

## COLL 1

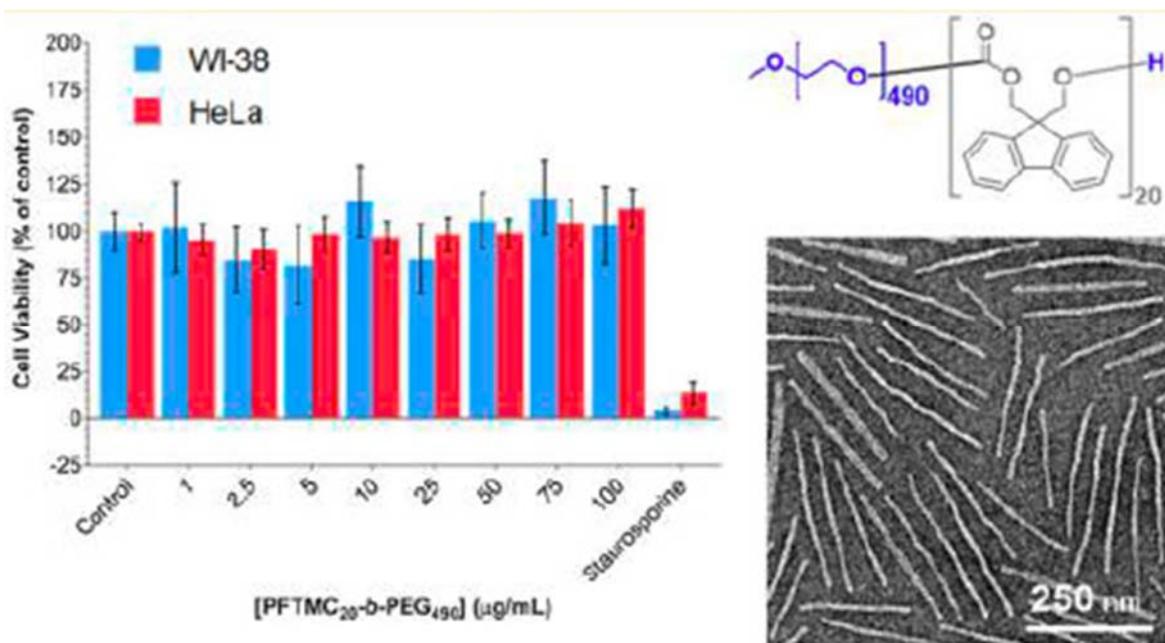
### Controlled self-assembly of polymeric amphiphiles driven by crystallization

**Ian Manners**, [imanners@uvic.ca](mailto:imanners@uvic.ca). Department of Chemistry, University of Victoria, Victoria, British Columbia, Canada

In this talk recent developments concerning a promising “seeded growth” route to well-defined 1D and 2D nano- and microparticles termed “living” crystallization-driven self-assembly (CDSA), will be described. Living CDSA can be regarded as a type of “living supramolecular polymerization” that is analogous to living covalent (e.g. anion initiated) polymerizations of molecular monomers but on a much longer length scale (typically, 10 nm – 5 microns). Living CDSA also shows analogies to biological “nucleation-elongation” processes such as amyloid fiber growth.

The building blocks or “monomers” used for living CDSA consist of a rapidly expanding range of crystallizable amphiphiles such as block copolymers, homopolymers with charged termini, or planar *pi*-stacking molecules with a wide variety of chemistries. The seeds used as “initiators” for living CDSA are usually prepared from preformed polydisperse 1D or 2D micelles by sonication.

Recent results indicate that through combination with the polymerization-induced self-assembly (PISA) method, living CDSA is scalable which will help enable applications in areas such as optoelectronics, catalysis, and biomedicine. Recent examples will be discussed.

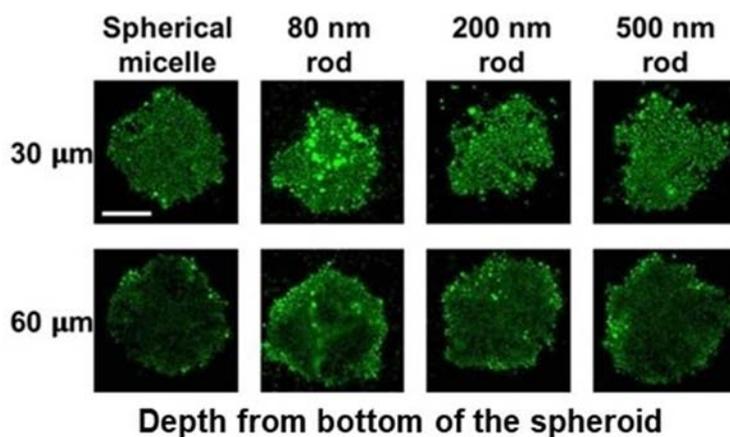


## COLL 2

### Rod-like block copolymer micelles for delivery of drugs and radionuclides to tumors

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Over the past 20 years there has been a strong interest in the use of elongated block copolymer micelles as drug delivery agents for potential applications in cancer therapy. Discher, for example, showed that long flexible micelles have long blood circulation times in animal models. Unfortunately, the examples in the literature have broad length distributions and could benefit from better characterization of the micelle dimensions. We have used crystallization-driven self-assembly to prepare a series of rod-like micelles from polyferrocenylsilane-*block*-poly(oligoethylene glycol methacrylate) (PFS<sub>27</sub>-*b*-POEGMA<sub>50</sub>). These micelle have narrow length distributions with lengths ranging from 80 nm to 2000 nm. The lengths and corona dimensions were characterized by TEM as well as multiangle static and dynamic light scattering. Introduction of amino groups in the corona allows the attachment of fluorescent dyes as well as chelators for radiometals. These micelles are non-toxic to two human breast cancer cell lines (MDA-MB-231 and MDA-MB-436). Most impressive, they show much deeper penetration into multicellular tumor spheroids (MCTS) of these two cell lines than spherical micelles of the same composition (at constant weight concentration) prepared by nanoprecipitation. The penetration depth is maximum for 80 nm and 200 nm long micelles.



## COLL 3

## **Polypeptide, RNA, and protein co-assemblies as delivery systems**

**Paula T. Hammond**, *hammond@mit.edu*. Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States

Poly(propargyl-L-glutamate) (PPLG), and similar functionalizable polypeptides subsequently introduced, have enabled a broad range of new approaches to design of artificial polypeptide systems with properties that engage or mimic biology. The resulting polymers can serve as interesting scaffolds for the generation of amphiphilic macromolecules capable of pH responsive drug delivery or oligomeric systems that encapsulate siRNA. Furthermore, these systems can be modified to optimize their interactions with protein-RNA complexes. The pre-encapsulation of the translational proteins complexed with mRNA can enhance mRNA translation within cells by multifold in comparison to release of mRNA alone. For example, we found that a unique series of polypeptides with variable charged side chain structures can enhance encapsulation of mRNA with EIF4E, with optimal systems yielding 70 to 80 times that of the mRNA alone. A key to these polymers is their ability to cooperatively bind RNA with the associated protein machinery needed for translation together to enhance translation. More recently, we have found similar kinds of enhancements for the delivery of siRNA via co-complexation with the Ago-2 protein to create a pre-assembled version of RISC complex, and with Poly-A binding protein with mRNA. These systems, and the potential role of such complexes in medical applications, will be discussed.

## **COLL 4**

### **DNA is not merely the secret of life: Semantomorphic science**

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We build branched DNA species joined using Watson-Crick base pairing to produce N-connected objects and lattices. We have used ligation to construct DNA topological targets, such as knots, polyhedral catenanes, Borromean rings and a Solomon's knot.

Nanorobotics is a key area of application. We have made robust 2-state and 3-state sequence-dependent programmable devices and bipedal walkers. We have constructed 2-dimensional DNA arrays with designed patterns from many different motifs. We have used pairs of 2-state devices to capture a variety of different DNA targets. We have constructed a molecular assembly line using a DNA origami layer and three 2-state devices, so that there are eight different states represented by their arrangements. We have demonstrated that all eight products are built. Recently, we connected the nanoscale with the microscale using DNA origami.

We have self-assembled a 3D crystalline array and reported its crystal structure to 4 Å resolution. We can use crystals with two molecules in the crystallographic repeat to control the color of the crystals. Rational design of intermolecular contacts has enabled

us to improve crystal resolution to better than 3 Å. We now do strand displacement in crystals to change their color, thereby making a 3D-based molecular machine. Thus, structural DNA nanotechnology has fulfilled its initial goal of controlling the internal structure of macroscopic constructs in three dimensions. A new era in nanoscale control awaits us.

## **COLL 5**

### **Coupling self-assembly of one-dimensional DNA fibers and fiber networks to regulating chemical reactions**

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In biological systems, self-assembly processes exhibit features such as robust performance across a wide range of physical conditions, controlled stepwise assembly of hierarchical structures, and self-repair. A key mechanism underlying these phenomena is the coupling of molecular self-assembly processes to signal transduction and gene expression networks. DNA nanotubes, for which Watson-Crick hybridization of DNA complexes drives growth of a cylindrical lattice, are a model system for understanding how coupling self-assembly processes to designed chemical reaction networks can make it possible to achieve similar features *in vitro* by design. I will describe how coupling “buffering” monomer concentration using a self-regulating chemical reaction can allow nanotubes to grow at a fixed rate for a wide range of monomer concentrations from DNA nanotube seeds to act as templates for growth, thus controlling where nanotubes assemble. I will also show of multivalent seeds and hierarchical assembly can be used to assemble hierarchical nanotube networks with control of assembly kinetics and network topology. Finally, I will show how when nanotubes are damaged via enzymatic degradation, incorporation of fresh monomers can heal this damage, allowing nanotube structures to persist for long periods of time in environments where their components are chemically unstable.

## **COLL 6**

### **Beyond Watson-Crick base pairing: DNA polymer hybrid self-assemblies**

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In recent years, great progress was achieved by folding nucleic acids into intricate 2D- and 3D nanostructures. However, the combination of DNA with other moieties like synthetic polymers or lipids allows the evolution of exciting functional polymer hybrids. Our group developed new DNA amphiphiles that can be either fabricated by electrostatic complexation or by covalently attaching hydrophobic units to the nucleic acids. The former class of materials yielded the first DNA thermotropic liquid crystals, which could be exploited further to construct smart bioelectronic devices. Moreover,

enveloping DNA with polyethylene glycol chains enabled the salt-free hybridization in water and transferring DNA in other organic media. Covalent attachment of hydrophobic units to DNA yielded amphiphiles that allow interfacing of the resulting assemblies with biological systems. This resulted in programmable cell uptake, controlled drug delivery and encoding of life animals with sequence information.

## **COLL 7**

### **Supramolecular polymerization of DNA origami nanostructures with peptides, proteins, and small molecules**

**Nicholas Stephanopoulos**, *nikosteph@gmail.com*. Arizona State University, Scottsdale, Arizona, United States

Supramolecular polymers, where monomeric units form higher-order assemblies through self-assembly, are an attractive platform for functional materials in biology, medicine, energy, and fundamental science. These materials have been constructed from polymers, proteins, peptides, or DNA, but hybrid systems that integrate more than one of these molecules are rare. We report on the supramolecular polymerization of DNA origami nanostructures using three self-assembled molecular systems: (1) a coiled-coil peptide heterodimer; (2) the host-guest interaction between adamantane and cucurbituril moieties; and (3) the binding interface between a nanobody and its protein target. In all cases, the DNA nanostructure provides a rigid building block with a tunable number of handles for attachment of the peptides, proteins, or small molecules. These species are in turn conjugated to complementary handles through site-specific chemistry, and several hierarchical self-assembly pathways are probed, including one-pot annealing, sequential assembly, and formation of alternating copolymers. The final assemblies merge the programmability of DNA nanotechnology with the unique molecular and self-assembly properties of the molecules tested, and will pave the way for hybrid nanomaterials with diverse functions.

## **COLL 8**

### **New strategies for stimuli-responsive liposomes**

**Michael Best**, *mdbest@utk.edu*, *Jinchao Lou*, *xiaoyu Zhang*. The University of Tennessee, Knoxville, Tennessee, United States

Liposomes are effective supramolecular nanocarriers that have been approved for clinical use due to their ability to encapsulate and enhance the delivery of therapeutic agents. Nevertheless, liposome delivery properties could be improved by exerting control over the release of encapsulated contents in an effort to enhance the targeting of diseased cells. Toward this end, this presentation will report new strategies for the development of stimuli-responsive liposomes for drug delivery applications. In these approaches, synthetic lipid switches are developed that undergo chemical or

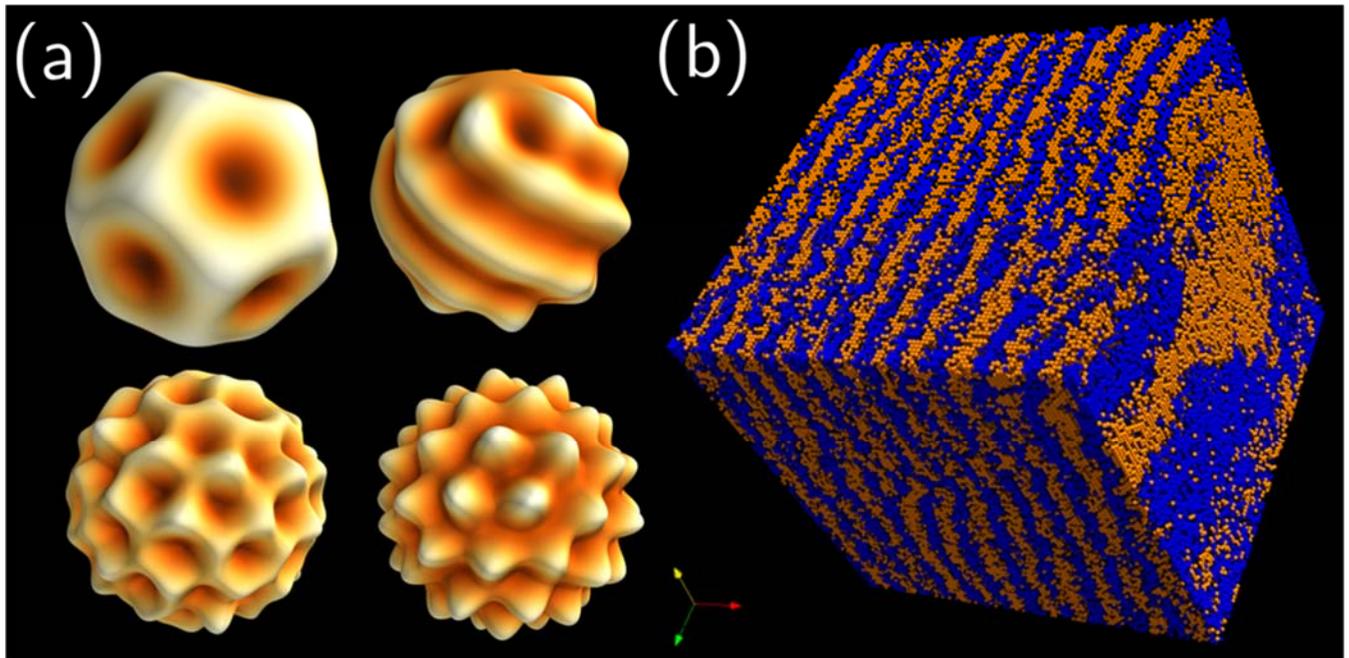
conformational changes in the presence of pathophysiological stimuli in a manner designed to perturb membrane properties and trigger content release. The design of stimuli-responsive lipid switches will be discussed, as will the analysis of liposome content release through techniques including dye release assays, DLS, STEM, and fluorescence microscopy.

## **COLL 9**

### **Modulated phases on spherical membranes and in strongly-driven systems**

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Spatially-modulated or patterned phases are found on many spherical biological objects including pollen grains, fungal spores, and insect egg shells. In many of these examples, biological membranes play a key role in the pattern formation. Phase-separating lipid vesicles may also exhibit spatially-modulated phases. Unlike a planar surface, the topology of a spherical surface induces defects in the patterns. We discuss the general principles of phase transitions to spatially-modulated phases on the surface of a sphere using a Landau-Brazovskii free energy approach. We then show how the general theory applies to pattern morphogenesis on the surface of biological membranes. Next, we examine phase separation in lipid vesicles with heterogeneous compositions in the presence of melatonin, a small molecule, using optical measurements and small angle neutron scattering. We show that high concentrations of melatonin preserve lipid domains. Finally, although modulated phases are often found at equilibrium, patterns may arise in far-from-equilibrium contexts. We discuss stripe formation in a driven lattice gas and propose a possible general theory of such patterns, contrasting the theory with the Landau-Brazovskii approach for equilibrium systems.



(a) Examples of spatially-modulated phases on spherical surfaces describable by a Landau-Brazovskii free energy (b) Striped phases in a driven, phase-separating lattice gas

## COLL 10

### Chemical activation of mechanosensitive channels in living bacteria

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As a defense against acute shifts in environmental osmolarity, biological cells employ a series of membrane gated proteins called mechanosensitive (MS) channels, which activate in response to lateral stress applied to the membrane. These MS channels act as safety valves and open transient pores in the membrane to permit a careful release of pressure following the onset of osmotic shock. It has recently been demonstrated that, in addition to mechanical forces, MS channels can also be chemically activated. Of particular interest, MS channels of large conductance (MscL) are known to be specific to the cytoplasmic membrane (CM) of bacteria and create ca. 3 nm wide transmembrane pores when open. Chemical activation of these MscL channels could therefore feasibly form the basis of a new antibiotic paradigm, whereby open channels could permit uptake of otherwise membrane impermeable antibiotic compounds. Herein, we demonstrate that the triphenyl methane dye, malachite green (MG), is capable of activating the bacterial MscL channels. To do this, we employed time-resolved second harmonic light scattering to interrogate the transport rate of MG across the CM in living bacteria. Specifically, we monitored the interaction of MG in ensemble suspensions of

wild type (Wt) and MscL knockout (KO) strains of *E. coli*. Experiments with the Wt strain revealed an MG concentration dependent increase in the CM transport rate. Conversely, experiments with the KO strain exhibited a constant CM transport rate, completely independent of the MG concentration. Given that the sole difference between these two bacterial strains is the relative presence of the MscL channel suggests that the enhanced transport rate observed in the Wt strain must originate from an interaction with the MscL channel.

## **COLL 11**

### **Cooperative adsorption: Environmental and biological consequences of organic enrichment by lipid films**

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Cooperative adsorption describes how insoluble monolayers enhance a soluble solute's surface activity relative to the solute's affinity for neat interfaces. Cooperative adsorption's consequences are far-reaching. Saccharide adsorption to lipid films has been proposed as a mechanism to account for the unusually high organic content reported in sea-spray aerosols, and cooperative adsorption is considered to be one mechanism responsible for concentrating cryoprotectants such as trehalose near cell membranes. Our recent studies of cooperative adsorption have examined the roles played by soluble solute charge and insoluble monolayer composition on cooperative adsorption. Surface specific vibrational sum frequency generation (VSFG) experiments show that monosaccharides such as the anionic glucuronic acid and cationic glucosamine both cooperatively adsorb to DPPC monolayers and induce a higher degree of order in the DPPC acyl chains with increasing saccharide concentration, regardless of charge. Independent surface tension experiments support these findings and show both saccharides to have a condensing effect on DPPC monolayers. Further evidence of cooperative adsorption comes from differential scanning calorimetry (DSC) experiments where glucuronic acid induces a second gel-liquid crystalline transition temperature (~1 degree C higher than the main transition) suggesting that cooperative adsorption leads to partial headgroup dehydration.

## **COLL 12**

### **Direct visualization of platelet integrins using anti-transmembrane domain peptides containing a blue fluorescent amino acid**

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Fluorescent-labeled antibodies and recombinant proteins containing a fluorescent reporter are commonly used to visualize proteins in situ, but the antibodies and reporters can perturb protein structure and function. To overcome this problem, we designed minimally perturbing blue fluorescent labels (4-cyanoindol [4CN] and 4-cyano-tryptophan [4CNtrp]) that enable the direct imaging of intrinsically-fluorescent proteins. Here, we used 4CN-labeled peptides to directly image integrins on the platelet surface. 4CN has unique photophysical properties: an absorption maximum at ~325 nm, an emission maximum at ~420 nm, a large fluorescence quantum yield (>0.8 in aqueous solution), a long fluorescence lifetime (ca. 13 ns), and good photostability. Previously, we described CHAMP (Computed Helical Anti-Membrane Protein) peptides that target integrin TM domains in a sequence-specific manner. Thus, the peptides anti- $\alpha$ IIb and anti- $\alpha$ v bind to the  $\alpha$ IIb and  $\alpha$ v TM domains, respectively, causing  $\alpha$ IIb $\beta$ 3 and  $\alpha$ v $\beta$ 3 activation. Anti- $\alpha$ IIb also causes  $\alpha$ IIb $\beta$ 3 clustering that we visualized using fluorescent-labeled anti- $\beta$ 3 monoclonal antibodies but only after the platelets were fixed to prevent antibody-induced clustering. Using solid-phase peptide synthesis, we generated CHAMP peptides labeled with 4CN at their N-termini (CN- $\alpha$ IIb, CN- $\alpha$ v, CN- $\beta$ 1). 4CN labeling did not prevent the ability of CN- $\alpha$ IIb to cause  $\alpha$ IIb $\beta$ 3-dependent platelet aggregation, CN- $\alpha$ v to cause  $\alpha$ v $\beta$ 3-dependent platelet adhesion to osteopontin, and CN- $\beta$ 1 to cause  $\alpha$ 2 $\beta$ 1-mediated platelet adhesion to collagen. We then used 2-photon confocal imaging to detect 4CN-containing integrins on the platelet surface. Compared to a 4CN-containing random peptide that uniformly decorated the platelet surface, CN-labeled CHAMP peptides were present as a limited number of discrete foci. To confirm that these foci represent CN-peptide containing integrins, we co-stained the cells with Alexa Fluor 458-labeled integrin-specific monoclonal antibodies and found that the CN-peptide and antibody fluorescence coincided. Thus, these studies demonstrate the specific direct imaging of integrins embedded in the platelet membrane using 4CN-labeled anti-integrin TM peptides. Because 4CN can readily be incorporated into proteins and peptides with little if any structural perturbation, 4CN-labeling provides a facile way to directly monitor protein behavior and protein-protein interactions in cellular environments.

## **COLL 13**

### **Structural origin of cholesterol induced phosphoinositide clustering**

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Phosphoinositide lipids (PIPs) are important mediators for an extraordinary array of cellular functions. Many of these cellular events are sensitive to cholesterol depletion

and it has been speculated that PIPs are raft associated. However, the stearyl/arachidonoyl acyl chain composition of PIPs is generally unfavorable for an accumulation in a liquid-ordered (lo) environment and PIPs fail to enrich in such phases. Nevertheless cholesterol promotes PIP domain formation in ternary PC/PIP/cholesterol lipid mixtures. To elucidate the structural origins of the PIP/cholesterol interaction, we have conducted all-atom simulations of PI(4,5)P<sub>2</sub>/cholesterol monolayers and validated our results using surface pressure/area experiments of Langmuir films. In contrast to PC monolayers, we find for PI(4,5)P<sub>2</sub> monolayers that cholesterol interacts significantly with the headgroups. On average, 20-25% of the cholesterol hydroxyl groups form hydrogen bonds with the PIP phosphodiester and the C2 and C6-hydroxyl groups of the inositol rings. The participation of cholesterol in the PIP headgroup hydrogen bond network leads to a stabilization of the PIP enriched domain. The inositol ring tilt angle (relative to the surface normal) is reduced in the presence of cholesterol. Furthermore, the acyl chain tilt angle is decreased and the acyl chain order is increased.

While lo phase (raft) domain formation is governed by the interaction of cholesterol with lipid chains, the origin of PIP domain formation is fundamentally different: it is the result of the participation of cholesterol in the intermolecular hydrogen bond network formed within the PIP headgroup region. This cholesterol stabilized hydrogen bond network is particularly sensitive to ion effects. Na<sup>+</sup> stabilizes the intermolecular hydrogen bond networks, while this is less pronounced for K<sup>+</sup>. Ca<sup>2+</sup> and cholesterol synergistically promote PIP domain formation.

## COLL 14

### Universal dynamics in liposomes

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Liposomes composed of phospholipids in its fluid phase are very mobile complex fluid like objects. Usually it is assumed that collective membrane motion and single lipid dynamics are connected with characteristic parameters that define the behavior of membranes, starting from vibrations of molecules to translational diffusion of liposomes. Since many length-scales are involved, typically membrane dynamics is studied by a variety of techniques, including NMR, neutron scattering, microscopy to name only a few out of many important tools.

Our presentation concentrates on the motion in the time scale region from around 0.01 to 100 ns and shows rather universal behavior that can be detected by several techniques. We concentrate on the fast lipid relaxation and the slower collective motion of the membrane and show the importance of correctly including the tail dynamics to obtain a better estimate of the bending modulus.

## COLL 15

## **Exploring the properties and dynamics of multi-MAC support structures for lipid bilayer membranes**

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The fragility of reconstituted lipid bilayer membranes often limits biotechnological applications. Previously, we have enhanced the mechanical properties of planar lipid bilayers using a single-layered, molecularly thin, minimal actin cortex (MAC). To further increase stress resistance, we are developing multi-layered MAC structures (multi-MACs) that can be cross-linked to arbitrary thicknesses while retaining an open network structure that enables rapid diffusive permeability to the bilayer. In this work, we describe the multi-MAC formation process in the context of a bilayer array on a microchip, as well as glass supported bilayers. We report on permeability tests that demonstrate molecular access to the bilayer remains unhindered by the presence of the multi-MAC. We describe achievement of permeability by controlling the openness of the F-actin network, which can be tailored using the density of linkage sites, the electrostatic interactions between linkers and filaments, and specific F-actin growth and deposition techniques. Interestingly, experiments measuring the conductivity of nanopores embedded in the bilayer suggests that multi-MACs designed with alternating layers of charge create ion-selective permeability. We also present results from single-molecule optical measurements that characterize the multi-MAC structure, dynamics, permeability, and the approximate pore size of the layered network.

### **COLL 16**

## **Supported biomimetic hybrid bilayers: pH-mediated interactions between glass and lipid-polymer vesicles**

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The formation of supported bilayers over rigid materials represents an essential step towards producing a wide range of biomimetic surfaces. One practical approach towards robust and stable biomimetic platforms is to generate hybrid bilayers that incorporate both lipids and block copolymer amphiphiles, for example DOPC mixed with amphiphilic poly(ethylene oxide-*b*-butadiene). The currently limited number of reports on the interaction of hybrid lipid and polymer vesicles with glass surfaces, describe substantially different conclusions under very similar conditions (i.e. same pH) – either bilayer formation or no interaction at all. In this study, we vary vesicle composition and solution pH in order to generate a broader picture of spontaneous hybrid lipid/polymer vesicle interactions with rigid supports. We have found significant pH-dependent

adsorption/fusion of hybrid and polymer vesicles that accounts for some of the seemingly contradictory results observed in the literature. Our results suggest that careful control of pH can result in substantially different types of interactions between hybrid vesicles and hydrophilic surfaces in order to create a range of robust biomimetic surfaces.

## **COLL 17**

### **Nanomaterial-based contrast agents for spectral X-ray imaging**

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Well-defined biomaterial- and polymer-stabilized lanthanide nanophosphors (NPhs) and metallic nanoparticles (NPs) are developed in our group as contrast agents for spectral X-ray imaging, highlighting the macromolecular and structural differences derived on computed tomography (CT), cell viability, solvent dispersibility, and further tunability. Taking advantage of the ability of spectral X-ray imaging with photon-counting detectors to perform image acquisition, analysis, and processing at different energy windows (bins), enhanced signal and pronounced separability can be obtained by our NPs and K-edge materials, improving sensitivity of CT imaging, and differentiation between aqueous solutions, phantoms, tissues, and contrast materials. Results from our research indicate achieved CT contrast comparable/higher than iodine, good cell viability, and ability to further tune the structure by engineering biofunctionalities and incorporating site-specific drugs. Comparison of our X-ray molecular probes with current contrast agents will be provided on CT numbers and cell viability, laying the groundwork for the development of the next generation CT-guided diagnostic nanomaterials.

## **COLL 18**

### **Gadolinium oxide nanoplates as T<sub>1</sub> MRI contrast agents**

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Approximately 30 – 50 % of all MRI procedures require contrast agents (CA) for image enhancement. Gadolinium chelate CA (GCCA), that reduce T<sub>1</sub> relaxation times of water protons are preferred by radiologists for clinical use. However, burgeoning issues with GCCA toxicity have led researchers to consider various alternatives. One such example, gadolinium-containing nanocrystals (GCN), have the potential to offer greater r<sub>1</sub> relaxivity, reduced toxicity, and other nano-related advantages. In particular, gadolinium oxide nanocrystals (GON), demonstrate promise as efficient T<sub>1</sub> MRI CA for various biomedical applications. However, a significant challenge to the efficacy of T<sub>1</sub>

CA is the tension between colloidal stability and surface-water accessibility. Here, Gd<sub>2</sub>O<sub>3</sub> nanoplates (GONP) are encapsulated with a novel amphiphilic co-polymer (PAMPS-LA) for good colloidal stability in biological media and water-accessible surfaces. As such, GONP exhibit exceptionally large  $r_1$  relaxivity ( $r_1 = 62.9 \text{ mM}^{-1}\text{s}^{-1}$ ) while maintaining a  $r_2/r_1$  of 1.17 at a clinically relevant field strength of 1.4 T. High GONP  $r_1$  relaxivity is attributed to the dominance of inner-sphere relaxation mechanisms at nanoplate edges based on shape anisotropy and systematic studies of  $r_1$  dependence on size (2, 5, and 12 nm) and magnetic field strength (1.4, 3, and 9.4 T). In vitro, GONP are readily taken into cells, maintain signal in the intracellular environment, and exhibit no significant cytotoxicity at clinically relevant dosages (10 – 100  $\mu\text{M}$  Gd). In vivo, GONP have blood circulation lifetimes comparable to GCCA and are cleared hepatically, which enables their application in the differentiation of non-alcoholic fatty liver disease (NAFLD) in mice using MRI.

## COLL 19

### Morphology control and SERS application of gold nanostars

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Plasmonic nanomaterials have received increasing interests due to their tunable optical properties and broad applications. For example, gold nanostars have unique plasmonic and catalytic properties that are associated with their sharp branches protruding on the surface. Typically, gold nanostars were fabricated with kinetically controlled approaches, and these star shape gold nanomaterials are thermodynamically unstable. In this presentation, I will present our research on controlling the morphology of gold nanostars, as well as the stabilization of nanostars with capping ligands. The impact of various capping ligands was studied using in-situ UV-vis spectra. We clearly observed that thiol ligands could bind strongly to gold nanostars and maintain gold nanomaterials with star-like morphology. In addition, we found that the gold nanostars are excellent colloidal substrates for surface-enhanced Raman scattering (SERS). Increased SERS enhancements were observed from the gold nanostars with sharp branches, and we can easily distinguish an addition of nanomolar 4-mercaptopyridine or various organic dyes. With further optimization, gold nanostars with superior SERS sensitivities and long-term stability could be perfect candidates in making security materials for a variety of anti-counterfeiting applications.

## COLL 20

### Room temperature green synthesis of reduced Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene nanosheets with enhanced conductivity and SERS activity

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MXenes are an emerging family of highly conductive 2D materials with additional functional properties introduced by surface terminations and show promise for frontier applications. Further modification of the structure and surface terminations makes MXenes even more appealing for practical applications. Herein, we report a facile, room temperature and environmentally friendly synthesis of reduced  $\text{Ti}_3\text{C}_2\text{T}_x$  MXene ( $r\text{-Ti}_3\text{C}_2\text{T}_x$ ) *via* a simple treatment with L-ascorbic acid. An examination of the surface-enhanced Raman scattering (SERS) activity reveals that the SERS enhancement factor of  $r\text{-Ti}_3\text{C}_2\text{T}_x$  is over an order of magnitude than that of regular  $\text{Ti}_3\text{C}_2\text{T}_x$ . In addition,  $r\text{-Ti}_3\text{C}_2\text{T}_x$  shows a paramagnetic behavior as well as a significant increase in electrical conductivity from  $1360 \text{ Sm}^{-1}$  in regular  $\text{Ti}_3\text{C}_2\text{T}_x$  to  $6870 \text{ Sm}^{-1}$  in the reduced version. The improved SERS activity of  $r\text{-Ti}_3\text{C}_2\text{T}_x$  could be attributed to the charge transfer interaction between the MXene surface and probe molecules, re-enforced by higher metallic conductivity. The finding of this study suggests that reduced MXene could be a superior choice over regular MXene, especially for applications that employ high electronic conductivity, such as electrode materials for batteries and supercapacitors, photodetectors, and SERS-based sensors.

## COLL 21

### Intracellular activation of bioorthogonal nanozymes through endosomal proteolysis of the protein corona

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Bioorthogonal activation of prodrugs provides a strategy for on-demand production of therapeutics. Intracellular activation provides a strategy to localize therapeutics, potentially minimizing off-target effects. In this study nanoparticles embedded with transition metal catalysts (nanozymes) were engineered to generate either 'hard' irreversible or 'soft' reversible coronas in serum. The hard corona effectively inhibited nanozyme activity, whereas only partial loss of activity was observed with the soft corona nanozymes. In both cases, complete activity was restored by treatment with protease. Intracellular activity mirrored this reactivation: endogenous proteases in the endosome provided intracellular activation of both nanozymes. The role of intracellular proteases in nanozyme reactivation was verified through the treatment of the cells with protease inhibitors, which prevented reactivation. Taken together, this study demonstrates the use of intracellular proteolysis as a strategy for the localization of therapeutic generation within cells.

## COLL 22

### **Toxicity and degradation of copper indium sulfide quantum dots *in vivo***

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There is a growing interest in near infrared (NIR, 700nm-900nm) imaging for both clinical and research applications, yet current NIR dyes tend to be dim, lack photostability, are less functionalizable, and can be toxic. Semiconductor quantum dots (QDs) can inherently circumvent many of these challenges; however, traditional QDs comprise toxic materials such as cadmium or lead.

Copper indium sulfide (CIS) QDs have emerged in the last decade as a non-toxic alternative; however, previous *in vivo* studies have been confounded by the presence of a zinc sulfide (ZnS) shell, which traps the CIS core by preventing degradation, thus causing accumulation in vital organs. This bioaccumulation greatly limits clinical translation: of the ~50 FDA-approved clinically-used nanomedicines, all are cleared from vital organs quickly.

For the first time, we assess the biodistribution and toxicity of unshelled CIS and partially zinc-alloyed CISZ QDs in a murine model at 1-day, 7-day, and 1-month timepoints. We show that bare CIS QDs breakdown quickly, with >75% of the initial dose being cleared by 1-month. Surprisingly, we also demonstrate a significant toxic response to these QDs as measured by organ weight, blood chemistry, and histology. Specifically, moderate doses of CIS particles (15mg/kg) induce severe hepatotoxicity and splenotoxicity. Similarly, CISZ demonstrated significant, but lower, toxicity compared to bare CIS. We examined the roots of this toxicity and degradation through *in vitro* studies on hepatocytes. Overall, our data suggests that reconsideration of CIS as a translatable QD system is required: degradation-based toxicity is an important aspect of biocompatibility that needs to be assessed in “non-toxic” QDs, if QDs are to ever be clinically successful.

## COLL 23

### **Soluble, multi-valent nano-self peptides increase phagocytosis of antibody-opsinized targets**

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Macrophages engulf a majority of particles that are injected, whereas our own cells including cancer cells inhibit such phagocytosis by displaying membrane protein CD47. Clinically, anti-CD47 blockade combined with cancer-targeting antibody is now showing

efficacy against cancer. Based on our previous study of CD47-derived polypeptides on particles that are phagocytosed minimally compared to control particles, we have now engineered shorter, soluble nano-Self oligopeptides in multivalent form to block CD47's receptor on macrophages, SIRP $\alpha$ . Bivalent oligos prove more potent as phagocytosis agonists of antibody-targeted cells ( $K_{\text{eff}} \sim 20$  nM) than monovalent oligos. Bivalents also exhibit a more stable hairpin-like structure, and out-compete monovalents in macrophage association, whereas scrambled oligos lack function. Soluble nano-Self oligos added to isolated macrophages also suppress a passivating phospho-Tyrosine signal, consistent with 'self' signaling through SIRP $\alpha$ . Bivalent nano-Self oligopeptides are thus a potential alternative to anti-CD47 blockade and promoting phagocytosis of 'self'.

## **COLL 24**

### **Peptide engineering for targeted, intracellular delivery of siRNA and proteins**

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Protein nanostructures with tunable chemistries would be extremely useful in a wide variety of applications ranging from biocatalysis to biopharma. Biopharmaceutical products are especially well-posed for impact: drugs such as monoclonal antibodies, peptides, and enzymes are rapidly transforming the global pharmaceutical industry, and biologics represented 35% of all new FDA approvals between 2010 and 2016. Moreover, the pipeline has a dearth of intracellular protein drug candidates, even though intracellular proteins comprise 61% of the proteome and have multiple predicted therapeutic applications. In fact, essentially all protein drugs to date have been restricted to vascular targets or targets on the cell surface, referred to as the 'accessible target space.'

We are designing peptide functionalization approaches in protein nanostructures that will enable improved control over intracellular targeting and delivery of siRNA and protein cargoes via improved control over the display of peptide ligands. Our specific goals are to demonstrate the use of versatile and modular protein engineering approaches (e.g., 'Tag/Catcher' chemistries; unnatural amino acid [UAA]/'click' chemistries) to create protein nanostructures that can be targeted and delivered with high efficiency, cell specificity, and no activity loss. Herein, we will describe approaches to enhance targeted protein delivery into inflammatory breast cancer (IBC) cells by tuning the number and density of epidermal growth factor receptor (EGFR) ligands, and by altering the size of the nanostructures used for delivery.

## **COLL 25**

### **Colloidal synthesis of light-emitting carbon dots and rods**

**Andrey Rogach**, *andrey.rogach@cityu.edu.hk*. City University of Hong Kong, Kowloon, Hong Kong

Carbon dots (CDs) – small crystalline or amorphous carbon-based nanoparticles – have attracted much attention as promising fluorescent materials for a wide range of applications, both in the biomedical fields and in optoelectronics. One of their widely accepted advantages is the simplicity of the formation of highly luminescent CDs from a wide variety of organic precursors. At the same time, several recent studies on these chemically synthesized CDs raised questions about the nature of the resulting products. Their strong fluorescence can arise due to the presence of molecular organic fluorophores, not necessary CDs, as was assumed in the earlier publications. On the other hand, purely carbon dot samples can be synthesized using seeded growth method, yielding CDs of the different sizes, through controlling the amount of seeds introduced into reaction mixture, alongside with the reaction time. This synthetic approach has been demonstrated to be an effective way to tune their optical properties: color-tunable fluorescence of CDs with blue, green, yellow, orange and red emission under UV excitation has been achieved, with the color depending on size of the  $\pi$ -conjugated domains in the CD graphitic core. Very recently, we have extended the family of the light-emitting colloidal carbon nanoparticles towards carbon nanorods with linearly polarized emission.

## **COLL 26**

### **Self-assembly of gold nanocrystals**

**Paul Mulvaney**, *mulvaney@unimelb.edu.au*. ARC Centre of Excellence in Exciton Science, School of Chemistry, University of Melbourne, Parkville, Victoria, Australia

Standard DLVO forces predict that particles will aggregate into either diffusion-limited structures or kinetically-controlled aggregates, once the interparticle potentials in a colloid system become attractive. Formation of ordered colloid assemblies is generally more complex. Here we will look at using poly-NIPAM capped gold particles to form well-defined structures. Temperature is used to tune the interparticle potential and the interparticle spacing. We show the formation of hexagonal superlattices that are centimetres in size that form within seconds. The pNIPAM also acts to modify surface plasmon interactions between the gold particles.

In a second approach we use lithographic templates to build arbitrary 2D arrays of single nanocrystals. We show that gold nanorods can be deposited vertically or horizontally. Molecular dynamics simulations are used to validate the approach, which employs electrophoretic deposition to assemble the arrays. The approach can be used for magnetic particles, insulators and semiconductor nanocrystals such as CdSe quantum dots.

## **COLL 27**

## **Rational construction of complex heterostructured nanoparticles using sequential partial cation exchange reactions**

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Many types of nanoparticles that are targeted for applications in energy, catalysis, medicine, and photonics require integration of multiple functional materials in precise locations. Synthetic routes to such heterostructured nanoparticles are available, but they remain limited in complexity, scope, and scalability. This talk will highlight our efforts to use sequential partial cation exchange reactions to synthesize a growing library of complex heterostructured nanoparticles. By applying multiple partial cation exchange reactions to copper sulfide nanoparticles, derivative nanoparticles having complex and asymmetric arrangements of materials and interfaces within the nanoparticles can be created. Crystal structure relationships among the various metal sulfide phases provide guidelines for predicting and controlling where cation exchange occurs and which interfaces form.

## **COLL 28**

### **Design of multifunctional nanomaterials and devices through nanocrystal self-assembly**

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The synthesis of monodisperse colloidal nanocrystals (NCs) with controlled composition, size, and shape provides ideal building blocks for the assembly of new thin films and devices. These monodisperse colloidal NCs can be thought of as "artificial atoms" with tunable electronic, optical, magnetic properties that are allowing the development of a new periodic table for design at the Mesoscale. In this talk, I will briefly outline the current state of the art in synthesis, purification, and integration of single-phase NCs and core-shell (heterostructures) NCs emphasizing the design of semiconductor building blocks with tunable shapes (spheres, rods, cubes, discs, octahedra, etc...). I will then share how these tailored NCs can be directed to assemble into single-component, binary, ternary NC superlattices providing a scalable route to the production of multifunctional thin films. The modular assembly of these NCs allows the desirable features of the underlying quantum phenomena to be retained and enhanced even as the interactions between the NCs allow new delocalized properties to emerge. Synergies in the electronic, optical coupling between NCs will be emphasized as we pushing toward the realization of artificial solids with a new 3D and structure and high mobilities ( $>30 \text{ cm}^2\text{V}^{-1}\text{S}^{-1}$ ) device integration. I will share specific case studies in thin-film transistors, thermoelectric materials and solution-processable photovoltaic devices build with these strongly coupled nanocrystal solids highlighting the recent developments in wafer-scale NC superlattice deposition and patterning may provide a path to scalable fabrication. In a final example of hetero-integration, I will present our

progress in the co-assembly of plasmonic resonators together with nanoscale emitters as a route to the scalable self-assembled MetaMaterials with novel linear and non-linear optical properties.

## **COLL 29**

### **Fabrication of intelligent colloidal photonic crystal hydrogels for sensing trace metal in seawater**

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Responsive hydrogel sensing materials have been fabricated using three dimensional (3D) polymerized colloidal photonic crystals (PCPCs) for highly sensitive and selective detection of hazardous metal ions in seawater at ultra-low concentration. Due to periodically ordered lattice of the embedded photonic crystals, the hydrogel diffracts light in visible spectral range according to the Bragg's law. When the hydrogel is functionalized by spatially distributed –SH groups through cleaving –S–S– bonds in grafted N,N'-cystaminebisacrylamide molecules, the functionalized hydrogel can selectively bind with mercury ions ( $\text{Hg}^{2+}$ ) to form –S–Hg–S– bridge bonds in seawater. The  $\text{Hg}^{2+}$  binding causes the volume of the hydrogel to shrink, corresponding to a wavelength shift of the light diffracted by the hydrogel, while the shifted wavelength is proportional to the amount of bound  $\text{Hg}^{2+}$  ions, which enables the quantitative evaluation of  $\text{Hg}^{2+}$  ions with a limit of detection at  $10^{-9}$  M level in seawater, as measured by a portable spectrometer. When the hydrogel is functionalized with crown ether molecules containing the smallest cavities, the grafted benzo-9-crown-3 can strongly and selectively chelate with beryllium ions ( $\text{Be}^{2+}$ ) in solution, which enables the detection of the smallest metal ions  $\text{Be}^{2+}$  quantitatively at a detection of limit of  $10^{-11}$  M in seawater. With this intelligent hydrogel sensors, we demonstrate a simple method for the rapid in situ monitoring and detection of hazardous metal ions such as  $\text{Hg}^{2+}$  and  $\text{Be}^{2+}$  at ultra-low concentrations in seawater.

## **COLL 30**

### **Massively-parallel tip-directed synthesis of complex polyelemental nanoparticle arrays**

*Andrey Ivankin<sup>1,2</sup>, aivankin@gmail.com, Pengcheng Chen<sup>3</sup>, Jingshan Du<sup>3</sup>, Liliang Huang<sup>3</sup>, Edward J. Kluender<sup>3</sup>, Chad A. Mirkin<sup>4</sup>.* (1) TERA-print, Skokie, Illinois, United States (2) International Institute for Nanotechnology, Northwestern University, Evanston, Illinois, United States (3) Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois, United States (4) Chemistry, Northwestern University, Wilmette, Illinois, United States

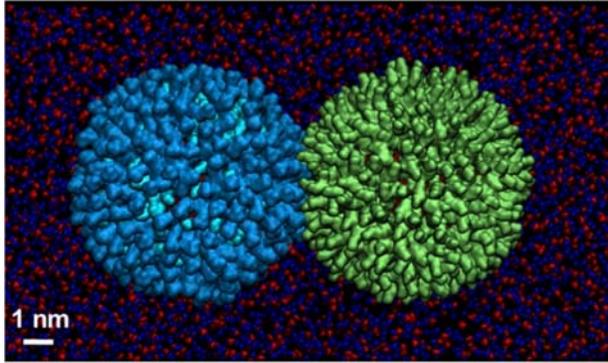
Polyelemental nanoparticles have applications in catalysis, plasmonics, light-harvesting, medical diagnostics and therapeutics, and electronics. Discovering the best nanoparticle architectures for a given application is, however, a daunting task, due to the enormous size of the nanomaterial parameter space and the lack of universal synthesis methods on the nanoscale. Cantilever-free scanning probe lithography (CF-SPL) in combination with block copolymer-based nanoparticle synthesis, a process termed scanning probe block co-polymer lithography (SPBCL), addresses many of these challenges. When SPBCL is integrated with polymer pen lithography (PPL), a way to deposit millions of discrete attoliter-volume nanoreactors loaded with metal precursors on a substrate in parallel is achieved, and each nanoreactor can be transformed into millions of spatially encoded functional nanoparticles. The composition and size of the nanoparticles can be precisely controlled by adjusting the type, ratio, and concentration of metal precursors loaded prior to printing. SPBCL has already been generalized to synthesize nanoparticles composed of metals, metal oxides, and semiconductors, and nanoparticles with up to seven elements and four phases have been successfully demonstrated. Not only has this strategy become extremely powerful for synthesizing densely packed arrays of complex and highly uniform nanoparticles, but more importantly, it has unlocked the possibility of rapidly creating libraries of millions of unique, spatially encoded nanoparticles with gradients of deliberately varied sizes and compositions. This combinatorial method of synthesizing nanoparticle “megalibraries” offers researchers a platform for identifying structures with desired physicochemical properties at a rate that was previously impossible to realize.

## **COLL 31**

### **Atomistic modeling of nanoparticles lattices formed at surfaces and bulks of liquids**

*Petr Kral, pkral@uic.edu.* University Illinois Chicago, Chicago, Illinois, United States

First, we discuss our modeling of binary systems of nanoparticles (NPs) which self-assemble at liquid surfaces. Our modeling reveals that NPs-liquid coupling energies form about 40% of the total lattice energy, which means that this coupling largely controls the types of NP-superlattices formed. We explain why different superlattices form and show why similar solvents can provide very different NPs self-assembly conditions. Next, we present our modeling of supercharged NPs that self-assemble in bulk solvents, and clarify the conditions under which different superionic lattices form. We use free energy calculations to predict the existence conditions of different superlattices and show that the computational results very well with the observed experimental data.



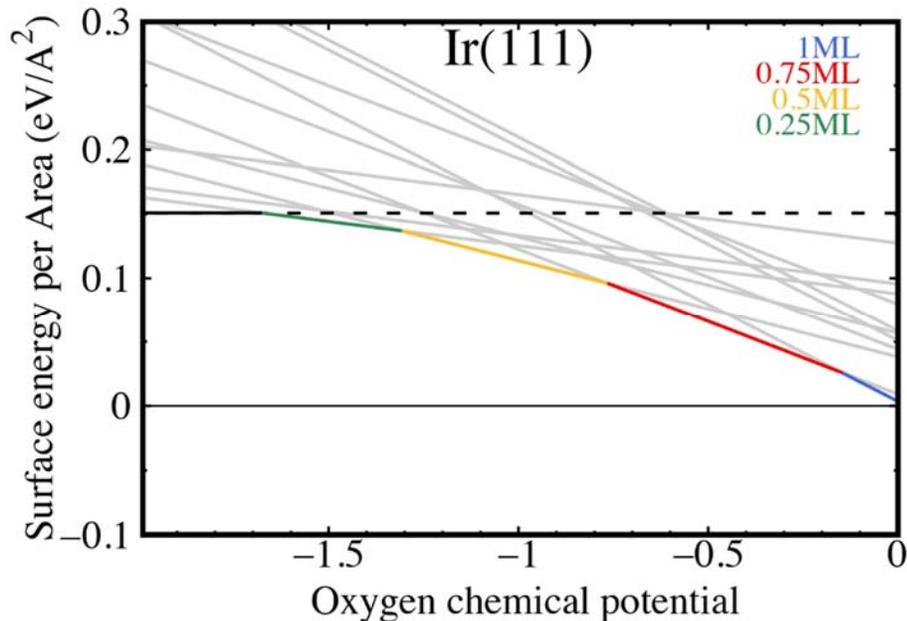
Self-assembly of superions in ionic solutions.

## COLL 32

### First-principles calculations on $\text{IrO}_3$ desorbability at high temperatures

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Since iridium has great mechanical properties and chemical inertness at high temperatures, it is broadly used as applications at high temperatures, such as spark plugs of an internal combustion engine or crucibles for single crystal growth. However, iridium is suffering from desorption as gaseous oxides, composed mainly of  $\text{IrO}_3$  at high temperatures. This problem accelerates the consumption of iridium. To solve this problem, we investigated  $\text{IrO}_3$  desorption by first-principles calculations based on density functional theory (DFT). The OpenMX is used as a first-principles calculation code with norm-conserving pseudopotentials and pseudo-atomic localized basis functions. The electronic exchange-correlation effect is treated by the first-principles GGA-PBE functional. As a result, we found that iridium desorption occurs not at low temperatures but at high temperatures. Also, we discovered that the Ir(111) surface is the most crucial surface on iridium desorption. We observed the reaction path of iridium desorption from nudged elastic band calculations.



Surface phase diagram on oxygen-adsorbed Ir(111) surface.

### COLL 33

#### Understanding wet chemical etching mechanisms for selective functionalization of graphitic surfaces

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For the synthesis of heterogeneous catalysts, surface functionalization (via area activation) of substrates using a bottom-up approach has gained great interest, due to the increasing control of the engineering surfaces on the atomic scale. This approach enables the creation of well-defined nanostructures otherwise unobtainable through the traditional lithographic (top-down) processes. The investigation of surface functionalization by acid etching of a well-defined graphite surface is presented. In this study, we report the effect of two different acids to produce oxide functional groups on highly oriented pyrolytic graphite (HOPG). Various concentrations of hydrochloric acid (HCl) and nitric acid (HNO<sub>3</sub>) were used to etch and functionalize the HOPG surface. X-Ray photoelectron spectroscopy (XPS) was used to investigate the binding energies and the HOPG surface functionalization. It was found that HCl acid etching produced both C=O and C-OH functional groups on the graphite surface and HNO<sub>3</sub> acid etching produced mainly C-OH functional groups. Density functional theory calculations confirmed the presence of oxygenated species in the C1s region. The surface

topography was investigated using scanning electron microscopy (SEM) and atomic force microscopy (AFM) imaging to find surprising differences in the etching mechanism that is discussed. These studies suggest that understanding the etching and functionalization mechanisms on 2D materials has potential for selective growth of metals/metal oxide films or nanostructures for new catalyst growth methods.

## COLL 34

### **Covalent functionalization of Si(111) surfaces with ferrocene and naphthalene diimide: Molecular strategies to control the electrochemical properties of hybrid interfaces**

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Development of functional molecular materials plays a pivotal role in the fabrication of smart integrated devices for contemporary applications such as in micro- and optoelectronics, information storage, photovoltaics, etc. In this regard, covalent functionalization of semiconducting surfaces, such as, doped silicon, with redox-active moieties offers new opportunities for applications which necessitate reversible charge storage at the molecular level. We have explored the extent to which structural properties and covalent anchoring strategies of redox-active systems based on ferrocene (Fc) and naphthalene diimide (NDI) tune the electrochemical properties of functionalized hydrogen-terminated Si(111) surfaces. Such hybrid interfaces were characterized comprehensively using atomic force microscopy, X-ray photoelectron spectroscopy and cyclic voltammetry. The electrochemical properties of Fc-functionalized Si interfaces depend significantly on the organic structural design and synthetic anchoring strategy. It emerges that a direct one-step photografting strategy offers considerably higher (ca. 25 times) surface coverage of organo-iron ( $1.25 \times 10^{-10}$  mol cm<sup>-2</sup>) as compared to divergent synthetic approaches that involve multiple post-synthetic modifications, for example, including Steglich esterification. In contrast, a synthetic strategy that involves thermal grafting of an aliphatic alkadiyne on Si-H followed by a Cu(I)-catalyzed “click” reaction with a ferrocenyl-azide results in one of the highest surface coverages ( $9.97 \times 10^{-10}$  mol cm<sup>-2</sup>) of organo-iron. Such high surface concentration leads to a remarkable anodic shift (350 mV) of the half-potential as compared to surfaces functionalized via direct photografting. This strategy was further extended to anchor an NDI-based electron-acceptor molecular system on Si-H. Confinement of NDI moieties on Si surfaces are associated with the emergence of intriguing electrochemical properties due to non-negligible aggregative interactions between the  $\pi$ -conjugated aromatic cores that facilitate delocalization of injected charges. The overall results offer access to novel redox-active hybrid Si interfaces with tunable electrochemical properties and are expected to constitute important additions to the gamut of microelectronics.

## COLL 35

### Scalable preparation of chiral metal surfaces for enantioselective processes

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Chiral surfaces are critical components of enantioselective heterogeneous processes such as those used to prepare enantiomerically pure pharmaceuticals. While the majority of chiral surfaces in practical use are based on achiral materials whose surfaces have been modified with enantiomerically pure chiral adsorbates, there are many inorganic materials with valuable surface properties that could be rendered enantiospecific, if their surfaces were intrinsically chiral. Such intrinsically chiral surfaces have been prepared in the laboratory and demonstrated to exhibit enantiospecific adsorption, surface chemistry, electron emission, etc. One of the key challenges to the practical implementation of such materials is the development of scalable methods for their production in high surface area, enantiomerically pure form. This perspective addresses possible paths to the scalable fabrication of chiral surfaces, recent developments over the past couple of years and future opportunities for progress.

## COLL 36

### Cycloalkane adsorption on symmetry compatible and frustrated surfaces

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There has been fundamental interest in cycloalkanes for decades from organic and physical chemists alike. Cyclopropane has been principally studied due to the molecule's unique planar structure that lends itself to bond angle strain and reactivities not seen in the other cycloalkanes. However, it is not well known how symmetry, or lack thereof, affects the rotational and vibrational dynamics or the adsorbate film growth process from the monolayer to bulk behavior. This study investigates the effect of surface symmetry on the molecule conformation and configuration as well as the layering of adsorbed cyclopropane molecules for comparison with other small ring alkanes. High resolution volumetric isotherms have been employed to observe the thermodynamics of cyclopropane film growth on graphite (similar symmetries) and (100) MgO (dissimilar symmetries) over a range of temperatures near the triple point of cyclopropane (145.6K). The isotherms have been analyzed to obtain thermodynamic properties (heats of adsorption, isosteric heats, differential entropies and enthalpies) and possible phase transitions. Molecular dynamic simulations of mono- and multilayers

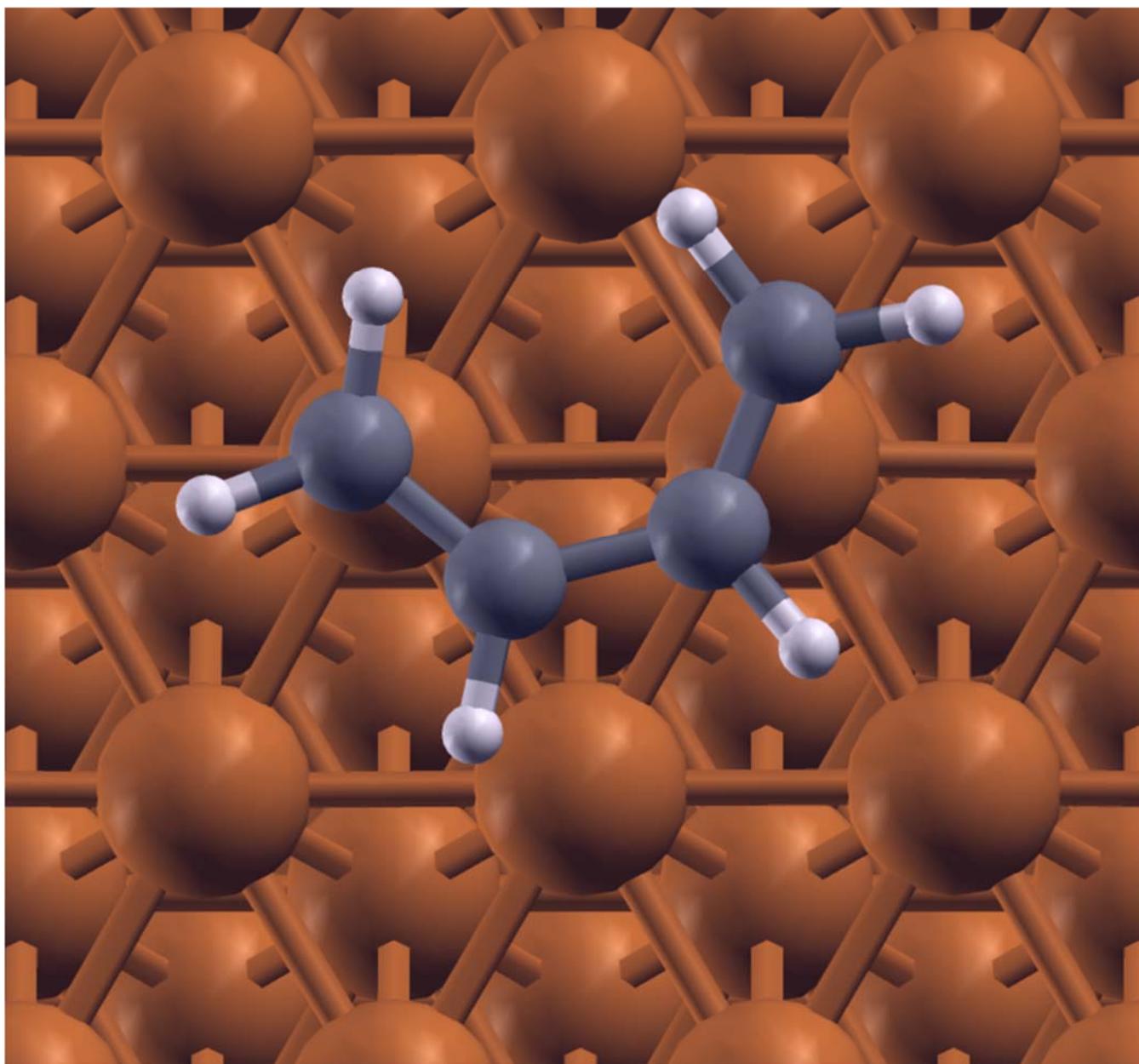
of cyclopropane have been used to obtain binding energies, molecular trajectories, pair-correlation function, and Z-distribution of molecules from the surface. Future neutron diffraction studies and inelastic neutron scattering studies will be used to investigate the microstructure and molecular vibrations in the adsorbed layers

## **COLL 37**

### **Adsorption of butadiene and butene isomers on Cu(111): Insights from DFT**

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Using periodic Density Functional Theory (DFT), we investigate the adsorption of the isomers of 1,4-butadiene and butene on Cu(111). Interestingly, cis-1,4-butadiene experiences a relatively large amount of bond elongation/shortening compared to the trans-isomer. The influence of surface coverage on this previously mentioned bond modulation is also explored.



**COLL 38**

**Thermodynamic, modeling, and neutron scattering investigation on the adsorption of rigid linear hydrocarbons on graphite and MgO (1 0 0)**

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The study of the structure and behavior of adsorbed systems of hydrocarbons have potential applications in important areas of research pertaining to energy storage and the production of efficient catalysts. Our research group has an interest in focusing on homologous series of adsorbed hydrocarbon systems and how their adsorption is affected by the combination of surface and molecular symmetries. Towards this goal, the investigation of a series of small, rigid, linear hydrocarbons is being conducted on surfaces of MgO (1 0 0) and graphite's basal plane. The first two of these molecules to be investigated are acetylene and allene, both of which are molecules that possess an unusually strong quadrupole moment, and similar, but not identical molecular symmetries. The thermodynamics and phase behavior of both systems have been investigated using high-resolution volumetric isotherms. Preliminary neutron diffraction data for acetylene on graphite have also provided more information about the film structures and phase transitions within this system. Lastly, molecular dynamics simulations have been used to help visualize and provide insight into the behavior of these films, from which we are able to examine molecules preferred orientations on the surfaces, molecular trajectories to examine film dynamics, and radial distribution functions to look at molecular ordering transitions.

## **COLL 39**

### **Nanoscale surface chemistry during N<sub>2</sub>O hydrogenation on Au-Ag model catalysts**

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Supported Au nanoparticles are outstanding catalysts for oxidation reactions, guaranteeing high activity and selectivity even at low temperatures, but an optimal size of 3-5 nm is necessary to ensure the O<sub>2</sub> splitting properties of the nanoparticles, and the use of bigger catalysts leads to lower efficiency. The presence of atomic oxygen being the key for Au-based catalysis, its concentration can be increased by changing the chemical composition of either the support or the catalyst itself. However, if the surface concentration of O(ads) is too important, it may result in a loss of selectivity. A more elegant way to balance out these two problems, namely O<sub>2</sub> dissociation vs selectivity-loss, is by alloying Au with Ag, allowing to obtain a catalyst with dual functionality. The efficiency of these systems has already been proven, but fundamental aspects on the structure, composition and their changes during reaction remains unanswered. Studies with field emission techniques, using sharp tips as models for single catalytic particles can give insights into these questions. Field Ion Microscopy (FIM) is used to image the surface of Au-8.8%at.Ag samples with atomic resolution, and Field Emission Microscopy (FEM) allows to image the sample with nanoscale resolution and during the reactive processes. In FEM, the electron emission depends on the work function of the metal and its crystallographic orientation, but more importantly on the presence of

adsorbates. Therefore, in presence of reactive gases, differences in the emission pattern give information about changes in the chemical composition of the adsorbate layer, i.e. the reaction dynamics.

We studied  $N_2O$  adsorption and hydrogenation during which a strong structure-reactivity relationship was observed. By comparison of the FIM and FEM micrographs, in a limited temperature range, adsorption and reaction are governed by the subsequent surface structure: facets of  $\{012\}$  orientations remain dark with a more active border. No permanent surface reconstructions were visible in FIM mode after reaction.

Correlative experiments with PhotoEmission Electron Microscopy (PEEM) lead to the conclusion that for Au-Ag systems, the presence of Ag is not sufficient to explain the exceptional activities observed for example on nanoporous Au-Ag foams. Low coordinated surface atoms, such as found on field emitter tips, contribute largely to the observed reactivity.

## **COLL 40**

### **Directed collision of F or $CF_2$ with $CF_3$ gives umbrella inversion of $CF_3$ followed by collinear ejection of F or $CF_2$**

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Scanning tunneling microscopy (STM) can identify the alignment of individual molecules at a surface, and can also induce reaction one molecule-at-a-time. In a recent STM study we have shown that low-energy electron-induced reaction of  $CF_3$  on Cu(110) at 4.6 K breaks the C-F bond lying along the copper row, producing opposed directed recoil of an F-atom and  $CF_2$  [1]. These energetic products can be 'projectiles' engaged in directed collision at selected impact parameter with a second adsorbate, the 'target' [1-2]. In the present case the target is another  $CF_3$  molecule adsorbed on the same copper row as the projectile, exclusively giving-zero-impact parameter collision dynamics. Here we show that if the projectile is an F-atom, the collision results in umbrella inversion of the  $CF_3$  target and gives an F-atom product that recoils in the direction of, and collinear with, the F- projectile. If the projectile is  $CF_2$ , the collision once again results in umbrella inversion of the  $CF_3$  target and in this case gives a  $CF_2$  product recoiling in the direction of, and collinear with, the  $CF_2$  projectile. Preliminary calculations suggest that the collinearity of projectile and product and the observed umbrella inversion of the target and can be explained as substitution by the projectile in the course of each reaction.

## **COLL 41**

### **Multi-electron reduction capacity and complexity in metal-organic redox assembly at surfaces**

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Metal-ligand complexation at surfaces utilizing redox-active ligands has been demonstrated to produce uniform single-atom metals centers in regular coordination networks, which are of interest for new surface chemistry and catalysis. Two key design considerations are the electron storage capacity of the ligand and the metal-coordinating pockets on the ligand. In an effort to move toward greater complexity in the systems, particularly dinuclear metal centers, our collaborative team has worked toward new ligand designs and assembly strategies. These systems are studied by scanning tunneling microscopy and X-ray photoelectron spectroscopy under ultra-high vacuum. Au(111) and other single crystal metal surfaces are used as pristine model supports to examine the on-surface redox chemistry and structure in detail. Here, I will present several examples of metal-ligand complexation at surfaces, including new results that advance these systems toward greater complexity.

## **COLL 42**

### **Rapid, selective, ambient growth and optimization of copper benzene-1,3,5-tricarboxylate (Cu-BTC) metal-organic framework thin films on a conductive metal oxide**

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Metal-organic frameworks (MOFs) exhibit tremendous promise in sensing applications such as the detection of gasses, molecules, temperature, and pH. However, the incorporation of MOFs onto various sensing platforms, such as optical fibers and quartz crystal microbalances, requires high-quality, well controlled thin film growth techniques that are flexible, scalable, and manufacturable. For this reason, there is a critical need for the ability to efficiently grow dense, uniform MOF films on a wide range of substrates. Here, a facile and rapid strategy to grow copper benzene-1,3,5-tricarboxylate (Cu-BTC) MOF thin films using the plasmonic substrate aluminum-doped zinc oxide (AZO) as a seed layer is demonstrated. The AZO templates Cu-BTC growth, with MOF formation only occurring on the AZO layer via a hydroxy double salt intermediate. As a result, growth chemicals can be recycled, minimizing waste. Remarkably, a dense Cu-BTC layer can be obtained within 10 minutes at room temperature and ambient conditions, circumventing energy-intensive heating steps and long reaction times. The formation pathway of the Cu-BTC films was investigated in detail, with the role of solvent growth conditions, pH, and the identity of the Cu salt anion analyzed extensively. We demonstrate that each of these variables can be exploited to systematically fine-tune both the packing density and size of the MOF crystals on AZO. The technique described here is rapid, tunable, selective, and applicable to a variety of substrates, providing a robust, versatile strategy for incorporating MOFs into sensing devices.

## COLL 43

### **Intrinsic thermal framework stability of UiO-67 metal-organic frameworks**

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Metal-Organic Frameworks (MOF) are robust hybrid materials with highly tunable geometries, allowing for direct control over chemical and physical properties making them suitable for a variety of filtration, catalytic and detection applications. While the ability to readily tune complex chemical and physical functionality is highly desirable for targeted applications, the thermal stability and impact on applications must also be considered. In this work, we provide a detailed characterization of the intrinsic thermal behavior of the UiO-67 series MOF and functional analogs using temperature-programmed FTIR and mass spectrometric techniques under ultra-high vacuum (UHV). The UiO-67 MOFs show reversible (< 473 K) and irreversible (up to 1273 K) thermal behavior, revealed in the IR spectra. When coupled with mass spectrometry, we have identified the evolution of key structural transformations during the degradation process, including: node dehydration and total node-linker separation. Additionally, we have demonstrated that functionalization of the organic linker reduces thermal stability in the order: UiO-67 > UiO-67-CH<sub>3</sub> > UiO-67-NH<sub>2</sub>. Moreover, thermal treatment impacts the uptake of selected probe analytes as defects develop and heal, and as the pore structure of the MOF transforms. These results provide a fundamental understanding of how the properties of these UiO-67 MOFs govern their thermal stability which is critical for the future development of ultra-stable MOFs and for the interpretation of binding interactions with guest-molecules.

## COLL 44

### **NMR relaxation, powder wettability and Hansen solubility parameters applied to colloidal materials**

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The ease with which particles can be dispersed in a liquid is dependent on the details of the liquid to be used and the surface chemistry of the particles. The particle wettability, as controlled by dispersion forces, dipole-dipole forces and hydrogen bonding is the primary influence. Being able to predict the appropriate liquids to use for a given particle is of considerable interest to the formulator; there has been much interest in semi-empirical routes to selecting the optimum solvent (or solvent mixture) for pigment particles

The Hansen Solubility Parameters (HSP) approach, originally devised to study polymer-solvent compatibility, can be applied to solid materials - and is then termed the HDP. Determination - traditionally by visual observation of sedimentation - is subjective, time-consuming, error prone and is only qualitative. Extinction profiles measured over centrifugation time are more quantitative; the influence of density and viscosity of different solvents employed must be accounted for and the solids concentration must be chosen with care.

NMR relaxation measurements are sensitive to the same intermolecular forces between solvent and particles with which HDP are concerned. We will show relaxation data obtained using various hydrophilic and hydrophobic powders dispersed in a range of polar and non-polar solvents in Hansen space.

Results suggest that a straightforward, quantitative, fast instrumental approach to determining the HDP of a nanomaterial is feasible and, further, that NMR relaxation can also discriminate between suspensions that may initially appear similar but exhibit different long-term colloidal stability. NMR relaxation measurements can be made at almost any industrially relevant solids concentration without requiring further sample preparation; any hydrogen-containing solvent can be used.

The ability to project solid-liquid interactions obtained by NMR relaxation into Hansen space is powerful, is much simpler and easier than sedimentation/centrifugation and can potentially provide formulators with a time-saving method to optimize and select the liquid composition (solvent plus surfactant additives) for desired particle suspension performance.

## **COLL 45**

### **Antiferromagnetic to ferromagnetic transition in geometrically frustrated quasi-two-dimensional colloidal crystals**

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We experimentally study the behavior of geometrically frustrated quasi-two-dimensional colloidal crystals with both attractive and repulsive interparticle interactions. We create a two-dimensional triangular lattice by confining a monolayer of close-packed micron-sized spheres between two parallel glass coverslips. The wall separation is slightly larger than one particle diameter, which facilitates buckling in the monolayer of particles. Each particle can occupy either a buckled up or down position on its lattice site, where neighboring particles favor opposite positions to maximize their free volume and hence frustrates the third neighbor. Thus, our system is analogous to the Ising antiferromagnet on a triangular lattice where particle up-down position is analogous to Ising spins. Using

video microscopy, we measure the temporal evolution of each "spin" and tune the "Ising coupling constant" by adjusting the interparticle interaction. Our preliminary results show the transition of this coupling constant from antiferromagnetic to ferromagnetic in our system.

## **COLL 46**

### **Stabilization of cationic aluminum hydroxide clusters in high pH environments with a CaCl<sub>2</sub>/L-arginine matrix**

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Polyaluminum Keggin structures and larger clusters have a number of applications in water treatment, clay pillaring, active pharmaceutical ingredients (APIs), and serve as model molecules to study mineral surfaces. However, only a few aluminum Keggin structures have been isolated which can be partially attributed to their metastable nature. In fact, small perturbations in aluminum concentration, temperature, pH, or a number of other factors can cause significant structural transformations leading to polydispersity, completely different structure moieties, degradation into aluminum chloride monomers or precipitation as bulk aluminum hydroxide. In this work, we report the unprecedented stabilization of one of the more common Keggin aluminum clusters, Keggin Al<sub>13-mer</sub>, in alkaline pH environments (*i.e.*, pH > 9) by utilizing a combination of CaCl<sub>2</sub> and L-arginine. Electronic structure calculations were employed and demonstrate favorable energies for binding configurations between calcium and L-arginine at ratios present in the high pH system. The discovery of soluble cationic polyaluminum clusters at pH > 7 unlocks a new realm of synthesis, mechanism, and application of aluminum clusters.

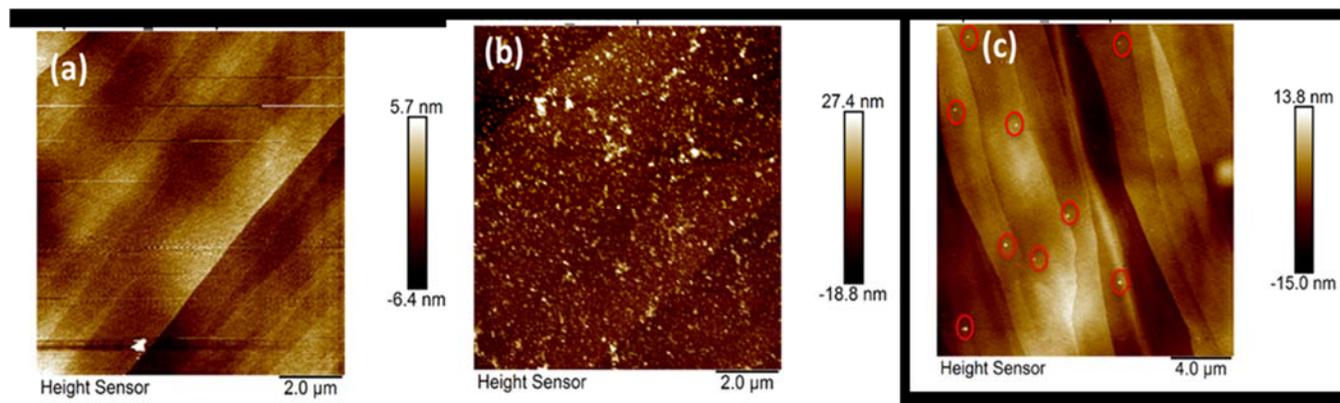
## **COLL 47**

### **Characterization of Colloidal, Mechanical and Electrochemical Properties of Nanobubbles in Water**

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Nanobubbles (NBs) in water exhibit many appealing characteristics, such as a long residence time of bubbles in water due to their low buoyancy and stability against coalesces, collapse or burst. Other characteristics are like long retention time in water empower reactions, enhanced mass transfer in processes such as ozonation or aeration to increase dissolved ozone and oxygen in water for reactions or pollutant degradation. In addition, NBs can exceed solubility barriers and reach supersaturated state for ozone, oxygen or other gases that may have low solubility in water. Therefore, NBs hold promise in green and sustainable engineering applications in diverse fields

(e.g., water/wastewater treatment, food processing, medical applications, and agriculture). NBs were generated by a ceramic membrane generation system in Zhang's laboratory at NJIT. The hydrodynamic diameters of NBs are around 200~400 nm depending on the injection gas pressure and surface hydrophobicity of the ceramic membrane. The colloidal sizes and zeta potentials of NBs were measured by dynamic light scattering (DLS). NBs that deposited on substrate surface (e.g., HOPG, mica or silicon wafer) were also imaged by atomic force microscopy (AFM). We have also sought to establish conditions for AFM nanomechanics measurements of NBs to determine the elastic modulus and internal pressure. We further analyzed the electrochemical (EC) activity of different NBs (e.g., oxygen, hydrogen, and nitrogen), using cyclic voltammetry (CV) and scanning electrochemical microscopy coupling with AFM (SECM-AFM), respectively.



AFM height images of HOPG surface (a) with a drop of DI water; HOPG surface with a drop of ONBs water (b) 1 hour after NBs generation; (c) 72 hours after generation.

## COLL 48

### Generation of anisotropic gold and gold-palladium bimetallic nanoparticles on functionalized surfaces

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Gold nanoparticle arrays catalyze alcohol oxidation reactions in methanol fuel cells. We have studied four different alcohols for potential replacement of methanol and two classes of alternative nanostructured surfaces compared to pure gold nanoparticles. Gold-palladium bimetallic nanoparticles are generated on TMSPP (trimethoxysilylpropyl (polyethyl enimine)) functionalized silicon and indium tin oxide (ITO) coated glass surfaces through reduction of surface bound metal ions ( $\text{AuCl}_4^-$  and  $\text{PdCl}_4^{2-}$ ) by appropriate reducing agent. The concentrations of gold and palladium precursors were

systematically varied in the surface attachment step of metal ions to generate nanoparticles with different mole ratios. The *in situ* synthesis of anisotropic gold nanorods on functionalized surfaces was derived from surface bound gold nanoparticle seeds of specific sizes. Gold seeds are generated on TMSPP functionalized silicon and ITO glass through adsorption of gold ions followed by reduction with a strong reducing agent. Surfaces with gold nanoparticle seeds are then submerged in growth solutions of cationic surfactant (cetyltrimethyl ammonium bromide CTAB & benzyldimethyl ammonium chloride BDAC), gold (III) trichloride, and weak reducing agent to direct the growth of anisotropic shapes. Length of exposure to the growth solution is varied. UV-Visible measurement shows shift in the surface plasmon absorption band due to varied Au:Ag ratio in bimetallic nanoparticles and for anisotropic growth of pure gold nanorods. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) are used follow the morphology of these structures. X-ray photoelectron spectroscopy (XPS) is used to measure the elemental composition of the bimetallic nanoparticles. The catalytic activity of all these nanostructured are assessed by cyclic voltammetry using different multi-carbon alcohols and polyalcohols.

## **COLL 49**

### **Stabilization of STRIPS bijels with mixtures of hydrophilic and hydrophobic nanoparticles**

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Bicontinuous interfacially jammed emulsion gels (bijels), in which the oil and water phases are continuous throughout the structure, have potential as media for simultaneous reaction and separation in continuous mode. Among the possible fabrication paths the solvent transfer-induced phase separation (STRIPS) method has proven to be a powerful approach to produce bijels in a continuous fashion with a broad selection of starting materials. STRIPS bijel formation involves the preparation of a precursor suspension which contains oil, water, nanoparticles and co-solvent, typically ethanol, that is injected in a water bath to trigger the oil-water phase separation. The successful formation of bicontinuous domains requires the use of neutral wetting particles which is achieved using nanoparticles with surfactant. However, this approach is not appropriate in applications that that require surfactant free environment such as enzymatically driven reactive separations. In this work, we use a pair of nanoparticles, one hydrophilic, the other hydrophobic to stabilize STRIPS bijels. We produce bijels using oil phases with broad ranges of polarity by simply changing the ratio of the two nanoparticles. We show how the ratio of the hydrophilic to hydrophobic nanoparticles required to form stable bijels changes as a function of the dielectric constant of the oil. Very non-polar oils require a smaller ratio than partially polar oils. If a sufficiently polar oil is selected, only the hydrophilic type of nanoparticles is necessary, thus simplifying

the procedure for STRIPS bijels manufacturing process. This approach widens that type of oils that can be used for the formation of STRIPS bijels. Moreover, the use of two different particles opens up the possibility to imbue the interface with two distinct functionalities that could be useful for reactive separation applications.

## **COLL 50**

### **Influence of nanoparticles on the dynamics and clustering of active colloids proximate to a boundary**

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Active colloidal particles regularly interact with surfaces in applications ranging from microfluidics to sensing. Herein, experiments and simulations were conducted to illustrate the impact of nanoparticles on the propulsion dynamics and clustering behavior of micrometer scale catalytic active Janus colloids near a boundary. The addition of either negatively charged 20 nm polystyrene particles or polyethylene glycol (PEG) of molecular weight 6K and 600K decreased the apparent propulsion of a Janus colloid at infinite dilution to near zero. These experiments were extended to more concentrated systems in which the same active Janus colloids, in the absence of added nanoparticles, formed clusters. The extent of clustering tended to increase with fuel concentration. Similar to the case of Janus colloids at infinite dilution, the addition of polymers had a dramatic impact on clustering behavior. Following the addition of either 6K or 600K PEG, clustering was significantly mitigated, with the higher molecular weight polymer having a more dramatic effect. Complementary agent-based simulations considering the impact of hydrodynamics for active Janus colloids were conducted in the range of separation distances inferred from experiment. These simulations showed that propulsion speed decreased monotonically with decreasing average separation distance and also that clustering was reduced with decreasing propulsion speed. Taken together, these experiments and simulations demonstrate the impact of depletion and conductivity arising from the addition of nanoparticles on the dynamics and clustering of active colloids proximate to a boundary.

## **COLL 51**

### **Three dimensional multiphasic structures via vaporization induced phase separation (VIPS)**

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Studies of bicontinuous interfacially jammed emulsion gels (bijels) have greatly expanded the possibilities of multiphasic systems. We have previously introduced the solvent transfer induced phase separation (STRIPS) method to prepare bijels from ternary mixtures of oil, water and co-solvent (ethanol). Although STRIPS enables continuous processing, the requirement of the outer aqueous phase limits their applications to liquid environments. Enabling production of bijels in air would further expand their applications in areas such as coatings and surface modification applications. In this work, we demonstrate a new method of producing three dimensional multiphasic structures (including bijels) via vapor-induced phase separation (VIPs). In VIPs, the evaporation of the co-solvent from a ternary mixture of oil, water and ethanol, induces phase separation. Particles present in the mixture attaches to the interface and arrests the phase separation between water and oil. VIPs enables the fabrication of films and coatings via spreading or spraying particle-laden suspension onto a surface without the need for an outer aqueous phase. The structure of VIPs films on different substrates are characterized, and the influence of initial composition, quenching depth and particle concentration are investigated.

## **COLL 52**

### **Symmetry-based discovery of multicomponent, two-dimensional colloidal crystals**

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We present a systematic method for the elucidation of crystalline ground states to calculate the phase behavior of multicomponent colloidal materials. In two-dimensions there are exactly seventeen “wallpaper groups” which represent distinct combinations of the isometries of a Euclidean plane. Using properties of these groups, we develop an algorithm to cover a plane with a fixed number of arbitrary components in all ways that satisfy a desired stoichiometric ratio. These combined symmetry-stoichiometry rules dramatically reduce the number of possible configurations, which generally suffer from a so-called “combinatorial explosion” otherwise making extensive, random structure searching computationally infeasible. These candidates represent a complete, systematic coverage of all wallpaper groups, which helps to ensure that the correct ground state is discovered. With subsequent continuum relaxation, this approach is able to predict crystal structures *in silico* for multicomponent colloidal mixtures. We use this approach to investigate the ground state phase behavior of multicomponent systems inspired by multifunctional DNA-coated colloidal mixtures, with a particular focus on stable, low-density “open” crystals. We demonstrate the approach for binary and ternary mixtures at zero ambient pressure in order to explore how complexity can be achieved

through the combination of many components with simple interactions rather than a smaller number of components with more complicated potentials.

## **COLL 53**

### **Engineering crystal morphology using an additive: Case study of stearic acid**

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Organic crystals are principal building blocks for food, pharmaceuticals, and consumer goods. Crucial performance characteristics such as stability of formulations, the color of pigments, *etc.* are decided by the choice of shape and size of the crystals. The desired morphology of the crystal can be achieved by tailoring the process parameters like cooling rate, shear rate, or use of additives. In this study, we tune the crystal shape and size of stearic acid crystals during crystallization. Highly deformed crystal structures can be obtained in the presence of additive during crystallization. The range of crystal shapes spans rhombic to fractal-like and spherulitic structures. For an increasing concentration of additive, the crystal morphologies observed in a sequence are: perfectly rhombic, deformed rhombic shape with needles at the edges, tree-like structure, densely branched tree-like structure and spherulitic structure. In addition, the higher the relative supersaturations of stearic acid, the higher the concentration of additive required for the shape transitions. This evolution of different crystal habits can be related to the facial growth rates of the crystals. The growth rates are dependent on the molecular interactions of solute and additive at the growing edge. Any instability and/or change in adsorption energies of solute (stearic acid) and additive at the growing interface affect the growth rate and eventually affect the crystal habit. In this talk, we present a framework to understand this change in morphology based on the mechanism of crystal growth due to the adsorption of additive on the growing interface of crystal.

## **COLL 54**

### **Computational modeling of colloidal nanocrystals: Equilibrium and far-from-equilibrium self-assembly**

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Colloidal nanocrystals offer a rich platform to design materials with many applications, from catalysis and drug delivery to electronics. These colloids are composed by a hard-core material surrounded by a soft, organic component. Experiments have shown that the collective dynamics of these nanocrystals can give place to self-assembled complex lattices. However, a complete description of the phase behavior of these materials is still lacking. In this work, we use a simple representation of a colloidal nanocrystal, and performed extensive Molecular Dynamics simulations to elucidate the phase behavior of

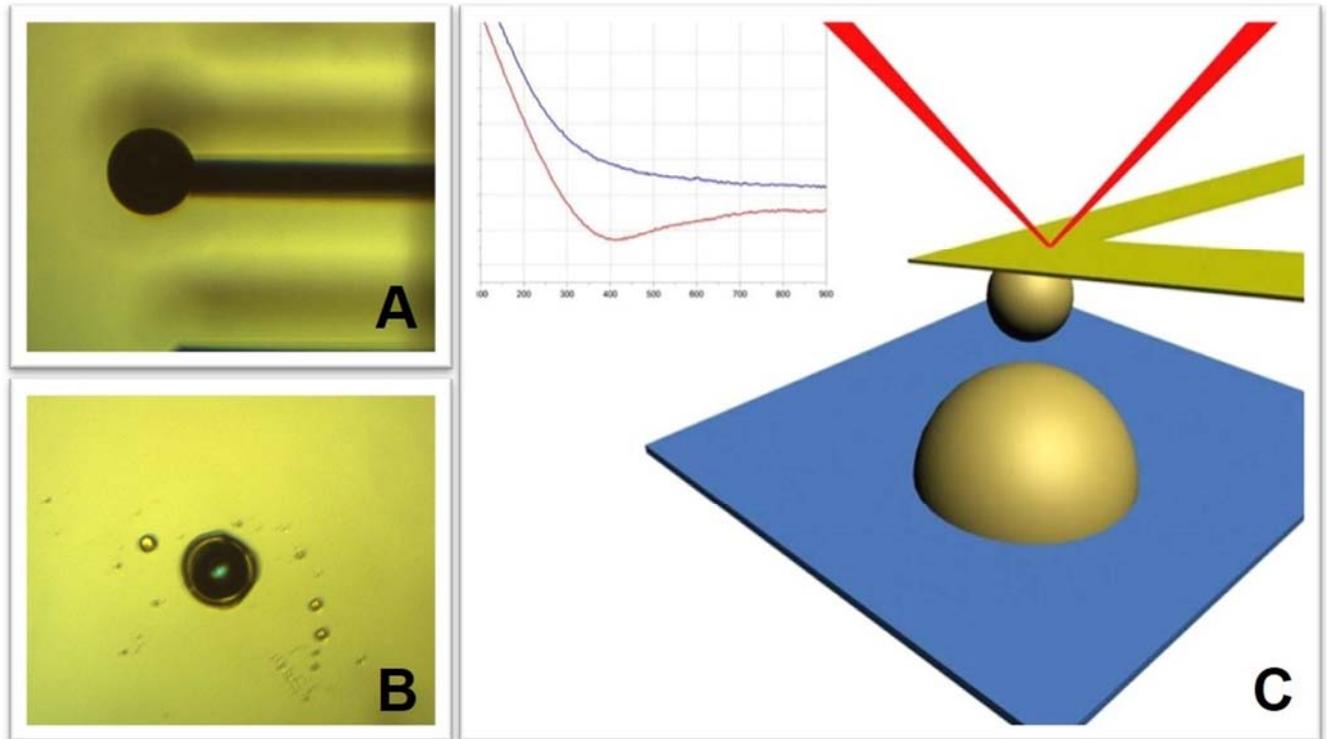
this model as experimentally-relevant parameters are varied. Our calculations found a rich repertoire of possible equilibrium colloidal arrangements: hexagonal, rhomboid, honeycomb, stripe phases, quasicrystals, and hierarchical self-assembled structures. Our results highlight the important role of the size of the soft shell on the equilibrium self-assembly. We use this model to represent thermo-responsive soft shells, and explore the far-from-equilibrium self-assembly in response to time-varying external temperature conditions.

## **COLL 55**

### **AFM study of colloidal forces between asymmetric hydrophobic bodies in aqueous solution**

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Particular attention is given to elucidating the interaction of both DLVO forces and non-DLVO forces present in colloidal systems due to its significance on emulsion stability. In this work, an experimental study was conducted to explore the forces effective between asymmetric hydrophobic bodies (particles, bubbles, oil droplets, solid surfaces) in aqueous solution with the application of Atomic Force Microscopy (AFM). Subsequently, analysis of the acquired force data was carried out based on Stokes–Reynolds–Young–Laplace theoretical model to provide an explicit understanding of the physical principles of forces related to such systems. The results show that van der Waals and electrical double-layer forces, in combination with hydrophobic force and other structure forces including steric hindrance stem from long-chain macromolecules, play a vital role in determining the state of the intervening liquid film. It turns out that the hydrophobic force between two hydrophobic bodies could be altered by changing the content of ethanol or glycerol in aqueous solution. We demonstrate that, with a subtle control of the continuous phase condition, the colloidal forces between dispersed bodies, and hence the stability of the colloidal system, could be suitably manipulated.



(A) The air bubble attached to AFM cantilever; (B) The lens formed by coalescence of bubble and oil droplet in aqueous solution; (C) Schematic of the force measurement by AFM.

## COLL 56

### Efficient trapping of fluorinated therapeutics at the air/water interface using fluororous interactions: Implications for medical microbubble design

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Fluorinated therapeutics are key for the diagnosis of neurodegenerative diseases (e.g. amyloid imaging) and treatment of cancers, calling for efficient carriers. Microbubbles show definite potential to deliver active compounds and are intensely investigated for their ability to cross the brain blood barrier, facilitating access to the nervous central system. However, their development is hindered by their limited pay-load as compared to emulsion droplets, liposomes, or nanoparticles.

We found that fluorocarbon gases can be extremely effective for promoting adsorption at the air/water interface of a wide range of molecules, including surfactants, phospholipids, proteins, biomarkers and diblock copolymers. As an important consequence, the encapsulation of such compounds in the shell of microbubbles is enabled or strongly facilitated, opening a new approach to drug delivery driven by hydrophobic interactions. We will focus on a series of *F*-nitrosoimidazoles taken as a model of a fluorinated bioactive agent, EF5, which is investigated in the clinic as a cell

hypoxia biomarker and a tracer for PET when radiolabeled with  $^{18}\text{F}$ . Using neutron reflectometry, we were able to demonstrate that substantial concentrations of these *F*-biomarkers (up to 1:1 molar ratio with respect to the phospholipid) can be trapped in the interfacial film. Interestingly, nanoparticles, including of iron oxide, carbon and cerium oxide, can also be recruited at a gas/water interface by fluorocarbons and form stable microbubbles. These new phenomena will be presented along with some of their perspectives of applications.

## COLL 57

### Tuning morphology of low fluorine-content reverse micelles in supercritical carbon dioxide by pressure, water content, and UV-light irradiation

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Our earlier studies found FC-HC hybrid surfactants FC6-HC $n$  having a perfluorohexyl chain and a hydrocarbon chain ( $n$ : hydrocarbon length) to be not only a super-efficient water solubilizer but also a CO<sub>2</sub>-thickener by formation of rod-like reverse micelles (RRMs) in scCO<sub>2</sub>. Aiming at exploring a lower fluorine content surfactant to be a more practical CO<sub>2</sub>-thickner, this study examine formation of RRM of the double C<sub>2</sub>F<sub>5</sub>-tail surfactant 2FG(EO)<sub>2</sub> and tuning its micelle morphology by water content, pressure and UV-light irradiation with a photochromic dye 1,3,3-trimethylindolino-6'-nitrobenzopyrrolospiran (SP).

The 50mM surfactant/7mM SP/D<sub>2</sub>O/CO<sub>2</sub> mixtures at 45 °C and 350 bar displayed SANS profiles for RRM at water-to-surfactant molar ratio ( $W_0$ ) = 5-10 and for lamellar liquid crystals with Bragg peaks with  $W_0$  = 20. With decreasing pressure from 350 bar to 200 bar, those SANS profiles for the molecular assemblies disappeared due to formation of a W/C macroemulsion or precipitation of the surfactant. By fitting theoretical curves of cylindrical particles to the SANS data, length of RRM was found to increase from 65 Å to 432 Å with loading water from  $W_0$  = 5 to 10, although the radius was almost same at 10.4-10.5 Å. UV-light irradiation at the wavelength 365 nm for 3 min also decrease RRM length at  $W_0$  = 10 by 36 Å due to photoisomerization of SP.

## COLL 58

### Perfluorinated surfactant micelle formation and structure in aqueous media

**Samhitha Kancharla**<sup>1</sup>, **Dmitry Bedrov**<sup>2</sup>, **Marina Tsianou**<sup>1</sup>, **Paschalis Alexandridis**<sup>1</sup>, [palexand@buffalo.edu](mailto:palexand@buffalo.edu). (1) SUNY Buffalo, Buffalo, New York, United States (2) Univ of Utah, Salt Lake City, Utah, United States

Fluorinated surfactants find niche applications because of their high chemical and thermal stability, their incompatibility with both water and hydrocarbons, and their unique ability to render surfaces non-stick. However, several widely used fluorinated surfactants have been found extremely resistant to degradation, accumulate in the environment, and have long half-lives in humans, consequently causing great concern. In the context of sequestering fluorinated surfactants from aqueous media, we research solution properties of fluorinated surfactants, with a focus on how such surfactants interact with (bind to) other molecules or particles/surfaces. We report here on ammonium perfluorooctanoate (APFO) micelle formation and structure in aqueous solutions and in the presence of various additives, probed with complementary experimental techniques (conductivity, surface tension, small-angle neutron scattering) and atomistic simulations. The results inform the fate and transport of per- & poly-fluoroalkyl substances (PFAS) in the environment.

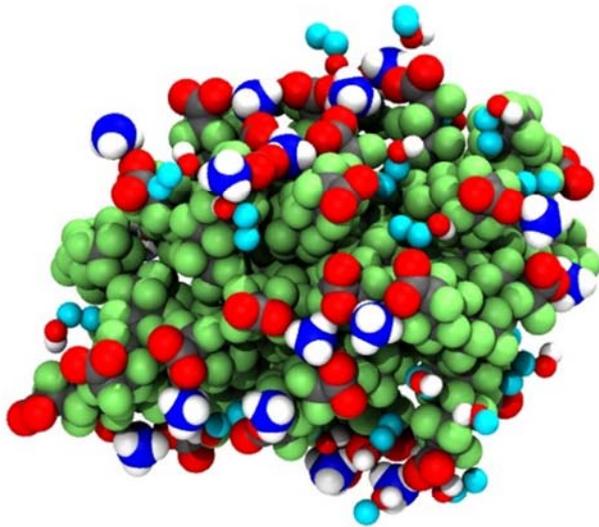
## **COLL 59**

### **Influence of Co-solvents on the structure of perfluorooctanoic acid micelles in water: Molecular dynamics simulation study**

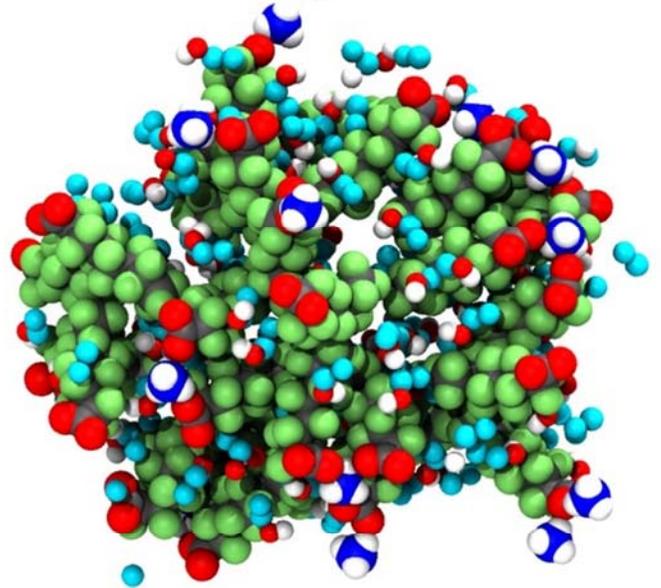
*Dengpan Dong*<sup>1</sup>, [dengpan.dong@utah.edu](mailto:dengpan.dong@utah.edu), *Dmitry Bedrov*<sup>2</sup>. (1) Materials Science and Engineering, University of Utah, Salt Lake City, Utah, United States (2) Univ of Utah, Salt Lake City, Utah, United States

The left-over of perfluorooctanoic ammonium (PFOA) in environment is responsible for recent water contamination cases in several states in the US. The EPA established the advisory level of PFOA in drinking water to be 70 ng/L. However, the limitations of traditional removal techniques e.g. activated carbon development of novel removal methods stimulate the interest in understanding the mechanism of PFOA micelle self-assembly. In this study, the self-assembly of PFOA micelle in water is systematically investigated using molecular dynamics simulations. Since ethanol is one the most commonly used cosolvents, the interplay between added ethanol and micelles is studied as a function of ethanol concentrations. The influence of other additive molecules, including urea, cyclodextrin, *etc* on the micelle morphology is also investigated. To understand the mechanistic interplay between PFOA and co-solvent characteristics, the dipole moment of model solvent additives is systematically varied to modify co-solvent hydrophobicity/hydrophilicity. The phase diagram with respect to scaled co-solvent properties and weight fraction of co-solvent has been derived.

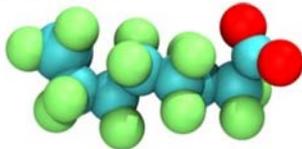
## Compact Packing



## Loose Packing



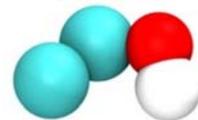
**PFOA**



**Ammonium**



**Ethanol**



Small molecules like ethanol play a significant role in controlling the morphology of PFOA micelles.

### COLL 60

#### Investigation of PFOA and PFOS enrichment mechanisms in sea spray aerosol proxy systems

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Perfluoroalkyl substances are man-made chemicals that have been widely used in industrial processes and military operations since World War II. While the exact toxicology of these substances has not been deciphered, perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) have been linked to liver, kidney, and testicular cancer, as well as hypertension and low birth weight in children. Additionally, PFOA and PFOS are persistent in the environment and are transported globally, as they are enriched in sea spray aerosol (SSA) particles over the Arctic Ocean. We aim to characterize the surface activity of PFOA and PFOS at SSA proxy surfaces to better understand the pollutant enrichment in SSA particles. Surface tensiometry and infrared reflection-absorption spectroscopy are used to determine the surface adsorption

constants via fitting to the Langmuir-Szyszkowski equation. PFOA and PFOS exhibit higher surface activity in the presence of divalent seawater cations. However, PFOA and PFOS surface activity is reduced when mixed with palmitic acid, a highly surface-active lipid found in SSA. Further study is underway to determine the impacts of other dissolved organic compounds on the interfacial activity of PFOA and PFOS at SSA proxy surfaces.

## **COLL 61**

### **Perfluorinated amphipolar polymers at interfaces**

*Markus Klapper, klapper@mpip-mainz.mpg.de, Katharina Kluthe, Thomas Schuster.*  
Max-Planck-Institute for Polymer Research, Mainz, Germany

Surface active compounds play a decisive role for various applications, such as emulsions, polymer dispersions and coatings. While in most cases one focuses on hydrophilic/ hydrophobic structures herein the use of perfluorinated amphiphiles is discussed. In four different examples, it is demonstrated that these molecules are very powerful surface active compounds. However, toxicity of the perfluoroalkyl compounds is a major concern and only short perfluoroalkyl chains can be tolerated. In particular, (i) fluorinated amphiphilic block copolymers were designed to stabilize nonaqueous emulsions even suitable for metallocene catalyzed polymerisations, (ii) statistical copolymers were utilized to functionalize and compatibilize the surface of inorganic nanoparticles, and finally (iii) terpolymers were applied to obtain superhydrophobic properties. The polymers and oligomers are characterized by NMR spectroscopy and diffusion studies. The self-assembly behavior is investigated by DLS.

The utilization of such fluorinated high *M.W.* amphiphiles based on small perfluoroalkyl subunits leads to materials having novel or enhanced interface active features, such as stabilization of a liquid-liquid-interface, surface modification and compatibilisation, and superhydrophobic properties. It is demonstrated that the properties can be optimized by free (statistical polymer) or by the more sophisticated controlled (block copolymer) radical polymerization. The composition of the copolymers can simply be changed by varying the monomer concentration. Depending on the application, optimized co- or terpolymers with hydrophobic and/or hydrophilic comonomers are synthesized.

(iv) In a final example short perfluoroalkyl-PEO compounds are presented to obtain surface active compounds matching the requirements for non-toxic perfluoro compounds with very fast diffusion coefficients. Such compounds are essential to avoid bubble formation in polymer coatings .

## **COLL 62**

### **Fuel for firefighting foam evaluations: Gasoline vs heptane**

**Arthur Snow**, *arthur.snow.ctr@nrl.navy.mil*, **Spencer Giles**, **Katherine Hinnant**, **John Farley**, **Ramagopal Ananth**. Chemistry Division, Naval Research Laboratory, Washington, District of Columbia, United States

Aqueous film-forming foams (AFFF) rapidly extinguish fuel fires and are generated from commercial surfactant concentrates. The most active component in AFFF formulations are fluorocarbon surfactants. The unique properties of these surfactants (low surface tension, hydrophobicity, oleophobicity, thermal stability) enable their formulations to form aqueous films and foams that spread very rapidly on burning hydrocarbon fuel surfaces, function as a very stable and excellent barrier to permeating hydrocarbon fuel vapors and thermally insulate the fuel surface from the combustion above. Since 2000, use of these fluorocarbon surfactants has been increasingly limited due to bioaccumulation and toxicity. In recent years research efforts have been initiated to develop fluorine-free foams (F3) to be used in place of AFFF for hydrocarbon pool fire suppression, and commercial F3 concentrates are becoming available. International standards for firefighting foam evaluation require qualifying tests in which a specific fuel, usually heptane, is prescribed. The US MilSpec standard is an exception and specifies alcohol-free gasoline as the test fuel. Our research has focused on utilization of siloxane surfactants in combination with alkyl polyglycoside surfactants in F3 formulations. These formulations are very effective on heptane pool fires. However, unlike AFFF formulations which are very effective on both heptane and gasoline fires, a large divergence in fire suppression effectiveness is observed when this F3 formulation is used on a gasoline fire. A testing of commercial F3 formulations also shows a similar fire extinction dependence on fuel identity. The origin of this gasoline-heptane divergent fire suppression behavior resides in the aromatics components of gasoline.

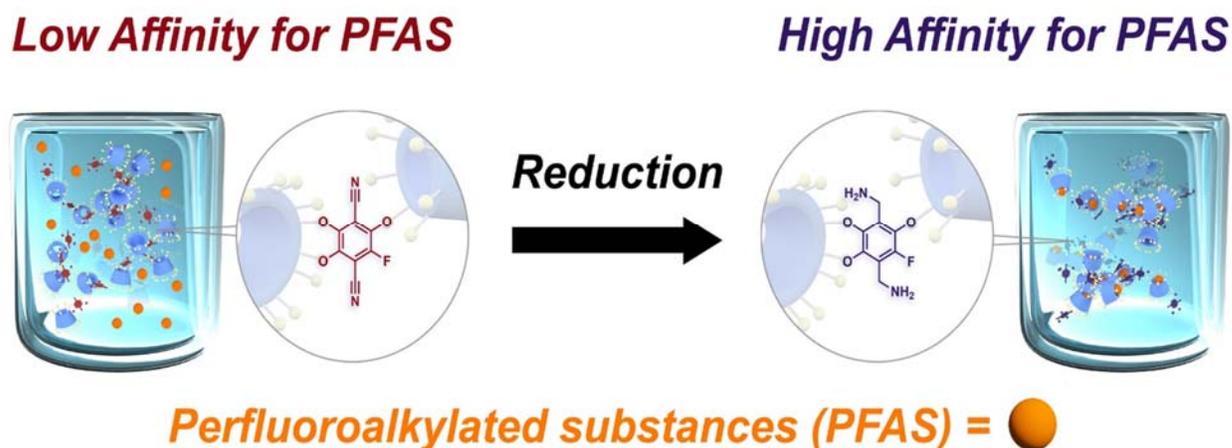
## **COLL 63**

### **Novel cyclodextrin-based adsorbents to remove per- and polyfluorinated alkyl substances from water**

**Max Klemes**<sup>1</sup>, **Yuhan Ling**<sup>2</sup>, **Casey Ching**<sup>2</sup>, **Leilei Xiao**<sup>1</sup>, **Damian E. Helbling**<sup>2</sup>, **William R. Dichtel**<sup>1</sup>, *wdichtel@northwestern.edu*. (1) Chemistry, Northwestern University, Wilmette, Illinois, United States (2) School of Civil and Environmental Engineering, Cornell University, Ithaca, New York, United States

Per- and polyfluorinated alkyl substances (PFASs), have come under increased scrutiny because of their environmental persistence and association with various health problems. A  $\beta$ -cyclodextrin polymer linked with tetrafluoroterephthalonitrile (TFN-CDP) has high affinity for cationic and many neutral MPs from contaminated water because of anionic groups incorporated during the polymerization. But TFN-CDP does not bind many anionic MPs strongly, including anionic PFASs. To address this shortcoming, we reduced the nitrile groups in TFN-CDP to primary amines, which reverses its affinity towards charged MPs. TFN-CDP exhibits adsorption distribution coefficients ( $\log K_D$  values) of 2-3 for cationic MPs and -0.5-1.5 for anionic MPs, whereas the reduced TFN-CDP exhibits  $\log K_D$  values of -0.5-1.5 for cationic MPs and 2-4 for anionic MPs, with

especially high affinity towards anionic PFASs. Kinetic studies of the removal of 10 anionic PFASs at environmentally relevant concentrations showed 80-98% removal of all contaminants after 30 min and was superior to commercial granular activated carbon. These findings demonstrate the scope and tunability of CD-based adsorbents derived from a single polymerization and the promise of novel adsorbents constructed from molecular receptors.



## COLL 64

**Particulate clay with a polyamine fluorocarbon polymer stationary phase as an adsorbent for the removal of perfluorinated chemicals from water**

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Perfluorinated chemicals (PFCs), including perfluorootanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) are organic compounds that have a fully or partially fluorinated carbon chain with a polar end group. These industrial compounds, with ubiquitous stable persistence in the environment, have been shown to cause adverse physiological effects. To date, various sorbents such as activated carbon, ion exchange resins, and clay have been reported for the removal of PFCs from water. We have shown a weak anion exchange (WAX) polymer derivatized with Kel-F 800, a co-

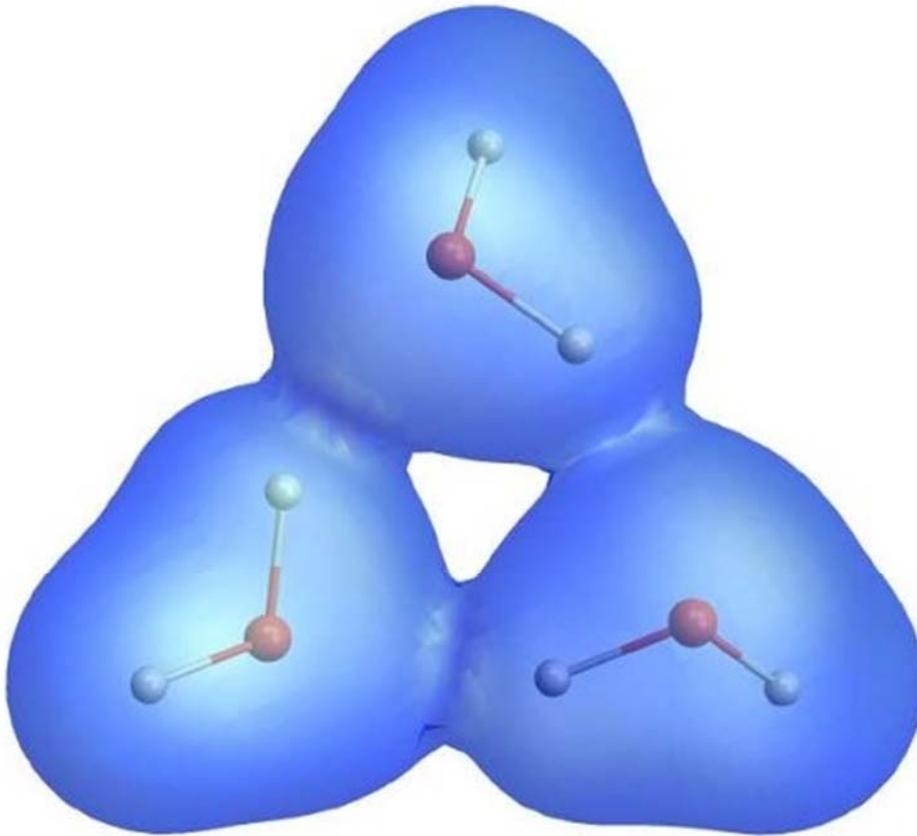
polymer of chlorotrifluoroethylene and vinylidene fluoride, is effective for selective removal of PFOA from water. However, this material is too expensive to be scaled up for preparative (industrial scale) removal of PFCs from water. It is known that palygorskite-montmorillonite (Pal-Mt) clay particles are effective in the removal of organic amines such as the pharmaceuticals carbamazepine, diphenhydramine, and atenolol from water through likely interaction with the silanol groups present in the clay structure. In addition, thermal recycling of this clay by heating to 500 °C, has been shown to be feasible. Pressure stability of these clay particles when packed in 100 x 4.6 mm ID columns is good permitting breakthrough data of pumped analyte solutions. Recently, we have discovered that Pal-Mt clay, after derivatization with a polyamine such as polyethyleneimine (PEI), can be functionalized with Kel-F 800 to promote fluorophilic interactions. Variation of the PEI molar mass and consideration of other polyamines to generate this WAX-fluorocarbon polymer clay adsorbent is under study. Column breakthrough studies are also planned to generate Thomas and Yoon-Nelson kinetic data.

## **COLL 65**

### **Visualizing chemistry: Atomic sizes and molecular shapes from the classical turning surface of the Kohn-Sham potential**

*Egor Ospadov*<sup>1</sup>, *Viktor N. Staroverov*<sup>2</sup>, *Jianmin Tao*<sup>3</sup>, ***John P. Perdew***<sup>4</sup>, *tuf25956@temple.edu*. (1) Quantum Benchmark, Inc., Kitchener, Ontario, Canada (2) Department of Chemistry, The University of Western Ontario, London, Ontario, Canada (3) Department of Physics, Temple University, Philadelphia, Pennsylvania, United States (4) Departments of Physics and Chemistry, Temple University, Philadelphia, Pennsylvania, United States

The Kohn-Sham potential is the effective multiplicative operator in a non-interacting Schrödinger equation that reproduces the ground-state electron density of a real interacting system. From this potential, the sizes and shapes of atoms, molecules, and clusters can be found in a non-arbitrary way that accords with chemical intuition, permitting a natural pictorial representation for chemistry and condensed matter physics. The surface of any electronic object is here taken to be the classical turning surface of the Kohn-Sham potential, which separates the classically allowed and classically forbidden regions for the electron of highest energy. Atomic and ionic radii defined in this way agree well with empirical estimates. The ratio of the actual equilibrium bond length for two atoms to the sum of their radii identifies the nature of the bond, as does the shape of the surface: perfectly fused for a covalent bond, seamed for an ionic bond, necked for a hydrogen bond, and separated for a van der Waals bond.

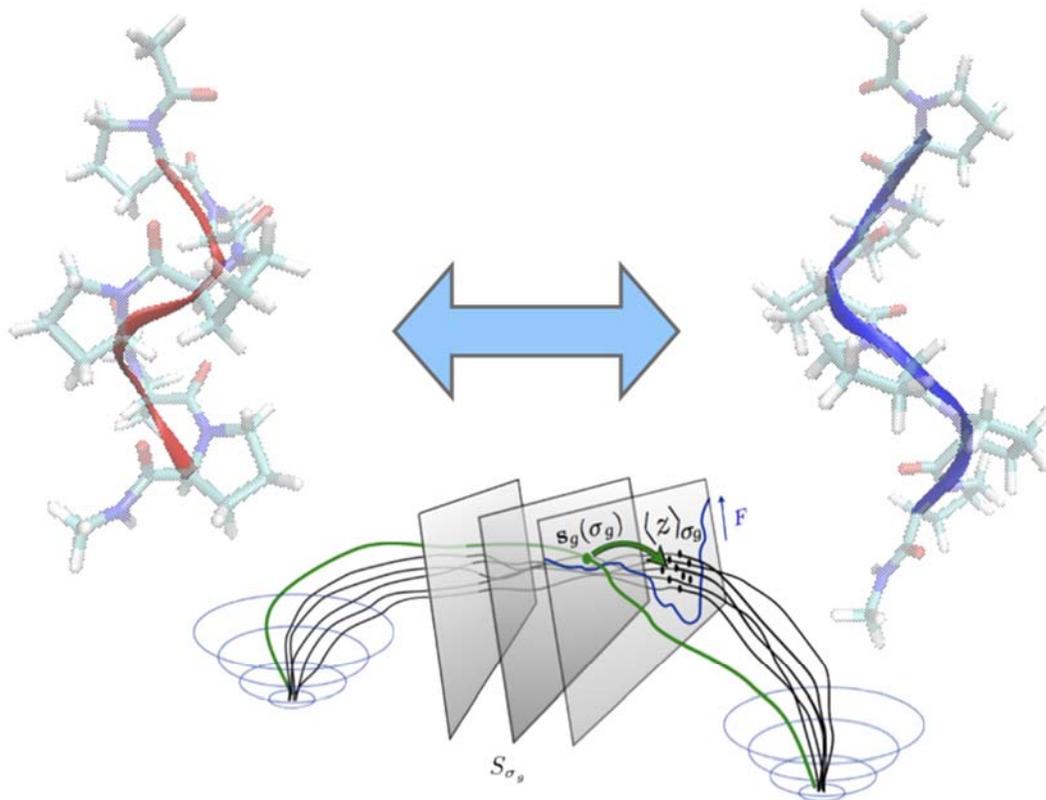


## COLL 66

### Path collective variables for exploring free energy landscapes of molecular transitions

*Alberto Pérez de Alba Ortíz, Ambuj Tiwari, Rakesh Puthenkalathil, **Bernd Ensing**, [b.ensing@uva.nl](mailto:b.ensing@uva.nl). FNWI/HIMS, University of Amsterdam, Amsterdam, Netherlands*

The invention of adaptive bias techniques, such as metadynamics, brought the possibility to explore efficiently the Landau free energy of a molecular transition as a function of more than one descriptive collective variable (CV). In the Klein group, we developed tools to find the minimum free energy paths that connect the stable states in the computed free energy landscapes, which eventually led to the invention of the versatile path-CV. A path-CV can adapt to the mean transition path on the fly during a biased dynamics simulation. After a brief history of finding transition paths, I will give an overview of the latest developments, such as the multiple walker and the multiple path extensions, illustrated with applications in catalysis, proton transfer reactions, polypeptide folding, and the Watson-Crick to Hoogsteen transition in DNA.



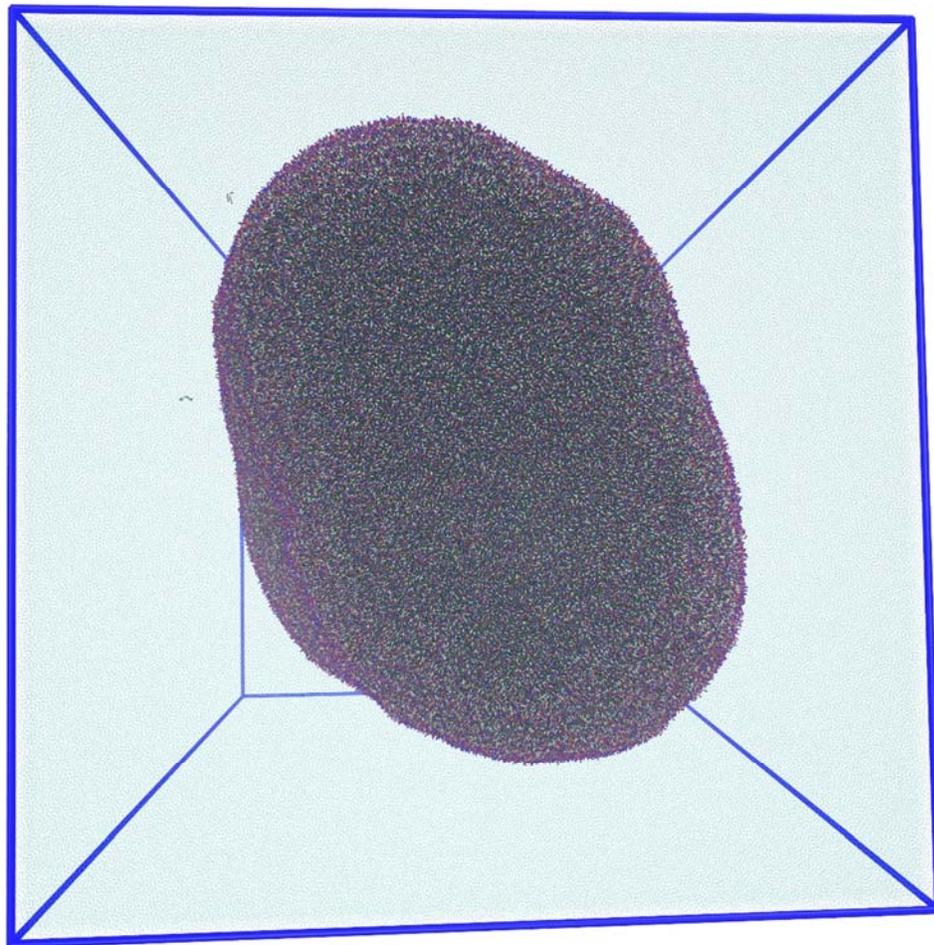
COLL 67

## Coarse-grained molecular dynamics of lipid self-assembly: Membranes, vesicles, lipid nanoparticles

**Wataru Shinoda**, [w.shinoda@chembio.nagoya-u.ac.jp](mailto:w.shinoda@chembio.nagoya-u.ac.jp). Department of Materials Chemistry, Nagoya University, Nagoya, Japan

We illustrate our coarse-grained (CG) molecular modeling of lipid assemblies. The CG model was early called Shinoda-DeVane-Klein (SDK) model and has been recently renamed SPICA force field, which reproduces reasonable interfacial and thermodynamic properties of lipid assembly such as surface/interfacial tension, density, solvation/transfer free energies as well as molecular distribution obtained from all-atom MD simulations. The SPICA FF also yields realistic elastic properties and line tension of

lipid membranes, which guarantees a quantitative prediction of morphology of lipid aggregates. A recent CG modeling of cholesterol and sphingomyelin (SM) successfully used to discuss the phase separation or domain formation within lipid membranes. Liquid ordered domains in two opposing leaflets are registered and anti-registered depending on the lipid species, suggesting the importance of hydrophobic mismatch and interdigitation. Inter-leaflet coupling is examined using long SM(LSM). We detected a striking effect of LSM on the phase state of the opposing leaflet. We also would like to talk on an extension of the SPICA FF for proteins and DNA/RNA. For the latter, we use the model for the simulation of lipid nanoparticles (LNPs), which is a great candidate of the nano-carrier for gene delivery. MD simulation with the SPICA FF can handle the molecular system of over 100 nm (Figure), which is large enough to accommodate ordinary LNPs.



## **COLL 68**

### **Accelerating first-principles based molecular dynamics simulations with machine learning**

**Ursula Roethlisberger**, *ursula.roethlisberger@epfl.ch*. Chemistry, EPFL, Lausanne, Switzerland

Density Functional based molecular dynamics simulations and their quantum mechanical/molecular mechanical (QM/MM) extensions are powerful tools for the investigation of quantum mechanical phenomena in extended systems. However, the time scale that can be covered in such simulations is still limited even when they are used in combination with enhanced sampling techniques. To make first-principles based simulations more efficient; we have developed a new highly flexible interface for multiscale simulations in CPMD together with novel schemes for the calculation of exact exchange within plane wave calculations. Through the extensive use of multiple-time step techniques and combinations with algorithms from artificial intelligence (AI), first-principles based molecular dynamics simulations can be sped up by several orders of magnitude. This combination of traditional computational chemistry methods with approaches from AI constitutes an exceptionally powerful recipe for next-generation first-principles based multiscale simulations. In this talk, some illustrative applications from biological systems to material science will be presented.

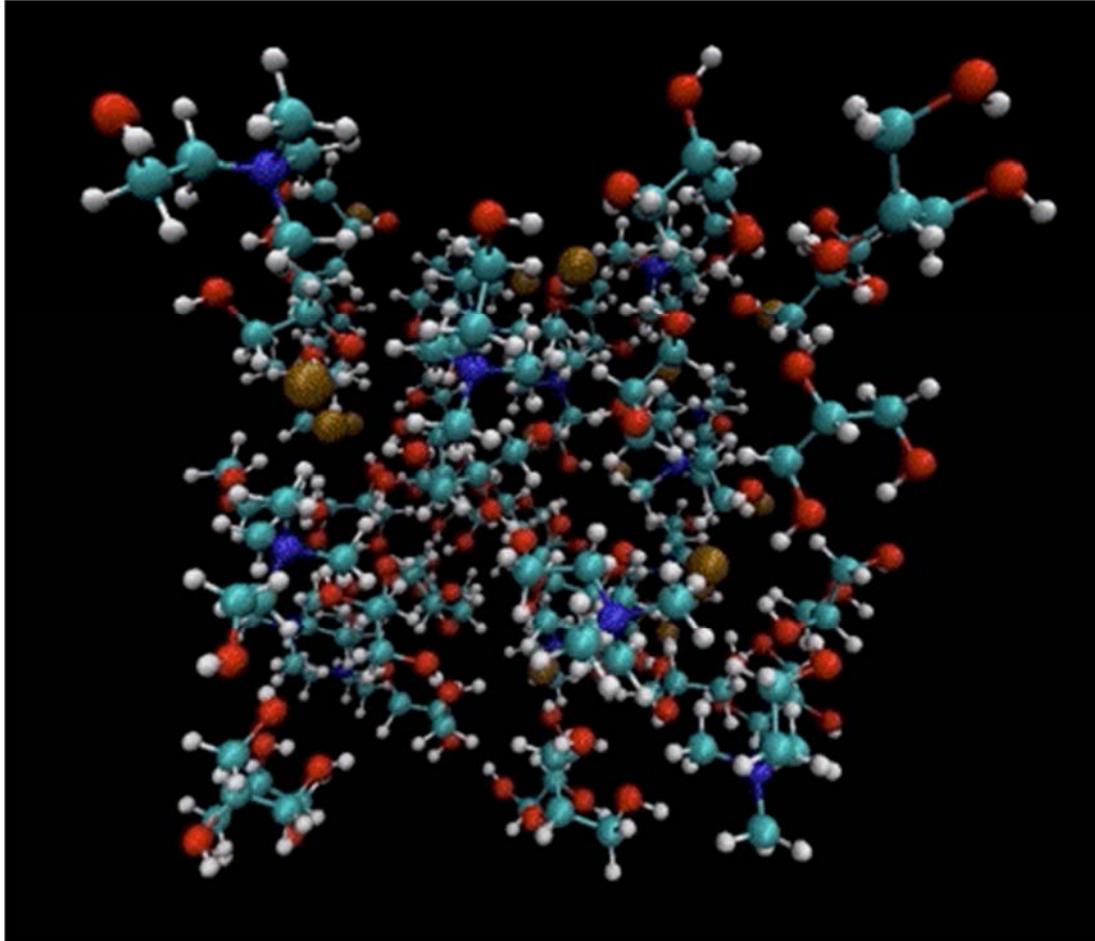
## **COLL 69**

### **Discovering design principles for anion exchange membranes and deep eutectic solvents using first-principles molecular dynamics**

**Mark E. Tuckerman**, *mark.tuckerman@nyu.edu*, *Tamar Zelovich*, *Brian Doherty*. New York University, New York, New York, United States

It is clear that in the identification and development of clean energy sources, a range of technologies will need to be leveraged. Electrochemical devices are an important part of this mix of technologies, and among these, batteries and fuel cells are of considerable interest. However, advancing these technologies requires discovering a set of rules for optimal design of the electrolytes used in these systems. In this talk, I will outline a strategy to discover these rules employing density-functional theory based first-principles molecular dynamics calculations. In the area of fuel cells, we have focused on the design of anion exchange membranes (AEMs) capable of exhibiting high hydroxide conductivity by examining the chemistry of pendant functional groups, the distance between them, width of aqueous pores, and temperature. In the area of breakthrough electrolytes for battery (and other) electrochemical applications, the focus has been on

deep eutectic solvents, specifically, on understanding their structure and charge transfer properties at electrode surfaces.



Snapshot from an ab initio molecular dynamics simulation of a (2:1) mixture of choline chloride and glycerol.

## **COLL 70**

### **Novel evaluation scheme of adhesion strength at the interface between liquid and polymer-grafted substrate**

**Masayuki Uranagase**, [uranagase.masayuki@nitech.ac.jp](mailto:uranagase.masayuki@nitech.ac.jp), **Shuji Ogata**. Nagoya Institute of Technology, Nagoya, Japan

In recent years, jointing materials using adhesive gathers much attention because this enables to joint with lightweight even for different materials. Not only laboratory experiments but molecular simulations are performed for understanding properties

related to adhesion. One of the applications of molecular simulations to adhesion problems is precise evaluation of the adhesion strength. Adhesion strength is quantitatively evaluated via the work of adhesion, which is defined by subtracting the interfacial free energy from the sum of surface free energies of each materials. Therefore, the free energy calculation using molecular simulation plays a key role for quantitative evaluation of adhesion strength.

For solid-liquid interface, several methods for evaluating interfacial free energy have already been proposed. Interfacial free energy can be obtained by integrating the free energy gradient, which is evaluated via molecular simulation, in the process of separating liquid atoms from the solid surface. Separation of liquid atoms can be done by applying artificial planar potential which acts on liquid atoms at the interface. Then, this potential is gradually shifted along the direction perpendicular to the interface. Although, this method works well when the solid surface is sufficiently flat, there is inefficiency if this method is applied to complex surfaces such as polymer grafted substrates, e.g., the planar potential should be shifted over long distance.

We developed the novel method to evaluate the work of adhesion using molecular simulation to improve this inefficiency. In this method, a set of spherical potentials instead of planar potential is introduced to separate liquid atoms from the solid surface according to its structure. This enables to reduce the number of evaluations of the free energy gradient. In addition, we considered the update scheme of parameters contained in potentials to suppress the variation in the free energy gradient, which contributes improvement of the accuracy of numerical integration. Then, we found that the parameters to suppress the variation in the free energy gradient can be adaptively determined. Therefore, this method can be applied without dependence on species of solid and liquid.

## **COLL 71**

### **Boosting *ab-initio* molecular dynamics with machine learning**

**Roberto Car**, [rcar@princeton.edu](mailto:rcar@princeton.edu). Princeton Univ, Princeton, New Jersey, United States

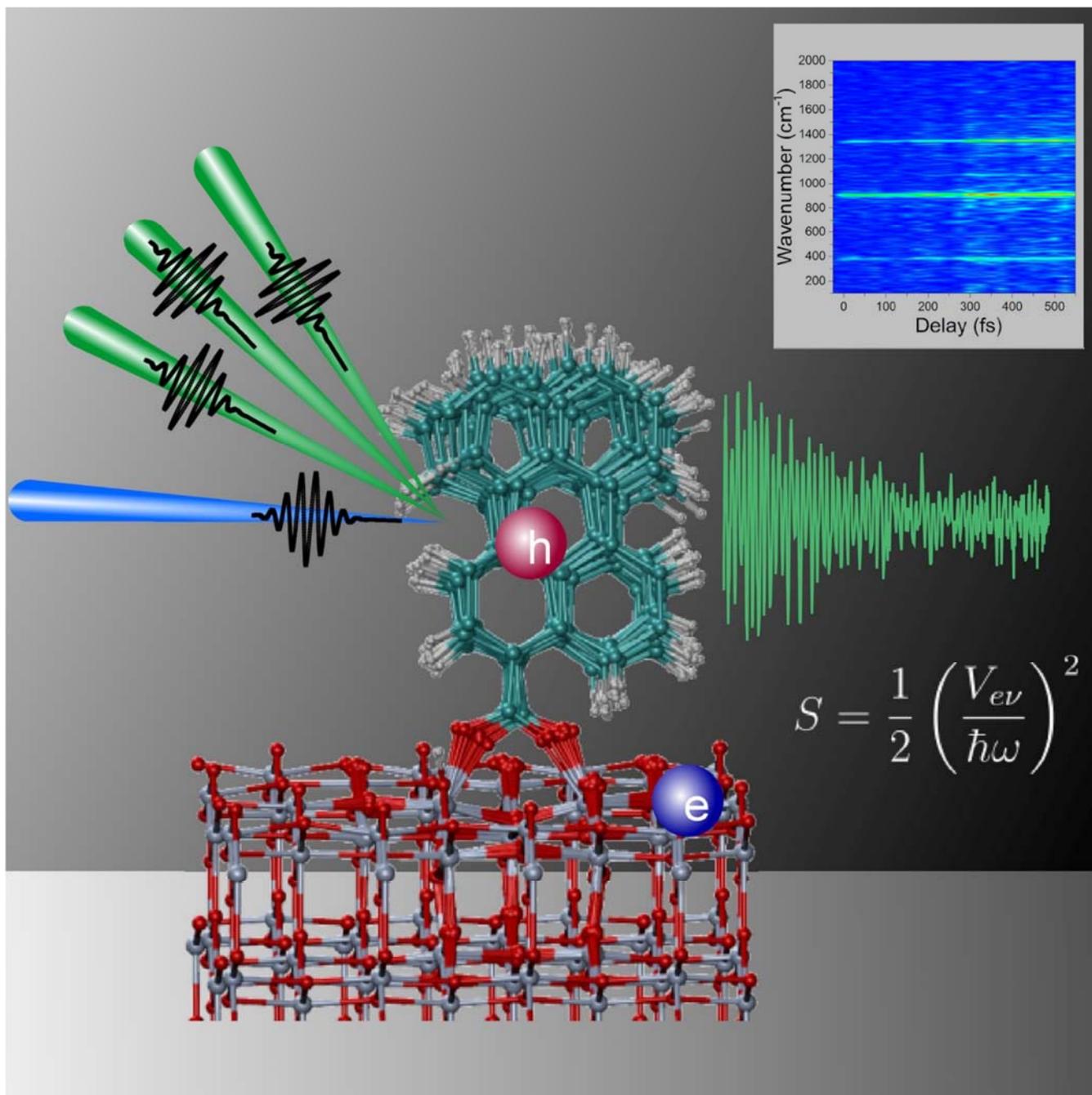
Accessible time and size scales severely limit the range of ab initio molecular dynamics simulations. Machine learning techniques are rapidly changing this state of affairs: deep neural networks learn the interatomic potential energy surface from ab-initio data and make possible simulations with quantum mechanical accuracy at the cost of empirical force fields. The scheme leads naturally to models that include partial electronic structure information, allowing us to access properties like the dielectric response functions measured in experiments. Moreover, with incremental learning techniques it becomes feasible to construct reactive potentials that work well over a vast range of thermodynamic conditions, such as the pressure and temperature regimes that characterize molecular and ionic phases of water.

**COLL 72**

**Ultrafast charge carrier dynamics at molecule-semiconductor interfaces**

**Lars Gundlach**, *larsg@udel.edu*. Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware, United States

**Ultrafast Charge Transfer Dynamics at Interfaces** is a critical process in surface catalysis, novel electronic applications and solar energy conversion. The fast kinetics (below 100 fs) and the inhomogeneous environment complicate identifying the parameters that dominate the reaction. We are investigating the influence of structural dynamics throughout the progression of heterogeneous electron transfer by monitoring coherent oscillations in the dynamic of the excited state and the molecular cation by pump-degenerate four-wave mixing spectroscopy of the photoexcited chromophore. I will present ultrafast spectroscopic studies of model systems with well-defined variations in electronic coupling, excess energy and dipole moment and address the importance of electronic-vibrational coupling for electron transfer.



COLL 73

1D chains: On-surface synthesis and transport properties

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Low dimensional materials offer very interesting material and physical properties due to reduced dimensionality. At present, 2D materials are the focus of attention. However, 1D systems often show far more exotic behavior, such as Tomonaga-Luttinger liquid, Peierls distortion, etc.. In this talk, we will present different classes of 1D molecular chains formed by on-surface synthesis, whose physical properties were investigated by low temperature UHV scanning probe microscopy supported by theoretical simulations. We will also discuss transport measurements of quasi free-standing molecular wires suspended between metallic probe and sample showing non-trivial transport properties on external stimuli (bias, light). The experimental observation will be rationalized by theoretical simulations.

## **COLL 74**

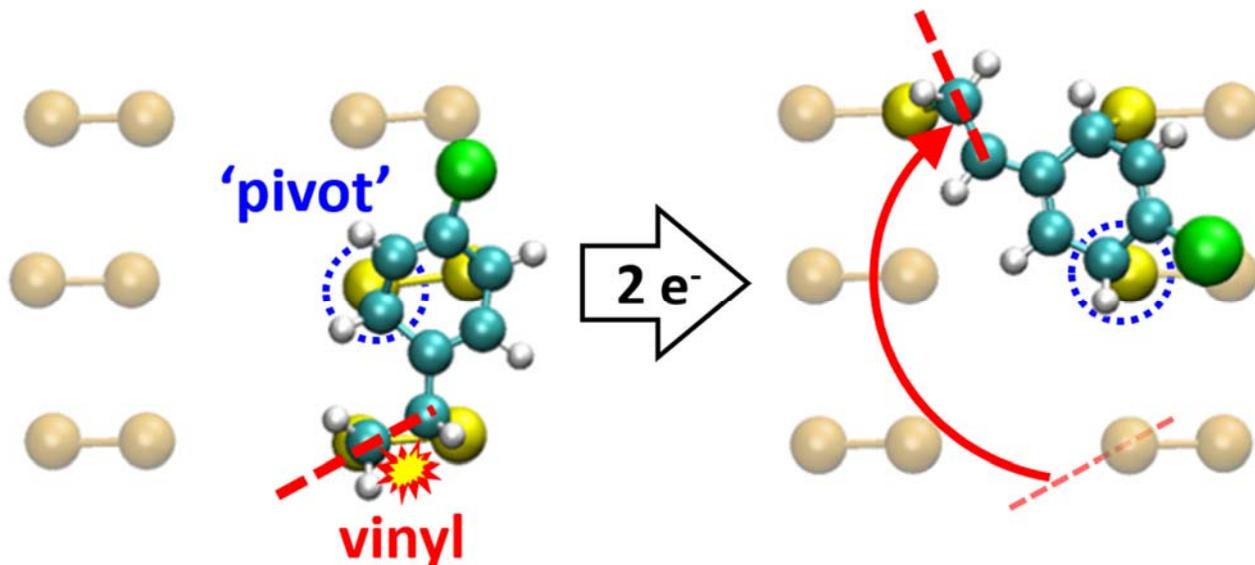
### **Electron-attachment gives unidirectional in-plane molecular rotation of *para*-chlorostyrene on Si(100)**

*Si Yue Guo*, [sguo@chem.utoronto.ca](mailto:sguo@chem.utoronto.ca), *Matthew J. Timm*, *Kai Huang*, *John C. Polanyi*.  
Chemistry, University of Toronto, Toronto, Ontario, Canada

The miniaturization of machines requires an understanding of the dynamics of molecular motions at the atomic level. Molecules on a variety of substrates behave analogously to molecular machines whose geometry results from the selective adsorption and reaction of the different functional groups within an intact molecule.

Here we report the observation of electron-induced unidirectional planar molecular rotation of *para*-chlorostyrene on Si(100), studied by scanning tunneling microscopy at room temperature, and by *ab initio* theory. This bifunctional molecule is shown to be favourable to electron-induced rotation, since the phenyl group acts as a pivot and the vinyl as lever arm. In the initial configuration both phenyl and vinyl are attached to silicon dimers along the same row of the substrate. The first electron from the STM tip is observed to induce a lateral shift of the vinyl to 'state 1' in which the vinyl is bound asymmetrically to one side of a silicon dimer. The second electron is found to give rise to a  $\sim 60^\circ$  rotation to 'state 2', a configuration in which the vinyl has swung around the phenyl to an adjacent dimer row.

The 'impulsive two-state' (I2S) model was employed to explain the conversion of the initial state to state 1 and subsequently, a further electron to explain the conversion of state 1 to state 2. These two successive impulses were computed by the I2S model to be the result of excitation to different configurations in an anionic excited state. Following the addition of the second electron, the repulsion between the asymmetric vinyl and the surface was shown to give rise to a torque with the magnitude and direction required to explain the observed rotation.



Asymmetric repulsion induces torque around 'pivot'

## COLL 75

### Excited states and rapid electron exchange at polymer-metal and molecule-metal interfaces

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Two classes of photoexcited interfaces were explored with the help of pump-probe transient absorption, ultrafast Kerr-gated fluorescence and single molecule fluorescence spectroscopy. The two systems consisted of: (A) bulk and highly diluted (single strand) conjugated organic polymer (P3HT) deposited on nanostructured Au substrates; (B) molecular electron acceptors anchored to Au nanoparticles with the help of alkyl thiol anchor groups. In the first case the polymer served as the light-absorbing species and the fate of the nascent exciton was largely determined by the proximity to the metal surface. Among others, a large increase of the triplet exciton population was observed in the presence of the metal, indicating an accelerated loss of the spin-spin correlation. We attribute this effect to rapid singlet exciton dissociation at the interface followed by energetically favorable charge carrier recombination to the triplet state, rather than to the acceleration of the intersystem crossing due to the metal-induced enhanced spin-orbit coupling. The single molecule fluorescence measurements revealed an average 5-fold increase of emission intensity for single strands of P3HT in the presence of Au nanowire arrays, with the strongest emitters exceeding the brightness of the reference by a factor of 40. The collected trajectories show that the same polymer strand is capable of exhibiting a wide range of enhancement levels, most likely depending on the initial location of the exciton with respect to the nearest Au nanowire.

In the case of molecular electron acceptors (viologens) anchored to Au nanoparticles, the plasmon band of the latter was photoexcited with a short laser pulse and subsequent spectral evolution of the viologen@Au assembly was followed. Alkyl thiol linkers of various length were used. For short linkers we were able to detect the characteristic spectrum of the viologen radical cation, which indicates that a fraction of the plasmonic hot electrons was captured by the acceptor. This spectroscopic observation is consistent with the growing body of plasmon-induced chemical reactions. Electron capture was not detected for long alkyl thiol linkers or in highly concentrated solutions of free viologens pointing to the short lifetime of the hot electrons. The analysis of these results is in progress.

## **COLL 76**

### **Relaxation rates of charge carriers response to chemical composition in PbX/CdX, X = S or Se, core/shell quantum dots**

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Colloidal quantum dots (QDs) have been heavily investigated for a range of applications including display technology, bio-imaging, and solar energy conversion. Traditional QDs are highly sensitive to environmental factors arising from dynamic passivation of surface atoms by ligands. Heterostructures nanoparticles such as core/shell QDs have been shown to reduce the sensitivity of the QD to environmental factors. Core/shell QDs are comprised of two semiconductors, in this work we study pseudo-type II (PbX)<sub>16</sub>/(CdX)<sub>52</sub>, X = S or Se, core/shell QDs. The chemical composition of the QDs control the excited state properties via manipulation of the ground state electronic properties. For solar energy conversion, the electronic properties of the pseudo-type II QDs can dramatically reduce the rate of charge carrier cooling. Non-adiabatic molecular dynamics simulations were performed showing that PbS/CdS charge carriers cool in approximately half the time compared to PbSe/CdSe QDs, which can be attributed to the reduced vibrational frequency of the metal chalcogenide bond vibration in PbSe/CdSe QDs. The reduced charge carrier cooling can aid in the efficiency of the solar cell by improving Carrier Multiplication (CM), generating multiple pairs of charge carriers from a single photon. CM must occur quicker compared to charge carrier cooling which makes PbSe/CdSe QDs are more suitable for solar energy conversion compared to PbS/CdS QDs.

## **COLL 77**

### **Dynamics of para-methyl red on surfaces**

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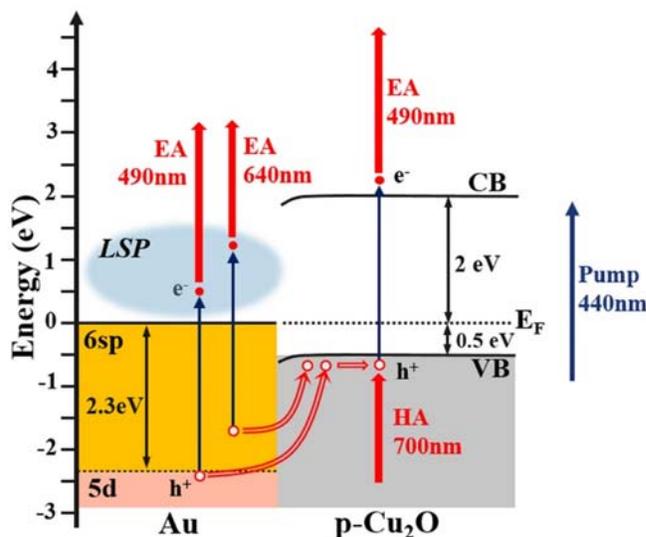
Molecular switches respond to external stimuli to induce a change in structure such as light causing isomerization. Anchoring a photoswitchable molecule to a surface allows for their structural and electronic changes to be harnessed for optical data storage or molecular electronics. Measuring and understanding the chemistry of molecular switches is necessary to optimize organic electronics. In solution para-methyl red isomerizes upon irradiation, but when it is adsorbed to TiO<sub>2</sub> theory predicts that electron transfer can compete with isomerization. Ultrafast transient absorption was utilized to understand the photoswitching properties of para-methyl red on surfaces.

## COLL 78

### **Ultrafast dynamics of plasmon-induced hot-hole transfer in Au/p-Cu<sub>2</sub>O heterostructures**

*Meng Jia*<sup>1</sup>, *mengj@udel.edu*, *Zhengxin Li*<sup>1</sup>, *Han Yan*<sup>1</sup>, *Joseph P. Avenoso*<sup>2</sup>, *Samantha Doble*<sup>1</sup>, *Lars Gundlach*<sup>1,2</sup>. (1) Chemistry and Biochemistry, University of Delaware, Newark, Delaware, United States (2) Physics and Astronomy, University of Delaware, Newark, Delaware, United States

Plasmonic metal/semiconductor heterostructures exhibit unique optoelectronic properties and many applications in energy harvesting, photodetectors, photocatalysts, and optoelectronic devices have been identified. To investigate the plasmon-induced hot-carriers dynamics at the metal/semiconductor interface is a great challenge and understanding the physics behind the hot-carrier transfer dynamics is currently a n important research topic. Numerous studies of hot-electron transfer processes have been published, however, the dynamics of plasmon-induced hot-hole transfer remains largely unclear and only few examples have been presented. Investigation on hot-hole-driven systems is needed to improve our understanding. Herein, we fabricate the gold/p-type cuprous oxide (Au/p-Cu<sub>2</sub>O) heterostructures and observe the plasmon-induced hot-hole transfer from Au nanoparticles to the valence band of p-Cu<sub>2</sub>O using ultrafast transient absorption spectroscopy (TAS). Compared with pure Au nanoparticle, an enhanced excited state hole absorption (HA) is clearly observed from the Au/p-Cu<sub>2</sub>O two-dimensional TAS map. The enhancement is attribute to the hot-hole collection in the valence band of p-Cu<sub>2</sub>O. We further observed a faster hot-electrons relaxation of Au/p-Cu<sub>2</sub>O compared with Au nanoparticles which is attribute to a parallel competing relaxation path that enable hot-electrons to be diverted into the valence band of p-Cu<sub>2</sub>O. The energy schematic mechanism of plasmon-induced hot-hole transfer at Au/p-Cu<sub>2</sub>O interface will be discussed.



## COLL 79

### Enhanced transport and carrier selectivity at silicon/perovskite interfaces enabled by ordered perylene monolayers

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Covalent, organic-functionalized interfaces offer the potential for robust, flexible, and tunable interfaces for a variety of applications including hetero-junction photovoltaics, organic field effect transistors, and optics. In the context of tandem-junction PV, we investigate low-temperature, monolayer functionalization of Si(111) with perylene derivatives to chemically and electrically tether MAPbI<sub>3</sub> thin films to the surface enabling flexible, carrier-selective interfaces. We covalently graft perylene dianhydride to surface via an imide linkage to surface-bound aniline. Secondary functionalization of the terminal anhydride with phenylenediamine yields A-type cation moieties that serve as a chemical hook for perovskite deposition. Ultraviolet Photoelectron Spectroscopy characterized the band-energy levels of functionalized surfaces. Transfection Infrared Spectroscopy and X-ray Photoelectron Spectroscopy probed each step of the surface functionalization and revealed high coverages of surface-attached perylenes. Current density-voltage measurements reveal that oxide-free, perylene-functionalized surfaces yielded improved energy conversion relative to aliphatic interfaces. We ascribe the efficiency improvements to reduced recombination and enhanced carrier transport. This work presents a bench top functionalization yielding soft, robust, electron transport layers to further integrate low-cost perovskites with mature silicon PV.

## COLL 80

## Avoiding the endosomal trap: Direct cytosolic delivery of biologic (and CRISPR-Cas9) through membrane fusion processes

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Therapeutic delivery of proteins and nucleic acids into cells is a difficult goal. Of the many challenges in the delivery process, perhaps the most demanding is providing these biologics with access to the cytosol. Most delivery strategies employ endosomal uptake, requiring endosomal escape for the payload biologics to be effective. In our research, we have developed strategies to deliver proteins and nucleic acids directly to the cytosol through fusion of nanomaterials with the cell membrane.

We have developed a nanoparticle-based delivery platform system that uses co-engineering of nanoparticles and proteins to deliver proteins directly into the cytosol. This platform co-assembles arginine-functionalized AuNPs with proteins modified with a glutamate (E-tag) chain. The resulting assemblies interact with cell membranes, delivering proteins into the cytosol through fusion with the cell membrane. This strategy has been applied to a wide range of proteins, and we have employed this system to co-deliver complete CRISPR machinery (Cas9 protein and guide RNA) for effective editing both in vitro and in vivo.



Delivery of CRISPR-Cas9 using coengineered nanoparticle-protein assemblies.

## COLL 81

### Non-covalent attachment of peptide drugs to gold nanoparticles for intracellular delivery utilizing host-guest chemistry

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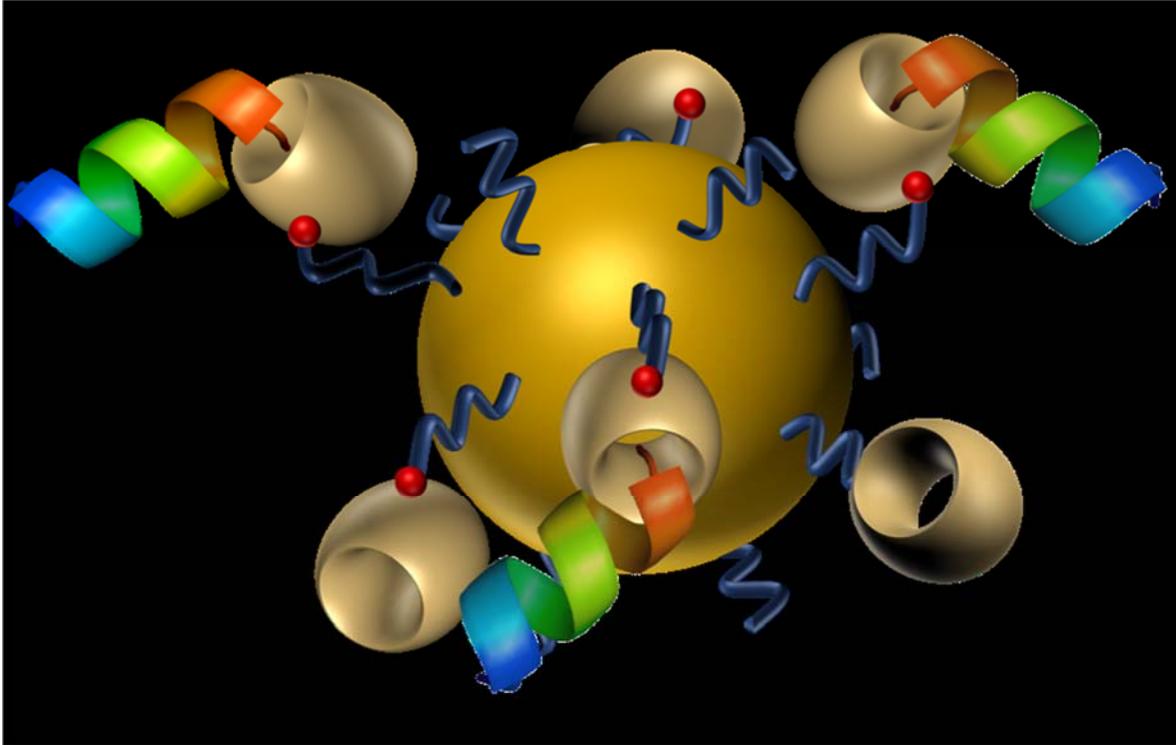
Gold nanoparticles (AuNPs) have shown huge promise for use in biotechnological applications on account of their low toxicity, ease of surface functionalisation and sensing capabilities. Acting as a nano-Trojan horse, AuNP delivery systems can cross the cell membrane, taking with it the therapeutics attached to their exterior.

This project aims to attach therapeutic and targeting peptides non-covalently to a AuNP surface through host-guest chemistry. Cucurbit[*n*]urils (CB[*n*]s) are a family of biocompatible macrocyclic host molecules consisting of *n* glycouril units. CB[7] has the highest water solubility of the family members and the ability to bind guests more strongly than  $\beta$ -cyclodextrin. This includes both synthetic and biomolecules such as N-terminal phenylalanine. Methodology for the functionalisation of CB[7] has been developed by Issacs, Ouari & Bardelang, Kim and Scherman, opening up possibilities for tethering to various chemical architectures.

Peptide sequences can be modified with a suitable CB[7] guest in order to introduce a binding site to an otherwise non-binding sequence. The simultaneous addition of targeting peptides results in a multivalent, multimodal NP surface. Multivalency can allow for super-selectivity to be designed into the system, resulting in a delivery platform that can target cells overexpressing a certain receptor whilst avoiding healthy cells.

Non-covalent conjugation to AuNPs allows for a facile 'mix and match' approach to surface functionalisation with such peptides, circumventing the need for new chemistries to be developed for each attachment. As the external decoration dictates the final outcome of the NP therapy, the same platform could be used to perform various tasks depending on the combination chosen. One combination of peptides could kill a cancer cell directly and another could elicit an immunogenic response.

This platform could have major consequences in the realm of personalised healthcare. With the ability to 'mix and match' therapeutics, combinations could be tailored and administered according to a patient's needs.



## COLL 82

### Assessing micrometastases as a target for nanoparticles using 3D microscopy and machine learning

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Metastasis of solid tumors is a key determinant of cancer patient survival. Targeting micrometastases using nanoparticles could offer a way to stop metastatic tumor growth before it causes excessive patient morbidity. However, nanoparticle delivery to micrometastases is difficult to investigate because micrometastases are small in size and lie deep within tissues. Here, we developed an imaging and image analysis workflow to analyze nanoparticle–cell interactions in metastatic tumors. This technique combines tissue clearing and 3D microscopy with machine learning-based image analysis to assess the physiology of micrometastases with single-cell resolution and quantify the delivery of nanoparticles within them. We show that nanoparticles access a higher proportion of cells in micrometastases (50% nanoparticle-positive cells) compared with primary tumors (17% nanoparticle-positive cells) because they reside close to blood vessels and require a small diffusion distance to reach all tumor cells. Furthermore, the high-throughput nature of our image analysis workflow allowed us to

profile the physiology and nanoparticle delivery of 1,301 micrometastases. This enabled us to use machine learning-based modeling to predict nanoparticle delivery to individual micrometastases based on their physiology. Our imaging method allows researchers to measure nanoparticle delivery to micrometastases and highlights an opportunity to target micrometastases with nanoparticles. The development of models to predict nanoparticle delivery based on micrometastasis physiology could enable personalized treatments based on the specific physiology of a patient's micrometastases.

## **COLL 83**

### **Dual-function of lipoic acid groups as surface anchors and sulfhydryl reactive sites on polymer-stabilized nanocolloids**

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Coating quantum dots and gold nanoparticles with polymer ligands presenting multiple lipoic acid (LA) anchors provides nanocolloids with remarkable colloidal and photophysical stability. Here, we show that the natural swelling of macromolecules imposes a coating configuration where a fraction of the lipoic acid groups stay free, and are targeted for activation and conjugation to molecules, using the reliable sulfhydryl-to-maleimide reaction. This implies that simple and efficient functionalization of nanocrystals can be achieved without introducing specific reactive groups in the coating. We apply a photoligation strategy to promote the dispersions of luminescent QDs and AuNPs in buffer media, and react the resulting materials with maleimide-Cy3 dye. We then use optical absorption and resonance energy transfer measurements to extract estimates for the fraction of accessible LA groups per QD or AuNP. In addition, we demonstrate the potential utility of this approach by constructing a ratiometric pH sensor made of QD-SNARF conjugates. Our ligand design combined with the photoligation strategy yield colloiddally stable dispersions of nanocrystals that present accessible reactive thiols, without introducing new functionalities, or requiring chemical reducing reagents, making them highly useful for use in applications such as biological sensing and imaging.

## **COLL 84**

### **Click chemistry-ready zwitterionic quantum dots exhibiting high DNA grafting efficiency**

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For use in biological applications, semiconductor quantum dots (QDs) must be transferred from their native organic phase into aqueous media. Polymeric or small molecule ligands facilitate water solubility while conferring colloidal stability through either steric hinderance or charge repulsion. We demonstrate a novel polymer functionalization that produces a carboxybetaine-like coating for QDs. This polymer formulation takes advantage of the high stability observed in nanoparticles exhibiting both positive and negative charges on their surface without requiring the synthesis or handling of small molecule zwitterions. This polymer coating uses readily available reagents to functionalize commercially available poly(anhydride maleic-*alt*-isobutylene) (PIMA) with a quaternary amine to balance charges from carboxylic acids on the polymer backbone, avoiding the synthetic and solubility challenges typically associated with working with zwitterionic moieties. The resulting particle surface charge is much closer to neutral than the similar, but more complicated, materials that inspired this work. In addition to the charge-based stabilization, the polymer also provides copper-free click-chemistry handles for subsequent biofunctionalization. As a demonstration of the ease with which this subsequent functionalization proceeds, we demonstrate the grafting of DNA oligomers to the surface of the QDs with >95 % efficiency, reducing the amount of DNA used for conjugation and eliminating the need to remove unbound DNA prior to use of the QD-DNA conjugate. The simplicity of the polymer preparation ensures that the coating approach will be accessible to a range of chemistry and biological research.

## **COLL 85**

### **Investigating thermodynamics and kinetic control mechanism for competitive protein adsorption to a nanoparticle surface**

*Rebecca Hill, beccaann.hill@gmail.com, Sarah Claxton, Katarina Boulet, Randy Perera, Taylor South, Rahul Yadav, Nicholas Fitzkee.* Chemistry, Mississippi State University, Starkville, Mississippi, United States

Due to their well-defined surface chemistry, nanoparticles (NPs) are of great interest, having found numerous biological applications, such as biosensing, bioimaging, and drug delivery. When NPs are exposed to biological fluids, the proteins in solution will compete to bind to the NP surface. However, it remains impossible to predict the competitive binding outcome of proteins to NPs, knowledge that would be useful for scientists wanting to target NPs to specific cells in the body. Here, NMR methods were used to investigate how proteins compete to bind to various NP surfaces, as well as to explore aspects of kinetic and thermodynamic control. Specifically, we use a  $^1\text{H}$ - $^{15}\text{N}$  HSQC technique to quantify AuNP binding for various mixtures of GB3 and Ubiquitin, two small model proteins, as well as Amidase and R2ab, two larger protein domains from *S. epidermidis* implicated in biofilm formation. Using CPMG relaxation experiments, we monitored the timescale of protein exchange with a pretreated, protein functionalized AuNP surface, as well as the protein exchange with SiNP surface. The AuNP surface was found to have a hard corona with no observable difference in the relaxation rates. However, SiNPs exhibit a soft corona with a measurable protein

dynamics ( $\Delta R_2$ ). Since the proteins harden quickly on AuNP surfaces, the mixtures were sampled at 1.5 h intervals to investigate and quantify the protein competition binding over time. Our results suggest that the competition is not kinetically controlled, but thermodynamically controlled as the competition between proteins leads to an increased surface exchange rate ( $\sim$ ms). This differs slightly from a previous study, where surface exchange was extremely slow (18 h). Together, our results suggest a mechanism by which NP surface character may change over time, and this may be an important consideration in the design of NP-based therapeutics.

## **COLL 86**

### **Assemblies of highly efficient iron oxide nanocubes for magnetic hyperthermia to treat tumors**

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To assemble magnetic nanoparticles into colloidal stable clusters has resulted useful in many fields of applications ranging from medicine to catalysis. Magnetic nanoparticles are also exploited in magnetic hyperthermia to convert, under an alternative magnetic field, magneto energy into thermal energy. This non-invasive heat modality is now in clinical practice, to treat solid tumors: it is based on the sensitivity of cancer tissues upon exposure to temperatures of 40-45°C. In our group we have developed cubic shaped iron oxide nanocubes with optimized magnetic properties. These nanocubes have 10 times better heating performance (measured in terms of specific absorption rate, SAR, values) than commercially available iron oxide nanoparticles.<sup>1</sup>

It has been theoretically explained that the chain-like configuration of magnetic nanoparticles have higher SAR values than isolated nanoparticles by favoring magnetic dipolar interactions.<sup>2</sup> At the same time, at the tumor, nanoparticles or nanoclusters are exposed to tumor tissue microenvironment, which could modify or degrade the magnetic heat performances of the magnetic materials. Therefore, the preservation of the heat ability (the SAR values) of magnetic nanoparticles even when associated to the tumor matrix or engulfed by tumor cells is crucial.

With this talk, I will overview the efforts of our team to cluster iron oxide nanocubes in different conformations from chain-like configuration to bi-dimensional and three-dimensional arrangements with size defined from less than 50 nm to mesoscale or to microscale size.<sup>3,4,5</sup> The evolution of the clusters and their SAR properties in presence of tumor cells or in intratumoral-like environment will also be shown.<sup>4,5</sup> Finally, an example of chain-like assembly of nanoparticles occurring at the tumor in an *in vivo* murine xenograft tumor model under alternating magnetic field, will be also reported and discussed.

## **COLL 87**

### **Lymphoid targeting of peptide antigen and TLR agonists by lipid nanoparticles**

**Dorien Van Lysebetten**, *dorien.vanlysebetten@ugent.be*, **Bruno De Geest**. Ghent University, Ghent, Belgium

The generation of robust T cell responses against tumor antigen requires antigen to be delivered to antigen presenting cells in lymphoid tissue in combination with innate activation stimuli. Here, we report on the design of lipid nanoparticles that allow for efficient lymphatic drainage in combination with co-delivery of peptide antigen and small molecule TLR agonists. Poly-L-glutamic acid (PGA) served as a scaffold for conjugation or either imidazoquinoline TLR7/8 agonist (TLRa) or peptide antigen. PGA-TLRa and PGA-peptide were subsequently formulated by electrostatic interaction into lipid nanoparticles using ionizable lipids and PEGylated lipids to provide colloidal stabilization. Field flow fractionation in combination with fluorescence and light scattering detection showed that lipid nanoparticles with a mean size of 60 nm were obtained with an encapsulation efficiency of PGA to be above 99 %. In vitro cell uptake and toxicity measurements strongly correlated with the pKa of the ionizable lipids, showing that ionizable lipids with a pKa below physiological pH were non-toxic while still allowing for cellular uptake. Also in vitro antigen and TLR agonist loaded nanoparticles were able to induce both innate immune activation and antigen presentation. In vivo experiments in mice showed strong accumulation of nanoparticles in draining lymphoid tissue and induction of localized innate immune activation in lymph nodes and in the spleen. Furthermore, we demonstrate that lipid nanoparticles can mount T cell responses against encapsulated peptide antigen. These findings strongly suggest that this nanoparticle design holds potential for the development of cancer vaccines.

## **COLL 88**

### **Nanoparticle-biomolecule interface in paper based immunoassays and rapid diagnostics**

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Nanoparticle-biomolecule conjugates have been studied for numerous applications in biology and medicine, including imaging agents, therapeutics, drug delivery vehicles, and contrast agents for imaging. One emerging area is the use of nanoparticles in paper based immunoassays, which are used as rapid diagnostics for infectious disease and many other applications including clinical tests, drug testing, and food safety. They can be administered at point of care and deployed in fieldable settings by non-experts. Predominantly, they provide a readout by eye because they use gold nanoparticles, which have a strong absorption due to their surface plasmon resonance, thus providing sample-to-answer times of minutes. However, the biotic-abiotic interface can result in undesirable side effects, especially for nanomaterials. In paper-based assays, there are numerous opportunities for non-specific adsorption, protein denaturation, protein corona formation, and steric hindrance. Unfortunately the impact of these interface issues are

false positives, and/or reduced sensitivity, which can have severe ramifications in a clinical setting. Furthermore, diagnostics are run in biological fluids such as blood, serum, or urine, where proteins are present at high concentrations, and thus a protein corona can form around the nanoparticle. Here, we will discuss interface issues such as bioconjugation and surface chemistry, and quantitatively assessing their impact on the paper diagnostic performance. We will also describe special issues for using high sensitivity detection methods, and also exploiting size-dependent nanoparticle properties.

## **COLL 89**

### **Programming lifecycles and dynamics in chemically powered out-of-equilibrium self-assemblies**

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Living self-organizing systems operate far-from-equilibrium and maintain functions by constant energy dissipation in adaptive steady states, and are orchestrated through feedback loops to allow tailored response in complex sensory landscapes.

In man-made self-assemblies we have mastered to a large extent near-equilibrium structure formation in space, and have gained an increasing understanding to construct very complex, hierarchically structured soft matter with responsive properties. This has allowed to create materials with advanced functionalities and switchability, inaccessible without sophisticated nano- and mesostructuration and delicate control over molecular interactions.

Some of the next steps in self-assembling systems are to approach multicomponent co-assembling systems, and to master temporal behavior as well as complex adaptation mechanisms. The latter require new types of internal control mechanisms, such as kinetic control over opposing reactions (built-up/destruction), the integration of feedback mechanisms, or the use of energy dissipation to sustain structures only as long as a chemical fuel is available. This ultimately goes along with a transition towards out-of-equilibrium complex systems, in which multiple components self-assemble dynamically in a non-linear and adaptive fashion.

In this talk I will present two conceptual pathways towards out-of-equilibrium systems, (i) driven environments and (ii) driven structures, which allow to program self-assemblies and materials with lifetimes and programmable steady state dynamics using feedback mechanisms and conversion dynamics of chemical fuels. This will be showcased for different self-assembling systems (polymers, peptides, DNA), and the connection to hydrogels and photonic materials demonstrates possibilities for new horizons in materials science.



## COLL 90

### Programming materials with classical conditioning algorithm

**Olli T. Ikkala**<sup>1</sup>, [olli.ikkala@aalto.fi](mailto:olli.ikkala@aalto.fi), **Hang Zhang**<sup>1</sup>, **Hao Zeng**<sup>2</sup>, **Arri Priimagi**<sup>2</sup>. (1) Dept of Applied Physics, Aalto University, Espoo, Finland (2) Faculty of Natural Science and Engineering, Tampere University, Tampere, Finland

In bioinspired materials there is a search for ever more complex functionalities. Could materials showing a response to a particular stimulus become responsive to another stimulus to which they are originally indifferent? Such a behavior would mimic the classical conditioning in behavioral psychology, one of the elementary forms of learning, originally shown by Pavlov in his experiments with dogs. Here we demonstrate two soft matter systems (a hydrogel and a liquid crystalline network) programmed to mimic classical conditioning (Zhang et al, Nat. Commun. 2019, 10, 3267; Zeng et al, submitted). The hydrogel consists of pH-sensitive Au-nanoparticles and merocyanine-based photoacid embedded in thermoresponsive agarose hydrogel. The liquid crystalline network actuator is prepared by photo-polymerization. Irradiation absorbing dye is applied on one actuator surface, i.e. asymmetrically. The hydrogel melts (response) upon heating (unconditioned stimulus) but does not melt upon irradiation (neutral stimulus). However, conditioning by simultaneous heating (leading to gel melting, thus promoting Au-nanoparticle dynamics) and irradiation (leading to proton release from the photoacid and pH change) leads to Au-nanoparticle chaining, and modified plasmonic absorption. Thus, irradiation leads to gel melting (conditioned stimulus), by selecting the irradiation wavelengths. The nanoparticle chaining acts as the memory, relevant for conditioning. Even forgetting is achieved by pushing the system out-of-equilibrium using systems chemistry, thus controlling the Au-nanoparticle chaining. On the other hand, the splay-aligned liquid crystalline networks bend upon heating (unconditioned response and stimulus) due to asymmetric thermal expansion. Irradiation is the neutral stimulus. But conditioning upon applying simultaneous heating and irradiation leads to diffusion of the dye into the bulk. The conditioning enhances the dye distribution, and thereafter also irradiation allows actuation (conditioned stimulus) due to more efficient radiation absorption. In this case, the modified dye distribution sets the memory. We foresee a wealth of possibilities for different materials systems,

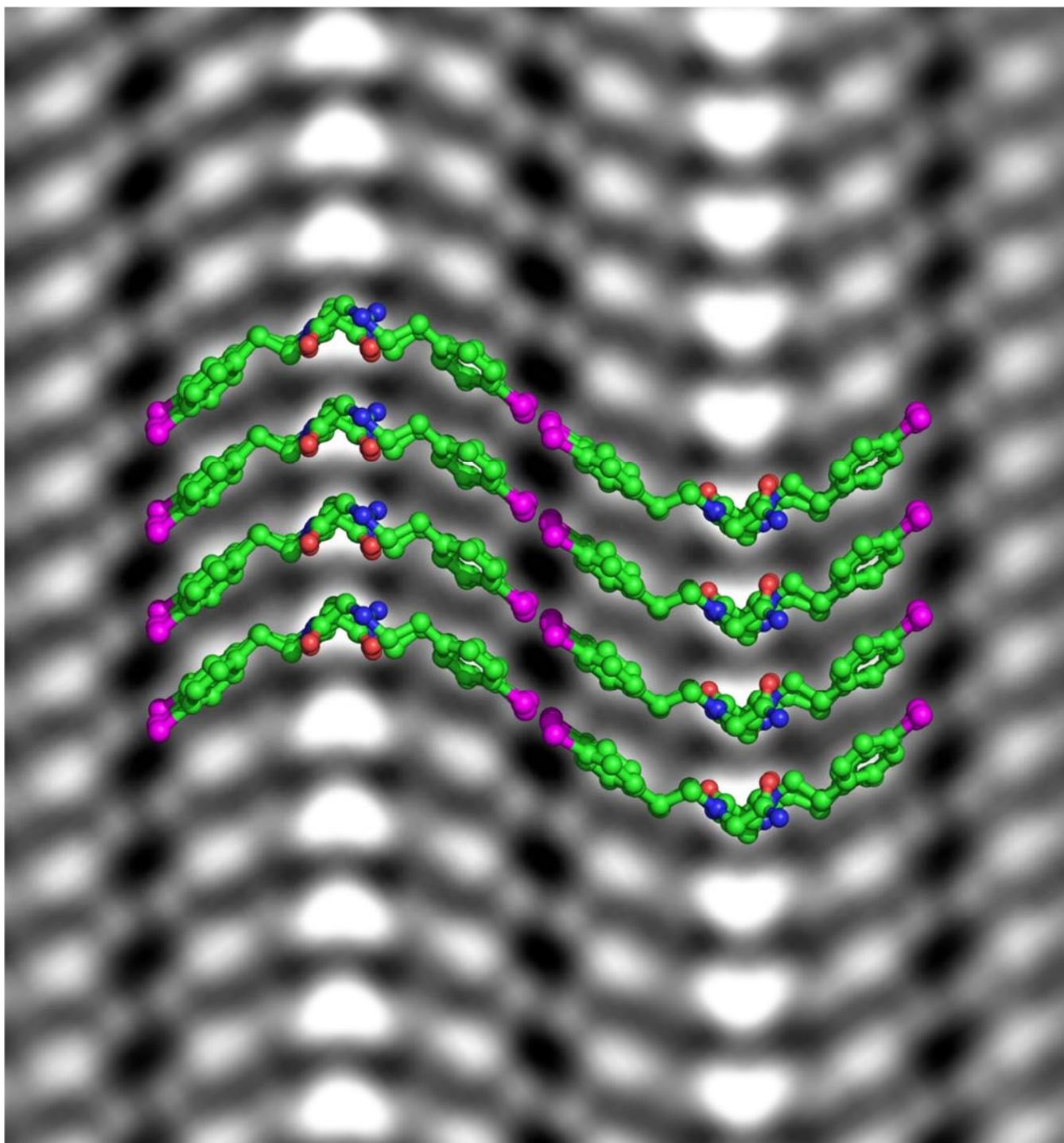
combinations of stimuli and different "memory" concepts for classically conditioned functional materials.

## **COLL 91**

### **Assembly of atomically defined nanostructures from sequence-defined peptoid polymers**

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A fundamental challenge in materials science is to create synthetic, organic nanostructures with the same architectural sophistication as proteins. One of the most exciting ways to do this is to mimic Nature, and synthesize sequence-defined, non-natural polymer chains that spontaneously fold and assemble into precise three-dimensional structures. Peptoid polymers offer a unique platform to advance this general approach. We developed an automated synthesis method, the solid-phase submonomer method, which can efficiently synthesize high-purity, sequence-defined peptoid polymers up to 50 monomers in length. The method uses readily available primary amine synthons, allowing hundreds of chemically diverse sidechains to be cheaply introduced. We use this method, along with computational modeling, to design, synthesize, assemble and engineer a variety of protein-mimetic nanostructures, and to probe fundamental questions in polymer physics. Here, we show by direct imaging using cryo-TEM, and X-ray scattering, that all known crystalline peptoid assemblies share a fundamental secondary structure motif based on a backbone fold containing all *cis*-amide bonds. This unexpected universality of peptoid backbone folding offers a unique opportunity to rationally design and engineer these materials to create robust, atomically-defined nanomaterials capable of protein-like functions.



High-resolution cryo-TEM of a peptoid monolayer nanosheet, resolving individual molecules packed into a planar lattice. Atomic models of the peptoid chain are shown superimposed (green), where individual bromine atoms are directly observed (magenta).

**COLL 92**

## **Elastin-like protein-globular protein fusion constructs as a method for high-throughput self-assembly of functional nanostructures**

**Bradley D. Olsen**, *bdolsen@mit.edu*, *Carolyn Mills*, *Erika Ding*. Chemical Engineering, MIT, Cambridge, Massachusetts, United States

The self-assembly of proteins into functional nanostructured materials offers the opportunity for substantial improvement in the performance of materials such as biocatalysts and biosensors. Typically, these materials are developed by adopting a protein that was previously optimized for function in solution and repurposing it in a solid state or interfacial context. However, this may not lead to optimum function of the overall material. Here, we show a method for preparing protein-based materials in high-throughput based on fusion protein self-assembly. First, we demonstrate that elastin-like protein (ELP) fusions, originally developed as solubility-enhancing tags, can also be engineered in order to promote self-assembly of the protein materials into block copolymer-like nanostructures, similarly to synthetic polymer-protein bioconjugates. The design of the ELP block to promote self-assembly, including charge and hydrophobicity, is explored. Then, we show that the use of the ELP as a protein purification tag enables high throughput material fabrication. In particular, the discovery of cononsolvency of the ELPs enables development of a precipitation-based purification process that can yield purified protein samples with very low residual salt, producing robust self-assembled structures. This process can be generalized to a variety of different proteins that are tolerant of the cononsolvent. The ability to use this technology in well plate format to generate material libraries is then demonstrated.

### **COLL 93**

## **Sonic design of self-assembling hierarchical biopolymers**

**Markus J. Buehler**, *mbuehler@MIT.EDU*. MIT, Cambridge, Massachusetts, United States

What if we could design materials that integrate powerful concepts of living organisms - self-organization, the ability to self-heal, tunability, and an amazing flexibility to create astounding material properties from abundant and inexpensive raw materials? This talk will present a review of bottom-up analysis and design of materials for various purposes - as structural materials such as bone in our body or for lightweight composites. These new materials are designed from the bottom up and through a close coupling of experiment and powerful computation as we assemble structures, atom by atom. We review case studies of joint experimental-computational work of biomimetic materials design, manufacturing and testing for the development of strong, tough and smart mutable materials for applications as protective coatings, cables and structural materials.

Modeling matter as resonating systems, this talk will then discuss the interface of material and sound, and present how we can transcend scales in space and time to

make the invisible accessible to our senses and to manipulate matter from different vantage points, using innovative agents such as AI interacting with human creativity. The impact of this work is the design and making of new materials, art and music, and a deep mathematical understanding of the functional underpinnings of disparate manifestations of hierarchical systems. Building on these concepts, using AI, we explore a new interface of human expression with learned behavior to better understand the physiology and disease etiology due to the misfolding of proteins, explore it as the basis to generative algorithms, and present musical compositions based on the natural soundings of amino acids and proteins.

Using sets of harmonic oscillations as a unifying description, model of disparate hierarchical systems are developed, and then used to illustrate competing concepts of order and disorder and how they are the basis to create functional cross-scale relationships. The insights from this theory explain practically relevant issues such as the strength of silk or the emergence of disease, and the creation of new art. The translation from various hierarchical systems into one another presents a paradigm to understand the emergence of properties in materials, language, visual art, music, and similar systems.

## **COLL 94**

### **Prediction of polyelectrolyte block copolymer morphologies**

**Yaroslava G. Yingling**, [yara\\_yingling@ncsu.edu](mailto:yara_yingling@ncsu.edu). Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina, United States

Responsive materials, which react to changes in the surrounding environment through specific property adjustments, will play an increasingly important part in a diverse range of applications. However, the mechanisms of responsiveness is difficult to characterize due to its inherent complexity and multiscale nature: stimuli triggers atomistic-level molecular changes that cause macroscopic response in physical and chemical properties of material. Modeling a responsive material presents a challenge with a large number of unknown variable parameters, such as chemical reactions kinetic or conformational changes as a function of environment, that is hard to measure directly. We have recently developed a method which is parameterized based on a single set of parameters, which allows for large-scale simulations of self-assembling polyelectrolytes materials and their morphological response to the changes in salt concentration. Polyelectrolyte block copolymers, which combine structural features of polyelectrolyte, block copolymers and surfactants, can self-assemble in a variety of nanoaggregates in aqueous environment, such as micelles, vesicles, lamellar mesophases or micellar aggregates. The morphology and size of formed aggregates are determined by the characteristically complex equilibrium of noncovalent forces and depends on variations in ionic strength or/and pH in the aqueous solution. Our methodology permit us to construct a morphological diagram of polyelectrolyte block copolymers and evaluate the size of aggregates obtained along with their responsive morphological transitions and scaling relation.

## **COLL 95**

### **Self-assembly in block copolymer systems**

**Ulrich B. Wiesner**, *ubw1@cornell.edu*. Materials Science and Engineering, Cornell University, Ithaca, New York, United States

The formation of polymer self-assembly derived functional nanomaterials is discussed from a combination of block copolymer self-assembly directed organic as well as inorganic nanoparticles. The talk will focus how the self-assembly based nanostructure control of amorphous macromolecules can be transcribed into functional materials generating emergent behavior in quantum materials as well as enabling applications in energy storage. The emphasis will be on the development of wet chemical methodologies, as opposed to top-down approaches, towards controlled nanostructures resulting in specific function. Experiments will be compared to theoretical predictions to provide physical insights into formation principles and specific properties. The aim of the described work is to understand the underlying fundamental chemical, thermodynamic and kinetic formation principles as well as nanostructure-property correlations enabling generalization of results over a wide class of materials systems. Work will cover structure formation at or close to the thermodynamic equilibrium as well as approaches where systems are driven away from equilibrium. Examples will include block copolymer self-assembly based mesoporous metallic structures as well as the first self-assembled quantum materials, e.g. in the form of superconductors, including the discussion of emergent behavior from the control of three-dimensionally periodic lattices including the so-called gyroid structure. Examples will further include the formation of block copolymer directed gyroidal mesoporous carbons for the realization of the first true three-dimensional (3D) battery architectures with all battery components having dimensions below 20 nm.

## **COLL 96**

### **Dynamics of a polymer network at intermediate distances**

**Haim Diamant**, *hdiamant@tau.ac.il*. School of Chemistry, Tel Aviv University, Tel Aviv, Israel

Beyond what length scale can a polymer network be considered a homogeneous bulk? With respect to the network's static structure, it is the mesh size. With respect to dynamics, we show that another, typically much larger, length scale is relevant. It is larger than the mesh size by a frequency-dependent factor, increasing with the ratio of the bulk viscosity to the solvent's viscosity. In-between the two lengths the network responds and fluctuates in a distinctive way, qualitatively different from that of the bulk. We demonstrate the consequences of this intermediate regime for several phenomena: (a) the displacement fluctuations of a particle embedded in a polymer network; (b) the correlated displacement fluctuations of two such particles; (c) the network's surface fluctuations; and (d) the fluctuations of a membrane in contact with a network. We

discuss how these results can be utilized to extract more information from microrheology experiments.

## **COLL 97**

### **Lipid chain entropy and exchange in the vicinity of G-protein coupled receptors**

**Alison Leonard**<sup>1</sup>, [aleon@udel.edu](mailto:aleon@udel.edu), **Alexander Sodt**<sup>2</sup>, **Edward Lyman**<sup>1</sup>. (1) Physics and Astronomy, University of Delaware, Newark, Delaware, United States (2) National Institutes of Health, Bethesda, Maryland, United States

The local lipid environment of the A<sub>2A</sub> adenosine receptor was recently reported to be enriched in unsaturated phosphatidyl choline (PC) during 30  $\mu$ sec of all atom simulation. Rhodopsin is also known to prefer solvation by unsaturated chains, suggesting this may be a generic feature of GPCRs. However, even with tens of  $\mu$ sec of trajectory data it is challenging to converge the first shell lipid composition of an integral membrane protein. This motivated the construction of a Markov State Model (MSM) for the local lipid composition, with states and transition rates obtained from the 30  $\mu$ sec trajectory data, permitting estimation of the timescale needed to relax the initial lipid composition. The thermodynamics of lipid-protein interactions were also assessed, comparing chain entropy of first shell and bulk lipids estimated within the context of a correlated rotational isomeric states-like model, in order to determine the entropic contribution to preferential solvation by unsaturated lipids. The analysis provides a new way to conceptualize the link between lipid structure and thermodynamics.

## **COLL 98**

### **Elastic and structural interactions of eCAPs WLBU2 and D8 with bacterial lipid membrane mimics**

**Stephanie A. Tristram-Nagle**<sup>1</sup>, [stn@cmu.edu](mailto:stn@cmu.edu), **Frank Heinrich**<sup>2,1</sup>, **Akari Kumagai**<sup>1</sup>, **Fernando Dupuy**<sup>3</sup>, **Robert Ernst**<sup>4</sup>, **Berthony Deslouches**<sup>5</sup>, **Peter Di**<sup>5</sup>. (1) Biol Phys Group, Physics, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States (2) Stop 6102, NIST Center for Neutron Research, Gaithersburg, Maryland, United States (3) INSIBIO, National University of Tucuman, San Miguel de Tucuman, Tucuman, Argentina (4) Dept. Microbial Pathogenesis, University of Maryland, Baltimore, Maryland, United States (5) Dept. Environmental and Occupational Health, University of Pittsburgh, Pittsburgh, Pennsylvania, United States

In this work, we focus on elastic and structural interactions of two novel engineered cationic antimicrobial peptides (eCAPs) each with four bacterial lipid membrane mimics. The linear eCAPs are WLBU2 and D8, each composed of 3 types of amino acids (tryptophan, arginine and valine) with a total length of 24 residues. In D8, all valines (8 in total) are the D-enantiomer. Both eCAPs demonstrate broad-spectrum antimicrobial activity and efficiently kill both gram-negative and gram-positive bacteria. Bending moduli, lipid chain order and membrane structure are obtained using x-ray diffuse

scattering (XDS) and the position of each peptide in the membrane is determined with neutron reflectivity (NR). We previously showed using CD and NMR that WLBU2 is primarily alpha-helical, while D8 is primarily random coil in membranes, which indicated that eCAP secondary structure is not a critical factor for bacterial killing, consistent with the diversity in secondary structures observed in natural antimicrobial peptides. However, membrane thinning and the dual location of both WLBU2 and D8 in the headgroup and in the hydrocarbon regions may lead to the membrane destabilization that causes killing of both gram-negative and -positive bacteria. Our published elastic results showed that both WLBU2 and D8 exhibit irregular, non-monotonic changes in bending moduli as a function of increasing concentration of peptide. We suggested that domains with different material moduli are juxtaposed, leading to unstable domain walls. It is possible that each peptide aligns within the domain walls in the hydrocarbon region of gram-negative and -positive bacteria. While neither peptide thins the gram-negative lipopolysaccharide outer membrane model, they both locate deep into its hydrocarbon region where they are primed for self-promoted uptake into the periplasm.

## **COLL 99**

### **Polymer gel-tethered lipid bilayer: Cell surface mimetic of tunable viscoelasticity**

**Christoph Naumann**, [canauman@iupui.edu](mailto:canauman@iupui.edu), **Kent Shils**. Chemistry and Chemical Biology, Indiana Purdue Univ, Indianapolis, Indiana, United States

It is now increasingly recognized that the stiffness of the surrounding tissue may have a profound influence on fate and function of anchorage-dependent cells. Previous advancements in the understanding of cellular mechanosensitivity in an extracellular environment have been made using linker-functionalized polymeric gels of adjustable stiffness. In contrast, less is known about processes about cellular mechanosensitivity in response to mechanical signals from neighboring cells, considered to be significant in processes, such as epithelial-mesenchymal transition and vascular leakage during inflammation. To overcome this shortcoming, we previously introduced the polymer-tethered lipid multi-bilayer as a cell surface mimetic of adjustable stiffness to explore processes of cellular mechanosensitivity of adhering/migrating cells. Here, we present recent results about the assembly and characterization the cadherin-functionalized polymer gel-tethered lipid bilayer (*PGTB*) system as an advanced cell surface mimetic for the analysis of cellular mechanosensitivity. Like other polymer-tethered membrane architectures, *PGTB* enable the dynamic assembly of individual cadherin molecules into cadherin linker clusters at cell-substrate linkages to enable cell spreading and migration. Moreover, unlike polymer-tethered lipid multi-bilayer systems, *PGTB* allow the adjustment of substrate stiffness over the whole physiologically relevant range. In particular, we will describe different *PGTB* assembly strategies and will discuss properties of plated cells, such as cell spreading and cell-substrate linkage distribution and dynamics.

## **COLL 100**

## **Exquisite sensitivity of PhD peptide activity to bilayer lipid composition**

*Sarah Y. Kim*<sup>1</sup>, *William C. Wimley*<sup>2</sup>, ***Kalina A. Hristova***<sup>1</sup>, *kh@jhu.edu*. (1) Johns Hopkins Univ, Baltimore, Maryland, United States (2) Tulane University Health SCI, New Orleans, Louisiana, United States

Peptides that self-assemble into pore-like structures in lipid bilayers could have utility in a variety of biotechnological and clinical applications due to their ability to breach the barrier imposed by lipid bilayers. To empower such discoveries, we use rationally designed peptide libraries and high-throughput screens to select peptides based on a particular property, in this case macromolecular-size bilayer poration. Towards this goal, we have identified the PhD peptides, which efficiently assemble into large pore-like structures when triggered by low pH. Subsequent biophysical characterization has revealed that the activity of these peptides is extremely sensitive to the composition of the lipid bilayer. Currently we are working to understand the principles of peptide-lipid interactions that underlie the observed exquisite sensitivity.

## **COLL 101**

### **Effect of very long chain polyunsaturated fatty acids on membrane structure and lipid flip-flop studied in model membranes**

***John C. Conboy***, *conboy@chem.utah.edu*. Univ of Utah, Salt Lake City, Utah, United States

Retinal membranes are comprised of a variety of phospholipids, proteins, and fatty acids. The presence of a unique class of lipids, which contain very-long chain polyunsaturated fatty acids (VLC-PUFAs), was first identified over two decades ago and has been implicated in maintaining healthy retinal function, particularly rod photoreceptors. In the retina, deficiencies in VLC-PUFAs stem generally from either low dietary intake of VLC-PUFAs or altered activity of the fatty acid elongase protein, ELOVL4, which synthesizes VLC-PUFAs in the endoplasmic reticulum. The studies described here were motivated by the need to characterize a biologically rare but influential membrane component found in the membrane of retinal cells. In an attempt to investigate the impact of VLC-PUFAs on lipid membrane properties, membrane packing in model VLC-PUFA:DSPC membranes were evaluated from pressure-area isotherms. Additionally, the compression moduli of VLC-PUFA:DSPC mixtures were determined, as it has been postulated that VLC-PUFA may modulate membrane rigidity as a key aspect of their biological function in the retinal membrane. In addition to the static perturbations to the membrane, the effect on lipid translocation (flip-flop) was also investigated by sum-frequency vibrational spectroscopy (SFVS).

## **COLL 102**

### **Microfluidic development of giant unilamellar vesicles encapsulating drugs for oral administration**

**Jing Fan**, *jfan1@ccny.cuny.edu*. City College of New York, New York, New York, United States

Liposomal encapsulation of drugs has been widely studied and commercialized over the past several decades. The key benefits of liposomal drug delivery include improved drug effectiveness and bioavailability, protection from degradation, and elongation of retention time. However, traditional liposome preparation methods, such as thin-film hydration and ethanol injection, usually lead to low encapsulation efficiency and heterogeneous size distribution. For example, the encapsulation efficiency for hydrophilic drugs in a liposome core is rarely above 30 %. These non-preferred features can be resolved quite well by microfluidic fabrication, as demonstrated by previous studies. In this work, with a self-secured, multilayered microcapillary device that we recently developed, we create thin-shell double-emulsion drops encapsulating several lipids or lipidic active substances in the middle fluid, and various drugs and nutrients against chronic fatigue syndrome (CFS) in both inner and middle fluids. The formula of this liposomal cocktail has been optimized by a separate study recently based on thin-film method and slightly modified to improve the stability of microfluidic encapsulation. Due to the large diameter of the microcapillary device and relatively slow flow rates, the double emulsion drops can stay a couple minutes in the capillary, experiencing the dewetting process. Therefore, uniform-sized liposomal vesicles can be directly collected from the outlet of the microfluidic device.

To further confirm the unilamellar structure of these vesicles, we add pore-forming proteins,  $\alpha$ -hemolysin ( $\alpha$ -HL), into the inner solution. Since the transmembrane segment of  $\alpha$ -HL spans a single bilayer in size, they only form nanometer-sized pores in unilamellar membranes. Since we encapsulate a self-fluorescent, small molecular drug in the core of the vesicles, we examine the fluorescence variation of vesicles both with and without  $\alpha$ -HL over 80 min after collection under a confocal microscope. The fluorescence intensity of the inner core for vesicles with  $\alpha$ -HL decreases by 60% after 80 min, while that of vesicles without  $\alpha$ -HL does not show any noticeable difference. This indicates the existence of nanopores on the vesicle membranes with  $\alpha$ -HL added and thus confirms the structure of a single bilayer of lipids.

## **COLL 103**

### **Model plasma membrane exhibits a microemulsion in both leaves providing a foundation for "RAFTS"**

**Michael Schick**<sup>1</sup>, *schick@phys.washington.edu*, **David Allender**<sup>1,2</sup>, **Ha Giang**<sup>3</sup>. (1) Physics, University of Washington, Seattle, Washington, United States (2) Physics, Kent State University, Kent, Ohio, United States (3) Viettel Aerospace Institute, Hanoi, Viet Nam

We consider a model lipid plasma membrane, one that describes the outer leaf as consisting of sphingomyelin, phosphatidylcholine, and cholesterol, and the inner leaf of phosphatidylethanolamine, phosphatidylserine, phosphatidylcholine, and cholesterol.

Their relative compositions are taken from experiment; the cholesterol freely interchanges between leaves. Fluctuations in local composition are coupled to fluctuations in the local membrane curvature, as in the Leibler-Andelman mechanism. Structure factors of components in both leaves display a peak at non-zero wavevector. This indicates that the disordered fluid membrane is characterized by structure of the corresponding wavelength. The scale is given by membrane properties: its bending modulus and its surface tension, that arises from the membrane's connections to the cytoskeleton. From measurements on the plasma membrane, this scale is on the order of 100 nm. We find that the membrane can be divided into two different kinds of domains that differ not only in their composition, but also in their curvature. The first domain in the outer, exoplasmic, leaf is rich in cholesterol and sphingomyelin, while the inner, cytoplasmic, leaf is rich in phosphatidylserine and phosphatidylcholine. The second kind of domain is rich in phosphatidylcholine in the outer leaf, and in cholesterol and phosphatidylethanolamine in the inner leaf. The theory provides a tenable basis for the origin of structure in the plasma membrane, and an illuminating picture of the organization of lipids therein.

## **COLL 104**

**Domains of synaptotagmin 1 are structurally disordered, coupled and are allosterically modulated by synaptic vesicle lipids: Each modulates the calcium ion sensing capabilities of synaptotagmin 1**

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Synaptotagmin 1 (Syt 1) is a synaptic vesicle-localized integral membrane protein that senses the calcium ion influx to trigger synchronous release of neurotransmitter. The family of synaptotagmins have a commonality of being comprised of two tandem repeat domains (C2 domains) that are covalently linked to the transmembrane region by a variable peptide linker. We propose a model of how the two cytosolic C2 domains of Syt 1 communicate to propagate the calcium ion binding signal that is allosterically modulated by both its variable linker as well as by synaptic lipids. We provide experimental evidence that is consistent with the variable linker of Syt 1 being a functional domain that modulates sensing of calcium ion. The variable linker of Syt 1 has the hallmarks of an intrinsically disordered region. Intriguingly, this finding of the variable linker being an intrinsically disordered region extends to other members of the synaptotagmin family. This newly defined intrinsically disordered region of Syt 1 was found to interact with membranes whose lipid composition mimics that of the synaptic vesicle. We also define how the overall plasticity of Syt 1 impacts its function in its sensing of calcium ion. The role of lipids in modulating the structural disorder, coupling, sensing of calcium ion and disruption of the membrane by Syt 1 calls into question current models of Syt 1 action.

## **COLL 105**

## **Molecular modeling of lipid-lipid interactions coupling to curvature: Cholesterol and gangliosides**

*Andrew Beaven, Kayla Sapp, Mitchell Dorrell, **Alexander Sodt**, alexander.sodt@nih.gov.* NICHD, National Institutes of Health, Bethesda, Maryland, United States

The energies of lipid membrane shapes are frequently modeled in terms of a lipid's spontaneous curvature. The conventional approach is that each lipid has a single intrinsic parameter, and that the spontaneous curvature of a mixture is the simple sum of its constituents. However, molecular simulations show that this assumption is violated by common lipids, for example, cholesterol and sphingolipids. In this study, we demonstrate how to interrogate the curvature coupling of long-lived configurations of GM1-GM1 dimers, yielding a spontaneous curvature more positive than the monomer form. Additionally, we show how cholesterol can behave in opposite ways depending on context: as either a positive or negative spontaneous curvature lipid.

### **COLL 106**

#### **Structure and dynamics in perovskite nanomaterials**

***William A. Tisdale**, tisdale@mit.edu.* Chemical Engineering, MIT, Cambridge, Massachusetts, United States

Hybrid organic-inorganic semiconductors, including halide perovskites and perovskite nanomaterials, are an exciting class of solution-processable materials that may be used in next-generation optoelectronic applications. When fabricated in a nanostructured form – either as layered 2D quantum wells or colloidal nanocrystals – these hybrid materials exhibit interesting behavior, revealing both quantum mechanical and classical composite effects. I will discuss the thermal, electronic, and excitonic properties of lead halide perovskite nanomaterials – and what these photophysical studies tell us about the interactions between organic and inorganic subphases of this interesting class of materials.

### **COLL 107**

#### **Controlling the optical and electronic properties of colloidal quantum dots using surface ligand chemistry**

***Matt C. Beard**, matt.beard@nrel.gov.* National Renewable Energy Lab, Golden, Colorado, United States

Colloidal semiconductor nanocrystals, specifically quantum dots (QDs), are of interest to numerous scientific disciplines due to their highly tunable optical and electronic properties. I will discuss our efforts in controlling the optical and electrical properties of QDs using various ligand chemistries. I will discuss how the ligand dipole moment can

impact ligand exchanges, the bandedge position, and the enhanced absorption. My taking advantage of ligand-ligand coupling on the QD surface we can construct Janus-ligand shell systems. I will discuss our demonstrated strategies for producing *n* and *p*-type PbSe colloidal QDs. We studied electronic impurity doping of colloidal PbSe quantum dots (QDs) using a post-synthetic cation exchange reaction in which  $\text{Pb}^{2+}$  cations are exchanged for either  $\text{Ag}^+$  or  $\text{In}^{3+}$  cations where varying the concentration of dopant ions exposed to the as-synthesized PbSe QDs controls the extent of exchange. The electronic impurity doped QDs exhibit the fundamental spectroscopic signatures associated with injecting a free charge carrier into a QD under equilibrium conditions, including a bleach of the first exciton transition and the appearance of a quantum-confined, low-energy intraband absorption feature. For  $\text{In}^{3+}$ , spectroelectrochemical measurements demonstrate characteristic *n*-type signatures, including both an induced absorption within the electrochemical bandgap and a shift of the Fermi-level towards the conduction band.

## COLL 108

### Making nanoparticles more efficient than bulk: Lessons from upconversion

**Bruce E. Cohen**<sup>1</sup>, [becohen@lbl.gov](mailto:becohen@lbl.gov), **Bining Tian**<sup>1</sup>, **David Garfield**<sup>1</sup>, **Angel Fernandez-Bravo**<sup>1</sup>, **Emory Chan**<sup>1</sup>, **Peter J. Schuck**<sup>2</sup>. (1) Molecular Foundry 67R5110, LBNL, Berkeley, California, United States (2) Columbia University, New York, New York, United States

Large surface areas are defining features of nanoscale materials, and energy losses associated with surfaces are often a major impediment to efficient performance. For nanocrystals that absorb and emit light, surface traps and quenchers may depress quantum efficiencies by orders of magnitude compared to bulk. Here, we describe 2 strategies to improve quantum yields of NIR-excited, lanthanide-doped upconverting nanoparticles (UCNPs) to be as good as, and better than, those measured in lanthanide-doped upconverting bulk materials. UCNPs convert 2 or more incident low energy photons to higher-energy emission and have proven to be among the most efficient multiphoton probes, but their emission efficiency is limited by energy migration to the surface, where capping ligands and proximal water effectively quench to depress quantum yields. First,<sup>1</sup> we have developed protein-sized, alloyed UCNPs (*a*UCNPs) that can be imaged at the single particle level at laser intensities under  $300 \text{ W/cm}^2$ , a *billion-fold lower* than needed for the best 2-photon fluorophores and over 300-fold lower than needed for comparably-sized doped UCNPs. Using single UCNP characterization and computational models of lanthanide energy transfer, we find that addition of inert epitaxial shells radically changes optimal lanthanide content from  $\text{Yb}^{3+}$ ,  $\text{Er}^{3+}$ -doped  $\text{NaYF}_4$  nanocrystals to fully alloyed compositions. Core/shell *a*UCNPs are brighter than comparably-sized doped UCNPs at all laser intensities tested, over 4 orders of magnitude, and show quantum yields higher than optimized bulk  $\text{Yb}^{3+}$ ,  $\text{Er}^{3+}$ -doped  $\text{NaYF}_4$ . A second strategy<sup>2</sup> for better-than-bulk quantum yields explores organic dye-sensitized UCNPs, in which we discover the critical mechanisms that enable NIR dye antennas to enhance upconverted emission. Using time-gated phosphorescence,

singlet lifetimes, DFT, and triplet quenching experiments, we find that increasing the lanthanide content in the UCNP shifts the primary energy donor from the dye singlet to its triplet, and the resultant triplets in turn mediate energy transfer into the nanocrystals. This symbiotic dye-lanthanide relationship results in dye–UCNP hybrids with >33,000-fold increases in brightness and 100-fold increases in quantum efficiency over dye-free UCNP.

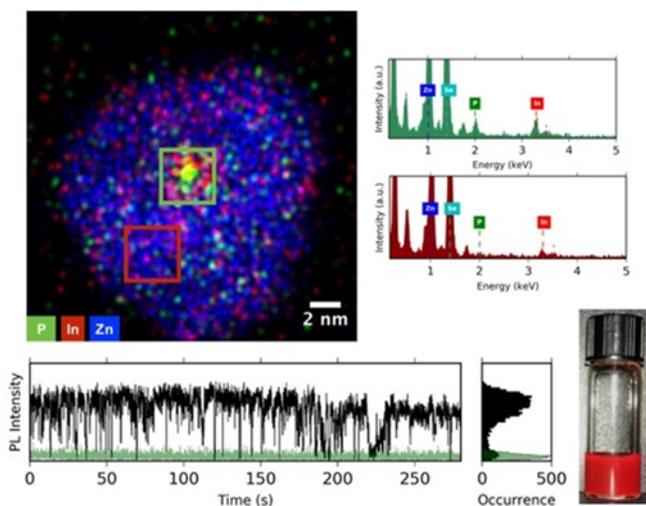
## **COLL 109**

### **Revealing the impact of shell composition and defects on colloidal quantum dot performance**

**James R. McBride**<sup>1</sup>, [james.r.mcbride@vanderbilt.edu](mailto:james.r.mcbride@vanderbilt.edu), **Sophia M. Click**<sup>1</sup>, **Nathaniel Freymeyer**<sup>2</sup>, **Matthew F. Chisholm**<sup>3</sup>, **Jennifer A. Hollingsworth**<sup>4</sup>, **Sandra J. Rosenthal**<sup>1</sup>.

(1) Chemistry, Vanderbilt University, Nashville, Tennessee, United States (2) Department of Chemistry, Vanderbilt University, Nashville, Tennessee, United States (3) Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States (4) Los Alamos National Laboratory, Los Alamos, New Mexico, United States

Core/shell nanocrystals or colloidal quantum dots have become highly complex nanoscale structures designed to achieve high brightness and prolonged photostability. Far removed from simple binary material systems such as CdSe/ZnS, modern quantum dots consist of complex chemical gradients, precisely defined interfacial layers and extreme shell thicknesses. While ensemble observations of the as-synthesized particles provide useful feedback, the ability to match a single quantum dots' optical behavior with its structure and chemical composition can revolutionize the chemist's ability to fine tune the synthesis to produce specific optical properties. To achieve this ability, we have developed an intuitive and reproducible method to correlate the atomic and chemical structure of individual colloidal nanocrystals with the same particle's fluorescence dynamics. With this correlation technique it is possible to identify sub-populations of structures that exhibit the desired photophysics and then use that knowledge to direct chemistry to produce quantum dots with specifically chosen optical behavior. In conjunction with advanced scanning transmission electron microscopy coupled with energy dispersive spectroscopy (STEM-EDS) the single particle photophysics of graded alloy CdZnSSe nanocrystals was obtained revealing that a thick and non-alloyed ZnS shell is required to achieve suppressed blinking and improved photostability. Defects identified as determinantal via the correlation methodology were observed for the first time with atomic resolution aberration-corrected STEM. Additionally, single particle spectroscopy, STEM-EDS and aberration-corrected STEM will be presented on thick-shelled InP quantum dots. The effect of indium incorporation into the shell on their structure and optical properties discussed.



Thick-shelled InP/ZnSe quantum dot: Chemical structure and blinking dynamics

## COLL 110

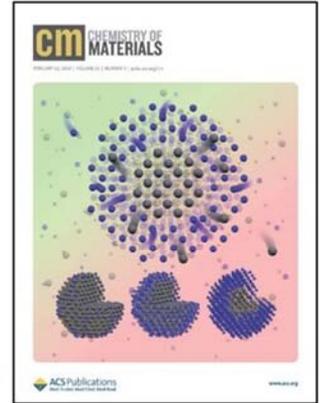
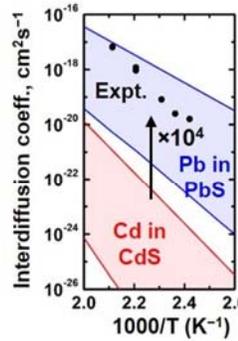
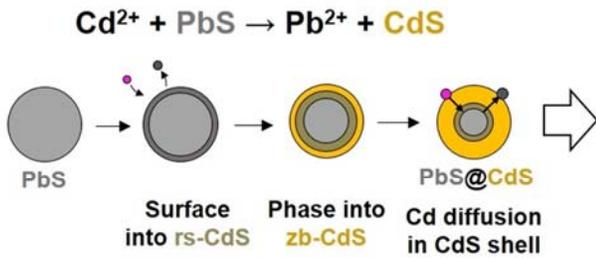
### Accelerated solid-state diffusion during cation exchange in PbS-CdS nanocrystals

**Richard D. Robinson**, [rdr82@cornell.edu](mailto:rdr82@cornell.edu). MSE Department, Cornell University, Ithaca, New York, United States

The phenomenology of solid-state transformations in nanoparticles is important for applications utilizing their reactivity and for investigations into how nearby interfaces interact with the defects responsible for mass transport. We directly interrogate the structure and reaction kinetics of lead sulfide (PbS) nanocrystals undergoing cation exchange in organic solution to cadmium sulfide (CdS) *via* x-ray diffraction (XRD). The epitaxial relationship of zincblende CdS to rocksalt PbS breaks the overall symmetry of the core-shell nanocrystal without requiring the loss of unit cell symmetry, leading to anomalous peak shifts in the diffraction pattern. Conversion occurs in three stages: (1) surface exchange to form a metastable rocksalt CdS shell, (2) crystallization of this shell to zincblende, and (3) diffusive transport of ions through the completed shell. The interdiffusion coefficient,  $D$ , for ions diffusing through the shell follows the Arrhenius relationship with an activation energy of 160-180 kJ mol<sup>-1</sup>, which exceeds that observed in many other experiments in diffusion in nanoparticles and is similar to values measured in bulk solids, suggesting the barrier to exchange is dominated by the energies of point defect formation rather than surface-bound reactions. However, the magnitude of  $D$  is larger by four orders of magnitude or more compared to the slowest diffusing species in our system (self-diffusion of Cd in CdS). This surprising result suggests interdiffusion is enhanced in nanocrystals, and possible mechanisms include high concentrations of induced extrinsic defects and/or increase in diffusive jump length through high-diffusivity paths. Cation exchange illustrates that the distinction between chemical diffusion in a potential gradient and diffusion at thermodynamic equilibrium has

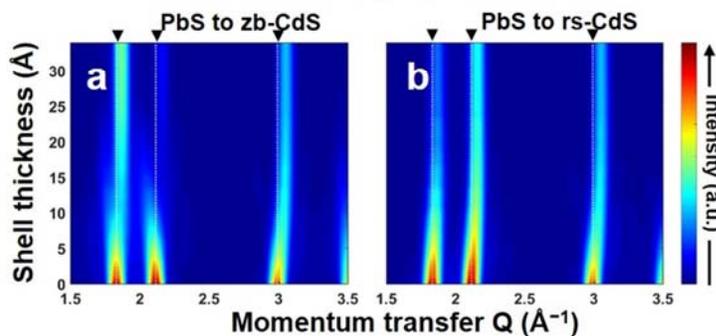
not been fully appreciated. Acceleration of interdiffusion in core-shell nanoparticles due to large chemical potential gradients will be important for understanding for nanoscale heterostructure formation and stability.

### Accelerated Diffusion in Nanomaterials

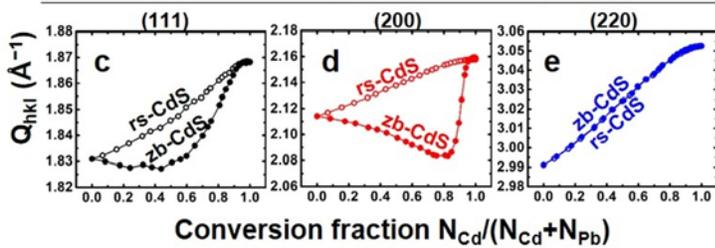


Diffusion is  $10^4$ x faster than bulk constants

### Debye scattering eq simulations



• *rs-CdS shell should show opposite shifts from zb-CdS shell*



• *Our experimental data consistent with initial metastable rs-CdS shell*

COLL 111

### Synthesis of $Cu_{2-x}S/PbS$ core/shell nanocrystals for infrared exciton-plasmon coupling

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Lead chalcogenide nanocrystals are an excellent material for infrared optoelectronics and have recently been commercialized in low-cost near-infrared cameras. However, they still remain limited by the absorption-extraction compromise and low photoluminescence quantum yields. One solution to these limitations is to combine an infrared plasmonic material with the lead chalcogenide into a core/shell nanocrystal, which will allow for exciton-plasmon coupling and optical enhancements via the Purcell effect. Doped plasmonic nanocrystals, such as copper chalcogenides, are good plasmonic materials for this purpose because they have plasmonic energies tunable throughout the near-infrared. Therefore, lead and copper chalcogenide core/shell nanocrystals, such as  $\text{Cu}_{2-x}\text{S}/\text{PbS}$ , are very desirable as a model system to controllably couple excitons and plasmons to enhance the optical properties of infrared nanocrystals.

We developed a novel synthetic method for  $\text{Cu}_{2-x}\text{S}/\text{PbS}$  core/shell nanocrystals, which deposits a PbS shell while maintaining the plasmonic character of the  $\text{Cu}_{2-x}\text{S}$  cores. Typical shell synthetic methods avoid homogenous nucleation of the shell material by the slow addition of precursors over a long reaction time. However, long reaction times (~hours) do not work for  $\text{Cu}_{2-x}\text{S}/\text{PbS}$  core/shell nanocrystals due to a Cu-to-Pb cation exchange, which destroys the plasmonic character of the  $\text{Cu}_{2-x}\text{S}$  cores. By simultaneously mixing the precursors with the  $\text{Cu}_{2-x}\text{S}$  cores, and limiting the reaction times and temperatures, we were able to deposit the PbS shell before cation exchange could destroy the  $\text{Cu}_{2-x}\text{S}$  plasmon. PbS nanocrystals do homogeneously nucleate, but they can be removed using size-selective precipitation. The effect of the PbS shell on the energy and intensity of the plasmon depends on the ligand type and copper vacancy concentration of the initial  $\text{Cu}_{2-x}\text{S}$  cores. This synthesis is the first step toward the realization of infrared exciton-plasmon coupling in uniform core/shell nanocrystals using doped plasmonic semiconductors.

## **COLL 112**

### **Alternative plasmonic nanomaterials as building blocks for purcell-enhanced emission in the infrared**

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Recent interest towards development of novel semiconducting materials with plasmonic properties is driven by their potential to advance applications ranging from light-based sensing and environmental testing to telecommunication technologies. A new class of infrared (IR)-active plasmonic material – spinel metal oxides (sp-MOs) – can address deficiencies of both metallic and semiconducting plasmonic nanomaterials in terms of control over spectral position, ease of fabrication, and environmental stability. As a

result of their unusual structure sp-MO systems support multiple doping modes for controlling free carrier density, which may afford unprecedented tunability in their plasmonic behavior. Finally, when paired with IR-active light-emitting semiconducting nanocrystals, i.e., quantum dots (QDs), sp-MOs may provide enhanced light emission by increasing radiative recombination rates through the well-known Purcell enhancement effect.

Here, we report synthesis and comprehensive characterization of novel plasmonic sp-MO nanocrystals, as well as their integration with IR-QDs resulting in hybrid assemblies with plasmonic-enhanced light emission properties. Here, we effectively “co-develop” IR emitters with supporting IR plasmonic semiconducting nanocrystals, and demonstrate for the first time plasmonics-enhanced emission from telecom-active QDs (up to five-fold enhancement to date). Using two sp-MO systems, we show how material composition, nanocrystal size and nanocrystal shape/faceting impact electronic behavior. We also use systematic exploration of synthesis parameters to establish key correlations between processing, structure and properties toward targeting plasmonic nanomaterials by-design.

## **COLL 113**

### **Dimensional confinement to control perovskite crystallographic phase**

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Phase diagrams depicting the equilibrium between different polymorphs of a crystalline material are commonly measured as a function of temperature and pressure; herein we explore dimensional confinement as an alternative dependent variable that likewise determines the phase equilibrium of metal halide solids. We develop and test the hypothesis that for solids with mixed covalent and ionic bonding, low-density, high-symmetry phases can be favored by restricting crystal dimensions to the nanoscale. In particular, we seek to render the perovskite phase of cesium lead iodide (CsPbI<sub>3</sub>) thermodynamically stable at standard temperature and pressure through nanostructuring, in order to exploit this structure's beneficial optoelectronic properties. Using first-principles calculations, we demonstrate that phase stability changes as a function of varying crystal size. Such calculations allow for the simultaneous quantification of short-range, orbital-orbital repulsive forces, which are hypothesized to favor low-density and high-symmetry phases as well as long-range electrostatic forces, which favor high-density. Experimentally, we show that the phase sequence can be inverted and equilibrium shifted by as much as 250 °C through various nanostructuring approaches, including colloidal nanocrystal co-assembly and crystallization within nanoporous scaffolds.

## **COLL 114**

## **Mercury chalcogenide nanoplatelets with tunable shortwave infrared defect emission**

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Despite broad applications in imaging, energy conversion and telecom, there are few nanoscale moieties that absorb and emit light efficiently in the shortwave infrared (1000-2000 nm or 1.24-0.62 eV). Quantum confined mercury chalcogenide (HgX) nanocrystals have size-tunable bandgaps through the SWIR, with 2 dimensional three monolayer HgTe nanoplatelets (NPLs) emitting in the near infrared (900 nm or 1.37 eV). Despite the fixed atomic confinement, we demonstrate previously unreported bright (QY>30%) tunable (900-1800 nm) infrared emission from 3ML HgX nanoplatelets. Spectroscopic characterization strongly suggest ligand exchange is accompanied with changes in NPL stoichiometry and eventual nanoparticle rearrangement, inducing thermodynamically controlled tunable trap/defect emission. Spectrally resolved photoluminescence demonstrate energy dependent lifetimes, with radiative rates 10 times faster than their PbX analogs. Coupled with their high quantum yield, HgX NPLs provides a potential platform novel optoelectronics in the SWIR.

### **COLL 115**

## **Synthesis of self-assembled nanoparticles from various types of precursors in aerosol droplets**

**Pratim Biswas**, *pratim.biswas@wustl.edu*, **Sukrant Dhawan**, **Hao Zhou**. Washington University in St. Louis, Saint Louis, Missouri, United States

Aerosol processes can be used to produce droplets with well controlled sizes. Depending on the nature of the precursors used (either dissolved species or nanoparticle inclusions), various morphologies of functional materials can be produced. By understanding the various mechanistic steps and then controlling the various operating parameters, self assembly resulting in specific structures have been obtained (Shah and Biswas, ACS Nano, 2014 ). Two types of systems will be described in this presentation.

The first system will examine the morphology of the resultant nanoparticles in an aerosol spray synthesis process. Based on the properties of the precursor such as solubility and decomposition rate, different time scales will be derived to predict the resultant structure of the nanoparticles. Regimes to produce hollow (core-shell) structures to solid structures will be described. Such spray aerosol processes find application in a variety of systems ranging from catalysis to energy materials.

The second system will examine the structure evolution in electrospray systems. Here the role of charge of the droplet on the evaporation process and the eventually

assembly will also be discussed. Systems to produce perovskite nanoparticles for solar energy harvesting will be discussed. In addition to specific composition, the evolution of the crystal phases of the resultant compounds will also be discussed.

## **COLL 116**

### **Hyperspectral imaging of nanoparticle attachment and growth**

**David S. Ginger**, *ginger@chem.washington.edu*. Dept of Chemistry, University of Washington, Seattle, Washington, United States

Plasmonic nanoparticles are exquisitely sensitive to their local environment. Here, we exploit this sensitivity to study bio-templated nucleation and growth of gold nanospheres and nanorods on engineered protein nanofibers. We benchmark optical darkfield microscopy data with electron microscopy, then apply massively parallel hyperspectral darkfield imaging to obtain statistics on particle attachment and growth kinetics as a function of charge state and solution chemistry. Finally, we explore stimulus-responsive behaviors and dynamic reconfiguration of the plasmonic properties of these systems to change their optical properties and assembly behaviors in response to light, heat, and chemical changes in the environment, extracting statistical information on the dynamic response from the darkfield data.

## **COLL 117**

### **Anisotropic chemistry on gold nanorods**

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Gold nanorods provide tunable plasmon modes that span the visible to the near-infrared part of the electromagnetic spectrum. Illumination at the plasmon band leads to localized electric fields at the surface of the nanorods, at different positions depending on illumination wavelength. Surface-enhanced X (Raman, fluorescence) spectroscopies rely on molecules being an optimum distance away from either the ends or sides of the nanorods. How can one achieve spatially selective chemistry on these colloidal objects? In this talk I will describe, briefly, the synthesis of gold nanorods of different absolute dimensions, and the strategies used to deposit material on either the sides or ends of the rods.

## **COLL 118**

### **Light-triggered changes in the solvation and interactions of metallic nanoparticles**

**Nicholas L. Abbott**, *nabbott@cornell.edu*. Smith School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, New York, United States

The structuring of solvent molecules near the surfaces of nanoparticles influences both equilibrium (self-assembly) and dynamic (transport) properties of nanoparticles. This presentation will report observations of light-induced changes in the solvation of metallic nanoparticles made by performing measurements of the hydrodynamic drag experienced by the nanoparticles during motion through a solvent. Specifically, by choosing temperatures that place isotropic solvents close to phase transitions to ordered liquid phases, and by tracking the motion of single-nanoparticles undergoing Brownian diffusion, we measure optically-induced changes in solvation of surface-functionalized gold nanoparticles to occur in a wavelength-specific and nanoparticle size-dependent manner. A range of experiments and calculations designed to test hypotheses regarding the underlying mechanism, including the effects of optical pressure, surface plasmon resonances and hot electrons, support the proposal that an ordered solvent corona is induced by interfacial electric fields generated by optically-induced hot electron-hole pairs. We confirm solvent restructuring by measuring changes in the surface plasmon resonances of surfaces decorated with gold islands. Overall, these results suggest new principles for optical manipulation of the interfacial ordering of solvents at the surfaces of nanoparticles.

## **COLL 119**

### **Structure determination of colloidal crystals in solution using small angle X-ray scattering**

**Byeongdu Lee**, *blee@aps.anl.gov*. Argonne National Laboratory, Lemont, Illinois, United States

Small angle x-ray scattering (SAXS) has been a key technique in the structure determination of colloidal crystals especially in solution. When the structure becomes complex, it is essential to accurately calculate its x-ray scattering pattern. In this presentation, recent advances of SAXS data analysis on colloidal crystals will be discussed. A focus will be more on particle position determination in the unit cell. Two approaches, model analysis and Fourier synthesis, will be reviewed along with examples on DNA-NP assemblies. Complimentary use of these two methods will significantly improve data analysis and reduce effort.

## **COLL 120**

### **Nanostructures synthesized using non-native block copolymer morphologies**

**Kevin G. Yager**, *kyager@bnl.gov*. Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York, United States

Functional nanostructures, including arrays of nanowires or nanodots, can be fabricated using self-assembly of block copolymers as templates. The range of structures that can be formed is correspondingly limited by the range of morphologies that block copolymers easily form. This talk will present a selection of emerging strategies for constructing three-dimensional nanostructures whose shapes and symmetries go beyond those of the bulk equilibrium diblock copolymer phase diagram. Photo-thermal methods are used to control block copolymer ordering histories; ordered layers can be stacked to yield new lattice symmetries. This can also be performed in a responsive mode, where each self-assembled layer templates the ones that follow. Finally, blending allows the self-assembling film morphology itself to be responsive to underlying guides. Taken together, these new motifs represent a toolbox for constructing 3D nanostructures with symmetries and complexity beyond conventional self-assembled morphologies.

## **COLL 121**

### **New insight into the role of Ag in the seed-mediated gold nanorods synthesis**

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The role of silver ions in seed-mediated gold nanorod (AuNR) syntheses has been investigated. The key silver intermediate which controls the AuNR aspect ratio was identified as a CTA-Ag-Br complex using UV-Vis spectroscopy. We systematically studied the AuNR growth solution preparation process and determined that the solubility of this CTA-Ag-Br complex intermediate is the limiting reagent, with a limiting solubility of 0.12 mM, in the preparation of AuNR. Additional AgNO<sub>3</sub> does not influence of the aspect ratio (length-to-width) of the resulting AuNR. The sequence of reagent addition is also a determinant in the evolution of the gold nanorod. The importance of CTA-Ag-Br complex in nanorod synthesis is further supported by the observation of nanoparticle formation when ascorbic acid is added before the formation of CTA-Ag-Br complex. mixing of AgNO<sub>3</sub> results in the formation of large quantities of (spherical) gold nanoparticles. This result sheds light on the understanding of the role of silver ions in AuNR syntheses and helps the design of new synthetic approaches to produce AuNR with large aspect ratios.

## **COLL 122**

### **Long-range order and templated deposition of alkoxy-pyrenes in monolayers of discrete oligoethylene-naphthalenediimide at the liquid/solid interface**

**José Augusto Berrocal**<sup>1</sup>, [jose.berrocal@unifr.ch](mailto:jose.berrocal@unifr.ch), **Bas F. de Waal**<sup>2</sup>, **Henriette Heideman**<sup>3</sup>, **Egbert W. Meijer**<sup>2</sup>, **Ben L Feringa**<sup>3</sup>. (1) Adolphe Merkle Institute, Fribourg, Switzerland (2) Institute for Complex Molecular Systems, Eindhoven University of

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Precise control over molecular self-assembly on surfaces holds promise for fundamental and technological advances in both supramolecular chemistry and materials. From the fundamental point of view, the understanding of the delicate interplay between the supramolecular forces operating on surface-based systems and its translation into molecular design principles can pave the way to defect-free self-assembled monolayers. This can subsequently resonate into a number of applications, such as smart surfaces that can reconfigure structure and properties in response to chemical/physical stimuli.

The defect-free engineering of surface-supported supramolecular assemblies on unconfined Highly Oriented Pyrolytic Graphite (HOPG) represents a major challenge in this field. So far, various approaches focused on limiting the number of domain boundaries and/or molecular defects to improve the organization of the 2D architectures generated. Alternatively, spatially confining the self-assembly process into nanocorrals created on HOPG afforded impressive results in terms of order, but only for very small areas.

In this contribution, we report the synthesis of two libraries of naphthalenediimides (NDIs) symmetrically functionalized with long aliphatic chains (C<sub>28</sub>-C<sub>55</sub> range) and their self-assembly at the 1-phenyloctane/HOPG (1-PO/HOPG) interface. The two NDI libraries possess long aliphatic chains and differ by the presence/absence of internal double bonds in each aliphatic chain (unsaturated and saturated compounds, respectively). All molecules assemble into lamellar arrangements with the NDI cores lying flat and forming 1D rows on the surface, while the carbon chains separate the 1D rows from each other. Importantly, the presence of the unsaturation plays a dominant role in the arrangement of the aliphatic chains, as it exclusively favors interdigitation. The fully saturated tails, instead, self-assemble into a combination of either interdigitated and non-interdigitated diagonal arrangements. The difference in packing between unsaturated and saturated chains is spectacularly amplified at the whole surface level and results in almost defect-free self-assembled monolayers in unconfined HOPG for the compounds featuring unsaturated chains. Finally, we show the application of one of these self-assembled monolayers at the 1-PO/HOPG interface as a template for the subsequent deposition of alkoxy-pyrenes with exquisite spatial control.

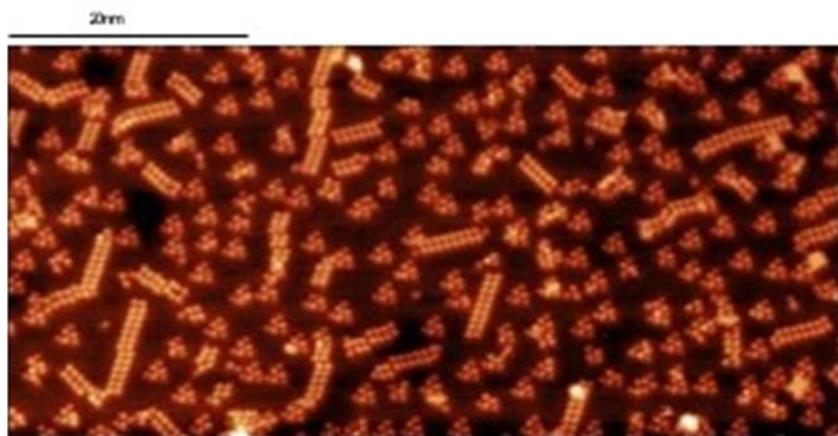
## **COLL 123**

### **Surface molecular assemblies of amino acids on Cu(111)**

**Constance Pfeiffer**, *crpfeiffer6@outlook.com*, **Nathan Guisinger**. Nanoscience and Technology, Argonne National Laboratory, Naperville, Illinois, United States

Amino acids are the building blocks of all proteins. The way in which they assemble on surfaces can give useful information for ways of controlling material symmetry to induce exotic behavior and provide methods to develop atomically manufactured molecular

networks for generating artificial condensed matter testbeds. Except for glycine, all nineteen of the other simple amino acids exhibit either D- or L- chirality. However, all proteins selectively use only the L-configuration of amino acids. In attempt to understand this selectively as well as obtain an understand of the molecular assemblies of amino acids on surfaces, we have studied several amino acids on a Cu(111) surface. With some amino acids, in particular tryptophan and threonine, one or two basic building blocks are observed. These building blocks have a distinct chirality depending on whether D- or L-configuration is adsorbed onto the surface. When a D/L racemic mixture is used, the building units separate out into individual D or L assemblies. Other amino acids such as serine, result in more complex molecular assemblies.



D-Threonine on Cu(111)

## **COLL 124**

### **Using EC-STM to obtain an understanding of amino acid interaction on Au(111)**

**Kennedy P. Boyd**, [kpb878@utulsa.edu](mailto:kpb878@utulsa.edu), *Jesse A. Phillips, Irene Baljak, Lauren K. Harville, Erin V. Iski*. Chemistry and Biochemistry, University of Tulsa, Jenks, Oklahoma, United States

Further investigation into the interaction of biomolecules on metallic surfaces can provide a better understanding of the origins of life and homochirality in biology. Many studies involving the adsorption of amino acids on metallic substrates have been observed using scanning tunneling microscopy (STM) and conducted in gas phase under ultra-high vacuum (UHV) in order to maintain a pristine surface. Many of these studies have reported that the interaction between the amino acids and the metallic surface results in the formation of 3D structures. These structures, or islands, are formed due to the binding of different functional groups of the biomolecule to diffusing metal adatoms. Although much can be learned from the studies conducted in UHV, it would be advantageous to conduct similar experiments in more biologically relevant

conditions. This investigation focuses on the study of five simple amino acids, as well as two modifications of a single amino acid, and their interaction with Au(111). These interactions were observed via *in situ* Electrochemical STM (EC-STM) at ambient temperature and in liquid. Importantly, ambient conditions provide a closer representation of the hypothesized environment in which homochirality originated. Results indicate that depending on the external potential applied, the amino acids either assisted in the formation of magic gold fingers or formed 3D adatom islands, similar to the UHV studies. It was also found that as the molecular weight of the amino acids increased, the island area increased as well. Moreover, an increase in island area was observed when the amino acid side chain changed from nonpolar to polar. By investigating these interactions via EC-STM, insight can be gained into the relevance UHV-STM studies as well as into a better understanding of the interaction of amino acids with metallic substrates.

## **COLL 125**

### **Surface-mediated crystal growth of aurous cyanide from molecular self-assembled monolayers**

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Self-assembled monolayers have been used to pattern surfaces at the nanometer scale. These patterns enable us to change the surface properties of materials. Our group uses surface functionalization and uses gold on many systems. Cyanide has a strong affinity towards gold; however, the basic chemical and physical properties of gold cyanide compounds remain largely unexplored. Unraveled by scanning tunneling microscopy, cyanides can form self-assembled monolayers on gold substrates when exposed to dilute concentrations of cyanide vapor with two distinct absorption geometries: carbon bound to gold and nitrogen bound to gold. Upon prolonged vapor-deposition, the self-assembled cyanide monolayers reconfigure into large-scale aurous cyanide (AuCN) crystals. Similar to our previous discoveries on self-assembled monolayers, we found two distinct morphologies. Those crystals have similar optical properties, but different cyanide vibrational modes. Therefore, we postulate the unit-cell also goes through a rearrangement and results in structures differing in the gold-cyanide orientations and long-range ordering. Overall, we expect our findings will lead to new insights for controlled surface-mediated crystal growth.

## **COLL 126**

### **Infrared nanospectroscopy at the graphene–electrolyte interface**

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A new methodology is presented to study the molecular structure of graphene–liquid interfaces with nanoscale spatial resolution. It is based on Fourier transform infrared nanospectroscopy (nano-FTIR), where the infrared (IR) field is plasmonically enhanced near the tip apex of an atomic force microscope (AFM). The graphene seals a liquid electrolyte reservoir while acting also as a working electrode. The photon transparency of graphene enables IR spectroscopy studies of its interface with liquids, including water, propylene carbonate, and aqueous ammonium sulfate electrolyte solutions. We illustrate the method by comparing IR spectra obtained by nano-FTIR and attenuated total reflection (ATR-FTIR) demonstrating that the nano-FTIR method makes it possible to determine changes in speciation and ion concentration in the electric double and diffuse layers as a function of bias.

## **COLL 127**

### **Molecular layers as functional interfaces to nanoporous gold**

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Nanoporous gold is a material with high conductivity and surface area, which makes it an interesting platform for surface chemistry. However, the nanoporous gold surface lacks the molecular functionality necessary for many applications. We have investigated molecular layer formation and properties on nanoporous gold, comparing reactions formed through the commonly used thiol attachments with direct carbon to gold bonds. We use infrared spectroscopy, cyclic voltammetry, and X-Ray photoelectron spectroscopy to show that the molecular layer ordering, density, and intermolecular interactions depend on the functionalization method and on the porosity of the underlying nanoporous gold substrate.

## **COLL 128**

### **Reversible self-assembled monolayers as a multivalent platform for virus detection and inhibition**

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Multivalency plays a major role in most biological molecular recognition processes. For instance, multivalent interactions are the driving force in virus attachment to the cell surface at the early stage of infection process. The development of new drugs with

multivalent ligand representation that will inhibit the virus-cell association is considered as an advantageous alternative for the treatment of severe viral infections such as Influenza. The design of such drugs includes the synthesis of complex compounds as dendrimers, fullerenes, polymers *etc.* and requires time-consuming multistep organic synthesis. Here we present a new concept for multivalent ligand representation, *reversible self-assembled monolayers*. These layers are pH-switchable version of self-assembled monolayers. Unlike SAMs, the rSAMs demonstrate lateral mobility and enhanced affinity towards hemagglutinin. These layers mimic the complex multivalent carbohydrate arrays present on the cellular surfaces thus represent an ideal platform for virus detection and for engineering of multivalent virus inhibitors.

## **COLL 129**

### **Quantifying nanoparticle surface chemistries' effect on association with biological models**

**Denise N. Williams**, [dwill3@umbc.edu](mailto:dwill3@umbc.edu), Zeev Rosenzweig. Chemistry and Biochemistry, University of Maryland, Baltimore County, Bowie, Maryland, United States

This presentation describes work investigating the impact of quantum dots' (QDs') surface chemistry on their interactions with model membranes and bacterial cells. QDs are continuously being incorporated into biological assay, imaging, targeting, and treatment technologies. The varying methods in use to attain the aqueous miscible QDs of these technologies result in inherently different QD surface chemistries. These different surface chemistries impact the ability of the QDs to interact with biological models. While it is common practice to determine affinity and association constants for specific QDs in their intended technology, this study aims to concurrently investigate the impact varying QD surface chemistries have on the association and interaction of QDs with biologically-relevant models. Our studies use various optical and surface probing techniques to characterize the QDs' surface chemistry and interaction with biological models, including dynamic light scattering, zeta potential, absorbance, emission, and FRET measurements. Our studies show how differences in charge, charge density, and surface ligand type may impact QD interactions with model membranes and human health-relevant bacterial and mammalian cells.

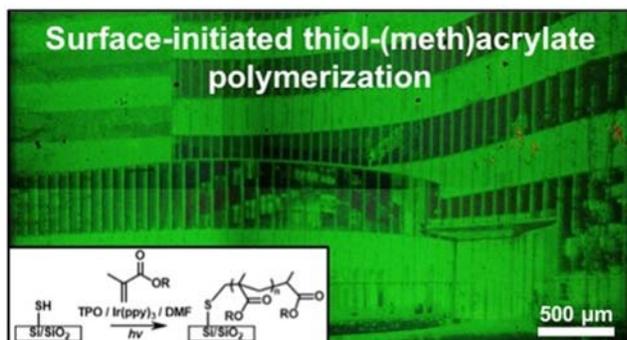
## **COLL 130**

### **Rapid optimization of surface chemistry in a novel photochemical printer: Surface-initiated thiol-acrylate photopolymerizations**

**Adam B. Braunschweig**, [adam.braunschweig@asrc.cuny.edu](mailto:adam.braunschweig@asrc.cuny.edu). Department of Chemistry, University of Miami, Coral Gables, Florida, United States

A major challenge in surface chemistry is the difficulty in which grafted-from polymerizations are optimized. Specifically, the roadblock is that finding the correct reaction conditions often requires trying tens or even hundreds of different reaction

conditions, and the effects of each reaction on brush height and composition must be tested on a separate surface, leading to high costs and low-throughput. Here we show how a new printer that combines an LED, a digital micromirror device (DMD), and an air-free reaction cell can be used to study the thiol-(meth)acrylate photopolymerization. The key advance of this platform is that hundreds of different reaction conditions can be tested on each surface, thereby rapidly accelerating the development and optimization of surface chemistry. With this printer we tested over 200 different reaction conditions to understand the role of light intensity, monomer concentration, and photocatalyst on polymer height. In addition, the ability to test so many reaction conditions lead to several serendipitous and surprising observations, including data that suggest that, under certain conditions, the thiol-(meth)acrylate shows the characteristic behaviors of a controlled radical polymerization.



## COLL 131

### Smooth and transparent hybrid films showing statically hydrophilic but dynamically hydrophobic behavior

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Smooth and transparent hydrophilic films showing excellent water sliding property were prepared using a sol-gel solution of 2-[methoxy (ethyleneoxy)<sub>10</sub>propyl]trimethoxysilane (PEG-M) and tetraethoxysilane (TEOS). The resulting films were statically hydrophilic (static water contact angles (CAs) were in the range of 30°–45°), but dynamically hydrophobic properties with low CA hysteresis ( $5^\circ \pm 1^\circ$ ), on which 50 μL of water droplet could move smoothly on an inclined surface (minimum sliding angle was 6°) without pinning and tailing. Due to the formation of this hybrid film on aluminum (Al) substrate, drainage performance during condensation and frosting/defrosting steps markedly improved compared with hydrophilic bare Al or hydrophobic perfluoroalkylsilane monolayer-covered Al surfaces (Figure1).

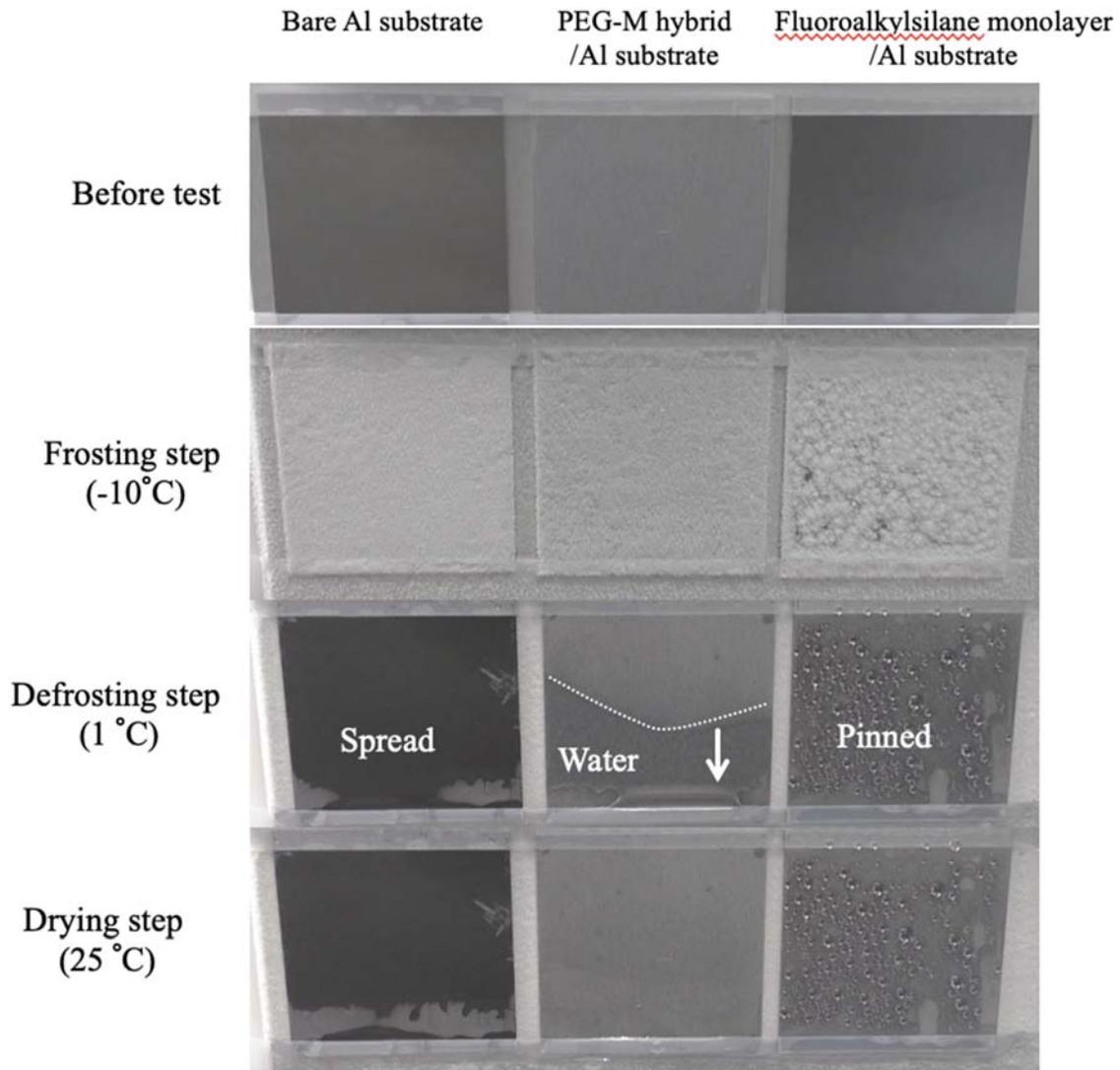


Figure 1. Frosting/defrosting behaviors of UV-ozone cleaned bare (left 4 images), PEG-M hybrid (middle 4 images) and fluoroalkylsilane monolayer (right 4 images) formed on finely polished aluminum (Al) substrates (50×50 mm<sup>2</sup>). The samples were firmly attached to an upright Peltier cooler (tilt angle of 90°).

**COLL 132**

**Atmospheric aging increases rigidity in sea spray aerosol proxy films**

**Kimberly A. Carter Fenk**, *carter-fenk.1@osu.edu*, **Heather C. Allen**. Chemistry & Biochemistry, The Ohio State University, Columbus, Ohio, United States

Saturated fatty acids comprise one of the most abundant and surface-active components of sea spray aerosol (SSA) during seasons of high biological productivity in the ocean. An organic film is formed on SSA surfaces, and particle aging in the marine boundary layer leads to changes in film morphology. Surface pressure – area isotherms and Brewster angle microscopy were used to investigate interfacial organization and morphology as a function of SSA aging. A fatty acid mixture composed of myristic acid (MA), palmitic acid (PA), and stearic acid (SA) at the molar ratio of 3 SA:4 PA:2 MA was used to model the dominant surfactant composition in fine SSA. An aqueous subphase of 0.4 M NaCl adjusted to pH 8.2, 5.6, and 2.0 was used to mimic the SSA aqueous core at various stages of particle aging. We show that the SSA proxy film differs in phase behavior and monolayer collapse from that of its individual fatty acid components. The proxy film exhibits intermediate rigidity at seawater pH and folds upon film compression, whereas at low pH the film becomes highly rigid and forms 3D nuclei upon monolayer collapse. Our results indicate that subphase composition and pH play a significant role in modulating SSA film morphology, which in turn impacts SSA reflectivity in the atmosphere.

### **COLL 133**

#### **Methodology to enhance absorption of thin films on ice using reflection-absorption infrared spectroscopy (RAIRS)**

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The detection of adsorbed molecules on ice at surface coverage similar to those encountered in environmental conditions requires high surface sensibility that few techniques can afford. An experimental methodology allowing a significant enhancement in the absorption from adsorbed molecules is demonstrated here. It exploits electric field standing wave (EFSW) effects intrinsic to grazing incidence Reflection Absorption Infrared Spectroscopy (RAIRS) where film thickness dependant optical interferences occur between the multiple reflected and transmitted IR beams at the film-vacuum and the substrate-film interfaces. As a case study, CH<sub>4</sub> is used as a probe molecule and deposited on a 20 ML thick dense amorphous solid water (ASW) film adsorbed onto underlayers of Ar of various thicknesses. These investigations reveal that an enhancement from 20 to 35 is achieved when destructive interference coincides with the absorption features of the adsorbate, that is the  $\nu_3$  and  $\nu_4$  modes of methane, respectively. Simulations using Fresnel transmission and reflection coefficients reproduce the Ar thickness dependant enhancement for CH<sub>4</sub> absorption bands and reveal that enhancement in the absorption by adsorbates occurs when the square modulus of the electric field at the film's surface reaches its minimum. Exploiting the EFSW allows the limit of detection of adsorbed molecules at the surface of ice coverage

to be reduced to 0.2 ML using CH<sub>4</sub> as a probe molecule which opens interesting perspectives for spectroscopic studies of heterogeneous atmospheric chemistry at coverages that are more representative of those found in the natural environment.

## **COLL 134**

### **Monitoring cellular trafficking of therapeutic nucleic acids in the real-time**

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The intracellular trafficking and delivery of nucleic acids in cells is a field of growing interest both from a fundamental standpoint and for therapeutic applications. Spectroscopic methods can be used to observe and quantitatively measure the extent of delivery of therapeutically active oligonucleotides both in vitro and in vivo. Here we present novel chemical design elements into a newly developed hybrid biomaterial called nucleic acid nanocapsule (NAN). These new modifications consist of optically activatable cross-linkers and fluorophore labeled surfactants that can be used for monitoring the trafficking of therapeutic nucleic acids (TNAs) in the cell. These new cross-linkers contain nitro-phenol cross-linkages that are incorporated into the NANs surface. Upon degradation of the NAN by enzymes, the extent of disassembly can be monitored spectroscopically due to the production of phenol ions. In a second parallel approach a fluorophore-labeled surfactant consisting of a solvatochromatic chromophore is present which can be utilized to track the movement of a surfactant-nucleic acid conjugate using a fluorescently labeled oligonucleotide cargo. Using these new chemical probes tailored to the NANs assembly and disassembly, mechanistic insights into the stability and degradation of NANs both in vitro and in cell culture can be studied effectively, providing new tools that will allow us to measure the cellular uptake, stability and trafficking of TNA conjugates intracellularly in real time.

## **COLL 135**

### **Self-assembly of bacterial quorum sensing signals in aqueous media: Integrated experimental and molecular dynamics study**

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Many species of bacteria communicate and coordinate group behaviors, including toxin production and surface fouling, through a process known as quorum sensing (QS). In Gram-negative bacteria, QS is regulated by *N*-acyl L-homoserine lactones (AHLs) that

possess a polar homoserine lactone head group and a nonpolar aliphatic tail. Past studies demonstrate that AHLs can aggregate in water or adsorb at interfaces, suggesting that molecular self-assembly could play a role in processes that govern bacterial communication. We used a combination of biophysical characterization and atomistic molecular dynamics (MD) simulations to characterize the self-assembly behaviors of 12 structurally-related AHLs. We used static light scattering and measurements of surface tension to determine that four natural AHLs (3-oxo-C8-AHL, 3-oxo-C12-AHL, C12-AHL, and C16-AHL) self-assemble in aqueous media and characterize their critical aggregation concentrations (CACs). Unbiased atomistic MD simulations demonstrated that 3-oxo-C12-AHL can self-assemble into spherical, cylindrical, or bilayer-like aggregates depending on the initial concentration of AHL molecules added to the system; alchemical free energy calculations were then used to predict thermodynamically preferred aggregate structures. Those calculations predicted that AHLs with 10 or 12 tail carbon atoms should form spherical micelles, and that AHLs with 14 or 16 tail carbon atoms should form vesicles in solution. Characterization of solutions of AHLs using transmission electron microscopy (TEM) revealed aggregates with sizes consistent with spherical micelles or small unilamellar vesicles for 3-oxo-C12-AHL and C12-AHL, and the formation of large vesicles (~250 nm) in solutions of C16-AHL. These experimental findings are in general agreement with our simulation predictions. When combined, our results provide new physical insight into the aggregation behavior of this important class of non-ionic amphiphile and suggest that aggregation could potentially play a role in mediating processes that enable bacteria to communicate.

## **COLL 136**

### **Micromotors for temporal control of signaling in bacterial cells**

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Magnetically-actuated micromotors have many potential applications in biological environments. Micromotors have many uses in cellular environments since they can be remotely actuated and precisely manipulated in biochemical fluids. Most cellular phenomena depend on biochemical signals. Therefore, various techniques have been developed for encapsulation and release of drugs, nutrients or other cargo using micromotors. However, localized targeting without payload leakage during transport is challenging. In this work, we present a light-controlled delivery system integrated with magnetic micromotors which overcomes this challenge. We synthesize a photolabile linker which releases a cell-to-cell signaling molecule when exposed to light. This system is integrated with magnetic micromotors, which can be steered to target locations in the cell culture. We demonstrate that gene expression in engineered bacterial cells is successfully activated when the signaling molecule is cleaved. This proposed method can be used for wide-ranging applications in the fields of engineering, biology, and medicine, in which the ability to target and release molecules on-demand to a particular location is important.

## COLL 137

### **Dynamic behavior of molecules on the lipid membranes studied with second harmonic generation and fluorescence**

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Understanding the interactions between the drug and dye molecules with the lipid membranes is crucial in cell imaging, designing new drugs and drug delivery vesicles. Recently, we used second harmonic generation method with interface selective and fluorescence spectroscopy to investigate the adsorbing, aggregating, embedding and cross-membrane transporting of some dye and drug molecules on the surface of vesicles [1, 2]. Based on these studies, we found that the ionic strength in the aqueous solutions notably influenced the adsorption and transportation behaviors of molecules on the vesicle surface. This proved that the majority of species in the cross-membrane transportation was charged form instead of neutral form. Also, we found that the anticancer drug, doxorubicin, formed molecular domains at the lipid interfaces. At high doxorubicin concentrations, these domains altered the permeability of the membrane.

## COLL 138

### **Liposomes encapsulating methotrexate: Methods for production and quantification**

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Liposomes have been considered the most suitable drug delivery system for a range of pharmaceutical and biomedical applications. The drugs encapsulated have several advantages such as the protection of drugs by degradation caused by the organism environment and the minimization of the potential side effects in the body.

The ethanol injection method is an interesting technique for scaling-up liposomes production, due to their simplicity, fast implementation, and reproducibility. However, only a very small percentage of a water-soluble drug can be passively encapsulated inside the formed vesicles. This problem led us to optimize the production of liposomes encapsulating methotrexate disodium salt, a hydrophilic drug, based on the principles of the ethanol injection method. After several optimizations, our results showed that it was possible to establish a new pre-concentration method for liposomes production, observing an increase in the encapsulation efficiency of methotrexate more than 10 times.

Furthermore, we established a rapid and easy method for quantification of drugs

encapsulated in liposomes, exploiting the advantages of  $^1\text{H}$  Nuclear Magnetic Resonance (NMR) spectrometry. Comparing the assay results obtained by quantitative NMR with conventional techniques Ultraviolet-Visible spectrophotometry and High-Performance Liquid Chromatography no significant differences in drug concentration were observed.

In summary, the present study offerings a promising liposomal production method for liposomes encapsulating methotrexate and even a simple quantitative NMR analysis method for quantification of drugs encapsulated in liposomes.

## **COLL 139**

### **Mapping the hydrophobicity and amino-acid affinities of monolayer-protected gold nanoparticles using molecular simulations**

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Monolayer-protected gold nanoparticles (GNPs) have attracted significant interest in biomedical applications because they can be detected *in vivo*, deliver drugs, and target specific sites in the body (e.g. cancer cells). GNPs are often covered by self-assembled monolayers (SAMs) consisting of ligands with a sulfur head group, alkane backbone, and terminal end groups. SAM-protected GNPs are advantageous because of their ease of fabrication and tunable properties, such as the gold core size, the ligand chain length, and ligand end group chemistry. However, a challenge that inhibits the use of GNPs in biomedical applications is the adsorption of proteins present in the blood onto the GNP surface, forming a “protein corona” that masks GNP surface properties. The protein corona can trigger the removal of GNPs by the immune system and influence interactions with cells or biomolecules. Therefore, predicting GNP-protein binding propensity is critical for the design of NPs that avoid undesirable protein adsorption. With approximately 3,700 different types of proteins in human blood, experimentally exploring factors affecting the interactions between each GNP-protein combination is time-consuming and cost-prohibitive, motivating the use of *in silico* techniques to narrow the GNP design space.

In this work, we use classical atomistic molecular simulations to model SAM-protected GNPs and understand how tuning GNP size and ligand properties can affect GNP surface properties relevant to protein adsorption. We develop a generalized system preparation workflow for SAM-protected GNPs and show how changing the end-functionalized groups of uniformly long alkanethiol SAMs can lead to heterogeneous surface properties even for single-component SAMs. We then map spatial variations in the hydrophobicity of the GNP surface, which has been found to be a critical parameter that correlates with immune response, and compare the hydrophobicity of small, high curvature GNPs with larger, planar GNPs. We then include representative amino acid moieties that range in polarity and charge to map potential protein binding sites on the

GNP surface. The computational tools developed here will help predict the effects of GNP functionalization on protein adsorption, opening avenues towards efficient screening of GNPs for selective protein binding.

## **COLL 140**

### **Characterization of oligo-peptide/nucleotide-based coacervates in various pH and salt concentration**

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Complex coacervates are organic-rich phases or droplets, formed by spontaneous liquid-liquid phase separation, when oppositely charged polyelectrolytes or biomolecules associate with each other via ionic pairing. Microenvironments inside coacervates could be different as compared to the surrounding dilute solution due to their higher local concentration of biomolecules and lower water content. This could impact physical properties such as viscosity, polarity and/or local pH. We are interested in learning how coacervate microenvironments could be controlled by overall solution composition such as salt concentration and pH, which can impact the degree of ionization of charged molecules. Internal microenvironments of coacervates formed from biologically relevant molecules such as oligopeptides and nucleotides, have not been explored under various solution conditions. Herein, we studied the local physical properties of coacervates as a function of salt concentration and pH using fluorescent indicators. We found that coacervates composed of oligopeptides and nucleotides can exhibit salt- and pH- resistance, and potentially could serve as pH-buffering microdroplets. These investigations provide fundamental understanding of oligo-peptide/nucleotide based coacervates, and could lead to design coacervates as protocells.

## **COLL 141**

### **Computationally designed coiled coil peptides as model charge-patterned colloidal particles**

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Peptides that are short sequences of amino acids are excellent candidates for biomaterial construction as they provide a diverse and tunable interaction landscape at

the nanoscale while also being relatively straightforward to synthesize and modify using lab-scale chemical procedures. Computational prediction of peptide sequences has enabled faster screening of sequences that facilitates deterministic biomaterial design. We demonstrate the utility of such computationally designed peptide assemblies as model colloidal systems for studying protein-protein interactions. Specifically, the assembly of artificial peptides that are predicted *in silico* to form  $\alpha$ -helical coiled coils also known as bundlemers will be discussed. The peptides tetramerize to form a robust anisotropic nanoparticle with a stable hydrophobic core and multiple surface exposed polar and charged side groups. These groups can be strategically placed or chemically modified to display different net charges and patterns on the bundlemer surface. Via a constant feedback cycle between experimental results and computational sequence prediction, we have tested multiple design rules for successful bundlemer construction displaying different net charges (+32e to -32e). Specifically, we have confirmed that the bundlemers are robust nanocylinders and are consistently  $\approx 4$  nm in length and  $\approx 2$  nm in diameter, making them ideal colloidal nanoparticles that can also mimic the complex protein surface. In-depth small angle scattering investigation shows that while bundlemers behave as repulsive colloidal particles that are sensitive to net bundlemer charge and consequently, on solution conditions such as peptide concentration, pH and ionic strength, their solution behavior is further impacted by the subtle sequence-driven charge patterns on their surface. This sequence-specific solution behavior of bundlemers puts them at the cross-section of polyampholyte, polyelectrolyte and colloids research, the sum of which is important for describing protein-protein interactions in a holistic manner. Important parallels between these systems in context of the computational design and resulting sequence-driven solution behavior of the model bundlemers will be discussed.

## **COLL 142**

### **Microfluidic production of biomimetic water-in-oil emulsion droplets utilizing aqueous phase separation**

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The living cell is a complex, crowded system comprised of distinct compartments, each of which house unique solution conditions. The non-ideal solution dynamics of these environments resulting from the high concentration of biological macromolecules can be modeled using segregative and associative aqueous phase separation, independent from the additional complexity of *in vivo* systems. By dispersing these solutions within a continuous oil phase, a large number of individual phase-separated aqueous emulsion droplets are produced. In this research, aqueous phase-separated water-in-oil emulsion droplets containing both neutral polymer phase separation utilizing poly(ethylene glycol) and dextran, as well as complex coacervation of protamine sulfate have been incorporated into a single system using a fluorinated oil-based continuous phase. Microfluidic production of these droplets enables controllable incorporation of individual polymer solutions, leading to phase-separated systems ranging in composition across

the phase diagram. This allows for control over the partitioning behavior of various biological molecules and probes within the droplets, as well as the potential encapsulation of bio-relevant reactions.

## **COLL 143**

### **Penetration mechanism through the stratum corneum depending on the structure of microemulsions**

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The performance of transdermal drug delivery systems are affected by the presence of stratum corneum (SC). Carriers such as microemulsions (MEs) have been developed as skin penetration enhancers. Although the main permeation route for MEs appears to be the pathway through the lipid layers between corneocytes, the interaction mechanism between MEs and lipid layers has not been clarified. In the lipid layers in SC, there are two types of lamellar structures, the long lamellar (L-La) and the short lamellar (S-La). Additionally, the alkyl chains in L-La and S-La are packed in a hexagonal array (Hex) and in an orthorhombic array (OR), respectively. Four types of MEs with different structures containing a deep eutectic solvent (DES) or H<sub>2</sub>O in the inner phase were prepared using two surfactants, Tween80 and Span20 (T3S1DES, T3S1H<sub>2</sub>O, T1S3DES, and T1S3H<sub>2</sub>O as indicated in Table1). Then, we evaluated which ME easily disturbed the lipid packing structures in SC by X-ray diffraction. The result showed that MEs at all compositions disturbed both Hex (d=0.41nm) and OR (d=0.37nm and 0.41nm) (Fig.1a, b), and T3S1H<sub>2</sub>O disturbed the lipid packing the most. We found that only T3S1H<sub>2</sub>O disturbed Hex more strongly because of a decrease in the ratio of the peak area of Hex to OR at 50 min after applying samples. Taking into account the result of skin penetration (Fig.1c), T3S1H<sub>2</sub>O appeared to mainly remain in Hex. For T3S1H<sub>2</sub>O, the hydrocarbon chains of the surfactants may easily interact with the lipid hydrocarbon chains in SC because the surfactants of ME are not packed densely (Table 1). The smallest ME (T1S3H<sub>2</sub>O) easily penetrates S-La because it appeared to easily pass through the narrow spaces of the intercellular lipid matrix. Hence, we concluded that the penetration mechanism depends on not only the sizes of MEs but also their aggregation numbers.

Sample name	Tween80 / Span 20 (wt / wt)	Inner phase	Structure	Aggregation number <sup>a</sup>
T3S1-DES	3 / 1	DES	Cylinder with 13 nm of cross-sectional diameter	>100
T3S1-H <sub>2</sub> O	3 / 1	H <sub>2</sub> O	Sphere with 14 nm of diameter	40
T1S3-DES	1 / 3	DES	Sphere with 13.6 nm of diameter	80
T1S3-H <sub>2</sub> O	1 / 3	H <sub>2</sub> O	Sphere with 8.2 nm of diameter	40

a) When N is larger than 100, the calculated SAXS profile is unchanged.

Table 1. The code names of the samples and their structures.

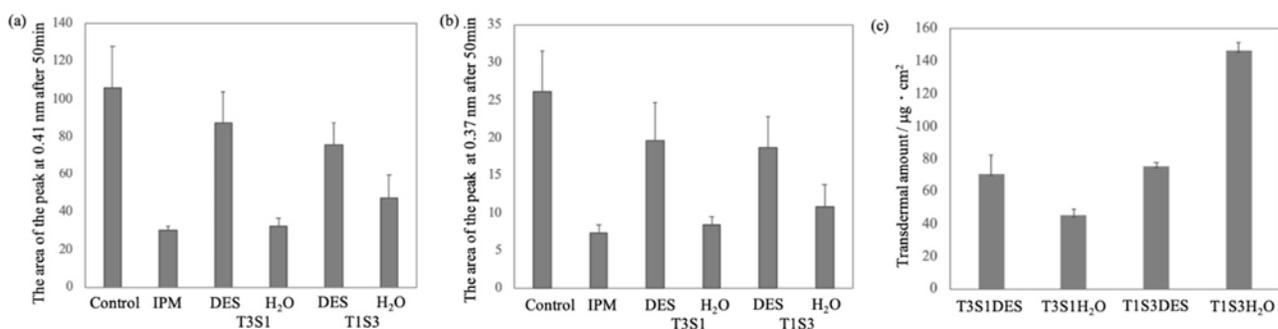


Fig.1 The area of each peak at 0.41 nm (a) and at 0.37 nm (b) at 50 min when applying each sample. (c) The transdermal amount of RSV through the hairless mouse epidermis after 24h. n=3.

## COLL 144

### Application of sophorolipid butyl ester as an antimicrobial surfactant

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Colloidal materials consisting of essential oils, food-grade surfactants and biopolymers, have attracted extensive attention due to their non-toxicity and antimicrobial activities; however, most of the systems investigated so far used commercial surfactants (Tween 80, modified starch and soy lecithin) that can only perform a simple function – stabilize the emulsion. In this work, sophorolipid butyl ester (SLBE), a biosurfactant produced from microbial fermentation, has been investigated. Notably, SLBE can perform dual functions, namely, stabilizing the emulsions while also being antimicrobial active. We have examined the use of SLBE as stabilizers of o/w emulsions containing oregano oil, and it has been found that SLBE was able to stabilize emulsions with oil concentrations

20 times that of the surfactant for almost a month. The addition of  $\gamma$ -polyglutamic acid (anionic polymer) to primary emulsions resulted in a decrease of oil droplet size, but an increase in creaming rate due to depletion flocculation, while the introduction of chitosan (cationic polymer) led to a significant decrease in both droplet size and the rate of creaming due to enhanced electrostatic repulsion. Further studies also showed that the application of SLBE could help increase materials' antimicrobial activity against typical pathogenic microorganisms, especially for gram-positive bacteria. These results demonstrated the ability of this naturally derived surfactant, SLBE, to endow materials with both high stability and good antimicrobial properties, making it very promising for food applications.

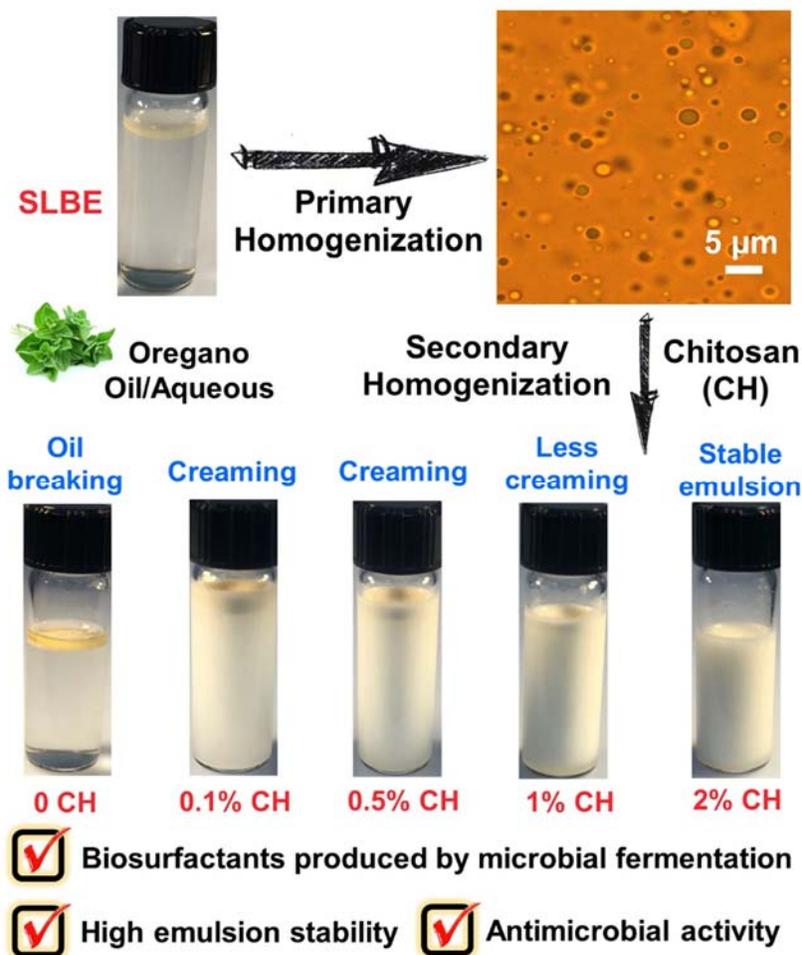


Figure 1. Schematic illustration of two-step homogenization involving SLBE and CH.

COLL 145

Langmuir monolayers of membrane lipids as model systems for investigating the mechanisms behind the healing properties of commercial natural products

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Molecular interactions of membrane lipids can be measured using the Langmuir Monolayer technique. In our lab in the chemistry department at Monmouth College, a private liberal arts college, we have been investigating the antibacterial properties of essential oils, propolis (a natural antibiotic made by bees) and CBD oil (cannabidiol). Monitoring the surface tension and molecular area of phospholipids at an air-water interface before and after the addition of these natural products helps determine the mechanism by which they act as an antibacterial or anti-inflammatory agent. Specifically, the phospholipid head and tail groups were varied as were the types of lipid systems which included *E. coli* lipid extract and brain lipid extract. Results predict that essential oils interact with the tail groups of the lipids as long as they can get in between the head groups. Previous research in our lab showed that honey affects membrane organization based on the charge of the membrane lipids which led us to analyze propolis. Current data is being gathered with mass spectrometry to identify the specific flavonoid compounds in the propolis for more targeted monolayer studies. The interactions between CBD oil and brain lipid extract has been our most recent area of study with regards to the interactions of membrane lipids and commercial natural products.

## **COLL 146**

### **Studies of surface chemistry of hybrid porous materials for tuning drug delivery efficacy and efficiency**

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Coronary artery disease (CAD) is a major leading cause of death in the United States. Suffering from plaque narrowing the blood vessel to lessen blood rate to organs, people with CAD have a higher chance of experiencing a heart attack and stroke. Our research focuses on using a porous structure of iron-containing metal-organic framework (MOF), Fe-MIL family, as a potential coating material for drug eluting stent (DES) to prevent CAD and minimize restenosis and thrombosis. Fe-MILs were composed of iron (III) clusters linked by terephthalate ligands with various crystal structures. Powder X-ray diffraction (XRD) was used to confirm the crystal lattice structure while ultraviolet-visible (UV-Vis) spectroscopy was used to examine and quantify the drug loading amounts in Fe-MILs. Here, we used ibuprofen as a model drug to represent other anti-inflammatory drugs. After comparing drug loading capacities of using various Fe-MILs, we construct a Fe-MIL-88B thin film on a 16-mercaptohexadecanoic acid (MHDA) functionalized gold

surface to study the drug loading and releasing kinetics using surface plasmon spectrometer (SPR) and quartz crystal microbalance (QCM). The chemical composition changes after each modification step were monitored by Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). The morphology of the resulting Fe-MIL-88B film before and after loading with the model drug was examined by scanning electron microscopy (SEM). Our study confirmed the use of surface-supportive MOF thin film for drug elution coating purposes.

## **COLL 147**

### **Solving the mystery between silver and silver nanoparticles: Who's toxic?**

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The growth in nanotechnology applications comprised of silver nanoparticles (AgNPs) has led to a significant interest in understanding their possible environmental and human health impacts. The diversity of commercially available AgNP products is often proprietary, not well-defined, and undergo rapid surface oxidation and dissolution of Ag<sup>+</sup> making their assessment difficult to study. Consequently, there is a gap in our current understanding of the relative contribution of physicochemical parameters such as shape, size, and surface coating to nanoparticle stability, nanoparticle-biological interactions (NBI), bio uptake, and ecotoxicity. Given the critical need to identify features of AgNPs over Ag<sup>+</sup> that induce toxicity and disrupt ecosystems, well-defined AgNPs with tightly-controlled size and shape that can be modified to tune Ag<sup>+</sup> release is of significant interest. Here we discuss the design of hybrid lipid-coated AgNPs of varying shapes and sizes that are differentially shielded from surface oxidation. We will present UV-Vis spectroscopy, transmission electron microscopy, and ICP-MS studies characterizing the stability of the hybrid lipid-coated AgNPs. We will present ICP-MS data evaluating the AgNPs for Ag<sup>+</sup> ion release and will show that AgNPs that are completely shielded from surface oxidation does not release Ag<sup>+</sup> ions. The toxicity and distribution of AgNPs in using zebrafish models will also be presented to identify features of AgNPs that drive toxicity, nanoparticle distribution, and NBI's. These studies will provide valuable information on the toxicity of AgNPs and Ag<sup>+</sup> ions release into its surroundings while also providing a potential template for designs on safer nanoparticles.

## **COLL 148**

### **Changes without exchanges: On-particle ligand chemistry with purpose-designed, as-synthesized ligands**

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The Niezgoda lab researches new quantum dot (QD) systems in which chemically interesting ligands are incorporated into syntheses of QDs themselves as new “native” ligands. As a prototype example of this theme, we present recent findings concerning a project that details the on-particle modification of a surface bound ligand. In this first-of-its-kind work, we synthesized a ligand molecule that is purposefully designed to contain a functional group that can undergo chemical transformation, rendering the ligand shell less physical bulky and altering the QD solubility. Findings from this project are germane to thin film QD studies in which surface passivation, suppression of trap states, and short ligand length are of crucial importance. This ligand, 9,10-dihydroxystearic acid (DHSA) is a fatty acid vicinal diol (glycol) prepared from the careful oxidation of oleic acid by undergraduate researchers. We then designed a synthesis for CdSSe alloy QDs *around* this DHSA ligand, taking in to account the heavily altered solubility and solution dynamics of the DHSA. This new solubility led us to develop a specific diphenylether/dimethyl formamide mixture that permitted growth and formation of solution stable QDs, which represents the first time such a solvent has been used in QD syntheses. This task required a rethinking of the possible solvent species—striving to achieve sufficiently high boiling point solvents with little to no nucleophilicity to form both the Cd<sup>2+</sup> as well as the QDs themselves. In this way, we were able to obtain size-tunable and solution-stable CdSSe QDs utilizing only DHSA as a ligand. Absorption and PL data shows good size dispersity and tunable fluorescence. Finally, we are able to effectively decrease the length of this ligand in half, *all while never removing or replacing the original binding group*. This is achieved through oxidative cleavage of the glycol with lead (IV) acetate (LTA) to two terminal aldehydes, with the acid aldehyde remaining bound to the QD, proven through FTIR spectroscopy. This further alters the solubility of the QDs, however they still remain stable in solution. HR-TEM images show decreased particle separation in monolayer QD films, resulting from the shortened carbon chains in the ligand molecules. Finally, ongoing research projects are discussed for the introduction of new functional groups to as-synthesized QDs, including “clickable” moieties for substrate-specific linkage without surface alteration.

## **COLL 149**

### **Reverse Micelles as simple model systems to investigate photophysical properties of probe molecules and biomolecule dynamics**

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Reverse Micelles (RMs) are thermodynamically stable, nanometer sized water droplets, composed of a pool of polar solvent (usually water), surrounded by a mono layer of surfactant, which is in turn solvated by a bulk, nonpolar solvent. This simple self-assembled structure is readily producible over wide range of sizes, generally characterized by the molar ratio of water to surfactant ( $w_0$ ):  $w_0 = [\text{H}_2\text{O}]/[\text{Surfactant}]$ . RMs can be used as a simple model system for biomolecule structure and dynamics studies in extracellular spaces and like biological membrane, RM is crowded and confined and

mimic the biological systems. RMs have also been extensively used as a model system to investigate photophysical properties of various fluorescent and solvatochromic dyes. The properties of the confined water inside RMs are significantly different than that of core water where water is free and can form as many hydrogen bonds it can. Therefore, it can be expected that the physicochemical properties of the probemolecules can be different in reverse micelle compared to bulk water.

In these experiments, we examined photophysical properties of fluorescent probemolecules in reverse micellar environments using various steady-state and time resolved spectroscopies. The results in reverse micellar environments of various size parameters were compared to that of in the bulk aqueous environment. We observed that for example, Cy5 dyes in the smallest of reverse micelles of size  $w_0 = 1$  probably undergoes aggregation as compared to the bigger RMs and in aqueous environments. These experiments in confined reverse micellar environments have provided us required protocols to investigate complex biomolecule dynamics for example protein folding and nucleic acid folding in connection with neurodegenerative diseases such as Alzheimer diseases (AD) and Huntington disease (HD) to name a few.

## **COLL 150**

### **Synthesis and characterization of “responsive” supramolecular nanocomposite materials for health and bio-inspired energy applications**

*Jason J. Keleher, KeleheJa@lewisu.edu.* Dept of Chem, Lewis University, Romeoville, Illinois, United States

Supramolecular nanocomposite materials have emerged as a leading interdisciplinary research area that exploits synergistic relationships at the nanoscale to enhance electrochemical properties of next-generation responsive systems. Therefore, mechanistic understanding tailored to the nuances involved in the synthesis and characterization of these complex ensemble materials with applications that range from antimicrobial wound management materials to electrodes for novel microbial fuel cell technologies is needed. This presentation will place particular emphasis on exploiting the “blurred” disciplinary boundaries as a model for the development of an active undergraduate research experience that highlights interdisciplinary problem solving, robust experimental design, and the development of essential critical thinking skills. More specifically, one focus area is the design of hydrogel nanocomposites which upon external stimuli (i.e. swelling and pH) will elicit an electrical response to serve as a diagnostic probe related to the integrity of the matrix for applications in wound management. This composite consists of a wound contact layer (hydrogel), an electrical contact layer (conductive NPs), and a conductive layer (polyaniline (PANI)) which ultimately produces the electrical response due to exudate uptake in the hydrogel layer. Moreover, due to the hydrogel’s intrinsic properties and conductivity these nanocomposites have additional applications as electrodes in microbial fuel cells (MFCs). These electrodes are synthesized via the in-situ photopolymerization of PANI throughout the hydrogel network to provide a uniform scaffold for bacteria docking to

ultimately allow for efficient electron transfer in the system. Initial results have shown comparable power output generation when compared to commercially available carbon-based materials. In addition, these composite materials have significantly reduced biofilm formation, thus increasing the overall efficiency and lifetime of the composite material.

## **COLL 151**

### **Bottom-up assembly of surface-anchored metal-organic framework thin films**

**Mary E. Anderson**, [maryelizabeth.anderson@furman.edu](mailto:maryelizabeth.anderson@furman.edu). Chemistry, Furman University, Greenville, South Carolina, United States

Toward the incorporation of nanomaterials into device structures, the overarching goal of this research is to investigate the driving forces directing the bottom-up solution-phase synthesis of nanomaterials. Our research examines both free-standing and surface-anchored nanomaterials to gain fundamental understanding about their growth, which is necessary to tune material properties and to integrate the material into hierarchical structures through low-energy processing techniques. Thin films of metal-organic frameworks (MOFs) can integrate the versatility and potential of the material directly into architectures for gas storage, chemical sensing, and energy storage. We investigate methods of fabrication for surface-anchored MOFs (e.g. HKUST-1, MOF-14, MOF-399) and determine thin film growth mechanisms primarily by characterization with atomic force microscopy. Research investigates synthetic variables to tailor film morphology, examines gas interactions with the MOF as a film compared to free-standing nanopowder, and studies MOF thin film formation and transport properties for potential integration into electrochemical devices. Current research continues to investigate other surMOF systems, technologically-relevant substrates, methods for patterning the MOF films, and the effect of post-synthetic modifications. This fundamental research is essential to develop design rules for the integration of these promising supramolecular nanomaterials into real-world applications.

## **COLL 152**

### **Self-assembly, mechanical and thermal properties of molecular gels derived from simply structured molecules as low molecular mass gelators**

**Ajay Mallia**, [amallia@ggc.edu](mailto:amallia@ggc.edu). School of Science and Technology, Georgia Gwinnett College, Lawrenceville, Georgia, United States

Simply structured molecules are very important to understand the mechanism of self-assembly and aggregation of molecules at different distance scales. Preparation and studies of N-(phenylalkyl)octadecanamides, N-(acridin-9-yl)alkanamides, and anthraquinone derivatives will be presented. Structure property correlations and morphology between the molecular structures of the gelators and the properties of their gels using spectroscopic and rheology will be discussed.

We thank Prof. Richard Weiss (Georgetown University) for the use of rheometer and polarizing optical microscope.

## **COLL 153**

### **Investigating novel colloidal sol-gel feedstocks for fabricating 3D-printed functional glass materials**

*Joel F. Destino, joeldestino@creighton.edu, Peter S. Palencia, Alexandra C. Vahle, Cameron J. Jayson, Samuel T. Fernandez, Bachtri T. Nguyen.* Chemistry, Creighton University, Omaha, Nebraska, United States

Over the past decade, the advancement of additive manufacturing or 3D printing has shown extraordinary potential to revolutionize many fields, including glass science. We present the development and characterization of sol-gel germania-silica or  $\text{GeO}_2\text{-SiO}_2$  feedstocks for fabricating glass by direct ink write (DIW) 3D printing.  $\text{GeO}_2\text{-SiO}_2$  feedstocks are of interest because silica-germania glass exhibits similar physical and optical properties of traditional silica glass, but with improved optical transmission and a tunable refractive index. We report an optimized sol-gel formulation for preparing 3D-printed silica-germania glass; and investigate the role of particle size, shape, and morphology by DLS, zeta-potential, and transmission electron microscopy. Spectroscopic studies are presented to reveal the structural evolution of germania-silica feedstocks from particles to glass. Furthermore, we present preliminary spectroscopic studies investigating particle-dispersant interactions towards improving our understanding of the fundamental interactions that govern colloidal stability and DIW feedstock quality.

## **COLL 154**

### **Modeling of interfaces involved in sustainable energy technologies**

*Emily A. Carter, eac@ucla.edu.* Office of the Chancellor, University of California, Los Angeles, Los Angeles, California, United States

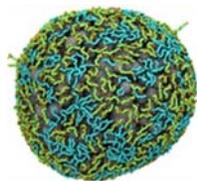
Mike Klein cares about the future of the planet and its inhabitants. Amazingly, he is – at 80 (!) – still working to inspire and train the next generation of scientists and engineers. He is indeed an inspiration, both as a university leader and a scientist who has investigated breathtakingly complicated phenomena in soft condensed matter. To honor him, I will present a few selections from my group's research into sustainable energy technologies, focusing on quantum mechanics based simulations of phenomena involving interfaces, to make a connection to Mike's work emphasizing the latter. Examples may include gas bubble formation in liquid metal alloy candidates for fusion reactor walls, (photo)electrocatalysis for renewable chemical and fuel production, among others.

## **COLL 155**

## Domain formation in charged polymer vesicles

*Kaushik Chakraborty*<sup>1,2</sup>, **Sharon Loverde**<sup>1,2</sup>, *sharon.loverde@csi.cuny.edu*. (1) City University of New York, New York, New York, United States (2) Department of Chemistry, CUNY College of Staten Island, Staten Island, New York, United States

Microphase separation can occur on a polymersome membrane surface. The phase behavior is dependent on the mixture of charged and uncharged diblock copolymers, as well as the salt concentration in solution [1]. Using molecular dynamics simulations, we evaluate the elastic properties of mixed charged and uncharged diblock copolymer membranes as a function of charged polymer concentration, for the case of divalent counterions in solution. We find that both the area elastic modulus and bending modulus increase as a function of charged copolymer concentration. We find that the membrane thickness decreases and the membrane overlap increases as a function of charged copolymer concentration. We next perform large-scale simulations of a nearly 40 nm polymersome and characterize the growth of domains over 500 ns simulation time. We calculate the potential of mean force to form domains using the self-coordination number of the polymers. We characterize the size, shape, and surface topology of the domains as they grow.



"Spotted" Polymersome.

## COLL 156

### Ionic liquid mixtures at polar and apolar interfaces

**Waruni V. Karunaratne**<sup>1</sup>, *warunivindhya-hapuarachchigedona@uiowa.edu*, *Claudio J. Margulis*<sup>2</sup>. (1) Department of Chemistry, University of Iowa, Iowa City, Iowa, United States (2) Dept of Chemistry, University of Iowa, Iowa City, Iowa, United States

Ionic Liquids (ILs), a class of molten salts with melting points below 100 °C, have unique chemical and physical properties which make them excellent candidates for various applications including in chemical synthesis, catalysis, tribology, electrochemistry and many other areas. Due to the nature of such applications, ILs are often exposed to various interfaces and forms of confinement including by air, vacuum, other liquids or solids. The structure and dynamics of ILs change when vicinal to boundaries and understanding these changes is critically relevant to said applications. During my presentation, I plan to show results from molecular dynamics simulations of an 'IL

mixture' based on the alkylimidazolium – alkylsulfate family of ions confined by vacuum and mica. Whereas vacuum represents a highly apolar boundary, mica instead is highly polar. Even though these interfaces are very different, and so are their corresponding adlayers, some of the IL features at the interface are similar including the decorrelation length scale.

## **COLL 157**

### **Hydrophilic/hydrophobic hydration at mineral-water and semi conductor-water interfaces revealed by DFT-MD simulations coupled to sum frequency generation vibrational spectroscopies**

**Marie P. Gaigeot**, *mgaigeot@univ-evry.fr*. LAMBE UMR8587, Universite d'Evry val d'Essonne, Bures sur Yvette, France

In this talk, we will present some of our most recent theoretical DFT-MD simulations on the hydration of mineral-water and semi-conductor oxide-water interfaces, and especially on how water can be accommodated at the interface when going from hydrophobic to hydrophilic surfaces, with consequences for e.g. chemical reactions at the interface (e.g. water splitting), adsorption of molecules at the interface, accommodation of electrolytes at the interface. We will show results on the BIL (Binding Interfacial Layer, i.e. the interfacial water) and DL (Diffuse Layer) water organization at hydrophobic/hydrophilic oxide-water interfaces, their spectroscopic SFG (Sum Frequency Generation) signatures, and the interplay/fight in between horizontal and vertical ordering of the water and some 'undisciplined' water behaviours at some of these interfaces. We will also show how nominal hydrophilic surfaces (e.g. silica) can have 'hydrophobic patches' over the surface and how these patches have direct spectroscopic SFG signatures of hydrophobicity.

## **COLL 158**

### **Electron traps, screening, and transport at liquid-solid interfaces**

**Richard C. Remsing**, *rremsing@gmail.com*. Chemistry and Chemical Biology, Rutgers University, New Brunswick, New Jersey, United States

Interfaces between semiconductors and soft, disordered materials like liquids are attracting interest as functional components of nanoscale devices for catalysis, solar energy conversion, and flexible electronics. The performance of these devices is often dictated by the influence of the soft material on the behavior of the charge carriers within the semiconductor, in addition to any sources of disorder (defects) present in the hard material. However, a detailed molecular-scale picture of the interplay among interfacial structure, charge carriers, and defects is difficult to ascertain with current approaches. In this talk, I will introduce an approach for modeling charge carriers in condensed phase systems. I will then discuss charge carrier trapping by defects in two-dimensional semiconductors, screening of these defects by interfacial liquids, and

effects on transport. I will conclude with a discussion of potential implications for nanodevices and future areas of development.

## **COLL 159**

### **Structure and chemistry of aqueous TiO<sub>2</sub>: Insights from simulations**

**Annabella Selloni**, *aselloni@princeton.edu*. Princeton Univ, Princeton, New Jersey, United States

Titanium dioxide (TiO<sub>2</sub>) is a naturally abundant, chemically stable, and environmentally compatible metal oxide, and also one of the most widely used photocatalysts for scientific and technological applications. Of particular relevance is the anatase phase of TiO<sub>2</sub>, which predominates at the nanoscale. Since TiO<sub>2</sub> photocatalysis usually takes place in humid or aqueous environment, the interface of anatase TiO<sub>2</sub> with water is of fundamental importance, e.g. for elucidating the not yet fully understood mechanisms of photochemical water splitting and UV-induced hydrophilicity. In this talk, I shall present recent applications of ab initio molecular dynamics (AIMD) to study the structure and dynamics of interfacial water on the majority anatase (101) surface, for which a number of experimental results have recently become available. I shall also discuss large scale simulations with a deep neural network interatomic potential trained on the AIMD results. These simulations show a dynamical equilibrium of molecular and dissociated water on the TiO<sub>2</sub> surface, consistent with the dissociation free energy estimate obtained from enhanced sampling techniques.

## **COLL 160**

### **Investigation of $\alpha$ -alumina(0001)/water interface in acidic or basic solutions using SCAN functional**

**Ruiyu Wang**<sup>1,4</sup>, *wangruiyuwry@gmail.com*, **Mark DelloStritto**<sup>1,4</sup>, **Vincenzo Carnevale**<sup>2,3</sup>, **Michael L. Klein**<sup>1,4,2</sup>, **Eric Borguet**<sup>1,4</sup>. (1) Department of Chemistry, Temple University, Philadelphia, Pennsylvania, United States (2) Inst Comp Molecular Science, Temple University, Philadelphia, Pennsylvania, United States (3) Department of Biology, Temple University, Philadelphia, Pennsylvania, United States (4) Center for Complex Materials from First Principles (CCM), Temple University, Philadelphia, Pennsylvania, United States

The chemistry of oxide/water interfaces differs greatly from that of bulk water and plays an important role in adsorption, catalysis, and environmental remediation. However, even simple questions, such as the effect of acidic/basic solutions on the interface, are not fully understood. In this work, we investigated charged  $\alpha$ -alumina(0001)/water interfaces using ab initio molecular dynamics simulations of PBE+TS and SCAN functionals, adding or removing a proton to the surface to simulate acidic and basic solutions, respectively. We find that in basic conditions, the deprotonated site on the

surface accepts a proton from solution, leaving an OH<sup>-</sup> group in the aqueous phase. This behavior is quite different from experimental interpretations but is consistent with other theoretical work. At the acidic surface, we surprisingly find no proton transfer between surface and solution with the SCAN functional, even though we observe it when using the PBE-TS functional; in basic solutions, both functionals predict that the proton vacancy diffuses readily across the interfacial waters. We then analyze the vibrational properties of the interface. In acidic conditions, we find that the vibrational frequency of protonated sites is distinct from that of neutral ones. In basic conditions, we observe an increase of vibration intensity in the low frequency region, in agreement with previous experimental results. This work constitutes the first atomistic description of the alumina/water interfaces in acidic/basic conditions. Importantly, our molecular dynamics simulations based on an accurate meta-GGA functional allowed us to describe explicitly proton transfer events and thus obtain a good agreement with experimental measurements.

## **COLL 161**

### **Atomistic and spectroscopic studies of aqueous:solid interfaces**

**Franz Geiger**, *geigerf@chem.northwestern.edu*. Dept of Chem Tech KG G6, Northwestern University, Evanston, Illinois, United States

This talk will review some of our recent advances in understanding charged aqueous:solid interfaces using atomistic computer simulations and nonlinear optical spectroscopy. Topics included concern lipid membranes and the charge state of adsorbed cationic species there, as well as spectral lineshape analyses at oxide:water interfaces.

## **COLL 162**

### **Semiconductor surface functionalization: From self-assembly to photoinitiated film growth**

**Stacey F. Bent**, *sbent@stanford.edu*. Dept of Chem Eng, Stanford, California, United States

Semiconductor surface science serves as the foundation for applications ranging from microelectronics to optoelectronics to bio-sensing. Given the importance of semiconductor materials in important technologies of today, being able to control their surface properties is key to future advances. One way to modify the surface properties of a semiconductor is by functionalizing it with organic monolayers, multilayers, and thin films. This talk will describe studies on the formation of organic layers at semiconductor surfaces, aimed at the ultimate goal of controlling subsequent fabrication processes. The presentation will examine two contrasting systems of functionalization. In one case, formation of well-ordered alkanethiolate multilayers occurs on a copper oxide surface by self-assembly after exposure of the surface to vapor alkanethiols. In the other example,

intentional attachment via carbon-carbon bond formation of covalently-bound organic multilayers is achieved on silicon through the process of photo-initiated molecular layer deposition (MLD). A combination of microscopy, spectroscopy, and x-ray scattering studies provides insight into both the functionalization mechanisms and the structure of the resulting organic films. The application of both types of layers to serve as resists for area selective deposition will also be described.

## **COLL 163**

### **Semiconductor surface chemistry beyond thermal activation: Surface reactions on Si(001) controlled by electronic and vibrational excitation**

*Michael Durr*<sup>1,2</sup>, *michael.duerr@ap.physik.uni-giessen.de*, *Gerson Mette*<sup>2</sup>, *Alexa Adamkiewicz*<sup>2</sup>, *Marcel Reutzel*<sup>2</sup>, *Ulrich Koert*<sup>2</sup>, *Ulrich Höfer*<sup>2</sup>. (1) Institute of Applied Physics, Justus Liebig University Giessen, Giessen, Germany (2) Philipps University Marburg, Marburg, Germany

The search for functional molecular architectures on surfaces calls for new strategies in controlling surface reactions. Here, we show for ether cleavage on Si(001) as a test system that controlled electronic and vibrational excitation can open reaction channels beyond thermally activated reaction schemes: tip-induced excitation of the system in an STM leads to new final products and the type of final products is controlled by selectively addressing different excitation channels: Above a threshold voltage of 2.5 V, direct electron transfer into the antibonding C-O orbital of the tetrahydrofuran (THF) molecules induces ether cleavage of the datively-bonded intermediate of THF on Si(001). Below the threshold, ether cleavage is induced by multiple excitation of vibrational modes. The distributions of final products are different when compared to thermal excitation and significantly differ for the two non-thermal excitation modes. The results thus demonstrate how the final reaction products can be controlled by means of the different excitation mechanisms which in turn can be selectively addressed by the tunneling voltage [1]. When we compare the results of THF with diethylether on Si(001), we find surprising differences. The comparison gives detailed insight into the driving forces of such chemical reactions of organic molecules on semiconductor surfaces.

## **COLL 164**

### **Gram-scale synthesis of functionalized crystalline silicon nanoparticles**

*Alyssa Van den Boom*, *Sidharam Pujari*, ***Han Zuilhof***, *han.zuilhof@wur.nl*. Lab of Organic Chemistry, Wageningen University, Wageningen, Netherlands

Functionalized silicon nanoparticles can be synthesized in a variety of ways. However, typically this process requires high temperatures and/or harsh reaction conditions. Recently we developed a novel route to obtain crystalline hydrogen-terminated silicon nanoparticles quickly in gram-scale quantities under mild reaction conditions. We will present this method, a range of functionalization methods including fast, room-

temperature procedures, and will discuss the effects of temperature on the outcomes of the synthesis as have become evident by a range of characterization methods..

## **COLL 165**

### **Versatile, scalable monolayer functionalization of carbon-based materials by radical-initiated grafting**

*Yongqian Zhang*<sup>2</sup>, *Ali Abbaspour Tamijani*<sup>3</sup>, *Bo Zhi*<sup>4</sup>, *Christy L. Haynes*<sup>4</sup>, *Sara E. Mason*<sup>3</sup>, **Robert J. Hamers**<sup>1</sup>, *rjhamers@wisc.edu*. (1) Univ of Wisconsin, Madison, Wisconsin, United States (2) Chemistry, University of Wisconsin- Madison, Madison, Wisconsin, United States (3) Chemistry, University of Iowa, Iowa City, Iowa, United States (4) Univ of Minnesota, Minneapolis, Minnesota, United States

Controlled functionalization of carbon-based materials such as diamond is challenging. Here, we describe the use of radical-based grafting to selectively functionalize carbon surfaces with self-terminating monolayers. Starting with H-terminated surfaces of nanodiamond, glassy carbon, and polymeric carbon dots, we demonstrate that the surfaces can be selectively functionalized by introducing a small amount of radical initiator into a reactant organic alkene. We find that this approach leads to formation of self-terminating monolayers with the molecules bound exclusively by the terminal carbon atom, as shown by detailed proton and carbon NMR studies. Density functional calculations show that the enthalpy change in abstracting an H atom from a H-terminated diamond surface is much lower than that required to remove an H atom from an organic alkene; as a result, the radical initiators selectively remove H atoms from the surface, which can then react with the terminal organic alkene. DFT calculations further show that the preference for bonding to the terminal side large arises from steric considerations, as forming a surface bond to the second carbon atom would result in a sterically constrained configuration of higher energy. Overall, these results demonstrate a new, scalable method for functionalization of carbon surfaces that can be applied to powders and non-planar surfaces.

## **COLL 166**

### **Physical passivation of silicon surfaces**

**Robert L. Opila**, *opila@udel.edu*, *Meixi Chen*, *James Hack*. Univ Delaware Dept MAT SCI, Newark, Delaware, United States

Physical passivation of semiconductor surfaces to limit recombination of excited electrons and holes is important in the function of devices. Quinhydrone in methanol is known to interact with hydrogen terminated Si surfaces to passivate them. In this work quinhydrone has been separated into its constituent parts, p-benzoquinone and hydroquinone, and each was dissolved in methanol in order to test the electrical passivation of the silicon surfaces. P-benzoquinone is the active component, however, hydroquinone solutions improve in performance when in contact with the substrates for

a longer duration. The effect of light was also examined. Substrates passivated with benzoquinone in full ambient light conditions displayed the highest effective carrier lifetimes. The passivation effect of solutions exposed to light during preparation, but with measurements taken in the dark, were compared with that of substrates passivated using a process completely performed in the dark. The passivation effect from these procedures is much less effective than full light passivation. It is confirmed that the presence of light facilitates the passivation. The presence of a free proton in the solution (i.e., the hydroxyl proton) is also found to play an important role in passivation. Surface analyses (XPS and FTIR) demonstrate that benzoquinone has reacted with the surface. Density functional calculations are consistent with a photoexcited benzoquinone species reacting with the surface. Surface photovoltage using both x-ray photoelectron spectroscopy and Kelvin probe techniques.

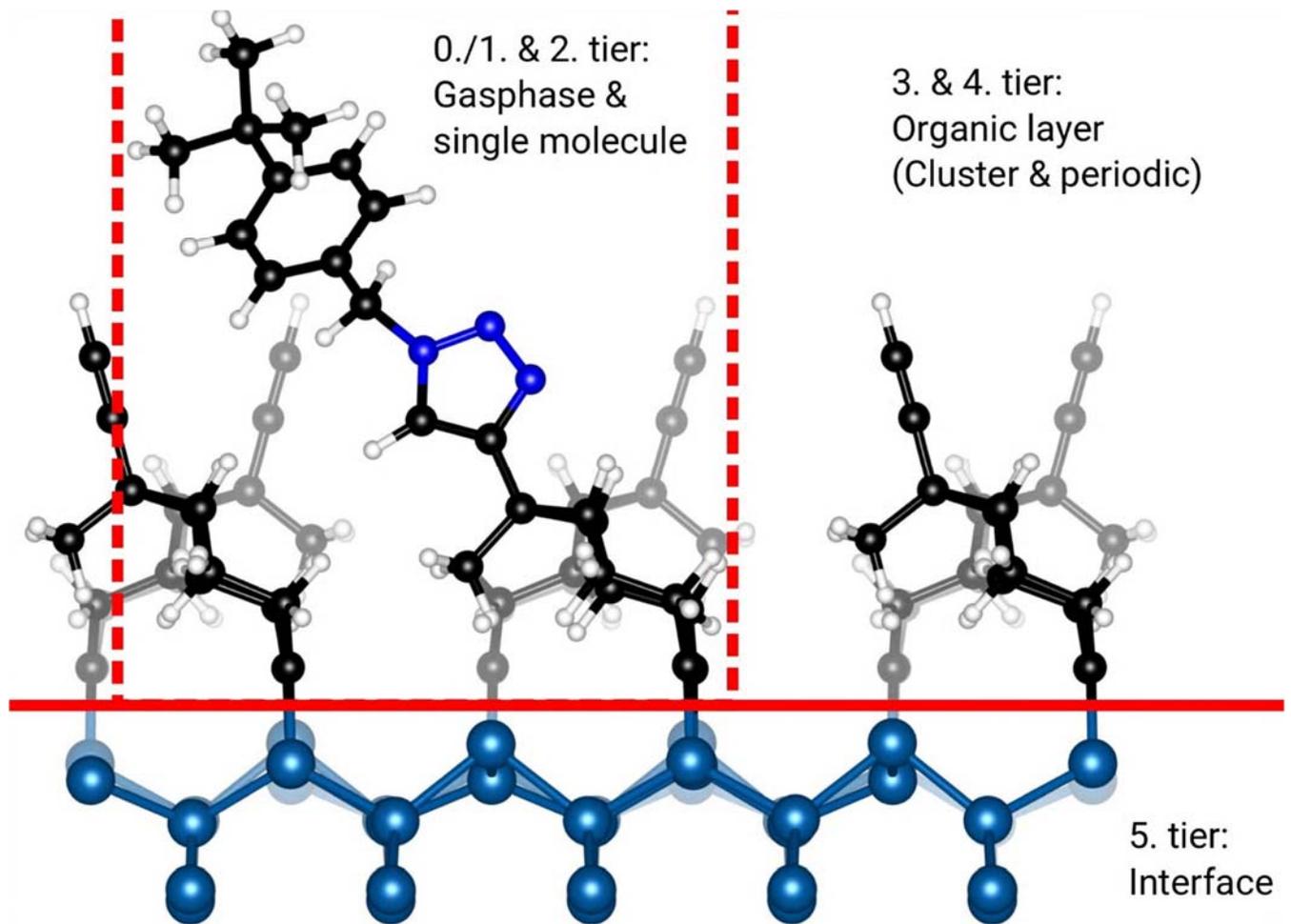
## **COLL 167**

### **One, two, many: From mono- and bifunctional molecules to multilayer structures on semiconductor surfaces by electronic structure theory**

*Ralf Tonner*, [tonner@chemie.uni-marburg.de](mailto:tonner@chemie.uni-marburg.de). Department of Chemistry, University of Marburg, Marburg, Germany

Fundamental investigations of semiconductor surface chemistry has delivered tremendous insight over decades on a broad range of organic adsorbates. Designing hybrid organic-inorganic interfaces now requires to move from fundamental studies of mostly monofunctional molecules to more complex substitution patterns. Further, reactivity beyond the contact layer needs to be addressed and suitable reactions need to be identified. The goal is to find promising routes toward well-defined interface structures from organic molecular building blocks while minimizing byproducts. By combining density functional theory (DFT), ab initio molecular dynamics (AIMD) and advanced electronic structure analyses (energy decomposition analysis for extended systems, pEDA), the design principles toward this goal are highlighted from a computational chemistry perspective for the model system of cyclooctyne on silicon and further model compounds. We will show that in many cases, we can understand the surface reactivity with molecular chemistry concepts like donor/acceptor-interactions, covalent and ionic bonding or aromaticity. Model building is shown to be a crucial step in the modelling of complex and flexible interfaces and efficient and accurate computational protocols will be presented.

Thus, based on a combination of quantitative modelling approaches and qualitative concepts guiding interpretation we highlight the continuing fascination of semiconductor surface chemistry.



Model building for computational investigations of hybrid interfaces

**COLL 168**

**Proximity-driven cell surface conjugation of nanoparticle by a combination of metabolic labeling and SPAAC**

**Bruno De Geest**, *br.degeest@ugent.be*, **Alexander Lamoot**. Ghent University, Ghent, Belgium

Covalent modification of the cell surface can be of interest for a wide variety of biomedical applications. Whereas common non-covalent ligand-receptor recognition involves a dynamic equilibrium between bound and unbound state, covalent conjugation results in a permanently bound state of the therapeutic molecule of interest. This could be of particular interest for drug molecules that exert their activity on the cell surface such as blocking of specific receptors, recruiting factors from the external medium to the cell surface or when using cells as a carrier to deliver a therapeutic payload to a specific

tissue. Here we present a strategy that allows for efficient cell surface conjugation of nanoparticles. Firstly, we aimed for a biorthogonal route based on strain promoted azide-alkyne cycloaddition (SPAAC) between cycloalkyne-functionalized nanoparticles and cells that are metabolically labelled with azides on their glycocalyx. We observed that, relatively to small molecule dye-labelled cycloalkynes, the reaction between cycloalkyne-functionalized nanoparticles and azido-labelled cells is extremely sluggish, due to sterical hindrance and the low concentration of the reaction partners. This issue could be circumvented using nanoparticles containing ionizable lipids with a pKa below physiological pH. Hence at pH 7.4 almost no association between cycloalkyne-functionalized nanoparticles and azido-labelled cells takes place, but at pH 5, where the ionizable lipids bear a cationic charge, strong nanoparticle adsorption takes place due to electrostatic interaction. Importantly, due to the close contact between cycloalkyne-functionalized nanoparticles and azido-labelled cells, SPAAC takes place and nanoparticles remain permanently bound to the cell surface. The latter is confirmed by performing washing steps at physiological pH that do not influence the amount of nanoparticles being bound to cells in case of cycloalkyne-functionalized nanoparticles and azido-labelled cells, whereas blank nanoparticles and/or blank cells are prone to massive loss of nanoparticles on their surface when the pH is increased.

## COLL 169

### **Development of polyzwitterion that responds to tumorous pH for effective delivery of nanomaterials to the deeper site in the tumor tissue**

*Hiroyasu Takemoto*<sup>1</sup>, [takemoto@res.titech.ac.jp](mailto:takemoto@res.titech.ac.jp), *Aziz Awaad*<sup>1</sup>, *Takahiro Nomoto*<sup>2</sup>, *Makoto Matsui*<sup>3</sup>, *Nobuhiro Nishiyama*<sup>1</sup>. (1) Tokyo Institute of Technology, Yokohama, Japan (2) Polymer Chemistry Division, Tokyo Institute of Technology, Yokohama, Japan (3) Institute of Innovative Research, Tokyo Institute of Technology, Yokohama, Kanagawa, Japan

Polyzwitterions offer an antifouling property when the net charge is neutral, and have been utilized for coating of nanomaterials. Thus, precisely regulated protonation behavior in the betaine structure in principle produces smart polyzwitterions with a switchable property to be interactive with surrounding substances in response to a site-specific pH (i.e., tumor in the present study). Herein, we report that surface engineering of nanomaterials using a polyzwitterion comprising 1,2-diaminoethane-based carboxybetaine with polyglutamate backbone (termed as PGlu(DET-Car)) enables tumor-selective delivery of the coated nanomaterials (Figure 1). The delivery performance of PGlu(DET-Car) is based on the stepwise protonation behavior of 1,2-diaminoethane moiety; 1,2-diaminoethane is mono-protonated at physiological pH, and the di-protonation is initiated at tumorous pH. When we coated gold nanoparticles (AuNs) with PGlu(DET-Car), the zeta potential of the coated AuNs (PGlu(DET-Car)-AuNs) was neutral at physiological pH 7.4, but became cationic at tumorous pH 6.5. Ultimately, the three times more PGlu(DET-Car)-AuNs accumulated in tumor tissues relative to PEG-coated system. Of note, the coated nanomaterials reached hypoxic regions in the tumor tissues, possibly due to the protonation of PGlu(DET-Car) along

the pathway to the distant area from the nearest blood vessels. The obtained results suggest that the performance of polyzwitterions can be tuned by the ionizable moieties in betaine structure, directed toward a molecular design of functional surface of nanomaterials.

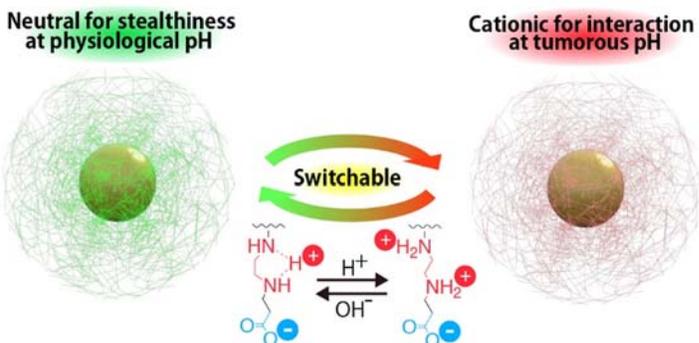


Illustration of the nanomaterials coated with developed polyzwitterion.

## COLL 170

### Nanobiosensors for disease biomarker detection

**Januka Budhathoki-Uprety**, [bjanuka@gmail.com](mailto:bjanuka@gmail.com). Textile Engineering, Chemistry and Science, North Carolina State University, Raleigh, North Carolina, United States

Biosensors are molecular tools that facilitate in disease diagnosis and monitoring of therapy for personal health managements. Single-walled carbon nanotubes have been investigated as emergent materials for nanobiosensors because of their outstanding photophysical properties such as excitation with visible/near-infrared light and non-bleaching emission in the near-infra red region, extreme optical sensitivity towards molecular recognition and tunable high surface area available for molecular interaction. We are developing tailored optical sensors based on fluorescent single-walled carbon nanotubes to enable them for the detection of disease biomarkers in biofluids such as blood, urine, sweat and tears. Our sensors can be integrated into portable, implantable and wearable devices for health monitoring.

## COLL 171

### Lateral flow assays with CdSe nanocrystals

**Paul Mulvaney**, [mulvaney@unimelb.edu.au](mailto:mulvaney@unimelb.edu.au). ARC Centre of Excellence in Exciton Science, School of Chemistry, University of Melbourne, Parkville, Victoria, Australia

Lateral flow assays (LFAs) are simple diagnostic strip tests used for routine Yes-No identification of pathogens or disease markers. The current pregnancy test kit used around the world is a typical example. Current lateral flow assays used colloidal gold as a red indicator for the presence of an analyte. However it has nanomolar sensitivity only. For targets at lower concentrations, this means that pre-concentration, filtering or other processing steps are required. An alternative is to use fluorescence based detection. We describe here the use of semiconductor nanocrystals as an alternative signalling element in LFAs. These allow an increase of at least 2 orders of magnitude in sensitivity.

## **COLL 172**

### **Promotion or prevention of protein corona around nanocolloids: Role of the surface coating**

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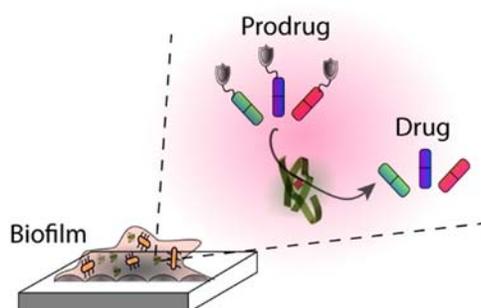
When nanocolloids are introduced into biological media, nonspecific interactions can promote adsorption of proteins around their surfaces, resulting in corona buildup. This can alter the materials behavior and ultimately their effectiveness when used for imaging or sensing applications. Understanding the corona buildup around these nanocolloids has been a challenge. We hereby investigate these interactions using two model systems: luminescent quantum dots and gold nanoparticles. We vary the nature of the hydrophilic block in the surface coating, while maintaining the same lipoic acid bidentate coordinating motif. We track changes in the mobility shift upon exposure of the nanocrystals to protein-rich media, using agarose gel electrophoresis and further complement them with light scattering measurements. We find that lipoic acid (which presents a carboxyl-terminated alkyl chain), either oxidized or reduced promote corona formation. Analysis of the gel mobility data as a function of protein concentrations yields information about the nature of the interactions. However, our data show that when a hydrophilic block made of polyethylene glycol chain or a zwitterion group is appended onto the lipoic acid, the coating drastically reduces corona build-up. Our results are supplemented with additional gel experiments using SDS-PAGE, which show that mainly soft corona forms around the lipoic acid-capped nanocrystals. These findings will be informative when designing nanocolloids with great potential for use in biological applications.

## **COLL 173**

### **Polymer-based bioorthogonal nanocatalysts for the treatment of bacterial biofilms**

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Bioorthogonal catalysis offers a unique strategy to modulate biological processes through the in situ generation of therapeutic agents. However, the direct application of bioorthogonal transition metal catalysts (TMCs) in complex media poses numerous challenges due to issues of limited biocompatibility, poor water solubility, and catalyst deactivation in biological environments. We report here the creation of catalytic “polyzymes”, comprised of self-assembled polymer na-noparticles engineered to encapsulate lipophilic TMCs. The incorporation of catalysts into these nanoparticle scaffolds creates water-soluble constructs that provide a protective environment for the catalyst. The potential therapeutic utility of these nanozymes was demonstrated through antimicrobial studies where a cationic nanozyme was able to penetrate into biofilms and eradicate embedded bacteria through the bioorthogonal activation of a pro-antibiotic.



## COLL 174

### Self-Assembly of biomimetic nanoparticles with amyloid peptides

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Bacterial biofilms represent an essential part of Earth's ecosystem that can cause multiple ecological, technological and health problems. The environmental resilience and sophisticated organization of biofilms acting like a multicellular organism are enabled by the extracellular matrix (ECM) that creates a protective network of biomolecules around the bacterial community. Current anti-biofilm agents can interfere with ECM production but, being based on small molecules, they can be degraded by

bacteria and rapidly diffuse away from biofilms. Both factors severely reduce their efficacy, while their toxicity to higher organisms create additional barriers to their practicality. In the past, we observed semi-selective self-assembly of inorganic nanoparticles (NPs) with a library of proteins that paved the way to their further experimental and computational studies. In this study, we report on the ability of graphene NPs (GNPs) to effectively disperse mature *Staphylococcus aureus* biofilms, interfering with the self-assembly of amyloid fibers - a key structural component of the ECM. Mimicking peptide-binding biomolecules, GNPs form supramolecular complexes with phenol soluble modulins (PSMs), the peptide monomers of amyloid fibers. Experimental and computational results show that GNPs efficiently dock near the *N*-terminus of the peptide and change the secondary structure of PSM, which disrupts their fibrillation and represents a novel strategy for mitigation of bacterial communities.

## **COLL 175**

### **Spectroscopic investigation of gold nanoparticle-protein interactions**

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The range of applications for the use of gold nanoparticles (AuNPs) has been rapidly growing and now includes such areas as diagnostics, catalysis, drug delivery and biological sensing. In this work, we examine the thermodynamic consequences of protein-nanoparticle binding using spectroscopic approaches. We monitored binding using UV-Vis spectroscopy for six proteins chosen based on their differing size and chemical properties bound to both 15 nm and 30 nm citrate-coated AuNPs. UV-Visible extinction and polarized resonance synchronous spectroscopy (PRS2) were used to monitor binding. The UV extinction maxima shifts with increasing protein concentration until saturation of the AuNPs occurs, and the wavelength shift was fit with two models: a Langmuir isotherm model and a mass action-derived model. Both models fit the data equally well; however, the models predict very different  $K_d$  values for 15 nm AuNPs. This difference in  $K_d$  value from the two fits is reduced as the nanoparticle size is increased. The PRS2 data monitor changes in scattering cross section size as protein concentration is increased, and an overlay of binding curves built from both the UV extinction maxima shift and the calculated cross section obtained from PRS2 scattering data are in quantitative agreement. Together, the data suggest two-state binding is sufficient to describe the initial adsorption process. Moreover, for the proteins studied, AuNP curvature is shown to play little role in protein adsorption, with protein type and size showing to be the major contributing factor.

## **COLL 176**

### **Novel approaches for quantum dot sensing**

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Optical sensing of environmental parameters like pH, ions or sugar becomes an increasingly important topic in nanobiomedical applications. Although many selective fluorescence dyes are already in use, the need for alternatives with higher stability, reliability and ability for parallel detection of various parameters is constantly growing. We will report a novel concept which fulfills these requirements and which is based on extremely stable quantum dot constructs. They consist of quantum dots surrounded by a stable shell of polyisoprene-polyethylene oxide diblock copolymer (PI-PEO). We introduced a non-fluorescent pH-indicator dye between the PI and PEO block, allowing a well controllable FRET process between the quantum dot and the dye. We could show that fluorescence lifetime is a very sensitive and reliable measure for the pH in biological environment. These novel sensor probes can further be conjugated to biological markers.

## **COLL 177**

### **PET-guided drug delivery from ultrasound-sensitive multilayer microcapsules**

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Radioisotope functionalized drug delivery vehicles capable of producing positron emission tomography (PET) imaging contrast have gained interest in the biomedical field due to the ability to track in vivo behavior of microcapsule therapeutics and the high sensitivity of detecting radionucleotide emissions for improved biodistribution quantification. However, the majority of current PET-guided theragnostic agents suffer from low loading capacities, poor retention of drug and stability over time, and time-limited PET imaging capability. To overcome these challenges, we have explored hollow microcapsules with a thin (<100 nm) multilayer shell as advanced theranostic delivery systems. The 3- $\mu$ m polymeric shells are fabricated via the aqueous multilayer assembly of a natural antioxidant, tannic acid (TA), and a poly(N-vinylpyrrolidone) (PVPON) copolymer containing monomer units functionalized with deferoxamine (DFO) to carry <sup>89</sup>Zr radioisotope which has a half-life of 3.3 days. We explored the effects of PVPON-DFO composition and localization within the capsule shell on the stability of the radioisotope chelation. The capsule properties were characterized by SEM, AFM and radio chromatography. We also show that anticancer drug doxorubicin encapsulated into the TA/PVPON-DFO microcapsule interior cavities can be released from the microcapsules in response to therapeutic ultrasound. Time-dependent in vivo

biodistribution of TA/PVPON-DFO-89Zr capsules were explored in healthy BALB/c mice and athymic nude mice for 7 days post-injection using PET imaging. These polymeric capsules with the capability for their extended in vivo PET-based tracking and ultrasound-induced drug release may provide an advanced platform for development of precision-targeted therapeutic carriers and could aid in the development of more effective drug delivery systems.

## **COLL 178**

### **Investigating the behavior of charged liposomal encapsulation on acoustically active colloidal particles**

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It has been shown that phase-change agents (PCA's) in the form of surfactant-coated liquid perfluorocarbon droplets nested within charged phospholipid bilayers of particular formulation exhibit improved non-linear acoustic response upon introduction of an electric field. However, the mechanism of alteration is not fully understood. We seek to understand the behavior of the lipids comprising these bilayers, through investigating their impact on the acoustic behavior of their contents. A liposomal encapsulation model developed employing well-characterized colloidal systems such as PEGylated microbubbles is to be extended to more complex systems involving PCA's. Finally, the impact of varying frequency and magnitude electric field on these systems yields insight into the energy- and time-scales of the alteration.

## **COLL 179**

### **Langmuir trough studies of the interactions between per- and polyfluoroalkyl substances (PFAS) and a model cell membrane**

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Bioaccumulative per- and polyfluoroalkyl substances (PFAS), a large class of highly fluorinated organic chemicals, are used as surfactants in industrial and commercial applications. Their resistance to degradation and their ubiquitous presence in water, soil, animals and humans are cause for concern. PFAS chemicals such as perfluorobutane sulfonate (PFBS) and the Gen-X replacement chemicals have the potential to adversely affect cellular functions. Examinations of PFAS are conducted in the presence of a model cell membrane, specifically monolayers of 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC), to better understand the alterations these chemicals may cause to the cell. This project reports surface pressure measurements obtained using a Langmuir trough to monitor changes in the fluidity and packing of a DPPC monolayer at the air-water interface upon addition of PFBS and Gen-X chemical

replacements to the aqueous phase. Preliminary results suggest that while PFBS is not surface active at the neat air-water interface, it alters the surface pressure vs. area isotherm of the DPPC monolayer.

## **COLL 180**

### **Polyacrylate microgels as antimicrobial agents**

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Polyacrylate microgels were prepared with altered material composition and explored as antimicrobial agents towards Gram-positive and –negative bacteria, such as *S. aureus* and *E. coli*. Microbroth dilution assays were used to determine the minimal inhibition concentration and the minimal bactericidal concentration. The obtained data are contrasted against vancomycin, which is a commonly used antimicrobial agents on the market. Interestingly, the crosslinking of the material, its polarity, and degree of crosslinking influence the interactions of the material with both types of bacteria. Preliminary insights in the mechanism of the bacterial interaction will be discussed.

## **COLL 181**

### **Bacterial adhesion and cell-envelope deformation during early-stage *S. aureus* biofilm formation**

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Bacterial adhesion to a surface is the first step in biofilm formation, and adhesive forces between the surface and a bacterium are believed to give rise to phenotypic changes associated with the planktonic-to-biofilm transition. To study the initial adhesion process, we use Focused-Ion-Beam (FIB) tomography coupled with backscattered scanning electron microscopy (SEM) to image *Staphylococcus aureus* (*S. aureus*) biofilms grown on Au-coated polystyrene (PS) and Au-coated PS modified by mixed thiols of triethylene glycol mono-11-mercaptoundecyl ether (EG<sub>3</sub>) and 1-Dodecanethiol (CH<sub>3</sub>). The FIB-SEM approach allows for the direct measurement of the contact area between individual bacteria and the substrate. This contact area is effectively zero on the EG<sub>3</sub> substrate but is nonzero on all of the other substrates and increases with increasing hydrophobicity. The contact area is highest on the unmodified gold, however, which indicates that other forces beyond hydrophobic ones are significant. The bacterial shape is affected by adhesion to the substrate, and the magnitude of bacterial deformation indicates that the adhesive forces are on the order of a few nN. This value is consistent with AFM force measurements reported in the literature. The resolution afforded by electron microscopy furthermore enables us to probe changes in the cell-envelope thickness. Relative to other parts of the same

bacterium away from the substrate, the bacterial cell envelope thickness decreases within and near the contact area. Envelope thinning supports the idea that mechanosensing due to stress-induced membrane thinning plays a role in the planktonic-to-biofilm transition associated with bacterial adhesion.

## **COLL 182**

### **Investigation of bacterial oxidative stress induced by lithium cobalt oxide nanosheets**

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The increasing demand for rechargeable batteries with improved stability and performance to accommodate the rapid expansion of mobile electronics and transportation calls for increased production of nanoscale transition metal oxides as cathode materials in lithium ion batteries. However, the biological impacts these transition metal oxides at the end of their user cycle are poorly understood. Hence, we investigate the biological impact of one of the most widely used cathode materials, Lithium Cobalt Oxide (LCO), on an environmentally beneficial model bacterium, *B. subtilis*, at the molecular level. Our results show that exposure to a sub-lethal dose of LCO causes significant amount of DNA damage, changes in expressions of oxidative stress genes in *B. subtilis*, and an increase in intracellular reactive oxygen species. Hence, we further investigate the identity of the specific type of ROS generated both in solution and intracellularly with a variety of molecular probes in a time-dependent manner. We identify that hydrogen peroxide is the major form of ROS in fresh LCO suspension, and the amount of hydrogen peroxide decreases over time as the suspension ages. The time-dependent measurements of solution ROS generated in LCO suspension enable us to identify the sources of intracellular ROS via a series of reactions resulting in oxidative damages to biomolecules.

## **COLL 183**

### **Engineering polymeric surfaces to combat bacterial adhesion with tunable nanostructure and stiffness**

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Biomimetic, bactericidal surfaces containing nano-protrusive structures have been recently shown to prevent pathogenic bacterial invasion by mitigating the growth of bacteria with the surface nanostructures. Previous work has indicated that protrusive nanostructures on hard surfaces with high stiffness exhibited ample bactericidal

efficiency by mechanically rupturing adhered bacterial membranes. Nonetheless, the nanostructure-induced bactericidal property has not been fully understood in soft materials, despite the prevalence of polymers in biomedical applications. It is of great importance to understand the correlation between the structural and mechanical properties of the designed polymer surfaces and their bactericidal performance for a rational design of biomedical implants and devices incorporating this approach. In this talk, we propose the development of polymeric surfaces with tunable nanostructures and stiffness to combat bacterial adhesion and growth without antibiotic treatment and antifouling agents. We fabricate bactericidal nanostructures at different aspect ratios of the protrusive pillars on hard silicon molds, then transfer the structure on polymeric surfaces by soft molding pattern transfer methods while tuning their mechanical properties by varying the polymerization processes. We investigate the effect of geometry and the mechanical properties (i.e. elastic modulus and bending stiffness) of the polymeric nanopillars on the antibacterial efficacy against both Gram-positive and Gram-negative bacteria. This work will provide insight to aid in solving the questions about whether the mechanical properties of the surface protrusive nanostructures have a critical role in determining bactericidal efficacy and what the critical stiffness of surface structures is to induce membrane rupture and subsequently kill the bacteria. The versatile fabrication methods also give practical insight to help develop bactericidal, medical surfaces made from polymers by engineering surface structures and mechanical properties.

## **COLL 184**

### **Understanding the roles of hollow silica in methane hydrate formation close to room temperature**

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One way to realize natural gas storage via hydrate technology is to form the hydrate at a condition close to room temperature. Although there are a few methods for natural gas storage and transportation, they are either subject to the loss of natural gas during transportation like using liquified natural gas or storage efficiency like compressed natural gas. Using hydrate technology to store natural gas in the solid form or solidified natural gas is believed to change the way natural gas stored and transported. Still, the condition to form natural gas or methane hydrates is somewhat slow and energy required to cool down the operation close to zero degree Celsius. There have been attempts in overcoming the above challenges through the use of promoters like tetrahydrofuran (THF), where the hydrate formation rate drastically increases. Recent findings on using hollow silica (HS) not only further enhance the formation rate but also shift the hydrate formation condition close to room temperature. This work reported how the presence of HS contributes to the such remarkable increase in the formation rate and temperature required to form the hydrates. Real time morphology during the hydrate formation obtained from this study helps shedding light on the role of HS in the formation.

## COLL 185

### Designing phase diagrams of two-dimensional colloids

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The ability to tailor effective interactions between colloids provides a platform to create advanced functional materials. A big challenge is the design of these effective interactions to generate target colloidal structures. In this work, we propose a methodology to select interaction potential parameters that are able to generate target phase behaviors. The methodology consists of four steps: 1) calculate the ground-state energy (zero temperature) of the desired particle arrays (square and triangular, in this work), 2) classify the systems by the lowest potential energy to find the more stable configurations, 3) make a pre-selection of the potential parameters that favor the desired geometry, 4) validate the selected parameters for temperatures above zero by using molecular simulations. As an illustrative example we used a square-shoulder + square-well potential. We build a phase diagram having vapor, liquid, hexagonal, square and rhombic phase. To our knowledge, this is the first simulation work for 2D systems where the full phase diagram is designed from simple considerations: the calculation of the ground state potential energy. The presented method could be applied to other potentials and to other geometrical arrays for two- or three- dimensional systems.

## COLL 186

### Gold-polymer nanocomposites as highly reactive catalysts in homocoupling reactions

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Gold nanoparticles (AuNPs) have been physically encapsulated into polymer particles to serve as highly reactive quasi-homogeneous catalysts in various types of chemical transformation reaction. Although diverse synthetic strategies have achieved great progress in designing catalytically active AuNPs, a major concern in most synthetic methods is the inevitable use of stabilizing or capping agents to prepare the colloidal form of AuNPs against their aggregation in solution unless they are supported onto stable substrates. Furthermore, the presence of stabilizing agents around AuNPs can often minimize and block the readily available active sites of AuNP surfaces, which can greatly reduce their catalytic performance. In this study, we prepared surfactant-free

and physically-embedded AuNPs within poly(N-isopropylacrylamide) particles *in situ* via a light-induced reduction method. The polymer particles did not possess any functional groups to induce strong interactions, but still provided a greatly improved stability to the embedded AuNPs, which resulted in reactive catalysts in homocoupling reactions in pure alcohol and alcohol-rich aqueous solvents under ambient aerobic conditions.

## **COLL 187**

### **Unique method for the phase transfer of aqueous gold nanoparticles to organic solvents**

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Nanoparticles prepared in organic solutions are useful for applications in catalysts as well as surface modifications with organic ligands. The synthesis of aqueous gold nanoparticles is a common procedure that is widely used, but still holds many flaws. As there are many protocols for the synthesis of aqueous nanoparticle solutions, the development of a general procedure for the phase transfer of nanoparticles could be useful.

In this research, we will disclose a new approach to the dispersion and stabilization of gold nanoparticles from aqueous to organic solution using alkylsilanes. The unique activity of poly(hydro)silanes inspired the investigation of monomeric hydrosilanes<sup>1</sup> as transfer agents. This transfer method utilizes n-butyldisilane to complete a ligand exchange, allowing the particles to flow into organic solution. No preliminary surface modifications of the nanoparticles is necessary to facilitate phase transfer using this method. Many published phase transfer protocols involve multi-step reactions, which require surface modifications prior to the nanoparticles being phase transferred. This method allows for transfer of particles without prior modifications or additional stabilizing agents. The gold and silver nanoparticles transferred using this protocol maintained their size and shape throughout the reaction. The transferred nanoparticles were analyzed using UV-Vis, FT-IR, TEM, and <sup>1</sup>HNMR and were found to remain stable even after prolonged storage.

## **COLL 188**

### **HPLC analysis of mono-, di-, and triglycine as a solvent for life**

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Andrew Lee, Sarah Maurer  
Central Connecticut State University, Department of Chemistry

The most common metric for assessing the habitability of a planet or moon is through

the amount of water that area possesses. While liquid water has not been found in abundance elsewhere in the solar system, lakes of liquid alkanes have been discovered on the moon Titan. This begs the question of could it be possible for life to form in other mediums? We tested mono-, di-, and triglycine for their solubility in decanol to better understand the role of Earth-like biomolecules in life in an oil phase. These molecules were partitioned at differing pH's: 1.5, 7, and 10 with the help of charged amphiphiles called phase transfer agents. The method used to detect the compounds was HILIC HPLC with charged aerosol detection. From the data acquired, none of the molecules were able to readily partition into the decanol phase without a phase transfer agent. With the presence of transfer agents however, glycine at high and medium pH was able to substantially partition into the decanol phase with di-, and triglycine being partially able to partition at higher pHs. These trials provide insight into the possibility of life existing in non-water fluids like that of oils and other hydrocarbons.

## **COLL 189**

### **Interaction of $\beta$ -lactoglobulin with lauryldimethylamine oxide and binary surfactant mixtures**

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Understanding the interactions between proteins and surfactants is important for the processing of foods, the formulation and development of pharmaceutical and cleaning products, the purification and analysis of proteins, and the solubilization and extraction of membrane proteins. Ionic surfactants, such as sodium dodecyl sulfate (SDS), are known to perturb protein tertiary and secondary structure at low concentrations. However, several nonionic surfactants, such as lauryldimethylamine oxide (LDAO), have been shown to weakly interact with proteins causing minimal change in protein structure. Understanding the interactions between surfactant mixtures and proteins is important for product formulation and development since the structure of the protein-surfactant complex can affect protein activity as well as emulsion and foam formation and stability. We used a variety of biophysical characterization methods to investigate the impact of SDS and LDAO, and their mixtures, on the structure of  $\beta$ -lactoglobulin ( $\beta$ LG). The tertiary and secondary structure of  $\beta$ LG was found to be significantly perturbed by SDS, LDAO and their mixtures, albeit at much higher concentrations for solutions that contain LDAO. Pyrene fluorescence showed that surfactant aggregates were formed in SDS and  $\beta$ LG mixtures at concentrations lower than the critical micelle concentration of SDS alone. The presence of  $\beta$ -lactoglobulin with LDAO did not change the concentration in which micelles were formed, and the unfolding of  $\beta$ LG occurred at concentrations of LDAO greater than the critical micelle concentration of LDAO alone. The impact of structure of the protein-surfactant complex on the equilibrium and dynamic surface tension will be presented.

## COLL 190

### Effects of characteristic of CO<sub>2</sub> flooding crude oil on foaming and defoaming behaviour

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CO<sub>2</sub> flooding enhances the recovery of crude oil effectively, but a large number of foams will generate in wellhead separator when the produced liquid releases gas due to depressurization, which will reduce the separator capacity. Contraposing the foaming problem of crude oil produced by CO<sub>2</sub> flooding, this paper provides some qualitative and quantitative insights through studying the effects of depressurization, temperature, wax precipitation characteristics, ratio of resin/asphaltene and other factors on the foaming characteristics of four sets of crude oils. A set of depressurization foam experimental device is developed. Experiments indicate that the larger pressure drop ratchet up the amount of foam generated and the defoaming rate. Differential scanning calorimetry (DSC) tests show that the defoaming rate has little relationship with the temperature before wax appearance temperature (WAT). But with the decrease of temperature after WAT, the precipitation of a small amount of wax crystals accelerates the burst of foam, while the further increased wax crystals stabilize the foam. The asphaltene stabilizes foam effectively, but the existence of abundant resin adsorbed on asphaltene surface reduces the stability of foam. The results provide guidance and reference for the research of CO<sub>2</sub> flooding technology, improvement of separator and foaming and defoaming mechanism of the crude oil.

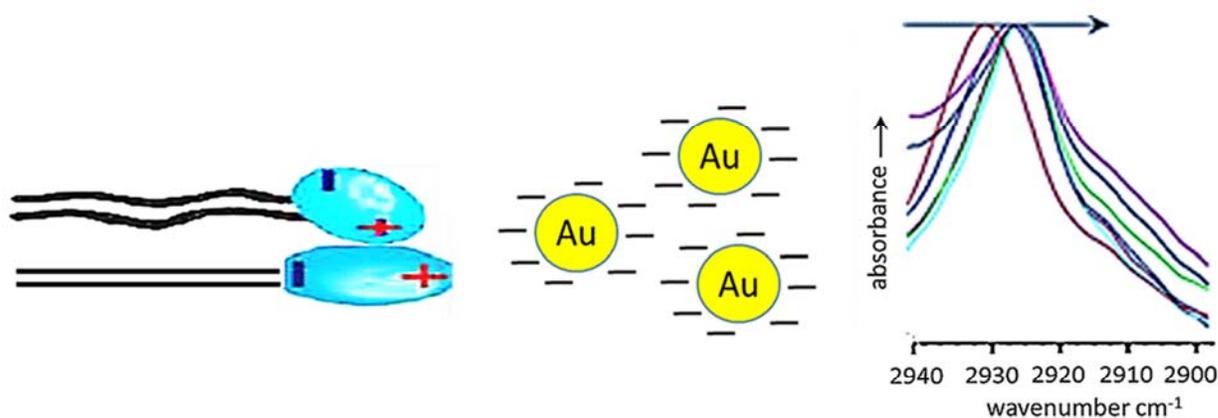
## COLL 191

### Absorption IR spectroscopy tracks the effect of gold nanoparticles on the ordering of phospholipids

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The interactions between a lipid bilayer and metal nanoparticles holds environmental and biomedical significance. Here, we probe the mechanism (of interaction) by following, spectroscopically, the dynamic ordering of a lipid layer from its constituent monomers in the presence of citrate stabilized gold nanoparticles (AuNPs). Individual solutions of DPPC (1,2-dipalmitoyl-sn-glycero-3-phosphatidylcholine) and DMPC (1,2-dimyristoyl-sn-glycero-3-phosphatidylcholine) in CDCl<sub>3</sub> are titrated with 0.5 μL aliquots of pure water, D<sub>2</sub>O and respective solutions with and without AuNPs. The gradual lipid

ordering is followed in separate FTIR experiments. Absorption bands for C-H, C=O and asymmetric  $\text{PO}_2^-$  vibrations are monitored throughout (the titration). The more pronounced shifting in band positions for C-H vibrations toward lower frequencies, consistent with transition to a more ordered crystalline orientation of  $\text{C}_{16}$  chains (on DPPC) on interaction with AuNPs, supports an electrostatic model of the lipid-AuNP orientation process. Our results are consistent with a recently reported electrostatic model of bilayer fluidity (in response in response to AuNP). Discussion of solvation mechanisms along with supportive hyperspectral imaging and UV/vis spectral results are presented.



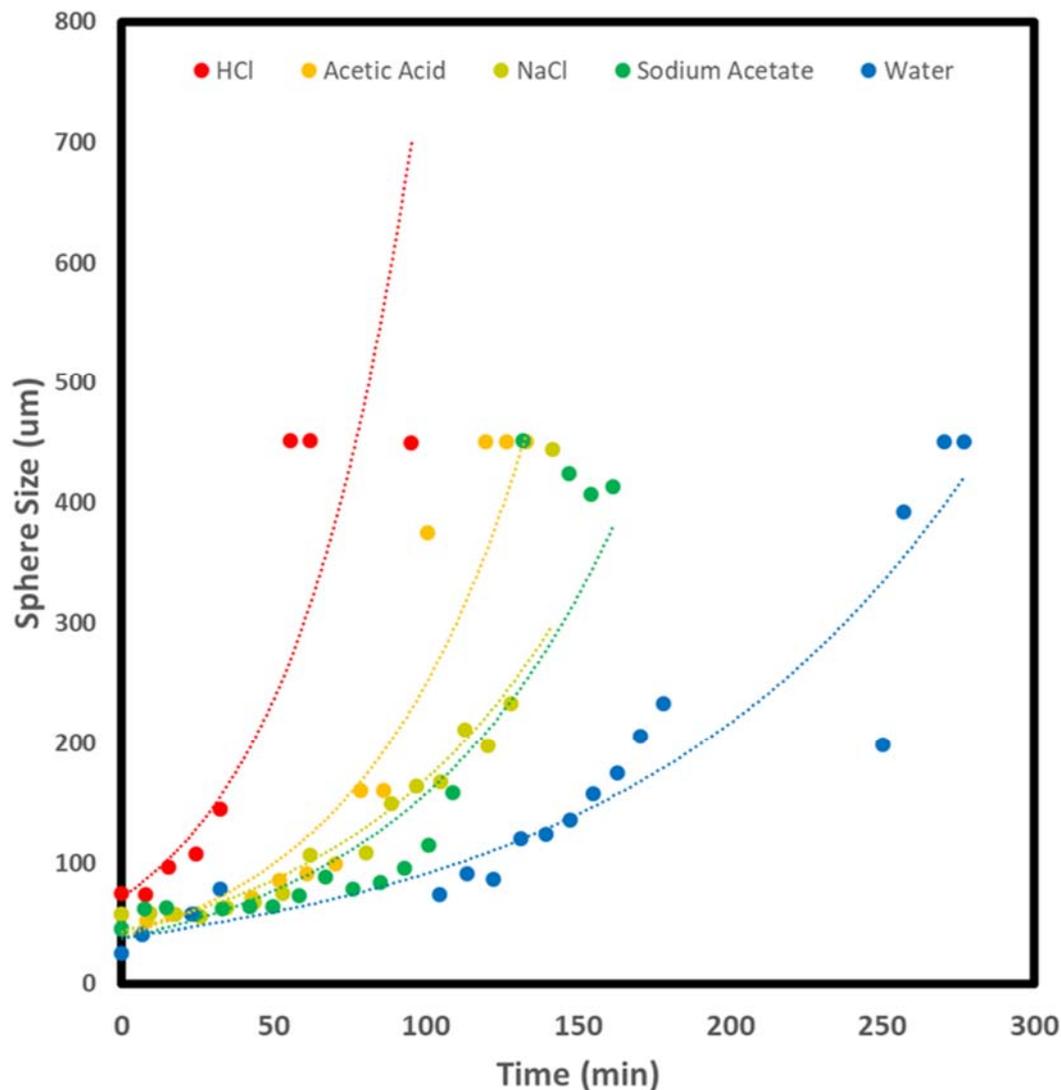
Scheme 1: Graphical depiction (not-to-scale) of citrate stabilized AuNP(s) interacting with zwitterionic DPPC; resulting shifts in hydrocarbon C-H vibrational frequencies.

## COLL 192

### Two dimensional surfactants and porous composite foams: Graphene and boron nitride

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Two dimensional (2D) surfactants are an intriguing class of materials that fall somewhere between traditional small molecule surfactants and solid particle/Pickering stabilizers. Analogous to small molecule surfactants, 2D surfactants spread at high energy interfaces to reduce the total energy of the system. Most Pickering stabilizers are low aspect ratio particles that adsorb to high energy interfaces, such as oil and water, to reduce the interfacial energy of the liquids. Graphene, as a 2D surfactant, spreads at the oil water interface to reduce the total energy of the system, but has a much higher aspect ratio than particle stabilizers. While 2D surfactants have yet to be observed adopting micellar or lamellar structures, they stabilize water-in-oil emulsions with tunable sphere sizes. The incorporation of graphene as a surfactant has enabled the fabrication of conductive polymer foams with properties based both on the monomer selected as an oil phase as well as the contents of the aqueous phase. Herein we explore the properties and stability of emulsions prepared with graphene as a 2D surfactant.



**COLL 193**

**Microstructure design of CTAC:FA and BTAC:FA lamellar gels for optimized rheological performance utilizing automated formulation platform**

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The cosmetic and consumer industry is very fast growing and mass customization has become an increasingly discussed topic within this industry. As demand grows for more customized products and as consumers become increasingly aware of the ingredients that go into their various day-to-day products, the need for more flexible processing and manufacturing methods has increased significantly. This is leading to the increasing utilization of automation across the cosmetic and consumer industry. This study highlights how a combination of a formulation automation platform and rheological characterization can be utilized to design and optimize the microstructure and rheological response of lamellar gels utilized in personal care products.

The microstructure and rheological response of Cetrimonium Chloride (CTAC) and Behentrimonium Chloride (BTAC) with Fatty Alcohol (FA) were investigated and optimized. These compositions are utilized as hair conditioners. The formulation composition was optimized through use of a formulation automation platform. Impact of the microstructure on the rheology was investigated in the formulated systems as well as during product in-use conditions of dilution. The microstructure breakdown during dilution and the maintenance of high viscosity, required for enhanced wet lubrication for hair conditioning performance was seen to be connected to the initial network connectivity of the lamellar gel structure and yield strength of the formulated products.

**Background**

- The Pharmaceutical and Cosmetic Industry is very fast growing and mass customization has become an increasingly discussed topic within the cosmetic industry.
- As demand grows for more customized products and as consumers become increasingly aware of the ingredients that go into their various day-to-day products, the need for more flexible processing and manufacturing methods has increased significantly.
- The size of the global hair care market is estimated at:
  - USD 75 billion in 2012
  - USD 122.28 billion by 2024
- Need to engineer performance of hair care products through high throughput formulation and advanced characterization.

**Objective**

- Optimize hair conditioner performance through variation of composition utilizing automated cosmetic formulation platform and advanced characterization techniques.
- Develop understanding of how performance (wet combing) of hair conditioner is affected by its rheology (i.e. Yield Stress).
- Controlled breakdown of the formulations (dilution) and its effect on wet combing.

**Experimental Design**

**Formulation Variables**

- Cetyltrimethylammonium Chloride or Cetyltrimethylammonium Chloride
- Dodecyltrimethylammonium Chloride or Hexadecyltrimethylammonium Chloride (CTAC)
- Cetyl Alcohol (CA)
- Surfactant/Fatty Alcohol Combinations
  - CTAC/Cetyl Alcohol
  - CTAC/Cetyl Alcohol
  - CTAC and BTAC were varied at 2% or 6% while Cetyl Alcohol was varied at 5% and 10%.

**Techniques (Figure 1)**

- Automated Formulation
  - ChemSpeed Flex (gamma)
  - MedSonic Technology
  - TA Instruments DHR3
- Temple Tester
  - TA Instruments MTT3.75

**Figure 1:** TA Instruments (left), ChemSpeed Flex Formax (right) and MedSonic Technology (right) Temple Tester (left).

**Result: Rheological Properties**

Composition variation to engineer the Microstructure and Yield Stress: the rheological behaviors of the mixtures were evaluated at following ratios:

- BTAC (CTAC) 2%/CA 5%
- BTAC (CTAC) 6%/CA 5%
- BTAC (CTAC) 2%/CA 10%
- BTAC (CTAC) 6%/CA 10%

**1. Yield Stress of BTAC/CA and CTAC/CA Formulations:**  
Yield Stress of the formulations were engineered through composition variation and the highest Yield Stress is recorded at 6% BTAC/10% CA\* in the BTAC system and recorded at 6% CTAC/10% CA\* in the CTAC Systems.

BTAC Formulations			CTAC Formulations		
Formulation	BTAC : CA (%)	Yield Stress (Pa)	Formulation	CTAC : CA (%)	Yield Stress (Pa)
1	2:5	125.938	5	2:5	31.7015
2	6:5	63.124	6	6:5	25.1714
3	2:10	158.497	7	2:10	19.9754
4	6:10	251.179	8	6:10	50.1402

**Result: Dilution Regime**

What effect does dilution have on formulation viscosity as we mimic some consumer actions?

**1a. BTAC formulation with lowest Yield Stress: 25%, 50%, 75% & 90% dilutions.**

**1b. BTAC formulation with highest Yield Stress: 25%, 50%, 75% & 90% dilutions.**

**Result: Dilution Regime**

**2a. CTAC formulation with lowest Yield Stress: 25%, 50%, 75% & 90% dilutions.**

**Formulation 7 Dilutions**

**2b. CTAC formulation with highest Yield Stress: 25%, 50%, 75% & 90% dilutions.**

**Formulation 8 Dilutions**

**Result: Effect of Yield Stress on Viscosity Breakdown**

Viscosity was measured at the highest shear rate of 100000 1/s and it can be observed that the higher the Yield Stress, the higher the dilution viscosity.

**Result: Effect of Yield Stress on Combing Force**

Formulations with highest yield stress in each system (6% BTAC/10% CA and 6% CTAC/10% CA) have the best effect on reducing overall combing force i.e. from dry hair stress to wet hair stress and after product is rinsed off.

BTAC : CA	Yield Stress (Pa)	% Reduction in Combing Force	CTAC : CA	Yield Stress (Pa)	% Reduction in Combing Force
6 : 5	63.124	88.76	2 : 10	19.975	65.04
6 : 10	251.2	94.6	6 : 10	50.14	88.2

**Conclusion**

- Yield Stress was found to have significant effect on dilution viscosity breakdown.
- Formulations with highest yield stress maintain high viscosity (high shear rate) on dilution impacting wet lubrication. This results in lower combing force.
- The overall performance of the hair conditioner can be engineered through optimization of the microstructure and microstructure breakdown on dilution.

**Future Study**

- Further explore the effect of substituting CTAC/BTAC with natural cationic surfactants and/or cationic polymers.
- Explore processing and formulation parameters further for optimization of the engineered microstructure through automated formulation platform.

**Acknowledgement**

We acknowledge the contribution of the following companies and institution for making this project possible:

- CHEMSPEED TECHNOLOGIES
- DIA-STRON
- TA INSTRUMENTS
- EVONIK POWER TO CREATE

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COLL 194

Engineering surface activity and bulk rheological performance through controlled interactions of biopolymers with biosurfactants

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Evolving consumer inclinations and expectations are now driving a wider range of non-toxic, sustainable and biodegradable innovations in the cosmetic and personal care industry. In addition, highly competitive nature of the cosmetic industry requires providing consumers with unexpected and novel sensory experiences to help further differentiate products. This requires generating novel textures and performance in foaming, cleansing etc. through modifications in surface activity and bulk rheological performance. In this study we explore the impact of three natural biopolymers Chitosan, Alginate and Pectin on surface activity and rheology of two biosurfactants Rhamnolipid

and Sophorolipid. The impact on the surface tension and surface elasticity at the air-water interface and bulk viscoelasticity and viscosity will be presented.

## **COLL 195**

### **Investigating the Influence of Polysorbate 20/80 and Poloxamer P188 on the surface & interfacial properties of Bovine Serum Albumin and Lysozyme**

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The current challenges faced in the formulation of high concentration protein-based therapeutics include protein stability, protein aggregation, and high viscosity. Although there has been significant progress in developing a mechanistic understanding of the protein systems themselves, the impact of other formulation components has been limited. Excipients like surfactants such as Polysorbates, or Poloxamers which are commonly utilized in bio-therapeutic formulations may potentially impact many of these aspects. This systematic study details the effect of these excipients on protein aggregation and corresponding effects on bulk and surface rheology evolution. Additionally, the impact on interfacial and surface properties has been limited in the range of formulation conditions and impacts on interfacial rheology have not been investigated in detail. In this study, we utilize a range of advanced characterization techniques such as surface/ interfacial rheometry, tensiometry, dynamic light scattering, as well as thermal aggregation studies to develop new insights into the impact of surfactants i.e. polysorbate 20, polysorbate 80 and poloxamer P188 on the aggregation behavior, rheology and interfacial and surface properties of Bovine Serum Albumin (BSA) and lysozyme. In conclusion, competitive adsorption between proteins and common excipient surfactants is dictated by the type of protein and its effective structuring/rigidity at the surface as reflected through surface elasticity. BSA was seen to exhibit a higher surface elasticity than lysozyme, and therefore has a more rigid structure and is more competitive at the interface. Poloxamer P188 does not exhibit high surface activity compared to proteins such as BSA or Lysozyme. Both PS 20 and PS 80 are able to displace BSA and Lysozyme at high concentrations. Rheological properties and thermal stability both seem to be impacted also by the choice of the surfactant. Thermal studies of BSA with each of the excipients show that the PS 20 results in the highest aggregation temperature. Additional studies are ongoing to understand the effects on thermal stability and rheology for lysozyme in the presence of these surfactants.

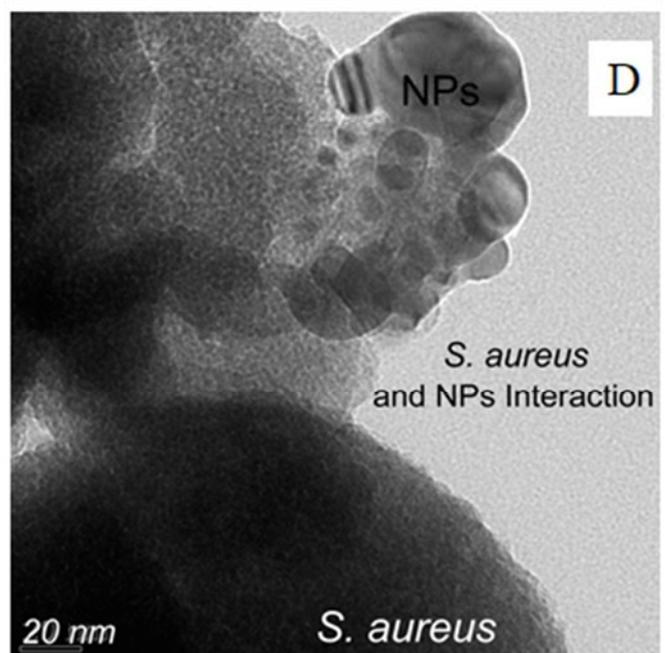
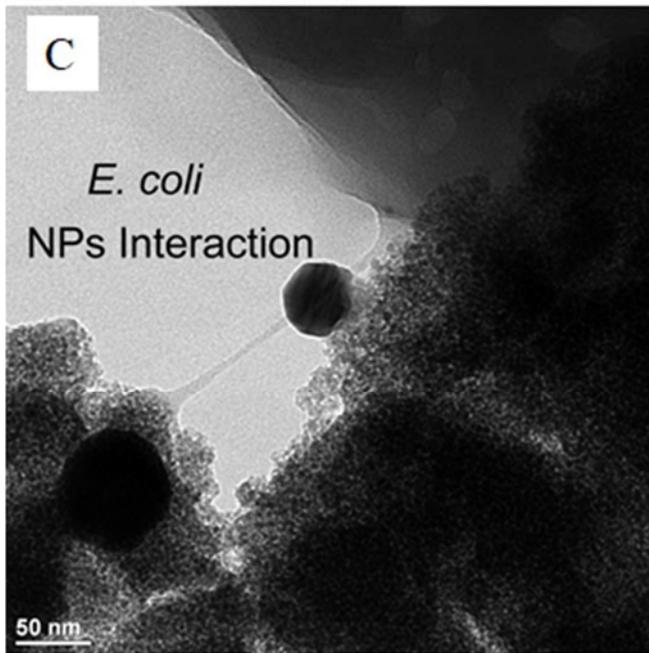
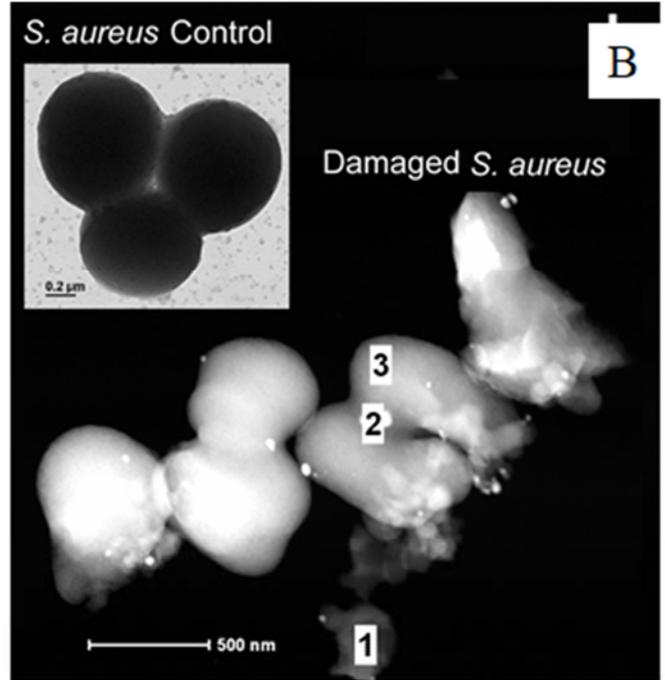
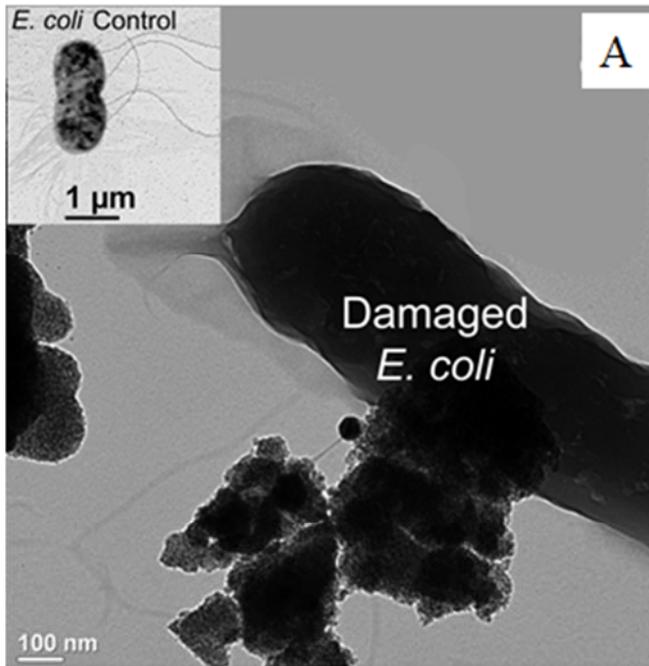
## **COLL 196**

### **Progressive approach on inactivation of bacteria using nanostructured composites**

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Silver insertion into titania offers a number of tangible advantages compared with transition metal oxides, when applied as nano-biocidal agents. These advantages relative to titania are effectiveness under visible light conditions, lower minimum bactericidal concentrations (MBC), lower incorporation of silver (relative to silver nanoparticles) and broad range of activity. Three concentration-dependant trends are observed, at very high nanoparticles ( $> 50,000$  ppm) concentrations, cellular lysis is observed, similar to that for bleach, suggesting that lipid oxidation is the major form of inactivation; at intermediate levels (MBC: 2.5 ppm to 20 ppm) inhibition is observed with minimal lysis, suggesting that other mechanisms, such as DNA fragmentation, protein and respiration inhibition or disruption of the membrane potential are more prominent in inactivating the microbe than lysis and at ultralow doses ( $< 2.5$  ppm) bacteriostatic like phenomenon is observed, suggesting some membrane damage inhibiting growth, but not extensive enough to cause cellular inactivation. Plausible mechanism of inactivation is offered to explain the observed events. Lastly, other advantages common with transition metal oxides are retained, such as long-term persistence and 100% metal recycling. Collectively, this approach can be applied where traditional disinfectant approaches are ineffective such as with antibiotic resistant bacteria, high sunlight where bleach is rapidly oxidized and has many potential benefits to the community in terms of a microbe-free water supply.



Evaluation of antibacteria efficacy (A, B) and interaction between *Escherichia coli* and Ag/TiO<sub>2</sub> (C), showing cytoplasmic membrane peeling (light to dark gray zone); and similar view for *Staphylococcus aureus*, also showing peeling (light grey regions, D).

## COLL 197

**Snowball-like sweeping removal of dropwise condensation propelled by gradient electric field**

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Dropletwise condensation plays an important role in nature and industrial applications, such as water harvesting, air conditioning, desalination, anti-fog and thermal management. The evolution of superhydrophobic surfaces promotes dropletwise condensation in easily removing condensing droplets to enhance mass and heat transfer. Droplet departure size is at small-scale through droplet jumping by releasing surface energy but the existence of vapor flow and gravity can lead to droplets return. Droplet sweeping by gravity can expose large re-nucleation area for next condensation, which takes a long growth and shedding cycle due to the droplets have to exceed the capillary length to take advantage of gravity. Here, we demonstrate that condensation micro-droplets could sweep on the horizontally placed surface spontaneously by implanted a gradient electric field into an electret with superhydrophobic surface. This sweeping movement can take place at much smaller size and earlier departure time compared to gravity shedding, which is attributed to the fact that coalescence-induced charging of condensing droplets at a very small length scale. Condensing droplets undergo coalescence-charging, snowball-like moving and self-propelling, the process repeats itself in a periodic manner. Utilizing a gradient electric field to propel the charged droplets to sweep other condensation droplets shift drop size distribution timely and lower surface coverage. This controlled sweeping behavior opens up a novel avenue for condensation enhancement.

**COLL 198**

### **Aggregation of gold nanoparticles induced by amino acids: Enhancement of colorimetric response by $\text{Cu}^{2+}$**

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Gold nanoparticles have an optical property that depends on the interparticle distance, and thus their aggregation can cause a noteworthy color change of the dispersion. This study investigated the aggregation of gold nanoparticles caused by various amino acids in order to develop a strategy for colorimetric detection of a biological reaction. We examined the colorimetric response of gold nanoparticles with varying concentrations of cysteine, cystine, arginine, aspartic acid, serine, and methionine solutions. The results demonstrated gradual color changes with increasing concentrations of cysteine but did not exhibit a noticeable change for other amino acids. We explored the effect of the nanoparticle size on the cysteine-induced aggregation and a smaller gold nanoparticle showed a lower detection limit than a larger one. Additionally, the sensitivity of the colorimetric response was significantly increased by adding  $\text{Cu}^{2+}$  to the examined dispersions due to the chelate formation between the metal ion and surface-immobilized

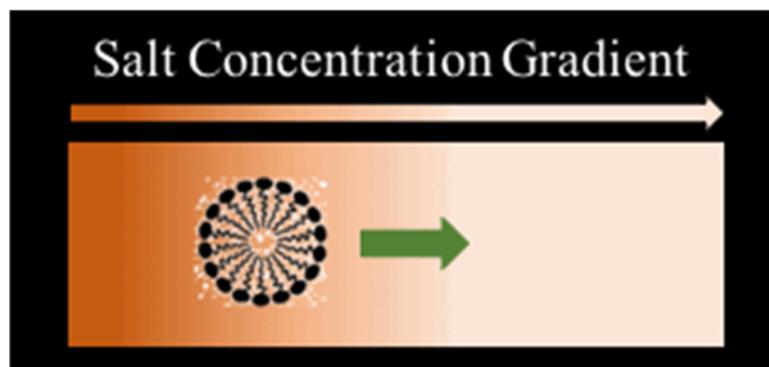
cysteines. The overall results demonstrate that the highly sensitive aggregation of gold nanoparticles caused by cysteine in the presence of  $\text{Cu}^{2+}$  ion has the potential to be used for selective chemical and biological sensing for specific analytes.

## COLL 199

### Salt-induced diffusiophoresis of a neutral micelle

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Diffusiophoresis is the migration of colloidal particles in a fluid due to concentration gradients of other solutes such as salts. Many recent studies have shown that this transport mechanism could be used for controlling particle motion, with potential applications in separation science, controlled release, microfluidics, and enhanced oil recovery. These applications are especially appealing for host particles such as micelles. In this work, Rayleigh interferometry was used to characterize diffusiophoresis of Tyloxapol, a nonionic PEG-based micellar system, in the presence of the strong salting-out agent, sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), in water at 25°C. Our results show that micelle diffusiophoresis occurs from high to low salt concentration. Another transport mechanism, denoted as salt osmotic diffusion, was also characterized. This process, which describes salt diffusion induced by micelle concentration gradients, was used to determine the thermodynamic driving force responsible for diffusiophoresis of this neutral particle. Our results were explained with a model based on PEG preferential hydration. At relatively high salt concentrations liquid-liquid demixing was observed even in dilute micellar solutions. Correspondingly, micelle normal diffusion was found to dramatically slow down near the phase-transition boundary while diffusiophoresis was not significantly affected. This implies that diffusiophoresis is the dominant diffusion mechanism for micelle transport close to the phase boundary. Our work provides guidance for the development of strategies to control the motion of micelles and PEG-based colloidal particles in general by applying salt concentration gradients.



Micelle migration from low to high salt concentrations

## **COLL 200**

### **Electrochemically triggered deposition of water suspended colloids**

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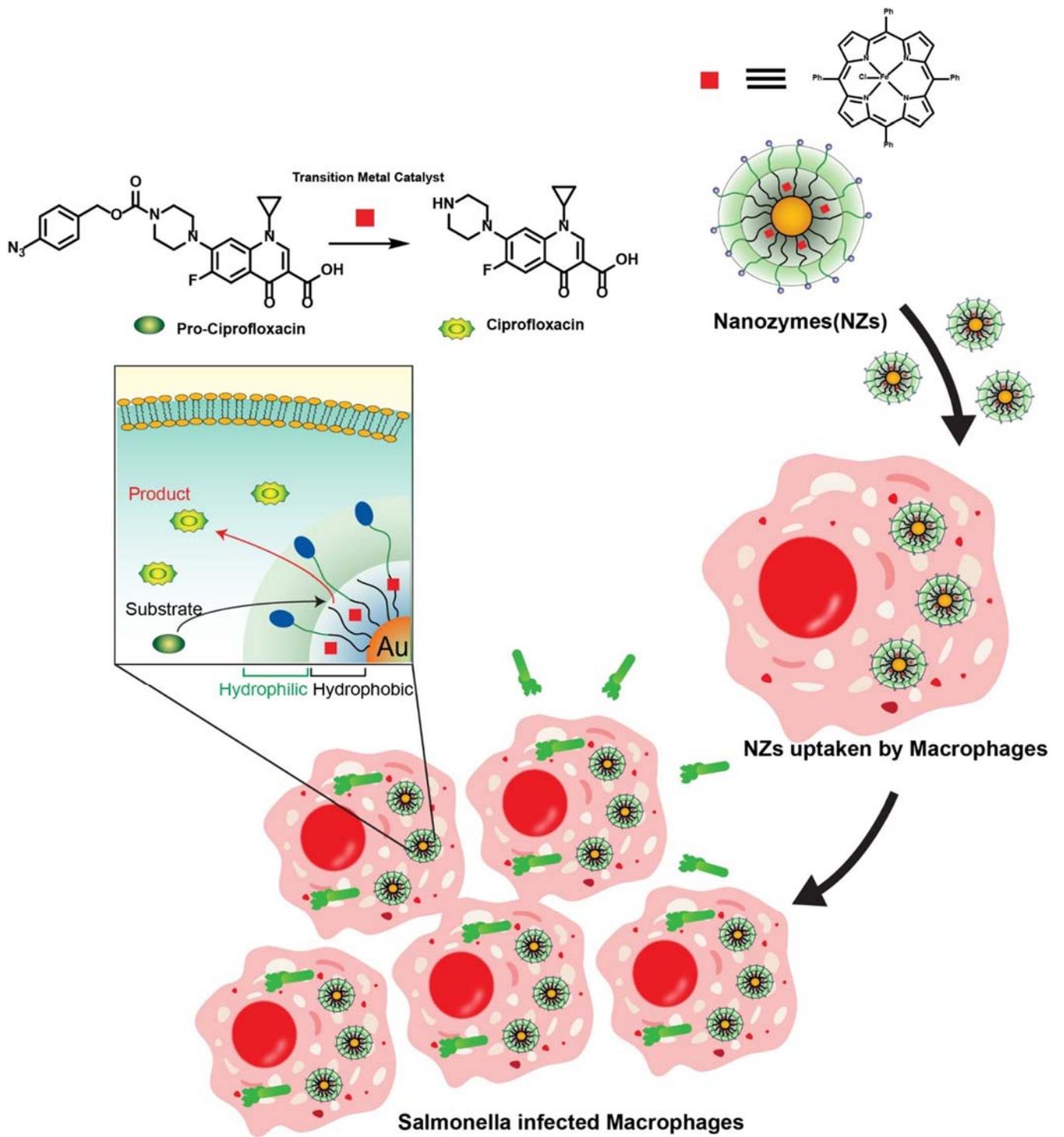
In this presentation, I will discuss our recent findings on using self-assembled monolayers of ferrocene to trigger fast and reliable surface deposition of colloidal particles. This method can afford deposition of polystyrene microspheres of different sizes ranging from 50 nm to 5  $\mu\text{m}$  as tested. This approach provides access to generate sophisticated patterns of deposited materials on electrode surface, an alternative to available surface patterning technologies with certain advantages to offer. Patterns can be created by attaching ferrocene thiol on gold through conventional microcontact printing followed by electrochemically triggered deposition of desired microspheres exclusively on thiol embedded region of the electrode. Voltametry and confocal laser microscopy was used to characterize and analyze the deposition process and thus resulted electrode surface. Effects of size and charge density of carboxylated polystyrene microspheres on deposition process, and deposition in presence of small ions are also discussed.

## **COLL 201**

### **Targeting of invading pathogenic bacteria using biorthogonal nanozymes**

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Intracellular infections, such as *Salmonella enterica* and *Listeria monocytogenes* present a major health threat. These intracellular pathogens invade and reproduce within host cells such as macrophages, providing protection of pathogens from host defenses and antibiotic therapy. We have used biorthogonal catalysis to effectively treat intracellular *Salmonella* infections. Nanozymes, comprised of gold nanoparticles loaded with transition-metal catalysts, were used to activate pro-antibiotics at the site of infection. These nanozymes were functionalized to specifically target macrophage cells, creating an effective, site-specific intracellular antibiotic treatment while avoiding off-target toxicity.



## **Controlling optical properties of complex emulsions via $\gamma$ -cyclodextrin degradation for colorimetric sensing applications**

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Structural coloration plays an important role in daily phenomena as one of the main mechanisms of color in nature and materials. Complex emulsion droplets consisting of hydrocarbon and fluorocarbon oils have previously been shown to exhibit iridescent structural color via total internal reflection based on the size, shape, composition, and orientation of the droplets. Our study works to further explore the optical properties of complex emulsion droplets and their applications given their reconfigurable properties in aqueous surfactant solution. An  $\alpha$  – amylase enzyme-responsive surfactant solution was modeled after a previous study by Zarzar, et al. and is composed of  $\gamma$  – cyclodextrin substrate, Triton X – 100 surfactant, and Capstone FS – 30 surfactant. This enzyme-responsive surfactant solution was utilized to quantify the sensitivity of O/O/W emulsion droplets for simple colorimetric sensing capabilities and enzyme activity through the correlation of color patterns to droplet shape, size, and volume ratio.

### **COLL 203**

## **Exploring the impact of $\beta$ -cyclodextrin infused cellulose-based composites for the remediation of persistent organic pollutants**

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Common remediation techniques for persistent organic pollutants involve absorptive processes, flocculation, and reverse osmosis to improve water quality. Though these methods are efficient they are costly and have limited adsorption capacity. Therefore, recent studies have shifted towards alternative methods using naturally abundant polymers, such as cellulose and its common derivatives, due to their high adsorptive properties and tunable morphology. While previous results have shown efficient remediation of organic dyes, the adsorption efficiency was hindered for persistent organic pollutants such as parabens. To enhance the non-covalent interactions, this work focuses on the addition of  $\beta$ -cyclodextrin ( $\beta$ -CD) to the bulk cellulose matrix. Results have shown significant remediation (> 50%) in short time periods (i.e. less than 1 hour) of both methylene blue (MB) and four different hydrocarbon substituted parabens. The addition of  $\beta$ -CD to the matrix showed changes in bulk polymer pore structure but did not have a significant effect on the overall remediation. To enhance the remediation efficiency this work focuses on modulating the surface energy by altering the pH during synthesis while controlling the morphology through the addition of  $\beta$ -CD. Initial results have shown improved adsorption of various persistent organic pollutants by increasing the surface hydroxyl concentration through base-assisted hydrolysis of the polymeric matrix. Modifications to the surface energy of the supramolecular

nanocomposites has shown to be a major driver in the modulation of remediation efficiency.

## **COLL 204**

### **Impact of formamide osmolytes on water in confinement: pH at the nanoscale**

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To investigate the impact of osmolytes on surfactant bound water nanodroplets, reverse micelle (RM) systems involving an anionic surfactant and mixed composition polar cores were studied. In RMs the surfactant bounds polar nanodroplets in a non-polar solvent. This study uses sodium 1,4-bis(2-ethylhexyl)-sulfosuccinate (AOT), a well-studied and common surfactant. To address the impact of osmolytes on water in confinement polar cores were varied from the typical 100% water to 100% formamide osmolyte. Visible and NMR spectroscopies were used to gather information about the systems. Characterization of absorption spectra of methyl orange spiked RMs provided measurements of pH within the polar core. As expected as the core becomes more basic as the ratio of formamide increases. Comparisons between confinement and bulk solutions of the same water:osmolyte composition shed light on the impact of confinement on proton transfer. Results comparing formamide, N-methylformamide, and N,N-dimethylformamide illustrate the impact of osmolyte structure in confined environments.

## **COLL 205**

### **Nanoparticle-enabled, waveguide-based, mid-infrared sensor for selective detection of gases**

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We report a waveguide-based optical sensor which enables multi-analyte detection of gases (methane, acetylene, acetone and ethanol) in the mid-infrared spectral region. Selectivity and sensitivity of detection was enabled by chemical functionalization of an amorphous silicon (a-Si) ridge waveguide with multilayers of ZnO and SiO<sub>2</sub> nanoparticles with diameters of 4.2 nm and 20 nm, respectively. The a-Si waveguide was prepared by complementary metal-oxide-semiconductor (CMOS) processes capable of wafer-scale device production. The nanoparticles were strategically assembled within the coatings using the layer-by-layer (LbL) technique, which enables the deposition of conformal coatings of controlled nanoscale thickness and composition.

The effect of varying size and surface charge of the nanoparticles on the thickness and morphology of the assembled films has been investigated. The assembled nanosized particles have provided a large surface area for gas adsorption and concentrated gas molecules within the evanescent field of the optical sensor, thus dramatically enhancing sensitivity of gas detection. Importantly, sensitivity of gas detection could be also enhanced by the deposition of a larger number of nanoparticle layers within LbL films. At the same time, selectivity of the detection was achieved through a combination of wavelength-specific sensing and preferential adsorption of gas molecules on specific type of nanoparticles (such as stronger adsorption of acetone vs. methane on ZnO nanoparticles). Selective and reversible sensing of methane, acetylene, acetone and ethanol using the nanoparticle-enabled waveguide-based platform has been demonstrated in the mid-infrared region.

## **COLL 206**

### **Functionalizing fabrics and textiles with giant polymer and lipid vesicles**

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Giant vesicles are structures larger than 1 micrometer that have self-assembled membranous walls composed of amphiphiles such as phospholipids, amphiphilic block copolymers or fatty acids. Giant vesicles are useful since they can encapsulate and protect hydrophilic cargo in their lumens and host hydrophobic molecules in their membranous walls. Giant vesicles are known to form from lamellar amphiphile films on a subset of solid surfaces under limited sets of conditions. Here we significantly expand on our demonstration that giant vesicles can form on cellulose paper. We show that a wide variety of commercially and technically important fabrics and textiles coated with dried amphiphile films and then exposed to water support the growth of giant vesicles. Fabrics that support the formation of giant vesicles in water include natural fibers such as cotton, wool, and silk, as well as synthetic fibers such as rayon, nylon, polyester, and glass fiber. Most of the giant vesicles remain trapped within the matrix of the fabric thus providing a means of retaining hydrophilic material while the fabric is immersed in water. Approximately 5 % of the giant vesicles are released from the fabrics when subjected to shear flow, thus allowing transport of both hydrophobic and hydrophilic cargo into the surrounding solution. Furthermore, the formation of giant vesicles occurs within minutes, enabling vesicle formation at the point of use. These results open new avenues into developing technologies that require control and release of hydrophilic and hydrophobic cargo such as bandages in wound healing.

## **COLL 207**

### **Preparation, gelation and DNA binding studies of N-(acridin-9-yl)alkanamides as low molecular mass gelators**

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Acridine derivatives are known to exhibit pharmacological properties and many biological functions. Preparation and characterization of N-(acridin-9-yl)alkanamides with varying carbon chain will be presented. Gelation studies show that 5 wt % N-(acridin-9-yl)docdecanamide and N-(acridin-9-yl)tetradecanamide gelate organic liquids (silicone oil, safflower oil and DMSO) and water. Correlation of gelation properties of hydro and organo gels as well as computational studies of complexation with DNA with N-(acridin-9-yl)alkanamides will be presented.

## **COLL 208**

### **Synthesis, self-assembly, gelation studies of anthraquinonylalkanamides based low molecular mass gelators**

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Anthraquinones can be found in various herbs<sup>1</sup> and have known to exhibit many biological functions.<sup>2</sup> Cleavage of DNA by irradiation of substituted anthraquinones are also reported.<sup>3</sup> Present study discuss the synthesis and gelation studies of anthraquinonylalkanamides as low molecular mass gelators. Low molecular mass gelators are viscoelastic materials that can be considered as an important class of soft materials. The gelator molecule aggregate *via* weak intermolecular interactions such as hydrogen bonding, Van der Waals interactions and  $\pi$ - $\pi$  stacking to form a three dimensional fibrillar network that can trap large amount of liquid. Anthraquinonylalkanamides with varying alkyl chain length have been synthesized and characterized. Gelation studies of synthesized compounds have been examined in 19 different polarity liquids. Correlations between the molecular structures of the anthraquinonylalkanamide gelators and the properties of their gels, including critical gelator concentrations, periods of stability, and gel-sol transition temperatures, thermodynamic and spectroscopic properties will be presented.

## **COLL 209**

### **Development of gold nanorod-peptide nanocomposites for phototriggered drug release to tumor cells**

**Rachel E. Daso**, *rdaso@fordham.edu*, **Ipsita A. Banerjee**. Department of Chemistry, Fordham University, Bronx, New York, United States

In this work, we have developed a new dual targeting nanocarrier system for targeting MCF-7 breast cancer cells. We synthesized a new amphiphatic peptide-based system where in Fluorenylmethoxycarbonyl protecting group was attached to the N-terminal of

the peptide sequence L-S-G-C-G-N-S that comprised of a tumor targeting peptide sequence. The product self-assembled into nanofibers under aqueous conditions in the diameter range of 200-300 nm. The nanofibers were then encapsulated with an estrogen receptor antagonist drug fulvestrant. In some cases, the nanofibers were first attached to gold nanorods (10 nm) and then encapsulated with the drug to facilitate photo-triggered drug release. SEM and AFM imaging were used to probe the morphology of the drug delivery vehicles and FTIR, UV-Vis and DSC confirmed the entrapment of the drug while XRD confirmed incorporation of the gold nanorods. Release studies indicated that irradiation of the drug-encapsulated gold nanorod-bound assemblies with near infra-red laser showed a two-fold higher drug release compared to those without irradiation over a period of two weeks. Cytotoxicity studies indicated that the irradiated assemblies showed higher cytotoxicity toward the breast cancer cells due to both the greater release of the drug and interactions between the drug delivery vehicles and the cells. Furthermore, cell blebbing and complete loss of actin stress fibers were observed. Additionally, cell invasion studies showed reduction in cell invasion compared to control cells upon irradiation. Thus, the formed drug delivery vehicles demonstrate potential in targeting breast tumor cells and may have applications in tumor targeting.

## **COLL 210**

### **Investigating position-dependent coupling between a fluorescent molecule and plasmonic nanoparticle in super-resolution imaging**

*Bianca Paranzino, [tuj46245@temple.edu](mailto:tuj46245@temple.edu), Katherine A. Willets.* Chemistry, Temple University, Turnersville, New Jersey, United States

Super-resolution imaging is potentially useful for obtaining information about the placement of ligands on the surfaces of metallic nanoparticles. While the resolution of optical microscopes is limited by the diffraction limit of light and is unable to resolve particles smaller than half the wavelength of light, super-resolution imaging overcomes this limitation by localizing individual emission events from fluorescent molecules attached to surface-bound ligands. A reconstructed image of the underlying nanoparticle is generated by mapping the localized positions. While the reconstructed images reproduce the orientation and shape of the nanoparticle, they are often smaller than the dimensions of the nanoparticle and provide unreliable spatial information about the ligand due to coupling between the fluorescent molecule and the plasmonic nanostructure. To investigate how the position of a fluorescent molecule on an anisotropic nanoparticle affects coupling, fluorophore-labeled DNA is bound to specific positions on the surface of selectively silica coated gold nanorods. The position of the fluorophore-labeled DNA can be controlled by blocking either the ends or the sides of a gold nanorod with silica. This provides the ability to study how the position of the fluorophore affects the coupling between a fluorescent molecule and plasmonic nanoparticle.

## **COLL 211**

## **Using defocused images to investigate fluorophore-plasmon coupling interactions and their relation to localization accuracy in super-resolution imaging**

**Abigail Crawford**, *tuj13296@temple.edu*, **Katherine A. Willets**. Chemistry, Temple University, Philadelphia, Pennsylvania, United States

Super-resolution imaging is a useful tool to gain information not only about the shape and orientation of metallic nanoparticles but also how fluorescent biological ligands bind to the surface. One major problem with the technique is that the reconstructed image is consistently smaller than the expected size of the particle. It is hypothesized that this error in localization may be due to coupling between the plasmon mode of the nanoparticle and the fluorophore. The degree to which they are coupled can be investigated by studying the orientation of the fluorescent emitter on the rod by defocused imaging.

## **COLL 212**

### **Investigating the reversibility of protein adsorption on gold nanoparticles and the role of free sulfhydryl**

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Adsorption of proteins to gold nanoparticles (AuNPs) and application of the resulting bioconjugates for diagnostics, therapeutics, and other biomedical applications have played a central role in early detections, prevention and treatment of many diseases. Our group and others have recently developed several AuNP-enabled immunoassays that rely on antibody-AuNP conjugates to selectively bind targeted antigens for detection. Improved sensitivity of these immunoassays can be enhanced by exploring the mechanisms of antibodies adsorption onto AuNPs for maximum binding to the antigens. Our group recently demonstrated that IgG has a stronger adsorption affinity to gold nanoparticles (AuNPs) than many other abundant blood plasma proteins, including fibrinogen, human serum albumin and transferrin. Nanoparticle tracking analysis (NTA) confirmed that IgG irreversibly binds to AuNPs and the adsorbed IgG is not displaced by other plasma proteins. The strength of the IgG-AuNP interaction goes beyond electrostatic attraction and is more consistent with chemisorption through the formation of Au-S bond between cysteine residues and a gold nanoparticle. We hypothesize that the number of free sulfhydryl groups present in a protein correlate with the protein-AuNP adsorption affinity. Moreover, we hypothesize that proteins containing free sulfhydryl groups are necessary to exhibit irreversible adsorption and to resist displacement by other proteins. In these subsequent studies, we are studying the ability of IgG to displace blood proteins adsorbed on AuNPs using complementary analytical techniques such as fluorescence, inductively coupled plasma optical emission

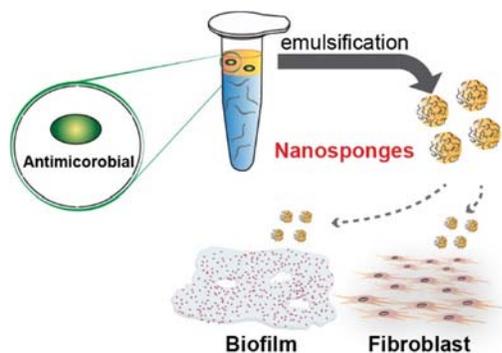
spectrometry and UV-vis extinction spectrophotometry. Results of the protein exchange studies are correlated with the experimentally measured number of accessible free sulfhydryl groups to elucidate the role of Au-S bonds in the formation of stable protein-AuNP conjugates. Insight gained into the mechanism of protein-AuNP adsorption will aid in the development of a predictive model to synthesize stable, sensitive, and well-orientated bioconjugates for biomedical applications.

## COLL 213

### Antimicrobial-loaded nanosponges for synergistic treatment of multidrug-resistant bacterial biofilms

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Multidrug-resistant bacteria (MDR) infections have emerged as a threat to public health. It has been estimated that MDR infections will result in 10 million casualties by 2050, overtaking cancer. Typically, bacteria accumulate to form biofilms. This biofilm hinders the penetration of antibiotics and facilitates development of drug resistance. Essential oils are a class of plant-derived phytochemicals which have excellent antimicrobial activity against dispersed bacteria. However, the utility of these phytochemicals as antimicrobial and antibiofilm agents is limited by their poor aqueous solubility and inherent stability issues. Herein, we report the fabrication of polymer-stabilized phytochemical nanosponges capable of effectively penetrating into biofilms. The antimicrobial properties of these nanosponges were further enhanced through loading small-molecule antimicrobials into the phytochemical payload. The incorporation of the antimicrobial agent inside the nanosponge results in an additive/synergistic combinations for treatment of biofilm-associated infections, providing complete elimination of bacteria in biofilms.



## COLL 214

### **Nanoparticles for surface enhanced Raman scattering detection of cell surface proteins**

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The multiplexed detection of cell surface proteins plays an integral role in the differentiation of cell types and diagnosis of disease. Currently, the use of flow cytometry to evaluate fluorescently labelled surface proteins is the gold standard technique for the diagnosis of diseases such as chronic lymphocytic leukemia, the most prevalent blood cancer in the western world. However, the number of proteins that can be detected at once is limited by the broad emission signals and there is a push to create Raman-based labels whose narrow spectral signatures allow for greater vmultiplexing. Detection methods focusing on the coupling of the localized surface plasmon resonances (LSPRs) of plasmonic surfaces with Raman active dyes as a way to generate probes have been shown to be the most promising methods to address the brightness limitation. To be practical alternatives to fluorescent markers, these probes must: 1. Produce strong & detectable SERS signals, 2. Produce signals that are consistent over time & between batches and a quantitative technique; 3. Demonstrate colloidal stability in physiological media, and 4. Specifically target proteins with minimal non-specific binding. We will describe 3 particle types: PEGylated gold core NP, liposome encapsulated gold nanoparticles, and j-aggregate metal core np.

The j-aggregate particles are especially bright. They exhibit an excitonic resonance that is key in setting up a strong electric field enhancement in the j-aggregate layer. The collective absorption of J-aggregates can tightly couple with LSPRs of NPs to result in greater SERS. In producing these, a cationic linker facilitates formation of J-aggregates on the NP surface. Silica encapsulation provides colloidal stability and brings dyes closer to surface to provide fluorescence quenching.

Liposomes composed of zwitterionic lipids limit biofouling and serve as a modular matrix to incorporate a variety of functional molecules. Dark field microscopy and SERS represent combined functionalities for targeted liposomal probes. Two methods of antibody conjugation to SERS liposomes are reported: (i) direct conjugation to functional groups on the SERS liposome surface, or (ii) post-insertion of lipid-functionalized antibody fragments (Fabs) into preformed SERS liposomes. In vitro experiments targeting both the lymphoma cell line LY10 and primary human chronic lymphocytic leukemia (CLL) cells demonstrate the usefulness of these probes as optical contrast agents.

## COLL 215

### **Exploring the interactions of ionic-liquid-peptide nanofiber gels and their potential biological applications**

**Rachel E. Daso**<sup>1</sup>, [rdaso@fordham.edu](mailto:rdaso@fordham.edu), **Margaret Whalen**<sup>1</sup>, **Marie F. Thomas**<sup>2</sup>, **Ipsita A. Banerjee**<sup>1</sup>. (1) Department of Chemistry, Fordham University, Rego Park, New York, United States (2) Department of Natural Sciences, Fordham University, New York, New York, United States

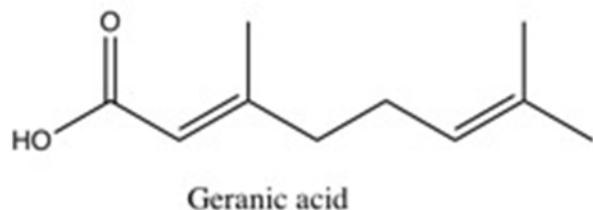
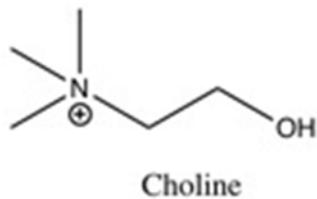
In this work, we have synthesized new tert-butyloxy carbonyl protected peptide amphiphiles that were functionalized with a short sequence of laminin to form Boc-pA-Lam. The functionalized amphiphiles were then self-assembled into nanofibrils and bound to ionic liquids to form nanogels. We examined the impact of varying structures of ionic liquids (IL) and the ratio of the ionic liquid to the nanofibrils and their effects on the properties of the nanogels. The formation of nanogels was confirmed by FTIR spectroscopy and electron microscopy. Thermal, electrical and mechanical properties were studied. The nanogels were found to enhance the tensile strength and modulus of the Boc-pA-Lam nanofibers. Thermal phase changes were also seen due to strong interactions between the IL-Boc-pA-Lam. The binding interactions between the ILs and the nanofibers was probed by surface plasmon resonance. Furthermore, we examined the interactions between rat neural cortical cells with the IL-Boc-pA-Lam. Results indicated that incorporation of Boc-pA-Lam with ILs reduced cytotoxicity and the hybrid composites efficiently adhered to the cells and thus may have potential applications as scaffolds.

## **COLL 216**

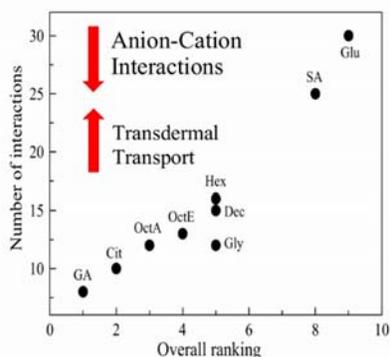
### **Elucidating design principles of ionic liquids for transdermal drug delivery**

**Eden Tanner**, [edentanner@seas.harvard.edu](mailto:edentanner@seas.harvard.edu), **Samir Mitragotri**. Harvard University, Cambridge, Massachusetts, United States

The recent application of ionic solvents, including Ionic Liquids and Deep Eutectic Solvents, to the biomedical context has brought the non-invasive transdermal delivery of pharmaceuticals closer to clinical realization. Choline and geranic acid based ionic liquids (CAGE, Figure 1) have shown excellent biocompatibility and the ability to carry large (ca. 6000 Da) molecules through to the dermis. Using two model drugs of differing hydrophilicities, acarbose and ruxolitinib, and 16 quaternary ammonium carboxylic acid ionic liquids, we examine the dependence of skin penetration on the chemical properties of ILs. We also examine the role of structurally different cations, including imidazolium and pyrrolidinium, on transport. We therefore evidence that systematic investigation of the cation and anion enables the task specific design of ionic solvents for transdermal drug delivery. This talk will elucidate the lessons learnt thus far on the role of stoichiometry and inter-ionic interactions in mediating transport, thus illustrating how delving into the chemistry of this solvent class can provide a straightforward, effective bioengineering design strategy in the use of ionic solvents in transdermal drug delivery applications.



Chemical structures of Choline and Geranic acid (CAGE).



The ionic liquids with the fewest interactions (as measured by 2D Nuclear Overhauser Effect Spectroscopy) show the best overall transport to the dermis.

## COLL 217

### Quantifying of gold nanoparticle based cytotoxicity induced by ionizing and visible radiation

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Nanomaterials are a rapidly growing field of study in biomedicine, in part due to their multimodal activities and their capacity for highly localized therapeutic effects. Two clinically used local treatments, radiotherapy and laser thermal therapy, can both be augmented through the use of Au nanomaterials. Studies on these materials are

extremely phenomenological due to nanoparticle heterogeneity and the complexity of biological systems. Even accurate quantification of the particle dose still results in bulk average biases, i.e. the effect on individual cells is not measured, but rather the effect on the overall population. In order to perform quantitative nanobiology, glass coverslips were uniformly coated at varying densities with Au nanoparticle preparations with different morphologies (spheres, rods, cages and urchins) and different mean particle sizes (5-50 nm). Consequently, the effect of a specific number of particles per unit area in contact with cells growing on the coated surfaces was ascertained. Laser heating was applied in graded exposures and the cell viability was assessed to estimate the number of particles per unit area of the membrane needed to achieve significant cell killing, with 55 nanocage/ $\mu\text{m}^2$  resulting in complete destruction of adherent cells with 10 min CW irradiation. Nanocages also showed the highest degree of radiosensitization on a per particle basis with a dose enhancement factor of 2 observed when roughly 500 particles were associated with each cell. Significant sensitization was observed with the other particle morphologies as well. Monte Carlo simulations of the electrons generated from the gold by the X-rays indicated that these electrons have the potential to completely travel through the cell and exert cytotoxic levels of bond breakage in important biomolecules such as DNA. This platform has been tested initially using only Au materials without any active molecules. Ultimately drug loading, surface modification, distance between cells and materials, and material modifications will be performed to develop a more comprehensive understanding of the nanotechnology/biology interface.

## **COLL 218**

### **Directional liquid transportation control on biomimetic surface**

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Inspired by the liquid uni-directional transportation on the peristome surface of *Nepenthes*, we fabricated a peristome-mimicking surface through high-resolution stereolithography and demonstrated the detailed uni-directional transportation mechanism from a micro-scaled view visualized through X-ray microscopy. Significantly, an overflow-controlled liquid uni-directional transportation mechanism is proposed and demonstrated. Unlike the canonical predictions for completely wetting liquids spreading symmetrically on a high-energy surface, liquids with varied surface tensions and viscosities can spontaneously propagate in a single preferred direction and pin in all others. In addition, we use this kind of 3D printed materials to separate micro-scaled water-in-oil droplets into pure phases, which is quite important in environmental protection, bioassays, and saving functional inks. So far, bulk oil-water separation has been achieved by membrane separation and sponge absorption. As a big advantage, we report that instead of the “plug-and-go” separation model, tiny water-in-oil droplets can be separated into pure water and oil droplets through “go-in-opposite ways” on curved peristome-mimetic surfaces, in milliseconds, without energy input. More importantly, this overflow controlled method can be applied to handle oil-in-oil droplets and viscous liquids with viscosities as high as hundreds of centipoises, which markedly

increases the range of applicable liquids for micro-scaled separation. Furthermore, the curved peristome-mimetic surface guides the separated drops in different directions with high efficiency. The fundamental understanding gained from this robust system enabled us to tailor advanced micro-computerized tomography scanning and stereolithography fabrication to mimic natural creatures and construct a wide variety of fluidic machines out of traditional materials.

## **COLL 219**

### **Kinetics of lipid monolayer assembly in the presence of MUS:OT amphiphilic nanoparticles**

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The interactions of engineered nanoparticles with the plasma membrane can be critical to cellular health and are recognized as an important consideration for drug delivery. While many charged nanoparticles generate cytotoxic pores in the membrane, or become trapped in endosomes, amphiphilic gold nanoparticles (AuNPs) functionalized in stripes with hydrophilic sulfonate (MUS) and hydrophobic octane (OT) ligands have been shown to passively translocate cell membranes and directly enter the cytoplasm. The specifics of membrane-nanoparticle interactions at the nanoscale are less well understood, and to this end, *in vitro* synthetic lipid bilayer experiments, including via use of the Droplet Interface Bilayer (DIB) approach to assemble bilayers between monolayer-coated water droplets in oil, hold promise for studying properties affecting particle fusion and translocation, such as ligand ratio, particle size, and membrane composition.

Currently, little is known about the kinetics of AuNP and lipid assembly at a hydrophilic/phobic interface, which affect nanoparticle fate and lipid membrane formation. Here we show via pendant drop goniometry that AuNPs, which are themselves only mildly surface active, rapidly reduce the interfacial tension of a lipid monolayer when both species are initially present in the aqueous phase. Further, we demonstrate the dependency of this effect on nanoparticle concentration and zeta potential, the degree of particle functionalization, and phospholipid type, including zwitterionic phosphocholine and negative phosphoglycerol headgroups. Interfacial kinetics are then investigated by incorporating lipids exclusively in the hydrophobic oil phase, which alters their adsorption mechanism to the monolayer. Finally, we use Langmuir trough compression to explore nanoparticle fate at equilibrium interfacial tension in each condition. Knowledge of lipids and amphiphilic AuNP co-assembly at the interface facilitates incorporation of nanoparticles with *in vitro* cell membrane models. Furthermore, understanding such interactions sheds insight on *in vivo* encounters between nanoparticles and biointerfaces.

## **COLL 220**

## **Peptoid microsphere coatings: Effects of helicity, temperature, pH, and ionic strength**

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Peptoids are peptidomimetic oligomers that predominantly harness similarities to peptides for biomimetic functionality. They have potential for use in biomedical applications and biosensors due to resistance to proteolytic degradation and low immunogenicity. The incorporation of chiral, aromatic side chains in the peptoid sequence allows for the formation of distinct secondary structures and self-assembly into supramolecular assemblies, including microspheres. Peptoid microspheres can be coated onto substrates for potential use in biosensor technologies, tissue engineering platforms, and drug-delivery systems. In order to be useful for these applications, the peptoid coatings must be robust under physiological conditions. In this study we report the effects of various conditions on the peptoid microsphere coatings, including (i) helicity, (ii) temperature (iii) pH, and (iv) ionic strength. These studies show that microsphere size decreases with increasing peptoid helicity and the positively charged side chains are positioned on the outside of the microspheres. The peptoid microsphere coatings are robust under physiological conditions but degrade in acidic conditions (pH < 7) and at low ionic strengths (< 150  $\mu$ M).

### **COLL 221**

#### **Poly(oxanorbornene)-coated CdTe quantum dots as antibacterial agents**

*Denise N. Williams*<sup>1</sup>, dwill3@umbc.edu, *Julia Saar*<sup>2</sup>, *Vera Bleicher*<sup>2,3</sup>, *Sibylle Rau*<sup>3</sup>, *Karen Lienkamp*<sup>4,2</sup>, *Zeev Rosenzweig*<sup>1</sup>. (1) Chemistry and Biochemistry, University of Maryland, Baltimore County, Bowie, Maryland, United States (2) Department of Microsystems Engineering (IMTEK), Albert-Ludwigs-Universität, Freiburg, Germany (3) Department of Operative Dentistry and Periodontology, Center for Dental Medicine of the Albert-Ludwigs-Universität, Freiburg, Germany (4) Freiburg Institute for Advanced Studies (FRIAS), Albert-Ludwigs-Universität, Freiburg, Germany

The increasing prevalence of multidrug resistant bacteria is a global human health challenge. Unfortunately, the development of traditional small molecules against drug resistant bacterial strains has been unable to fill the drug pipeline with treatments ready for clinical use. For this reason scientists are taking new approaches to antibacterial drug design, including the one pursued in our research: combining antimicrobial polymers and antibacterial nanoparticles into conjugates that could lead to synergistic activity against bacterial growth. The polymers we use are a series of synthetic mimics of antimicrobial peptides based on poly(oxanorbornene)s (PONs) which alone have selective, tunable, broad-spectrum activity against bacteria -including against some bacterial strains for which we are observing increasing cases of drug resistance. The nanoparticles in this study are 2.4eV bandgap CdTe quantum dots (QDs) which have

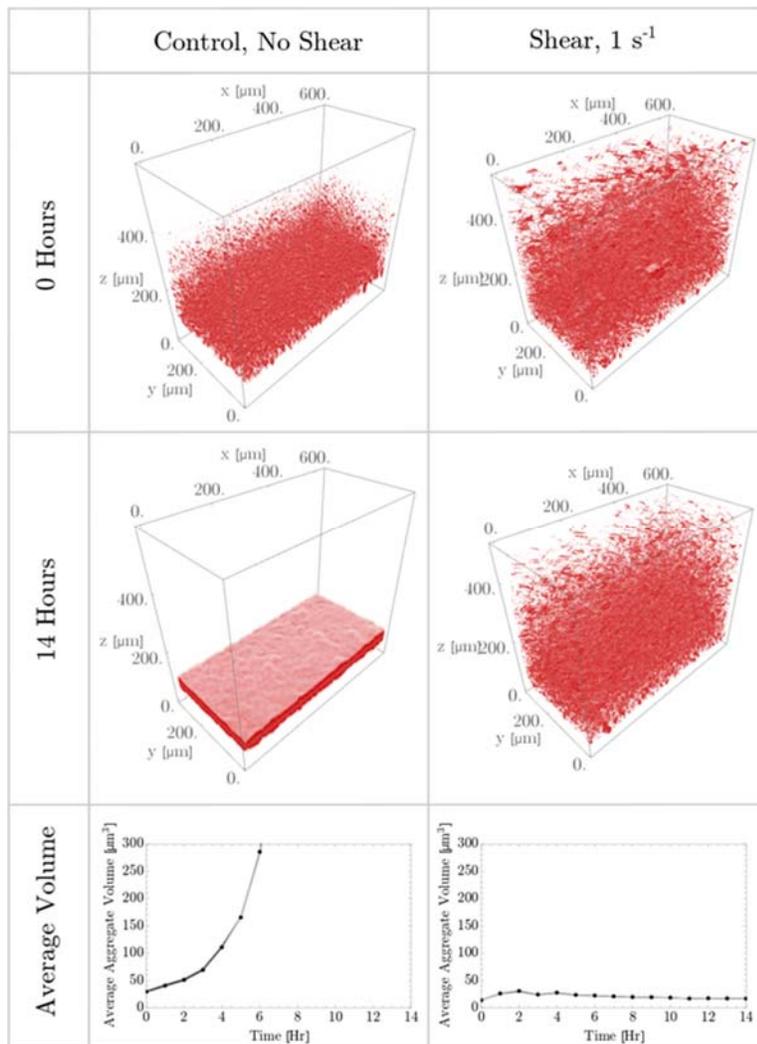
optimal light-activated antibacterial activity compared to other QD materials and sizes, and also have demonstrated activity against some drug-resistant bacterial strains. We conjugated PONs of varying amine/alkyl ratios to CdTe QDs, and then compared the conjugates' activity against *Escherichia coli* and human red blood cells to that of free PONs and CdTe QDs. The conjugates -particularly those of higher amine density- had significantly lower minimum inhibitory concentrations than the free PONs or QDs. Equally important, the conjugates had decreased hemolytic activity compared to free PONs, leading to higher therapeutic indexes against *E. coli*. These outcomes highlight the potential for higher (and therefore more effective) concentrations of PONs to be used in antibacterial treatments while in conjugate form, with less concern for off-target effects.

## **COLL 222**

### **Investigating colloidal transport in biological polymer solutions under shear and the ensuing CaOS**

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Diverse settings involve the transport of particulates in polymer solutions; a key biological example is mucociliary clearance in the lungs, in which mucus mediates the removal of environmental contaminants from, and the delivery of therapeutics to, the airways. However, how particulates behave in such systems is surprisingly poorly understood, and this is particularly problematic when considering diseased lungs. Here, we present an experimental platform—Capillary Oscillatory Shear (CaOS)—to probe the structure and dynamics of particulates in polymer solutions under shear. We find that particulates aggregate due to polymer-induced depletion attraction, eventually reaching a steady-state aggregate size that depends on particle size and the imposed shear rate. Surprisingly, however, our results cannot be described by a simple competition between attractive depletion forces and shear-induced breakup. Our work thus reveals interesting new physics, and provides guidelines for key biological applications: for example, to predict how inhaled therapeutics behave in the lungs.



Left side column represents controlled experiment of colloids in a polymer solution; over time, the colloids settle due to gravity. The right side column represents colloids in a polymer solution under a shear rate of  $1 \text{ s}^{-1}$ . The colloid aggregates under shear reach a steady-state aggregate size, demonstrated by the bottom graphs.

## COLL 223

### Enzyme encapsulation in porous silica nanoparticles for potential therapeutic applications

**Annie Y. Heble**, [anniex.yang@utsouthwestern.edu](mailto:anniex.yang@utsouthwestern.edu), **Khaled A. Nasr**, **Aditi Mulgaonkar**, **Amanda M. Armstrong**, **Xiankai Sun**, **Robert F. Mattrey**, **Jacques Lux**. Radiology, University of Texas Southwestern Medical Center, Dallas, Texas, United States

Enzymes are biological catalysts that have many promising biomedical applications. However, they are rapidly degraded and can lead to immune responses when

administered intravenously, thereby limiting their usefulness *in vivo*. There is a need for a versatile enzyme-encapsulation strategy to increase the biological half-life and effectiveness of enzymes.

We developed two approaches to encapsulate enzymes in nanoporous silica nanoparticles that shield the enzyme from large biomacromolecules while allowing the entrance of small molecules. We hypothesize that our encapsulation methods will improve enzyme stability and eliminate immune responses from the body.

In the first approach, we directly modified the surface of the enzyme to generate a silica precursor, then coated it with silica by hydrolyzing tetraethyl orthosilicate (TEOS) followed by conjugating polyethylene glycol (PEG) groups. In the second approach, we used reverse emulsion conditions by dispersing an aqueous solution of enzyme in decane, with CO-520 and hexanol as surfactant and cosurfactant respectively. Then, we added TEOS and base to grow the silica network, followed by conjugation of PEG groups. We used catalase as a model enzyme because its ability to degrade hydrogen peroxide to oxygen has potential applications for the detection of inflammation and radiosensitization of tumors.

We encapsulated catalase in silica nanoparticles of approximately 100 nm, as characterized with dynamic light scattering, nanoparticle tracking analysis, and transmission electron microscopy. We measured catalase activity electrochemically and demonstrated their protection from proteolysis. We radiolabeled the particles with  $^{89}\text{Zr}$  to determine their biodistribution in tumor-bearing mice. Finally, we conjugated anti-EpCAM antibodies and demonstrated their targeting against hepatocyte-derived carcinoma cells *in vitro*.

We demonstrated that we encapsulated catalase in nanoporous silica nanoparticles with high activity and optimal protection, along with the ability to conjugate antibodies for targeting properties. We are currently evaluating the potential of this formulation *in vivo* for the radiosensitization of tumors.

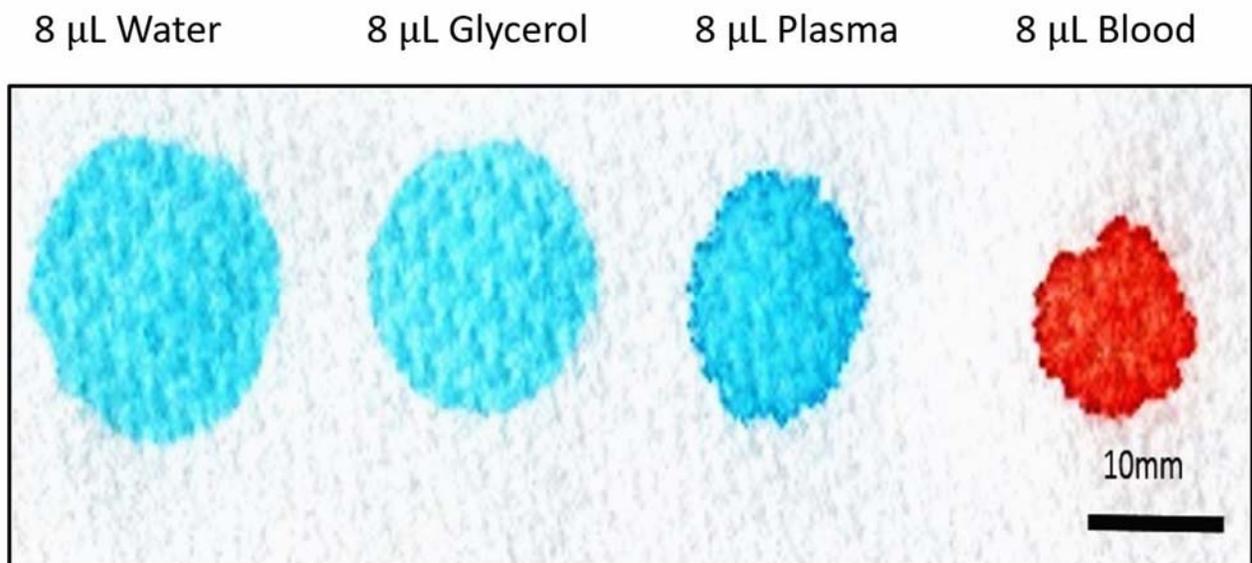
## **COLL 224**

### **Understanding the wicking of blood in paper-based diagnostics**

**Michael Hertaeg**<sup>1</sup>, [michael.hertaeg@monash.edu](mailto:michael.hertaeg@monash.edu), **Joseph Berry**<sup>2</sup>, **Rico F. Tabor**<sup>3</sup>, **Gil Garnier**<sup>1</sup>. (1) Chemical Engineering, Monash University, Melbourne, Victoria, Australia (2) Department of Chemical and Biomolecular Engineering and the Particulate Fluids Processing Centre, University of Melbourne, Melbourne, Victoria, Australia (3) Chemistry, Monash University, Melbourne, Victoria, Australia

Paper-based diagnostics can offer significant advantages over traditional microfluidic devices. This is due to their low manufacturing cost and relative simplicity that means they can be operated by untrained individuals outside of a lab setting. Although several products are currently in production, much of their design has been optimized by trial and error. Past research has shown that visual analysis of the size and shape of stains caused by drops of biological fluids on paper can be the basis of highly reproducible and sensitive diagnostic devices. Many devices rely on the wicking of a sessile droplet on paper to analyse or communicate results.

In this presentation, the wicking behaviour of sessile droplets of blood is analysed experimentally and modelled from first principles. Fluid mechanics models predicting the radial wicking of simple fluids are available. However, blood components such as cells and proteins alter this process significantly. This is because the time frame of protein adsorption at the solid-liquid and liquid-gas interfaces matches that of wicking in paper, adding two transient terms of normally constant properties. This research combines experiments and simulations to study stain growth after drops of blood and its components are deposited on paper. Particular emphasis is placed on the adsorption of blood proteins onto paper fibres and why the corresponding change in surface chemistry has a significant effect on the redistribution of fluid in the later stages of stain growth.



Stains on paper produced by equal sized droplets of different fluids

## COLL 225

### Hydrazide-modified hyaluronic acid enables the safe-by-design engineering of antimicrobial metal-based nanomaterials

**Guillem Ferreres Cabanes**, [guillem.ferreres@upc.edu](mailto:guillem.ferreres@upc.edu), *Sílvia Pérez-Rafael, Kristina Ivanova, Juan Torrent-Burgués, Tzanko Tzanov*. Chemical engineering, Universitat Politècnica de Catalunya, Terrassa, Spain

Antimicrobial resistance (AMR) is a serious threat to the global public health. The enormous and irresponsible use of antibiotics has promoted the development of different antibiotic resistance mechanisms in bacteria, leading to an abruptly reduction

on the efficacy of conventional antibiotic drugs. In the context of AMR threat, research initiatives have been focused on engineering new and more efficient antimicrobial agents that eliminate bacteria through non-specific mechanisms unlikely to promote the apparition of resistance.

Hybrid biopolymer-metal nanomaterials are gaining significant attention due to their wide antimicrobial spectrum and lower toxicity compared to the stand-alone metal-based counterparts. Some natural polymers possess inherent antibacterial activity and when used in the nanomaterials synthesis, they improve the stability and enhance the materials antimicrobial efficacy, mainly due to the improved interaction with bacterial membrane leading to membrane damage and bacterial death.

In this study, we modified the biopolymer hyaluronic acid (HA) with adipic acid dihydrazide (ADH), designing a dual functional biopolymer that interacts with metals to form safe to human cells stand-alone nanomaterials and self-assembled nanocoatings with improved antibacterial and antibiofilm activities. The amino-functionalized HA was able to reduce silver (Ag), obtaining stable hybrid biopolymer capped AgNPs that are active against Gram-positive *S. aureus* and Gram-negative *E. coli*, without affecting the human skin cell lines. Furthermore, the enhanced interaction between ADH-modified HA and metals (copper and cobalt) lead to the coordination-driven self-assembly of hybrid multi-layered coatings on silicone surface in layer-by-layer fashion. These materials demonstrated improved antifouling and antibacterial activities against medically relevant bacteria. This antimicrobial approach appears suitable for functionalization of surfaces such as hospital textiles, water treatment membranes and implantable medical devices, ensuring a safer environment for both patients and healthy population.

## **COLL 226**

### **One-step ultrasound assisted synthesis of farnesol nanoparticles for bacterial eradication and disruption of drug-resistant biofilms**

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The antimicrobial resistance is constantly growing healthcare issue associated with increased mortality and morbidity, and huge financial loss. Moreover, the ability of the bacteria to encase in biofilm structures, surrounded by extracellular polymeric matrix (EPM), is the reason for persistent bacterial infections that are up to 1000x more resistant to the existing antibiotics than the free-floating cells. *Staphylococcus aureus* (*S. aureus*) is one of the most common causes of life-threatening infections, able to adapt rapidly, developing resistance to the currently available at the practice antibiotics. In this line, the development of alternative therapeutic strategies for managing *S. aureus* associated difficult-to-treat infections is a challenge. Herein, novel nanoparticles (NPs), loaded with natural bactericide farnesol, have been generated using high intensity

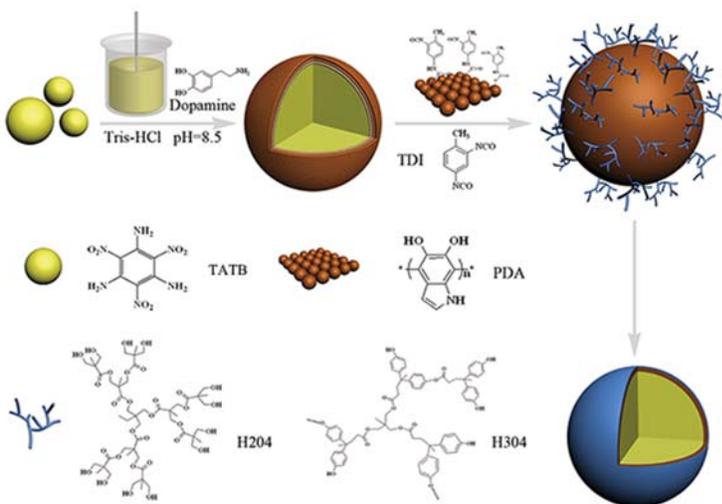
ultrasound and their ability to control *S. aureus* pathogen was evaluated. The developed antibiotic free NPs demonstrated strong affinity to the bacterial membrane and completely eradicated *S. aureus* bacteria, up to 8 logs reduction was achieved within less than 1 h of contact. The farnesol NPs were able to inhibit the *S. aureus* attachment and biofilm formation by 100 %. Furthermore, these NPs penetrated with the otherwise antibiotic resistant *S. aureus* biofilms, eradicating 80 % of the total biofilm mass at very low concentration of the active agent. These antibacterial and antibiofilm farnesol NPs did not cause skin tissue irritation (100% viability) and did not induce inflammation in 3D skin model. These results suggested the farnesol NPs might be a promising strategy to prevent and treat *S. aureus* infections.

## **COLL 227**

### **Grafting hyperbranched polyester on the energetic crystals: Enhanced mechanical properties in highly-loaded polymer based composites**

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The interfacial strength usually plays a key role for exhibiting great effects on mechanical performances. In this work, typical energetic crystal 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) was firmly coated by the strong adhesion of polydopamine (PDA), then two HBPs with fatty and aromatic structure were grafted onto the surface of TATB, by using the hydroxyl groups of the PDA layer as secondary reaction platform. Four highly-loaded polymer based energetic composites (solid loading was 95%) were prepared with fluoropolymer binders as substrate. The results showed that the surface of grafted samples with 0.5 wt.% HBP was more easily wetted by non-polar liquid. Improved storage modulus and creep resistance properties were exhibited in polymer bonded explosives (PBXs). The static mechanical properties of tensile and compressive strength were increased significantly by 26.5% and 19.8%, respectively, due to the strong interfacial reinforcement of HBPs.



Schematic diagram of grafting process for pTATB@HBP

## COLL 228

### Lignin-mediated sonochemical synthesis of biocompatible tellurium nanoparticles with antimicrobial properties

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Overuse of antibiotics has led to the surge of multiple drug resistant bacterial strains which are already responsible for more than half a million deaths globally each year. As a consequence, the effectiveness of antibiotics for the treatment of bacterial infections has rapidly decreased, resulting in prolonged illness and even death. Therefore, there is an urgent need of developing alternative antimicrobials to face microbial infections while preventing the antibiotic resistance in bacteria.

The use of metals such as silver, silver ammonium tellurite and potassium iodotellurite as antibacterial compounds has been reported throughout history even prior to the use of antibiotics. In recent years, in the search of antibiotic alternatives, these metals have regained interest in form of nanoparticles (NPs). Among the different metal NPs, tellurium nanostructures have gained attention due to their antibacterial activity and their lack of cytotoxicity. Moreover, tellurium has been applied in the development of novel materials such as fluorescent quantum dots (CdTe), opening the door to the development of theranostic materials for medical applications.

Traditional chemical and physical synthesis methods for the production of tellurium nanostructures have significant drawbacks as involve high temperature and pressures, acidic pH and the use of toxic reducing agents such as hydrazine or ammonia. The use of environmentally-friendly reducing agents for the synthesis of metal NPs has been

recently explored. Lignin, which is the second major component of wood, is a by-product from paper manufacturing industry rarely used for valorization. This aromatic polymer is a promising candidate as a reducing agent due to the variety of chemical groups that it possesses, including phenolic and aliphatic hydroxyl groups. Moreover, the use of organic molecules is known to reduce the cytotoxicity associated to metal nanoparticles.

In this work, we propose a facile sonochemistry approach to synthesize tellurium nanoparticles (TeNPs) using Kraft lignin as a reducing agent. The TeNPs were found to possess bacteriostatic activity against *Pseudomonas aeruginosa* and *Staphylococcus aureus*, and shown strong bactericidal effect against *Escherichia coli*. The capacity of killing bacteria, together with their biocompatibility, make these nanoparticles a promising antimicrobial agent for the treatment of bacterial infection.

## **COLL 229**

### **Multilayered enzyme/antimicrobial peptide decorated silica nanoparticles for controlling bacterial infection**

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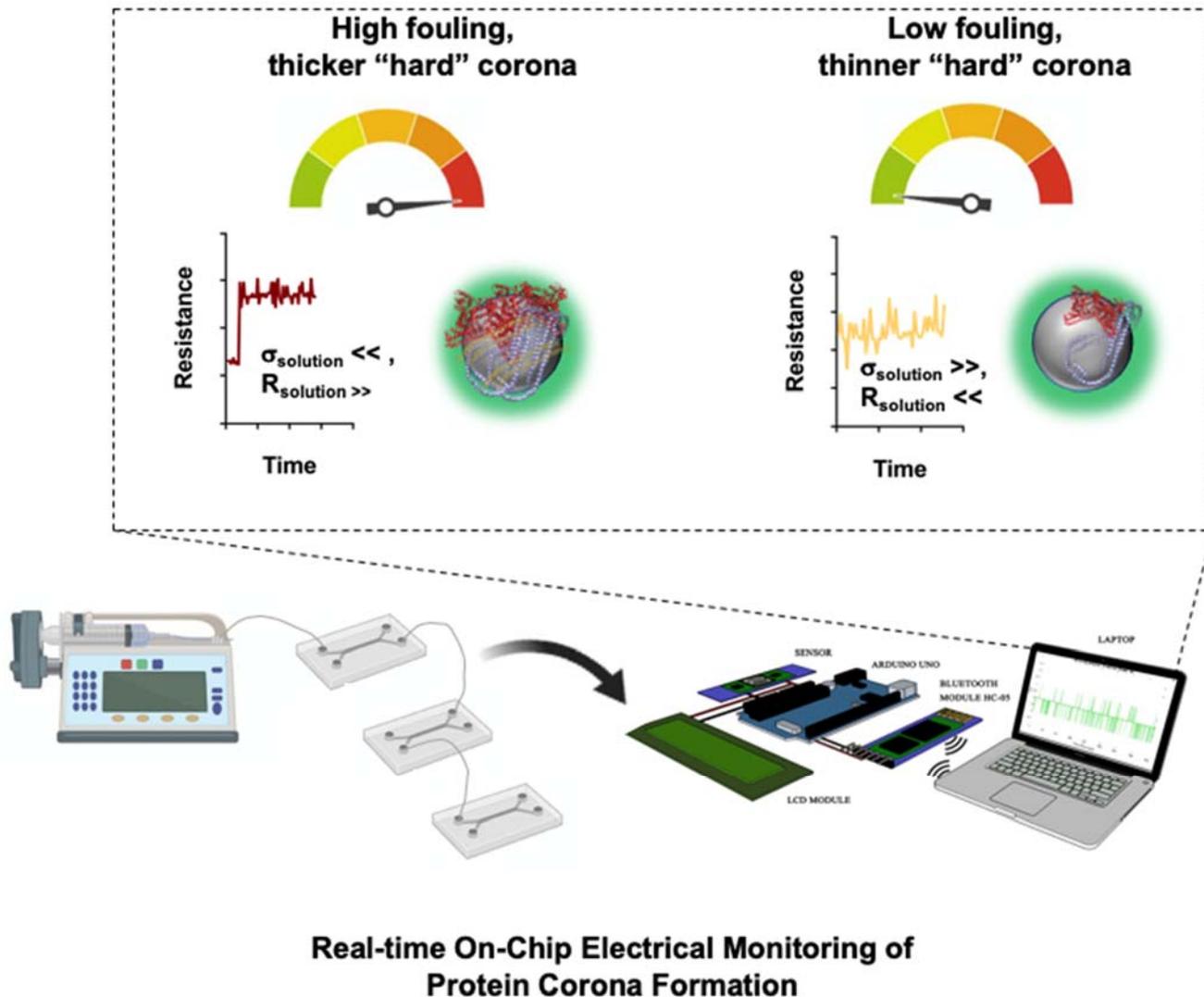
The wide spread of antimicrobial resistance (AMR) is one of the global public health threats accounting for the enhanced morbidity and mortality, time of hospitalization and huge financial burden. The ability of bacteria to embed into biofilm structures diminishes the effectiveness of the existing drugs, due to the limited penetration through the biofilm extracellular polymeric matrix, causing difficult-to-treat infections. To date, there is an urgent need to develop alternative therapeutic approaches to manage bacterial infections and AMR occurrence. Nano-formulated antibacterials possess improved activity compared to their bulk counterparts, due to the enhanced interaction with bacterial membrane and easy access to the target site. They represent the most promising antibacterial approach with lower potential for development of new resistant mechanisms.

In this study, porous silica-based NPs, which were produced from silica-rich rice husks agriculture residues, were sequentially decorated with antibacterial enzyme lysozyme and peptide polymyxin B. The bactericidal actives were deposited in a multilayered fashion with biocompatible hyaluronic acid onto the inert silica NP template using high intensity ultrasound as a driving force for the rapid layers' assembly. The inclusion of lysozyme and polymyxin into the multilayered NPs shell resulted in the formation of stable hybrid nanoantibacterials with high bactericidal activity towards *Pseudomonas aeruginosa* and *Staphylococcus aureus* at very low actives concentrations, taking advantage of the nano-form. The engineered NPs inhibited the establishment of drug resistant biofilms by more than 90 % and did not induce toxicity towards human cells. The balance between the effective bacterial elimination and biocompatibility make these NPs valuable alternatives to fight AMR infections and spread of resistance.

**Machine-learning and wavelet transform assisted on-chip electrical monitoring of real-time “soft” and “hard” protein corona formation in carbon nanoparticles**

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When nanoparticles (NPs) encounter a biological fluid, proteins, lipids, and other biomolecules adsorb on the nanoscale surface consequently leading to the evolution of a protein shell or “corona”. The corona formed is dynamic in nature and depends on the “synthetic identity” of the NPs, thereby ultimately affecting their biological response. In this paper, an integrated microfluidic platform coupled with electrical resistance measurement setup is developed to monitor and investigate the real-time formation of a biomolecular corona of carbon nanoparticles and effectively discriminated “soft” vs. “hard” corona formation stages based on their nanoscale surface chemistries when combined with a time-frequency tool known as wavelet transform (WT) and machine-learning (ML) techniques. Additionally, the corona and its composition were studied using different techniques such as dynamic light scattering, nanoparticle tracking analysis, zeta potential, excitation-emission profiles, 1D SDS-PAGE and subsequently, LC-MS analysis. We further demonstrated the protein corona formation process influences the cellular internalization process and is also dependent on pH of the system, paving a way for synthesizing robust pH-controlled drug delivery system. Our dynamic setup has paved a potential avenue in controlling the adsorption of proteins on NPs by tailoring the chemical motifs at its surface could be a valuable tool with promising therapeutic benefits in drug delivery and targeted cancer treatment in the near future



**Scheme 1.** Real-time on-chip monitoring of the protein corona formation on carbon nanoparticles having varied surface chemistry. Further classifications of “soft” and “hard” corona were done by utilizing machine-learning and wavelet transform on the collected data.

**COLL 231**

**Modulating nanoparticle size to understand factors affecting hemostatic efficacy and maximize survival**

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Polymeric particle-based hemostats have been demonstrated to be an attractive technology to halt bleeding through extensive testing in animal models, ranging from arterial injury to blast trauma. While the results of these *in vivo* experiments have been well documented and utilized to develop subsequent generations of hemostats, the effect of particle-target interactions and their predictive capabilities for *in vivo* performance has yet to be fully explored. In this work, the size of GRGDS-conjugated PEG-b-PLGA nanoparticles was tuned and its effect on platelet binding, particle adherence to wound-mimetic surfaces, aggregation capability, biodistribution, and circulation lifetime were systematically assessed using various *in vitro* and *in vivo* experiments. Smaller and intermediate-sized nanoparticles were all found to specifically bind a larger number of activated platelets when compared to larger (>300 nm) particles, while incubation of these larger particles on collagen and activated platelet-coated surfaces led to a higher total mass of polymer bound. Intermediate particle diameters led to the greatest number of platelets aggregated on a surface relative to agonist-only positive controls. Finally, larger particles experienced faster clearance and higher pulmonary accumulation per organ mass in an uninjured murine model, whereas smaller particles exhibited longer circulation and retention times and increased accumulation in the liver. These results indicate that tuning particle size provides a key handle for engineering the performance of particle-based hemostat systems, with specific size offering optimal performance depending on the desired outcome.

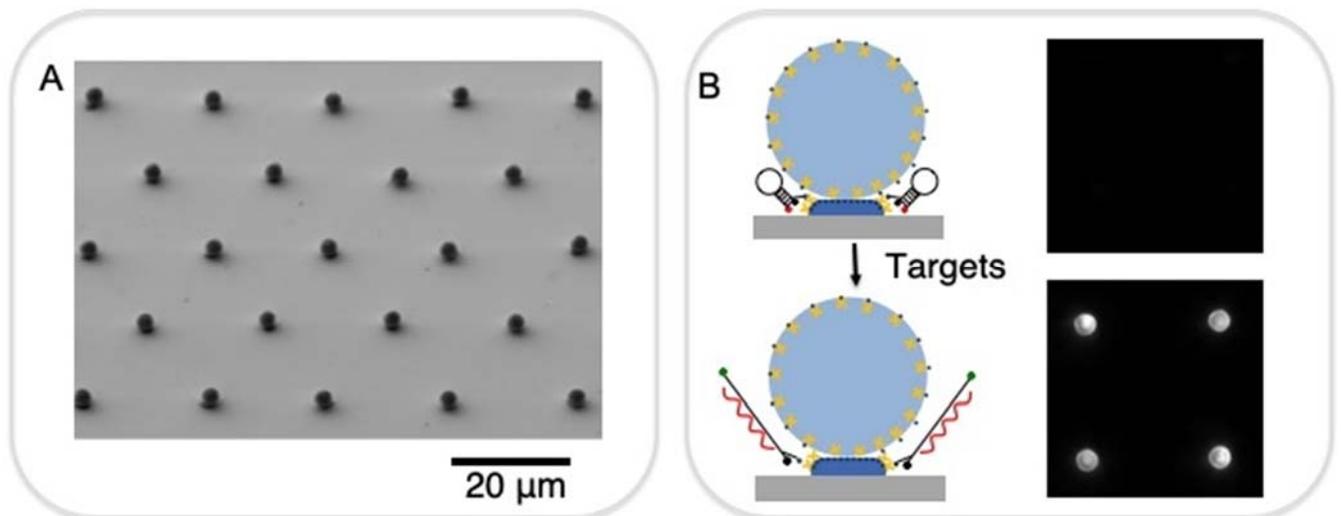
## **COLL 232**

### **Self-assembled microsphere-on-microgel array for nucleic acid detection**

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Self-assembled microsphere arrays have gained increasing interest for their unique properties in photonic and sensing applications, but their application to nucleic acid detection has not been well explored. Fluorescence-based techniques are widely used in nucleic acid detection, but their relatively low signal intensities hinder their use in point-of-care (POC) testing where inexpensive and low-numerical aperture lenses are likely to be used. To overcome this fundamental challenge, we are exploring a new materials platform for nucleic acid test development using self-assembled microspheres to create a microlens array that can amplify fluorescent signals generated from surface-tethered molecular beacons. First, we create an array of microgels patterned on silicon or glass surfaces using e-beam lithography of biotin-terminated poly(ethylene glycol) thin films. Streptavidin-functionalized polystyrene microspheres can bind to these

microgels and thus form an array of microspheres on functional microgels. We show that biotinylated molecular beacon (MB) detection probes can be co-localized with the microspheres on the microgels. We have previously shown that, in contrast to traditional microarray spotting directly onto a solid substrate, tethering to microgels maintains oligonucleotide probes in a highly hydrated and conformational unconstrained state, and microgel-tethered MBs can thus achieve signal-to-background levels comparable to those characteristic of untethered MB probes in solution. Co-tethering microsphere and MBs enhances the collection of fluorescent intensity generated by hybridized MBs. We find that a tethered microsphere increases the collected intensity 1.5 and 10 times depending on the specific pattern size and areal density of microgels. The highest signal increase occurs when a single microsphere is tethered to a single isolated microgel. These findings suggest a pathway towards very high-density microarrays compatible with simple point-of-care diagnostic systems.



## COLL 233

### Polymer modification of bioprosthetic heart valves to mitigate structural degeneration

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At present, there are no medical therapies for structural heart valve disease, leaving surgical valve repair or replacement as the only treatment options. Bioprosthetic heart valves (BHVs) made from glutaraldehyde-crosslinked tissues, such as bovine pericardium (BP), represent the most widely used heart valve prostheses. While

effective short-term at restoring hemodynamic flow, these devices undergo structural valve degeneration (SVD) eventually resulting in their failure. This is accelerated in the pediatric patient population. We hypothesize that an inflammatory response triggered by the accumulation of advanced glycation endproducts (AGE) in BHV is a key mechanism to the failure of heterograft valve prostheses.

In this work, we explore the covalent modification of glutaraldehyde-fixed BP with polyethylene glycol (PEG) to protect the tissue from glycation and the accumulation of glycated serum proteins, attenuating the subsequent inflammatory response. Modification of BP was achieved through carbodiimide reaction between amino-terminated PEG and carboxylic groups of BP. PEG coated samples demonstrated reduced albumin infiltration and glycation *in vitro* relative to unmodified tissues, as evident by fluorescent albumin uptake and immunohistochemistry staining for AGE. The anti-inflammatory effects of PEG coating were evaluated *in vitro* using activated human monocytes (THP-1). Cells were seeded on the surface of control and PEG-modified BP after exposure to albumin under accelerated glycation conditions, for 24 hours, then washed and placed in resazurin containing media to estimate the amount of viable adherent cells; an 80% reduction in cell count was observed in PEG-modified vs. control BP samples. Analysis of cell media showed a marked increase ( $215 \pm 11\%$ ) of TNF $\alpha$  levels in control BP samples relative to nonglycated samples. Samples protected with PEG did not exhibit quantifiable changes in TNF $\alpha$  production ( $0 \pm 8\%$ ). The results of these studies provide support of our hypothesis on the role of serum proteins in AGE-mediated SVD. Our findings offer experimental evidence establishing the feasibility and effectiveness of PEG modification as a strategy for improving integrity and durability of implantable cardiovascular devices. Furthermore, this work has the potential to make BHV viable for application in pediatric patients.

#### **COLL 234**

##### **"Smart" zero-valent iron delivery nanosystem for MRI guided cancer therapy**

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The iron-catalyzed Fenton-type reaction has been widely used to generate reactive oxygen species (ROS) from hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) for cancer therapy. However, the Fe<sup>2+</sup>-catalyzed Fenton reaction is inefficient in physiological condition, limiting its therapeutic application. Many efforts have been made to increase intracellular H<sub>2</sub>O<sub>2</sub> level in order to improve the Fenton mediated therapy efficacy. Here, we developed an intelligent zero-valent iron reservoir with ultrahigh Fenton catalytic activity and selectivity in weak acidic tumor microenvironment. The system demonstrated superior tumor inhibition with an IC<sub>50</sub> around 20  $\mu\text{g}_{\text{Fe}}/\text{ml}$  for HepG2 cells. A single intravenous injection (1 mg/kg) could trigger the Fenton-type reaction for tumor suppression with high efficacy.

#### **COLL 235**

## **Monitoring drug loading and releasing in MIL-88B(Fe) films modified gold substrates using surface plasmon methods**

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A large portion of patients experience coronary artery disease (CAD) caused by atherosclerosis. One of the treatments of CAD is to utilize stents to restore blood flow. Compared to traditional bare metal stents (BMS), polymer-based drug eluting stents (DES) can minimize restenosis symptoms, however they may cause late-stent thrombosis. A significant amount of effort has been devoted to design polymer-free stent by introducing biodegradable drug eluting materials, such as metal-organic framework (MOF). MOFs are composed of repeating units of metal ions connected by organic linkers by forming porous three-dimensional structures. Known for their high surface area and versatile properties, selective MOFs show great potential applications in drug delivery systems. Certain MOFs have exhibited prominent results through their high drug capacity, uniform topography, and flexible structures. Our research investigated iron-based MIL-88B, a type of MOF, as a drug delivery system with ibuprofen as a model drug. We studied ibuprofen encapsulation and delivering properties on MIL-88B(Fe) films attached on a chemically functionalized Au surface. MIL-88B(Fe) film was prepared through a direct crystallization method using the mother solution from solvothermal synthesis. The film was implemented on an Au surface with a COOH-terminated self-assembled monolayer (SAM). Surface plasmon resonance (SPR) was used to monitor the drug loading and kinetic eluting behaviors on MIL-88B(Fe) films.

**COLL 236**

## **Synthesis and targeting of ubiquicidin linked Ag-Cu nanoparticles to *S. aureus* in osteoblast infection**

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Alloy nanoparticles (NPs) of Silver-Copper (Ag-Cu) are shown to have potent antibacterial activity due to the release of Ag<sup>+</sup> and Cu<sup>+</sup> ions, but the toxic effect of the nanoparticles may extend to the host cells. The targeting of the NPs to the causative agent can decrease the toxicity of the NPs to the host cells. This study focusses on the synthesis and functionalization of Ag-Cu with Ubiquicidin (Ag-Cu-Ubi). Ubiquicidin is a protein molecule that can target and bind to *Staphylococcus aureus* (*S. aureus*). *S. aureus* is the most prominent causative agent that results in bone infection called osteomyelitis. *S. aureus* is an intracellular pathogen and has developed mechanisms to

evade antibiotic treatment and immune response. The antibiotic treatment in intracellular infection may become ineffective due to low intake and diffusion of antibiotics by the host cells. Also, the development of bacterial resistance can lead to ineffective antibiotic treatment. However, the ions released from the nanoparticles can penetrate the host cells. Therefore, our treatment strategy involves the release of ions at the site of infection where the concentration of *S. aureus* is high. In this work, *S. aureus* is targeted by the functionalization of the NPs with Ubiquicidin that can specifically bind to bacteria like *S. aureus*. The *in vitro* studies have shown that Ag-Cu-Ubi NPs have an antibacterial effect against *S. aureus* but was slightly less when compared to the non-functionalized Ag-Cu. Furthermore, the targeting NPs were also efficient in clearing a major percentage of infection in *S. aureus*-infected osteoblasts after 24 hours of incubation. Moreover, the strategy of targeting *S. aureus* reduces the dose of NPs for treatment and proportionally lower NP toxicity to host cells which can contribute to clinical osteomyelitis management and needs to be further studied employing *in vivo* animal models.

## COLL 237

### Nano-size dependent aggregation of Amyloid beta 1-40 peptide-coated gold colloid

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The mechanism of aggregation of Amyloid beta 1-40 ( $A\beta_{1-40}$ ) coated gold nano-particles ranging between 10 nm to 100 nm were investigated. The  $A\beta_{1-40}$  – coated nano-gold colloids aggregate at a particular pH value ( $pH_0$ ) due to the unfolded conformation of a peptide resulting in peptide networking. The formation of the aggregation can be identified by the red-shift of gold SPR (Surface Plasmon Resonance) band. Therefore, a spectroscopic investigation as a function of the concentration of  $A\beta_{1-40}$  allowed us to monitor gold aggregation process quantitatively for the first time. The aggregation mechanism was considered to be a nano-size dependent. For example, the 20 nm gold colloid particle exhibited sharp rise of aggregation formation at  $\gamma_{20\text{ nm}} = [\text{number of } A\beta_{1-40}] / [\text{number of gold colloid}] \sim 400$  with  $\lambda^{(1)} \sim 0.5$  nm/pmol, where  $\lambda^{(1)}$  is the first derivative of SPR peak wavelength as a function of concentration of  $A\beta_{1-40}$ . On the other hand, the 50 nm gold colloid particle exhibited very moderate rise with  $\lambda^{(1)} \sim 0.01$  at  $\gamma_{50\text{ nm}} = \sim 20,000$ . Considering the square of two gold colloidal size is 6.25 (*i.e.*,  $(50\text{ nm}/20\text{ nm})^2 = 6.25$ ),  $\gamma_{50\text{ nm}} / \gamma_{20\text{ nm}} = \sim 50$  is remarkably large and implying that the amount of  $A\beta_{1-40}$  required to complete full aggregation process is not simply described by an individual core gold colloidal size but by a core consisting of a multiple gold colloids. A drastic difference in the slope between two sizes indicate different aggregation processes. A sharper rise may indicate an instantaneous aggregation mechanism, and a moderate rise may be associated with a gradual growth (growing snow-ball).

## COLL 238

## **Hypersonic-assisted thermodynamic re-organization of silica microparticles on inkjet-printed protein films**

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Separation and sorting of analytes such as micron-sized particles is of key importance in areas that involve chemical or biological analysis such as food and chemical processing, medical diagnostics, and environmental assessment. Hydrodynamic approaches have undergone rapid developments over the last decade due to the numerous applications of fluidic systems in above-mentioned applications. However, these systems face numerous challenges due to limited control on the flow rate and flow mode. Translocation of particles on surfaces is a major challenge in such systems as most laminar flow systems cannot provide the necessary drag force. Our strategy utilizes acoustic force generated through a hypersonic resonator to achieve translocation of negatively charged particles along charged protein surfaces. We demonstrate our ability to sort particles on the basis of size with high efficiency. This strategy provides an efficient and inexpensive alternative for size-based sorting of analytes in a small volume and therefore has potential applications in diagnostic devices.

**COLL 239**

## **Sharkskin mimicked polymeric membranes**

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With recent advancements of science and technology, new discoveries have been made showing that the nature has provided every means for wellbeing of humans. One of these means are antimicrobial micro-structures. Investigations among marine animals showed that sharks stay completely free of any microorganism attachment, hence completely immune from microbial infections. Further research revealed that sharkskin reduces drag force due to its surface micro-structure which led to some speculations among scientists that the unique morphology might be responsible for prevention of microorganism attachment. Herein we decided to investigate the biological properties of sharkskin morphology by mimicking its surface micro-topography using polymeric membranes.

In this regard, we have fabricated bio-mimicked structures using soft lithography and solvent casting methods. We aimed to investigate physicochemical and mechanical of sharkskin mimicked micro-patterned polymeric membranes. Among commonly used polymers Chitosan (CH) was chosen due to its potentials for mimicking micro and nano-structures along with its excellent biological properties.

Mechanical, physical and chemical properties of fabricated membranes were tested as the first step of our study. Elongation at break and Tensile Strength tests were conducted for mechanical characterization. As for physical and chemical characterizations, swelling test, Surface Energy measurement, Fourier-transform infrared spectroscopy (FTIR), X-Ray Photoelectron Spectroscopy (XPS), and Raman Spectroscopy were used. So far, our results have shown significant differences among our groups. Thus, in vitro experiments were conducted in order to evaluate cellular responses of mammalian cells along with bactericidal properties using Gram-positive *Staphylococcus aureus* bacterial strains as model bacteria and Human Dermal Fibroblast and Human Keratinocyte cell lines for the cell culture experiments.

## **COLL 240**

### **Surface modification of silk fibroin to control protein deposition**

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Silk fibroin is a high molecular weight protein that is fabricated by certain species of insects and arachnids, including *Bombyx mori* silkworms. *B. mori* fibroin consists of hydrophilic blocks that can be modified using different chemistries and hydrophobic blocks that are capable of hydrogen bonding, which results physical crosslinking to form beta sheet secondary structures. This physical crosslinking provides unique opportunity to tune the mechanical and degradation properties of the protein-based materials. In addition to its tunable properties, silk fibroin has been shown to be biocompatible in a variety of biomedical applications. This work utilizes surface-initiated atom transfer radical polymerization to grow grafted polymers from the surface of silk fibroin films. This approach was found to lead to higher degrees of substitution compared to existing methods to functionalize silk fibroin. The surfaces of silk fibroin were first oxidized with ammonium persulfate and ultraviolet light to introduce hydroxyl groups, which increased the reactive sites for grafting. Hydrophilic polymers containing varying types and amounts of charges (cationic, anionic, zwitterionic, and polymers lacking charge), were synthesized and characterized for their ability to tailor the protein adsorption to silk surfaces. A reduction in water contact angle was observed after oxidation and each polymerization, indicating successful surface modification. Further characterization by

attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy showed the formation of new vibrations after grafting, and atomic force microscopy showed that the morphology of the chains exhibited globular conformations. The adsorption of bovine serum albumin and fibrinogen was lower for the zwitterionic silk films compared to the positively or negatively charged films. The manipulation of surface charges on silk fibroin thus provides a route for degradable and controlled protein attachment to implantable biomaterials.

## **COLL 241**

### **Using iron-containing metal-organic frameworks as drug-eluting stent coating**

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Coronary artery disease (CAD) is the number one cause of death nationally. One method of treatment for this disease is through balloon angioplasty along with stent implantation to restore blood flow. In this work, two types of iron-containing metal-organic frameworks (Fe-MOFs) were studied: MIL-53 and MIL-88B. Both materials are composed of iron (III) ligands connected by benzene dicarboxylate linkers by forming three-dimensional structures. MIL-53 is formed through homogeneous nucleation while MIL-88B through heterogeneous nucleation. The different nucleation pathways result in MIL-53 with one-dimensional channels and MIL-88B with a three-dimensional cage. By controlling the crystal structure, we were able to tune drug loading and releasing patterns with ibuprofen as a model drug. We observed that MIL-53 is able to take up larger amounts of ibuprofen than MIL-88B per mg of material. However, the drug elution process is much slower observed for the MIL-88B system compared to its analog material. This indicates that MIL-88B with complex 3D cages is beneficial for regulating drug release in a controlled manner. After identifying the chemical and structural features that influence drug release profiles, we constructed a thin film drug delivery system with MIL-88B. We modified several suitable surface platforms (with specific chemical features) that can be used to construct MIL-88B films. These platforms include COOH-terminated gold and OH-functionalized medical grade stainless-steel substrates. The drug loading/releasing with MIL-88B films were studied in terms of drug encapsulation amount, mass transfer efficiency, and cumulative releasing. The knowledge acquired from these studies will benefit future *in vivo* studies of Fe-MOF thin film as a drug-eluting stent coating, in addition to the creation of new thin-film materials with potential applications in medical devices. This work aims to enhance the scientific understanding of surface and interface interactions between general three-dimensional materials and assorted therapeutic agents. The results will lead to new insights and guide future drug-eluting materials design.

## **COLL 242**

### **Measuring the interaction of polyglutamine peptides with lipid membranes**

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Huntington's disease (HD) is a fatal neurodegenerative genetic disorder, deteriorating both the patient's physical and mental abilities and ultimately resulting in death. There is currently no cure for the disease, only treatments to alleviate symptoms. HD is caused by huntingtin (htt) protein misfolding that results in oligomeric and fibrillar aggregates. The misfolding is the result of a genetic mutation that leads to an expanded polyglutamine (polyQ) domain near the N-terminus of htt. The htt polyQ region is flanked by a 17 amino acid N-terminal sequence (Nt17) and a proline-rich region, both of which play a role in the aggregation process. Nt17 interacts with cell membranes, resulting in an interest in understanding the htt binding mechanism and subsequent effects on both protein aggregation and membrane structure. Because abnormalities in lipid metabolism have been found in HD patients, it is important to understand the role of the membrane composition in this interaction. To provide mechanistic insight to protein-membrane binding and subsequent htt aggregation, two complementary techniques were used: circular dichroism (CD) to measure protein secondary structure and isothermal titration calorimetry (ITC) to quantify thermodynamic parameters. The cell membrane was modeled with large unilamellar vesicles (LUVs) composed of varying ratios of total brain lipid extract, zwitterionic phosphatidylcholine (PC), and negatively charged phosphatidylserine (PS) lipids. Nt17 membrane binding was monitored with CD by following the transition from solution phase random coil to interfacial alpha helical structures. The magnitude and kinetics of peptide binding correlate with the proportion of negatively charged lipid indicating the role of electrostatics and membrane composition in this interaction. Additionally, ITC data will be presented to provide insight to the enthalpy and htt-vesicle binding stoichiometry.

### **COLL 243**

#### **Functionalized polystyrene nanoparticles alter the structure and stability of model cell membranes**

**Paige Ashey**, *ashepa01@gettysburg.edu*, **David Van Doren**, **Shelli L. Frey**. Chemistry, Gettysburg College, Gettysburg, Pennsylvania, United States

Nanoparticles (NPs) possess unique material properties that make them ideal for applications ranging from increasing transparency and protection of sunscreen to transporting drugs across cell membranes without causing damage to the cell itself. Since the interactions of NPs with biological membranes have not been fully characterized to correlate surface characteristics and size with mode of action, model cell membranes in the presence of NPs were monitored using fluorescence microscopy. Giant unilamellar vesicles (GUVs) composed of 1:1:1 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC):dipalmitoylphosphatidylcholine (DPPC):cholesterol were prepared via electroformation with fluorescent TR-DHPE and exposed to NPs either during the vesicle formation process or after stable vesicles were formed. The concentration of 40 and 60 nm functionalized polystyrene NPs was varied to determine

the effects of vesicle size distribution and morphology changes. Polystyrene particles functionalized with positively charged amine groups were shown to limit the size of stable GUVs when introduced during and after vesicle formation. Aminated NPs distributed around and within the membrane also resulted in extruded lipid tubules extending from the vesicle structure. Negatively charged particles, functionalized with carboxyl groups, did not produce a dramatic effect compared to the control system. In both cases, high NP concentration completely prevented GUV formation, indicating a concentration dependent effect. The effect of nanoparticles on the membrane material properties, as determined by phase separation morphology and transition temperatures, will also be discussed.

## **COLL 244**

### **Effect of biomimetic additives on pore structure modulation in alginate-based hydrogels for applications in wound management materials**

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Biomimetic hydrogel materials have become of great interest in many disciplines of research due to their fluid uptake capacity, tensile strength, non-cytotoxicity, and biodegradability. These supramolecular composites are typically comprised of naturally derived polymers such as alginate as well as cross-linking agents which arrange themselves non-covalently providing structural tunability to the final composite. This research will attempt to decode critical interactions of alginate with biomimetic cross-linking agents such as sugars and amino acids. It has been determined that the incorporation of structurally diverse amino acid-Ca<sup>2+</sup> complexes into the alginate backbone, macromolecularly alter the pore structure, driving the overall efficacy of the hydrogel matrix. As the concentration and hydrodynamic radius of the additive was increased, there was a significant decrease in the pore size via increased non-covalent interactions such as hydrogen bonding and  $\pi$ - $\pi$  stacking. This attributed to a resultant decrease in the initial rate of swell in the presence of aqueous media due to capillary forces within the hydrogel composite. The pore size-tunability is directly correlated with the materials ability to swell due to an inverse relationship between the cross-linking density and degree of swelling (DOS). One such example, at a fixed additive concentration phenylalanine exhibited an initial swell rate of ~279.5%/min, and glycine had a swell rate of ~436.9%/min. Their corresponding pore sizes were 1.72 $\mu$ m and 5.31 $\mu$ m, respectively. Furthermore, although the structural properties of the material can be finely tuned based on the biomimetic additive (amino acid or sugar), all resultant hydrogels were found to proliferate cell growth of adult human dermal fibroblasts.

## **COLL 245**

### **Elastic moduli and collective dynamics of phospholipids are revealed by solid-state <sup>2</sup>H NMR spectroscopy**

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Solid-state deuterium NMR spectroscopy is a powerful method in colloid and surface chemistry for addressing how material properties emerge from atomistic level interactions of surfactants and lipid membranes. Here we show that solid-state <sup>2</sup>H NMR relaxation provides atomistically resolved information about the structure and dynamics of flexible phospholipids in the liquid-crystalline state. For lamellar mesophases, the average structure is manifested by the segmental order parameters ( $S_{CD}$ ) of the lipid molecules. Material properties are obtained from measurements of static lipid deformations, and thermal motions in liquid-crystalline membranes are directly related to membrane mechanical properties via the fluctuation-dissipation theorem. Because of the temporal range of solid-state <sup>2</sup>H NMR relaxation methods, the hierarchical dynamics of liquid-crystalline membranes have become accessible. Model-free interpretation of the functional dependence of spin-lattice relaxation rates ( $R_{1Z}$ ) on the  $S_{CD}$  order parameters informs the composite lipid dynamics in the liquid-disordered (ld) state. Our approach reveals that membrane elasticity involves bilayer deformations over a range of length scales, from the nanoscale down to the size of the flexible lipid segments. Elastic membrane deformations involve director fluctuations that are characterized by a square-law dependence of the nuclear spin relaxation rates on the segmental order parameters, and by their dependence on the magnetic field strength (Larmor frequency). We establish how NMR relaxation guides the continued development of atomistic and coarse-grained molecular mechanics force fields. Collective bilayer excitations are emergent over mesoscopic length scales that elucidate how membrane mechanics are governed by the lipid acyl chains, polar head groups, cholesterol, and proteins. Solid-state <sup>2</sup>H NMR relaxation studies further reveal lipid-specific effects of cholesterol on the bending rigidities of both saturated (DMPC) and unsaturated (POPC and DOPC) bilayers in the liquid-disordered (ld) state in terms of their viscoelastic properties. Future conceptual advances and theoretical reductions will enhance our understanding of hierarchical biomembrane dynamics through a synergistic integration of NMR measurements, molecular simulations, and neutron scattering studies.

## **COLL 246**

### **A<sub>2A</sub> adenosine receptor activation studied by all-atom simulation**

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G protein-coupled receptors (GPCRs) are the largest class of membrane proteins and are involved in a wide variety of physiological processes, making them targets of around 30-50% of medicinal drugs. The A<sub>2A</sub> adenosine receptor is activated by extracellular adenosine, and activates the stimulatory G-protein G<sub>s</sub>. To better understand the activation cycle, 5 microsecond simulations were performed for the A<sub>2A</sub> adenosine receptor bound to NECA in two states: with a “mini G protein” bound, and without G protein. Analysis of helix RMSD distributions suggests a special role for helix 3 in the return of the protein to the inactive state. Analysis of contacts formed and broken during the simulation between the mini G protein and the receptor, and comparison to the crystal structure identifies several new contacts formed between the third intracellular loop and the mini G protein and suggests the conformational change of the mini G protein after GDP unbinds from its binding interface. Pathways of coupled side chain conformations between the mini G protein and the ligand binding site were identified by a mutual information analysis.

## **COLL 247**

### **Complex coacervation as a model for membraneless organelles: Effects of macromolecular crowding on the formation and behaviors of polypeptide coacervates**

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Intracellular environments are crowded with various biological macromolecules, which can contribute to aqueous phase separation within cells. This process can lead to the formation of RNA- and protein-rich liquid membraneless organelles *in vivo*, such as processing bodies and stress granules in the cytoplasm, as well as Cajal bodies and nucleoli in the nucleus. There are still many unknowns surrounding how liquid organelles form and function, so creating cellular mimics to study membraneless organelles *in vitro* is an attractive option for scientists, as we can remove some of the complexity of living cells without surrendering a comparable cellular environment. In this research, complex coacervation, a type of associative phase separation, is used as a physicochemical model for understanding the behaviors and compartmentalization abilities of liquid membraneless organelles in eukaryotic cells. Complex coacervates were formed from oppositely charged polypeptides and introduced to aqueous solutions containing neutral crowding agents, including poly(ethylene glycol) (PEG) 8 kDa, ethylene glycol (EG), Ficoll 70 kDa, and sucrose. Increasing the amount of PEG, EG, and Ficoll in samples resulted in a lower charge ratio required for coacervation, indicating that coacervates easily formed. Conversely, sucrose increased the charge ratio required for phase separation, suggesting that interactions between the polypeptides and sucrose molecules hindered coacervation. Macromolecular crowding also stabilized coacervates in increasing concentrations of NaCl, as PEG and Ficoll crowders caused the coacervate phase to persist in higher concentrations of NaCl, compared to samples lacking crowders. Additionally, we observed evidence that

crowding molecules impacted the physical morphology of the coacervate phase. These preliminary results demonstrate that crowding-induced effects can influence the phase behavior and physical properties of peptide-based coacervates. These findings also suggest that potential consequences of the high concentrations of intracellular macromolecules and cosolutes should be considered in the formation of liquid organelles in cells.

## **COLL 248**

### **Comparison of antipsychotic drug and peptoid adsorption to lipid membranes using second harmonic generation**

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We tracked the adsorption of drugs and peptoids to lipid membranes by utilizing second harmonic generation, a nonlinear optical method. Recent studies were conducted using the antipsychotic drug chlorpromazine to quantify its adsorption to supported lipid bilayers. Comparisons were made to analogous peptoid structures to better understand structure-activity relationships. Studies were conducted in biologically-relevant buffer and temperature conditions to provide insight into how chemical structure, size, and charge impact interactions with lipid membranes in natural biological systems.

## **COLL 249**

### **Carbon accumulation at model biological interfaces: Changes to lipid film structure and organization**

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The effects of fine particulate matter (< 2.5  $\mu\text{m}$  in diameter,  $\text{PM}_{2.5}$ ), particularly black carbon (BC) aerosols, on biological membrane structure, organization and function remain poorly characterized despite the risks that these particles pose to human health and the environment. In order to gain a predictive understanding of how non-biological, nano-sized materials impact membrane organization and function, findings presented in this work use model systems to examine how different sized carbon nanoparticles (CNPs) affect the properties of lipid films adsorbed to aqueous – air interfaces as well as lipid bilayers in vesicles. Data from surface tension measurements show that carbon loadings up to 5% in lipid monolayers increase the isothermal compressibility, with higher loadings and smaller sizes of CNPs appearing more like pure DPPC while lower loadings and larger sizes of CNPs have a more extreme effect on monolayer rigidity. Differential scanning calorimetry (DSC) measurements indicate that CNPs in aqueous solution do not significantly change DPPC bilayer melting temperature, although the gel-

liquid crystalline transition temperature does broaden slightly with less CNP loading and larger CNP size. These results are supported with complementary surface specific vibrational sum frequency generation (VSFG) experiments. Together, findings presented in this work illustrate how a combination of independent measurement techniques can begin to identify a subtle but measurable particulate affinity for lipid membranes and how these associations depend sensitively on a lipid film's thermodynamic state.

## **COLL 250**

### **Designing self-assembled high-efficiency lipid nanodiscs for the encapsulation of graphene family materials**

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Graphene family materials (GFMs), such as graphene and fullerenes, have shown promising photo-theranostic efficacy for tumor imaging and therapy. However, their strong hydrophobic nature limits their bioavailability and overall therapeutic efficacy when used *in vivo*. Bicelles, which are self-assembling, discoidal phospholipid nanostructures with a hydrophobic core, can be used to deliver hydrophobic drugs and molecules. Herein, we present a facile method for the encapsulation of graphene and fullerene in bicelles. Using small angle X-ray scattering, we further investigated the sub-particle structure of the bicelle in order to determine the impact of GFM encapsulation on the bicelle stability and structure. While lower concentrations of graphene encapsulation produced stable bicelles solutions, higher concentrations led to the formation of a mixture of bicelles and multilamellar vesicles. Fullerene encapsulation, even at exceptionally high concentrations, only produced bicelle solutions. Further, we found that fullerenes preferred to orient themselves around the rim of the bicelle, which is consistent with our previous data for the encapsulation of other small spherical particles.

## **COLL 251**

### **Development of minimal actin cortices (MACs) on lipid bilayers for ion channel electrophysiological recordings**

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Artificial lipid bilayers are an important tool in the world of biointerfaces. However, a major impediment to the adoption of techniques involving biomembrane synthesis is their inherent instability and fragility. One method for reducing membrane fragility is by supporting the lipid bilayer with a network of actin filaments also called a MAC (minimal

actin cortex). Such networks can be layered indefinitely, forming increasingly thick and dense networks upon the bilayer. While previous work on MAC formation focuses on a glass supported bilayer, recently our lab has transferred this procedure to bilayers painted across a small aperture. Transfer of the procedure to an aperture based bilayer allows for simultaneous electronic and fluorescent recordings. Simultaneous electronic and fluorescent recordings confirms the compatibility of MAC formation with techniques involving capacitance measurements, nanopore conductivity, along with many others.

## **COLL 252**

### **Novel lipids based on cyanuric chloride for drug, gene, and vaccine delivery**

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To develop a simple and inexpensive class of lipids for therapeutic delivery, we exploited the reactivity of cyanuric chloride to build a library of novel lipids. Cyanuric chloride lipids were designed using a convergent and divergent synthetic scheme. In the convergent scheme, protected small molecule headgroups were reacted with cyanuric chloride using diisopropylethylamine as a base to form a monochlorotriazine. The products of these reactions were then reacted with a secondary aliphatic amine that served as the lipid tail. In the divergent scheme, the secondary aliphatic amine tail was reacted with cyanuric chloride to form a dichlorotriazine, which was reacted with various nucleophilic headgroups to form the final lipid. The resulting compounds were analyzed using NMR and mass spectroscopy and further analysis was performed to understand the biophysical characteristics of the compounds. Through these strategies, a small library of synthetic lipids was developed using beta-alanine, diaminopropane, cysteamine, dimethyldiaminopropane and morpholine headgroups. Lipids containing morpholine failed to form liposomes at a 50% mixture with helper lipids (PC or cholesterol). However, non-cyclical headgroups yielded nanoparticles of 60-100 nm diameters. Our work demonstrates that cyanuric chloride can serve as a linker between hydrocarbon tails and a diversity of head groups in the synthesis of lipids that can be used to form liposomes. By combining various headgroup moieties, these nanoparticles have potential use in a variety of applications including drug and nucleic acid delivery, as well as vaccine development.

## **COLL 253**

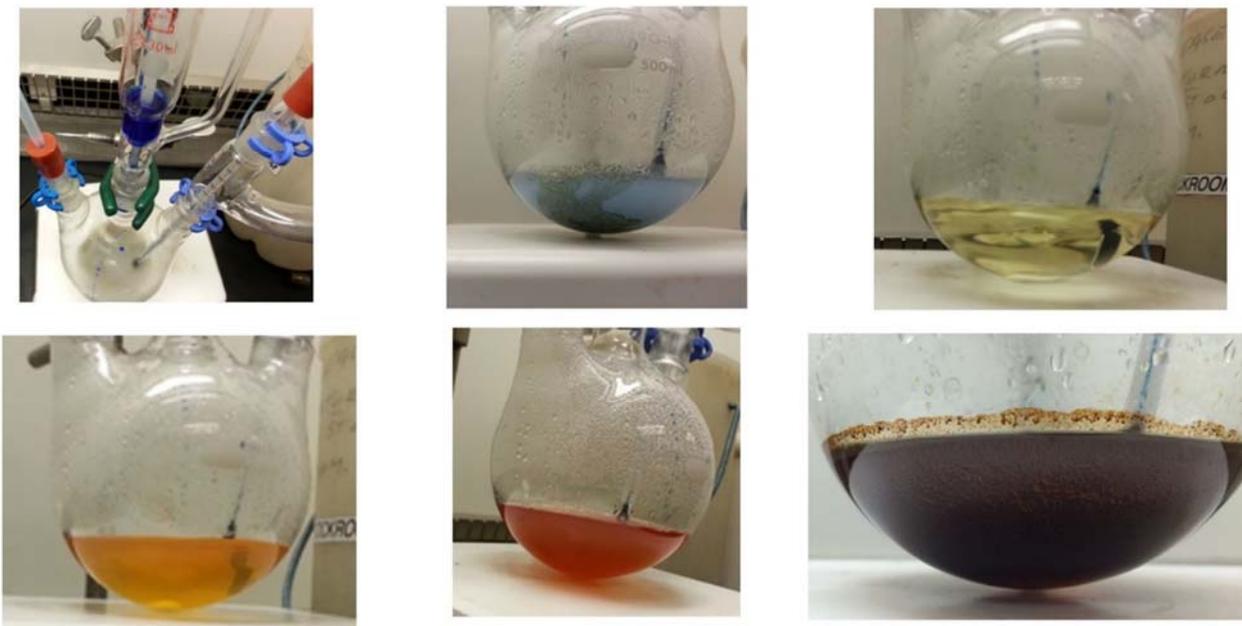
### **Copper cluster nanoparticles protected using glutathione**

**Aris V. Rubio**<sup>1</sup>, *arisrubio1@gmail.com*, **German P. Villa**<sup>2</sup>, **Marco Alvarez**<sup>1</sup>, **Glen Baghdasarian**<sup>1</sup>. (1) Los Angeles City College, Los Angeles, California, United States (2) Biology, University of Texas at San Antonio, San Antonio, Texas, United States

Copper cluster macromolecules are nanoscale materials comprised of a copper core or frame enclosed by a mantle of stabilizing ligands. Its exploration offers advancement in

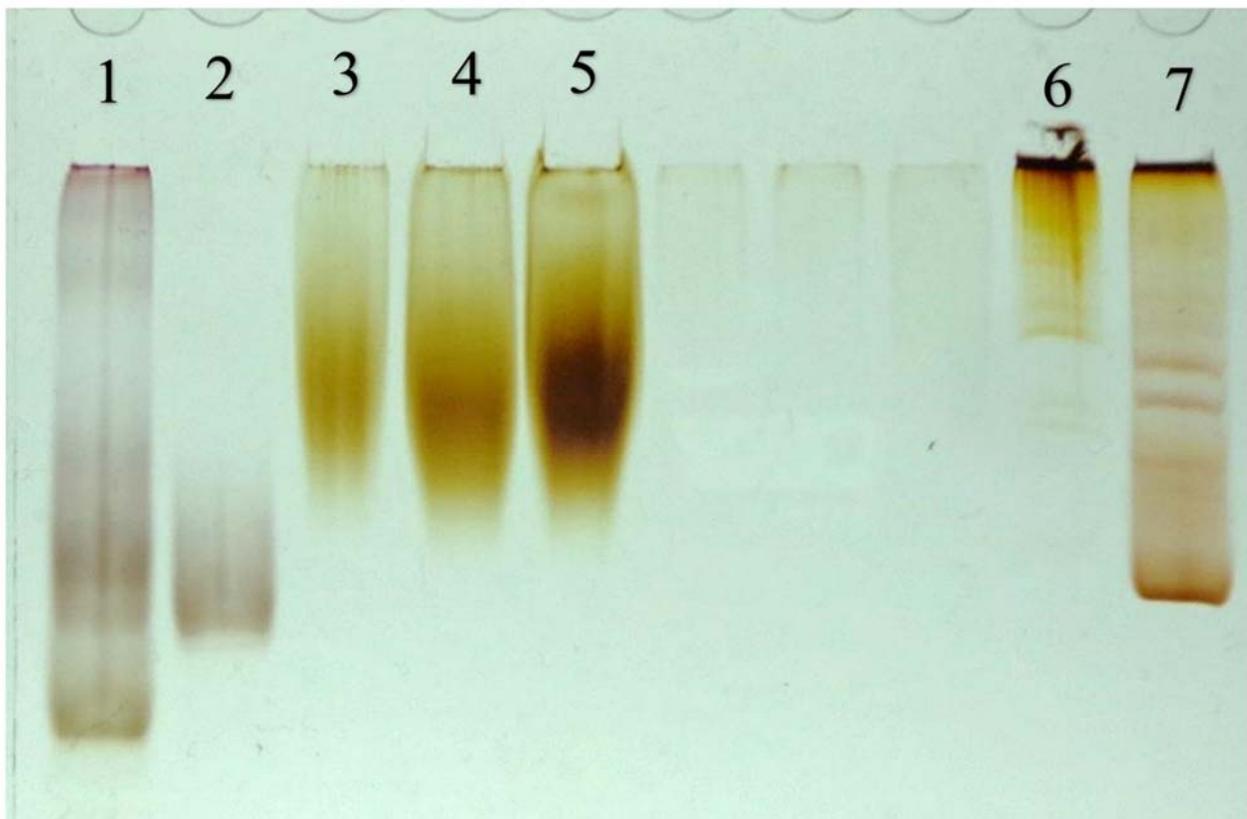
various fields from electronics and energy to medicine. Copper clusters have potential to further progress in fundamental chemistry as catalysts, reducing agents, corrosion inhibitors, and petroleum sweeteners, for instance. Nanoscale materials were synthesized from copper salts using borohydride reducing agents, and a protecting ligands to optimize their composition, structure, size, and reactivity. Results demonstrated glutathione is an excellent stabilizing ligand for the macromolecule. When prepared in anaerobic alkaline conditions, the nanoparticle is air stable for months at a time, and it shows high cohesion as judged by its melting point ( $>250^{\circ}\text{C}$ ). Polyacrylamide gel electrophoresis shows monodispersity at less than 3nm diameter, and surprisingly, UV-Vis spectrometry demonstrates the material absorbs strongly in the near infrared ( $>1100\text{nm}$ ).

**Figure 1: Synthesis of CuGSH CCC's**



Reaction of copper ammonia complex ( $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ ) with glutathione in the presence of sodium borohydride. The copper was introduced into the glutathione within an anaerobic environment. Reaction resulted in a color progression from clear, blue, pale yellow, orange, red, then brownish-black. The material is water soluble and can be purified through sequential washes using cold methanol.

**Figure 2: Gel electrophoresis of CuGSH CCC's**



1. CTRL Au102-pMBA (Stock#1) (2ul+2ul glycerol 50%); 2. Au144-pMBA (2ul+2ul glycerol 50%); 3. CuGHS-10x (1ul); 4. CuGHS-10x (2ul); 5. CuGHS-10x (3ul); 6. Ag-pMBA (#1) (2ul+2ul glycerol 50%); 7. Ag-pMBA (#2) (2ul+2ul glycerol 50%); GEL 15% (19:1), TBE, 110V, 90min

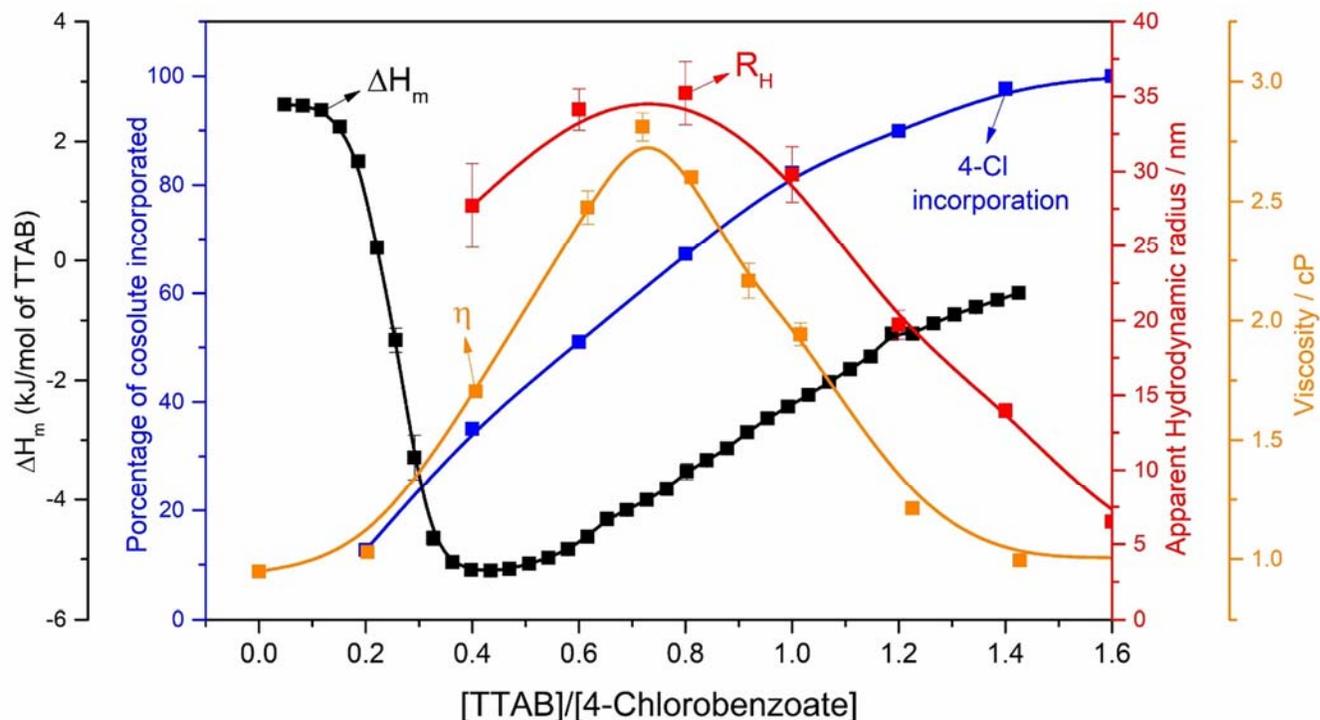
## COLL 254

### Formation of wormlike micelles with tetradecyltrimethylammonium bromide and 4-halogenbenzoates

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Wormlike micelles (WLM) are elongated self-assembly structures that can reach hundreds of nanometers in length and solutions containing WLM has wide applications in various fields, such as drug delivery, enhanced oil recovery, rheology control, drag reduction agents and many home care, personal care and cosmetic products. Its formation is based on noncovalent interactions such as hydrophobic, electrostatic screening,  $\pi$ - $\pi$  stacking, hydrogen bonding among others. The elongated structures are

dynamic and they are continuously breaking and recombining. The formation of wormlike micelles in aqueous solution with cationic surfactant is highly favored in the presence of hydrotropes such as derivatives of benzoate. In this study, we used tetradecyltrimethylammonium bromide (TTAB) and 4-halogen benzoates, such as 4-fluorobenzoate, 4-chlorobenzoate, 4-bromobenzoate and 4-iodobenzoate, to form the wormlike micelles in aqueous solution and understand the implications that the change of the halogen atom brings for the formation of wormlike micelles. Besides that, the calorimetry profile of this type of aggregate is not fully understood and by comparing the results obtained by isothermal titration calorimetry with rheometry, dynamic light scattering,  $^1\text{H}$  chemical shift and diffusion coefficient in nuclear magnetic resonance and cryogenic transmission electron microscopy, it is possible to propose a possible interpretation for the calorimetric profile.



## COLL 255

### General approach to the synthesis of hetero-dimers of metal nanoparticles through site-selected protection and growth

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Hetero-dimers of metal nanoparticles are widely sought for applications in photonics, sensing, and catalysis. In this work, we demonstrate a general approach to the fabrication of hetero-dimers of metal nanoparticles by leveraging the concept of site-selected growth under the protection of an inert material. When styrene is polymerized in the presence of Au nanoparticles, the resultant polystyrene (PS) can be controlled to grow only from one portion of the surface of a nanoparticle. Free of PS, the remaining portion can serve as an active site for the heterogeneous nucleation and growth of the second metal. After dissolving the PS component, we obtain hetero-dimers of metal nanoparticles with tunable elemental compositions and controllable physical dimensions. The contact area between the two metals can also be maneuvered by adjusting the concentration of divinylbenzene used for co-polymerization with styrene. Using this method, we have prepared Au-Ag, Au-Pd, and Au-Pt hetero-dimers and further investigated their plasmonic properties. The capability of this approach should be extendible to the fabrication of hetero-dimers with a broader range of compositions and properties.

#### **COLL 256**

#### **Lead-free, zero-dimensional perovskite-analogue nanocrystals with rich post-synthetic transformation reactions**

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The unique crystal structure and optoelectronic properties of zero-dimensional perovskite-analogues have attracted a great amount of research interest in recent years. However, much of the 0D perovskite-analogues contain lead, making them hazardous for the environment. Herein, we report a facile synthesis towards a lead-free perovskite-analogue, Cs<sub>3</sub>BiX<sub>6</sub> NC (X=Cl, Br). We observe a broad photoluminescence peak centered at 390 nm, which we tentatively assign to the photoluminescence of self-trapped exciton. Furthermore, we demonstrate that the Cs<sub>3</sub>BiX<sub>6</sub> NCs can transform into other bismuth-based perovskite-analogues nanocrystals *via* facile anion exchange or metal ion insertion reactions. The high activity and the preservation of nanoscale structure made Cs<sub>3</sub>BiX<sub>6</sub> NCs potential reaction precursors towards other bismuth-based perovskite-analogue nanocrystals that are hard to obtain otherwise. This work presented here can inspire insight into the structure-property relationship for 0D perovskite-analogue nanomaterials and promote the fabrication of perovskite optoelectronic devices.

#### **COLL 257**

## **Use of digestive ripening to synthesize quantum dot alloy nano particles**

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Quantum Dots(QDs) are nanoscale semiconductor particles, having size dependent electronic and optical properties. As the size of QDs increases, there band gap decreases, and a higher wavelength of light is emitted when they fluoresce. Digestive Ripening (DR) is known to convert polydisperse nanocrystals to monodisperse ones via fusion/coalescence and intraparticle growth. The goal of the experiment was to use DR technique on two different type of QDs together to find how they behave. The hypothesis was that the two different QDs would grow together in the same crystal structure forming a QD alloy. The two different QDs were subjected to DR inducing condition. The color of light emitted by QDs under UV red shifted after treatment. This is evidence for growth in size. The wavelength of emission spectrum and Transmission Electron Microscope(TEM) images before and after treatment also supported this conclusion. Furthermore, X-Ray powder diffraction(XRD) was conducted before and after treatment to compare the crystal structures. The peak from XRD of CdS+CdSe QD product after treatment was in between initial peaks of CdS and CdSe QDs. This is the evidence for formation of CdSe<sub>x</sub>S<sub>1-x</sub> QD alloy. Other combinations did not provide conclusive data.

## **COLL 258**

### **Submicrometer nitridated titania spheres with extraordinary plasmonic photothermal conversion efficiencies for solar seawater desalination**

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The past decade has seen a fast growth in the field of localized surface plasmon resonance (LSPR). Plasmonic nanoparticles have been researched and applied in various areas. The field of nanoplasmonics has been dominated by noble metal nanoparticles since its emergence. However, the high cost and poor stability of noble metals greatly hinder their applications. New types of plasmonic materials have been studied recently. In this work, we have chemically synthesized submicrometer nitridated titania (TiO<sub>x</sub>N<sub>1-x</sub>) spheres and evaluated their plasmonic properties. The submicrometer TiO<sub>x</sub>N<sub>1-x</sub> spheres are produced by calcining submicrometer titania spheres in NH<sub>3</sub> milligram scale. The scattering spectra of various TiO<sub>x</sub>N<sub>1-x</sub> spheres are measured by dark-field spectroscopy and compared by Mie theory calculations, which are found to be broad. The absorption spectrum of the TiO<sub>x</sub>N<sub>1-x</sub> powder is nearly flat with the value over 90%. The ultrahigh absorption capability makes our sample promising in photothermal conversion applications. We can even control the properties of the TiO<sub>x</sub>N<sub>1-x</sub> samples by varying the calcination temperature. This result is of fundamental importance to the

understanding of the plasmon resonance in nitridated metal oxide nanomaterials.

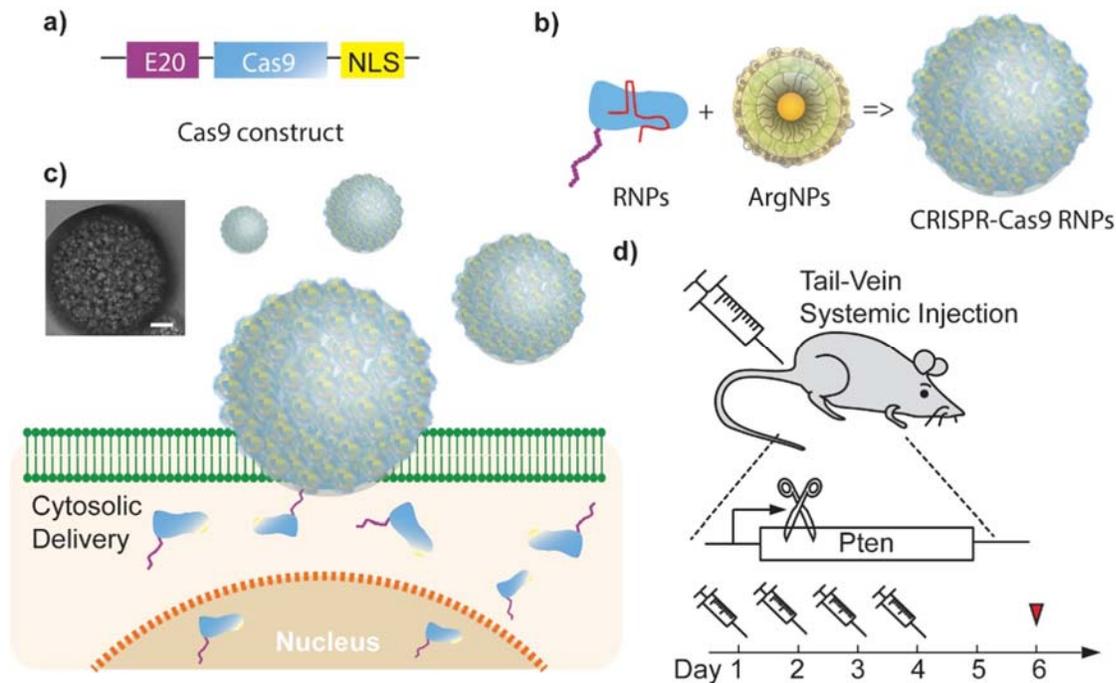
We also demonstrated the application of the submicrometer  $\text{TiO}_x\text{N}_{1-x}$  spheres in solar seawater desalination. Polymer films containing the  $\text{TiO}_x\text{N}_{1-x}$  spheres are prepared. A water vaporization device is assembled by integrating the film with a piece of tissue paper and packaging foam. The device can float on water and transport it to the film. The water trapped in the film can be vaporized efficiently under sunlight owing to the plasmonic photothermal conversion effect of the submicrometer  $\text{TiO}_x\text{N}_{1-x}$  spheres. A water vaporization rate of  $\sim 2.9 \text{ kg h}^{-1} \text{ m}^{-2}$  has been achieved, with a solar energy conversion efficiency reaching 96%. These values are comparable to the world records. We have also designed a steam collection device and have it tested in real conditions. The concentrations of the different metal cations in the seawater and the desalinated water are measured. The cation concentrations in the desalinated water are found to satisfy the WTO standard for drinking water. Our new plasmonic nanomaterials and their world-record-comparable vaporization performance are expected to generate a high impact in the field of nanoplasmonics, in seawater desalination, as well as in environmental waste water treatment.

## **COLL 259**

### ***In vivo* editing of macrophages through systemic delivery of CRISPR/Cas9 RNP-nanoparticle nanoassemblies**

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Macrophages are key components of the host immune system with crucial roles in the response to and treatment of disease. Targeted modification of the macrophage genome using CRISPR/Cas9 technology could provide a powerful technique for the treatment of diseases through transient immune modulation. However, there are significant physiological, cellular, and intracellular barriers to effective delivery of the CRISPR machinery that have restricted *in vivo* Cas9 protein-based approaches to local/topical delivery applications. We utilized our gold nanoparticle (AuNP)-based self-assembled delivery platform for systemic (tail-vein) administration of the CRISPR/Cas9 machinery. We observed highly selective delivery to macrophage cells of the liver and spleen, with concurrent gene editing efficiency of >8%, and no observed negative immunological effects.

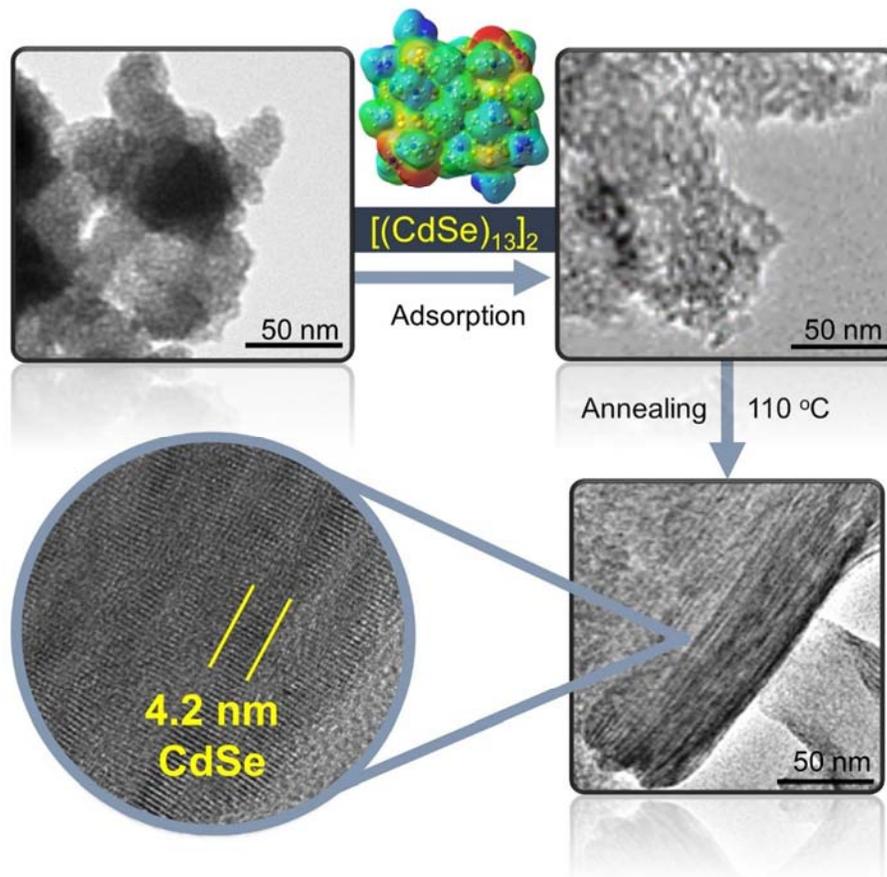


## COLL 260

### Spatially-confined CdSe nanowires in mesopores

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Here we grow CdSe nanowires into mesoporous materials via interfacial interaction between silanols and molecular CdSe precursor. Magic-sized nanocluster  $(\text{CdSe})_{13}$  is an air-stable precursor which can be adsorbed and chemically bonded into mesoporous zeolite and graphene-derived materials (MZNs, MGNs) of high surface area ( $> 900 \text{ m}^2/\text{g}$ ) and enlarged pore sizes ( $> 5 \text{ nm}$ ). With tunable mesopore diameters and morphology, spatially-confined CdSe nanowires can be grown vertically into nanochannels of mesoporous zeolite thin films (MZTFs). Spatial confinement and transformation of 0D CdSe into orientated 1D nanowires are realized via surface manipulation of mesopores as well as designs of CdSe precursors with suitable molecular interaction.



Formation pathway of CdSe nanowires via spatial confinement of  $[(\text{CdSe})_{13}]_2$  into mesoporous materials.

## COLL 261

### Platinum recycling for synthesis of Pt-based electrocatalysts

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Platinum is an ideal catalyst for various chemical reactions. For example, proton-exchange membrane fuel cells contain Pt-based nanoparticles due to the sluggish kinetics of oxygen reduction reaction (ORR). However, Pt resource is scarce, and produced in limited areas. Therefore, recycling plays a key role for resource security as well as enhancement of the ORR activity. In hydrometallurgical Pt recovery process, Pt in spent materials is dissolved into acidic solution followed by forming Pt-ammonium

compound to be separated from other metal species. Then, pure Pt is recovered via heat treatment. When recovered Pt is used for synthesis of renewed material, pure Pt is redissolved to prepare general Pt precursor. The current recycling process is complicated, and is not always worth the cost. Moreover, reactive and toxic aqua regia, which releases nitrosyl chloride, nitrogen dioxide, and chlorine, is used to leach stable Pt. Herein, we propose a closed Pt cycle system by connecting recycling process with material synthesis. The system is composed of two research topics: (1) synthesis of active Pt-based electrocatalyst directly from Pt-ammonium compound, which is generated as recycling intermediate, (2) and development of green recycling process without harmful aqua regia. In future, spent material will be starting material.

## **COLL 262**

### **One pot route to functionalized gold nanogels**

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Gold nanoparticles (AuNPs) can be used in many different applications due to their optoelectronic properties. Their optoelectronic properties can be changed by changing their size, shape, surface chemistry or aggregation state. They can be used as therapeutic agents, as drug delivery agents, as sensory probes, as conductors, as well as catalysts.

The purpose of this research is to create functionalized gold nanogels for their application in catalysis. The novelty of our process is that the reduction and stabilization of gold nanoparticles is accomplished in one-step in presence of alkoxy silane-substituted polyethylenimine under mild reaction conditions. The versatility of the process is demonstrated by the fact that one can synthesize such particles in different solvents. First, in a one-pot reaction of gold salts with Trimethoxysilylpropyl modified Polyethylenimine (TMSP-PEI) was carried out under optimized reaction conditions, which led to the TMSPEI stabilized AuNPs. It was observed that amounts of TMSP-PEI have a marked effect on the size of resulting nanoparticles. Further polymerization of TMSP-PEI using sol-gel technique led to the formation of gold nano gels under various reaction conditions. We will present the results of these investigations as well as characterization of all new materials using various spectroscopic techniques. We will also present our studies of the physical and chemical properties of gold nanogels. In addition, we will also present our preliminary studies of the catalytic activity of these gels for effecting the reduction of 4-nitrophenol to 4-aminophenol.

## **COLL 263**

### **Morphology- and size-dependence of pressure-induced phase transition in semiconductor nanocrystals and their self-assembled arrays**

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In recent years, high pressure investigation of structural and property changes of nanomaterials have been of great interest in the field of materials science. Studies have shown that hydrostatic pressure can induce reversible and non-reversible crystal structural phase transitions, and under certain conditions, sintering of pre-ordered nanocrystal arrays leads to higher order structures. However, how the particle size and shape affect such pressure-dependent process have not been widely investigated nor well understood. CdS is one of the most studied wide band gap semiconductor materials and has found many applications in opto-electronic devices. Only a handful of examples are available studying the high-pressure behavior of CdS nanoparticles. Therefore, in this study, we choose CdS nanoparticles as a model material to investigate the high-pressure behavior of nanoparticles with various sizes and shapes. Characterization with in-situ small and wide-angle X-ray scattering measurements under high pressure suggest that both the reversibility of phase transition and phase transition pressure are closely related to the particle size and shape. Further characterizations with transmission electron microscopy show that external pressure can decrease the nanoparticle separation distance and induce sintering and coalescence of the nanoparticles into new nanostructures. This work provides detailed information over the relationship between nanoparticle structures and their high-pressure phase transition property, which can serve as guidelines for future materials design.

## **COLL 264**

### **Magnetic iron oxide nanocubes: Effect of annealing on the formation of a monolayer**

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Over the last decade, nanoparticles have become particles of great research interest because of their inherent chemical compositions such as size, shape, ability to be coated by other molecules and control over their magnetic properties. Assembly of these particles into a monolayer allows their properties to be harnessed and applied in various fields of studies. One method that has been adopted to enable this monolayer formation is the annealing of nanoparticles.

The goal of this experiment was to anneal decanoic acid coated iron oxide nanocubes at different temperatures and time intervals, to find the optimal conditions for the formation of a smooth monolayer. Using the spin casting method, the magnetic iron oxide nanocubes were spun onto a Transmission Electron Microscopy (TEM) grid, where they were subjected to different conditions of plasma cleaning, temperatures and

annealing times. The grids were then imaged under TEM at different magnifications. Using the program, Image J, it was found that the nanocubes maintained their shape and the mean cubic length of 15.5 nm at temperatures ranging from 100 – 150 °C. The results so far indicates that plasma cleaning of TEM grids can hinder the formation of a uniform monolayer. This could be due to the unfavorable interaction between hydrophobic decanoic acid coating of nanocubes and the hydrophilic TEM grid.

## **COLL 265**

### **Controlling atom arrangement in ternary metal chalcogenide nanoparticles using precursor oxidation state**

*Emily A. Eikley*<sup>1</sup>, *eae40@pitt.edu*, *Xing Yee Gan*<sup>1</sup>, *Derrick Kaseman*<sup>1</sup>, *Corban Murphey*<sup>1</sup>, *Scott Crawford*<sup>1</sup>, *Kathryn Johnston*<sup>1</sup>, *Sadegh Yazdi*<sup>2</sup>, *Jill Millstone*<sup>1</sup>. (1) University of Pittsburgh, Pittsburgh, Pennsylvania, United States (2) University of Colorado Boulder, Boulder, Colorado, United States

Composition is a well-known variable that controls material properties across length scales and has helped lead to the wide range of applications of metal chalcogenides. As the material composition is made more complex by the introduction of additional elements, challenges in controlling atom position emerge, which is especially crucial at the nanoscale. Several synthetic strategies have been identified as promising routes to access metal chalcogenide nanoparticles of various compositions. Of these, cation exchange is particularly versatile in accessing compositionally complex metal chalcogenide nanoparticles. Single reaction vessel syntheses have been less explored for complex metal chalcogenides, although they are desirable for their scalability, and ultimately, the translation of these materials into everyday technologies. Here, these two methods are investigated to identify mechanistic principles that can be used to access the widest variety of material compositions with the least number of synthetic steps. Specifically, we study nanoparticles containing copper, silver, and selenium elements synthesized using both cation exchange and a single reaction vessel method. Initially, we show that the cation exchange and single reaction vessel methods yield particles with tunable compositions but different atom arrangements. We then identify the main factor in the single reaction vessel synthesis that dictates atom arrangement in the final nanoparticle structures: copper precursor oxidation state. Specifically, we demonstrate that by controlling precursor chemistries, the single reaction vessel pathway can be used alone to access these two different atom arrangements in the resulting nanoparticle samples. Taken together, these results demonstrate the importance in identifying synthetic parameters that control atom position and the benefits of manipulating these factors to control final nanoparticle architecture.

## **COLL 266**

### **Bottom-up assembly of DNA: Silica nanocomposites into micrometer-sized hollow spheres**

**Yong Hu**, *yonghu2018@gmail.com*. karlsruhe institute of technology, Karlsruhe, Germany

Although DNA nanotechnology has developed into a highly innovative and lively field of research at the interface between chemistry, materials science, and biotechnology, there is still a great need for methodological approaches for bridging the size regime of DNA nanostructures with that of micrometer- and millimeter-sized units for practical applications. We report on novel hierarchically structured composite materials from silica nanoparticles and DNA polymers that can be obtained by self-assembly through the clamped hybridization chain reaction. The nanocomposite materials can be assembled into thin layers within microfluidically generated water-in-oil droplets to produce mechanically stabilized hollow spheres with uniform size distributions at high throughput rates. The fact that cells can be encapsulated in these microcontainers suggests that our concept not only contributes to the further development of supramolecular bottom-up manufacturing, but can also be exploited for applications in the life sciences.

#### **COLL 267**

##### **Size mapping of PLGA nanoparticles as a function of organic and water compositions**

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Different sizes of poly(lactic-co-glycolic acid) (PLGA) nanoparticles (NPs) were synthesized via single emulsion under different solvent conditions. Of the factors tested were organic to water phase and DCM:DMSO ratios. Results from Dynamic Light Scattering (DLS) show that NP sizes increase when the DMSO concentration was increased, and the NP sizes decreased when the organic phase to water ratio increased.

#### **COLL 268**

##### **Synthesis of colloidal gold nanoplates and their plasmon coupling with gold nanospheres**

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Noble metal nanocrystals have attracted extensive attention for their wide potential applications, including photothermal therapy, chemical and biological sensing, and plasmon-enhanced spectroscopies, because of their localized surface plasmon resonances (LSPRs). The LSPR frequency is highly dependent on the shape and size of metal nanocrystals and the dielectric property of their surrounding environment.

Among variously shaped Au nanocrystals, nanoplates (NPLs) offer significant advantages in their asymmetric geometry as well as rich plasmon resonance modes. Strong electric field enhancements can be generated at their sharp corners and straight edges. Au NPLs with large-area flat surfaces are the ideal building blocks for constructing plasmonic assemblies, which are beneficial for the manipulation of the optical responses of plasmon-coupled nanostructures and the development of plasmon-based optical devices.

Herein we report on a wet-chemistry method for the facile synthesis of highly uniform hexagonal Au NPLs with tailorable thicknesses. By controlling the amount of the Au precursor, their thicknesses can be readily varied in the range from 10 nm to 50 nm. The dipolar plasmon resonance can be correspondingly varied from the visible to near-infrared region. The chemically synthesized Au NPLs possess a single-crystalline nature and atomically flat surfaces. Moreover, the surface of the Au NPLs can be dramatically altered by plasma treatment under specific conditions, with their overall shape and plasmon resonance remaining nearly unchanged. The flat NPLs are further assembled with Au nanospheres (NSs) to form heterodimers using different thiol molecules as the linkers. When the molecular junction is formed with insulating molecules that have only one thiol group, the Au NPL–NS heterodimer shows a distinct Fano resonance with a deep dip. When the insulating molecules are replaced with dithiol molecules that are conductive, a large blueshift of the scattering spectral peak is observed. The blueshift results from the occurrence of a higher-order charge transfer mode because of the conductive molecular junction. Taken together, these results will be important not only for understanding the properties of the Au NPLs but also for developing Au NPL-based plasmonic applications, such as surface-enhanced spectroscopies, optical switching and solar energy harvesting.

## **COLL 269**

### **Stability limits of biologically relevant nanoparticle coatings under varying chemical environments**

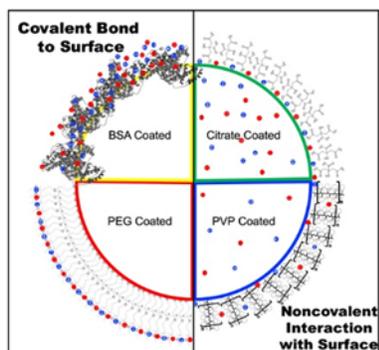
**Catherine J. Munro**, *Catherine.munro.90@gmail.com*, **Naha Rizk**, *nahla.rizk@ku.ac.ae*, **Matthew N. Martin**. Department of Physics, Khalifa University, Abu Dhabi, Abu Dhabi, United Arab Emirates

Biological applications involving nanoparticles (NPs) are inherently limited by their coating molecules' stability and biocompatibility. NPs can encounter harsh acidic, basic, or salt conditions that completely destabilize the dispersion, rendering their material properties useless. The chemical thresholds and mechanisms for coating breakdown and ensuing reactions (dissolution, agglomeration, and sedimentation) are poorly understood. This lack of knowledge severely limits the implementation of these NPs into assays or drug delivery systems.

Here we present the stability of NPs in different environmental conditions, functionalized with different biologically relevant coatings. Stable AuNPs (and inherently unstable AgNPs) are synthesized and coated with biocompatible molecules: trisodium citrate,

BSA, PVP, and PEG. Using time-resolved UV-Vis, DLS, and TEM the breaking point of the protective coatings is elucidated in the presence of HNO<sub>3</sub>, HCl, NaCl, and NaOH. Additionally, effects of solution temperature and pH during the coating process are studied to understand how synthesis conditions alter the surface coating and dispersion's resilience. By surveying these common coatings and grafting processes in the presence of comprehensive destabilizing conditions, we gain deeper insights into the stabilization of NPs by molecular coatings.

The choice of coating drastically affects the NPs stability. Specifically, the coating's conformation in solution and molecular association with the NP surface need to be studied to better understand what enhances NP stability. We propose that by exploiting the inherent chemical properties of the coating molecule we can mitigate diffusion channels that allow destabilizing ions to reach the NP surface by providing more obstructed transport pathways; and that these pathways are dictated by how the coating molecule associates with the NP surface and how many "neutralization sites" exist within the coating molecule.



## COLL 270

### Colloidal nanostructures through polyol synthesis and their functional assemblies for SERS sensing applications

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Polyol process has provided detailed insight for precise shape control of silver nanostructures. However, despite the significant progress in studying shape control and polyol process, research in this context *via* 1,3-propanediol has been explored to a limited extent. In this study, we explore the versatile properties of 1,3-propanediol-based

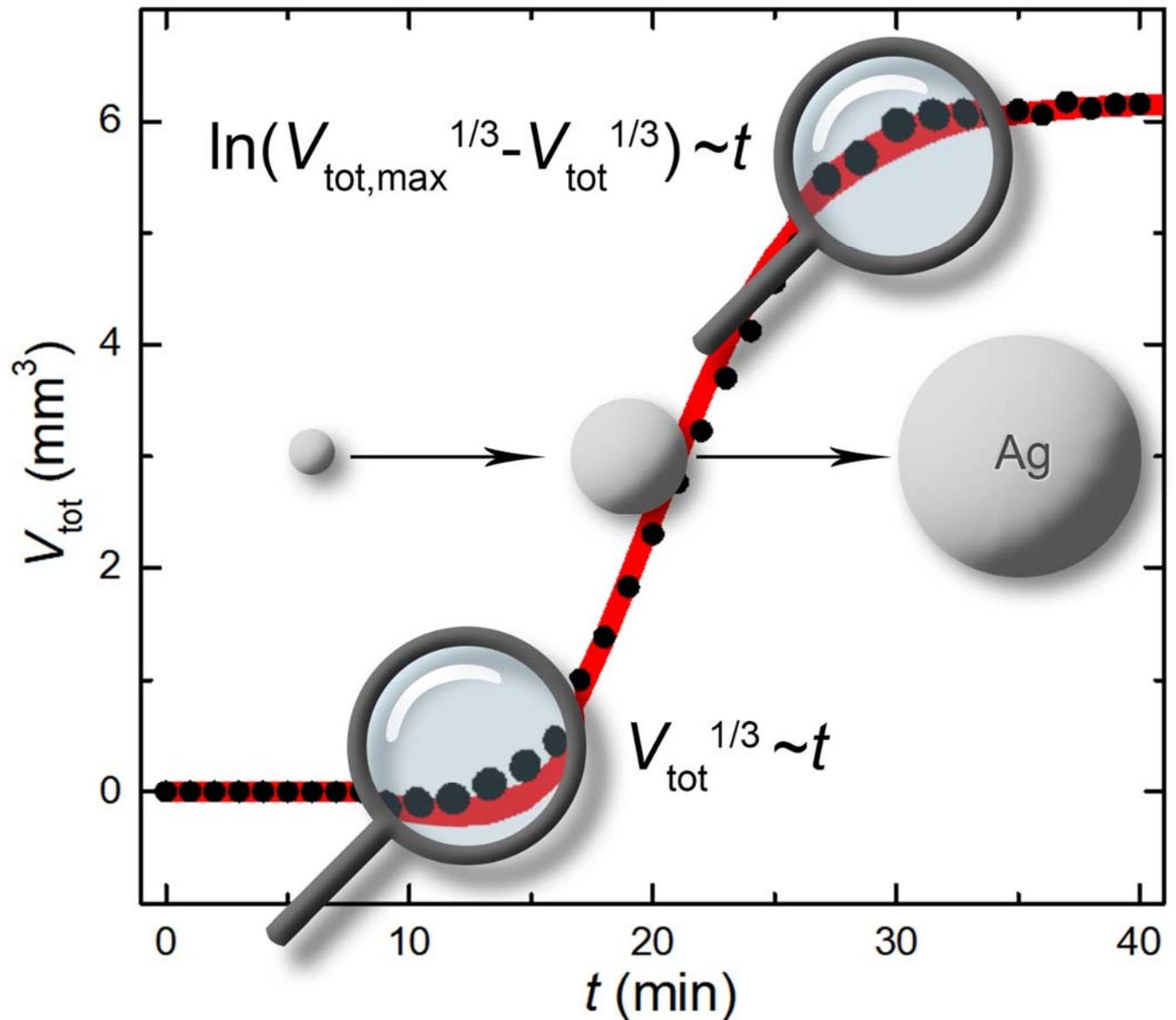
polyol synthesis in order to investigate the tunability of shapes of silver nanostructures. The type, strength and concentration of reducing agents as well as the presence of polyvinylpyrrolidone (PVP) contribute advanced effects for precise tuning in nanostructures formation. We found that the high yield of monodispersed nanorods occurs as a result of precise combination of mild reducing agents and moderate molecular weight of PVP at a defined reaction temperature in 1,3-propanediol. Similarly, monodispersed nanocubes formation is dependent on PVP with high molecular weight dissolved in 1,3-propanediol. The self-seeding synthesis process is the generation of Single-crystal seed which is believed to form uniform nanocubes. On the other hand, nanorods are the product obtained in the form of Penta twinned seeds. Beyond the structural aspect, in-situ surface functionalization helps to form layer-by-layer assembly system for the potential sensing applications. The assembly process *via* metal-catalyzed metal enforcement was performed on the surface of nanorods, nanocubes, multi-faceted nanoparticles and nanobullets and analyzed using surface-enhanced Raman scattering (SERS) sensing.

## **COLL 271**

### **Determine growth kinetics of colloidal nanoparticles by a fully quantitative model**

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Colloidal nanoparticle synthesis has reached a level of empirical maturity with a consensus that growing well-defined colloidal nanoparticles depends on “kinetics control”. However, quantitative study of growth kinetics of colloidal nanoparticles is still missing and virtually unexplored, and rational control over growth kinetics for synthesizing colloidal nanoparticles with desirable properties on demand remains challenging. In this presentation, a strategy has been developed for analyzing growth kinetics of colloidal metal nanoparticle quantitatively by focusing both the very early and the very late growth stages, at which the size of growing nanoparticles and the reaction time follow linear functions. Applying this extreme-condition model to a microwave-assistant synthesis of colloidal silver nanoparticles, for the first time, results in the determination of intrinsic kinetics parameters involving in the growth of the silver nanoparticles. The diffusion coefficient ( $D$ ) of the precursor species containing  $\text{Ag}^+$  is  $4.9 \times 10^{-14} \text{ m}^2/\text{s}$  and the surface reaction rate constant ( $k$ ) of the precursor species on the surface of the growing silver nanoparticles is  $8.7 \times 10^{-8} \text{ m/s}$  in an ethylene glycol solution containing 0.15 M polyvinylpyrrolidone at 140 °C. The extreme-condition model is ready to deconvolute the intrinsic kinetics parameters of growing colloidal nanoparticles once the enlargement rate of the nanoparticles can be experimentally measured in real time and with high temporal resolution. Availability of the high-fidelity values of  $k$  and  $D$  will provide the crucial information to guide the design and synthesis of colloidal metal nanoparticles with the desirable properties.



COLL 272

### Synthesis of heterostructured nanoparticles in ionic liquids

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This presentation will describe methods for synthesis of heterostructured nanoparticles in the ionic liquids 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and 1-

butyl-3-methylimidazolium methylsulfate. We will discuss deposition of noble metal particles onto a ligand-capped semiconductor nanorod substrate using an ionic liquid as the solvent and sacrificial reducing agent, characterization of the resulting materials, and the effect on photocatalytic performance. We will then discuss our recent progress towards using only ionic liquids and metal salts for the total synthesis of core/shell semiconductor particles with attached noble metal cocatalysts and comparison of photocatalytic efficiency with ligand-capped particles. Finally, we will discuss our recent progress towards shape control of metal nanoparticles using task-specific ionic liquids. It is our goal to establish new methodologies that will be generally applicable to synthesis of heterostructured nanoparticles in ionic liquids to improve particle surface availability, catalytic performance, and incorporation of these materials into devices.

## **COLL 273**

### **Formation of non-noble metals in organic liquids via laser ablation**

**Cory Trout**<sup>1</sup>, [cjt122@scarletmail.rutgers.edu](mailto:cjt122@scarletmail.rutgers.edu), **Paul Kumpf**<sup>1</sup>, **Julianne C. Griepenburg**<sup>2</sup>, **Sean M. O'Malley**<sup>1</sup>. (1) Physics, Rutgers University Camden, Sicklerville, New Jersey, United States (2) Physics, Rutgers University-Camden, Cherry Hill, New Jersey, United States

Pulsed Laser Ablation in Liquid (PLAL) offers a reproducible method to manufacture nanoparticles (NPs) with a desired size distribution and surface chemistry. While the synthesis of NPs in aqueous solutions is well understood, the effects of photodegradation and surface modification in organic solvents during PLAL warrants further investigation. The formation of a hot plasma during the laser ablation in water process results in hydroxyl formation that readily oxidizes metals such as iron, titanium, and copper. Herein, we investigate the structure and surface chemistry of these metals ablated in organic liquids, e.g. acetone, toluene, and alkanes, and relate these properties to characteristic features of the PLAL process such as plasma and cavitation bubble formation. A combination of time-resolved spectroscopy and shadowgraphy are used to track the evolution of these features, while manipulating the level of dissolved gases in the liquid via a custom ablation chamber to control the degree of oxidation.

## **COLL 274**

### **Synthesis and characterization of functionalized nanocomposite abrasive particles for chemical mechanical planarization (CMP) applications**

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Chemical mechanical planarization (CMP) is a process used to achieve angstrom-level uniformity of semiconductor devices which has played a critical role in the extension of Moore's Law. The CMP process utilizes a nanoparticle dispersion (known as a slurry) that contains abrasives, rate enhancing additives, and critical metal passivation

chemistry, coupled with a mechanical force to remove excess topography. Traditional abrasives used in Cu CMP such as silica ( $\text{SiO}_2$ ) can aid in the mass transport process but can aggregate or adsorb to the surface which can cause defects such as scratching, and low material removal rate (MRR) selectivity can lead to dishing and erosion. Specifically, through silicon vias (TSV) are necessary to produce 3D integrated circuit devices; however, due to the large Cu overburden, TSV requires high MRR, low dishing, high selectivity, low defectivity, and uniform surface topography. This work focuses on developing multi-functional reactive nanocomposite abrasive particles to transport chemistry to the surface to enhance overall CMP performance. These pressure-responsive particles are synthesized by functionalizing  $\text{SiO}_2$  with strong Cu chelators as the inner layer which becomes exposed after reaching a pressure threshold and removing the outermost layer consisting of a weak Cu chelator. The  $\text{SiO}_2$  core is initially functionalized by covalently bonding aminosilanes, which then non-covalently interact with additives containing Cu complexing functional groups. Results indicate that these nanocomposites must strike a synergistic balance between chemical activity and the ability to form passivation films at the Cu interface is critical to controlling MRR. Utilizing potentiodynamic scans it was determined that the activation energy of film formation shows a direct correlation to controlled MRR and reduced defectivity.

## **COLL 275**

### ***In situ* monitoring of retrograde crystallization of perovskite-phase $\text{MAPbI}_3$**

**Ryan F. Barrett**, [rfb45@drexel.edu](mailto:rfb45@drexel.edu), Aaron T. Fafarman. Chemical and Biological Engineering, Drexel University, Philadelphia, Pennsylvania, United States

Climate change, declining oil reserves, and the increasing world power demand have provided the impetus for developing cheap, scalable, and efficient renewable energy technology; solar energy in particular has massive potential for replacing fossil fuel dependence due to its versatility and rapid rate of improvement. In this field, lead halide perovskites have emerged as a class of promising alternatives to petroleum and coal due to their low cost of synthesis and highly desirable electronic structure. These materials exhibit the uncommon phenomenon of thermally retrograde solubility, also known as inverse temperature crystallization, whereby their solubility in certain solvents *decreases* with increased temperature. This has the potential for significantly expanding the processing options for crystallizing halide perovskites into high quality thin films in a high-throughput, low-cost manner. The synthesis of uniform, void-free polycrystalline thin films requires precise control over the independent processes of nucleation and crystal growth. To quantify the temperature dependence of the rates of both of these processes, *in situ* monitoring of perovskite formation under optical microscope was performed over a range of processing and system conditions. By directly observing heterogeneous crystallization and subsequent growth at high temperatures, we show how concentration and temperature affect crystal nucleation and growth. We observed two different products of retrograde crystallization as a function of precursor concentration: the direct crystallization of the desired cubic perovskite phase of  $\text{MAPbI}_3$ ,

or alternatively, an additional yellow, needle-like crystal which converts into the perovskite phase with increased temperature. The avenue of growth plays a major role in grain formation and surface coverage and thus we posit it is an important predictor of the end performance of a fabricated device.

## **COLL 276**

### **Amphiphilic polymeric micelles for delivery of docetaxel and carbonic anhydrase inhibitors**

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The project describes the use of amphiphilic diblock co-polymer PEGPCL as a delivery system for docetaxel and carbonic anhydrase inhibitors. We studied the influence of drug nature and the impact of polymer to drug ratio on the loading and release properties of the PEGPCL polymeric micelles. We succeeded in optimizing protocols for efficient loading carbonic anhydrase inhibitors and/or docetaxel into stable polymeric micelles with controlled release rates.

## **COLL 277**

### **Electrochemical controllable preparation of preferentially oriented porphyrin MOF films and their electrocatalytic properties**

*Qi Li, nanokingdom@163.com, Feng Bai.* Key Laboratory for Special Functional Materials of Ministry of Education, National & Local Joint Engineering Research Center for High-efficiency Display and Lighting Technology, School of Materials Science and Engineering, and Collaborative Innovation Center of Nano Functional Materials and Applications, Henan University, Kai Feng, Henan, China

Creating highly oriented metal-organic framework (MOF) nanosheets has attracted extensive interest. However, it still remains a great challenge to synthesize highly oriented MOF nanosheets with controlled thickness. The uniform porphyrin-based metal-organic framework cross nanosheet array (P-MOF CNSA) films with highly orientation have been controllable synthesized and grown in situ on various conductive substrates by the environmentally friendly electrochemical reduction method at ambient temperature. The highly oriented P-MOF CNSA film is endowed with excellent crystalline, spatial network structure and hierarchical three-dimensional pore structure, which is conducive to charge transfer and material transmission and suitable for use as an electrochemical catalyst. The application performance of electrochemical catalysis and electrochemical sensor of the thin film was described in detail. The P-MOF CNSA films on conductive substrate could be used directly as an electrochemical sensor, and showed wide linear range, low limit of detection high sensitivity and good anti-interference performance. Importantly, *ab* plane of the porphyrin MOF perpendicular to

substrate was first reported by electrochemical reduction. The results provide an excellent demonstration of how to exercise in a facile way fine control of the assembly of molecule-based hybrid objects, which is a key issue for the future use of MOFs in potential applications in nanodevices.

## **COLL 278**

### **Molecular dynamics study of fiber-epoxy interphase with monolayer silane**

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Using all-atom molecular dynamics (MD) simulations, we are investigating the interactions of epoxy-amine resin with the glass fiber (especially silica) surface in the presence of monolayer glycidoxypropyltrimethoxy silane (GPS). To develop the atomistic model, first we deposit GPS molecules on the silica surface at different number densities and react them with the silica surface through a condensation reaction. A mixture of Epon828-Jeffamine<sup>®</sup> D-230 is then put on the silica surface and equilibrated to predict the epoxy-amine diffusion into the monolayer silane using the general AMBER force field. Epoxide-amine curing reaction among the epoxy, silane and amine are modeled using the cross-linking algorithm. The model is then subjected to Mode-I, Mode-II and Mixed-Mode loading with the reactive force field ReaxFF to predict the stress-strain responses and failure loci within the interphase. Strain-rate and GPS bond-density dependent 3D Mixed-Mode traction surface (please see the attached image) will be developed to bridge length scale in the continuum level micro-mechanics modeling. Detailed morphology of the interphase at the atomistic scale will also be reported.

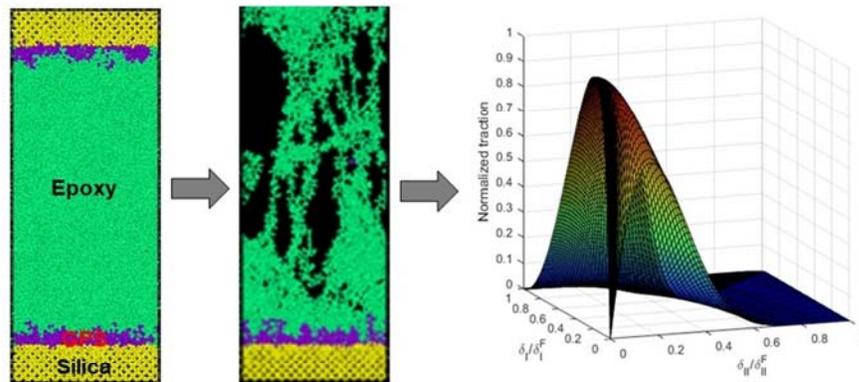


Fig.: Fiber-Matrix Interphase Modeling to Develop 3D Traction Surface

COLL 279

### Evaluation of adsorption characteristics of alpha olefin sulfonate and internal olefin sulfonates at oil-water interfaces: Molecular dynamics simulation study

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In order to displace the large volume of remaining hydrocarbons in reservoirs which cannot be recovered by conventional ways, the enhanced oil recovery (EOR) technology has been developed. The EOR technologies contain chemical flooding, gas injection, thermal recovery and other methods. Surfactants play an important role in chemical flooding and its key mechanism is to reduce the oil-water interfacial tension. Anionic surfactants are ideal components for oil displacement because most of the chemical flooding work has been conducted in sandstone and the negatively charged sandstone prevents the anionic surfactant from adsorbing on the surface of the formations. Several experimental studies have proved that alpha olefin sulfonate (AOS) and internal olefin sulfonates (IOS) have good oil displacement performance. However, there are few molecular dynamics simulations for the aggregation properties of AOS and IOS at the oil-water interface. AOS and IOS have the same and simple hydrophilic

headgroup which minimizes the influence of hydrophilic groups on the interfacial properties of surfactants, allowing us to focus on the difference between twin-tailed structures and single-chain structures.

In this work, we use the molecular dynamics simulation method to investigate the adsorption characteristic of surfactant molecules at oil-water interface. Anionic surfactants IOS and AOS are selected to compare the effects of different molecular structures on adsorption processes. We are going to study the morphology of the surfactant monolayer, the stability of the hydrophilic group in the aqueous phase and the miscibility of the hydrophobic tails with oil molecules to compare the interface properties of the two surfactants. Octane, decane and dodecane molecules are selected to represent oil phase to compare the effects of different oils on surfactant monolayers. Besides, we plan to add inorganic salts to the system to explore the effect of salinity on the interfacial properties of surfactants. Detailed information obtained from mass density distribution, interfacial tension calculation, solvent accessible surface area calculation, hydrogen bond analysis, radial distribution function and effective alkyl tail length can help us to understand the effect of molecular architecture of surfactant molecules on the interface performance.

## **COLL 280**

### **Computational investigation of CO<sub>2</sub>/CH<sub>4</sub> separation in novel mechanically robust 3D graphene-supported ionic liquid membranes**

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Porous 3D graphene (3DGr) is an unconventional support material for supported ionic liquid membranes (SILMs) with superior mechanical properties, as confirmed by recent molecular dynamics (MD) simulations. In this work, we used MD/Grand Canonical Monte Carlo (MD/GCMC) simulations to investigate the CO<sub>2</sub>/CH<sub>4</sub> separation performance of both pristine 3DGr and 3DGr-supported IL ([EMIM][TF<sub>2</sub>N]) membranes as a function of pressure, with bulk ionic liquid (IL) selected as benchmark. We calculated the ratios of Henry's law constants in single-gas simulations and CO<sub>2</sub>/CH<sub>4</sub> membrane selectivities in gas pair (1:1 molar ratio) simulations as a function of pressure. Once our computational data was validated with experiments, we found that the gas separation performance of 3DGr-supported IL (3DGr-IL) membranes to be very promising. For example, we observed a slightly higher selectivity for the 3DGr-IL membrane than for the benchmark membrane (selectivity of 10-15 in the pressure range of 0.25-10 bar). In short, our results indicate that the gas separation performance of 3DGr-supported IL membrane matches or exceeds that of the benchmark membrane, i.e., bulk IL. Given the excellent mechanical properties of 3DGr, we, therefore, propose the use of this unconventional material as a promising mechanically robust support for IL membranes with excellent CO<sub>2</sub>/CH<sub>4</sub> separation performance.

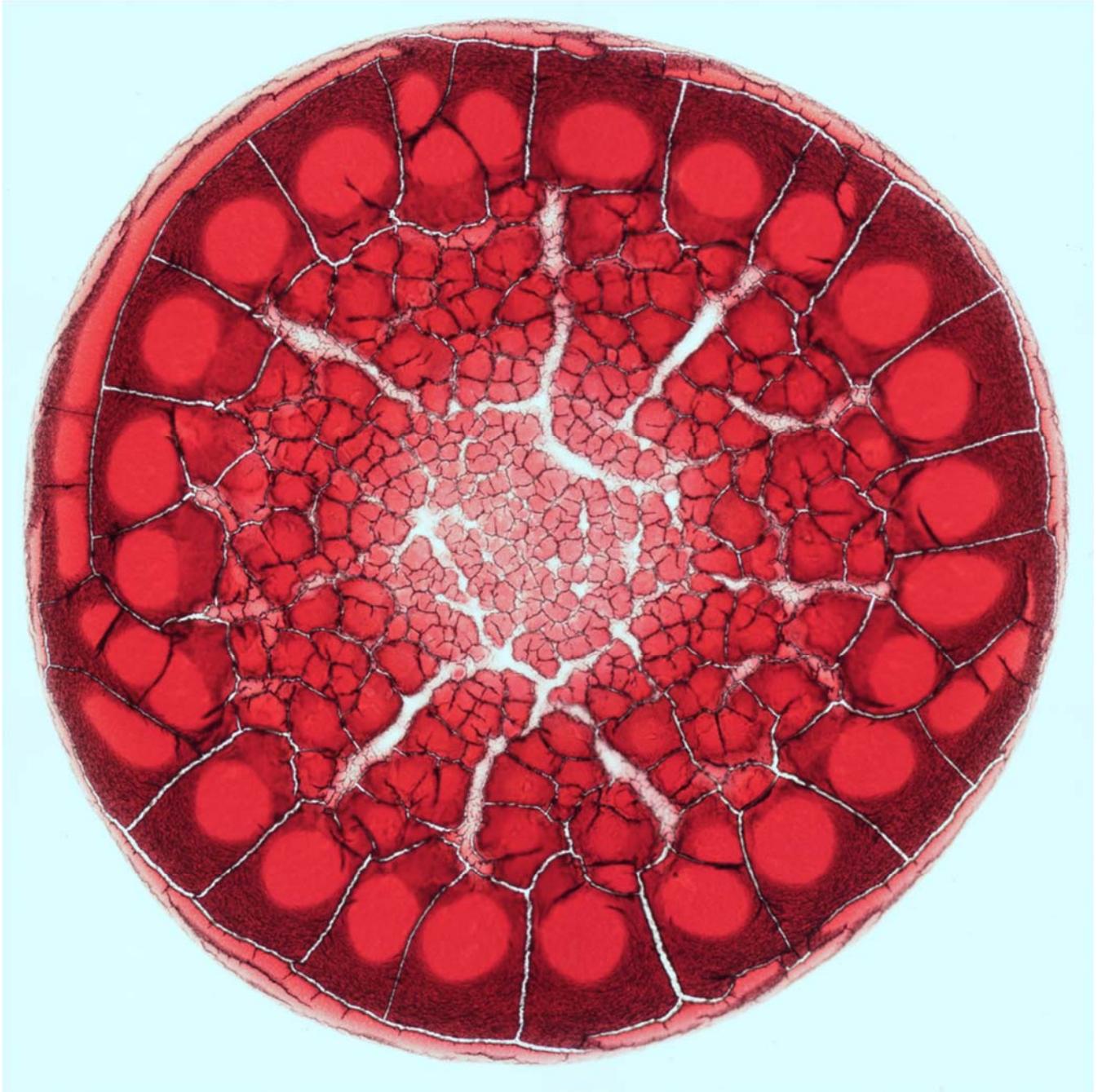
**Modelling patterns in dried blood drops for diagnostics**

**Michael Hertaeg**<sup>1</sup>, *michael.hertaeg@monash.edu*, **Alexander F. Routh**<sup>3</sup>, **Rico F. Tabor**<sup>2</sup>, **Gil Garnier**<sup>1</sup>. (1) Chemical Engineering, Monash University, Melbourne, Victoria, Australia (2) Chemistry, Monash University, Melbourne, Victoria, Australia (3) Dept of Chemical Engineering and Biotechnology, University of Cambridge, Cambridge, United Kingdom

The coffee ring effect can be observed in many particle suspension systems. This is where the constituents of a pinned sessile drop are deposited preferentially around the circumference of a stain left after the liquid has evaporated. This phenomena has been shown to be highly dependent on the initial particle concentration and contact angle of the suspension. The effect is also seen in the dried deposits of whole blood. As low red cell concentration is a symptom of some types of anaemia, drying blood samples on a range of surfaces and visually comparing the patterns formed is proposed to be a new rapid, low-cost diagnostic tool.

In the first part of this presentation the effect of the independent variables affecting coffee ring formation with blood is demonstrated experimentally. In the second, a fluid mechanics model of the process is presented.

During blood drop drying, two phases are present: a central fluid region and a deformable porous outer region where the particles (red blood cells) have consolidated. As drying continues this inner region shrinks and the outer region grows. A numerical model was developed to predict the evolution and final height profile in thin droplets containing flexible particles. The model is based on coupling lubrication theory assuming infinite vertical diffusion in the centre region, with a Darcy's law continuum model in the outer region.



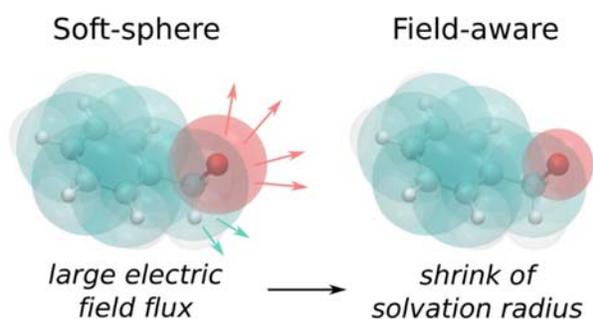
Blood drop dried on glass

**COLL 282**

**Field-aware interfaces in continuum solvation**

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The continuum embedding approach has seen a rapid influx of interest from the condensed matter community in recent years. Within this field, many successful models have focused on providing a transferable representation of the interface that characterizes the continuum region. We present here a number of additions that aim to provide an implicit consideration of charged species and compounds with highly polarized regions, in an effort to further expand on the capabilities of continuum models. These advances follow recent approaches of using the electric field as an effective proxy for the localized charge surrounding a specific region. This “field-aware” approach is applied first to the recently proposed soft-sphere continuum solvation (SSCS) method. The radius of each soft-sphere composing the interface is allowed to readjust as a function of the value of the field flux through its surface. The self-consistent continuum solvation (SCCS) method is modified in a similar manner; here, the interface is directly shaped by the electronic density, which is temporarily scaled by the electric field component perpendicular to the density gradient. In both cases, a complex dependence of the interface function on both the electronic and ionic degrees of freedom of the solute is introduced. Analytic derivatives of the new interface are thus implemented during optimization procedures (SCF and geometry optimization). Application of the field-aware procedure to molecular compounds showing pathological behaviors with the standard SSCS approach show that significant improvements can be achieved by specifically tuning the newly introduced parameters.



Field-aware effect on the soft-sphere interface

## COLL 283

### Molecular dynamics simulations of CO<sub>2</sub> foam film stabilized by different kind of surfactants

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There have been many experimental and simulation studies on stability of CO<sub>2</sub> foam, as it can be used for underground storage of greenhouse gas CO<sub>2</sub> while enhancing oil recovery. However, poor stability of CO<sub>2</sub> foam film is a critical challenge which limits its wide applications. It is necessary to understand the adsorption state and molecular behavior of surfactants at CO<sub>2</sub>/water interface for studying the microcosmic mechanism of CO<sub>2</sub> foam stability. Meanwhile, in order to improve the field application of CO<sub>2</sub> foam, it is also significant to explore the influence of temperature and pressure. The forming process and stability mechanism of CO<sub>2</sub> foam film at molecular level can be obtained by molecular dynamics simulation.

This research includes:

- (1) The isobaric-isothermal ensemble (NPT) equilibrium simulation system of CO<sub>2</sub> foam film under high temperature and high pressure conditions is established (initial and final configuration is shown in figure.1 ), and the interfacial tension (IFT) of CO<sub>2</sub>/surfactant/water system is calculated by isobaric-isothermal-isointerface-area ensemble (NPnAT) simulation to evaluate the stability of CO<sub>2</sub> foam film.
- (2) Analyze molecular configuration of different kind of surfactants (includes anionic, cationic, nonionic and zwitterionic) adsorbed at the interface of CO<sub>2</sub> and water, compare their differences to explore the microscopic mechanism of stabilizing CO<sub>2</sub> foam.
- (3) Analyze the influences of temperature and pressure on the equilibrium adsorption state and molecule behaviors of CO<sub>2</sub> foam film stabilized by different surfactants.

Through the works mentioned above, we got these conclusions:

- (1) Under high surfactant concentration, surfactant molecules could form tight monolayer to reduce interfacial tension (IFT) of CO<sub>2</sub>/water interface, and hinder the diffusion of CO<sub>2</sub> molecules through water layer, to stabilize foam film.
- (2) With temperature increase, interfacial tension rise and CO<sub>2</sub> molecules move rapidly, foam become unstable.
- (3) high pressure is conducive to foam stability, as molecules move slow and interfacial tension is low.

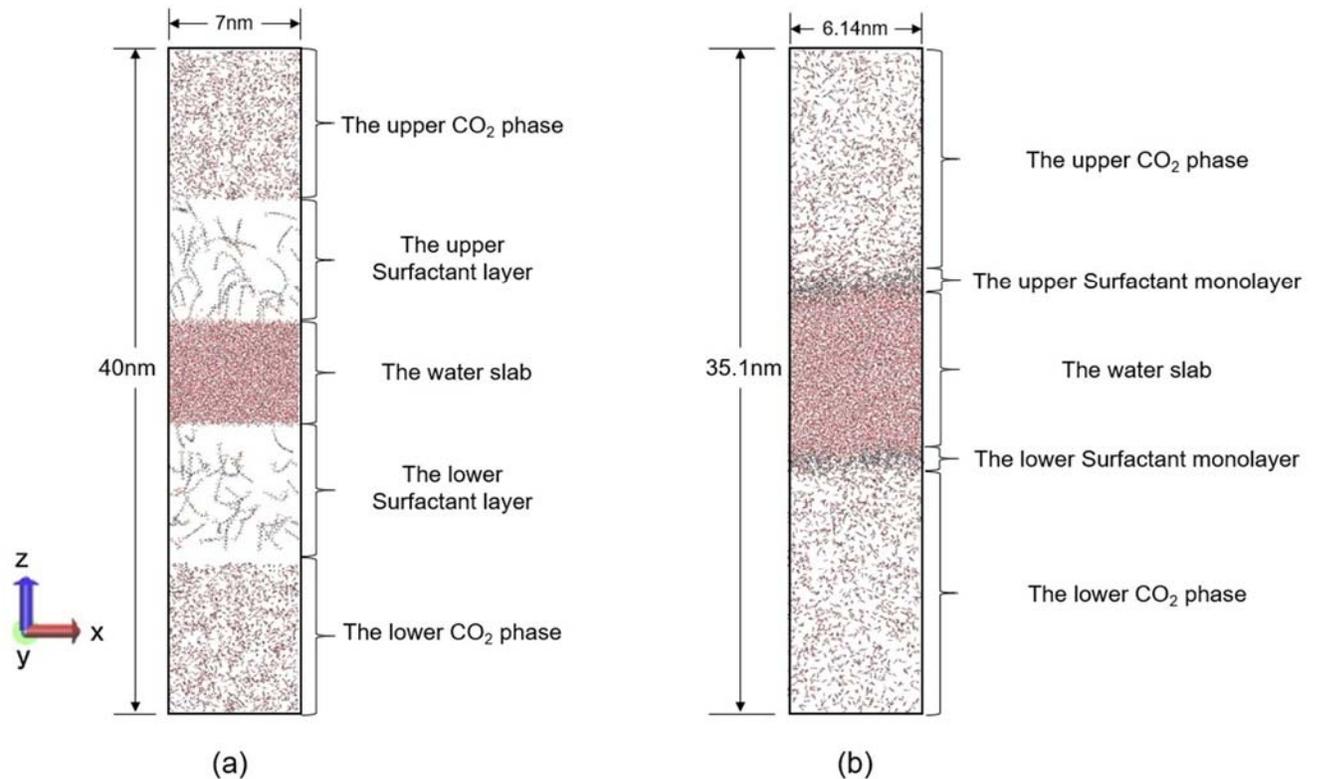


Figure.1. Molecular configuration of CO<sub>2</sub> foam stabilized by surfactant sodium dodecyl sulfate (a) initial configuration (b) final configuration.

## COLL 284

### Molecular dynamics study on the micellization of carboxylate surfactants

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From the time the molecular dynamics (MD) simulation technique was first applied to surfactant assemblies, numerous studies on surfactants with computational tools has been carried out. The size-dependent free energy of association for micelle-forming surfactants controls the critical micelle concentration and the concentration-dependent distribution of micelle sizes. We have developed an analysis approach (PEACH method) to calculate cluster free energy profiles from cluster statistics of molecular dynamics simulations with only one or two micelles.

This research project aims to investigate into the fundamental thermodynamics of the micellization process of several typical fatty acid surfactants. Regarding this type of surfactants, experimental results from different techniques have shown inconsistent or contradictory properties of average micelle sizes, critical micelle concentration and

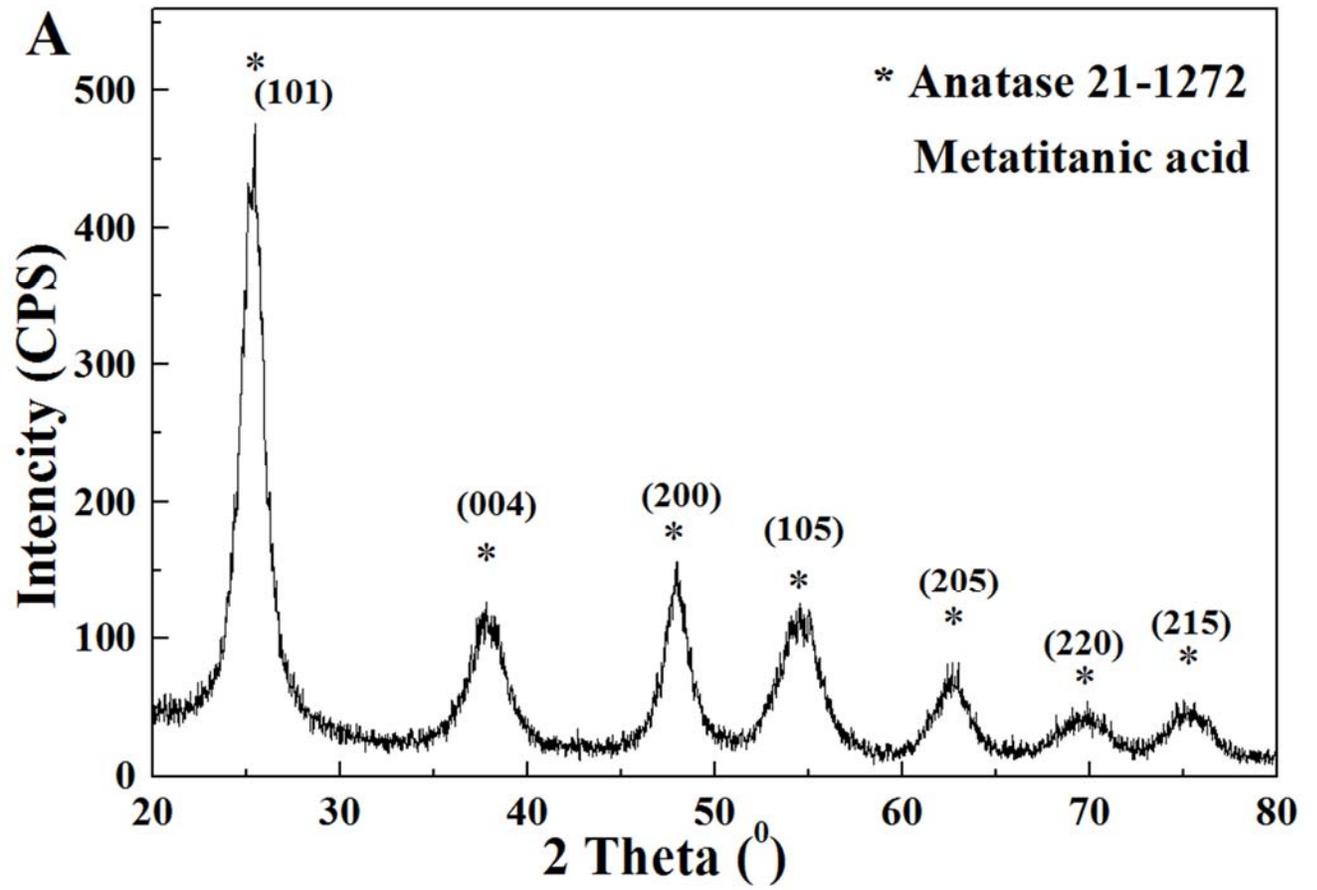
counterion binding affinity. In this project, we simulate the equilibrium behaviors of octanoate/decanoate micelles with Na<sup>+</sup> and K<sup>+</sup>. Using PEACH, we obtained the cluster free energy profiles with respect to cluster sizes and number of bound counterions. Free energies of assembly were consistent with simple phenomenological models, whose parameters were used to generate enthalpograms that are comparable to experimental results from isothermal titration calorimetry (ITC). By taking into account the full range of clusters formed, the phenomenological models may prove effective in resolving experimental inconsistencies.

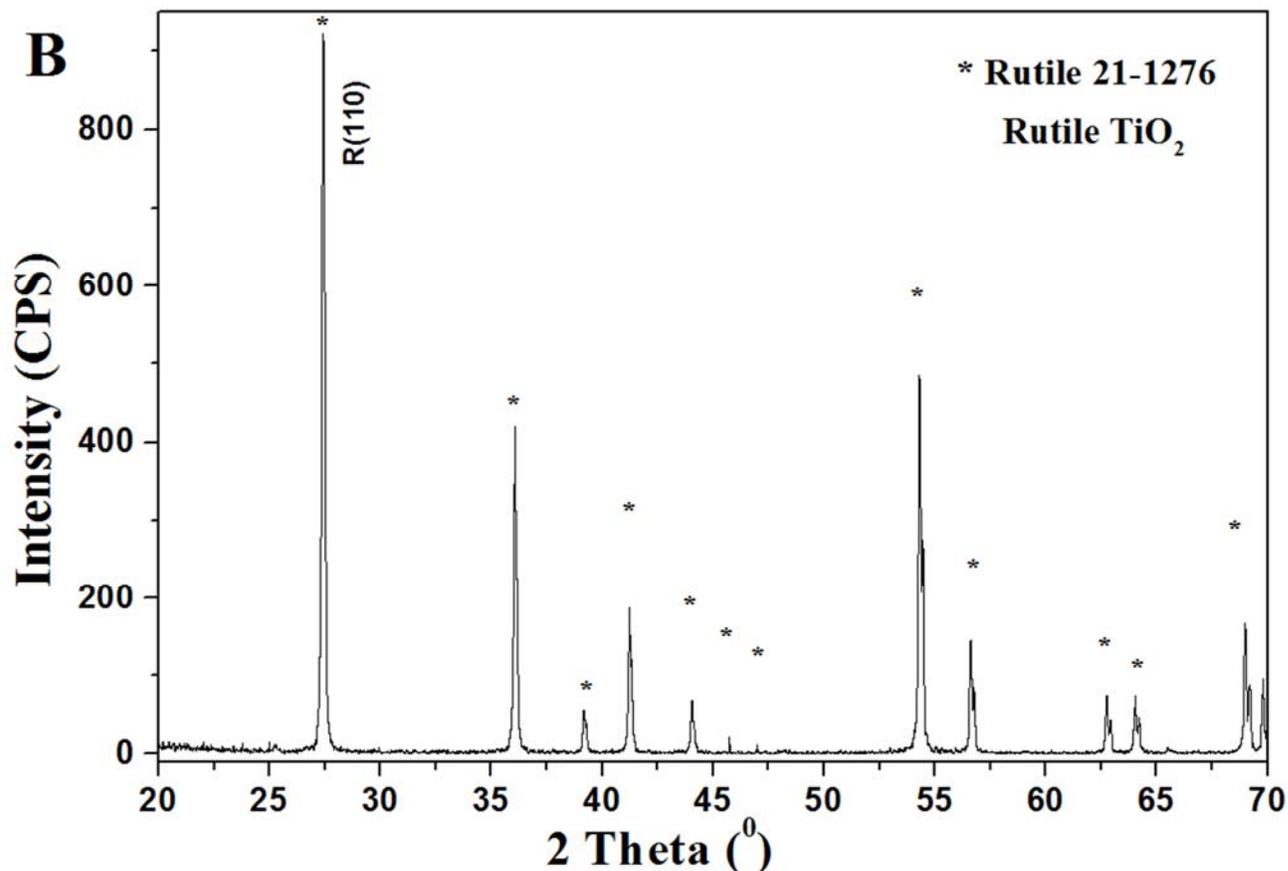
## **COLL 285**

### **Particle size distribution characterization conditions for metatitanic acid by photon correlation spectroscopy**

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The particle size and its distribution of metatitanic acid determines the particle size distribution and pigment properties of titanium dioxide pigment, it is great important to characterize the particle size distribution of metatitanic acid particles. Using metatitanic acid slurry hydrolyzed from industrial low concentration titanyl sulfate solution via short sulfate process as research object, the effects of dispersing media, dispersant and dispersing conditions on the particle size distribution by photon correlation spectroscopy were investigated. Proper dispersion media, dispersant and its concentration, ultrasonic vibration would all improve the Zeta potential of metatitanic acid particles, enhance the repulsion between particles and strengthen particle dispersion. The optimal dispersion conditions for metatitanic acid were slurry dosage of 0.044 g, 50 ml of 0.05% aqueous sodium hexametaphosphate solution, mechanical stirring time of 2 min, ultrasonic vibration time of 5 min. After thorough dispersion, the particle size distribution of metatitanic acid must be determined immediately.





COLL 286

### Synthesis and characterization of L1<sub>0</sub> bimetallic and trimetallic nanocrystal catalysts for electrocatalytic oxygen reduction reaction

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The proton exchange membrane fuel cell (PEMFC) is a critical technology to enhance the clean, sustainable production of energy by converting fuels directly into electricity. However, practical application remains challenging because of the high cost and low durability of the cathode catalysts that perform oxygen reduction reaction (ORR). Efforts have been placed on the study of alloys that adopt an intermetallic structure to reduce the usage of precious metal, improve the ORR reaction rate, and catalyst stability in a

corrosive environment. The addition of a third element to form ternary catalysts further shows improved ORR reaction rates and promotes the structural transition from disordered to ordered intermetallic structure with reducing transition temperature and inhibiting particle grain growth. In this contribution, monodisperse bimetallic (PtCo) and trimetallic (PtCoAg) nanocrystals (NCs) with tunable compositions of Co and Ag are synthesized *via* solvothermal methods. This synthetic method allows good control over particle compositions with homogeneity achieved at the atomic scale. The transformation from A1 to L1<sub>0</sub> phase was achieved via thermal annealing using a conventional oven and the structure of catalysts was characterized by a variety of techniques, including transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy in high-angle annular dark-field scanning transmission electron microscopy (STEM-EDS), small-angle X-ray scattering (SAXS), X-ray diffraction (XRD), and inductively coupled plasma-optical emission spectrometry (ICP-OES). The correlation between compositions and the degree of ordering was established and further correlated with the ORR activities.

## **COLL 287**

### **Docetaxel nanomedicine based on biologic-responsive polymers for glioblastoma chemotherapy**

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Glioblastoma is among the brain cancers with highest prevalence and mortality worldwide. Docetaxel is one of the most effective chemotherapeutics against glioblastoma, although it presents pharmacokinetic constraints mainly due to its low solubility and poor blood-brain barrier (BBB) permeation. This project proposes a biologic-responsive nanomedicine to circumvent these inadequacies based on docetaxel-loaded nanoparticles for glioblastoma treatment. The developed nanomedicine comprises a poly(lactic-co-glycolic) acid (PLGA) core and a polyethylene glycol (PEG) shielding of long- and short-length. The long-length PEG possesses an Angiopep-2 moiety for BBB targeting (low-density lipoprotein receptor) and is able to dissociate in the acidic pH of BBB endosomes, hence sterically de-protecting the short-length PEG coupled with L-histidine for further glioblastoma targeting (L-type amino acid transporter 1) upon brain arrival. The chemical synthesis achieved a total purity value of around 70% and 90% for the long- and short-length PEG, respectively, as demonstrated by different characterization techniques such as nuclear magnetic resonance (NMR), Fourier-transform infrared spectroscopy (FTIR), gel permeation chromatography (GPC) and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS). Preliminary work has focused the production of docetaxel-loaded nanoparticles post-polymer synthesis through a microfluidic technique using 80%, 10% and 10% of PLGA, long- and short-length PEG, respectively. Nanoparticles' physicochemical characterization has demonstrated around 100 nm average size and

0.1 polydispersity index. Overall, the current need to accelerate drug delivery to glioblastoma, bypassing the BBB and targeting tumor tissue of brain, places this system in a privileged position in the field of translational nanomedicines. This work also lays foundation for future biologic-responsive delivery of other therapeutics to a range of pathologies.

## **COLL 288**

### **Influence of chemically-functionalized gold nanoparticles on emulsions of thermotropic liquid crystals**

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Past studies have reported that confinement of LCs within micrometer-sized droplets dispersed in aqueous phases (e.g., LC-in-water emulsions) provides a versatile platform for the design of droplet-based LC sensors that can respond sensitively to the presence of amphiphilic analytes present in aqueous environments. Here, we report studies aimed at characterizing the adsorption and interaction of chemically-functionalized gold nanoparticles (AuNPs) with LC emulsions as a potential approach to design responsive materials with (i) tunable sensitivity to aqueous analytes and (ii) improved colloidal stability. Our approach makes use of AuNPs functionalized with binary mixtures of self-assembled monolayers of alkanethiols displaying polar (i.e., hydroxyl or amine) and non-polar (methyl) groups to trigger changes in LC droplet configurations that can be readily observed using polarized light. Our results show that these AuNPs trigger bipolar-to-radial ordering transitions in LC droplets in ways that depend upon nanoparticle surface composition and the identity and charge state of the polar functional groups. Additional studies have focused on characterizing the extent to which the adsorption of AuNPs to LC droplet interfaces can confer colloidal stability to the droplets and the preparation of LC-in-water emulsions with enhanced colloidal stability, which could facilitate their application as droplet-based sensors in complex media, including cellular environments.

## **COLL 289**

### **Speciating Ag(I) and AgNPs in the leachate of AgNP-impregnated fibers**

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Silver nanoparticles (AgNPs) are one of the most common engineered nanomaterials found in consumer products. Silver's antimicrobial and antibacterial properties make AgNPs a desirable material to incorporate into products in the fields of medicine, food

packaging, cosmetics, and textiles. AgNPs incorporated into textiles are currently of special interest, as the fate of these AgNPs in environmental and biological systems once released from the textile is poorly characterized. In order to better understand how these AgNPs will interact with environmental and biological systems, it is important to understand the release mechanism of silver from such fabrics; specifically, whether Ag(I), AgNPs, or a combination of both are released and the release rate of each species. It has been well documented that these variables change from product-to-product, depending on how the AgNPs were originally incorporated into the textile. The unpredictability of silver release, coupled with the increase in AgNP consumer products available every year, necessitate the development of cheap and efficient analytical methods to characterize silver release in order to better understand the potential environmental and biological implications of such release.

Current techniques that analyze silver release from nano-enabled products are often expensive, require extensive sample preparation, and cannot simultaneously determine the amount of Ag(I) and AgNPs present. However, by coupling two inexpensive and efficient electrochemical techniques linear sweep stripping voltammetry (LSSV) and particle-impact voltammetry (PIV) to an orthogonal technique, UV-Vis spectroscopy, these issues can be addressed. Electrochemistry is an extremely powerful technique to analyze AgNPs in solution. In this work, we demonstrate that a novel technique (LSSV-PIV/UV-Vis) is able to simultaneously determine the concentrations of Ag(I) and AgNPs in the leachate of AgNP-impregnated textiles exposed to simulated sweat with comparable limits of detection to techniques currently used in the field.

## **COLL 290**

### **Interactions of $\beta$ -cyclodextrin modified gold nanoparticles with human serum albumin at single molecule level**

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Gold nanoparticles (AuNPs) have remained a research topic because of their extensive range of applications which includes biosensing, cancer therapy, and drug delivery. In biological applications one of the most pertinent interactions is the corona formation (proteins/NPs complex). This project focused on studying the interactions of human serum albumin (HSA), the most abundant protein in human blood, with AuNPs using fluorescence correlation spectroscopy (FCS). Atto655 was used as a probe, because its absorption and emission are in the red region, away from AuNP plasmonic absorption. We proposed that through FCS detailed information could be obtained about the interaction of HSA with AuNP and how these interactions change with NPs' surface modification at the single molecule level. Results demonstrate that the emission of Atto655, i.e. the average number of molecules ( $\langle N \rangle$ ) and the brightness, decreases in the presence of  $\beta$ -cyclodextrin-AuNP (bCDAuNP) and Citrate-AuNP (cAuNP). Addition of HSA (0-100nM) to Atto655:bCDAuNP induces a recovery of free  $\langle N \rangle$ , while for Atto655:cAuNP remains low. When HSA is added to polyethylene glycol (PEG) modified AuNPs,  $\langle N \rangle$  remains constant. Thus, the information gathered at single molecule level

provides a better understanding of the binding mechanism of macromolecules to AuNPs.

## **COLL 291**

### **Self-organization and swarm behavior in active matter: Combined computational-experimental analysis of the intelligence-information interplay**

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Swarm behavior is a nonequilibrium phenomenon that takes place in a wide range of biological and natural systems. Swarming involves the emergence of intelligent collective behavior and leads to highly energy-efficient assemblies. Here, we combine computational and experimental methods to unravel and control self-organization and swarming in active matter systems of light-activated and shape-changing colloidal particles. Using a multi-scale simulation framework to model the assembly process in active matter and recent advances in the determination of nonequilibrium entropies, the computational analysis sheds light on the intelligence-information link in active assemblies. This is achieved through the calculation of an entropy characteristic of the configuration of the assembly (degree of organization) through machine learning and pattern recognition, and of an entropy measuring the information contained in the assembly (bits or shannons) through a Kolmogorov complexity approach. The assembly rules identified here will provide the blueprint for a bottom up approach to micro- and nanorobotics, with active particles swarming and forming large assemblies to perform macroscopic tasks.

## **COLL 292**

### **Quasi-spherical gold nanoparticles synthesis and applications**

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Nanoparticles exhibit different properties based on their chemical composition, shape, and size. Uniform, quasi-spherical gold nanoparticles were synthesized using a modified Frens method with chloroauric acid and trisodium citrate and glutathione as ligands. The goal of this research was to study the optical properties of these gold nanoparticles and utilize them for optical trapping studies. During the synthesis, trisodium citrate concentration, tris buffer concentration, and temperature were manipulated to stabilize the nanoparticles, increase uniformity, and decrease particle size. In addition, glutathione (GSH) was used as a second ligand to further decrease the

nanoparticle size. The results of the work as a function of GSH, citrate ion and tris concentrations will be presented.

## **COLL 293**

### **Photolysis of organic dyes at the polymeric colloidal-aqueous interface**

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Photo-degradation is an important process that can chemically transform and thereby influence the distribution of harmful compounds in natural waters. Organic contaminants are not only dissolved in the aquatic medium but can also be adsorbed onto the surfaces of colloids, which can include particulate natural organic matter (NOM). While photolytic investigations of organic dyes in bulk aqueous samples are ample, knowledge of photolysis of organic dyes physisorbed onto polymeric particles suspended in aqueous solution is lacking. Fundamental questions, such as what is the influence of adsorption strength (physi- vs. chemi- sorption), surface population, and possible orientation of the adsorbate on the rate of light mediated degradation, demand answers. In this study, we used a surface selective laser technique, namely, second harmonic generation (SHG) spectroscopy, to investigate photo-degradation of malachite green (MG) adsorbed at the surface of carboxyl functionalized latex particles. Our results demonstrate that MG, an environmental contaminant, exhibits a markedly different photolytic rate at the particle-aqueous interface. The photolytic rate of MG upon UV exposure appears to be faster at the surface than when it is dissolved in aqueous solution. Surface coverage dependent rate studies also demonstrate possible influence of re-adsorption of MG from the aqueous solution. The surface SHG versus bulk UV-Vis rate studies, along with mass spectrometry data, indicate that de-methylated photo-products show surface proclivity and can have an impact on the overall surface photo-degradation rate. It will be shown that SHG can serve as a powerful technique to elucidate NOM surface mediated photolytic reactions. SHG studies on distinct dye molecules also provide the potential to decipher the influence of molecular orientation on surface photolysis.

## **COLL 294**

### **Investigating lattice strain impact on the alloyed surface of small Au@PdPt core-shell nanoparticles**

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States (4) ShanghaiTech, Shanghai, China (5) Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts, United States

We investigated lattice strain on alloyed surfaces using ~10 nm core-shell nanoparticles with controlled size, shape, and composition. We developed a wet-chemistry method for synthesizing small octahedral PdPt alloy nanoparticles and Au@PdPt core-shell nanoparticles with Pd-Pt alloy shells and Au cores. Upon introduction of the Au core, the size and shape of the overall nanostructure and the composition of the alloyed PdPt were maintained, enabling the use of the electrooxidation of formic acid as a probe to compare the surface structures with different lattice strain. We have found that the structure of the alloyed surface is indeed impacted by the lattice strain generated by the Au core. To further reveal the impact of lattice strain, we fine-tuned the shell thickness. Then, we used synchrotron-based x-ray diffraction to investigate the degree of lattice strain and compared the observations with the results of the formic acid electrooxidation, observing a volcano relationship between peak current density and lattice strain.

## **COLL 295**

### **Solid-phase synthesis as a strategy to investigate protein adsorption to gold nanoparticles**

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Bioconjugation of antibodies onto gold nanoparticles is of great interest due to the implications on novel, cost-effective bioanalytical assays. Critical to the success of such assays is the immobilization of antibody to reliably synthesize stable conjugates. Understanding this fundamental interaction between antibody and gold nanoparticle is essential for successful downstream applications. The effects of pH, ionic strength, and protein concentration are factors that affect the antibody loading, orientation, and overall conjugate stability. However, electrostatic bridging of nanoparticles by protein at certain pHs and moderate to high ionic strength restricts mechanistic studies of protein adsorption to a narrow set of solution conditions. Here we explore solid-phase synthesis as a novel pathway to systematically investigate the adsorption of antibodies to AuNPs. With this approach, gold nanoparticles are immobilized on an APTES-modified glass surface prior to the addition of antibody to limit the possible modes of aggregation and allow for further studies of incubation conditions inaccessible by conventional synthetic pathways. Protein adsorption to AuNPs is systematically investigated as a function of solution pH and ionic strength, and the resulting bioconjugates are characterized by nanoparticle-tracking analysis (NTA), dynamic light scattering (DLS), and UV-vis extinction spectrophotometry. Experimental results show an excitingly well-behaved solid-phase conjugate that may be synthesized in conditions that would otherwise lead to premature aggregation in conventionally synthesized conjugates.

## COLL 296

### **Durable lubricant-infused ZnO nanowire surfaces via capillary rise infiltration (CaRI)**

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Slippery lubricant-infused porous surfaces (SLIPS) can be used in a wide range of applications such as self-cleaning windows, anti-icing surfaces, anti-biofouling, and anti-corrosion coatings. For SLIPS surfaces to be used more widely in practical applications, it is critical to enhance the stability of lubricant layer, while maintaining scalable manufacturability and minimizing potentially negative environmental impacts. In this study, we describe a robust method for the fabrication of durable SLIPS by inducing the capillary rise infiltration of silicon oil into honeycomb-like micropatterns of ZnO nanowires (NWs), which exhibit self-cleaning and self-healing properties. The honeycomb-like micropatterns of ZnO NWs, which formed via a capillarity-driven coalescence of long nanowires during drying step, serve as the porous template for wicking and retaining of are used as porous substrates to the silicon oil through capillary force. The effects of nanowires orientation on the infiltration rate of silicon oil as well as the wetting and the mobility of water droplets are also investigated. The as-prepared SLIPS can exhibit self-healing properties against small surface damage due to the self-recovery property of the oil. This study presents a new way of using capillarity to create durable SLIPS for self-cleaning and self-repairing properties.

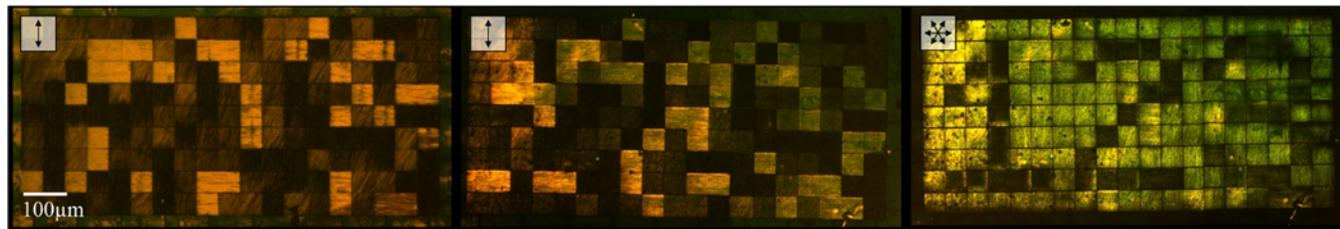
## COLL 297

### **Higher-order molecular and alignment control of self-assembling donor-acceptor columnar liquid crystals (DACLCs)**

**Harper Wallace**, [wallac\\_h1@denison.edu](mailto:wallac_h1@denison.edu), **Joseph J. Reczek**. Chem Dept, Ebaugh Labs, Denison University, Granville, Ohio, United States

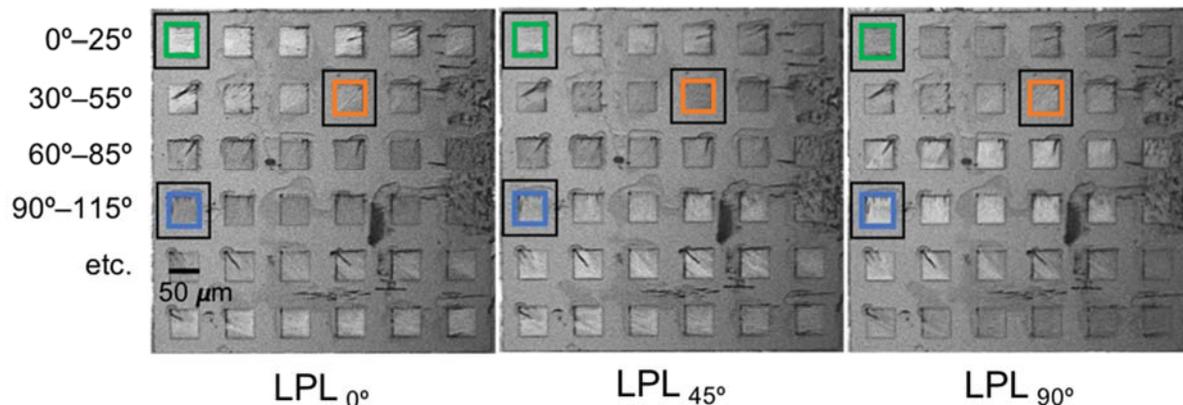
Functional control over the orientation of liquid crystals has become an operating principle for modern computer-display technologies, and it promises to play an important role in the development of novel organic electronics and wearables. In particular, emerging chemistries involving the self-assembly of organic-based molecular components have the potential to significantly increase versatility and function of future technologies. Donor acceptor columnar liquid crystals (DACLCs) are one such class of versatile, self-assembling liquid crystals. We have previously shown that thermal-gradient-based alignment techniques can achieve a fine degree of control over the orientation of DACLC columns in films. In addition, well-aligned regions of DACLC films exhibit strong dichroism when exposed to linearly polarized light. Here, we illustrate how the combination of these functional properties offers great potential for DACLC applications in data storage and encryption, based on optical readout. In addition, we

discuss the synthesis of core-asymmetric component molecules and their incorporation into new DACLC materials capable of higher-order thermal and magnetic-field-based control over molecular orientation and material alignment.

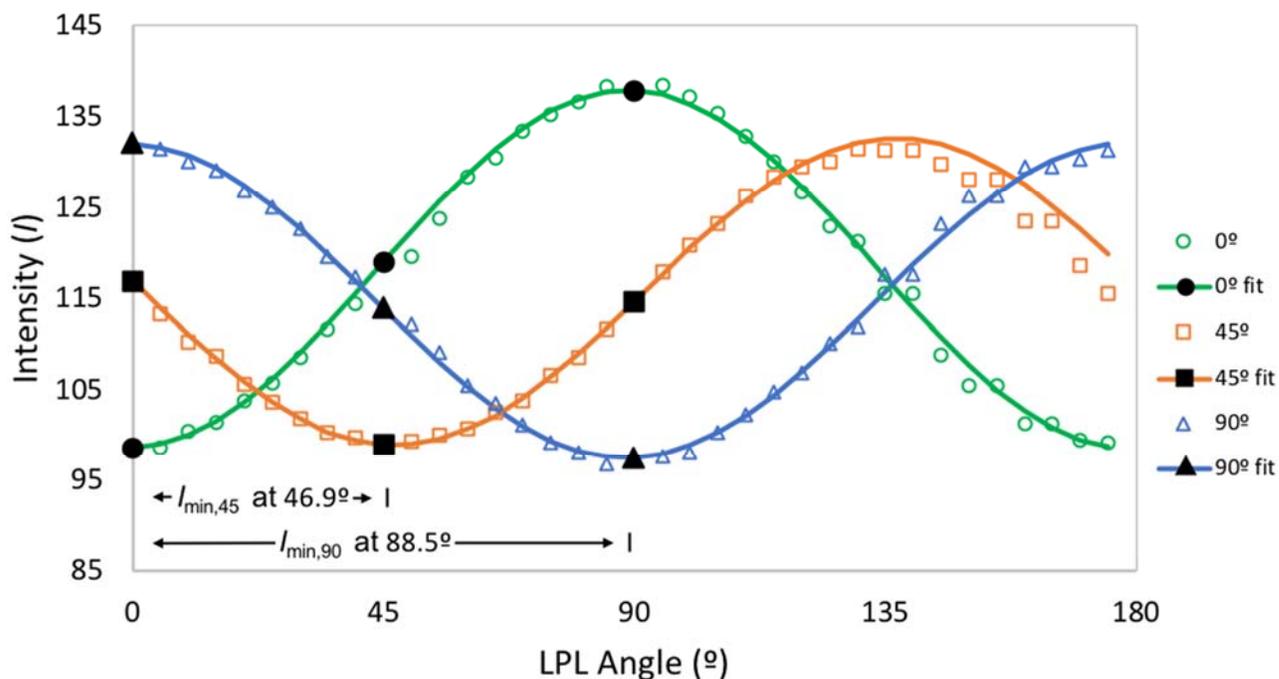


Two-film overlay encryption application.

### Test cells written in 5° increments



### Cell alignment readout using three LPL images



Optical data readout in base-19.

### COLL 298

### Metal mediated polymerization of various rhodanines to create new morphologies

**Gurjeet K. Longia**<sup>1</sup>, longiag1@wpunj.edu, **Moni Chauhan**<sup>2</sup>, **Saleh Jaser**<sup>2</sup>, **Bhanu P. Chauhan**<sup>1</sup>. (1) Department of Chemistry, William Patterson University, Wayne, New

Jersey, United States (2) Chemistry, Queensborough Community College of CUNY, Staten Island, New York, United States

Rhodanine is known to possess antimicrobial, antibacterial, and antiviral advantages and can be used in many different applications. On the other hand, very little is known about its polymeric analog polyrhodanine (pR). It is expected that polyrhodanine (pR), a conjugated polymer, will inherit medicinal properties of rhodanine along with electrical and optical properties of conjugated polymers.

In our recent work,<sup>a</sup> we explored the polymerization of rhodanine with copper acetate and were surprised to learn that very rich and unique materials such as core-shell micro- and nano-particles can be generated under appropriate conditions. Such core-shell structures have a large surface area, and tunable particle diameter, which makes them good candidates for applications in medicine, biology and industry. This has led us to systematically investigate the reactivity of various rhodanine precursors with copper-based complexes.

In this presentation, we will disclose the results of our exploration of the reactivity of complexes with four derivatives of rhodanine, namely 3-aminorhodanine, 3-methylrhodanine, 5-(4-dimethylbenzylidene) rhodanine and rhodanine-3-acetic acid. To our surprise, we found that different morphologies could be obtained under different reaction conditions. By reacting different copper complexes with different derivatives of rhodanine, we were able to synthesize morphologies such as spherical, core-shell, and rods. These reactions were carried out in ethanol, and monitored at different temperatures. The spectroscopic analysis of the resulting materials was carried out using UV-Vis, FT-IR, SEM and TEM techniques. In addition, their stability, solubility and optical properties were also investigated.

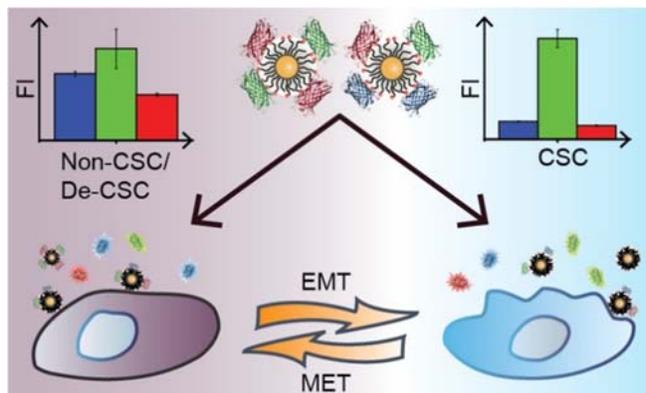
## **COLL 299**

### **Rapid phenotyping of cancer stem cells using multichannel nanosensor arrays**

*Aritra Nath Chattopadhyay<sup>1</sup>, aritrathch@umass.edu, Yingying Geng<sup>1</sup>, Hira L. Goel<sup>2</sup>, Arthur Mercurio<sup>2</sup>, Vincent M. Rotello<sup>1</sup>.* (1) Chemistry, University of Massachusetts Amherst, Amherst, Massachusetts, United States (2) Molecular, Cell and Cancer Biology, University of Massachusetts Medical School Worcester, Worcester, Massachusetts, United States

Cancer stem cells (CSCs) contribute to multidrug resistance, tumor recurrence and metastasis, making them prime therapeutic targets. Their ability to differentiate and lose stem cell properties makes them challenging to study. Currently, there is no simple assay that can capture and trace the dynamic phenotypic changes on the CSC surface. Here, we report rapid discrimination of breast CSCs from non-CSCs using a nanoparticle-fluorescent-protein based sensor array. This nanosensor uses a hypothesis-free, signature-based approach to identify complex bioanalytes, such as phenotypes of CSCs. Through selective interactions with the target analyte, a unique fluorescence response signature was generated and further used for rapid

discrimination of CSCs from non-CSCs, as well CSCs that had differentiated *in vitro* in two breast cancer models. In this work, we demonstrate the feasibility of using the nanosensor to phenotype CSCs and monitor their fate. Furthermore, this approach provides a novel area for therapeutic interventions against these challenging targets.



## COLL 300

### Closer look at confined water: Use of Overhauser Dynamic Nuclear Polarization to study nanoscale water dynamics in aerosol-OT reverse micelle model systems

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Experimental studies of interfacial water are complicated by the inescapable presence of bulk water. Over the past decade, Overhauser Dynamic Nuclear Polarization (ODNP) has demonstrated remarkable aptitude for overcoming this problem. ODNP relies on chemistry to place a spin probe in a known location and on spin physics to read out the dynamics of water within 5-15 Å of that location, thereby extracting the interfacial water signal from the bulk. As a simple but important model system, we have selected AOT (Aerosol-OT, dioctyl sulfosuccinate sodium salt) reverse micelles (RMs) employing ODNP with the amphiphilic spin label CAT-16 (4-(N,N'-dimethyl-N-(hexadecyl)) ammonium- 2,2',6,6'-tetramethylpiperidine-1-oxyl salt) to extract the interfacial water signal and TEMPO-sulfate to extract the RM core water signal. These results will offer a unique perspective on nanoscale water dynamics and provide benchmark measurements important to ODNP analysis of confined water in other, more complex material systems with less defined morphology. Here we present the development of a home-built NMR spectrometer and probe designed for ODNP measurements, as well as the design of a Python library that permits facile implementation of complex pulse sequences. We demonstrate the utility of modern NMR relaxometry techniques, in

particular 2-Dimensional Inverse Laplace Transform (2D-ILT)  $^1\text{H}$  and  $^2\text{H}$  NMR relaxometry. In order to observe translational dynamics, ODNP requires an NMR resonance frequency near 15 MHz, an unusually low frequency that gives rise to obvious challenges for NMR sensitivity and for chemical shift resolution. Therefore, we demonstrate the ability of the 2D-ILT to separate water signal from that of other chemical species, and culminate with the first sensitive and selective measurements of ODNP inside the reverse micelle environment.

## **COLL 301**

### **Ligand substitution on colloidal quantum dots: Mechanistic study**

**Serena Rolland**<sup>1</sup>, *rollse01@luther.edu*, **Emily Reasoner**<sup>2</sup>, **Nathan Campbell**<sup>1</sup>, **Molly Wilker**<sup>1</sup>. (1) Luther College, Burnsville, Minnesota, United States (2) University of Wisconsin - Madison, Madison, Wisconsin, United States

There has been an increased emphasis on understanding nanocrystal surface chemistry and the way that these surfaces interact with diverse solvent environments for broadening applications. To control the surface chemistry of nanocrystals, a deeper understanding of the mechanism of ligand binding and the conditions that control the rate of this process are necessary. In this study, native ligands on CdSe quantum dots were substituted for shorter ligands using a series of bifunctional molecules with consistent thiol anchoring groups and changing secondary functional groups. As new ligands were added to the as-synthesized nanocrystal solutions, nanocrystal band-edge fluorescence was analyzed for evidence of quenching, which is characteristic of thiol ligand binding. The ligand exchange was more quantitatively measured by using  $^1\text{H}$  NMR. The  $^1\text{H}$  NMR peaks of the free ligand and the nanocrystal-bound ligand were monitored and used to calculate equilibrium constants. Further, the importance of the ligand deprotonation step in this mechanism was clarified by varying the pH of the ligand solutions before substitution. These results were used to gain insight into the ligand binding mechanisms and to understand how the strength of binding is influenced by ligand functionality.

## **COLL 302**

### **Optimization of polydopamine adhesiveness during thin film fabrication**

**Katherine R. Kolozsvari**, *koloz22k@mtholyoke.edu*, **Wei Chen**. Chemistry Dept, Mount Holyoke College, South Hadley, Massachusetts, United States

In the last decade, polydopamine (PDA) has become a subject of considerable scientific interest due to its universal adhesive properties. Dip coating, the traditional method of adhesion, does not allow for investigation into the adhesiveness of PDA at any given time point as the substrate and PDA solution are in continuous contact until a desired thickness of PDA is achieved. By utilizing a spin-coating method, we aim to determine how PDA adhesiveness changes over time. This would inform both dip coating and

other adhesion methods, such as spray coating, as researchers could allow a PDA solution to age to its optimal reactivity level before introducing it to substrates of interest. As PDA is a universal adhesive, we analyzed three different substrates, silicon dioxide, polydimethylsiloxane, and aminopropylmethylsiloxane-dimethylsiloxane copolymer to warrant that conclusions drawn are relevant to substrates with varying hydrophilicity and interactions with PDA. We also designed a modified dip-coating method which mimics the timing and DA concentration used in the spin-coating protocol to ensure that our results are widely applicable and not inherent to the spin-coating method itself.

## **COLL 303**

### **Atomic force microscopy (AFM) characterizations of semiconductor nanomaterials and solar cell electrodes**

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Scanning probe microscopy (SPM) represents a powerful tool in nanoscience and nanotechnology. As a popular SPM technique, atomic force microscopy (AFM) has been widely used in many fields including biology, chemistry, physics and materials. In this poster, we first introduce AFM working principle, including the different operational modes of AFM, how AFM can image surface morphology, and continue to describe the sample preparation and procedure of carrying out an AFM experiment. Then, we will present some experimental data on the characterization of different nanomaterials (such as NiWO<sub>4</sub>, TiO<sub>2</sub>) and solar cell electrodes using tapping mode AFM imaging technique. The high-resolution AFM images show that morphology and size of NiWO<sub>4</sub> nanomaterials can be determined. One experiment shows the ability of AFM in determining the hollow-sphere nanoparticles, which is difficult to be determined by other technique such as TEM. AFM also can help reveal different surface morphology before and after depositing TiO<sub>2</sub> and platinum nanomaterials on solar cell electrode surface.

## **COLL 304**

### **Elucidation of conditions for metastable poly(vinyl alcohol) thin films on polydimethylsiloxane substrates**

*Yuxin Jiang*, [jiang46y@mtholyoke.edu](mailto:jiang46y@mtholyoke.edu), *Wei Chen*. Chemistry Dept, Mount Holyoke College, South Hadley, Massachusetts, United States

The metastability of a thin film refers to the co-existence of stable and unstable states as a function of film thickness. The film is unstable at low film thicknesses, whereas at large thicknesses, the film is stable unless heterogeneous nucleation takes place. Poly(vinyl alcohol) (PVOH) thin films were chosen in this research as PVOH is a water-soluble, thermally stable, atactic yet semi-crystalline polymer. Polydimethylsiloxane (PDMS) polymer was chosen as the substrate material because it has an extremely low glass transition temperature and can modulate the extent of the instability that it exerts

on the PVOH thin films. Film-preparation methods included both static adsorption and dynamic spin coating. As-prepared and thermally annealed thin films were analyzed using contact angle goniometry, ellipsometry, optical microscopy, and atomic force microscopy. PDMS molecular weight, PVOH solution concentration, spin rate, and thermal annealing allowed the control of the PVOH film thickness and morphology. Among the parameters probed, PDMS molecular weight plays a substantial role in controlling the stability of the PVOH thin films. Metastability was observed when PDMS molecular weights between ~200 Da and ~2000 Da were employed.

## **COLL 305**

### **Preparation of stable poly(vinyl alcohol) thin films from aqueous solution on silicon wafer**

**Margaret Minett**, *minet22m@mtholyoke.edu*, **Wei Chen**. Chemistry Dept, Mount Holyoke College, South Hadley, Massachusetts, United States

An understanding of film stability is useful in crafting predictable film morphologies, which have a wide range of applications extending from self-assembled nanostructures to coatings for engineered materials. The stability of a thin film on a solid support is affected by the nature of the thin film and the underlying substrate as well as their interactions. Thin films are commonly prepared by depositing organic solutions of nonpolar materials onto silicon wafer (SiO<sub>2</sub>); aqueous solutions are rarely used due to the destabilizing polar interactions during solvent evaporation leading to dewetting. In this study, hydrophilic and semi-crystalline poly(vinyl alcohol) (PVOH) thin films from aqueous solution were fabricated on SiO<sub>2</sub> via spin casting. Experimental parameters including PVOH concentration, PVOH degree of hydrolysis, spin rate, and thermal annealing were probed. The PVOH thin films appeared to be continuous under all the conditions examined, demonstrating the stable nature of the PVOH-SiO<sub>2</sub> system. The extensive hydrogen bonding between the films and the substrate as well as the crystallization within the thin films appear to play more dominant roles than the destabilizing polar interactions during solvent evaporation in dictating thin film stability.

## **COLL 306**

### **Optimizing AgGaS<sub>2</sub> nanocrystal thin films for photoelectrochemical hydrogen generation**

**Harrison Worster**, *hdworster@mail.roanoke.edu*, **Steven Hughes**. Chemistry, Roanoke College, Salem, Virginia, United States

The modern day demands for energy are increasing rapidly. One possible solution for this demand is utilizing photocatalysts to facilitate the generation of hydrogen gas via water splitting. In this work, silver gallium sulfide (AGS) nanocrystals were demonstrated to work as a photocatalyst for water splitting by photoelectrochemical techniques. Various AGS and AGS nanocrystal derivatives were synthesized and

isolated for use in producing thin films by drop-coating and spin-coating. These films were submerged in a pH buffered solution and exposed to high intensity ultraviolet light during linear sweep voltammetry to determine their viability as a photocatalytic system. While the chemical system does appear to be photoactive, the current challenge is optimizing the film architecture in order to determine the actual potential of AGS as a water-splitting photocatalyst. This research highlights these optimization efforts in both nanocrystal network formation and film preparation technique to improve photoelectrochemical performance.

## **COLL 307**

### **Producing steam at room temperature with solar radiation and metal nanoparticles**

**Laura Huff**, *lrh4@geneseo.edu*, **Adelaide Weidner**, *aw32@geneseo.edu*, **Jeffrey J. Peterson**. Chemistry, SUNY Geneseo, Geneseo, New York, United States

Gold nanoparticles are well-known light absorbers that efficiently generate heat under photoexcitation. For example, when suspended in water, these particles radiate enough heat to generate water vapor upon being exposed to sunlight, without bulk heating of the solution. Solar-powered steam generators would facilitate, for example, electricity-free water purification and sterilization of instruments and waste in regions without well-established energy grids. This investigation focuses on optimizing the efficiency of photothermal steam generation by controlling the geometry of SiO<sub>2</sub>/Au core/shell nanoparticles. SiO<sub>2</sub>/Au core/shell nanoparticles were synthesized, characterized by transmission electron microscopy and UV-Vis absorbance, and irradiated by a solar simulator in a temperature-pressure recording assay. The synthesized SiO<sub>2</sub>/Au core nanoparticles produced a higher efficiency of steam generation than our research group had previously accomplished and point to future directions for further optimizations.

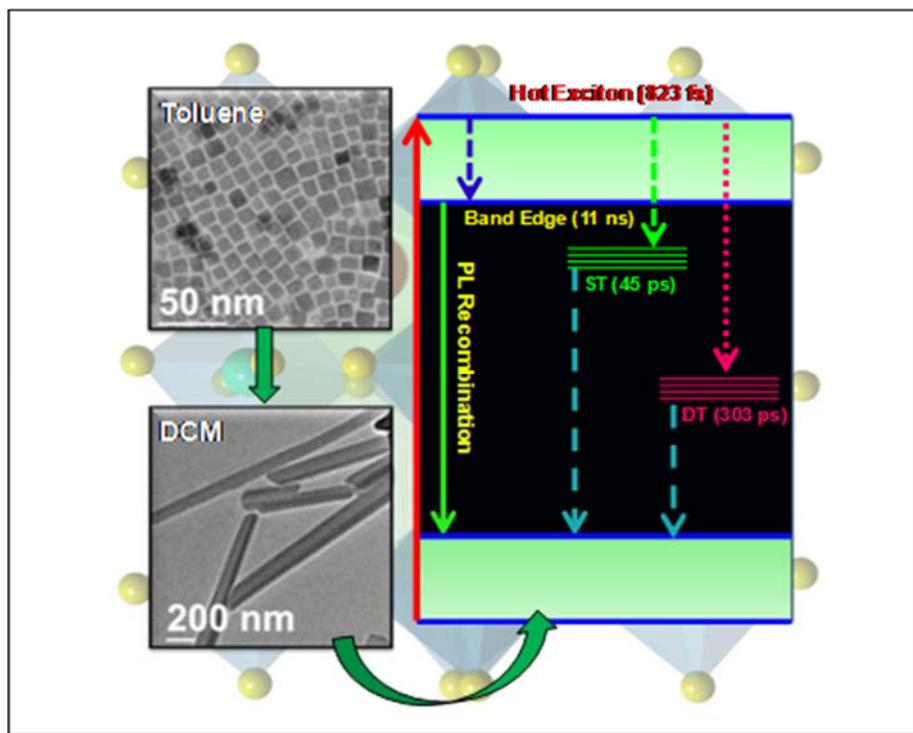
## **COLL 308**

### **Ultrafast photo-induced processes in perovskite nanocrystals**

**Goutam Ghosh**, *msgg@iacs.res.in*, **Amitava Patra**. school of materials science, indian association for the cultivation of science, Kolkata, India

The worldwide accolades to the ongoing research activity on lead halide perovskite nanocrystals (LHP NCs) which shows unprecedented success in photovoltaic as well as optoelectronic applications are primarily due to the engrossing photophysical characteristics of these novel materials. The defect tolerance nature and the prolonged carrier lifetime are the major enabling factors, being described to be unique as well as complex compared to other conventional semiconductor NCs. However, despite the rapid progress in the device application, the fundamental molecular level understanding of the ultrafast processes triggered by light still remain obscure. We have employed the femtosecond pump-probe technique to deconvolute the dynamics of photoexcited

carriers of perovskite NCs of different shapes. Subsequent investigation of the spectral and temporal data has been carried out using singular value decomposition (SVD) based global and target analysis to obtain a model based description with precisely estimated rate constants and excited state species-related spectral signature. It surfaces from our research that trap states play an important role in the carrier relaxation dynamics of perovskite NCs of dissimilar shapes. In addition we will present a brief overview of crucial ultrafast photo-induced processes, namely hot-carrier relaxation, hot-carrier extraction, carrier trapping and carrier extraction from band edge states within perovskite NCs and across the interface of different heterostructure containing perovskites. With our knowledge and expertise of the fundamental photophysics of perovskite NCs, we have designed hybrid systems composed of two dimensional CdSe quantum well and perovskite NCs, wherein enhanced charge separation due to photo-induced electron transfer occurs. Summarily, fundamental understanding of the charge transfer dynamics may open up new avenues to design efficient light-harvesting system based on these novel optoelectronic materials.



COLL 309

Impact of chemically functionalized gold nanoparticles on oil-water emulsion stability

**Gabriel Sanchez**, *gabriel.sanchez10@upr.edu*, Lucas Capre, Claribel Acevedo.  
Chemical Engineering , University of Puerto Rico-Mayaguez, Mayaguez, Puerto Rico

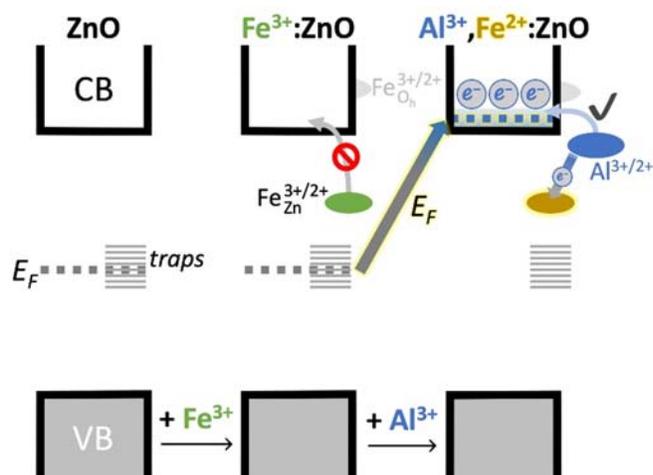
Nanoparticles chemically modified to be surface-active can adsorb strongly at the oil-water interface to stabilize emulsions. Polar and nonpolar groups can be incorporated onto the nanoparticle surfaces to tune particle surface properties. Here, we report studies aimed characterizing the adsorption of chemically functionalized gold nanoparticles (AuNPs) at the oil-water interface to stabilize emulsions. Our approach makes use of AuNPs functionalized with binary mixtures of self-assembled monolayers of alkanethiols displaying polar (i.e., hydroxyl or amine) and non-polar (methyl) groups to modulate the adsorption of the AuNPs at the oil-water interface. Interfacial tension measurements and emulsion stability studies using optical microscopy and dynamic light scattering methods are conducted to assess interfacial behavior. Our results show that the nature of the polar groups and nanoparticle surface composition (ratio of polar to nonpolar groups) influences adsorption of the AuNPs at the oil-water interface and their ability to stabilize emulsions. Additional studies have focused on investigating the effect of variables such as emulsification method and ionic strength on the stability of emulsions using chemically functionalized AuNPs.

## **COLL 310**

### **Air-stable n-type Fe-doped ZnO colloidal nanocrystals**

**ENES BUZ**, *ebuz@umass.edu*, Dongming Zhou, Kevin R. Kittilstved. Department of Chemistry, University of Massachusetts Amherst, Amherst, Massachusetts, United States

The oxidation state of Fe dopants in ZnO nanostructures or bulk powders is reported as a mixture of both 2+ and 3+ in the majority of experimental studies. We utilize the codoping method to control the oxidation state of Fe dopants via the introduction of Al dopants. Several novel features are observed including the disappearance of the characteristic electron paramagnetic resonance (EPR) signatures of Fe<sup>3+</sup> upon activation of Al<sup>3+</sup> donor defects in the ZnO lattice and the appearance of localized surface plasmon feature, indicating excess free carriers in Al and Fe codoped ZnO nanocrystals and confirming the substitutional Al<sup>3+</sup> doping. These spectral changes suggest that Al<sup>3+</sup> doping results in a reduction of Fe<sup>3+</sup> dopants to the EPR-silent Fe<sup>2+</sup> dopants that are stable under ambient conditions. These colloidal nanocrystals provide a potential building block for manipulating the magneto-optical properties and plasmon responses in colloidal nanocrystals and higher-order nanostructures.



## COLL 311

### Development of catalytic chromia-based aerogels

**Fiona T. Fitzgerald**<sup>1</sup>, [fitzgerf@union.edu](mailto:fitzgerf@union.edu), **Mary K. Carroll**<sup>1</sup>, **Ann M. Anderson**<sup>2</sup>, **Bradford A. Bruno**<sup>2</sup>. (1) Dept of Chemistry, Union College, Schenectady, New York, United States (2) Dept of Mechanical Engineering, Union College, Schenectady, New York, United States

Over one billion automobiles are in use around the world, the majority of which employ internal combustion engines. Catalytic converters are used to convert the toxic compounds found in car exhaust -- carbon monoxide, nitrogen oxides (NO<sub>x</sub>) and hydrocarbons -- to less harmful gases. The typical catalytic converter employs as catalysts expensive raw materials (platinum, palladium and/or rhodium) wash-coated onto an alumina-based ceramic substrate. Aerogel materials have high surface area and thermal stability, properties that make them attractive for catalysis applications. Aerogels made with transition metal oxides are candidates to replace platinum in the catalytic converter. Chromium oxide (chromia) materials have demonstrated catalytic activity in other applications due to favorable redox chemistry, stability and selectivity. In this work, sol-gel synthesis techniques are adapted to a patented rapid supercritical extraction (RSCE) method to fabricate chromia and chromia-based catalytic aerogels. In one example of a co-precursor technique, a mixture (1:5 mole ratio) of chromium(III) to aluminum salt in ethanol is reacted with a proton scavenger to induce gelation. Following solvent exchanges of the wet gels with absolute ethanol, RSCE processing yields chromia-alumina aerogels. Observed shrinkage is higher than for copper-containing aerogels fabricated via the same process. Physical characterization via several methods, including XRD and SEM, is performed on the materials as prepared and following calcination, and catalytic performance of promising materials is evaluated using an in-house-constructed testbed in which the aerogel materials are exposed to

simulated automotive exhaust under temperature conditions that approximate those experienced in a catalytic converter.

## **COLL 312**

### **Investigation of structural changes in mixed-metal catalytic aerogels at elevated temperatures**

**Thomas F. Andre**<sup>1</sup>, [andret@union.edu](mailto:andret@union.edu), **Mary K. Carroll**<sup>1</sup>, **Ann M. Anderson**<sup>2</sup>. (1) Dept of Chemistry, Union College, Schenectady, New York, United States (2) Dept of Mechanical Engineering, Union College, Schenectady, New York, United States

Aerogels possess physical properties that make them appealing for applications in catalysis. They have a low density as well as high surface area and porosity. Alumina-based aerogels also have high thermal stability. Most catalytic converters currently in use in automobiles employ precious metals such as platinum, palladium, and rhodium as 'three-way' catalysts to oxidize carbon monoxide (CO) and unburned hydrocarbons (HCs) and reduce nitrogen oxides (NOx). These precious metals are expensive due to their low abundance in the earth's crust. Aerogels containing more abundant catalytic metals such as copper or nickel could be a less expensive alternative to the modern solution. In prior work, copper-, nickel-, and cobalt-containing silica and alumina aerogels have demonstrated three-way catalytic ability. These mixed-metal catalytic materials are readily fabricated from metal salts using an epoxide-assisted sol-gel synthetic approach with subsequent processing via a patented rapid supercritical extraction (RSCE) method to yield aerogels. Although the aerogels are predominantly amorphous, scanning electron microscopy (SEM) and powder X-ray diffraction (XRD) analyses of the catalytic aerogels demonstrate convincingly that the materials have transition-metal-containing microcrystalline components. In order to develop a fundamental understanding of catalytic aerogel materials, it is necessary to identify the forms that are present at the elevated temperatures employed in catalytic converters. In this presentation, a comparison of powder XRD patterns of mixed-metal RSCE aerogels is made. Differences observed in the XRD patterns and SEM images for these materials as-prepared and following calcination (up to 800 °C) and subsequent catalytic testing (up to 600 °C) provide convincing evidence of the chemical and structural changes that have occurred. Through the use of powder x-ray diffraction (XRD) with thermal control, the microcrystalline components that are present at elevated temperatures can be identified.

## **COLL 313**

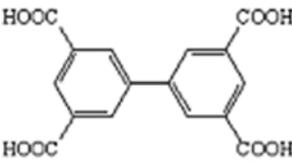
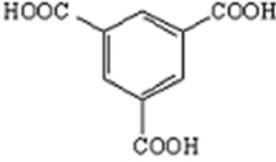
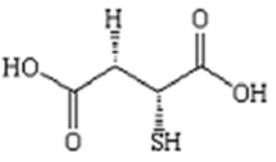
### **Nanostructured covalent organometallic polyhedron (COP) agents used to detect fingerprints from the non-porous surfaces**

**Pete Villarreal**<sup>1</sup>, [pete.villarreal@students.tamuk.edu](mailto:pete.villarreal@students.tamuk.edu), **Jack Ocheltree**<sup>1</sup>, [jack.ocheltree@students.tamuk.edu](mailto:jack.ocheltree@students.tamuk.edu), **Haiqiu Zhang**<sup>1,2</sup>, **Sajid Bashir**<sup>1</sup>, **Jingbo L. Liu**<sup>1</sup>. (1)

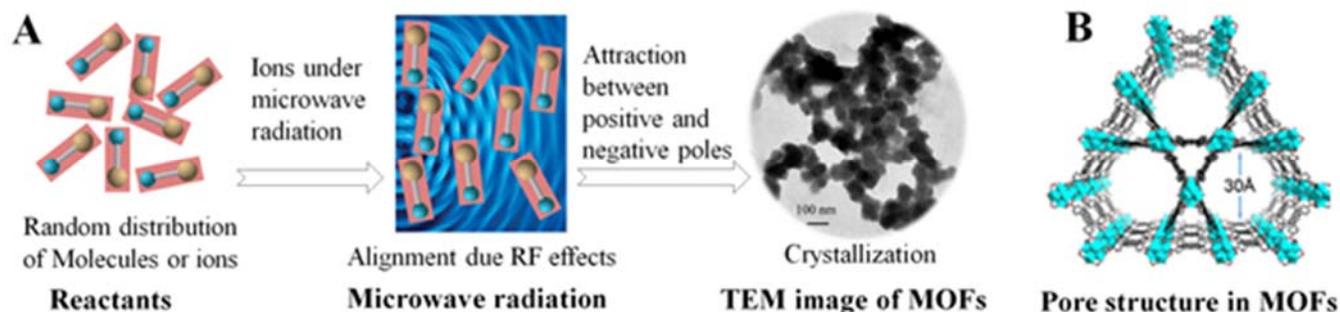
Chemistry, Texas A&M University-Kingsville, Kingsville, Texas, United States (2)  
 Chemistry, Heilongjiang University, Harbin, Heilongjiang, China

A colloidal wet-chemistry was employed to prepare covalent organometallic polyhedron (COPs). A complex between metal cation ( $M^{n+}$ ) and multi-coordinate ligands (M-COPs) was found to be formed with a coupling of hydrophilic active sizes into the substructure. These substructures are highly stable, enabling the COPs to be stable in air and water, enhancing print residue detection and selectivity, due to various carboxylates that can interact with amino acids in fingerprint residues. The interaction between prints and M-COPs was found to occur within 5-30 s, enabling the rapid detection of fingerprints from non-porous and porous surfaces. The sensitivity and visibility of latent prints were used to increase by impregnating fluorescent dye into COP's pore by a post-modification. This technique allows for encapsulation of M-COPs by dyes to emit different colors when 'hemiketalized' with the amino acid in fingerprint residue. **Fig. 1** lists the ligands, dyes and metal ions, which have been used to produce COP DAs to improve sensitivity, selectivity and detection speed.

This study indicated that the microwave-assisted colloidal chemistry was optimal method in the producing of well-crystallized COPs. The charge attraction developed during microwave radiation is the driving force for the nucleation, leading to the crystallization and growth. The fluorescent COFs (3 formulations) with highly porous nanostructures (**Fig. 2**) were generated in a short period under microwave radiation. Functional groups of  $-NH_2$  and  $-C=O$  can be introduced into the COP pores. These groups were found react with  $1^\circ$  and  $2^\circ$  amines in amino acids present in the papillary exudate forming hemiketals. The fluorescent emission yield can be used as a quantitative evaluation of the fingerprints detection thresholds.

Ligands			
	[1,1'-biphenyl]-3,3',5,5'-tetracarboxylic acid	benzene-1,3,5-tricarboxylic acid	(R)-2-mercaptosuccinic acid
Dyes	Rhodamine 6G	Guinea Green B	Eosin B
Metal ions	$Zn^{2+}$	$Ag^+$	

*The selected multi-dentate ligands, three families of fluorescent dyes and two metal ions*



The synthesis of MOFs using the microwave-assisted colloidal chemistry and different formulations of COPs with controllable pores.

## COLL 314

### Characterizing optical transitions in inverted core/shell ZnSe/CdSe quantum dots

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Traditional core/shell quantum dots (QDs) consist of a smaller band gap core and wider band gap shell (eg, CdSe/ZnS QDs), confining excitons within the core of the particle and isolating them from the QD surface. Inverted core/shell heterostructures reverse this geometry, placing the smaller band gap material in the outer shell and isolating excitons near the QD surface. Such structures could be used for certain technological applications, such as photocatalysts for electron transfer reactions or QD lasers; however, they have been significantly less explored than their traditional counterparts. ZnSe/CdSe core/shell were synthesized using a sequential ion layer adsorption-reaction (SILAR) technique, enabling independent control of the both core and shell thicknesses. The capped core/shell nanoparticles were characterized via UV/Vis and low temperature photoluminescence excitation spectroscopies, TEM imaging, and time-resolved fluorescence measurements. The optical transitions will be compared to core-only CdSe QDs and potential applications of the inverted core/shell QDs will be discussed.

## COLL 315

### Removal of organic contaminants from water by using the polypropylene-based monoliths

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Water pollution is putting in danger the human and marine life. One of the major sources of water pollution is the organic contaminants that are being contributed by the rapidly growing industries and the offshore movements of the oil. There is a need to

develop such materials that can selectively adsorb these toxic chemicals or filter out from the water. A propylene-based magnetic monolith was synthesized for the static and dynamic separation of non-polar organic contaminants from the water. The polypropylene-based magnetic monolith was obtained by the combination of the polystyrene, polystyrene and magnetic nanoparticles. The developed monolith was characterized by various advanced materials such as FTIR, EDX and BET and Raman spectroscopy. The introduction of the magnetic nanoparticles enhances the surface roughness, improves stability and surface area (33 to 221 m<sup>2</sup>/g). The magnetic behavior of the monolith provides a chance to direct it at a specific position for adsorption of the non-polar organic contaminants. The magnetic polypropylene monolith has displayed a water contact angle of 146°. The absorption capacity was found up to 1517%. A high flux of 13365 Lm<sup>-2</sup>h<sup>-1</sup> was found during the separation of the non-polar hydrocarbons from the water.

## **COLL 316**

### **Synthesis and characterization of conductive mesoporous silica**

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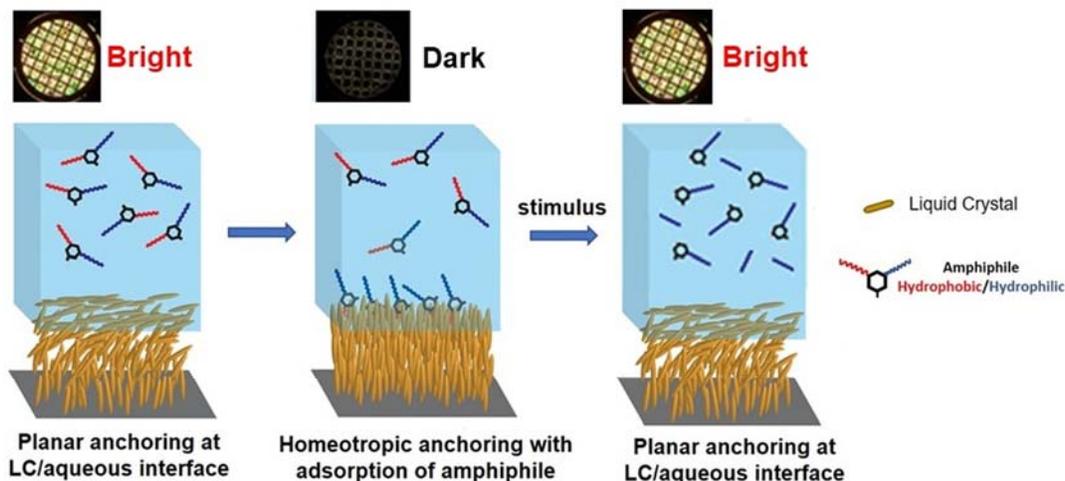
Mesoporous silica particles with tunable pores, high surface area, and ease of surface chemistry modifications are versatile for a range of functions from serving as a carrier molecule for therapeutics to chemosensors. Here we propose the synthesis of polypyrrole functionalized mesoporous silica, specifically ultraporous mesoporous silica nanoparticles, with large pores in the size regime of both mesopores and macropores as determined by scanning electron microscopy and porosimetry analysis by N<sub>2</sub> (g) adsorption and desorption. Surface functionalization of the mesoporous silica with polypyrrole occurs upon polymerization of pyrrole in an aqueous reaction in the presence of sodium nitrite and acetic acid to give a monolayer of conductive polymer as characterized by energy dispersive x-ray and electrochemical studies. The resulting novel material with high surface area and large pores can be leveraged for the binding of therapeutics or as a composite material consisting of insulating silica and conductive polypyrrole for electrochemical sensors.

## **COLL 317**

### **Anchoring transitions induced by stimuli-responsive amphiphiles at the liquid crystal-water interface**

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Liquid crystals are one of the most fascinating soft matter with extensive applications in electronic displays owing to their optical properties. Their long-range orientational order and reorganizing abilities are well studied with a solid interface. However, the cooperative reorientation (anchoring) of liquid crystals at an interface with water in response to subtle molecular level change is still puzzling. It is known that surfactants, polymers, and amphiphiles can adsorb at the liquid crystal-water interface and induce a homeotropic anchoring. Although, we lack the structural design guidelines for these molecules to predict the anchoring behavior. To resolve this problem, we have systematically designed and synthesized a library of amphiphiles and tested the effect of various structural factors such as variable aliphatic tail length, linker rigidity on the anchoring behavior. This unravels how the cooperative association of amphiphiles seen in a three-dimensional system manifests itself in the two-dimensional system. In addition, it broadens the understanding of the molecular design and helps with predicting the anchoring behavior of stimuli-responsive amphiphiles. We have developed protein-sensitive amphiphiles that show homeotropic anchoring at the liquid crystal-water interface and exhibits planar anchoring upon the introduction of a protein. This system can be used to sense various levels of protein concentrations and has future applications in biomolecular sensing.



## **Electron-beam-induced orthogonal functionality in biotinylated poly(ethylene glycol) thin films**

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Patterning surfaces with multiple functionalities at nano- and micro-length scales is important to an array of bio-interactive applications including the control of cell signaling and cooperative reaction cascades in detection and diagnostics. Methods based on electron-beam (e-beam) lithography are of particular interest, because e-beam lithography can flexibly pattern features with lateral dimensions as small as a few nanometers in user-controlled shapes. We and others have studied poly(ethylene glycol) [PEG] as an additive resist for bio-interactive patterning applications. Under appropriate conditions, electron irradiation can both cross-link a solvent-cast homopolymer PEG thin film as well as graft it to the underlying substrate to form micro- and nano-gel structures. To separate surface-grafting, cross-linking, and chemical functionality, we studied the effects of 2 keV electrons on thin films of PEG end-functionalized with hydroxyls (PEG-OH) or biotins (PEG-B). Similarities in the dose-dependent thickness changes of the patterned PEGs indicate that surface grafting and cross-linking primarily involve the ethylene oxide main chain. Higher doses create thicker patterns with more biotin, but the concurrent increase in thiol reactivity indicates that cross-linking competes with biotin degradation. The dose window for optimal e-beam patterning of biotinylated PEG is very narrow. Biotin is entirely consumed at higher doses. Its modified functionality is reactive with 5-((2-(and-3)-S-(acetylmercapto)succinoyl) amino) (SAMSA). This effect creates a dose-dependent orthogonal functionality that can be patterned from a single precursor thin film.

### **COLL 319**

## **Nickel-palladium phosphide catalysts for the selective hydrogenation of alkynes**

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The selective hydrogenation of alkyne impurities in alkene streams is of critical importance to the chemical industry for which high-purity monomer feedstocks are needed. Current industrial catalysts are based on palladium (usually alloyed with silver) because of their combination of high activity and selectivity, but the use of noble metals results in high catalyst cost. Nickel phosphides ( $\text{Ni}_x\text{P}_y$ ) have emerged as a new class of catalysts for a range of processes, including hydrogenation reactions. The current study focuses on the selective hydrogenation of phenyl acetylene to styrene over different crystalline phases of nickel phosphide ( $\text{Ni}_3\text{P}$ ,  $\text{Ni}_{12}\text{P}_5$ ,  $\text{Ni}_2\text{P}$ ,  $\text{Ni}_5\text{P}_4$ ), and the effect of low-level Pd substitution. The synthesis and characterization (XRD, XPS, chemisorption) of silica-supported  $\text{Ni}_3\text{P}$ ,  $\text{Ni}_{12}\text{P}_5$ ,  $\text{Ni}_2\text{P}$  will be discussed, as will efforts to prepare the P-rich  $\text{Ni}_5\text{P}_4$  phase. The catalysts were prepared by incipient wetness impregnation onto a

high surface area silica support followed by temperature-programmed reduction (TPR) in flowing hydrogen. Analysis of XRD line broadening indicates average  $Ni_xP_y$  crystallite sizes in the 4-5 nm range. Catalytic reactor studies reveal a trend of decreasing hydrogenation activity and increasing styrene selectivity with increasing P/Ni molar ratio, which can be ascribed to ligand and ensemble effects associated with the different bonding environments of Ni in the  $Ni_xP_y$  phases. The successful synthesis of single-phase  $Ni_{1.95}Pd_{0.05}P/SiO_2$  has been verified by XRD, with small shifts of XRD peaks to lower Bragg angles indicative of Pd substitution for Ni in the  $Ni_2P$  lattice. Catalytic results for the Pd-substituted  $Ni_xP_y/SiO_2$  catalysts (Pd/Ni = 0.01-0.05) will be compared with those for the  $Ni_xP_y/SiO_2$  catalysts, with insights gained from XPS and chemisorption ( $CO$ ,  $H_2$ ) measurements used to help understand the role of the substituted Pd atoms.

## **COLL 320**

### **Surface modification of gold nanorods to enhance the detection of $Hg^{2+}$**

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Gold Nanorods (AuNR) have demonstrated a unique facility for the detection of mercury due to their plasmonic properties and the propensity for mercury and gold to form an amalgamation. Prevalent methods for the synthesis of AuNR's utilize high concentrations of cetyl trimethylammonium bromide (CTAB). CTAB was exchanged for polyethylene glycol thiol (PEG) as a capping agent on the AuNR's resulting in much better stability and a significant increase in both sensitivity and selectivity for detection of mercury (II) over CTAB-coated AuNR's. It was discovered that the sensitivity of PEG coated AuNR's to mercury (II) could be as much as tripled with incubation of the PEG coated AuNR's. This increased sensitivity has been attributed to the preferential removal of PEG from the tips of AuNR's by the formation of a complex between PEG and mercury (II). Removal of surface PEG has the combined effect of lowering the surface stability of the AuNRs as well as exposing more rod surface for mercury adsorption. Scanning Transmission Electron Microscopy (STEM) analysis has confirmed that this causes increased change of AuNR morphology over the same mercury (II) concentration without PEG removal.

## **COLL 321**

### **Surface initiated atom transfer radical polymerization (SI-ATRP) for corrosion resistant surfaces on stainless steel 316L**

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Stainless steel 316L is a commonly employed alloy with high corrosion resistance due to the chromium content. However, in marine environments it is susceptible to pitting corrosion due to the presence of chloride ions leading to a breakdown on the passive oxide layer. Surface initiated atom transfer radical polymerization (SI-ATRP) in conjunction with self-assembled monolayers (SAMs) were used to produce films of poly(methyl acrylate), poly(methyl methacrylate), and poly(styrene) covalently bound to the surface of stainless steel 316L. This was accomplished by immobilization of an SI-ATRP initiator on hydroxyl terminated SAMs, followed by surface-initiated polymerization. The ordering of the alkyl chains, immobilization of the bromoisobutryl bromide, and the successful synthesis of the polymer films on the surface were characterized by diffuse reflectance infrared Fourier transform spectroscopy. The films were characterized with cyclic voltammetry, electrochemical impedance spectroscopy and atomic force microscopy. Modifications resulted in polymer films with up to 0.99 fractional coverage and protection efficiency of up to 99.6%. Future work aims to form block copolymers in an effort to enhance the surface properties of stainless steel 316L.

## **COLL 322**

### **Reservoir on a chip: Microfluidics for rapid study of viscosity of N<sub>2</sub> foams with brines of different ions content**

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Generating in-situ foam is regarded as one of the most promising techniques to overcome gas mobility issues and improve sweep efficiency in both miscible and immiscible gas injection enhanced oil recovery (EOR) processes. Gravity override, viscous fingering and channeling through permeable zones are the major limiting factors that can impair the efficiency of gas floods, mainly due to low density and viscosity of the gas relative to reservoir fluids. Generating strong and stable foam while injecting gas is one way to achieve in-depth conformance improvement in the reservoir. Underground conditions in oil and gas reservoirs around the world are different. Temperature, pressure and salinity of the water available for use can vary significantly. Therefore foams need to be developed specifically for conditions based in the field of application. During research and development phase, conventionally used methods to study foams under reservoir conditions are time consuming and costly, especially when large number of formulations need to be tested. This study demonstrates utilization of a microfluidics device to rapidly evaluate foams when produced utilizing different surfactants in brines with different ions content. Results from microfluidics experiments are also compared to data from conventional foam rheometer and demonstrate that foam viscosity and stability can be significantly altered by changing the type of ions present in brines.

## **COLL 323**

## **Photocatalytic activity of hybrid metal/semiconductor nanostructures with varied morphologies**

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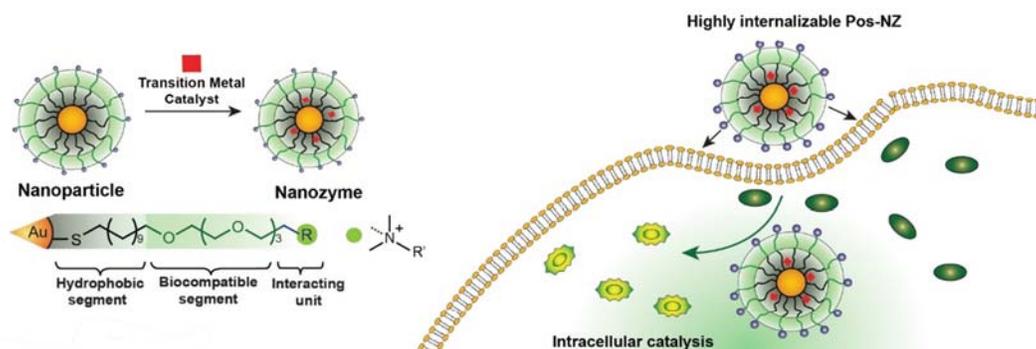
Hybrid metal-semiconductors nanoparticles offer many optical and electronic advantages that play important roles in photocatalysis. In order to create the hybrid metal-semiconductor catalysts, CdSe quantum dots, nanorods and nanoplatelets are synthesized using organometallic hot injection reactions and Au nanoparticles with different dimensions are reduced onto the CdSe nanocrystal surface. The dye methyl viologen is photocatalytically reduced by the Au tipped CdSe heterostructures. This investigation focuses on optimizing the catalytic properties of Au tipped CdSe by varying the morphology of CdSe and the size of Au nanoparticles. The photocatalytic activity of the hybrid Au-CdSe nanostructures are characterized via UV-Vis absorption and fluorescence spectroscopy. The structural properties of the hybrid materials have been studied using high resolution transmission electron microscopy and powder x-ray diffraction.

### **COLL 324**

## **Eradication of cancer cells through combination therapy using bioorthogonal nanozymes and pro-drug**

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Multidrug resistance (MDR), narrow therapeutic windows and the undesired side effects of available anticancer drugs are major limitations in cancer treatment. MDR is considered a major obstacle in cancer treatment due to metastatic tumors that develop resistance to chemotherapy. Nanoparticle-mediated combination therapy with anticancer drugs can induce synergistic drug action and prevent the onset of drug resistance. We have developed a bioorthogonal combination therapeutic approach that uses 'nanozymes' that employ hydrophobic environments in nanoparticle scaffolds to encapsulate transition metal catalysts (TMCs), These nanozyme platforms solubilize the TMCs and protect it from degradation in complex biological environments leading to in situ activation of pro-drug to effectively combat drug resistance and enhance killing of cancer cells. The use of these systems to activate prodrugs and imaging agents in cells and other biosystems will be presented



## COLL 325

### Synthesis of InSe nanosheets and nanoparticles by semi bottom-up method and exposing them to human health relevant organisms

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Nanoparticles are particles with diameters between 1 to 100 nm in size. Similarly, nanosheets are layered two-dimensional nanostructures with thickness ranging from 1 to 100 nm. These layered materials are defined as solids with strong in-plane chemical bonds and weak out-of-plane van der Waals bonds. Both nanosheets and nanoparticles have properties completely different from their bulk precursors. They represent a diverse and largely untapped source of nanosystems with exotic electronic, electrochemical and photonic properties. Additionally, they have high specific surface areas which are important properties for electronics such as transistors, sensors, etc. The goal of the study is to investigate the interactions of emerging 2D materials and model membranes and living organisms in the environment. This presentation focuses on InSe, a 2D material with potential use in optoelectronic applications. The presentation will describe the synthesis and characterization of InSe 2D materials using a recently developed semi bottom up synthesis method. This method, which was recently reported by Motolo and co-workers from the University of the Witwatersrand,

South Africa, enables us to produce InSe 2D nanosheets with greater control of flake size, thickness and morphology compared to InSe nanosheets that are formed using mechanical or chemical exfoliation methods. Experiments to determine the impact of InSe 2D materials with varying size, thickness and morphology on zebrafish embryo development are on-going.

## **COLL 326**

### **Thermal treatment of collagen films in fluoruous media for enhancement of mechanical and enzymatic stability**

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Collagen is widely used in the fabrication of biomaterials as it is the primary component of the extracellular matrix. For this reason, it has a wide variety of biomedical applications such as tissue engineering scaffolds, drug delivery patches etc. However, a major drawback of collagen-based materials is their susceptibility to mechanical failure during handling, which limits their applicability to biomaterials. Chemical or physical treatment can improve the mechanical properties of collagen however, these processes can create issues of cytotoxicity or denaturation. We report an alternative approach to enhance the stability and mechanical properties of collagen through thermal treatment in fluoruous media. Our treatment significantly increases mechanical strength, reduces rate of proteolytic degradation, and provides high cell biocompatibility while preventing denaturation.

## **COLL 327**

### **Supported Ni-Au colloid precursors for active, selective, and stable alkyne partial hydrogenation catalysts**

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Bimetallic NiAu catalysts have garnered broad interest for various reactions including selective hydrogenations and selective oxidations. However, studies of this bimetallic system have been limited due to the bulk immiscibility of the two metals that makes catalyst synthesis a challenge. Our group has developed a solution phase synthesis using oleylamine-capped Ni nanoparticles that are formed using a colloid method. The optimized Ni synthesis led to particles with a narrow size distribution ( $4.7 \pm 0.4$  nm). Gold was added to the Ni nanoparticles via galvanic displacement before they are

deposited onto a commercial alumina to yield new bimetallic heterogeneous catalysts. While this process yielded bimetallic nanocomposites, large particle size growth and the production of small Au particles was also observed. The supported NiAu catalysts were more active than Au for 1-octyne partial hydrogenation, and largely maintained the high alkene selectivity associated with Au catalysts (90% alkene selectivity at 95% conversion). When operated at lower space velocities, the NiAu catalysts also had reduced propensity to over-hydrogenate the alkene, allowing for wider operating ranges with high alkene yields when compared to Ni catalysts alone. Stability testing showed the bimetallic catalyst activity increased significantly over the first ~15 hours on stream and remained stable for one week. In control experiments, NiAu catalyst performance was compared with reactivity over Au/NiO and with physical mixtures of Au/Al<sub>2</sub>O<sub>3</sub> and Ni/Al<sub>2</sub>O<sub>3</sub> catalysts. Only the NiAu catalysts prepared through the colloid synthesis showed the enhanced activity and selectivity. The reactivity and characterization studies suggest that the active catalysts are likely composed of bimetallic NiAu particles that have heavily enriched Au surfaces.

## **COLL 328**

### **Aggregation and photophysical properties of cyanine dyes in confined reverse micellar environments**

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The aggregation and photo physical properties of fluorescent Cyanine dyes in aqueous and confined reverse-micellar environments were investigated by using steady-state UV-Vis absorption and emission and time-resolved fluorescence spectroscopic techniques. The fluorescent dye molecules were encapsulated in reverse micelles of various sizes. The photo physical properties of the dyes in water as well as in reverse micelles of various sizes were examined by analyzing various photophysical parameters such as quantum yields, band shifts and fluorescence life time etc. Our observation shows that Cy5 dye probably undergoes aggregation inside the smallest reverse micelle of size, which is very significant. Cy5 does behave differently in bigger reverse micelle and in aqueous environment.

## **COLL 329**

### **Plasmonic monitoring of DOTAP liposome fusion**

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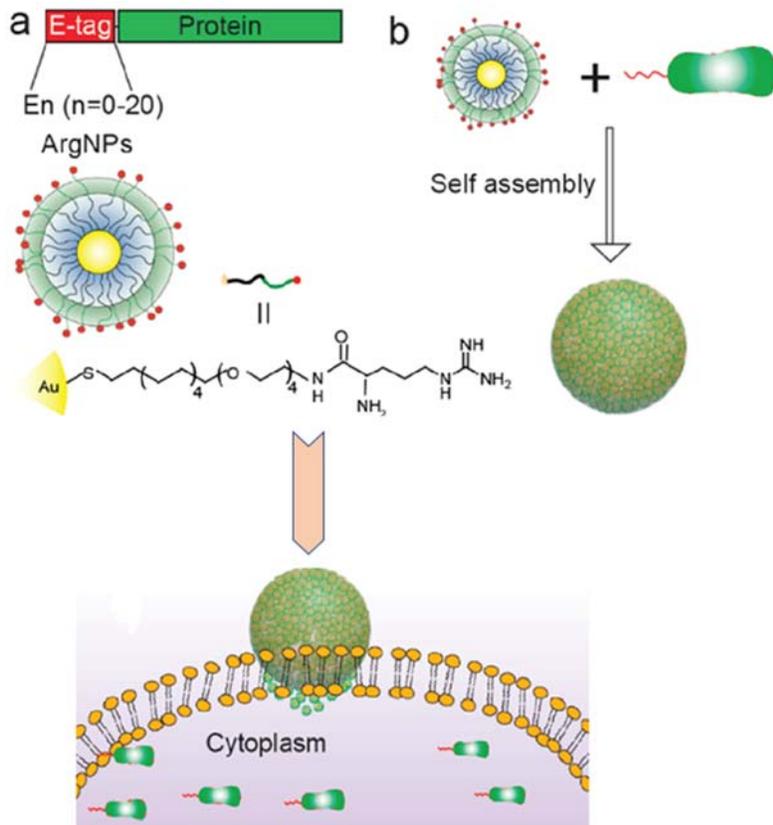
Materials and inorganic systems have been widely characterized via plasmonics, but this analytical method has further potential in analyzing more biological components. As many biological substrates are limited conformationally to certain active states, it is important to ensure the substrates are in a state reflective of their in vivo character. There is evidence to support that this can be done by monitoring liposomes covered in gold nanoparticles with surface enhanced raman spectroscopy (SERS). Few steps have been taken to characterize a component of such analytical methods, and it is important to understand the behavior of these nanoparticle-plated liposomes before they can be used as an analytical tool. We have taken steps to further characterize these liposomes. DOTAP liposomes are synthesized, gold nanoparticles are secured to the outside, and SERS/LSPR (localized surface plasmon resonance) measurements are taken of the samples. Measurements taken of the substrates have given findings in quantifying fusion rates of the nanoparticle coated liposomes and show exciting potential for further uses of nanoparticle coated liposomes.

## **COLL 330**

### **Direct cytosolic protein delivery using versatile nano-carrier platform**

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Delivery of active therapeutic proteins into cells is a challenging task. The majority of current protein delivery vehicles enter the cell by endocytotic pathways and become entrapped into endo/lysosomes, ultimately leading to degradation of the cargo. We have developed a protein-nanoparticle nanoassembly system to deliver proteins directly to the cytosol and evade endosomal entrapment. In this strategy proteins -engineered with oligo-glutamic acid tags (E-tags), were self-assembled with oppositely charged arginine-functionalized gold nanoparticles (2 nm core diameter) via electrostatic interaction. Using this strategy, we demonstrated delivery of five proteins of different size and charge, including active Cre recombinase (pI = 9.60, MW = 38.5 kDa), and granzyme A (pI = 9.14, MW = 29.0 kDa). We also achieved delivery of CRISPR/Cas9 demonstrating highly efficient cytosolic delivery ~90% and gene editing. Evolution of this platform and integration into therapeutic and imaging strategies will be presented.



Schematic representation of the nanoparticle-protein self-assembly

## COLL 331

### Investigating the interparticle spatial properties and phase behavior of DNA-mediated nanoparticle assemblies with incorporated temperature sensitive copolymers

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The degree of crystallinity and the interspatial properties of various lengths of DNA-on gold nanoparticles is studied as a function of temperature, along with the effects the addition of a thermally responsive copolymer plays on the rate of assembly, the degree of ordering and interparticle separation of the DNA-mediated assemblies. Small-angle x-ray scattering was used to aid in determining the crystallinity and interspatial properties of the assemblies. The addition of polymer was found to disrupt long-range ordering and extend interparticle separation, while temperature tended to disrupt base stacking interactions, expanding pure DNA spacer regions, and compression the DNA upon the addition of polymer due to the thermal response of the polymer and entanglement with the spacer.

## COLL 332

### **Integration of nanofillers into 3D conducting polymer nanocomposites for enhanced mechanical and electrochemical properties: Applications in energy storage and conversion**

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Conducting polymers such as polyaniline (PANI) and polypyrrole (PPy) have enhanced chemical and mechanical properties for the basis of lightweight and configurable battery electrodes when combined with nanofillers. Recent research has shown that the integration of organic and inorganic nanofillers into PANi has enhanced structural stability and electrical conductivity resulting in higher charge density and charge transport. This project specifically explores covalent and non-covalent functionalization of graphene, graphene oxide, and carbon nanotubes (single-walled and multi-walled) as nanofillers with PANi and PPy to form 3D nanocomposites. The current challenges with electrodes made from conducting polymers is that they lack good charge rate capability and experience voltage decay. Nanofillers have potential to enhance the electrical conductivity as well as the mechanical properties of these conducting polymers. Mechanical properties such as modulus, stiffness, creep, and stress relaxation will be investigated using a dynamic mechanical analyzer. Chemical and materials characterization will be done using Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analyzer (TGA), and Differential Scanning Calorimeter (DSC). This electrode would produce a high-energy, lightweight battery which could advance current battery technology.

## COLL 333

### **Influence of lipid composition on physicochemical properties, stability, loading and interaction with amphiphilic proteins in phospholipid-based liposomes**

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The objective of this study was to analyze the impact of lipid composition on formulation ability (methods and outcomes), physicochemical properties (size, polydispersity, homogeneity), stability and dynamics, drug loading, and on interaction with amphiphilic

proteins in a series of phospholipid-based liposomes generated from saturated glycerophospholipids DMPC and DSPC.

### **COLL 334**

#### **Electronic and hydrodynamic properties of Texas red dyes in confined reverse micellar environments**

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The electronic and hydrodynamic properties of fluorescent Texas red dyes have been investigated in confined and crowded reverse micellar environments. Various steady-state and time-resolved spectroscopic techniques such as UV-Vis absorption, fluorescence emission, Fluorescence Anisotropy, Dynamic Light Scattering (DLS) as well as Time Correlated Single Photon Counting (TCSPC) techniques were employed to determine various photophysical parameters such as quantum yield, fluorescence lifetime, aggregation number and band shift etc. The results obtained in confined environments were compared with the results in aqueous environments. Our experimental observation shows that Texas red behaves very differently in reverse micellar environment as compared to aqueous environment. Since reverse micelle mimics the cellular environment, our findings can be used as a protocol to study biomolecule dynamics inside confined reverse micellar environment.

### **COLL 335**

#### **Enhancing enzyme immobilization on graphene oxide surface using metal-organic frameworks for large-substrate biocatalysis**

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Immobilizing enzymes for biocatalysis offers enhanced stability, reusability, and catalytic efficiency, therefore improving cost-efficiency. However, most applications of immobilized enzymes must be carried out in relatively mild conditions because the enzymes are largely exposed to the reaction medium. This places limitations on reactions that may denature the protein such as: elevated temperature, organic solvents, and/or extreme pHs. This paper endeavors to overcome these limitations using Graphene oxide (GO) and Metal-Organic Frameworks (MOF). We used two different pairs of metals and ligands to form the co-crystals in aqueous phase. We tested the enzyme/GO/MOF composites using a T4 lysozyme (T4L) to catalyze the hydrolysis of  $\beta$ -1,4 glycosidic bonds of bacterial cell walls. In comparison to ZIF-based GO composites, the pH stability of the GO-CaBDC composite is significantly enhanced. Other advantages include enzyme-friendly synthesis environment, low toxicity, and easy

handling. Also, we probed the orientation of T4L on the surface of GO/ZIF and GO/CaBDC using Site-Directed Spin Labeling Electron Paramagnetic Resonance spectroscopy.

### **COLL 336**

#### **Combining experiment and density functional theory to understand transition metal oxide reduction mechanisms in chemical-looping combustion**

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Chemical-looping combustion (CLC) has developed significant interest over the recent years because of its ability to capture nearly 100% of the carbon dioxide produced from hydrocarbon combustion. CLC uses oxygen from reducible transition metal oxides to react with the hydrocarbons in the absence of air. This allows for the CO<sub>2</sub> product to be easily captured without the need of expensive gas phase separation techniques used today. Before being used at the industry level, these metal oxides have to show high reactivity with thermal and mechanical stability. Experimental work has shown these transition metal oxides may follow two different reduction processes. Through the Nucleation and Nuclei Growth Model (NNGM) reduction of the metal first occurs inside the particle bulk before being seen on the surface. The Uniform Shrinking Core Model (USCM) shows reduction occurs at the surface before slowly working its way towards the bulk. To increase metal oxide reactivity, an understanding of why they tend to reduce through different methods is needed. In this work, DFT + *U* methodology is used to obtain an understanding of the reduction along the catalysis' surface through oxygen vacancies and electronic structure. We find that transition metal oxides which reduce through the NNGM process show a favorability for an oxygen vacancy along its subsurface compared to its surface. The opposite is seen for transition metal oxides that reduce through the USCM. The surface electronic structure is then studied through the inclusion of band centers of the oxygen and metal states. This method allows for the prediction of transition metal oxide reduction mechanisms and defines a tunable parameter that can be used to increase reactivity.

### **COLL 337**

#### **Hammett studies on supported Au nanoparticle catalysts**

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The activity of different types of supported Au catalysts is greatly affected by the electronic properties of the nanoparticle. Hammett Studies can be used to directly probe

the active site electronics of Au nanoparticle catalysts. Previous Hammett Studies using benzyl alcohol oxidation as a probe reaction have been conducted to examine differences in Au nanoparticle active site electronics on different metal oxide supports. The addition of Ni and Cu to create Au bimetallic catalysts is expected to change the activity and also electronic properties of the nanoparticles, and this change can be observed using Hammett Studies. Therefore, a new probe reaction for Hammett Studies which is the oxidation of 1-phenylethanol has been developed to characterize the electronics of these Ni-Au and Cu-Au bimetallic catalysts. 1-phenylethanol concentration studies examining the reactivity of several supported Au catalysts (Au/TiO<sub>2</sub>, Au/Al<sub>2</sub>O<sub>3</sub>, Au/ZnO, Au/SiO<sub>2</sub>) were performed, and showed that the reaction was largely insensitive to the reactant concentration. Hammett studies with several of the monometallic catalysts using 1-phenylethanol oxidation have begun, and the preliminary results are similar to the Hammett studies using benzyl alcohol oxidation. However, the 1-phenylethanol oxidation reaction appears to be potentially a more sensitive probe than the benzyl alcohol oxidation reaction. This work is currently being extended to Ni-Au and Cu-Au bimetallic catalysts.

## **COLL 338**

### **Effect of thermal activation on analyte uptake capacity of zirconium-based metal organic framework**

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Many applications of Metal Organic Frameworks (MOFs) would benefit from a fundamental understanding of thermal effects of the MOF on analyte adsorption. An important step in the use of a MOF is activation to remove the synthesis solvent. Studying the effects of thermal activation on UiO-67, a 12-connected zirconium-based metal organic framework, Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(COO)<sub>12</sub>, and its interactions with polar molecules allow us to interpret the strength and nature of analyte-MOF interactions and its uptake capacity. In this study, we compare the interactions of two polar analytes (ammonia and acetone) with UiO-67 MOFs following successive thermal activations. We hypothesize that increasing the activation temperature will lead to structural changes, including the formation of defects within the MOF. Using temperature programmed desorption-mass spectrometry, we can compare the distribution of adsorption sites and energies of desorption for the various analytes. Our studies reveal an increase in acetone uptake capacity and a change in the shape of the thermal desorption profile as the activation temperature is increased, suggesting a redistribution of adsorption sites. A decrease in the binding energy for acetone as activation temperature increases appears to be due to the loss of a high energy binding site. Using Infrared Spectroscopy (IR), the interactions of acetone and ammonia with various sites on the MOF are revealed; IR spectra show reversible hydrogen bonding between each analyte and the MOF. Thus,

we conclude that UiO-67 series of MOFs are capable of capturing both ammonia and acetone with little structural impact to the MOF and that thermal activation increases its uptake capacity.

## **COLL 339**

### **Confined fabrication of double perovskite quantum dots in metal-organic framework: Applications in solar photovoltaics**

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In the last few years, there has been a rising interest in metal-organic frameworks (MOF) for the purpose of enclosing guest molecules. These nanoporous MOF structures consist of a metallic ion connected by organic ligands. In addition, in recent times, there has been also an interest in halide perovskites which have excellent optoelectronic properties. However, two major problems have plagued the development of halide perovskites for optical applications namely: the presence of hazardous lead and stability. In this work, we have tried to address both these problems with the help of metal-organic frameworks and double halide perovskites. Recently, "double halide perovskites" have been developed in which two divalent 'Pb<sup>2+</sup>' cations are replaced with one monovalent and trivalent cation, generating quaternary  $A_2M^+M^3+X_6$  compounds. The problems in double perovskite structures are the same as that of normal halide perovskite. In this work, we have tried to encapsulate double perovskite quantum dots within nanoporous metal-organic frameworks. To fabricate Cs<sub>2</sub>AgInCl<sub>6</sub> quantum dots (QD), we have followed an earlier reported process by Manna et al. MOF thin films were deposited on a clean ITO substrate via LBL process. Zinc Nitrate and TCPP solution in DMF were spin-coated on ITO substrate. The deposited MOF was annealed at a temperature of 80 degrees to remove any residual solvent. Coated substrates were immersed for 10 mins in a solution comprising of ligands, Ag and In chloride salts. Diffusion of perovskite precursor in the micropores of MOF takes place which allows confined reaction and growth of the perovskite quantum dots. After washing with ethanol, the coated substrates were dipped in hot Cs-Oleate Solution, leading to the formation of confined quantum dots in the size range of MOF nanopores. Structural characterization of the sample was done by XRD which revealed strong peaks identical to the one reported before. Optical properties were determined by UV-vis spectrometry and PL spectrometry. Stability measurements showed significant PL emission for more than 20 days. Relatively, as-synthesized QDs decompose within hours due to agglomeration of nanoparticles, thereby losing their properties. At room temperature, Cs<sub>2</sub>AgInCl<sub>6</sub> @Zn-TCPP thin film shows emission at 470-490 nm, upon excitation at 350 nm, which is a 70 nm blue-shift from its powder sample (560 nm). The blue shift in the thin films confirms the encapsulating nature of the metal-organic frameworks.

## **COLL 340**

## Understanding the role of intrinsic and extrinsic defects on acetone interactions with isorecticular zirconium metal-organic frameworks

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Three dimensional Metal Organic Frameworks (MOFs) are a valuable class of porous, crystalline materials. However, their chemical and structural properties can deviate from the ideal framework through the formation of defects. Understanding the role of defects in MOFs is of fundamental interest as they play a crucial role in dictating their thermal and chemical properties. In this work, we subject the isorecticular zirconium MOFs, UiO-66 and UiO-67, to a variety of conditions in order to modify the defect concentration, both intrinsically and extrinsically. We define an intrinsic defect as structural deviations resulting from synthesis and extrinsic defects as post-synthetic structural changes resulting from heating. We investigate the relationship between defect generation and acetone binding under controlled conditions by monitoring analyte-MOF interactions via Temperature Programmed Desorption-Mass Spectrometry (TPD-MS) and Temperature Programmed IR (TP-IR) spectroscopy. TPD-MS studies performed on a high-defect UiO-66 (100 degrees Celsius synthesis) reveal differences in the relative distribution of acetone adsorption sites compared to that of a low-defect UiO-66 (220 degrees Celsius synthesis), suggesting that defects have a significant influence on the strength and nature of acetone binding interactions. Additionally, TPD-MS spectra of acetone adsorption on the highly-defective UiO-66 MOF reveals evidence for irreversible binding, suggesting chemisorption of acetone. *In situ* IR spectroscopy provides insight into how the structure of the MOF changes following successive thermal activations. We hypothesize that the concentration of defects can be increased by varying the sample activation temperature. Our results indicate that acetone binding interactions with the MOF are influenced by sample activation temperature. These studies further our understanding of MOF defects and their role in gas adsorption.

### COLL 341

#### Thermal analysis of metal-organic frameworks and their interactions with simple molecules

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Toxic industrial chemicals (TICs) are hazardous to humans and the environment upon exposure. Thus, technologies and materials that can mitigate their effects are necessary. Metal-Organic Frameworks (MOFs) are three-dimensional, crystalline, porous materials that are made of metal ions or clusters connected by organic linkers. High surface areas, porosity, and facile functionalization are desirable traits of MOFs

which make them capable of capturing, transporting and degrading TICs. In order to develop suitable MOF materials for preventive applications, preliminary studies of MOF-analyte interactions are essential to understand the fundamental MOF-analyte interactions. In this work, we probe the preference of analyte binding for acidic or basic functionalities present on MOFs. Two MOFs, a zinc 3-aminotriazole oxalate based MOF (ZnAtzOx) and an amine functionalized zirconium MOF (UiO-67-NH<sub>2</sub>) are used, containing carboxylate (acidic) and amine (basic) groups in their organic linkers, respectively. *In-situ* Temperature Programmed Desorption – Mass Spectrometry (TPD-MS) and Temperature Programmed Infrared Spectroscopy (TP-IR) experiments were performed under Ultra-High Vacuum (UHV) conditions, and the interactions of acetone and ammonia with the carboxylate and amine functional groups were monitored. Our results suggest that acetone preferentially binds to UiO-67-NH<sub>2</sub> as observed in the TPD-MS profiles. Acetone desorption from UiO-67-NH<sub>2</sub> was observed from two binding sites; however, for ZnAtzOx only one binding site was observed. We hypothesize that ammonia will have stronger adsorption to ZnAtzOx compared to UiO-67-NH<sub>2</sub>, due to the more favorable ammonia interactions with the 3-aminotriazole groups on ZnAtzOx. Our results indicate that the intrinsic framework structure and composition are likely contributors to the overall thermal stability of the material.

## **COLL 342**

### **Highly sensitive colorimetric immunoassay utilizing enzyme-catalyzed Ag growth on surface of Au nanoparticle-assembly SiO<sub>2</sub> structure**

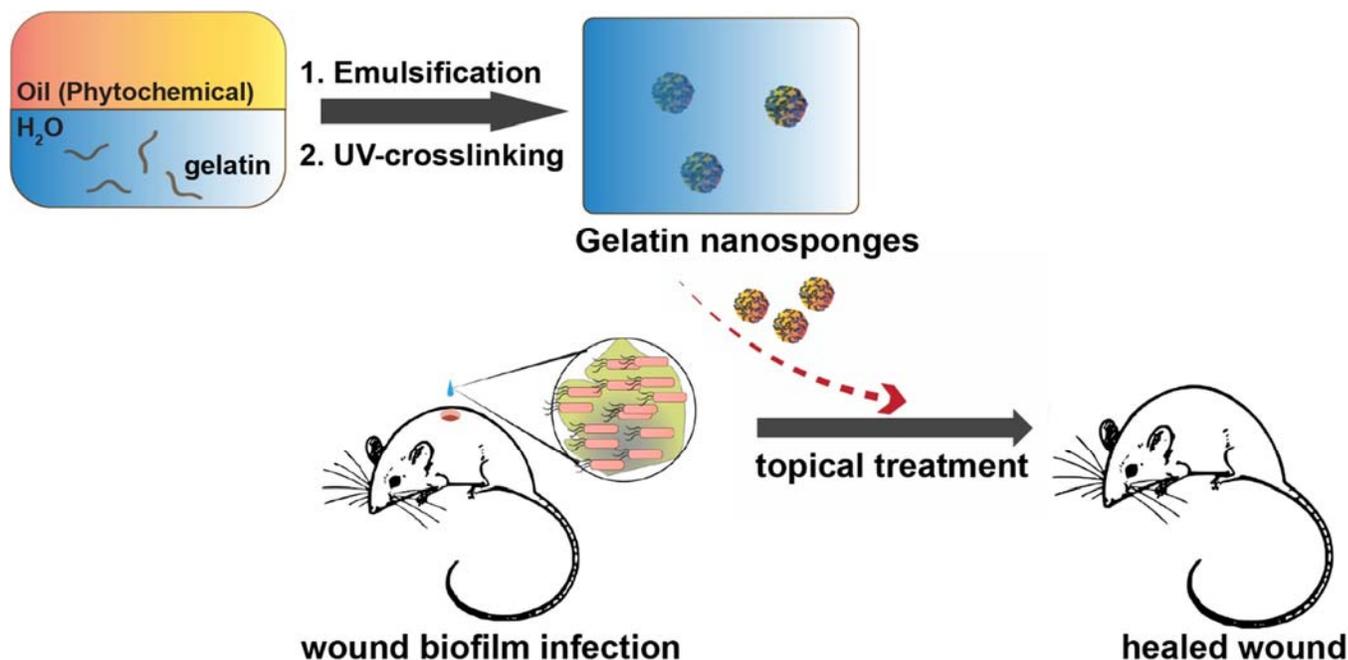
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Signal amplification of immunoassay using nanoparticles (NP) has attracted for enhancing the sensitivity and increasing the limit of detection. Among other nanomaterials, gold nanoparticles (Au NPs) is usually utilized signal amplification of immunoassay because of the excellent characteristics such as easy surface modification, chemical inertness and biocompatibility. The development of highly sensitive and quantitative Au NP-based immunoassays, however, was limited due to the narrowness of the dynamic linear range of Au NP-based immunoassays. In this study, we developed a new colorimetric immunoassay with broad dynamic range based on utilizing an alkaline phosphatase (AP)-catalyzed Ag growth on Au NP-assembled SiO<sub>2</sub> (SiO<sub>2</sub>@Au@Ag). In the presence of antigen (IgG) and catalysis of AP, incorporating the reduction of 2-phospho-L-ascorbic acid to ascorbic acid, cause convert Ag<sup>+</sup> ion to Ag coating on the surface of Au NPs embedded SiO<sub>2</sub>. This alloy structure amplified the signal of immunoassay by increase of the absorbance intensity signal of SiO<sub>2</sub>@Au@Ag at 430 nm in the presence of antigen. Based on the sandwich enzyme-linked immunosorbent assay (ELISA), this approach was demonstrated by the quantification of IgG. This method showed a detection limit of  $1.4 \times 10^{-13}$  M, which is hundred times higher dynamic range than that of conventional colorimetric immunoassays. The signal amplification method through the formation of SiO<sub>2</sub>@Au@Ag structures opens a new strategy for in vitro diagnosis of target proteins with the naked eye.

**All-natural crosslinked nanosponges for the topical treatment of wound biofilms**

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Wound infections are a serious threat to public health. Treatment of these wounds is complicated by formation of biofilms that are resistant to antibiotic penetration, as the wound bed is an ideal surface for attachment of microbes. Debridement of the infected tissue coupled with aggressive long-term antimicrobial treatments are currently used to treat wound biofilms. However, these strategies are ineffective, invasive, costly, and are susceptible to drug resistance development. Phytochemicals present a promising alternative to traditional antimicrobial agents against drug resistant bacteria and biofilms. However, their poor aqueous solubility limits their biomedical applications. Here, we report the use of gelatin as a biopolymer scaffold to stabilize phytochemicals and facilitate their delivery into biofilms. The resulting gelatin nanosponges (G-NS) were able to penetrate and eradicate both Gram-positive and -negative biofilms while having negligible toxicity to mammalian cells. Furthermore, G-NS facilitated healing of biofilm-infected wound in an *in vivo* murine wound biofilm model. The antimicrobial efficacy of G-NS coupled with the biosafety of the platform make these systems uniquely promising for the topical treatment of wound biofilms.



COLL 344

### Deposition and characterization of peptoid-gold nanoparticle composite films assembled at fluid interfaces

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The ability to detect water pollutant levels rapidly and accurately is critical to assessing their immediate impacts on human health. Traditional surface enhanced Raman scattering (SERS) sensors based on colloidal gold nanoparticles (AuNPs) have successfully been used to detect low levels of pollutants in water. However, these sensors can be highly unstable when in the presence of complex sample matrices like those found in environmental samples. SERS sensors based on highly ordered two-dimensional AuNP arrays have the potential to overcome these limitations, but reproducibly preparing these arrays still remains a challenge. This study focuses on preparing highly ordered two-dimensional AuNP arrays at the air-water and oil-water interface using a combination of hydrophobically modified AuNPs and amphiphilic peptoid polymers. Peptoids are a relatively new class of peptidomimetics that are easily synthesized, more stable than peptides, and can be programmed to bind targets like pollutants with high sensitivity. The peptoid-AuNP composite arrays were assembled in a Langmuir Trough where surface pressure vs. area measurements were used to investigate the interactions between the peptoid and AuNP ligands. Raman spectroscopy, atomic force microscopy, and scanning electron microscopy were used to characterize composite films that had been deposited on solid substrates using the

Langmuir-Blodgett method. Initial results suggest that the peptoid impacts the ordering of the AuNPs in composite films. These studies are critical to providing information on how the film will behave as a functional SERS sensor.

## **COLL 345**

### **Investigation of nanomaterial's safety through transpiration study in plants**

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Nanomaterials are very significant in several fields such as biomedicine and electronics because they have enhanced physicochemical properties due to their extremely small size and larger surface area compared to their bulk counterparts. When certain properties of nanomaterials are fine-tuned, designed and produced to solve specific problems, they are called “engineered nanomaterials”. Although engineered nanomaterials are promising in numerous applications, there is one major concern--- there is no complete knowledge on the possible adverse effects of these nanomaterials on immunological, inflammatory and regulatory systems of people.

Nanomaterials can be inhaled without even noticing because of their very small size. For instance, humans are exposed to nanomaterials by its release to the environment such as during manufacturing, use and disposal. Nanomaterials can get into the water streams and soil, eventually interacting with plants. This research focuses on transpiration study of plants which are fed by engineered nanomaterial dispersion considering inhalation is a major way of human exposure to nanomaterials.

## **COLL 346**

### **Furthering understanding of the impact of ligand composition on protein corona formation around Au nanoparticles**

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Coatings on nanoparticles in biological environments have a large impact on the dynamics and stability of the nanoparticles. The destinations, potential function, and the

amount of time the nanoparticles circulate in blood streams can be changed by the presence of ligands attached to the nanoparticle surface, or the formation and content of protein coronas that regularly form around nanoparticles. In this study, molecular dynamics is used to study how different ligands behave in solution and interact with proteins. The effect of altering the chemical end groups of ligands on their behavior in solution is explored in detail. Specifically, changing the number of carbon atoms at the end of an alkyl-PEG-alkyl chain was found to have a large impact on the structure of the ligands at the ligand-water interface, potentially altering ligand-protein interactions. Nanoparticles coated in alkyl-PEG-butanamide, alkyl-PEG-glucosamide, and PEG<sub>2000</sub> are found to each have a distinct conformation in solution which impacts their interactions with Bovine Serum Albumin and Concanavalin A. PEGylated chains ending in glucosamine result in a rough surface, capable of forming many weak unspecific non-covalent bonds with proteins and allows moderate water penetration into the ligand coating. PEGylated chains with a butanamide end group present a varied surface, with the majority being an ordered smooth hydrophobic surface at the water-nanoparticle interface, allowing little water penetration, while disordered sections result in water penetration into the ligand layer. PEG<sub>2000</sub> creates a very loose and disordered surface, where water can penetrate to the gold nanoparticle surface. The CHARMM36-Interface force field is used throughout all simulations which yields interfacial properties directly comparable to experimental measurements. The study is driven by experimental results and is expected to lead to new insight into how protein-ligand interactions work, as well as increasing understanding of how ligand conformations can affect their interactions with the environment. This will open doors to designing ligands with the goal of forming specific protein coronas to be able to control the destination of therapeutic nanoparticles.

## **COLL 347**

### **Biomimetic 2D template mediated recognition and stabilization of peptide form super $\alpha$ -helices**

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The fabrication of secondary structure peptides in presence of artificial material through a specific and selective alloy has been a challenging problem. Biomimetic, the template graphene oxide (GO) and other 2D charge materials can also be used as a receptor for molecular surface recognition. The tunable properties GOs which can utilize as site-specific interactions to generate protein mimicking unnatural systems. Our aim, to designed different side chain residue peptides which consist specific recognizer such as amino acid residue at suitable interval i.e., arginine and aspartic acid for electrostatic recognition and phenylalanine for hydrophobic recognition that induced to appear secondary conformations. Based on the nature of peptides the secondary conformation can be control the edge vs surface materials, which may give the valuable information in biology.

## **COLL 348**

### **Impact of hydrophobicity/hydrophilicity on PAMAM dendrimer-lipid bilayer interactions**

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Biomaterials based on dendrimer, highly branched synthetic macromolecule, have been extensively studied in applications such as drug carriers, imaging agents, and gene delivery vehicles. One of the major challenges in using dendrimers in biomedical applications is understanding their cytotoxicity, cellular uptake, and cellular membrane interaction in relation to their size and surface modification. Studies of modified dendrimers interacting with controlled compositions of lipids in a model lipid bilayer were conducted in order to better understand the dendrimer cellular uptake mechanism. In this study, Generation 3-5 poly(amidoamine) (G3-5 PAMAM) dendrimers were used with amine terminated surface functionalization and with fluorescein isothiocyanate (FITC) and poly(ethylene glycol) (PEG) modification in order to determine how altering the degree of hydrophobicity/hydrophilicity on a macromolecule impacts the interaction of the macromolecule with the bilayer. Water permeability, a sensitive probe for the lipid bilayer structure, was measured on the models of the biological membrane made by the Droplet Interface Bilayer method. Combined with Confocal Raman Microspectroscopic and Differential Scanning Calorimetric studies, this study provides insights on the nature and extent of the interaction between PAMAM dendrimer and cell membrane.

## **COLL 349**

### **Custom PLA/PLGA nanoparticles for bio-applications**

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In the past two decades poly lactic-*co*-glycolic acid (PLGA) and polylactic acid (PLA) polymers have attracted enormous attention due to their tunable mechanical properties, biocompatibility, biodegradability, and safe profile (FDA approved) that make them the most popular choice for clinical applications. Of interest is the nanoparticle (NP) compositions prepared from these polymers. Since these polymers, biodegrade through the hydrolysis of ester linkages giving rise to benign lactic and glycolic acid, they are extremely popular in drug delivery. The size and the surface of NPs can be tuned to include targeting capabilities.

The Chemical and Nanoparticle Core (CNSC) at The University of Pennsylvania has long been interested in the property control of such NPs with the aim to enable novel formulations suitable for drug delivery and imaging. Our findings from the core scientists' unique perspective will be presented.

## **COLL 350**

### **Effect of peptoid monolayers on functionalized gold nanoparticle film assembly at the oil-water interface**

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Gold nanoparticles (AuNPs) that are ordered in two-dimensional (2D) arrays have been shown to exhibit optoelectronic properties that make them useful in a variety of technologies, including sensors for pollutants. These properties depend on the way the particles are arranged within the array. Previous work has shown that AuNPs can be simply and inexpensively assembled into 2D arrays at fluid interfaces using a Langmuir trough, but controlling the exact patterning of the AuNPs at the interface remains a challenge. Our research focuses on controlling the assembly of hydrophobic AuNPs at fluid interfaces using amphiphilic peptoids that readily form highly ordered monolayers. To study whether peptoid monolayers effectively control the 2D assembly of dodecanethiol ligated and phenylethanethiol ligated 5nm AuNPs, we use the Langmuir-Blodgett method to transfer composite films from fluid surfaces to silicon thermal oxide wafers. The deposited films are then characterized using optical microscopy and AFM imaging. Preliminary results show that the AuNPs do not completely cover the peptoid monolayer, but instead assemble into regions in which they are densely packed. In these regions, the AuNP ligands integrate into the peptoid monolayer. The peptoid-AuNP composite films are more uniform than those of only peptoid or only nanoparticle, and the peptoid-dodecanethiol AuNP composite films demonstrate a more uniform film than those with phenylethanethiol AuNPs. The flower-like pattern observed with the peptoid-phenylethanethiol composite film is likely due to the pi-pi interactions between the peptoid and the phenylethanethiol AuNPs.

## **COLL 351**

### **Optimizing gold nanoparticle-fluorophore interactions to minimize fluorescence quenching**

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Gold nanoparticles (AuNPs) are widely explored for many biomedical research applications such as drug delivery, imaging, and fluorescence-based assays or sensors. Their surface modification allows for the attachment of targeting moieties for site-directed delivery to specific tissues and cells as well as fluorescent markers for visualizing uptake and retention in cellular environments. The overall goal is to design nanomaterials that are soluble in biological environments, non-toxic, stable, and fluorescent with no or minimal background fluorescence. While there exist many types of AuNP-fluorophore conjugates, the challenge with these is that the fluorescence

behavior is altered upon surface conjugation. The fluorophore can interact with the AuNP surface to either undergo quenching or fluorescence enhancement depending on the physical property of the AuNP (size or shape) and the organic dye. There is still a critical need to determine how the size and shape affect the fluorescence behavior. More importantly, what features of dye and AuNP are needed to optimize the fluorescence behavior. Here we will present fluorescence spectroscopy studies evaluating the effect of AuNP size and shape on the fluorescence behavior of a variety of dyes. We will also present studies evaluating the impact of the donor-acceptor distance and concentration of dye on fluorescence quenching by AuNPs. We expect these studies will provide users with important design rules for designing AuNP-fluorophore conjugates for various applications where the features of the AuNP and fluorophores are equally important.

## **COLL 352**

### **Novel near infrared molecular probe provides rapid *in vivo* readout of thrombin activation**

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Thrombin is a serine protease and regulator of hemostasis that plays a critical role in the formation of obstructive blood clots, that is a life-threatening condition associated with numerous diseases. To detect thrombi in living animals, we design and conjugate thrombin-sensitive peptide substrates to the surface of Polylysine. The Thrombin imaging agent consists of a polymer backbone derivatized with multiple copies of a Thrombin-cleavable peptide substrate containing a NIR fluorochrome, resulting in strong intramolecular quenching at baseline. After enzymatic cleavage, the fluorochromes separate, resulting in substantial amplification of the NIR fluorescence (NIRF) signal. For the present study, the highly specific CatK peptide substrate was used to construct the Thrombin-activatable NIRF agent. In the presence of Thrombin, this peptide substrate undergoes cleavage between the Arginine and Serine residues. This Thrombin-specific peptide substrate resists scission *in vitro* by a wide range of proteases and does not undergo cleavage by other enzymes.

Thrombin activity can be imaged *in vivo* by using this novel thrombin-activatable and thrombin-specific NIR molecular probe. The thrombin probe could enhance the understanding of the role of thrombin in thrombogenesis and other homeostatic and pathological conditions.

## **COLL 353**

### **Comparative assessment of different lipoplex pegylation strategies**

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The study will present our recent results in PEGylation of lipoplexes using different strategies of PEGylated conjugate insertion, together with physicochemical and biological properties of generated PEGylated lipoplexes, in a comparative manner.

## **COLL 354**

### **Competition of organic ligands on gold nanostars**

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Counterfeiting is a massive industry that sucks money out of legal markets and hurts consumers. To combat the ever-evolving industry, more complex anti-counterfeit measures must be developed. One such development is using different combinations and concentrations of organic ligands in solution with plasmonic gold nanostars as anti-counterfeiting SERS tags, which can be then analyzed through principle component analysis (PCA). The purpose of this project is to further understand how the surface-enhanced Raman scattering (SERS) signals from different organic ligands impact each other in order to synthesize more complex anti-counterfeiting tags. The distinct SERS signals of 4-mercaptobenzoic acid and malachite green make these ligands excellent candidates for the SERS security tags. By exploring how the concentrations of these two ligands impact the Raman spectra, we can use trace amount of ligands to produce SERS security tags, which will result in differentiable SERS spectra. The large number of molecular combinations coupled with the PCA technology necessary to analyze the SERS security tags would make these nanostars an ideal candidate for a new generation of anti-counterfeit measures.

## **COLL 355**

### **Magneto-optical characterization of magnetic nanoparticles confined in a lyotropic liquid crystalline matrix**

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Hybrid complex fluids composed of iron oxide magnetic nanoparticles (MNPs) and liquid crystals have unique properties of interest for applications such as drug delivery and information storage. When MNPs are incorporated into a liquid crystalline phase, their positions and orientations are confined, which can result in a different magnetic response compared to MNPs in an aqueous environment. Here, we study the magnetic response of iron oxide MNPs confined in a bicontinuous cubic lyotropic liquid crystalline (LLC) matrix using an AC Faraday rotation setup. We explore MNP magnetic response as a function of MNP size (15, 20, 25, and 200 nm) and MNP concentration in the LLC matrix. We compare these results to the behavior of the same MNPs in aqueous solutions, which provides insight on the effects of LLC confinement on MNP magnetic response. Furthermore, we investigate the influence of MNP functionalization on their response in an LLC phase. This work may have implications in the development of MNP-containing complex fluids with targeted properties and lends itself to future fundamental investigations into the magnetic response of MNPs confined in different LLC phases.

## **COLL 356**

### **Mesoporous organosilica nanotubes templated by judiciously selected Pluronic surfactants**

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Commonly used, commercially available poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) Pluronic P123 surfactant (EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>) was reported earlier to be suitable as micellar template for organosilica nanotubes, but the resulting nanotube products were significantly curved and/or locally formed bundles. This inadequate quality of the nanotube product is most likely due to insufficient size of poly(ethylene oxide) (PEO) block that forms the micelle corona, the latter being a space for the framework formation and the agent to stabilize the nanotubes against consolidation into bundles through the retention of free ends of PEO blocks on the nanotube periphery. While the quality of the nanotube products can be greatly enhanced using mixtures of appropriate Pluronic surfactants, one providing long PEO blocks and the other one promoting the formation of cylindrical micelles, we hypothesized that an appropriate selection of a single Pluronic surfactant may also allow one to template high-quality organosilica nanotubes. Such a surfactant would need to have sufficiently long PEO blocks to promote the formation of a stable organosilica framework and to prevent consolidation, and a significant fraction of poly(propylene oxide) (PPO) component to facilitate the formation of cylindrical micelles. In our study, single Pluronic surfactants swollen by ethylbenzene were used for synthesis of ethylene-bridged organosilica mesoporous nanotubes with tunable inner diameters. The products were characterized by using transmission electron microscopy, nitrogen adsorption and solid-state NMR. Using the combination of Pluronic P105 (EO<sub>37</sub>PO<sub>56</sub>EO<sub>37</sub>) as surfactant and

ethylbenzene as a micelle swelling agent, a series of ethylene-bridged organosilica nanotubes were obtained with tunable inner diameters from ~10 to ~20 nm, as the initial synthesis temperature decreased from 20 to 15°C. The nanotubes synthesized under appropriate conditions had very uniform diameters and did not have much tendency to form bundles. At 16-20°C, the nanotubes had negligible nanosphere contamination. Moreover, the combination of Pluronic P104 (EO<sub>27</sub>PO<sub>61</sub>EO<sub>27</sub>) and ethylbenzene afforded much larger ethylene-bridged organosilica nanotubes, with inner tube diameter ~25 nm, although there were quite many nanospheres present in the product. This study showed a promising way for synthesizing high quality organosilica nanotubes.

## **COLL 357**

### **Tuning sol-gel GeO<sub>2</sub> and core-shell GeO<sub>2</sub>-SiO<sub>2</sub> reaction conditions to optimize particle properties for use in 3D printing glass optics**

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We report the formulation of sol-gel derived GeO<sub>2</sub> and GeO<sub>2</sub>-SiO<sub>2</sub> core-shell colloidal suspensions for use as feedstocks in direct ink write (DIW) 3D printed glass optics. Germania-silica or GeO<sub>2</sub>-SiO<sub>2</sub> colloidal feedstocks are of interest because silica-germania glass exhibits similar physical and optical properties of traditional silica glass, but with reduced wavefront error or scatter loss. Additionally, the refractive index of SiO<sub>2</sub>-GeO<sub>2</sub> can be readily tuned by proportionally increasing the amount of Ge-dopant. While existing reports of sol-gel GeO<sub>2</sub> particle formulations do exist in the literature, there is no comprehensive investigation that accounts for the combination of factors important for use as DIW glass feedstocks. As a result, we have surveyed a wide range of reaction conditions (i.e., H<sub>2</sub>O, catalyst, and temperature) to determine the optimal sol-gel GeO<sub>2</sub> particle formulation. Optimization was evaluated by studying particle size, shape, and morphology using DLS and TEM. From our optimized GeO<sub>2</sub> sols, we have also identified multiple pathways to prepare core-shell GeO<sub>2</sub>-SiO<sub>2</sub> particles of various shapes and sizes as shown by TEM. We have also demonstrated proof-of-concept that these particles are viable DIW glass feedstocks. Ongoing research includes studying the chemical characterization of the core and core-shell particles at various stages of particle growth and glass formation.

## **COLL 358**

### **Direct functionalization of graphene nanoplatelets and their effect on dispersion and mechanical properties**

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Graphene is a carbon-based material with  $sp^2$ -hybridized carbon atoms arranged in a hexagonal lattice. Due to its multifunctional properties, *i.e.* high conductivity, hydrophobicity, tensile strength, barrier, *etc*; graphene has shown to be a promising material in a variety of fields. Introduction of surface functional groups can help to enhance the multifunctional properties. Both amination and fluorination of graphene nanoplatelets was performed without the use of pre-treatment with strong oxidizers. Amination of graphene was performed with urea as the amine source and eco-friendly solvents. Fluorination of graphene (FG) was done using direct gas fluorination with a dilute mixture of  $F_2/N_2$  at room temperature. The fluorine content can be adjusted by altering either the pressure or the time of the reaction. Surface functionalization was determined through analytical techniques, including FTIR, XPS, SEM-XRF, and TGA. Both AG and FG materials were composited in a 2K epoxy resin to observe their effect on mechanical properties. After functionalization the tensile strength of both composites increased versus pristine material. Additionally, dispersion studies were performed with both functionalized graphene materials to observe their effect on dispersion stability. AG showed stability in dispersions with NMP, DMF, and ethylene glycol for 60 days. These studies show that through functionalization the properties of graphene can be enhanced.

## **COLL 359**

### **Large-scale patterned plasmonic nanoparticle assemblies**

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We use a scalable, and robust soft lithographic technique, chemical lift-off lithography, to pattern plasmonic gold nanoparticles (AuNPs). Specifically, mercaptoalkanol-functionalized AuNPs are self-assembled on a liquid-liquid interface then are subsequently transferred onto desired substrates. Click-chemistry between an activated polydimethylsiloxane (PDMS) stamps and the mercaptoalkanol are utilized to form strong covalent bonds in the patterned region of the stamp. Upon "lifting-off" the PDMS stamps, large-scale plasmonic structures with gold nanoparticles as building blocks exhibits collective optical properties based on the design of the pattern. Using this method, we have arranged AuNPs into micron-size linear chains and square spiral over millimeter-sized substrates. Those structures are capable of coupling to other materials (*i.e.* 2d transition metal dichalcogenides) to enhance their optical performance. The developed approach enables robust fabrication of wafer-scale functional architectures with pre-programmed plasmonic properties.

## **COLL 360**

### **Controlled synthesis and transfer of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene nanosheets with SERS performance**

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Surface-enhanced Raman scattering (SERS) is a molecule-specific and highly sensitive spectroscopic technique widely used for chemical and biological sensing. Herein, we report a facile approach to synthesize and transfer Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> nanosheets onto Si and SiO<sub>2</sub>/Si substrates. The structure and SERS performance of the individual Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> nanosheets were characterized by co-localized measurements using a combined atomic force microscopy (AFM)-Raman spectroscopy system. Our results indicate that the SERS performance of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> nanosheets is thickness contingent, and the enhancement factor of some nanosheets reaches up to 106, which is comparable to the best non-noble metal SERS substrates being reported in the literature. Unexpectedly, a small enhancement of silicon Raman peak was also observed, which might be explained by the generation of non-resonant plasmons in Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> nanosheets, resulting from the physical proximity of the laser irradiated MXene sheets and the silicon substrate. The plasmonic contribution to SERS activity of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> nanosheets was further confirmed by molecular dynamics simulation. The findings reported here shed new light on the optimization of substrate thickness in developing highly flexible and sensitive sensing platforms based on MXenes.

## **COLL 361**

### **Synthesis of colloidal quantum dot-based heterostructures for photon upconversion**

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Photon upconversion is a process by which two or more low-energy photons are absorbed and one higher-energy photon is emitted by a material. Materials that can achieve photon upconversion are desirable for many applications such as optoelectronic devices, drug delivery, and photovoltaics. A key advantage of using semiconductor nanoparticles for photon upconversion is their wide tunability in structure, which consequently affects their absorption and emission properties. We have synthesized colloidal quantum dot (QD) heterostructures for this purpose, in which two QDs with different bandgaps are separated by a wide-bandgap nanorod. While our

CdSe(Te)/CdS/CdSe core/rod/emitter structures demonstrate near-infrared (NIR)-to-visible photon upconversion, their upconversion efficiencies show significant room for improvement. The performance of these structures can be enhanced through a better understanding of their underlying properties and the effect of these properties on upconversion efficiency. While we can further our understanding through theoretical modeling, we must also consider the constraints of available synthesis techniques. Synthesis parameters such as ion precursors, organic ligands, reaction time, and temperature, among others, can be tuned within well-studied procedures to create structures with the desired composition, structure, and resulting optical behavior. For example, introducing a bandgap gradient along the nanorod through doping has been found to funnel carriers to the emitter, increasing both quantum yield and upconversion efficiency. We have therefore studied an “inverted” emitter/rod/core structure which allows this gradient to form more naturally during synthesis. We have also found that charge carrier separation can be improved by controlling the position of the core along the rod and by optimizing the length of the rod. This has led us to explore spherical CdTe/CdS/CdSe core/shell/shell structures with varying shell thicknesses and gradients to further tune absorption and emission wavelengths. We present these synthesis methods, the resulting structures, and their impact on upconversion performance as characterized by TEM, absorbance, and photoluminescence measurements. We describe how further upconversion performance enhancement can be achieved through improved structural control, which will allow for future incorporation into various photonic device applications.

## **COLL 362**

### **Thermodynamic stability of perovskite-phase CsPbI<sub>3</sub> enforced by nanotemplating**

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Perovskite phase cesium lead iodide CsPbI<sub>3</sub> has emerged as a promising all-inorganic photovoltaic (PV) absorber material for its remarkable optoelectronic properties such as optimal band gap, high absorptivity, high charge carrier lifetime and solution processability, all desired qualities for PV cells. However, under ambient conditions, CsPbI<sub>3</sub> transforms into a high density, non-functional, non-perovskite yellow phase. Researchers have observed that perovskite-phase CsPbI<sub>3</sub> is more stable in the form of quantum dots and thin films. Proceeding with the hypothesis that this is an effect of reduced dimensionality, we have sought a robust approach for enforcing controlled nanostructure. To do so, we synthesized CsPbI<sub>3</sub> in the pores of prefabricated anodized aluminum oxide (AAO) membranes to restrict crystal growth. Nano-structuring thus provides a truncated crystal lattice, which we hypothesize weakens the impact of the long-range, compressive electrostatic forces that act upon the CsPbI<sub>3</sub> unit cell. Under such reduced compression, a lower density, expanded lattice, namely the black perovskite phase, is favored. Herein is described a systematic study of phase transition thermodynamics of CsPbI<sub>3</sub> as a function of crystal confinement dimension, for perovskite synthesized in AAO scaffolds with pore sizes ranging from 10-250 nm. X-ray

diffraction is employed to quantify the resulting expansion of the lattice. We found a 250 C drop in the phase transition temperature as a consequence of nano-templating in AAO with pore sizes lower than 80nm; crystals synthesized in larger pores showed standard phase transition temperature of 330 C, consistent with bulk CsPbI<sub>3</sub>. This approach could potentially stabilize the functional perovskite phase of CsPbI<sub>3</sub> at near ambient conditions.

## **COLL 363**

### **Amine functionalization and *in situ* reduction of carbon nanotubes nanonetworks for solar electrode applications**

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Carbon nanotube (CNT) nanonetworks offer impressive promise for clean energy applications owing to ballistic electron transport and tunable conductivity. However, many envisioned CNT-based electronic devices have not yet been commercialized because of the limited water processability of CNTs. A widely accepted method to increase the aqueous phase polydispersity involves functionalization that introduces hydrophilic groups to the exterior surfaces of CNTs. This functionalization frequently employs harsh reaction conditions using strong acids and oxidizing agents that can damage nanostructures, leading to defects and reduced conductivity. We report here alternative, nondestructive syntheses that create connected conductive carbon self-assemblies using noncovalently attached amines, as compared to destructively functionalized CNTs with covalently bonded amine groups. These amine grafted/functionalized CNT nanomaterials were mixed with both surfactants and Laponite™ nanoparticles to produce stable colloidal dispersions. Solid composites containing CNT networks were cast through aqueous phase self-assembly on various substrates including indium tin oxide and aluminum coated electrodes for the development of bulk heterojunction solar nanocomposites. The nanocomposite films containing destructively functionalized CNTs were subsequently reduced in-situ to restore conductivity and to establish conductive pathways. Nanocomposite electrical performances were investigated by conductive atomic force microscopy (cAFM) and surface morphologies were studied using tapping mode AFM analyses. Amine functionalization of CNTs, when combined with dispersing agents and surfactants, has proven successful for fabricating water processable conductive nanocomposite films for solar electrodes.

## **COLL 364**

### **Computationally guided synthesis of manganese substituted ferrites**

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Metal substituted ferrite nanoparticles ( $MxFe_{3-x}O_4$ ,  $M = Mn, Co, Ni, \text{ or } Zn$ ) have been synthesized and applied for a variety of biomedical applications such as magnetic hyperthermia treatment, drug delivery, and MRI contrast agents with tunable magnetic properties comparing to iron oxide. To optimize the magnetic performance of the materials, we performed quantum chemical simulations through VASP and computationally optimize the lattice parameters (LPs) of different compositions and configurations of substituted metal ferrites to find the correlation between a material's composition and its magnetic properties. As a result, we found that computationally optimized LPs generally matched the experimentally observed LPs well. Composition was shown to affect the optimal LP differently based on the substituted metal. While configuration (spinel or inverse spinel) did not significantly impact the optimal LP, randomized distribution impacted magnetic moment greatly. To validate the computational model and back feed the model with experimental data manganese ferrite particles with different compositions were synthesized via chemical reaction and characterized afterwards. Ultimately, better understanding of the lattice parameter enhances our ability to tune ferrites' magnetic properties and eventually allows for a calibrated computational model of substituted metal ferrites.

## **COLL 365**

### **Atomic-scale imaging of a free-standing monolayer clay mineral nanosheet by aberration-corrected scanning transmission electron microscopy**

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Direct imaging of single atoms or molecules on/inside low-dimensional nanomaterials has been significantly progressed owing to the recent development of an aberration corrected electron microscopy. Anionic-charged two-dimensional (2D) clay mineral nanosheets were used in this study as a host material to build a supramolecular 2D assembly of cationic guests via electrostatic interaction, which were successfully characterized by spectroscopic techniques. For deeper understanding of clay-based supramolecular chemistry, direct imaging of the clay nanosheet and its molecular complexes in atomic-scale is the key issue. However, atomic-scale imaging of the clay nanosheet and its molecular complexes by electron microscopy has not been achieved, since clay minerals are typically sensitive to an electron beam irradiation. Here, the first atomic-scale imaging of a free-standing monolayer clay mineral nanosheet by annular dark field (ADF) imaging on aberration-corrected scanning transmission electron microscope (STEM) is demonstrated. ADF-STEM measurement was conducted at an acceleration voltage of 300 kV using a FEI Titan Cubed G2. STEM samples were prepared by dropping a solution containing well-dispersed aqueous suspension of the montmorillonite (MMT, Figure) nanosheet onto a carbon-coated Cu

grid. The monolayer MMT nanosheet was stably observable under the optimum conditions, while typical bulk clay minerals are highly sensitive to an electron beam irradiation during the electron micrography. Moreover, to understand the stability of monolayer MMT nanosheet during the electron beam irradiation, we analyzed the decrease of Selected Area Electron Diffraction (SAED) intensity with TEM mode which showed the higher stability of monolayer than stacked tri-layers.

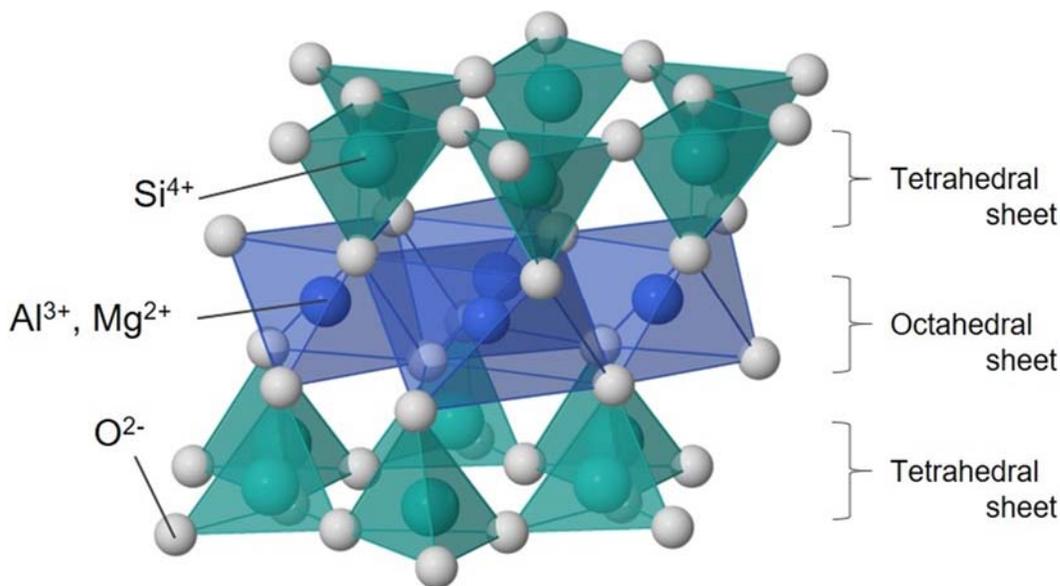


Figure. Unit structure of the montmorillonite nanosheet.

## COLL 366

### Chemically deposited and photodeposited Ag nanoparticles on rutile TiO<sub>2</sub>

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For catalytic or photocatalytic purposes, semiconductors are functionalized by metal nanoparticles that are deposited by chemical reduction or by photodeposition. In chemical reduction, positive metal ions are reduced by electron donors in reaction solution, forming nanoparticles that adhere to the semiconductor surface. In photodeposition, positive metal ions are reduced by the photoexcited electrons from the semiconductor conduction band and deposited on the semiconductor surface. In this comparative study, Ag nanoparticles were photodeposited or chemically deposited onto 100nm rutile TiO<sub>2</sub> powder (semiconductor). Trisodium citrate was used as both the reducing agent and protection group to generate hemispherical Ag seeds on the surface

of TiO<sub>2</sub>. Ascorbic acid and poly(sodium 4-styrene sulfonate) were served as protection groups added subsequently to continue growing Ag hemispherical seeds on TiO<sub>2</sub> into Ag nanoprisms. Mass loading, size distribution, and optical spectra of deposited Ag nanoparticles were measured by Flame Atomic Absorption, Transmission Electron Microscopy, and UV-visible Absorption.

## **COLL 367**

### **Metal nanocluster modify the band gap and maintain the ultrathin nature of semiconducting two-dimensional materials**

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Modifying the bandgap of semiconducting two-dimensional materials (S2DM), such as monolayer molybdenum disulfide (MoS<sub>2</sub>) is useful in ultrathin optoelectronic applications. Electron doping is an efficient technique to alter the electronic bandgap and change the exciton binding energy of MoS<sub>2</sub>, thus modifying the optical bandgap. Photoexcited silver nanoclusters (AgNCs) can produce a large number of energetic hot-electrons with a lifetime in the hundreds of picoseconds time scale. These hot-electrons can inject into the conduction band of a single-layered MoS<sub>2</sub> thereby modifying its optoelectrical properties when AgNCs come in contact with the sheet. Additionally, increasing AgNCs coverage density on MoS<sub>2</sub> surface increases the electron doping density. At low AgNCs coverage density, the absorption and photoluminescence (PL) spectrums of MoS<sub>2</sub> are red shifted as a result of bandgap renormalization. The magnitude of the redshift increases as the coverage density of AgNCs is increased before blue-shifting remarkably at high AgNCs coverage. The blue shift is attributed to the population of the high energy dark excitonic states. The optical band gap of monolayer MoS<sub>2</sub> is also tuned by integration with silver nanodisk (AgND). Unlike the high efficiency and controllable modification of bandgap of MoS<sub>2</sub> by AgNCs, photoexcited AgNDs exhibit opposing effects on the bandgap of MoS<sub>2</sub>. Photoexcited AgNDs produce a strong electromagnetic field, which changes the spin-orbital coupling inside the MoS<sub>2</sub> and so the electronic bandgap of MoS<sub>2</sub>. The plasmon field decays generating hot-electrons which cross the nanoparticle/MoS<sub>2</sub> Schottky barrier and inject into the conduction band of MoS<sub>2</sub> within a hundred femtoseconds. Hot-electron of AgNDs ascribes its limitation to that delay the electron injections process lead to the relaxation of hot-electrons, which generates heat that induces the transformation of 2H semiconducting MoS<sub>2</sub> into metallic 1T.

## **COLL 368**

## **Efficiency of Ni-Mo-P nanoalloys catalysts with various compositions and crystal structures towards hydrogen evolution reactions**

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Hydrogen is a clean and environment-friendly fuel. The current predominant industrial technique for hydrogen production is steam reforming which depends on fossil fuel that is on its way of depletion and produces the greenhouse gas as a byproduct. On the other hand, the clean substitute, electrolysis takes only 4% of hydrogen production, because of the high cost of the noble metal electrodes used. Transition metals electrodes and their phosphides showed good comparable activity along with low-cost, high durability, abundance and ease of fabrication. Recently, we have synthesized Ni-Mo alloy NPs and studied their characteristics as high efficiency, durable water splitting catalyst. Upon phosphidation, the phosphide changes the catalyst surface, creating localized negative charges that attract protons that facilitates their coupling for hydrogen production. Herein, we have used colloidal synthesis to produce two distinct crystal structures of Ni-Mo-P alloy NPs with a varying Mo composition (0-18%), and morphology at moderately high temperatures. In addition, electrocatalytic activity and durability were investigated by recording overpotentials, Tafel slopes and chronoamperometry using linear sweep voltammetry (LSV). The effect of synthetic and physical parameters on electrocatalytic activity and efficiency of hydrogen reduction reactions will be explained.

**COLL 369**

## **Microwave assisted synthesis of cesium lead halide nanoplatelets**

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In this presentation, we will describe the effect of solubility and microwave synthesis in the preparation of 2-dimensional (2-D) all-inorganic CsPbBr<sub>3</sub> perovskite nanoparticles (NPs). In this study, we synthesized 2-D CsPbBr<sub>3</sub> nanoplatelets in benzyl ether (BE) using a synthetic microwave with precise control over temperature ramping and cooling, while similar synthesis in 1-octadecene (ODE) produced 0-D perovskite quantum dots. In addition, CsPbBr<sub>x</sub>I<sub>3-x</sub> perovskite NPs with tunable band gap and narrow emission were synthesized using different ratios of halide precursors in either solvent. Size and morphology of the 2-D nanoplatelets were investigated using TEM and AFM and their crystal structure was confirmed using XRD. To shed light on the lateral growth mechanism of the nanoplatelets, we performed Benesi-Hildebrand analysis to calculate the equilibrium constant of lead halide complexes in the presence of BE and ODE. Our

study indicated that shape and optical properties of perovskite NPs can be tuned with control over the solubility of the precursors.

## **COLL 370**

### **Comparative study of the environmental exposure of common lithium ion cathode materials coated with iron oxide**

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As efforts towards global energy sustainability increase, there has become a higher demand for energy storage products. A common cathode material used in commercial energy storage products is LiCoO<sub>2</sub> (LCO). LCO has become quite costly as the global supply of lithium and cobalt is limited. To improve costs for these materials the cobalt can be replaced with other transition metals to improve stability and performance, such as been studied with LiNi<sub>x</sub>Mn<sub>y</sub>Co(1-x-y)O<sub>2</sub> (NMC), with reduced costs compared to LCO. Due to the current lack of recycling infrastructure for these materials there is a high risk of environmental exposure. Previous work done by the Center for Sustainable Nanotechnology has shown that is exposure is damaging to biological systems because of the release of toxic ions from the cathode surface. To deter the environmental impact of these materials the release of ions should be hindered. Studies on iron oxide coatings for cathode materials have shown improved results on the electrochemical performance of the cell. Studying the properties of these coatings may be a way to enhance the performance of these materials and mitigate their potential environmental impact (by limiting ion release).

The properties of the two cathode materials (NMC and LCO) are compared using the analytical techniques of x-ray photoelectron spectroscopy, powder x-ray diffraction, ICP-OES, and electrochemical cell testing. Both materials are coated with iron oxide to observe any changes in dissolution, electrical potential, and structure. These tests give insight into the sustainable properties of the iron oxide coated cathode materials. Preliminary results show that the presence of the iron oxide coating on similar materials will impact dissolution and improve electrochemical performance. Using iron oxide as a coating will serve as a simple, bulk, inexpensive coating that can improve the industrial uses of these materials and reduce their impact on environmental systems.

## **COLL 371**

### **Stimuli-responsive poly(4-vinylpyridine) hydrogel structure and hydration via neutron reflectometry**

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This work studies the effect of film fabrication parameters on the structure of highly-responsive multilayer films of poly(4-vinylpyridine), used to form neutral single-component nanothick hydrogels. The effect of crosslinking degree and chain deposition on hydration and thickness are probed with neutron reflectometry (NR). The benefit of NR in hydrogel experiments is that it allows the elucidation of internal structure in a way not available using photon-based measurements. Neutrons interact directly with the nuclei of constituent atoms and, using isotopic substitution, can be made sensitive to specific polymer layers and to the presence of water. By using polymers or solvents containing deuterium, resolution of internal structure at the nanometer scale is possible. This capability allows us to understand well-stratified films and hydrogels as unified structures, enabling us to resolve polymer layers with distinct chemistries, or to see the way stimuli-responsive polymers absorb water. This view, coupled with more conventional techniques such as ellipsometry, deepens our understanding of these materials. Specifically, NR has been used to track internal changes as pH passes through the pKa, driving the film between its hydrophobic basic and hydrophilic acid states.

Films of PVP can undergo an over 10-fold increase in volume at low pH if deposited through the spin-assisted layer-by-layer (LbL) technique, which results in high-entropy stratified layers. The degree of swelling and collapse are closely related to the method used to deposit the layers (either spinning or dipping) and the degree of crosslinking (4% of crosslinked backbone groups versus 7%). The least-crosslinked hydrogel with high stratification can increase volume 11.5 fold versus the dry film, corresponding to a  $0.91 \pm 0.05$  D<sub>2</sub>O volume fraction. Above the pKa, the volume increase is 3 fold, consisting of  $0.60 \pm 0.01$  water. In addition to gross swelling, proton/deuteron contrast highlights the distribution of water throughout the film.

## **COLL 372**

### **Toward sequential assembly of finite 1-D origami arrays of sensing nanostructures**

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There are several possible routes to the synthesis of complex macromolecular assemblies. These approaches can be parsed along a continuum arranged according to the information content of the building blocks. "One pot" self-assembly can be enabled if the building blocks have sufficient information content. In the approach reported here, minimal spatial/localization information is encoded in the building blocks, requiring that

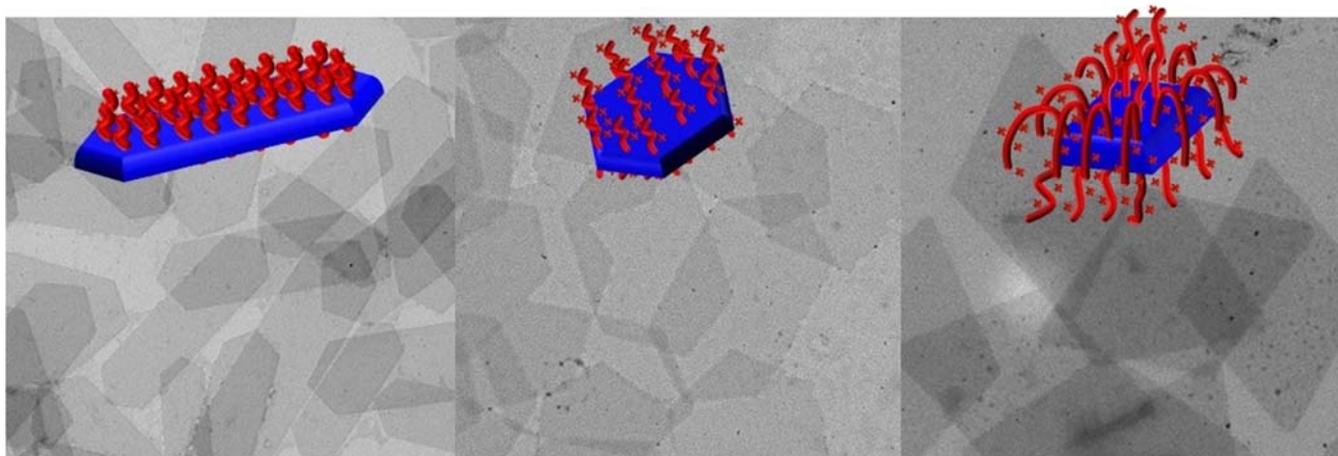
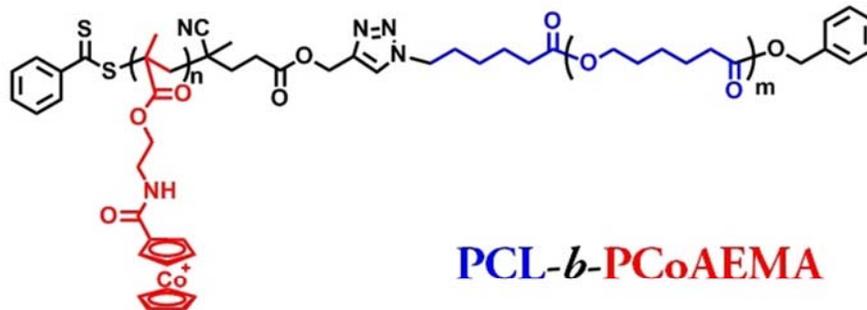
such spatial information must be encoded through the sequence in which assembly reactions are performed. Several parameters, including building block concentrations, building block programming, "build solution" composition and thermal annealing protocols were studied in order to optimize yield. Fidelity of the intended constructs and yield were determined using atomic force microscopy, fluorescence microscopy and gel electrophoresis.

### **COLL 373**

#### **Two dimensional structures from cobaltocenium-containing block copolymers by crystallization-driven self-assembly**

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Self-assembly of Block copolymer (BCP) provides a robust method to construct a variety of micellar morphologies, ranging from spheres to vesicles. Crystallization-Driven Self-assembly (CDSA), one of the methods for the preparation of nano-objects, has attracted a great deal of interest due to its unique ability for dimensional control over 1D, 2D, and 3D nano-objects. Metallopolymers have been utilized in CDSA. I will present CDSA of cobaltocenium-containing block copolymers, poly(caprolactone)-*b*-poly(cobaltocenium amidoethyl methacrylate) (PCL-*b*-PCoAEMA), which can form 2D hexagonal platelet structures in protic solvents. By changing the composition of block copolymers, the block copolymers self-assembled into various two-dimensional platelets, from hexagons to diamonds.



2D platelets from CDSA of PCL-*b*-PCoAEMA

## COLL 374

### Polymersome drug nanocarriers from temperature-sensitive poly(N-vinylcaprolactam) block copolymers

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Naturally occurring self-assembled biological carriers (e.g., cell membranes, exosomes) that provide a nanometer-thin hydrophobic barrier to protect and transport cargo have inspired the development of new nanosized polymeric vesicles (polymersomes) for advancing the field of precision therapy. Polymersomes have demonstrated increased mechanical stability, efficient drug entrapment, and controllable stimuli-triggered delivery of cargo. Herein, we present synthesis and assembly of polymersomes from thermally responsive poly(N-vinylcaprolactam)-*block*-poly(N-vinylpyrrolidone), poly(N-vinylpyrrolidone)-*block*-poly(3-methyl-N-vinylcaprolactam), and poly(N-vinylcaprolactam)-*block*-poly(dimethylsiloxane)-*block*-poly(N-vinylcaprolactam) block copolymers and explore their biomedical potential. The poly(N-vinylcaprolactam)<sub>n</sub>-*block*-

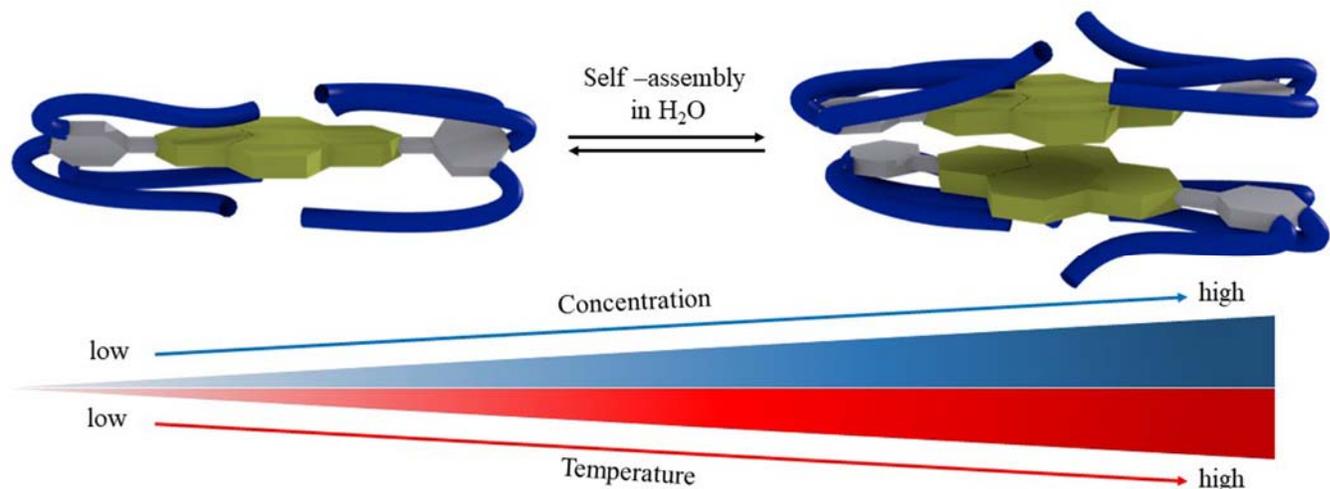
poly(N-vinylpyrrolidone)<sub>m</sub> polymersomes are synthesized by stabilizing the vesicular morphology of the diblock copolymers via hydrogen bonding with an antioxidant, tannic acid (TA), at 48 °C. The size of the TA-locked (PVCL<sub>179</sub>-PVPON<sub>m</sub>) polymersomes is controlled by the PVPON chain length and TA:PVPON molar unit ratio. These TA-locked polymersomes can encapsulate and store the anticancer drug doxorubicin (DOX) and higher molecular weight rigid molecules (e.g., dextran). Encapsulated DOX can be released in the nuclei of tumor cells after 6-h incubation via biodegradation of the TA shell. For PVCL-PDMS-PVCL triblock copolymer polymersomes, increasing the temperature above the LCST of PVCL results in gradual vesicle shrinkage leading to sustained drug release. *In vivo* transthoracic electrocardiography of mice injected with the DOX-loaded PMVC-*block*-PVPON polymersomes and liposomes followed by necropsy analysis revealed that while free DOX was toxic to the mice at low and high doses after 14 days, and showed detrimental effects to the heart left ventricle, neither liposomal or polymersomal DOX showed direct evidence of cardiotoxicity at low DOX dose. However, both analyses revealed the detrimental effects of liposomal DOX at a higher DOX dose unlike that for DOX-(PMVC-*block*-PVPON) polymersomes. Our results provide the evidence for superior stability of synthetic polymersomes *in vivo* and show a great promise for development of the next generation of advanced therapeutics carriers with minimal side effects.

## COLL 375

### Aggregation of amphiphilic naphthalene and perylene bisimides in water: Thermodynamic analysis

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The ability to control the thermodynamic driving forces of self-assembly is key to the development of functional and in particular thermoresponsive materials. This is especially challenging in water due to the solvophobic effects which dictate association. Herein, we present naphthalene and perylene bisimides whose aggregation is observed either upon heating or cooling depending on the connection of solubilising side chains to the  $\pi$ -cores. Rylene bisimides, where phenyl substituent with three oligoethylene glycol (OEG) chains are attached directly to the hydrophobic  $\pi$ -cores undergo association at elevated temperatures with a favorable entropy as revealed by UV-vis spectroscopy and calorimetric measurements. In contrast, rylene bisimides where the phenyl substituent with three OEG chains are attached via a methylene spacer unit self-assemble upon cooling. This surprisingly different thermodynamic signature for quite similar molecules will be explained by the different hydration of the hydrophobic cores and the OEG side chains as well as by structural peculiarities.



**Figure 1.** Schematic illustration of the self-assembly of an OEG-functionalized naphthalene bisimide undergoing an entropically driven aggregation in water.

## COLL 376

### Molecular doping of Si(100)

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Miniaturization of feature sizes is a driving force in the semiconductor industry and has been key in enabling small, low-cost high-powered computing devices. As feature sizes approach the sub-10 nm, new challenges need to be overcome to achieve the benchmarks set by the International Roadmap for Devices and Systems. Current state of the art atomically precise advanced manufacturing (APAM) has successfully demonstrated the formation of devices with atomically sharp features and doping concentrations that exceed the solid solubility of dopant in Si, but the scale-up of these methods is hindered by the specialized UHV equipment required in the current APAM process. On the other hand, molecular monolayer doping (MLD), is a scalable method which utilizes wet chemistry and rapid thermal annealing to produce doped surfaces, however MLD lacks the high doping concentration of APAM methods. The overall goal of this work is to develop new wet chemistry methods, inspired by the MLD process, to produce doping characteristics analogous to those of APAM. This poster will address current experimental progress.

## COLL 377

### Reactions of boron- and nitrogen-containing compounds with Cl-terminated Si(100) surface

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Interaction of boron-containing compounds, including boron trichloride and 4-fluorophenyl boronic acid, and nitrogen-based compounds, hydrazine, with Cl-terminated Si(100) surface were studied in order to understand the interaction of these molecules with the surface for designing possible silicon doping processes. The reactions reported utilized Cl-terminated Si(100) surface prepared by wet chemistry methods and selected comparisons were made with the H-terminated Si(100). The process was followed by X-ray photoelectron spectroscopy (XPS). Within the reaction conditions investigated, boron trichloride does not react with the H-terminated surface, but it does react with the Cl-terminated surface where a peak for B 1s around 193 eV corresponding to (B-O)<sub>x</sub> species was recorded. A reaction of hydrazine with Cl-terminated Si(100) and Hydrogen-terminated Si (100) in a liquid phase was performed in order to compare the reactivity of these surfaces and infer differences with previously investigated reactions of this compound with Si(111) crystal face. Finally, a reaction of 4-Fluorophenyl Boronic acid was studied on both H- and Cl-terminated Si(100) surfaces. This compound reacts preferentially with the Cl-terminated Si(100), as confirmed by observation of a B 1s peak at 191.2 eV and F 1s peak at 689.3 eV. Density functional theory was utilized to supplement the analysis and identify major surface species resulting from these reactions. This work provides a new pathway to obtain a defined functionalized silicon surface with different boron and nitrogen compounds that can be used for further functionalization or as a mean of selective doping.

## **COLL 378**

### **Functionalization of silicon with photo-sensitive carbene precursors for patterning monomolecular phosphorus-based dopant species**

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The ability to efficiently couple pattern-specific monolayers with dopants that demonstrate great structural variability is desired in the manufacturing of novel logic switching elements. In this study, we demonstrate a reliable protocol for the delivery of a phosphorus-based dopant onto functionalized silicon with spatial control at the microscale. This method relies on selective surface reactions of immobilized carbene species with phosphine derivatives. This bilayered system provides terminal functionalities that can be photochemically modified via UV-assisted contact printing

between the functionalized surface and an elastomeric stamp inked with the molecular dopant. Spectroscopic measurements combined with electron microscopy was used to characterize the dopant attachment and patterning ability of this technique. Several notable features are observed in the resulting spectra that are indicative of the bonding behavior between dopant and carbene monolayer including an increase in the atomic percentage of phosphorus atoms on the surface observed after photochemical printing. Microscopic analysis of the corresponding surface structures demonstrates high fidelity pattern transfer. Our approach to atomic precision surface processing has the potential to inform future development of next-generation devices in applications such as; quantum electronics, surface passivation, optics, biomedical devices, and sensors.

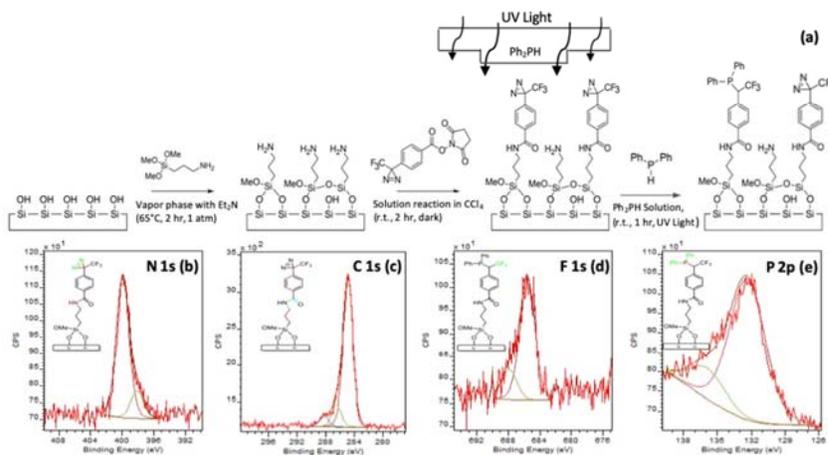


Figure 1. (a) Schematic showing the functionalization and doping strategy employed in this study. XPS spectra for (b) N 1s on NHS-terminated surface, (c) C 1s on NHS-terminated surface, (d) F 1s on P-doped surface, and (e) P 2p on P-doped surface.

## COLL 379

### Conducting polymer based potentiometric affinity biosensor

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There is a considerable interest and a high commercial demand for a cost-effective, rapid, point-of-use diagnostic technology for disease, food quality, and environmental pollutants. Delays caused by conventional tools of analysis can often lead to serious consequences either in terms of the control of a pathogen, disease or financial penalty. Biosensors are powerful and rapid analytical tools with applications in medicine, environmental diagnostics, and food/processing industries. Electrochemical (EC) biosensors where conducting polymers are used for signal transduction is a rich area of enquiry. Doped, electrically conducting polypyrrole (Ppy) has gained considerable recognition as a signal transducing element in the field. Described is a flexible, lightweight, and rugged biosensor composed of electrochemically deposited polypyrrole on screen-printed carbon electrodes that displays superior performance characteristics towards detecting antigens in real-life samples (e.g., TSH assay). Such as whole blood and serum. Also described are approaches to overcome challenges to signal sensitivity/selectivity, device miniaturization, minimizing non-specific binding, and reducing signal-to-noise variation. Our potentiometric sandwich-type ELISA biosensor detects enzyme-labelled immuno-complexes formed at the surface of polypyrrole coated on screen-printed carbon electrode.

## **COLL 380**

### **Understanding the mechanism of atomic layer etching of CoFeB alloy thin films using diketones**

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Atomic layer etching of Co/Fe alloys has a number of applications particularly in random access memory technology. The initial steps of the etching of CoFeB thin films with diketones (1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hfacH) and 2,4-pentanedione (acacH)) were studied using in situ temperature-programmed desorption (TPD). The surfaces produced following these steps were characterized using X-ray photoelectron spectroscopy (XPS) supplemented with microscopic investigations. It is shown that starting with oxidized or halogenated surfaces is essential to form volatile products, and halogenation improves the kinetic of this reaction. By investigating the desorbing products, it is revealed that metals are oxidized to their higher oxidation states during the etching process. However, the overall mechanism is quite complicated and depends on the specific starting surface. For example, the surfaces that have both oxygen and chlorine present yield the products that contain simultaneously both the organic ligand and the halogen, as a result of thermal dry etching. In addition, annealing the surface at elevated temperatures results in substantial morphology changes.

## **COLL 381**

### **Structure-function properties of WO<sub>3</sub> nanosheets**

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Low dielectric constant semiconductors offer the possibility to study and image surface decays processes (such as the space-charge region). These processes, largely determine the surface properties, both chemical and physical. We have achieved controllable synthesis of WO<sub>3</sub> nanosheets with different layer thickness, mono-layer, double-layer and triple-layer WO<sub>3</sub> nanosheets, even thicker WO<sub>3</sub> nanoplatelets ranging from 10 nm to 50 nm. Employing Kelvin probe force microscopy (KPFM) and electrostatic force microscopy (EFM), we have experimentally studied the effect of the size of the WO<sub>3</sub> nanoparticles on the formation of space-charge region and generation of surface electronic states by mapping of their work function and the surface charge density. The thickness dependent- electronic properties of WO<sub>3</sub> nanosheets were also studied. Theory side, we derived basic surface slabs containing more than 200 atoms by cutting along the (001) and (100) plane of bulk WO<sub>3</sub> and adding a 15 Å vacuum layer as well as some other models containing a surface O vacancy on all slab models. Additionally, to study the relation between the particle size and density of surface electrons we employed multilayer slab models by constructing extra 1, 2, 3, and 4 layers on the original 4 layers-models. The results of both experimental and computational characterizations will be presented.

## **COLL 382**

### **Building a budget friendly drop shape analysis system to be used on nanoparticle treated surfaces**

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Smaller Chemistry departments all around the country are often limited by funding and cannot afford the technology needed to research new topics. However, building budget friendly versions of these devices can prove to be a viable option for research, and as a result, allows Chemistry to become more accessible. This Drop Shape Analysis device runs on MATLAB and is comprised of relatively inexpensive components that can be found at a local hardware store. We tested the accuracy and precision of this device by comparing experimental contact angles of water with different silanes with known values. We found this device to be crucial in our research in nanoparticles and colloids.



Binary photograph of water droplet placed on a silane treated glass slide

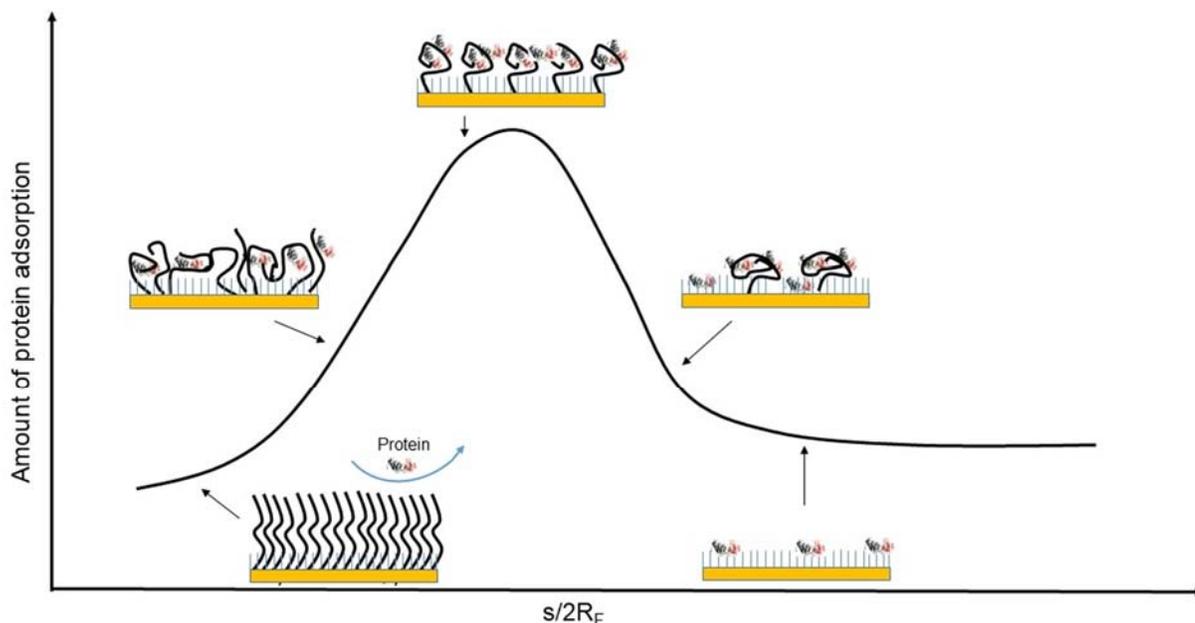
**COLL 383**

**Protein adsorption on grafted zwitterionic polymer thin films**

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This study demonstrates that protein adsorption on end-grafted poly(sulfobetaine) thin films depends on the grafting density, molecular weight, and ionic strength. Zwitterionic polymers contain cationic and anionic groups, and reportedly exhibit ultralow non-specific fouling (protein adsorption) and excellent biocompatibility. This picture contrasts with a recent report that soluble pSB chains bind proteins and alter their folding stability. To address this apparent contradiction, we investigated the dependence of protein adsorption on the chain grafting parameters: namely, the grafting density, molecular weight and ionic strength. Studies compared the adsorption of PGK (phosphoglycerate kinase) and positively charged Lysozyme versus the scaled grafting parameter  $s/2R_F$ . Here,  $s$  is the distance between grafting sites, and  $R_F$  is the Flory radius. With both proteins, plots of the adsorbed protein amount versus  $s/2R_F$  exhibits a bell shaped curve, with a maximum near  $s/2R_F \sim 1$  and an amplitude that decreases with ionic strength. This behavior is qualitatively consistent with theoretical models for colloid interactions with weakly attractive, grafted chains. In such models, adsorption is controlled by competition between protein-segment attraction and osmotic repulsion, which prevents protein insertion into the brush. The model predicts a bell shaped adsorption curve, as we observe experimentally in our studies. Our results confirm that proteins do adsorb to pSB thin films. They also suggest an underlying mechanism. Comparison with polymer models further identify design rules for pSB films that effectively repel protein.



Schematic diagram of protein adsorption mechanism on grafted zwitterionic polymers.

## COLL 384

### Investigation of 2-cyclohexenylcyclohexanone corrosion inhibitor as surfactant

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All effective inhibitors are strong surfactants. Generally a surface activity of the nonionic surfactants can be determined by interaction of surfactant molecules with metal or the interaction of these molecules with a solution. However overwhelming majority of works on the adsorption mechanism relates the adsorption just to interaction of surfactant and metal.

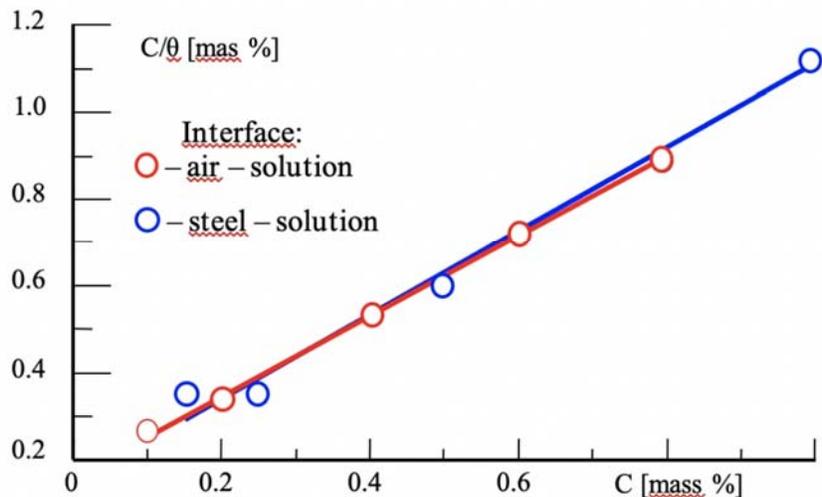
Here the mechanism of nonionic surfactant adsorption is investigated, as an example, the adsorption of 2-cyclohexenylcyclohexanone on steel in 1 M acid chloride solution and on these solution - air interface.

Adsorption on the solution - steel interface is investigated by Electrochemical Impedance Spectroscopy technique. The maximum bubble pressure technique is applied for investigation of surface tension on solution - air interface.

If inhibitor adsorption follows to the Langmuir adsorption isotherm, the surface coverage  $\theta$  calculate by Equation (1), where  $C$  is the surfactant concentration and  $K_{ad}$  is the adsorption constant. For air - solution interface, the  $\theta$  value calculate by Equation (2), where  $\Gamma$  is the adsorption value and  $\Gamma_{\infty}$  is the limiting adsorption value. For steel - solution interface, the  $\theta$  value calculate by equation (3), where  $R_{corr}$  is the corrosion resistance without inhibitor and  $R_{corr(inh)}$  is the corrosion resistance at the inhibitor presence.

Inhibitor adsorption isotherms for air - solution and steel - solution interfaces (Figure) well agree to Equation 1. Slopes of straight lines (0.92 and 0.97) well agree with a theoretical (unit) slope. Hence the Langmuir adsorption takes place both on the steel surface and on the air - solution interface.

The values  $K_{ad}$  for air - solution (0.16 mass %) and steel - solution (0.15 mass %) interfaces practically coincide. Therefore it is possible to make the guess that the 2-cyclohexenylcyclohexanone adsorption does not depend on an adsorbent nature, but depends on the interaction of 2-cyclohexenylcyclohexanone with solution. It is possible to explain this effect by a solvophobic solvation of surfactant organic molecules and entropic tendency of displacement of the adsorbate from solution volume to the phase interface.



$$\theta = \frac{K_{ad}C}{1 + K_{ad}C} \quad \text{or} \quad \frac{C}{\theta} = \frac{1}{K_{ad}} + C \quad (1)$$

$$\theta = \Gamma / \Gamma_{\infty} \quad (2)$$

$$(1 - \theta) = \frac{R_{corr}}{R_{corr(inh)}} \quad (3)$$

## COLL 385

### Temperature dependent investigation of thiolated DNA on gold nanoparticle arrays

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Super-resolution imaging is used to explore the effect of temperature on thiolated DNA bound to gold nanostructures. For these studies mixed monolayers of thiolated DNA and short alkane thiols were self-assembled on nanosphere lithographically produced gold nanoparticle arrays. The effects of thermal pre-treatments on the nature of transient binding interactions between surface tethered and solution phase strands of DNA is explored using DNA-PAINT. These studies reveal how elevated temperatures affect thiolated DNA bound to gold.

## COLL 386

### Single-molecule optical imaging of electrochemical reactions on the surface of plasmonic nanoparticle electrodes

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Super-resolution fluorescence imaging is used as an optical readout to investigate single molecule electrochemical events on the surface of plasmonic nanoparticle electrodes. The fluorescence of single Cresyl Violet molecules is monitored as the molecule changes between an emissive and non-emissive form based on its redox state. This provides the ability to monitor site-specific single molecule oxidation events on the surface of nanoparticle electrodes, providing powerful information about intra-particle heterogeneity and its impact on electrochemical reactions.

## **COLL 387**

### **Simultaneous sonochemical functionalization of urinary catheters with biofilm matrix degrading amylase and antibacterial zinc oxide nanoparticles for prevention of bacterial infections**

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Catheter-associated urinary tract infections (CAUTIs), caused by the biofilm formation on the indwelling catheters, worsen the problem with the resistance development, being the most common infections in the patients in health care facilities. Bacterial biofilms account for 60 % of CAUTIs and are global treat to the human health due to their resistance to antibiotics, leading to increased time of hospitalization, significant medical costs and poor treatment outcomes. The need to control and prevent CAUTIs calls for development of novel antibiofilm strategies with low probability for selection of new resistant strain. In this work, urinary catheters were simultaneously coated with adhesives-degrading antibiofilm enzyme amylase and antibacterial zinc oxide (ZnO) nanoparticles (NPs) in a one-step ultrasound assisted process.

The coating of these two compounds on the same surfaces resulted in a strong synergism and significantly reduced the biofilm formation of *Escherichia coli* and *Staphylococcus aureus* by 54 % and 80 %, respectively. Moreover, these nanocoatings demonstrated stability and impeded the bacterial attachment and biofilm formation on the catheters under dynamic conditions. The developed coated catheters did not induced toxicity towards human fibroblast cells line BJ-5ta, HaCaT keratinocytes, and demonstrated 100 % biocompatibility over 7 days incubation. Taken together, such catheter with co-therapeutic compounds of amylase and ZnO NPs could be promising strategy for prevention and control the CAUTIs.

## **COLL 388**

### **Unusual behavior of a polymer bearing a guanidium analog**

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The guanidinium ion is a positively charged moiety known for being one of nature's powerful denaturants. It has also been recently proven that it can form strong ionic interactions. We have made a polymer containing a guanidinium analog that has a sulfur atom replacing the NH group: 2-(4-vinylbenzyl) isothiuronium chloride (VBT). The VBT was also copolymerized with 3-((2-acrylamidoethyl) dimethylammonio) propane-1-sulfonate (AEDAPS), a zwitterionic monomer with a sulfonate group. Throughout the synthesis, it was found that the positively charged VBT can interact strongly with the sulfonate group, even though it is part of a zwitterion charge pair. The isothiuronium behavior in the presence of salt will be discussed in addition to its ability to form strongly associated complexes with weakly negative zwitterionic groups. Understanding isothiuronium specific interactions can shed light on the stability of these materials.

## **COLL 389**

### **VSFS studies of glyoxal and its surface-active oligomers at the air-water interface**

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Glyoxal (GL) is one of the most abundant atmospheric aldehydes and contributes significantly to the formation of aqueous secondary organic aerosol (aqSOA). However, the molecular nature of GL in these aerosol is not well understood due to its proclivity towards hydration and oligomerization reactions. GL can hydrate at each of its two carbonyl moieties to form the GL tetrol in solution. Furthermore, it readily self-reacts to form GL dimers, trimers, and other larger molecular weight oligomers. While GL itself would not be expected to be particularly surface active, its oligomer products may well be and thus they would have the potential to affect the interfacial properties of the aqSOA in which they reside. For this reason, vibrational sum frequency (VSF) spectroscopy, a surface selective technique, has been employed to investigate GL at the air-water water interface in combination with Wilhelmy plate surface tensiometry. The results do indeed show surface-active species and VSF spectra contain contributions attributed to GL oligomers. This work provides much need information necessary to understand and model the atmospheric fate of GL containing aqSOA.

## **COLL 390**

### **Nanoscale chemical and mechanical imaging via peak force infrared microscopy**

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Despite Abbe's optical diffraction limit impedes nanometer-scale spatial resolution for conventional microscopy and spectroscopy, the combination of scanning probe microscopy and laser illumination provides new ways to beat the diffraction limit. One of

these imaging techniques, infrared scattering-type scanning near-field optical microscopy (s-SNOM), is to demodulate the near-field light scattering signal from a metallic AFM tip to locally enhance the optical field and probe the polaritonic properties of the sample. The other family of high spatial resolution imaging technique is action- or force-based infrared microscopy, which measures the light-induced thermal expansions in the sample or the photo-induced force from the dipole-dipole interaction between the tip and sample.

Recently our research group developed a new type of scanning probe microscopy: peak force infrared microscopy (PFIR). It combines the peak force tapping (an operation mode of AFM from Bruker Nano) with a synchronized pulsed mid-infrared light source, and enables chemical imaging, broadband spectroscopy and mechanical mapping at a spatial resolution  $\sim 10$  nm. I will describe the mechanism and technical details of PFIR microscopy, and its applications in characterizing soft polymers, urban aerosols (particulate matter PM<sub>2.5</sub>), as well as biological samples. The high spatial resolution and multimodal characterization ability of PFIR microscopy will provide a powerful analytical tool for explorations at the nanoscale across wide disciplines.

## **COLL 391**

### **Interactions between nanoparticles and extreme pressure additives: Toward high performance low viscosity lubricants**

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Improving energy efficiency in the transportation sector is a major avenue towards both economic growth and the reduction of greenhouse gas emissions. Low viscosity (LV) lubricants that reduce viscous losses can boost automotive efficiency, but the resulting thinner lubricating films increase the risk of boundary contact, requiring antiwear (AW) additives for surface protection. We have recently shown that zirconium oxide (ZrO<sub>2</sub>) nanoparticle (NP) additives in lubricant base oils produce stable, optically transparent dispersions that form AW tribofilms in sliding contacts. In these microscale sliding contacts, ZrO<sub>2</sub> NP additives develop tribofilms through a tribosintering mechanism, with a linear dependence on contact pressure. However, their performance in a fully formulated LV gear oil remains unknown, since co-additives in such oils can impact tribofilm growth rate and mechanisms through synergistic or antagonistic chemical interactions with the NPs. To understand interactions with such additives, particularly sulfur- and phosphorous-containing AW and anti-scuffing compounds, we evaluate tribofilm growth across different length scales comparing ZrO<sub>2</sub> NP behavior in pure base oil to a fully formulated LV gear oil with and without ZrO<sub>2</sub> NPs. We use a mini traction machine (MTM) to understand the effect of slide-to-roll ratio (SRR) on tribofilm growth rate in macroscale contacts. Additionally, we use *in situ* atomic force microscopy (AFM) tribofilm generation experiments to help assess the impact of NP/co-additive

interactions on contact-stress dependent film growth in microscale contacts. We further characterize the structure of ZrO<sub>2</sub> tribofilms with cross-sectional transmission electron microscopy (TEM). We find that surface-active co-additives do not prevent ZrO<sub>2</sub> tribofilm nucleation and growth. Moreover, we observe NP/co-additive interactions synergistic to tribofilm development. We will discuss the proposed underlying mechanisms for these differences in ZrO<sub>2</sub> behavior. Overall, understanding ZrO<sub>2</sub> NP behavior in a LV gear oil aids in improving vehicle efficiency while maintaining component durability.

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## **COLL 392**

### **Modification of inorganic oxides with poly(hydridomethyl)siloxanes as a scaffold for mixed functional surfaces**

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Reactions of siloxane polymers and monomers with inorganic oxide surfaces have become increasingly prominent over the last several years with the growing acceptance that the siloxane bond can serve as a reactive, functional group. However, while these reagents create well-characterized low-hysteresis surfaces, they do not provide further opportunities for additional modification or tailoring of the surface properties. Poly(hydridomethylsiloxane)s (PHMS), however, have been shown to react with a wide variety of inorganic oxide surfaces, while possessing the hydridosilane groups which create the potential for further modifications. Herein, we describe the preparation of PHMS-modified silica and titania surfaces, along with subsequent modifications of these interfaces via platinum-catalyzed hydrosilylation reactions. Resulting surfaces are characterized by contact angle goniometry, ellipsometry and x-ray photoelectron spectroscopy (XPS) and show the presence of additional functional groups, such as amines, perfluoroalkanes, and carboxylic acids. This technique has been applied to produce surfaces featuring both hydrophobic and hydrophilic groups which have a profound effect on wettability.

## **COLL 393**

### **Hydrophobization and acid resistance of silica surfaces through reaction with alternating carbosiloxane polymers**

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Siloxane polymers are widely used in commercial products due to their versatility, stability, and low cost. When chemically bonded with metals, they generate hydrophobic surfaces, applicable for water-repellent coatings. While several studies have utilized functionalized silicones, there is limited research on siloxane-containing inorganic-

organic “hybrid” polymers and their potential as chemically resistant, hydrophobic interfaces. In this research, fourteen “hybrid” siloxane polymers were prepared from divinyl-terminated compounds and hydridosiloxanes using a one-pot process. Results from infrared spectroscopy (IR) established that the polymers were successfully synthesized; all contained characteristics of both siloxanes and organic polymers. Each polymer, along with two commercially available polymers, was reacted with the surface of silicon wafers. Thickness and contact angle measurements revealed that all sixteen polymers reacted with wafers, resulting in unique properties depending on the chemical groups present in the polymers. The acid-resistance of these “hybrid” polymers was examined by submerging samples in hydrochloric acid solutions. In comparison to traditional siloxane polymers, these “hybrid” polymers showed a smaller change in surface properties. Overall, fourteen novel polymers were fabricated and were reacted with silica wafers to fabricate hydrophobic surfaces. They are viable candidates commercial use as various water-repellent, anticorrosive, and UV-resistant surfaces. Our polymer coatings demonstrated increased stability when submerged in HCl solutions, demonstrating potential as hydrophobic modifiers for use in extreme conditions.

#### **COLL 394**

##### **Study of insulin interactions with lipids and the effects of pH on insulin aggregation using student-made Brewster angle microscope**

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Insulin is a polypeptide hormone produced in the beta cells of the pancreas. It consists of two peptide chains: the hydrophilic chain A which is comprised of 21 amino acid residues, and the hydrophobic chain B which is comprised of 30 amino acids. This amphiphilic property of insulin allows it to orient at the air-water interface and form monolayers that can be studied using the Langmuir monolayer technique. In solution, insulin tends to aggregate to form multimers, commonly dimers through hydrogen bonding between the C-termini of the B chains. These can then aggregate to form higher oligomers such as the hexamer formed in the presence of the Zn<sup>2+</sup> ion. The effects of pH on this oligomer aggregation was studied at the air-water interface with and without the presence of zinc. Additionally, insulin's interactions with lipids commonly found within the cell membrane such as dipalmitoylphosphatidylcholine (DPPC) and cholesterol were also investigated. An improved student-made Brewster angle microscope has been created in order to eventually visualize these interactions and aggregations in comparison to previous BAM data in our lab.

#### **COLL 395**

## Determination of point of zero charge of perovskites and oxides using second harmonic generation

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Second Harmonic Generation (SHG) using a femtosecond Ti:sapphire oscillator was employed to determine points of zero charge (PZC) of centrosymmetric SrTiO<sub>3</sub> perovskite and non-centrosymmetric z-cut alpha quartz. The interfaces of these materials in contact with water were studied with varying bulk water pH and NaCl concentration. For the SrTiO<sub>3</sub> perovskite, we found that the surface is positively and negatively charged below and above pH 10, respectively. We also found that increasing NaCl concentration impacts SHG response by a combination of changing the ordering of water molecules at the interface with SrTiO<sub>3</sub> and the depth of sampling the nonlinear optical response. For the non-centrosymmetric quartz, the SHG signal from the bulk was dominant over that from the interface. The rotational dependence of quartz SHG was collected to reveal the interfacial response. In this case, the surface was found to be neutral in the acidic pH range of 2-4. These results enable us to explore a wide range of oxides with the purpose of understanding the *in-situ* surface behavior of these materials.

### COLL 396

## Calorimetric study of oxalate and citrate adsorption on hematite nanoparticles under different pH and ionic strength values

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Organic acids-metal oxides interfaces are ubiquitous in environmental systems and play a fundamental role in the bioavailability of nutrient, overall soil fertility and adsorption of other natural and anthropogenic contaminants. This study investigates the effect of pH and ionic strength on the adsorption of oxalate and citrate on hematite nanoparticles. Using flow microcalorimetry, the heats of adsorption  $Q_{ads}$  in  $\text{mJ}\cdot\text{mg}^{-1}$  were measured at pH values of  $4\pm 0.02$  and  $6\pm 0.02$ , and four background solutions concentrations of 1 mM, 10 mM, 100 mM, and 1000mM.

Results indicate that background electrolytes significantly impact the adsorption of oxyanions. For oxalic acid,  $Q_{ads}$  decreases with ionic strength until it reaches a plateau for a background concentration of 100 mM KCl. On another hand,  $Q_{ads}$  for citrate increases with increasing background concentration. Increasing pH resulted in an overall decrease of  $Q_{ads}$  for both. The contrasting trends highlight the underlying different adsorption mechanisms for these two oxyanions where citrate forms a mix of

inner- and outer-sphere complexes, while oxalate forms mostly outer-sphere complexes.

This study showcases the importance of considering background electrolytes in studies of adsorption as they can have either an inhibiting or a stimulating effect on organic acids adsorption.

## **COLL 397**

### **Surface chirality study of a manganese salen complex via internal heterodyne doubly-resonant sum-frequency generation spectroscopy**

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Chiral salen transition metal complexes have been increasing in popularity due to their wide range of applications as catalysts for asymmetric epoxidation reactions. The study of surface chirality is of high interest because it influences the enantioselectivity of the catalyst during heterogeneous catalysis. In addition, molecular chirality is directly related to configuration and conformation of molecules, and therefore their functional properties. Heterodyne Detected Doubly-Resonant Chiral SFG, an interface specific highly sensitive technique has been applied to have a better understanding on both molecular electronic and vibrational structures of the chiral Jacobsen catalyst while being able to distinguish between its enantiomers by referring to their phase. The role of the central metal in proximity to the surface in the chirality and the effect of its electronic properties in the d-d and metal to ligand charge transfer electronic transitions coupling is examined.

## **COLL 398**

### **Hierarchical nanoparticle assemblies in thin films: Study kinetic effects**

**Ting Xu**, [tingxu@berkeley.edu](mailto:tingxu@berkeley.edu). Material Sci Eng, UC Berkeley, Berkeley, California, United States

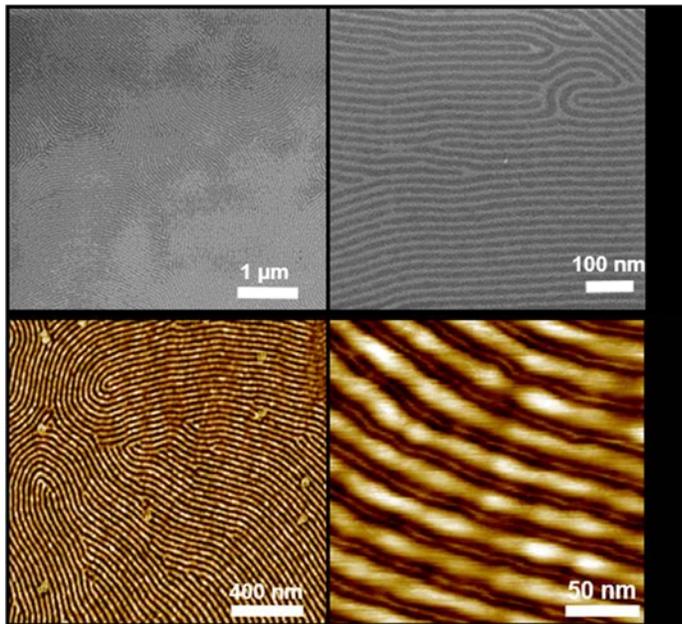
Numerous approaches have been explored to generate spatially organized assemblies of nanofillers with high precision. The current challenge is to narrow the gap between what can be fabricated and the required spatial arrangement of each building block to access targeted properties. Nonequilibrium structures in nanocomposites provide possibilities to modulate the organization of nanofillers beyond the phase diagram and to fabricate functional materials with targeted properties. However, multicomponent systems, such as nanocomposites, have complex phase diagrams and kinetic pathways. I will discuss our recent work in thin films of supramolecular nanocomposites and how to kinetic pathway can affect the their behaviors in flat and patterned surfaces.

**COLL 399**

## **Nanoscale thin oxide films for nanoelectronics**

**Mick A. Morris**, *MORRISM2@tcd.ie*. AMBER & School of Chemistry, Trinity College Dublin, Dublin, Dublin, Ireland

Thin film oxides have an important role in semiconductor and nanoelectronic fabrication. Deposition of oxide films is by techniques such as spin-on, chemical vapour deposition and atomic layer deposition as well as epitaxial methods where precise structural definition is required. Further, metal oxides such as nickel oxide are being used as high contrast etch masks during fabrication of the nanocircuitry. They may also have future importance in generation of oxide based devices for logic and memory (including memristors) particularly for active layers above CMOS. Making coherent thin films of oxides for silicon electronics is challenging, particularly at the lower temperatures needed to be sustainable above CMOS – around 400 to 450C maximum. Further, patterning of complex oxides can be extremely challenging if composition and structure is not going to be compromised. In recent years we have pioneered a process where oxide films can be created by a process of infiltration. Here, a polymer brush (a polymer molecule with a chain termination group that can be bound to the substrate surface) is exposed to a solution of a metal salt-solvent combination that will swell the polymer and allow infiltration of metal ions. The swollen film is then exposed to reactive oxygen (plasma or UV-ozone) to remove polymer and form the oxide film. The films show very high coverage, uniformity and coherence with thicknesses of 2 to 20 nm. In this paper we will show recent progress in defining a range of materials. We will also describe the infiltration of self-assembled block copolymer films that allow selective inclusion and direct writing of device patterns of oxides. These have been use to make copper oxide based devices as transistor like circuitry. Typical images of these wires are shown in Figure 1. The potential for these techniques to deliver disruptive progress in the creation of future electronic devices is discussed.



## COLL 400

### Self-assembled stimuli-responsive copolymer colloids

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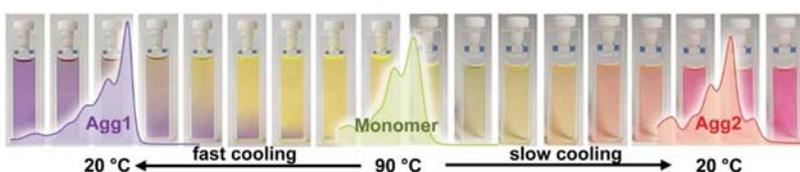
The precise control of colloidal morphologies remains to be challenging, especially when specific stimuli-responsive properties are desired. Taking advantage of the heterogeneous nature of emulsion polymerization, surfactant-free heterogeneous radical polymerization (HRP) was developed to synthesize ultra-high molecular weight amphiphilic block copolymers. This one-step process resulted in amphiphilic block copolymers that form thermochromic inverse micelles in organic solvents capable of selectively scattering light as a function of temperature. This approach was also utilized to synthesize polymer nanowires *via* in-situ self-assembly of amphiphilic block copolymers. This kinetically controlled directional growth may lead to many industrial applications, including synthesis of other block copolymers, polymeric nanowire latexes and other morphologies. This talk will also outline recent advances in stimuli-responsive colloidal nanoparticles/nanorods and their self-assemblies that lead to shape-tunable Janus and gibbous or inverse-gibbous nanoparticles as well as nanowires.

## COLL 401

### Supramolecular polymorphism in aggregates of tetra-bay-acyloxy functionalized perylene bisimides

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Perylene bisimides (PBIs) are amongst the most studied colorants in supramolecular chemistry due to their unmatched combination of favorable optical and redox properties in the monomeric as well as self-assembled states. These features can be finely tuned by chemical modification of the monomeric building blocks. In this regard, we recently reported 1,6,7,12-tetraalkoxy- and 1,6,7,12-tetrahydroxy-substituted PBIs which were successfully applied in organic solar cells. Now we report on tetra-acyloxy functionalized PBIs which exhibit free NH groups in imide position for hydrogen bond-directed self-assembly. In our contribution we will show that this new modification enables the formation of two types of polymorphic dye aggregates with distinct optical and morphological features in solution as well as the solid state. The contrasting self-assembly behavior is achieved by adjusting the cooling rate applied to a hot solution of monomers in a non-polar solvent (Figure 1). Our further studies are directed towards deriving structure-function relationships for these aggregates and applying them as materials for organic electronics and photovoltaics.



Formation of two polymorphs by applying different cooling rates to a hot solution of monomers.

## COLL 402

### Self-assembly and interaction in polymer nanocarriers for drug delivery applications

**Domenico Lombardo**, lombardo@ipcf.cnr.it. IPCF - Istituto per i Processi chimico - Fisici, CNR - Consiglio Nazionale delle Ricerche, Messina, Italy

Polymer based, nanosized particles (such as dendrimers and polymers micelles) can be successfully used for the solubilisation of various poorly soluble therapeutic drugs, and demonstrate a variety of attractive properties in drug delivery and nanomedicine applications. Dendrimers are a class of multi-functional polymers consisting of highly ramified (dendritic) macromolecules, that provide a source of surface functionality and interior void space. Their multivalent surface functionalities, that can be linked to drug molecules or ligands, makes them well-suited for use as carrier of therapeutic molecules in drug delivery applications. Polymeric micelles formed by amphiphilic block copolymers, are of a special interest as they possess high stability (both in vitro and in vivo), and good biocompatibility. These systems combine an enhanced colloidal stability

together with the inclusion and transport properties of host-guest (drug carrier) systems, and represent promising classes of nanomaterials suitable for advanced applications in the field of biotechnology and nanomedicine. Understanding the fundamental physico-chemical properties of those polymer-based systems, in terms of interaction strength, colloidal stability, nanocarriers size and morphology, stimulates the development of formulation polymeric nanocarriers with enhanced properties, such as the drug encapsulating capacity, prolonged circulation time, and colloidal stability in the human body environments. We present some recent results which show how the effective intra- and inter-particles interactions, as well as the solution environment conditions, are crucial parameters for the modulation of the degree of structural organization in solution, suitable for a number of potential applications in the field of biotechnology and nanomedicine.

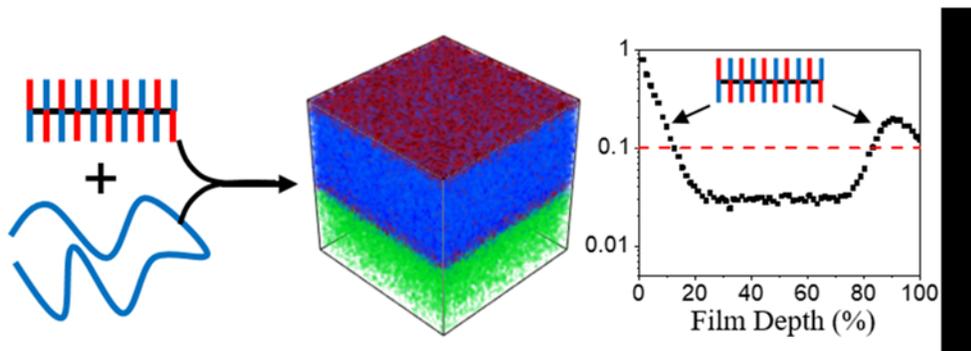
## **COLL 403**

### **Development of bottlebrush copolymers as surface-active additives**

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The use of architecturally complex copolymer additives provides a versatile approach to decoupling surface and bulk chemistries, enabling the introduction of new surface properties or functionalities. As examples, the preferential segregation of a component to an air surface or substrate can be leveraged for antifouling properties, orienting block copolymer films, and tailoring the properties of organic electronic devices. In this presentation, we show that bottlebrush polymers provide a convenient platform for the design of surface-active polymer additives. Bottlebrush polymers have polymeric side chains densely grafted to a linear polymer, and this molecular architecture enables tuning entropic and enthalpic interactions with other polymers and with surfaces. The strength of the entropic attraction towards surfaces can be tuned in blends of bottlebrush and linear polymers by varying the number of bottlebrush side chains, the length of the bottlebrush side chains, and the length of the linear polymer host, and enthalpic interactions can be controlled by incorporating different side chain and side chain end-group chemistries. We present studies of bottlebrush polymers blended with linear polymers to understand the role of enthalpic and entropic effects that can drive segregation to film interfaces. Time-of-flight secondary ion mass spectroscopy (ToF-SIMS) is used to quantify the distribution of bottlebrushes through the film thickness as a function of homopolymer type, homopolymer molecular weight, and processing conditions. Modeling using the self-consistent field theory (SCFT) highlighted effects of conformational entropy and enthalpic interactions in driving segregation of the bottlebrush additives toward interfaces. Furthermore, enthalpic interactions were predicted to cause lateral phase segregation in cases where the homopolymer is preferred over the bottlebrush copolymer at the substrate, an effect that was also

observed in experiments. This study demonstrates that bottlebrush copolymer additives can be designed to spontaneously segregate to surfaces in thermal blends, providing a possible route to decouple surface properties from bulk properties.



## COLL 404

### Self-assembly of block copolymers to photonic crystals

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Photonic crystals are periodic dielectric materials that possess a photonic bandgap. This presentation will discuss the design of block copolymer composite materials and their self-assembly to photonic crystals that can reflect light from the UV, across the visible, and into the IR. The application of these materials as thermoplastic build materials in 3D printing and heat-reflective window coatings to reduce cooling loads in warm climates will be presented.

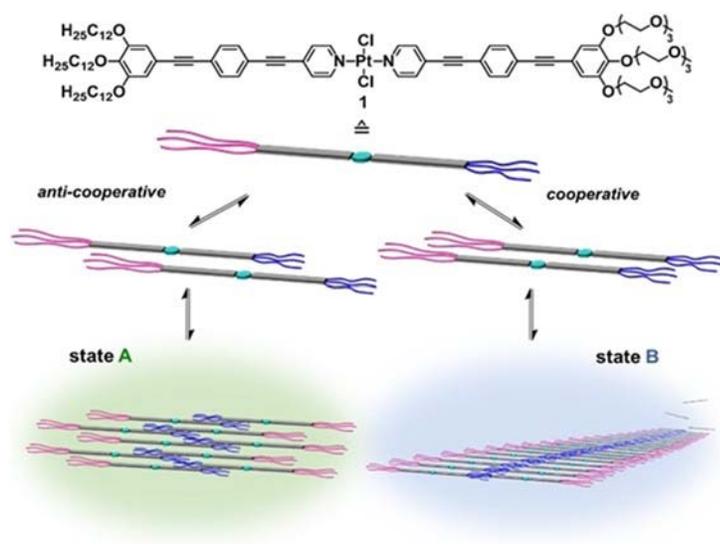
## COLL 405

### Pathway selection in metallosupramolecular polymers

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Self-assemblies of metal complexes have gained considerable attention not only because of the inherent properties of the metal ions but also due to the versatility of non-covalent interactions when a metal fragment is part of the molecular design. Our group has investigated the thermodynamically controlled supramolecular polymerization of oligophenyleneethynylene (OPE)-based dichlo(bis)pyridyl Pd(II) and Pt(II) metal complexes both in polar and non-polar media. However, recent work in the field of self-

assembly reveals that a given building block can often form more than a single aggregate species depending on different experimental conditions. The existence of competing aggregation pathways, a phenomenon termed *pathway complexity*, has been observed for various types of organic dyes, but less attention has been devoted to metal-based homologues. In this abstract, recent work on pathway complexity in self-assembling OPE-based Pt(II) complexes with either hydrophobic or amphiphilic nature will be described. For example, amphiphilic Pt(II) complex **1** self-assembles in methylcyclohexane into two competing aggregates (anti-cooperative aggregate **A** and cooperative aggregate **B**, Scheme 1) with different molecular packing (long- vs. medium-slipped) that can be isolated controlling the temperature and the addition of a co-solvent.



**Scheme 1.** Chemical Structure of **1** and cartoon representation of the competing aggregation pathways

## COLL 406

### Contiguous nanostructured cellulose substrates produce quantitatively high yields of giant vesicles in low and high salt solutions

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Since reports of their assembly from purified phospholipids more than half a century ago, single-walled phospholipid vesicles larger than 1 micrometer in diameter also called giant unilamellar vesicles (GUVs) have been objects of fascination due to their resemblance to minimal biological cells. Nevertheless, basic information such as the influence of fabrication technique and conditions of growth on the yields and sizes of GUVs is lacking. I will describe a quantitative framework that we developed to

systematically measure the 'fractional yields' and sizes of GUVs produced through generic thin film hydration techniques. The fractional yield — the molar yield of lipids harvested as GUVs divided by the molar amount of lipids initially deposited on the substrate — allows fair inter- and intra-technique comparisons. Comparison of the fractional yield of giant vesicles obtained from gentle hydration, electroformation, gel-assisted hydration, and paper-assisted lipid hydration in aqueous solutions (PAPYRUS) showed that PAPYRUS on nanocellulose papers produces superior fractional yields of GUVs in both low salt and high salt solutions. Using artificial blood as a prototypical manufacturing challenge to concretize the requisite numbers and sizes of GUVs, we find that PAPYRUS on nanocellulose paper is several orders of magnitude cheaper than other extant techniques for growing GUVs. We also use the measured differences in fractional yield to obtain insights on the process of formation of GUVs for the different techniques.

## **COLL 407**

### **Lipid/protein nano-assemblies entrapped within mesoporous gels**

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Entrapment of biomembranes in mesoporous metal oxide gels has proven to be a challenge, as current and previous techniques utilize liposomes as biological membrane hosts. The instability of liposomes in mesoporous gels is attributed to their size and altered environment upon entrapment within the nanometer scale pores (5-50 nm). We have overcome these barriers by entrapping nanometer-scale lipid/protein assemblies - nanolipoprotein particles, bacteriorhodopsin (BR) purple membrane fragments, and copolymer-stabilized lipid nanodiscs. We have investigated the phase behavior of the lipids in addition to the structure, localization, and environmental polarity of the involved proteins mainly by spectroscopy methods. Our results indicate that near room temperature these gel-entrapped lipid/protein assemblies remain intact, with only slightly altered lipid and protein structure and dynamics. We then compare the thermal stability of gel-entrapped BR in purple membrane or lipid nanodiscs and find differences related to oligomeric states of the protein.

## **COLL 408**

### **Single-molecule imaging of cells detecting nutrients in their local environment**

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The gut microbiota is made up of thousands of organisms whose composition is dictated by the available nutrients. The *Bacteroides thetaiotaomicron* starch utilization system (Sus) is a prototype for glycan uptake by the bacteria. Interestingly, Sus includes five outer-membrane proteins (OMPs) which interact to bind and transport

starch. Although the molecular mechanisms of this system are well known, the dynamics and cooperativity of the Sus OMPs are still not fully understood. Based on new super-resolution fluorescence microscopy methods to locate, track, and analyze single molecules in living anaerobes, we have shown that the SusG enzyme explores the cell surface but slows upon interaction with starch. Furthermore, we have seen that the SusE and SusF OMPs are immobile on the cell surface even when other members of the system are knocked out and under multiple different growth conditions. These measurements suggest a new paradigm for protein complex formation: binding proteins form immobile complexes that transiently associate with a mobile enzyme partner. Thus, we are now testing and completing the paradigm for glycan uptake by measuring and understanding the dynamical interactions essential for carbohydrate catabolism in the human gut microbiome, with extensions to determining the response of three different carbohydrate utilization systems in diverse carbohydrate environments. Overall, our results provide fundamental insight of relevance to human health and disease.

## **COLL 409**

### **High content imaging to identify novel pharmacological modulators of membrane rafts**

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Cholesterol- and sphingolipid-enriched membrane nanodomains known as membrane rafts are widely recognized for their role in regulating membrane protein trafficking and function. The movement of specific proteins into or out of rafts has also been linked to a number of diseases. Despite this, few methods to experimentally perturb rafts currently exist, and we still lack a clear understanding of how rafts control cellular functions. To address these long-standing questions, we are utilizing giant plasma membrane vesicles (GPMVs) as a model to investigate mechanisms controlling raft structure, composition, and function. Isolated from the plasma membrane of live cells in the form of cell-sized vesicles, GPMVs maintain the compositional complexity of cell membranes, yet are capable of forming coexisting raft-like and non-raft phases that can be readily visualized by fluorescence microscopy. Here, I will describe new computational approaches developed in our group to facilitate high content imaging of rafts in GPMVs and discuss how we are using these methods to perform unbiased high throughput screens of small molecule libraries to discover new pharmacological approaches to manipulate raft structure and function. Ultimately, these studies should lead to the development of new classes of raft modulators that can be used to address the many still-unanswered questions about these poorly understood structures in biological membranes.

## **COLL 410**

### **Development of easy, fast, and stable cell imaging methods**

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It is difficult to image the cell membrane of a live cell for a prolonged period of time because of the cellular internalization of fluorescent dyes. Commercially available cell imaging agents can produce clear cell membrane images initially, but the images will soon become smeared due to the internalization of such materials by cells. Here we developed an easy, fast and stable cell imaging method, utilizing glycol chitosan (GC), polyethylene glycol (PEG), cholesterol, and fluorescent molecules such as FITC through the multi-site anchoring strategy. The developed material is a polymer bearing many PEG-cholesterol side chains which can insert into the cell membrane, and therefore the cell internalization is much slower. It was shown that the cell membrane can be imaged clearly within five minutes using this material and the high quality images can be obtained after many hours. The components of this GC-derived material can be slightly changed for many other purposes. For example, a similar compound can be used to image the surfaces of bacterial, mammalian, and fungal cells. Drugs molecules can be incorporated into such imaging materials to deliver drugs to cell surfaces to kill bacteria and cancer cells. Therefore, in addition to the imaging function, such materials can be used for therapeutic purpose as well.

## **COLL 411**

### **Loss of smooth muscle alpha-actin impairs cellular mechanosensing**

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Vascular smooth muscle cells in the aorta play an integral role in regulating vessel wall contractility and matrix deposition in the medial layer. Recent studies show that mutations in genes associated with actomyosin apparatus reduce smooth muscle contractility, increasing susceptibility to thoracic aneurysm development. These mutations are associated with impaired vascular smooth muscle cell function, which may lead to decreased ability of the cell to sense matrix-mediated mechanical stimuli. This study investigates how loss of smooth muscle alpha-actin affects cell adhesion. We tested the hypothesis that a loss of smooth muscle alpha-actin decreases cell adhesion to the matrix. Confocal and total internal reflection fluorescence microscopy were used to quantify actin and focal adhesion fluorescence, respectively, in wild-type and smooth muscle alpha-actin null cells. Our results showed that in absence of smooth muscle alpha-actin, there is a compensatory increase in smooth muscle gamma-actin. Moreover, specific integrin recruitment at cell-matrix adhesions was reduced in alpha-

actin null cells. These findings suggest a dysfunctional vascular smooth muscle cell-matrix cross-talk and cellular mechanosensing in alpha-actin null cells.

## **COLL 412**

### **Biomolecular and particle interactions with curve model membranes**

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Non-lamellar lipid aqueous phases, such as reverse cubic or hexagonal phases, are ubiquitous in nature and they present a curve lipid aqueous interface on the nanoscale. The role of curvature for biomolecular and particle interactions has been increasingly recognized. Planar biomimetic membranes can be prepared by deposition onto flat surfaces. Here we will show that using nanostructured surfaces, i.e. surfaces with an array of silicon nanowires (diameter 90 nm), we can deposit a phospholipid bilayer, consisting of mixtures of dioleoylphosphatidyl choline and dioleoylphosphatidyl ethanolamine. The interaction of proteins with these curved lipid bilayers will be discussed in terms of confocal fluorescence microscopy, Grazing Incidence Small Angle Neutron Scattering (GISANS) and neutron reflectometry. This includes both specific in terms of streptavidin-biotin and non-specific using  $\alpha$ -synuclein. We also show that we are able to prepare lipid mesophase surface films with controlled and tuneable structure, which allows us to study the interaction of nanoparticles with lamellar and non-lamellar lipid films. We used spin-coated layers of glycerol monooleate (GMO), forming a cubic phase, and mixtures of GMO/diphosphatidylcholine (DOPC) forming a lamellar phase. These membranes can be used to mimic the inorganic nanoparticles (NPs)-membrane interaction. Such studies provide relevant insights on the main factors implied in cellular trafficking and cytotoxic effects, but this type of particles are also used in nanomedicine to enhance imaging and also in therapeutic applications. The structural effects on the lipid films of gold nanoparticles (AuNPs) of different shape and surface functionalization have been studied using Neutron Reflectometry. The results will be discussed in terms of particle shape and functionalization and the curvature of the lipid aqueous interface.

## **COLL 413**

### **Nanoplastic interactions with biomembranes: Effects of surface charge and protein corona passivation**

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Plastic waste can break down to produce micro- and nano-scale particles that present health threats to wildlife and humans. The modes by which nanoplastics interact with biological systems have yet to be fully characterized; however, the small size and high surface energy of these materials suggests that they likely have the capacity to penetrate biological barriers, including the cell plasma membrane. Here, we study the interaction of polystyrene nanoparticles (PNPs) with cellular and model biomembranes. Using confocal microscopy techniques, we investigated how PNPs with varying surface charge bound to and disrupted the membranes of 293T cells in culture, giant plasma membrane vesicles (GPMVs) derived from these cells, and giant unilamellar vesicles (GUVs) fabricated from synthetic and naturally-derived lipids.

Upon exposure to the body, PNPs acquire a biomolecular corona composed primarily of serum proteins. By incubating PNPs in human serum, we have identified an ensemble of ~30 proteins that represent the primary corona constituents. The association of these proteins with PNPs depends on the PNP charge and the protein pI. We incubated PNPs with 293T cells; PNP association with cell plasma membranes is most pronounced for particles with positive surface charge and can be reduced by the presence of a corona.

To isolate the role that lipid bilayer composition plays in membrane-particle interactions, we built biomimetic GUVs from lipids extracted from brain, heart, and liver tissue. We also derived GPMVs from 293T cells. As with intact cells, biomimetic membranes were most aggressively attacked by positively charged PNPs. The presence of a corona reduced PNP-membrane interactions. Finally, we investigated the capacity of PNPs to permeabilize biomembranes. In all membranes investigated, incubation with PNPs significantly compromised the barrier properties of biomembranes, with the presence of a corona providing minimal protection against permeabilization.

We have performed a broad-ranging investigation of the capacity of nanoplastics to bind to and permeabilize biomembranes, both with naive surfaces and with associated protein coronas. The results show that PNPs can damage biomembranes in a wide range of conditions, suggesting that nanoplastics represent a persistent and significant environmental toxicity concern.

## **COLL 414**

### **Can we dispense with sphingolipids?**

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Glycosphingolipids are ubiquitously present in mammalian cells. Obtaining sphingolipid-free cells appears to be very difficult, if not impossible, because sphingolipids appear to

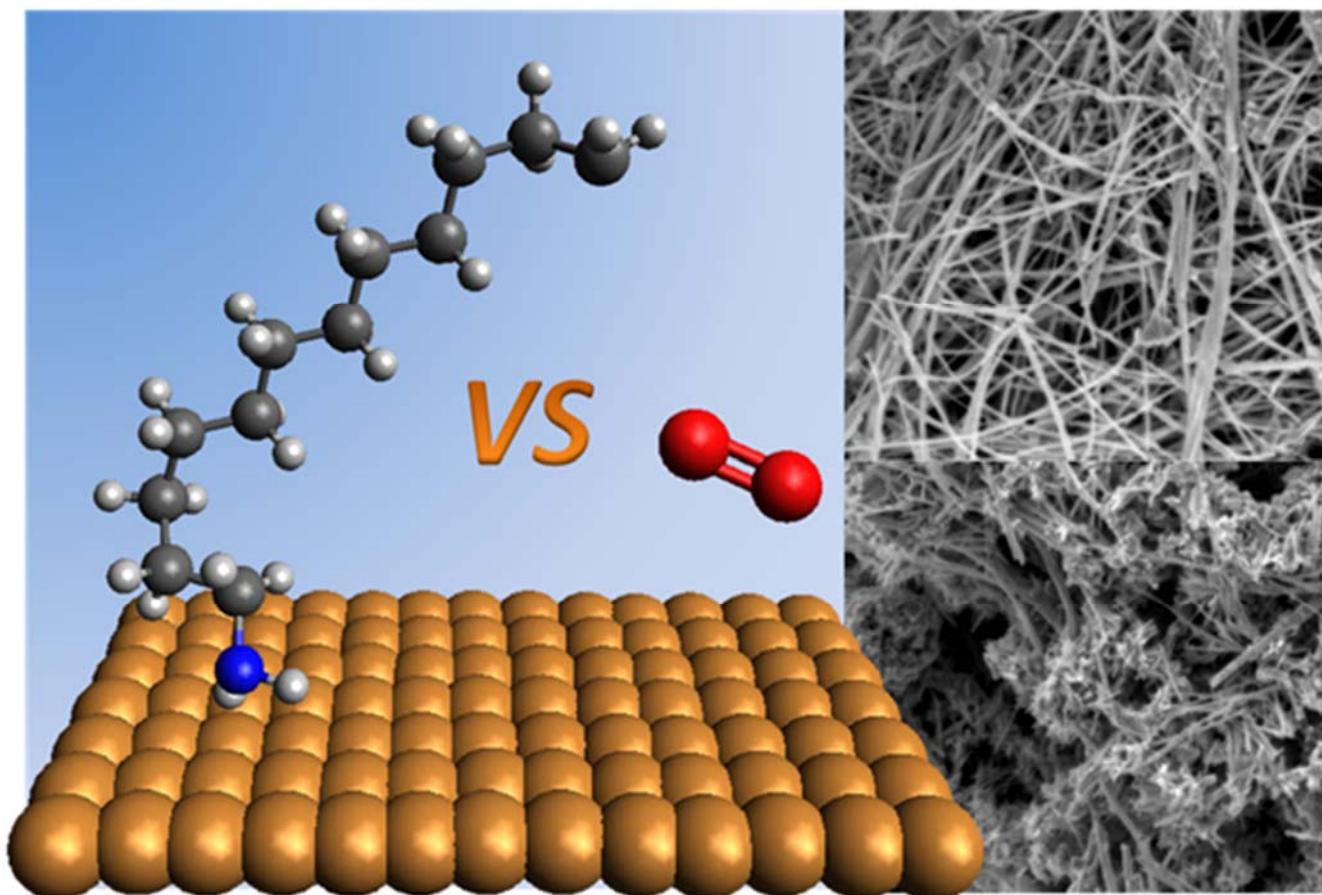
be essential for cell growth and survival. One way to explore this problem would be the use of cell lines deficient in sphingolipid synthesis. Following this idea CHO cells were mutated by Hanada *et al.* to suppress serine palmitoyltransferase, the first enzyme in sphingosine synthesis, while maintaining the capability of taking up and metabolizing exogenous sphingoid bases from the culture medium (LYB cell line). In this study wild type CHO and mutant LYB cells have been adapted to grow in a medium containing very low fetal bovine serum (FBS) concentrations (down to 0.04% instead of the usual 10%) to reduce, if not suppress, external uptake of lipids. Laurdan fluorescence measurements have been performed to measure membrane fluidity/rigidity, showing a significant decrease in the rigidity of LYB cells. Moreover, AFM force spectroscopy has shown statistically significant differences in nanomechanical properties in response to AFM tip-mediated sample breakthrough. A significantly lower force is required to penetrate samples obtained from LYB cells as compared with CHO ones. Mass spectroscopic analyses help in understanding the redistribution undergone by the LYB membrane cell lipids. In short, sphingomyelin is reduced by 65% in LYB grown in 0.04% FBS containing medium, as compared to those grown in 10% FBS. This leads to a cellular homeostatic response that makes LYB cells synthesize significantly more saturated glycerophospholipids and less polyunsaturated ones. Our results support the idea that LYB cells try to compensate the loss of membrane rigidity due to sphingomyelin decrease through an increase in fatty acid saturation, although with only partial success.

## **COLL 415**

### **Oxidation resistant copper nanowires with sustained electrical and electro-chemical properties**

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Recent rapid advances in flexible electronics, batteries, sensors and catalytic systems demand high performance electrical and electrochemical materials that are stable in an aqueous or humid environment. Copper nanowire (Cu NW) has been considered as an attractive “building block” for nano-device fabrication owing to their outstanding physical, electrical and chemical properties. The poor oxidation resistance of Cu NWs compromises their intended performance in real world applications despite their excellent properties and low cost. It remains a challenge for Cu NWs to be oxidation resistant while maintaining good electrical/electrochemical properties. In this work, several short chain ligands and long chain polymers were chosen to decorate Cu NW surfaces to minimize oxidation. With proper molecular design of the chain length and binding strength, the oxidation resistance of Cu NWs can be greatly enhanced without compromising their electrical and electrochemical properties. Implication of the present research toward preparation of high performance Cu NW-based devices for various microelectronic applications will be discussed.



COLL 416

### Encapsulation of gold nanoparticles into controlled homopolymer particles for catalytic applications

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Central to the success of AuNP-based catalytic systems is the effective modification to enhance their catalytically active sites, long-term stability, and applicability in green reaction environments. We report an *in situ* method to effectively encapsulate multiple gold nanoparticles (AuNPs) within functional-group-free poly(N-isopropylacrylamide) particles, which are developed as reactive quasi-homogeneous catalysts for carbon-carbon bond-forming reactions under base-free aerobic conditions. Unlike supported and embedded metal nanoparticles, the surfaces of the encapsulated AuNPs are nearly free from the reducing/stabilizing agents that can often serve as a physical barrier in

catalytic reactions (e.g., minimizing the role of the adsorbed reducing/stabilizing agents and maximizing the active sites of the loaded AuNPs as a catalyst). Given these features, employing these composite particles in the homocoupling of arylboronic acid derivatives results in an unexpectedly high catalytic activity and selectivity in EtOH. Investigating these types of materials and reaction conditions can lead to the development of robust, versatile, and environmentally-friendly catalytic systems.

## **COLL 417**

### **Robust nickel nanoparticles shielded from surface oxidation**

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Nickel nanoparticles (NiNPs) have recently gained wide popularity due to its wide use in catalysis, alloys, coatings, magnetic fluids, anodes of fuel cells, and imaging agents. Their nanometallic properties of small size and shape tunability, conductivity, and magneticity all in tandem with relative low-cost has given the NiNPs an edge over more REDOX-stable transition metals. However, it is also well-known that NiNPs and their alloy derivatives undergo degradation and release of Ni<sup>2+</sup> ions, which have huge environmental and human health impacts since Ni<sup>2+</sup> ions are known to be toxic. The environmental impacts of NiNPs independent of their Ni<sup>2+</sup> leaching are challenging at best. Studies designed to evaluate the nanoparticle-specific effects of NiNPs have been limited because of their propensity to undergo Ni<sup>2+</sup> dissolution. Design strategies for controlling Ni<sup>2+</sup> ion release from NiNPs are minimal to non-existent and are important if we are to understand how the physicochemical properties (size, shape, surface coating, and area) NiNPs play a role in toxicity. Here, we will present a design a strategy for synthesizing robust NiNPs capable of withstanding surface oxidation and Ni<sup>2+</sup> ion release at room temperature in aqueous solution. By utilizing a variety of coatings, including surfactants, lipids, and thiols, we are able to shield the NiNP from oxidizing conditions, yielding monodispersed NiNPs that are stable for months. The robustness of shielding is verified using UV-Vis spectroscopy and inductively coupled plasma mass spectrometry (ICP-MS), while size and shape of the particles are confirmed via dynamic light scattering (DLS) and transmission electron microscopy (TEM). With these NiNPs Robust NiNPs opens the door for many types of applications in catalysis, coating, and bioimaging as well as toxicological studies.

## **COLL 418**

### **Elucidating the stability of ligand-protected Au Nanoclusters under electrochemical reduction of CO<sub>2</sub>**

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Ligand-protected gold nanoclusters (NCs) are a novel class of particles that have attracted great interest in the field of catalysis due to their atomically precise structure, high surface-to-volume ratio, and unique electronic structure. In particular, the anionic thiolate-protected Au<sub>25</sub> NC, [Au<sub>25</sub>(SR)<sub>18</sub>]<sup>1-</sup>, with partially lost ligands, has been demonstrated to act as an active catalyst for the electrochemical reduction of CO<sub>2</sub>. However, the stability of this and other thiolate-protected NCs after partial ligand removal remains elusive. Using density functional theory (DFT) calculations and the recently developed thermodynamic stability model (TSM), we investigate the stability of [Au<sub>25</sub>(SR)<sub>18</sub>]<sup>1-</sup>, [Au<sub>18</sub>(SR)<sub>14</sub>]<sup>0</sup>, [Au<sub>23</sub>(SR)<sub>16</sub>]<sup>1-</sup>, and [Au<sub>28</sub>(SR)<sub>20</sub>]<sup>0</sup> NCs when a single ligand (–R or –SR) is removed from the surface. Additionally, we examine the stability of the partially protected NCs upon the adsorption of CO<sub>2</sub> reduction reaction intermediates (H, CO, and COOH) on the S or Au active site generated after single –R or –SR ligand removal respectively. Our results reveal that the partially protected Au<sub>25</sub> NC shows the highest stability compared to the other partially protected NCs. We find that the presence of the COOH intermediate on the generated active sites stabilizes the Au<sub>25</sub> NC almost as well as the removed ligands. Moreover, time-dependent DFT calculations reveal that the adsorption of CO and COOH on a Au active site leads to a red-shifting of the lowest-energy peak in the photoabsorption spectrum of [Au<sub>25</sub>(SR)<sub>18</sub>]<sup>1-</sup>. This observation may aid the detection of reaction intermediates during electrochemical catalytic reduction of CO<sub>2</sub>. Importantly, this study demonstrates the robustness of the Au<sub>25</sub> NC and offers a novel way to address stability of ligand protected NCs during electrocatalytic reaction conditions.

## COLL 419

### Manipulating energy transfer at the surface of PbS nanocrystals

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The current solar energy marketplace is dominated by silicon; however, the efficiency of these cells is substantially hampered by silicon's poor ability to absorb energy below its bandgap at 1.14 eV. A process called photon upconversion, that uses pairs of incoherent, low-energy photons to produce higher energy photons, can combat this issue by converting the sun's infrared rays into light that can be absorbed by silicon. However, an efficient system that can upconvert infrared to visible light for this purpose remains elusive. To address this need, we have investigated perylene-3,4,9,10-tetracarboxylic diimide (PDI) molecules that have been attached to the surface of lead sulfide (PbS) quantum dots as a potential system of infrared upconversion. Upon low-energy excitation of a PbS quantum dot, it can pass its energy to an interfaced PDI molecule, placing the molecule into a dark, spin-triplet excited state. Pairs of these triplet-excited molecules can subsequently pool their energy to form a high-energy, emissive spin-singlet state. Using ultrafast transient absorption, we investigated the photoexcited dynamics of this system in solution, expecting to observe triplet formation based on the energetic alignment of PDI and PbS electronic states. Instead, we saw single electron transfer from PbS to PDI

at an intrinsic rate of ~30 ps, evidenced by the formation of PDI anions. Importantly, we found that by tuning the energy levels of the PbS quantum dots relative to vacuum by attaching cinnamate ligands with large dipole moments to their surface, we can adjust the PbS-to-PDI electron transfer rate by nearly an order of magnitude. Our findings indicate that by changing the relative energy levels between PbS and PDI in our complex, heterogeneous system, we can selectively modify the PbS:PDI interface towards favoring either charge or energy transfer. This widely diversifies the range of applications that our system could potentially address, from upconversion via triplet formation to catalysis via excited anion formation. Furthermore, our work highlights the importance of considering relative energy levels when designing inorganic:organic interfaces for triplet energy and/or charge transfer, which we believe will guide future efforts to design high-efficiency light harvesting technologies.

## **COLL 420**

### **Pseudocarbynes: Polyynes stabilized by metal clusters**

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Pseudocarbynes are a new class of molecules/materials that we define as finite sp-hybridized carbon chains stabilized through non-covalent interactions with metal clusters. These exciting and innovative materials are expected to approach the unprecedented strength, elastic modulus, and stiffness of carbyne, which has defied isolation and characterization for over a century. We optimized a procedure to synthesize pseudocarbynes via the finely controlled laser ablation of a liquid/metal interface, where clusters and one-dimensional carbon chains self-assemble from colloidal solutions into new mesomaterials that bridge the molecular and materials realms. The non-covalent interaction between sp-carbon and small metal clusters is characterized by strong signatures in UV-vis, Raman, and infrared spectroscopies. These experimental measurements are supported by density functional theory (DFT) calculations that highlight a strong tendency of small metal clusters to interact with the sides of the -C≡C- chains. X-ray powder diffraction and high-resolution electron microscopy demonstrate the long-range crystallinity of the materials. I will present our progress in expanding the range of pseudocarbynes by incorporating a variety of metal clusters in their production.

## **COLL 421**

### **Elucidating how photoexcited semiconductor nanocrystals drive redox enzyme catalysis**

**Gordana Dukovic**, *gordana.dukovic@colorado.edu*. Dept of Chemistry and Biochemistry, University of Colorado Boulder, Boulder, Colorado, United States

This presentation will focus on the coupling of semiconductor nanocrystals as light absorbers with redox catalysts for multi-electron transfer reactions to drive solar photochemistry. Reactions of interest include H<sub>2</sub> generation, CO<sub>2</sub> reduction, N<sub>2</sub> fixation, and water oxidation. This presentation will summarize how nanocrystal excited state behavior and surface chemistry impact the rates and efficiencies of photoexcited electron transfer from CdS nanorods to the enzyme hydrogenase, which catalyzes proton reduction to H<sub>2</sub>. A combination of transient absorption spectroscopy and kinetic modeling allowed us to quantitatively understand the competition between electron transfer and the excited state relaxation processes in the CdS nanorods, and the relationship between these processes and the overall photochemical H<sub>2</sub> formation. These insights will then be applied to a more catalytically complex system: CdS nanorods complexed with an oxidoreductase that catalyzes formation of carbon-carbon bonds via CO<sub>2</sub> reduction. The presentation will feature our most recent results on charge transfer between semiconductor nanocrystals and redox enzymes.

## **COLL 422**

### **Nanoscale photoinduced charge transfer with individual quantum dots: Tunability through synthesis, interface design, and interaction with charge traps**

**Mircea Cotlet**, *cotlet@bnl.gov*. Brookhaven National Laboratory, Upton, New York, United States

Semiconducting colloidal quantum dots (QDs) provide an excellent platform for nanoscale charge-transfer studies. Because of their size-dependent optoelectronic properties, which one can tune via chemical synthesis and because of their versatility in surface ligand exchange, QDs can be coupled with various acceptor moieties to create hybrids with controlled type (electron or hole), direction, and rate of charge flow, depending on the foreseen application, either solar harvesting, light emitting, or biosensing. I will present several examples of QD-hybrids with controllable rate of charge transfer which were obtained by various approaches, including (i) by changing the QD core size and shell thickness, (ii) by the insertion of molecular linkers and dielectric spacers between QD and the acceptor component and (iii) by subjecting QDs to external factors such as intense electric fields or alternate optical excitation energy which can bias QD's internal charge transfer with surface charge traps [1].

## **COLL 423**

### **Designing inorganic nanomaterials for energy applications**

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For the last 10 years, we have focused on the architecture engineering of oxide-based nanomaterials for their applications to lithium ion battery, fuel cell electrocatalysis, and photocatalysis. We reported the first demonstration of galvanic replacement reactions in metal oxide nanocrystals, and synthesized hollow nanocrystals of various multimetallic oxides including  $\text{Mn}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$ . We report a simple synthetic method of carbon-based hybrid cellular nanosheets loaded with  $\text{SnO}_2$  nanoparticles. These oxide-based nanomaterials exhibited very high specific capacity and good cyclability for lithium ion battery anodes. We designed hollow anatase  $\text{TiO}_2$  nanostructures composed of interconnected  $\sim 5$  nm-sized nanocrystals, which individually reach the theoretical lithium storage limit and maintain a stable capacity during prolonged cycling. We present a synthesis of highly durable and active electrocatalysts based on ordered fct-PtFe nanoparticles and FeP nanoparticles coated with N-doped carbon shell. We designed and synthesized highly active and stable Fe-N-C catalyst for oxygen reduction reaction. We also report on the design and synthesis of highly active and stable  $\text{Co-N}_4(\text{O})$  moiety incorporated in nitrogen-doped graphene ( $\text{Co}_1\text{-NG}(\text{O})$ ) that exhibits a record-high kinetic current density and mass activity with unprecedented stability ( $>110$  h) for electrochemical  $\text{H}_2\text{O}_2$  production (Revised for *Nature Mater.*). We synthesized multigrain nanocrystals consisting of  $\text{Co}_3\text{O}_4$  nanocube cores and  $\text{Mn}_3\text{O}_4$  shells that are separated into mutually orthogonal multiple grains. At the sharp edges of the  $\text{Co}_3\text{O}_4$  nanocubes, we observed that tilt boundaries of the  $\text{Mn}_3\text{O}_4$  grains exist in the form of disclinations due to a large geometric misfit between adjacent tetragonal  $\text{Mn}_3\text{O}_4$  grains (*Nature* in press). By taking advantage of the uniform grain boundary defect structures, we obtained a correlation between the defects and the resulting electrocatalytic behavior for the oxygen reduction reaction. We report on the designed synthesis of highly active  $\text{TiO}_2$  photocatalysts incorporated with single copper atoms ( $\text{Cu/TiO}_2$ ) that exhibit reversible and cooperative photoactivation process, and enhanced photocatalytic hydrogen generation activity.

## **COLL 424**

### **Molten inorganic salts as solvents and reactive media for colloidal chemistry**

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Many functional nanomaterials used for catalysis, healthcare, solid-state lighting, and displays are synthesized by colloidal techniques. The scope of chemical transformations accessible to colloidal chemists is determined by the stability of solvents and surfactants used as a reaction medium. For example, very few traditional solvents can handle temperatures above 400 C, while many inorganic phases require even higher temperatures to form. We recently reported a novel class of colloidal systems, colloids in molten inorganic salts. Nanoparticles of different transition metals, semiconductors, oxides, and magnetic materials can form true colloids in molten inorganic salts. The colloidal stability of nanoparticles in molten salts could not be explained by traditional electrostatic and steric stabilization mechanisms. Our experimental studies and simulations point to the importance of the long-range ion correlations in the molten salt

near the nanocrystal interface.

In addition to the fundamental exploration of new colloidal systems, molten salts expand the boundaries for solution synthesis of many hard-to-crystallize nanomaterials that have been out of reach for colloidal chemists. We have used molten salts to synthesize colloidal GaAs,  $\text{In}_x\text{Ga}_{1-x}\text{As}$ , and  $\text{In}_x\text{Ga}_{1-x}\text{P}$  quantum dots, which resisted numerous synthetic attempts for over two decades. By further developing colloidal chemistry in molten salts, we are working to enable synthetic routes toward novel covalent functional nanomaterials.

## **COLL 425**

### **DNA-programmed interfacial nanoparticle assembly**

**Robert Macfarlane**, *rmacfarl@mit.edu*. Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States

The programmability of DNA makes it an attractive structure-directing ligand for the assembly of nanoparticle superlattices with unique structure-dependent physical phenomena. While DNA base pairing has enabled the development of materials with nanometer-scale precision in nanoparticle placement and independent control over particle size, lattice parameters, and crystal symmetry, manipulating the macroscopic shape of the lattices remains challenging. By pairing this “bottom-up” assembly method with “top-down” lithographic techniques and assembling nanoparticle superlattices on a patterned substrate, complete control over crystal size, shape, orientation and unit cell structure can be realized. The key challenges in developing this technique are to first understand how different design factors affect the assembly process in this broken-symmetry system that is assembled at an interface, and subsequently develop structure-property relationships that correlate the above mentioned design parameters with the resulting overall material structure. Here, we examine both at-equilibrium deposition processes capable of generating single crystals with well-defined shapes, as well as post-deposition annealing to transform disordered particle arrangements into crystalline arrays. Using a combination of X-ray diffraction and electron microscopy techniques, both surface morphology and internal thin film structure are examined to provide an understanding of the mechanisms of particle crystallization under conditions where crystal growth is anisotropic due to a boundary condition. This novel method for controlling particle assembly draws several strong analogies to traditionally atomic epitaxy/heteroepitaxy, providing a useful tool for understanding thin film growth processes. As a result, we are able to realize 3D architectures of arbitrary domain geometry and size, thereby making materials with unprecedented precision across multiple length scales.

## **COLL 426**

### **Designing Au nanocrystal assemblies for optical metamaterials**

**Cherie R. Kagan**, [kagan@seas.upenn.edu](mailto:kagan@seas.upenn.edu). Dept of ESE MSE, Univ of Pennsylvania, Philadelphia, Pennsylvania, United States

Colloidal Au nanocrystals (NCs) are known for their size- and shape-dependent localized surface plasmon resonances. Here, we explore the optical properties of Au NC assemblies as we control their number, arrangement, and inter-particle distance and then exploit their properties in the design of optical metamaterials. For example, we use lithography to define size- and shape-engineered topographical templates for the directed assembly of NC oligomer “metamolecules.” We map the evolution in energy and strength of electric and magnetic dipole modes as we increase the number of nearest neighbor shells in close-packed spherical NC assemblies and as we construct trimers of nanorods that assemble along the edges of equilateral triangles to form open structures. These NC assemblies can also show chiroptical responses. We also use chemical exchange of the long ligands used in NC synthesis with more compact ligand chemistries to bring neighboring NCs into proximity and increases interparticle coupling. This ligand-controlled coupling allows us to tailor a dielectric-to-metal phase transition seen by a  $10^{10}$  range in DC conductivity and a dielectric permittivity ranging from everywhere positive to everywhere negative across the whole range of optical frequencies. We realize a “diluted metal” with optical properties not found in the bulk metal analog, presenting a new axis in plasmonic materials design and the realization of optical properties akin to next-generation metamaterials. We harness the solution-processability and physical properties of colloidal plasmonic NCs to imprint NC superstructures for large-area, active metamaterials. We demonstrate quarter-wave plates with extreme bandwidths and high polarization conversion efficiencies in the near- to-mid infrared. By juxtaposing plasmonic NCs and bulk materials, we exploit their different chemical and mechanical properties to transform lithographically-defined two-dimensional structures, upon ligand exchange, into three-dimensional structures and optical metamaterials.

## **COLL 427**

### **Shape regulation of high-index facet nanoparticles by dealloying**

**Chad A. Mirkin**, [chadnano@northwestern.edu](mailto:chadnano@northwestern.edu). Chemistry, Northwestern University, Wilmette, Illinois, United States

For many reactions catalyzed by metallic nanoparticles, the more-exposed metal atoms on high-index faces can be more active than the metal atoms on smooth, low-index faces. Surface ligands can be used to stabilize high-index surfaces, but they can also be hard to remove. We report the solid-state synthesis of tetrahedral (THH) nanoparticles (~10 to ~500 nanometers) with high-index faces. THH particles composed of platinum (Pt), palladium, rhodium, nickel, and cobalt, as well as a library of bimetallic compositions, were synthesized on silicon wafers and on catalytic supports via a ligand-free, solid-state reaction that used trace elements [antimony (Sb), bismuth (Bi), lead (Pb), or tellurium] to stabilize high-index facets. Both simulation and experiment confirmed that this method stabilized the {210} planes. A study of the PtSb system

showed that the tetrahedron shape resulted from the evaporative removal of Sb from the initial alloy—a shape-regulating process fundamentally different from solution-phase, ligand-dependent processes. The current density at a fixed potential for the electro-oxidation of formic acid with a commercial Pt/carbon catalyst increased by a factor of 20 after transformation with Bi into THH particles.

## **COLL 428**

### **New developments in chiral inorganic nanostructures**

**Nicholas Kotov**, *kotov@umich.edu*. University of Michigan, Ann Arbor, Michigan, United States

The early observation of strong circular dichroism for individual nanoparticles and their assemblies have developed into a rapidly expanding field of chiral inorganic nanostructures. The chiral inorganic nanostructures encompass sophisticated constructs from metals, semiconductors, ceramics, and nanocarbons with multiple chiral geometries with characteristic scales from *Ångströms* to microns. Such versatility enables their functional engineering over a broad range of physical and chemical properties inspiring multiple technological realizations exemplified by biosensing and optoelectronics.

This talk will address (1) the origin of the uniquely high values of optical anisotropy; (2) the mechanisms of chirality transfer in inorganic materials; and (3) differences/similarities with chiral supramolecular, liquid crystal, and biological assemblies. The role of chiral inorganic nanostructures in homochirality of life on Earth will be briefly discussed. In that respect, long-range correlations and critical phenomena in chiral nanoassemblies leading to the emergence of geometrically complex structures will be demonstrated.

The novel venues for practical realizations of chiral nanoassemblies included in the talk will be photocatalytic C-C coupling in biomimetic chiral supraparticles and polarization spectroscopy in terahertz spectral window with chiroplasmonic kirigami composites.

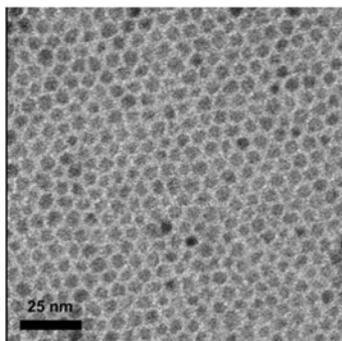
## **COLL 429**

### **Colloidal synthesis of germanium nanocrystal quantum dots with size-tunable near-infrared photoluminescence**

*Jungchul Noh, Hyungyun Kim, Tushti Shah, Brian A. Korgel*, *korgel@che.utexas.edu*. University of Texas at Austin, Austin, Texas, United States

We report a colloidal synthesis of alkyl-passivated germanium (Ge) nanocrystals with widely tunable size. Average diameters range from 3 to 18 nm and the nanocrystals exhibit band edge near infrared (NIR) photoluminescence (PL). The synthesis involves the heating-up of GeI<sub>2</sub> in a mixture of oleylamine (OLAm) and octadecene (ODE). Nanocrystal growth proceeds by two sequential mechanistic steps at low and then high

temperature. First, OLAm promotes the decomposition of GeI<sub>2</sub> to Ge at relatively low temperature to lead to nanocrystal nucleation and growth. OLAm also serves as a capping ligand. Its reversible bonding to Ge allows nanocrystals to grow in this low temperature range. Growth then terminates when the temperature becomes hot enough to induce hydrogermylation of ODE. OLAm ligands are displaced by a layer of covalently bonded alkyl groups. The nanocrystal size is tuned by adjusting the reactant concentrations and heating rate. The largest nanocrystals (>11 nm) are obtained by adding trioctylphosphine (TOP) to further modify the GeI<sub>2</sub> decomposition rate. The optical properties of these Ge nanocrystals quantum dots are compared to two-dimensional Ge nanosheet structures with organic ligand passivation.



Transmission electron microscope (TEM) image of a monolayer of organic ligand-passivated Ge nanocrystals.

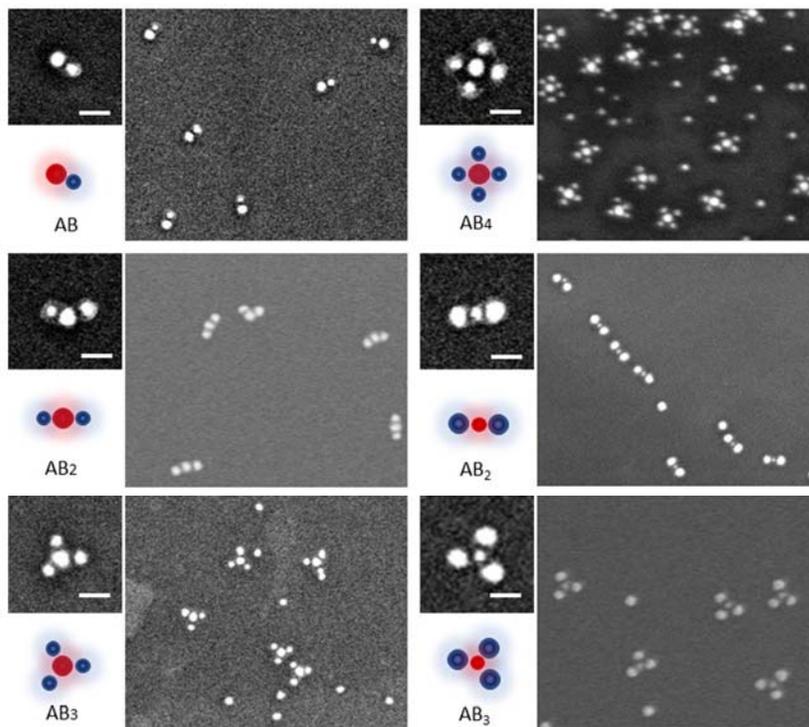
## **COLL 430**

### **Controlled self-assembly of water-soluble, “hairy”, inorganic nanoparticles (HINPs) into supracolloids with defined valence**

**Kyle Webb**<sup>1</sup>, [kylewebb031693@yahoo.com](mailto:kylewebb031693@yahoo.com), **Zhihong Nie**<sup>2</sup>. (1) Chemistry, The University of Maryland, College Park, College Park, Maryland, United States (2) Macromolecular Science, Fudan University, Shanghai, China

Nature has developed clever and intricate strategies to assemble simple building blocks into complex architectures, ranging from stacking in tubulin to complex twisting and folding in DNA. Drawing inspiration, much research has been done to mimic this molecular programming to develop well-defined nanoscale structures via nanoparticle (NP) self-assembly. However, architectures remain largely simplistic due to the isotropic nature of established assembly protocols. Consequently, we have developed a new self-assembly technique that utilizes favorable Lewis acid/base interactions, Cu(I)-catalyzed azide-alkyne cycloaddition, or host-guest interactions between block-copolymers (BCPs) tethered to the surface of AuNPs. AuNPs are synthesized via reduction of a gold precursor, using sodium citrate as both a reducing and capping agent. Concurrently, thiol-terminated BCPs are synthesized via Reversible Addition-

Fragmentation Chain-Transfer (RAFT) polymerization, with desired functionalities incorporated into the polymer backbone. Subsequently, these BCPs are tethered to the NP surface through ligand exchange, achieving hairy inorganic NPs (HINPs). We demonstrate, that through careful tuning of the BCP length and particle concentrations, we can control the interactions between particles, yielding structures (ie. dimers, trimers, tetramers, etc.) with high yields. Particularly intriguing is the ability to then transfer these structures into aqueous media without loss of structural integrity. Additionally, the use of reversible interactions yields structures that can be controllably assembled and disassembled using various stimuli.



Representative colloidal structures (scale bars are 50nm)

## COLL 431

### Plasmonic colloids and biosensing

**Luis Liz Marzan**, [llizmarzan@cicbiomagune.es](mailto:llizmarzan@cicbiomagune.es). CIC biomaGUNE, Donostia - San Sebastian, Spain

The field of Nanoplasmonics focuses on the manipulation of light using materials with significantly smaller sizes than the radiation wavelength. This is typically achieved using nanostructured metals, since they can very efficiently absorb and scatter light because

of their ability to support coherent oscillations of free (conduction) electrons. Although the remarkable optical response of “finely divided” metals is well known since more than 150 years ago, the recent development of sophisticated characterization techniques and modeling methods has dramatically reactivated the field. An essential pillar behind the development of nanoplasmonics is the great advance in fabrication methods, which have achieved an exquisite control over the composition and morphology of nanostructured metals. In particular, Colloid Chemistry has the advantage of simplicity and large scale production, while offering a number of parameters that can be used as a handle to direct not only nanoparticle morphology but also surface properties and subsequent processing. This talk will provide an overview of “colloidal nanoplasmonics” as a sufficiently mature field to bridge the basic fabrication of nanoplasmonic building blocks, all the way to devices that can be used for real applications in biosensing.

## **COLL 432**

### **Probing bioconjugation chemistry in colloidal materials**

**Chris D. Spicer**, *chris.spicer@york.ac.uk*. Department of Chemistry, University of York, York, United Kingdom

Colloidal materials are powerful platforms for biomedicine, providing substrates for sensing and tissue engineering. To increase the potency and sensitivity of these materials it is important to maximise their ability to interact with biological environments. This is commonly achieved through the attachment or encapsulation of biomolecules that are able to mediate recognition. The interface between colloid and biomolecule is therefore a critical design feature when looking to maximise the efficacy of the resultant biomaterials. Here, I will present our efforts to develop and study bioconjugation chemistries both on the surface and in the interior of colloidal materials. This will focus on the design of fluorescence-based reporters for conjugation, allowing us to monitor biorthogonal reactions within the colloidal phase, as well as interrogate the kinetics, stability and responsiveness of dynamic covalent linkages within the dilute concentration regimes often required for biomolecule-material functionalisation.

## **COLL 433**

### **Encoding high bioactivity in supramolecular nanostructures**

**Samuel I. Stupp**, *s-stupp@northwestern.edu*. Northwestern University, Evanston, Illinois, United States

Bioactive nanostructures can play critical roles in tissue regeneration, disease therapies, targeted drug delivery, and anti-microbial activity, among other biomedical functions. An important mechanism to encode bioactivity is to design structures that activate receptors for cell signaling and therefore function as protein mimics. Alternatively, nanostructures can be designed to amplify signaling by proteins such as growth factors. Ideally such systems should be fully and safely biodegradable and have

greater half-lives than their protein counterparts. This lecture will describe a broad platform of bioactive supramolecular nanostructures built with a toolbox of peptides, peptide amphiphiles, glycans, nucleic acids, and metallic clusters. One of the examples to be described involves nanostructures that bind growth factors in specific ways to enhance regeneration of musculoskeletal tissues. Other examples will include nanostructures that activate important neural receptors, deliver therapeutic peptides and gases, or provide anti-microbial protection.

## **COLL 434**

### **Novel antivirals**

**Francesco Stellacci**, *francesco.stellacci@epfl.ch*. Institute of Materials, EPFL, Lausanne, Switzerland

There are a large number of viral infections against which we have no vaccine and no drug. Years of research in antivirals have resulted only in a handful of success stories. It will be showed that a novel approach to fight viral infections extracellularly is possible. The approach is based on the targeting of highly conserved viral domains and the consequent application of a strong hydrophobic contact that lead sot irreversible damage of the virions. It will be argued that the approach is general as it can be used to fight a large number of different viruses and it can be applied to many compounds. The mechanism of action and the design rules for the compounds will be discussed.

## **COLL 435**

### **Glucose-responsive smart insulin patch**

**Zhen Gu**, *guzhenlab@gmail.com*. University of California, Los Angeles, Los Angeles, California, United States

A glucose-responsive insulin delivery system that mimics beta cell function holds great promise to enhance health and improve the quality of life for people with type 1 and advanced type 2 diabetes. In this talk, I will introduce our innovation development of smart insulin patches, integrating glucose-responsive micro-/nano-formulations with painless microneedle-mediated transdermal devices. A variety of systems with different response mechanisms will be discussed and compared, including hypoxia-responsive, vesicle fusion-based, glucose transporter-mediated and charge switchable polymer-based formulations. A latest coin-sized smart insulin patch can regulate blood glucose levels of a diabetic minipig model (>25 kg) for over 20 hours.

## **COLL 436**

### **Multicompartmental protein nanoparticles for targeted drug delivery**

**Joerg Lahann**, *lahann@umich.edu*. Univ of Michigan, Ann Arbor, Michigan, United States

Multicompartmental drug nanocarriers are monolithic particles that are comprised of distinct polymer domains. In case of bicompartamental nanocarriers, i.e. two distinct domains, the nanocarriers feature two equally sized hemispheres. Preparation of multicompartmental nanocarriers with sizes ranging from 100 nm to microns can be achieved using electrohydrodynamic (EHD) co-jetting. Nanocarriers that are made of two distinct base polymers can combine orthogonal properties, including distinct degradation mechanisms, that will lead to the controlled release of binary combinations of drugs from the same particle. Moreover, addition of orthogonally functionalized polymers allows for selective targeting of one hemisphere only. In addition to multicompartmental nanocarriers comprised of synthetic polymers, EHD co-jetting has been employed to prepare multicompartmental protein nanoparticles. These protein nanoparticles have been evaluated as drug carriers for combination therapy in breast cancer and glioblastoma. In addition, the conceptual role of protein nanoparticles for cancer immunotherapies will be addressed.

## **COLL 437**

### **Zinc oxide particles release nitric oxide from endogenous and exogenous nitric oxide prodrugs**

**Rona Chandrawati**, *rona.chandrawati@unsw.edu.au*. School of Chemical Engineering, University of New South Wales (UNSW Sydney), Sydney, New South Wales, Australia

Nitric oxide (NO) is a potent biological molecule that contributes to a wide spectrum of physiological system, including cardiovascular system, immune system, central nervous system, and outflow physiology. However, NO delivery technology remains severely limited due to the physiological properties of NO: 1) NO has a short half-life in human tissues (seconds); 2) NO can only diffuse over short distances (~100  $\mu\text{m}$ ), thus limiting its action to only areas near the source of delivery; and 3) NO can exert protective or deleterious effects depending on its concentration. Current strategies for NO delivery focus on encapsulation of NO donors into pre-fabricated scaffolds or an enzyme-prodrug therapy approach. The former is limited by the finite pool of NO donors available, while the latter is challenged by the inherent low stability of natural enzymes. Enzyme mimics are attractive substitutes for their natural counterparts in diverse biomedical applications because they have excellent stability against biological degradation, high temperature, and extreme pH conditions compared with natural enzymes. In this work, we provide the first report of zinc oxide (ZnO) with innate glutathione peroxidase and glycosidase activities that catalytically decompose endogenous (GSNO) and exogenous ( $\beta$ -gal-NONOate) NO donors to generate NO at physiological conditions. Through ZnO approach, we envision that sustained NO delivery could be achieved by relying on life-long pools of GSNO, and when needed, on-demand NO delivery at the desired levels of NO could be realized by externally administered  $\beta$ -gal-NONOate. By tuning the concentrations of ZnO particles and NO

prodrugs, physiologically relevant NO levels were generated. ZnO preserved its catalytic property for 6 months and retained 55% of the initial activity after 10 months. We further demonstrated the activity of ZnO in generating NO from NO prodrugs in human serum. Our findings may open new routes to the next generation of NO-releasing biomaterials and devices in diverse biomedical applications.

## **COLL 438**

### **Assembly and degradation of inorganic nanoparticle in biological environment**

**Wolfgang J. Parak**<sup>1,2</sup>, [wolfgang.parak@uni-hamburg.de](mailto:wolfgang.parak@uni-hamburg.de). (1) CHyN, Universitaet Hamburg, Hamburg, Germany (2) CIC Biomagune, San Sebastian, Spain

In solution, nanoparticles may be conceptually compartmentalized into cores and engineered surface coatings. Recent advances allow for simple and accurate characterization of nanoparticle cores and surface shells. After introduction into complex biological environment, adsorption of biological molecules to the nanoparticle surface as well as a loss of original surface components occur. Thus, colloidal nanoparticles in the context of biological environment are hybrid materials with complex structure, which may result in different chemical, physical, and biological outcomes as compared to the original engineered nanoparticles. In this perspective, we will discuss building up an engineered inorganic nanoparticle from its inside core to its outside surface, and following its degradation in biological environment from its outside to its inside. This will involve the way to synthesize selected inorganic nanoparticles. Then, we will discuss the environmental changes upon exposure of these nanoparticles to biological media and their uptake by cells. Next, the intracellular fate of nanoparticles and their degradation will be discussed. Based on the examples the need to see nanoparticles in the context of biological environment as dynamic hybrid materials will be highlighted.

## **COLL 439**

### **Rapid, large-volume, thermally controlled 3D printing using a mobile liquid interface**

**Chad A. Mirkin**, [chadnano@northwestern.edu](mailto:chadnano@northwestern.edu). Chemistry, Northwestern University, Wilmette, Illinois, United States

We report a stereolithographic three-dimensional printing approach for polymeric components that uses a mobile liquid interface (a fluorinated oil) to reduce the adhesive forces between the interface and the printed object, thereby allowing for a continuous and rapid print process, regardless of polymeric precursor. The bed area is not size-restricted by thermal limitations because the flowing oil allows for direct cooling across the entire print area. Continuous vertical print rates exceeding 430 millimeters per hour with a volumetric throughput of 100 liters per hour have been demonstrated, and proof-of-concept structures made from hard plastics, ceramic precursors, and elastomers have been printed. Taken together, these advances in throughput, mobile interface

design, and materials generality, which were enabled by the tailoring of the chemistry at interfaces and surfaces, solve several problems associated with large-area, large-object 3D printing.

## **COLL 440**

### **Inverse-opal structures for photonic, catalytic, and sensing applications**

**Joanna Aizenberg**, *jaiz@seas.harvard.edu*. Harvard University, Cambridge, Massachusetts, United States

This presentation will introduce a sol-gel co-assembly approach that results in large-scale, highly ordered coatings with embedded, uniformly distributed, and accessible nanoparticles. The unique coloration of these inverse opal films combines iridescence with plasmonic effects. The composition and optical properties of these films are demonstrated to be locally tunable using selective functionalization of the doped opals. The latter exhibit a sharply defined threshold wettability for infiltration. This liquid-specific wetting behavior naturally couples to macroscopic color changes. We are exploiting this effect in the development of simple and low-cost colorimetric indicators for liquid detection and encryption, as a tag for low-cost monitoring of tampering or material aging, and in the design of novel, highly stable heterogeneous catalysts.

## **COLL 441**

### **Nanolaminated multiresonant plasmonics for multimodal nano-bio interface**

**wei zhou**, *wzh@vt.edu*. Electrical and Computer Engineering, Virginia Tech, Blacksburg, Virginia, United States

In this talk, Dr. Zhou will discuss innovative concepts and approaches to design, fabricate, and exploit nanolaminated multiresonant plasmonics devices for biomedical applications. Out-of-plane engineered multiresonant plasmonics can control light flows and enhance light-matter interactions at multiple different wavelengths, and thus can potentially be used as multifunctional wavelength-multiplexed optical nanosensors and nanotransducers in biological systems. We investigated a new type of multilayered metal-insulator optical nanocavities that can support multiple localized plasmon resonances with ultra-small mode volumes. The number of resonance peaks and their resonance wavelengths can be controlled by simple geometric design rules. The innovations discussed in this talk could be inspiring for the development toward multimodal optical-electrical nano-bio interface for applications including implantable flexible bio-integrated nanosystems, lab-on-a-chip biomedical architectures, and handheld point-of-care diagnostics platforms.

## **COLL 442**

## **Tuning biomolecular display on nanostructured surfaces for high-performance sensing**

**Shana O. Kelley**, *shana.kelley@utoronto.ca*. Univ Toronto Fac of Pharmacy, Toronto, Ontario, Canada

Controlled nanostructuring of electrode surfaces can be used to enhance biomolecular capture rates and efficiencies. By immobilizing biomolecules on nanostructured surfaces, high-performance biomolecular detection systems can be developed to facilitate rapid biomarker analysis and the detection of infectious pathogens. We have developed electrochemical assays that are able to detect nucleic acids, proteins and small molecules, with universally high sensitivity levels (*Nature Chemistry* 2012) and have applied this approach in a variety of areas including noninvasive monitoring via Liquid Biopsy (*Nature Chemistry* 2015). This talk will highlight how electrodeposited metals can be used to create high-performance sensors that can be applied to a broad collection of clinically-relevant analytes, and will discuss how surface morphology, surface area and molecular diffusion can affect the detection limits obtained. Recent progress linking these sensors with gene circuits (*Nature Chemistry* 2019) and reagentless readout will be discussed.

### **COLL 443**

## **Exploring chemical dynamics at the soft-hard interfaces**

**Bozhi Tian**, *btian@uchicago.edu*. Chemistry Department, the University of Chicago, Chicago, Illinois, United States

Although there are numerous studies on either hard or soft materials, our understanding of the fundamentals at hard/soft interfaces has been limited. As different types of energy (such as electrostatic, mechanical, thermal, and chemical energies) display diverse scaling behaviors and can converge, an appropriate selection of the length scale is critical for promoting new scientific discoveries across these interfaces. Our group integrates material science with biophysics to study several hard/soft interfaces. We synthesize new materials and probe interfacial dynamics, with particular focus at the sub-micrometer and sub-cellular length scales. In this talk, I will focus on the interfaces that enabled non-genetic, freestanding, and semiconductor-based biological modulation. I will also discuss some recent work that exploits the dynamic behaviors of granular materials in polymeric matrices. I will end the talk by proposing several new scientific and engineering approaches to improving our fundamental understanding of the (bio)chemical processes at soft/hard interfaces and to exploring new applications of these interfacial (bio)chemical processes.

### **COLL 444**

## **What do ligands look like on gold nanocrystals?**

**Catherine J. Murphy**, *murphycj@illinois.edu*. Box 59-6, Univ of Illinois at Urbana-Champaign, Urbana, Illinois, United States

Organic ligands are frequently required to stabilize inorganic nanomaterials in colloidal solution. Yet compared to the many measurements that scientists perform to learn about the “hard stuff”, there are far fewer measurements to learn about the “soft stuff” at the surface of inorganic nanocrystals. In this talk I will describe two different methods – STEM EELS and NMR – that can give insight into ligand density at different positions around individual anisotropic gold nanocrystals (in the case of STEM EELS) and average ligand densities and headgroup mobilities in solution (NMR).

#### **COLL 445**

##### **Investigating the stability and orientation of antibody adsorbed onto gold nanoparticles**

**Jeremy D. Driskell**, *jdriske@ilstu.edu*, *Guadalupe Ruiz*, *Kiran Tripathi*, *Nicki Ryan*, *Kylie Rutschke*, *Samuel Okyem*, *Olatunde Awotunde*. Department of Chemistry, Illinois State University, Normal, Illinois, United States

Antibody-gold nanoparticle (AuNP) conjugates are central to many emerging nanobiotechnology applications. Immobilization of the antibody on the AuNP surface to provide a robust interaction, facilitate colloidal stability, and provide proper orientation of the antibody is critical to realize the potential benefits of these novel platforms. Recent studies have demonstrated that localized regions of charge on the antibody are responsible for the orientation of the immobilized protein. In this presentation, we will describe efforts to modulate the surface charge of an antibody using solution pH and measure the impact of protein charge on adsorption. The adsorption affinity between the antibody and AuNP was extracted from adsorption isotherms generated via nanoparticle tracking analysis (NTA) and was found to be independent of the protein charge. However, differences in the measured thickness of the protein layer suggest that protein charge impacts the orientation of the immobilized antibody. An enzyme-mediated assay was developed to confirm pH-dependent orientation. Adsorption dynamics of ubiquitous plasma proteins to AuNPs were also analyzed and compared to antibody adsorption. The antibody displayed the greatest affinity for the AuNP among the tested plasma proteins. Moreover, the enzyme-mediated assay confirmed that antibody irreversibly adsorbed to AuNPs and resisted displacement under the stress of a physiological environment. This work provides additional insight into the mechanism of antibody adsorption and better defines the capabilities and potential limitations of antibody-AuNP conjugates in emerging bioanalytical technologies.

#### **COLL 446**

##### **Biomimetic self-assembly: Nanoliter aqueous microdroplet**

**Sunghee Lee**, [slee@iona.edu](mailto:slee@iona.edu). Chemistry, Iona College, New Rochelle, New York, United States

Amphiphilic molecules can spontaneously self-assemble into bilayer nanostructures at a liquid-liquid interface. This presentation features systems that mimic the structure and function of the cell membrane using self-assembly. These systems are constituted by the interface of a pair of contacting aqueous nanoliter droplets, each of which is covered with a lipid monolayer. These droplet interface bilayer (DIB) systems offer a powerful and controllable model for studying the fundamental physical chemistry of lipid bilayers. Using the DIB as a model biomembrane, we report results for rates of water transport across the bilayer interface that illuminate the exquisite interplay between structural factors of the bilayer and its chemical environment: water permeability parameters provide important insights into the aggregate structure of these soft membranes. The permeability of the DIB system allows us to probe the extent to which nanoparticles and small molecules may bind or perturb the lipid bilayer. This successful demonstration of soft surface engineering at the aqueous nanoliter droplet will provide important insights into the understanding of the lipid bilayer, an essential component of cellular membranes, and its interactions with surroundings.

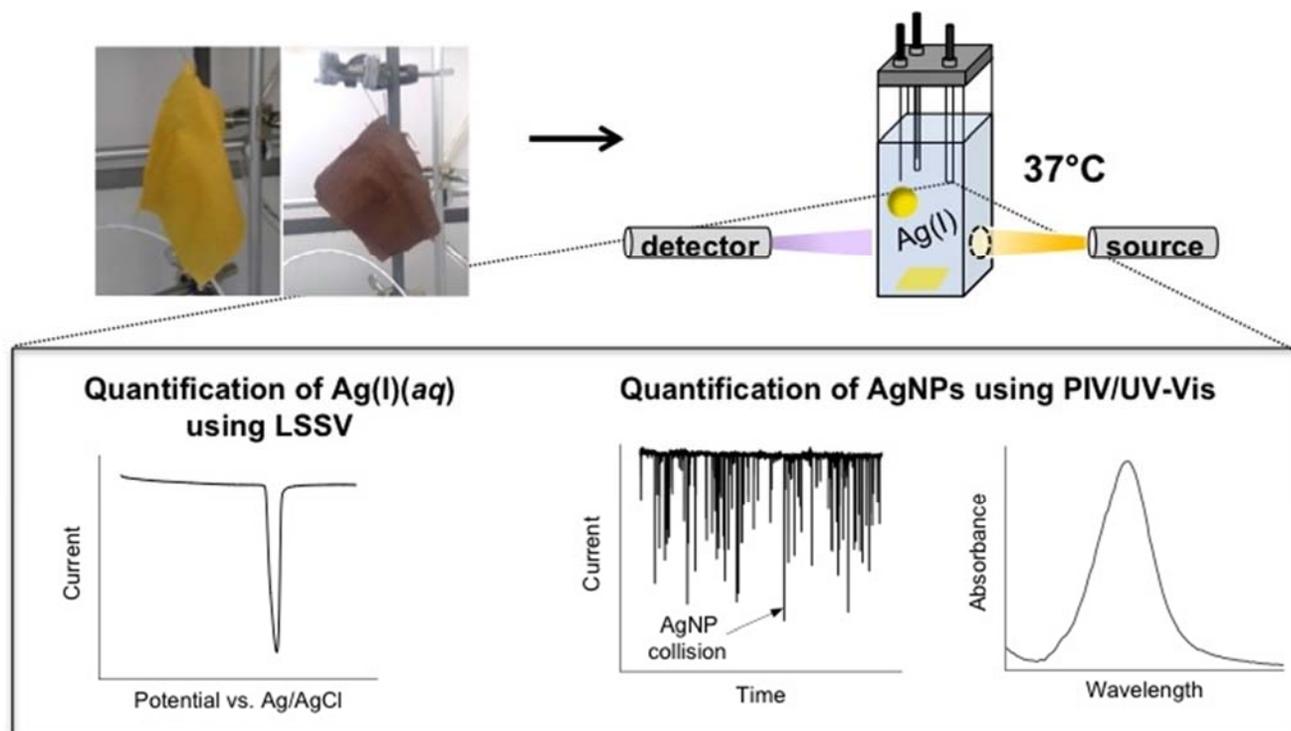
#### **COLL 447**

#### **Development of a novel analytical method for the *in situ* quantification and speciation of Ag(I) and AgNPs released from nano-enabled textiles**

**Zachary J. O'Dell**, **Laela Ezra**, **Dan Boehmler**, **Kathryn R. Riley**, [kriley1@swarthmore.edu](mailto:kriley1@swarthmore.edu). Department of Chemistry and Biochemistry, Swarthmore College, Swarthmore, Pennsylvania, United States

The unique properties of engineered nanomaterials (ENMs) have enabled their increased use for a range of environmental, medicinal, and commercial applications. However, ENMs can undergo many transformations in environmental and biological matrices (e.g. dissolution, aggregation, adsorption of small molecules, etc.), which alter their physicochemical properties. In order to fully characterize ENM properties in relevant matrices, *in situ* analytical tools are needed. We have developed a highly reproducible linear sweep stripping voltammetry (LSSV) method to quantify silver nanoparticle (AgNP) dissolution kinetics in real-time. Separately, we have developed a technique that integrates UV-vis spectroscopy with particle-impact voltammetry (PIV/UV-vis) to monitor changes in the bulk AgNP suspension and at the single particle scale, respectively. In the present work, we have coupled our LSSV and PIV/UV-vis techniques to speciate dissolved Ag(I)(aq) and in-tact AgNPs released from AgNP-impregnated textiles in real-time. Specifically, since AgNPs are frequently incorporated in sports-performance clothing, we have evaluated silver release from cotton fabrics exposed to simulated sweat solutions in order to mimic a release and human exposure scenario. We have evaluated the effect of various solution conditions (e.g., temperature, ionic strength, pH, the presence of biomolecules) on Ag(I)(aq) and AgNP release. The

development of this novel analytical tool and the insights gained regarding  $\text{Ag(I)(aq)}$  and AgNP release will be presented.



Schematic of PIV-UV-vis. A swatch of AgNP-impregnated fabric is placed into a PIV/UV-vis cuvette containing simulated sweat solution. LSSV tandem PIV/UV-vis is carried out to quantify the concentrations of dissolved  $\text{Ag(I)(aq)}$  and AgNPs, respectively, that are released from the textile over time.

## COLL 448

### Tuning the dimensionality of polyaniline nanomaterials using Laponite™ hydrogels

**Michael E. Hagerman**, [hagerman@union.edu](mailto:hagerman@union.edu). Chemistry, Union College, Schenectady, New York, United States

Owing to their tunable conductivity and environmental stability, polyaniline nanocomposites have found practical applications as clean energy nanomaterials including supercapacitors, sensors, and solar cells. In order to achieve the desired properties for these nanotechnology applications, morphosynthesis parameters including concentration, reaction time, pH, temperature, and template have been varied to optimize dimensionality. We are currently exploring the use of Laponite™ nanoparticle hydrogels to direct the self-assembly and dimensionality of polyaniline

nanomaterials. One dimensional fibrillar nanorods and two dimensional nanosheets were synthesized using aniline and anilinium hydrochloride monomeric precursors exposed to free standing vanadium(V) exchanged clay hydrogels. Water-dispersible polyaniline nanosheets were grown at the interfacial regions between the aqueous layer and the clay hydrogel. In addition, polyaniline nanofibers became interwoven within the mesoporous spaces of the silicate host matrices creating high surface area nanocomposites. Scanning electron microscopy coupled with energy dispersive spectroscopy and atomic force microscopy were employed to verify syntheses and study nanocomposite surface morphologies. Polyaniline polymerization at clay hydrogel interfaces offers a new route to tune polymer dimensionality and to realize anisotropic self-assembled nanostructures with high potential to improve charge transport and energy storage capabilities.

## **COLL 449**

### **Hydrogenation reactions over metal phosphide catalysts**

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Metal phosphides (e.g. Ni<sub>2</sub>P, MoP, Co<sub>2</sub>P) have attracted interest as the active phase of catalysts with potential for application in a number of catalytic processes. The current study focuses on the development of metal phosphide catalysts for the selective hydrogenation of alkynes (to alkenes) and for the hydrogenation of carbon dioxide (to CO). For the selective hydrogenation studies, the focus is on different crystalline phases of silica-supported nickel phosphide (Ni<sub>3</sub>P, Ni<sub>12</sub>P<sub>5</sub>, Ni<sub>2</sub>P, Ni<sub>5</sub>P<sub>4</sub>) and the synthesis and characterization (XRD, XPS, SEM, chemisorption) of these catalysts will be described. The characterization results will be correlated with the hydrogenation properties of the Ni<sub>x</sub>P<sub>y</sub>/SiO<sub>2</sub> catalysts for the conversion of phenylacetylene. The activity and selectivity show a strong dependence on the composition of the Ni<sub>x</sub>P<sub>y</sub> phase (P/Ni molar ratio). For the CO<sub>2</sub> hydrogenation studies, the preparation and characterization of titania-supported In-Ga phosphides (In<sub>1-x</sub>Ga<sub>x</sub>P) will be described. The photophysical and surface properties of the In-Ga phosphide catalysts will be used to gain insight into their activity and selectivity for the photocatalytic conversion of CO<sub>2</sub>.

## **COLL 450**

### **Polymer thin-film stability studies using spin coating**

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Polymer thin films are ubiquitous in everyday life and central to numerous industrial applications. Stability is often desirable, however, controlled dewetting can also be beneficial. In this research, the stability of poly(vinyl alcohol) (PVOH) thin films spin-

coated on silicon wafer-supported polydimethylsiloxane (PDMS) substrates was examined. PDMS is hydrophobic and a liquid at room temperature, while silicon is hydrophilic and a rigid solid. In the four-layer air/PVOH/PDMS/SiO<sub>2</sub> system, the effective interactions between the PVOH film and the PDMS/SiO<sub>2</sub> substrate as well as the effective mobility of the substrate were tuned by adjusting PDMS layer thickness. PVOH thin films exhibit stable, to metastable, to unstable states as PDMS thickness increases from 0 to 11 nm. In the three regimes, PVOH film thickness shows respective exponents of -1, -1/2, and 0 in the scaling relationship with spin rate, deviating from the -1/2 exponent reported by Meyerhofer. In the presentation, we will also demonstrate that spin coating is not only a facile method for fabricating stable thin films, but also provides a unique means of generating globally ordered dewetted morphologies that are the outcome of spin symmetry and temporally and spatially adjustable drying rates. It provides access to various kinetically trapped morphological states that are critical in the study of thin-film stability.

## **COLL 451**

### **Characterization of electrogenerated hexacyanoferrate thin films**

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Metal hexacyanoferrates (HCFs) have gained increasing interest as materials for advanced battery applications, as they provide enhanced stability due to their open framework structure and potential for reduced cost by use of earth-abundant materials. We produce a variety of electrogenerated HCF thin films by modifying electrodeposited Ni and Ni-based alloys in the presences of hexacyanoferrate. Structural and chemical analysis along with electrochemical testing provides information on how the fabrication methods affect the charge storage and transport properties of the materials. For NiCo- and NiCu-based HCF, the results were compared to Ni-HCF to explore the effects of the addition of alloying metals. For Ni-HCF, atomic force microscopy measurements before and after the HCF electroformation allowed insight into the impacts of the underlying structure on the charge storage. AC measurements of the charge transfer process were compared to other electrochemical techniques to help determine the charge transport kinetics. X-ray spectroscopic measurements of the total amount of Fe in Ni-HCF were correlated with electrochemical measurements to assess the amount of active material present.

## **COLL 452**

### **Nano engineering of rhodanine stabilized metallic nanostructures**

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Rhodanines are an interesting class of compounds, which possess broad spectrum of pharmacological activities. In last decade, this class of compounds have generated huge amount of interest due to their antibacterial, antiviral, antihistaminic and anticorrosion properties. Hybridization of polyrhodanine with inorganic complexes can provides materials with promising and attractive properties for their application in new and diverse technologies.

Last year<sup>a</sup>, our research group discovered that rhodanine could be converted to polyrhodanine in a very selective manner under mild reaction conditions in presence of stoichiometric amount of copper acetate. Surprisingly, we found that depending on the reaction conditions, we were able to engineer the hybrid rhodanine copper polymer to create core shell nanostructures, very desirable yet difficult morphologies to achieve. In this Presentation, we will present the results of our further investigations of the polymerization of various rhodanine structures to polyrhodanines (pRh) in presence of various metal complexes. We will discuss the morphology of the resulting materials and their characterization by various techniques such as NMR, IR, UV-Vis, TEM and SEM. We will also forward the mechanistic proposal as well as our investigations to support the mechanisms involve in formation of various nanostructures.

## **COLL 453**

### **Enzyme-based *in situ* synthesis, stabilization and activity of gold nanoparticles for biological applications**

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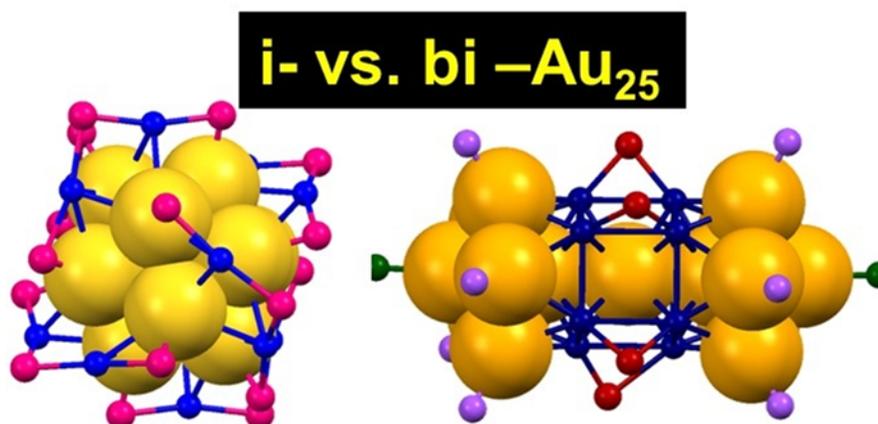
Stabilization and activity of biomolecules such as proteins and nucleic acids is very crucial in applications such as biosensing and drug delivery. In this presentation, the *in-situ* synthesis and stabilization of enzyme-modified gold nanoparticles without the use of activators or organic stabilizers will be discussed. The enzyme acted not only as a reducing agent of the gold salt precursor, but also as a stabilizing agent of the resulting gold nanoparticles. The enzyme/nanoparticle conjugates were coated with poly(ethyleneimine) (PEI), a well-known cationic polymer used for transfection purposes. Further, the activity of the resulting PEI-coated enzyme/nanoparticles conjugates was evaluated. The activity of these nanoparticle conjugates were compared with those prepared from the well-known method of synthesizing gold nanoparticles via citrate reduction followed by stabilization with organic molecules (mercaptoundecanoic acid (MUA)). The residual activity of the enzyme was much longer for the PEI-enzyme/nanoparticle conjugates than for the PEI-enzyme/MUA nanoparticle conjugates. The nanoconjugates were characterized by Dynamic Light Scattering, UV-Vis spectroscopy, IR spectroscopy and Transmission Electron Microscopy (TEM).

## **COLL 454**

## Super atom gold clusters: Optical and electrochemical properties

**Mary Devadas**, [mdevadas@towson.edu](mailto:mdevadas@towson.edu). Department of Chemistry, Towson University, Towson, Maryland, United States

Super atom gold clusters are important from the standpoint of affording directional electron transfer. Our focus is on Au<sub>25</sub> and Au<sub>144</sub> species. In this presentation we compare clusters of Au<sub>25</sub> with the icosahedral and bi-icosahedral crystal structures. Extensive characterization was carried out on the systems to optically and electrochemically characterize the system. These clusters were then subjected to focused ligand exchange/direct synthesis with chromophoric ligands to transform the clusters to possess higher quantum yields. Two-photon cross-section measurements were done to indirectly prove covalent bonding of the chromophore along with fluorescence and electrochemistry. Dye loading was quantified using HNMR. These quantum sized monolayer protected gold clusters can be exploited for applications in catalysis, solar energy harvesting, imaging agents and sensors.



COLL 455

### Computational modeling of light-modulated ligands bound to their neuronal receptor targets

*Alba Nin Hill*<sup>3,4</sup>, *Galyna Maleeva*<sup>5,6</sup>, *Alexandre Gomila-Juaneda*<sup>6</sup>, *Daniel Wutz*<sup>7</sup>, *Karin Rustler*<sup>7</sup>, *Antoni Bautista-Barrufet*<sup>6</sup>, *Xavier Rovira*<sup>6,8</sup>, *Miquel Bosch*<sup>6</sup>, *Petra Scholze*<sup>9</sup>, *Franck Peiretti*<sup>10</sup>, *Carme Rovira*<sup>3,4,11</sup>, *Burkhard König*<sup>7</sup>, *Pau Gorostiza*<sup>6,11</sup>, *Piotr Bregestovski*<sup>5,12</sup>, **Mercedes Alfonso-Prieto**<sup>1,2</sup>, [malfonsoprieto@gmail.com](mailto:malfonsoprieto@gmail.com). (1) INM-9/IAS-5 Computational Biomedicine, Forschungszentrum Juelich, Juelich, North-Rhine-Westfalia, Germany (2) C. and O. Vogt Institute for Brain Research, Heinrich Heine

University Düsseldorf, Düsseldorf, Germany (3) Department of Inorganic and Organic Chemistry, University of Barcelona, Barcelona, Spain (4) Institute of Theoretical and Computational Chemistry, University of Barcelona, Barcelona, Spain (5) Institut de Neurosciences des Systèmes, Aix-Marseille University, Marseille, France (6) Institute for Bioengineering of Catalonia, Barcelona Institute of Science and Technology, Barcelona, Spain (7) Institute of Organic Chemistry, University of Regensburg, Regensburg, Germany (8) University of Vic, Vic, Spain (9) Department of Pathobiology of the Nervous System, Center for Brain Research, Medical University Vienna, Vienna, Austria (10) INSERM 1263, INRA 1260, C2VN, Aix University Marseille, Marseille, France (11) Catalan Institution for Research and Advanced Studies, Barcelona, Spain (12) Open Lab of Motor Neurorehabilitation, Kazan Federal University, Kazan, Russian Federation

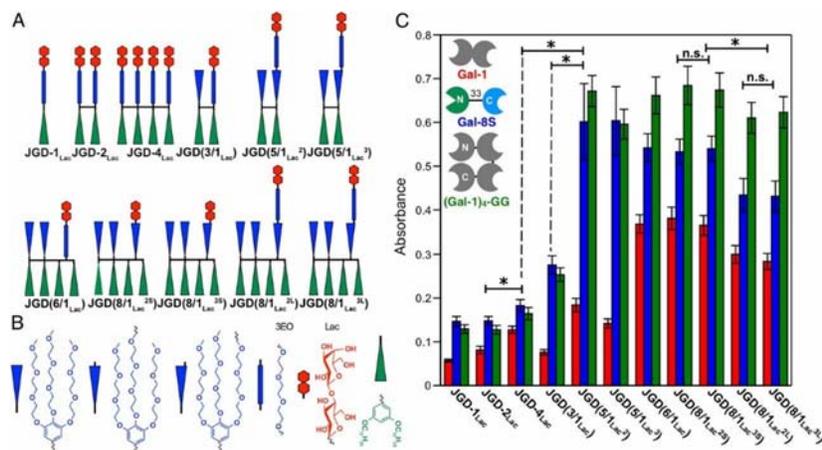
Light-modulated or photoswitchable ligands are molecules that change their conformation (e.g. cis-trans isomerization) with light of specific wavelength. This change modifies binding to their target receptor, thus opening the way for controlled receptor regulation, both in space and time. Recently, we have applied a multidisciplinary approach to design, synthesize and functionally characterize photoswitchable ligands targeting GABA and glycine receptors, the main ion channels involved in inhibitory neurotransmission in the brain. Experimental characterization combines *in vivo* tadpole behavioral assays (to screen photoswitchable molecules potentially affecting inhibitory neurotransmission) and *in vitro* electrophysiology and mutagenesis experiments (to identify the receptors most likely targeted by these ligands and their putative binding site). In parallel, computational modeling has provided a molecular explanation for the light-dependent effect and the receptor selectivity of these photoswitchable ligands. The discovery of improved light-modulated ligands opens the way towards the development of drug-based phototherapies and pharmacological tools to understand inhibitory circuits in intact animals.

## **COLL 456**

### **New functions based on sequence-defined and mixed-ligand strategies**

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Very few synthetic methods and methodologies apply to more than one discipline of science. This lecture will discuss the elaboration of the sequence-defined and mixed-ligand concepts and discuss them with examples that will create new functions in Chemical and Biological Sciences.



## COLL 457

### Ions in solution: From intrinsic to collective properties

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Herein, I will discuss the fundamentals of the theory of solvation and demonstrate both quantitative and qualitative difference based on the choice of the interaction potential. Using the tools of molecular simulation, we utilize both *ab initio* interaction potentials based in quantum mechanics and accepted classical potentials connecting to reduced models for solvation, such as Born theory, providing insight into the validity of piecewise linear models for ion solvation. We discuss the challenges of connecting experiments that elucidate the first solvation shell via extended x-ray absorptions fine structure (EXAFS) to molecular simulation of monovalent cations. Here, we will propose new metrics and methods to correct quantum density functional theory using better estimates of the ion-water binding energy to be obtained by higher level electronic structure methods to obtain accurate single ion free energies. Additional complexities are encountered at the level of ion-pairing where differences between classical and quantum descriptions of molecular interaction suggest dramatically different solution thermodynamics. We explore the connection between the free energy of ion-pairing and collective phenomena such as clustering. Additional emphasis will be on long-range collective properties of electrolyte solutions.

## COLL 458

## **Monolayer protected gold nanoparticles, on the move!**

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The self-assembly of a monolayer of ligands on the surface of noble metal nanoparticles allows the realization of ordered and complex molecular structures, with applications that span from materials science and electronics, to bioimaging, nanomedicine, and even catalysis. In this context, we use extensive MD simulations to analyze the dynamics of differently functionalized monolayer-protected gold nanoparticles. We will introduce NanoModeler, which is the first platform to automate and standardize the construction and parametrization of realistic models for atomistic simulations of gold NPs and gold nanoclusters. We will also show that MD simulations have revealed how functionalized coating thiols can self-organize to form transient pockets in the nanoparticle's monolayer, which can explain the selectivity and sensitivity observed for different organic analytes in NMR chemosensing experiments. Our findings and current efforts advocate for the rational design of tailored coating groups to form specific recognition binding sites on monolayer-protected gold nanoparticles.

### **COLL 459**

#### **Photo- and mechano-sensitive lipids: Properties and applications**

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Photosensitive lipids, with an azobenzene group incorporated into one of the lipid tails, can be switched from the trans to the cis form leading to significant changes in the bilayer properties, facilitating drug release. The two leaflets in diamidophospholipids interdigitate in the gel phase, leading to stiff membranes; this stiffness leads to faceted vesicles which are mechanosensitive, again facilitating drug release. The physical properties of these photo- and mechano-sensitive membranes and their applications will be discussed.

### **COLL 460**

#### **How is electronic energy converted to heat in semiconductor nanocrystals?**

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Non-radiative recombination limits the efficiencies of semiconductor-based optoelectronic devices and photocatalysts by converting useful electronic energy into heat. It has been known for more than half a century that such recombination is facilitated by defects, but theoretical prediction of exactly which defects promote non-radiative recombination remains a challenge. In order to develop a predictive understanding of the role specific defects play in semiconductor photophysics, we are investigating the hypothesis that conical intersections introduced by defects form pathways for recombination. We will present recent developments in the computational identification of such defect-induced conical intersections. Fast and stable graphics processing unit accelerated multireference electronic structure codes enable the identification of these defects, and new nonadiabatic molecular dynamics methods allow us to model dynamics in their vicinities. These tools have enabled us to identify defect-induced conical intersections in silicon nanomaterials, lead-halide perovskites, and colloidal chalcogenide nanomaterials. Through analysis of these intersections, we can understand how the structures of these materials determine their photophysical properties.

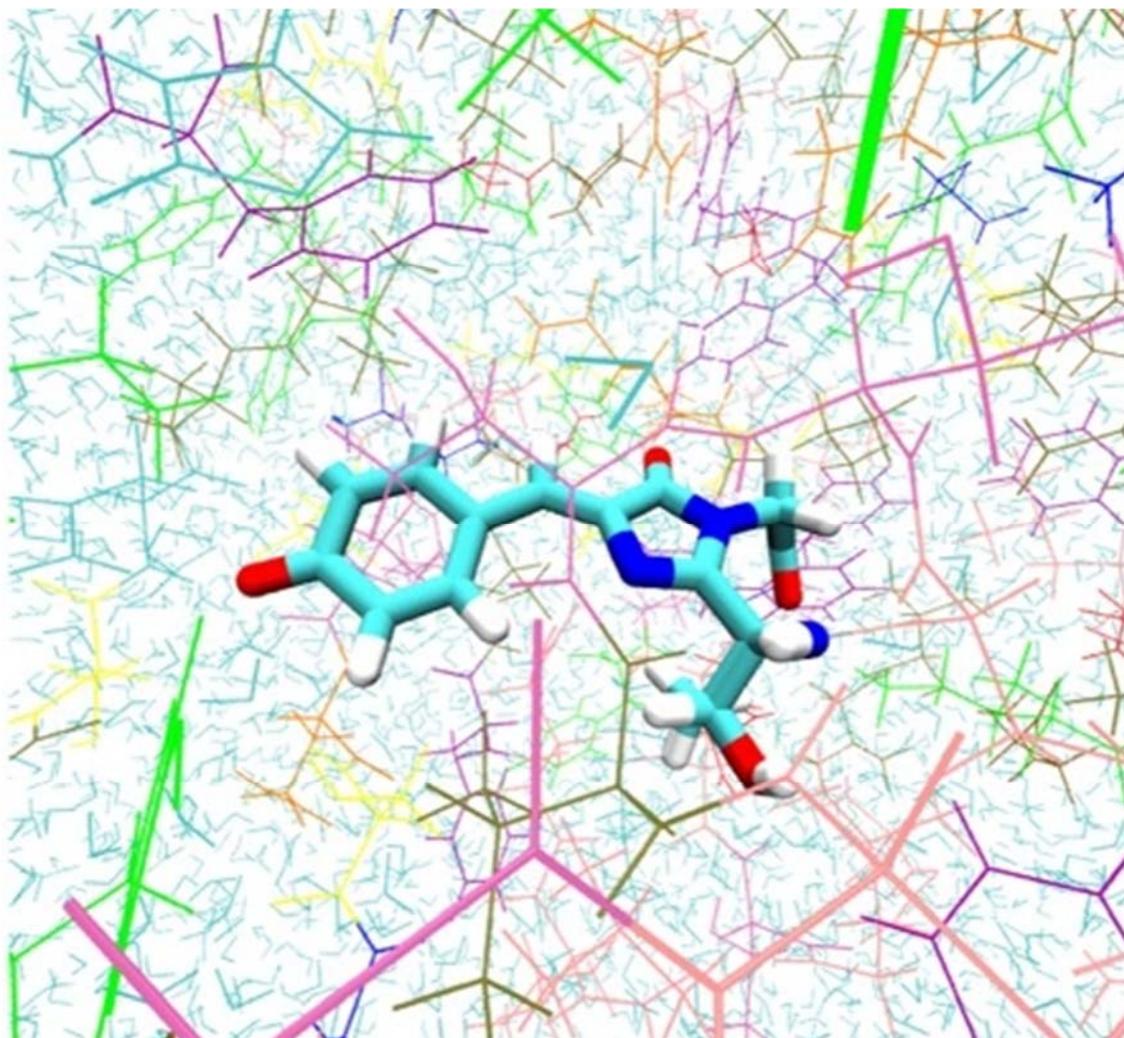
## **COLL 461**

### **Translating the message in spectroscopic probes of conjugated molecular materials**

*Peter J. Rossky*, [peter.rossky@rice.edu](mailto:peter.rossky@rice.edu). Chemistry, Rice University, Houston, Texas, United States

Over recent decades, there have been a steadily increasing number of studies on electronically conjugated materials for use in solar photovoltaic cells, organic transistors, and fluorescent probes. Progress in using semiconducting polymers has been limited by a fundamental lack of knowledge at the nanoscale underlying variations in electro-optical behavior. Hence, in contrast to familiar silicon-based technology, there is a dearth of principles to drive the bottom-up design of material building blocks.

Experiments probe such materials by their response to light, i.e., spectroscopically. The challenge is to interpret the observations in molecular terms. Computational modeling based on the physics of atomistic details and explicit electronic structure is ideally suited to enabling this connection of spectra to structure, since the connection in modeling is unambiguous while the experiment provides a strong constraint on the validity of the model. In this presentation, I will discuss examples of conjugated molecular material systems studied by theoretical, modeling, and experimental approaches that elucidate both atomistic and electronic structure and dynamics in a way inaccessible to either theory or experiment alone. Examples from the area of conjugated polymers and also from biosensors based on GFP will be presented.



**COLL 462**

**Atomistic arsine-silicon surface chemistry studies for atomic-scale semiconductor device fabrication**

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In recent years, atomic-scale device fabrication has been achieved using scanning tunneling microscopy (STM) hydrogen resist lithography. This technique exploits the atomic resolution of the STM to precisely position individual dopant atoms in silicon (Si). Specifically, a hydrogen passivation layer is patterned with the STM tip and used as a

resist to spatially confine the surface chemical reaction of a dopant precursor molecule on the Si(001) surface. Development of this technique has required an atomistic understanding of the precursor molecule chemistry on both the bare and hydrogen adsorbed silicon surfaces. Traditionally this technique has used phosphine ( $\text{PH}_3$ ) as a precursor for doping of phosphorus (P) atoms in silicon. Recently we have expanded the technique to include atomic-scale doping of arsenic (As) atoms, using arsine ( $\text{AsH}_3$ ) as a precursor molecule. Introducing arsenic as a second dopant species has been accomplished by developing an atomistic understanding of the surface chemistry of arsine on the Si(001) surface.

We have performed detailed surface chemistry studies of the  $\text{AsH}_3/\text{Si}(001)$  system using STM, density functional theory, and kinetic Monte Carlo simulations. We show that a number of subtle, but important differences exist in the  $\text{XH}_3/\text{Si}(001)$  systems when changing dopant X from P to As i.e. phosphine to arsine. These differences, primarily resulting from the more rapid rate of dissociation of  $\text{AsH}_3$  and a lower diffusivity of As atoms in Si, have important implications for advanced device fabrication strategies. Also of great technological importance to device fabrication is the evolution of the interface formed between a heavily doped silicon surface and an epitaxial silicon capping layer. We use secondary ion mass spectroscopy and electrical transport measurements to examine properties of this interface, in particular the segregation and electrical activation of the dopants. Finally, we provide a first demonstration of nanoscale device structure patterning in Si using the two unique donor species (P and As) within a single Si plane.

## **COLL 463**

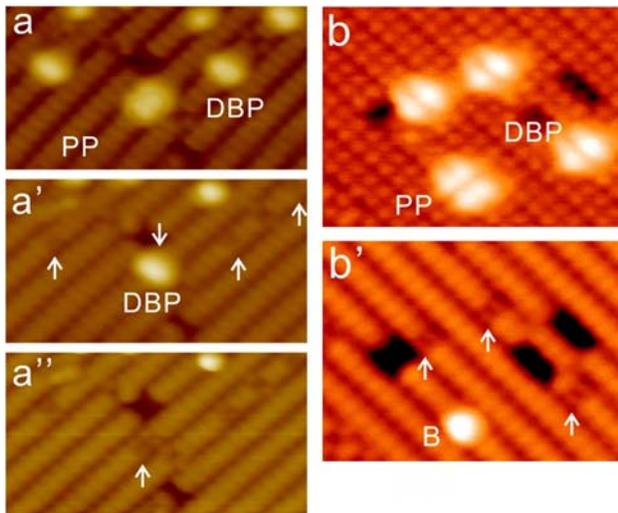
### **Atomically precise control and understanding of each dissociative adsorption event of multiatomic molecules on single, paired, and arrays of reactive sites on the Si(100) surface**

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Isolated, paired, and clustered dangling bonds can be precisely prepared on a Si(100) surface as well-defined chemically-reactive sites for chemisorption of prototypical molecules, such as  $\text{I}_2$ ,  $\text{Cl}_2$ , HCl diatomic and  $\text{H}_2\text{O}$  triatomic molecules. The surrounding dangling bonds around a designed reactant configuration can be passivated by hydrogen-, chlorine-, and iodine-termination. Following exposure to these molecules at room temperature, the adsorbate configurations on these reactive sites are been examined using scanning tunneling microscopy (STM) and DFT calculations.

As an example, on clean Si(100), three types (type-I, type-II, and type-M) of  $\text{I}_2$  adsorption pathways are been identified, consistent with previous findings. However, the results from H- and I-masked Si(100) shows that at least two dangling bonds in the same row and in close proximity ( $< 4 \text{ \AA}$ ) are needed to trigger chemisorption and that dissociative adsorption is the dominant mechanism. Contrary to its major role on clean Si(100), the type-II adsorption is not observed when the two needed dangling bonds are

surrounded by H-adatoms. For HCl adsorption, we have found that adsorption of either H or Cl is possible on an isolated dangling bond, which is forbidden from simple energetic calculation. For H<sub>2</sub>O on Cl-terminated surface, H-Si-o-Si-OH configuration are common on a paired dangling bonds. These findings indicate that a seemingly simple chemisorption reaction on reactive sites involves not only the sites themselves but also the relevant surrounding bonds and adatoms.



STM images before (a, b) and after (a', b') about 0.24 L I<sub>2</sub> exposure to DBPs. (a'') was taken after an additional 0.24 L I<sub>2</sub> dose on the surface of (a'). PP indicates two adjacent DBPs. An arrow points to a new mono-iodide species after I<sub>2</sub> adsorption on a DBP.

## COLL 464

### Halogen-based chemistry for atomic-precision device fabrication

**Robert E. Butera**, [rbutera@lps.umd.edu](mailto:rbutera@lps.umd.edu). Laboratory for Physical Sciences, College Park, Maryland, United States

The ability of the scanning tunneling microscope to fabricate atomic-scale devices in silicon has been well-demonstrated. However, the application of this technique to fabricate devices other than phosphorous-based qubits in silicon has suffered from the lack of demonstrated chemistry compatible with the overall process flow and innovative device designs that harness performance gains achievable at the atomic-level. Halogen-based chemistry provides a relatively unexplored, yet promising, path towards atomic precision advanced manufacturing (APAM) of silicon-based electronic devices that has the potential to expand the application space into additional fields beyond quantum computing. The halogen-silicon system has been well-studied due to the prevalent use of halogen-based plasmas for silicon device processing and, more recently, for its role in the functionalization of silicon surfaces. Compared to hydrogen,

the large size and bond polarity of halogen adsorbates on silicon surfaces results in surface ordering and additional reaction pathways that can be accessed and leveraged to enhance the APAM process. This talk will present results of adsorption, lithographic patterning, etching, surface functionalization, and stability of halogen-based resists in ambient environments leading to the development of a process flow that is not inherently confined to ultra-high vacuum environments and facilitates the development of novel silicon-based electronic devices.

## COLL 465

### **(H,OH)-Si(001)-2x1 as a model surface for the study of ammonia adsorption on hydroxylated surfaces with real-time XPS**

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Water-terminated Si(001)-2×1, which presents well-identified OH patterns, is the ideal surface to study H-bond formation both at experimental and theoretical levels. Not only can H-bonding be tracked by a vibrational spectroscopies, but, *and this is the novelty*, XPS combined to DFT calculations can also provide a detailed information on the bonding configurations, especially their H acceptor or donor nature.

As the chosen probe molecule, ammonia, bounds relatively weakly with the hydroxyls and as (minority) chemisorbed species may be evolved due to intrinsic or extrinsic (beam damage) processes, real-time XPS measurements in the presence of the gas (under  $5 \times 10^{-9}$  mbar at 120 K) were instrumental to understand the adsorption processes and their time and pressure dependence.

We have demonstrated that the hydroxyl O 1s and ammonia N 1s XPS core-levels are highly informative of the formation of H-bonds between surface OHs and the ammonia molecule. The spectra interpretation relies on DFT calculations that provide the adsorption energies of the ammonia molecule under different configurations (periodic slab DFT) and the corresponding core-level binding energies (periodic DFT and cluster quantum chemistry). It is remarkable that, despite the methodological differences, both theoretical approaches lead to practically identical binding energy shifts. In all the geometries with the *lowest* adsorption energies (i.e. the most tightly bound), ammonia makes a double acceptor-donor bond with two surface hydroxyls. Similar bonding geometries were replicated using silicon clusters DFT calculations. When the N 1s experimental binding energy measured at 120 K is compared to the (periodic and cluster DFT) binding energy calculations, it only matches with the double (acceptor/donor) H-bond in striped and checkerboard patterns. Purely dative geometries are not observed in the N 1s spectra. Finally, donor-donor geometries are not considered as they cannot be present on the surface at 120 K due to their far too high calculated adsorption energy (they are the less tightly bound).

Until now, the (large) effects of H-bonding on oxygen and nitrogen core-level binding

energies have been insufficiently addressed in the XPS literature, probably because of the lack of theoretical support. We hope that the present work will stimulate further XPS studies, in contexts where H-bonding is of primary importance, from water/solid interfaces to supramolecular chemistry.

## **COLL 466**

### **Surface chemistries for atomic precision advanced manufacturing**

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The massively increasing cost and technical challenges of further scaling down silicon devices below 10 nm has led to the search for alternative materials and processes. This has created an opportunity for atomic precision advanced manufacturing (APAM), which combines scanning probe techniques and surface chemistries to explore and realize atomic-scale devices with enhanced performance and new functionality. Here, I overview current, state-of-the-art APAM technology and discuss key challenges moving forward that can be addressed by new silicon surface processes and chemistries. In particular, key opportunities exist in developing APAM from a non-scalable, ultra-high vacuum-based learning platform limited to a single resist and dopant combination towards a more flexible platform encompassing scalable lithographies and doping chemistries.

## **COLL 467**

### **From single molecule to molecular devices: Silicon surface as a study platform**

**damien riedel**, [damien.riedel@u-psud.fr](mailto:damien.riedel@u-psud.fr). INP, CNRS, Orsay, France

One of the most challenging Graal in nanosciences resides in our ability to design, control, and operate functionalized devices at the nanoscale. While various techniques are used to reach this goal, several drawbacks still remain difficult to tackle. In this quest, the silicon surface remains a tremendous versatile playground to meet this challenge. During this talk, after a quick overview of the actual state-of-the-art, I will firstly present some recent finding that allow to perform and run a 2D device made of single atom quantum dots. This atomic structure offers the possibility to be reversibly switched to an ON and OFF state, mimicking the well-known transistor function[1]. I will also address our abilities to control the manipulation and formation of molecular dyads

to study charge transfer processes at the nanoscale. We have shown recently that non-bonding FeTPP homodimers adsorbed on a semi-insulating CaF<sub>2</sub>/Si(100) layer can be used to investigate charge transfer at the nanoscale [2]. In particular, we have demonstrated that the dynamics in relation to the excitation position can rule the charge transfer efficiency that mainly follows anti-Kasha rule.

## **COLL 468**

### **Hydrogenic states in silicon and black phosphorus**

**Steven R. Schofield**, *s.schofield@ucl.ac.uk*. London Centre for Nanotechnology, University College London, London, United Kingdom

The ability to control hydrogenic states in semiconductors and two-dimensional materials opens a pathway to novel atomic-scale electronic devices for applications including quantum information processing. The prototypical hydrogenic semiconductor defect is the substitutional group-V donor in silicon. Our group has recently developed the capability to position arsenic donors in silicon with nanometre accuracy [1], which is the first such development since the ability to position phosphorus atoms in silicon with nanometre accuracy was established in the early 2000s [2]. There is currently strong interest in developing similar capabilities to position other impurity species in silicon. Bismuth is the heaviest of the group-V atoms, and also forms the deepest of the substitutional single donor species in silicon, with a binding energy of > 70 meV. For this reason, bismuth is particularly attractive as an impurity for atomic-scale quantum electronic devices in silicon. In this talk, I will present recent work exploring pathways to the controlled positioning of bismuth in silicon. I will also discuss the properties of hydrogenic states in semiconductors, and to what extent we are able to resolve the spatial and electronic structures of these defects with scanning tunnelling microscopy and spectroscopy. The latter part will include a discussion of our recent work imaging and identifying hydrogenic impurities in the two-dimensional Van der Waals material, black phosphorus.

## **COLL 469**

### **Colloidal plasmonic metal nanoplates and nanocups**

**Jianfang Wang**, *jfwang@phy.cuhk.edu.hk*. Department of Physics, The Chinese University of Hong Kong, Shatin, New Territory, Hong Kong

I will describe two new types of colloidal plasmonic metal nanoparticles, i.e., gold nanoplates and nanocups, which have been synthesized recently in our group. Owing to their crystallinity and particular geometry, gold nanoplates are very attractive for assembly with other nanoscale components. For example, gold nanoplates are preferred for assembly with two-dimensional semiconductor nanosheets to study plasmon-exciton interactions, plasmon-enhanced spectroscopy in two-dimensional nanomaterials, and plasmon-enhanced optoelectronic devices based on two-

dimensional nanomaterials. We have developed methods for the synthesis of hexagonal and circular gold nanoplates with plasmon wavelengths controllable in the visible and near-infrared regions. Hexagonal gold nanoplates exhibit large electric field enhancement at the sharp corners and straight edges. They exhibit Fano resonance with deposited on high-dielectric-constant substrates. When gold nanospheres are assembled with hexagonal gold nanoplates at the corners and edges, strong Fano resonance with its dip reaching the background is produced. In addition, we have assembled gold nanospheres on the top of gold nanoplates to form molecule-bridged plasmonic junctions. The junctions bridged with conductive and non-conductive molecules exhibit distinct plasmonic responses. The plasmonic response of the junctions gapped with polyaniline can be reversibly switched. Moreover, we have developed methods for the synthesis of colloidal gold nanocups that exhibit strong magnetic plasmon resonance. Both of the overall and opening sizes of the nanocups can be adjusted. The nanocups with small opening can hold desired species inside, such as medicinal drugs. The gold nanocups also exhibit interesting depth-dependent second-harmonic generation responses. The most-efficient second-harmonic generation of the gold nanocups is experimentally observed when the normalized depth is adjusted to  $\sim 0.78$ . The maximal second-harmonic generation can be attributed to the joint action of the optimized magnetic plasmon resonance and the “lightning-rod effect” of the gold nanocups.

## **COLL 470**

### **Nanoparticle carriers of Notch-1 antibodies and ABT-737 inhibit triple-negative breast cancer tumor growth *in vivo* to extend survival**

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Novel therapies are needed to combat triple-negative breast cancer (TNBC), as this aggressive disease is unsusceptible to current targeted or hormonal therapies. To meet this need, we have developed poly(lactic co-glycolic acid) (PLGA) nanoparticles (NPs) that are loaded with the Bcl-2 inhibitor ABT-737 (ABT) and functionalized with Notch-1 (N1) antibodies. Both Bcl-2 anti-apoptotic proteins and N1 receptors are overexpressed by TNBC cells and contribute to disease progression. We hypothesized that the N1 antibodies on these NPs could enable both TNBC cell-specific binding and suppress Notch signaling by locking the N1 receptors in a ligand unresponsive state. This would potentiate ABT, as Notch inhibition upregulates Noxa, a protein that counteracts ABT resistance. We present *in vitro* and *in vivo* data that show N1-ABT-NPs can induce TNBC cell death and reduce tumor burden in mice.

PLGA NPs loaded with ABT or DiD fluorophores were synthesized by single emulsion solvent evaporation, then coated with N1 or IgG antibodies by EDC chemistry. Flow cytometry revealed that N1-DiD-NPs displayed 3-fold higher uptake by MDA-MB-231 TNBC cells than IgG-DiD-NPs. N1-DiD-NPs also exhibited no appreciable binding to non-cancerous MCF-10A cells that lack N1 overexpression. An MTT assay showed the

IC<sub>50</sub> of N1-ABT-NPs was 1.6 μM, substantially lower than that of IgG-ABT-NPs (IC<sub>50</sub>= 3.2 μM) or freely delivered ABT and N1 antibodies (IC<sub>50</sub>=2.6 μM). qRT-PCR demonstrated IgG-ABT-NPs did not alter the expression of Noxa or Hes5 (an indicator of Notch activity), but they did suppress Bcl-2, indicating successful ABT release. By comparison, N1-ABT-NPs reduced Bcl-2 mRNA by 70%, suppressed Hes5 by 65%, and upregulated Noxa 2.6-fold.

To test the NPs *in vivo*, MDA-MB-231 cells were injected in the flank of female nude mice. When tumor diameter reached 5 mm, saline, IgG-ABT-NPs, or N1-ABT-NPs at 10 mg ABT/kg were intravenously injected 1x/week for a tumor growth inhibition study or 2x/week for a survival study. When given 1x/week, N1-ABT-NPs reduced tumor volume by 20% within 1 week, and this reduction was maintained through 3 weeks. When given 2x/week, N1-ABT-NPs improved animal survival to 88.9%, versus 46.9% for IgG-ABT-NPs and 44.4% for saline.

In conclusion, N1-ABT-NPs can effectively regulate both Bcl-2 and Notch signaling to induce TNBC cell death *in vitro*. These NPs can also reduce tumor volume *in vivo* to extend animal survival, indicating they are a potent treatment for TNBC.

## **COLL 471**

### **Biodegradation of bi-labelled polymer-coated rare-earth nanoparticles in adherent cell cultures**

**Neus Feliu**<sup>1</sup>, [neus.feliu@physnet.uni-hamburg.de](mailto:neus.feliu@physnet.uni-hamburg.de), **Wolfgang J. Parak**<sup>1,2</sup>. (1) CHyN, Universitaet Hamburg, Hamburg, Germany (2) CIC Biomagune, San Sebastian, Spain

The fate of polymer-coated Eu- and Bi-doped GdVO<sub>4</sub> nanoparticles of cubic shape upon cellular internalization was investigated. After having been endocytosed by cells, the cubic Eu- and Bi-doped GdVO<sub>4</sub> nanoparticle cores partly dissolved and were reshaped to rounded structures, which in control experiments could be ascribed to the acidic conditions present in endosomes/lysosomes. With ongoing time, there was a significant reduction in the amount of internalized nanoparticles *per* cell due to proliferation. This was of higher extent than nanoparticle exocytosis. Data of the study are compatible with the scenario that endosomal/lysosomal enzymes may partly digest the polymer shell around the nanoparticle cores, with enhanced exocytosis of the polymer fragments as compared to the nanoparticle cores.

## **COLL 472**

### **Supramolecular self-assembly and bioconjugation of gold nanoparticles**

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In this communication, recent results regarding the development of biomolecular conjugation of colloidal gold nanoparticles (AuNPs) with different functionalities and morphologies will be presented. We will show herein that the strategy of bioconjugation can be controlled by using supramolecular interactions in solution, such as hydrogen bonding,<sup>1</sup> hydrophobic interactions,<sup>2</sup> and complex coordination.<sup>3</sup> The use of thiol-functionalized supramolecules to stabilize the surface of AuNPs can induce the spontaneous formation of supramolecular complexes or polymers,<sup>4</sup> which provides large and homogenous close packing of AuNPs, both in solution and interfaces. Once formed, the self-assembled superstructures have shown excellent levels of reversibility. The pH-, temperature- and pressure-controlled self-assembly may offer excellent functional nanomaterials in sensing,<sup>4</sup> photothermal therapy<sup>1</sup> and molecular and nanoparticle delivery.<sup>2,3</sup>

## **COLL 473**

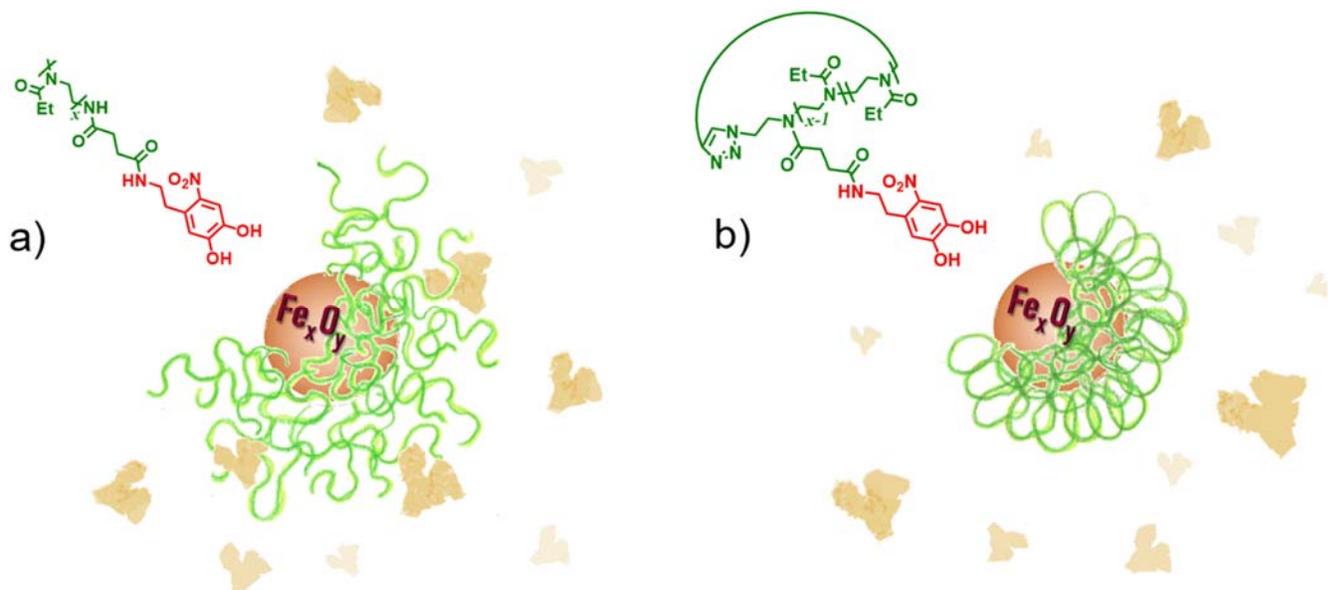
### **Polymer brush topology and core size control formation of protein corona and functionalized nanoparticle avidity**

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Monodisperse iron oxide nanoparticles can be grafted with very dense and stable polymer brushes using nitrodopamine anchor chemistry. This allows us to explore the effect of nanoparticle size, curvature, polymer shell chemistry, and polymer shell topology on their interaction with proteins. We have applied this to explore the limits of polymer brushes of poly(ethylene glycol), poly(2-alkyl-oxazoline), and poly(*N*-isopropyl acrylamide) to avoid adsorption of a protein corona on nanoparticles in the size range of 5-20 nm.

We use isothermal titration calorimetry and supporting techniques to demonstrate the weak association of blood serum proteins on polymer-grafted nanoparticles that are assumed to have stealth properties. We also report the first results on the complete suppression of protein adsorption on polymer-grafted nanoparticles using such ultrasensitive measurements of protein interactions. The protein adsorption strongly depends on polymer brush grafting density also for very high grafting densities but is less dependent on polymer chain length due to the high curvature of small nanoparticles. Full suppression of protein adsorption is only achieved for dense grafting of polymers with a cyclic topology that yields the highest polymer segment density close to the core.

Finally, we demonstrate that the binding avidity of biofunctionalized nanoparticles is not only determined by the binding affinity of the functional ligand. For accurate prediction of the nanoparticle avidity, the contribution of the van der Waals potential of the polymer brush-stabilized nanoparticle must be considered. The van der Waal potential of nanoparticles is also strongly dependent on the size and polarizability of the core.



(a) Linear PEOXA-Fe<sub>x</sub>O<sub>y</sub> and (b) cyclic PEOXA-Fe<sub>x</sub>O<sub>y</sub> NPs show different interactions with serum proteins. While cyclic PEOXA shells completely suppress protein adsorption, interactions of proteins with linear brush shells cannot be prevented entirely.

## COLL 474

### Bioconjugation of nanoparticles with controlled ligand density

*Neus Feliu*<sup>1</sup>, **Wolfgang J. Parak**<sup>1,2</sup>, [wolfgang.parak@uni-hamburg.de](mailto:wolfgang.parak@uni-hamburg.de). (1) CHyN, Universitaet Hamburg, Hamburg, Germany (2) CIC Biomagune, San Sebastian, Spain

Nanoparticles modified with ligands for specific targeting towards receptors expressed on the surface of target cells are discussed in literature towards improved delivery strategies. In such concepts the ligand density on the surface of the nanoparticles plays an important role. How many ligand *per* nanoparticle are best for the most efficient delivery. Importantly, this number may be different for *in vitro* and *in vivo* scenarios. In the review first virus as "biological" nanoparticles are analyzed towards their ligand density, which is then compared to the ligand density of engineered nanoparticles. Then, experiments are reviewed in which *in vitro* and *in vivo* nanoparticle delivery has been analyzed in terms of ligand density. These results help to understand which ligand densities should be attempted for better targeting. Finally synthetic methods for controlling the ligand density of nanoparticles are described.

## COLL 475

### Exploring dynamic confinement based on molecular recognition for sensing and biomedicine

**Oren A. Scherman**, *oas23@cam.ac.uk*. Melville Laboratory for Polymer Synthesis, Department of Chemistry, University of Cambridge, Cambridge, Cambridgeshire, United Kingdom

Molecular recognition based on host-guest interactions is a powerful tool to create well-defined nanostructured architectures for controlled spatial confinement of chemical species. We have shown that cucurbit[*n*]uril (CB[*n*]; *n*=5-8) macrocycles are promising host systems to develop supramolecular building blocks, as well as controlled polymer architectures for integration into complex dynamic networks and assembly at hybrid inorganic-organic interfaces. These robust ~1 nm<sup>3</sup> host molecules form dynamic, yet stable complexes with guest moieties in aqueous media exhibiting a wide range of binding affinities (10<sup>3</sup>-10<sup>15</sup> M<sup>-1</sup>). We have gained fundamental understanding into how to exploit these macrocycles to bring together a variety of chemical entities through host-guest complexation, including small molecules in solution and at polymer-polymer, polymer-colloid or colloid-colloid interfaces. Moreover, our expertise extends to the use of CB[*n*] as a “molecular glue” to direct and control the self-assembly of metallic and semiconducting nanoparticles (NPs).

Unlike other laborious and time-consuming approaches such as surface modification with classical organic ligands, CB[*n*]s are able to rapidly (< 3s) and uniformly assemble NPs in solution, acting as robust molecular spacers for the controlled assembly *via* electrostatic interactions. We have extensively explored this assembly strategy to construct uniform NP assemblies, which afford plasmonic “hot-spots” of highly-controlled geometry, ideal for Surface Enhanced Raman Spectroscopy (SERS) applications. We have shown great potential of the resultant hybrid SERS-substrates for the detection of extracted chemical entities and precisely placed within the hot-spots. This approach was further developed towards quantitative multiplexing for the detection of neurotransmitters in biological fluids. We further explore CB[*n*]-based molecular recognition to: (i) spatially confine biologically active entities at the interface of metal NPs as well as (ii) functionalisation of selected antibodies to yield macrocyclic-antibody conjugates. This has led to the development of novel NP based vehicles for targeted drug delivery as well to modulate the lifetime of endogenous insulin. These approaches open a plethora of new possibilities for construction of hybrid systems for sensing applications and in nanotheranostics as well as the development of new medicines and therapies.

## **COLL 476**

### **Site-specific nanobody conjugation for targeted drug delivery to protumoral tumor-associated macrophages**

*Maximilian Scherger*<sup>1</sup>, *Evangelia Bolli*<sup>2</sup>, *Jo A. Van Ginderachter*<sup>2</sup>, **Lutz Nuhn**<sup>1</sup>, *lutz.nuhn@mpip-mainz.mpg.de*. (1) Max Planck Institute for Polymer Research, Mainz, Germany (2) Lab of Cellular and Molecular Immunology, Vrije Universiteit Brussels, Brussels, Belgium

Nanobodies are one of the smallest available single chain antigen binding fragments derived from camelid heavy chain-only antibodies. With a molecular weight of about 15kDA they are 10 times smaller than conventional antibodies. They can be produced recombinantly and genetically engineered to provide chemical functionalities for site-specific protein modification. In this study, nanobodies were used to target the macrophage mannose receptor (MMR, CD206) overexpressed on tumor-associated macrophages (TAMs). Those type of immune cells govern chronic cancer-associated inflammations and establish immunosuppressive tumor microenvironment. Strategies to repolarize TAMs and trigger an antitumoral activity can be followed by using the targeting potential of anti-MMR/CD206 specific nanobodies engineered with a C-terminal cysteine. They can be site-specifically modified via maleimide chemistry under reducing conditions without interfering with their internal disulfides. Thus, one single fluorescent dye can be coupled to the nanobody, for instance, to monitor the recruitment of TAMs into immunosuppressive cancers. Additionally, immune modulating small molecules can be ligated to the nanobodies to stimulate the immune system of the tumor microenvironment after systemic injection. Alternatively, nanobodies can further be attached to the surface of nanogels loaded with multiple immune modulating molecules in order to trigger TAM repolarization after peritumoral injection. In summary, we believe that our nanobody approach may pave the road for targeted modulation of pro-tumoral TAMs during cancer immunotherapy.

## **COLL 477**

### **Dipole-modulated downconversion colloidal nanoparticles as label-free biological sensors**

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Ultrasensitive detection of proteins and biomolecules has been previously achieved by optically active colloidal nanoparticles (NPs) using the principles of Forster resonance energy transfer (FRET). However, the inherent need for labeling the target analyte in these assays hinders their applicability in point-of-use (POU) diagnostics. To address the challenges of current FRET-based sensors, we have developed a  $\text{YVO}_4:\text{Eu}^{3+}|\text{YVO}_4:\text{Bi}^{3+}$  core-shell (CS) nanoarchitecture that exhibits adaptive downconversion (DC) luminescence upon modification with polarized surface ligands. It was demonstrated that the luminescent signal of the CSNPs could be systematically decreased or increased based on the direction and magnitude of the dipole moment. In this work, a label-free NP-based sensor was developed that utilizes DC luminescence and surface electric dipoles as a novel approach for the detection of avidin. The surface of the CSNPs was functionalized with biotin using carboxylic acid chemistry instead of capping ligands or crosslinking agents, which requires complex reaction chemistries. Fourier-transform infrared spectroscopy (FTIR) and zeta-potential measurements verified the successful conjugation of biotin to the NP surface. In order to develop the avidin binding assay, the surface coverage of the biotin decorated NPs was measured to be  $0.35 \mu\text{mol}.\text{mg}^{-1}$  based on the thermogravimetric analysis (TGA) performed on the

biotinylated CSNPs. The long-lived luminescence of  $\text{Eu}^{3+}$ -doped biotinylated NPs was effectively quenched in the presence of avidin in a concentration-dependent manner. The NP sensor exhibited high avidin selectivity and sensitivity with a limit of detection (LOD) of 7.8 nM, a signal-to-noise ratio (SNR) of 25.1, and a wide dynamic range (1 nM-10  $\mu\text{M}$ ) in deionized (DI) water. The application of the assay in a complex biological matrix of growth medium supplemented with 10% serum was then verified with good avidin sensitivity (LOD of 34.7 nM and SNR of 11.7). The robustness of the assay was evaluated by comparing the intensity values of known avidin concentration and the values predicted by the calibration curve with a variance of 9% in water and 5% in medium with serum. Overall, this inexpensive and label-free NP sensor has the potential to be coupled with different surface ligands for the detection of small molecules, enzymes, antibodies, and aptamers with high sensitivity and reliability in clinical and POC diagnosis settings.

## **COLL 478**

### **Self-assembly of genetically encoded stimulus responsive polymers into nanoparticles**

**Ashutosh Chilkoti**, *chilkoti@duke.edu*. Duke Univ, Durham, North Carolina, United States

This talk will cover work in my laboratory over the past decade on the molecular design of genetically encoded stimulus responsive elastin-like polypeptides (ELPs) that self-assemble into micelles with diverse and tunable morphology. Below a characteristic inverse transition temperature ( $T_t$ ), ELPs –peptide polymers composed of VPGXG repeats– are soluble in aqueous solution, but when the temperature is raised above their  $T_t$ , they desolvate and undergo phase separation. We have exploited ELPs to create stimulus responsive micelles via three approaches. In the first approach, we have designed diblock ELPs with two ELP blocks with different hydrophobicity's that self-assemble into spherical micelles with an increase in temperature above the critical micellization temperature of the diblock polymer. I will introduce the concept of “blockiness” in ELP diblock block copolymer design and demonstrate how it can be used to tune the morphology of self-assembled nanostructures. In a second approach, we have encoded multiple copies of hydrophobic residues with the sequence  $(\text{VPGXG})_n(\text{XGG})_8$  where X = W, Y, or F and show that these highly asymmetric amphiphiles spontaneously self-assemble into rod-like micelles depending on the specific hydrophobic residue. Finally, we have created a diblock copolymer of an ELP fused to a resilin-like polypeptide (RLP) that exhibits upper critical solution temperature transition (UCST) phase behavior. By systematically varying the weight fraction of the hydrophilic ELP block and molecular weight of the ELP-RLP diblock polypeptide, we have designed micelles of different morphologies ranging from spherical to worm-like that present a human wild-type 10<sup>th</sup> fibronectin domain (Fn3) on the corona of the micelles. The avidity of these Fn3 decorated micelles for the  $\alpha_v\beta_3$  integrin is a strong function of shape. The binding avidity of the most elongated worm-like micelle for the  $\alpha_v\beta_3$  integrin is 1000-fold higher than a ELP-RLP diblock that

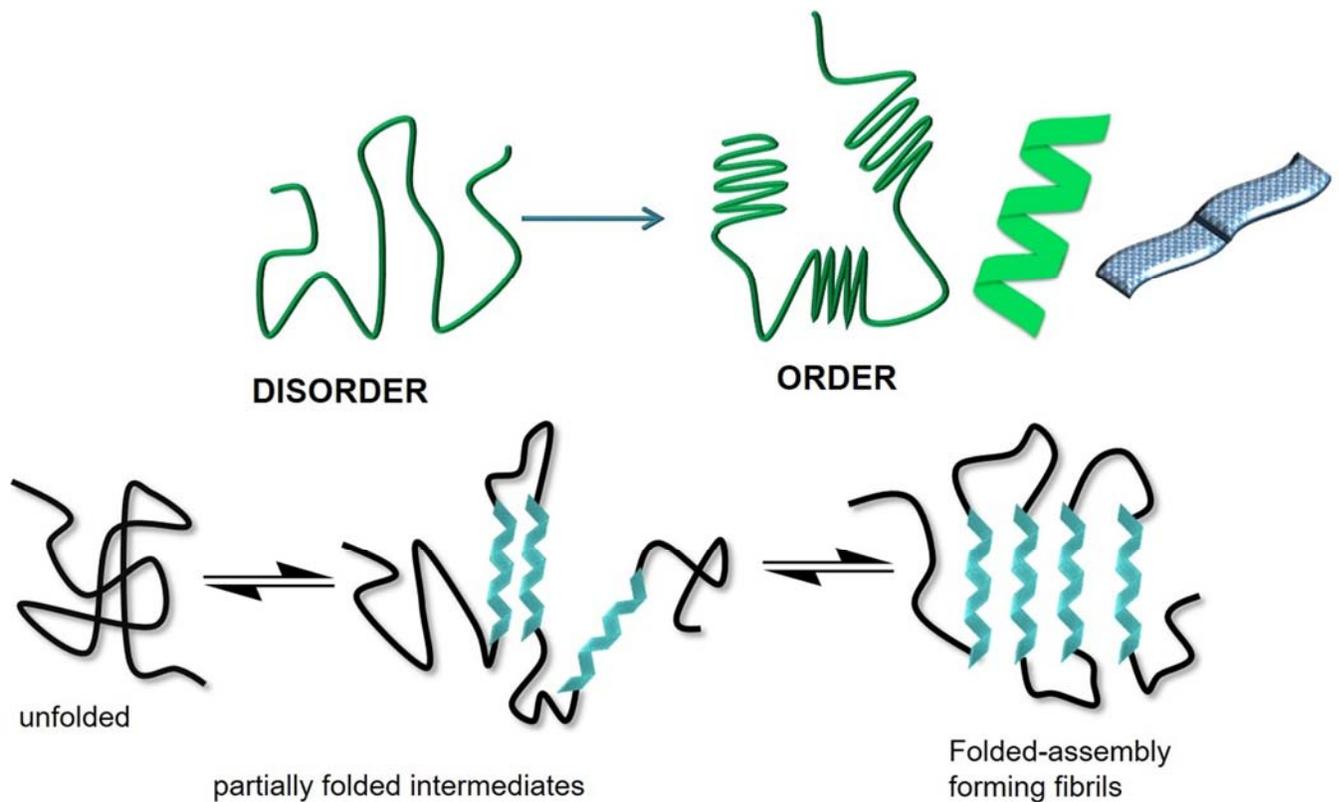
does not self-assemble into micelles and hence only presents a single copy of the Fn3 domain. These results provide perhaps the clearest demonstration yet of how nanoparticle size, shape, binding affinity and cell uptake can be programmed at the sequence level of a polypeptide.

## **COLL 479**

### **Modulating fibrillar assembly processes of proteins and peptides by polymers and folding elements**

**Wolfgang H. Binder**<sup>1</sup>, [wolfgang.binder@chemie.uni-halle.de](mailto:wolfgang.binder@chemie.uni-halle.de), **Zhanna Evgrafova**<sup>1</sup>, **Merve Canalp**<sup>1</sup>, **Bruno Voigt**<sup>1</sup>, **Jochen Balbach**<sup>2</sup>. (1) Faculty of Natural Sciences II, Martin-Luther University Halle-Wittenberg, Halle, Germany (2) University of Halle, Halle, Germany

Fibrillar aggregation and/or misfolding of peptides and proteins has received increasing attention due to the involvement of these molecules in a variety of neurodegenerative diseases, such as Alzheimer's, Parkinson's and prion diseases. The underlying assembly pathways are often nucleation driven, leading to complex fibrous assemblies. We have taken the challenge to interfere with such fibrillation pathways either via synthetic model systems, or by designing artificial hybrid-molecules, composed of amyloid- and polymer/oligomer segments. We here discuss both approaches in terms of synthetic analogues, steric shielding, protein assembly, as well as conformational analysis. Starting from model-polymer systems, containing artificial folding elements, prepared by RAFT-/ROP/ADMET-polymerization, polymers or oligomers are attached to specific positions of assembling proteins, such as amyloid-Aβ-40 and parathyroid-hormone, PTH. These hybrid-systems, also composed of temperature-sensitive polymers and assembling proteins allow to understand the proteins conformation, subsequently modulating its assembly, as shown for parathyroid-hormone PTH and amyloid-Aβ-40. Another approach uses artificial beta-turns, embedded into amyloid-Aβ-40 peptides. It is shown that both, the chemical nature as well as the positioning of artificial beta-turn mimetics strongly influences the subsequent fibrillation-behavior, often leading to the beta-crosssheet as the thermodynamically most favorable conformation.



## COLL 480

### Self-assembly of biomimetic polypeptide and protein based copolymers: From conformational control to functional biomaterials

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En route for highly functional biomaterials and nanodevices, amphiphilic block copolymer structures are gaining in complexity and precision in their macromolecular structure. In addition to their intrinsic self-assembly properties, they may include stimuli-responsiveness possibly in addition to relevant biological functions. By combining the self-assembly properties of block copolymers together with the richness of function-bearing peptides, polypeptide and proteins, we aim at creating functional biomaterials. We were interested in designing copolymers able to self-assemble into well-defined micelles and vesicles that can advantageously be loaded with drugs and present a surface with multivalent presentation of bioactive building blocks that were shown to target specific cell receptors. We will especially focus on how the conformation and

responsiveness of polypeptide-based materials can allow deep control in self-assembly processes.

## **COLL 481**

### **Amphiphilic block copolymers to tailor the biology-materials interface**

*Amanda Leonardi*<sup>1</sup>, **Christopher K. Ober**<sup>1</sup>, [cko3@cornell.edu](mailto:cko3@cornell.edu), *Hellen Papananou*<sup>2</sup>, *Rachel A. Segalman*<sup>2</sup>. (1) Cornell Univ, Ithaca, New York, United States (2) Chemical Engineering, UCSB, Santa Barbara, California, United States

The ability to rapidly transform a substrate from a hard, structural material to a soft, hydrogel structure over the course of a few tens of nanometers makes polymers elegant materials for tailoring the biology-materials interface. The use of amphiphilic block copolymers to form surface brushes provides most of the benefits of “grown from” polymer brushes with the ability to coat large area surfaces. Surfaces used for anti-fouling coatings are an example of brush like, large area application. Prior studies have shown that amphiphilic brush surfaces (with both polar and non-polar groups) provide a broad range of anti-fouling properties. Here we describe new approaches to surface active block copolymers and discuss strategies to tune surface properties and surface placement while introducing active units that interfere with the biochemistry of fouling. Polymers are made by living anionic polymerization and modified using “click” chemistry.

## **COLL 482**

### **Assembly of polymers with nanocellulose: Polyelectrolyte complexes to CNC surface modification**

*Nasreen Khan*, *Manali Banerjee*, **Blair Brettmann**, [blair.brettmann@mse.gatech.edu](mailto:blair.brettmann@mse.gatech.edu). Georgia Tech, Atlanta, Georgia, United States

Cellulose nanomaterials have a high surface area covered with hydroxyl groups, which makes them attractive for tailored molecular interactions, such as hydrogen bonding and electrostatic, as well as for further chemical modification. We specifically examine how the charged cellulose nanomaterials interact with polymers to lead to assembled structures, such as gels and dense aggregated phases, working to improve the use of this sustainable material for a variety of industries. We have studied oppositely charged polyelectrolyte systems including anionic poly(acrylic acid) (PAA)/ cationic poly(allylamine) (PAH) for the regimes where they form precipitate, coacervate, or soluble phase in the presence of negatively charged cellulose nanofibrils (CNFs). The timescale of assembly of coacervates and precipitates with cellulose depends on the order of addition of the polycation and polyanion and on the nature of the polyelectrolytes. To better understand the molecular mechanisms behind this, we have also performed simulations on the interactions of the complexes with CNFs. Through this work, we aim to control assembly of CNFs in a paper suspension in order to improve sustainability in

the paper-making process, while more broadly providing important perspective to coacervate assembly with particles. In related work, we modify the surface of CNCs to design gels in organic solvents, examining how the extent of surface modification and gel strength depend on the CNC source and purification methods, with the aim to develop robust, consistent and homogeneous CNC organogels for use in pharmaceutical applications.

## **COLL 483**

### **Density control in receptor-functionalized surfaces**

*Jurriaan Huskens, j.huskens@utwente.nl, Jacopo Movilli, Daniele Di Iorio.* University of Twente, Enschede, Netherlands

Control over the probe density is important for optimal performance of biosensing devices. The probe density not only provides possible binding sites for the analyte, but also affects the accessibility of the analyte toward the probe surface by the occurrence of steric and electrostatic effects. In particular, in DNA sensing, the density of probes, which usually consist of complementary single strand DNA (ssDNA), is affected by electrostatic repulsion leading to decreased hybridization efficiency at increased probe densities.

The type of immobilization technique affects the density and distribution of the probes on a sensing surface. Many methods aim to control the probe density at the surface modification step, requiring characterization of the probe density and the hybridization efficiency after sample preparation using difficult surface-analytical techniques.

Here we present two methods that allow density control in a preceding synthetic or mixing step, upon which analysis is conveniently achieved using solution-analytical techniques and which is followed by a straightforward surface immobilization step of a single compound or assembly that provides a reproducible density upon adsorption.

As a first example, the formation of DNA biorecognition surfaces prepared by the deposition of modified poly(L-lysine) polymers with various ratios of OEG and maleimide (Mal) moieties (PLL-OEG-Mal) on surfaces, so that the probe density control is achieved during a preceding and simple synthetic step, where the degree of functionalization is readily analyzed and quantified by <sup>1</sup>H NMR. This chemistry will be illustrated using PNA/DNA probe binding and subsequent DNA hybridization.

In a second example, supported lipid bilayers are described in which a small and tuneable fraction of a receptor-modified lipid is added to provide density control. This chemistry is illustrated using the multivalent binding of the influenza virus.

## **COLL 484**

## Origin of saloplasticity in complexed polyelectrolytes

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(1) Florida State Univ, Tallahassee, Florida, United States (2) Chemistry & Biochemistry, Florida State University, Tallahassee, Florida, United States

Oppositely-charged polymers readily self-assemble into complexes when they are mixed in solution. This spontaneous association, driven mainly by the release of counterions, leads to well mixed blends of polyelectrolytes, and is sometimes termed “coacervation.” While the overall mechanism for pairing of opposite charges on repeat units can be ascribed to electrostatics, the enthalpic contribution to the driving force of assembly from water can actually be attributed to changes in water structure around paired charges. The reversible aspect of polyelectrolyte assembly is illustrated by a gradual unpairing of charges as the external salt concentration is increased. This reversible doping by salt, termed saloplasticity, controls all of the physical and mechanical properties of the material. This talk will illustrate the concept of saloplasticity and will show how a “sticky association” theory of polymers can be extended to complexes to predict their dynamics as a function of salt doping.

## COLL 485

### Patterning charges and complex coacervation

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Understanding how chemical sequence affects the self-assembly of polymers is a grand challenge across materials science and biology. The complexity of a near infinite number of sequence permutations is made even more difficult because of the convergence of interactions across a wide range of length-scales. In particular, electrostatic interactions are long-range, and compete with shorter-range effects such as van der Waals forces, hydrogen bonding, etc. From a materials science perspective, we draw inspiration from membraneless organelles, which involve sequence-specific intrinsically disordered proteins that interact via weak, multivalent interactions to achieve transient liquid-liquid phase separation in cells. We have utilized polypeptides as sequence-controlled polymers to study how variations the patterning or presentation of charges and other chemical functionalities can modulate the potential for liquid-liquid phase separation via complex coacervation. We have further examined how the patterning of oppositely-charged groups can facilitate or suppress the self-coacervation of polyampholytes. Our experimental efforts are supported by the parallel development of computational approaches for modeling and predicting the phase behavior of

patterned polymeric materials. These efforts have identified an initial set of molecular-level design rules for the tailored creation of materials based on polyelectrolyte complexation, and have relevance for materials in biology and for real-world applications.

## **COLL 486**

### **Principles of tension- and curvature-controlled solid domain interactions on vesicle membranes: From biomolecular constructs to responsive materials**

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In biomembranes, the interactions of molecules across neighboring raft domains is thought to be mediated by membrane curvature. In the solid-containing membranes of interest for applications requiring dynamic materials patterning, these curvature-mediated interactions can form the basis for new responsive patterned materials having dynamic connectivity. This talk demonstrates, based on new experimental findings, how interactions between membrane domains depend on specific variables: domain sizes, global membrane curvature (vesicle size), and local curvature (depending on excess area or “floppiness”). Depending on the ranges of these variables, interactions can be switched from attractive to repulsive, leading to two dimensional aggregation of domains in some cases and ordering in others. We demonstrate how control of curvature mediates the distance between rigid domains, potentially of importance in cells (when proteins impart domain stiffness and resistance to shear) and materials alike.

## **COLL 487**

### **Molecular insight into the potential cytotoxicity of hydrophobic nanosheets**

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Two-dimensional nanomaterials could cause structural disruption and cytotoxic effects to cells, which greatly challenges their promising biomedical applications including biosensing, bioimaging, and drug delivery. Here, interactions between lipid liposomes and hydrophobic nanosheets is studied utilizing coarse-grained (CG) molecular dynamics (MD) simulations. The simulations reveal a variety of interaction morphologies that depend on the size and the orientation of nanosheets. Dynamic and thermodynamic analyses on the morphology evolution clarify and provide insights into molecule motions such as “nanosheet rotation”, “lipid extraction”, “lipid flip-flop”, and “lipid spreading”. Driven by these molecule motions, hydrophobic nanosheets cause morphology changes of liposomes. The lipid bilayer structure can be corrugated, and the overall liposome sphere can be split or collapsed by large nanosheets. In addition,

nanosheets embedded into lipid bilayers greatly weaken the fluidity of lipids, and this effect can be cumulatively enhanced as nanosheets continuously intrude. To further explore the membrane properties affected by the insertion of nanosheet, six different single component lipid membranes are examined. The insertion of nanosheet to the membrane affects the structural and mechanical properties of the bilayers. The bending moduli of the six bilayers all increase. The corresponding molecular mechanism is that the acyl chains of local lipid molecules re-orient and become more ordered after the insertion of the nanosheet. Particularly, the fluid-gel phase transition occurs in the DMPC bilayer. These results could facilitate molecular-level understanding of the cytotoxicity of nanomaterials, provide insight for the design of safer nano-carrier, antibiotics and other bio-nanotechnology applications, and help future nanotoxicology studies associating computational modeling with experiments.

## **COLL 488**

### **Unbiased identification of the liposome protein corona using photoaffinity based chemoproteomics**

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Protein adsorption to the surface of a nanoparticle can fundamentally alter the character, behavior and fate of a nanoparticle *in vivo*. Unfortunately, current invasive methods to isolate and characterise the protein corona of a nanoparticle are unable to resolve key, individual protein-nanoparticle interactions. As such, the link between the “synthetic” and the “biological” identity of any given nanoparticle remains opaque. Herein, we report an unbiased photoaffinity-based approach to capture, quantify and characterise the hard protein corona of a liposome in its native state. Compared to common centrifugation methods used to isolate nanoparticle-protein complexes, our photoaffinity approach reveals not only reduced total protein binding to liposome surfaces but also considerably shorter lists of individually bound proteins. Identified proteins do not follow protein abundance patterns of human serum, as is generally the case for centrifugation methods, but are instead dominated by soluble and abundant apolipoproteins that have evolved to recognise the lipidic surface of circulating lipoproteins. Correlating the identified liposome protein coronas to *in vivo* fate, our findings fundamentally question the general significance of the protein corona in determining the behavior of nanoparticles *in vivo*. In particular, the almost total absence of proteins adsorbed to freely circulating, near neutral liposomes, as well as the dominance of direct electrostatic interactions between charged nanoparticles and cells *in vivo*, suggest the protein corona plays a less important role in determining the *in vivo* fate of many nanoparticles than previously thought.

## **COLL 489**

### **Physical properties of membranes and membrane mimics: Potential impact on membrane protein structure**

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The specific and solvent interactions between lipids and membrane proteins that stabilize fold and function are not well understood. To begin to understand the interactions between proteins and the solvent environment, the physical properties of the environments used to stabilize membrane protein folds need to be understood. The structure, shape, and dynamics of micelles, bicelles, and membranes will be presented and compared. The impact the differences and similarities of these environments have on membrane protein structure will be explored.

## **COLL 490**

### **Regulation of phospholipase C $\beta$ activity at the membrane**

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Phospholipase C $\beta$  (PLC $\beta$ ) hydrolyzes phosphatidylinositol-4,5-bisphosphate at the plasma membrane to regulate intracellular Ca<sup>2+</sup> and activate pathways involved in proliferation and survival. Aberrant PLC $\beta$  activity in the cardiovascular system is associated with arrhythmias, hypertrophy, and heart failure. Under basal conditions, PLC $\beta$  enzymes are maintained in a catalytically quiescent state. Upon stimulation of G protein-coupled receptors (GPCRs), PLC $\beta$  is activated through direct interactions with the heterotrimeric G protein subunits G $\alpha_q$  and G $\beta\gamma$ . However, maximum stimulation of lipase activity is only achieved in the presence of cellular membranes. The molecular basis by which the membrane and its properties contribute to PLC $\beta$  adsorption and activity under basal and G protein-stimulating conditions is poorly understood. Using compressed lipid monolayers as a model membrane system, we used an innovative combination of atomic force microscopy, mass spectroscopy, and biochemical assays to begin understanding how the membrane, PLC $\beta$  regulatory elements, and G $\alpha_q$  coordinately regulate PLC $\beta$  activity. These studies provide new structure-based insights in our understanding of interfacial activation mechanisms in this critical enzyme.

## **COLL 491**

### **Structure and shape transitions in PEGylated paclitaxel-loaded cationic liposomes enhances delivery and cytotoxicity to human cancer cells**

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Cationic Liposomes (CLs) are synthetic vectors for nucleic acid (NA) and drug delivery applications. CLs may be complexed with nucleic acids (DNA or short interfering RNA) for gene delivery and silencing, or used as vectors of cytotoxic hydrophobic drugs in

cancer therapeutics. Primary among hydrophobic drugs is paclitaxel (PTX) a mitotic inhibitor that halts the proliferation of tumor cells during the cell cycle and induces cell death. We will describe the effect of PEGylation of paclitaxel-loaded cationic liposome (CL<sub>PTX</sub>) nanoparticles (NPs) on structure and NP shape, which, in turn, lead to modified interactions with human cancer cells and a dramatic enhancement of PTX delivery and cytotoxicity compared to bare CL<sub>PTX</sub> NPs. This enhancement occurs even though the PEG-chain coating the NP is in the mushroom to brush transition regime. These results are in contrast to PEGylated CL-DNA NPs employed in gene therapeutics, where the PEG coat suppresses cell entry.

## COLL 492

### Solid-state deuterium NMR spectroscopy reveals emergent bending energies of lipid membranes

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Phospholipids are examples of biological liquid crystals exhibiting long-range order in their molecular organization, with interactions at mesoscopic length scales playing a key role in the emergence of mechanical properties of lipid membranes. The average structure is obtained from solid-state <sup>2</sup>H NMR lineshapes that yield segmental order parameters ( $S_{CD}$ ) for the individual acyl segments, which are related to the average membrane properties such as area/lipid and spontaneous curvature. On the other hand, thermal motions in liquid-crystalline membranes are obtained from spin-lattice relaxations as a function of the order parameter  $S_{CD}$ . These collective dynamics are related to the membrane mechanical properties by the fluctuation-dissipation theorem. Model-free interpretation of the functional dependence of spin-lattice relaxation rates ( $R_{1Z}$ ) on the segmental  $S_{CD}$  order parameters informs the liquid-crystalline material properties of the lipid bilayer. Variation of both average and dynamic properties with key compositional membrane parameters reveal how the membrane mechanical properties emerge from the intermolecular interactions. These compositional variables include the lipid polar head groups, acyl chains, and cholesterol, which are accessible at the atomistic level using solid-state <sup>2</sup>H NMR spectroscopy. For instance, mixtures of DPPE and DPPC show bending elasticities that depend on the molar ratio of PE to PC head groups in the liquid-disordered (ld) state. For the acyl chains, the emergent bending energy follows the sequence DOPC < POPC < DMPC. Furthermore, solid-state <sup>2</sup>H NMR studies of the effect of cholesterol on the bending rigidities of both saturated (DMPC) and unsaturated (POPC and DOPC) bilayers in the liquid-ordered (lo) state reveal phospholipid-specific effects on the membrane viscoelastic properties. The square-law

functional dependence of the  $R_{1z}$  relaxation rates on the segmental  $S_{CD}$  order parameters (Fermi's Golden Rule), indicates membrane stiffening with increasing cholesterol content. Studies of membranes with different lipids (e.g., POPC vs. DOPC) reveal that the cholesterol-induced stiffening depends on acyl chain unsaturation. Solid-state  $^2H$  NMR probes emergent bending energies of lipid bilayers on mesoscopic length scales, consistent with a flexible surface model (FSM) for the influences of the soft matter on membrane proteins such as ion channels, receptors, and transporters.

## **COLL 493**

### **Mechanism of cholesterol-induced shifts of GPCR activation**

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It was reported that activation of many rhodopsin-like G protein-coupled membrane receptors (GPCR) is sensitive to cholesterol content of the membranes into which they are imbedded. Crystallographic studies indicate existence of specific sites on GPCR for preferential interaction with cholesterol. It was suggested that such specific interactions are responsible for shifts in function of GPCR to activate G protein. On the other hand, cholesterol may act on GPCR via changes of membrane properties. Plasma membranes may contain high concentrations of cholesterol, a molecule that is known to increase bilayer thickness, seen as increase of chain order parameters, and to alter membrane elastic properties. Furthermore, at the proper concentration, cholesterol may facilitate lateral segregation of lipids into cholesterol-depleted and -enriched regions, such as lipid domains or clusters (also called rafts). We reconstituted bovine rhodopsin into unsaturated phosphatidylcholine bilayers with hydrocarbon chain lengths from 14 - 20 carbon atoms at cholesterol concentrations from 0 to 30 mol%. Lipid order parameters were measured by  $^2H$  NMR and photoactivation of rhodopsin was measured by following the ratio of metarhodopsin-II (MII)/metarhodopsin I (MI) concentrations by spectrophotometry. The MII photointermediate is capable of activating G protein, setting off a biochemical amplification cascade that results in the visual signal. It was observed that action of cholesterol on the MII/MI equilibrium depends on hydrophobic thickness of lipid bilayers. While addition of cholesterol to bilayers with a hydrophobic thickness less than 27 Å favored MII formation, thicker bilayers shifted the MII/MI equilibrium towards MI. Effects increased steadily with cholesterol content, suggesting that changes in properties of the lipid matrix surrounding rhodopsin are responsible for the effect. There is evidence that addition of cholesterol to membranes with a hydrophobic thickness larger than 27 Å results in aggregation of rhodopsin molecules. Implication of observations for function of GPCR under physiologically relevant conditions will be discussed.

## **COLL 494**

### **Efficacious bicelle/PNA nanodisc for antisense**

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We report an efficacious discoidal bicelle platform which entraps peptide nucleic acids (PNAs). PNAs are artificial DNA-like molecules consisting of pyrimidine or purine nucleobases attached to a highly flexible pseudopeptide backbone and have remarkable potential in gene editing and targeting. However, endocytosis of PNAs is a challenge in developing their broader therapeutic applications. The newly developed disc-like nanocarriers made of lipid bicelles (i.e., dipalmitoyl phosphatidylcholine/dihexanoyl phosphatidylcholine/dipalmitoyl phosphatidylglycerol) and PNA show efficient delivery of PNAs (targeting microRNA 210 and 155) into the cells. Negatively-charged bicelle is more adaptable to entrap the PNAs without affecting the discoidal morphology, while the positively charged mixture transforms the bicelles into irregular vesicles after the incorporation of PNA. Small-angle X-ray scattering and negatively-stained transmission electron microscopy were applied to characterize the structure of the nano-platform as well as the location of PNA in the nanodiscs, providing insight into how the hydrophobic region of PNAs interacts with bicelles. The outcomes of flow cytometry and confocal microscopy indicated superior transfection efficiency of bicelles containing dye conjugated anti-miR PNAs. Functional analysis also confirmed miR inhibition by PNA oligomers delivered by bicelles. The nanodiscoidal complex opens a new pathway to deliver PNAs, which, on their own, are challenging to be endocytosed into cells.

## **COLL 495**

### **4D printed nanoparticle hydrogel composites**

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Multi-length scale materials possessing structure spanning the nano- to macro-scale can only genuinely be achieved through the integration of bottom-up self-assembly of molecular amphiphiles with top-down additive manufacturing such as 3D printing. To date, only a few reports describing the 3D printing of self-organizing molecules (supramolecular organization) have appeared. To address this deficiency, in this presentation we report the synthesis of self-assembling feedstocks applicable to vat-photopolymerization 3D printing. Visible light printing of self-assembled multicomponent amphiphilic complex fluids containing both a macro-monomer and metal ions readily yield fabrication of nanostructured metal (plasmonic) nanoparticle hydrogels that undergo reversible shape transformation upon varying hydration levels, thus producing 4D printed composites. The discrete shape states achieved are spatially non-uniform

(i.e., not simply uniform volumetric expansion and contraction) making them ideal candidates for further development as shape-shifting nanocomposites.

## **COLL 496**

### **Stress induced mesoscale assembly of nanoparticles for active nanostructures**

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Due to the size- and shape-dependent properties, nanoparticles have been successfully used as functional building blocks to fabricate 1-3D ordered assemblies for the development of artificial metamaterials. At ambient pressure, entropy driven self-assembly of monosized or binary nanoparticles generally results in polycrystalline 2- or 3D close-packed arrangements, and extensive efforts have been made to develop structural perfection of nanoparticle arrays or 'single crystal-like' domain structures with precise long range order for their definite advantages for electron transport. To date, fabrications of ordered nanoparticle assemblies have been relied on specific interparticle chemical or physical interactions such as van der Waals interactions, dipole-dipole interaction, chemical reactions, etc. Recently we have discovered a pressure-induced assembly method to engineer nanoparticle assembly at mesoscale and to fabricate new nanoparticle architectures without relying on specific nanoparticle interactions. We show that under a hydrostatic pressure field, the unit cell dimension of a 3D ordered nanoparticle arrays can be manipulated to reversibly shrink, allowing fine-tuning of interparticle separation distance. Under a uniaxial pressure field, nanoparticles are forced to contact and coalesce, forming hierarchical nanostructures. Depending on the orientation of the initial nanoparticle arrays, 1-3D ordered nanostructures including nanorod, nanowire, and nanoporous network can be fabricated through the pressure-induced self-assembly method. Guided by computational simulations, we were able to rationalize the pressure-induced self-assembly of nanoparticle arrays for predictable nanostructures. Moreover, we discovered for the first time a transition from an ordered polycrystalline nanoparticle mesophase to quasi-single crystalline nanoparticle lattices induced by PDA process. Exerting pressure-dependent control over the structure of nanoparticle arrays provides a unique and robust system to understand collective chemical and physical characteristics and to develop novel electronic and photonic behavior for energy transduction related applications.

## **COLL 497**

### **Order and transport in 3D epitaxially-connected colloidal quantum dot superlattices**

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Colloidal quantum dots (QDs) that are epitaxially interconnected (necked or partially fused) to form highly-ordered, highly-coupled superlattices are an exciting new class of materials for optoelectronics. These epitaxially-fused QD superlattices (epi-SLs), which are typically made by self-assembly and ligand exchange on a liquid surface followed by stamp transfer to a solid substrate (the Langmuir-Schaefer technique), promise to combine the size-tunable photophysics and solution processability of QDs with delocalized, bulk-like carrier transport.

In this talk, I describe recent progress in making epi-SLs of sufficient spatial and energetic order to delocalize carriers into mini-bands. I discuss the fabrication of high-quality 3D epi-SL films, along with the determination of their structure (the complete superlattice unit cell) and physical formation pathway from the parent oleate-capped SL using a combination of X-ray scattering and correlative electron microscopy and diffraction of single SL grains. The oleate- to epi-SL phase transition occurs by nearly-pure translation of the QDs with minimal rotational motion, resulting in a rhombohedrally-distorted simple cubic epi-SL with fusion along the PbSe {100} facets. This simple translational phase transition is made possible by the rhombohedral distortion of the initial oleate-capped SL and results in  $>5 \mu\text{m}$  epi-SL grains free of linear or planar defects. While large epi-SL grains are useful, several types of intra-grain structural defects conspire to reduce order within the grains and localize charge carriers. Quantitative characterization of these intra-grain defects and a better understanding of the molecular processes involved in epi-SL formation have enabled fabrication improvements that enhance intra-grain order and overall film uniformity. Measurements probing mini-band formation and the impact of SL surface chemistry on charge transport will be highlighted.

## **COLL 498**

### **High resolution electron microscopy imaging of metallic helical nanowires**

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The packing of tetrahedra into nanoparticles has been well reported and controlled for icosahedral and decahedral synthesis, but more arcane is the packing of tetrahedra into nanowires. Icosahedral nanoparticles contain a characteristic “fan-like” contrast in Scanning Transmission Electron Microscopy (STEM) images, which is formed by the packing pattern of the tetrahedral units within the structure. Tetrahedra can similarly pack into an aperiodic helical structure forming nanowires. This structure, known as a variant of the Boerdijk-Coxeter-Bernal (BCB) helix, can be synthesized from Au alloys. The same “fan-like” contrast is dominant in STEM images of ultrathin AuAg nanowires, indicating that icosahedral packing is present in this system. The AuAg alloyed nanowires exhibit a unique structural transformation from a polycrystalline aperiodic helical structure to a double helix when induced with Pd precursor. This structural

transformation occurs simultaneously with a surface transformation. As the twisting advances, the wire surface roughens. We report a workflow to carefully control the surface and helical features of Pd-induced AuAg nanowires. This work combines electron microscopy techniques, such as High-Resolution STEM, STEM-Energy Dispersive X-Ray Spectroscopy (STEM-EDS), and Electron Tomography to characterize the structural transformation of this system. Ultimately, an understanding of this transformation will lead improved synthetic control of chiral systems for applications in plasmonics and catalysis.

## **COLL 499**

### **Detailed structural engineering of copper fine particles for conductive materials**

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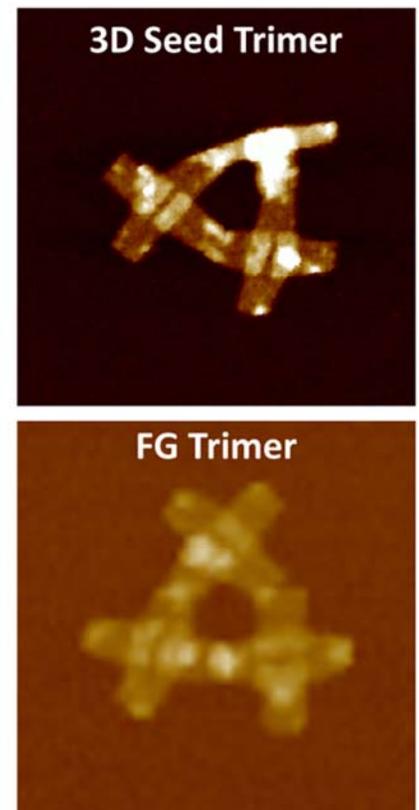
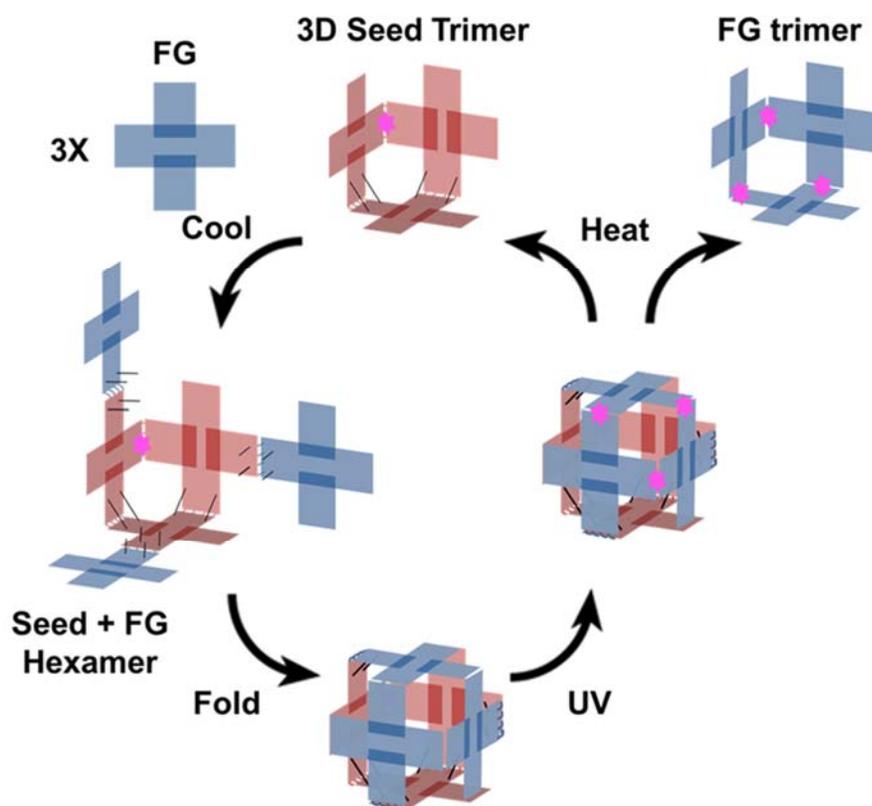
Preparation and structural engineering of nanoparticles and fine particles of metallic copper by solution-based strategies will be discussed in this paper. Biopolymer, such as gelatin, other polymers and surfactants can be applied as stabilizing reagent to maintain the particle surface in metallic conditions and control the detailed particle structure. Gelatin stabilized copper fine particles could be successfully applied as the materials for the inner electrode of multi-layered ceramic capacitor by using a high-temperature annealing process. However, as for the more widely used applications, in the field of printed electronics as well as organic electronics and dye-bonding of circuit tips, copper conductive particles for low-temperature sintering has become widely demanded. Smaller nanosized particles can be one of the good candidates for low melting temperature sintering, but in the case of copper, smaller particles can hardly be used for this purpose because they are readily oxidized. Therefore, we apply structural engineering including crystal engineering and surface engineering for copper fine particles prepared by solution-based strategies. We used the transition metal oxides as the precursors for solution syntheses of these particles which is useful for mass production. Preparation of copper fine particles in this study was carried out by hydrazine chemical reduction of CuO micro particles. This chemical process is a low temperature process, the particles are consisted of small crystalline grains. At the grain boundary in the copper fine particles, the diffusion of copper atoms becomes higher. Therefore, lower temperature sintering can be applied even the particle sizes bigger than 100 nm. Some of our particles contains slightly oxidized surface. These slightly oxidized states can be reduced readily in the presence using some reductive small molecules and metallic surface which is important for necking and sintering generates. We can apply this strategy of the structural engineering of copper fine particles for the application of electro-conductive and dye-bonding.

## **COLL 500**

### **3D self-replication of DNA nanostructures**

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Self-replication is a natural process that can generate materials and pass along information. We have seen several examples of artificial self-replication in which the template assembles, organizes and directs formation of the target nanostructure. However, the self-assembly procedure increases the template's dimensionality, which makes it challenging to template and replicate a 3D object. Here, we report the direct self-replication of a 3D object. First, we fabricate our 3D object: a three face cube corner by folding a planer self-assembled set of three DNA origami tiles. This three face cube corner is our template. The replication proceeds by self-assembling three daughter origami tiles to three edges of the cube corner. DNA single strands on each cube face and daughter tile hybridize to fold the tiles inward and complete the cubic box. The daughter tiles are then cross-linked into a new cube corner. Heating releases the two complementary cube corners. This method provides a general bottom-up approach for conducting high-order self-replication by organizing the materials *via* folding. Considering that the 3D DNA nanostructure is a functional platform, this type of 3D self-replication is expected to produce new materials, such as chiral plasmonic nanomaterials, by passing the steric information through successive generations.



## **COLL 501**

### **Semiconducting nanosurfactants for additive printing of colloidal particles**

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2D/3D printing of colloidal particles has emerged as a powerful tool for fast prototyping of functional electronics and devices. Surfactant, as an active ingredient of inks, plays a significant role in many printing processes due to its ability of reducing the interfacial tension between solvents and nanoparticles. However, the residual of organic surfactants in printed devices limits the overall functionalities of the nanomaterials, requiring the post-treatments (e.g. thermal sintering) to remove organic surfactants. Therefore, one practical barrier to the large-scale application of nanoparticle-based inks is the development of compatible ink additives such that they may not compromise or even improve the performance of printed devices. Here, we report a graphene quantum dot nanosurfactant that is able to stabilize graphene in aqueous dispersion via  $\pi$ - $\pi$  stacking interaction. Such nanosurfactant-stabilized graphene dispersion is readily printable using a commercial aerosol jet printer. In addition, the suitable band gap of graphene quantum dots enables the printed composite with intriguing optoelectrical activity. Taking advantage of the aerosol jet printing, the formulated composite ink can be directly printed on various types of substrates for the prototyping of multiple optoelectrical devices, thus opening new design opportunities for functional inks as well as high-performance devices.

## **COLL 502**

### **Capturing structural transitions in surfactant adsorption isotherms at solid/solution interfaces**

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Although adsorption isotherms of surfactants are critical in determining the relationship between the interfacial properties and structures of surfactants, providing quantitative predictions of the isotherms remains challenging. This is especially true for adsorption at hard interfaces such as on 2D layered materials or on nanoparticles where simulation techniques developed for fluid-fluid interfaces do not apply. In this work, we predict non-ideal adsorption at a solid-solution interface with a molecular thermodynamic theory (MTT) model that utilizes molecular dynamics (MD) simulations for the determination of free energy parameters in the MTT. Furthermore, the MTT/MD model provides atomistic insights into non-ideal behavior of surfactant molecules by capturing structural phases

of the surfactants at different concentrations. Our approach captures structural transitions from the ideal state at low concentrations and then to the critical surface aggregation concentration (CSAC) and finally through the critical micelle concentration (CMC). We validate our model against the original MTT model by comparing predicted adsorption isotherms of a simplified surfactant system from both approaches. We further substantiate the applicability of our model in complex systems by providing the adsorption isotherms in an aqueous sodium dodecyl sulfate(SDS)-graphene system, in good agreement with experimental observations of the CSAC for the same system.

## **COLL 503**

### **Immersion and clustering of cylindrical nanoparticles at liquid-air interfaces**

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Self-assembly of nanoparticles (NPs) at liquid surfaces is strongly influenced by coupling between the NP and liquid. This effect can be particularly complex for anisotropic NPs, as has been shown for nanocubes (NCs) by analytical methods and molecular dynamics simulations. These simulations reveal that the strength of ligand-solvent interactions determines the immersion and orientation of cubic NPs at the liquid-air surface, with three immersion regimes observed: NCs can sit flat on the liquid surface (weak), be partly immersed in a tilted orientation (intermediate), or be fully immersed except for the top facet (strong), determining the self-assembly of NCs on liquid surfaces. Here, molecular dynamics simulations have been performed using the MARTINI coarse-grained force field to investigate similar behavior in cylindrical NPs.

## **COLL 504**

### **Bottom-up approaches for precisely nanostructuring hybrid organic/inorganic multi-component composites for organic photovoltaics**

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Nanostructuring organic polymers and organic/inorganic hybrid materials and control of blend morphologies at the molecular level have become the prerequisites for organic photovoltaics (OPVs) that are widely perceived as low-cost alternative energy sources. To achieve all-around high performance, multiple organic and inorganic entities, each designed for specific functions, are commonly incorporated into a single device. Current state-of-the-art approaches to morphology control in these multi-component systems typically involve physical blending and optimization via thermal/solvent annealing. Such trial-and-error approaches are however highly system dependent, lack controllability on

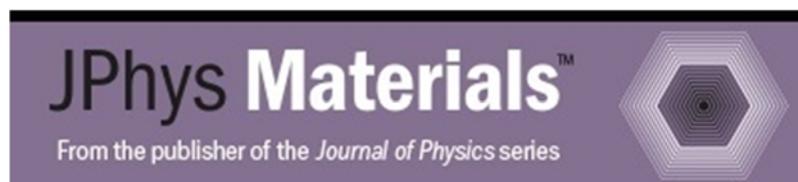
the molecular level and generally lead to morphologies at only thermodynamically metastable states. We present herein our efforts in developing a versatile toolbox employing supramolecular chemistry that is capable of precisely nanostructuring multi-component organic/inorganic hybrid materials through self-assembly processes. Specifically, we show that well-defined core-shell composite nanofibers (NFs) containing precisely placed conjugated polymers, inorganic quantum dots and fullerene derivatives, can be obtained through cooperation of orthogonal non-covalent interactions including conjugated polymer crystallization, fullerene aggregation, hydrogen bonding interactions and metal-ligand coordination. OPV devices applying these NFs display much improved efficiencies and stability over their conventional bulk heterojunction (BHJ) counterparts.

## **COLL 505**

### **Introducing *JPhys Materials*: New open access journal from IOP Publishing for leading interdisciplinary research in materials science**

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Research is increasingly a collaborative enterprise, breaking traditional subject boundaries and journals must evolve to reflect these changes. *JPhys Materials* is an innovative new open access journal for high quality research in materials science, focusing in particular on interdisciplinary and multidisciplinary approaches. It builds on the strength and prestige of IOP Publishing's Journal of Physics series, which celebrated 50 years of publishing in 2017. The journal showcases the most significant and exciting developments in materials science research and applies open science principles to encourage maximum collaboration, reproducibility and dissemination of research. The journal offers rapid peer review and is also committed to supporting gender and geographic diversity across the global materials science community, maximising the reach and visibility of authors' work. *JPhys Materials* is firmly focused on a community-oriented approach to communicating science and is not driven by funders, institutions or for-profit corporations.



# IOP Publishing

## COLL 506

### **Designed synthesis and assembly of inorganic nanomaterials for medical applications**

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We demonstrated that ceria nanoparticles and ceria–zirconia nanoparticles can work as therapeutic antioxidants to treat various nasty diseases including ischemic stroke, Alzheimer’s disease, sepsis, and Parkinson’s disease.<sup>1</sup> We developed a click reaction-assisted immune cell targeting (CRAIT) strategy to deliver drug-loaded nanoparticles deep into tumor interiors, reducing tumor burden in an aggressive 4T1 breast cancer model without any systemic toxicity.<sup>2</sup> We report a highly sensitive and selective K<sup>+</sup> nanosensor that can quantitatively monitor extracellular K<sup>+</sup> concentration changes in the brains of freely moving mice experiencing epileptic seizures.<sup>3</sup> We introduced electromechanical cardioplasty using an epicardial mesh made of electrically conductive and elastic Ag nanowire-rubber composite material to resemble the innate cardiac tissue and confer cardiac conduction system function.<sup>4</sup>

## COLL 507

### **Directly correlating synthesis parameters with nanostructure and optical properties in advanced colloidal quantum dots**

**Jennifer A. Hollingsworth**, [jenn@lanl.gov](mailto:jenn@lanl.gov). Center for Integrated Nanotechnologies, Los Alamos National Laboratory, Los Alamos, New Mexico, United States

Solution-processed quantum dots (QDs) are finding applications in a wide-range of technologies from display and lighting to photovoltaics and photodetectors. We take advantage of an expanded “structural toolbox” to synthesize QDs with novel and optimized photophysical properties, especially bright and stable emission in the visible and infrared. We use advanced heterostructuring that employs bandgap engineering, thick (“giant”) or asymmetric shell growth, interfacial alloying, etc. In this way, we have synthesized QDs for which non-radiative processes, such as blinking, Auger recombination and photobleaching, have been reduced or even “turned off” at room

temperature and exposed to air (e.g., *J. Am. Chem. Soc.* 2012, 134, 9634; *Nano Lett.* 2012, 12, 5545; *J. Am. Chem. Soc.* 2017, 139, 11081; *Nature Commun.* 2017, 8, 15083; *Adv. Funct. Mater.* 2019, 29, 1809111). As part of this effort, we have developed new methods for evaluating processing-structure-function correlations toward materials-by-design. In this talk, I will discuss: (1) a “single-QD stress test” used to evaluate photodegradation processes (*ACS Nano* 2018, 12, 4206), and (2) an “inside-out” approach to establishing processing-structure-function correlations. First, by testing QDs at the level of single nanocrystals under controlled photon flux and temperature, we directly identify degradation mechanisms and associated reaction kinetics, which is not possible relying on device testing alone. Moreover, we calculate activation energies for the photo-degradation processes specific to a QD composition or a QD synthesis procedure. Second, by performing multimodal characterization, we pinpoint the nanocrystal structural/chemical features responsible for desired vs. non-optimal properties, and their origin in processing. Taken together, the techniques enable a faster progression from nano-synthesis to ideal functional nanostructures.

## **COLL 508**

### **Cluster assembly pathways to gibbsite nucleation and crystal growth**

**Xin Zhang**, [xin.zhang@pnnl.gov](mailto:xin.zhang@pnnl.gov). Pacific Northwest National Laboratory, Richland, Washington, United States

Gibbsite ( $\alpha$ -Al(OH)<sub>3</sub>) is an important archetype hydroxide of aluminum in nature that also plays diverse roles across a plethora of industrial applications. In addition, gibbsite is a prominent component of high-level nuclear waste stored in large quantities at the Hanford Site, WA and at the Savannah River Site, SC, with future processing plans dependent on developing a predictive understanding of its nucleation, crystal growth, dissolution and transformation in solution conditions. However, mechanisms of gibbsite nucleation and crystal growth remain poorly understood. In this work, *in situ* magic angle spinning nuclear magnetic resonance (MAS-NMR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray absorption spectroscopy (XAS), Electropray ionization (ESI)-Mass, high resolution powder X-ray diffraction (XRD), and X-ray Pair Distribution Function (PDF) techniques were used to explore the nucleation and crystal growth mechanisms of gibbsite from amorphous aluminum hydroxide precursors in details. By focusing on understanding the role of aluminum coordination change dynamics from tetrahedral in solution to octahedral in solids and vice versa, and by quantifying intermediate polyoxoaluminate cluster formation, some unifying principles governing these transformations emerge. Furthermore, various advanced techniques reveal the transformation and aggregation of aluminum clusters during the hydrothermal process, which indicate cluster assembly pathways to gibbsite nucleation and crystal growth. These findings are important for developing new methods to morphology and size controlled synthesis of gibbsite nanoparticles, and may aid in the design of chemical processes for managing the aluminum inventory in nuclear waste.

## **COLL 509**

## **Self-assembled optical and energy materials**

**Ullrich Steiner**, *ullrich.steiner@unifr.ch*. Adolphe Merkle Institute, Fribourg, Fribourg, Switzerland

Polymer self-assembly enables the creation of well-defined morphologies on the 10-nm length scale. Translating these structural motives into functional materials is however a challenge. My presentation will provide an overview over the translation of polymer self-assembly into inorganic materials, with the aim to create functionalities not normally found in polymeric materials. These include the management of light propagation in photonic and plasmonic materials and the creation of morphologies that improve the properties of photovoltaic and energy storage materials.

### **COLL 510**

#### **Nanoparticle self-assembly: From oligomers to mesoscale structures**

**Antonios Kanaras**, *antoniskan@gmail.com*. University of Southampton, Southampton, United Kingdom

Controlling nanoparticle self-assembly in a very effective and easy way has many applications in several scientific fields such as nanophotonics and metamaterials, nanoelectronics and nanodiagnostics.<sup>1</sup> In particular the employment of DNA as a scaffold for the organization of nanoparticles is exceptionally attractive and has been utilized to arrange nanoparticles into dimers, trimers or more complex structures.<sup>2</sup>

In this presentation I will discuss recent progress in my group related to the development of new tools to control the self-assembly of nanoparticle oligomers and mesoscale structures based on chemical and photochemical methods.<sup>3-5</sup>

### **COLL 511**

#### **Development of surface composition and ordering during reverse-emulsion assembly of binary colloidal particle mixtures**

**Christian Heil**<sup>1</sup>, *heil@udel.edu*, **Thomas E. Gartner**<sup>1</sup>, **Arthi Jayaraman**<sup>1,2</sup>. (1) Chemical and Biomolecular Engineering, University of Delaware, Newark, Delaware, United States (2) Materials Science and Engineering, University of Delaware, Newark, Delaware, United States

Nanoparticle assembly at a fluid-fluid interface is a proven route to precisely engineer organic/inorganic materials with controlled optical properties. In this talk, we will present our recent work using coarse-grained Langevin dynamics simulation that mimics reverse-emulsion (aqueous droplet in octanol) directed assembly of binary nanoparticle mixtures into supraballs. We model a binary mixture of silica and synthetic melanin particles in implicit solvent within a shrinking spherical confinement to replicate the

shrinking reverse-emulsion droplet as the water diffuses from inside the droplet into the octanol phase. The simulation protocol captures the physics of this reverse-emulsion assembly by reproducing the experimental observation of melanin and/or smaller nanoparticles enriching the water-octanol interface. For all binary mixtures, we observe enrichment of the melanin particles at the supraball surface as compared to interior of supraball. This enrichment decreases with increasing melanin/silica size ratio. We observe appreciable crystalline ordering only in systems where the particles are of similar size and that particle size dispersity, finite assembly timescale, and curvature of the supraball surface all serve to suppress particle ordering. These findings serve as design rules for tailoring the supraballs for structural color applications and improve our fundamental understanding of particle assembly near curved interfaces.

## **COLL 512**

### **Biomimetic nanomaterials for neuroprosthetic devices**

**Nicholas Kotov**, *kotov@umich.edu*. University of Michigan, Ann Arbor, Michigan, United States

Materials with difficult-to-attain combination of multiple properties - mechanical, electrical, optical, chemical, transport, and biological – represent the quintessential bottleneck neuroprosthetic devices. Nanocomposites with molecular, nano-, meso-, and microscale levels of structural engineering can address these requirements, which can be demonstrated on the basis of layered biomimetic nanocomposites from nanoparticles, nanoshells, and carbon nanotubes. Besides mechanical robustness making possible their implantation, the biomimetic nanocomposites can exceed charge injection capacity and other key electrochemical characteristics of gold, IrO<sub>x</sub> and other materials used currently for neural stimulation. Small dimensions of the nanocomposite electrodes afford marked reduction of the scar tissue formation around implants. Photoactive multilayer from semiconductor particles were used to grow neuron precursor cells on them. It was found that light adsorbed in the nanoparticle layers results in the electrical excitation of the neurons making this system a functional analog of retina. Cartilage-like nanocomposites from aramid nanofibers also provide the long-term corrosion-resistant protection for a wide range of neuroprosthetic devices.

## **COLL 513**

### **Taking cyclodextrin metal-organic frameworks from the research laboratory to the market place**

**James F. Stoddart**, *stoddart@northwestern.edu*. Department of Chemistry, Northwestern University, Evanston, Illinois, United States

Porous metal-organic frameworks (MOFs) have been studied in the context of a wide variety of applications, particularly in relation to molecular storage and separation sciences. In 2010, we reported a green, renewable framework material composed of  $\gamma$ -

cyclodextrin ( $\gamma$ -CD) and alkali metal salts—namely, CD-MOF. These cubic CD-MOFs are (i) stable to the removal of solvents, (ii) permanently porous, with surface areas of  $\sim 1200 \text{ m}^2 \text{ g}^{-1}$ , and (iii) capable of storing gases and small molecules within their pores. They have been shown to facilitate the separation of mixtures of alkyl/aromatic compounds, including the BTEX mixture (benzene, toluene, ethylbenzene, and the regioisomers of xylene), into their pure components, in both the liquid and gas phases, in an energy-efficient manner which could have implications for the petrochemical industry. In particular, CD-MOF has the ability to separate a wide variety of mixtures, including ethylbenzene from styrene, haloaromatics, terpinenes, pinenes and other chiral compounds. Since CD-MOF is a homochiral framework, it is also able to resolve the enantiomers of chiral analytes, including those of limonene and 1-phenylethanol. In 2017, we incorporated ibuprofen within CD-MOF-1 either by (i) a crystallization process using the potassium salt of ibuprofen as the alkali cation source for production of the MOF or by (ii) absorption and deprotonation of the free-acid, leading to an uptake of 23–26 wt % of ibuprofen within the CD-MOF. These inexpensive, green, nanoporous materials exhibit absorption properties which make them realistic candidates for commercial development, not least of all because edible derivatives, fit for human consumption, can be prepared entirely from food-grade ingredients. In this lecture, the story of CD-MOFs will be presented, as we venture from the lab to the market place.

## **COLL 514**

### **Programming medical treatment one nanolayer at a time**

**Paula T. Hammond**, [hammond@mit.edu](mailto:hammond@mit.edu). Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States

By alternating positively and negatively charged molecules in sequence, it is possible to generate thin films one nano-layer at a time while controlling the composition of the film with great precision. This electrostatic layer-by-layer (LBL) process is a simple and elegant method of constructing highly tailored ultrathin polymer and organic-inorganic composite thin films. We have used this method to develop thin films that can encapsulate and release proteins and biologic drugs such as growth factors with highly preserved activity from the surfaces of biomedical implants or wound dressings with sustained release over periods of several days. We have engineered coatings that yield release of different drugs, DNA or protein, resulting in highly tunable multi-agent delivery nanolayered release systems for tissue engineering, biomedical devices, and wound healing applications. Depending on the nature of the LbL assembly, we can generate thin films that rapidly release proteins or peptides within minutes for rapid hemostasis to stop bleeding in soldiers on the battlefield, or release growth factors that help to regenerate bone in defects where bone may no longer grow. Finally, the manipulation of charge to target other tissues, in particular cartilage, is an important means of targeting the joint for osteoarthritis. We have generated unimolecular charged systems that can be precisely tuned to achieve deep penetration into avascular tissues such as cartilage to enable extended release treatments for cartilage regeneration.

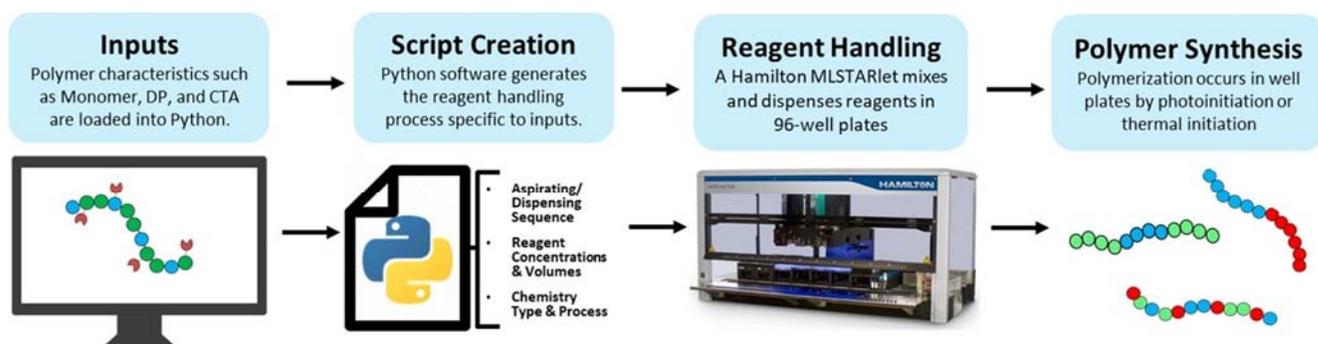
These and other uses of controlled polyelectrolytes and their complexes for delivery within tissues and across barriers will be addressed.

## COLL 515

### Automation and machine learning: Big data tools to engineer biofunctional polymers

**Adam J. Gormley**, *adam.gormley@rutgers.edu*. Biomedical Engineering, Rutgers University, Piscataway, New Jersey, United States

Synthetic polymers have played a key role in medicine and drug delivery for the last 50 years. Their ability to be uniquely tailored for very specific formulation needs makes them highly powerful tools. Here, we talk about how these material parameters can be tuned with incredible precision to achieve highly diverse characteristics. Recent advances in oxygen tolerant controlled/living radical polymer chemistry have also enabled a new and exciting ability to make polymer libraries using laboratory automation. Coupling this custom polymer automation with machine learning now allows us to sort through a very large range of characteristics to identify highly valuable compositions. This enables a transition from 'screening' experiments to intelligent profiling of quantitative structure-activity relationships (QSAR). In effect, we believe this unique set of tools may significantly enable the emerging field of polymer informatics, particularly for biomedical applications.



Automated process for oxygen tolerant controlled/living radical polymer chemistry

## COLL 516

### Disarming bacteria the natural way

**Laura L. Kiessling**, *kiesslin@mit.edu*. Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States

Antibiotic resistance is a global health emergency. Bactericidal drugs with specific cellular targets promote the emergence of drug-resistant pathogens. The global tally due to antibiotic-resistant bacteria is 10 million deaths annually, underscoring the need for innovative anti-infection strategies that do not drive the emergence of resistance. Mucins are highly glycosylated proteins that reside at the barrier between animal tissues and the microbiome. Mucins neutralize pathogen virulence to assist in host defense. Understanding the attributes of mucins responsible for taming pathogens could lead to fundamentally new strategies to regulate pathogenic bacteria. Our goal is to synthesize polymers for mechanistic studies and to capture critical bacterial disarming properties. Using ring-opening metathesis polymerization (ROMP), we generated defined polymers that can block toxin activity. Intriguingly, the backbone structure was critical for activity. This seminar outlines how polymer architecture influences the function of these mucin mimics.

## **COLL 517**

### **Granular hydrogels for biomedical applications**

**Jason A. Burdick**, [burdick2@seas.upenn.edu](mailto:burdick2@seas.upenn.edu). 240 Skirkanich Hall, Univ Pennsylvania, Philadelphia, Pennsylvania, United States

Hydrogels represent a class of biomaterials that have great promise for the repair of tissues, particularly due to our ability to engineer their biophysical and biochemical properties. Hydrogels can provide instructive signals through material properties alone (e.g., mechanics, degradation, structure) or through the delivery of therapeutics that can influence tissue morphogenesis and repair. In recent years, we have transitioned from traditional hydrogels to granular hydrogels that are comprised of smaller hydrogel units (i.e., microgels). Granular hydrogels have advantages in that they can be designed through heterogeneous microgels to introduce complexity to the material, they support cell invasion through the space between microgels, and they can be packed together to act as solids that can be easily extruded through a syringe.

Here, I will give examples of the design and use of granular hydrogels based on hyaluronic acid for use as injectable therapeutics, as well as in 3D printing. Microfluidic devices are used to fabricate the microgels using photoinitiated thiol-ene reactions or radical polymerizations for intraparticle crosslinking where crosslinkers can be stable or responsive to local proteases. For cardiac therapeutics, we injected heterogeneous granular hydrogels into the myocardium and showed selective microgel degradation to release factors and introduce porosity for cellular ingrowth. In 3D printing, we jammed together microgels to form shear-thinning and self-healing hydrogels that could be printed either onto surfaces or within other hydrogels. These could be cell-laden or stabilized where necessary with secondary crosslinking. Most recently, we designed these granular hydrogels to be conductive, through an in situ metal reduction process of silver onto microgels and then jamming into solids with high conductivity due to increased surface area when compared to traditional hydrogels. Overall, the granular hydrogel design opens up new opportunities in the design of functional hydrogels in biomedical applications.

## **COLL 518**

### **Nano-enabled immunotherapy for cancer and the treatment of allergic and autoimmune disease**

**Andre Nel**, *anel@mednet.ucla.edu*. Division of Nanomedicine, Department of Medicine, University of California Los Angeles, Los Angeles, California, United States

Nanoparticles have made a big impact on the development of immunotherapy for cancer and serious allergic disorders, demonstrating the ability to develop new therapeutics that are capable of boosting immunogenic effects in the setting of “cold” tumor microenvironments in solid cancers, as well as the ability to induce tolerogenic effects that suppress antigen-specific immune hyperreactivity in the setting of asthma or autoimmune disease. I will describe cancer immunotherapy from the perspective of inducing immunogenic cell death (ICD) by silicasome carriers and liposomes that provide an endogenous vaccination approach through the delivery of chemotherapeutic agents in combination with other active pharmaceutical ingredients. Immunogenic cell death leads to the activation of cytotoxic T-cells by the generation of “eat-me” and immunological danger signals, which can be further propagated at the TME delivery site by additional interference in checkpoint and immune metabolic pathways. This intervention can increase the number of immunotherapy responders to checkpoint inhibitors, in addition to inducing immune memory that can eradicate tumor metastases. The second part of my talk will focus on the induction of antigen-specific immune tolerance by liver-targeting tolerogenic nanoparticles, which leads to the generation of antigen-specific regulatory T cells and that can suppress allergic inflammation in the lung and autoimmune disease processes. Moreover, both treatment modalities, i.e., ICD-inducing nanocarriers and liver-targeting tolerogenic nanoparticles, can be used on the translational side to generate new therapeutics that can be implemented to treat two major disease processes by using contrasting design features.

## **COLL 519**

### **Bringing the digital revolution to polymer manufacturing**

**Joseph M. DeSimone**<sup>1,2,3</sup>, *joe@carbon3d.com*. (1) Chemistry, The University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, United States (2) Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina, United States (3) Carbon, Inc., Redwood City, California, United States

Although digital technologies shape our modern world, the production of polymer products relies largely on age-old molding techniques. A major reason for this is that additive methods have not delivered a meaningful alternative to traditional processes—until now. In this talk, I will describe Carbon Digital Light Synthesis™ (DLS) technology, which embodies a convergence of advances in software, hardware, and materials to bring the digital revolution to polymer additive manufacturing.

DLS uses software-controlled chemistry to produce commercial quality parts rapidly and at scale. Layerless parts 'grow' continuously from a pool of resin, formed by light. Compatible with a wide range of polymers, Carbon DLS opens major opportunities for innovative—and previously unmakeable—products across industries, as well as valuable opportunities for product light-weighting and de-materialization, accelerated product design cycles, and local-for-local manufacturing.

## **COLL 520**

### **Light-harvesting applications of nanoparticles**

**Naomi J. Halas**, [halas@rice.edu](mailto:halas@rice.edu). Rice Univ Ece Dept, Houston, Texas, United States

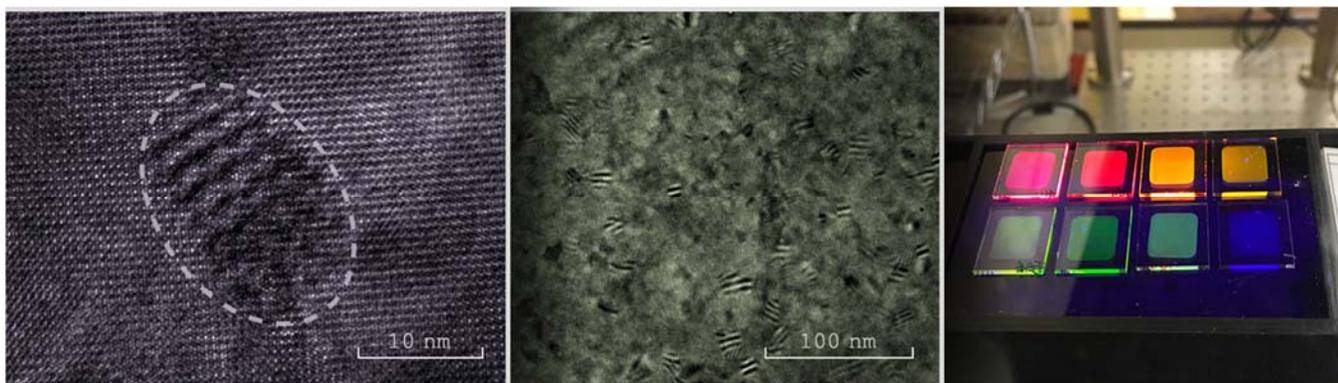
The interaction of light with nanoparticles and nanostructures has been a topic of increasing interest within the chemistry community, and a topic of increasing impact in terms of applications. We will discuss several light-based applications of nanoparticles, such as nanomedicine in clinical trials, photocatalysis with “antenna-reactor” nanocomplexes, and applications dependent upon phase change, in particular, solar water remediation.

## **COLL 521**

### **Could composite halide perovskites provide a stable solution?**

**Hanwei Gao**, [hgao3@fsu.edu](mailto:hgao3@fsu.edu). Physics, Florida State University, Tallahassee, Florida, United States

Halide perovskites have shown their promises in a variety of optoelectronic applications, from solar cells, light emitting diodes, to photodetectors. This new class of optoelectronic materials exhibit superb optical and electrical properties such as long diffusion length, high carrier mobility, strong optical absorption, and tunable bandgap. Despite the successful demonstrations reported so far, perovskite-based devices with high performance and stability still remain challenging. We discovered that perovskites in form of composites can sometime outperform the pure perovskites with improved material stability. In this talk, I will focus on the correlation between the crystal phases and the microscopic structures, as well as the favorable physical properties we have observed in composite perovskites.



## COLL 522

### Integrating catalysis-critical transport functions within nanoarchitected platforms

**Debra R. Rolison**, [rolison@nrl.navy.mil](mailto:rolison@nrl.navy.mil). Surface Chemistry, U.S. Naval Research Laboratory, Arlington, Virginia, United States

Our team at the U.S. Naval Research Laboratory studies the effect on catalytic activity of wiring multiple transport and reactivity functionality into practical, not model, mesoscale architectures. We exploit sol-gel-derived aerogels as a hierarchical platform—structurally complex, but functionally simple in which the mesoporous network (for facile molecular flux to internal sites) is co-continuous with a covalently bonded nanoparticle network (that serves as a long-range electrical conduit). Such a platform offers the means to query how electronic, ionic, and molecular transport within the nanoarchitecture affects the elementary reaction steps that underlie catalytic efficacy. We focus on evaluating energy conversion-relevant catalytic oxidations at gold nanoparticle (Au NP)-modified oxide aerogels and copper nanoparticle (Cu NP)-modified oxide aerogels in the dark and under visible-illumination to stimulate the plasmonic character of the metal NPs. We show that the Au||TiO<sub>2</sub> interfacial design strongly impacts charge carrier (electron and proton) transport over mesoscale distances in catalytic guest-host architecture and affects the presence of electron paramagnetic resonance-visible oxygen vacancies in the oxide network. Hierarchical nanoarchitectures provide a tunable platform with which to develop comprehensive mechanistic understanding that will allow us to design next-generation catalytic architectures with superior performance.

## COLL 523

### Deterministic routes to assembly of functional materials into complex, three dimensional architectures

**John A. Rogers**, *jrogers@northwestern.edu*. Materials Science and Engineering, Northwestern University, Evanston, Illinois, United States

Complex, three dimensional (3D) assemblies of nanomaterials provide sophisticated, essential functions in even the most basic forms of life. Compelling opportunities exist for analogous 3D structures in man-made devices, but existing design options are highly constrained by comparatively primitive capabilities in fabrication and growth. A recent collection of advances in chemistry, materials science and mechanical engineering provide broad access to diverse, highly engineered classes of 3D architectures, with characteristic dimensions that range from nanometers to centimeters, across areas that span square centimeters or more. The approach relies on geometric transformation of preformed two dimensional (2D) precursor micro/nanostructures into extended 3D layouts by controlled processes of substrate-induced compressive buckling, where the bonding configurations, thickness distributions and other parameters control the final configurations. This talk reviews the key concepts, and focuses on the most recent developments with example applications at the bio-interface.

#### **COLL 524**

##### **Programmable synthesis of hybrid inorganic colloids**

**Mikhail Zamkov**, *zamkovm@bgsu.edu*. BGSU, Bowling Green, Ohio, United States

I will discuss a novel, non-conjugation strategy for integrating inorganic nanocrystals into multi-component hybrid colloids. The synthetic innovation lies in stimulating the viscoelastic behavior of inorganic nanocrystals, which causes dissimilar colloids to bond at hybrid interfaces in a controllable manner. This process is initiated by the introduction of ion-solubilizing molecules to colloidal solutions that, under thermal activation, promote nanoparticle coalescence into clusters of two, three, or more domains. Once a desired size of a nanoparticle cluster is formed, the process is thermally switched off. The ability to assemble pre-fabricated inorganic colloids permits a programmable design of multifunctional nanostructures, where a particular selection of materials can be optimized to perform catalytic, sensing, light-emitting, or energy converting functions. The employment of the viscoelastic fusion as an assembly strategy has allowed expanding the range of possible hybrid inorganic geometries, including novel bimetallic, Janus, non-core/shell, and other multi-domain heterostructures. We expect that this work would be important both to the basic science and material engineering applications as the programmable assembly of inorganic colloids can potentially affect a wide range of emerging technologies.

#### **COLL 525**

##### **Investigation of nanoparticle surface properties that impact interactions with model bacteria**

**Vivian Feng**, [feng@augsborg.edu](mailto:feng@augsborg.edu). Chemistry, Augsburg College, Minneapolis, Minnesota, United States

Fundamental understandings of how bacteria interact with nanomaterials with various surface chemistry provide important insights into designing materials with desirable properties in biomedical, pharmaceutical and consumer products. As one of the primary modes of nanomaterial interaction with bacteria involves contact with the bacterial cell surface, we take a molecular approach by placing the surface chemistry of both the cells and the nanoparticles on equal footing, and examining factors that govern their interactions. This talk will focus on recent studies from my group that investigate how engineered nanoparticles with various surface functionalities result in different interactions with both Gram-positive and Gram-negative bacterial models that induce toxicity through surface binding and membrane damage. Our results show that although cationic nanoparticles often result in greater surface binding and interactions with bacterial cells, the mechanism of interactions depends on both cell surface components (such as lipopolysaccharides and teichoic acids) and the molecular conformations of the nanoparticle surface ligands.

## **COLL 526**

### ***In situ* generated metal nanoparticles as two-dimensional assemblies, core-shell structure and biosensor**

**Krisanu Bandyopadhyay**, [krisanu@umich.edu](mailto:krisanu@umich.edu). Department of Natural Sciences, University of Michigan-Dearborn, Dearborn, Michigan, United States

Metallic and bi-metallic nanoparticles like gold, platinum, palladium, Au-Pt and Au-Pd of specific size immobilized on solid support has seen remarkable growth due to their different potential applications. Thus, there is a considerable interest for investigating a general preparative route to engineer aggregation-resistant metallic nanoparticles for various applications. The present study deals with *in situ* formation of two-dimensional assemblies of metallic and bi-metallic nanoparticles on functionalized surfaces. Electrochemical investigations of these nanoparticles revealed a highly efficient catalytic activity for many long-chain and poly alcohols including methanol, ethanol, 1-propanol, 2-propanol, ethylene glycol, and glycerol. In another application of this *in situ* metal nanoparticle synthesis, gold and palladium nanoshells have been synthesized successfully by reducing surface bound palladium and gold ions onto ~200 nm diameter silica core. The method for generating such nanoshells is based on seed-mediated growth technique. This present method reports the first time synthesis of palladium nanoshell from surface bound palladium nanoparticles seeds compare to earlier reports that use gold nanoparticles as seed to generate final palladium shell. In addition, the current study also involves synthesis of gold nanoshells on silica cores that are less than 100 nm diameter. Previous work has shown the successful synthesis of gold nanoshell on a ~200 nm silica core using the present seed mediated synthesis procedure. Gold nanoshells with a smaller core may find increased application in photo-thermal therapeutic studies. Finally, palladium nanoparticle assemblies generated on

indium tin oxide (ITO) coated glass surfaces are applied towards detection of Dopamine (DA), an important neurotransmitter in the mammalian central nervous system. The sensing performance of the present biosensor is measured electrochemically using differential pulse voltammetry (DPV) and impedance spectroscopy, at different concentrations of dopamine in solution. The biosensor has shown a remarkably low detection limit for DA and a linear response over a wide concentration range. In addition, specificity of this biosensor for DA detection is also explored in presence of ascorbic acid (AA).

## **COLL 527**

### **Charge transfer capabilities of hybrid metal: Semiconductor nanomaterials architectures**

**Rabeka Alam**, *alamr@geneseo.edu*. Chemistry, SUNY Geneseo, Geneseo, New York, United States

Visible light photocatalysis is a useful method for using solar energy to promote chemical reactions. Nanomaterials with hybrid metal – semiconductors architectures provide an unique system to perform such catalysis due to their interesting optical and electronic properties. Metal – semiconductor architectures were prepared by directly anchoring Au nanoparticles on the surface of CdSe quantum dots, nanorods, and nanoplatelets. This investigation focuses on optimizing the catalytic properties of Au tipped CdSe by varying the shape of CdSe and the size of Au nanoparticles. The photocatalytic activity of the hybrid Au-CdSe nanostructures are characterized via UV-Vis absorption and fluorescence spectroscopy. The structural properties of the hybrid materials have been studied using high resolution transmission electron microscopy and powder x-ray diffraction.

## **COLL 528**

### **Aerogels! Engaging undergraduate students in cross-disciplinary research**

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Aerogels are mesoporous materials with extraordinary properties that render them interesting to study at a fundamental level and useful for a wide variety of applications. The typical approach to fabricating an aerogel starts with formation of a colloidal solution that gels to form a continuous polymer network. The pores in the network are filled with a liquid mixture: substances that are left over from the precursor mixture or formed as byproducts of the condensation reactions. If the solvent mixture in the pores can be extracted from the gel matrix without causing significant pore collapse, an aerogel results. Understanding novel materials fully and utilizing them effectively requires expertise from multiple STEM fields. We began collaborating in 2001-02, each

contributing our discipline-specific experience. Working with faculty colleagues and undergraduate students, we have invented and patented a novel rapid supercritical extraction (RSCE) method for aerogel fabrication, undertaken fundamental studies of this process, and explored the use of RSCE aerogels for a number of applications, including chemical sensing, drag reduction, catalysis and fenestration. To date, we have involved 150 undergraduate students and several high-school students in aerogel research. Working as part of an intellectually vibrant and diverse cross-disciplinary team facilitates continued professional development of faculty members, stimulates and inspires students and fosters interest in STEM careers. This presentation will highlight ongoing projects in areas as diverse as employing catalytic aerogels to mitigate automotive pollution and designing works of aerogel art.

## **COLL 529**

### **Characterization of the factors that influence nanocrystal surface ligand exchange dynamics**

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With their unique optical and physical properties, colloidal semiconductor nanocrystals are used in a wide range of applications. Most applications require post-synthetic modification of the nanocrystal surface for compatibility with the intended environment. Despite the many recent advances in nanocrystal surface functionalization, an understanding of the ligand exchange reaction dynamics remains limited. This is because a typical ligand replacement process involves the introduction of a large excess of new ligand under conditions that promote fast, complete exchange of ligand molecules. In order to examine the factors, beyond concentration, that control the rates of ligand removal and attachment, we slowed the exchange reaction and studied it using established spectroscopic techniques. By monitoring the reaction as it occurs, we have determined that the exchange reaction can be controlled through ligand choice, solvent environment, and nanocrystal anisotropy. Using this increased understanding of ligand exchange dynamics, we have stabilized colloidal nanocrystals after partial ligand replacement and introduced consecutive ligand molecules to create mixed ligand monolayers on nanocrystal surfaces.

## **COLL 530**

### **Siloxanes as useful modification agents for inorganic oxides: Simple techniques and applications towards conformal, multi-functional interfaces**

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Over the past decade, the siloxane bond has seen increased use as a chemical functional group, despite being previously and mistakenly ignored due its incredible thermal stability. However, the siloxane bond readily reacts with acids and bases,

making it a prime candidate for reactions with inorganic oxides, whose interfaces contain such moieties. In this way, covalent attachment of a wide range of unique interfaces is possible through simple acid-base chemistry, given the large number of siloxane-containing molecules. Here, we explore several of these surfaces, such as those with negligible contact angle hysteresis, thermally and chemically resilient coatings, as well as scaffolding siloxanes which allow for the introduction of additional functional groups. The techniques used in these studies are simple, robust and versatile making them applicable to a number of different interfaces depending on the application.

## **COLL 531**

### **Tuning acidity of graphene oxide for the reduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> using physical hole defects**

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Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is an important chemical for bleaching in the pulp and paper industry as well as the production of detergents. 2.2 million tonnes are produced annually. Its industrial production is catalyzed by anthrahydroquinone (AHQ), an anthracene molecule with OH groups on either side of the central ring, in a homogeneous mixture where the economics of the process depends heavily on the regeneration of the catalyst and separation of H<sub>2</sub>O<sub>2</sub> from the solvents. Using density functional theory, we explore how this process might be catalyzed heterogeneously using other fullerene structures, like graphene oxide. We have found that the acidity of graphene oxide plays a large role in catalysis and that this acidity can be tuned by the size of the physical hole defect directly adjacent to surface OH-groups. This presentation will highlight the instrumental role that undergraduate research students have played in probing how different fullerene structures, such as pristine graphene oxide sheets, graphene oxide sheets with physical hole defects, and graphene nanoribbons, influence surface OH-group acidity and ultimately the activation energy to reduce O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub>. These results suggest an interesting case where we can modify the acidity of graphene oxide based catalysts as a function of the size of a physical hole defect to produce ideal catalytic conditions for specific reactions.

## **COLL 532**

### **Functional approach to solubility parameter computations**

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Solubility parameter (SP) methods have proven very useful in an array of theoretical and practical applications. From an applications standpoint, SPs are a practical and

convenient way to evaluate polymer solubility in organic solvents, as well as the miscibility of polymer-polymer and polymer-nanoparticle blends. While this approach has been applied in a multitude of polymer and material settings, current methods for accurately determining the SPs of a solute suffer from theoretical and computational deficiencies that have led to many on-going investigations that seek improvement in fundamental and applied solubility parameter theory. To overcome some of these issues, an approach that makes use of accurate solubility data to construct a three-dimensional solubility function,  $f$ , is presented. The principles of the functional solubility parameter (FSP) approach are discussed and procedures for generating the solubility function and FSPs are described using PCBM and P3HT solubility data. Recent results using intrinsic viscosity as a measure of solvent-polymer affinity for FSP calculations of the polyester polycaprolactone (PCL) are also presented.

### **COLL 533**

#### **Spectroscopic assessment of the conformational dynamics of the M2 proton channel**

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The M2 protein of the Influenza A virus mediates the acidification of the virion interior at low pH conditions, a step vital to viral replication. High-resolution structural studies reveal that the transmembrane (TM) portion of the M2 protein is composed of four identical helices, forming an asymmetric channel that opens and allows unidirectional proton passage when the environment of the virus becomes acidic. Due to many previous studies, we now know a great deal about the structural architecture underlying the proton conduction function of the M2 protein, especially the role of two pore-lining gates, the His37 and Trp41 tetrads. However, the conformational dynamics of the M2 proton channel, especially those controlling the rate of its action, have been much less studied, preventing us from achieving a complete understanding of its action mechanism. In this talk, we will discuss our recent efforts in this regards, with a focus on highlighting results obtained with both infrared (IR) and single-molecule fluorescence techniques. Taken together, these results suggest that a large-scale conformational motion near the Trp41 cluster may play a key role in regulating the proton conduction rate of the channel, as it allows more water molecules to fill the cavity below the His37 cluster.

### **COLL 534**

#### **Multilevel modeling of cellular networks in biomedicine**

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One of the main challenges of current biology is to integrate the available genetic, biochemical, molecular, and structural information into a physiologically relevant description of cellular and supracellular processes. Computational modeling has emerged as a promising tool for transforming molecular detail into a more integrated form of understanding complex behavior. In this talk, I will draw examples from the recent work of my laboratory to discuss the state-of-the-art on modeling of biological processes at different temporal and spatial scales, going from molecular interactions to the assembly of macromolecular complexes on DNA and the stochastic dynamics of the resulting gene regulation networks. I will discuss our recent results on the study of genetic and signal transduction networks, including gene regulation by the RXR nuclear receptor and signal processing in the TGF-beta pathway.

### **COLL 535**

#### **Interfacial ion atmosphere around highly charged surfaces in aqueous solution**

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The characteristics of the interface between highly charged surface in aqueous solution in the presence of multivalent metal ions are less than well understood. We have developed generalization of Manning condensation model that quantitatively describes the interfacial ion atmosphere around RNA and DNA in the presence of divalent and monovalent metal cations. Various predictions of the model would be tested against all-atom explicit solvent simulations, experimental data, and Manning model.

### **COLL 536**

#### **Integrative modeling at the protein-membrane interface**

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Biological membranes represent the selective barrier of every cell: they shape organelles, steer vesicles trafficking and modulate interactions with integral and peripheral proteins. Thus, capturing their complexity in terms of lipids composition, concentration and chemical features is crucial to accurately describe protein-membrane interactions. Molecular modelling and multiscale molecular simulations seamlessly integrated with biophysical/biochemical and structural biology experiments have the potential to characterize the protein-membrane interface at the molecular level. We used this approach to study the functional membrane-binding properties of several protein systems, as those involved in CoQ bio-synthesis at the mitochondrial inner membrane and human acyl protein thioesterases that catalyze S-depalmitoylation regulating protein trafficking across intracellular membranes.

### **COLL 537**

## Far from ideal: Specific binding in lipid phases

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The theory of receptor–ligand binding equilibria has long been well-established in biochemistry, and was primarily constructed to describe dilute aqueous solutions. In contrast, biologically and pharmacologically relevant protein–ligand interactions often occur in complex environments, including lamellar phases like membranes. The plasma membrane comprises a highly heterogeneous lipid "solvent" that varies over time (due to modulation by the cell) and varies over space (due to lamellar structure, domain formation within the membrane, and lipid sorting by transmembrane proteins). Traditional formalisms for receptor-ligand binding employ overly specific assumptions that are violated within this environment. These assumptions also make interpretation of calculated binding free energies more difficult. I will present a more generalized framework for predicting site occupancies at an arbitrary ligand concentration that discards and/or circumvents these assumptions.

Our theoretical framework separates ligand-solvent interactions from ligand-receptor interactions and treats both sets of interactions with equivalent rigor. Consequently, existing microscopic models for complex liquid mixtures (in the absence of protein) can be consistently incorporated. When combined with Alchemical Free Energy Perturbation calculations or other methods that decompose binding processes into separate legs of the thermodynamics cycle, this approach allows for an efficient and powerful prediction of dose-response across a range of concentrations. As an example, I will present occupancy predictions for cholesterol binding sites on various GPCRs, over a range of concentrations. These calculations used a fraction of the computational cost required by a physical pathway method like umbrella sampling. For lower-affinity sites, the non-ideality of cholesterol in the membrane introduces detectable and surprising signatures into the binding curve.

## COLL 538

### Computational design of dendronized nanoparticles

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Many drug delivery strategies are dependent upon the adsorption and transport of charged, therapeutic biomolecules. Our focus is steered towards developing stable nanoparticles (NPs) encompassing multiple molecular species that endow

electrostatically-induced interfacial binding of specific biomolecules. We are interested in understanding the role of the architecture and composition of the molecular species on the morphological characteristics of the NPs. We study multicomponent NPs encompassing phospholipids and lipids bearing hyper-branched polyelectrolytic (namely, polyamidoamine (PAMAM)) dendrons via the Molecular Dynamics simulation technique. For each dendron generation, we identify a threshold critical concentration of dendrons, beyond which we obtain unstable NPs. Additionally, we quantify the driving forces responsible for unstable NP morphology under various circumstances. Our observations could potentially frame an understanding of forces incurred by a mixed NP morphology due to hyper-branched polyelectrolytes. This can guide experimentalists in designing stable NP morphologies optimized with interfacial binding abilities.

### **COLL 539**

#### **Principles governing catalytic activity of self-assembled short peptides**

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Molecular self-assembly provides a chemical strategy for the synthesis of nanostructures by using the principles of nature, and peptides serve as the promising building block to construct adaptable molecular architectures. Recently, a series of hepta-peptides with alternative hydrophobic and hydrophilic residues were reported to form amyloid-like structures, which were capable of catalyzing acyl ester hydrolysis with remarkable efficiency. However, it remains elusive about the atomic structures of the fibrils: what is the origin of the sequence-dependent catalytic activity? How does the ester hydrolysis catalyzed by the fibril? In this work, the atomic structure of the aggregates was determined by using molecular modelling and further validated by solid-state NMR experiments, where the fibril with high activity adopts twisted parallel configuration within each layer, and the one with low activity is in flat antiparallel configuration. The polymorphism originates from the interactions between different regions of the building block peptides, where the delicate balance between rigidity and flexibility plays an important role. We further show that the p-nitrophenylacetate (pNPA) hydrolysis reactions catalyzed by two different fibrils follow similar mechanism, and the difference in microenvironment at the active site between the natural enzyme and the present self-assembled fibrils should account for the different catalytic activities. The present work provides atomic understanding of the structure and function of self-assembled fibrils formed with short-peptides, and thus sheds new insight on designing aggregates with better functions.

### **COLL 540**

#### ***De novo* design of functional proteins**

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The de novo design of proteins with bespoke structures and functions critically tests our understanding of the underlying chemical processes. Impressive progress has been made in the design of proteins that fold into predetermined three-dimensional structures, and in the design of proteins that engage in protein-protein interactions. By contrast, the classical problem of designing proteins that tightly and specifically bind densely functionalized, flexible small molecules rich in polar atoms has proven very difficult. We are using a fragment-based approach to design ligand-binding proteins: First, the ligand of interest is deconvoluted into a collection of fragments. In the second step, we use unsupervised learning methods to find the modes by which proteins interact with such fragments to assure they are efficiently sampled. To design a ligand-binding protein, we construct a large number of target backbones, using parametric equations to define the backbone conformation. The sequence of the binding site and the orientation of the target ligand within a backbone are next designed in a hierarchic set of computations. We begin by satisfying the most difficult interactions involving the ligand's polar groups, which are need to be accommodated by highly directional hydrogen-bonded interactions. The computation then progresses to optimize shape complementarity and to introduce hydrophobic interactions; in parallel, the core of the protein is designed within the same calculation to assure that the designed tertiary structure supports the precise positioning of the critical sidechains in the active site. We demonstrate the success of this approach through the design of metallo-organic cofactors and a protein that binds the FDA-approved factor Xa-binding drug, apixaban. Crystal structures of the complexes confirm the designs and demonstrate the specificity of the design.

## **COLL 541**

### **Pt-Sn clusters on TiO<sub>2</sub>: Growth and activity for selective hydrogenation reactions**

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Pt-Sn bimetallic catalysts are known to be selective catalysts for the hydrogenation of unsaturated aldehydes to the corresponding alcohols, which are important intermediates in the pharmaceuticals, flavor and fragrance industries. These catalysts are therefore also good candidates for the selective hydrogenation of furfural to furfuryl alcohol, which is a reaction of interest in biomass reforming. The desirable selectivity of oxide-supported Pt-Sn clusters compared to pure Pt has been attributed to a number of factors, including electronic effects, bifunctional effects, and the role of Sn oxide. Vapor-deposited Pt-Sn clusters supported on TiO<sub>2</sub>(110) are investigated in ultrahigh vacuum (UHV) as model systems for understanding selective hydrogenation of furfural, and catalytic activity is studied in a microreactor (P~ 1 atm) coupled to the UHV chamber. Scanning tunneling microscopy experiments demonstrate that exclusively bimetallic clusters can be prepared by sequential deposition of Sn and Pt. Strong interactions between Sn and TiO<sub>2</sub> lead to oxidation of Sn at the cluster-support interface

as well as evidence for reduction of titania. Due to the lower surface free energy of Sn compared to Pt, the surfaces of the bimetallic clusters are Sn-rich, regardless of the order of deposition. Studies of furfural hydrogenation on Pt-Sn alloy surfaces show that the addition of Sn to Pt increases selectivity for furfuryl alcohol and prevents the catalyst from deactivating.

## **COLL 542**

### **Chemistry of TiO<sub>2</sub> surfaces in aqueous and ambient environments**

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Earth-abundant metal oxide nanocrystals have attracted a great deal of attention for environmental remediation and photocatalysis because they are inexpensive, they are typically very stable under reactive conditions, and their semiconducting nature enables efficient generation of long-lived photocarriers that can initiate chemical reactions. Nevertheless, an atomic-scale understanding of their reactivity in ambient and aqueous environments has proven elusive. I will review our work in developing “new eyes” for nanocatalysis to enable an atomic-scale understanding of their reactivity in ambient and aqueous environments.

Previous researchers have shown that fluorine-containing precursors can be used as shape-directing agents in TiO<sub>2</sub> synthesis, leading to the production of highly reactive crystals of controlled shape. But is this high reactivity a function of the exposed facets, the fluorine termination of the crystals, or both? To probe this question, we have produced passivated TiO<sub>2</sub> surfaces in which fluorine blocks the undercoordinated surface cation sites. Nevertheless, these fluorine-terminated TiO<sub>2</sub> surfaces display higher photoreactivity than comparable “clean” surfaces. Possible origins of this behavior will be discussed.

We have also investigated the structure of solution-deposited monolayers on TiO<sub>2</sub> and demonstrated a rational approach to tuning intermolecular interactions and enabling long-range ordering. We show that simple electrostatic insights can be used to engineer away unfavorable intermolecular interactions, producing monolayers with exceptional long-range ordering. Quantitative measurements of the intermolecular interaction energies from molecularly resolved STM images are a factor of ~7 larger than those predicted by dispersion-corrected density functional theory (DFT). This finding suggests a new path to the production of highly ordered monolayers and superstructures of large molecules.

## **COLL 543**

### **Interfacial electron transfer of perylene based chromophores bound to TiO<sub>2</sub>**

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Interfacial electron transfer or heterogeneous electron transfer is the key to many applications, such as photocatalysis, photovoltaic, energy storage, and molecular electronics. Photoabsorption and interfacial electron transfer of perylene based chromophores binding on TiO<sub>2</sub> anatase with different bridge group is frequently studied to understand the process. This perspective reports recent developments on measuring ultrafast electron transfer dynamics with ultrafast transient absorption, and high energy vibrational mode with pump-degenerate four wave mixing. The improvements in minimizing the group velocity dispersion on the pump and probe beam make it possible to measure shorter dynamics of electron transfer on transient absorption measurement. While the coherent artifact measurement gives a fixed universal time zero for all wavelengths on a TA map.

#### **COLL 544**

#### **Carboxylic anchoring dyes do not adsorb directly onto TiO<sub>2</sub> particles in protic solvents**

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Adsorption of the carboxylic anchoring dye, para-ethyl red (p-ER), onto TiO<sub>2</sub> nanoparticles in protic vs aprotic solvents was studied *in-situ* using the surface-specific technique, second harmonic light scattering (SHS). Two different adsorption schemes were proposed to account for p-ER interactions with TiO<sub>2</sub> under different solvent environments. In aprotic solvents, p-ER adsorbs directly onto TiO<sub>2</sub>. Conversely, in protic solvents, in which solvent molecules bind stronger than p-ER with TiO<sub>2</sub>, the dye molecules adsorb onto the solvent shell around the particle but not directly to the TiO<sub>2</sub> surface. In addition, a portion of the p-ER molecules forms hydrogen bonds with the protic solvent molecules. The two different adsorption models reproduce the measured adsorption isotherms detected by SHS. Specifically, the p-ER molecules adsorb with a smaller free energy change and a larger density in protic solvents than in aprotic solvents. Our results indicate that protic solvents are undesirable for administering adsorption of carboxylic dyes in dye-sensitized solar cell applications as the dye molecules do not directly adsorb onto the TiO<sub>2</sub> particle.

#### **COLL 545**

#### **Well-defined nanographene-based systems for catalytic applications**

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Improving energy efficiency of electrocatalytic CO<sub>2</sub> conversion to useful chemicals poses a significant scientific challenge. Recently we have reported on using a derivatized colloidal nanographene as a ligand to form a rhenium-based molecular complex to tackle this challenge, leading to significantly improved CO<sub>2</sub> reduction potential. In this work, we have performed theoretical computations, based on dispersion-corrected density functional theory, to investigate the roles of the nanographene ligand in the reduction and the reaction pathways. Remarkably, our results show that the rhenium metal center merely provides a binding site for CO<sub>2</sub> and a conduit for electron transfer between the nanographene ligand and the substrate instead of changing its own oxidation state in the processes. The size-dependence of the graphene ligand on the redox and catalytic properties of the system have been explored. The implications of our findings for electrocatalysis and photocatalysis using similar graphene-based ligands will be discussed in this presentation.

## **COLL 546**

### **Activating single-layer MoS<sub>2</sub> for conversion of syn gas to higher alcohols: Insights from theory**

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There is an on-going quest for cheap and abundant catalysts that would facilitate hydrogenation of CO<sub>2</sub>, an abundant greenhouse gas in the Earth's atmosphere, and CO, a poisonous exhaust, into fuels and chemicals that are traditionally derived from petroleum. Interestingly, the high attention paid to two dimensional (2D) materials, because of their promising optoelectronic properties has also resulted in their consideration as promising catalysts for a variety of reactions. This is not surprising because of the high surface to volume ratio, structural stability and flexibility, and possible large-scale production of 2D materials. In this talk I will present results of our density functional theory based calculations of the hydrogenation of CO and CO<sub>2</sub> to methanol, ethanol and methane on a popular transition metal dichalcogenide: molybdenum disulfide (MoS<sub>2</sub>). I will highlight the important role that defects [1] (S vacancy) and transition metal nanoparticles [2] play without which the basal planes of these materials would remain inert. It will be shown that while S vacancies could facilitate CO hydrogenation, the reactivity and product selectivity is further improved by both a Cu substrate or adsorbed Au nanoparticles. The relative importance thermodynamics and kinetics in predicting activity and reaction selectivity and turn over frequencies will also be discussed. Insights obtained from characteristics of the local electronic structure, calculated using density functional theory, provide some descriptors of reaction activity and product selectivity. Contact will be made with ongoing experiments.

## COLL 547

### **Modulating $\pi$ - $\pi$ stacking of naphthalene bisimide ligand architectures for electron transfer in nanocrystal hybrid materials**

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Investigation of charge transfer in quantum dot (QD) systems is of great interest due to applications in light emitting devices, photocatalytic systems, and solar cells. To optimize these materials, the relationship between capping ligand and charge transfer has been studied. A series of ligands were specifically designed to allow for direct comparison between  $\pi$ - $\pi$ stacking of electron accepting naphthalene bisimide (NBI), where one ligand allows for these interactions at high surface coverages, and a comparable ligand uses steric bulk to inhibit these interactions. These hybrid materials were studied using UV-Vis, fluorescence, and transient absorption spectroscopy. Interestingly, the sample with the fastest electron transfer was not the sample with the most NBI  $\pi$ - $\pi$ stacking, it was instead where these ligands were mixed amongst oleic acid, breaking up H-aggregates between the NBI groups. This phenomena is most likely due to H-aggregate formation between the NBI groups, as this would lead to alterations in the HOMO/LUMO gap between the aggregated and non-aggregated forms of the ligands on the QD surfaces.

## COLL 548

### **Carbonic anhydrase inhibitors-conjugated colloidal systems for doxorubicin delivery to hypoxic tumors**

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The uncontrolled growth of tumors often places their cells far away from blood vessels, thus becoming hypoxic. Hypoxia triggers the expression of many proteins, pumps, and transporters required for cellular adaptation to low  $P_{O_2}$  and survival. Among them are the membrane-bound isozymes of carbonic anhydrase (CA), especially CA IX. CA IX is over-expressed in many hypoxic tumors and was confirmed as a valuable epitope for targeting of drug delivery systems to these malignancies [1-3].

We will present our most recent results towards targeting of two types of colloidal nanoparticles, namely gold nanoparticles and liposomes, towards hypoxic tumors via

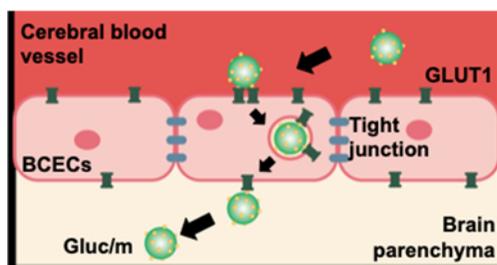
conjugation of these colloidal nanosystems with CA IX inhibitors. We will present the chemistries used for conjugation, the formulation strategies and the in vitro and in vivo results obtained with these targeted nanosystems towards doxorubicin delivery to breast and ovarian hypoxic tumors.

## **COLL 549**

### **Quantitative analysis of targeting ability for glucose decorated polymeric micelle penetrating blood-brain barrier**

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Precisely programmed block copolymers self-assembly nano-structures such as micelles, vesicles and nanotubes in aqueous solution, have attracted increasing interests from all over the world as the biomaterial which has potential mainly for medical applications. Most typical example is the polymeric micelles with distinctive core-shell architecture, have great potential as drug delivery systems (DDS) to cancer and other intractable diseases. Hydrophilic shell provides polymeric micelles with stealth effect against foreign body recognition system in the body, while inner core works as a nano-reservoir of various cargo compounds. The polymeric micelle provides a promising system for delivery of therapeutic or diagnostic agents to diseased parts of the body, particularly solid cancers which have blood vessels with enhanced permeability, and some clinical trials are currently in progress. Though the polymeric micelle also has a potential for therapeutics of central nervous system (CNS) disorders by delivering antibodies, nucleic acids, proteins and so on, through the barrier of a blood vessel with unenhanced permeability remains a challenging task. Especially, for the development of DDS to the CNS, blood brain barrier (BBB) is the obstacle, which excludes most drugs with the tight junction between brain capillary endothelial cells (BCECs). Recently our group developed glucose decorated polymeric micelles (Gluc/m) targeting glucose transporter 1 (GLUT1). GLUT1 is highly expressed on the BCECs and its localization can be manipulated by controlling the blood glucose level. Optimizing glucose ligand density on the surface of Gluc/m and glycemic control, Gluc/m achieved 6 %dose/g accumulation in the brain and attained its high BBB penetrating ability. For further development of Gluc/m as a carrier of various types of drugs, chain length of hydrophilic segment of polymeric micelle was changed to increase the structural stability of Gluc/m and BBB penetration of Gluc/m was investigated.



Conceptual scheme of BBB penetration of Gluc/m

## COLL 550

### Control of gold nanoparticle growth on ferritin proteins

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Novel biomaterial heterostructures synthesized from cage-like ferritin proteins have seen an increased interest due to their potential uses in biomedical and environmental remediation applications. These structures offer controllable building blocks, where the nature of the protein cage can be altered, the native iron oxide core replaced with other transition metals, and the attachment of plasmonic nanoparticles on the interior or exterior of the cage can be achieved. To further the understanding of the conductive nature of ferritin, we aimed to generate a plasmonic gold nanoparticle (AuNP) on the exterior of a 100% heavy chain ferritin cage (HFtn). Both our group and others have generated AuNP on primarily light chain ferritin cages (Ftn), an attachment which is expected to occur on a lone cysteine residue residing in the pores of the protein. However in HFtn, more cysteine groups, located both on the pore and on the surface of the protein, alter the AuNP growth strategy. Characterized by UV-Vis, TEM, and DLS the results show that modified cysteine groups prevent the growth of AuNP but the presence of too many cysteine groups results in aggregated heterostructure solutions, induced by inter-structure Au-S attractions. By mutating the most solvent-exposed cysteine to an arginine (C90R-HFtn), this work demonstrates a “goldilocks” protein that supports AuNP growth but remains stable as a colloid heterostructure.

## COLL 551

### Bioconjugation of nanoparticles and their applications

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A critical aspect of the use of nanoparticles in biomedical applications relates to their surface chemistry. The nature of interaction of ligands with the nanoparticle surface, their hydrophilicity/hydrophobicity, their length, charge and density around the nanoparticles surface are critical factors that contribute to the performance of nanoparticles in biomedical applications. This talk will discuss a series of nanoparticles designs created in our lab where accurate manipulation of the nanoparticle surface chemistry results to functional nanoparticles and defines their fate in various biomedical systems.

## **COLL 552**

### **Antibody-targeted protein nanoparticles: Selective activation of the antioxidant response element**

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The mechanisms by which cells sense and respond to varying levels of environmental oxygen are amongst the most conserved in all of biology and have recently been recognized with the 2019 Nobel Prize in Physiology or Medicine. While detection of hypoxia has received the most attention, the transcriptional response to oxidative stress, driven largely by a cis-acting element in the promoters of a number of antioxidant and detoxifying enzymes, is arguably of similar importance to the survival of multicellular organisms. While a number of electrophilic small molecule drugs like the polyphenol curcumin have been identified as activators of the antioxidant response element (ARE), their clinical utility has been limited by poor pharmacokinetics and rapid entry into nearly all cell types. Given the ubiquitous nature of the ARE, these characteristics have largely prevented selective activation at intended sites of therapeutic action and inevitably resulted in dose-limiting off-target side effects. While a number of drug delivery systems have been adapted to increase the plasma stability of curcumin and/or facilitate its distribution to tumors or sites of oxidative stress, none have convincingly shown the ability to selectively activate antioxidant gene expression in cells expressing specific surface determinants

Here we report the development of an affinity-ligand targeted protein nanoparticle system capable of accomplishing this elusive goal. Physical characterization of the resulting nanoparticles included measuring size and morphology via dynamic light scattering (DLS) and scanning electron microscopy (SEM). The quantification of conjugation efficiency to the particle surface, performed using radioactively labeled antibodies, together with biodistribution experiments, allowed for an optimized system to be developed facilitating increased lung targeting following systemic administration.

Finally, encapsulating the hydrophobic small molecule, curcumin, we demonstrate a sustained and selective activation of the ARE signaling pathway in endothelial cells.

## **COLL 553**

### **Self-assembled bio conjugated silica assembly in the treatment of drug resistance cancer**

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Drugs resistance by cancerous cells are often said to be more responsible for cancer patient's death. Tumor cells develop drug resistance to chemotherapeutic drugs that lead to a failure or inefficient action of the drug on cancer cells and unregulated action on normal cells. The widely explored bio conjugation strategies are explored to advance the controlled drug delivery and duration of drug delivery, while targeting explicit locations of the body (such as tumors) for therapy, to get rid from drug resistance by the tumors. We aimed to develop bioconjugated silica nano assembly that improve anticancer drug targeting and tackle the drug resistance without moderate toxicological effects. In our preclinical toxicology experiments, we utilized the intended clinical administration route, i.e. intravenous injection, throughout the studies with the normal and HTC116/DR tumor-bearing mice models. The overall study revealed best strategy against drug resistance cancer cells and tissues developed by these nano assembly. The nano assembly is an encapsulation of various anticancer moieties in single modality to reduces the toxic drug concentration in normal host tissues and increases the concentration of active drug within the tumor. The present work achieved this goal and overcome the barrier of targeting nanomedicine using antibodies. Therefore, we developed here the alternative targeted multi cargo delivery systems which is important implications for future novel anticancer therapeutics. *In vivo* trails with exact chemoresistance tumor model with different types of tumors such as breast tumor is currently being developed by our group to show the efficacy of present formulation on various cancers.

## **COLL 554**

### **Membrane wrapped plasmonic nanoparticles quantify cell surface receptor clustering and reveal lipid-mediated intracellular fates**

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Zwitterionic lipids when self-assembled around a noble metal nanoparticle can reduce corona formation and keep surface conjugated targeting moieties accessible for interacting with cell surface receptors. We demonstrate in this paper that the unique optical properties of the nanoparticle core facilitate not only a characterization of nanoparticle uptake and binding but also allow for a quantification of the spatial

heterogeneity of the targeted cell surface on the single cell level. We show for the example of the epidermal growth factor receptor (EGFR) that the distance-dependent plasmon coupling between nanoparticles targeted to cell surface receptors allow for a reliable quantification of receptor clustering. We validate and benchmark the plasmon coupling approach with fluorescence superresolution fluorescence microscopy. In addition to providing superb optical properties, membrane-wrapped nanoparticles are nanoscale scaffolds that allow for a rational variation of the ligand (in this case epidermal growth factor, EGF) presented on the surface. We took advantage of the nanoparticles' ability to resolve EGFR clustering and to control the local density of EGF to demonstrate that EGF ligand density and nanoparticle clustering cooperate to achieve a multivalent amplification of EGFR activation. In addition to passivating plasmonic nanoparticle cores, some lipids are by themselves bioactive and can target specific surface receptors. We show in this paper that ganglioside – GM3 – functionalized nanoparticles allow a selective targeting of CD169-expressing myeloid cells (macrophages and dendritic cells) *in vitro* and *in vivo*. The GM3-CD169-controlled intracellular fate is further investigated on the single cell level. We demonstrate that the lipid-receptor interactions allow targeting of non-lysosomal compartments that share distinct similarities with virus containing compartments.

## **COLL 555**

### **Role of EGFR clustering in ROS-mediated signal activation**

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The epidermal growth factor receptor (EGFR) is overexpressed and dysregulated in many cancers and its activation is related to the spatial and temporal regulation of the receptor. Formation of EGFR oligomers and higher-ordered structures on the length scale of tens to hundreds of nanometers are critical for modulating cell signaling outcomes. An aspect of the spatial regulation of EGFR that is not well understood is the role of EGFR clustering in reactive oxygen species (ROS) mediated receptor activation. To address the interplay between EGFR clustering and ROS generation, we use plasmonic gold nanoparticles (NPs) conjugated with EGF as a tool for controlling the multivalent presentation of EGF ligands on the NPs. In this work, we will demonstrate that NP-EGF of different sizes and ligand densities can provide a viable strategy for controlling the spatiotemporal regulation of activated EGFR and ROS mediated EGFR activation.

## **COLL 556**

### **SNAP, click, and catch: New strategies for nanocrystal bioconjugation**

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Functionalization of inorganic nanocrystals is essential for their practical application in living systems, but standard bioconjugation chemistry is often incompatible with nanocrystals and their passivation layers. We report 3 new methods for covalent attachment of biomolecules to inorganic nanocrystals, designed to maintain nanocrystal optical properties and permit protein-specific targeting in cells. First, we have synthesized novel covalent protein labeling ligands that are specially optimized for use with inorganic nanocrystals.<sup>1</sup> These hydrophilic benzylguanine ligands (i.e., SNAP tags) covalently modify SNAP tag protein chimeras within live cells ~10-fold more efficiently than existing SNAP tags. This specific and improved protein labeling allows intracellular single-molecule imaging of kinesin motors and dual-color quantum dot (QD) labeling of kinesin heads to track its stepping movement in live cells. Second, the copper-catalyzed azide-alkyne cycloaddition (CuAAC) is among the most useful methods for ligating molecules to surfaces, but has been largely useless for QDs because Cu ions quickly and irreversibly quench QD fluorescence. To discover non-quenching synthetic conditions for Cu-catalyzed click reactions on QD surfaces,<sup>2</sup> we developed a combinatorial fluorescence assay to screen over 2000 reaction conditions to identify conditions for complete coupling without significant quenching, which are compatible with both common QD polymer surfaces and with various azide/alkyne pairs. Applied to the conjugation of a K<sup>+</sup> channel-specific peptidyl toxin to CdSe/ZnS QDs, we synthesize unquenched QD conjugates and image their specific and voltage-dependent affinity for K<sup>+</sup> channels in live cells. Finally, we have exploited SpyCatcher-Spytag isopeptide bond formation reactions to label 2-dimensional S-layer protein sheets both *in vitro* and on the surfaces *C. crescentus* bacteria. S-layer sheets displaying SpyTag sequences show high labeling efficiencies (>70%) of either SpyCatcher-coated upconverting nanoparticles (UCNPs) or QDs. This method combines 2 genetically encoded elements and is orthogonal to both SNAP and click bioconjugation, allowing a significant expansion of complexity possible in inorganic-living hybrids.

## **COLL 557**

### **Utilizing meta-analysis to understand the cellular toxicity of cadmium containing quantum dots**

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Understanding the complex relationships between the properties of engineered nanomaterials such as nanoparticles and their toxicity is critical for both environmental and health risk analysis. This task continues to be severely hampered by inherent material diversity, heterogeneity of published data, and limited sampling within individual

studies. A meta-analytical approach for analyzing pertinent knowledge from published studies was previously developed to focus on the cellular toxicity of Cd-containing semiconductor quantum dots (QDs). This encompassed more than 300 publications and yielded 1,741 cell viability-related data samples, each with 24 qualitative and quantitative attributes describing the material properties and experimental conditions. Applying random forest regression models to this data showed that toxicity was closely correlated with several QD surface properties including shell material, ligand and surface modifications, diameter, assay type, and cellular exposure time. Subsequently, a Bayesian Network (BN) resource for meta-analysis of nanomaterial toxicity was also tested for exploring the cellular toxicity of Cd-containing QDs. Here, the dataset was significantly expanded to include 517 publications comprising 3,028 cell viability data samples and 837 IC<sub>50</sub> values. BN-QD toxicity models were developed using both continuous or numerical and categorical attributes and confirmed many of the previous findings along with providing insight on unique material-toxicity conditional relationships. Continued data extraction has now expanded the base data set to encompass ca. 600 published reports. We will report on the analysis of this expanded data set and how it correlates with previous findings. Unique subsets of the overall data set will also be subjected to more focused analysis to better understand the nuances of complex conditional toxicity relationships. This approach of integrating quantitative and categorical data from the literature can help develop methods for predicting the toxicity of engineered nanomaterials. Moreover, the body of evidence for a given nanomaterial can be continuously updated as more studies become available.

## **COLL 558**

### **Bespoke functional polymer colloids via polymerization-induced self-assembly**

**Steven P. Armes**, *s.p.ames@sheffield.ac.uk*. Univ of Sheffield Dept of Chem, Sheffield, United Kingdom

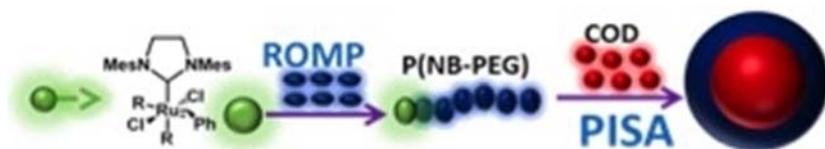
Polymerization-induced self-assembly (PISA) is a powerful and versatile technique for the rational synthesis of concentrated dispersions of block copolymer nano-objects of controllable size, shape and surface chemistry. PISA can be conducted in aqueous media using reversible addition-fragmentation chain transfer (RAFT) polymerization. In this context, RAFT aqueous dispersion polymerization formulations are rather scarce because there are relatively few water-miscible vinyl monomers that form water-insoluble polymers. However, such syntheses afford various examples of stimulus-responsive nano-objects that undergo morphological transitions on varying the solution pH or temperature. For example, herein we report a new diblock copolymer of fixed composition that can form spheres, worms or vesicles simply by varying the solution temperature. A second aqueous PISA formulation affords new cationic sterically-stabilized nanoparticles that are exceptionally tolerant towards added salt, remaining colloidally stable at up to 4.0 M KCl. Finally, we show that cross-linked spherical nanoparticles prepared directly in mineral oil can act as highly lubricious additives that enable the formulation of next-generation ultralow viscosity engine oils.

## COLL 559

### Polymerization-induced self-assembly (PISA) of 1,5-cyclooctadiene using ring opening metathesis polymerization (ROMP)

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Ring opening metathesis polymerization (ROMP) is a technique that allows the synthesis of well-defined linear polyolefins. Polymerization-induced self-assembly (PISA) involves the synthesis of amphiphilic block copolymers: a hydrophilic block is first polymerized homogeneously in solution (usually water) followed by polymerization of a second hydrophobic block, resulting in a diblock copolymer that self-assembles. We present the development of ROMP in PISA through the synthesis of amphiphilic block polyolefins based on P(NB-PEG)-*b*-PCOD using a new water-soluble PEGylated ruthenium alkylidene catalyst that was designed to undergo phase transfer from the aqueous phase to the monomer droplets or polymer particles following activation. In the first step, a water-soluble modified-norbornene monomer was polymerized in water, then 1,5-cyclooctadiene (COD) was added to the system to produce amphiphilic block polyolefins. By varying the concentrations of hydrophilic versus hydrophobic monomer, stable latexes with final particles of ~200 nm diameter were prepared. The formation of amphiphilic block polyolefins was confirmed from GPC analysis, showing in every case quite clean chain extensions. TEM analysis confirmed that spheres particles were obtained under the conditions presented here. The ratio of the hydrophilic:hydrophobic monomers plays an important role in determining particle size. In order to achieve relatively small particles (~200 nm), a minimum concentration of hydrophilic monomer is needed (30 mol%). It is established that the PEG chains present on NB-PEG monomer provide stability to the particles.

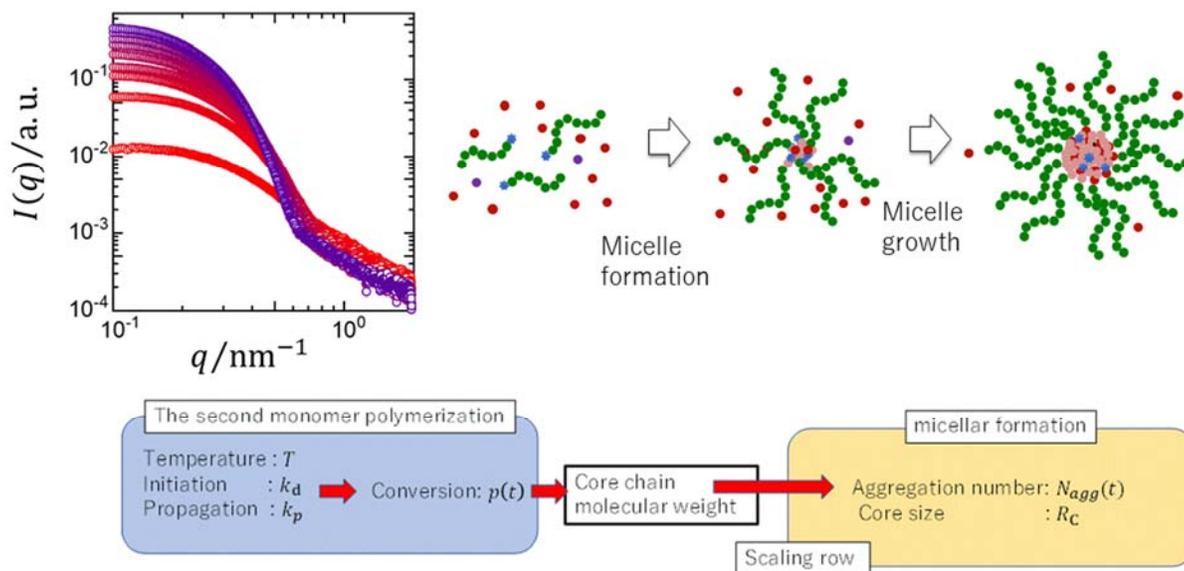


## COLL 560

### Kinetical analysis of RAFT-polymerization-induced self-assembly by decoupling chain propagation and micelle formation

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Upon extending a hydrophobic polymer chain from the end of a preceding hydrophilic chain in aqueous solutions, the resultant block copolymers may eventually undergo self-assembly owing to microphase separation and further chain propagation continues in the newly formed hydrophobic polymer rich domain. This process is referred to as polymerization-induced self-assembly (PISA). Its kinetics consists of polymerization and micelle formation/growth, possibly leading to a highly complex process of structural development. In this study, we studied PISA in aqueous solution accompanied by the reversible addition fragmentation chain transfer (RAFT) polymerization of poly(*N*-acryloylmorpholine)-*b*-poly(*N*-acryloylthiomorpholine). By using *in situ* small-angle X-ray scattering (SAXS) and nuclear magnetic resonance spectroscopy (NMR), we found that the kinetics of the two above-mentioned events can be decoupled when the following conditions are satisfied: (i) the time scale of the micelle formation/growth is much shorter than that of the polymerization, (ii) the micellar core is swollen by solvent so as not to interfere with the monomer supply into the core, and (iii) the core formation or segregation of the hydrophobic block occurs at quite an early stage. As a result, the rate constants characterizing RAFT do not change during PISA and the overall micellar structural development can be quantitatively described by a simple kinetic model.

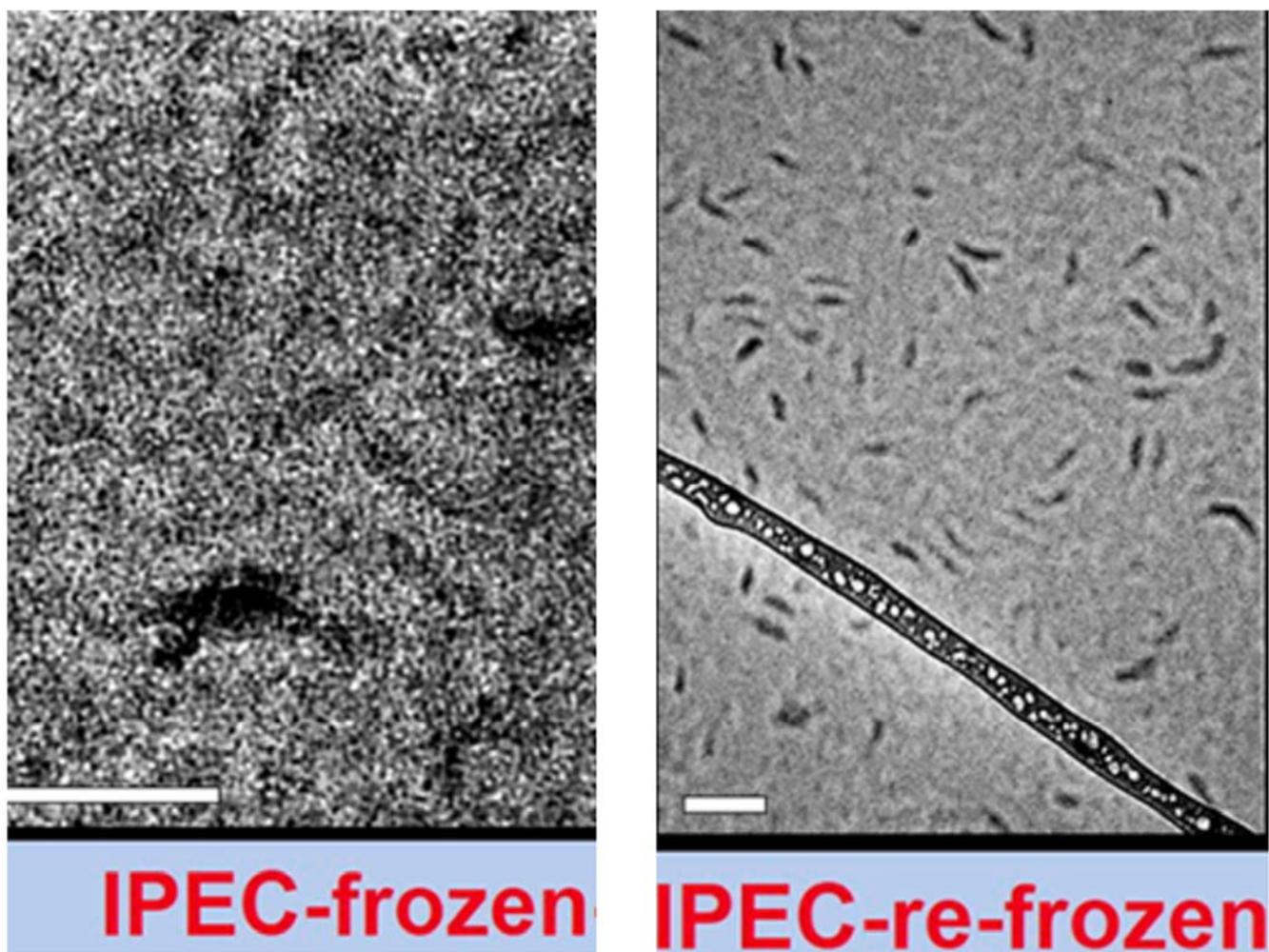


**COLL 561**

### **Triggering and recycling of nonequilibrium micelles**

*Claudia Dähling*<sup>1</sup>, *Alexander Steinschulte*<sup>1</sup>, *Judith Houston*<sup>3</sup>, *Aurel Radulescu*<sup>4</sup>, *Markus Drechsler*<sup>5</sup>, *Monia Brugnoni*<sup>1</sup>, *Hideharu Mori*<sup>6</sup>, *Dmitry Pergushov*<sup>7</sup>, **Felix Plamper**<sup>2</sup>, *felix.plamper@chemie.tu-freiberg.de*. (1) Institute of Physical Chemistry, RWTH Aachen University, Aachen, Germany (2) Institute of Physical Chemistry, TU Bergakademie Freiberg, Freiberg, Germany (3) European Spallation Source, Lund, Sweden (4) Juelich Centre for Neutron Science, Garching, Germany (5) Univ Bayreuth MC2, Bayreuth Bayern, Germany (6) Yamagata University, Yonezawa, Japan (7) Lomonosov Moscow State University, Moscow, Russian Federation

It is challenging to reliably create self-assemblies of different morphologies of the same polymer at the same final conditions (same ingredients, composition, temperature, etc.). It involves pathway-dependent preparation strategies geared towards defined nonequilibrium states. In the best case, the resulting metastable micelles would be kinetically stable for a long time, but would allow a triggered transition at will, which would entice pronounced property changes of the colloidal suspension on the way towards equilibrium at otherwise constant conditions. Even more challenging is the recreation of the original nonequilibrium micelles. As a solution to these problems, we propose an interpolyelectrolyte complex (IPEC) exhibiting spherical star-like or cylindrical micelles in the same conditions. This method relies on a temperature-induced structural change at equilibrated conditions due to the presence of a plasticizer. Removal of the plasticizer leads to a kinetic freezing, preserving some morphological features also at other conditions, where these micelles are not the equilibrium structure. Then, addition of plasticizer allows a return to the equilibrium state. This preparation and triggering cycle can be repeated at will, envisioning possible application in nanotechnology or triggered-release applications.



Original nonequilibrium micelles (left) and micelles after triggering (right) towards spherical micelles and reestablishing the nonequilibrium state (both are cryo-TEM images; scale bar 100 nm)

## **COLL 562**

### **Block copolymer micelles modulated by ionic liquids: Thermodynamics and structure**

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Ionic liquids (ILs), organic salts that are fluid at ambient conditions, are a novel class of compounds with a combinatorially great chemical diversity and unique properties. The very low volatility and high thermal and chemical stability that many ILs exhibit render them promising as solvents in diverse applications. We are interested in the self-

assembly properties in ionic liquids of block polymers, in particular those of the poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) family, commercially available as Poloxamers or Pluronics. We consider here aqueous solutions of a relatively hydrophobic PEO-PPO-PEO block copolymer (Pluronic P123) with the representative ionic liquids ethylammonium nitrate (EAN) (protic IL) or 1-butyl-3-methylimidazolium tetrafluoroborate (BmimBF<sub>4</sub>) (aprotic IL). We report on the amphiphilic block copolymer micellization thermodynamics (obtained from isothermal titration calorimetry, ITC) and micelle structure (obtained from small-angle neutron scattering, SANS), and discuss the observed IL effects in the context of the underlying intermolecular interactions between PEO-PPO-PEO and IL, PEO-PPO-PEO and water, and IL and water. We further compare the effects of ionic liquid electrolytes to those of classic electrolytes.

### **COLL 563**

#### **Do we understand the early stages of self-assembly in copolymer materials?**

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Process-directed self-assembly refers to processes that reproducibly trap the kinetics of structure formation that ensues after a sudden change (“quench”) of the thermodynamic state into a desired, (meta)stable target state. In this context, the short-time kinetics of structure evolution is important because it templates the morphology at later stages, but it poses challenges for a theoretical description in terms of continuum models such as dynamic SCFT or D-DFT.

Examining simple, prototypical examples, we highlight the importance of the early stage kinetics and illustrate the difficulties of dynamic SCFT to describe collective structure formation on the time scale of the single-chain relaxation time. Strategies how dynamic SCFT can be generalized to include the consequences of the subdiffusive short-time dynamics of the individual chains for the collective kinetics will be discussed.

### **COLL 564**

#### **Microfluidics synthesis of drug-loaded hybridosomes**

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The design of nanoscale reservoirs for efficient delivery of drugs and nucleic acids to cells is an enduring challenge in materials for medicine. Drug-loaded liposomes and polymersomes have enabled numerous FDA approved systems for several diseases. However, many of the applications of these self-assembling molecular materials encapsulating hydrophobic drugs are discontinued. This is because small hydrophobic drugs are difficult to disperse in either liposome or polymersome membranes tending to

aggregate and crystallize out of the nanoscale reservoirs. In this work, we use X-ray scattering, NMR, and electron microscopy to show that multi-layers of lipids and polymers provide an interesting environment that hinders hydrophobic drug crystallization and boosts permeation. These materials are very promising for the formulation of hydrophobic drugs and we show that such complex hybrid membrane reservoirs can be synthesized into sub-100 nm sizes by means of a microfluidics reactor.

## **COLL 565**

### **Platonic micelles: Molecular packing and thermodynamics**

**Ramanathan Nagarajan**, *ramanathan.nagarajan.civ@mail.mil*, Yenny Cardona Quintero. CCDC Soldier Center, Natick, Massachusetts, United States

Formation of micelles of discrete aggregation numbers 4, 6, 8, 12 and 20, paralleling the number of faces of Platonic solids, has been recently reported. These discrete aggregation numbers have been rationalized by invoking the problem of close packing of non-overlapping circles (representing amphiphile head groups) on a spherical surface (representing the micelle), giving rise to maximum coverage of the surface by the head groups. In this paper we examine, (i) whether a controlling role for the effective surface coverage of head groups, used to rationalize the Platonic micelles, is consistent with a more complete thermodynamic treatment of micelle formation, taking into account system entropy and head group repulsions; (ii) whether the close packing of the head groups on the micelle surface is compatible with the tails completely filling the micelle core; and (iii) what factors determine the specific aggregation number an amphiphile achieves at equilibrium, from among the multiplicity of the Platonic aggregation numbers.

## **COLL 566**

### **Tethered-type lipid bilayer membranes on graphene oxide**

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Lipid bilayer is a fundamental structure of cell membranes, and lateral and transversal distribution of lipid molecules are key factors during the transportation of materials and signals through the cell membrane. We have studied lipid bilayer membranes on graphene oxide (GO). GO has a unique fluorescence quenching property, and applied to biosensing recently. We have reported that less-fluid components localized on GO in multi-component lipid bilayer membranes on a SiO<sub>2</sub>/Si substrate partly covered with GO. In this study, we formed a tethered-type lipid bilayer on a chemically modified graphene oxide (GO), and investigated the localization effect of GO and the lateral diffusion in the tethered bilayer.

GO was prepared by the chemical exfoliation of graphite particles, and spin-coated on a

thermally oxidized SiO<sub>2</sub>/Si substrate. The GO/SiO<sub>2</sub>/Si substrate was treated with 1-pyrenebutyric acid N-hydroxysuccinimide ester, followed by 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride, and streptavidin. Atomic force microscope topographies showed that the GO flakes were covered with streptavidin molecules, which were observed as ~3 nm high protrusions, while bare SiO<sub>2</sub> regions were kept flat.

We prepared a planar lipid bilayer membrane comprising of 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC), biotin-N-1,2-dipalmitoyl-sn-glycero-3-phosphoethanolamine (biotin-DPPE) and lissamine rhodamine B-N-DPPE (Rb-DPPE) (100:1:0.5) by the vesicle fusion method. AFM topographies showed flat morphology on the GO flake surface, and shape of streptavidin molecules were not observed. The GO flake region was higher than the surrounding lipid bilayer membrane on the bare SiO<sub>2</sub> region by 7.1 nm. It corresponds to a thickness of GO (~1.5 nm thick) modified with streptavidin (~6 nm in diameter). A lipid bilayer consisting of DOPC, poly(ethylene) glycol-DPPE (PEG-DPPE) and biotin-DPPE (97.5:2.5:1) showed that the localization effect of GO did not appear on the streptavidin-modified GO, while PEG-DPPE domains were localized on non-modified GO. We conclude that a planar tethered-type lipid bilayer formed on the streptavidin-modified GO, and streptavidin worked as a spacer between the lipid bilayer and GO. We also describe the fluorescence quenching efficiency of lipid bilayers on GO with and without streptavidin modification.

## **COLL 567**

### **Intracellular transport of TiO<sub>2</sub> nanoparticle-containing lysosomes**

**Christine K. Payne**, *christine.payne@duke.edu*. Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina, United States

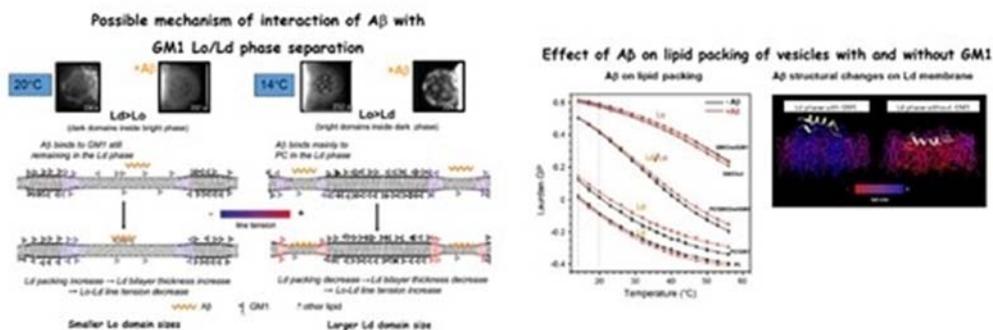
Lysosomes are membrane-bound intracellular vesicles with a low pH and high concentration of enzymes. These organelles are essential for the processing of intracellular cargos ranging from nutrients to viruses. Our recent work with TiO<sub>2</sub> nanoparticles shows, using a combination of fluorescence and electron microscopy, that these nanoparticles accumulate in lysosomes resulting in a 2-fold increase in lysosome diameter. We have used single particle tracking fluorescence microscopy to characterize the motion of these enlarged vesicles with the goal of understanding how increased lysosome diameter affects the global cellular response to TiO<sub>2</sub> nanoparticles. Beyond nanoparticle-cell interactions, an understanding of lysosomal transport is important for fundamental cellular biophysics as well as human health and disease, specifically lysosomal storage disorders.

## **COLL 568**

### **Alzheimer's disease amyloid- $\beta$ peptide and the sphingolipids: From lipid domain pattern to functioning**

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Alzheimer's disease (AD) is characterized by an amazing interplay between numerous aspects of AD, the membrane lipid composition and metabolism, and, the overproduction of the amyloid-beta peptide (A $\beta$ ). This has even led to the hypothesis that the nonpathological role of A $\beta$  and its parent protein might be that of regulators of lipid homeostasis. The most documented lipids involved in AD are sphingolipids and cholesterol. The first AD related suspected lipid from sphingolipid family is the ganglioside GM1 (GM1). A specific A $\beta$ -GM1 complex found in early AD brains, suggested that GM1-bound A $\beta$  may serve as a seed for the formation of toxic amyloid fibrils. Here, we present our results regarding the interaction of A $\beta$ (1–42) with GM1-containing biphasic, liquid ordered/liquid disordered phase (Lo/Ld) giant vesicles. Our fluorescence co-localization experiments confirm that A $\beta$ (1–42) binds preferentially to the Ld phase. The effect of A $\beta$  on the Lo/Ld size dynamics is studied using photoinduced spinodal decomposition which mimics the nanodomain/microdomain raft coalescence. A $\beta$ (1–42) affects the kinetics of the coarsening phase and the size of the resulting microdomains, depending on which phase, Lo, or, Ld, is in a majority. Our fluorimetric measurements on large unilamellar vesicles using the probe Laurdan indicate that A $\beta$ (1–42) binding respectively increases or decreases the packing of the Ld phase in the presence or absence of GM1. The differential effects of A $\beta$ (1–42) on spinodal decomposition are accordingly interpreted as resulting from distinct effects of the peptide on the Lo/Ld line tension modulated by GM1. In all, this study confirms that A $\beta$ (1–42) binds preferentially to the non-raft Ld phase of membranes even in the presence of the ganglioside GM1. Finally, having in mind that the dynamics of raft nano-micro-domains is instrumental in many cell signaling processes, it appears that many neuron signaling processes might be affected at various stages of AD by mechanism related to the kinetics of phase coarsening.



## **Membrane curvature underlies topography-induced intracellular signaling**

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Surface topography profoundly influences cell adhesion, differentiation, and stem cell fate control. Numerous studies using a variety of materials demonstrate that nanoscale topographies change the intracellular organization of actin cytoskeleton and a broad range of cellular dynamics in live cells. However, the underlying molecular mechanism is not well understood, leaving why actin cytoskeleton responds to topographical features unexplained and therefore preventing researchers from predicting optimal topographic features for desired cell behavior. We recently demonstrate that topography-induced membrane curvature plays a crucial role in modulating intracellular actin organization. By inducing precisely controlled membrane curvatures using engineered vertical nanostructures as topographies, we find that actin fibers form at the sites of nanostructures in a curvature-dependent manner with an upper limit for the diameter of curvature at ~400 nm. Nanotopography-induced actin fibers are branched actin nucleated by the Arp2/3 complex and are mediated by a curvature-sensing protein FBP17. Our study reveals that the formation of nanotopography-induced actin fibers drastically reduces the amount of stress fibers and mature focal adhesions. These findings establish the membrane curvature as a key linkage between surface topography and topography-induced cell signaling and behavior.

### **COLL 570**

#### **Exploring the behavior of PI(4,5)P2 using supported lipid bilayers**

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Phosphatidylinositol 4,5-bisphosphate, PI(4,5)P2, typically resides in the inner leaflet of the plasma membrane of living cells and is involved in a wide variety of biological processes. These range from serving as a second messenger to cytoskeletal attachment. As such, it is important to explore the behavior of this lipid in model membrane systems to obtain molecular level details on how it interacts with other lipids, membrane-bound proteins as well as aqueous proteins. PI(4,5)P2 is highly charged at physiological pH and protrudes above the plane of the membrane surface. As such, it interacts strongly with divalent metal cations like  $Mg^{2+}$  and  $Ca^{2+}$ . In this talk, we will employ supported bilayer systems to explore the mechanisms concerning how this lipid can interact with its external environment. Vibrational sum frequency spectroscopy, fluorescence microscopy, and related interfacial diagnostic results will be provided.

### **COLL 571**

#### **Interactions of cells and cell spheroids with biomimetic polyzwitterions**

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Polyzwitterions, containing either phosphorylcholine (PC) groups or sulfobetaine (SB) moieties form an important class of biomaterials with outstanding non-fouling properties and compatibility with blood and other body fluids. The presence of zwitterions on polymer chains strongly affects their solution properties and their assembly in the form of nanoparticles in aqueous media. Placed in contact with live cells they forgo endocytotic cell entry pathways and pass the cell membrane by translocation. Details of the translocation mechanism vary depending on the nature of the zwitterionic group and of the polymer architecture. In the case of a fluorescein-labeled random copolymer of 3-dimethyl(methacryloyloxyethyl)ammonium propane sulfonate and poly(ethyleneglycol) methacrylate, p(DMPAS-ran-PEGMA), the uptake mechanism is dominated by dipole-dipole interactions between the phosphorylcholine moieties of the cell membrane and the sulfobetaines of the polymers. The polymers p(DMAPS-ran-PEGMA) labeled with the cationic Rhodamine B preferentially localize in mitochondria, an important characteristic for drug delivery applications.

Although, most PC-polymers are obtained de-novo from PC-containing monomers, it is often advantageous to prepare them by post-modification of preformed natural or synthetic polymers. The introduction of PC groups strongly affects the solution properties of polymers and, more importantly, the presence of PC groups on interfaces can be detected by cells: chitosan is known for its bioadhesive characteristic, whereas PC-modified chitosan substrates tend to be cell repellents: they promote cell-cell adhesion over cell/substrate adhesion, triggering the formation of 3D cell aggregates. Films of chitosans bearing zwitterions other than PC groups, such as sulfobetaines, exhibit similar properties, bringing support to the generic non-fouling characteristics of the zwitterion functionality, independently of chemical composition. These characteristics suggest the use of PC-modified chitosans in 2D- or 3D-templates for tissue engineering.

## **COLL 572**

### **Hybrid photosynthetic system of natural plant thylakoids and synthetic lipids reconstituted into a supported microscale membrane array**

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Thylakoid membranes in the chloroplast of plants, algae, and cyanobacteria are the powerhouse of the photosynthesis capturing the solar energy and converting it into chemical energies. Although their overall structures and functions have been extensively studied, the intrinsically heterogeneous and dynamic two-dimensional (2D) membrane structures are not fully understood. Investigating native thylakoid

membranes *in vivo* is difficult due to their small sizes and limited external access to the chloroplast interior, while the bottom-up approaches based on model systems have been hampered by the sheer complexity of the native membrane. Here we try to fill the gap by reconstituting the whole thylakoid membrane into a patterned substrate-supported planer bilayer. A mixture of thylakoid membrane purified from spinach and synthetic phospholipid (DOPC) vesicles spontaneously formed a laterally continuous and fluid 2D membrane in the scaffold of patterned polymeric bilayer. Chlorophyll fluorescence arising from photosystem II (PSII) recovered after photobleaching, suggesting that the membrane components are laterally mobile. The electron transfer activity of PSII was retained as confirmed by the changes in chlorophyll fluorescence in the presence of the electron acceptors and/ or inhibitors. Furthermore, we confirmed the electron transfer activity of photosystem I (PSI) by observing the generation of NADPH in the presence of water-soluble ferredoxin and ferredoxin-NADP<sup>+</sup> reductase. The lateral mobility of membrane-bound molecules and the functional reconstitution of major photosystems support the feasibility of reconstituted thylakoid-synthetic lipid hybrid membranes as the experimental platform to study the 2D organization and molecular machinery of photosynthesis.

## **COLL 573**

### **Systemic effects of engineering the cell membrane composition in *Bacillus subtilis***

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Engineering bacterial cells to contain defined fatty acid compositions within their cell membranes establishes an *in vivo* experimental platform to study membrane biophysics. Yet before fully realizing the potential of this system, it is prudent to understand the systemic changes in cells induced by the labeling procedure itself. In this work, analysis of cellular membrane compositions was paired with shotgun proteomics to assess how the proteome changes in response to the directed incorporation of exogenous fatty acids (*n*16:0 and *antiiso*15:0) into the membrane of *Bacillus subtilis*. This labeling was previously used in experiments showing lateral heterogeneity in the distribution of these fatty acids in the plane of the membrane, suggesting lateral organization on the order of 40 nm. The current analysis reveals an alteration in lipid headgroup distribution, with an increase in phosphatidylglycerol lipids and decrease in phosphatidylethanolamine lipids, possibly providing a fluidizing effect on the cell membrane. Changes in the abundance of enzymes involved in fatty acid biosynthesis and degradation are observed; along with decreases in the abundance of cell wall biosynthesis enzymes, the well-known lipid raft-associated protein flotillin, and the actin-like protein MreB. These results illustrate the active regulation of cell membrane properties beyond the fatty acid content and some of the many implications of modulating cell membrane fatty acid composition - deepening the understanding of this experimental platform and forthcoming results from its use.

## **COLL 574**

### **Asymmetric lipid bilayers: Insights from leaflet-specific structural studies**

**Georg Pabst**, *georg.pabst@uni-graz.at*. Institute of Molecular Biosciences, University of Graz, Graz, Austria

Lipid-only mimics of biological membranes serve as valuable platforms for studying the functional role of membrane lipids and their coupling to protein function under chemically and experimentally well-defined conditions. Of recent, we have advanced protocols for producing lipid vesicles with an asymmetric distribution of lipids, similar to that found in natural membranes, which are amenable for broad variety of experimental techniques. To study their biophysical properties, we have focused on scattering techniques capable of interrogating leaflet-specific structure on the sub-nanometer scale. Combining small-angle neutron and X-ray scattering techniques with advanced data analysis tools allowed us to gain insight into contributions from lipid chemistry to transbilayer coupling mechanisms. For example, lipids with fluid unsaturated hydrocarbons caused a softening of rigid disaturated lipids, but also the intrinsic lipid curvature was found to play a significant role in interleaflet coupling. Additionally, I will report on the effects of hydrocarbon chain interdigitation and discuss effects of membrane asymmetry on the activity of membrane active compounds and protein function.

## **COLL 575**

### **Investigating plasmonic nanomaterials via ssNMR**

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Localized surface plasmon resonance research has been extended from noble metals to doped metal oxide nanoparticles. Unlike noble metal nanoparticles, the carrier density of metal oxide semiconductors can be tuned by intrinsic or extrinsic doping methods. This makes these materials increasingly versatile, but also complex in that these dopants can lie interstitially or at various sites within the crystal lattice. Understanding the distribution (surface vs. core), site symmetry, and influence on carrier density of these dopants is crucial to the development of plasmonic semiconductor nanomaterials. Here, we utilize ssNMR to probe plasmonic n-type  $\text{In}_2\text{O}_3$  nanocrystals in order to examine the dopant properties. Samples are fully characterized via UV-Vis-NIR, FTIR, pXRD, ICP-MS, and TEM.

## **COLL 576**

### **Surface chemistry and gel permeation chromatography purification of $\text{CsPbBr}_3$ nanocrystals with high quantum yield and colloidal stability**

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United States

Inorganic halide perovskites such as CsPbX<sub>3</sub> have emerged as a better alternative for various optoelectronic applications due to their ease of preparation, narrow emission peak widths, short radiative lifetimes and remarkably high quantum yield in colloidal solution. However, the progress in their exploration has been hindered in different areas such as stability and providing an effective purification that can maintain or improve their external quantum efficiency. The ionic character of CsPbX<sub>3</sub> makes them very sensitive to polar solvents which usually compromise their structural integrity. Here, we report the use of gel permeation chromatography for effective purification of CsPbBr<sub>3</sub> nanocrystals and study the effects of this purification on ligand populations and their optoelectronic properties. We also show that near-unity quantum yield and high colloidal stability can be achieved for CsPbBr<sub>3</sub> using gel-permeation chromatography. We take our ability to manipulate the particles in this way to explore several post-synthetic reactions.

## **COLL 577**

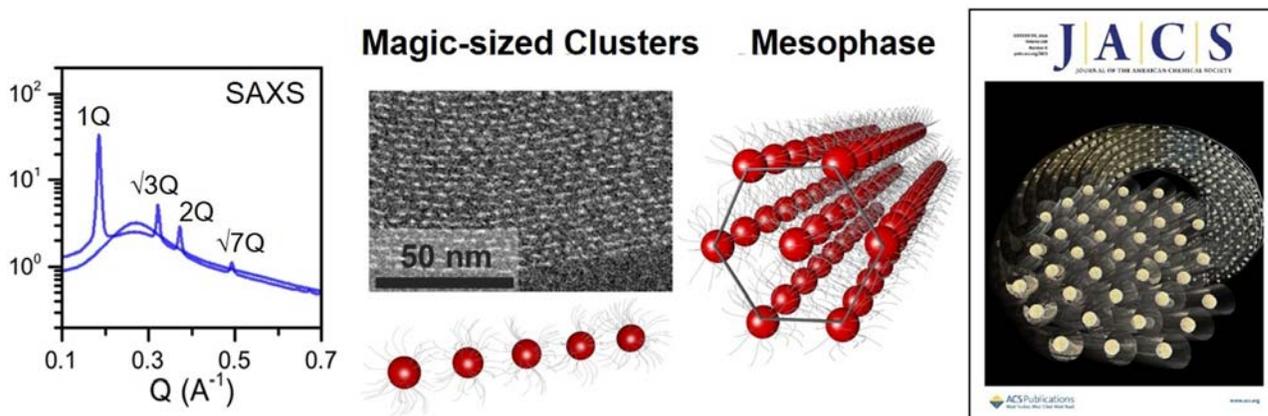
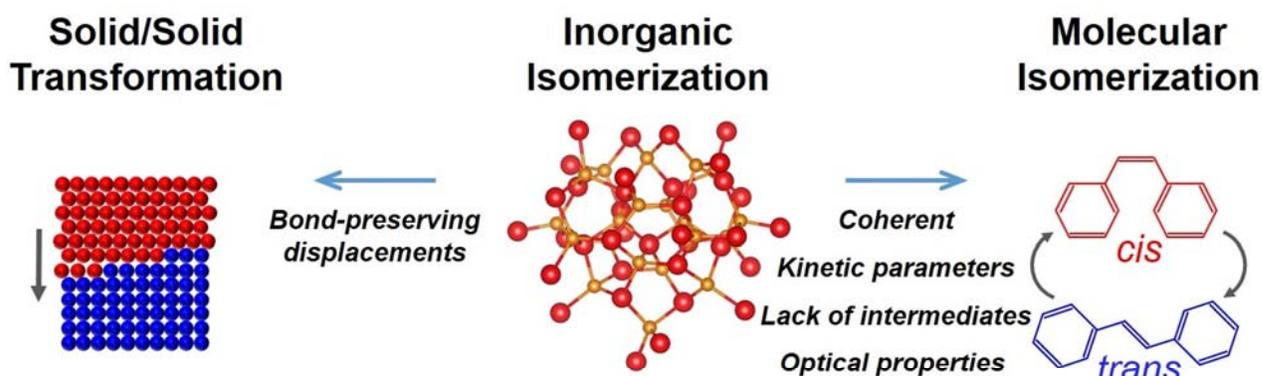
### **Chemically reversible isomerization in inorganic magic sized clusters**

**Richard D. Robinson**, *rdr82@cornell.edu*. MSE Department, Cornell University, Ithaca, New York, United States

Structural transformations are ubiquitous at all length scales in chemistry, spanning from isomerization reactions of small molecules to solid-solid transformations in bulk crystals, which have generally been studied in isolation. Despite attempts to merge understanding of these disparate regimes by reducing domain size in solids to nanocrystalline dimensions, bulk-like solid-solid transformation behavior still predominates at length scales approaching those of molecules. In-between small molecules and nanocrystals, magic-sized clusters (MSCs) provide an advantageous experimental platform to study isomerization in well-defined atomically precise systems. We show here that a reversible transformation between CdS cluster isomers with distinct stable configurations possesses essential characteristics of both solid-solid transformations and molecular isomerization reactions. These isomers, termed  $\alpha$ - and  $\beta$ -(Cd<sub>2</sub>S)<sub>x</sub>, interconvert ( $\alpha$ -to- $\beta$ / $\beta$ -to- $\alpha$ ) reversibly, as identified by a 140 meV shift in the species' excitonic energy gap. A characteristic displacive reconfiguration of the inorganic core (solid-solid transformation), as evidenced by our reconstruction of the atomic pair distribution function from x-ray scattering, accompanies the change in electronic structures. The first order kinetics of the transformation—indicative of molecular isomerization—are driven by a distortion of the ligand binding motifs due to the presence of hydroxyl species in the ligand shell. Chemical control over the surface energy boundary conditions *via* adsorbates appears to be the exclusive determinant of “phase” stability in this system. The reversible transformation of MSCs reported here presents the missing bridge between molecular isomerization and solid-solid transformations. Manipulation of MSCs, which serve as seeds and as a monomer

reservoir in nanocrystal growth, will provide an additional strategy for control over the structure of colloidal nanocrystals.

## The missing link between bulk phase transformations and molecular isomerization



COLL 578

### Time resolved x-ray spectroscopy of ZnSe semiconductor nanocrystals: Understanding the role of surface ligands on dynamical properties

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Many groups have been investigating both how the choice of non-solvent and multiple steps during the purification processes of semiconductor nanocrystals (NCs) can affect both the optical properties and the ligand surface density. Based on an approach for the classification of covalent compounds suggested by M. L. H Green, molecules that are able to act in role of ligands for NCs are categorized by the specific interaction with the particle surface and include X-type, L-type, and Z-type. X-type ligands are only replaceable by ligands of the same kind owing to the fact that NCs are metal rich on the surface rendering them positively charged, so the new ligand has to be able to maintain the charge balance of the system. TOPO and alkylamines are frequently utilized ligands of the L-type variety, and in the case of II-VI nanocrystals, primary amines tend to prefer the Se sites over the metal sites. Our group has been investigating the use of ethanol (EtOH) as the non-solvent during the cleaning process of II-VI NCs coated with TOPO and stearic acid. Unlike the reports using methanol during the purification process, the photoluminescence quantum yield (PLQY) measurement on EtOH purified samples do not exhibit any degradation in the PLQY, even after many purification steps. In general, during the washing steps, the TOPO (L-type ligand) is removed in the early stages of cleaning, followed by stearate (X-type ligand) removal, although the amount of stearate removed from the NCs surface reaches a plateau after a few washing steps. The competition between both surface ligand densities with our suggested model of preferential desorption of L-type over X-type ligands from NC surfaces should influence the optical properties strongly, and thusly the charge carrier dynamics. In our current work, we have performed x-ray transient absorption spectroscopy to further understand the charge carrier dynamics of ZnSe nanocrystals as a function of surface ligand coverage. We use above band gap excitation from a femtosecond laser and probe the decay dynamics at both the Se and Zn K-edges. The x-ray data points towards evidence for a photoinduced charge transfer from Se sites to Zn sites that depends directly in the surface ligand density.

## **COLL 579**

### **Colloidal synthesis of phase-tunable transition metal dichalcogenide nanocrystals**

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Transition metal dichalcogenides (TMDs) can host a variety of phases, each with a unique electronic structure, allowing access to a compositionally and electronically diverse set of 2D materials. Among these materials, the metastable 1T' (2M) phase of WSe<sub>2</sub> has recently gained attention due to its potential application as a quantum spin hall insulator operable at room temperature. This metastable phase, however, is difficult to access via traditional synthetic methods due to the low barrier for conversion to the thermodynamically favored 2H phase. Colloidal chemistry is uniquely poised for the synthesis of metastable phases because conditions can be chosen to access kinetic growth regimes. We have previously shown that control over the size and phase of

colloidal WSe<sub>2</sub> nanocrystals can be achieved by careful choice of ligand. Specifically, increasing the amount of coordinating ligand (oleic acid) present during synthesis leads to larger nanocrystals with increasing contribution from the 1T' (2M) phase. This talk will review the influence of ligand coordination on the phase of colloiddally synthesized WSe<sub>2</sub> nanocrystals and will discuss the extension of this chemistry to the synthesis of other group-VI TMDs, including WS<sub>2</sub> and MoSe<sub>2</sub>.

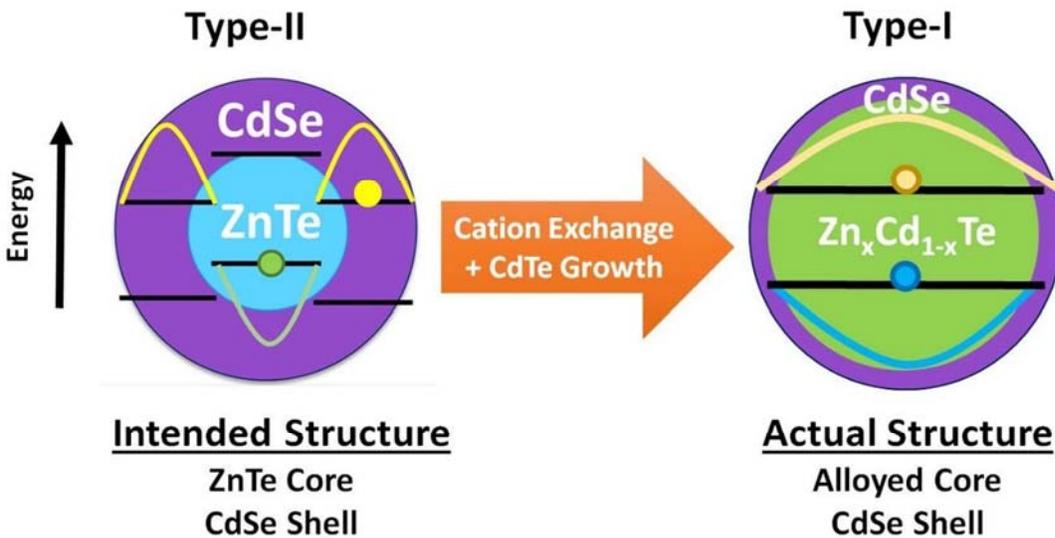
## COLL 580

### Deciphering the hidden complexity of heterostructured nanocrystals

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Colloidal semiconductor nanocrystals exhibit size dependent optoelectronic properties due to quantum-confined excited states. The charge-carrier distribution and recombination rate in nanocrystals can be tuned by addition of a shell. The precise control over charge-carrier localization and recombination dynamics make these materials interesting candidates for photovoltaics, lasers, LEDs, and biomedical imaging. X-ray absorption spectroscopy (XAS) is ideally suited for probing the internal structure of multicomponent materials because of its elemental specificity and sensitivity to local structure of the absorbing atom. The extended X-ray absorption fine structure (EXAFS) can ascertain coordination numbers, distinguish between types of scattered atoms, and calculate bond lengths in the local (~6 Å) environment of the absorbing atom.

We show that ZnTe/CdSe core/shell quantum dots synthesized by standard literature procedures have an alloyed Zn<sub>x</sub>Cd<sub>1-x</sub>Te core. We individually probed the Zn, Te, Cd, and Se X-ray absorption K-edges and performed a global EXAFS fitting analysis in order to extract the first-shell bond distances. We combine our XAS results with transmission electron microscopy (TEM) sizing and elemental analyses, which allows us to propose models of the internal particle structure. Our multimodal characterization approach confirms **(1)** the presence of Cd-Te bonds, **(2)** cation alloying in the core, and **(3)** a patchy pure-phase CdSe shell. We synthesized particles of different shell thicknesses and performed synthetic control studies that allowed us to discard a ZnTe/CdTe/CdSe core/shell/shell structure and confirm the alloyed core/shell structure. We extend our structural analysis with electronic band structure calculations and UV/vis absorption spectroscopy, demonstrating that the alloyed Zn<sub>x</sub>Cd<sub>1-x</sub>Te/CdSe core/shell quantum dots exhibit a type-I band alignment, different from the predicted type-II band alignment of the intended ZnTe/CdSe core/shell quantum dots. This study highlights the power of XAS for understanding the internal structure of heterogenous nanoparticles.



**COLL 581**

### **Non-classical growth mechanism of nanoparticles resolved by liquid phase TEM**

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For the past few decades, nanoparticles of various sizes, shapes, and compositions have been synthesized and utilized in many different applications. However, due to a lack of analytical methods that can obtain in-situ structural information at the nanoscale level, many of their growth mechanism are not understood well. The liquid phase transmission electron microscopy (TEM) offers an opportunity to directly observe chemical reactions that occur in solution. Here we present application of liquid phase TEM to study growth of colloidal nanoparticles. We focus on recent *in situ* TEM studies of nanoparticle growth which reveal important roles of non-classical crystallization pathways in the entire formation process. Our in-situ observations with liquid phase TEM elucidate different types of non-classical pathway, including two-step nucleation, amorphous-to-crystalline transition, and coalescence of clusters, are involved in different conditions of nanoparticle synthesis.

**COLL 582**

## **Unraveling the energy landscape of tetrahedral InP nanocrystals**

**Sohee Jeong**, *s.jeong@skku.edu*. Department of Energy Science, Sungkyunkwan University, Suwon, Korea (the Republic of)

Synthesis of colloidal nanocrystals (NCs) is considered as a sequential chemical reaction. The entire energy landscape in the colloidal NCs is predominantly determined by the surface free energy and surface stabilization energy for the bare surface facets and ligands passivated facets, respectively. The evolution of the NCs is driven continuously by reducing surface energy during the growth process, determining the exposed facets and ultimately inducing the final shapes. Here, the insights into the surface energy driven reaction pathway of InP tetrahedral nanocrystals will be shared allowing more precise control over the morphology as well as size.

### **COLL 583**

## **Galvanic replacement with chemically heterogeneous templates**

**Sara E. Skrabalak**, *sskrabal@indiana.edu*. Chemistry, Indiana University, Bloomington, Indiana, United States

Galvanic replacement of sacrificial metal nanoparticles is a versatile route toward nanomaterials with complex compositions and architectures. In most demonstrations, the oxidation of monometallic templates by ions of a more noble metal is studied, having provided a route to multimetallic nanocatalysts and contrast enhancement agents. However multimetallic templates offer more than one type of reaction site. This presentation will outline the processes involved during galvanic replacement with Janus-style AgPd dimers and intermetallic nanoparticles. Interestingly, the galvanic replacement is found to be selective with multimetallic nanocrystals and solid-state diffusion processes influence the final multimetallic distribution. These results enhance our understanding of how the galvanic replacement process can be used to achieve nanostructures with increasingly more complex structures and compositions.

### **COLL 584**

## **Small gold nanorods and protected small silver nanorods**

**Luis Liz Marzan**, *lizmarzan@cicbiomagune.es*. CIC biomaGUNE, Donostia - San Sebastian, Spain

Seeded-growth methods have provided us with an extensive library of anisotropic metal nanoparticles, among which gold nanorods are arguably the most extensively used ones. The main reason behind this choice is the possibility of fine-tuning the frequency of the longitudinal localized surface plasmon band (LSPR), through the aspect ratio of the particles. Such a tunability is essential toward a variety of applications, including medical diagnosis and therapy.

Some such applications require not only tuning the LSPR into a biological transparency window, but also adjusting the ratio between absorption and scattering, which requires a tight control over particle size.

We present synthetic strategies toward the synthesis of both gold and silver nanorods with small dimensions and high quality, in terms of optical and morphological monodispersity. Due to the limited chemical stability of silver nanoparticles, which readily oxidize in aqueous and media (biofluids in particular), we also present a protocol for polymer encapsulation that warrants long-term stability in highly oxidizing environments, as well as negligible cytotoxicity.

## **COLL 585**

### **Importance of unbound ligand in determining nanocrystal superlattice structure and orientation**

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Significant theoretical work has been devoted to understanding why colloidal nanocrystals (NCs) form the diverse set of structures they do. This research has focused on the ratio of ligand shell to core size, core faceting, ligand coverage, and processing conditions as controllable parameters. Here, we demonstrate the central role unbound/free ligands play in tuning NC superlattice (SL) structure. We perform a series of controlled additions of unbound oleic acid ligands to solutions of identically sized, oleate-capped PbS NCs with differing ligand coverages and track the structures formed upon deposition via spin-coating with grazing-incidence small-angle X-ray scattering (GISAXS). The unbound ligand swells the bound ligand-shell and tunes the SL continuously with increasing addition of ligand from a body-centered cubic (BCC) phase, through a series of body-centered tetragonal (BCT) phases, to the face-centered cubic (FCC) symmetry. We establish limitations on the range of tunability based on Flory-Rehner theory of gel-swelling. Molecular dynamics simulations of single NCs confirm the unbound ligand readily swells the bound ligand-shell over all exposed NC facets, even without explicit rebinding to the NC surface. Furthermore, we explain the disruption of SL orientation relative to the substrate observed for high volume fraction samples by considering the early-time dynamics of spin-coating viscous solutions. This study establishes the ability to rationally tune SL structure through the addition of unbound ligand and highlights the importance of fully characterizing the bound and unbound ligand populations in a batch of NCs to successfully predict SL structure. This opens the door to new functionality of NC assemblies through the incorporation of free ligand.

## **COLL 586**

### **Unique reshaping behavior of gold nanoprisms in the presence of cetyltrimethylammonium chloride**

**Yuchen Wang**, *wyc93112@gmail.com*, **Shu Yang**. Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States

Gold nanoparticles (AuNPs) with their unique surface plasmon resonance (SPR) properties have been widely applied in enhanced spectroscopies, biosensors, photothermal therapy, and solar light harvesting. The SPR properties of AuNPs are highly dependent on the particle size and shape. It has been shown that AuNPs can be oxidized by Au(III) in the presence of cetyltrimethylammonium bromide (CTAB) due to the strong binding between them. Oxidation occurs preferentially at the surface sites with higher curvatures, leading to transformation of gold nanoprisms to gold nanodisks. Here, we report that when the CTAB is replaced by cetyltrimethylammonium chloride (CTAC), a unique reshaping behavior is observed. The gold nanoprisms first undergo conventional etching of the tips of the gold nanoprisms (~60 nm edge length), leading to the shift of plasmon peak from 648 nm to 556 nm. However, after a certain period of time, the shape of gold nanoprisms is recovered, accompanied with plasmon peak shifting back to 632 nm. High-resolution transmission electron microscopy (TEM) and selected area diffraction (SAED) images at different stages indicate the crystallinity of gold is preserved. Preliminary in-situ UV-vis spectroscopy study suggests redeposition of gold atoms on gold nanoprisms, leading to recovery of the shape. More detailed study of the reshaping mechanism is ongoing.

**COLL 587**

### **Understanding the synthesis mechanism of silver-glutathione monolayer-protected clusters**

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Silver monolayer-protected clusters (MPCs), also known as molecular nanoparticles, have significant potential for next generation technological applications (nano-carrier for drug delivery, bio-imaging, photovoltaics, etc.). The syntheses of this class of nanoparticles are not yet well understood, however, so designing syntheses to produce specific technologically important MPC products remains a challenge. Syntheses can be designed and controlled more easily if the synthetic mechanism is known. Two different synthetic mechanisms have been proposed, namely the “size focusing” and “condensation” models, but we have observed that silver-glutathione (Ag:SG) MPC formation is not compatible with these models. Rather, the mechanism for Ag:SG MPC formation progressed through the growth of smaller sizes into larger sizes of previously known species. Here, we describe a new “sequential growth” model of MPC synthesis wherein their formation involves the growth of smaller species into larger species, sequentially, from one known size to another. This sequential growth pathway progresses through a potential energy landscape that is defined by thermodynamic preferences for stable sizes (controlled by choices of metals, ligands, solvents, etc.) and their associated kinetic barriers to the transformation of one size into another. It was

also found that oxidation reactions played an important role in the synthesis of Ag:SG MPCs, which will also be discussed. Together, this work begins to better define the mechanisms of silver MPC synthesis.

## **COLL 588**

### **Chemical reaction mechanisms of tin telluride nanocrystals**

**Sean W. O'Neill**<sup>1</sup>, [sean.oneill@rochester.edu](mailto:sean.oneill@rochester.edu), **Malik Hamilton**<sup>2</sup>, **Todd Krauss**<sup>1</sup>. (1) University of Rochester, Rochester, New York, United States (2) Knox College, Galesburg, Illinois, United States

Colloidal semiconductor nanocrystals (NCs) historically are attractive because of their tunable band gap, ease of synthesis, and promise as solution-processable materials for a number of technologies. While much NC research has focused on cadmium and lead chalcogenide materials, many other semiconductor NCs are of potential interest. One such example is the semiconductor tin telluride (SnTe). Bulk SnTe has several interesting and somewhat idiosyncratic qualities including an inverted (i.e., negative) bandgap, a typically p-doped character arising from intrinsic Sn vacancies, and its categorization as a topological crystalline insulator. As a narrow bandgap semiconductor, SnTe holds promise for use in several applications, including in infrared photodetectors. However, limited evidence exists on how the unusual properties of SnTe manifest themselves at the nanoscale. For example, contrary to the expected Sn deficiency in the bulk, several studies have reported a Sn rich composition for SnTe nanostructures arising from surface oxidation.

In this presentation we will provide a thorough characterization of the composition and resultant photophysical qualities of colloidal SnTe NCs. In-depth characterization was conducted by means of various spectroscopic techniques (e.g., NIR-absorption spectroscopy, FTIR, EDS, XPS, XRD, NMR). Special care was taken to perform all syntheses in an inert atmosphere to prevent rapid oxidation. Yet, we found that the Sn:Te ratio as determined with both EDS and XPS was greater than one, indicating that the NCs were Sn rich. This off-stoichiometry was exacerbated with increased air exposure. Chemical analyses also consistently indicated elevated levels of Si, attributed to trimethylsilyl-containing synthesis byproducts. Furthermore, we investigated SnTe NC chemical reaction mechanisms using <sup>119</sup>Sn and <sup>31</sup>P NMR, following the evolution of the bis(bis(trimethylsilyl)amino tin (bisbisSn) and trioctylphosphine telluride (TOPTe) precursors over the course of the reaction. We found that approximately 50% of the bisbisSn formed various byproducts, while TOPTe largely decomposed into trioctylphosphine which did not further react nor form additional compounds. The implications of these results on final NC properties will be discussed.

## **COLL 589**

### **Sterically encumbered phosphine precursors for InP quantum dot synthesis**

Hashini Chandrasiri, **Preston T. Snee**, [sneep@uic.edu](mailto:sneep@uic.edu). Chemistry, University of Illinois at Chicago, Chicago, Illinois, United States

Bright III-V semiconductor quantum dots are of recent interest due to the lack of significantly toxic elements (i.e. cadmium). While great advancements have been made towards preparing high quantum yield InP materials, most synthetic protocols create QDs with poor color saturation. A potential cause is the use of overly reactive phosphorus precursors such as tris-trimethylsilyl phosphine,  $(\text{TMS})_3\text{P}$ . Presented is an attempt to mollify the reactivity of  $(\text{TMS})_3\text{P}$  via the use of larger ligands, specifically triethyl and tributyl silanes. The reagent tris-triethylsilyl phosphine  $(\text{TES})_3\text{P}$  results in brighter InP QDs with narrower emission spectra. Furthermore, the synthesis of larger, red-emitting dots is more facile with  $(\text{TES})_3\text{P}$  compared to  $(\text{TMS})_3\text{P}$ . However, the butyl analog was not as effective for InP QD preparation, causing us to conclude that sterically encumbering the  $\text{P}^{3-}$  anion is not the final solution for preparing color-saturated III-V QDs.



Increasing the size of phosphide anion ligands results in InP QDs with improved optical properties (higher quantum yield, red-shifted emission with better color saturation).

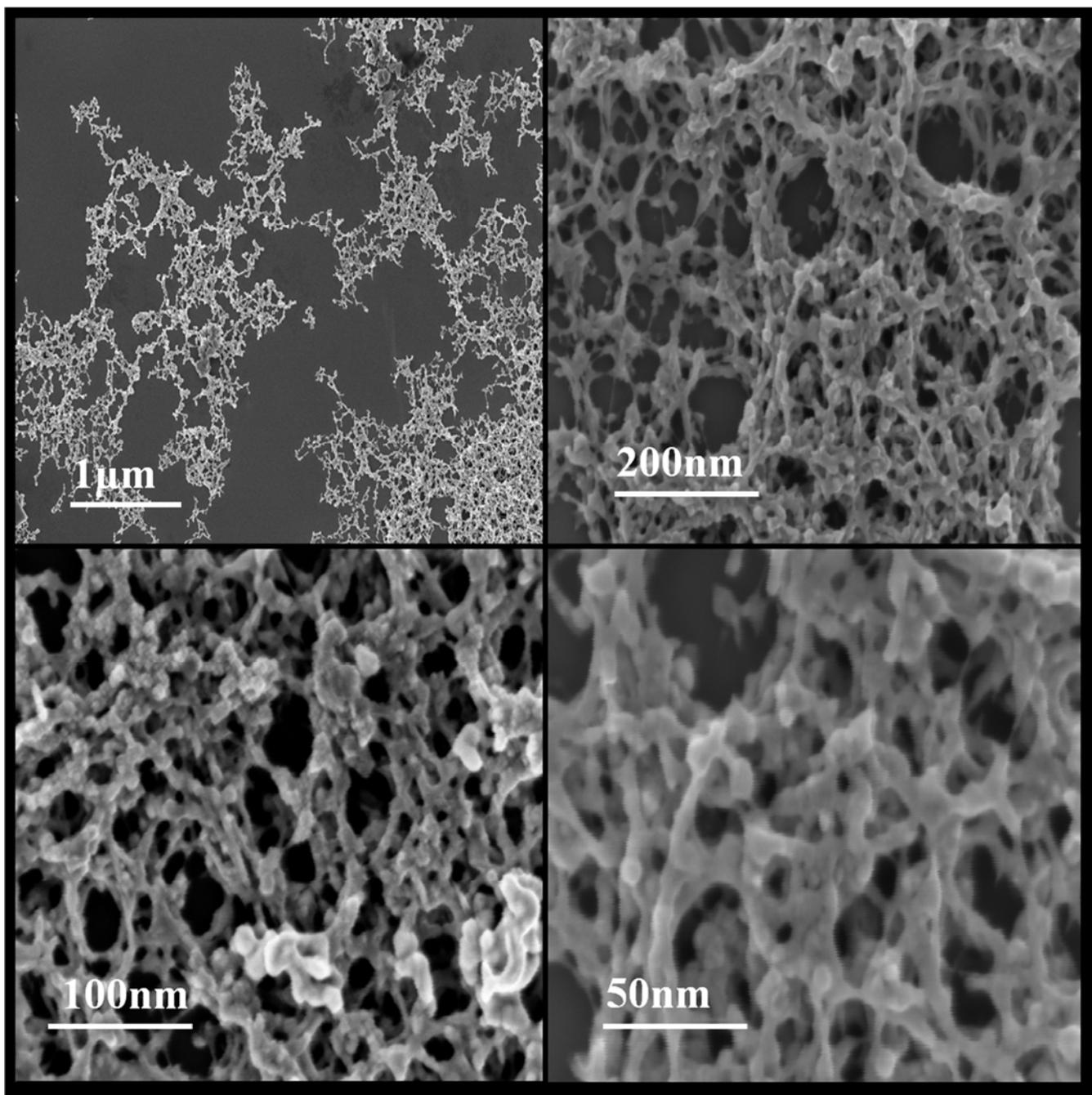
## COLL 590

**Crystal engineering to fabricate twin boundary induced highly strained network of Au doped Ag nanorod with excellent catalytic efficiency: Bridging application from catalysis to sensing for early detection of dengue serotype-2 and its related metabolites in human serum**

**Sandip K. De**, [sandipdey.444@gmail.com](mailto:sandipdey.444@gmail.com). Chemical Sciences Division, Saha Institute of Nuclear Physics, Saltlake, India

Fabrication of Au doped Ag nanorod with a central twin boundary have been done by a new synthetic protocol. The Bimetallic Au@Ag rod then assembled to form a network type structure with multiple porous crystal sites (low coordinated atomic sites like stepped surface, terrace, grain boundary, twin boundary etc). Dengue serotype-2

related metabolites like L-tryptophan, Blood glucose, vitamin K , vitamin d<sub>3</sub>, vitamin C , Uric Acid have been oxidized electrochemically to get characteristic peak of each analytes in human serum. It was found that Differential Pulse Voltammetry, Chronoamperometry, Electrochemical Impedance Spectroscopy are able to generate a linear calibration plot of each analytes in the physiological concentration level when the Au@Ag network is used as an electrode material to catalyze the reaction. Besides we have also performed aptamer based sensing of real Dengue-2 infected blood both by electrochemically and spectroscopically. The sensing limit of direct virus (serotype2) is well agreed with common lab methods like PCR. The sensitivity was cross checked in presence of other viruses like Dengue-3, Japanese Encephalities etc. Therefore a non-enzymatic protocol has been developed for early detection of Dengue-2 with low cost and high sensitivity,



**COLL 591**

**Two-dimensional nanoparticle assemblies with atomic-level precision**

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In nature, biological particles, such as virus capsids, are inspirational examples for hierarchical self-assembly with exceptional thermodynamic stability. They follow the principle of genetic economy, efficiency, and error-free structure formation using the concept of subunit based self-assembly. Related self-assembly concepts have been widely explored in supramolecular chemistry using molecular-level building blocks. However, a similar approach using colloidal-level building blocks such as inorganic nanoparticles has certain limitations due to challenges in controlling their size, shape, interactions, and stability. Despite tremendous progress in the field of NPs, achieving a combination of precision, reproducibility, and reliability is a formidable challenge in many branches of material science. In this presentation, we will discuss the self-assembly of atomically precise gold and silver nanoparticles into two- and three-dimensional (2D and 3D) superstructures (**Fig. 1**). Further, we will show how to extract three-dimensional details of such assemblies at near-atomic resolution using transmission electron microscopy (TEM) tomographic reconstruction. Finally, we show the application of nanoparticle superstructures in bioimaging and photocatalysis.

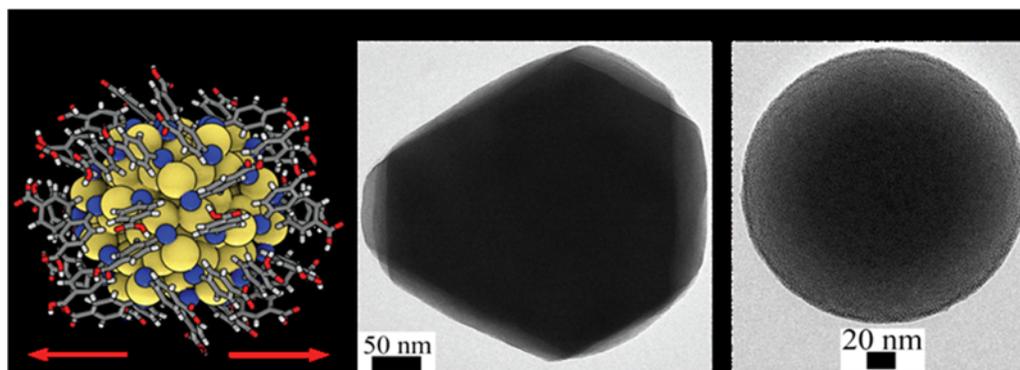


Figure 1. The solid-state structure of a gold nanocluster and TEM micrographs of self-assembled 2D nanosheets and capsid-like structures.

## COLL 592

### Mixing-controlled synthesis of metal halide perovskite nanocrystals

**Milad Abolhasani**, [abolhasani@ncsu.edu](mailto:abolhasani@ncsu.edu). Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina, United States

The emergence of organic/inorganic metal-halide perovskite nanocrystals (i.e., quantum dots) as a new class of semiconducting materials with unique optoelectronic properties, have enabled breakthrough applications at device scales in photonic devices.<sup>1</sup> Precise bandgap engineering of perovskite nanocrystals, similar to well-studied II-VI and IV-VI semiconductor nanocrystals will facilitate their adoption in next-generation devices. Further development of perovskite nanocrystals for impactful applications in energy<sup>2</sup> and chemical<sup>3</sup> technologies strongly benefits from a better understanding of different

mechanisms involved during the early-stage formation and growth kinetics of these exciting nanocrystals.

In this work, we developed and utilized a modular microfluidic platform for fundamental studies of the colloidal synthesis of metal lead halide perovskite nanocrystals using in situ absorption/fluorescence spectroscopy.<sup>4</sup> Decoupling of the spectral monitoring probe and the reaction time (residence time) within the microfluidic reactor enables a systematic study of the effect of early-stage precursor mixing timescale on the nucleation and growth of perovskite nanocrystals. Utilizing the developed microfluidic strategy, we systematically studied the mass transfer-controlled perovskite nanocrystal synthesis over 4 orders of magnitude change in the reaction timescales (15 ms to 5 min). The fundamental understanding of the process-structure-property relationships of the perovskite nanocrystals enabled by the time- and material-efficient microfluidic strategy will be utilized to develop the design principles for the on-demand synthesis of engineered perovskite nanocrystals for direct utilization in solution-processed photonic devices.

## **COLL 593**

### **Industry-academe dialogue**

***Kathleen J. Stebe***<sup>1</sup>, *kstebe@seas.upenn.edu*, ***Matthew L. Lynch***<sup>2</sup>, *lynch.ml@pg.com*.

(1) Chem Biomole Dept Rm 311A, Univ of Pennsylvania, Philadelphia, Pennsylvania, United States (2) Procter & Gamble Company, Cincinnati, Ohio, United States

In this session, we present a dialogue between industry and academe, with the goal of communicating industry views and needs to academic researchers and doctoral students interested in careers in industrial R&D. This event will focus on three topics: 1) Myths and Facts in Industrial R&D; 2) What is industry interested in?; 3) What drives a successful industrial career? This will take the form of a panel discussion which will include Gerard Baillely, VP Corporate Functions, the Procter & Gamble Company, Eric Kaler, President, University of Minnesota, and representatives from national funding agencies, and professors who have experience in interacting with industrial R&D. This panel will be moderated by Kate Stebe - Chair-Elect Colloid Division, Deputy Dean, University of Pennsylvania and Matthew Lynch - Vice-Chair Colloid Division, the Procter & Gamble Company. We hope to engage students, faculty, industrial scientists and engineers.

## **COLL 594**

### **Grand challenges for nanophotonics: Steering and riding light**

***Harry Atwater***, *haa@caltech.edu*. Applied Physics, Caltech, South Pasadena, California, United States

Research in nanophotonics is yielding advances towards grand challenges that have not previously been achievable. A first grand challenge is realization of comprehensively

tunable metasurface nanoantenna arrays, which are enabling dynamic, active control of the constitutive properties of light – amplitude, phase, wavevector and polarization – opening new applications such as phased-array optical beam steering, visible light modulation for communication and thermal radiation management. I will discuss the concept of a ‘universal’ metasurface, i.e, one whose properties are arbitrarily reprogrammable, performing a wide array of functions, including lenses with reconfigurable focal lengths and beam-steering devices. A second grand challenge for nanophotonics is design of spacecraft capable of reaching the stars beyond our solar system, since light itself is the only fuel capable of propelling spacecraft to the relativistic speeds needed to achieve interstellar travel. I will show that this audacious concept may be closer than we imagine, if advances in nanophotonic materials can enable key concepts for spacecraft propulsion, and communications.

## **COLL 595**

### **Electronic, multiplexed neurochemical monitoring**

**Anne M. Andrews**, [aandrews@mednet.ucla.edu](mailto:aandrews@mednet.ucla.edu). Mailbox 77, UCLA Neuroscience Bldg, Los Angeles, California, United States

To investigate chemical neurotransmission at scales wherein information is encoded, micro- to nanoscale sensors are needed for multiplexed and selective readouts of extracellular neurotransmitter concentrations with fast response times. We design, develop, and deploy sensing architectures that approach these critical attributes. We have developed electronic biosensors to investigate neurochemical signaling (and for other biosensing applications that involve biologically important small-molecule targets). Neurotransmitter recognition is by aptamers (oligonucleotide receptors) linked to field-effect transistor (FET) arrays for electronic signal transduction. We lithographically fabricate FETs on silicon microprobes for acute, multiplexed *in vivo* sensing. Moreover, we pattern FETs on soft materials to produce neuroprobes for chronic implantation. We assess brain tissue damage caused by probes constructed of different materials and sizes; minimizing tissue damage is hypothesized to lead to more stable recordings. Probes are implanted for neurochemical recordings in awake animals to enable decoding of behaviorally relevant information.

## **COLL 596**

### **Next-generation upconverting nanoparticles for low-threshold micro- and nano-lasing**

**Peter J. Schuck**, [p.j.schuck@columbia.edu](mailto:p.j.schuck@columbia.edu). Mechanical Engineering, Columbia University, New York, New York, United States

The development of low-threshold anti-Stokes miniature lasers is driven by a strong need: these lasers typically operate within unconventional environments that are highly susceptible to photodamage and/or unwanted autofluorescence generated by UV/visible

excitation. However, efforts on this front have been precluded by the higher energy losses and thermal instabilities encountered as cavity dimensions push to wavelength – and subwavelength – scales. Excitingly, we find that integrating solid-state, lanthanide-based UCNP as gain media within small laser platforms not only solves these problems but revolutionizes the intrinsic limits of lanthanide upconversion—which is constrained by optically forbidden transitions—by coherently coupling the quantum emitters. Working with the Odom group, we combine UCNP and plasmonic arrays to demonstrate continuous-wave, room temperature upconverting sub-wavelength lasing with thresholds several orders of magnitude lower than observed in any existing small lasers. These nanolasers have dimensions and power requirements that are sufficiently small to function within cells and tissues, smartphones, extraterrestrial sensors, or on-chip quantum circuitry – offering immediate relevance to in vivo biomedical, quantum optics, and nanophotonics applications.

## **COLL 597**

### **Organometallic precursors for FEBID and FIBID of nanostructures**

**Lisa McElwee-White**, *lmwhite@chem.ufl.edu*. Department of Chemistry, University of Florida, Gainesville, Florida, United States

Focused electron beam induced deposition (FEBID) and focused ion beam induced deposition (FIBID) can create metal-containing nanostructures by using charged particles to induce local decomposition of organometallic precursors. We are using mechanistic insights from electron- and ion-induced reactivity on surfaces to design organometallic precursors specifically for FEBID and FIBID. Synthesis of the candidate precursor complexes and evaluation of their reactivity with electrons and ions under UHV and steady state deposition conditions allows us to identify privileged ligands for use in FEBID and FIBID. Examples will be taken from deposition of Ru, Au, Pt and alloys.

## **COLL 598**

### **Optical properties of 2D and 3D plasmonic nanoparticle arrays**

**George C. Schatz**, *g-schatz@northwestern.edu*. Chemistry, Northwestern University, Evanston, Illinois, United States

This talk will overview the interplay between optics, plasmonics, and excitonics for systems that consist of arrays of gold, silver or aluminum nanoparticles in 1D, 2D and 3D. Two kinds of arrays will be considered, those involving DNA-linked nanoparticles in 3D with subwavelength particle spacings, and those involving 2D arrays of particles where the spacing satisfies a diffraction condition that produces hybrid plasmon-photonic excitations known as lattice plasmons. The emphasis of the DNA-linked nanoparticle structures is on describing scattering and extinction experiments where issues such as effective medium approximations and Fabry-Perot cavity modes are

important. I also describe DNA-linked structures with embedded dyes, and structures that combine magnetic and plasmonic properties.

The studies of lattice plasmons include unusual extinction and scattering properties of the lattices that include quadrupole resonance effects for aluminum lattices, and lattice plasmon lasers in which laser dyes are added to the nanoparticle lattices and where the theory needs to combine electrodynamics with a quantum description of the dye photophysics. I will also talk about recent work on exciton transfer between dye molecules that is mediated by plasmonic nanoparticles, and about how array topology properties can be used to advantage in determining lattice plasmon properties.

## **COLL 599**

### **Lignin nanoparticles as a sustainable oil dispersant**

**Amber Pete**, *apete4@lsu.edu*, *Jin G. Lee*, *Bhuvnesh Bharti*, *Michael G. Benton*.  
Chemical Engineering, Louisiana State University, Baton Rouge, Louisiana, United States

The large-scale oil spills have repeatedly occurred and adversely affected our environment, and ecosystem. The primary method used for managing oil spills is to “dissolve” the spilled oil in water in form of emulsion droplets. Here an amphiphilic emulsifier is generally used to stabilize oil-water interface and initiate the formation of oil-in-water emulsion. However, recent studies have shown that the commercially used emulsifiers for oil spill cleanup processes have adversely affected our environment, and there is an immediate need to find new, ecofriendly alternatives to currently used emulsifiers. Here, we present nanoparticles synthesized from plant biopolymers as a new class of biocompatible emulsifiers, which allow for managing oil spills in a rapid and ecofriendly manner. We demonstrate the ability of plant-based nanomaterials to stabilize emulsion droplets using chitosan coated lignin nanoparticles as a model system. We also show the effect of presence of the lignin-chitosan composite nanoparticles on the metabolic activity of *Alcanivorax borkumensis*, and corresponding biofilm formation at the oil-water interface. The study presents a new design principle of engineering materials using plant-based precursors, and provides much-desired sustainable alternative to currently used harsh chemical emulsifiers.

## **COLL 600**

### **How staphylococcal autolysin interacts with surfaces during biofilm formation**

**Nicholas Fitzkee**, *nfitzkee@chemistry.msstate.edu*, *Rahul Yadav*, *Randy Perera*, *Taylor South*. Chem Dept Hand Lab Rm 1115, Mississippi State University, Mississippi State, Mississippi, United States

Every year, over 1.5 million Americans are affected by a healthcare related infection. The source of many of these infections is an implanted medical device, where bacteria

can colonize to form biofilms. During the earliest stages of biofilm formation, proteins and other molecules on the bacterial surface spontaneously adsorb to the medical device, but the molecular determinants of this process are unclear. Autolysin (AtlE) is an extracellular protein from *S. epidermidis* that has been implicated in bacterial attachment during biofilm formation. AtlE has multiple domains, each of which may be important for surface binding. Here, we use NMR spectroscopy to identify the structure-function-surface relationships in bacterial attachment. Fibrinogen- and fibronectin-coated nanoparticles are engineered to model inorganic surfaces coated with human blood proteins. Then, NMR, light scattering, and conventional spectroscopies are used to understand the interaction between AtlE and these model surfaces. Focusing on the AtlE amidase (Ami) and R2ab domains, we have determined that both domains contain dynamic regions, making them good candidates for surface attachment. Both proteins readily coat fibrinogen-functionalized nanoparticles, and binding kinetics are slow on the NMR timescale. Additionally, we have carried out titrations with fibrinogen and fibronectin, and these titrations suggest a potential surface of interaction for R2ab and Ami. When both R2ab and Ami are mixed together, they can compete for the same surface, revealing a complex interplay involving both thermodynamic and kinetic control. Moreover, surface binding of Ami may be modulated by solution conditions, as this domain exhibits altered dynamics when the extracellular zinc concentration is elevated. Together, our results show how protein biophysics and surface chemistry can be leveraged to understand the complexities of biofilm formation.

## **COLL 601**

### ***Staphylococcus aureus* adhesion is mechanosensitive to soft materials**

*Irene Kurtz, Kristopher K. kcolewe@ecs.umass.edu, Jessica D. Schiffman, schiffman@ecs.umass.edu.* 159 Goessmann Lab, UMass Amherst Dept Chem Engr, Amherst, Massachusetts, United States

Biofilm-related infections are a class of notoriously difficult to treat healthcare-associated infections, which commonly develop on the surface of implanted medical devices. Despite lacking visual, auditory, and olfactory perception, bacteria detect and settle on surfaces, however, how the intrinsic properties of materials affect the initial adhesion microorganisms remains relatively unknown. By unveiling the structure-property relationships between polymer materials and microbial adhesion, we could guide the design of materials a priori to resist the adhesion of infection causing microorganisms, such as *Staphylococcus aureus*. In this presentation, I will discuss the effect that fundamental properties of polymer coatings (i.e., molecular architecture, stiffness, and thickness) have on the surface-associated transport of bacteria and on the adhesion of bacteria under quiescent conditions. By decoupling the effects of molecular architecture, stiffness, and thickness from coating chemistry, we have unlocked specific structure-property relationships that can be tailored to control the degree of bacterial adhesion and subsequently, reduce the formation of biofilms. By fundamentally understanding the interactions between microorganisms and engineered materials, we can reduce the spread of microbial resistant genes and the use of

commercial antimicrobials in applications from biomaterials to water purification membranes.

## **COLL 602**

### **Bacterial motility and chemotaxis near oil-water interfaces**

**Roseanne M. Ford**, *rnf3f@virginia.edu*. University of Virginia, Charlottesville, Virginia, United States

Oil-water interfaces are critical features in bioremediation of environmental contaminants. A chemical dispersant was used to breakup oil into small droplets (10-100 microns in diameter) to enhance biodegradation of oil released into the Gulf of Mexico following the Deepwater Horizon tragedy. Removal of groundwater contaminants is especially challenging for residual oil-phase ganglia trapped within the soil matrix that leach out over long periods of time and pollute groundwater reservoirs. Microbes that accumulate at these oil-water interfaces facilitate biodegradation.

Motility and chemotaxis are physical processes that can bring bacteria into close contact with oil-water interfaces. Chemotactic bacteria are able to sense chemical gradients in their surroundings and swim toward localized hydrocarbon sources that they perceive to be beneficial to their survival. We quantify the extent to which these processes facilitate transport of bacteria from the bulk aqueous fluid to oil-water interfaces within porous media. Our fundamental approach, which combines laboratory experiments, multi-scale modeling and computer simulation is broadly applicable.

Microbial interactions with oil-water interfaces were studied in three experimental systems: a sand-packed column, a pore network, and a single pore. Breakthrough curves from a pulse input of bacteria into a column with residual oil-phase ganglia showed greater retention of chemotactic bacteria than non-chemotactic. Chemotactic bacteria responded to chemoattractants released from the oil phase ganglia and moved from the bulk fluid to the interface. To more directly observe the accumulation of chemotactic bacteria near an oil-water interface a microfluidic device with trapped oil droplets above a network of pores was used. Again, chemotactic bacteria were retained at oil-water interfaces within the device to a greater extent than non-chemotactic bacteria in control experiments. Finally, the accumulation of chemotactic bacteria near a single pore containing an oil-phase chemoattractant was analyzed and found to be dependent on the shear rate of the bacterial suspension flowing by the interface. Mathematical models and computer simulations were applied to the experimental systems to quantify the extent to which motility and chemotaxis contributed to the transport of bacteria to the oil-water interface.

## **COLL 603**

### **Holography demonstrates force-modulation of fimbriated bacteria adhesion without specific bonds**

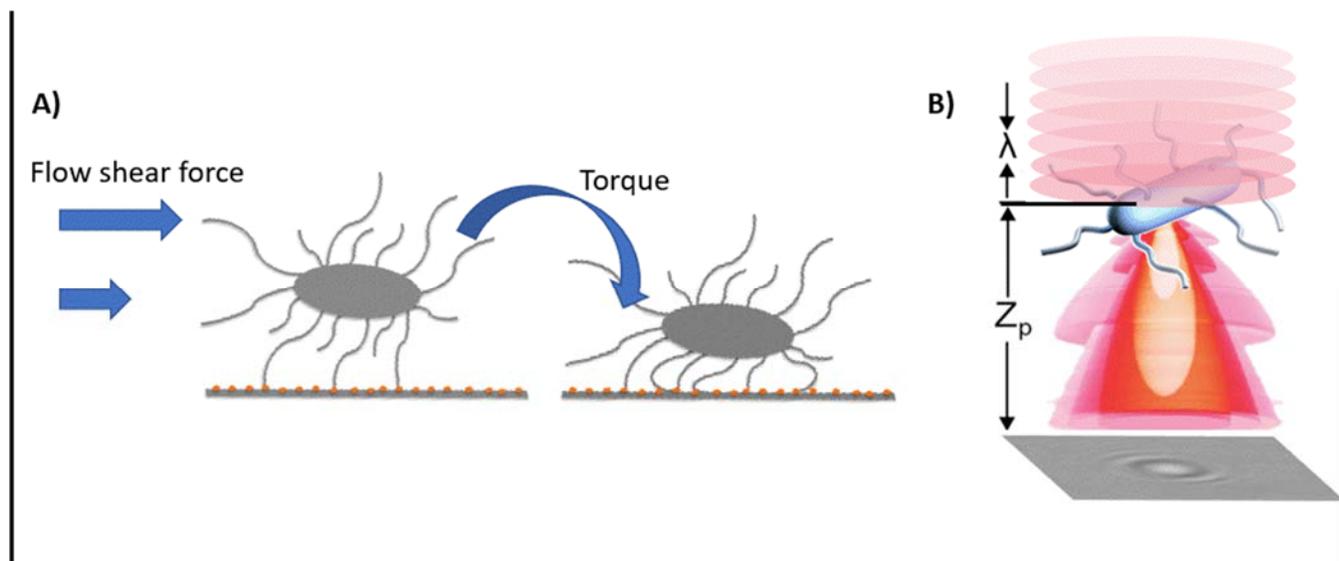
**Erik Reimhult**<sup>1</sup>, [erik.reimhult@gmail.com](mailto:erik.reimhult@gmail.com), Anders Lundgren<sup>2</sup>, Peter van Oostrum<sup>1</sup>. (1) Dept. of Nanobiotechnology, University of Natural Resources and Life Sciences, Vienna, Austria (2) University of Gothenburg, Gothenburg, Sweden

Many bacteria interact with surfaces *via* long ( $\mu\text{m}$ ) and thin (nm) tethers called fimbriae or pili. We investigated the role of fimbriae in the interaction of *Escherichia coli* (*E. coli*) under shear with surfaces displaying different densities of nanoscopic mannose or hydrophobic domains. The tip of type I fimbriae forms specific bonds with domains of mannose, implicated in so-called catch bonds, while only non-specific bonds can form to hydrophobic patches of the same dimensions.

We applied a newly developed extension of digital phase-contrast holographic microscopy and cytometry to map 3D trajectories of *E. coli* over these surfaces. This technique can be used to measure a position with  $\sim 50$  nm precision at high time resolution, *i.e.*, velocity, as well as size, orientation, and density. Flow shear forces acting on the bacteria were measured by resolving the laminar shear flow profile from the movement of free-flowing bacteria. This technique presents a new efficient tool to analyze bacteria interactions with surfaces quantitatively.

We show that fimbriated *E. coli* undergo a rolling motion on surfaces, *irrespective of binding specificity*, which is controlled by the fimbriae binding strength and the number of fimbriae forming bonds with the surface. The rolling motion slows down and eventually stops in response to *increasing* the flow rate. The loss of translational motion is caused by a shear force-induced push of the bacteria toward the interface. Pushing the bacteria closer to the surface increases the binding valency as shorter fimbriae now can bind to the surface.

Our data thus suggest that fimbriae allow bacteria to explore different surface niches, responding both to the affinity to and the number of available contact points, as well as to flow. In contrast to other force-controlled binding mechanisms, *e.g.*, catch-bonds, force modulation of the binding valency is *generic*; it is not limited to a specific interaction, but merely dependent on general properties such as the number, length distribution and mechanical properties of the tethers (fimbriae) forming bonds. We argue that this effect may be ubiquitous in biology and play an essential but overlooked role in cellular interactions under physiological conditions.



## COLL 604

### Controlling bacteria-material interactions via polyelectrolyte microgels

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Preventing the bacterial colonization of tissue-contacting biomedical devices is a key scientific challenge rich with potential clinical impact. Much research has concentrated on antimicrobial modification of device surfaces either by incorporating continuous elution mechanisms or by covalent surface tethering. Both strategies have shortcomings. As an alternative, we are studying a microgel-based approach that can flexibly modulate the bacteria-interactive surface properties. Microgels provide a controllable combination of size, soft mechanical properties, and network behavior. Notably, polyelectrolyte microgels can be electrostatically deposited to form sub-monolayer microgel coatings on complex 3-D device surfaces. Much of the underlying surface remains exposed to interact with mammalian cells and promote healing while the microgels impart antimicrobial properties to inhibit infection. We have shown that the size and spatial distribution of antifouling PEG-based microgels critically controls the competing requirements for bacterial repulsion and tissue-cell adhesion and proliferation. Incorporating antimicrobials into the microgels brings a second line of defence against bacterial colonization. To this end, we have concentrated on colloidal poly(acid) microgels such as poly(acrylic acid) (PAA) synthesized by suspension polymerization or membrane emulsification. After deposition, their internal negative charge enables loading by cationic antimicrobials via a second self-assembly step driven by antimicrobial-microgel complexation. Analogous to a cation exchange column, the drugs remain complexed when exposed to salt-free buffer at pH 7.4 but can be

released as the ionic strength is increased. Importantly, we have identified several antimicrobials, notably antimicrobial peptides with high positive charge and hydrophobicity, that remain sequestered under physiological pH and ionic strength for weeks or more. These antimicrobials are nevertheless released when the loaded microgels are contacted by bacteria, a process that kills the bacteria. We speculate that this antimicrobial is driven by the high concentration of negative charge and hydrophobicity associated with the bacterial cell envelope. Tissue cells such as osteoblasts or macrophages are, however, unable to similarly trigger release. Such bacteria-triggered release represents a new mechanism with which to create a so-called self-defensive surface with which to prevent device infection.

## **COLL 605**

### **Adhesion of bacteria at surfactant-decorated oil/water interfaces**

*Narendra K. Dewangan, Jacinta Conrad, jconrad@uh.edu. S222 Engineering Building 1, University of Houston, Houston, Texas, United States*

Interactions between bacteria and oil/water interfaces underpin technologies in wastewater treatment, in bioremediation, and in droplet microfluidics for pathogen detection, antibiotic susceptibility, and biotechnological selection. How the presence of surfactants, used to stabilize droplets or alter their size and interfacial tension, influence adhesion remains incompletely understood. Here, I will describe experiments in which we use microfluidics and microscopy to characterize adhesion of bacteria at the interface of dispersed hydrocarbons. We use as model organisms several species of marine bacteria that are found near oil spills and can degrade hydrocarbons, including *Halomonas titanicae*, *Shewanella haliotis*, *Marinobacter hydrocarbonoclasticus*. Specifically, I will show that adhesion of non-motile *M. hydrocarbonoclasticus* depends on droplet radius and surfactant type and concentration and can be modeled using Langmuir adsorption, and that (chemotactic) motility enhances the accumulation of bacteria on the interface. Finally, I will show that adherent, motile marine bacteria can be used to drive rotation of droplets near surfaces. These results demonstrate that surfactants can strongly alter bacterial interactions with and accumulation on dispersed hydrocarbons, with consequences for active manipulation of droplets.

## **COLL 606**

### **Fluid motion induced by driven and active colloids at interfaces**

*Nicholas G. Chisholm, nick.g.chisholm@gmail.com, Mehdi Molaei, Jiayi Deng, Tianyi Yao, John C. Crocker, Kathleen J. Stebe. Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States*

Colloid motion is altered by adsorption to fluid interfaces, allowing for boundary guidance or directed assembly. This is particularly interesting for colloidal motion driven by external fields (driven colloids) or for self-propelled objects (active colloids or

swimmers). However, the influence of a fluid interface on these hydrodynamic phenomena is relatively unexplored. We theoretically quantify the flows generated by interfacially trapped colloids by developing an appropriate flow singularity model for both driven and active colloids. The Reynolds and capillary numbers are assumed small, as is typical for colloidal systems involving an air- or oil-water interface, so interface deformation is neglected. We consider an ideal “clean” interface characterized solely by a uniform interfacial tension. We also consider an incompressible fluid interface, as can occur even for trace surfactant adsorption. Theoretical results are compared with experimental flow fields generated by (1) a microbead undergoing thermal motion, (2) a magnetic disk forced to translate at constant velocity, and (3) actively swimming *P. Aeruginosa* bacteria. Our results will be useful in future work on the use of active colloids to direct and enhance transport at interfaces.

## **COLL 607**

### **Response of marine bacteria to microplastics**

**Mary Machado**<sup>2</sup>, [mary\\_machado@brown.edu](mailto:mary_machado@brown.edu), **Tania Oliveira**<sup>1</sup>, **Gina Vimbela**<sup>2</sup>, **Anubhav Tripathi**<sup>2</sup>, **Arijit Bose**<sup>1</sup>. (1) University of Rhode Island, Kingston, Rhode Island, United States (2) brown university, Providence, Rhode Island, United States

Microplastics are a ubiquitous and damaging pollutant in the marine environment. However, few studies have focused on the interactions between plastic particles and marine bacteria. The objective of this study was to measure the responses of a characteristic marine organism (*Synechococcus elongatus* pcc 7002) to an anthropogenic stressor (polyethylene nanoparticles and microparticles) using molecular techniques and scanning electron microscopy. Polyethylene microparticles and polyethylene nanoparticles have effects on rRNA and tRNA stability within the cyanobacteria and on the expression of esterase genes. It contains the first characterization of variation of total RNA and shows increased degradation of RNA at increased exposure to nanoparticles and microparticles. Further experiments on esterase expression showed increased expression of these genes at 5 days in nanoparticle samples and at 10 days in microparticle samples. The formation of biofilms was revealed by electron microscopy.

## **COLL 608**

### **Alkali metal-liquid ammonia solutions: From blue electrolytes to bronze metals**

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The electronic structure of alkali metal – liquid ammonia mixtures at concentrations spanning from blue electrolytes to bronze colored metallic solutions is characterized by means of photoelectron spectroscopy in liquid microjets aided by ab initio molecular

dynamics simulations and quantum chemical calculations. The experimental PE signature of ammoniated electrons and dielectrons with vertical detachment energy of about 2 eV is in agreement with calculations. By comparing solutions of different alkali metals at low to intermediate concentrations, we show that the vertical detachment energy is only weakly sensitive to pairing with an alkali metal cation. This is confirmed by electronic structure calculations, which also show that the transition from the ammoniated electron to dielectron regimes is connected with a minor change of vertical detachment energy.

Upon increasing the alkali metal concentration, the photoelectron peak at ~2 eV broadens asymmetrically toward higher binding energies, which primarily signifies a build-up of a metallic conduction band. The present study shows that this electrolyte-to-metal transition is a gradual process rather than an abrupt first order transition. From the molecular point of view, the transition may be understood in a simplified way as a coalescence of individual solvated electrons and dielectrons upon increasing alkali metal doping, with the metallic behavior appearing at the threshold of percolation.

## **COLL 609**

### **Path integral approach to a strong coupling solution of a coarse grained electronic structure describes water's properties from ice to the supercritical regime**

**G J. Martyna**, *glenn.martyna@pimperlinc.com*. Pimpernel Science, Software and Information Technology, Yorktown Heights, New York, United States

Recently, a new atomistic simulation method has been introduced, the quantum Drude oscillator model (QDO), which coarse-grains the electronic structure of a complex chemical system into a set of distributed quantum oscillators. The model thereby contains, within Gaussian Statistics, all long-range force diagrams – many-body polarization and dispersion beyond the dipole approximation as well as cross interactions – leading to high transferability across many different chemical environments. That is all collective fluctuations in the N-body problem giving rise to long-range interactions are included. This responsiveness means the model can be parameterized to single molecule and dimer properties only, permitting the properties of condensed phase systems to naturally emerge as predictions. An efficient linear scale path integral method provides a strong coupling solution, keeping all diagrams and collective fluctuations allows the method to be applied to simulate large scale condensed systems such as water [4-5] with low overhead compared to standard atomistic models while including all long force diagrams.

In this lecture, the QDO model is described and its predictions of water's properties from the super-cooled regime to ice to the gas-liquid coexistence to the super critical regime including an outstanding prediction of critical point and temperature of maximum density, presented. Given the model's success, the physics underlying the model is then compared in more detail to other descriptions including dipole polarizable models, fixed point charge models, and the classical Drude model, and the reasons for the

outstanding predictions of the QDO treatment discussed in a form a suitable for the general audience.

## **COLL 610**

### **Interphase human chromosome exhibits out of equilibrium glassy dynamics**

**Dave Thirumalai**, *dave.thirumalai@gmail.com*. Department of Chemistry, University of Texas at Austin, Austin, Texas, United States

The structural organization of the condensed chromosomes is being revealed using chromosome conformation capture experiments and super-resolution imaging techniques. Fingerprints of their three-dimensional organization on length scale from about hundred kilo base pairs to millions of base pairs have emerged using advances in Hi-C and super-resolution microscopy. I will describe using a minimal Chromosome Copolymer Model (CCM) with two loci types corresponding to euchromatin and heterochromatin that the dynamics is similar to that observed in glasses. Chromosome organization is hierarchical involving the formation of chromosome droplets (CDs) on short genomic scale followed by coalescence of the CDs, reminiscent of Ostwald ripening. Glassy landscapes for the condensed active chromosomes might provide a balance between genomic conformational stability and biological functions.

## **COLL 611**

### **Rearrangements in supercooled liquids and reconfiguration of liquid crystal oligomer drops**

**Arjun G. Yodh**, *yodh@physics.upenn.edu*. University of Pennsylvania, Philadelphia, Pennsylvania, United States

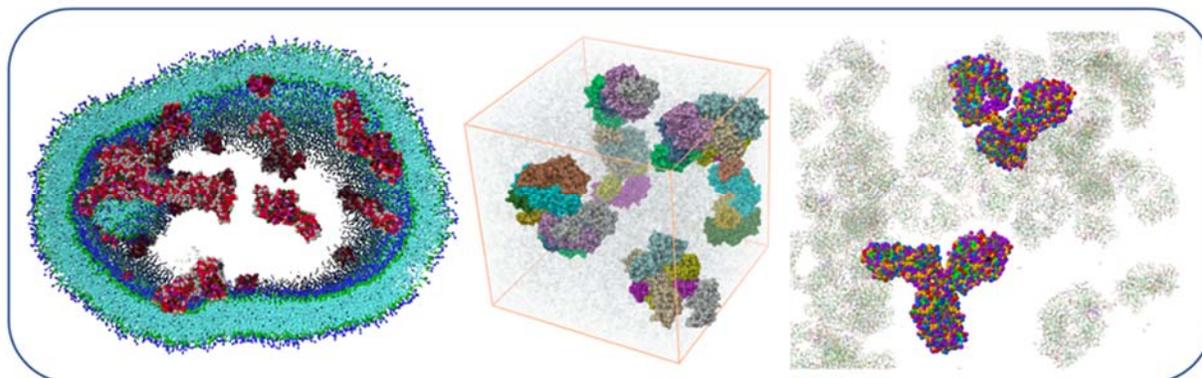
I will describe two experiments that probe softness, rearrangement, and reconfiguration in disordered soft matter. The first set of experiments employ video microscopy to probe structure and dynamics in colloidal supercooled liquids and elucidate the origin of non-exponential relaxation in these systems. The second set of experiments involve drops containing liquid crystal oligomers; these drops exhibit remarkable shape transitions with variation in temperature (and variation of other parameters) that are facilitated by oligomer polydispersity.

## **COLL 612**

### **Structured solutions and drug delivery**

**John Shelley**, *John.Shelley@schrodinger.com*. Development, Schrödinger, Inc., Tigard, Oregon, United States

Structured solutions, which are inhomogeneous on the supramolecular scale are present in diverse applications, including cleaning products, food, living organisms, materials and pharmaceuticals, to name a few. While experimental techniques are useful and necessary for studying such systems, often information on the molecular associations within and between such structures is limited. That information is crucial for industry to go beyond a purely empirical way to characterize and optimize these systems and enable a more rational and structure-based approach. For many applications molecular dynamics can fairly routinely produce supra-molecular information on these length-scales and there is enough overlap between simulation and experiment results to provide useful cross-checks. This approach does not eliminate the need for experiment, however, it should help reduce and focus those tests on the most promising directions. The complementarity between the two approaches should also efficiently yield a broad understanding of the complex behavior of these systems and how to best exploit it. While atomistic models can sometimes be used, more efficient mixed all-atom/coarse-grained, pure coarse-grained and meso-scale modeling methods permit us to dramatically expand the types of problems that can be addressed. This talk will review some applications in both small-molecule drug and biologics drug development: including lipid formulation as well as peptide aggregation and the viscosity of concentrated protein solutions.



**COLL 613**

**From molecular dissociation to crystal nucleation: Next generation methods for sampling rare events in all-atom resolution**

**Bruce J. Berne**<sup>1</sup>, [bb8@columbia.edu](mailto:bb8@columbia.edu), **Pratyush Tiwary**<sup>2</sup>. (1) Columbia Univ, New York, New York, United States (2) Chemistry and Biochemistry, University of Maryland at College Park, College Park, Maryland, United States

Processes such as the nucleation of a crystal or the association/dissociation of molecular complexes are so slow that they can not be studied using straightforward all-atom simulation techniques. Thankfully, over the decades several enhanced sampling algorithms have been proposed that can perform sampling of such rare events in an accelerated but controllable manner. However, a large class of these methods (arguably all?) need an a priori, at least approximate, sense of a low-dimensional reaction coordinate (RC) even before performing the sampling. In order to deal with this cyclic problem where one needs extensive sampling of the rare events to know the RC, but also needs to know the RC in the first place to perform sampling, it is thus extremely desirable to construct methods that learn the RC as they perform the sampling. In this talk we will be describing recent methods that learn reaction coordinate on the fly as they sample the landscape. This will include our method SGOOP that uses a Maximum Caliber (or path entropy) framework to solve the problem. We will also illustrate applications to different challenging real-world problems

## **COLL 614**

### **Molecular simulations probing the distribution of molecules: Phases, mesophases, and interfaces**

*J. I. Siepmann, siepmann@umn.edu.* Chemistry, University of Minnesota, Minneapolis, Minnesota, United States

Monte Carlo and molecular dynamics simulations with molecular-mechanics and coarse-grained force fields can provide much needed molecular-level information on the partitioning of molecules between bulk phases, the adsorption of molecules at interfaces, and the distribution of molecules between different regions in microheterogeneous systems. This talk will highlight insights from molecular simulation on liquid-liquid extraction, uptake in lamellar surfactant phases, retention in reversed-phase liquid chromatography, and self-assembly of high-chi block oligomers.

## **COLL 615**

### **Novel approaches to form organic-inorganic interfaces on metal oxides: Controlling reactivity, concentration of functional groups, and substrate morphology**

*Andrew V. Teplyakov, andrewt@udel.edu.* Chemistry and Biochemistry, University of Delaware, Newark, Delaware, United States

Recent interest towards controlled formation of organic-inorganic interfaces, fueled by modern development in molecular electronics, single atom catalysis, and high-selectivity sensing, affected greatly the approaches used for chemical surface modification. Despite substantial progress in synthetic capabilities to build a variety of precursor molecules, there are a number of major issues remaining. This presentation will describe recent developments in surface organic sensitization of metal oxide materials

that allow for controlling surface chemical functionalities (and their concentration) and for preserving the morphology of the substrate. The first step of the two-step method in the novel approach utilizes exposure of the oxide material to gas-phase propiolic acid, as a means to introduce carbon-carbon triple bond as a reactive functionality. This chemical group can further be modified with "click" chemistry. The approach preserves the morphology of otherwise brittle nanostructured materials (including ZnO and CuO) and allows to control surface chemical functionality by using a mixture of propiolic and acetic acids as a surface modifier in the first step. In fact, on CuO, this modification scheme does not require additional catalyst or even solvent. We use multiple analytical spectroscopic and microscopic techniques combined with computational investigations to understand the challenges of molecular-level control over the desired structures and processes.

## **COLL 616**

### **Building a new materials toolkit: Using surface chemistry to direct the morphology and deposition of thin films and nanoobjects**

**Amy V. Walker**, [amy.walker@utdallas.edu](mailto:amy.walker@utdallas.edu). Materials Science and Engineering, University of Texas at Dallas, Richardson, Texas, United States

Novel and advanced materials and devices for sensors, actuators, molecular and organic electronics, photovoltaics have many exciting applications including in healthcare, electronics, and energy harvesting and generation. However, for these to become integrated into everyday practical devices there are many challenges to be addressed. Perhaps the largest challenge is to direct and control the deposition of materials from the molecular scale to the mesoscale. Further these materials, whether nano-objects or thin films must be integrated into complex functional structures in a predictable and controlled way. In this talk we will describe our recent progress in synthesizing *in situ* with precise placement both nano-objects and films of two-dimensional materials, in particular transition metal dichalcogenides. We exploit our understanding of the common features of gas-phase and solution-based deposition methods to formulate design guidelines to control the *in situ* synthesis and placement of these complex materials with nanoscale precision, and to develop new faster, precise deposition processes.

## **COLL 617**

### **Monolayer assembly, film morphology, and charge transport of organic semiconductor layers and films**

**Steven L. Tait**, [tait@indiana.edu](mailto:tait@indiana.edu). Indiana University, Bloomington, Indiana, United States

Surface-assisted molecular self-assembly is a powerful strategy for forming molecular-scale architectures on surfaces, which have potential applications as molecular semi-

conductors. Understanding the intermolecular interactions on a surface can help predict packing, stacking, charge transport, and other key properties and allow for new molecular designs to be tailored for a required organic semiconductor function. This presentation will compare studies of a series of molecules related to tris(*N*-phenyltriazole) (**TPT**). TPT was shown by our group to exhibit exception stacking characteristics with planar stacking through > 20 molecular layers by donor–acceptor (D–A) type intermolecular  $\pi$ – $\pi$  contacts between the electron-deficient tris(triazole) core and electron-rich peripheral phenyl units. We investigated an expanded family of **TPT**-based molecules with variations made on the peripheral aryl groups to modulate the molecular electron distribution and examine the impact on molecular packing and charge-transport properties. Molecular-resolution scanning tunneling microscopy was used to compare the molecular packing in the monolayer and to investigate the effects that the structural and electronic modifications have on the stacking in subsequent layers. Conductivity measurements were made using the four-point probe van der Pauw technique to demonstrate charge transport properties comparable to pentacene. Although molecular packing is clearly impacted by the chemical structure, we find that the charge transport efficiency is quite tolerant to small variations in the molecular structure.

## **COLL 618**

### **Unusual electronic structure and surface properties of transparent conducting oxide semiconductors**

**Chris F. McConville**, [chris.mcconville@rmit.edu.au](mailto:chris.mcconville@rmit.edu.au). Physics, RMIT University, Melbourne, Victoria, Australia

Oxide semiconductors have become of great technological interest and importance in recent years with opportunities to improve both the existing materials and their potential device applications. This is particularly true for a sub-group of materials that display both optical transparency and high electrical conductivity, so-called transparent conducting oxides (TCOs). The fact that some of these materials, such indium tin oxide (ITO) have been around for many years and seen significant industrial use as transparent conductors in a relatively low quality form, has perhaps contributed to the belated recognition of using these materials as semiconductors in their own right. Here, examples from the surface and bulk electronic properties of several epitaxially grown oxide semiconductors ( $\text{In}_2\text{O}_3$ , CdO and ZnO) will be discussed along with the effects of modifying their surfaces by controlled adsorption. The valence band density of states and the surface electronic properties of these TCO's have been studied using high-resolution synchrotron radiation angle-resolved photoemission (SR-ARPES) and core-level photoemission spectroscopy with hard x-rays (HAXPES), and these data are compared with theoretical DFT band structure calculations. A common property of these oxide semiconductors is the presence of a significant electron accumulation layer at the surface. While this is similarly found at the surfaces of materials such as InN and In-rich InGaN, it is in marked contrast to the electron depletion typically observed at the surfaces of conventional III-V, II-VI and Group IV semiconductor materials. More

unusual still is the quantized nature of this surface 2D electron gas. The origins of this phenomenon will be discussed in terms of the band structure and intrinsic properties of these materials.

## **COLL 619**

### **Interface engineering for electronic applications: Surface chemistry of 2D materials for doping and contacts and Si anodes for SEI formation on batteries**

**Christina A. Hacker**<sup>1</sup>, [christina.hacker@nist.gov](mailto:christina.hacker@nist.gov), *Saya Takeuchi*<sup>1,2</sup>, *Siyuan Zhang*<sup>1,2</sup>.  
(1) Stop 8120, NIST, Gaithersburg, Maryland, United States (2) Theiss Research, La Jolla, California, United States

Incorporation of novel materials into electronic paradigms enables transformative potential in applications ranging from memory, batteries, catalysts, flexible devices, and alternative computing paradigms. In order to take advantage of the promising properties of these components, a holistic study of the fundamental components, as well as their impact on the final device properties are important. As interfaces continue to dominate the electrical performance, the ability to adjust the interface for desired properties becomes more critical. Molecular layers offer a versatile means of tuning interfacial electronic, chemical, physical, and magnetic properties. This talk will focus on our work with engineering interfaces for nanoelectronic and battery applications. Transition metal dichalcogenides are promising for nanoelectronic and optoelectronic applications and we have investigated the role of organic molecules in doping the charge carriers as well as optimizing metal contacts for device performance. In the area of batteries, much focus is on the promise of silicon anodes while there are several scientific challenges to overcome, including lifetime reliability. Paramount among this is the understanding of the surface-electrolyte-interphase (SEI) with cycling. We will describe the impact surface functionalization conditions have on the resulting SEI formation and electronics of silicon anodes.

## **COLL 620**

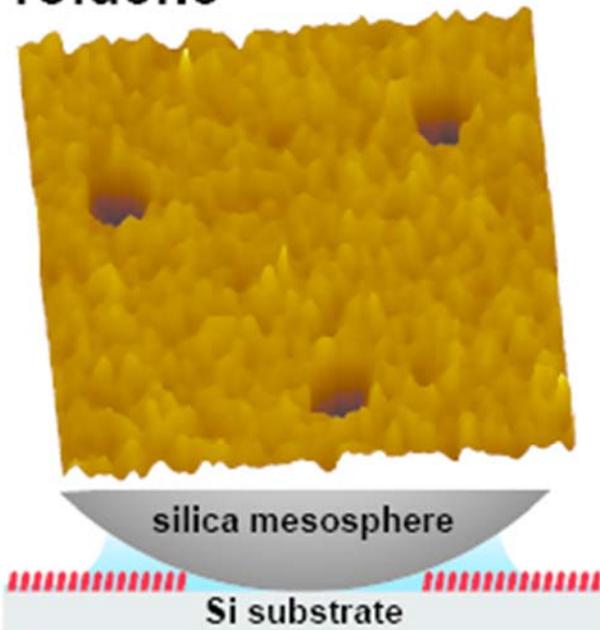
### **Organosilane nanostructure fabrication on semiconductor substrates using particle lithography: Influence of solvent and surface water**

**Thomas J. Mullen**, [tj.mullen@unf.edu](mailto:tj.mullen@unf.edu). Department of Chemistry, University of North Florida, Jacksonville, Florida, United States

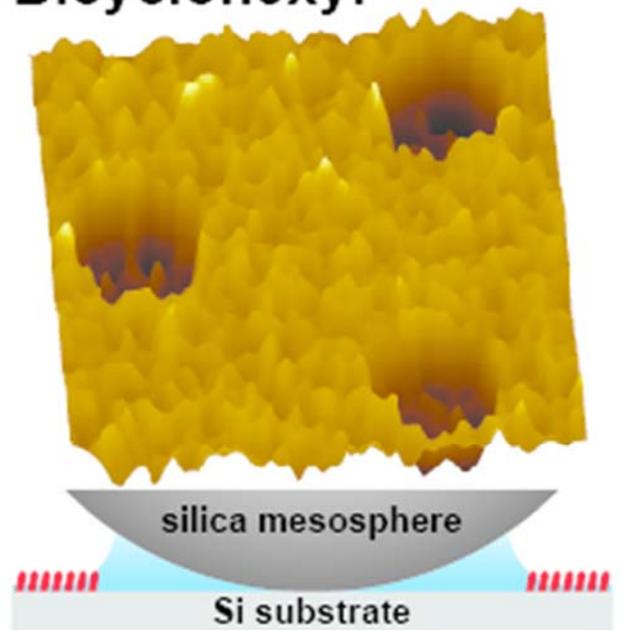
Patterned organosilane monolayers on semiconductor substrates serve as molecular platforms for electronic, optical, and sensing applications. Among the numerous strategies to pattern organosilane monolayers, particle lithography offers a high throughput means to fabricate arrays of organosilane nanopatterns across large areas. However, the size and features of organosilane nanopatterns is typically dependent on the mesospheres used during particle lithography. Herein, we demonstrate that the utility of particle lithography for generating organosilane nanostructures can be

enhanced by tailoring sample preparation. First, we explore the influence of solvent on the formation of nanopores within organosilane monolayers using particle lithography. We find that smaller nanopores within organosilane monolayers are generated from anhydrous toluene solutions composition and larger nanopores are generated from bicyclohexyl solutions. Second, we investigate various substrate drying conditions and correlate the resulting organosilane nanopatterns (nanopores, pillars, and rings) fabricated using particle lithography to surface water. These insights into the influence of solvent and surface water demonstrates an additional level of hierarchical control over organosilane nanostructure formation on semiconductor substrates and enables a broader range of nanostructures that can be fabricated.

## Toluene

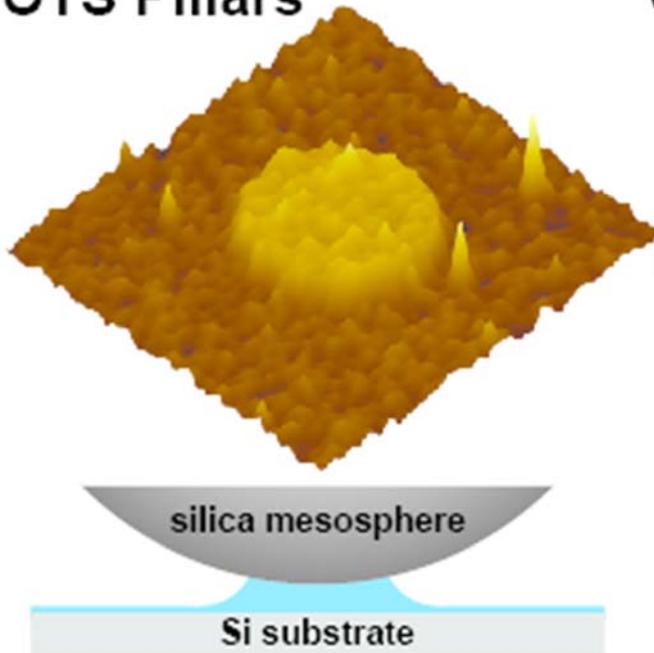


## Bicyclohexyl

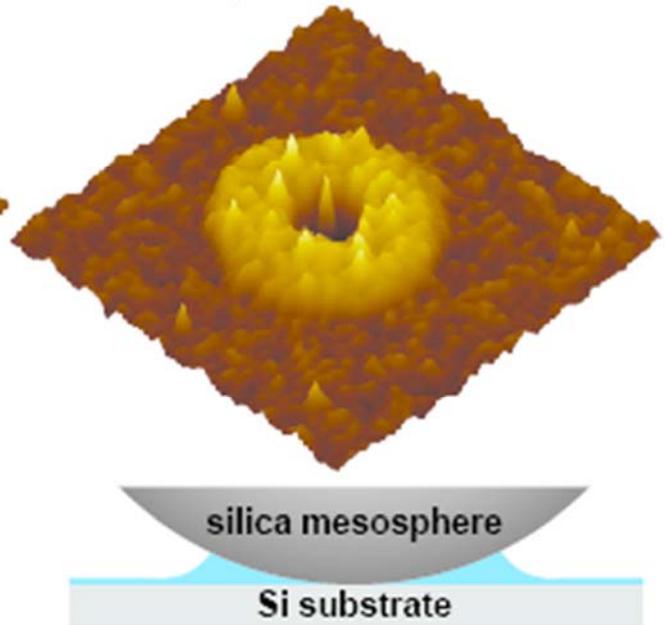


■ water meniscus    / OTS molecules

## OTS Pillars



## OTS Rings



COLL 621

### Role of hydroxy-substituted benzenes as rate enhancement additives for shallow trench isolation (STI) chemical mechanical planarization (CMP): Structure activity relationship (SAR)

*Katherine Wortman-Otto, katherinemwortmano@lewisu.edu, Jason J. Keleher. Dept of Chem, Lewis University, Romeoville, Illinois, United States*

As device feature size and complexity continues to advance beyond the 10-nm node, understanding the molecular level interactions during the fabrication steps becomes of utmost importance. In order to keep up with stringent market demands, device manufacturing has shifted from traditional 2D-NAND structures to multi-component 3D-NAND architecture. This transition has led to an increase in device performance via packing density, computing power, and memory storage which has significantly increased the number of process steps used in device fabrication. One critical attribute of these 3D-NAND structures is the electrical isolation of active components which can be achieved through a process known as Shallow Trench Isolation (STI) Chemical Mechanical Planarization (CMP). This planarization step looks at actively removing an oxide overburden left after the deposition process while selectively stopping on a  $\text{Si}_3\text{N}_4$  barrier layer. The angstrom-level uniformity in STI CMP is achieved through the synergistic balance of an applied mechanical force and the incorporation of a colloidal dispersion containing ceria ( $\text{CeO}_2$ ) nanoparticles, rheology modifiers, and stability additives. Research in this arena has emphasized the importance of additives with

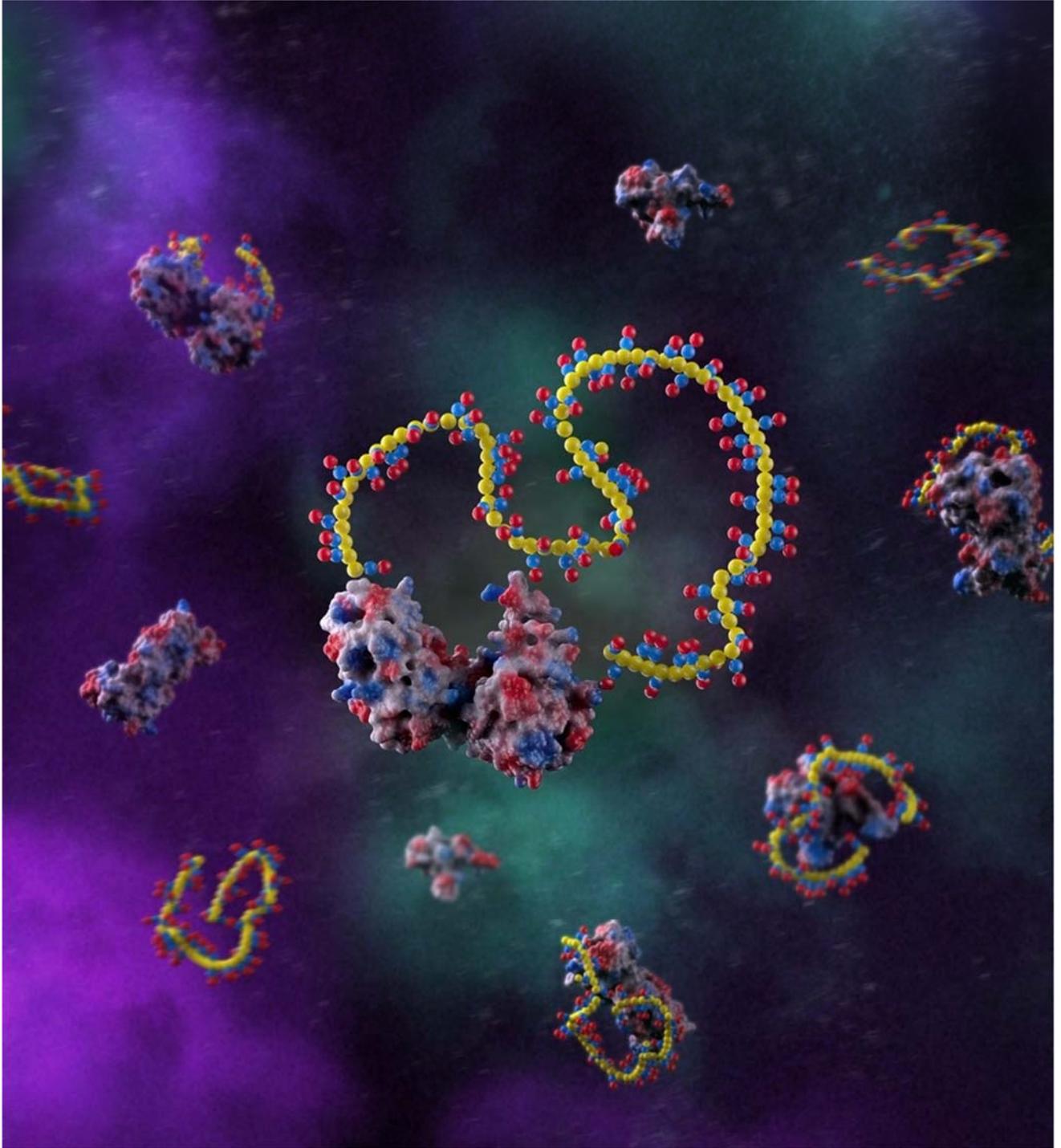
carboxylic acid, amine, and amino acid functionality in order to not only boost material removal rate (MRR) and enhance selectivity, but also limit defectivity and control final device topography. While the mechanism behind these additives is still of great debate, results have shown the importance of additive surface adsorption, nanoparticle surface redox properties, and slurry macro-environment. Using a suite of dynamic, analytical techniques this research explored the structure activity relationship (SAR) with hydroxy-substituted aromatic compounds as slurry additives for STI CMP. Results indicate a strong correlation between additive structure, slurry macro-environment, adsorption kinetics, and redox properties to the overall CMP performance. More specifically, balancing the surface oxygen vacancies (redox reactions) with dissolved oxygen content has shown to dramatically alter MRR and reduce defectivity.

## **COLL 622**

### **Tuning protein interactions with zwitterionic poly(sulfobetaine)**

**Deborah E. Leckband<sup>1</sup>**, [leckband@illinois.edu](mailto:leckband@illinois.edu), **Tajin S. Ahmed<sup>1</sup>**, **Lydia Kisley<sup>2</sup>**, **Drishti Guin<sup>4</sup>**, **Kali A. Miller<sup>5</sup>**, **Martin Gruebele<sup>3</sup>**. (1) University of Illinois, Urbana, Illinois, United States (2) Physics, Case Western Reserve University, Cleveland, Ohio, United States (3) Univ of Illinois, Urbana, Illinois, United States (4) Box 93-6 MC-712, University of Illinois Urbana-Champaign, Urbana, Illinois, United States (5) Chemistry, University of Illinois at Urbana-Champaign, Champaign, Illinois, United States

Zwitterionic polymers have been widely reported to be ultra low fouling, protein resistant, biocompatible materials. Here we report evidence that proteins directly interact with soluble, zwitterionic poly(sulfobetaine) (pSB) and also adsorb to end-grafted pSB thin films. Studies monitored the impact of soluble pSB chains on protein structure and stability, by quantifying temperature-dependent changes in the tryptophan fluorescence of a model protein phosphoglycerate kinase (PGK). Results demonstrated that pSB binds PGK directly (Figure) and reduces the unfolding temperature, in a concentration dependent manner. Two additional proteins similarly bind pSB, but the quantitative effects on the unfolding temperature depend on the protein identity. In order to reconcile these findings with the reported ultra low fouling properties of pSB thin films, we quantified the adsorption of proteins on end-grafted pSB coatings, as a function of the polymer grafting density, molecular weight, and ionic strength. The protein adsorption signatures agree qualitatively with polymer models for colloid interactions with weakly binding, grafted polymers. The results suggest that zwitterionic polymers do not universally repel proteins, but that the protein resistance of zwitterionic coatings will depend on the polymer grafting conditions.



Protein binding to zwitterionic polymers in solution

**COLL 623**

**Rapid “hard” serum albumin coronas: towards personalized surfaces**

**Joseph B. Schlenoff**, *schlen@chem.fsu.edu*, *Jose Delgado*, *Richard L. Surmaitis*.  
Florida State Univ, Tallahassee, Florida, United States

The formation of an adsorbed layer of proteins normally occurs quickly when a synthetic surface is exposed to physiological media. A “soft” coating or corona of easily-exchanged proteins is thought to reside on top of a more persistent “hard” corona. The distinction between “soft” and “hard” can be imprecise, since many proteins exchange given enough time. Here, we discuss a method to rapidly induce a hard corona of serum albumin on a surface using an ultrathin polyelectrolyte multilayer with aromatic sulfonates as the terminal functional group. In contrast to surface carboxylates, sulfonates hold on to serum albumin and prevent full displacement by self-exchange or by spontaneous desorption with solutions containing high salt concentration. In comparison, surfaces decorated with carboxylate groups permit displacement of the first monolayer of adsorbed albumin, presumably allowing cell-adhesive proteins such as fibronectin to adsorb. Because of this, cells adhere and proliferate on carboxylate-terminated surfaces, including the widely-employed “tissue culture plastic.” On multilayers terminated with sulfonate, cells adhere poorly and form quasispherical clusters, which have potential for use in stem cell culture. The production of biocompatible cell-repelling surfaces has promise for preparing personalized surfaces which mirror the serum chemistry of individuals.

## **COLL 624**

### **Interaction of PrP(106-126) with model cell membranes**

**Jordyn Markle**, *markjo04@gettysburg.edu*, *Shelli L. Frey*. Chemistry, Gettysburg College, Gettysburg, Pennsylvania, United States

When abnormal forms of prion protein accumulate in the brain, spongiform encephalopathies, a group of fatal neurodegenerative diseases, may result. Prion protein (PrP) is thought to function in copper transport and cell signaling and is associated with cell membranes through a C-terminal glycolipid anchor. Prion protein (PrP<sup>C</sup>) may unfold and refold into an abnormal structure (PrP<sup>Sc</sup>), leading to differing physical properties and function. PrP<sup>C</sup> folded in its wild type form is highly  $\alpha$ -helical, while PrP<sup>Sc</sup> contains more  $\beta$ -sheet structures that lead to misfolded non-functioning aggregates. These differing structures result in their differing characteristics; PrP<sup>C</sup> is easily degradable, while PrP<sup>Sc</sup> is highly insoluble and demonstrates resistance to digestion. To investigate the role that lipid membranes have in this secondary structure conversion to PrP<sup>Sc</sup>, a combination of calcein permeability assays, circular dichroism (CD) to monitor peptide secondary structure, and isothermal titration calorimetry (ITC) were performed on PrP(106-126), a short peptide fragment of PrP that recapitulates many of the known features of PrP<sup>Sc</sup>, in conjunction with negatively charged small unilamellar vesicles, a model system for neuronal membranes. At physiologically relevant concentrations, monomeric PrP(106-126) does not cause an increase in membrane permeability or disruption. The lipid interface does induce significant

secondary structure transformation of PrP(106-126) which scales with concentration of negatively charged lipid, indicating that membrane composition affects the peptide-membrane binding mechanism. Additionally, results will be presented on the thermodynamic binding parameters upon addition of PrP(106-126) to model membranes and how the process is affected by membrane composition and spontaneous curvature.

## **COLL 625**

### **Protein toxin sorting on the bacterial cell membrane**

**Angela Brown**, [acb313@lehigh.edu](mailto:acb313@lehigh.edu), **Justin B. Nice**. Chemical and Biomolecular Engineering, Lehigh University, Bethlehem, Pennsylvania, United States

Gram-negative bacteria release nanoscale outer membrane vesicles (OMVs) throughout growth to serve various functions, including delivery of toxins to both host and bacterial cells. Although the OMV is derived directly from the bacterial outer membrane (OM), numerous reports have demonstrated that the protein and lipid composition of the OMVs and OM can differ substantially. In particular, bacterial toxins are often reported to be enriched in the OMV relative to the OM. We have previously observed that the leukotoxin (LtxA) produced by *Aggregatibacter actinomycetemcomitans* associates with the surface of OMVs in a much higher concentration than on the OM. Here, we undertook a series of studies to investigate this sorting process. We observed that *A. actinomycetemcomitans* releases two populations of vesicles, one highly abundant population with diameters of approximately 100 nm, and a less abundant population with diameters of approximately 350 nm. We separated the two vesicle populations and measured the LtxA, protein, and nucleic acid compositions of both. The protein composition of the large and small OMVs is quite similar with the distinct exception of LtxA, which is found to be present in large amounts on the large OMVs and only in small quantities on the small OMVs. The large OMVs also contain significant amounts of surface-associated DNA. The outer leaflet of the OMV consists primarily of lipopolysaccharide (LPS); we therefore hypothesized that variations in the LPS structure between the OM, large OMVs, and small OMVs regulate binding of DNA and subsequent binding of LtxA. To study this, we purified LPS from the large and small OMVs and measured the chemical structures using matrix-assisted laser desorption/ionization (MALDI)-mass spectrometry (MS). Our results demonstrate that the LPS structures in the two OMV populations is distinct. Together, these results demonstrate a mechanism by which a bacterial protein (toxin) is sorted to specific secreted vesicles due to variations in the toxin's membrane affinity.

## **COLL 626**

### **Bioconjugates: *In silico* perspective**

**Coray M. Colina**, [colina@chem.ufl.edu](mailto:colina@chem.ufl.edu). Chemistry and Materials Science and Engineering, University of Florida, Gainesville, Florida, United States

Understanding the biomolecule-polymer interface is critical for the development of next-generation biomaterials, protein technologies and drug delivery. Understanding the interactions of the polymer with residues on the protein surface as a function of time will pave the road to the development of new materials. Molecular simulations are a powerful tool to complement and enhanced experimental findings, helping to reveal the fundamental interactions that drive these materials.

Many atomistic and coarse-grained models have been independently developed for polymers and proteins. However, only a handful of models have been used at the protein-polymer interface level over different time and length scales to determine the effect of their interactions. In this talk, we will discuss the current state-of-the art of these models, both at the atomistic and meso-scale level, from PEGylated systems to the novel polymer-protein system made by ATRP.

## **COLL 627**

### **Optimizing blood-compatible materials: Protein interactions with nanostructured and polymer brush surfaces**

*Matt Kipper*, [mkipper@engr.colostate.edu](mailto:mkipper@engr.colostate.edu). Dept of Chem Biol Engineering, Colorado State University, Fort Collins, Colorado, United States

The inside surfaces of blood vessels is the only material known to be completely compatible with flowing whole blood for long-term contact. This surface is dominated by the vascular endothelial glycocalyx—containing proteoglycans and glycosaminoglycans. We are developing new surfaces that mimic key features of this surface, which includes the dense assembly of polyanionic polysaccharides. These bioinspired surfaces have unique interactions with blood proteins, leading us to investigate these protein-surface interactions in detail. In particular, time-resolved, single-molecule video microscopy provides details of protein surface interactions that yield new insights into the phenomena that give rise to blood compatibility.

Surfaces modified with colloidal nanoparticles formed from the electrostatic complexation of glycosaminoglycans (which are polyelectrolytes) can be used to form structures that mimic the macromolecular assembly of the vascular endothelial glycocalyx. These nanostructured surfaces prevent the adsorption of fibrin fibers, which could lead to reduced blood clotting. We can also describe in detail the kinetics of protein adsorption to and desorption from these surfaces providing insights for the design of a new class of blood-compatible materials.

## **COLL 628**

### **Tuning protein interactions with polyions for cellular compartmentalization**

*Vivian Yeong*, *Jouwen Wang*, *Allie Obermeyer*, [aco2134@columbia.edu](mailto:aco2134@columbia.edu). Chemical Engineering, Columbia University, New York, New York, United States

Protein de-mixing has recently been implicated in the organization of cellular components. These phase separated membraneless organelles create distinct environments that are essential to cellular processes ranging from cell signaling to genome organization and gene expression. Several membraneless organelles appear to have the same physical properties as complex coacervates – liquid-liquid phase separated mixtures of oppositely charged polyelectrolytes. However, protein polymers differ significantly from synthetic polyelectrolytes. Proteins are amphoteric, have low charge density, and frequently adopt a globular folded structure. These differences impact the complexation and phase separation of proteins with polyelectrolytes. We are motivated to understand protein complex coacervation in order to enable new biological applications of these materials. Toward this end, we are interested in utilizing the physical phenomenon of complex coacervation and principles underlying the formation of liquid-like biological condensates to create synthetic membraneless organelles. We have investigated the complex coacervation of engineered proteins with biological polyelectrolytes to determine predictive design rules for protein phase separation. We employ these design rules to create synthetic organelles by promoting phase separation of engineered proteins in *E. coli*.

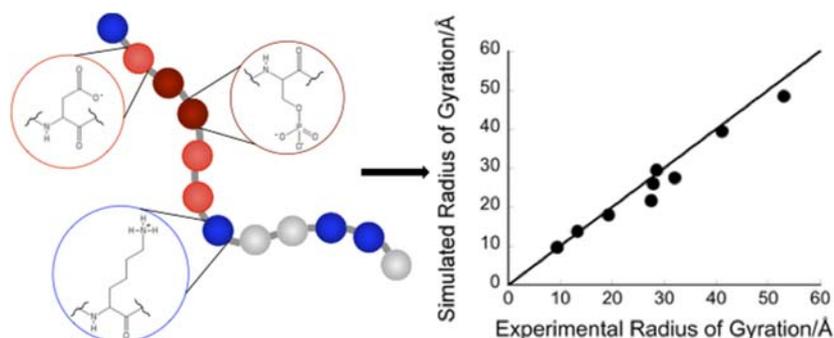
## **COLL 629**

### **From solution behaviour to interaction with lipid bilayers: Building a tool-box for understanding intrinsically disordered proteins**

**Marie Skepö**, [marie.skepo@teokem.lu.se](mailto:marie.skepo@teokem.lu.se). Theoretical Chemistry, Lund University, Lund, Sweden

Intrinsically disordered proteins, IDPs, are characterized by a lack of stable tertiary structure. More recently it has been shown that ~30% of all proteins in eukaryotic organisms belong to this group of proteins, and that IDPs are involved in a large number of central biological processes and diseases. This discovery challenged the traditional protein structure paradigm, which stated that a specific well-defined structure was required for the correct function of a protein. Instead, in solution IDPs adopt a heterogeneous ensemble of conformations, which can be altered by crowding and through interaction with membranes. Biochemical evidence has since shown that IDPs are functional, and that the lack of folded structures is related to their functions. There is a great interest in the research community in the structure-function relationship for IDPs. One hypothesis is that upon adsorption to surfaces, such as membranes, IDPs might adopt a more specific/folded structure, that modulates function. Hence, it is of interest to relate the properties of IDPs in solution with their properties in the adsorbed state and their interactions with biological membranes. To be able to obtain a molecular understanding of IDPs, it is useful to combine experimental solution-based techniques such as X-ray scattering, and neutron spectroscopy, with surface adsorption techniques such as neutron reflectivity, ellipsometry, and QCM-D. Additional insight into the effects of absorption can be gained by computer simulations using both atomistic and coarse-grained modelling. In this talk I will present our research regarding IDPs with respect to

their structural, thermodynamical, and dynamical properties in solution, and the effects thereon upon adsorption to surfaces and lipid bilayers.



Schematic representation of the coarse-grained model used for intrinsically disordered proteins, as well as the simulated versus the experimental radii of gyration. The latter were determined by small angle x-ray scattering.

## COLL 630

**Award Address (ACS Award in Colloid Chemistry sponsored by the Colgate-Palmolive Company). Engineering the bio-material interface for biosensing applications**

**Molly Stevens**, *m.stevens@imperial.ac.uk*. South Kensington Campus, Imperial College London, London, United Kingdom

This talk will provide an overview of our recent developments in the design of colloids to detect disease biomarkers, such as abnormally regulated enzymes, to extend the detection window for early disease diagnostics. This talk will describe our research on the design of polymeric and inorganic nanomaterials for developing sensitive detection assays that are simple, cost-effective and easy to deploy to the point-of-care. We are exploiting the sensing capabilities of nanoparticles to engineer paper-based lateral flow immunoassays (LFIAs) and nanosensors for in vivo disease diagnostics that produce a colorimetric response ideal for naked eye read-out. We can integrate our nanomaterial based assays into smartphone enabled tests for point-of-care cancer diagnostics and monitoring of disease progression and response to treatment. Recent developments in this and other contexts will be discussed.

## COLL 631

**Award Address (ACS Award in Surface Chemistry sponsored by The Procter & Gamble Company). Chemistry on three-dimensional surfaces**

**Teri W. Odom**, *todom@northwestern.edu*. Northwestern University, Evanston, Illinois, United States

This talk will describe three-dimensional structured nanoscale materials that exhibit extraordinary physical properties. These architectures show organized structure and function over multiple length scales, with independent control over each order of magnitude. We will discuss periodic hybrid nanostructures that can manipulate light-matter in unprecedented ways and three-dimensional substrates from two-dimensional sheets that show area-specific chemical reactivity and mechanical properties.

## **COLL 632**

**Award Adress (ACS Award for Research at an Undergraduate Institution sponsored by Research Corporation for Science Advancement). Fluorescence delineation of self-assembled aggregates of amphiphilic surfactants and chromonic dyes**

**Kerry K. Karukstis**, *Kerry\_Karukstis@hmc.edu*. Harvey Mudd College, Claremont, California, United States

A unifying focus of my research is the study of classes of amphiphilic molecules that have the ability to self-assemble into complex three-dimensional structures using transient intermolecular forces when placed in water and other solvents. My undergraduates and I have pioneered the practice of examining the complete emission spectrum of an extrinsic fluorescent probe to reveal heterogeneity in the probe distribution and thereby efficiently characterize the diverse microregions of amphiphilic aggregates. The basis for this approach is the fact that an overall fluorescence spectrum is the sum of the emission spectra of a fluorophore in its multiple environments within a given system. We use the fluorophore prodan (6-propionyl-2-(dimethylamino)-naphthalene) which has the potential to distribute throughout the diverse microregions of self-assembled aggregates as a consequence of its solubility in a variety of media. Furthermore, unlike many fluorophores, prodan exhibits an extreme sensitivity of its maximum emission wavelength to its environment. We have used prodan to characterize a wide variety of surfactant aggregates including aqueous micelles with cationic, anionic, zwitterionic, and nonionic headgroups; reverse micelles of varying water pool size; unilamellar vesicles of varying dimension; liquid crystalline mesophases of amphiphilic alkyl glucosides; supramolecular assemblies of polymeric dendrimers and surfactants; and aggregates of chromonic dyes.

We have also used this spectroscopic approach to construct thermodynamically correct binary surfactant-water phase diagrams representing phase behavior as a function of surfactant concentration and temperature. In a study of aqueous mixtures of n-octyl- $\beta$ -D-glucoside, we highlighted several significant advantages of this method including the use of a single technique to demarcate distinct single-phase and multi-phase regions of a binary system in a rapid and streamlined fashion. This presentation will feature some of the key findings of my undergraduate research students throughout my career.

## **COLL 633**

### **Dynamic plasmonics**

**Laura Na-Liu**, *na.liu@kip.uni-heidelberg.de*. Kirchhoff Institute for Physics, University of Heidelberg, Heidelberg, Germany

A prerequisite to build advanced nanophotonic architectures is the ability to precisely control the organization of different optical elements, such as metal nanoparticles, fluorophores, semiconductor nanocrystals, and others in space. To this end, DNA origami represents an ideal construction platform owing to its unique sequence specificity and structural versatility. I will present sequentially a diverse set of DNA-assembled nanophotonic systems according to their characteristic optical properties. I will also discuss about the inevitable evolution from static to dynamic devices along with the fast development of this inter-disciplinary field. Finally, possible future directions and perspectives on the challenges will be elucidated.

## **COLL 634**

### **Incorporation of liquid nanodomains into polymeric films for pharmaceutical applications**

**Eva Abramov**, *eva.abramov@mail.huji.ac.il*, **Nissim Garti**. Casali Center of Applied Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel

The pharmaceutical applications of microemulsion (ME) as drug delivery vehicles are gaining scientific interests due to their high solubilization potential for both lipophilic and hydrophilic drugs and enhanced penetration ability. However, the dermal application of MEs is limited because they cannot guarantee slow and controlled release of the drugs. This study proposes to incorporate the modified ME structures, or nanodomains (NDs), into a bio polymeric films, which allow slow and controlled release of nanodroplets along with the solubilized drug. Curcumin, hydrophobic polyphenol, served as the guest molecule in the loaded systems in our study.

Films were prepared by embedding empty and curcumin-loaded MEs. It was significant to verify the persistence of the nanostructure upon the dissolution of the film, mimicking its behavior with a human physiological aqueous environment. For this purpose, the films were dissolved, and the reconstituted ND structure was compared with the ND structure before film formation. Detailed investigation of nanodomain systems was performed by SAX, EPR, Cryo-TEM, DLS, SD-NMR techniques, which shed light on the structural and dynamical properties of the NDs before film formation and after film reconstitution. Ex-vivo release study was performed using Franz cell method and pigs skin. The most important finding of this study is that NDs structure after film redissolution is reversible and film forming process is reconstructive by allowing the intactness of nanodomain structure and the bioactive curcumin solubilization into the nanodroplet/water interface after film redissolution.

The combined techniques confirmed that NDs embedded film may be used as a

platform for solid reservoir of liquid nanodomains which enables controlled release of drug-loaded nanodomains.

## **COLL 635**

### **Roles of surface wetting and bulk diffusion in the contamination of polymer composite thin films by distilled mustard blister agent, HD**

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This work focuses on determining physicochemical interactions that influence the resistance of materials to chemical contamination, specifically for the case of a liquid phase chemical warfare agent exposed to polymer composite materials. The degree and type of retention is a function of wetting behavior at the material surface as well as the propensity for penetration of the liquid phase into the bulk layers of the exposed material. Experimental work has been performed to study the interaction of a liquid chemical agent, specifically, HD (bis(2-chloroethyl) sulfide, distilled mustard blister agent), and its associated chemical simulants, with polyurethane-based thin films. The materials studied include polyurethane-based coatings, which can be treated as high solids loaded polymer composites. Optical microscopy, atomic force microscopy, dynamic contact angle, and FTIR-ATR have been used to track how HD can become entrained in surface and near-surface capillary networks as well as transport into bulk polymer through molecular diffusion as a function of variations in polymer binder and solids loading in the composite. The understanding garnered from considering chemical retention not only informs next generation decontamination approaches but also the design of new coatings formulations that are tuned for chemical resistance, reduced decontamination burden, and mitigated hazard for warfighter personnel.

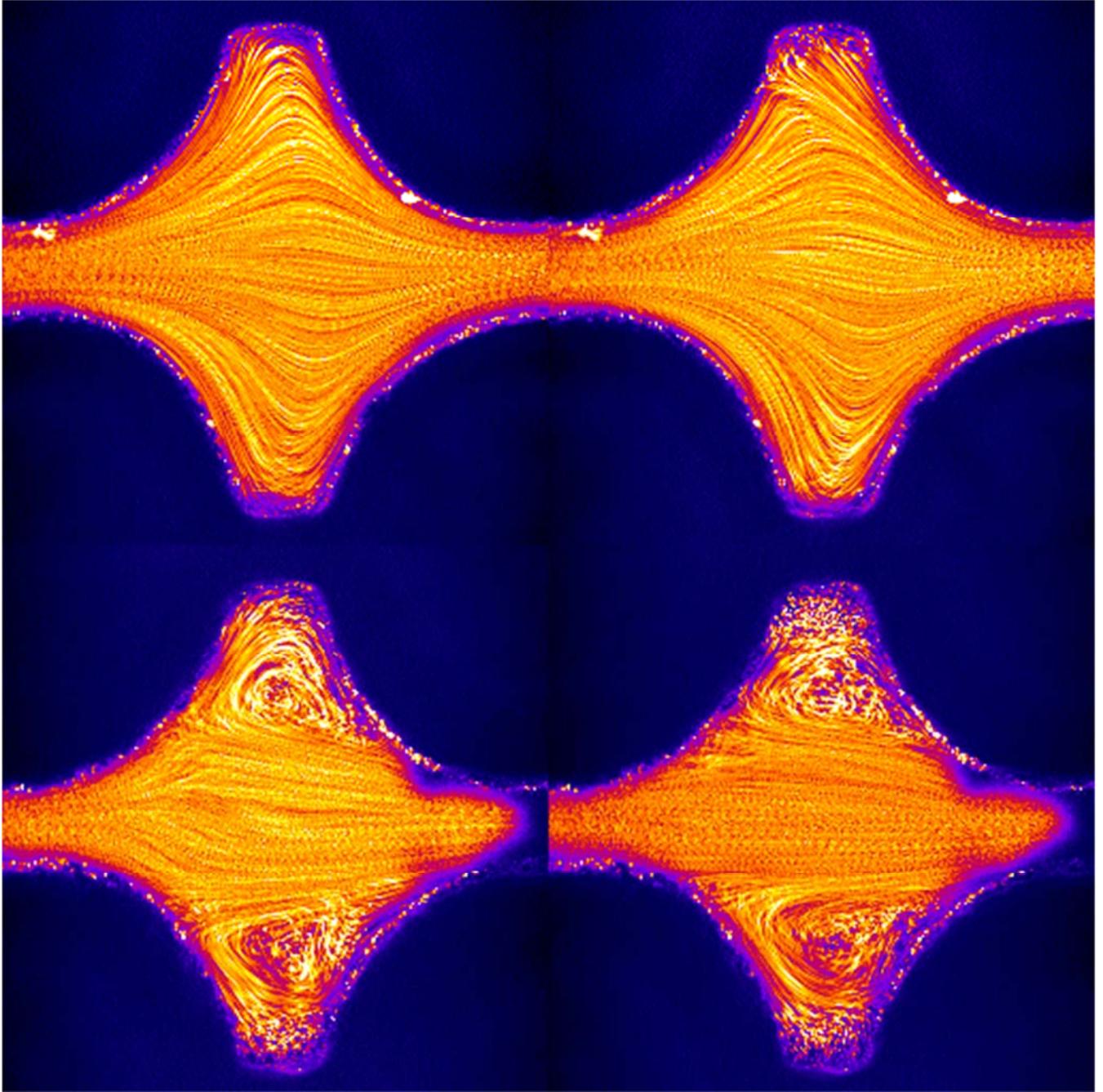
## **COLL 636**

### **Bistability in the flow of polymer solutions in porous media**

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Polymer solutions are often injected in porous media to improve enhanced oil recovery or groundwater remediation efforts, but these applications are limited by an incomplete understanding of the underlying physics. In particular, the removal of oil or contaminants from an aquifer is often limited by the formation of preferential flow pathways that bypass large regions, leaving them untreated. These bypassed regions can potentially be treated using polymers, which are believed to dynamically redirect the flow.

In a tortuous pore space, polymers are elongated dynamically by the extensional and shear fields. At sufficiently high flow rates, polymer elongation cannot keep up with the changing flow field in the tortuous pore space, producing an unstable flow with strong spatial and temporal fluctuations. These flow fluctuations are surprising, because the flows have negligible inertia ( $Re \ll 1$ ) and hence the flow is typically assumed laminar. In particular, it is still poorly understood how the spatio-temporal characteristics of this flow state depend on pore geometry. We shed light on this question by systematically varying the spacing between pores. We find that when the pore spacing is large, unstable eddies form upstream of each pore, similar to the case of an isolated pore. By contrast, when the pore spacing is sufficiently small, the flow exhibits a surprising bistability, stochastically switching between two distinct flow states. We hypothesize that this unusual behavior arises from the interplay between the retention of polymer strain between pores, hysteresis in polymer conformations, and fluctuations in the flow. Our results help to elucidate the rich array of flow behaviors that can arise in polymer solution flow through porous media.



**COLL 637**

**Controlled delivery and release for biopolymer degradation**

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The encapsulation and controlled release of active ingredients is critical in a variety of industrially important applications. These applications include delivery of agricultural and pharmaceutical actives, catalysts, components such as enzymes, fragrances or emollients for consumer and personal products, and actives delivery to aid in oil and gas production. The function of a controlled delivery system is to protect or isolate the actives from other reactants or from external conditions (humidity, UV light) until the active is needed, and to provide a trigger mechanism to release the actives on demand. The morphology of the encapsulated system (core-shell or matrix) and the release mechanism are key features that must be designed and optimized to meet the application requirements. This paper will highlight the design of an encapsulated oxidant for oil and gas applications. The robust encapsulation system successfully enables the delivery of an oxidant in harsh down-well conditions which provides a controlled degradation of a key biopolymer when triggered. A similar approach may be leveraged for encapsulation and controlled release needs in other technology spaces.

## **COLL 638**

### **Phase behaviour of rod-polymer mixtures**

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Dispersions of colloidal rod-like particles, like tobacco mosaic or feline distemper viruses, cellulose nanocrystals, or boehmite rods, can demix into two or more coexisting phases upon addition of non-adsorbing polymers. This polymer-mediated phase separation is the result of excluded volume interactions between the polymers and the rods and can be described by Free Volume Theory (FVT). We extend FVT to predict the liquid crystalline phase behaviour of dispersions containing hard rods mixed with non-adsorbing polymers up to dense phases, including the smectic and crystal phase states. By only taking into account excluded volume interactions a remarkably rich phase behaviour is found. Among the results we find four- and five-phase coexistences. It will be discussed whether this finding contradicts the Gibbs' phase rule in our system, from which a maximum of three coexisting phases is naively expected.

## **COLL 639**

### **Molecular mechanisms of complex boundary lubrication behavior for multifunctional associative polymer viscosity modifiers**

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The drive towards better fuel economy through lower viscosity engine oils places increased importance on reducing friction in the so-called boundary regime, where direct solid-solid contact can lead to increased wear and friction. Intriguingly, functionalized olefin copolymers (FOCP) containing a small fraction of polar, aromatic groups are found to reduce wear and improve the efficiency of real engines in addition to improving their viscosity stability vs. temperature. We have utilized a suite of surface-sensitive techniques to elucidate the molecular-level origins of this friction reduction. Quartz crystal microbalance with dissipation monitoring measurements demonstrate that FOCP forms viscoelastic layers at steel-oil interfaces with significantly higher irreversibly adsorbed masses compared to equivalent non-functionalized olefin copolymers (OCP). These adsorbed FOCP layers display a complex, non-monotonic relationship between bulk FOCP concentration and nanoscale friction measured by colloidal probe atomic force microscopy (AFM). In addition, intermediate concentrations of FOCP are significantly more lubricious than polymer-free oil (PAO4) or equivalent OCP solutions. To understand this behavior, we performed quasi-static normal force AFM measurements, which showed that the adsorbed FOCP function as a repulsive, steric barrier upon approach of the probe, and induces a long-range adhesion upon its retraction. The magnitude and range of both repulsion and adhesion increase monotonically with increasing FOCP concentration. Bulk rheology measurements indicate that the polar functional groups form associative bonds which promote stronger repulsive and adhesive interactions with increasing bulk FOCP concentration by increasing the adsorbed mass and the number of adhesive interpolymer bridges respectively. The importance of association between bulk and surface FOCP is further highlighted by the reduction in friction and adhesion between adsorbed FOCP layers when non-associative OCP replaces the bulk FOCP. Together, these results demonstrate that the steric barrier reduces friction while adhesive bridges increase it, with competition between both processes leading to the observed non-monotonicity.

## **COLL 640**

### **Role of voids and porosity on the transport of macromolecules through 3D printed materials**

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Additive manufacturing or 3D printing is of interest for supplying personal protective gear on-demand during field use because it can dramatically reduce the logistics and supply chain burden. However, materials formed via 3D printing are inherently porous and may contain interconnected voids that affect the degree to which they can serve as protective material from toxic chemicals. In this study we seek a fundamental understanding of how porosity and voids affect migration of solvents and particles through materials. We present our results on experimental and computational

measurements of permeability of solvents through a pore network inside solid materials with varying morphologies. Detailed characterization of solvent transport provides an understanding of the mechanism of how voids structure and connectivity affect the solvent flow traversing the network. Here we present the comparison between in situ and in silico permeability measurements and discuss the mechanisms of solvent transport in porous materials.

## **COLL 641**

### **Layer-by-layer deposition and covalent attachment of PEGylated gold nanoparticles (AuNPs) on aminized glass**

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Gold nanoparticles (AuNPs) are an attractive option as scaffolds for loading biomolecules and drugs due to their high surface area and ability to be functionalized for targeted payload release. Gold nanoparticles have also been shown to form thin films on surfaces when appropriately functionalized. This study describes the layer-by-layer formation of uniform AuNP films on aminized glass surfaces via electrostatic deposition followed by covalent conjugation using 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) coupling to form stable multilayer films. AuNPs are synthesized using a citrate reduction method and subsequently functionalized with 5kD amine-terminated and carboxyl-terminated polyethylene glycol (PEG) spacers. Glass slides are aminized using (3-Aminopropyl)triethoxysilane (ATPES) and incubated in a solution of carboxylated AuNPs. Following formation of a thin film via electrostatic adhesion, the slides are dipped into a separate container with EDC coupling reagents. The process is repeated with aminized AuNPs to form alternating layers of carboxyl and amine conjugated AuNPs. The use of this two-step method produces a more uniform film compared to direct conjugation of each AuNP layer. The use of PEG molecules enhances the stability of the AuNPs while providing antifouling properties. We analyze the particles using UV-Vis spectroscopy, dynamic light scattering (DLS), Zeta potential, and TEM instrumentation. The functionalized glass slides are analyzed using X-ray photoelectron spectroscopy, contact angle ellipsometry, and atomic force microscopy (AFM). We also determine the antifouling capabilities using fluorescence spectroscopy of fluorescently tagged BSA protein. Successful formation of these stable multilayer AuNP films provides a novel scaffold for drug release from a surface as well as a platform for biodetection.

## **COLL 642**

### **Shear strength enhancement of carbon fiber composite via oxygen plasma treatment**

**zhongyao zhang**<sup>1</sup>, [zzhng158@illinois.edu](mailto:zzhng158@illinois.edu), Jennifer L. Wilson<sup>2</sup>, Brian R. Kitt<sup>2</sup>, David Flaherty<sup>1</sup>. (1) Dept. of Chemical and Biomolecular Engineering, University of Illinois, Urbana, Illinois, United States (2) Spirit AeroSystems, Wichita, Kansas, United States

Surface properties (e.g., surface morphology and chemical moieties) are reported to affect shear strength of carbon fiber composites and influence their applications in aerospace, automotive industry, and wind energy.<sup>1</sup> Plasma treatments are excellent methods to modify surfaces of composites for stronger bond line shear strengths.<sup>2</sup> However, the relationship between surface properties and shear strength is still elusive. Here, oxygen plasma treatment (oxygen flowrate 25 sccm, pressure 220mTorr; March CS-1701, Nordson March) is investigated as an efficient and environmentally-benign surface preparation method for aerospace-utilized carbon fiber composites. After plasma-treated composites are cured with epoxy adhesive, an increase of 10% in in-plane shear strength (from 24.2 MPa to 26.6 MPa) is observed based on the lap shear test. Fracture surfaces of composites show mixed failure modes including adhesive, cohesive, and substrate failure. Surface profilometry and atomic force microscopy confirm that surface roughness of carbon fiber composite increases by two times after plasma treatment, suggesting stronger mechanical interlocking at composite-adhesive interfaces. X-ray photoelectron spectroscopy (XPS) shows an increase of nitrogen feature in N1s spectra centering from 400.6 eV to 400.8 eV, which is attributed to imide groups. These imide groups are further hydrolyzed into amines and bonded by Texas Red sulfonyl chloride dye that can be detected by confocal fluorescence microscopy. It turns out that more dyes are grafted onto carbon fiber composites after plasma treatment, suggesting more imide groups on plasma-treated surfaces. We propose that aniline derivatives (confirmed from both material data sheet and XPS) on composite surfaces are oxidized into imides during plasma treatment, which can subsequently react with phenol derivatives and epoxy groups in adhesive and form stronger interfacial chemical bonding. Both stronger mechanical interlocking and interfacial chemical bonding can contribute to the enhancement of bonding of carbon fiber composite. These results suggest oxygen plasma treatment as a surface preparation method can be potentially incorporated into composite bonding processes to enhance structural capabilities.

## **COLL 643**

### **Functionalization of supramolecular hydrogels via *in-situ* photopolymerization of polyaniline for electrochemical sensing applications**

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Hydrogels are currently used in a variety of fields due to their well-defined structure, swellability, and biocompatibility. These supramolecular networks can be further functionalized (either surface or within matrix) with additives such as metal ions,

organic/inorganic crosslinkers, antimicrobial agents, nanoparticles, and conductive polymers to promote responsive characteristics. This work focuses on incorporating conductive polymers (i.e. polyaniline (PANI)) in agar/alginate hydrogels to develop a functionalized network which is responsive to external stimuli such as pH, ions, and oxygen diffusion. More specifically, PANI is integrated within a bulk hydrogel network by utilizing the photoreduction of  $\text{Fe}^{3+}$  to initiate the polymerization of aniline. Results have shown that with an increased concentration of monomer in the system there is a greater presence of oligomers ultimately resulting in less efficient electron transfer. Moreover, the resultant hydrogel's conductivity has been found to be highly dependent on the surrounding environment. To exploit this property the electrical response of the hydrogel is monitored as a function of ion concentration and pH to determine its sensitivity to these changes. Initial results have shown that as a greater amount of ions diffuse through the hydrogel the electron density is increased and therefore enhances the conductivity via p-doping. Additionally, as the pH of the surrounding environment becomes more basic the hydrogel loses conductivity due to the conversion of PANI to the emeraldine base form.

## **COLL 644**

### **Photoacoustically active colloids for medical imaging**

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Acoustic imaging is broadly accessible with good penetration depths and video frame rates. Unfortunately, wider use of ultrasound is limited by poor contrast of target issue versus background. Here, I will describe my lab's efforts to improve contrast via customized contrast agents and photoacoustic imaging. Photoacoustic imaging is a particularly powerful tool that combines the contrast of optics with the temporal and spatial resolution of ultrasound: It is "light in/sound out" as opposed to traditional "sound in/sound out" ultrasound. My group has developed novel materials and optical excitation sources that improve photoacoustic ultrasound for use in medicine. First, I will describe our work using photoacoustics to guide therapy in treating multidrug-resistant bacteria with plasmonic materials that are responsive to reactive oxygen species upregulated in infection. Second, I will overview our efforts using silica- and melanin-based structures for acoustic cell tracking to understand the fate and engraftment of transplanted cells. Finally, I will describe contrast agent-free translational efforts including in wound care and oral health.

## **COLL 645**

### **Molecular photoacoustic reporters for early diagnosis of kidney injury**

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Kidney plays a crucial role in removing xenobiotics and metabolic wastes from blood into urine and maintaining body fluid and electrolyte homeostasis. Such an intense metabolic activity makes kidney highly vulnerable to systemic insults. Thus, renal impairment (RI) often occurs for patients with ischaemia, sepsis or nephrotoxin exposure. With a high morbidity and mortality, RI places an increasing economic burden on healthcare system. Thus, real-time monitoring of kidney dysfunction is imperative not only to preclude nephrotoxic drugs from entering the market but also to timely conduct renoprotective interventions to prevent the progression into severe complications such as end stage kidney disease (ESKD) in hospital.

We here report highly renal-clearable molecular photoacoustic reporters for real-time noninvasive imaging of kidney dysfunction in murine model. The reporters contain two key functional components: photoacoustic moiety and renal-clearance-enabling moiety. The photoacoustic reporters can be activated by RI-associated biomarkers and change their photoacoustic signal wavelengths. This enables early detection of RI in living mice before obvious tissue damage. We have validated the sensing and selectivity of the reporters in solution first, and then examined their renal clearance efficiencies in living mice after intravenous injection. At last, we demonstrate their proof-of-concept in the mouse model of drug-induced kidney injury.

Thus, this study not only introduces a new class of molecular renal reporters but also provides useful molecular guidelines for deep-tissue optical imaging of pathological processes at molecular level in the kidneys of living animals.

## **COLL 646**

### **Optically modulatable contrast agents for background-free photoacoustic and ultrasound imaging**

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To overcome the most significant deficiencies of conventional and contrast-enhanced imaging – low contrast and sensitivity, we introduced a new class of contrast agents – nanometer scale particles that are capable of systemic delivery and penetration into tissue, and then, once they reach the target site, generating sufficient photoacoustic and ultrasound contrast upon user-controlled optical activation. These contrast agents – perfluorocarbon nanodroplets, silica nanoparticles doped with optically modulatable photoabsorbers, and gas-generating plasmonic nanoparticles covered by azide compounds, are stable at physiological temperatures, biocompatible, and nearly monodisperse in size. Given the unique properties of these particles, our imaging approach is drastically different from that of conventional imaging. Specifically, deterministically time-varying photoacoustic or ultrasound signals from nanoparticles can be demodulated to selectively recover high contrast, background-free photoacoustic and ultrasound images. Furthermore, these particles allow for multiplexed molecular imaging by permitting user-controlled laser triggering of distinct color-coded populations

of contrast agents via tuning of the incident laser irradiation to match optical absorption of the particles. This presentation, via examples, will discuss synthesis and optimization of the optically modulatable contrast agents, and their applications in diagnostic imaging and image-guided therapy.

## **COLL 647**

### **Organic nanoprobes for photoacoustic imaging in biomedical applications**

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Photoacoustic imaging techniques, which combine the high sensitivity and contrast of optical imaging with good tissue penetration ability of ultrasound, have shown great potential in versatile biomedical applications. To acquire desired functional information from photoacoustic imaging, researchers have been dedicated to exploring novel contrast agents using different materials. It is generally considered that the large absorption coefficient at long wavelength and high nonradiative nature of contrast agents are two dominant factors to yield strong photoacoustic signals.<sup>1</sup> Recently, we have designed a series of semiconducting polymers with large absorption coefficient in the near-infrared (NIR) region. In addition, we have demonstrated their exciting performance in stem cell tracking, tumor detection and treatment, and precise nanoparticle delivery. For instance, the photoacoustic cell trackers allow researchers to monitor the delivery and engraftment of stem cell-derived cardiomyocytes in beating mouse hearts with high resolution.<sup>2,3</sup> On the other hand, we also discovered that NIR light can facilitate the precise and efficient delivery of photoacoustic nanoparticles to specific tumor tissues *via* a transient vascular barrier opening process, which opening a new door in nanoparticle-based delivery system. In this talk, the speaker will introduce our recent progresses in exploration of advanced photoacoustic nanoprobes and their biomedical application.

## **COLL 648**

### **Dynamic optical absorption from antibody-indocyanine green conjugates for specific spectroscopic photoacoustic molecular imaging**

*Katheryne Wilson, wilsonk2@stanford.edu.* Radiology, Stanford University, Stanford, California, United States

Photoacoustic imaging is an emerging modality that allows for optical contrast at typically ultrasonic depths up to a few centimeters. Inherently a molecular imaging modality, photoacoustic imaging contrast is proportionate to optical absorption, dependent on molecular structure, of photoabsorbers within a tissue of interest. Furthermore, as photoacoustic imaging is an optical imaging modality, multiwavelength photoacoustic imaging allows for resolving of individual chromophores based on their

associated absorption spectra. In living tissue, endogenous photoacoustic contrast is dominated by oxygenated and deoxygenated hemoglobin. Therefore, to examine other molecular targets, exogenous contrast agents are critically needed. Here, antibody-indocyanine green (ICG) conjugates are discussed for their ability to undergo near infrared shifts in optical absorption *in vivo* once bound to their cellular molecular targets and internalized. These shifts allow for highly sensitive and specific spectroscopic photoacoustic molecular imaging due to suppression of both endogenous hemoglobin signal and signal from freely circulating agent. Synthesis and characterization of antibody-ICG conjugates, *in vitro* analysis of optical absorption shifts, and an extensive, multi-control, *in vivo* study to differentiate breast carcinomas and ductal carcinomas *in situ* from normal mammary epithelium in a murine model of breast cancer development are described. Leveraging antibody-ICG contrast agents and their dynamic optical absorption spectra with photoacoustic imaging may allow for earlier detection of cancers in screening and intraoperative scenarios.

## **COLL 649**

### **Formulating Photoacoustic Agents with High Contrast at 1064 nm**

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Surfactant-stripped micelles have been formed with various near infrared dyes, including a commercially available cyanine fluoroalkylphosphate salt dye (CyFaP). This enables high contrast photoacoustic imaging in the second near infrared window (NIR-II). The co-loading of Coenzyme Q10 into surfactant-stripped CyFaP (ss-CyFaP) micelles improves yield, storage stability and results in a peak absorption wavelength in the NIR-II window close to the 1064 nm output of Nd-YAG lasers used for photoacoustic imaging. Aqueous ss-CyFaP dispersions exhibit intense NIR-II optical absorption, calculated to be greater than 500 at 1064 nm. ss-CyFaP is detected through 12 cm of chicken breast tissue with PAI. In preclinical animal models, ss-CyFaP is visualized in draining lymph nodes of rats through 3.1 cm of overlaid chicken breast tissue. Following intravenous administration, ss-CyFaP accumulates in neoplastic tissues of mice and rats bearing orthotopic mammary tumors without observation of acute toxic side effects. ss-CyFaP is imaged through whole compressed human breasts in three female volunteers at depths of 2.6 to 5.1 cm. Taken together, these data show that ss-CyFaP is an accessible contrast agent for deep tissue photoacoustic imaging in the NIR-II window. Other NIR-II contrast agents will be discussed as well, including edible contrast agents capable of rapid human translation.

## **COLL 650**

### **Chemical approaches to enhance the photoacoustic properties of stimulus-responsive probes**

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Photoacoustic (PA) dyes, which absorb near-infrared (NIR) light to generate an ultrasonic signal, can be detected at centimeter depths in tissues with significantly higher resolution than dyes imaged with fluorescence-based methods. As such, PA agents show great promise as research tools for the study of live-animal disease models. However, the development of activatable PA probes has been hampered by the relative scarcity of appropriate PA-active molecular platforms with properties that can be manipulated in a rational manner. Herein we report the chemical tuning of the aza-BODIPY dye platform with respect to their absorbance, fluorescence, and PA properties. We identified a two promising scaffolds: 1) conformationally-restricted aza-BODIPY (CRaB) dyes and 2) sterically relaxed aza-BODIPY dyes that prioritizes three criteria necessary for the design of stimulus-responsive dyes with optimal ratiometric PA response: absorbance at NIR wavelengths, strong PA intensity, and large  $\Delta\lambda$  upon interaction with the desired stimulus. Using these scaffolds, we synthesized chemically diverse stimulus-responsive PA probes and demonstrated between 2- and 8-fold improvements in theoretical ratiometric response in vitro. This suggests that improvements in PA parameters are generalizable. Finally, we validated the in vitro turnover of each PA probe and demonstrated the in vivo potential of these scaffolds by direct comparison to an established probes for the detection of tumor properties.

## **COLL 651**

### **Anomalous small angle X-ray scattering study of macroion aggratation and quantitative counterion distribution around macroion**

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Counterion atmosphere condensed around charged macromolecules (nucleic acids, proteins, polyelectrolytes) is important of their self-assembly behaviors in solution. While other technique can hardly achieve, anomalous small angle X-ray scattering (ASAXS) can provide numbers and spatial distribution of counterions around macroion.  $\{\text{Mo}_{132}\}$ , a spherical negatively charged macroion undergoing aggregation in aqueous solution with monovalent  $\text{Rb}^+$  but not with divalent  $\text{Sr}^{2+}$ , was used as model of macroions to investigate the interaction between macroions and small counterions by ASAXS. The counterion distribution was obtained at sub-angstrom resolution and compared with classical theoretical prediction. Combined with  $^{87}\text{Rb}$  NMR, isothermal titration calorimetry, and other characterizations, the results show that  $\text{Rb}^+$  can chemically bind with  $\{\text{Mo}_{132}\}$ , replace the original counterions, and neutralize most of negative charges, while  $\text{Sr}^{2+}$  only loosely associate. While the Coulomb force dominate the interactions between macroions and counterions in most cases, the energy penalty of breaking the

hydration shell can be significant upon the association of divalent counterion with macroion.

## **COLL 652**

### **Kinetic phase diagrams of polystyrene-b-poly(ethylene oxide) in solution**

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Block copolymers have been widely used to form templates with different morphologies, such as spherical micelles, cylindrical micelles and vesicles. While the self-assembly process of block copolymers in bulk has been thoroughly explored, the same process in solution remains widely used but poorly understood. This is due the fact that the dynamics plays an important role on the final morphology adopted by the polymer, leading to kinetically trapped systems.

The best strategy to reach a desired structure via self-assembly of block copolymers in solution has proven to be an educated trial and error approach. While varying the blocks ratio or blocks nature can promote a change in morphology, this approach is time consuming as new polymers need to be synthesized and sometimes not a possibility when the polymer has a desired functionality.

In this paper we will report phase diagrams for a polystyrene-b-poly(ethylene oxide) block copolymer by changing the particle preparation method instead of changing the polymer type. We will study the effect of changing concentration, temperature and the scale of the process. A detailed analysis of the structures will be performed by advanced electron microscopy techniques such as (cryo)-electron microscopy and (cryo)-electron tomography.

We aim to discuss the importance of producing phase diagrams of block copolymers in solution and aim to find relationships between the kinetically trapped structures and the thermodynamics of block copolymer self-assembly.

## **COLL 653**

### **Self-assembly of short-chain polyelectrolyte block copolymers into fluid biomimetic membranes**

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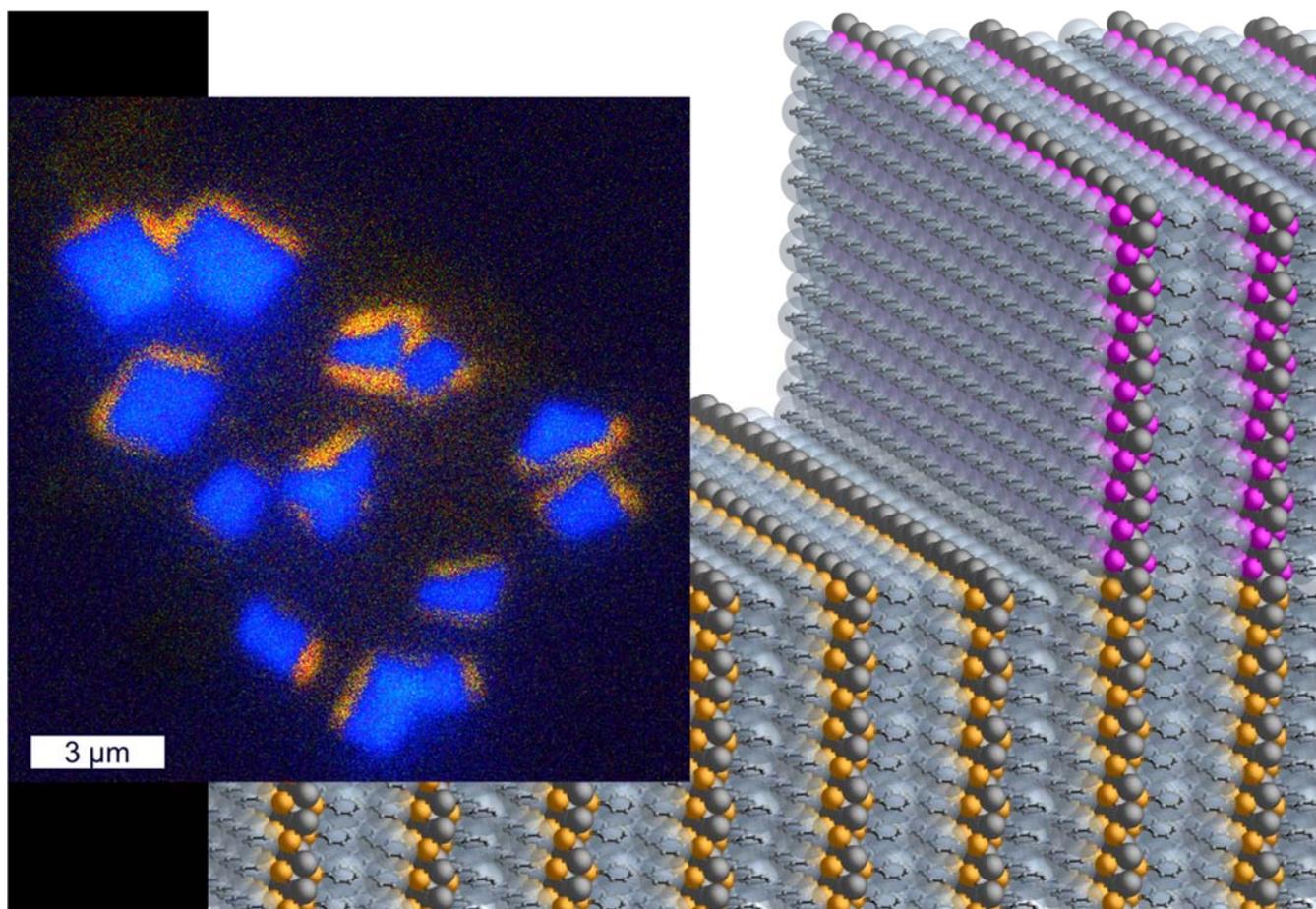
Amphiphilic block copolymers have been used to assemble extended polymer bilayers and polymersomes that mimic cellular membranes. These biomimetic structures are typically composed of block copolymers with molecular weights much larger than lipids and/or with high glass transition temperatures, leading to polymer membranes that lack the hallmark fluidity of biological membranes. This fluidity is key for a range of applications, from controlled drug release to polymer membrane-based diagnostics. Here, we show that a low molecular weight poly(butadiene)-*block*-poly(acrylic acid) (pBd-pAA) can self-assemble into supported polymer bilayers that exhibit environment-dependent fluidity. Micelles of the pBd-pAA form bilayers on pristine hydrophilic glass. We characterize the fluidity of these pBd-pAA membranes doped with a small percentage of fluorescently labeled lipid using fluorescence recovery after photobleaching (FRAP) and compare this fluidity to a prototypical lipid membrane of 1,3-bis(sn-3'-phosphatidyl)-sn-glycero-2'-phosphocholine (DOPC). pBd-pAA bilayers were found to exhibit diffusion coefficients of about  $10 \mu\text{m}^2/\text{s}$  in buffered aqueous solutions both above and below the pKa of poly(acrylic acid). These diffusion coefficients are more than five times greater than for DOPC membranes. The surface hydrophobicity can be tuned to toggle between pBd-pAA monolayer and bilayer formation. I will also report our investigation of the pH dependence of pBd-pAA membrane fluidity and thickness.

## **COLL 654**

### **Heteroepitaxy at metal-organic chalcogenolate coordination polymer interfaces**

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Heterostructured nanomaterials have attracted considerable interest as a paradigm for leveraging the emergence of new properties in ultrathin or nanoscaled materials for the exploitation of dissimilar functionality for the development of new applications. For example, core-shell morphologies have been exploited in nanocrystals, in hybrid coordination polymer network systems like MOFs, and recently in lateral and vertical heterostructures of 2D ultrathin materials. Especially in the case of hybrid materials, this rapid proliferation of new paradigms in material design has led to considerable opportunities for tailored material systems for specific applications, including catalysis, gas phase separations, and semiconductor devices. The particular advantage of hybrid nanostructures have attracted interest for controlling the chemical functionality and physics of a material from the bottom up. Here we present epitaxy in the homologous series of silver benzenechalcogenolates, [AgSPh], [AgSePh], and [AgTePh]. Synthetic, structural, and optoelectronic properties are examined.



## COLL 655

### Internal structure of nanocarriers containing drug hydrophobic ion pairs dictates drug release

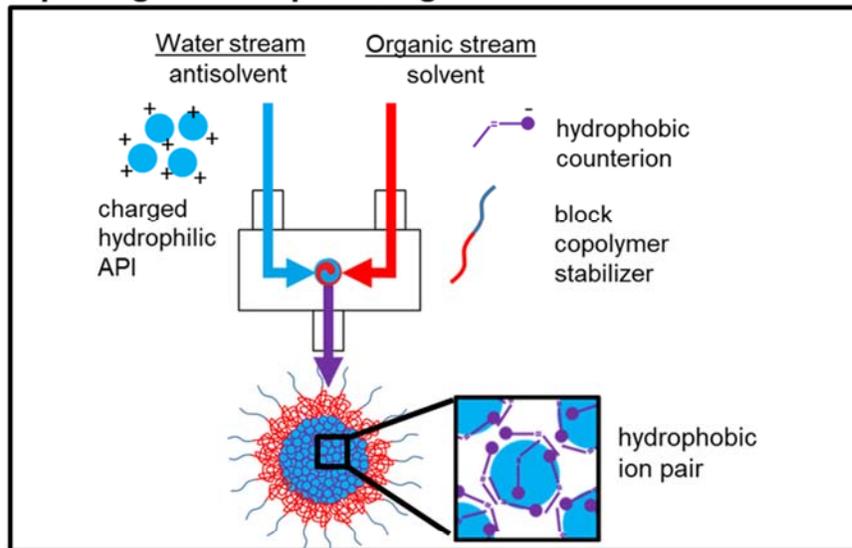
**Kurt Ristroph**<sup>1</sup>, [ristroph@princeton.edu](mailto:ristroph@princeton.edu), **Malinda Salim**<sup>2</sup>, **Brian Wilson**<sup>1</sup>, **Andrew Clulow**<sup>2</sup>, **Ben Boyd**<sup>2</sup>, **Robert K. Prudhomme**<sup>3</sup>. (1) Princeton University, Princeton, New Jersey, United States (2) Monash Institute of Pharmaceutical Sciences, Melbourne, Victoria, Australia (3) Dept. of Chemical Biological Engineering, Princeton University, Princeton, New Jersey, United States

Hydrophobic ion pairing is the process of forming temporary water-insoluble species from charged hydrophilic molecules by ionically complexing them with oppositely-charged surfactants. The technique has gained prominence as a method of encapsulating charged small molecule and peptide/protein therapeutics, which are otherwise difficult to efficiently encapsulate at high loadings, into nanocarriers. We previously demonstrated a process combining hydrophobic ion pairing with the continuous nanoparticle formulation technique Flash NanoPrecipitation to encapsulate

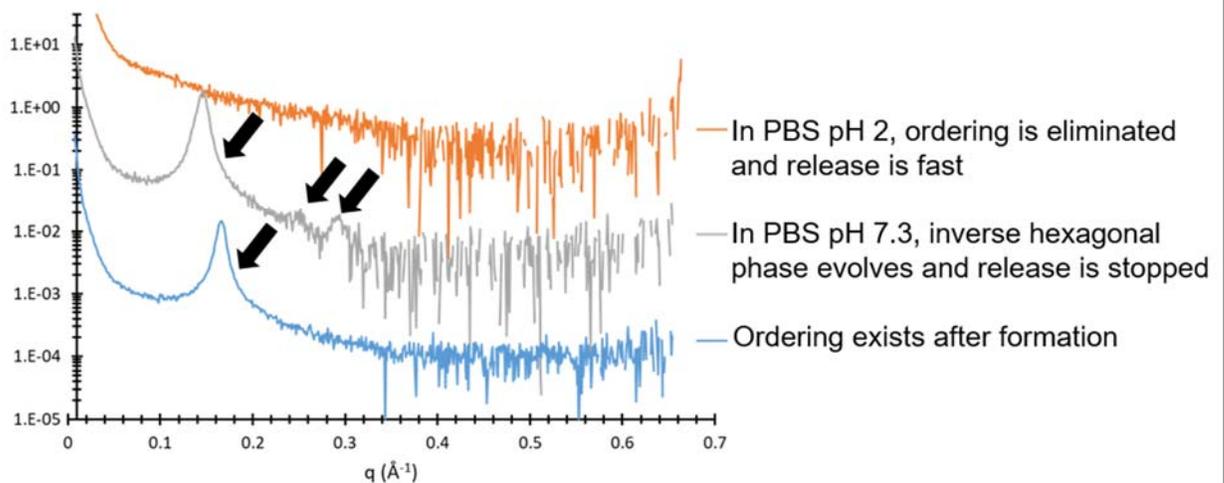
the peptide polymyxin B into nanoparticles. The release of polymyxin B from the particles was found to depend on factors such as pH, salt, and the ratio of polymyxin to surfactant.

We here describe and provide experimental evidence of a mechanism responsible for the polymyxin release behavior: the formation of ordered liquid crystalline structures within the nanocarrier core. Synchrotron small-angle x-ray scattering was used to characterize the nanocarriers under a series of salt and pH conditions and at multiple polymyxin:surfactant charge ratios. Ordering was observed in the system immediately after particle formation and was found to depend on the charge ratio. The ordering was shown to be dynamic and to correspond with drug release. At low pH, ordering is eliminated and fast release occurs. At neutral pH, a formulation with excess surfactant developed an inverse hexagonal phase that stopped peptide release. The same inverse hexagonal phase did not evolve under the same conditions for a formulation without excess surfactant, and release was not stopped. This relationship between internal ordering and drug release in systems containing hydrophobic ion pairs offers useful mechanistic insight into the stimulus-responsive release profiles that have been reported in similar systems in the literature.

## Flash NanoPrecipitation with hydrophobic ion pairing for encapsulating water-soluble molecules



**SAXS demonstrates internal ordering that is dynamic and stimulus-responsive**



COLL 656

**Self-assembly of poloxamer block copolymers: From thermodynamics, to nanostructure, to function, to formulations**

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Block copolymers exhibit an innate ability to organize from the nanoscale across to the mesoscale. Selective solvents provide valuable degrees of freedom for controlling the morphology and, hence, structure/property relationships; furthermore, solvents can dramatically affect the molecular mobility and the dynamics of structural transformations. The presentation will utilize research findings on “model” block copolymers of the poly(ethylene oxide)-poly(propylene oxide) (PEO-PPO) family, commercially available as Pluronics or Poloxamers, to discuss: (1) the basic self-assembly elements, i.e., micelles, in terms of the thermodynamics and interactions underlying their formation and disassembly in aqueous solvents (selective for PEO), and their nano-scale structure and dynamics, (2) the adsorption of block copolymers on surfaces macroscopic and nanoscale, hard and soft, and how the adsorbed layer structure can be related to the polymer organization in the bulk solution, (3) ordered micelles, i.e., lyotropic liquid crystal structures, in the context of their range of stability as affected by the block copolymer conformation and various additives (e.g., glycols, nanoparticles), and their structural transformations under shear, and (4) how the equilibrium phase behavior can inform processing paths for the preparation of kinetically stabilized emulsions and nanoparticles, and templates for nanomaterials synthesis. The self-assembly properties of PEO-PPO block copolymers in selective solvents are compared to those of low-molecular weight nonionic surfactants, and to block copolymers organizing in the absence of solvents.

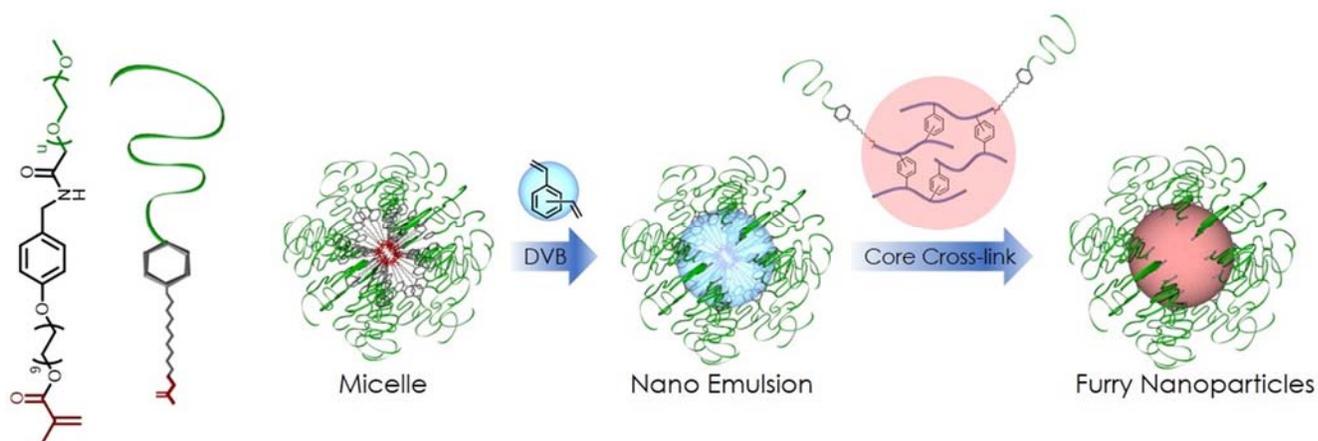
## **COLL 657**

### **Furry nanoparticles: Cross-linked nanoparticles prepared via nanoemulsions and their robust stability *in vivo***

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Self-assembled nanoparticles including micelles and liposomes have been studied as drug carriers and practically applied in clinics. However, their drug efficacy is not very high *in vivo*. This is due to the unstable nature caused by the dynamic self-assembly system. Those particles would easily be decomposed after administrating into blood stream by dilution effects, interacting with plasma proteins, and the high shear stress in blood vessels.

In this study, we have prepared an amphiphilic compound bearing poly(ethylene oxide) (PEO) as a hydrophilic part and methacryloyl group at the end of alkyl chain. Radical polymerization was conducted for the nanoemulsion composed of the amphiphile and divinyl benzene (DVB), producing cross-linked nanoparticles bearing PEO chains. We named the particles furry nanoparticles (f-NPs) and characterized their structures using small angle scattering measurements. The particle stability was improved compared to that of the micelle composed of the amphiphile while the structure remained in core-shell structures just like that of the micelle. Further, the size of f-NPs and their drug loading ratio can be easily controlled by changing the molar ratio of the amphiphile to DVB. The particle stability *in vivo* was also compared to that of the micelle.



## COLL 658

### Effect of a competitive solvent and chain architecture on binding enthalpy and chain intermixing in hydrogen-bonded assemblies

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We demonstrate the effect of a small-molecule/hydrogen-bonding competitor and polymer chain architecture on the heat of complexation of hydrogen-bonding polymers in aqueous solutions, as well as on deposition of these molecules within layer-by-layer (LbL) films. The effect of a hydrogen-bonding small molecule --- dimethyl sulfoxide (DMSO) --- was explored with poly(methacrylic acid) (PMAA) binding with poly(vinylpyrrolidone) (PVP), while the role of chain architecture was explored using linear PMAA interacting with poly(ethylene oxide) of linear and star-like architectures. Isothermal titration calorimetry demonstrated that endothermic, entropy-driven binding between PMAA and PVP in water switches to exothermic binding dominated by hydrogen-bonding interactions when concentration of DMSO in aqueous solution increase above ~25 vol % DMSO. The growth of LbL films at surfaces measured by ellipsometry was also strongly impacted by the presence of DMSO. The polymer mass deposited within the bilayer first increased as a result of the weakening of polymer-polymer binding by a competitive solvent, but deposition was fully inhibited at high DMSO concentrations. Neutron reflectometry revealed enhanced interpenetration of deuterated PMAA chains within a hydrogenated LbL matrix at increasing concentrations of DMSO, corroborating the ellipsometry results. We also explored the role of the molecular architecture of hydrogen-bonding polymers on intermolecular binding and LbL film growth. These studies, performed with systems composed of PMAA and linear or 6-arm PEO chains, revealed an increased content of PMAA in polymer complexes, as

well as increased enthalpy of complexation in the case of linear-star association, probably resulting from the beaded necklace complex architecture. The distinct structure of PMAA/star PEO complexes leads to slower deposition of these complexes within LbL films as compared to complexes of linear counterparts of these polymers.

## **COLL 659**

### **Polymer micelles: Controlling the spatial distribution of guest compounds and the stability using added free polymers**

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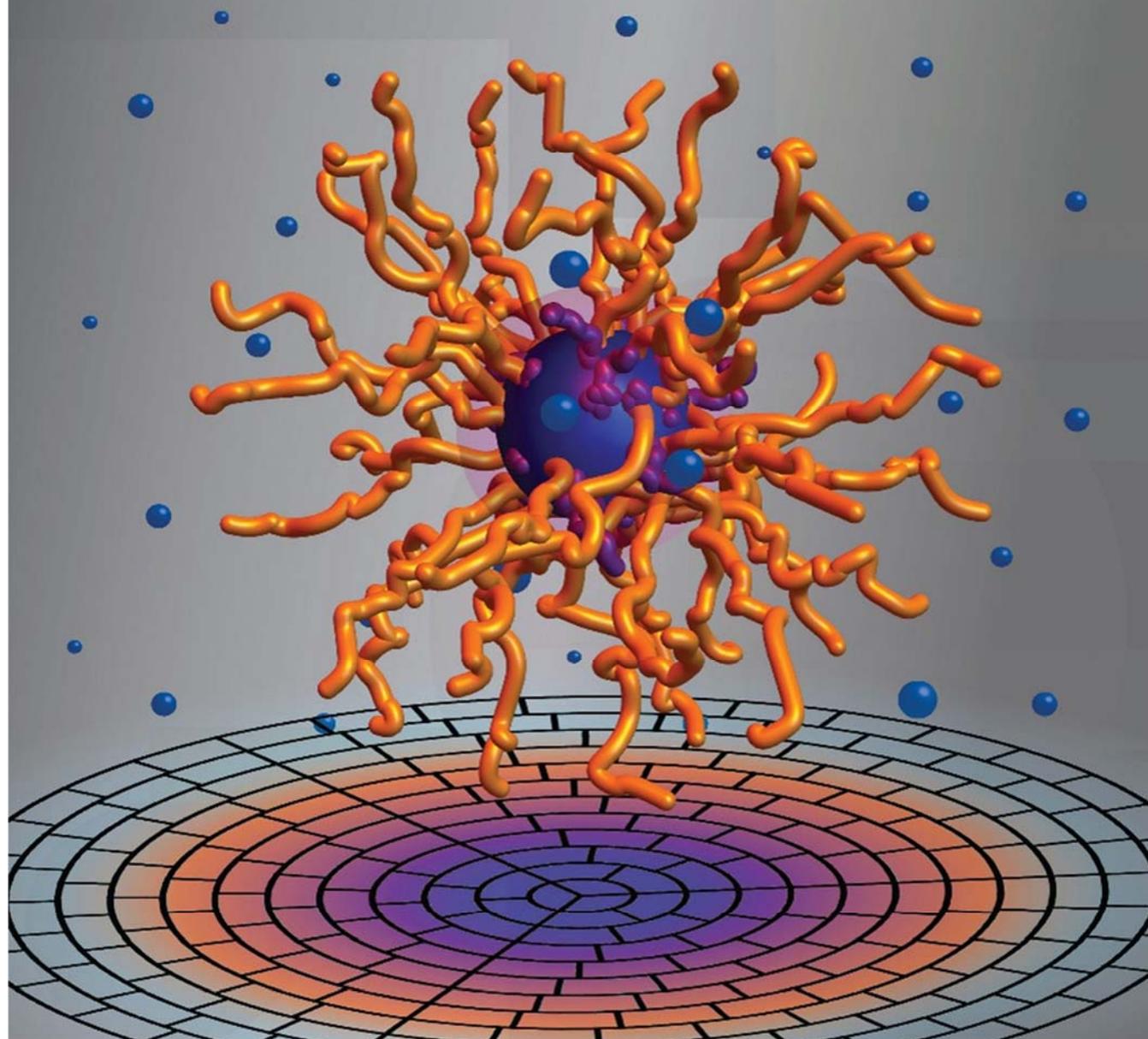
Controlling solubilization of lyophobic compounds in block copolymer micelles is a key aspect in the design of drug delivery systems with tailored release properties. Using self-consistent field (SCF) computations we show that solubilization is regulated by a complex interplay between enthalpic and entropic contributions, and that the spatial distribution can be controlled by the concentration and the solubility of the guest compound in the dispersion medium. A characteristic change in size and mass of the micelles upon solubilization is predicted. It is shown how this can be used experimentally as a fingerprint to assess spatial distribution indirectly. Using SCF we also study how micelles respond to other components in solution is scarce. Results will be reported on the colloidal stability of micelle suspensions in presence of (homo)polymers. A simple, yet insightful, polymer mediated micelle-micelle interaction is extracted via the changes in the micelle-unimer equilibrium with varying the inter-micelle distance in presence of homopolymer. For different polymer-to-micelle size ratios, model crew-cut and starlike micelles are studied, for both homopolymer depletion and adsorption from/into the corona. The fluffy nature of the corona may prevent depletion-induced destabilization of the micellar suspension. Adsorption of polymers into the corona induces bridging aggregation between micelles. Crew-cut micelles have a narrower yet denser corona, hence penetration of guest compounds into the coronal domain is less pronounced than for starlike micelles. This makes crew-cut micelles more suitable for applications in crowded environments, such as drug delivery. The trends observed for the colloidal stability of crew-cut micelles qualitatively match with experimental observations.

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## COLL 660

### **Mediation of co-assembly of peptides with different functionalities via a common peptide backbone**

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The self-assembly of peptides has been extensively studied over the past three decades. Through these studies, a multitude of nano- and biotechnological applications has been devised. Most of these studies center on the use of a single self-assembling peptide to confer a desired property. In principle, it is possible to design a multifunctional peptide that can (1) undergo self-assembly into the desired macromolecular structure and (2) display the functional groups that will confer the desired properties upon the peptide material. However, this will almost necessitate a complex synthesis of the multifunctional peptide while juggling the different chemistries of the functional groups. Another approach that might be more feasible, and is gaining popularity, is the co-assembly of different molecules to furnish a complex macromolecule with desired properties. In nature, this is manifest in the assembly of various enzymes, e.g. the tRNA ligase, from their component polypeptide moieties. Currently, however, studies on the co-assembly of peptides are still limited. In this talk, I discuss our initial studies into the utility of a common pentapeptide backbone to mediate the co-assembly of analogous hexapeptides with different C-terminal amino acids. Using a combination of circular dichroism (CD) spectroscopy, attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy, and transmission electron microscopy, we have been able to infer that the co-assembly of hexapeptides with a common backbone can indeed transpire, but that this is dependent to a small extent on the C-terminal amino acids. This represents the first step in elucidating the structure-co-assembly relationship among the oligopeptides towards the bottom-up fabrication of a complex peptide material.

## COLL 661

### **Unravelling protein mediated lipid dynamics using fluorescence correlation spectroscopy and molecular dynamics simulations: Influence of pore formation and crowding**

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Pore forming toxins are a class of proteins implicated in a wide range of virulent bacterial infections and diseases. These toxins bind to target membranes and subsequently oligomerize to form functional pores that eventually lead to cell lysis. Using three component (DOPC:DPPE:Cholesterol) supported lipid bilayers we study the influence of Listerolysin binding and pore formation on the underlying lipid dynamics and reorganization. Listerolysin (LLO) binds predominantly to the liquid disordered phase present on the bilayer and a non-monotonic trend in the lipid diffusivity as a function of LLO concentration is observed using FCS. The lipid diffusivity increases to a maximum value and decreases upon further increase in LLO concentration. We attribute the increase in diffusivity due to the formation of membrane inserted pores which fluidize the membrane as well as due to loss of lipids during the transition from a pre-pore to a membrane inserted pore state. The decrease in diffusivities at higher concentrations is attributed to crowding effects. All atom molecular dynamics simulations carried out with partially formed membrane inserted arcs reveal the increase in diffusivity due the presence of membrane inserted beta sheets of the LLO pore. Lipid diffusivities are significantly lowered when the LLO protein is placed in a pre-inserted conformational state. Cholesterol re-organization and leaflet dependent dynamics and mobilities illustrate the changes induced in the lipid environment during pore formation. Our study provides novel insights into membrane mediated protein interactions and the intimate reorganization of lipids during protein binding and pore formation.

## **COLL 662**

### **Interplay of membrane tension and osmotic pressure in modulating $\alpha$ -synuclein binding**

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$\alpha$ -Synuclein, an abundant protein found in the presynaptic terminal of neuronal axons and its dysfunction is fundamentally linked to Parkinson's disease. While  $\alpha$ -Synuclein is accepted to peripherally bind to the membrane of highly curved synaptic vesicles, there is increasing evidence that  $\alpha$ -Synuclein can subsequently regulate the size and architecture of synaptic vesicle "pools" through an unknown mechanism. Here, we present strong evidence that  $\alpha$ -Synuclein (at biologically relevant concentrations) disrupts inter-membrane interactions between synaptic vesicle-mimics at physiological salt and temperature conditions through a combination of synchrotron small-angle X-ray scattering (SAXS) and X-ray photon correlation spectroscopy (XPCS). Our results further indicate that the disordered C-terminal domain, much like grafted polymers on surface, predominantly contribute to steric stabilization of lipid membrane surfaces.

Using SAXS, we have further examined  $\alpha$ -Synuclein -bound SSLBs under depletion force induced by polyethylene glycol and found the critical osmotic pressure at which SSLBs aggregate to a condensed state. Under high salt conditions up to 1M NaCl, the critical pressure decreases significantly but remains higher than that required to condense SSLBs without  $\alpha$ S. The  $\alpha$ S-induced steric stabilization is therefore a result of both steric and electrostatic repulsion.

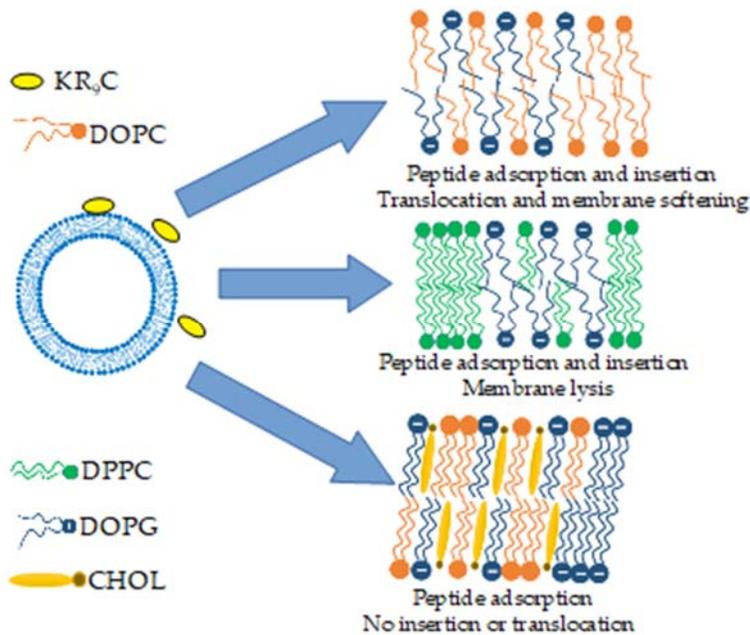
## **COLL 663**

### **Interaction of a polyarginine peptide with membranes of different mechanical properties**

*Natalia Wilke*<sup>1</sup>, *wilke@fcq.unc.edu.ar*, *Matias Crosio*<sup>1</sup>, *Matias Via*<sup>2</sup>, *Candelaria Camara*<sup>3</sup>, *Agustin Mangiarotti*<sup>1</sup>, *Del Popolo Mario*<sup>2</sup>. (1) Departamento de Quimica Biologica Ranwel Caputto, CIQUIBIC, Cordoba, Cordoba, Argentina (2) ICB-CONICET & Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Cuyo, Mendoza, Mendoza, Argentina (3) Departamento de Fisicoquímica, INFIQC, Cordoba, Cordoba, Argentina

The membrane translocation efficiency of Cell Penetrating Peptides (CPPs) has been largely studied, and poly-arginines have been highlighted as particularly active CPPs, especially upon negatively charged membranes. Here we inquire about the influence of membrane mechanical properties in poly-arginine adsorption, penetration and translocation, as well as the subsequent effect on the host membrane. For this, we selected anionic membranes exhibiting different rigidity and fluidity, and exposed them to the nona-arginine KR<sub>9</sub>C. Three different membrane compositions were investigated, all of them having 50% of the anionic lipid DOPG, thus ensuring a high affinity of the peptide for membrane surfaces. The remaining 50% was a saturated PC (DPPC), an unsaturated PC (DOPC) or a mixture of DOPC with cholesterol. Peptide-membrane interactions were studied using four complementary models for membranes: Langmuir monolayers, Large Unilamellar Vesicles, Black Lipid Membranes and Giant Unilamellar Vesicles. The patterns of interaction of KR<sub>9</sub>C varied within the different membrane compositions. The peptide strongly adsorbed on membranes with cholesterol, but did not incorporate or translocate them. KR<sub>9</sub>C stabilized phase segregation in DPPC/DOPG films and promoted vesicle rupture. DOPC/DOPG appeared as the better host for peptide translocation: KR<sub>9</sub>C adsorbed, inserted and translocated these membranes without breaking them, despite softening was observed.

In cell membranes, a great variety of compositions coexist transiently in small patches, each one with different mechanical properties. Thus, pre-concentration of CPP may occur in a region enriched in cholesterol, whilst the peptide inserts in a neighbor region depleted of cholesterol. Under this point of view, the patchwork like organization of the membrane would act synergistically enhancing peptide translocation.



## COLL 664

### Cholesterol stiffens saturated and unsaturated phosphocholine membranes

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Cholesterol is a critical component of eukaryotic cell membranes and a key molecule in controlling membrane fluidity, packing state, and various membrane functions. It also plays a regulatory role in antibiotic drug resistance by augmenting the mechanical properties of its host membrane against structural damage. Structurally, cholesterol exhibits a *universal condensing effect* on fluid lipid membranes (saturated and unsaturated), manifested in increased membrane thickness and smaller area per lipid. However, the effects of cholesterol on membrane mechanics have, so far, been presumed to be *non-universal*. While cholesterol is widely accepted to have a strong stiffening effect on saturated lipid membranes, its effects on unsaturated lipid membranes remain controversial and, in some cases, challenge our understanding of the mechanisms governing membrane mechanics. For instance, previous studies on dimonounsaturated lipids, such as DOPC, showed that cholesterol has virtually no effect on the bending rigidity modulus,  $\kappa$ , despite clear evidence of a condensing effect. In contrast, we recently showed, using neutron spin echo (NSE) spectroscopy, that cholesterol results in a non-trivial stiffening of DOPC membranes over NSE length/time scales. Direct NSE measurements of bending dynamics in DOPC membranes with increasing cholesterol content yielded increasing trends in  $\kappa$  up to  $\sim 3$ -fold increase at 50 mol% cholesterol. Here, we report similar results from solid state  $^2\text{H-NMR}$  spectroscopy which unambiguously show a gradual decrease in the square-law dependence of spin lattice relaxation rates ( $R_{1Z}$ ) on segmental order parameters ( $S_{CD}$ ), indicating cholesterol-induced membrane stiffening. Analysis of these results in the context of fluctuation-dissipation theorem yields the same trends in  $\kappa$  as observed by NSE. Parallel studies on membranes with different lipid unsaturation (e.g. POPC vs. DOPC) indicate that the degree of cholesterol-induced stiffening depends on chain unsaturation. Our dynamical results, as well as structural SANS/SAXS and ESR data, are in excellent agreement with real-space fluctuation analysis from molecular dynamics simulations on cognate DOPC-cholesterol bilayers and with standard theories of membrane mechanics. These findings have significant biological implications and encourage a reassessment of mechanical measurements of cholesterol-containing membranes over length and time scales that are relevant to biological processes.

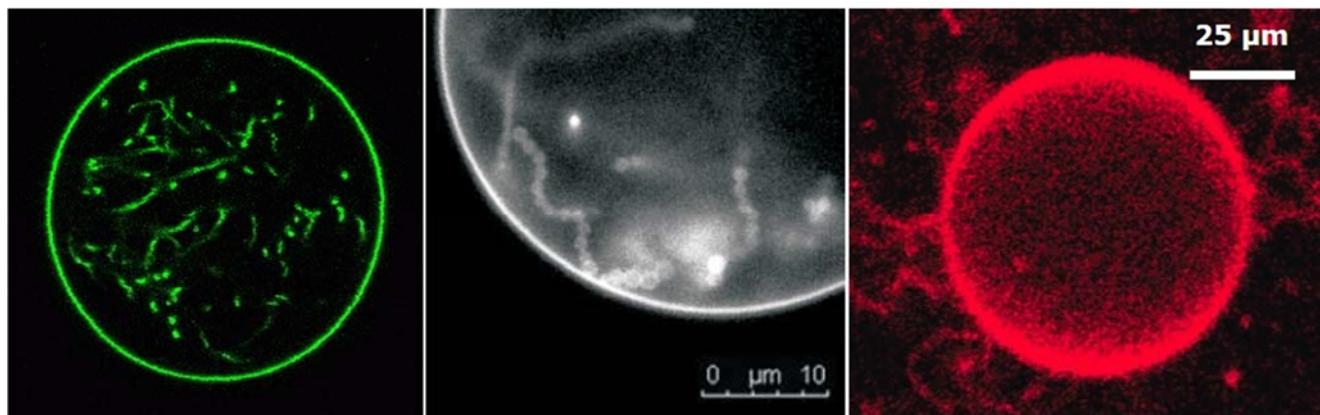
## **COLL 665**

### **Curving in or out: Membrane remodeling and spontaneous curvature generation by ions, (sugar)lipids, polymers and proteins**

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Membranes in cell exhibit a large variation in curvature. Very often, curvature generation is associated with the activity of specific protein species. We will demonstrate that spontaneous curvature is readily generated by various other asymmetries across the membrane which plausibly represent a governing factor in defining shapes of membrane organelles and in remodeling them. As a workbench, we employ giant vesicles, with sizes in the 10-100  $\mu\text{m}$  range. In this talk, we will introduce approaches employing giant vesicles to precisely quantify the membrane spontaneous

curvature. Several examples for spontaneous curvature generation will be discussed: asymmetric distribution of ions on both sides of the membrane, asymmetry in lipid distribution in the two membrane leaflets, membrane insertion and desorption of the ganglioside GM1 or of photo-sensitive molecules, and asymmetric adsorption of poly(ethylene glycol). All these example systems modulate the membrane shape dramatically as expressed in the spontaneous formation of cylindrical or necklace-like lipid nanotubes (see figure). Finally, we will show how spontaneous curvature generation by protein adsorption at low surface density is able to modulate membrane morphology and topology to the extent of inducing vesicle fission.



Lipid tubes in giant vesicles. Tubes can be thin and cylindrical (left, right) or necklace-like (middle). Inward tubes (left, middle) signify negative spontaneous curvature and outward ones (right) indicate positive spontaneous curvature.

## **COLL 666**

### **Motion of objects embedded in lipid bilayer membranes: Diffusion, advection and effective viscosity**

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A regularized Stokeslet scheme for calculating transport properties of objects embedded within membranes will be presented. The methodology is quite versatile and can be applied both to membranes suspended within an aqueous bulk and also to supported membranes. The technique has been used to interpret single particle tracking measurements of lipids in supported bilayers, which will be discussed.

## **COLL 667**

### **Lipid molecular diffusion and membrane viscosity measured by quasi-elastic neutron scattering**

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Molecular transport properties in two-dimensional membranes are characterized by the molecular size of the diffusing object,  $R$ , the molecular diffusion constant,  $D$ , and the membrane viscosity,  $\eta_m$ . Continuum hydrodynamic models, such as Saffman and Delbrück theory, are well accepted to model molecular diffusion in membranes when  $R$  is relatively large compared to the membrane constituent molecules. The model assumes continuum solvent and membrane fields, characterized by their viscosities  $\eta$  and  $\eta_m$ , and cylindrical molecules with the size  $R$  and the thickness corresponding to that of the membrane as a diffusing object. When  $R$  becomes small, such a continuum picture breaks down, and some theories predict existence of additional contributions to the drag due to the effects from the molecular order parameter or interactions. Experimental observations for such a contribution have never been achieved yet, as an experiment beyond hydrodynamics is challenging. Here, we employ incoherent and coherent quasi-elastic neutron scattering techniques to access such conditions. The neutron backscattering technique was used to estimate  $D$  from the self-motion of H atoms in membranes by measuring incoherent neutron scattering. On the other hand,  $\eta_m$  was determined from the collective membrane fluctuations by measuring coherent neutron spin echo signals. Interestingly, the temperature dependences of  $D$  and  $\eta_m$  show some differences, despite our expectation that the same frictional forces dictate these two parameters. Furthermore, a direct comparison between these two parameters indicates that additional drag on top of the hydrodynamic drag is necessary to explain the observed data.

## **COLL 668**

### **Local enrichment of unsaturated chains around the A<sub>2A</sub> adenosine receptor**

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Two 15  $\mu$ sec all-atom simulations of the A<sub>2A</sub> adenosine receptor were obtained in a ternary mixture of cholesterol, saturated, and unsaturated phosphatidylcholine lipids. An analysis of local lipid solvation is reported on the basis of a Voronoi tessellation of the upper and lower leaflets, identifying first and second solvation shells. The local environment of both the inactive state and the partially active state of the receptor are significantly enriched in unsaturated chains but depleted in cholesterol and saturated chains, relative to the bulk membrane composition. In spite of the local depletion of cholesterol, the partially active receptor binds cholesterol at three locations during the entire simulation trajectory. These long-lived interactions represent the extreme of a very broad distribution of first solvation shell lipid lifetimes, confounding sharp

distinctions between lipid interactions. The broad distributions of lifetimes also make equilibrating the local lipid environment difficult, necessitating long simulation times.

## **COLL 669**

### **Amine/acid mixtures: Their nanostructure and its role in extraction processes**

**Mark N. Kobrak**<sup>1,2</sup>, [mkobrak@brooklyn.cuny.edu](mailto:mkobrak@brooklyn.cuny.edu). (1) Chemistry, Brooklyn College of CUNY, Brooklyn, New York, United States (2) Chemistry, Graduate Center of CUNY, New York, New York, United States

Mixtures of amines and carboxylic acids have long been known to possess unusual physicochemical properties that depend strongly on the mole ratio of acid to amine. We use small angle x-ray scattering to show that these systems form nanostructures, and that the emergence of these nanostructures can be used to understand physicochemical observations. We further demonstrate that, when these mixtures are used to extract metals from water via liquid-liquid extraction, the structures change in ways that are closely related to the extraction mechanism. A particularly important phenomenon in this regard is the Hofmeister effect, which can be exploited to increase extraction yields. The results suggest novel strategies for designing liquid media to enhance metal recovery from aqueous phase.

## **COLL 670**

### **New nanostructures for X-ray nanochemistry**

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New nanostructures are made to facilitate the research in the field of X-ray nanochemistry, which is a discipline that studies how to harvest X-rays using nanomaterials. Several types of nanomaterials are discussed and compared, which are produced using novel methods. These materials as well as the approaches can be used in other applications.

## **COLL 671**

### **Development of field-operable quantum dot chemosensors: For gas-phase explosive signatures**

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The detection of explosives is a primary concern for homeland security as well as military operations. Development of a chemosensor that is field-operable drives this

research. Quenching of quantum dot fluorescence in solution with explosives has already been demonstrated. This work takes specific polymers in solution with various types of quantum dots and electrospins the solution into fiber-sensors to detect gas phase explosive signatures. Characterization of these sensors shows that the fibers are doped with the quantum dots. The characterization includes atomic force microscopy, fluorescence spectroscopy, and SEM-EDX. The fiber-sensors were exposed to the headspace vapors of different explosives to determine which combination of polymers and quantum dot type is the most selective for a given explosive.

## **COLL 672**

### **Fabrication of core-shell carbon polymer dots with stable fluorescence in polymers and potential applications as a sensor of chromium(VI)**

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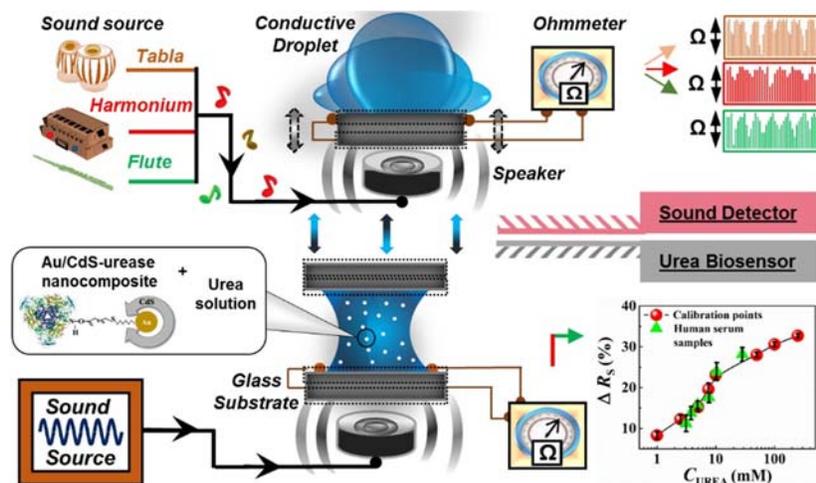
Fluorescent carbon dots have attracted great attention due to their good luminescence and low toxicity. Here, blue fluorescent core-shell structured carbon polymer dots (CPDs) with high stability in a wide pH range, long storage time, and excellent fluorescence in various solvents and even in polymers were prepared by hydrothermal synthesis of dendritic tris(2-aminoethyl)amine (TAEA) and citric acid. The CPDs core structure provides strong fluorescent luminescence, a shell structure of the core possesses high amount of dendritic primary amino groups connected by ethylene groups to the core. This unique structure prevents aggregation of the cores and self-quenching effect of CPDs. As a result, the CPDs have high fluorescence in both aqueous and hydrophobic solutions and even as pure solid-state powder. In addition, the CPDs are also insensitive to pH of solutions, and the fluorescence intensity of the solution was stable in the pH range of 4-14. The carbon polymer dots (CPDs) were covalently incorporated onto poly(vinyl alcohol-co-ethylene) (PVA-co-PE) nanofibers to fabricate novel nanofibrous membrane sensors to detect trace amount of heavy metal ions in drinking water systems. The membrane sensor was assembled in a syringe filter cell as a sensor unit used together with a volumetric syringe, and fluorescent color changes of the sensors responding to concentrations of Cr<sup>6+</sup> can be differentiated by naked eyes. The sensor system possesses features of instant detection, low cost, environment-friendliness, and high sensitivity to quantitatively measure Cr<sup>6+</sup> in a concentration range of 1-50 ppb, which is much lower than federal permissible limit of Cr<sup>6+</sup> in drinking water. Moreover, the used sensor could be refreshed and reused many times without obvious fluorescence loss and nanofibrous membrane damage by simply exposing to a 20 μM Vitamin C (VC) solution. The fluorescent color changes of the sensors could be read by using an app on a smartphone, which is simple, convenient and suitable for more accurate household operation, showing great application prospect for on-site instant detection of Cr<sup>6+</sup> in drinking water.

## **COLL 673**

## Oscillatory microdroplet constituted urea biosensor stimulated by acoustic waves

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This work presents a proof of concept point-of-care urea biosensor that incorporates a facile but robust detection technique and by virtue of its configuration, is also disposable. To substantiate, variations in the electrical resistance across a conducting water microdroplet placed on a glass substrate was observed when it was subjected to sinusoidal acoustic waves at its natural frequency. It was observed that for a 10  $\mu\text{L}$  droplet resting on a glass substrate, acoustic waves of  $\sim 320$  Hz frequency caused the maximum deformation and subsequently the maximum change in electrical resistance of the droplet. For the biosensing application, the conducting water microdroplet was loaded with a suspension of urease-linked gold/cadmium sulfide nanocomposite. Upon adding urea solution in the droplet under the influence of acoustics waves, the changing electrical resistance could be effectively correlated with the changing urea concentration. The nanocomposite enhanced enzymatic reaction followed faster first-order reaction kinetics than Michaelis-Menten pathway because of: firstly, nanocomposites presence acted as a scaffold for the enzyme moieties providing them with stability, enhanced interfacial area and secondly, oscillatory behavior of the microdroplet in a confined system resulted in formation of vortices that improved the mixing characteristics. Studies were also performed utilizing various concentrations of urea [1-150 mM] with a fixed enzyme concentration, to prepare a calibration chart which was eventually utilized for determining unknown urea concentration in human serum samples. Thus the potential of this setup as a urea biosensor was demonstrated. Additionally, this setup's utility could also be extended to another diverse application such as sound sensing without much alteration to the system's geometry. Upon exposing the droplet to different sounds issuing from three distinct Indian classical instruments, variations in the electrical resistance of the droplet could interestingly, follow the different musical notes and the rhythmic cycles. Thus the microdroplet setup could also be employed as a sound sensor.



## COLL 674

### Dumbbell-like silica coated gold nanorods and their plasmonic properties

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A great deal of attention has been attracted by silica-coated gold nanorods with dumbbell morphology due to their applications in sensing and biological imaging. We report a detailed study on the deposition of silica in dumbbell morphology onto gold nanorods. The morphology of the silica shell can be controlled to form cylindrical or dumbbell shapes. Shape control is accomplished by manipulating the synergetic effect of cationic surfactant and concentration of silica precursor. Precise control of available silica precursor along with the rate of diffusion of silica precursor through the solution allows the deposition of silica on gold surfaces. These silica shell morphologies were also investigated for their effects on the performance of surface-enhanced Raman scattering (SERS). The dumbbell morphology of silica-coated rods was found to have substantial enhancement of SERS compared to the cylindrical morphology. This study demonstrates a methodology to precisely control the dumbbell morphology of silica coated gold nanorods, thus opening up promising avenues for the applications of these plasmonic nanomaterials.

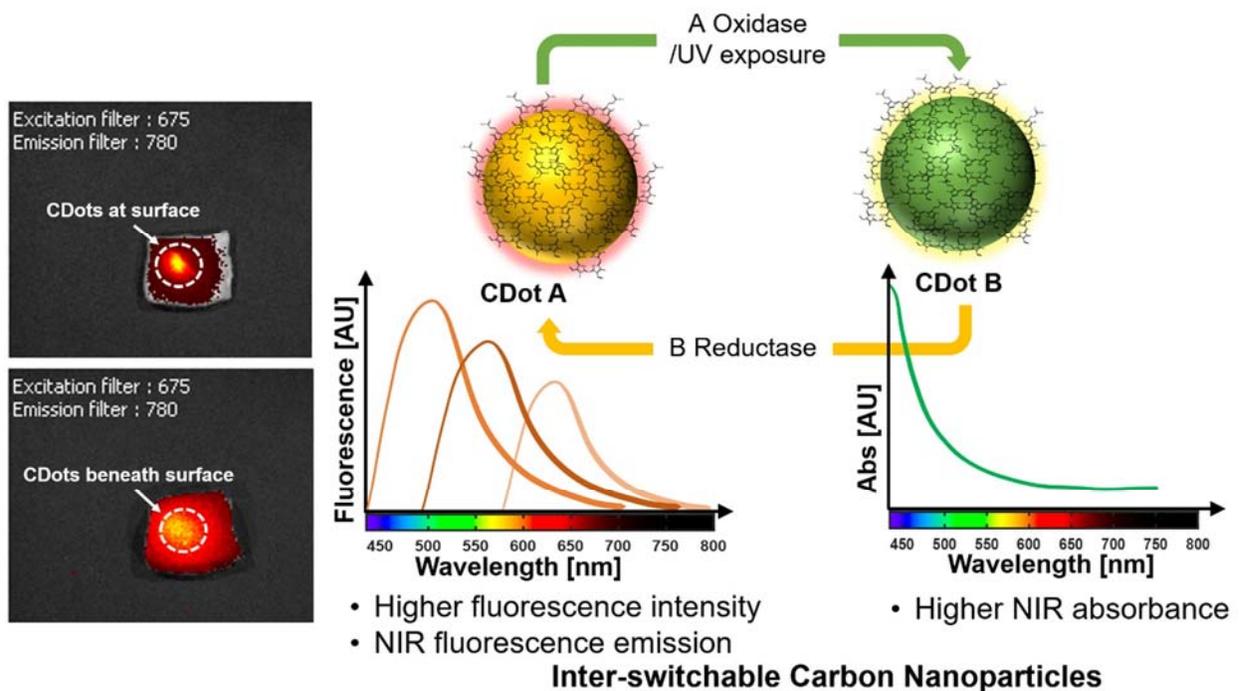
## COLL 675

### Enzymatically and photolytically inter-switchable carbon dots with near-infrared fluorescence emission

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Nanoparticle-based biological mimics are a promising tool for the development of drugs, sensors, and catalysts. These mimics are typically created through functionalization of nanoparticle surfaces using ligands or macromolecules. We sought to instead develop biologically mimicking nanoparticles in a single-step synthesis method without the need for further surface functionalization post-synthesis. Towards this aim, we reveal the design of a dual stimuli-responsive system where two discrete classes of biologically-mimicking carbon nanoparticles are transposable. Carbon nanoparticles or carbon dots provide a promising platform for biomimicking due to their relatively simple synthesis procedure, stable fluorescence which can be advantageous in studying naturally-occurring phytochromes, and known biocompatibility. Through rational selection of carbon dot precursors, we have obtained carbon dots whose absorbance and fluorescence behaviors can be inter-switched in response to enzymes or ultraviolet irradiation. At the same time, these carbon dots provide strong near-infrared fluorescence emission with potential applications in biological imaging. The inter-switching behaviors of these carbon dots was evaluated using UV-visible spectroscopy, fluorescence spectroscopy, transmission electron microscopy, and mass spectrometry, and strong near-infrared fluorescence emission was demonstrated in *ex vivo* experiments.



Enzymatically and photolytically inter-switchable carbon dots

## **COLL 676**

### **Oxidation and stabilization of colloidal 2D MXene nanosheets**

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MXenes, such as  $Ti_3C_2T_x$  and  $Ti_2CT_x$ , are fascinating 2D nanomaterials with an attractive combination of functional properties suitable for applications such as batteries, supercapacitors, and sensors. However, fabrication of devices and functional coatings based on MXenes remains challenging as they are prone to oxidize and degrade rapidly in aqueous and humid environments. MXenes have been found reacting with water molecules and dissolved oxygen resulting in structural and chemical degradations. We examined the oxidation of MXene nanosheets in various media (air, liquid, and solid) via multiple types of measurements to assess their performance and shelf stability. The degree of MXene oxidation was found being directly reflected on the electrochemical property and structural changes such as electrical conductivity and the Ti(IV) content detected by X-ray Photoelectron Spectroscopy. The oxidation rate of MXene nanosheets was observed fastest in liquid media and slowest in solid media and can be accelerated by exposure to UV light. We discovered that the oxidation rate can also be influenced by the presenting ions in MXene dispersions. More importantly, we demonstrated an effective method to retard the oxidation of colloidal  $Ti_3C_2T_x$  and  $Ti_2CT_x$  MXene nanosheets by introducing antioxidants such as sodium L-ascorbate, ascorbic acid, and tannic acid. The success of the method is evident in the stable morphology, less-changed structure, and colloidal stability of MXene nanosheets. Even in the presence of water and dissolved oxygen, the electrical conductivity of  $Ti_3C_2T_x$  nanosheets treated with sodium L-ascorbate was orders of magnitude higher as compared to untreated ones after long storage. The conductivity changes also reveal that the resistance to oxidation persists in the dehydrated MXenes as well. The experimental findings are supported by reactive molecular dynamics simulation (ReaxFF). Our findings have the potential to be generalized to protect other types of MXenes as well and solve the most pressing challenge in the field of MXene engineering.

## **COLL 677**

### **Detection of bio-analytes by using two-dimensional nano sensor array**

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Implementation of 2D materials in detection of bio analytes is highly advantageous in the field of sensing because of its high surface to volume ratio. We have designed our sensor array with different cationic two-dimensional MoS<sub>2</sub> where surface modification was achieved by thiolated ligands. 15 different proteins were discriminated at 50 nM with detection limit of 5 nM. The sensor system has also executed in biofluids such as saliva and serum. Further, different types of drug susceptible and drug resistance bacteria were detected successfully at OD = 0.05. We found out the mechanism of sensing through optical and electrodynamic study which indicates the interaction of bacteria with the sensor system was tuned by non-electrostatic interactions. The optimized sensor system also has good discrimination ability towards bacterial cellular components i.e. bacteria lysates. We believed that the above system can be widely used in the detection of other bio-analytes which we are currently exploring.

## **COLL 678**

### **Label-free pathogen detection based on yttrium doped carbon nanoparticles up to single-cell resolution**

**MAHA a. ALAFEEF**, *alafeef2@illinois.edu*, *Ketan Dighe*, *Dipanjan Pan*. Bioengineering, UNIVERSITY OF ILLINOIS, Urbana, Illinois, United States

The capability to detect bacteria at a low cell density is critical to prevent the delay in therapeutic intervention and to avoid the emergence of antibiotic-resistant species. Till date, great advancement has been made to develop a sensing platform for rapid and reliable bacterial detection. However, critical requirements i.e. limit of detection (LOD), fast time of response (TOR), ultra-sensitivity with high reproducibility and ability to distinguish between bacterial strains have yet to be met within a single sensing platform. In this contribution, we present a novel label-free sensor based on pH-sensitive fluorescent yttrium doped carbon nanoparticles (YCNPs) embedded in agarose that can rapidly and accurately detect and discriminate pathogens in real-time. The developed sensor matrix presented pH-triggered aggregation-induced emission quenching of YCNPs in a wide pH range. This can be explained by the generate Y(III)-phenolic complexed state. An important characteristic of metal-phenolic coordination is its pH-dependent behavior, which would allow a reversible change in the particle size, leading eventually to change the optical signal. When the pH decreased from 10.0 to 4.0, the fluorescence of the matrix decreased linearly ( $R^2 = 0.9229$ ). The sensor 's high sensitivity in a physiologically relevant pH range enables to monitor the presence of live pathogens to single-cell resolution. In addition, the 3D matrix sensor showed low cytotoxicity and long stability (>30 days). Moreover, the YCNPs platform is stable over several hours (5h) in complex medium and does not alter the bacterial growth, allowing real-time monitoring of bacterial growth with a small volume (100  $\mu$ L) and rapid response time (25 min). Furthermore, using machine learning assisted tools, different bacterial strains with various cell densities were discriminated with an accuracy of

almost 100%. Moreover, blends of pathogens and pathogen in a real-world sample can also be identified accurately. Thus, enabling the sensor to provide fast and reliable pathogen information for clinical decisions and allow continuous monitoring of infectious disease trends.

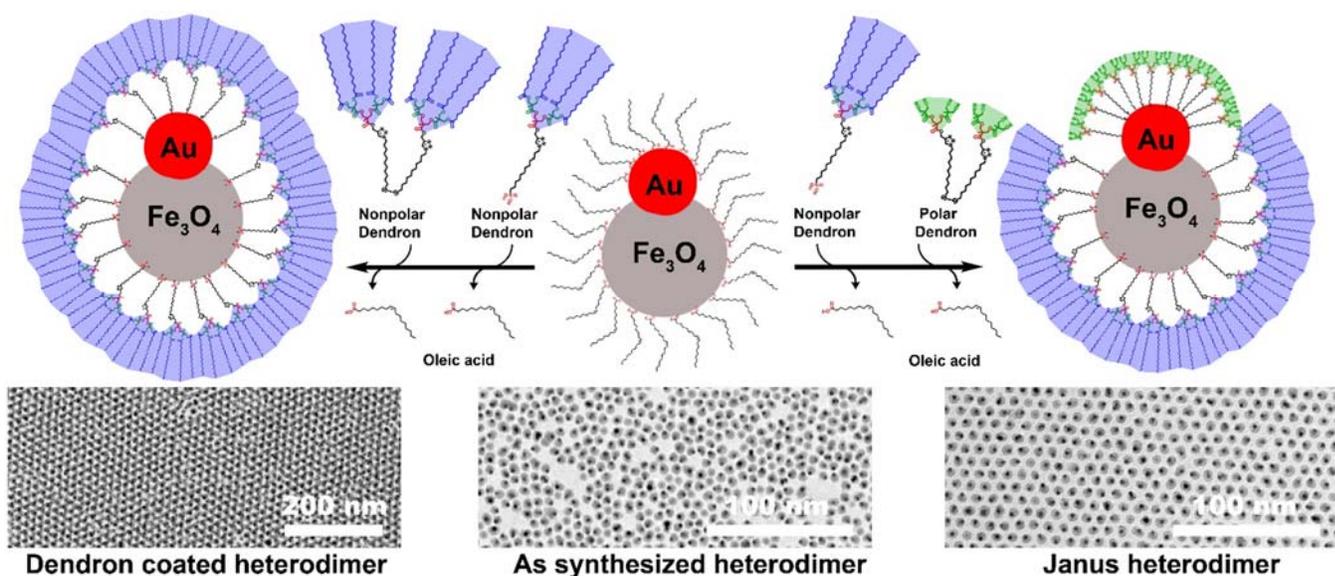
## **COLL 679**

### **Janus heterodimers: Preparation, surface modification, and self-assembly**

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Janus nanoparticles (NPs) often referred to as nano-sized analogs of molecular surfactants are amphiphilic structures with potential applications in materials science, biomedicine, and catalysis and their synthesis and self-assembly into complex architectures remain challenging. We have recently demonstrated the preparation of Janus heterodimers *via* asymmetric functionalization of Fe<sub>3</sub>O<sub>4</sub>-Pt and Fe<sub>3</sub>O<sub>4</sub>-Au heterodimeric NPs. The hydrophobic and hydrophilic dendritic ligands that have phosphonic acid and disulfide surface binding groups selectively coat the iron oxide and platinum (or gold) parts of the heterodimer, respectively. Such an approach allows simple and efficient preparation of amphiphilic structures. Moreover, liquid-air interface self-assembly studies of each ligand exchange step revealed a drastic improvement in film crystallinity suggesting the dendronization induced improvement of the whole particle polydispersity.

The ligands design, NP surface modification strategy, and their self-assembly properties will be presented.



COLL 680

### Transforming silver chlorobromide nanocubes into hollow nanostructures

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Hollow nanostructures are of great interest due to their unique geometry and associated properties compared to their solid counterparts. The availability of controllable synthesis approaches and their mechanistic understanding enables designing materials with enhanced properties. Out of several synthesis strategies, the use of templates which can act as a physical support or transform after appropriate chemical reaction shows promising ways to obtain desired geometry. Silver chlorobromide nanocubes have shown promise as a class of sacrificial template for the synthesis of silver-based hollow nanostructures through chemical transformation reactions. Strong chemical bonding between silver and sulfur enables the transformation of AgCl<sub>0.5</sub>Br<sub>0.5</sub> nanocubes into hollow nanoshells of silver-sulfur compounds. During these transformations, factors such as the crystalline structure and nature of the shell material influence the reaction kinetics, and thus the structural and morphological evolution of the hollow structures. Herein, we present the hollowing mechanism and associated reaction kinetics for the controlled conversion of AgCl<sub>0.5</sub>Br<sub>0.5</sub> nanocubes into hollow nanostructures. The use of sulfide anions (S<sup>2-</sup>) and benzenethiolate anions (BT<sup>-</sup>) for the anion exchange reaction with halide ions have been compared to illustrate the hollowing mechanisms. The S<sup>2-</sup> ions are comparable in size to the halide ions, resulting in a nano-scale Kirkendall effect that is mainly responsible for the formation of hollow Ag<sub>2</sub>S nanoshells. In contrast, the Kirkendall effect is absent from forming hollow nanoshells of silver benzenethiolate (AgBT) because the much large size of BT<sup>-</sup> ions relative to halide ions hinders their

diffusion in the solid AgBT lattice. The molecular-type layered structure of AgBT also disfavors both the inward and outward diffusion of ions through the AgBT shells, thus leading to an overall reduction in the kinetics of the transformation reaction. The transformation reaction is driven only by the dissolution of  $\text{AgCl}_{0.5}\text{Br}_{0.5}$  and reprecipitation of  $\text{Ag}^+$  and  $\text{BT}^-$  ions. These results allow for the understanding of underlying factors in hollowing mechanisms to enable the controlled synthesis of well-defined hollow nanostructures with desired properties for a broad range of potential applications.

## **COLL 681**

### **Molecular engineering of semiconductor and plasmonic nanocrystal interfaces through host-guest recognition motifs**

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We demonstrate ultrafine engineering of nanocrystal (NC) interfaces in an aqueous environment through supramolecular functionalization, which unlocks molecular recognition motifs revealing detailed insights into dynamic host-guest interactions at surface-confined binding centres. Highly luminescent semiconductor indium phosphide zinc sulfide core-shell NCs (InP/ZnS NCs) are decorated with cucurbit[*n*]uril macrocycles (CB[*n*]s) leading to self-limiting self-assembly of colloidally-stable dynamic hybrid aggregates. The resultant hybrids are utilized for interfacial encapsulation processes in which surface-bound CB[*n*] molecules work as a host system to spatially confine selected guest molecules (*i.e.*, cobaltocenium and adamantylamine), facilitating interfacial electron transfer processes. This fundamental understanding of host-guest chemistry at NC interfaces paves the way to controlled binding of chemical species that exhibit low or even no affinity to nanoparticulate materials.

We further employ the self-limiting character of CB[*n*]-mediated aggregation of the InP/ZnS NCs for the formation of controlled hybrid aggregates consisting of two types of NCs (*i.e.*, semiconductor and plasmonic) through rapid self-assembly. InP/ZnS core-shell NCs (3 nm) are efficient assembly-modulators in CB[*n*]-triggered aggregation of plasmonic Au NCs (5-60 nm). These core-shell NCs act as both a functional nanoparticle surfactant and photocatalytic absorber, which adhere onto the surface of the larger Au NCs and kinetically arrest growth of emerging plasmonic aggregates. Within the described self-limiting assembly, the photoactive semiconductor NCs become an integral part of the overall structure and function of the resultant hybrid supraparticles. The CB[*n*]-mediated coupling of semiconducting NCs serves as an attractive tool to facilitate control of aggregation processes as well as optical and plasmonic properties of the resultant colloidal assemblies. The colloidally-integrated semiconductor/metal hybrids represent a powerful prototype multifunctional SERS-based assay for photochemical processes.

Controlling the efficiency of supramolecular engineering of NC interfaces opens a plethora of possibilities for ultrafine nanoparticle functionalization and construction of hybrid systems for sensing applications as well as next-generation (photo)catalysis, optoelectronics and nanophotonics.

## **COLL 682**

### **Environmentally stable CsPbBr<sub>3</sub>/TiO<sub>2</sub> core/shell nanocrystals with enhanced charge transport properties**

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Inherent poor stability of perovskite nanocrystals (NCs) is the main impediment preventing broad applications of the materials. Here, TiO<sub>2</sub> shell coated CsPbBr<sub>3</sub> core/shell NCs were realized through the encapsulation of colloidal CsPbBr<sub>3</sub> NCs with titanium precursor, followed by calcination at 300 °C. The nearly monodispersed CsPbBr<sub>3</sub>/TiO<sub>2</sub> core/shell NCs show excellent water stability for at least 3 months with the size, structure, morphology and optical properties remaining identical. In addition, TiO<sub>2</sub> shell coating can effectively suppress anion exchange and photo-degradation, therefore dramatically improving the chemical stability and photo-stability of the core CsPbBr<sub>3</sub> NCs. More importantly, photoluminescence (PL) and (photo)electrochemical characterizations exhibit increased charge separation efficiency due to the electrical conductivity of the TiO<sub>2</sub> shell, hence leading to an improved photoelectric activity in water. This study opens new possibilities for optoelectronic and photocatalytic applications of perovskites-based NCs in aqueous phase.

## **COLL 683**

### **Dendrimer directed nanocrystal assembly**

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Nanocrystal (NC) self-assembly into ordered superlattices is a crucial area of investigation in nanotechnology due to its direct implications on the resulting properties of these materials. Typically, self-assemblies are dictated by NC-NC interactions, however it has been shown that the organic surface ligands can play a major role in

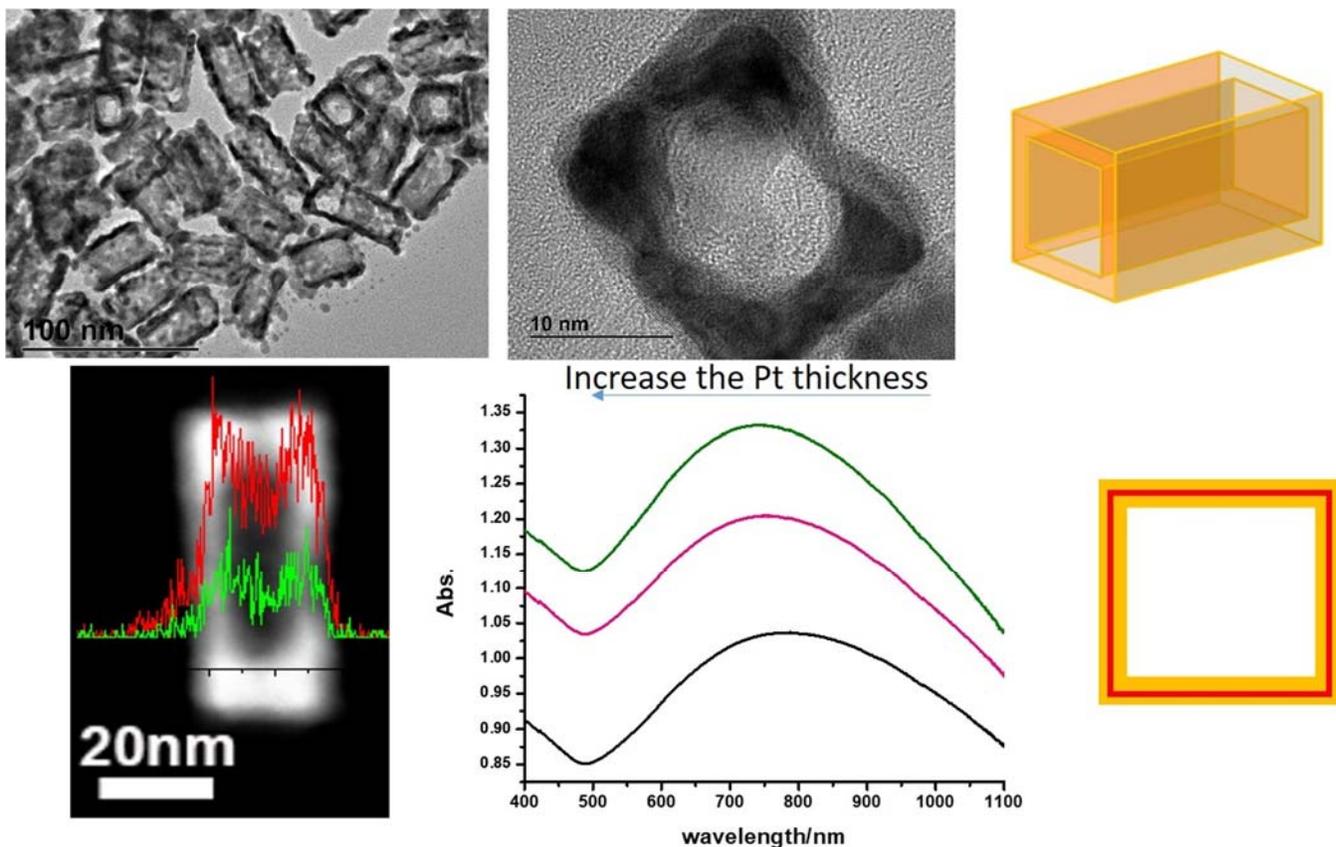
superlattice formation. In this study, a series of dendrimer ligands are used to direct nanoplate assembly into a directionally offset 3D architecture. The nanoplate films were evaluated with TEM tilt tomography and GISAXS experiments to probe the structure over a centimeter length scale, which were found to have high levels of uniformity. This 3D architecture is due to the non-trivial corona around the plates that changes with ligand architecture, which was confirmed with Monte Carlo simulations to characterize the ligand shells around the nanoplates. For larger, branched ligands, such as dendrimers, a lock-and-key type mechanism is found for the 3D assembly, as the steric bulk of the ligands on the corners and edges of the plates direct this unique architecture. Our developed level of understanding and modeling will help guide design frameworks to achieve targeted assemblies of NCs through a predictive model.

## **COLL 684**

### **Synthesis of sub-100 nm Pt-Au nanotube with tunable SPR band and investigation of its photothermal bactericidal activity**

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Hollow gold nanomaterials have been widely investigated as photothermal transduction agents (PTAs) in the biomedical field due to the advantages of: 1. high biocompatibility and low toxicity; 2. high photothermal conversion efficiency; 3. tunable optical absorption range in the NIR window I and II. Moreover, the inner cavity of the hollow structures guarantees a high cargo loading efficiency. Thus, gold nanoshell, gold nanocage and gold nanoring have been widely studied. However, anisotropic gold hollow structures, such as Au nanotube, are more favored due to its higher cellular uptake efficiency. In my research, anisotropic sub- 100 nm Pt-Au nanotube supported by ultrathin Pt layer was designed and synthesized by a polymer direct template method. The localized surface plasmon resonance (LSPR) band of the nanotube structure can be tuned from 650 nm- 1000 nm. The factors that influence the optical properties were comprehensively investigated. Both experimental results and DFT simulation demonstrated that the LSPR band of nanotubes highly depends on the aspect ratio of the nanotube, the ratio between wall thickness and diameter of the inner cavity as well as the contribution from the layer thickness of the ultra-thin Pt metallic substrate. Importantly, the hybrid Pt-Au coaxial tubular nanostructure exhibited excellent photothermal stability under different laser irradiation conditions compared to pure Au nanorods and can be used as photothermal bactericidal agents. These results point out a potential design based on noble metal materials as recyclable wound dressing materials.



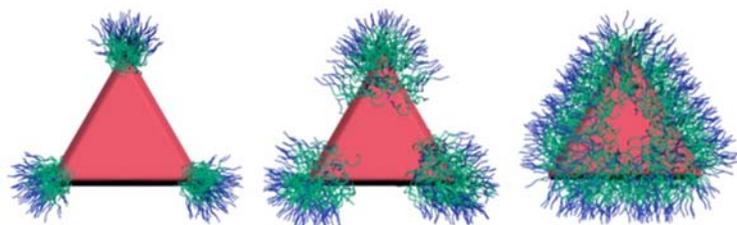
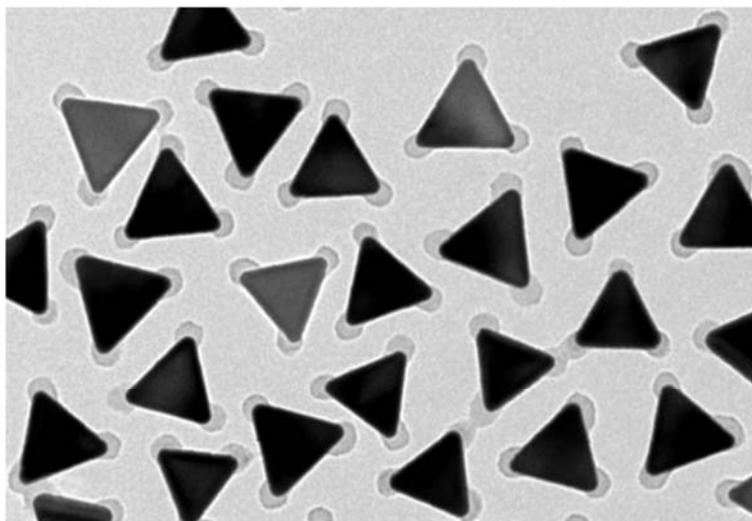
## COLL 685

### One-pot polymer patch deposition on gold nanoparticles via ligand island formation

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Precise control of surface patches on nanoparticles (NPs) can realize the great potentials of patchy NPs in directed assembly, catalysis and drug delivery. The prevailing synthetic methods of patchy NPs rely on the post-adsorption reorganization of uniformly coated ligands on NPs, which involve multiple steps to trigger the patch formation and lack the molecular-level control of ligands. Here, we apply the concept of “island formation” established for planar substrates, where ligands laterally cluster as they adsorb, to prepare patchy NPs with precise patterns and patch sizes *via* a one-pot

process. Using gold triangular nanoprisms and 2-naphthalenethiols (2-NAT) as a prototypical system, we show that the preferential adsorption of 2-NAT on the prism tips leads to formation of tip patches. We demonstrate that the tip-patched prisms can assemble into unexpected assemblies due to the patch-patch interactions. We also showcase this island formation mechanism as a generalizable strategy to pattern functional patches on NPs of other anisotropic shapes. The highly tunable surface patches, in addition to the plentiful NP core shape and composition, are expected to bring new possibilities towards the design of hybrid anisotropic NPs with directional interparticle interactions for applications in directed assembly and reconfigurable materials.



(top) A low-magnification TEM image of the as-synthesized tip-patched gold prisms, and (bottom) schematics of patchy prisms with various patch shapes, which can be readily synthesized by tuning the ligand island growth.

**COLL 686**

**Forming libraries of magnetic multicore nanoparticles with tunable dimensions and their biomedical applications**

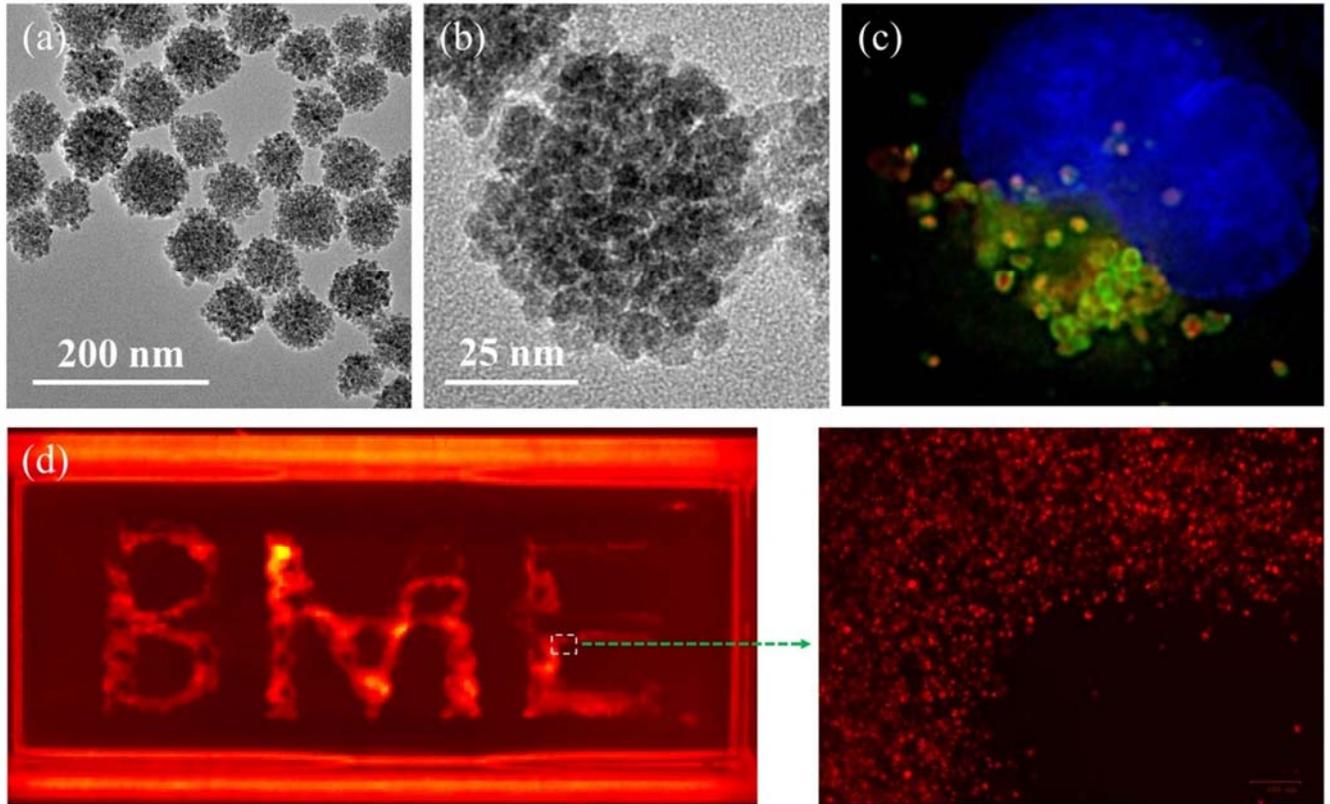
**Zhen Xiao**<sup>1</sup>, [zhen\\_xiao@brown.edu](mailto:zhen_xiao@brown.edu), **Qingbo Zhang**<sup>2,1</sup>, **Vicki L. Colvin**<sup>1</sup>. (1) Chemistry, Brown University, Providence, Rhode Island, United States (2) Chemistry, Rice University, Houston, Texas, United States

The development of magnetic nanomaterials has been of great interest over the past decades. Applications include magnetic resonance imaging, drug loading and targeted delivery, and hyperthermia agents for cancer treatment. Here we report a systematic approach for forming libraries of multicore iron oxide nanoparticle clusters with superior susceptibility, to meet the demand of different optimization of magnetic properties.

The clusters are aggregates of small nanocrystals (primary particles) as shown by TEM, Figure (a) and (b). We have synthesized a library of multicore iron oxide nanoparticles whose primary particle size and cluster dimension can be independently controlled by the reaction temperature and mass of added water, respectively. Both the cluster size and primary particle size can vary over a wide range. The clusters are superparamagnetic as indicated by VSM. At low applied magnetic fields on the order of Gauss, the magnetization of the multicore sample was much greater than that of the single-core nanoparticle, suggesting a superior susceptibility.

To demonstrate their potential for bioapplications, we functionalized the clusters with polyethylene glycol (PEG) and fluorescent Dil, and cultivated U2OS cells with the clusters. The result can be as seen in Fig (c). The centering blue area was the nucleus of the cancer cell. The green dots were the lysosome while the red dots were the Dil labeled clusters.

These cells were then placed on magnetic stickers with the shape of BME, and after 15 min the cells formed a pattern that was consistent with the magnet, as seen in Fig (d). The clusters successfully entering the cell membranes indicates their promising applications for biomedicines. Our preliminary experimental results shown here are very promising for biomedical applications, and a systematic investigation is underway.



**COLL 687**

### **Binary superlattices of plasmonic and excitonic nanocrystals for infrared optical metamaterials**

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Self-assembled nanocrystal superlattices offer exceptional control over the coupling between nanocrystals, just as solid-state crystals tailor the bonding between atoms. By assembling nanocrystals of different optical properties (e.g. plasmonic, excitonic, or dielectric), a wealth of binary superlattice metamaterials can be formed with new properties.

In this work, we add infrared plasmonic  $\text{Cu}_{2-x}\text{S}$  nanocrystals to the relatively limited library of materials that have been successfully incorporated into binary superlattices. We create a variety of binary superlattices with small plasmonic ( $\text{Cu}_{2-x}\text{S}$ ) nanocrystals and large excitonic (PbS) nanocrystals, both resonant in the infrared. Then, by controlling the surface chemistry of large  $\text{Cu}_{2-x}\text{S}$  nanocrystals, we are able to produce

structurally analogous superlattices of large  $\text{Cu}_{2-x}\text{S}$  and small PbS nanocrystals. Transmission electron microscopy (TEM) and grazing-incidence small-angle X-ray scattering (GISAXS) are used to characterize the superlattices. This synthetic achievement is the first step toward understanding how infrared plasmonic and excitonic nanocrystals couple in well-defined lattices that display a variety of symmetries and stoichiometries.

## **COLL 688**

### **Core-shell polyzymes as an approach towards polymeric nanoparticles for intracellular bioorthogonal catalysis**

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We have developed an all-polymeric nanoparticle as delivery scaffold for bioorthogonal catalysts. We synthesized polymeric backbones to generate nanostructured core-shell particles. In this approach the polymeric chains have been designed to present two distinct segments: a hydrophilic block and a hydrophobic one. In polar media these polymers self-assemble into stable nanoparticles with a hydrophobic core ideal for encapsulation of hydrophobic catalysts (see Figure 1). The synthetic strategies adopted for the preparation of the polymeric chains are based on controlled polymerizations, as reliable techniques to generate well-defined block copolymers. The bioorthogonal catalyst, a hydrophobic metal complex, is stably hosted in the nanoparticle core while the hydrophilic chains in the external shell provide stability to the particle in physiological environment. This system provides a platform for pro-drug activation, applicable for different therapeutic treatments, included multi-drug-resistant bacterial infections.

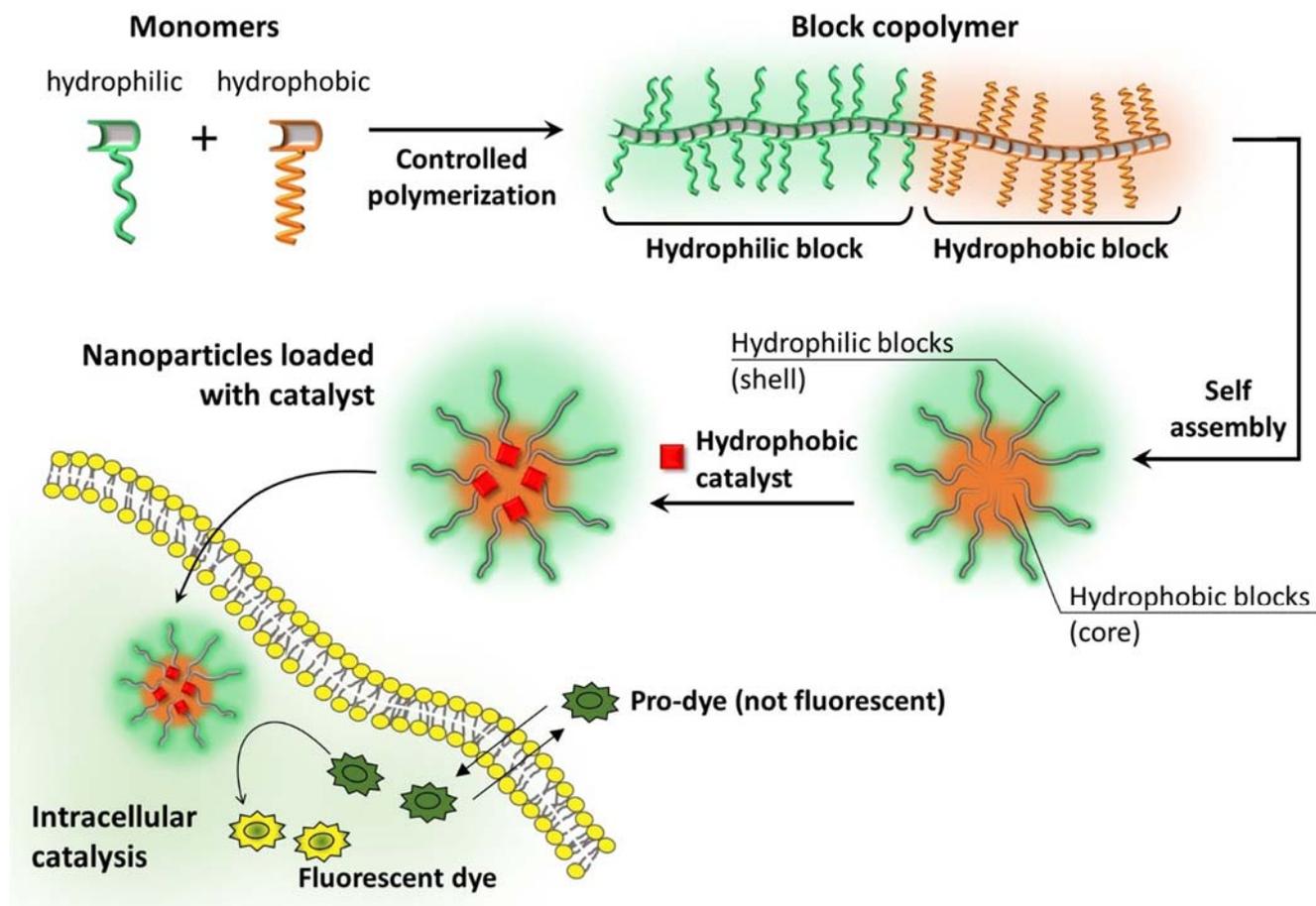


Figure 1

**COLL 689**

### **Chemical model studies of water-membrane interactions**

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Given the ongoing global economic growth, we can assume that our need for clean water will also keep growing, presenting a significant challenge. Among other water purification technologies, reverse osmosis (RO) desalination is key in solving this challenge. RO relies on a semipermeable polymer membrane that allows the diffusion of water, but not sodium or chloride ions. A better understanding of the surface chemistry is needed to combat surface degradation through unwanted accumulation of either mineral scales or biomass, so-called fouling.

A layer-by-layer preparation reported by Christopher Stafford[1], provides reproducible

polymer thin films with appropriately smooth surfaces to enable fundamental surface studies. Using ambient pressure X-ray photoelectron spectroscopy, we study the chemical makeup of this ultrathin model system, allowing a comparison to commercial membranes. We then show the interaction of water with these functional groups, providing clues about the nature of the solution-diffusion mechanism that is typically assigned to these membranes. A careful investigation of the radiation damage needs to be taken into account, both for studies in ultrahigh vacuum and in water vapor. These studies provide the foundation for ongoing investigations of the chemical interplay of polymer membrane, water and various contaminants.

## **COLL 690**

### **Investigation of insulin conformations and interactions with cell membrane lipids with Langmuir monolayers and Brewster angle microscopy**

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The effects of conformation and metal cation on insulin's aggregation into hexamers were studied at the air-water interface using the Langmuir monolayer technique. In the presence of divalent metal cations, typically zinc, insulin tends to aggregate into hexamers. The effects of other metal cations were tested on insulin at physiological pH and temperature. Each of the metal cations was also studied with each insulin's three conformations, T<sub>6</sub>, T<sub>3</sub>R<sub>3</sub>, and R<sub>3</sub>, to see how insulin's conformation affects its aggregation and interactions among hexamers. Compression-relaxation hysteresis was performed under each condition to determine the stability of each insulin conformation - metal cation combination's monolayer. Additionally, the hysteresis also allowed for the study of insulin's dissociation in the presence of a chelating agent, ethylenediaminetetraacetic acid (EDTA). Insulin's interactions with common constituents of the cell membrane (DPPC, DPPS, and Cholesterol) were also studied. A student-built Brewster angle microscope was used to visualize the insulin monolayers and identify any discernible features present among the various monolayers.

## **COLL 691**

### **Bioinspired coatings based on naturally occurring chlorophyll**

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& Computer Engineering, University of Massachusetts Lowell, Lowell, Massachusetts, United States (6) Plastics Engineering, University of Massachusetts Lowell, Lowell, Massachusetts, United States

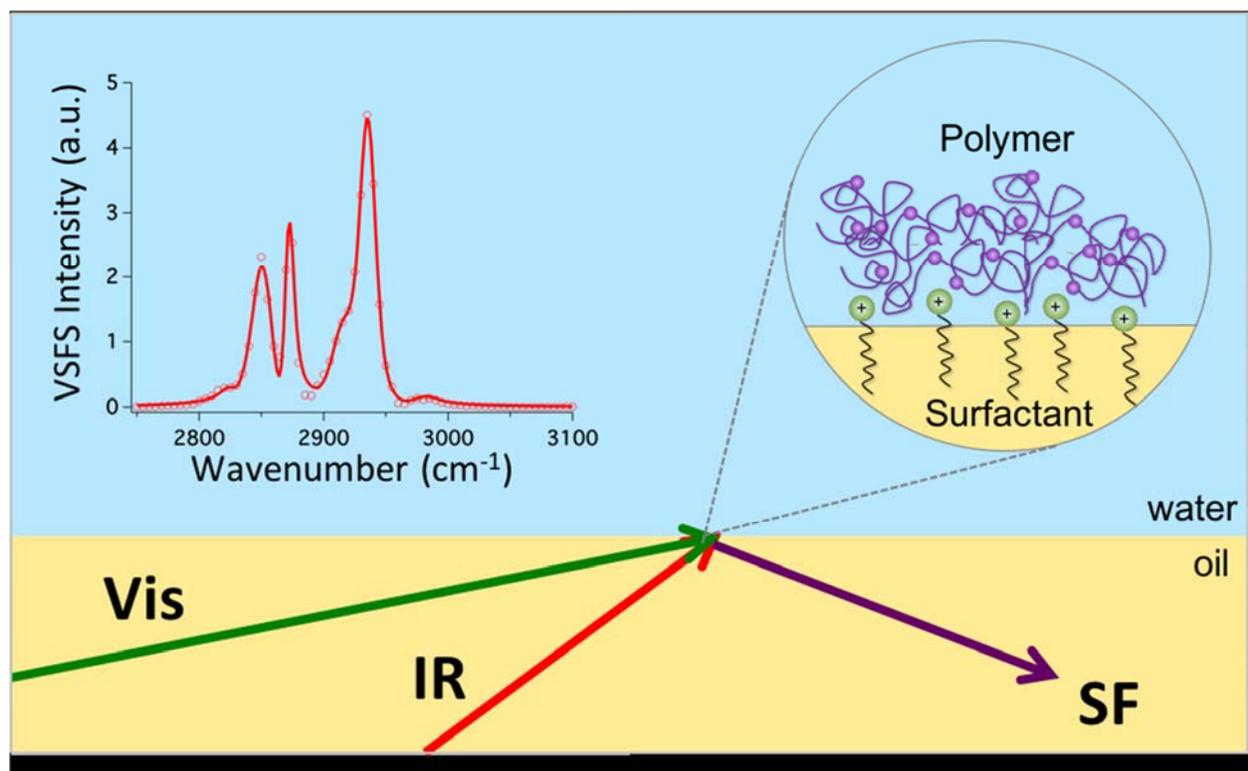
The development of durable dyed fabrics from safer materials are of interest for numerous military and civilian applications. Chlorophyll is a pigment which is available in large quantities from natural sources such as plants and green algae. However, the water insolubility and instability at high temperature renders this pigment not suitable for coating applications. Here we report a method to encapsulate chlorophyll using cyclodextrins with the goal of functionalization of the encapsulated pigment onto surface of fabrics like Cotton and Nylon-Cotton blends. Chlorophyll-cyclodextrin interaction helps improve not only the water solubility of the pigment but also its photo and thermal stability. The surface characterization of textile was performed using Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDX), and Fourier-Transform Infrared Spectroscopy (FTIR). Stability and spectral characteristics of the pigment were also evaluated. Thermogravimetric Analyzer (TGA) was used to study the temperature stability of the pigment. This research opens new possibilities that allows use of safer, low cost and durable natural dyes for fabric coatings.

## **COLL 692**

### **Adsorption and net structure of polymer-surfactant complexes at the oil/water interface as induced by their specific intermolecular interactions**

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Systems such as targeted drug delivery and functionalized polymer films utilize mixed chemical systems to manipulate desirable surface properties at a molecular level. Mixed systems allow particular chemical functionalization at the surface that cannot be achieved without the interaction between multiple chemical species. Because many surface chemistry applications rely on the specifics of chemical adsorption at buried liquid/liquid interfaces, a molecular-level understanding of the structure of adsorbed complexes from mixed systems at the surface is needed. The studies discussed herein reveal the interfacial complexation of nonionic polymer/surfactant mixed systems at the buried oil/water interface through the use of the surface-specific nonlinear experimental technique of vibrational sum frequency spectroscopy. Where hydrophobic interactions are found to affect the amount of chemical adsorption at the interface, the charge-dipole interactions between the surfactant headgroup and the polymer functional groups are responsible for the specific net structure the molecules adopt at the surface.



COLL 693

### Real-time adsorption of expansin on the surface of cellulose: Effect of pH, temperature and products during enzymatic hydrolysis of lignocellulose

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Biological pretreatment is a safe and environmentally friendly method for disrupting recalcitrant lignocellulose structures. Expansin and expansin-like proteins are proteins that can disrupt hydrogen bond of cellulose and open up the cellulose structure. They also display significant synergism when mixed with enzymes that catalyze cellulose and hemicellulose chain scission into sugars. However, the adsorption behavior and mechanism of expansin family proteins under pH, temperature and products during enzymatic hydrolysis of lignocellulose is yet unknown. Therefore, in this work, we investigated the effect of products, pH, and temperature on the adsorption of *Bacillus subtilis* expansin (*BsEXLX1*) on cellulose using quartz crystal microgravimetry with dissipation (QCM-D). Cellobiose and xylose in low concentration enhanced *BsEXLX1* adsorption, whereas they disrupted adsorption at high concentration. Arabinose and mannose continuously inhibited adsorption which gradually increased with increasing concentration. Glucose and galactose have no obvious influence on *BsEXLX1*

adsorption. Contact angle (CA) measurements and atomic force microscopy (AFM) of cellulose upon *BsEXLX1* adsorption in the presence of sugars showed that both hydrophilicity and roughness increased with *BsEXLX1* treatment. Improve temperature can increase the initial adsorption rate and irreversible amount of *BsEXLX1* adsorbed onto the cellulose. Acidic pH (4.8) was found to favor adsorption, whereas neutral and alkaline pH (10) favored desorption, which is useful to guide the process of *BsEXLX1* recovery. The results give us the ability to modulate and control expansin adsorption and provide insights into effective expansin use during enzymatic hydrolysis of lignocellulose in for example biorefineries.

## **COLL 694**

### **Genomic DNA coated 3D printed devices for chemotherapy**

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Since the discovery of chemotherapy, researchers around the world have been actively developing new and more effective chemotherapeutic agents to better treat cancer. Traditionally, chemotherapeutic agents work by interfering with cell division. However, by virtue of their mechanism of action, healthy normal cells can also be targeted and destroyed. As a result, while chemotherapy is an effective way of managing cancer, the resulting side effects limits its use. One approach currently taken to reduce these side effects is to deliver the chemotherapy drugs directly to the tumor. While this has been effective in reducing systemic toxicity, more can be done to improve this. Ideally, a device that could sequester any unreacted chemotherapy agents could be installed "downstream" of the tumor prior to them entering systemic circulation. Such drug-capture materials have yet to be realized due to the difficulty in achieving materials that have the right surface chemistry and geometry for blood flow.

Working together with medical doctors, computational fluid dynamics experts, and material chemists, we demonstrate the fabrication of DNA coated 3D printed materials that can be used to capture doxorubicin, a commonly used DNA-targeting chemotherapy agent. We discuss the concept behind the device, the use of 3D printed materials as an ideal substrate, and the chemistries considered in drug binding. To achieve scalability of these devices, we developed a method of coating cheaply available genomic DNA to these materials, a departure from commonly used synthetic DNA. The efficacy of these coated materials were demonstrated in PBS, where we observed a marked decrease in doxorubicin concentration over a period of 20 minutes, highlighting the viability of this as a method of drug capture. We also discuss the in-vitro stability of these DNA coatings, with approximately 400 pg of DNA lost/ mm<sup>2</sup> of coated material over 30 minutes in PBS at 37 C.



Left: Doxorubicin stock solution. Right: Doxorubicin solution with DNA coated materials after 20 minutes

**COLL 695**

### **Highly-tunable carbon fiber interfaces for high performance thermoplastic prepreg**

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Typical commercial surface treatments for continuous carbon fibers are often unavailable for short fibers. As such, there is little variety of chopped fiber surfaces leading to non-ideal coating solutions which result in poor interfacial compatibility between fibers and matrix. In this work we develop a method of applying a highly effective coating using a high throughput technique for chopped carbon fibers. We show the ability to tune both the coating thickness and chemical functionality using processing

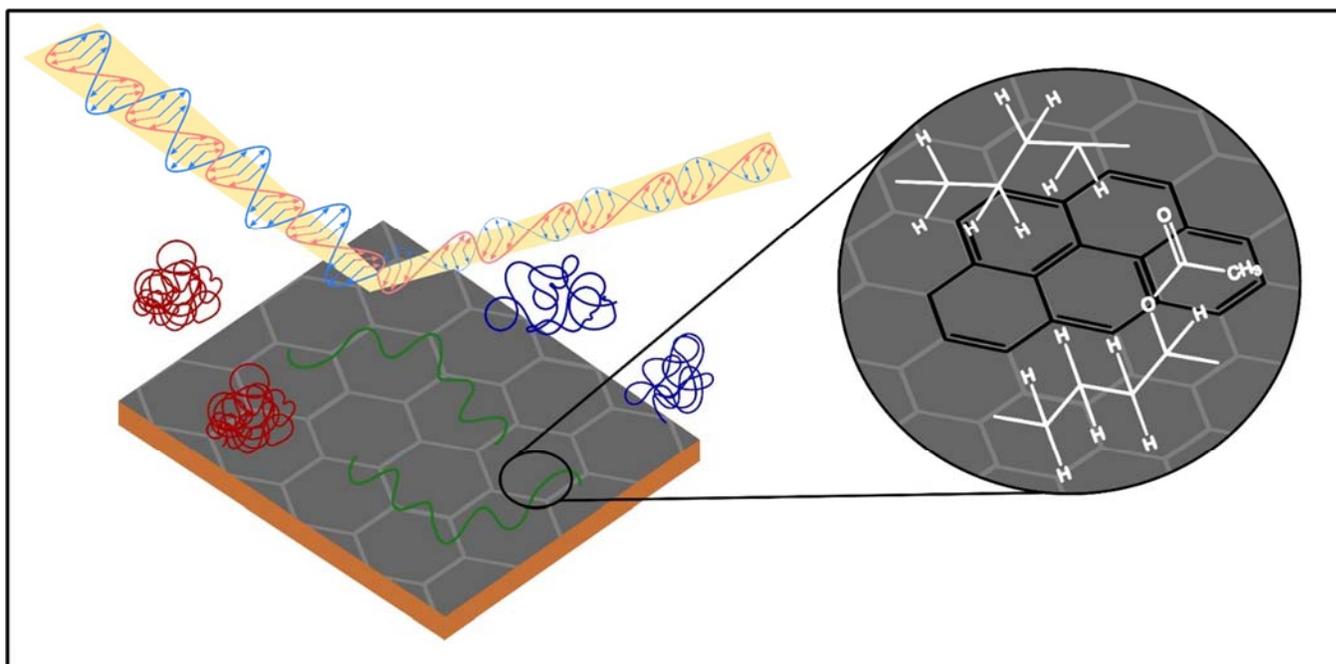
parameters. The coatings are evaluated using EDS and X-ray photoelectron spectroscopy (XPS) for uniformity and composition. Using this technique, thermoplastic composites are highlighted showing an increase in interfacial shear strength (IFSS) of 25 MPa. This process shows promise for increasing the throughput of surface treatment of chopped fiber on the industrial scale. With this technique, we hope to increase the overall performance of commercial, discontinuous composites as well as expand the possibilities of carbon fiber technologies.

## **COLL 696**

### **Molecular rationale of graphene-polymer interactions and the effect of solvent on graphene transfer**

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High-yield production of graphene-polymer devices requires robust, reliable transfer of chemical-vapor-deposition-grown graphene from the metal growth substrate to polymer films. Transfer success directly depends on the adhesion strength between graphene and the polymer relative to that between graphene and its native metal substrate. We demonstrate control over graphene-polymer adhesion by using solvent-polymer interactions to create favorable electrostatic interactions at the graphene-polymer interface. Using polarization modulated infrared reflection absorption spectroscopy (PM-IRRAS), we observe polymer chain rearrangement at the interface with neat single-layer graphene relative to the arrangement at the interface with copper. These data are measured for pressed unmodified polymer films soaked in different solvents, and we further demonstrate that polymer-solvent interactions can be used to control the polymer rearrangement induced at the graphene interface. Our results indicate the possibility of engineering solvent-polymer interactions to optimize graphene-transfer fidelity via interfacial interactions, and pave the way towards high-yield production of devices using graphene-polymer films.



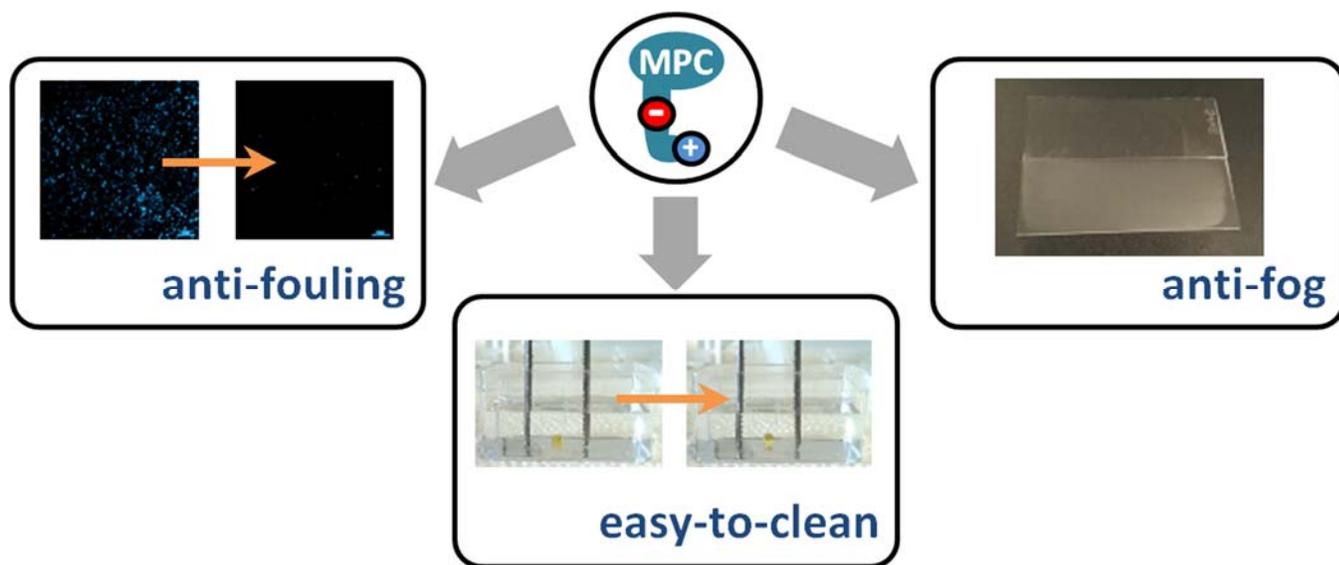
**COLL 697**

### **Control of structure property-relations of multi-functional polymer films based on zwitterionic phosphorylcholines**

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Functional polymer nano films, like stimuli-responsive polymer brushes, comb-like polymers or cross-linked polymer networks, are a group of smart surface coatings for the design of intelligent interfaces. Such innovative surface coatings will have to adopt additional intelligent functions preferentially simultaneously. These films are generated by a one step “grafting-to” approach of specifically designed and synthesized co-polymers allowing the modification of surfaces with preformed and most notably well-defined macromolecules. As an example for such a system, a novel multi-functional coating with simultaneous easy-to-clean, non-fouling as well as anti-fog properties based on co-polymers consisting of zwitterionic phosphorylcholine groups (MPC) and benzophenone units (BPO) as anchor and UV cross-linking agent will be presented. A series of co-polymers with different contents of BPO was synthesized by atom transfer radical polymerisation with the aim to investigate the mechanism that leads to the desired functionality of the coating on the base of an evaluation of the structure-property relationships of the MPC-BPO-coatings. By using atomic force microscopy (AFM), infrared spectroscopy (ATR-FTIR), contact angle measurements, and *in-situ* spectroscopic ellipsometry we demonstrate that the chemical composition of the polymer, the degree of crosslinking as well as thin film properties like thickness, degree

of swelling and wettability are crucial for the adjustment of the film function. A detailed study of the influence of various parameters, which are relevant for the control of the desired surface functions, will be presented. Therewith it can deliver guidance for future work in the field of functional polymeric nano films. Furthermore it will be shown that the developed MPC-based coatings can be applied to technical surfaces like cellulose and foils, and how the developed thin film forming process can be transferred from the lab to a technical coating process. The quality and durability of the desired surface functions was also one aspect of our investigations.



## COLL 698

### Adsorption of rare earth elements (REEs) by DNA functionalized mesoporous carbon

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The seventeen rare earth elements (REEs), comprised of yttrium, scandium, and the 15 lanthanides, are a group of chemically similar elements used in the manufacture of a wide array of modern products and their usages is expected to grow dramatically over the next two decades. Due to worsening of supply risks, recovery and reuse of REEs from the end-of-life products have been considered as an accepted strategy to maintain the supply-demand balance. Commonly, the separation of REEs is carried out by solvent extraction. However, this operation is not well suited to removing small concentrations of REEs (as would be found in waste streams), is time consuming, expensive, and can produce toxic and radioactive byproducts. Adsorption has been

recently gaining interest as a promising alternative to solvent extraction of REEs. Past research has demonstrated that phosphorous and oxygen-based functionalities have a strong affinity toward REE; molecules containing large numbers of these functionalities, such as DNA, may prove to be an ideal active site in development of a sorbent capable of extracting REEs through adsorption. In order to develop such a novel sorbent, commercially available and amine terminated single-stranded DNA was grafted onto carboxylated mesoporous carbon, which was characterized with conventional techniques. Equilibrium and kinetic studies of the adsorption of neodymium (Nd(III)) on this DNA functionalized carbon was performed, and the adsorbed amounts were measured by ICP-MS. The chemical interactions between the phosphate and oxygen functionalities with Nd (III) were investigated by Extended x-ray absorption fine structure (EXAFS). Lastly, a batch equilibrium study was conducted with a commercially available aqueous solution of 16 REEs to investigate the selectivity of each REE to this sorbent. Finally, similar studies with pristine mesoporous carbon demonstrated that DNA-functionalized carbons adsorb significantly higher amounts of rare earth elements thereby confirming the positive role of DNA in capturing REEs.

## **COLL 699**

### **Polyphenol-inspired coatings for membrane surface engineering**

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Plant polyphenols, such as tannic acid (TA), epigallocatechin gallate (EGCG), and gallic acid (GA), with high content of catechol/pyrogallol groups have been verified to form multifunctional coatings ascribed to the oxidative oligomerization of polyphenol precursors under mild conditions. They show great potentials as green building blocks for material engineering. Herein, we focused on the fabrication and modification of membranes taking advantages of polyphenol-inspired coatings.

Firstly we facilely fabricated low-pressure electroneutral loose nanofiltration (NF) membranes via co-deposition of EGCG and polyethyleneimine (PEI) on polyethersulfone (PES) ultrafiltration substrates. It exhibited desired performance in the context of textile wastewater treatment and yielded high pure water permeability. Moreover, the membranes exhibited good organic solvent resistance, structural stability together with favorable performance in dealing with textile effluent.

Following this work, EGCG involved coatings were further employed to fabricate dense NF membranes via the co-deposition of ECGG/PEI followed with cross-linking by trimesoyl chloride (TMC) onto hydrophilic microporous polytetrafluoroethylene (PTFE) substrate for water softening and remediation. The optimal NF membrane prepared at EGCG/PEI coating time of 6 h, EGCG/PEI mass ratio of 1:2 and TMC concentration of 0.2 wt% possessed a defect-free and negatively-charged selective layer with stokes radius of 0.46 nm. Moreover, the membrane exhibited good structural stability when

treated by ethanol as well as good long-term performance stability.

In addition, TA was also employed for membrane surface engineering. Hydrophobic polyvinylidene fluoride (PVDF) membranes were modified by one-step co-deposition of TA and a newly synthesized zwitterionic micromolecule substance (DEDAPS). The resultant PVDF membrane showed superhydrophilicity and underwater superoleophobicity. Furthermore, it possessed high pure water permeability of 4701.6 L/(m<sup>2</sup> h bar) and excellent separation performance for several oil-in-water emulsions. Moreover, the oil rejection and FRR were kept beyond 96% in 6 cycle tests and 14-day long-term stability tests.

## **COLL 700**

### **From molecular arrangement to macroscopic wetting of solid-confined ionic liquids**

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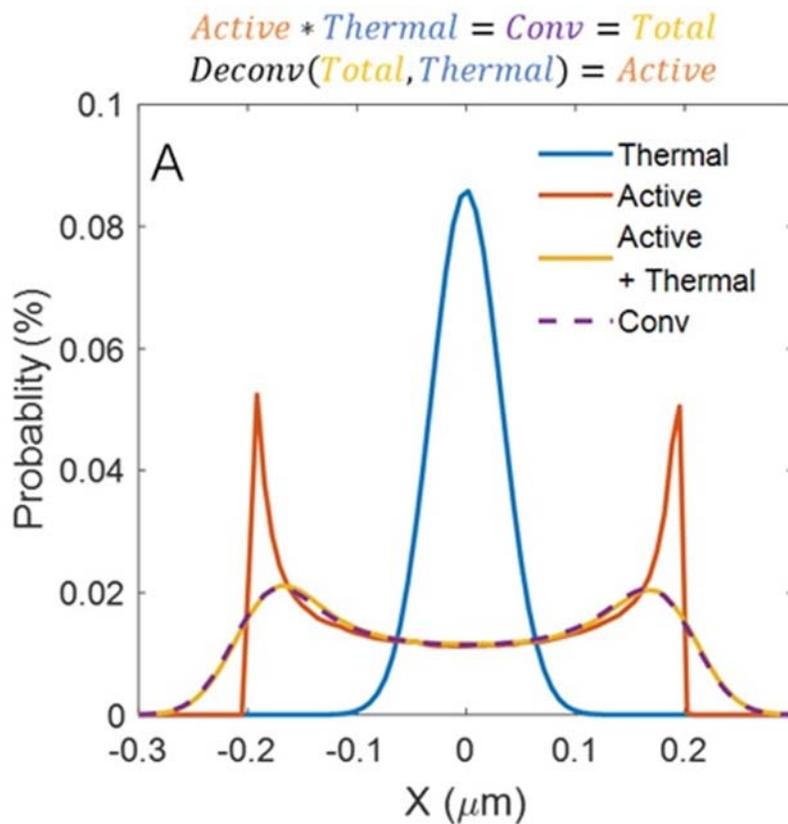
To optimize the wetting performance of ionic liquids (ILs) on solid surfaces, which is important in catalysis, lubrication, and energy storage, it is critical to control the molecular arrangement of ILs at the IL/solid interface. Here we report direct experimental evidence showing that tuning humidity is a novel and effective approach to manipulate the molecular arrangement and thus controlling the macroscopic wettability of ILs on the mica surface. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), contact angle testing, and atomic force microscopy (AFM) results showed that, under various relative humidity (RH), the molecular arrangement of nanometer-thick ILs on mica could be droplet, “pancake”, or extended layering. Meanwhile, the macroscopic wettability increases with RH. With the increase of RH, more water adsorbs on the mica surface, which dissolves and mobilizes K<sup>+</sup> on the mica. As a result, the cations of ILs occupy the empty spot left by the K<sup>+</sup> and initiate the layering of ILs. The water-enabled ion exchange and IL layering processes result in not only the decrease of the IL contact angle on mica but also the time-dependent contact angle. Additionally, it has been revealed that the growth of the nanometer-thick IL film on mica is unique. Initially, the IL film only covers more solid surface area while the thickness of the covered area remains constant. Then the thickness increases by double layering of the ion pairs. The findings here potentially provide new dimensions tailoring the performance of ILs at the IL/solid interface.

## **COLL 701**

### **Extract non-thermal fluctuation of active colloid particles in a quadratic potential well by deconvolution**

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A colloidal suspension of active Brownian particles (ABPs) driven by controllable forces into directed or persistent motions can serve as a model for understanding the biological systems. Such persistent motions generate non-thermal fluctuation that behaves differently from thermal fluctuation. 1-D position histograms of an active particle in a quadratic potential well reveal a splitting from a single peak of the ABP's positional distribution to a bimodal distribution. However, non-thermal and thermal fluctuations coexist. Decoupling the non-thermal from the thermal contributions to the overall histogram is non-trivial because the overall histogram is a convolution of the two contributions. If the thermal fluctuation can be determined independently, we show deconvolution or denoise algorithms can be used to extract the active fluctuation from the overall histogram. The talk will report the use of a single, induced-charge electrophoretic (ICEP) metallic Janus particle, confined in a quadratic potential well as a model ABP system to test our deconvolution method. The non-thermal fluctuations reveal physical parameters of the ABPs, including the ballistic speed, and the propelling force.



Histogram of particle position (HPP). Thermal noise (solid blue line), active noise (orange solid line),

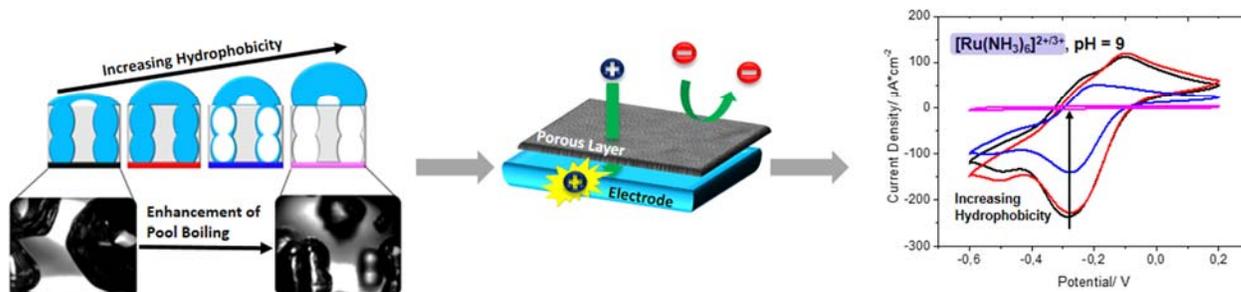
active +thermal noise (yellow solid line) and the convolution (purple dash line) between the histogram of thermal noise and histogram of active noise.

## **COLL 702**

### **Interplay between wetting and transport in mesoporous thin films**

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The development of nanoporous materials has received enormous attention during the last decades due to their technological relevance in e.g. energy- and water-management. These applications strongly rely on the transport processes within nanoporous materials which are tightly and mutually connected to wetting properties. In nano-confined space the interactions between molecules and surface are dominant, leading to extraordinary transport phenomena differing from bulk-like behaviour, particularly when the dimensions of the nanopores are close to the Debye screening length or hydrophobic interactions are involved. Thus, the understanding and design of the wetting-transport and wetting-charge-transport interplay in nanometer sized pores is a key step to improve nanopore transport related performance. To systematically understand and design this interplay of nanopore wetting and transport we use chemical functionalization to gradually adjust the wetting properties of mesoporous silica thin films, which can be prepared by coating or gravure printing processes. The mutual influence of wetting on liquid imbibition, condensation, and molecular transport as well as on boiling is investigated. As a key result two different ion transport mechanisms are proposed, which emerge from three defined wetting regimes as well as a threshold hydrophobicity suppressing pore accessibility. At the threshold hydrophobicity the pores are closed due to their wetting behavior but can be opened e.g. by electrostatic attraction. Furthermore, boiling-experiments show a clear increase of nucleation site density upon changing the wettability of the mesoporous surfaces from hydrophilic to hydrophobic. These results give insights into the complex interplay of pore wall functionalization, wetting, and charge determining nanopore properties. We expect these results to impact applications such as ionic transport relevant in smart water-management concepts and heat transport essential for cooling by boiling.



## COLL 703

### Magnetic single- and dual-resonant relaxometry to probe the dynamics of water molecules under confinement

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Overhauser Dynamic Nuclear Polarization (ODNP) isolates the translational motion of water near a selectively placed spin label, and reads out the result through variable enhancement of NMR (Nuclear Magnetic Resonance) signal. ODNP does not rely on higher-order spectroscopic effects, requires only a simple, versatile, and non-perturbative labeling strategy, and functions seamlessly in opaque, viscous, and other “dirty” systems. Despite previous applications to biological and polymer systems, ODNP still possesses many fundamental capabilities and a flexibility that remain largely untapped. In particular, it offers a window into understanding water confinement and the role it plays in a vast range of applications, from the binding of proteins to syntheses inside reverse micelles. However, these studies require the development of extensions to ODNP that can properly map out the behavior of surface and confined water across different compartments and phases in highly heterogeneous and/or porous materials. Emphasizing reverse micelles as model systems, we describe our progress towards measurements in highly phase-heterogeneous and confined systems and we include

comparisons to molecular modeling simulations. By integrating ODNP with modern NMR relaxometry techniques, we facilitate its deployment in the reverse micelle, and demonstrate that it can work synergistically with  $^2\text{H}$  NMR relaxometry and  $^1\text{H}$  NMR diffusometry. Specifically, ODNP measures intra-micelle translational dynamics,  $^1\text{H}$  NMR measures translational Brownian diffusion of reverse micelles in organic phase, and  $^2\text{H}$  NMR measures the rotational motion of motionally restricted water molecules. We discuss how such a multi-modal relaxometry strategy offers unique insights into the dynamics of reverse micelles, and discuss applying the methodology to other confined environments and synthetic soft materials systems.

## **COLL 704**

### **Experimental and computational VSFS studies on the influence of NaCl on methylglyoxal surface adsorption and hydration state at the air-water interface**

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Atmospheric aerosol have important and extensive effects on the environment. However, many of the processes that lead to the formation of aerosol, particularly aqueous secondary organic aerosol (aqSOA), remain poorly understood due to the complex processing of secondary organic constituents within the aerosol phase leading to hydration, oligomerization, and other reaction products. As the molecular composition of aerosol can significantly influence their properties, it is vital we increase our understanding of how such molecules behave in aqSOA systems. Vibrational sum-frequency (VSF) spectroscopy, a surface sensitive technique, can provide information about interfacial molecular populations and behaviors. Complementary experimental surface tensiometry and computational calculations afford further insights into these systems. A combination of these methods is utilized to investigate methylglyoxal at the air-water interface as a model for aqSOA. Methylglyoxal (MG) is an abundant and atmospherically important aldehyde that is known to participate in SOA formation. MG exists in an equilibrium of two hydration states in bulk water: a single hydrated diol and a doubly hydrated tetrol. Our studies of MG at the neat air-water interface determined that the diol to tetrol ratio is greater at the interface than in the bulk, favoring the diol. Here we present our preliminary studies on MG with non-reactive salts, which indicate an even greater shift in the equilibrium, further favoring the MG diol. This work has important implications for understanding MG's atmospheric fate and in turn the formation and aging of aqSOA.

## **COLL 705**

## **Modeling the impact and bounce of droplets at a horizontal solid plate considering the convection-diffusion behavior of surfactant**

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Droplet-wall interactions play an important role in many multiphase processes of the chemical, petroleum and pharmaceutical industries. This paper focuses on the dynamic microscopic mechanism of the deformable oil-water interface. Based on the mechanical behavior of dispersed droplets and interface properties under the influence of surfactant, the dynamic interaction during the collision between a droplet and a horizontal solid surface in aqueous solution is studied.

A theoretical model has been developed to analyze a droplet rise at a certain speed in aqueous solution and subsequent impact and bounce against a horizontal solid surface, by taking into account the driving force, hydrodynamic drag, inertial added mass effect and drainage of the thin film between the drop and the interface. The quantitative adsorption process of surfactant molecules at the oil-water interface and the convection-diffusion behavior of absorbed surfactant were simulated by coupling the effect of fluid flow inside droplet.

The trajectory and the deformation of the droplet and the dynamic distribution of surfactants at the interface during the collision were effectively predicted. The results demonstrate that the convection and diffusion of the absorbed surfactant molecules play an important role in the evolution of the interfacial deformation and the dynamic interaction forces at a relatively high collision velocity. That is, it can inhibit the impact process of droplets and promote the bounce process of droplets. Meanwhile, with an increase in the bulk concentration of surfactant, the mobility of the interaction interfaces is suppressed by the interfacial tension gradient and the interface behaves as immobile.

**COLL 706**

## **Single particle motion in dilute colloidal suspensions**

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We use fluorescence microscopy to study the dynamics of a Brownian probe particle driven by a constant external force through dilute colloidal suspensions with hard-sphere interparticle potential. As the probe particle moves through the colloidal suspension it collides with colloidal particles deforming the equilibrium suspension microstructure. The shape and the range of this distortion is determined by the volume fraction of the colloidal suspension and by the relative strength of the external force with respect to the entropic restoring force of the colloidal particles. We find that the average velocity of the probe particle is linear with the external force and it decreases with increasing volume fraction. Moreover, there is an increasing anisotropy with increasing

forcing between the velocity fluctuations of the probe particle oriented parallel vs. transverse to the imposed force. At high forcing, there is an increased probability of collisions on the front of the probe particle, and although these will partially contribute to transverse velocity fluctuations, they mainly contribute to parallel velocity fluctuations causing pronounced anisotropy. We compare our results with force-induced diffusion measured by Brownian dynamics simulations. Future studies will include studying probe particle dynamics in colloidal suspensions with a range of interparticle attractive strengths.

## **COLL 707**

### **Janus droplet impacting on superamphiphobic surfaces**

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Drop splashing on solid surfaces is crucial in many practical applications, such as spray-coating, ink-jet printing, fuel combustion, agriculture irrigation and pesticide spraying. In this work, Janus droplets splashing and rim instability on a superamphiphobic surface were investigated using high-speed photography. A striking phenomenon is observed: splashing can be promoted by increasing the viscosity of the half of a water drop, realized by introducing a glycerin drop into a water drop. The viscosity ratio of the resulted *Janus* drop greatly affects the splashing threshold of velocity and the corrugations on the expanding rim. The effect of enhancement can be tuned by the viscosity of the added glycerin. Experimental results and theoretical analysis support that the introduction of the glycerin part conduces to the spreading phase of the water part. The discrepancy in pressure of the glycerin and water part is discovered to be responsible for the increased expansion area triggering instability.

## **COLL 708**

### **Encapsulation of water droplet with silica precursor in o/w emulsions by SPG method**

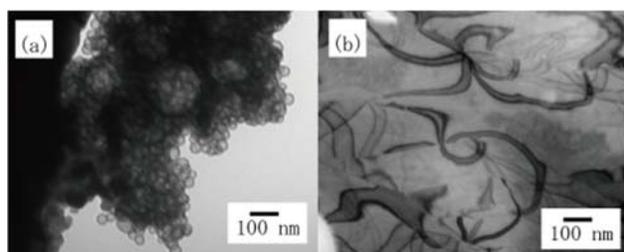
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Polymer capsules with submicron size are synthesized by encapsulation of emulsion droplets. We have synthesized silica capsules by encapsulation of water droplet of w/o emulsion with perhydropolysilazane (PHPS), which is a precursor of silica. The capsules with a range of 25 to 40 nm in diameter were obtained from the emulsion prepared by ultrasonication, and it was difficult to control the capsule size widely. SPG method is another approach for encapsulation.

It is known that the size of capsules is controlled by the pore size of SPG membrane. In this study, we aimed to control the size and the shape of the silica capsules by using SPG method for emulsion preparation. For encapsulation, NaCl aq. was added to

pentane containing PHPS and surfactants through SPG membrane. Surfactants were added to the pentane solution. The effect to pore size of SPG membrane, the HLB of surfactant, the concentration of PHPS in the pentane solution and the injection rate of aqueous phase on the size and shape of capsules were investigated. The sizes of droplet and capsules in solution were measured by dynamic light scattering. The size and shape of capsule, and shell thickness were determined by transmission electron microscopy.

Figure 1 shows the TEM images of capsules. The capsules with arrow size distribution were synthesized by the SPG membrane (Figure 1a). It was found that very small capsules were homogeneously formed by SPG method even though the pore size of the SPG membrane was larger than 5  $\mu\text{m}$ . Tube like capsules were obtained by increasing the injection rate (Figure 1b). The details of structural control were investigated.



TEM images of the capsules synthesized with PHPS by SPG method

## COLL 709

### Influence of polyelectrolyte architecture on the electro-kinetics and dewaterability of industrial MBR activated sludge

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Improvement of sludge dewaterability is greatly hindered by the presence of large amount of water molecules trapped in sludge as a result of its strong hydrophilic characteristics. This study investigates the influence of linear and branched structures of polyacrylamide (PAM) with different charge density (CD) on the electro-kinetics, dewatering and volume reduction of highly stable industrial membrane bioreactor (MBR) sludge. The presence of PAM has induced intensive impact on the flocculation behaviour of the sludge as revealed by supernatant turbidity, zeta potential, capillary suction time (CST), flocs size and settleability. Enhancement of the flocculation and dewatering of sludge is correlated to the surface charge neutralization and bridging mechanisms. The highest optimum dose is obtained as 70  $\text{mg}\cdot\text{L}^{-1}$  for linear PAM of 40%

CD whereas the lowest value is determined as 30 mg.L<sup>-1</sup> for branched PAMs. In all cases, turbidity removal of 99.9% and CST reduction of 51-64% are attained where the linear PAMs revealed the highest CST reduction. As per the flocs formation, higher PAM dose results in bigger flocs until the saturation point, beyond which the surface saturation occurs. The sludge percent volume reduction is measured and correlated to the flocs size and PAM dose. At an optimum PAM's dose, bigger flocs resulted in higher percent volume reduction, however, at a unified PAM's dose, branched structure of PAM achieved higher percentage volume reduction having smaller flocs size. Overall, the branched structure of polyacrylamide was more efficient in flocculation of MBR sludge at lower dose of 30 mg.L<sup>-1</sup> for both 40 and 60% CD and attaining the highest percentage volume reduction of 58%.

## **COLL 710**

### **Evidence for surface-active pyruvic acid oligomers products at the air-water interface: Combined experimental and computational VSFS study**

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Aqueous secondary organic aerosol (aqSOA) are among the most ubiquitous environmental systems and their impacts on the climate and overall environment can be far reaching. The secondary organics within aqSOA significantly influence their formation, structure, and characteristics. However, much of this influence remains poorly understood due lack of knowledge about the aqueous phase processing these organics undergo after partitioning into the aerosol phase. In particular, small atmospheric dicarbonyls that contribute to aqSOA formation can further react in the aqueous phase to form hydrated species and oligomers. The vast number of potential reaction pathways resulting from this means that the molecular nature of many of the organics at aerosol interfaces is largely unknown. A prime example of this is pyruvic acid (PA), which despite being better known for its biological significance, is also an abundant atmospheric secondary organic. Literature studies have revealed that in aqueous solutions, PA has two populated hydration species, the unhydrated alpha-keto acid form and a singly hydrated triol form. Previous studies by the Richmond lab have shown that such an hydration equilibrium can be depth dependent and can potentially affect the interfacial properties of the system. Interestingly, the neat-PA systems revealed higher than anticipated surface activity and VSF spectra provided significant evidence of surface-active oligomeric species at the interface. The experimental VSF spectra contain strong responses arising from vibrational modes of functional groups not found in the monomeric forms, establishing the presence of oligomers. The presence of favorable oligomeric reaction products in the bulk are well documented for PA, but the relative surface affinity of such species has not been previously studied. As these larger molecular weight species can have substantial impacts on aerosol properties, these are significant findings for the atmospheric community.

## COLL 711

### **Aqueous exfoliation of $\alpha$ -zirconium phosphate using mixed tetraalkylammonium hydroxides**

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$\alpha$ -Zirconium phosphate ( $\alpha$ -ZrP), as a layered material, has found widespread application for its ease of intercalation and exfoliation. Herein we focus on the aqueous intercalation/exfoliation using tetraalkylammonium hydroxide (TXAOH) and their mixtures. The size of the cations dramatically influences how they diffuse into the center of the galleries of the  $\alpha$ -ZrP nanosheets and affect the overall progress/degree of the intercalation/exfoliation.

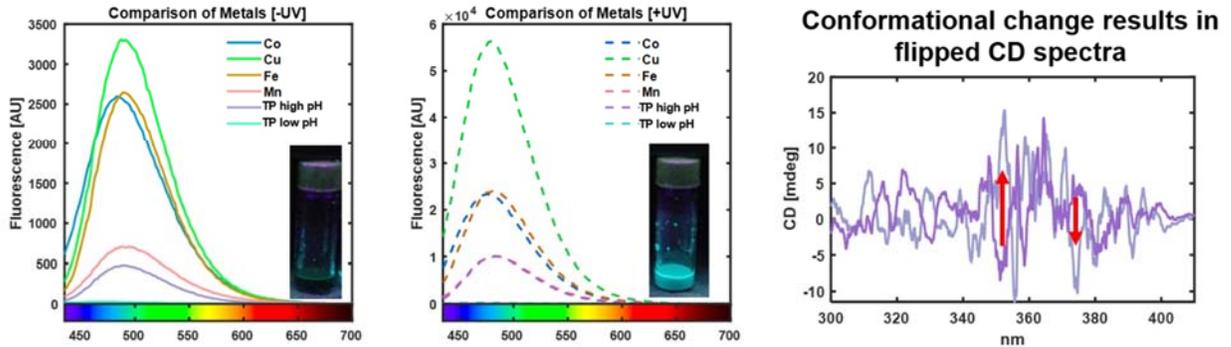
## COLL 712

### **UV-trained and metal-enhanced fluorescence of tetrapyrroles and tetrapyrrole-based nanoparticles**

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Tetrapyrroles (TPs) have been known to undergo conformational changes in response to stimuli such as UV irradiation or metal chelation. However, in contrast to previous reports of tetrapyrrole photodegradation behavior, we have determined that the conformational changes in some TPs exposed to UV irradiation actually lead to enhanced fluorescence emission without degradation into other products. This enhanced fluorescence can be further complimented with the chelation of metals. These observations were further evaluated in crosslinked TP nanoparticles, at the bulk state and at the single-particle level. TPs and TP-derived NPs were characterized using UV-visible spectroscopy, fluorescence spectroscopy, transmission electron microscopy, mass spectrometry, and circular dichroism. TP conformational change was confirmed with circular dichroism, and their ability to withstand photodegradation was confirmed with mass spectrometry. These findings suggest that UV irradiation and metal chelation can be utilized to “train” TPs for enhanced fluorescence at selected wavelengths.

**UV Exposure and metal chelation separately lead to “trained” enhanced fluorescence due to conformational changes in tetrapyrrole**



UV-trained and metal-enhanced fluorescence of tetrapyrroles

**COLL 713**

**Controlled delivery of signaling molecules using magnetic micromotors**

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Most cellular phenomena depend on biochemical signals. Therefore, various techniques have been developed for encapsulation and release of drugs, nutrients or other cargo using microrobots. However, localized targeting without payload leakage during transport is challenging. In this work, we present a light-controlled delivery system integrated with magnetic micromotors which overcomes this challenge. We synthesize a photolabile linker which releases a cell-to-cell signaling molecule when exposed to light. This system is integrated with magnetic micromotors, which can be steered to target locations in the cell culture. We demonstrate that gene expression in engineered bacterial cells is successfully activated when the signaling molecule is cleaved. This proposed method can be used for wide-ranging applications in the fields of engineering, biology, and medicine, in which the ability to target and release molecules on-demand to a particular location is important.

**COLL 714**

**Glycoconjugate-functionalized magnetic nanoparticles: Tool for selective killing of targeted bacteria via magnetically hyperthermia**

**Benjamin D. Fellows**<sup>1</sup>, **Cedric Taylor**<sup>2</sup>, **Anna Samstag**<sup>2</sup>, **Tzuen-Rong Tzeng**<sup>2</sup>, **Olin T. Mefford**<sup>1</sup>, *mefford@clemson.edu*. (1) Materials Science and Engineering, Clemson University, Clemson, South Carolina, United States (2) Department of Biological Sciences, Clemson University, Clemson, South Carolina, United States

New technologies utilizing nontraditional antibiotic mechanisms are urgently needed to combat the increasingly common appearance of multi-drug resistant bacteria. Drug resistant bacteria is a worldwide problem as the number of drug resistant pathogens grows with each year. The World Health Organization developed the Global Action Plan on Antimicrobial Resistance (AMR) in 2015 to control the spread and impact of antimicrobial resistance. In addition, the economic cost of AMR to be approximately 3.1% of global output gross domestic product. To put this in prospective, the cost of cancer represents 1.5% of global GDP. This work explores the feasibility of using magnetically hyperthermia to selectively kill enterotoxigenic *Escherichia coli* strain K99 (EC K99) as a model for antibiotic resistant bacteria.

Click ready magnetic nanoparticles were synthesized and functionalized with bacteria-specific glycoconjugate for adherence to EC K99. When mixtures containing both EC K99 and the GM3-MNPs were exposed to alternate magnetic fields (31 kA/m, 207 KHz), a clinically relevant 3-log reduction in colony forming units (CFUs) of EC K99 was achieved in 120 minutes. Bacterial selectivity of the treatment was shown using a mixed culture experiment including both receptor positive EC K99 and receptor negative EC O157. Targeted cell death of the EC K99 was seen after treatment of the mixed culture with minimal damage to EC O157. Cell death of EC K99 was further supported by the intracellular adenosine triphosphate (ATP) levels which were considerably reduced when incubated with GM3-MNPs and treated with MagMED. These results suggest that GM3-MNPs induced glycoconjugate targeting along with MagMED can be potentially used as a targeted nontraditional antibiotic treatment platform to inactivate/kill bacterial pathogens, with minimal impact on normal microflora and the affected body region/tissue.

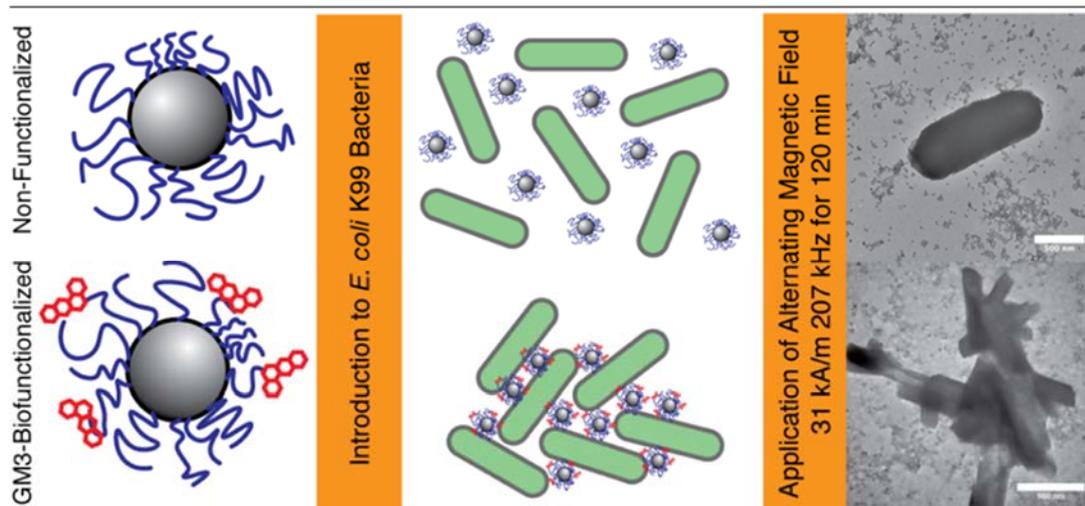


Figure 1: (left) Cartoon representation on functionalized and non-functionalized magnetic nanoparticles (center) representation of aggregation of the GM3-functionalized, but no aggregation with the non-functionalized particles (right) TEM image of cellular destruction following targeted treatment of *E. coli*

## **COLL 715**

### **Bacterial interactions with quaternary ammonium surfactants**

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In the field of microbiology, the efficacy of a biocidal active can be represented by different quantities. Often used are the minimum inhibitory concentration (i.e. “MIC”), which measures the minimum concentration of biocide above which the growth of a bacterial population is inhibited; and the minimum bactericidal concentration (“MBC”) beyond which bacteria are killed. Different actives are usually ranked against these quantities and different bacteria and fungi, to reflect how efficient and broad they are as antibacterial agents.

Bleach and alcohol are generally used as the first measure to control bacterial growth; they are cheap, available and easy to implement at industrial levels. Their mechanism, based on oxidation, leaves nothing to the imagination: efficacy is directly related to the dose added. On the other hand, the use of more complex molecules, such as quaternized surfactants, which belong to the field of Soft Matter, had led to fascinating questions that only such objects could pose. Of particular interest is the way by which biocidal efficacy relates to all thermodynamic aspects of such actives being surfactants which can self-assemble, lower surface/interfacial tensions... Unlike bleach or short-chain alcohols, surfactants present several different attributes of thermodynamic origin, which may impact (positively or negatively) their efficiency as biocides: a critical micellar concentration (“CMC”) or concentration under which surfactants exist as “unimers”, and as micelles above; a the micelle aggregation number, i.e. the number of surfactant unimers involved in a single micelle; a micelles of particular shape. To be efficacious, must cationic surfactants be in a free “unimer” state, or present as micelles? Do MBCs need to be above or below the CMC, as a general rule, or is it more complex than that? Another question of interest lies in the membrane activity of such surfactants. While it is well accepted that they kill bacteria by contact, disrupting the cell membrane as soon as they touch it, numerous questions remain to be answered. How do their structures affect the bacteria membrane disruption? What is the contact time impact on their biocidal activity? Can the same quaternary ammonium surfactant be involved in consecutive bacterial death? We will provide different examples of cases where such questions, at the interface between soft matter and biology, pose a challenge for the scientist.

## **COLL 716**

### **Towards an antimicrobial flexible nanopillar hydrogel film with tunable stiffness**

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Over a billion people worldwide have skin and nail fungal infections, more than 150 million of which are serious, invasive fungal infections. Such fungal infections have morbidity and mortality rates as high as 38% in the general population, much higher than bacterial infections. These fungal infections are usually caused by injuries contaminated by soil, allowing invasive molds into the wound area, and have been reported in people who have sustained injuries involving agriculture, industrial accidents, and combat. A notable fungal infection is fungal keratitis, which has ~1 million new cases annually worldwide. Some of the most common pathogens causing fungal keratitis are invasive molds such as *Aspergillus fumigatus* and *Fusarium oxysporum*. The current method to prevent microbial infection are overused chemical solutions that lead to antimicrobial resistance. Natural, nanotextured surfaces such as those on cicada wings have been found to cause bacterial and fungal cell rupture and death. These antimicrobial nanotextures are pillars ~100 nm in diameter, about 1000 times smaller than a strand of hair.

Nanostructured surfaces have been reported by many groups to inhibit microbial growth. However, these previous reports have been about stiff, not flexible surfaces, and are not desirable in many applications, such as a bandage. Here, we report the use of a naturally sourced, recyclable material, chitosan, from crustacean shells to form an antimicrobial, flexible, soft nanopillar surface. We examined the growth of pathogenic fungi on these hydrogel surfaces. After 24 hours, we found fewer viable fungi on the nanopillar surfaces compared to flat hydrogel surfaces. We conclude that flexible, nanopattern hydrogel films from chitosan inhibit fungal growth and are a promising future bandage material.

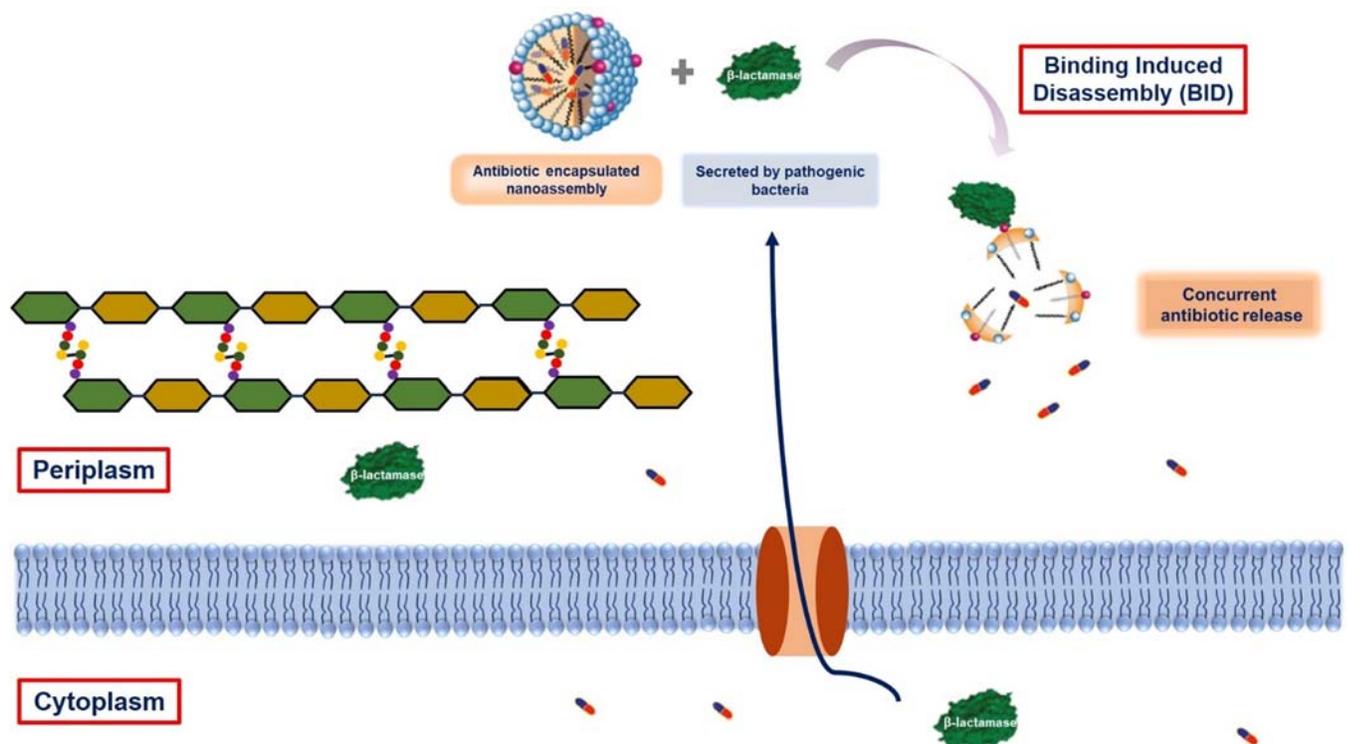
## COLL 717

### Enzyme responsive supramolecular approach for strain-selective killing of pathogenic bacteria

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Broad-spectrum antibiotics indiscriminately kill both pathogenic and beneficial bacteria alike, which facilitates in promoting antibiotic resistance and dysbiosis in the host microbiota. Therefore, developing alternate approaches that specifically target pathogenic bacteria without harming the beneficial ones are on demand.  $\beta$ -lactamases are enzymes that hydrolyze  $\beta$ -lactam class antibiotics, conferring resistance to a wide

group of bacteria, including pathogenic *Staphylococcus aureus*. Here we report a  $\beta$ -lactamase enzyme responsive dendrimer based nanoassembly for the delivery of broad-spectrum antibiotics in a narrow fashion.  $\beta$ -lactamase enzymes bind to the antibiotic loaded nanoassemblies, undergo disassembly, leading to the concurrent release of encapsulated antibiotics. Using the antibiotics loaded supramolecular strategy, enhanced potency of the antibiotics and bacterial strain-selective antibiotic release were achieved. We further demonstrate the strain-selective killing of pathogenic *Staphylococcus aureus* over commensal *Escherichia coli* in a co-culture model. Thus,  $\beta$ -lactamase responsive nanoassembly platform has the potential to selectively eradicate pathogenic bacteria with minimal impact on natural microbiome.



COLL 718

### Rational design of anti-fouling surfaces to control bacterial biofilms

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Bacterial biofilms are a major cause of chronic infections associated with implanted medical devices and biomaterials. However, controlling biofilm formation remains challenging due to the high-level tolerance of biofilm cells to antibiotics and disinfecting

agents. To overcome this grand challenge, we investigated how material properties affect bacterial adhesion using polymers with varying stiffness and specific topographic patterns. Based on the obtained results, we proposed a set of principles for rational design of antifouling surfaces and validated the design using protruding hexagonal patterns, which were found reduce biofilm formation of *Escherichia coli* by around 90%. Inspired by these findings, we further developed a new strategy based on dynamic topography using biocompatible shape memory polymers with micron-scale topographies. These surfaces can both prevent bacterial adhesion and remove established biofilms through rapid change in surface topography triggered by moderate shift in temperature, thereby offering more prolonged antifouling properties. We demonstrate that this strategy can achieve a total reduction of *Pseudomonas aeruginosa* biofilms by 99.9% compared to the static flat control. It was also found effective against biofilms of *Staphylococcus aureus* and an uropathogenic strain of *Escherichia coli*. Such biofilm removal also sensitized the detached cells to conventional antibiotics, demonstrating a synergistic effect. Based on these findings, we further developed a new anti-fouling strategy using active topography with programmable beating of micron-size pillars. This approach demonstrated a similar level of antifouling activities as dynamic topography, but does not require temperature change and offers better long-term protection. A prototype catheter based on this design remained clean for more than 30 days under constant challenge of artificial urine with inoculated bacteria, while the control catheters were completely blocked within 5 days. Possible applications of such technologies will be discussed.

## **COLL 719**

### **Interactions of motile bacteria with interfaces of liquid crystals**

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This presentation will describe an experimental study of the interactions of motile bacteria with the interfaces of liquid crystals, leading to the design of soft materials that provide self-regulated release of bioactive agents in response to mechanical stresses generated by motile bacterial cells. The presentation will have two parts. First, it will address how interfacial shear stresses generated by the swimming motion of bacteria can cause liquid crystals to reorient from an initial tangential orientation, leading to optical reporting of the arrival of bacteria. Second, the presentation will describe how micrometer-sized aqueous droplets can be sequestered within liquid crystals, and then preprogrammed, through an interplay of elastic and electrical double-layer forces, to be ejected from the liquid crystal when the liquid crystal reorients under the influence of interfacial shear stresses generated by bacteria. When the aqueous microdroplets contain antimicrobial compounds, we demonstrate that the behavior of the liquid crystalline material becomes self-regulating of its interaction with bacteria, as cell death results in cessation of the trigger (mechanical shear stresses of the moving bacteria) that ejects the microdroplets: cell death is also reported by the optical response of the liquid crystalline material.

## COLL 720

### **Fabrication of oil-infused anti-biofouling coatings on the surfaces of flexible polymer tubing**

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Advances toward the design of liquid-infused surfaces (LIS) or slippery liquid-infused porous surfaces (SLIPS)—materials fabricated by the infusion of oily lubricants into chemically compatible porous or textured surfaces—have led to new classes of synthetic materials with robust and mechanically-compliant anti-fouling properties. Several reports demonstrate that these materials can resist adhesion and colonization by microorganisms and prevent the formation of fungal or bacterial biofilms in both static and flowing media. Here, we report strategies for the fabrication of anti-biofouling SLIPS on the outside and inside (luminal) surfaces of flexible polymer tubing typically used to design catheters or transport fluids in commercial and industrial contexts. Our approach is based on the infusion of hydrophobic oils into rough and nanoporous polymer matrices fabricated by reactive/covalent layer-by-layer assembly. These methods can be used to fabricate slippery coatings on the surfaces of flexible tubing up to one meter in length. These coatings retain their antifouling properties upon repeated flexing, bending, and coiling, and after (i) ethylene oxide sterilization, (ii) contact with blood or simulated urine, and (iii) exposure to flow conditions for periods of weeks to months. Our results reveal these SLIPS-coated tubes to prevent the formation of bacterial biofilms (>95% relative to uncoated controls) upon exposure to cultures of *Staphylococcus aureus* for up to seven days, and that the anti-biofouling properties of these tubes can be improved and prolonged by adopting additional strategies that permit the sustained release of broad-spectrum antimicrobial agents. These approaches are scalable and could provide new anti-biofouling solutions for a broad range of applications, including clinical (catheters) and industrial (food processing) scenarios in which the fouling of flexible tubing is endemic. Results highlighting the potential of these materials in these applied contexts will be discussed.

## COLL 721

### **Probing bacterial-surface interactions of antimicrobial nanocomposites by utilizing an epi-fluorescence optical tweezer**

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Current antimicrobial susceptibility methods such as Kirby-Bauer disk diffusion and broth dilution are typically used to evaluate the leaching-based microbial inhibition of antibacterial surfaces and materials. While these traditional methods are useful in determining the antimicrobial efficiency (AME) of these nanocomposites, they are limited to an end-point evaluation, population analysis and substrate restrictions. This research emphasizes the importance of understanding the effects of bacterial susceptibility on wound management materials and the mechanism behind cell death. To probe these bacterial interactions, this study utilized an epi-fluorescence optical tweezer to dock a single *E. coli* cell on the surface of metal nanoparticle (NP) infused alginate-calcium hydrogel. These results showed that cell death occurred when bacteria were in direct contact with antimicrobial agents embedded in the polymer matrix. More specifically, Ag-TiO<sub>2</sub> NP hydrogels with larger pores sizes exhibited significant improvement of antibacterial activity with increased cell death kinetics. This is due to a greater probability of cells coming in contact with the Ag-TiO<sub>2</sub> NPs in the hydrogel matrix. Furthermore, the observed mode of cell death was caused by bacteria-NP oxidation on the cell surface, allowing for Ag<sup>+</sup> to diffuse through the cell and causing cell lysis. When coupled with traditional methods of antibacterial testing, the epi-fluorescence optical tweezer can effectively unravel the mechanism that drives the AME in materials for the development of novel antimicrobial composites in wound management applications.

## **COLL 722**

### **Solid and solution based reactivity of polyoxometalate and tungsten peroxo species**

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Wells-Dawson hetero-metal substituted polyoxometalates (POMs) are effective in aqueous decontamination solutions against organic CWA simulants. Rapid oxidation of the organophosphate simulant Demeton-S is achieved with aqueous solutions of hydrogen peroxide containing Ni(II) and Zr(IV) substituted polyoxometalates. Moving beyond polyoxometalate hydrogen peroxide solution base decontamination, tungsten peroxo species have been synthesized and utilized as both solid phase and solution based decontamination agents. Facile synthetic schemes for both polyoxometalates and tungsten peroxo species make them ideal for utilization on larger scales. Spectroscopic analysis of the synthesized materials matched that presented in the literature, confirming synthesis. Simulant challenges for the synthetic materials in both solution and as solids were performed in order to assess their decontamination capacity. Chromatography coupled with mass spectroscopy was utilized for the analysis of the reaction progress and for confirmation of byproduct formation from challenge experiments.

## COLL 723

### Impact of atmospheric contamination on zirconium (hydr)oxide surface chemistry using *operando* infrared spectroscopy

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Zirconium (hydr)oxide ( $Zr(OH)_4$ ) is an amorphous powder with both acidic and basic active sites that shows great promise for broad-spectrum sequestration and decontamination of toxic chemicals and chemical warfare agents. However, these highly active sites have previously been shown to react with common environmental components forming surface bound adsorbates that could reduce reactivity or compromise the decomposition capacity of  $Zr(OH)_4$ .

This presentation discusses the surface reactions of  $Zr(OH)_4$  with  $CO_2$ ,  $SO_2$ , and  $NO_2$  under ambient conditions using attenuated total reflectance (ATR) spectroscopy in real-time. The contaminated  $Zr(OH)_4$  is then challenged by a chemical warfare agent surrogate, dimethyl methylphosphonate (DMMP), to safely simulate the chemical warfare agent Sarin. The impact of these atmospheric gases on the decomposition of DMMP is discussed.

## COLL 724

### Impact of defect sites in Zr-based MOFs for chemical warfare agent degradation

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Metal-organic frameworks (MOFs) are a class of crystalline, highly porous material composed of metal nodes connected by organic molecules to form 1-, 2-, or 3-D structures. MOFs have shown potential in a wide range of applications due to their high porosity and synthetic tunability. Zirconium-based MOFs have recently shown improvements to bind and degrade chemical warfare agents (CWAs) likely due to nucleophilic attack by the phosphate group to open  $Zr^{IV}$  sites in the MOF node. For this to occur diffusion to and from catalytic sites in the MOF is crucial for the reaction to occur. As a result, defect sites, caused by missing MOF linkers or nodes, have a significant impact on substrate diffusion, number of catalytic active sites and potential mechanisms for CWA degradation. To better understand how defect sites impact reactivity towards CWA degradation a series of Zr-based MOFs has been synthesized with increasing amounts of defects. For this study, the UiO series was chosen due to their ability to tolerate a large amount of defect sites while maintaining long range crystallinity. The synthesis of UiO-66 at different defect levels will be discussed, as well as investigation of isopropanol diffusion as a proxy for potential CWAs.

## **COLL 725**

### **Tuning the photocatalytic activity of metal-organic frameworks toward the oxidation of sulfur mustard in military relevant conditions**

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Recently, much work has been done in developing metal-organic frameworks (MOFs) that are photoactive for many applications including photocatalytic oxidation. NU-1000 is of particular interest due to the ability of the 1,3,6,8-tetrakis( p-benzoic acid)pyrene (H<sub>4</sub>TBAPy) linker to generate singlet oxygen upon exposure to UV or blue light, and its large (3.1 nm) pores, that allow larger substrates to diffuse in. However, the ability of the pyrene moiety to absorb longer wavelengths of light and produce singlet oxygen efficiently is limited in its unperturbed state. Herein, various strategies to enhance the efficiency of singlet oxygen generation through H<sub>4</sub>TBAPy linker modification and absorption of the entire spectrum of visible light through post-synthetic incorporation of co-photosensitizers will be discussed. Through simple MOF modifications, photocatalytic rate enhancement of more than an order of magnitude has been achieved for the photocatalytic degradation of sulfur mustard under military relevant conditions over NU-1000.

## **COLL 726**

### **Rapid screening and development of MOFs for degradation of warfare agents**

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Metal-organic frameworks (MOFs) have received increased attention as catalytic materials for capturing and degrading chemical warfare agents (CWAs). In this presentation, we will discuss our efforts to develop high-throughput screening (HTS) to identify MOFs with CWA degradation activity, and to use these HTS methods to develop structure-activity relationships (SAR). HTS has helped to find distinguishing features of some MOFs that result in high CWA degradation activity. Furthermore, efforts to incorporate these active materials into useful form factors (e.g., polymers, fibers) will also be described.



## COLL 727

### Decomposition of chemical warfare agent simulants by photochemical and chemical mechanisms: New materials and approaches

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Optically enhanced catalytic decomposition has the potential to impact for both immediate and far-reaching technologies. Here, we (i) examine oxidation of 2-chloroethyl ethyl sulfide (CEES) residing on the surface of TiO<sub>2</sub>-surrounded plasmonic Au nanostars (NS) and nanorods (NR), driven by optical excitation, as well as (ii) probe photocatalytic activity of plasmonic TiN nanoparticles, embedded in TiO<sub>2</sub> (TiN/TiO<sub>2</sub>) for the electrochemical oxidation of CH<sub>3</sub>OH. Refractory nitride plasmonics offer the potential to realize enhanced light interactions for photo-driven chemistry with materials systems that are thermally rugged, inexpensive, and potentially catalytic. TiN and ZrN have been shown to exhibit plasmonic resonances similar to those of Au. Visible light excitation of Au-NS/TiO<sub>2</sub> and Au-NR/TiO<sub>2</sub> films has resulted in minimal to no oxidation of surface residing CEES. Surprisingly, the greatest oxidation was observed for TiO<sub>2</sub> nanoparticles immobilized on SiO<sub>2</sub> spheres alone. In a parallel effort the decomposition of another CWA simulant, Demeton-S, by home-made TiN and ZrN nanoparticles, both under visible light excitation, and in the dark was examined. The decomposition of Demeton-S by TiN nanoparticles occurs via hydrolysis route, resulting in formation of the disulfide and thiol products. The reactivity was found to be independent of light exposure.

Plasmon-driven photocatalysis by TiN/TiO<sub>2</sub> of commercial and in-house synthesized TiN nanoparticles have been compared for their ability to enhance CH<sub>3</sub>OH oxidation to that of conventional Au nanoparticles for feasibility. Although the photon-to-carrier conversion efficiencies were low (~10<sup>-4</sup> %), the reaction rates were enhanced by a factor of 4 in the visible and near-infrared for Au and TiN, respectively, compared to a pure TiO<sub>2</sub> control. The spectral dependence of reaction rate enhancement followed the

nanoparticle extinction spectra and a linear power-dependence identifies a photo-excited carrier mechanism. Electromagnetic simulations of Au, TiN and ZrN optical properties are performed in order to facilitate the results interpretation.

## **COLL 728**

### **Capture and transport of nerve agent simulants within UiO-67 MOFs**

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Porous Metal-Organic Frameworks (MOFs) have potential as superior sorbent materials capable of capturing, transporting and neutralizing hazardous chemical agents. The UiO family of MOFs, in particular, offer a high degree of chemical, structural and thermal stabilities making them amenable for a wide-range of protective applications. A combination of Temperature-Programmed Desorption Mass Spectrometry (TPD-MS) and *in situ* FTIR spectroscopy was applied to understand the uptake, transport and desorption interactions of the nerve agent simulants, dimethyl methylphosphonate (DMMP) and isopropanol with UiO-series MOFs. Isopropanol has been suggested as a simple and benign alternative to some traditional CWA simulants, providing detailed information on the structure-activity relationship of key structural functionality of live agents and MOFs, while minimizing experimental exposure risk. This multi-technique approach enables a fundamental understanding of chemical warfare agent (CWA) simulant interactions with single component MOFs and informs the rational design of stratified MOF materials with diverse functionality capable of selectively transporting an analyte of interest through various MOF strata. Ultimately, this provides information necessary for the design of materials with selective analyte uptake and transport mechanisms necessary for the catalytic degradation within a stratified MOF core.

## **COLL 729**

### **Spectroscopic investigations of sarin adsorption and decomposition on metal oxides, metal hydroxides, and metal organic frameworks under vacuum and ambient conditions**

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Current events have increased awareness of the threat that chemical warfare agents (CWAs) pose to the warfighter and civilian populations. Advances in material design for filtration, warfighter uniforms, and decontamination solutions have become increasingly

necessary to protect the warfighter from CWA exposure. Here we have evaluated a number of promising materials including metal oxides, hydroxides, and metal organic frameworks (MOFs) varying in pore size against the nerve agent, Sarin (GB). We found partial GB decomposition occurs on all of these materials, with strong bidentate product species formation. Additionally, both structural and environmental factors play a role in GB decomposition on the surface. For example, GB capacity increases with increasing porosity; while, linker exchange increases GB decomposition. Environmental contaminants such as NO<sub>2</sub>(g) also affect GB adsorption onto the surface. These CWA interactions with the surface are observed in-situ using several spectroscopy techniques such as transmission infrared spectroscopy (TIR), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), X-ray photoelectron spectroscopy (XPS), and Microbreakthrough experiments. These studies will facilitate the determination of design parameters governing adsorption, diffusion, and decomposition in advanced nanoporous materials.

## **COLL 730**

### **New *operando* studies of chemical agent interaction with MOFs and POMs at the gas-surface interface, and studies of HD catalysts**

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Continued use of Chemical Warfare Agents (CWAs) and other toxic chemicals continue despite contravening international law. Recent examples include the use of Sarin (GB), Sulfur Mustard (HD), Chlorine and allegedly incapacitating agents on civilians in Syria. Previously in modern history CWAs have also been used on a large scale in Japan (GB/VX) and in Iraq (GB). Furthermore, has been at least one assassination (using VX) in Malaysia. These incidents demonstrate the continued need for protective filters, protective suits, and decontamination materials for a wide variety of threat agents. While current decontamination solutions, military and civilian filters, and protective clothing do offer excellent protection; research continues on novel materials and multifunctional materials that might improve protection, reduce cost, or reduce weight or thermal burden on the user. The US Army CCDC Chemical Biological Center (CBC) has been applying recent advances in ambient pressure and *operando* methods in order to study the interaction of live agents at the gas-surface interface on novel materials. This talk will mostly focus on the application of Diffuse Reflectance Infrared Spectroscopy (DRIFTS) used for *operando* chemical agent (GB/HD) studies on Zr-based metal organic frameworks (MOFs) but will also focus on emerging work on HD oxidation catalysts recently studied in collaboration with multiple universities and at a national laboratory.

## **COLL 731**

## **Design of a “nanoscale boiling chip”: Science behind and applications of functionalized mesoporous silica nanoparticles for acoustic cavitation and nanoparticle propulsion**

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Ultrasound is widely applied in medical diagnosis and therapy due to its safety, high penetration depth, and low cost. In order to improve the contrast of sonographs and efficiency of ultrasound therapy, echogenic gas bodies or droplets (with diameters from 200 nm to 10  $\mu\text{m}$ ) are often used. However, because their inherent Laplace pressure limits both size and stability these fluid-filled colloids, they are not stable in circulation and have difficulty penetrating effectively into target tissues. Here we will present our work designing silica nanoparticles of  $\sim 100$  nm with surfaces that have been rationally designed to nucleate ultrasound-responsive microbubbles under reduced acoustic pressures. This talk will discuss three aspects of this work. First, a comprehensive study was undertaken to determine the effect of structure on bubble nucleation and cavitation. A series of mesoporous silica nanoparticles were synthesized with sizes around 100 nm, each containing different morphologies. From these studies, the effects of nanoparticle porosity, surface roughness, hydrophobicity, and hydrophilic surface modification on acoustic cavitation inception by porous nanoparticles were determined. Second, particles with a hexagonal, small pore morphology were utilized for imaging in complex media while resisting protein fouling. Because the combination of surface roughness and hydrophobicity was necessary for nucleating bubble cavitation, proteins such as albumin adhering to the surface of the nanoparticle would be expected to quench signal entirely. The nanoparticles were found to provide effective image contrast even in whole blood and long-term storage. Finally, the therapeutic efficacy of the particles was determined by utilizing a phospholipid monolayer that was functionalized with PEG-lipid. The nanoparticles were uptaken into cancer cells by receptor-mediated endocytosis, and the cells with uptaken particles were killed selectively under HIFU insonation, as compared to cells without nanoparticles. Similar results were shown for destruction of blood clots. Thus, these studies show how small nanoparticles can sensitize both bubble formation and cell death, thus overcoming the inherent Laplace limit found with fluid-filled particles.

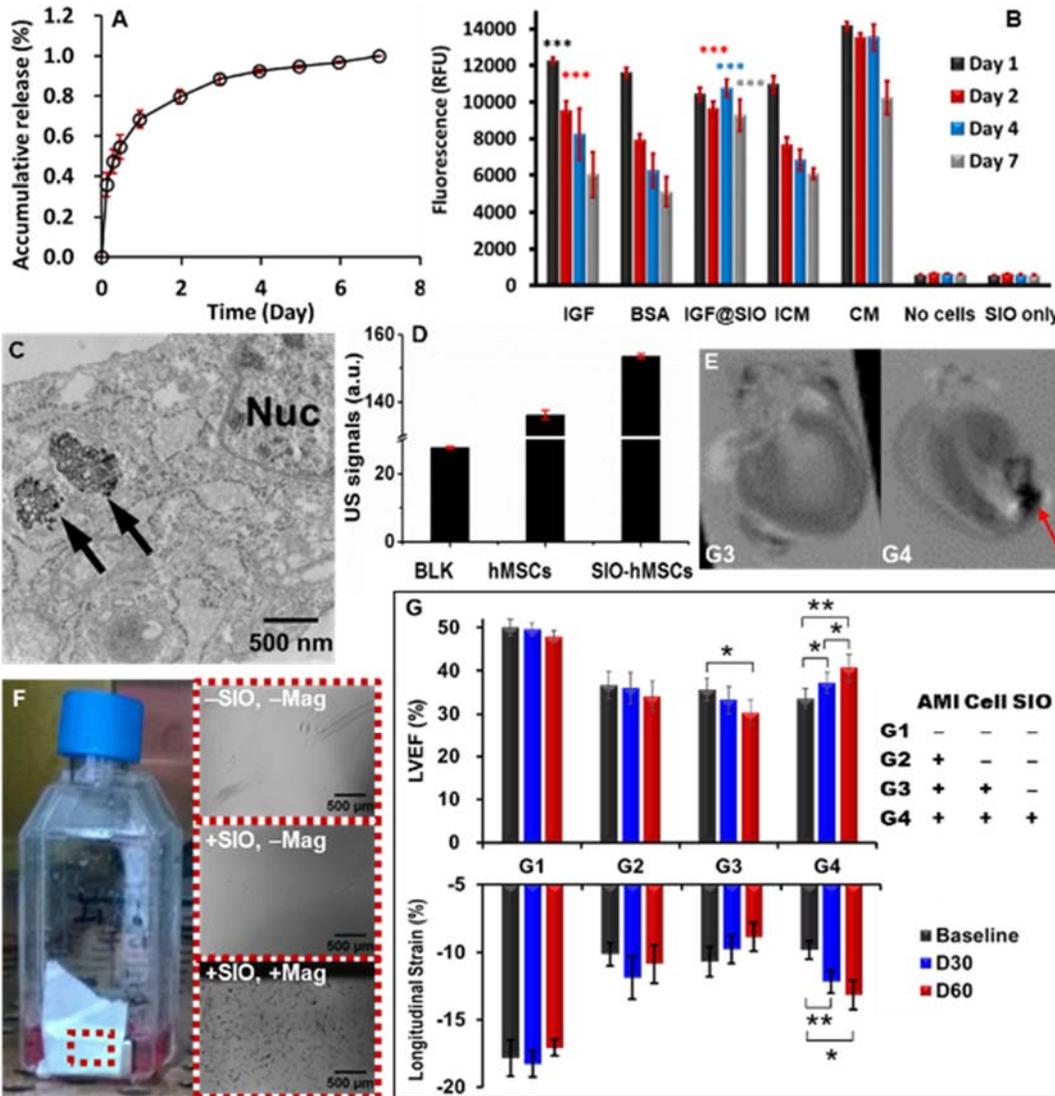
### **COLL 732**

## **Acoustically active multifunctional nanomaterials improving stem cells therapy efficacy in myocardial infarcted mice**

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Stem cells have great potential in regenerative medicine but have had relatively low clinical efficacy due to mis-injections, low cell retention, and poor cell viability after

transplantation. Here, we prepared a nanoparticle (SIO) to overcome these limitations: SIO served as a slow-release reservoir for pro-survival agent IGF-I. It also produced ultrasound and MRI signal for cell monitoring and helped immobilize cells in the affected area via a magnet. The viability of human mesenchymal stem cells (hMSCs) incubated with 1 mg/ml SIO was 99%, and a proliferation assay showed that the doubling time for labeled and unlabeled hMSCs were 2.31 and 2.27 days. The loading capacity was around 1.89  $\mu\text{g}$  IGF/mg SIO. While IGF-loaded SIO (IGF@SIO) has a burst release in the first 12 hours, there was sustained release for up to one week (**Fig. 1A**). IGF@SIO increased the hMSCs survival for one week compared to free IGF (**Fig. 1B**). SIO-labeling increased ultrasound and MRI signals of hMSCs(**Fig. 1C-E**). Moreover, a magnet could direct SIO-labeled cell growth (**Fig. 1F**) and increased SIO retention in mice heart by approximately 77%. *In vivo* studies with a mouse model of myocardial infarction showed that IGF@SIO-labeled hMSCs significantly increased the heart functions compared to hMSCs only (**Fig. 1G**).



**Fig. 1** (A) Release profile of IGF from SIO. Error bars: standard deviations of triplicates. (B) IGF@SIO increased hMSCs survivability. Error bars: standard deviations of eight replicates. (C) TEM image of SIO labeled hMSCs. Arrows indicate SIO. (D) SIO increased ultrasound signal of hMSCs. Error bars: standard deviations of five regions of interests. (E) SIO increased the *in vivo* MRI signal of hMSCs, indicated by the red arrow. (F) Magnet enabled SIO-labeled hMSCs grow on the side of flask. (G) SIO-labeled cell increased heart functions of myocardial infarcted mice on day 30 and 60. Error bars: standard errors (n=12).

## COLL 733

### Surface engineering of mesoporous silica nanoparticles to create highly echogenic nanoscale ultrasound contrast agents

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Due to its safety, low cost, high tissue penetration depth, and real-time imaging capability, ultrasound imaging is widely used in the clinic. Ultrasound contrast agents (UCAs), such as lipid stabilized perfluorocarbon microbubbles, can greatly enhance the ultrasound signal and enable molecular imaging of the disease-related biomarkers. However, their large size and poor stability in the circulation limit their use in the vascular space. To expand the applications of molecular ultrasound imaging beyond vasculature, robust UCAs with sizes small enough for extravasation from circulation (<200 nm) should be developed. One such promising candidate is the amphiphilic (e. g. lipids or amphiphilic polymers) coated hydrophobic mesoporous silica nanoparticles (MSNs). At their hydrophobic interfaces, such nanoparticles can stabilize gas-pockets, which can nucleate echogenic micrometer-sized bubbles under reduced acoustic pressures. In addition, their surfaces can be modified to improve their biocompatibility and for biomarker targeting. However, previously developed amphiphilic coated hydrophobic MSNs require high acoustic pressures to nucleate the echogenic bubbles. Thus, a high intensity focused ultrasound (HIFU) transducer is usually applied to provide such high acoustic pressures for contrast enhancement. The use of HIFU transducer not only complicates the ultrasound imaging instrumentation but also limits the imaging volume to the focal volume of the HIFU transducer (typically a few mm<sup>3</sup>). Here, we developed a method to prepare amphiphilic coated hydrophobic MSNs that can generate echogenic bubbles at relatively low acoustic pressures, which can be achieved by using conventional medical ultrasound instruments. Using this method, we prepared 50 nm UCAs that can enhance the contrast of B-mode ultrasound images, at mechanical indices (MI) as low as 0.7 (well below the FDA limit of 1.9), when dispersed in buffer solutions, serum, or tissue-mimicking gel phantoms at particle concentrations down to 10 µg/mL.

## **COLL 734**

### **Perfluorobutane nanoemulsions facilitated transcranial ablation**

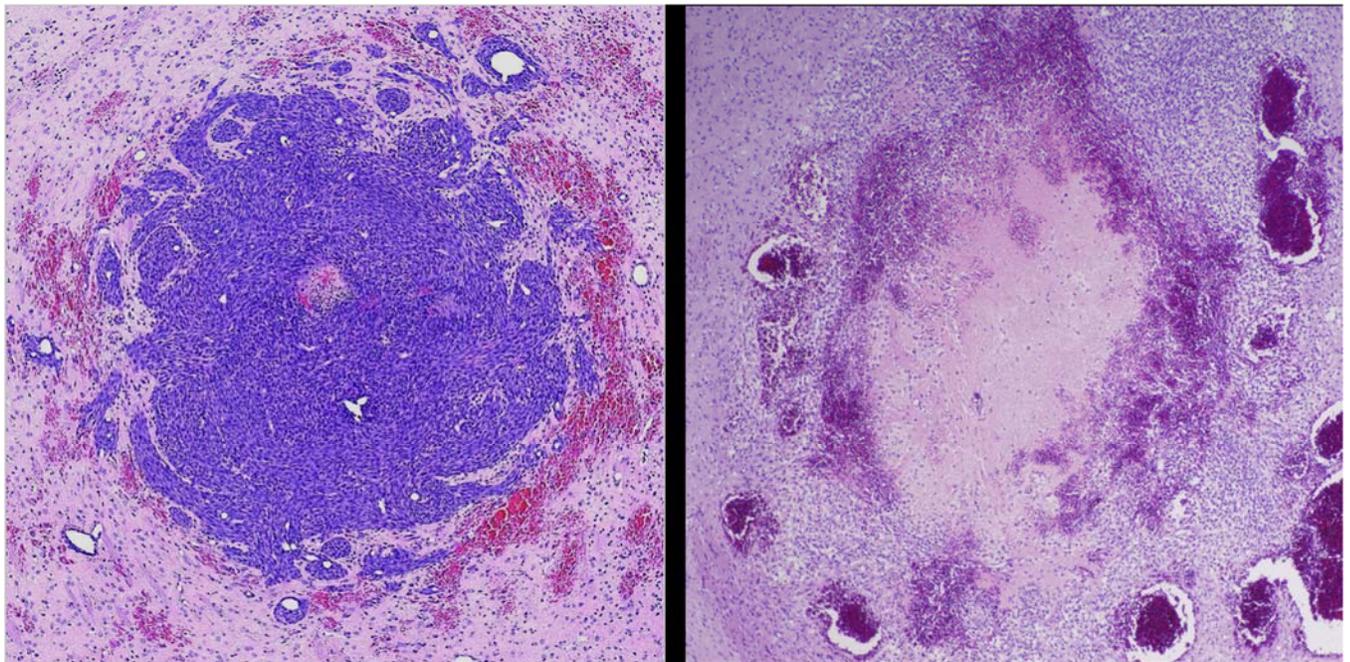
**Chenguang Peng**<sup>1,2</sup>, *pcg11@bu.edu*, *tao sun*<sup>2</sup>, *Chanikarn Power*<sup>2</sup>, *Yongzhi Zhang*<sup>2</sup>, *Tyrone Porter*<sup>3</sup>, *Nathan Mcdannold*<sup>2</sup>. (1) Biomedical Engineering, Boston University, Boston, Massachusetts, United States (2) Brigham and Women's hospital, Boston, Massachusetts, United States (3) Boston University, Boston, Massachusetts, United States

**Introduction:** Ultrasound nonthermal ablation is an emerging noninvasive technique to perform functional neurosurgery. To achieve enough cavitation for ablation purpose, microbubbles (MBs) are introduced through intravenous injection which could enhance ultrasound energy deposition. However, MBs are existed systemically after injection and could prevent the ultrasound wave to reach the focus. This would result in unwanted pre-focal damage at eloquent brain regions like cortex. We proposed to use an ultrasound activatable agent – perfluorobutane phase shift nanoemulsions (PFB PSNE)

that would only be activated at the focus of ultrasound and thus prevent pre-focal damage.

**Materials and Methods:** The PFB PSNE were synthesized by compressing (~45 psi) the MBs under dry ice bath (-10~-15 °C). Sonications were performed using two high intensity focused ultrasound (HIFU) transducers operating at 837 kHz. In each sonication, we started with a ramping pressure pulses (pressure ranging from 0.9 to 2.1 MPa) to determine the cavitation threshold. The peak negative pressures were fixed at the determined threshold (~2.1 MPa for PSNE and ~0.8 MPa for MBs) to sonicate for another 90 seconds. Two rats were sonicated with PFB PSNE and the other two served as control. The tumors were sonicated 8 days after the implantation and animals were sacrificed at day 13 to harvest the brains. The tumor growth was evaluated with magnetic resonance imaging (MRI) and hematoxylin and eosin stain and the result indicated localized microhemorrhage at targeted region

**Results and Discussion:** The PFB PSNE facilitated ablation generated a well-defined round-shape lesion at targeted area that was more compact than MBs facilitated ablation. After 3D reconstruction from stack of 2D images , it appeared that the lesion from PSNE group was more localized than MBs group (3x3x4 mm of PFB PSNE VS 5x9x7 mm for MBs). On contrary, MBs group showed apparent damages in the cortex region (Figure 1D). Interestingly, the damage of PFB PSNE ablation appears to be much more significant in tumors than in healthy rats which indicates an enhanced tumor killing capability.



## **COLL 735**

### **Cavitation-enhanced drug delivery: Microscale transport from nanoscale particles**

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Tumour physiology presents a formidable barrier to the delivery of current and emerging anticancer therapeutics, by virtue of the elevated intratumoural pressure, sparse vascularity and dense extracellular matrix. Recent clinical studies have demonstrated that ultrasound-mediated mild hyperthermia in combination with thermosensitive liposomal carriers can significantly improve drug delivery to tumours, but this approach is only directly applicable to therapeutic classes suitable for liposomal encapsulation. Seeking to exploit the mechanical effects of ultrasound, it is first demonstrated that the occurrence of cavitation-induced microstreaming in blood vessels enables the transport of nanomedicines to hundreds of microns from the vessel wall, but that this occurs only in the presence of inertial rather than non-inertial cavitation. This observation motivates the need to develop cavitation nuclei which are capable of 'following' unmodified therapeutics into tumours, rather than being confined to the vasculature; and the opportunity to modify the property of the nanomedicines themselves in order to maximize their transport through cavitation-induced microstreaming. A new type of cavitation-inducing gas-stabilized solid sub-micron particles has been developed that permits sustained cavitation activity throughout the tumour volume, significantly enhancing delivery and efficacy of last-generation anti-cancer agents. Further modification of these agents by applying a gold coating that increases their density is found to yield further enhancements in tumour penetration and delivery. These observations demand further mechanistic investigation of cavitation-induced microstreaming from a variety of agents including solid gas-stabilising particles, nanodroplets and microbubbles and its impact on the transport of nanoparticles of different density, shape and charge.

## **COLL 736**

### **Development of pH-sensitive microbubbles for ultrasound cancer detection**

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Melanoma is a common skin cancer that accounts for 4% of all skin cancers. It spreads through the lymphatics, requiring sentinel lymph node (SLN) needle or surgical biopsy for staging, which is either inaccurate or highly invasive. There is therefore a need to develop a noninvasive and highly accurate method for staging the SLN.

Our objective is to develop a bioresponsive ultrasound (US) contrast agent to map the lymph duct, aid in the recognition of the sentinel node, and detect nodal tumors by producing dramatic signal enhancement in response to the acidic tumor

microenvironment. One of the current challenges of lymphosonography is that contrast enhancement is transient, as microbubbles (MBs) rapidly wash out of the lymphatics. Thus, we aim to create a targeted agent for long lasting enhancement. We decided to decorate the MB's shell with hyaluronic acid (HA), a naturally occurring polysaccharide. HA serves a two-fold purpose; it targets the lymphatic vessel endothelial 1 receptor (LYVE-1), a CD44 homolog, and provides a biocompatible polymeric scaffold for crosslinking.

We hypothesized that crosslinking MBs' shells with an acid-cleavable linker will decrease their elasticity, reducing their ability to generate a harmonic signal at physiological pH. This elasticity will be restored in acidic environments.

We have validated HA conjugation to MBs by fluorescence microscopy and demonstrated that HA-conjugated MBs target CD44+ cells *in vitro* and show sustained signal in the lymph node *in vivo* compared to Definity (5.8-fold increase in half-life). Additionally, we have shown that, when crosslinked with a pH-sensitive crosslinkers, HA-MBs show a reduced harmonic signal at pH 7.4, which increases when exposed to acid.

Our data suggests that we have developed targeted US contrast agents for lymphography as well as pH-activatable MBs. Importantly, we believe that we will be able to tune this platform to be responsive to other biomarkers of disease such as enzymes, ROS, and reducing conditions.

## **COLL 737**

### **Intravenous immunoglobulin aggregation induced by cavitation resulting from mechanical shock: Effect of surface wettability**

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Despite the significant clinical benefits of therapeutic proteins, the existence of aggregation-prone regions in most of the proteins' sequences often results in nucleation of protein aggregation. The protein aggregation provokes adverse immune responses and anaphylaxis in patients and typically can be formed via the conformational changes due to different stress conditions. Such stresses include elevated temperature, surface adsorption, increased ionic strength, low pH, etc. In addition to the environmental factors, the protein aggregation may also arise from cavitation events which can occur during protein formulation administration and transportation. In this study, we investigated the effect of cavitation (induced by mechanical shock) on the stability of Intravenous Immunoglobulin (IVIG), as a model therapeutic protein. In addition, the effect of surface wettability (glass vials functionalized with hydrophobic and hydrophilic surface chemistries) on protein aggregation and particulates formation of IVIG was studied. To monitor the cavitation events and bubble collapsing in vials containing the

IVIG formulation, a high-speed camera was used following the application of controlled mechanical shock using a shock test tower. The mechanically-shocked IVIG formulations were analyzed for aggregation using fluorescent-based assay (Bis-ANS; fluorescent probe for nonpolar cavities in proteins) and size exclusion chromatography and for particle formation using microflow imaging (FlowCam). The protein adsorption on surfaces was also quantified by high-performance liquid chromatography. The results indicated that when containers of liquid protein formulations experience mechanical shock, cavitation occurs followed by bubble collapsing and microjets impinging the surfaces, which leads to particle formation. Further, the hydrophilic surface chemistry resulted in lower protein adsorption and lower protein aggregation and particulate formation compared to hydrophobic surface chemistry which enhanced the protein adsorption and aggregation. We envision the understanding gained through this work can lead to developing new interfacial coatings and chemistries that can prevent the mechanical shock-induced formation of particulates in protein solutions.

### **COLL 738**

#### **Mediating enzyme structure and dynamics on polymer brushes by tuning the enzyme-brush interface**

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Despite their widespread use in biocatalysis, the marginal stability of lipases can significantly limit their catalytic performance in industrial biotransformations. Here, we demonstrate that this limitation can be overcome by immobilization on poly(sulfobetaine methacrylate) (PSBMA) polymer brushes. Specifically, the immobilization of *Bacillus subtilis* lipase A (lipA) on PSBMA brushes resulted in a 100-fold enhancement in turnover frequency relative to ambient conditions at the temperature optimum of the immobilized enzyme, which was also improved by immobilization. This significant enhancement in catalytic performance was due to the structural stabilization of lipA as well as changes in lipA conformational dynamics as measured using single-molecule Förster resonance energy transfer. Interestingly, the enhancement in catalytic performance of lipases depended strongly on the chemistry of the brush. These findings demonstrate that tuning the brush chemistry can lead to marked improvements in the catalytic efficiency of immobilized lipases, which may have major ramifications in industrial biocatalysis. Moreover, our results illuminated an important tradeoff between stability and activity as a function of the decrease in structural dynamics of the immobilized lipA.

### **COLL 739**

#### **Computational investigation and design of the bio/nano interface**

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Determining the orientation and conformation of an adsorbed biomolecule at an inorganic interface remains a grand challenge in studies of interest to materials science, medicine and biotechnology. For example, metallic implants are often covered with an oxide layer, which offers high affinity binding – both specific and non-specific – to biomaterials.

Due to lack of a general approach, either computational or experimental, to study structure, thermodynamics and kinetics of the bio/nano interface, advances in the field are often left to chance discovery vs detailed mechanistic understanding. This talk will describe recent advances from our group in fundamental science and engineering of interfacial phenomena of complex peptides at inorganic interfaces using multiscale molecular dynamics simulations.

The talk will present computational methods for determining the structure and thermodynamics of a bound peptide, experimental validation of the accuracy of the methods, and a series of examples of increasing complexity including titania binding peptides, proteins involved in the mineralization of bone and integration of implants.

## **COLL 740**

### **Organic matrix-mediated growth and control of a pathologic biomineral**

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The morphological evolution of biominerals grown in organic matrices, and the interaction of such matrices with the inorganic surfaces are important for understanding biomineralization processes and for developing bioinspired materials. In this work, we employ hydrogels as model organic matrices and a ‘double-diffusion’ method to mimic the formation of calcium oxalate, the major constituent of kidney stones. Gel-mediated crystallization provides a great way to vary the local supersaturation through controlling the diffusion rate of the reacting ions. We study the nucleation, growth, type of polymorph, orientation and aggregation of the calcium oxalate particles as affected by the gel density, reservoir concentrations, and molar stock solution ratio. We also explore the inhibitory effects of anionic macromolecules or small organic molecules on the biomineral formation. These findings help our understanding of the mechanism of polymer incorporation in biomineral aggregates, and provide insights into the formation of organic-inorganic composite biomaterials. Furthermore, they guide the design and synthesis of therapeutic agents (modifiers with molecular recognition for crystal faces) to control biomineralization associated diseases.

## **COLL 741**

### **Selected DNA aptamers as mineralization templates and affinity reagents for calcium biomaterials**

**Aren E. Gerdon**, *gerdoar@emmanuel.edu*. Chemistry, Emmanuel College, Boston, Massachusetts, United States

DNA aptamers have been widely studied as affinity reagents and in sensor development for small molecule, DNA, protein, and cellular targets, but have not been widely used in relation to materials chemistry. We have recently identified several new DNA aptamers selected for their ability to bind to biomaterials as well as promote and control biomaterials synthesis. These aptamers have been demonstrated to influence kinetics, morphology, and crystallinity of calcium phosphate and calcium carbonate mineralization. They have also been shown to selectively label crystalline hydroxyapatite over amorphous calcium phosphate. Novel Precipitation SELEX as well as traditional affinity SELEX protocols were used in identifying these aptamers and mechanisms of interaction have focused around the prevalence for these aptamers to contain a high percent of G nucleotides, likely resulting in G-quadruplex secondary structure formation. Both heterogeneous and homogenous mineralization conditions have been studied and concentration-dependent enhancement or inhibition of mineralization has been observed. Current research efforts focus on implementing DNA aptamers into hierarchical structures and observing the influence of DNA aptamers in traditional collagen mineralization formats.

## **COLL 742**

### **Hydroxyapatite nanoparticle-stabilized polyHIPEs as osteoinductive bone grafts**

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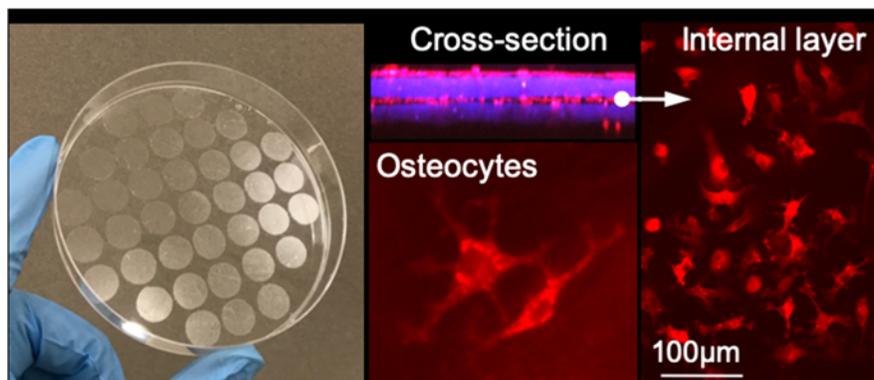
Our laboratory has developed an emulsion templating method that generates high porosity scaffolds that are both biodegradable and injectable. The biodegradable macromers used in these high internal phase emulsions (HIPEs) were designed to polymerize at body temperature and have a low viscosity prior to cure, eliminating the use of toxic solvents common in fabricating biodegradable polyHIPEs. New methodology in collaboration with Technion University was developed to eliminate surfactant from these injectable bone grafts. Hydroxyapatite nanoparticles were modified to permit HIPE stabilization and the resulting porous monoliths were characterized. PolyHIPE scaffolds were evaluated as bone grafts by assessing compressive properties, pore architecture, and degradation profile using standard methodology. In addition, material-induced osteogenic differentiation of human mesenchymal stem cells supported the osteoinductive character of these grafts. In summary, this emulsion templating platform can be used to generate injectable porous materials with clinically relevant properties that can be used to improve bone regeneration.

## **COLL 743**

## Engineering natural bone matrix to reproduce interface biology at bone and marrow

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The surface of trabecular bone represents a distinct biomaterial interface where the hardest (bone) and softest (marrow) tissues co-exist while undergoing repeated remodeling via bone-resorbing osteoclasts and bone-forming osteoblasts. Accumulating data indicate that osteocytes beneath bone surface play a critical role in regulating the surface cell activities via secreting a set of soluble factors. However, investigating how surface and subsurface cells interact and regulate bone surface biology remains challenging due to anatomical inaccessibility of the inner surface of bone cavities and lengthy nature of bone remodeling. It is imperative to develop in vitro tissue models that can recapitulate bone tissue complexity and associated bone surface remodeling process. In this talk, I will introduce a new type of tissue-engineered trabecular bone model that represents both surface and subsurface cellular and extracellular complexity in a controlled and analytical manner. Mature bone consists of multiple layers of lamella bone, and bone is the best biomaterial to reproduce bone tissue biology. Having this mindset, we first developed a process to generate a thin section of demineralized bovine compact bone that supported the aligned adhesion of osteoblasts and structural mineral deposition. We then exploited tissue-engineering strategies to induce osteoblast-to-osteocyte differentiation via stacking multiple layers of osteoblasts pre-seeded demineralized bone paper and subsequently applying cyclic mechanical compression under hypoxic milieu. This additive manufacturing enabled control of the thickness of the trabecular bone tissue models with osteocytes. Finally, we demonstrated how subsurface osteocytes direct surface osteogenic and hematopoietic cellular activity in the context of chemical and mechanical stimulation. We envision that an established bone tissue model is expected to advance bioengineering trabecular bone for basic and applied researches significantly.



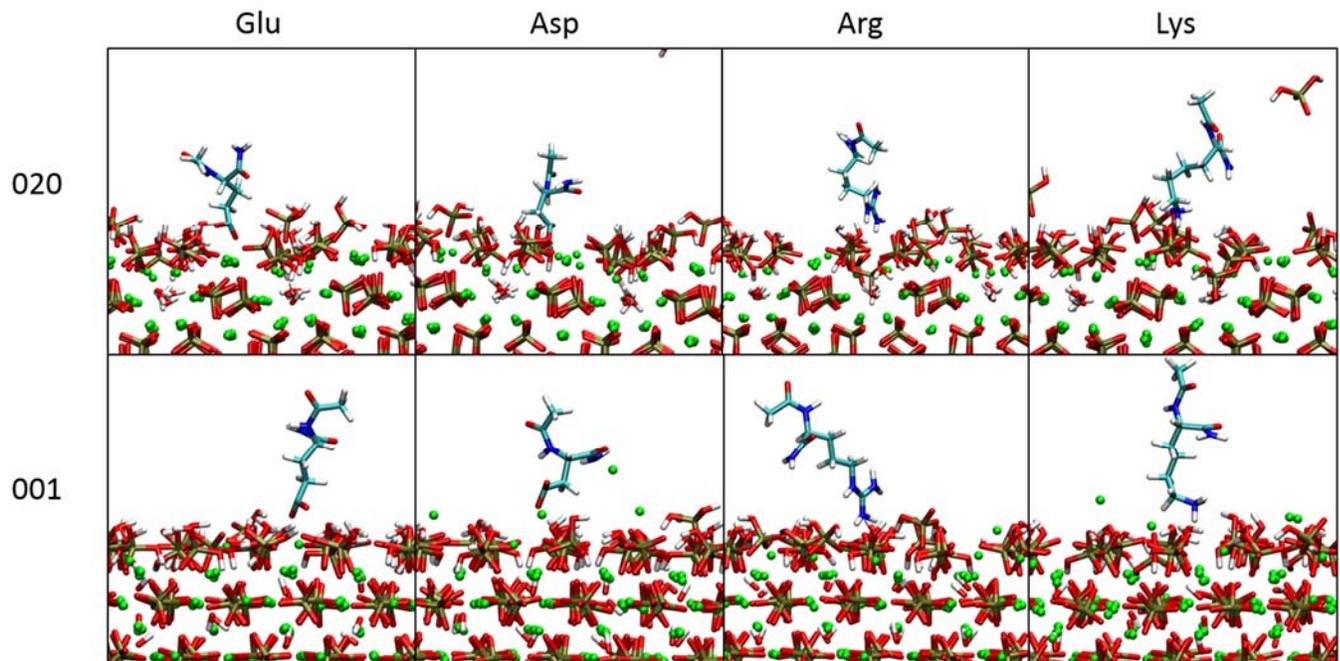
Demineralized bone paper and osteoblast-to-osteocyte differentiation.

## **COLL 744**

### **Insights into the binding of all 20 natural amino acids to (hkl) facets of hydroxyapatite as a function of pH**

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Mineralization of hydroxyapatite is a complex and highly controlled process involving interactions of biological and mineral components. Understanding the basic interactions between individual amino acids and hydroxyapatite at the (020) and (001) surfaces at pH 5 and 7 is a key part of understanding the mineralization process, which will eventually be used to aid in peptide design to control growth of biomimetic materials. In this study a combination of both unrestrained and steered molecular dynamics simulations utilizing CHARMM36 and Interface force field parameters are used to study the dynamic nature of hydroxyapatite, as well as the binding conformations of capped amino acids onto various hydroxyapatite surfaces. In depth analysis is also performed on citric acid due to its known presence on the surface of hydroxyapatite in physiological conditions. Binding site preferences, conformations, and affinities as a function of pH and surface facet are reported. Significant binding differences found between uncharged and charged amino acids are explained. Binding conformations and affinities of arginine, glutamic acid, aspartic acid, citric acid, and lysine are quantified and explored in greater detail. The results provide valuable insights into the affinity and binding mechanisms of the components that make up larger biological structures such as peptides and proteins, to hydroxyapatite surfaces. The results will be useful in designing peptides to target specific bone facets for growth as well as possibly offering the ability to target specific bone sites where infections exist.



Representative binding conformations of selected capped amino acids on (020) and (001) hydroxyapatite facets.

## COLL 745

### Disruption of lipid vesicles induced by amphiphilic Janus particles

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Understanding interfaces between nanomaterials and biological systems is critical to recognizing mechanisms of nanomaterial environmental impact. Extensive research has been dedicated to understanding potentially cytotoxic effects of engineered nanomaterials with uniform surface chemistry. In contrast, significantly less attention has been given to understand biological impacts of nanomaterials with anisotropic surface chemistry. Our group has recently validated spatial organization of surface chemistry is important by demonstrating that amphiphilic Janus nanoparticles rupture supported lipid bilayers with greater efficacy than uniform amphiphilic nanoparticles. Considering the complex morphology of cell membranes, we now ask: How is Janus nanoparticle-membrane interaction affected when membranes are free-standing and curved? We apply fluorescence microscopy techniques to probe nanoparticle influence on giant unilamellar vesicle morphology and membrane integrity. In addition, we combine experiments with coarse grain simulations to understand molecular

mechanisms by which amphiphilic Janus nanoparticles, beyond a concentration threshold, induce membrane pores and vesicle morphological defects.

## **COLL 746**

### **Self-assembled organic dye aggregates in polymersomes with high loadings**

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Self-assembled organic aggregates are encapsulated into polymersomes also formed by self-assembly step to form novel hierarchical nanocomposite materials with exceptionally high payloads for advanced function. Clinical translation of photoacoustic imaging (PAI) has been limited by the lack of sensitive near infrared (NIR) contrast agents with low toxicity. Herein, 50 nm “J aggregates” of FDA approved indocyanine green (ICG) with strong NIR absorbance were encapsulated at high loadings up to 70% within small 77 nm polymersomes (nanocapsules) composed of poly(lactide-co-glycolide-*b*-polyethylene glycol) (PLGA-*b*-PEG) bilayers. During self-assembly of the polymersomes, loss of ICG from the ICG J aggregates was minimized by strategic design of the various interfacial interactions to control the dewetting of the polymersomes from oil droplets dispersed in water. Remarkably, the ICG J aggregates occupied most of the volume of the polymersomes and with low polydispersities for both the J aggregates and the polymersomes. The high loadings enabled PAI of cancer cells with high specificity and a high detection limit. The encapsulated J aggregates were protected against dissociation by the polymersome shell for 24 hours in 100% fetal bovine serum enabling cancer imaging. The self-assembly concepts in this study may be generalized to design numerous types of hierarchical polymersomes with high payloads of self-assembled organic aggregates.

## **COLL 747**

### **Soft materials synthesis from template-polymerized polyelectrolyte complexes**

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Polymerization along macromolecular templates (i.e., template polymerization) occurs when the parent polymer templates and growing daughter chains associate through electrostatic, hydrophobic and/or hydrogen bonding interactions. Such polymerization has been used to create materials across different lengthscales, ranging from nanoparticles to macroscopic gels. To illustrate some applications of this technique,

here we present three examples of template polymerization use in our lab: (1) photodirected assembly of custom-shaped polyelectrolyte complexes (PECs); (2) use of these PECs as shape-directing templates for other soft materials; and (3) assembly of PEC nanoparticles with highly tunable size. Custom-shaped 3-D PECs with either microscale or macroscopic dimensions are prepared through photolithographic directed assembly, via photopolymerization of an anionic monomer in the presence of a polycation, which generates PECs whose shapes reflect the photoirradiation pattern. Besides their own stimulus-responsive properties (e.g., ability to change shape or dissolve on demand with changes in pH or ionic strength), these custom-shaped PECs can be used as sacrificial, structure-directing templates for other materials. To this end, we have recently shown how these PECs can direct the shape of thermoreversible gels. Such custom-shaped gel formation was achieved by adding agarose to the anionic monomer/polycation/photoinitiator precursor solutions. Upon photopatterning of these gelled mixtures, which causes photolithographically generated PECs to form inside agarose gels, the hydrogels surrounding the PECs are melted (through heating) and washed away. Dissolving the PEC templates in concentrated salt solutions then generates custom-shaped agarose gels whose shapes and sizes match those of their parent PEC templates. Lastly, we show how thermal template polymerization can, when performed at low polymer concentrations, be used to prepare colloidal PEC particles with narrow size distributions and highly tunable average sizes. Systematic analysis of compositional effects on this process reveals formation of particles ranging from ~20 nm (which, to our knowledge, is significantly smaller than the template polymerization-derived PECs reported to date) to micron-scale dimensions. Collectively, these findings indicate template polymerization to be an accessible and versatile tool for directing soft materials structure.

## **COLL 748**

### **Polydiacetylene-based sensors to detect food spoilage**

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Polydiacetylenes (PDAs) are a class of conjugated polymers with unique optical properties that make them excellent materials for the construction of colorimetric sensors. Amphiphilic diacetylene (DA) monomers self-assemble to form vesicular structures in aqueous solution, and in organized structures, neighboring DA monomers polymerize when exposed to 254 nm UV light to form alternating ene-yne polymer chains. Polymerization typically yields blue-phase PDAs with a characteristic absorption peak at ~640 nm. Chemical and biological recognition events can induce a blue-to-red color transition of PDA (absorption peak of red-phase PDAs at ~540 nm), which can be easily detected by the naked eye. In this work, we report synthesis and applications of PDA films on food packaging that enable low-cost, easy monitoring of food (e.g. meat and milk) spoilage without the need of specialized equipment. We investigated a range of DA monomers with different lengths of alkyl spacer and alkyl tail. To fabricate the film sensors, we stabilized PDA vesicles in polymer matrix. By optimizing film fabrication

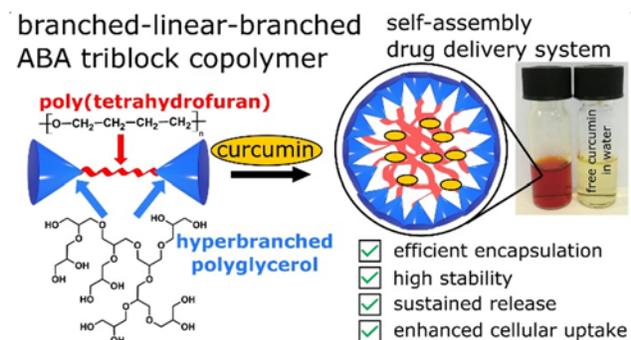
process, we were able to increase the local concentration of PDA vesicles at the surface of the film, thus enhancing response time and sensitivity of PDA to byproducts of bacteria. We successfully demonstrated the application of this method as colorimetric food sensors by integrating them into the plastic packaging of food container stored at -20 °C, 4 °C, and room temperature. At all temperatures, the sensors exhibited a distinctive blue-to-red color transition to indicate food spoilage. The PDA sensors will provide a real time indication of actual food quality, surpassing the function of traditional date marking tools that provide an indication of expected shelf life.

## COLL 749

### Amphiphilic hyperbranched-linear-hyperbranched ABA block copolymers with nanomicellar self-assembly as novel drug solubilization agents

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Unique novel amphiphilic ABA triblock copolymers with hydrophilic hyperbranched polyglycerol (HbPG) outer and hydrophobic poly(tetrahydrofuran) (PTHF) middle were synthesized via an unprecedented route by ring-opening multibranching polymerization of glycidol using amine-telechelic PTHF as macroinitiator. These hyperbranched-linear-hyperbranched block copolymers possess low critical micelle concentrations (cmc) and micellar self-assembling resulting in nanomicelles with 13-15 nm diameters with narrow size distribution. These nanomicelles have high colloidal stability against changes in temperature. With a natural drug, curcumin, of low water solubility, high solubilization efficiency (>700) was observed. In addition to the high and efficient drug encapsulation, good stability, sustained curcumin release and no toxicity were found. *In vitro* bioactivity investigations with the curcumin loaded nanomicelles indicate good cellular uptake.



## COLL 750

### Impact of the wet-dry cycle on polyelectrolyte complex coacervates

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The self-assembly of oppositely charged polyelectrolytes yields different morphologies ranging from solids to liquids. In certain conditions defined, among others, by the polymer concentration and ionic strength in solution, polycation and polyanion complexation leads to liquid-like phase separated entities termed coacervates. In the latter, polymer-rich droplets suspended in a dilute surrounding have been suggested as plausible protocellular models. This work investigates the prospect of complex coacervates as protocells in an environmental scenario proposed for the early Earth: the wet-dry cycle. Periods of dehydration and rehydration have been shown to drive the formation of different types of chemical functionalities opening the door for an increase in molecular complexity. Here, experiments show that this process leads to a change in the composition of complex coacervates and, depending on the starting point, could drive the solution into a two- or one-phase system. Along the way, the partitioning of a guest molecule between the two phases is probed and its diffusion within the concentrated phase, and between the phases, is measured. While more mobility is observed as salt concentration increases, the trend in the guest polymer concentration within the coacervate is not immediately evident as it either decreases or stays constant depending on the amount added initially. This range of behaviors, seen during the drying of a single mixture, is compared to observations in different compositions mimicking those obtained throughout the dehydration process. The comparison showcases how one cycle can lead to moving through various positions on the phase diagram for a coacervate system. Further experiments explore additional compositional changes as well as the effects of multiple cycles. From a fundamental perspective, this study demonstrates the need for a better understanding of guest molecules interactions within coacervates. More broadly, it establishes a framework to examine the impact of wet-dry cycling on the structure and reactivity in non-membranous compartments.

## COLL 751

### From monomer sequence to self-assembly in polyelectrolyte coacervation

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Oppositely-charged polyelectrolytes can undergo an associative phase separation known as complex coacervation, forming dense polymer phases that maximize favorable electrostatic interactions. This interaction motif can be harnessed to drive polymer assembly, via the incorporation of opposite charges on pairs of block copolymers. Coacervation is thus widely used in the self-assembly of structures such as gels and micelles, motivated by creating compartments capable of carrying hydrophilic cargo, or structures that are responsive to a variety of environmental stimuli. Despite the utility of this method of self-assembly, there remain fundamental questions about how molecular and environmental parameters govern phase behavior.

We will present a recent theory developed to describe the equilibrium phase behavior of complex coacervation, which is capable of predicting both the correlated molecular structure of the bulk coacervate phase as well as matching experimental phase diagrams. We incorporate this model into a self-consistent field theory (SCFT) of polyelectrolyte self-assembly, to predict phase behaviors over a wide range of molecular parameters (chain lengths, block fractions) and environmental parameters (salt, polymer concentrations). We predict a correspondence between salt concentration in charge-driven assembly and temperature in solvophobicity-driven assembly, due to the analogous role of salt in weakening the governing interactions. We also show the limits of blockiness, mapping out the transition between micro-phase separated and macro-phase separated polymers as the sequence of monomers on a polyelectrolyte changes from alternating to blocky. This demonstrates the existence of a critical blockiness, that demarcates the micro-phase and macro-phase separation as a function of block number, size, and salt concentration. Ultimately, this highlights the promise of monomer sequence as a tunable parameter in coacervation, due to the subtle interplay of the local electrostatic environment around a polyelectrolyte and its location within a self-assembled structure.

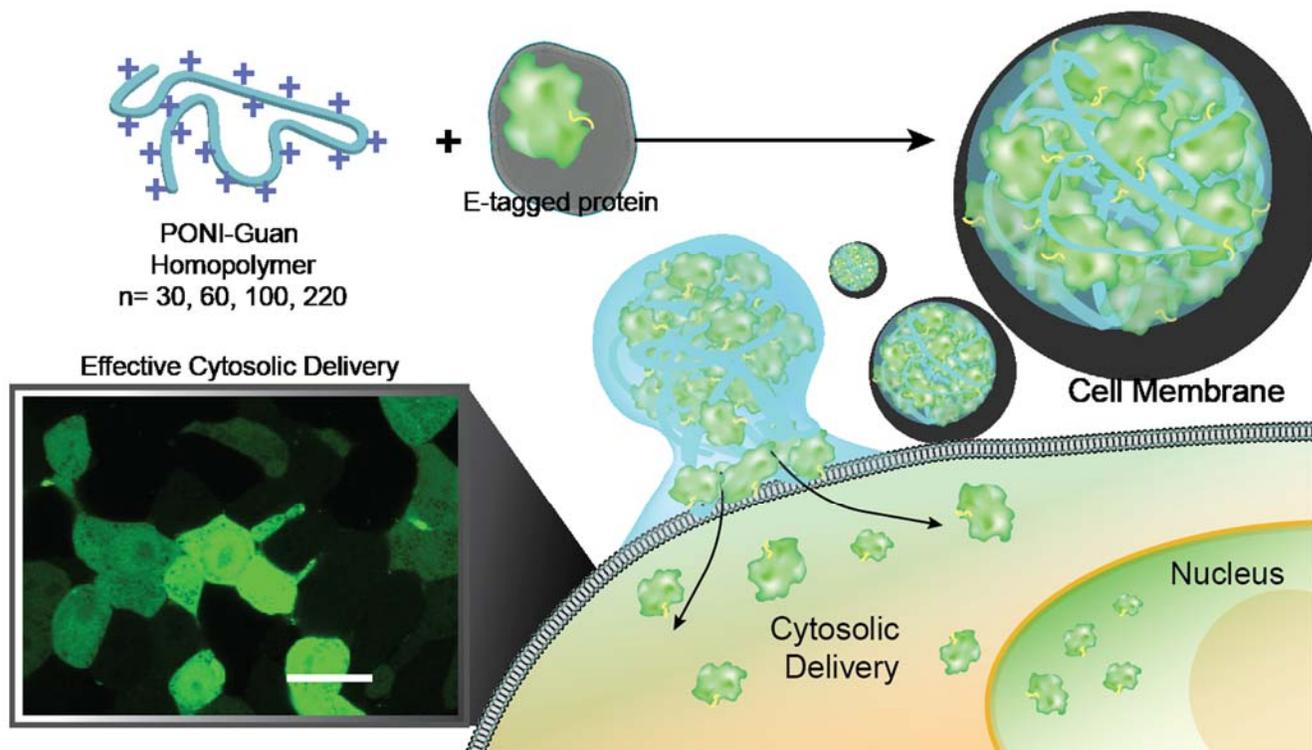
## **COLL 752**

### **Rationally designed polymers for intracellular protein delivery**

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Nanocarrier-mediated intracellular protein delivery is a promising strategy for treatment of disease, but is hindered by limitations to chemical design space and endosomal entrapment of delivered protein cargo. We developed a robust polymeric-protein nanocomposite (PPNC) platform to achieve direct cytosolic protein delivery, as demonstrated by imaging flow imaging cytometry. We synthesized a library of semi-rigid homopolymers with varying molecular weights and cationic functionality to electrostatically bind to and deliver co-engineered proteins featuring anionic glutamate 'E-tags' to the cytosol of mammalian cells. These PPNC platforms demonstrated effective intracellular protein delivery for proteins of ranging size and charge, including

an active therapeutic endonuclease (Cre recombinase) and a multimeric fluorescent protein (tdTomato). Higher molecular weight polymers demonstrate a larger range of effective formulations for protein delivery under serum conditions, making them robust agents for therapeutic protein delivery with potential for clinical translatability.



## COLL 753

### From order to disorder: Computational design of triblock amphiphiles that self-assemble with 1-nm domains

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The directed self-assembly (DSA) of block copolymers provides great opportunities in creating ordered nanostructure arrays with sub-10 nm feature sizes. Further miniaturization in the periodicity can be aided by amphiphilic, liquid-crystalline (LC)

molecules that incorporate highly incompatible segments. The formation of these LC phases is dictated by short-range intermolecular forces and shape anisotropy. In this work, molecular dynamics (MD) simulations with transferable force fields were used as a predictive tool to design a class of symmetric “triblock” amphiphiles containing polyalcohol and hydrocarbon blocks. In the solvent-free state, these molecules exhibit thermotropic liquid crystalline behavior, and are capable of self-assembling into ordered morphologies including lamellae and perforated lamellae. The periodic domain sizes for these morphologies are as small as 1.2 nm. At higher temperatures in the vicinity of the order-disorder transition, the disordered phases are found to be locally segregated, but without long-range order. Analysis of the hydrogen-bonded networks reveals the presence of co-continuous structures with even smaller characteristic dimensions than their ordered phases. Structural analysis provides molecular-level details in both ordered and disordered states, and their phase behavior and structure are also compared with symmetric triblock copolymers.

## **COLL 754**

### **Peptide controlled assembly of anion exchange ionomer thin films on electrode surfaces for promoting microphase separation and ionic conductivity**

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In electrochemical devices such as water electrolyzers and fuel cells, the network and morphology of the conductive ionomers within electrodes are critical for ion delivery and mass transport, significantly influencing the device performance. Most studies investigate these materials as bulk polymer electrolyte membranes and comparatively little attention has been given to their behavior on electrode surfaces as thin films. Anion exchange membrane fuel cells and water electrolyzers (AEMFCs and AEMWEs) would allow the use of non-precious group metals and enable low-cost systems, yet, even less is known about thin films of anion exchange ionomer (AEI). Protein engineering is emerging as a powerful nanomanufacturing tool to control the organization of components on electrodes. In this work, we propose that it can be applied to ionomer control, demonstrating that sequence defined elastin-like peptides assembled on electrode surfaces, and/or solvent vapor annealing processing, alters the microstructure configuration of assembled thin films of anion exchange ionomer. It is observed that peptide forms a uniform monolayer on metal surface, and moderately sized microphase separated ionic domains of the AEI are obtained either by modifying the electrode with peptides or solvent vapor annealing, increasing in-plane ionic conductivity of the thin film. Interestingly, the use of peptide modified electrodes in conjunction with solvent vapor annealing yields excessively large ionic grains that compromise ionic conductivity. Overall, the sequence defined peptides could serve as a tool for controlling electrode architecture, and judicious use of the peptides adsorbed to electrode surfaces, or

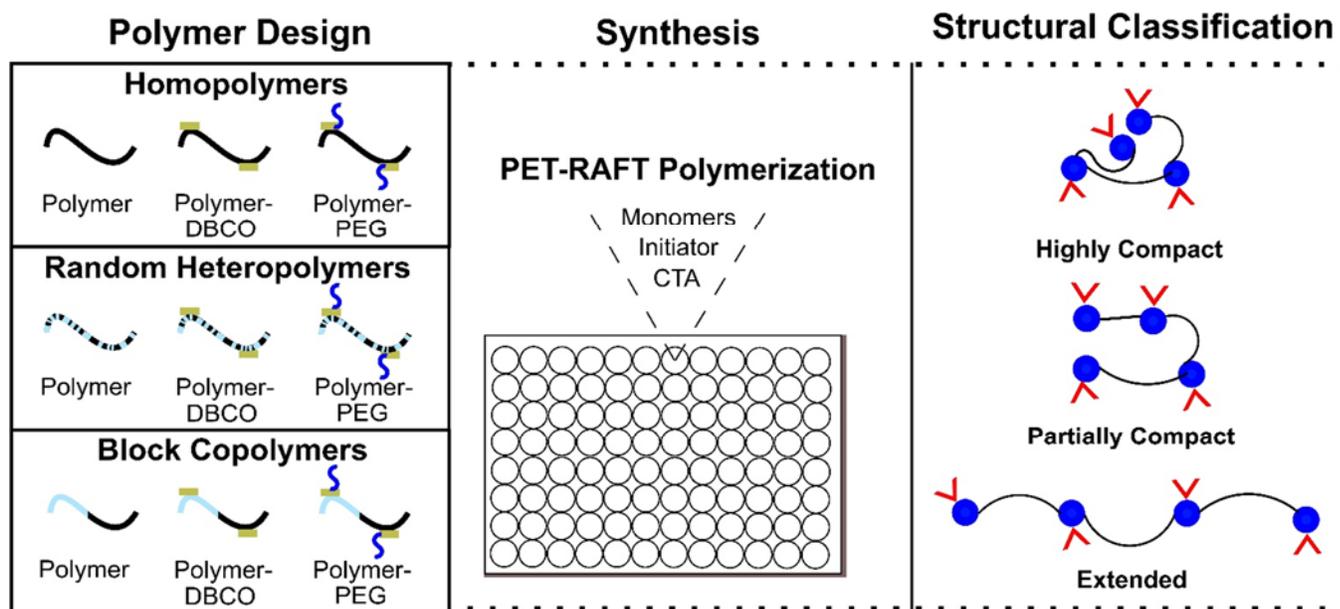
solvent vapor annealing, encourage the appropriate microstructures in thin film AEs resulting in improved ionic conductivity.

## **COLL 755**

### **High throughput tools to study the assembly of single-chain polymer nanoparticles**

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From protein science, it is well understood that ordered folding and 3D structure mainly arises from balanced and noncovalent polar and nonpolar interactions, such as hydrogen bonding. Similarly, it is understood that single-chain polymer nanoparticles (SCNPs) will also compact and become more rigid with greater hydrophobicity and intrachain hydrogen bonding. Here, we couple high throughput photoinduced electron/energy transfer reversible addition-fragmentation chain-transfer (PET-RAFT) polymerization with high throughput small-angle X-ray scattering (SAXS) to characterize a large combinatorial library (>450) of several homopolymers, random heteropolymers, block copolymers, PEG-conjugated polymers, and other polymer-functionalized polymers. Coupling these two high throughput tools enables us to study the major influence(s) for compactness and flexibility in higher breadth than ever before possible. Not surprisingly, we found that many were either highly disordered in solution, in the case of a highly hydrophilic polymer, or insoluble if too hydrophobic. Remarkably, we also found a small group (9/457) of PEG-functionalized random heteropolymers and block copolymers that exhibited compactness and flexibility similar to that of bovine serum albumin (BSA) by dynamic light scattering (DLS), NMR, and SAXS. In general, we found that describing a rough association between compactness and flexibility parameters ( $R_g/R_h$  and Porod Exponent, respectively) with  $\log P$ , a quantity that describes hydrophobicity, helps to demonstrate and predict material parameters that lead to SCNPs with greater compactness, rigidity, and stability. Future implementation of this combinatorial and high throughput approach for characterizing SCNPs will allow for the creation of detailed design parameters for well-defined macromolecular chemistry.



COLL 756

### Unusual complete unbinding of single-tail tethered lipids

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In lipid physics, multilamellar vesicles (MLVs) with a fixed  $d$ -spacing are commonly observed in the aqueous solution of zwitterionic lipids if their packing parameter is close to 1. The theory is well-established based on a thermodynamic equilibrium between the van der Waal attraction and the repulsion originated from the Coulombic interaction and thermal undulation. The minimal energy (including entropic contribution) is normally obtained for a structure of MLV for the bilayer composed of Zwitterionic long-chain lipids. However, the bilayers of MLV could decouple from each other (known as “unbinding”) if the repulsion is much higher than the attraction. Recently, tethered Archaea inspired (AI) lipids have drawn many researchers’ attention for their high stability at high temperature and acidic environment. Here, we report an unexpected unbinding behavior of a single-tail tethered AI lipid (referred to as “D143” later), which has 32 carbons on the tethered chain and 16 carbons on each of the two non-tethered chains (Fig. 1a), an identical structure of tethering two 1,2-di-O-hexadecyl-sn-glycero-3-phosphocholine, Di-C<sub>16</sub>-ether-PC (Fig. 1b, referred to as “DC<sub>16</sub>ePC”) between a tail of the two at the end carbons. MLV with a well-defined  $d$ -spacing has been found in

DC<sub>16</sub>ePC via a small/wide angle X-ray scattering study, while D143 shows large unbinding lamellae. Since both D143 and DC<sub>16</sub>ePC are zwitterionic lipids (*i.e.*, no net Coulombic force) and presumably have similar van der Waal attraction because of the chemical similarity. Further, the higher melting transition of D143 (67.5°C) than DC<sub>16</sub>ePC (44°C) seemingly suggests that the gel phase of tethered lipid is more stable, thus possibly more rigid and less thermal undulation. Based on the basic principle of lipid physics, the complete unbinding of D143 is unexpected. In this presentation, I will discuss over several possible reasons for this unusual behavior of this single-tail tethered lipid.

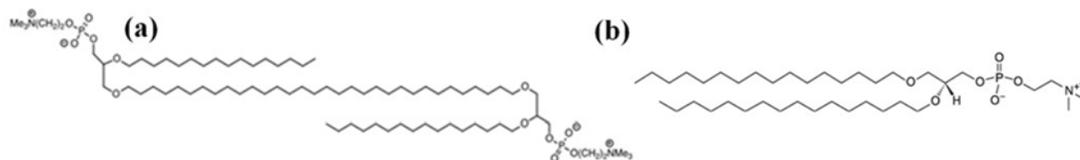


Figure. 1 Molecular structure of (a) D143 and (b) DC<sub>16</sub>ePC

Figure. 1 Molecular structure of (a) D143 and (b) DC<sub>16</sub>ePC

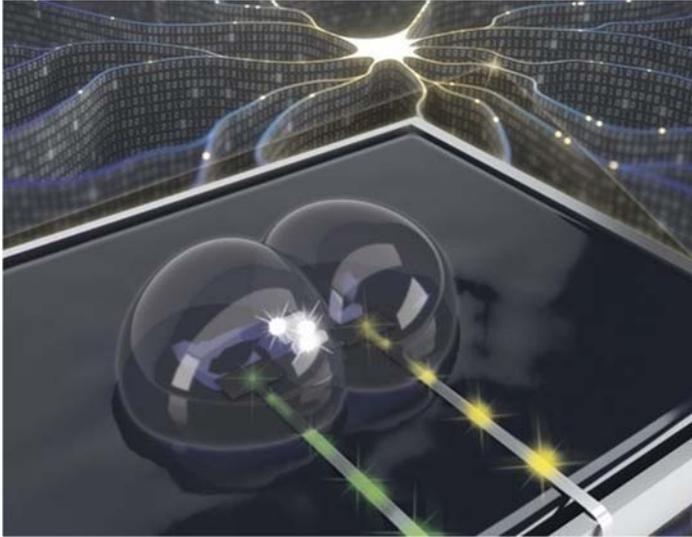
## COLL 757

### Memory and learning in biomolecular soft materials

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Neuromorphic elements have been predominantly solid-state devices which simulate the resistive and capacitive behaviors needed for neural networks and brain-inspired computing, but in non-brain-like ways. This talk will describe ways we are integrating lipid and polymer bilayer membranes with micro- and nanofabrication to develop fundamentally new types of neuromorphic elements that have the composition (biomolecules), structure (biomembranes), and switching mechanism (voltage-sensitive ion channels) of real biological synapses, and operate at lower power than the current state-of-the-art. Our devices consist of insulating, nm-thick lipid or polymer-based bilayer membranes that assemble at the interfaces of two or more aqueous droplets in oil, and that have demonstrated both memristive and memcapacitive behaviors, including memory resistance and capacitance, synaptic functions such as paired-pulse facilitation and depression, spike rate dependent plasticity, voltage-dependent inactivation and recovery, and charging hysteresis. These behaviors are linked to electrostriction, an electromechanical phenomenon that encompasses both electrowetting and electrocompression in the membrane, which are changes in membrane area and thickness due to charging in the presence of electric fields. Electrostriction results in a voltage-dependent capacitive susceptibility that replaces the more familiar concept of static capacitance, which, up to now, has dominated electrophysiological descriptions and characterizations of biomembranes. In this picture, biomembranes are not just equivalent  $RC$  circuits dependent only on ionic currents controlled by the conductance (resistance) of ion channels. Large capacitive currents from small voltage inputs can be generated as well for the development of neuromorphic computing elements exhibiting both short-term and long-term synaptic plasticity.



## **COLL 758**

### **Carotenoids promote lateral packing and condensation of lipid membranes**

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Carotenoids are pigment molecules that protect biomembranes against degradation. Recently, it has been suggested that carotenoids are involved in the formation of bacterial functional membrane microdomains. However, the molecular details of how carotenoids modulate the physical properties of biomembranes are unknown. To this end, we have conducted a series of molecular dynamics simulations of different biologically-relevant membranes in the presence of different amounts of either  $\beta$ -carotene or zeaxanthin. The results reveal that carotenoids have similar effects as cholesterol on regulating the behavior of fluid-phase membranes. Carotenoids are found to compact the bilayer via these two competing mechanisms, to either compress or interdigitate the lipid tails of opposing monolayers. However, the degree to which these competing mechanisms are utilized depends on the bilayer phase and the carotenoid identity. Overall, the simulation results provide compelling evidence that carotenoids can function as sterol substitutes and facilitate the formation of functional microdomains in prokaryotic membranes.

## **COLL 759**

### **Lipid domain in freestanding bilayer lipid membrane on microwell depending on glycolipids concentration**

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The lipid domains in biological cell membrane play a very important role in the localization and function of membrane proteins. If such a lipid domain can be reconstituted in freestanding membrane on nano-, microstructure substrates, it is expected to develop into nanobiodevices that measure and utilize the functions of membrane proteins. However, the liquid disordered (Ld) phase was localized on the freestanding membrane on SiO<sub>2</sub>/Si microwell.<sup>1</sup> On the other hand, hydrophilic polymer chains at the lipid head, such as that of glycolipids, affects membrane fluidity and domain formation in supported membrane.<sup>2</sup> In this study, we found lipid domain formation in phase separated freestanding membrane was affected by concentration of ganglioside GM1 (GM1), one of glycolipids. At a GM1 concentration ( $C_{GM1}$ ) of 0 mol%, the liquid ordered (Lo) domain in the freestanding membrane diminished over time and disappear as with the previous study.<sup>1</sup> In the GM1-containing membrane, the diminishing rate of the Lo domain decreased at  $C_{GM1} = 0.5\%$ . With  $C_{GM1} = 5\%$ , the Lo domain in the freestanding membrane appeared and grew over time. We observed the presence of GM1 in the membrane by staining GM1 with fluorescence-tagged cholera toxin subunit B. GM1 was present in the Lo phase at  $C_{GM1} = 0.5\%$ , but was also present in the Ld phase at  $C_{GM1} = 0.5\%$ . It is indicate that GM1 in Ld phase switched the preferential domain in the freestanding membrane from Ld phase to Lo phase. This result can be expected as a technique for controlling the phase separation structure on the freestanding membrane.

## COLL 760

### **Dynamical oligomerisation of histidine rich intrinsically disordered proteins is regulated through zinc-histidine interactions**

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The mouth is the first portion of the alimentary canal, it functions in the initial stage of food digestion. Saliva is found in the mouth where it serves several purposes including in the initiating the preliminary stages of digestion, maintaining the mineral phases of teeth, and protecting against antigens. Consequently, saliva is a complex biological fluid that contains both proteins and ions which are required to regulate these processes. Histatin 5 is a histidine rich antimicrobial protein found in saliva, and one of the first lines of defence in the innate immune system. Histatin 5 has been widely classified as an intrinsically disordered protein (IDP), which means that it maintains its function without adopting a folded conformation. IDPs are known to form functional oligomers and in some cases, insoluble disease related aggregates. It is therefore vital to understand processes and mechanisms that control pathway distribution. The exact mechanism

through which Histatin 5 performs its antimicrobial function is not yet precisely understood. We show that Histatin 5 can interact with membrane mimetics and that this interaction is promoted by the presence of the zinc divalent cation. Divalent cations found in saliva, including  $Zn^{2+}$ , can initiate IDP oligomerisation through the interaction with histidine residues. We apply a multi-disciplinary approach, using small angle X-ray scattering, nuclear magnetic resonance spectroscopy, calorimetry, and Monte Carlo simulations to show that Histatin 5 forms highly dynamic oligomers in the presence of Zn(II). The process is critically dependent upon interaction between Zn(II) ions, and distinct histidine rich binding motifs, which allows for thermodynamic switching between the states. We propose that the interaction between zinc and histidine residues may be important for membrane interactions and the consequent antimicrobial activity of Histatin 5.

## **COLL 761**

### **Membrane fusion studies of liposomes comprised of pure synthetic, Archaea-inspired bipolar lipids**

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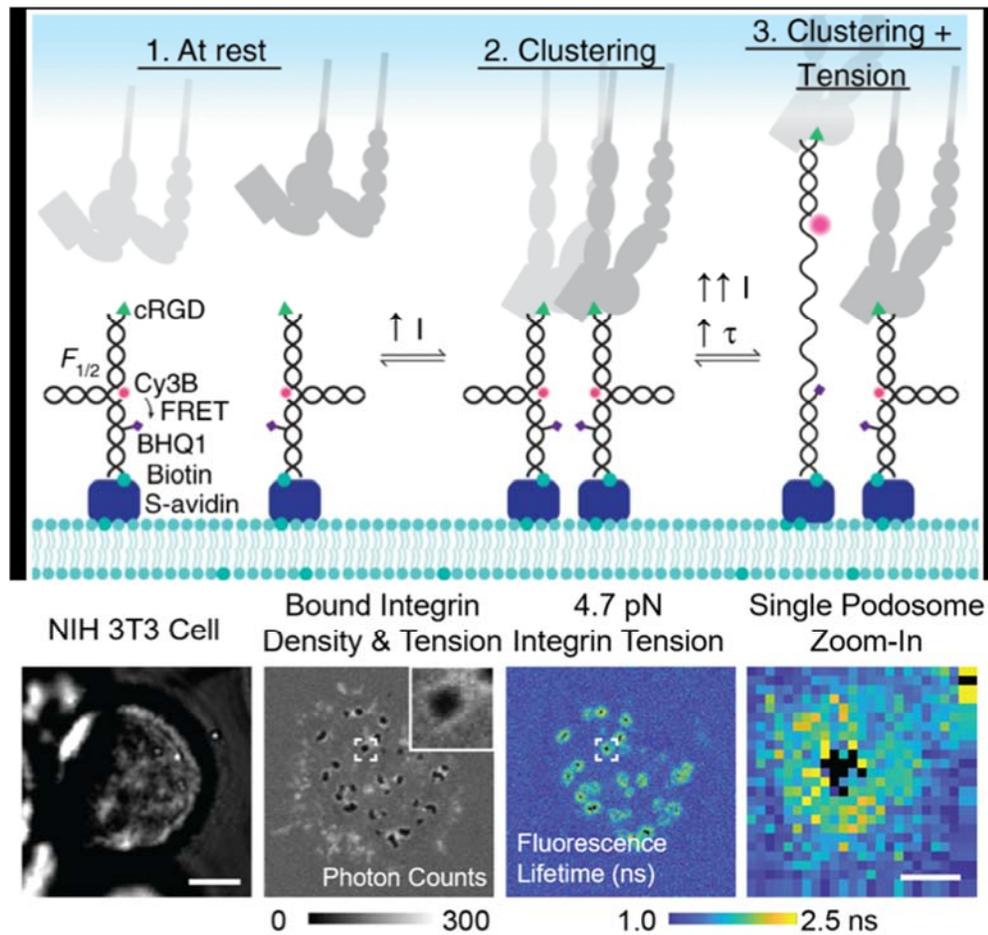
This presentation will describe results from membrane fusion studies of liposomes made from pure synthetic tetraether bipolar lipids. We previously showed that liposomes made of these Archaea-inspired lipids exhibited exceptionally low permeability to small molecules due to their ability to form more tightly packed membranes compared to monopolar lipids. Here, we demonstrate that liposomes made from synthetic bipolar lipids can be made to undergo membrane fusion events, which is typically accompanied by leakage of liposomal content when using monopolar lipids. Interestingly, calcium-mediated fusion of tetraether lipids containing phosphatidic acid headgroups occurs without content leakage, which contrasts the 80% leakage of content from liposomes formed from commercial monopolar lipids under the same fusogenic conditions. Solid-state NMR spectroscopy studies of deuterated analogs of the bipolar lipids provides some structural insight into the potential mechanism of membrane fusion associated with these lipids.

## **COLL 762**

### **DNA mechanotechnology shows that integrin receptors apply pN forces in podosomes formed on supported lipid membranes**

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Podosomes are ubiquitous cellular structures important to diverse processes including cell invasion, migration, bone resorption, and immune surveillance. Structurally, podosomes consist of a protrusive actin core surrounded by adhesion proteins. Although podosome protrusion forces have been quantified, the magnitude, spatial distribution, and orientation of the opposing tensile forces remain poorly characterized. Here we use DNA nanotechnology to create probes that measure and manipulate podosome tensile forces with molecular piconewton (pN) resolution. Specifically, Molecular Tension-Fluorescence Lifetime Imaging Microscopy (MT-FLIM) produces maps of the cellular adhesive landscape, revealing ring-like tensile forces surrounding podosome cores. Photocleavable adhesion ligands, breakable DNA force probes, and pharmacological inhibition demonstrate local mechanical coupling between integrin tension and actin protrusion. Thus, podosomes use pN integrin forces to sense and respond to substrate mechanics. This work improves our understanding of podosome mechanotransduction and contributes tools that are widely applicable for studying receptor mechanics at dynamic interfaces.



## COLL 763

### Uncoupling between the lipid membrane dynamics of differing hierarchical levels

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Diverse biological functions of biomembranes are made possible by their rich dynamical behaviors across multiple scales. While the potential coupling between the dynamics of differing scales may underlie the machineries regulating the biomembrane-involving processes, the mechanism and even the existence of this coupling remains an open question, despite the latter being taken for granted. Via inelastic neutron scattering, we examined dynamics across multiple scales for the lipid membranes whose dynamic behaviors were perturbed by configurational changes at two membrane regions. Surprisingly, the dynamic behavior of individual lipid molecules and their collective motions were not always coupled. This suggests that the expected causal relation between the dynamics of the differing hierarchical levels does not exist and that an apparent coupling can emerge by manipulating certain membrane configurations. The finding provides insight on biomembrane modeling and how cells might individually or concertedly control the multiscale membrane dynamics to regulate their functions.

## COLL 764

### Effects of domains on matrix dynamics in phase-separated model membranes

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Lipid bilayers form the matrix of biological cell membranes and exhibit a rich spectrum of dynamics, from molecular motions to collective undulations associated with

spatiotemporal signaling and various membrane functions. Understanding how various dynamic modes influence membrane behavior is crucial in uncovering the design rules of cell membranes and their use in future technologies. However, the large variety of lipids and the inherent heterogeneity of biological membranes poses a challenge to any meaningful experimental study of membrane dynamics, warranting the use of simple but realistic model membranes which exhibit the phenomena of interest. Previous neutron spin-echo spectroscopy (NSE) studies on model membranes have provided some insights into the hierarchy of membrane dynamics, in terms of correlation between collective membrane fluctuations and viscoelastic membrane properties. These studies demonstrated that thickness fluctuation modes (~100ns) are dictated by membrane viscosity, which simultaneously governs fast (ps) lipid diffusion. Here, we focus on the manifestation of these dynamic modes in model phase-separating lipid membranes, composed of DMPC:DSPC mixtures. Specifically, we aim to understand the effect of domain formation/growth on hierarchical matrix dynamics using selective lipid deuteration and different neutron spectroscopy techniques. NSE measurements on DMPC:DSPC-d83 (70:30 mol%) show that the bending rigidity of the DMPC-rich matrix gradually increases with decreasing temperature – as the fully-fluid membrane approaches the upper phase transition (i.e. with the formation of transient DSPC clusters) – and increases further in the phase coexistence region with the growth of DSPC domains. Analogous studies on DMPC-d54:DSPC-d83 membranes show pronounced matrix thickness fluctuations in the fully-fluid phase and drastic suppression of fluctuation mode in the gel-fluid coexistence phase, even when the DMPC-rich matrix is still in its fluid phase. Complimentary neutron backscattering measurements are utilized for selective investigations of lipid diffusion in the DMPC-rich matrix. Taken as a whole, our results indicate a dynamical coupling mechanism between lipid domains and their host matrix, as further illustrated by coarse-grained MD simulations. These observations suggest that domain formation influences membrane properties beyond local effects.

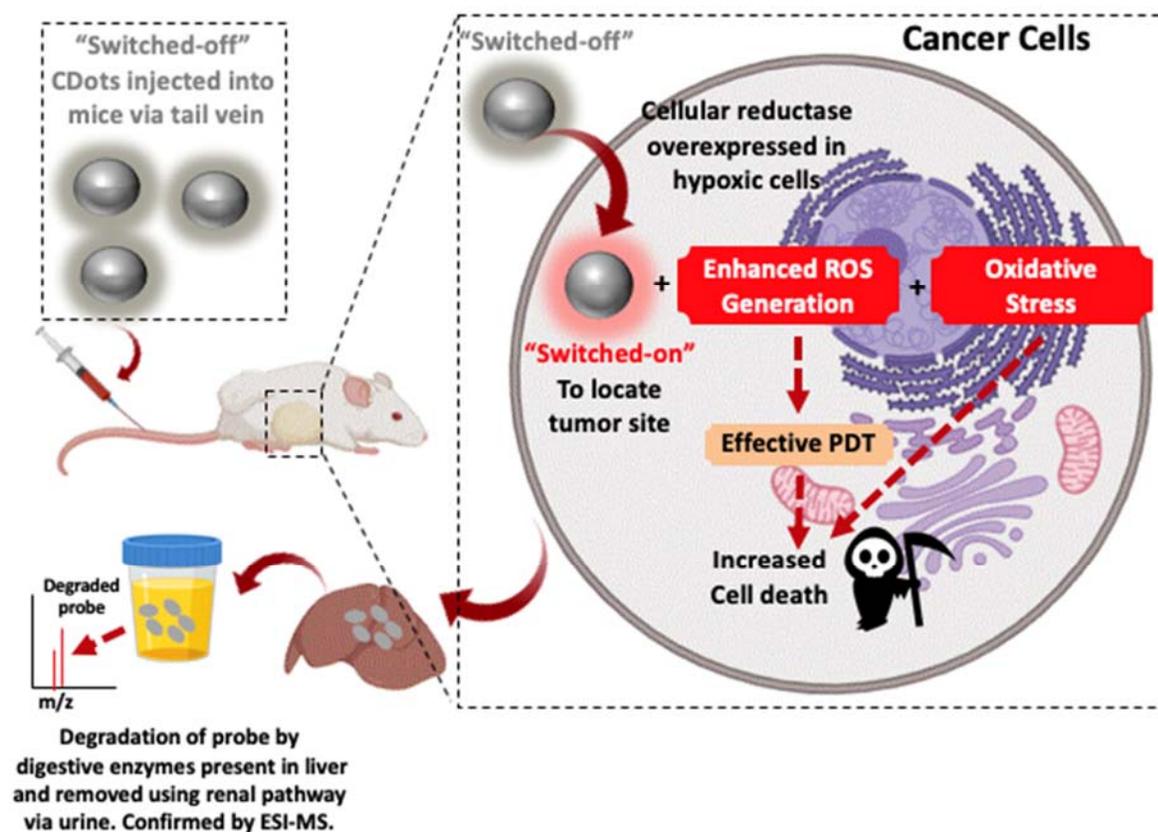
## **COLL 765**

### **Biodegradable, photodynamic-responsive, near-infrared fluorescent carbon dot probes for Hypoxia detection**

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Hypoxia is a condition where the tissue environment is deprived of adequate oxygen supply. Aside from cancerous tumors, it is often a common indicator of other diseases including cardiovascular diseases. Not only is the detection of hypoxia critical for early detection of solid tumors, but hypoxia is also often an indicator of resistance to chemotherapy. Therefore, it is imperative to be able to detect hypoxia via a sensitive, noninvasive, and *in vivo* imaging method for early detection. Currently, the primary

technique for hypoxia detection is to use an oxygen-sensitive electrode, which however is highly invasive. Other studies have considered the use of PET and SPECT to image hypoxia markers labeled with radiotracers. Though, specific and accurate detection of hypoxia can be difficult with this method due to the very small oxygen concentration necessary from the build-up of these probes at the tumor. Conversely, for detection of hypoxia *in vivo*, several fluorescent-based probes have been utilized over the last few years, however, these probes, (e.g. indocyanine green), have suffered from low quantum yield and rapid fluorescence lost. In this work, we have synthesized a probe, which is non-fluorescent in normoxic environments but is highly fluorescent in the NIR region in hypoxic environments. Additionally, during this conversion step, probes release ROS species which increases the oxidative stress and leads to increased cell death and tumors getting ablated when combined with photodynamic therapy. We have also shown that these probes are completely digested by different enzymes present in the liver so that it can be safely removed from the body via the renal pathway. Hence, for the first time, a versatile and promising probe for hypoxia detection was developed that (a) would selectively emit NIR fluorescence in cancerous tumors, (b) is responsive to photothermal therapy for tumor ablation, and (c) was completely biodegradable by digestive enzymes present in the body.



**Scheme 1.** Schematic illustration of the switchability of the probe in vivo.

## COLL 766

### **Controlled gold nanoparticle (AuNP) aggregation: Aggregate toxicity in NaCl**

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This presentation reports on the synthesis of quality mixed ligand shell gold nanoparticles (AuNPs) and their stability in monovalent polyelectrolyte solutions. There is currently a significant effort to clarify the bio-interactions of engineered nanoparticles with molecules, cells, and tissues. These studies could provide a foundation for connecting the physiochemical properties of engineered nanomaterials with their environmental stability. We have synthesized 6 nm AuNPs coated with a mixed monolayer of thiols: mercaptoethoxyethoxyethanol (MEEE, neutral), mercaptohexanoic acid (negatively-charged) and mercaptopentyltrimethyl ammonium (MPTMA, positively-charged) of varying ratios. The composition of the AuNP's surface chemistry influences how they interact with environmental systems. Here, we studied the stability of the functionalized gold nanoparticles against aggregation in a monovalent polyelectrolyte (NaCl) solution using absorbance spectroscopy and dynamic light scattering to determine critical coagulation coefficients and the rate of NP aggregation as a function of surface chemistry. We find that AuNPs possessing mixed ligand shells (mixtures of MEEE and  $\omega$ -functionalized charged thiols) show greater stability against aggregation, compared to monolayers composed of charged thiols alone.

## COLL 767

### **Array-based on differential switchable photoluminescence of macromolecularly “caged” carbon nanoparticles for the discrimination of human cells**

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Cellular discrimination techniques have been extensively explored in the past, many of which are predominantly based on the use of probes (e.g. antibodies, aptamers) which specifically target cellular biomarkers. Although this technique is powerful when there is a strong relationship between the biomarker and the cell of interest, the expression of the cellular biomarkers is usually governed by a complex combination of multicellular processes. Thus, ambiguous information regarding cell state may be obtained by analyzing biomarkers. Cells exhibit a unique molecular composition on their surface, which represents a “signature”-like molecular profile. This unique cell signature can tell us about different cell states such as cancer, metabolic disease, or stem cell differentiation. In this work, we demonstrate the use of polyethyleneimine (PEI)

encapsulated (“caged”) bare-surface carbon nanoparticles (CNPs) to obtain a unique cell signature. The encapsulation (“caging”) of bare-surface CNPs with charged cationic polymers leads to efficient photoluminescence (PL) quenching which is reversible by counterionic macromolecular caging and decaging at the nanoscale. The caged carbons can regain their emission through interaction with anionic surfactant molecules in human cells, providing a unique PL recovery pattern for each type of cell. In this work, we focus on breast cancer as our disease model. Breast cancer is one of the most prevalent malignancies and the leading cause of death amongst women worldwide<sup>1</sup>. Although the outcomes of early screening and treatment of breast cancer has improved significantly in recent years, current diagnostic methods and therapies still have unconquered limitations, especially when it comes to triple-negative breast cancer (TNBC). As a heterogeneous group of breast cancer, TNBCs demonstrate aggressive clinical behavior, high risk of metastasis, and rapid death after diagnosis with no effective standard therapy approved by the U.S. Food and Drug Administration (FDA). By utilizing a machine-learning algorithm, we are able to separate TNBC from non-TNBC cells with 94.4% accuracy. Therefore, this work points toward a new approach of identifying cells based on their cellular signature, which could offer an unprecedented cell sensing technique markedly different from conventional biomarker-based sensing. Furthermore, this approach offers insight into the biological processes and gives us the opportunity to better diagnose diseases.

## **COLL 768**

### **Encapsulation of low melting point metal nano/micro particle phase change materials for thermal energy storage**

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Phase change materials (PCMs) can be used for high-density heat absorption and release during transition in state of matter without fluctuation in working temperature, behaving as good candidates for thermal energy storage in a broad range of applications, like solar energy storage, waste heat harvest, temperature control for electronic devices and catalyst performance, etc. The most studied convention PCMs, such as organic compounds, inorganic salts and salt hydrates, are facing the following problems: (1) low thermal conductivity, resulting in the slow response to the heat source; (2) limited range of working temperature. Metal PCMs show high thermal conductivity and thermal energy storage density by weight, which are good candidates for the rapid heat storage in compact systems. For better use of PCMs, various forms like powder, paste, slurry and nanofluid, need to be designed, in which PCMs are decreased to micro or nano scale in size. To keep the designated form and avoid leakage or sintering of metallic PCMs in nano or micro scale, structure design like creating stable isolation or protection is an effective way to stabilize the PCM structure and morphology during melt-freeze cyclic operation. The purpose of this research is to design the isolation/protection oxide structures for stabilizing low melting point metallic PCM micro/nano particles, thus, to effectively enhance their thermal stability during the

melt-freeze cyclic working condition.

Silica and alumina as stable oxide materials are chosen for the stabilization of low melting point metal nanoparticle (NP) and microparticle PCM. The Sn NPs@SiO<sub>2</sub> particles were prepared by hydrogen reduction process of SnCl<sub>2</sub>-absorbed porous silica spheres, which had the silica spherical structure with Sn nanoparticles distributed (Figure 1a). The Sn@Al<sub>2</sub>O<sub>3</sub> PCM particles with core-shell structure (Figure 1b) were fabricated in a 3-step method, including hydrothermal synthesis of SnO<sub>2</sub> particles, boehmite treatment, air calcination and hydrogen reduction. The as-formed structures as well as formation mechanisms of both Sn NPs@SiO<sub>2</sub> and Sn@Al<sub>2</sub>O<sub>3</sub> were investigated. Furthermore, thermal energy storage properties and thermal stability were carefully examined. Both silica matrix and alumina shell act as the key roles for the enhancement of thermal storage stability of metal PCM. Our results show the great potential of Sn-based PCM particles in the high-temperature applications which are not suitable for organic PCMs.

## **COLL 769**

### **Plasmon-enhanced chemical conversion using copper selenide nanoparticles**

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From artificial photosynthesis to photovoltaics, designing materials that use light to drive chemical reactions has been a holy grail of materials science research. The first step in any of these processes is the absorption of incident light. A unique method of light absorption and subsequent transformation, is a phenomenon termed, “localized surface plasmon resonance (LSPR)” which is a light-matter interaction that exists at the nanoscale and can enhance a wide variety of technologies including ultrasensitive detection and catalytic reactions. While most widely-observed and studied in noble metal nanomaterials, recently, degenerately doped semiconductor nanoparticles have been identified as a class of alternative plasmonic nanomaterials. These materials have the added benefit of being derived from earth abundant, low-cost elements. Additionally, degenerately doped semiconductor nanomaterials allow one to access LSPRs that span a uniquely broad spectral range, from the ultraviolet into the far infrared (300 – 10000 nm). Like with all nanoscale phenomenon, the LSPR is tunable by changing particle size, shape, and even surface chemistry, but these relationships are largely unknown for these new, earth-abundant materials. Here, we synthesize and demonstrate the LSPR tunability of air-stable degenerately doped copper selenide (Cu<sub>2</sub>Se) nanoparticles. We quantitatively access the LSPR and correlate its spectral features with changes in the nanoparticle structure that can be controlled chemically. We then specifically study the surface chemistry of Cu<sub>2</sub>Se nanoparticles, which clarifies the site of potential catalytic behavior. We then combine our synthetic and analytical discoveries

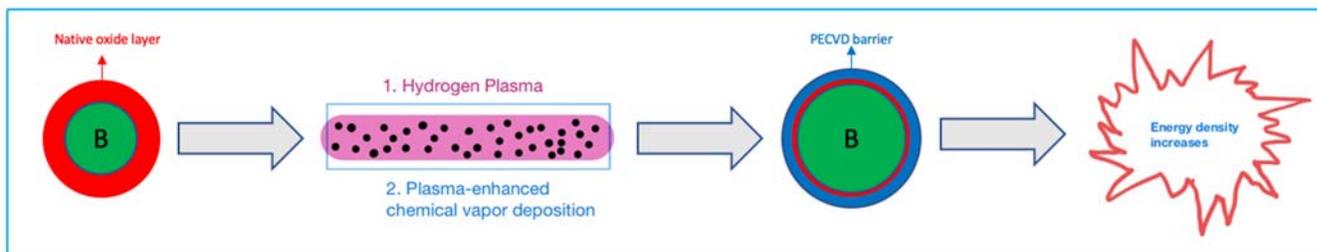
to demonstrate, for the first time, plasmon-driven chemical conversion on the surface of this new plasmonic material class.

## **COLL 770**

### **Nanoenergetics by plasma processing**

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Metal and metalloid particles are capable of releasing huge amounts of energy by oxidation and can be added to propellants in low concentrations to extract more energy in volume-limited propulsion systems. Nanometer sized metal powders have distinct advantages of fast ignition, more complete combustion and enhanced heat transfer rates. Boron nanoparticles have drawn maximum attention of researchers to be used as energy additives because of their high volumetric and gravimetric heats of combustion. However, there are some roadblocks in harnessing this energetic potential of boron nanoparticles. Due to their high reactivity, native oxide layer is present on their surface which impedes the combustion performance by creating a diffusion barrier for further oxidation of core. Also, boron powders are hydrophilic in nature and to get a stable dispersion in non-polar fuels, boron surface needs to be functionalized with polymer having non-polar properties. We have developed a unique method of reducing oxide layer from the surface of boron nanoparticles using non-thermal hydrogen plasma and creating a passivation barrier using plasma-enhanced chemical vapor deposition to prevent re-oxidation of the surface and to ameliorate dispersion stability. This method is a dry in-situ process which exposes the particles to minimum number of reagents and no post-processing separations are needed. This method converts native boron oxide to boron and hence energetic potential of boron can be enhanced. Passivation barrier provides flexibility of operation according to the chemistry of the jet fuel. High resolution scanning transmission electron microscopy (STEM), energy dispersive spectroscopy (EDS) in high angle annular dark field (HAADF) imaging and x-ray photoelectron spectroscopy (XPS) are used to show evidence of surface oxide reduction to boron. This enrichment of boron in the sample leads to increase in the enthalpy of oxidation which is shown by using thermal analysis methods such as differential scanning calorimetry and thermogravimetric analysis. STEM-EDS suggests that hydrogen plasma treatment for 120 minutes reduces the oxygen concentration by 93% which leads to the 19% increase in energy density of boron nanoparticles as evident from thermal analysis.



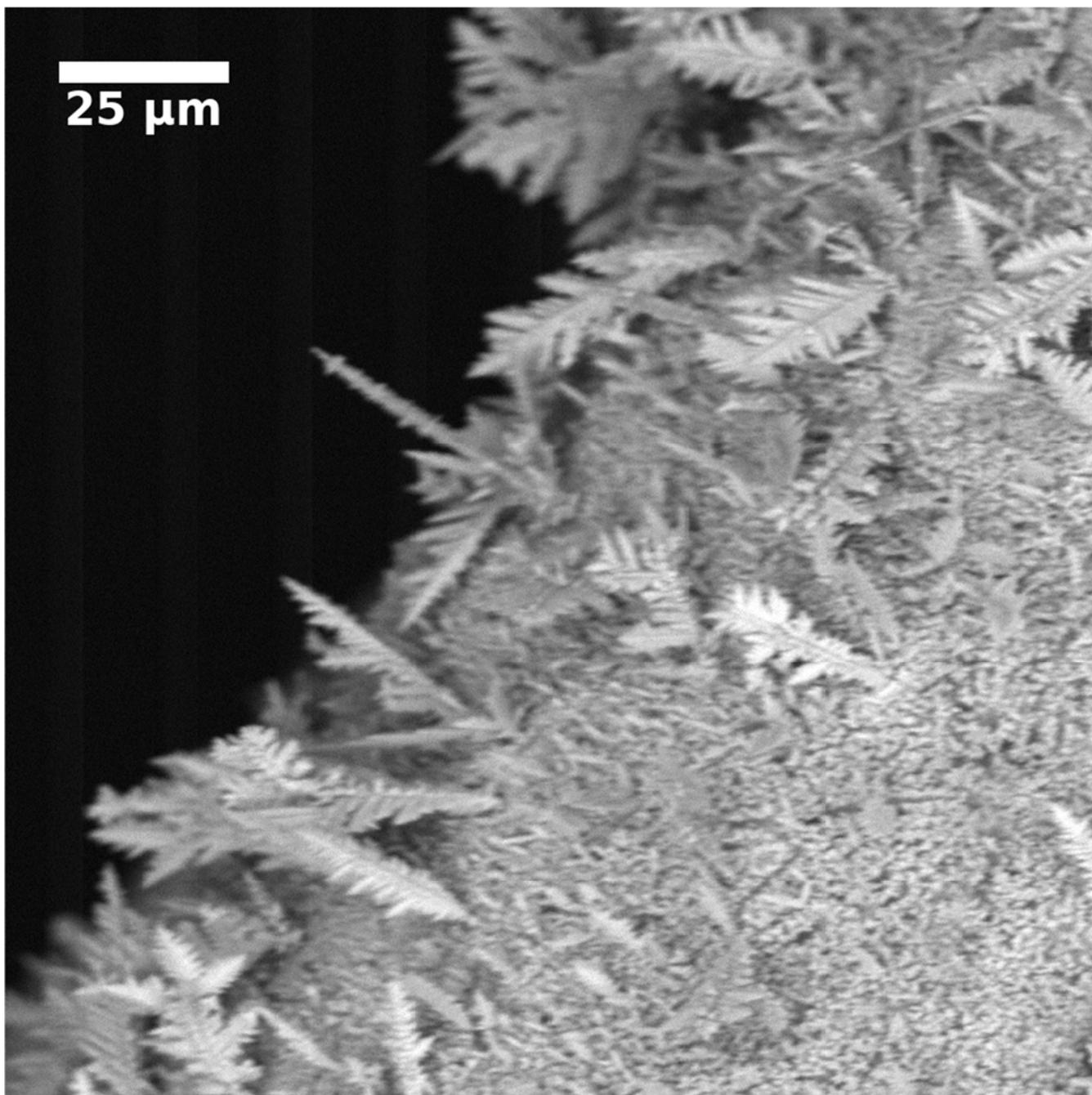
## COLL 771

### Modified surface-limited redox replacement for template-free nanodeposition

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An electrochemical deposition technique that can fabricate intricate nanostructured geometries without the need for a sacrificial template or corrosive solutions is presented. Using a modified surface limited redox replacement (SLRR) approach, dendritic features can be grown directly on a conductive substrate in order to prepare high surface area electrodes. The technique leverages the generally undesired defect growth in electrodeposition towards controlled three-dimensional metal growth. In the present study, gold with feature sizes on the order of 100 nm has been prepared using a sacrificial lead cation. In situ demonstration of mass growth on the surface is illustrated using a quartz crystalline microbalance. Subsequent characterization with underpotential deposition emphasizes the change in surface area. Scanning electron microscopy coupled with energy dispersive X-ray analysis confirms the desired feature sizes and composition.

This work is primarily motivated by the current trends towards miniaturization of analytical platforms, in particular translation of electrochemical sensors to microfluidic devices. Prior research has shown that highly porous gold surfaces prevent large biomolecules, such as proteins, from fouling the electrode surface. By adjusting the geometry of the electrode to filter such molecules, preliminary preconcentration or separations steps that commonly lead to sample loss can be avoided.



A representative scanning electron micrograph of the substrate after deposition.

**COLL 772**

**Exploiting the physiochemical interactions between single-walled carbon nanotubes and hydrogel microspheres to afford chirally pure nanotubes**

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Single-walled carbon-nanotubes (SWNTs) exhibit unique electronic, optical, and mechanical properties; however, a narrow availability of chirally pure (single electronic structure) material can limit effective integration within novel devices and schemes. This work focuses on understanding, modeling, and advancing methodology used to generate preparative quantities of single-chirality SWNT: the iterative adsorption/desorption of SWNT from aqueous surfactant suspensions to/from hydrogel microspheres. Commercially available hydrogel microspheres (Sephacryl S200) were sorted by radius and exposed to SWNT, affording a direct correlation between microsphere surface area and quantity of SWNT adsorbed using differential absorbance spectroscopy. This relationship elucidates a SWNT/gel purification scheme interaction mechanism exclusively involving the gel surface. High-concentration surfactant was used to elute SWNT from the gel with desorption efficiencies dependent on both SWNT chirality and hydrogel microsphere radius, ranging from 25–45%. A thermodynamic model for SWNT desorption that accounts for hydrogel microsphere curvature effects is presented and suggests that (when compared with experimental data) SWNT with greater than ~41% of their length adsorbed to a hydrogel surface bind irreversibly, while others are desorbed in the presence of high-concentration surfactant. These findings inspired the generation and application of mechanically fractured hydrogel microspheres (exhibiting greater surface area) for use as SWNT purification media in per-iteration quantities far less than traditional gels. A 10-iteration SWNT purification procedure demonstrated a marked improvement in process efficiency, as mechanically fractured gels afford a 10-fold reduction in gel-media use (the major expense of the process) while yielding equivalent SWNT purification.

## **COLL 773**

### **Increasing the antimicrobial properties of GO-CS membrane for using in water treatment**

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Energy-efficient and effective wastewater treatment for water purification and reuse remains a tremendous challenge because safe and reliable approaches are often capital and energy intensive. The capital/energy costs come from costs associated with membrane fouling, membrane cleaning, membrane pre-treatment (e.g., disinfection), and over-engineering of systems with the limited range of commercially-available options. The production of clean water from wastewater for municipal or industrial reuse requires the removal of a wide range of organic and inorganic contaminants, including many hazardous and toxic substances (e.g., heavy metals, carcinogens, pharmaceuticals, etc.). Membrane-based water filtration is often an optimal choice because the membranes provide a physical barrier to contaminants, unlike other

processes such as adsorption or coagulation. Membrane filtration is also a better choice than thermally-driven separation processes, such as distillation, which require large energy input to drive the phase-change separation process.

So, we are working on developing a PVA/CSGO membrane. The ultimate goal for this novel material is to create a membrane with a broad contaminant rejection while decreasing energy and fouling cost. The anti-microbial properties of the PVA/CSGO membrane allow this type of membrane to be used broadly for disinfection in wastewater treatment processes. There is a need for removal of viruses, bacteria, and other microbes during wastewater treatment. This project aims to address this critical need, where we will demonstrate contaminant rejection performance that is comparable to RO/NF rejection and we will demonstrate pressure requirements, resistance to fouling, and anti-microbial properties that enable achievement of >50% reduction in pumping (energy) costs.

## **COLL 774**

### **Electrophoretic plasmonic ink for dynamic color display**

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Benefitting from their distinct plasmon resonance properties, metal nanostructures exhibit rich and durable colors. The strong confinement of the electromagnetic energy to the nanoscale by plasmonic nanomaterials further enables the extremely high spatial resolution of the plasmonic color. Plasmonic nanostructures are therefore very promising for full-color, dynamic reflective displays with high refreshing rates and high color contrast. The advent of plasmonic color display devices holds great promise for further commercialization in electronic paper and wearable screens. However, the development of dynamic plasmonic display is currently limited by the challenges in large-scale preparation of plasmonic colors, which should be of low cost and high compatibility with integrated circuit technologies.

At present, the most successfully industrialized commodity that uses small particles as pixels for real-time display is the electrophoretic display device, which, represented by products from E-Ink and Sipix, takes advantage of the movement of charged pigments or dielectric particles driven by electric field. Plasmonic nanocrystals can work as advantageous nanoscale colorful ink, overcoming the limitations of traditional electrophoretic display, such as insufficient resolution and slow switching speeds. Herein we demonstrate a dynamic color display realized by the electrophoretic control of the movement of plasmonic nanocrystal ink. Plasmonic nanocrystals with various colors, including Au nanorods (red), Au nanospheres (60 nm for green, 80 nm for yellow), Au/Ag core/shell nanospheres (blue) are prepared. They are further modified to avoid aggregation in organic solvents and attraction onto the transparent electrodes. By applying a voltage of 2.25 V, electrophoresis dominates the collective movement of the plasmonic ink. We demonstrate the dynamic control of the plasmonic color and characterize the device performance by real-time particle tracking, scattering spectroscopy monitoring, and normalized RGB analysis. The complete assembly and

disassembly of the nanocrystals from the display surface can be realized within 30 s, leading to the generation of a type of high-contrast and high-saturation color display. In summary, we have solved the key technical issues of using plasmonic ink in electrophoretic displays. These nanocrystals can be further assembled into microcapsules or microcups to create commercially available full-color display devices.

## **COLL 775**

### **Local luminescent probing of nanoparticle surface temperature via $\text{Eu}^{3+}$ decay time on $\text{Y}_2\text{O}_3$ hosts**

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Magnetic nanoparticles (NPs) such as iron oxide ( $\text{Fe}_3\text{O}_4$ ) generate local heating under an alternating magnetic field (AMF), and they have been used for targeted cancer treatment, drug delivery, thermal polymerization, and catalysis. Despite the advances in the development of thermal probes that are not susceptible to an AMF, it is still very challenging to quantify the temperature on the surface of the nanoparticle instead of relying on bulk measurements to quantify heat transfer. Currently, temperature measurements require concentrated NPs solutions, adding external factors to the analysis, such as interparticle interaction, heat dissipation through the medium, and heat losses to the environment. Additionally, the indirect surface temperature measurements involving functionalized NPs with thermo-sensitive molecules are unable to withstand high temperatures without degradation, hindering our ability to probe temperatures above 70 °C. To avoid high-temperature decomposition of the molecular probe, this work proposes the use of a temperature-dependent, luminescent solid shell (i.e.  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ ) as a luminescent probe. By incorporating this shell on the NPs, the surface temperature can be quantified based on the change in luminescent intensity. In this work, monodisperse and morphologically-controlled  $\text{Fe}_3\text{O}_4$  NPs are synthesized via colloidal routes. Optically active  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  shell are then deposited on the surface via seeded growth methods to maintain the shape of the NPs. These structures are characterized via Transmission Electron Microscopy and X-ray Diffraction to confirm preservation of the shape and phase of the  $\text{Fe}_3\text{O}_4$  core and conformal shell deposition. After obtaining core-shell nanoarchitectures, *in situ* photoluminescent (PL) spectroscopy is performed at various temperatures, allowing calibration and correlation of NP temperature by monitoring Eu emission intensity and decay time. Subsequently, the particles are excited using an AMF during the PL measurements, and the luminescent response is compared to the thermal reference providing a direct temperature reading of the NP surface. Given the small shell thickness (~5 nm) the luminescent properties measured are an accurate representation of the surface behavior, allowing high-resolution thermal monitoring without the need for concentrated nanoparticle solutions or macroscopic temperature increase. This method can be used to standardize commonly reported Specific Loss Power (SLP) values of magnetic NPs.

## **COLL 776**

## Synthesis of core/shell nanoparticles in ionic liquids

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This presentation will describe the synthesis of CdS/ZnS core/shell nanoparticles using the Successive Ionic Layer Adsorption and Reaction (SILAR) method with octadecene and oleic acid, and adaptation of this method to ionic liquids. We will discuss the effects of using different precursors (e.g., Cd, bulk CdS, Zn, CdO, Cd(OAc)<sub>2</sub>, ZnO, and Zn(OAc)<sub>2</sub>) for nanoparticle synthesis, and necessary procedural changes for nanoparticle synthesis going from octadecene and oleic acid to the ionic liquid 1-butyl-3-methylimidazolium methylsulfate [bmim][MeSO<sub>4</sub>]. We will then discuss our recent progress towards metal/semiconductor photocatalysts synthesized using ionic liquids. Methods to isolate particles from the ionic liquid and characterization of these materials by transmission electron microscopy, UV-visible spectroscopy, and fluorimetry will be presented.

## COLL 777

### Seed-mediated continuous synthesis of ferrite nanoparticles with sophisticated designed structures

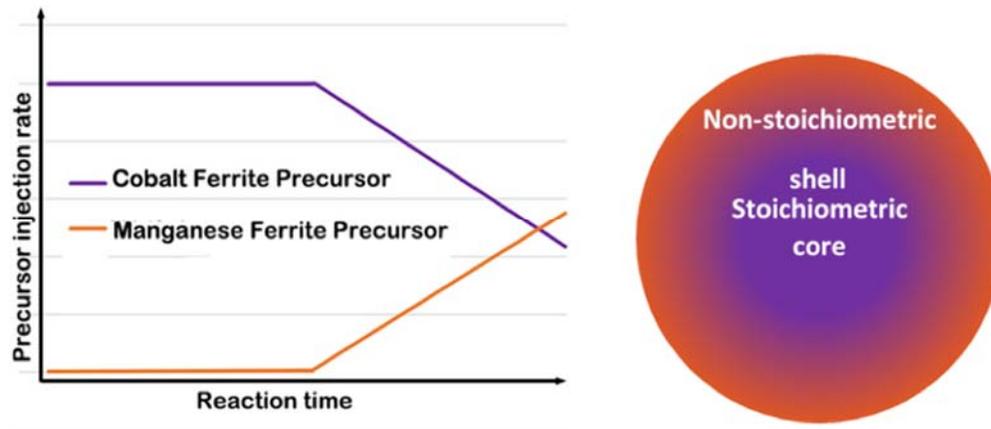
**Zichun Yan**<sup>1</sup>, *zichuny@g.clemson.edu*, Sara Fitzgerald<sup>2</sup>, Thomas Crawford<sup>2</sup>, Olin T. Mefford<sup>1</sup>. (1) Materials Science and Engineering, Clemson University, Clemson, South Carolina, United States (2) Department of Physics and Astronomy, University of South Carolina, Columbia, South Carolina, United States

Iron oxides (i.e. magnetite (Fe<sub>3</sub>O<sub>4</sub>) and maghemite (γ-Fe<sub>2</sub>O<sub>3</sub>) magnetic nanoparticles are extensively studied for their wide range of biomedical applications, including imaging, diagnostics, drug delivery, and therapy. We have been exploring the synthesis of substituted/doped metal ferrites (M<sub>x</sub>Fe<sub>3-x</sub>O<sub>4</sub>, M = Mn, Co, Ni, or Zn) in order to offer a wide range of properties through control over the composition, size and structures to meet the requirements of specific applications.

We adapted the “Extended LaMer” technique to synthesize multi-dopant ferrite nanoparticles. The composition and structure of the particles were altered by changing the pumping rate and the species of the precursors. The synthesis begins with a seeding process of thermal decomposition of metal acetylacetonates and followed by a continuous injection of metal oleate precursors at 350°C.

The results showed a well-controlled size and composition and the magnetic properties are promising. The composition of the particles will be analyzed by electron energy loss spectroscopy (EELS) and energy dispersive X-ray spectroscopy (EDS) to confirm the existence of core-gradient shell structure. Magnetic properties, such as saturation

magnetization, blocking temperature, and effective anisotropy were then measured and calculated based on vibrating sample magnetometer (VSM) and zero field cooling/ field cooling (ZFC/FC) measurements.



Representative image of control of precursors to produce gradient particles.

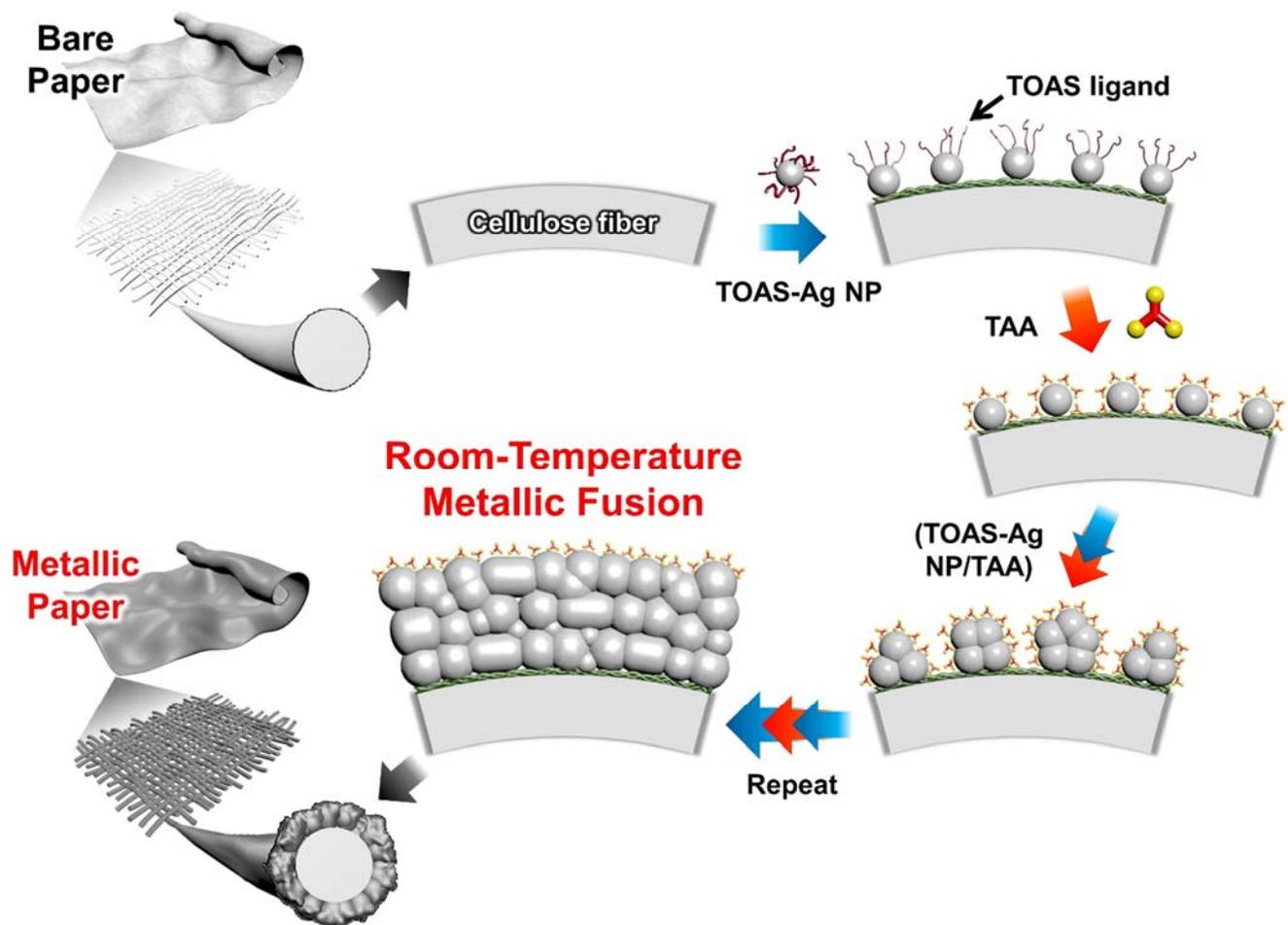
## COLL 778

### Highly conductive paper electrodes using metallic fusion of multilayered silver nanoparticles at room temperature

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For the preparation of highly conductive electrodes, various silver (Ag) nanomaterials have been deposited onto substrates using solution-based processes. However, the obtained electrodes exhibit a limited electrical conductivity owing to the bulky/insulating organic ligands between neighboring Ag nanomaterials, and resultantly require post-sintering processes to further improve the electrical properties. Herein, we report an entirely different approach of preparing electrodes with bulk metal-like conductivity using a metallic fusion of multilayered Ag nanoparticles (NPs) at room temperature. For this study, the newly synthesized tetraoctylammonium thiosulfate (TOAS)-stabilized Ag NPs are layer-by-layer (LbL)- assembled with small amine-functionalized molecules (tris(2-aminoethyl)amine, TAA) (**Figure 1**). During LbL assembly, the bulky TOAS ligands bound to the surface of Ag NPs are almost completely exchanged with small TAA linkers, significantly decreasing the separation distance between adjacent Ag NPs. In this case, the metallic fusion is strongly induced in the multilayered Ag NPs at room temperature without additional treatments due to both the minimized interparticle distance and the low cohesive energy of Ag NPs. Consequently, the prepared electrodes exhibit an extremely high electrical conductivity of  $\sim 1.60 \times 10^5 \text{ S cm}^{-1}$  (bulk Ag:  $\sim 6.30 \times 10^5 \text{ S cm}^{-1}$ ). Furthermore, our approach can be effectively applied to

porous paper or textile substrates by depositing Ag NPs over the entire surface ranging from the exterior to the interior. The insulating papers can be successfully converted to the highly conductive metallic papers, which can be used as three-dimensional current collectors for flexible/wearable energy-storage devices.



COLL 779

### Synthesis of monodisperse intermetallic nanoparticles via size refocusing

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Due to their ordered crystal structures and high structural stability, intermetallic nanoparticles are useful for their enhanced catalytic, magnetic, and optical properties.

Synthetic routes towards intermetallic nanoparticles includes thermal annealing of the disordered counterpart in atmosphere (or vacuum) and colloidal syntheses, where the phase transformation is attained in the solution phase. While both methods can generate intermetallic nanoparticles, there is difficulty achieving the monodispersity needed to exploit the properties of intermetallic nanoparticles for various applications. Here, overgrowth on random alloy AuCu nanoparticles facilitated formation of monodisperse intermetallic AuCu nanoparticles by size refocusing. Size refocusing has been used in syntheses of semiconductor and upconverting nanocrystals to achieve highly monodisperse nanocrystals. Now size refocusing has been realized as a mechanism to achieve the disorder-to-order phase transformation in multimetallic nanoparticles. A time evolution experiment of the phase transformation, where reaction aliquots were analyzed with transmission electron microscopy and powder x-ray diffraction, revealed the generation and dissolution of small nanoparticles along with an increase in average size of the nanoparticles and the achievement of the ordered phase. This work furthers our knowledge of the formation of intermetallic nanoparticles in colloidal syntheses, which could accelerate our advancements in electrocatalysis and magnetic storage devices.

## **COLL 780**

### **Synthesis of uncapped noble metal nanoparticles by laser reduction in liquid**

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Uncapped, or “naked” metal nanoparticles have pure metal/oxide surfaces that are amenable to subsequent conjugation with biocompatible ligands and provide active surface sites for catalysis. This presentation will highlight my group’s recent work on the synthesis of uncapped “naked” Au, Pd, and Ag nanoparticles by femtosecond laser-induced reduction of salt precursors in aqueous solution. Focusing femtosecond laser pulses into a condensed medium produces a dense plasma containing electrons and radicals that can reduce metal ions to neutral metal atoms, which coalesce into nanoparticles. For Au, Pd, and Ag salts, distinct reduction mechanisms operate that depend on one or more of the following reactive species: hydrated electrons, hydroxyl radicals, hydrogen peroxide, and hydrogen molecules. Following a discussion of these mechanisms, I will present chemical strategies for controlling the plasma composition by changing the solution pH and adding radical scavengers. Each metal requires distinct solution chemistry to effectively manipulate the nanoparticle sizes and morphologies. For instance, adding hydroxyl radical scavengers during reduction of  $\text{KAuCl}_4$  enables control over Au nanoparticle size distributions, while the choice of Pd salt determines the morphologies of Pd nanoparticles.

## **COLL 781**

### **Cross-linking approach to stabilizing stimuli-responsive colloidal crystals engineered with DNA**

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Two DNA-cross-linking reagents, bis-chloroethylnitrosourea and 8-methoxypsoralen, are used to covalently cross-link interstrand base pairs in DNA bonds that, in part, define colloidal crystals engineered with DNA. The irreversible linkages formed increase the chemical and thermal stability of the crystals and do not significantly affect their long-range order, as evidenced by small-angle X-ray scattering data. The post-modified crystals are stable in environments that the pre-modified structures are not, including solvents that encompass a broad range of polarities from ethanol to hexanes, and in aqueous media at pH 0 and 14. Interestingly, the cross-linked DNA bonds within these crystals still retain their flexibility, which is reflected by a solvent-dependent reversible change in lattice parameter. Since these organic cross-linking reagents, in comparison with inorganic approaches (use of silver ions or SiO<sub>2</sub>), have marginal effects on the composition and properties of the crystals, they provide an attractive alternative for stabilizing colloidal crystals engineered with DNA and make them potentially useful in a broader range of media.

## **COLL 782**

### **Structuring of rod-shaped nanoparticles using Langmuir-Blodgett assembly and investigation of their anisotropic properties**

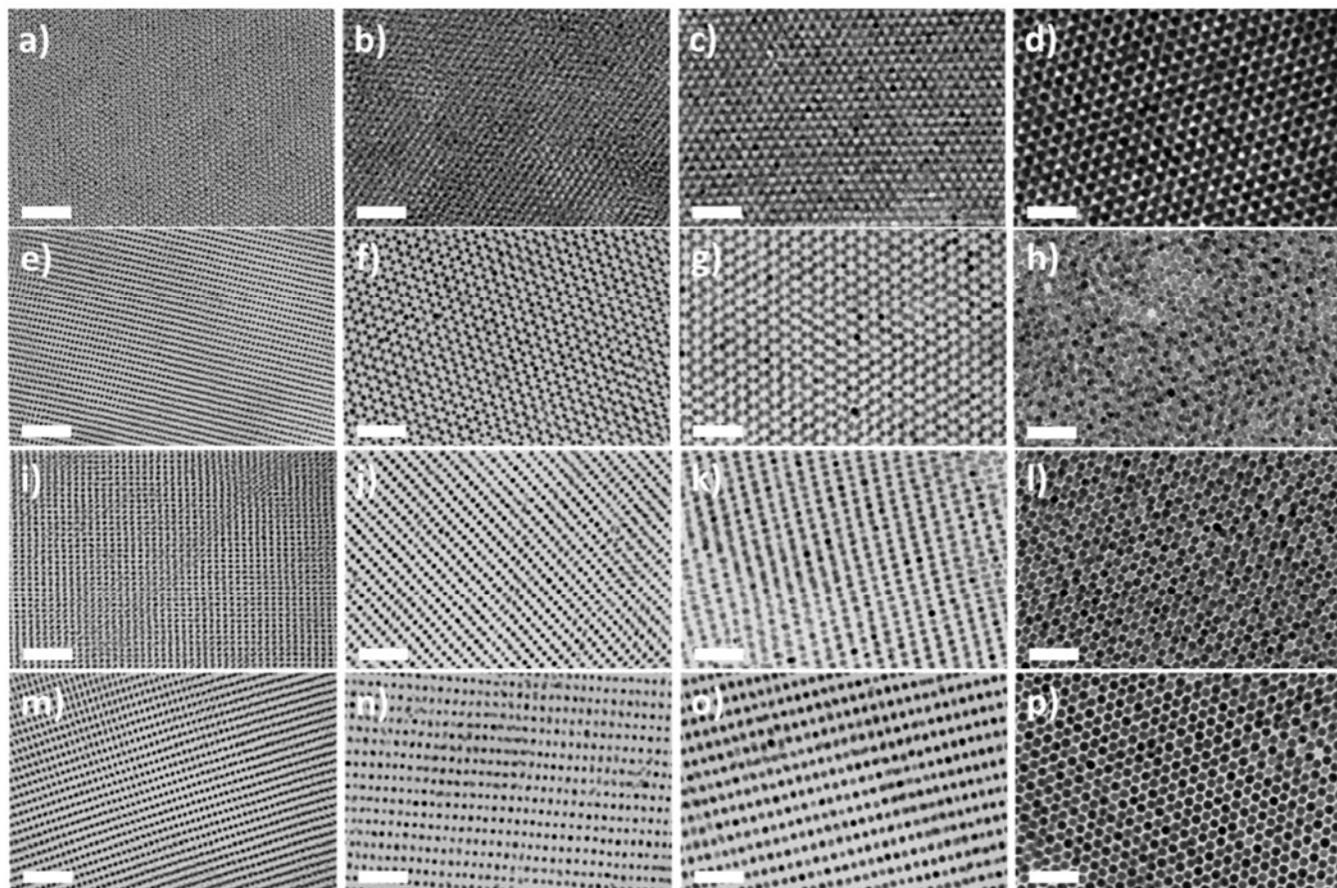
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Using Langmuir-Blodgett (LB) assembly, it is possible to control the packing density and orientation of nanoparticles in a monolayer level at the air/water interface, and then transfer to a solid substrate. In the presence of nanoparticles, the compression-isotherm profile is significantly modified, implying structural changes of LB films. In this study, we identified topographic effects of rod-shaped nanoparticles on the modification of compression-isotherm, specifically when nanoparticles are electrostatically adsorbed beneath the air/ionic surfactant/water interface. The arrangements of nanoparticles and ionic surfactants as well as topographical corrugation of the air/liquid interface during the LB compression were analyzed using in situ sum frequency generation spectroscopy. In addition, we elucidated the interplay between compression- and flow-induced alignment of rod-shaped nanoparticles during the LB deposition. In the case of uniaxially aligned cellulose nanocrystals in the LB film, their optical and frictional anisotropic properties were characterized using spectroscopic ellipsometer and atomic force microscopy, respectively. We expect that findings of this study will inform the preparation of uniform arrangements of LB films made of nanoparticles, with related impact on their material properties.

**Effective softness-dependent self-assembly behavior of polymer-grafted nanocrystals**

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Colloidal nanocrystals (NCs) have received great attention as building blocks for developing new metamaterials. Material properties of NCs are strongly dependent not only on size-, shape-, composition, but also assembled structure, which suggests the importance of understanding self-assembly behavior of NCs. Here, we demonstrate control of polystyrene-coated Au NC (Au@PS) superlattice symmetry by changing molecular weight ( $M_n$ ) of PS and diameter of Au. Au@PS nanoparticles were prepared by simple ligand exchange with thiol-terminated PS, which yielded the interparticle distance from a few nm to more than 10 nm. The Au@PS particles were then self-assembled using liquid-air interface self-assembly technique. Transmission electron microscopy images and grazing incidence small-angle X-ray scattering measurements revealed well-ordered Au@PS particles in long range. In particular, symmetry transitions were clearly observed from hexagonal close packing (hcp) to body centered cubic (bcc) symmetry as either  $M_n$  of PS increases or diameter of NCs decreases (**Figure 1**). Such structural transition was explained by “effective softness” model,<sup>1</sup> which includes concentrated polymer brush (CPB) regime around NC surface as part of “hard core.” Finally, we will show how the interparticle distance can be theoretically predicted by combining the optimal packing model (OPM) and the effective softness model.



**Figure 1.** TEM images of self-assembled a) 2.9nm@2k, b) 5.6nm@2k, c) 7.1nm@2k, d) 9.6nm@2k, e) 2.9nm@4k, f) 5.6nm@4k, g) 7.1nm@4k, h) 9.6nm@4k, i) 2.9nm@6k, j) 5.6nm@6k, k) 7.1nm@6k, and l) 9.6nm@6k, m) 2.9nm@8k, n) 5.6nm@8k, o) 7.1nm@8k, and p) 9.6nm@8k Au@PS nanoparticles.

## COLL 784

### Visualizing the electrochemical impact of sulfide adlayer formation on single silver nanoparticles

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The formation of sulfide adlayers at the surface of silver nanoparticles has been shown to be a critical-initial step in the growth of monolayer coverage of silver sulfide ( $\text{Ag}_2\text{S}$ ). Growth of  $\text{Ag}_2\text{S}$  is a mechanism that is known to weaken the electrochemical performance of silver nanoparticles, therefore, understanding how sulfide adlayers form is of great interest when considering the abundance of sulfide in the environment and the numerous catalytic applications of silver nanoparticles. The silver-sulfide adlayer complex ( $\text{Ag-SH}$ ) is formed when hydrosulfide ( $\text{HS}^-$ ) in solution adsorbs to the surface of silver nanoparticles. Here, correlated dark-field optical imaging and electrochemical

methods are used to investigate the reductive-stripping of adsorbed sulfide adlayers at the surface of individual silver nanoparticles and its subsequent effect on the electrodisolution kinetics of silver nanoparticles. This study provides information about how modified surfaces influence electrochemical performance of metal nanoparticles.

## **COLL 785**

### **Computational study of the brightening of II-IV quantum dots via hydride treatment**

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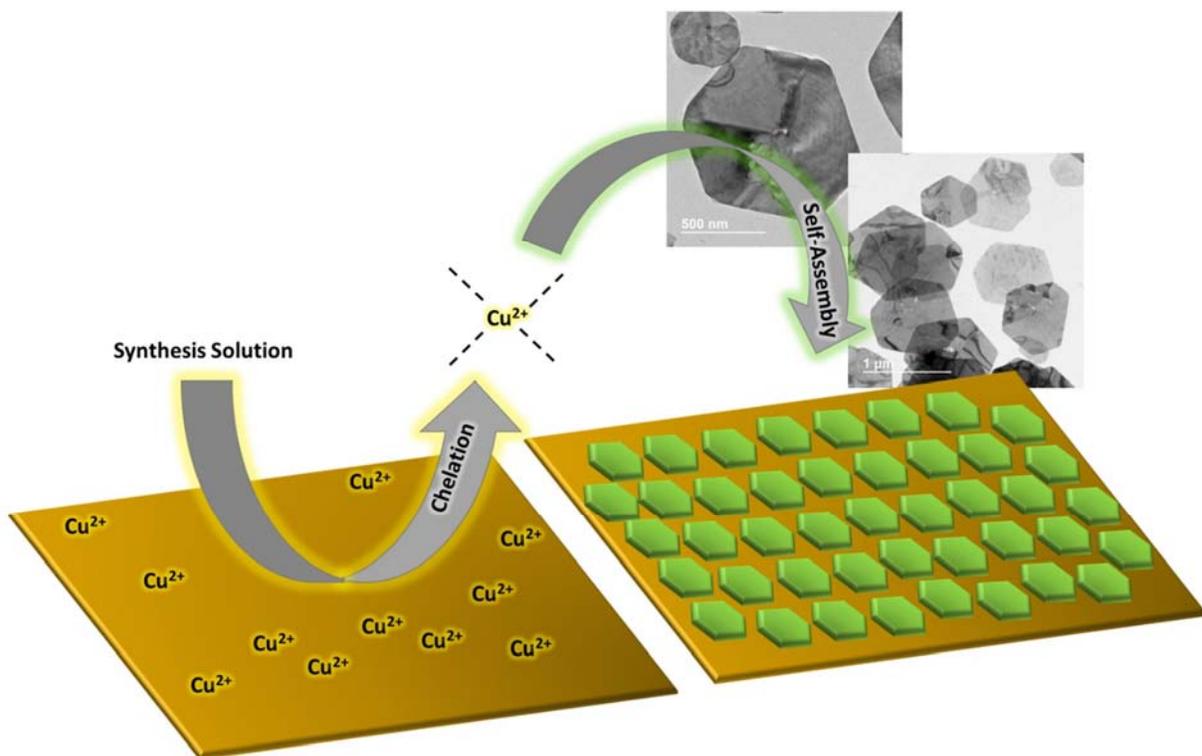
Colloidal Quantum Dots (QDs) have attracted the attention of the scientific and industrial communities for their wide range of applications including display technology, bioimaging, light harvesting, quantum computing, and miniature lasers. QDs are suited for these application due to: one pot synthesis with abundant precursors and solvents, size-tunable optical response, and high photostability. The ability of QDs' to harvest and emit light is sensitive to its surface morphology and environment. Thus, QDs' optical properties can be manipulated by surface modification. In particular, it was observed that the quantum yield of photoluminesces (QYPL) of cadmium chalcogenides QDs can increase by 55.7 times when treated with hydride-generating compounds. Investigating the mechanism for the enhancement in the QYPL is complicated due to complex surface chemistry. Here, we report on the effect of hydride anion ( $H^-$ ) on the morphology, electronic structure, and optical spectra of small Cd-Se clusters investigated by density functional theory (DFT) and time-dependent DFT. Results of our calculations reveal that  $H^-$  interaction with the QDs' surface gives rise to two main chemical changes: removal surface Se anions as  $H_2Se$ , and coordinates with surface Cd cations. When  $H^-$  removes surface Se anions the surface becomes Cd-enriched. Future treatment results in surface Cd passivated by  $H^-$  which leads to a significant increase in the oscillator strength of the first excited singlet state ( $S_1$ ) compared to the original QDs. The increase in oscillator strength indicates the elimination of hole and electron trap states from the band gap of the QDs, thereby decreasing the contribution of non-radiative electron-hole recombination and the increase QYPL of cadmium chalcogenides QDs.

## **COLL 786**

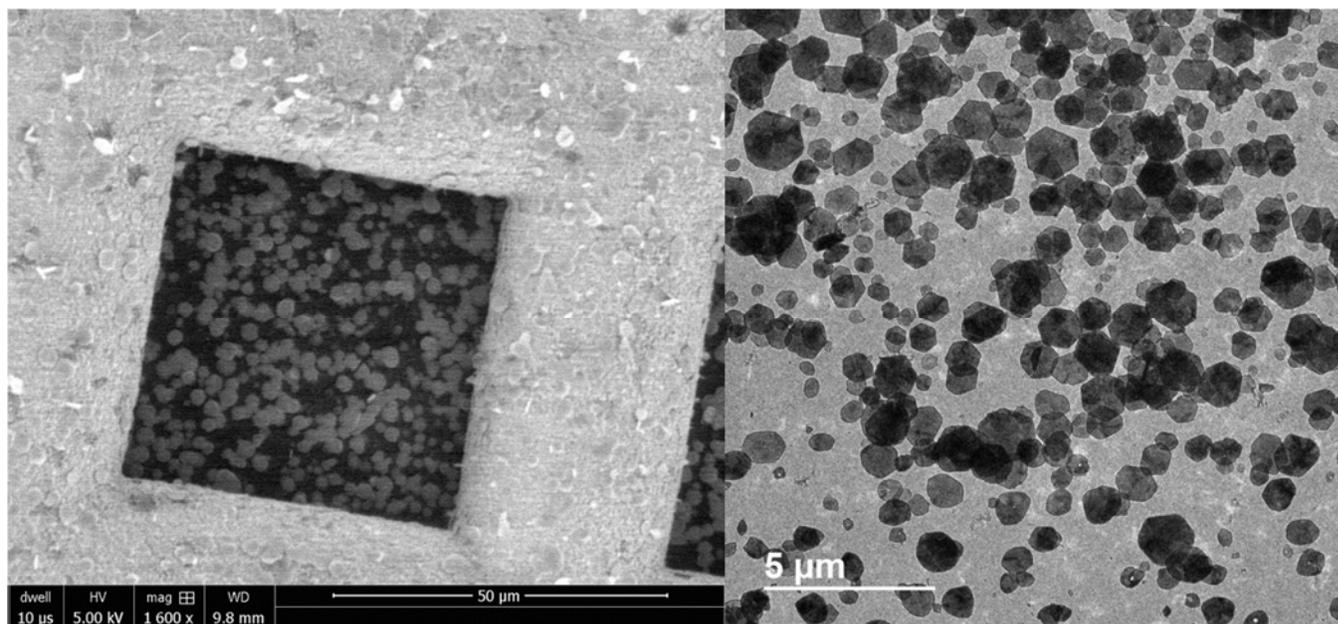
### **Surface-directed self-assembly of metal-chelated nanoplatelets**

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In-situ assembly of two-dimensional nanomaterials has a number of applications in sensors, disease therapies, and environmental management. We have developed a remarkably simple method for the self-assembly of metal-chelated nanoplatelets on a variety of metal surfaces. Using a one-step synthesis method, the application of a chelator-containing solution to a flat metal surface and subsequent drying of the solution results in the formation of metal-chelated 2-dimensional hexagonal nanoplatelets directly upon the metal surface. The results were reproducible on various metal surfaces, including copper tape and copper transmission electron microscopy grids. The ability of this method to be adapted to other metals was also explored. The effects of various synthesis parameters and metallic precursors were evaluated using transmission electron microscopy and scanning electron microscopy.



Synthesis schematic for copper-chelated nanoplatelets



Left: Scanning electron microscopy (SEM) image of copper nanoplatelets formed directly on a transmission electron microscopy (TEM) grid. Right: TEM image of copper nanoplatelets.

## COLL 787

### Diversifying solvent selection for thermodynamic surface energy analyses

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Surface energy analyses are a mature and well established subset of surface chemistry which can utilize the Owens-Wendt and/or van Oss-Chaudhury-Good (OCG) thermodynamic approaches to determine the degree of solvent interaction with a surface via goniometry. Using two fully characterized solvents (i.e., nonpolar and polar), the Owens-Wendt approach can use a simple algebraic approach to determine the total surface free energy ( $\gamma_s$ ), the Lifshitz-van der Waals component ( $\gamma_s^{LW}$ ), and the Lewis acid/base component ( $\gamma_s^{AB}$ ). To date, the OCG thermodynamic approach has used a similar algebraic approach but with three fully characterized solvents (i.e., nonpolar, monopolar, and bipolar). Unfortunately, the assumption of solvent monopolarity can introduce significant deviations in the overall Lewis acid/base component ( $\gamma_s^{AB}$ ), the acid component ( $\gamma_s^+$ ), and the base component ( $\gamma_s^-$ ). Furthermore, the preferred monopolar solvents (e.g., DMSO) often negatively affect many substrates causing further surface energy deviations. Therefore, we introduce a linear algebraic approach to simultaneously solve for all variables without assuming monopolarity thereby allowing for more solvent choices depending on the substrate. To demonstrate the linear algebraic model and efficacy thereof, we use silicone acrylate coatings as a model

system and further show how the results can be used effectively with Cassie's equation to more accurately predict the surface energy of various silicone formulations.

## **COLL 788**

### **Molecular polarizability in open ensemble simulations of aqueous nanoconfinements under electric field**

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Molecular polarizabilities at aqueous interfaces, especially under the effect of an electric field, play a vital role in our understanding of energy storage devices such as electric double layer capacitors. Conventional atomistic force fields typically average out the effect of these polarizabilities, which can influence the outcome of a molecular simulation. Our work concerns non-trivial methodological developments of expanded ensemble Monte Carlo simulations for open systems with long-ranged multibody interactions. We consider both fixed-charge, SPC/E-JC, and polarizable, BK3-AH, models of water and ions in a hydrophobic pore which are subjected to an electric field. Molecular exchanges are allowed with an unperturbed bulk environment. Results with the BK3 water model in neat-aqueous systems capture the ~10% reduction of molecular dipoles within the surface layer near the hydrophobic pore walls analogous to reported quantum mechanical calculations at water/vapor interfaces. Inclusion of polarizability affects the interfacial dielectric behavior and weakens the electric-field dependence of water absorption at pragmatically relevant porosities. Structural differences between fixed-charge and polarizable models were captured in Molecular Dynamics simulations for a set of closed systems. The use of polarizable force field indicates an enhanced response of interfacial ion distributions to applied electric field. Additionally, fixed-charge water experiences a more dramatic orientation-bias near the interface than its polarizable counterpart.

## **COLL 789**

### **Protic liquid solvents at the hydrophilic mineral/liquid interface probed by sum frequency generation spectroscopy**

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We Investigate the orientation and structuring of strong protic solvents as a model system for separation techniques. Hydrophilic interaction liquid chromatography (HILIC)

is an alternative mode to high performance liquid chromatography (HPLC) for separating highly polar and amphiphilic analytes. However, inconsistency of retention mechanism contributions has limited the advancement of the separation technique. The consensus is that both the liquid/liquid and solid/liquid interfaces may play a vital role in shedding light to these contributions. Knowing the specific molecular organization near surfaces may pave way to understanding the functional role of the liquid solvent mixture adsorbed at the interface. Surface selective vibrational sum-frequency generation (VSFG) is a second order ultrafast spectroscopic technique suitable for such studies, where the interfacial layers are selectively probed. We present here spectroscopic measurements of a double-layer formation of liquid methanol at the interface as well as probing the interfacial organization of water at the hydrophilic silica/liquid interface. Measurements of the methyl region of liquid methanol on hydrophilic surfaces have remained elusive, but here we report the first observation on the CH stretch spectrum.

## **COLL 790**

### **Electrospray deposition of phenyl modified melting gel coatings**

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Melting gels (MG) are hybrid polysilsesquioxanes that possess glass transition temperatures at ~28 °C and consolidation temperatures at ~150°C, above which they irreversibly transform into hybrid-organic inorganic silica-based glasses. MGs are synthesized via a sol-gel process using a monosubstituted alkoxide such as phenyltriethoxysilane (PhTES) along with a di-substituted alkoxide such as dipheyl-diethoxysilane (DPhDES). In this study MGs with 87%PhTES-13%DPhDES were prepared at different pHs (pH=1, 1.5, and 2.5). The properties of the MGs, such as glass transition temperatures, consolidation temperatures, and weight loss, were correlated with the pH during synthesis, which, in turn, is linked to their degree of polycondensation. The main advantage of MGs is their processing ability. MGs can be processed as a thermoplastic melt into a desired form and then converted into a permanent structure based on this property. In our study, melting gel coatings were prepared by electrospray deposition to observe the kinetic behavior arising from different experimental conditions and to see how these affect the final morphologies of the hybrid glasses coatings. Due to the electrostatic breakup mechanism present in electrospray, the resulting sprays had uniform droplets down to hundreds of nanometers. By using dilute loadings of 1 wt% in 2-butanone, these microdroplets delivered extremely small quantities of material at a continuous rate. Control of spray composition, voltage polarity, substrate temperature, flow rate, and collection distance,

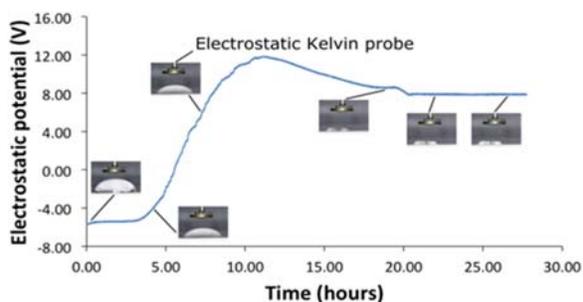
leads to adjustments in the dynamic evolution of solvent evaporation and MG consolidation. The results reveal that these can be used to controllably tune surface structure from dense, to cellular, to superhydrophobic fractal coatings. The thickness and the uniformity of the coatings are directly correlated with the pH during the synthesis of the melting gels. In addition, manipulation of charge dissipation during deposition enables control of the thickness of the coatings. FT-IR studies confirm that the chemical structure of the coatings is affected by the pH, the temperature, and the time of consolidation.

## **COLL 791**

### **Spontaneous mosaic of charges and high potential gradients on dielectric surfaces formed by evaporating liquid drops**

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Electrostatics is an old area of scientific research that lagged behind most other areas of natural sciences and especially chemistry and physics, during the 20th century. The role of interfaces as important sites for electric charge accumulation or exchange is well established in solid-solid, liquid-liquid and liquid-solid systems. However, this is not the case for gas-liquid or gas-solid interfaces. Water with excess charge is the outcome of many different events triggered by electric fields or by interfacial phenomena that produce non-electro-neutral water, either liquid, solid or vapor, due to excess  $H^+$  or  $OH^-$  concentration. As interfaces are recognized sites for electrification, we used a very simple apparatus to measure the electrostatic charge during phase transition at liquid-gas and solid-gas interfaces. The experiment consists on recording the electrostatic charge of a water drop on polytetrafluoroethylene (PTFE) during evaporation. This is simply done with a Kelvin probe and an optical microscope. Well-controlled experiments as shown in the figure attached reveal that when a drop of water is positioned on top of PTFE surface the electrostatic potential remains pretty stable until the drop has reached roughly half of its volume. After that, the electrostatic potential starts to increase significantly reaching high positive potentials + 12 V and high potential gradients. Finally, there is a slight electrostatic potential decreasing, reaching a plateau when there is no more water on PTFE. This equilibrium electrostatic potential is very stable and did no change even after 21 days of measurement. Experiments done in microscale with a Kelvin Probe Force Microscopy confirms the macroscopic results. At this point we speculate that the asymmetric partitioning of hydroxide and hydronium ions from water autolysis play a key role on the spontaneous charge build-up on dielectric surfaces by the evaporation of water and considering the ubiquitousness of water formation/evaporation on many systems, this discovery may be extremely relevant from atmospheric sciences to ESD control in electronic industry.



## COLL 792

### VSFS studies of the synergistic co-adsorption of CTAB and hexanol at the oil-water interface

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Synergistic mixed surfactant systems have proven to be highly tunable emulsifiers and are increasingly being utilized at the oil-water interface in a variety of applications ranging from oil-spill remediation to drug delivery. Of particular interest are mixtures of surfactants with dissimilar polar head groups, which offer additional avenues of control. However, the full potential of these systems cannot be realized without a deeper understanding of the interplay between their hydrophobic and electrostatic effects, which are not yet well understood. In an effort to bridge this knowledge gap, this work examines the cooperative molecular interactions between a cationic surfactant cetyltrimethylammonium bromide (CTAB) and a non-ionic alcohol (1-hexanol) at the buried oil-water interface. This is done using surface-specific vibrational sum frequency spectroscopy (VSFS) in combination with surface tensiometry and computational methods. Firstly, selective deuteration of CTAB was used to precisely differentiate resonances arising from the CTAB head and tail and later between the CTAB headgroup and hexanol. The results show that hexanol in isolation is highly disordered at the interface, but becomes increasingly ordered with concentration as it intercalates between CTAB. In turn, more CTAB is able to partition to the interface due to the neutral hexanol screening the positive charges between its headgroups. This work offers a unique insight into the behavior of CTAB and hexanol at the oil-water interface and brings attention to significant implications regarding the impact of interfacial ordering on surface tensiometry measurements for nonionic surfactants.

## COLL 793

### Molecular investigation of the three phase contact line friction of electrowetted nanodroplet

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Electric field induced spreading of nanodroplet is simulated using molecular dynamics (MD) simulation to understand the physics of molecular motion near the three phase contact line (TPCL). Electric field assisted droplet movement has a wide range of application starting from electrochemical cells, membrane ion channels, to modification and characterisation of biological cells on Lab-on-a-chip based micro-fluidic devices. When electric field induced droplet moves on a surface it encounters various resistive forces and contact line friction force is found to be the dominating one, which controls the droplet movement. The origin of this contact line friction (CLF) force is molecular in nature and can be explained from the molecular movement near the TPCL. However, there is a dearth on the understanding of the CLF from its origin. In the present study, MD simulation has been performed on the spreading of a nanodroplet on a solid surface to unveil the CLF from its origin. In MD regime the solid surface is characterised by adjusting the depth of the potential well ( $\epsilon$ ) of liquid-solid Lennard-Jones interaction parameter. Our finding show, with variation in electric field (in the direction parallel to the surface), the droplet footprint and the contact angle (both leading & trailing) changes significantly. At 1V/nm electric field, 50% increase in the droplet footprint area and 32% decrease in contact angle is observed. A faster dynamic response of spreading in presence of electric field on a hydrophobic surface is observed. Movement of the TPCL during the spreading of the droplet is resisted by the CLF force which is manifested by TPCL friction coefficient  $\zeta$ , which is a function of the temperature, equilibrium frequency ( $k^0$ ) and average molecular displacement ( $\lambda$ ). The equilibrium frequency during the TPCL movement is affected by the temperature, substrate property or presence of any external disturbances, which lead to an alteration of  $\zeta$ . It is observed that  $\zeta$  reduces by 20% with 1V/nm electric field. Significant decrease in  $\zeta$  (~39%) with only 20K increase in temperature is observed for electrowetted nanodroplet. The alteration of CLF with temperature will have a potential application towards the characterisation of surfaces for electric field induced nanodroplet spreading.

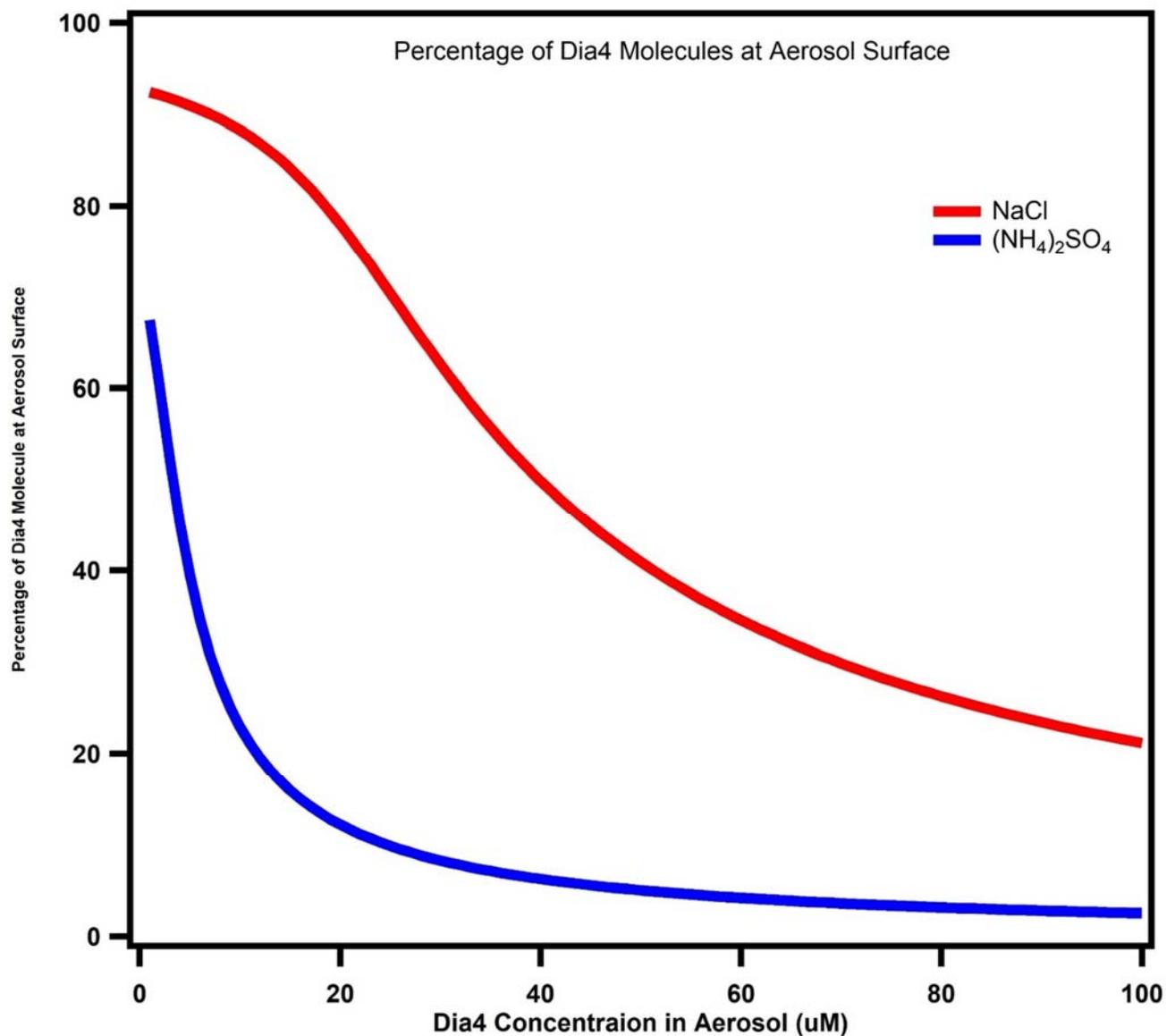
**COLL 794**

### **Molecular surface bulk equilibrium in aerosols**

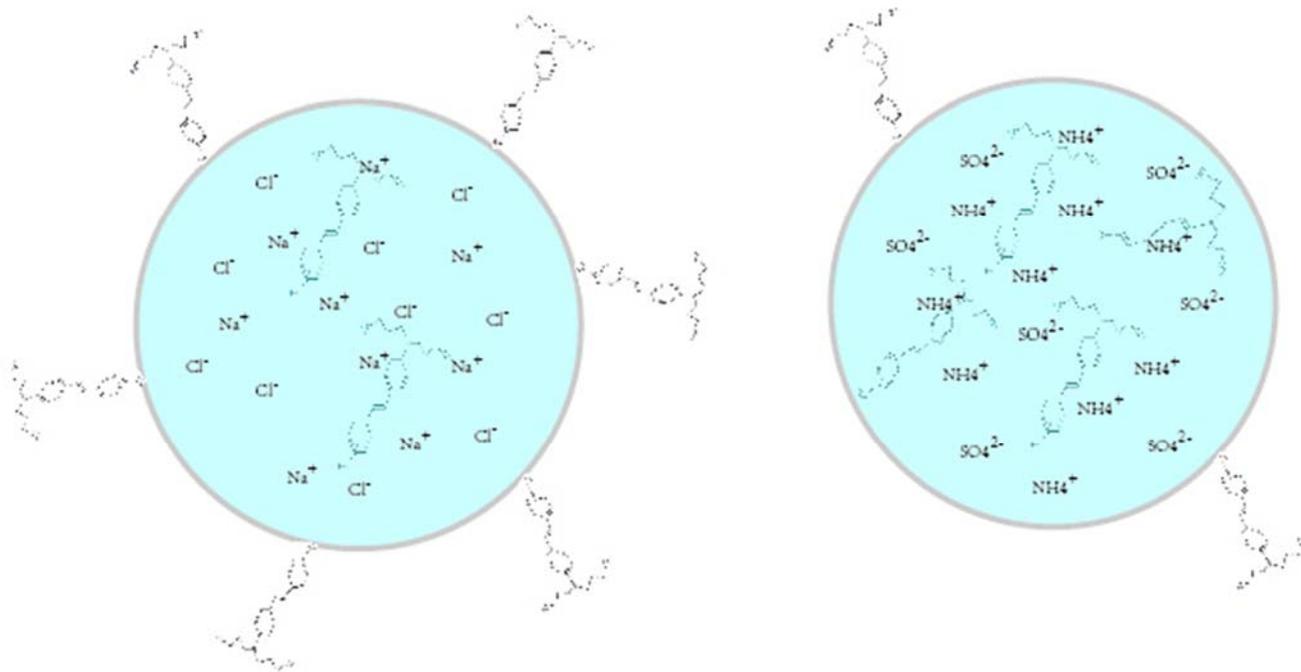
**Yuhao Wu**<sup>1</sup>, [yuhao.wu@temple.edu](mailto:yuhao.wu@temple.edu), **Yajing Wu**<sup>2</sup>, **Jianqiang Ma**<sup>1</sup>, **Hai-Lung Dai**<sup>3</sup>. (1) Chemistry, Temple University, Philadelphia, Pennsylvania, United States (2) Department of Chemistry, Temple Univ, Philadelphia, Pennsylvania, United States (3) CST Office of the Dean, Temple University, Philadelphia, Pennsylvania, United States

Atmosphere aerosols play an important role on global climate. It is essential to learn the composition, formation and reactions in aerosols. Air-water interface contribute a lot to aerosol properties since surface to volume ratio is aerosols is very high. In this work, we used second harmonic scattering (SHS), a surface specific tool, to study organic molecule equilibrium between aerosol bulk and interface. We generate aerosols using

TSI 3076 aerosol generator and use trans-4-[4-(dibutylamino)styryl]-1-methylpyridinium iodide (DIA4) dye to mimic organic molecules in aerosols. Second harmonic scattering (SHS) signal from aerosol air-water interface has been detected. We use modified Langmuir Model to fit the isotherm. The fitting result shows that dye concentration on aerosol surface is much higher than bulk and NaCl and  $\text{NH}_4\text{SO}_4$  have different impacts on dye equilibrium in aerosols. Besides, we do concentration correction of aerosols. Result shows that dye concentration in aerosols is higher than dye concentration in stock solution when using aerosol generator to generate aerosols. Because aerosol generation involve surface process and surface dye concentration is higher than bulk.



Based on modified Langmuir fitting parameters --  $N_{max}$  and rate constant  $k$ , we could simulate surface dye molecules vs. total dye molecules. Result shows that at low dye concentration, most of the molecules are all at aerosol surface. And different salt will affect the ratio of surface molecules.



In Sodium Chloride aerosols, more dye molecules are on the aerosol surface than bulk. However, in Ammonium Sulfate aerosols, dye molecules on surface are fewer.

## COLL 795

### Mechanisms underlying the simultaneous formation of hydrogen peroxide and reducing behavior in microdroplets of water

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Exciting reports on the simultaneous formation of hydrogen peroxide ( $H_2O_2$ ) and reduction of pyruvate, fumarate, lipoic acid, and oxaloacetate in microdroplets of water produced by pneumatic shearing of water (without electrical voltage or oxidizing or reducing agents) have appeared. These unexpected behaviors of water have been attributed to the air-water interface and used to speculate atmospheric and prebiotic phenomena, respectively,  $H_2O_2$  in nighttime clouds and the origins of life. Here, we systematically investigate these claims through microdroplets of water produced by:

pneumatic sprays, electrosprays, and electropneumatic sprays, and the results are analyzed by mass spectrometry, nuclear magnetic resonance, gas-chromatography, high-speed imaging, and laser diffraction. We show that there is a correlation between the applied pressure, the surface area of microdroplets, and the H<sub>2</sub>O<sub>2</sub> production, but the interfacial area is not the causation for the production of H<sub>2</sub>O<sub>2</sub>.

## **COLL 796**

### **Tunable aggregation-induced emission as an indicator of intermolecular distance in supramolecular assembly**

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Measuring the intermolecular distance in supramolecular structures in solution is important as well as challenging, especially for distance below 1.0 nm. The fluorescence emission is helpful in indicating intermolecular distances due to its sensitivity to the microenvironment, and the aggregation-induced emission (AIE) luminophores are especially useful against fluorescence quench in assembly and aggregation states. Herein, polyhedral oligomeric silsesquioxane (POSS) macroionic hybrids were synthesized with AIE luminophores (Tetraphenylethene, TPE or Tetra(biphenyl-4-yl)ethene, TPPE) chemically incorporated. The charged macromolecules self-assemble into hollow spherical blackberry-type stable supramolecular structures through the regulation of the electrostatic interactions. Macromolecules in the single-layered shell are closer to each other when assembled into spheres of larger size. The fluorescence emission was enhanced when more hybrids were involved in the assembly. The hybrid containing TPPE exhibits emission wavelength shift when macromolecules are closer to each other, due to the restriction of multiple rotatable C-C bonds connecting phenyl rings. Assembly in mixed solvent showed a more significant and tunable emission change in response to different intermolecular distances.

## **COLL 797**

### **Dipole-emitting semiconductor nanorods for luminescent solar concentrators**

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Luminescent solar concentrators (LSCs), those featuring quantum dots in particular, have gained much interest as a promising technology for improving the efficiency of

photovoltaic cells. These devices provide optical concentration via absorption and reemission of light from fluorophores embedded in dielectric media. Here, we introduce a strategy for integrating highly luminescent aligned semiconductor nanorods into an LSC in order to improve performance through enhanced light trapping. The proposed device features aligned CdSe/CdS dot-in-rod nanoparticles embedded in an optically transparent polymer matrix. This talk will discuss how an AC electric field is used to achieve maximum alignment in a colloidal dispersion of nanorods. We monitor the optical response of samples under field alignment to gain quantitative insight into the degree of alignment. By measuring the time-dependent change in fluorescence anisotropy, we have calculated the average deviation of nanorods at maximum alignment to be  $22^\circ$  with respect to the field vector. Dispersing the nanorods in a UV-curable resin allows samples to be immobilized under an electric field. While dynamic alignment has been demonstrated in both solution and resin media, maintaining alignment during the curing process has been a major challenge. With further optimization, we believe that this novel approach can help surpass limiting efficiencies for LSC-photovoltaic systems.

## **COLL 798**

### **RF mediated release of fluorophores from magnetic nanoparticles by hysteretic heating**

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Improved spatiotemporal control of drug release can address common concerns such as acute toxicity from therapeutics and off target effects of drugs. The ability of magnetic nanoparticles (MNPs) to generate heat locally in response to alternating magnetic field radio frequency (AMF-RF), its recognized bio-compatibility, and use in clinical practice, make MNPs appealing candidates for biomedical applications. By tethering therapeutics to the surface of magnetic nanoparticles via a thermally labile linker (i.e. a retro-Diels Alder cycloadduct), one could theoretically cage a therapeutic in an inactive state on the surface of nanoparticles, and have subsequent control over the therapeutics release by stimulation from a specific AMF-RF. Additionally, one could use the same linker, different therapeutics, and different nanoparticles in the same solution

for sequential release of therapeutics from different sized and/or composition nanoparticles.

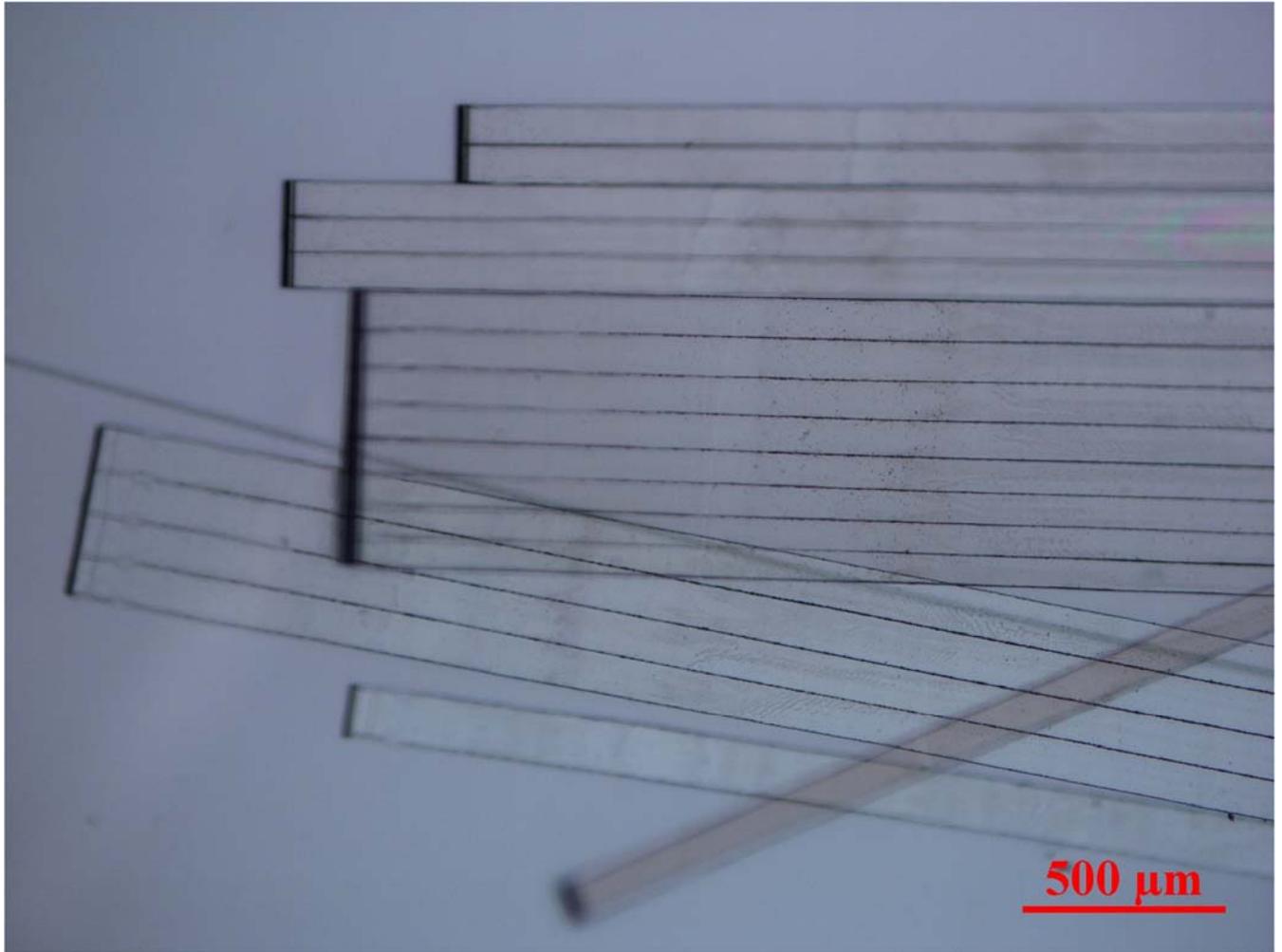
In this study, controlled release of fluorophore analogues from different size and composition magnetic nanoparticles were demonstrated using similar Diels-Alder linkers. Differential heating of different sized and composition nanoparticles for heteroplexed temporal controlled release of conjugated fluorophores from the surface of nanoparticles was demonstrated. By exploiting the differences in size and composition of nanoparticles ( $MFe_2O_4$  ( $M = Fe, Co$ )), we were able to control the amount of hysteretic heating occurring with distinct sets of magnetic nanoparticles using the same AMF-RF. Using thermally labile retro-Diels-Alder linkers conjugated to the surface of nanoparticles, the fluorescent payload from the different nanoparticles disengaged when sufficient energy was locally generated during hysteretic heating.  $^1H$ ,  $^{13}C$  NMR, ESI-MS, and SIMS characterized the thermally responsive fluorescent linkers used in this study; the Diels Alder cycloadducts were modeled using DFT computations. The localized heating ( $<60^\circ$ ) from the different nanoparticle compositions, drove the retro-Diels-Alder reaction at different times resulting in higher release rates of fluorophores from  $CoFe_2O_4$  vs  $Fe_3O_4$  nanoparticles.

## **COLL 799**

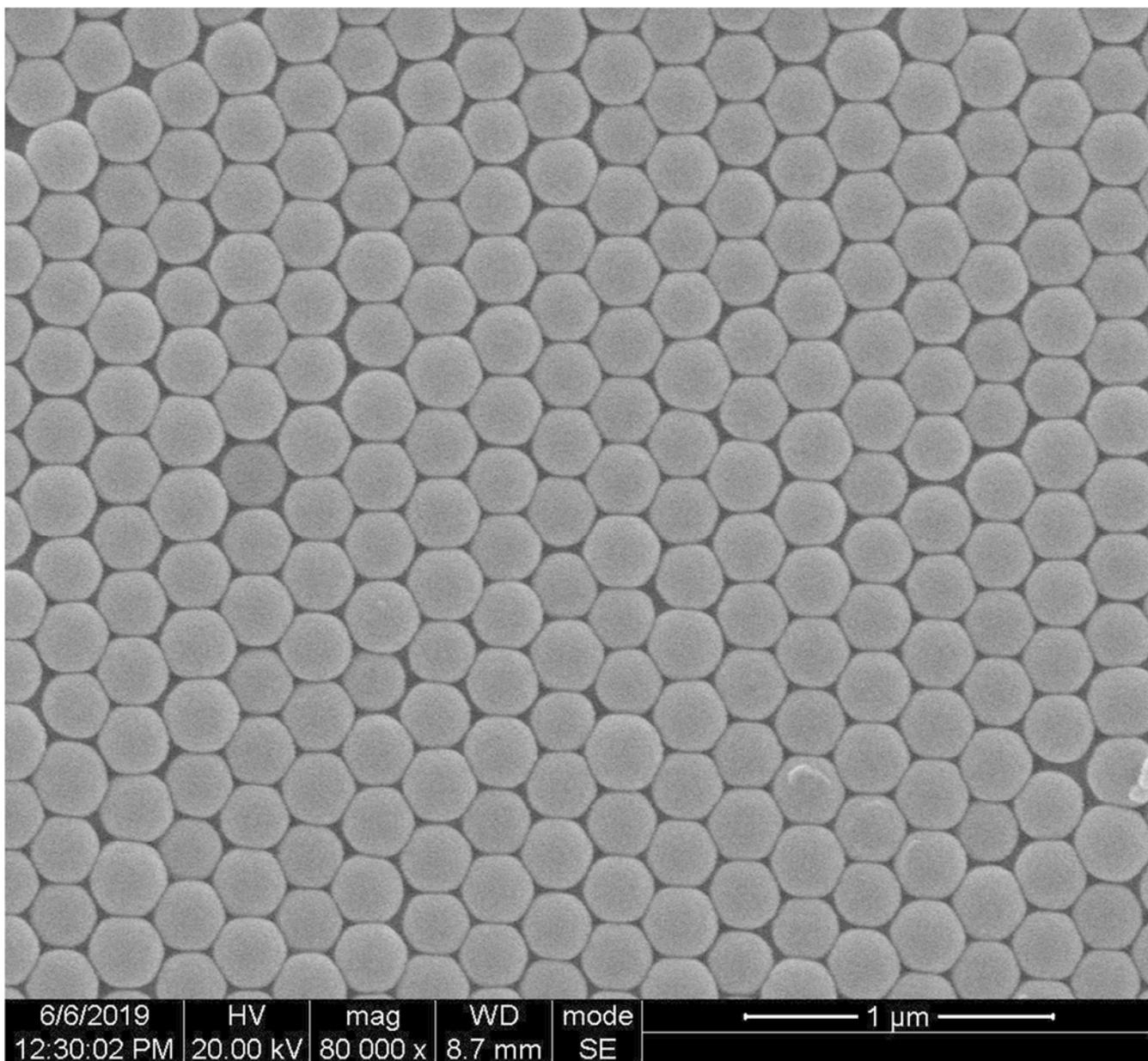
### **Crack-induced colloidal rods**

*Jingli Xie, jinglixie@163.com, Xu Deng.* University of Electronic Science and Technology of China, Chengdu, Sichuan, China

While a wet film containing colloidal nanoparticles (NPs) drying on a substrate, it often generates cracks. Crack formation is found useful in a variety of industrial products and techniques, including clay, ceramic coating and lithology. Herein, by tuning this crack formation carefully, we are able to obtain robust and highly transparent rods composed of colloidal NPs with uniform width and thickness. The morphology of these rods are strongly affected by solvent composition, NPs volume fraction and vial radius. Their mechanical property can be further reinforced by annealing. Further, these rods are used as probes for Surface-enhanced Raman scattering (SERS) detection making use of their rich nanostructured surface. This strategy for colloidal rods preparation is simple and might be further developed in large-scale, providing new opportunities for many technological fields.



An optical image of colloidal rods



An SEM image of the well-ordered colloidal rods.

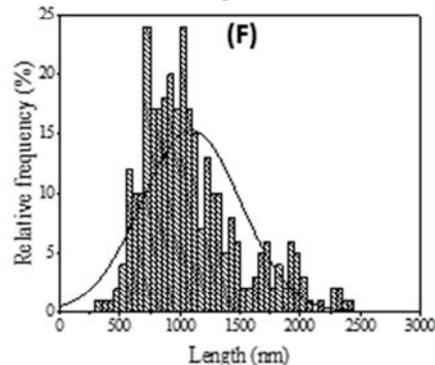
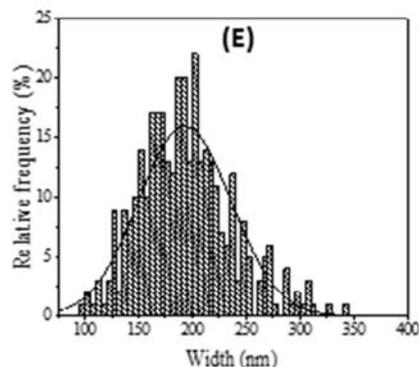
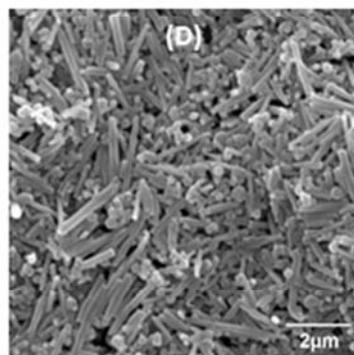
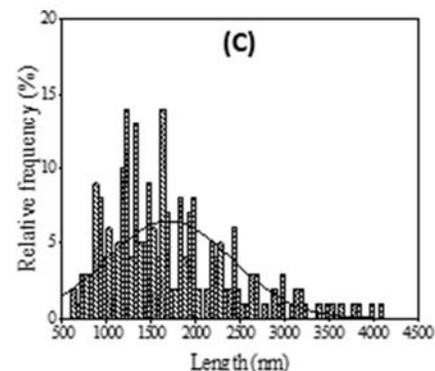
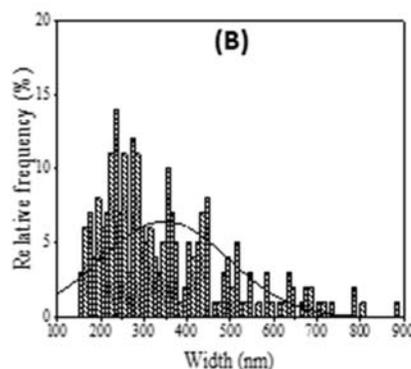
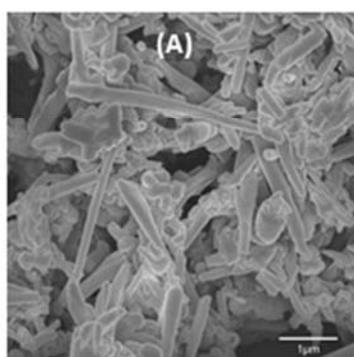
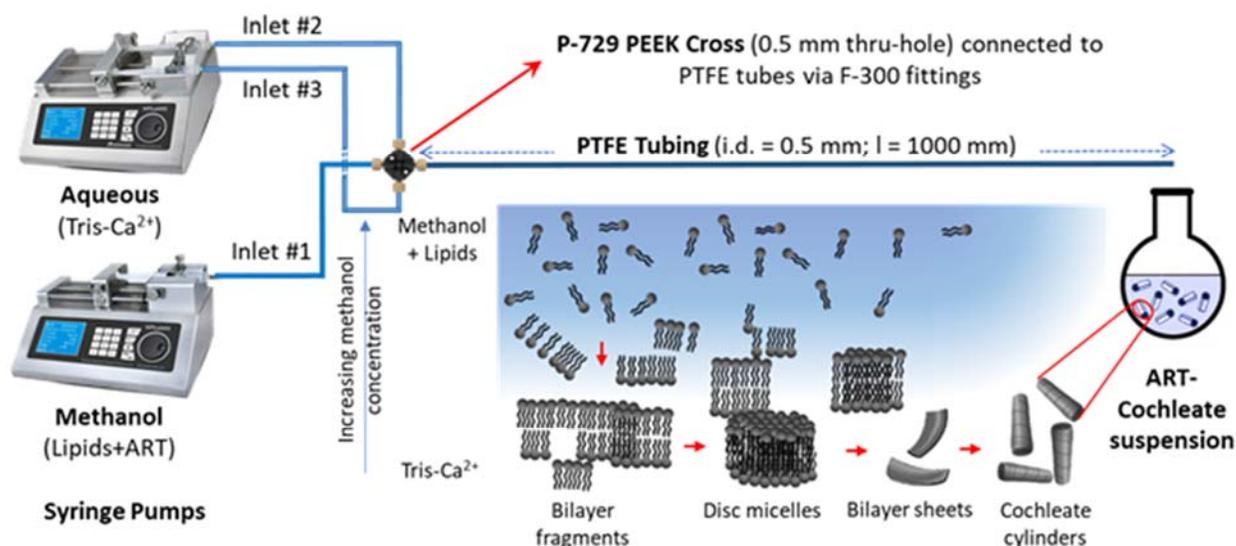
## **COLL 800**

**Continuous production of supramolecular cochleates using facile off-the-shelf flow focusing device**

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Lipid are gaining increasing interest as colloidal drug-carriers. Cochleates are a class of supramolecular structures consisted of large and continuous sheets of lipid bilayers rolled up to form cylinder-like solid particulates. They offer great potential as a vehicle for the oral delivery of drugs with low bioavailability, due to their high drug encapsulation, controlled-release capabilities and mechanical resilience. However, their preparation relies on conventional batch processes that are complex, time consuming and lack batch-to-batch reproducibility; presenting a bottleneck for clinical translation. We report an efficient continuous preparation process for artemisinin-loaded cochleates (ART-cochleates) using inexpensive off-the-shelf flow focusing device. By carefully controlling the flow focusing parameters, we showed along with the mechanism that, ART-cochleates of uniform and tuneable size (~180 nm in width and ~1030 nm in length) were obtained with low dispersity (0.18 in width and 0.27 in length), narrow size distribution and high reproducibility compared to the batch process. The device achieved high throughput of 11.5 g/day with ART encapsulation of  $64.24 \pm 2.5$  % and loading of  $83.37 \pm 3.68$  mg ART/g of cochleates. Art-cochleates were non-toxic and showed sustained in-vitro release of ART with effective transepithelial permeability across intestinal Caco-2 monolayer (~60% and ~25% transport for pure ART and ART-cochleates, respectively) resulting in better in-vitro bioavailability. Hence, the off-the-shelf device is envisioned to be highly promising platform for continuous and high-throughput manufacturing of drug-loaded cochleates in a controlled and reproducible manner. It has potential to enable clinical translation of drug-loaded cochleates with predicable drug release, absorption and bioavailability.

## Continuous production of supramolecular cochleates using facile off-the-shelf flow focusing device



Representative SEM of ART-cochleates in prepared in batch (A). Representative particle size distribution in width and length of the cochleates prepared in batch, (B) and (C), respectively. SEM of ART-cochleates prepared in-flow at total volumetric flow rate ( $Q_t$ ) of 8.0 mL/min and flow rate ratio (FRR) of 3.0 (D). Representative particle size distribution of ART-cochleates prepared in-flow in width (E) and length (F).

- ✓ Continuous production of ART-cochleates with high-throughput
  - ✓ Simple, scalable and inexpensive off-the-shelf device
  - ✓ Excellent particle size control, ART-loading and encapsulation
    - ✓ Non-toxic to intestinal Caco-2 cells
    - ✓ Sustained ART-release and better bioavailability

## COLL 801

### **Assembly of covalently-linked quantum dot heterostructures: Characterization of excited-state charge-transfer dynamics in dispersed and multilayered systems**

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Semiconductor quantum dots (QDs) are prime candidates as harvesters of light and donors of excited charge carriers for solar energy conversion. Our group's recent efforts have established the validity of utilizing carbodiimide-mediated coupling chemistry to selectively tether two QDs through the formation of an amide bond between the terminal functional groups of capping ligands. The unique properties of QDs can be exploited to tune energetic offsets to promote interfacial charge transfer between QDs. We previously reported on excited-state hole transfer in dispersed CdS/CdSe QD heterostructures, which exhibit quasi-type-I energetic offsets. Unfortunately, type-I energetic offsets rely on the excitation of one QD component, which promotes recombination as a result of charge transfer occurring in only one direction. To address this issue, we synthesized and characterized CdSe/CdTe QD heterostructures, which exhibit type-II energetics. Type-II energetics promote interfacial charge separation, irrespective of which constituent QD is initially excited. Moreover, the CdSe/CdTe QD heterostructures afford enhanced control over the thermodynamic driving forces for charge transfer. Within these systems photogenerated holes are transferred from CdSe to CdTe on timescales of  $10^{-8}$  s.

In an effort to further extend charge separation and to slow charge recombination, we have prepared ternary heterostructures. A covalently-linked bilayer of QDs was immobilized on a metal oxide substrate to promote an additional stepwise excited-state charge transfer process, facilitating extended spatial separation of charge carriers and longer charge-separated state lifetimes.

Dynamic quenching of emission was observed in heterostructure-modified thin films, consistent with excited-state charge transfer. Rate constants for photoinduced hole transfer between QDs are on the order of  $10^7$  s<sup>-1</sup>. CdSe/CdTe heterostructures exhibit bidirectional charge transfer, in which the rate constant for photoinduced electron transfer from CdTe to CdSe was estimated to be on the order of  $10^8$  s<sup>-1</sup>. These results demonstrate that carbodiimide-mediated coupling chemistry can be used to immobilize QD multilayers on metal oxide substrates, and that such assemblies undergo rapid charge transfer to facilitate extended charge separation. This presentation will highlight these recent results as well as our ongoing time-resolved spectroscopic characterization of photoinduced charge transfer in CdSe/CdTe systems.

## COLL 802

## **Effect of duty cycle on self-assembling superparamagnetic colloids in the toggled-field**

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Engineering magnetorheological fluids with an external field is motivated by building colloidal structures with an enhanced packing and periodicity. Superparamagnetic colloidal particles are assembled in toggled magnetic fields by switching on and off the field repeatedly. At sufficiently high field strengths, the suspension begins to form a microstructure, and its fluidic behavior experiences a solid to gel-like state transition. The suspension is then further condensed into droplet-like domains by a competition between the time-averaged bulk and surface energies. In this study, the effect of the duty cycle of the toggled field is investigated where four general structures are observed after enough assembly time is given: fluid, columnar, percolated, and ellipsoidal-shaped structure. Two distinct kinetic pathways are observed. The microstructure forms the ellipsoidal state by diffusion-driven particle aggregation in an early stage and the growth rate increases at a breakthrough time. By contrast, for columnar- and percolated-states, initially aggregated structures are arrested and no rate transition occurs. Interestingly, under a small range of assembly conditions (1.5-3.5 Hz, 0.2 duty cycle ratio), a new class of wavy-shaped microstructures is formed which exhibits the rotational emergent dynamics with continuous coalescence and breakup processes. These dynamics are analyzed by toggling external field that causes an asymmetric combination of ballistic and diffusive motion.

### **COLL 803**

#### **Synthesis and characterization of water-soluble phosphine gold nanoclusters**

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Great advancement in the synthesis of ultrasmall gold nanoclusters (AuNC) has resulted in the wide application of these materials in various fields including catalysis, nanoelectronics and nanomedicine. Several passivating ligands of AuNC have been successfully employed, including phosphines, thiolates, and more recently *N*-heterocyclic carbenes. Of these, the meta-stable phosphine-capped AuNC (PGC) have shown the most interesting biological activities as antitumor and antibacterial agents, mirroring the activity of their corresponding gold (I) complexes. The reduced stability of PGCs presents a challenge in synthesis and characterization, requiring controlled reaction and purification conditions particularly in aqueous media. In this work, we present several synthetic strategies of PGCs capped with aliphatic and aromatic water-soluble functional groups and demonstrate their application as biologically active compounds.

## **COLL 804**

### **Equilibrium assembly of metal oxide nanocrystals using dynamic covalent chemistry**

**Manuel N. Dominguez**<sup>1</sup>, [domingun@email.usca.edu](mailto:domingun@email.usca.edu), **Josef Maier**<sup>1</sup>, **Stephanie Valenzuela**<sup>1</sup>, **Michael Howard**<sup>2</sup>, **Delia J. Milliron**<sup>2</sup>, **Eric V. Anslyn**<sup>3</sup>, **Thomas Truskett**<sup>4</sup>. (1) Chemistry, The University of Texas at Austin, Austin, Texas, United States (2) Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas, United States (3) A1590 NHB 5.114, UTexas Chem and Biochem, Austin, Texas, United States (4) Department of Chemical Engineering, University of Texas at Austin, Austin, Texas, United States

Nanocrystals exhibit unique optical and electrical properties that make them a key component for next-generation optoelectronic devices. Assembling these nanocrystals through gelation allows them to retain their nanoscale properties while they are employed in multiscale architectures. However, nanocrystal assembly through gelation is typically irreversible, offers little control over the size of nanocrystal clusters and is non-specific to a particular linker. Here, we demonstrate that by using dynamic covalent chemistry one can introduce specific interactions between nanocrystals to achieve an assembly size from small clusters to a larger gel network, with a reversible manner. To establish these interactions, we functionalize the nanocrystals with peptide synthesized ligands having aldehyde functional groups and pair them with a complimentary linker molecule having di-hydrazide functional groups to form networks. This pairing forms a di-hydrazone product which enables the link between nanocrystals and offers a wide control over the size of the network formed. Moreover, the introduction of a capping molecule allows the network to delink forming smaller clusters and possibly returning them to a discrete nanocrystal state. This work aims to introduce a technique to form programmable gel assemblies from a variety of nanocrystals with different compositions.

## **COLL 805**

### **Swimming behavior of bacteria increases number and duration of bacterial-surface engagements**

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Because motility is associated with bacterial pathogenesis, there is general interest in studying the interactions of swimming bacteria with biomaterial surfaces. *E. coli*, a bacterial type associated with disease and biomaterial infections, includes motile phenotypes that swim using a bundle of several flagella. When in close proximity to a surface the swimming behavior of bacteria is affected by the presence of the wall.

This work studies the initial dynamic interactions that occur between *Escherichia coli* and a model non-adhesive Poly-L-lysine-poly(ethylene glycol) random graft co-polymer in the presence of shear flow. By studying the interactions between this non-adhesive surface and single bacteria in the presence of shear flow this talk will show the likely mechanisms for bacteria- surface engagement and disengagement.

To accomplish this, we designed a model *Escherichia coli* system that allows for the decoupling of bacteria motility with the presence of flagella. By using bacteria strains that have separately knocked out the production of flagella and the flagella motor we were able to show how swimming of *Escherichia coli* increases both the frequency of bacteria encountering a surface and the durations of the resulting engagements, near a single wall in shear flow, due to hydrodynamic and potentially due to short lived interactions between polyethylene glycol and the cell. This swimming effect was decoupled from the effect of flagella interactions. It was found that the presence of flagella, when not active, producing steric kicks, increasing the escape frequency and as a result reducing surface engagements length.

## **COLL 806**

### **Gallery of trajectories for motile bacteria at fluid interfaces**

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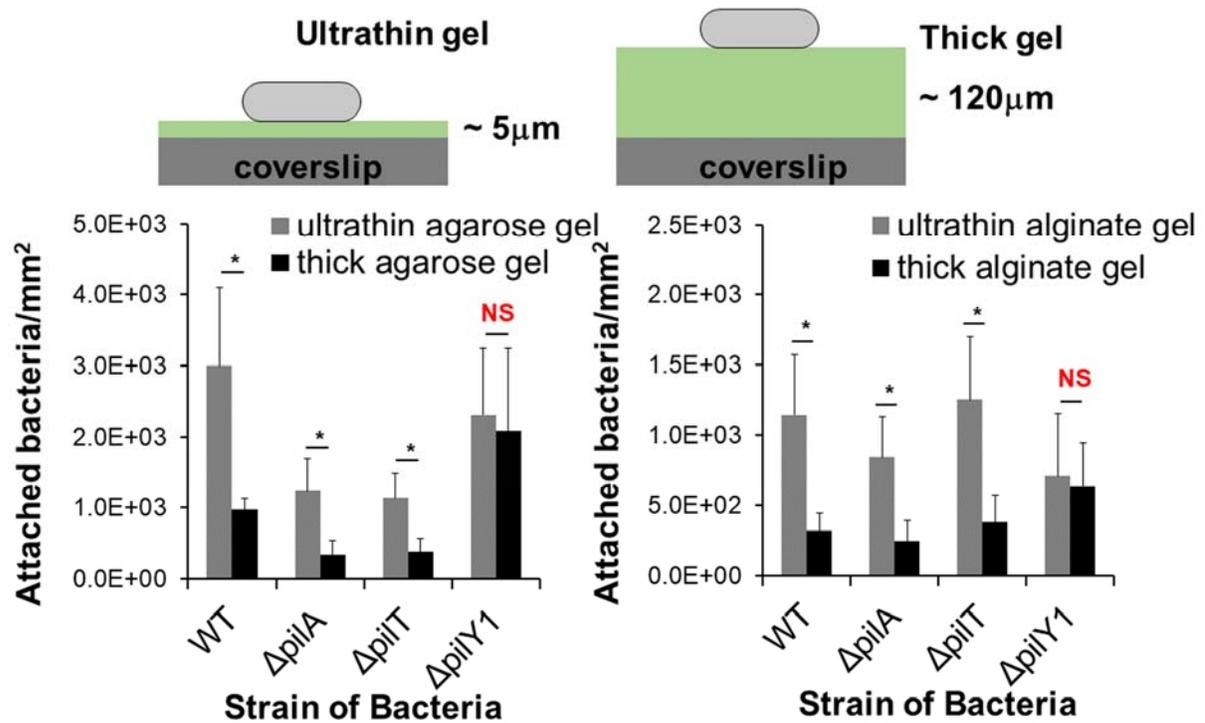
Active colloids can accumulate at fluid interfaces and move in manners strongly influenced by this complex 2D fluid environment. We seek to understand their motions and their consequences to develop building blocks for 2D materials that are truly surface *active*. Bacteria are important examples of active or self-propelled colloids. Because of their directed motion, they can become trapped and swim adjacent to the interface via hydrodynamic interactions, or they can adsorb directly and swim in an adhered state. We study *Pseudomonas aeruginosa* PAO1 on or near hexadecane-water interfaces as a model system. In addition to characterizing the ensemble behavior of the bacteria, we have observed a gallery of distinct trajectories of individual swimmers on and near fluid interfaces. These include Brownian diffusive paths, curvilinear trajectories including curly paths with radii of curvatures larger than the cell body length and rapid pirouette motions with radii of curvature comparable to the cell body length. Finally, we see interfacial visitors that come and go from the interfacial plane. We characterize these individual swimmer motions and propose the relevant implications on microrobots and interfacial transportation.

## **COLL 807**

### **Bacterial mechanosensing upon attachment to gels of different stiffness: Tale of two (or more?) steps**

**Vernita D. Gordon**, [gordon@chaos.utexas.edu](mailto:gordon@chaos.utexas.edu), *Liyun Wang*, *Jacob Blacutt*. University of Texas at Austin, Austin, Texas, United States

The attachment of bacteria to a surface is often a key initial step in the development of biofilms, communities of bacteria that are significant contributors to disease, fouling, and damage to the built environment. Recently, work from several groups has indicated that bacteria may be able to sense and respond to mechanical cues from their environment. Understanding how bacteria sense surface attachment and, in response, begin the process of biofilm initiation, has the potential to give rise to new avenues to biofilm prevention; such understanding would also be a major advance in basic science, since very little is known about bacterial mechanosensing. Here, we examine the relationship between substrate stiffness, mechanical deformation of the bacterial cell, accumulation of bacteria on the surface, and dynamics of the cyclic-di-GMP intracellular signal that is widely used as a second messenger to control biofilm development. Our model organism for these studies is *Pseudomonas aeruginosa*, a widely-used model organism for biofilm development and a common hospital-acquired pathogen. We find that when the chemistry of a gel substrate (alginate, agarose, or cross-linked poly-ethylene glycol) is held constant but the effective elasticity is varied, bacteria accumulate more on, and activate cyclic-di-GMP signaling earlier on, a stiffer substrate. We further show that the response to the substrate mechanics at times greater than one hour after attachment depends on different cellular structures than does the response to substrate mechanics at times less than one hour after attachment. This shows that bacterial mechanosensing leading to biofilm development is likely a multi-step process involving more than one sensory element.



## COLL 808

### Reversible attachment, surface sensing, and memory in early bacterial biofilm development

**Gerard Wong**, [gclwong@seas.ucla.edu](mailto:gclwong@seas.ucla.edu). bioengineering, chemistry, UCLA, Los Angeles, California, United States

Bacterial biofilms are integrated communities of cells that adhere to surfaces and are fundamental to the ecology and biology of bacteria. Although they possess the machinery to sense, adhere to, and proliferate on surfaces, it is commonly observed that bacteria initially have a difficult time attaching to a surface: Free-swimming, planktonic bacteria exhibit a variable and seemingly random period of transient surface attachment known as “reversible attachment” before committing to a surface, which is not well understood. Using community tracking methods at single-cell resolution, lineage reconstruction techniques, and an exactly soluble stochastic model, we show that different strains develop different coordinated social solutions to surface attachment: Besides attaching itself to the surface, *P. aeruginosa* PA01 cells use a strategy that also facilitates attachment of spatial neighbors, whereas *P. aeruginosa* PA14 cells use a complementary strategy that facilitates continued attachment of their progeny. We also investigate how these cells eventually commit to the surface via the pivotal process of “irreversible attachment”, by elucidating the interplay between surface

sensing, multigenerational memory via secondary messengers, and resultant modulation of motility appendages and exopolysaccharide production.

## **COLL 809**

### **Impact of variations in soft non-adhesive coatings on the swimming character and surface contact of *E. coli***

**Maria M. Santore**, [santore@mail.pse.umass.edu](mailto:santore@mail.pse.umass.edu), Molly Shave. Dept of Polymer Science, University of Massachusetts, Amherst, Massachusetts, United States

*E. coli* and some other common motile bacteria swim via the rotation of multiple flagella which bundle together through the rotation of motors at the base of the flagella. Near a rigid surface, these cells swim in clockwise circles in quiescent conditions but at air-water interfaces, they circle in the opposite direction. Near minimally adhesive biomaterial surfaces in gentle flow (10-20 s<sup>-1</sup> wall shear rate), relevant to infections on biomedical devices, we find that these cells travel mostly in lines in the flow direction and circular swimming is not apparent. Importantly, the character of this linear travel is highly dependent on the mechanics and water content of nonadhesive coatings on the wall of the flow chamber. This talk demonstrates how polyethylene glycol (PEG), hydrogels or brushes containing 50-90% water and varying in modulus from O(100-1000 kPa), influences swimming character. First, it is clear, based on relatively slow cell velocities and smooth near-surface trajectories, that swimming cells approach within nanometers of the coating surface (as defined by the point of zero shear). Motile cells travel more slowly (by a few  $\mu\text{m/s}$ ) than a non-motile flagella-containing control strain. Both motile and control cells escape the surface with a frequency on the order of a second, but the motile cells have a high probability of returning to the surface (90%) compared with non-motile cells which act diffusively near stiff hydrogels and brushes. By contrast, near the watery soft hydrogels, the return efficiency of swimming cells matches the diffusive character of non-motile controls, suggesting an influence of the material on the fundamental swimming character of the cells as one possible explanation.

## **COLL 810**

### **Bacterial interactions with soft medical device materials**

*sang lee*<sup>1</sup>, *Hao Wang*<sup>1</sup>, *Yi Wang*<sup>1</sup>, *Shin Hainsworth*<sup>1</sup>, *Dacheng Ren*<sup>2</sup>, ***kenneth s. phillips***<sup>1</sup>, [Kenneth.Phillips@fda.hhs.gov](mailto:Kenneth.Phillips@fda.hhs.gov). (1) CDRH/OSEL/DBCMS, US Food and Drug Administration, Silver Spring, Maryland, United States (2) Syracuse University, Syracuse, New York, United States

The Office of Science and Engineering Laboratories (OSEL) in FDA's Center for Devices and Radiological Health is accelerating patient access to innovative, safe and effective medical devices through best-in-the-world regulatory science. Researchers in the Biofilms Research Group, in OSEL's Division of Biology, Chemistry and Materials

Science, have studied a number of bacteria-soft materials interaction issues related to medical devices—including dermal fillers and breast implants. We will discuss how the viscoelastic properties of ultrasoft cosmetic filler products played important and unexpected roles in bacterial adhesion and colonization, with as much as a four-log difference in surface area adhesion levels. We will show how this research resulted in specific suggestions to clinicians on how to reduce the risk of infections associated with permanent dermal fillers. We will also report more recent research results for bacterial adhesion to textured silicone breast implant materials. Some researchers believe that bacterial adhesion to textured materials may be associated with a higher rate of lymphoma that is found primarily with textured breast implants. Related to this concern, we will present emerging results that suggest a mechanism for bacterial adhesion on textured implants. Finally, we will discuss key concepts for realistic biofilm testing in the context of medical devices.

## **COLL 811**

### **Bacteria as living patchy colloids: Phenotypic heterogeneity in surface adhesion**

**Wilson Poon**, *W.Poon@ed.ac.uk*. University of Edinburgh, Edinburgh, United Kingdom

Understanding and controlling the surface adhesion of pathogenic bacteria is of urgent biomedical importance. However, many aspects of this process remain unclear (for example, microscopic details of the initial adhesion and possible variations between individual cells). Using a new high-throughput method, we identify and follow many single cells within a clonal population of *Escherichia coli* near a glass surface. We find strong phenotypic heterogeneities: A fraction of the cells remain in the free (planktonic) state, whereas others adhere with an adhesion strength that itself exhibits phenotypic heterogeneity. We explain our observations using a patchy colloid model; cells bind with localized, adhesive patches, and the strength of adhesion is determined by the number of patches: Nonadherers have no patches, weak adherers bind with a single patch only, and strong adherers bind via a single or multiple patches. We discuss possible implications of our results for controlling bacterial adhesion in biomedical and other applications.

## **COLL 812**

### **Surface energy analyses to inform the inhibition of biofilm formation**

**Thomas B. Cavitt**, *tbcavitt@lipscomb.edu*, **Jasmine G. Carlisle**, **Daniel S. Oskin**, **Verena N. Ghebranious**, **Emily B. Henry**, **Wenting Wei**. Chemistry and Biochemistry, Lipscomb University, Nashville, Tennessee, United States

Biofilms, found in various surfaces, are the habitat of 95% of the earth's bacteria and successfully protect bacteria from many antibiotics. By inhibiting biofilm formation, the propagation of infectious bacteria could be deterred. However, inhibiting biofilm formation is difficult in that it is a symbiotic, dual determinant system involving 1) the

substrate surface and 2) bacterial adhesins. In our research group, we coupled surface analyses via contact angle measurements with a linear algebraic method to solve the Owens-Wendt and van Oss-Chaudhury-Good equations to determine the surface energy profile of both the substrate surface and collagen, a representative bacterial adhesin. Based on the surface energy profiles and Cassie's equation for formulated surfaces, we can posit a substrate composition that will inhibit biofilm formation of specific bacteria. Herein, we will briefly describe some of our results and the implications thereof regarding the inhibition biofilm formation.

## **COLL 813**

### **Probing interactions between synthetic bilgewater emulsion and biofilms**

**Xiao-Ying Yu**, [xiaoying.yu@pnnl.gov](mailto:xiaoying.yu@pnnl.gov), **Jiyoung Son**. Pacific Northwest National Laboratory, Richland, Washington, United States

Bilgewater, an oil-in-water (O/W) emulsion, is a persistent pollutant released to the ocean from the lowest part of ships. Microbes play an important role in the ocean. We hypothesize that microbes release organics and act as a source of surfactants and affect bilgewater formation or weakening. We present the first systematic study of emulsions and biofilms and investigate the effects of biofilms on bilgewater emulsions. A Navy O/W emulsion consisting of three oils and a detergent mixture was used as the synthetic bilgewater model. Of particular interest we compared bilgewater interactions with and without *Pseudomonas*. Biofilms were cultured in a microchannel to allow healthy culture. Once a thick layer of biofilms was formed in a microreactor, the medium solution was changed to a mixture consisting of 50 % bilgewater emulsion. Dispersed biofilms were collected at 24 hrs. and 48 hrs. after emulsions were introduced into the channel. Bilgewater emulsions, biofilms, and mixtures of bilgewater emulsions and biofilms were analyzed using multiple *in situ* and *ex situ* techniques including time-of-flight secondary ion mass spectrometry (ToF-SIMS), scanning electron microscopy (SEM), and optical microscopy. Our findings indicate that biofilms change the chemical makeup of the emulsion surface compositions and emulsion droplet size distribution, confirming the hypothesis that extracellular polymeric substance (EPS) related components released from biofilms can function as surfactants and change the oil-in-water interfaces.

## **COLL 814**

### ***In operando* Identification of active catalytic species during hydrolysis of DMNP by zirconium MOFs**

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Zirconium based metal organic frameworks (MOFs), such as UiO-67, are potential candidates for applications in chemical warfare agent mitigation due to their ability to hydrolyze dimethyl nitrophenyl phosphate (DMNP), a simulant of Soman (GD). However, the exact mechanism of catalytic action and the nature of the active catalytic sites is unclear. A critical evaluation of the activity of the precursors,  $ZrCl_4$  and the organic linker biphenyl dicarboxylic acid (BPDC), under basic aqueous conditions reveals key mechanistic details of the hydrolysis of DMNP by UiO-67 MOFs. Using  $ZrCl_4$  the reaction proceeds to completion on a similar timescale as the UiO-67 MOFs. However, BPDC linkers show no activity towards the hydrolysis of DMNP. We hypothesize that *in situ* conversion of  $ZrCl_4$  to zirconium-oxy-hydroxide, after dissolution in basic aqueous medium, provides the catalytic centers necessary for the reaction. Similar studies performed using  $Zr(OH)_4$  and  $HfCl_4$  provide key insights into the behavior of different metals and their role in the mechanism of DMNP hydrolysis. In comparison to the MOFs, the longer half-life of DMNP hydrolysis by  $Zr(OH)_4$  can be attributed to the aggregation of  $Zr(OH)_4$  forming larger crystallites in the solution thereby reducing the effective surface area available for the hydrolysis. Our studies provide insight into the mechanism of DMNP hydrolysis by zirconium-MOFs, revealing evidence for the active catalytic species, the MOF node, driving the reaction and aids in synthesizing hybrid materials with superior properties and better catalytic activities.

## **COLL 815**

### **Programmable and smart sponges**

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Metal-organic frameworks (MOFs) are a class of solid-state materials built up from metal-based nodes and organic linkers. They exhibit permanent porosity and unprecedented surface areas which can be readily tuned through coordination chemistry at the inorganic node and/or organic chemistry at the linkers. The high porosities, tunability, and stability are highly attractive in the context of catalysis. As exemplified by many catalytic enzyme assemblies in nature, site-isolation is a powerful strategy for performing catalytic reactions. MOFs provide an exciting platform for deploying catalysts in a site-isolated fashion and the cavities surrounding them can be engineered to conceptually mimic enzymes. This talk will address new advances in the synthesis and catalytic activity of MOF and POM@MOF materials developed at Northwestern University

## **COLL 816**

## Controlling the reactivity of the $[P_8W_{48}O_{184}]^{40-}$ inorganic ring and its assembly into POMzite inorganic frameworks

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Polyoxometalate (POM)-based materials are a family of compounds known for their rich structural diversity and properties. Over the years many synthetic strategies have been developed to control the self-assembly of the POMs as effective anionic molecular inorganic building blocks. One of the most recent successes of this strategy was made possible by using the superlacunary cyclic heteropolyanion  $[P_8W_{48}O_{184}]^{40-}$  (abbreviated as  $\{P_8W_{48}\}$ ) as a building block for the construction of intrinsically porous all-inorganic framework materials, named POMzites. Polyoxometalate-based framework materials, or POMzites, are an emerging class of configurable all-inorganic porous materials and in this talk I will give an overview of the structural types, synthesis, and how design may allow a range of new applications, as well as the new science that is emerging from the exploration of these materials.

### COLL 817

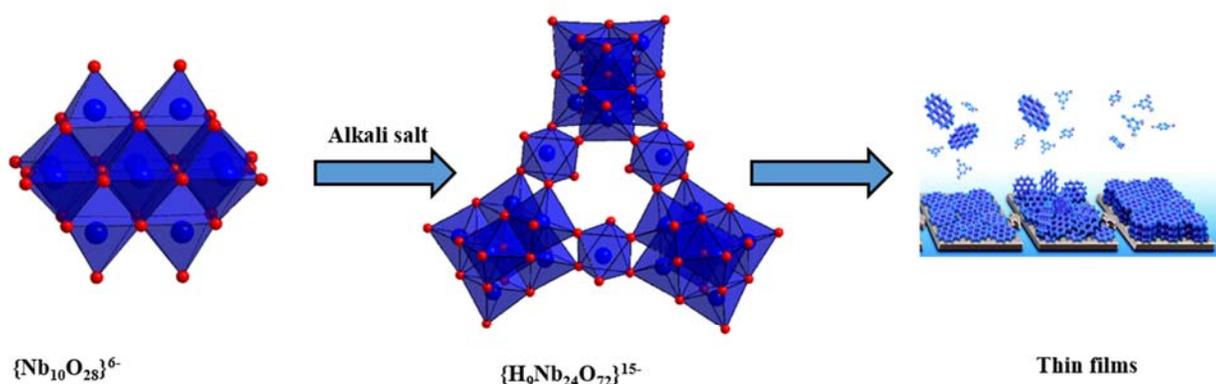
#### Advanced functional films from $\{Nb_{24}\}$ polyoxometalates

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Polyoxometalates (POMs) are usually soluble in water and are good precursors for thin film deposition, to be preserved in the molecular form or converted to a related metal oxide. These thin films can be used for piezo and ferroelectric response, energy storage, optical coating, catalysts, dielectrics, etc. In our research, we are interested in developing aqueous deposition chemistries for niobate thin film and thin films with intact POM clusters. Current foci include potassium sodium niobate ( $K_{0.5}Na_{0.5}NbO_3$  or KNN), lithium niobate ( $LiNbO_3$ ), niobium oxide ( $Nb_2O_5$ ) and films containing the intact POMs. The KNN thin films are promising lead-free alternatives for PZT materials.  $LiNbO_3$  thin films have optical properties.  $\{Nb_{24}\}$  POMs can be used for catalysis and  $Nb_2O_5$  thin films can have a variety of applications including catalysts, dielectrics, etc. We are also interested in comparing the catalytic activity of  $\{Nb_{24}\}$  in solution,  $\{Nb_{24}\}$  thin films within a polymer matrix and  $Nb_2O_5$  from Nb-POMs, to help understand catalytic mechanisms. We are studying DFP (nerve agent simulant) degradation, with these three media.

Prior aqueous deposition studies of niobate thin films from alkali salts of small POMs presented problems included crystallization of the films at higher concentrations and poor solubility. This leads to multilayer deposition processes and rough films morphologies.  $\{Nb_{24}\}$  is highly soluble with all counterions and shows promise in catalytic activity. We will present solution deposition of  $\{Nb_{24}\}$  with potassium/sodium, lithium, calcium and ammonium salts as a precursor, in order to design protocol for

LiNbO<sub>3</sub>, KNN and Nb<sub>2</sub>O<sub>5</sub> thin films, as well as intact {Nb<sub>24</sub>}. Solution characterization includes Raman and SAXS. The thin film characterization will include XRD, AFM, and Ellipsometry. For comparative thin films and solution catalytic studies of {Nb<sub>24</sub>}, we will use <sup>31</sup>P NMR to monitor DFP degradation.



COLL 818

**Metal-organic framework (MOF) structure, ligand dynamics, and electrochemical behavior as supercapacitor electrodes**

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Metal-organic frameworks (MOFs) are crystalline, highly porous materials that consist of coordination bonds between transition-metal cations and multidentate organic linkers. These 3-dimensional material architectures are exceptionally customizable for a broad range of applications owing to the diverse array of possible metal cluster centers and corresponding ligands. MOFs are ideally suited as active materials in electrodes of ultracapacitors, which rely on the electrosorption of ions into nanopores to store electrochemical energy. Since they offer high specific surface areas in excess of 1,500 m<sup>2</sup>/g, and we can tailor pore widths to accommodate electrolyte ions, MOF capabilities

can lead to energy storage devices with substantially improved power and energy densities. The fundamental material properties, including electrical conductivity, porosity, electrochemical stability, and intermolecular interactions at electrode/electrolyte interfaces all influence the viabilities of individual members of this family of 3-dimensional material structures for this application. They all depend on the individual chemistries of the metal cations and the corresponding organic bridges, as well as the dynamics of the ligands at different timescales. These insights will enable MOF electrodes to operate with non-aqueous electrolytes, and, subsequently, widen the operating potential windows of ultracapacitors and enhance their operating capabilities.

We developed novel insights into the structure and electrochemical performance of three distinct MOFs: 1)  $Zr_6O_4(OH)_4$  cluster with a 2,2'-bipyridine-5,5'-dicarboxylate ligand; 2) Ni cluster with a 2,3,6,7,10,11-hexaiminotriphenylene ligand; 3)  $Co(H_2O)_2/H_2O$  cluster with hexamethylenetetramine and 2,3,5,6-tetrafluoroterephthalic acid ligands. We rely on solid state NMR measurements to derive the structure and dynamics of each ligand with respect to its specific metal cation center. We derive the fundamental band structure of these MOFs with DFT calculations. We correlate these material properties with electrochemical capacitance, rate handling, and impedance performance using 1-ethyl-3-methylimidazolium bis(trifluorosulfonyl)imide ionic liquid electrolyte. Our findings highlight unique capabilities of these novel structures for energy storage.

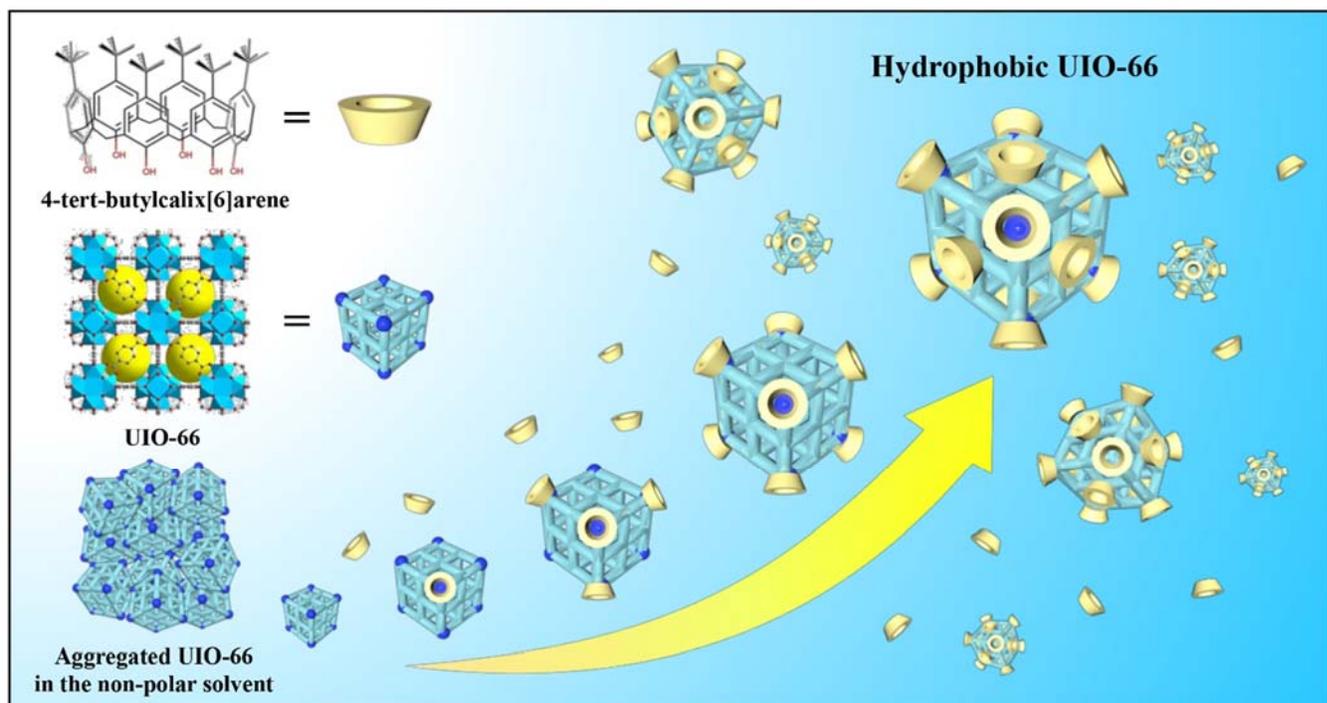
## COLL 819

### Surface and porosity modification of UIO-66 nanostructures using calixarenes

*Uiseok Jeong*<sup>1</sup>, *Nesibe Dogan*<sup>1,2</sup>, *Mousumi Garai*<sup>1</sup>, *Thien S. Nguyen*<sup>1</sup>, *James F. Stoddart*<sup>3</sup>, **Cafer T. Yavuz**<sup>1</sup>, *yavuz@kaist.ac.kr*. (1) KAIST, Daejeon, Korea (the Republic of) (2) Sorbonne University, Paris, France (3) Department of Chemistry, Northwestern University, Evanston, Illinois, United States

MOFs are commonly hydrophilic because of their formation which positive charged metal ion combined with negative charged organic linkers. UIO-66, a popular MOF example, is zirconium based MOF consisting of zirconium metal ion with terephthalic acid as a linker. Due to the Zr-O and OH bonds, UIO-66 has high affinity with polar solvent groups. Most recently, much have been attempted to obtain hydrophobically stabilized MOFs in order to mix with non-polar polymers. The common approaches are functionalizing of MOF surface using by hydrophobic ligands or mixing with hydrophobic compounds such as carbon, polydimethylsiloxane, and silica. However, these types of MOFs necessarily demonstrated decreased adsorption capacity, catalytic activity and unexpected influence to their structure and pore channel on the surfaces. To solve these problems, we sought to find a substance that protects the porosity and accessibility of MOFs. Here we report a surface modification route for MOFs to disperse in the non-polar solvent and separate the small particles from the mixture. We focused on the UIO-66 MOF particle with 4-tertbutylcalix[n]arenes. As synthesized UIO-66 with different amount of calix[n]arene conditions (0 to 30 wt%) were investigated in toluene. Adsorption isotherms, particles dispersity, particle size distributions, and kinetics have

been studied in detail. We show that supramolecular amphiphilic structures can effectively form stable colloidal dispersions of MOFs provided that their sites are larger than the pore openings. Our findings could lead to universal methodology to form non-polar stable dispersion of MOFs, to be used particularly in mixed matrix membranes.



## COLL 820

### Surface-catalyzed solvent-free “click” cycloaddition demonstrated for CuO nanowires sensitization

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The two-step surface sensitization of metal oxide nanomaterials (MONMs) has been demonstrated to be an efficient process allowing for selective attachment of a wide variety of target functionalities with simultaneous preservation of well-designed surface morphologies. In the first step, the surface was modified with a robust chemical “hook”, such as an alkyne functionality connected to a carboxylic group in prop-2-ynoic (propionic) acid, which can be utilized to react with an azide functionalized sensitizer introduced in the second step as a Cu(I) catalyzed click reaction. The use of this approach on nanostructured copper oxides (NCOs) not only resulted in a successful

morphology preserving modification, but also has demonstrated that surface Cu(I) can be obtained during the process and promote a surface-catalyzed click reaction without additional copper catalyst, which also make this process can be carried out without solvent as a “dry click” reaction. This solvent-free surface-catalyzed “dry click” reaction was studied by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Fourier Transform Infrared Spectroscopy (FTIR), solid-state nuclear magnetic resonance (ss-NMR), along with computational investigation using Density Functional Theory (DFT) implemented in the Vienna Ab initio Simulation Package (VASP).

## **COLL 821**

### **Acetone as a probe for UiO-67 series MOFs**

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The large scale production of industrial solvents poses an increasing human and environmental health hazard in the event of a chemical spill, thus highlighting the need for superior protective materials capable of mitigating potentially devastating impact. Metal-Organic Frameworks (MOFs) are a class of porous materials created by joining inorganic metal clusters with organic linkers, which can be easily functionalized to provide varying chemical and physical properties. In this work, we investigate acetone sorption on UiO-67 series MOFs. The highly sensitive carbonyl functionality of acetone renders this simple molecule an ideal probe for understanding MOF-analyte interactions (e.g. adsorption, desorption and diffusion mechanisms) and provides a framework for understanding the interaction of more complex systems. Using temperature programmed mass spectrometric and infrared spectroscopic techniques under controlled vacuum and temperature, we have identified a variety of MOF parameters, such as activation temperature and linker functionality, that influence the strength and nature of acetone binding. Using temperature programmed desorption mass spectrometry, we have determined that modification of the organic linker increases acetone binding strength as: UiO-67 < UiO-67-CH<sub>3</sub> < UiO-67-NH<sub>2</sub>. Moreover, as the sample activation temperature is varied, defects are introduced the framework that facilitate acetone binding. When coupled with *in situ* FTIR spectroscopy, hydrogen bonding interactions with the bridging free hydroxyls on the inorganic node and to linker functional groups are identified and monitored as a function of sample activation temperature revealing the impact of intrinsic MOF structural changes on acetone binding.

## **COLL 822**

### **Mechanistic study of the secondary cation release from Li(Ni<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>)O<sub>2</sub>**

**Diamond T. Jones**<sup>1</sup>, [diamond-jones@uiowa.edu](mailto:diamond-jones@uiowa.edu), **Joseph Bennett**<sup>2</sup>, **Robert J. Hamers**<sup>3</sup>, **Sara E. Mason**<sup>1</sup>. (1) Chemistry, University of Iowa, Iowa City, Iowa, United States (2) Chemistry and Biochemistry, University of Maryland Baltimore County, Baltimore, Maryland, United States (3) Univ of Wisconsin, Madison, Wisconsin, United States

Nanoscale complex metal oxides have transformed how technology is used around the globe. The most widespread examples are the electroactive components of Li-ion batteries found in portable electronic devices and electric cars. Lack of recycling infrastructure of these batteries will lead to their disposal in landfills, and finally ending up in the aqueous environment. In this work, we focus on the materials found in a Li-ion battery cathode,  $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$  (NMC). Previous work has shown that exposure of model organisms to nanoscale NMC can have adverse effects on survival owing to dissolution of metal ions. An Mn enriched lattice is left over after 72 hours of exposure. To understand the dissolution mechanism, we have developed an analysis, which combines DFT-computed total energies and experimentally adjustable reaction conditions to compute the surface dissolution of complex metal oxides. Using this method, we captured the observed incongruent dissolution of metals from the lattice,  $\text{Li}^+ \gg \text{Ni} > \text{Co} > \text{Mn}$ . However, to understand the persistence of Mn in the lattice, we further explore the thermodynamics of metal release from an already vacant surface. We also considered the effects of surface healing (reprotonation), oxidation state and site proximity to vacancies on metal release. We find that it is more favorable to release metals that are closest to the vacancy site after at least one reprotonation event on the surface. Using electronic structure calculations, we find that Ni and Co have the greatest fluctuation in oxidation states and are thermodynamically favorable to be removed after an initial Ni-OH or Co-OH unit is removed. Alternatively, releasing Mn from a defect surface is never favorable. By modeling the pathways of secondary cation release, the persistence of Mn in the lattice is further explained and advances molecular-level understanding of how these nanosheets transform in aqueous environments.

## **COLL 823**

### **Ultrasound-active theranostic microcapsules for imaging guided chemotherapy**

**Eugenia P. Kharlampieva**, [ekharlam@uab.edu](mailto:ekharlam@uab.edu). Department of Chemistry, University of Alabama at Birmingham, Birmingham, Alabama, United States

Ultrasound-triggered drug delivery offers a non-invasive alternative to both surgical resection and systemic drug delivery allowing higher drug concentrations at tumor sites and reduced side effects. This talk focuses on hollow polyphenolic particles (capsules) capable of delivering anticancer therapeutics upon high-power therapeutic and low-power diagnostic ultrasound irradiation. These capsules are comprised of hydrogen-bonded multilayers of poly(N-vinylpyrrolidone) and a natural polyphenol, tannic acid deposited on sacrificial submicron templates. We will discuss capsule potential to serve as powerful contrast-enhanced imaging agents utilizing ultrasound (US), positron emission tomography (PET), and magnetic resonance imaging (MRI) modalities. We will

also present capsule immunomodulatory capabilities to dissipate free radicals and influence immune responses for prolong circulation in the blood. Due to the customizable size, composition, effective contrast, high payload concentrations, and ultrasound-guided delivery, these polyphenolic capsules represent an attractive platform for advancing the field of theranostic agents and controlled treatment in general.

## COLL 824

### Imaging the laser-triggered release of therapies from nanodroplets for the treatment of preeclampsia

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Preeclampsia, which is characterized by new onset hypertension during pregnancy, affects up to 8% of all pregnancies and is a leading cause of maternal and fetal mortality. Currently, adequate treatments for preeclampsia do not exist. The underlying physiological trigger for the development of preeclampsia is believed to be abnormal placental development, which results in reduced blood perfusion and placental ischemia. To address this underlying placental ischemia, we are developing methods to deliver therapeutics to the placenta. We have investigated the ability of perfluorocarbon nanodroplets to deliver oxygen to the placenta. These nanodroplets have a lipid outer shell incorporating indocyanine green, which acts as a photothermal trigger for oxygen release when exposed to laser light. Additionally, the nanodroplets act as both photoacoustic and ultrasound imaging contrast agents. The nanodroplets were labeled with folic acid to enhance placental accumulation. The results show that the nanodroplets, used to treat a rat model of preeclampsia, led to an increase in placental oxygenation, as detected using spectral photoacoustic imaging. These results indicate that triggered, non-invasive delivery of therapeutics is a feasible strategy to improve treatments for preeclampsia. Ongoing work is continuing to investigate the spatial and temporal properties of the nanodroplet drug delivery.

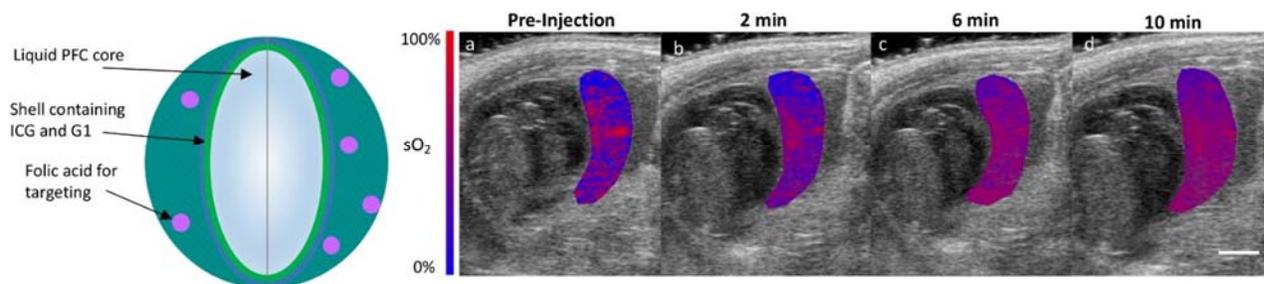


Figure 1: (a) Structure and design of nanodroplet; Ultrasound and spectral photoacoustic imaging of a

placenta in a preeclamptic rat, showing (b) initial placental ischemia and then an increase in oxygenation as the nanodroplets are triggered and release oxygen which was loaded into the nanodroplet.

## **COLL 825**

### **Development of novel polyplex-conjugated microbubbles as vectors for gene delivery**

**Sina Khorsandi**, *sina.khorsandi@utsouthwestern.edu*, **Richa Pandey**, **Robert F. Mattrey**, **Jacques Lux**. UT Southwestern Medical Center, Dallas, Texas, United States

Gene therapy holds the promise of providing single treatment curative benefits for diseases that currently require repeated infusions. The majority of clinical gene therapies make use of viral vectors which are limited by potential mutagenesis, immunogenicity, and non-specific delivery. Non-viral gene therapy utilizing microbubbles (MBs) and ultrasound has the potential to address these limitations. MBs are clinically used ultrasound contrast agents that have been frequently cited as promising vehicles for targeted drug delivery. It has been shown that a collapsing bubble will produce local shock waves, water jets, and shear forces that will permeabilize nearby cell membranes, allowing the direct delivery of nucleic acids or other therapeutics into the cell's cytosol. This phenomenon, termed sonoporation, will not only allow for spatial control of delivery using ultrasound but will also allow for high delivery efficiency since the drug will be bypassing endocytosis. Several examples of gene delivery utilizing cationic MBs have already been reported in the literature. However, due to their limited surface area and poor interaction, these cationic MBs only weakly bind DNA. Conjugating biocompatible cationic polymers onto the surface of MBs will not only increase DNA binding due to a larger surface area, but will also shield the DNA from serum proteins.

Here we report the development of polyplex-conjugated microbubbles utilizing spermine-conjugated dextran as a non-toxic polymer to complex DNA. Conjugating cationic polymers onto the surface of MBs will allow for tighter binding and increased loading of DNA as it will intertwine with the polymer instead of lying flat on the surface of the bubble. Using this platform, we achieved a 10-fold increase in DNA packing as compared to previous cationic MB formulations and are currently exploring its application to other nucleic acids.

## **COLL 826**

### **Potential of cancer therapies with drug-loaded bubbles and droplets: Challenges and opportunities**

**Naomi Matsuura**, *naomi.matsuura@utoronto.ca*. University of Toronto, Toronto, Ontario, Canada

Cancer is a leading cause of death worldwide. Chemotherapy is a key treatment for many cancers, but systemic distribution of chemotherapy into normal tissue risks dose-

limiting toxicity. Addition of anti-vascular therapy that damages tumor blood vessels can improve outcomes over chemotherapy alone, but also further increases toxicity. Better targeting of chemotherapeutic and anti-vascular therapy remains a significant clinical challenge in cancer therapy.

Non-invasive, therapeutic ultrasound has been previously used to cavitate ultrasound contrast agents (i.e., microbubbles) to potentiate chemotherapy by either increasing local tumour blood vessel permeability to allow co-injected drugs to diffuse preferentially into tumour tissue, and by causing local tumour vessel damage for mechanically-induced vascular disruption therapy which has shown to profoundly increase the efficacy of anticancer drugs.

In this talk, the development of new acoustically-active agents (i.e., droplets and bubbles) that are capable of both carrying therapeutic concentrations of a chemotherapeutic drug and can be cavitated for drug release and vascular damage will be introduced. Agents that are entirely composed of FDA-approved components are preferred as they may permit expedited translation into clinical use. Tradeoffs between size, stability, drug-loading, and *in vivo* performance between droplets and bubbles will be overviewed. Challenges and opportunities identified through recent efforts towards achieving cancer therapy potentiation in small animal cancer models will also be discussed.

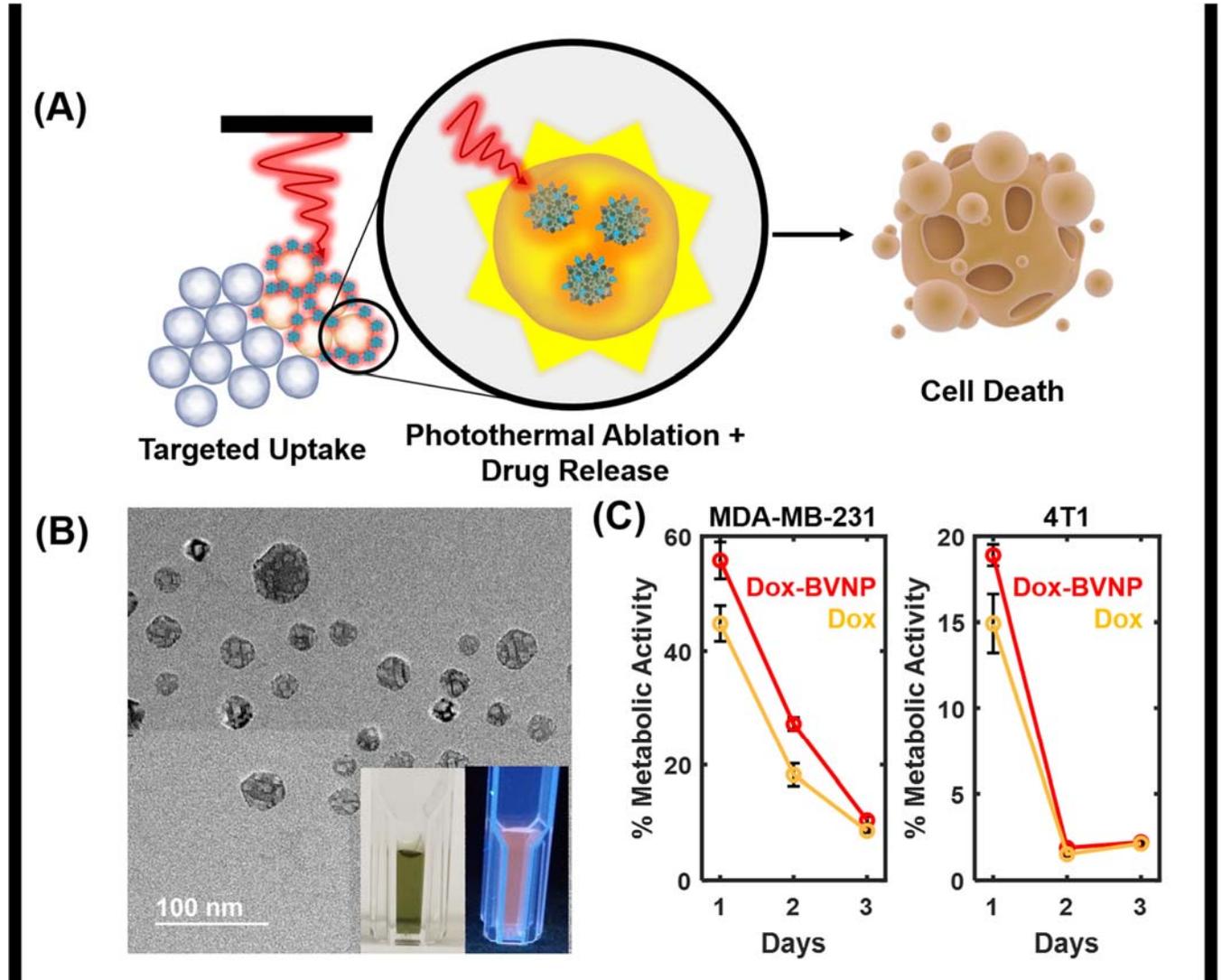
## **COLL 827**

### **Self-assembled drug-loaded biliverdin nanoparticles for combinatorial cancer therapy and photoacoustic imaging**

*Parinaz Fathi*<sup>1</sup>, *pfathi2@illinois.edu*, *Nicholas W. Pino*<sup>2</sup>, *Hailey Knox*<sup>2</sup>, *Mandy Esch*<sup>4</sup>, *Jeff Chan*<sup>3</sup>, *Dipanjan Pan*<sup>1</sup>. (1) Bioengineering, University of Illinois, Urbana, Illinois, United States (2) Chemistry, University of Illinois at Urbana Champaign, Urbana, Illinois, United States (3) Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States (4) National Institute of Standards and Technology, Gaithersburg, Maryland, United States

Recently, we reported the synthesis of biodegradable photoacoustic nanoparticles formed by nanoprecipitation of biliverdin, an endogenous chromophore (Fathi et al., ACS Nano, 2019). In further work, we have utilized these nanoparticles for targeted delivery of chemotherapeutic agents for treatment of triple-negative breast cancer. We have demonstrated that doxorubicin-loaded biliverdin nanoparticles (Dox-BVNPs) provide a platform for controlled release of doxorubicin, while also maintaining a high near-infrared absorbance, providing photoacoustic and fluorescent imaging contrast. The therapeutic efficacy of these nanoparticles was demonstrated in both MDA-MB-231 and 4T1 breast cancer cells, and their uptake mechanism was determined through inhibitor studies. Dox-BVNPs were extensively characterized with UV-visible spectroscopy, fluorescence spectroscopy, FT-IR spectroscopy, transmission electron

microscopy, scanning electron microscopy, and zeta potential measurements. Data on Dox-BVNP *in vitro* and *in vivo* image-guided therapy will also be presented.



**(A)** Dox-BVNPs for drug delivery, photothermal therapy, fluorescence imaging, and photoacoustic imaging. **(B)** Transmission Electron Microscopy (TEM) image of Dox-BVNPs. Inset depicts Dox-BVNPs under white light and UV illumination. **(C)** MTT assays demonstrate that Dox-BVNPs allow for controlled release of doxorubicin for treatment of triple-negative breast cancer.

## COLL 828

### Echogenic xenon microbubbles for ultrasound-mediated theranostic applications

**Rajarshi Chattaraj**<sup>1</sup>, [rajarshi.chattaraj@colorado.edu](mailto:rajarshi.chattaraj@colorado.edu), **Misun Hwang**<sup>3</sup>, **Daniel A. Hammer**<sup>1</sup>, **Chandra Sehgal**<sup>2</sup>, **Daeyeon Lee**<sup>2</sup>. (1) Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States (2) University of Penn, Philadelphia, Pennsylvania, United States (3) Children's Hospital of Philadelphia, Philadelphia, Pennsylvania, United States

Noble gases, especially xenon, have been shown to have cytoprotective effects in treating hypoxic ischemic injuries. Current Xe inhalation trials are expensive and prolonged. Recent efforts to locally deliver Xe with ultrasound-activated Xe-containing liposomes suffer from weak ultrasound response and low Xe payload due to the gas being confined between the bilayer. To address these issues, we have developed noble gas (xenon, argon) containing microbubbles (MBs) encapsulated by optimized phospholipid shell compositions capable of high payload and acoustic contrast. Unlike perfluorocarbons (standard gas for contrast MBs), Xe and Ar (higher water solubility) experience a greater chemical potential gradient to diffuse out of the bubble into the aqueous phase. The long-chain lipid DBPC (C22:0) with a rigid packing structure, is found to be the only one capable of producing stable bubbles within a 1-10  $\mu\text{m}$  diameter range when using a high-energy, open-to-atmosphere method like probe-sonication. However, due to its lower membrane residence time, shorter-chain DSPC (C18:0) is able to form 1-10  $\mu\text{m}$  bubbles by a lower-energy, closed-system, shaking method. The quantity of Xe encapsulated is determined by gas chromatography-mass spectrometry (GC-MS). DBPC+DSPE-PEG5000 MBs, as produced by sonication and size-isolated by differential centrifugation, were found to provide excellent non-linear (bubble-specific) ultrasound contrast, lasting 3-5 min in phantom studies. When injected retro-orbitally into a mouse vein, a bolus of Xe bubbles provide distinct and high contrast in both cardiac (pre-lung) and renal (post-lung) imaging settings. Ongoing studies are exploring the imaging and therapeutic capability of Xe bubbles in a traumatic brain injury model in pigs. In summary, this report presents a matrix of rigorously optimized shell-composition parameters for formulation of pure Xe and Ar microbubbles. We also demonstrate prolonged *in vivo* echogenicity of such bubbles for the first time, making these agents promising carriers for image-guided localized gas delivery.

## **COLL 829**

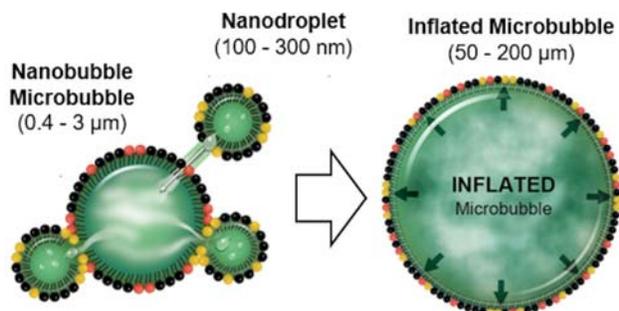
### **Potential side effects and opportunities of co-existence of microbubbles and perfluorocarbon nanodroplets in the circulation**

**Carlos J. Brambila**<sup>1</sup>, **Jacques Lux**<sup>1</sup>, **Robert F. Mattrey**<sup>1</sup>, **Dustin Boyd**<sup>1</sup>, **Mark A. Borden**<sup>2</sup>, **Caroline de Gracia Lux**<sup>1</sup>, [Caroline.Lux@UTSouthwestern.edu](mailto:Caroline.Lux@UTSouthwestern.edu). (1) Radiology, UT Southwestern Medical Center, Dallas, Texas, United States (2) Mechanical Engineering, University of Colorado, Boulder, Colorado, United States

Acoustic droplet vaporization was introduced to embolize tumors with large

microbubbles (MBs) non-invasively by converting  $\sim 2 \mu\text{m}$  perfluorocarbon (PFC) droplets within the feeding artery, and more recently cavitating  $\sim 300 \text{ nm}$  nanodroplets (NDs) to improve their detection by ultrasound (US). However, despite the introduction of this technology 20 years ago, it has not been translated to the clinic mostly because of efficacy and side-effects, some of which remains unexplained. This talk will describe a new theory and validate a new theranostic platform that can achieve all the benefits of acoustic ND vaporization, but without the need for US activation.

We demonstrated for the first time that the observed acoustic droplet vaporization side effects are due to the thermodynamically driven evaporation of liquid PFC from droplets to nearby bubbles and the fusion of their shell components resulting in microbubble volume expansion up to 6 orders of magnitude. US imaging confirmed that when liquid PFC NDs come in close proximity to PFC gas-filled nanobubbles, the latter inflate to become visible on US without the need for US activation. Microscopy showed MB expansion under stationary and flow conditions, and showed that inflated MBs can occlude a  $200 \mu\text{m}$  tube. Flow cytometry showed that not only did PFC transfer from NDs to MBs, but also the shell lipids and lipophilic payloads transferred. When NDs were targeted to MBs, the same rate and degree of inflation occurred at 1/10th the ND dose. We believe that this translatable approach will be able to occlude tumor vessels from inside out, and do so without the need to visualize tumors since no US activation is needed. Equally exciting, controlled microbubble inflation to a specific desired size will enable diagnostic applications without the potential of occluding vital vessels.



## COLL 830

### Effect of CaS nanostructures in the proliferation, survival and cell cycle of human adenocarcinoma and normal fibroblast cells *in vitro*

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We report on the effect of naked CaS nanostructures on the proliferation and survival rate of carcinoma cancer cells and normal fibroblasts *in vitro*. The CaS nanostructures are prepared via the microwave mediated decomposition of dimethyl sulfoxide (DMSO)

in the presence of calcium acetate  $\text{Ca}(\text{CH}_3\text{CO}_2)_2$ . Light scattering measurements revealed that dispersions contain CaS nanostructures in the size range of a few Å to about 1 nanometers are formed when DMSO is decomposed in the presence of  $\text{Ca}(\text{CH}_3\text{CO}_2)_2$ , consistent with  $(\text{CaS})_n$  clusters ( $n=1-4$ ). We found that a single dose of CaS nanoclusters smaller than 0.8 nm in diameter does not affect the survival and growth rate of normal fibroblasts and inhibits the proliferation rate of carcinoma cells *in vitro*. Larger CaS nanoparticles, approximately  $(1.1 \pm 0.2)$  nm in diameter, have a similar effect on carcinoma cell proliferation and survival rate. The CaS nanoclusters have little effect in the normal fibroblasts cell cycle. Human carcinoma cells treated with the CaS nanocluster dispersion exhibited a decreased ability to properly enter the cell cycle marked by a decrease in cell concentration in G0/G1 phase in the first 24 hours and an increase in cells held in the SubG1 and G0/G1 phases up to 72-hours post treatment. Apoptosis and necrotic channels were found to play significant roles in the death of human carcinoma exposed to the CaS nanoclusters. Effects on normal fibroblasts appeared to be short lived and non-detrimental. The interaction of CaS with several functional groups was further investigated using theoretical calculations. CaS is predicted by calculations at the DFT/B3LYP/6-311G level of theory to interact with thiol, hydroxide, amino, carboxylic acid, ammonium and carboxylate functional groups. None of these interactions are predicted to result in the dissociation of CaS. Thermodynamic considerations and experimental measurements, on the other hand, are consistent with the dissociation of CaS into  $\text{Ca}^{2+}$  ions and  $\text{H}_2\text{S}$  in acidic media, both of which are known to cause apoptosis or cell death. Passive uptake and intracellular pH levels of carcinoma cells are proposed to result in the observed selectivity of CaS to inhibit cancer cell proliferation with no significant effect on normal fibroblast cells. The results encourage further research with other cell lines *in vitro* as well as *in vivo* to translate this nanotechnology into clinical use.

## **COLL 831**

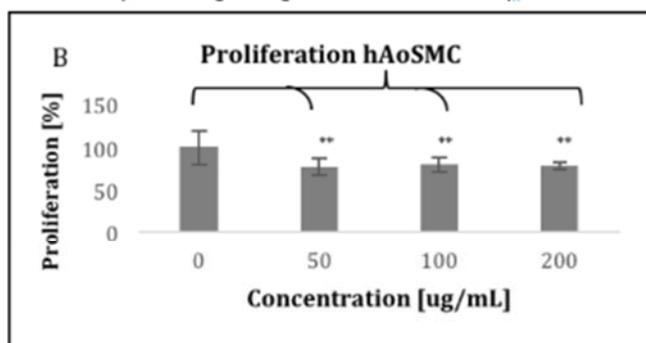
### **Using heparin-coated magnetic nanoparticles to treat neointimal hyperplasia**

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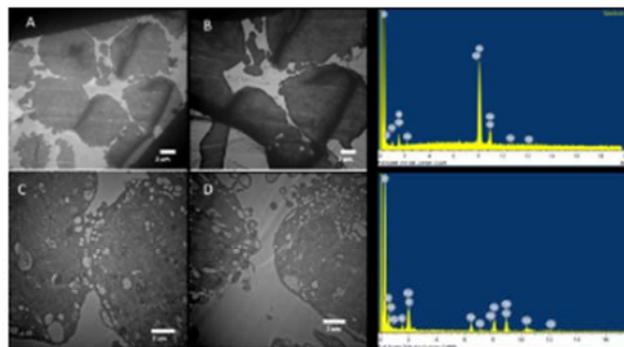
Currently the leading cause of death in both the United States and worldwide, cardiovascular disease continues to grow in prevalence and overall healthcare burden. Current treatment options for coronary artery disease include percutaneous devices, which are associated with high rates of restenosis. Two of the main causes of restenosis are neointimal hyperplasia and thrombosis.<sup>1</sup> We designed a drug delivery system to treat neointimal hyperplasia and prevent restenosis through preventing the proliferation and dedifferentiation of VSMCs and promoting endothelialization. We propose using heparin-coated magnetic nanoparticles (HMNP) to deliver heparin to a magnetizable stent under an external magnetic field. Heparin has been shown to reduce the proliferation of VSMCs and promote the proliferation of endothelial cells. Our preliminary *in vitro* and *in vivo* studies have shown that our HMNP are non-toxic. *In vitro*

studies have shown that HMNP reduce the proliferation of VSMCs and increase the proliferation of endothelial cells.

In vitro results show a trend of an increase in the proliferation of for human endothelial cells (hUVECs) compared to the control and a reduction in the proliferation of the human vascular smooth muscle cells (hAoSMCs) compared to the control. The results did not show a statistically significant change at the low concentrations used. At higher concentrations, the cell proliferation was statistically reduced ( $\alpha=0.001$ ) compared to the control. (Figure 1) TEM images showed that the particles were uptaken by the cells through pinocytosis and were internalized inside the cells in endosomes. EDX data showed iron presence inside the experimental sample, while the control did not show any iron presence. (Figure 2) Viability studies on both cell lines showed no statistically significant difference ( $\alpha=0.05$ ) between the control and treated groups. Finally, the proposed particles have been shown in the past to be non-toxic both in vitro and in vivo.



**Figure 1:** Proliferation of hAoSMC after treatment with heparin-coated magnetic nanoparticles. ¶



**Figure 2:** TEM and EDX results show the uptake of heparin-coated magnetic nanoparticles by hUVECs. Top: Control, Bottom: 200 ug/mL. ¶

## COLL 832

### Controlling microbial dynamics with nanomaterials and substrate conductive biointerfaces

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The attempts to eliminate infections using antibiotics become abortive because of the versatility of the microorganisms. Microbes secrete enzymes to inactivate the antimicrobials, modify their genetic and phenotypic make-up to persist throughout irregular and ineffective treatments, or develop biofilms to escape the immune system. Consequently, the rapid spread of multi-drug resistant pathogens continues to challenge

the treatment of infections with conventional methods. Here, we present novel strategies to eradicate multidrug-resistant microbes with substrate conductive interfaces and nanomaterials. This talk will discuss an electrochemical approach to eradicate opportunistic pathogens (e.g. *Pseudomonas aeruginosa* PAO1, *Candida albicans*) associated with many infections. The electrochemical technology (ECT) alters the metabolic response of cells to sensitize the pathogens to subsequent antibiotic treatments. We also explore the ability of Ni@SiO<sub>2</sub> nanoparticles to promote the controlled-release of biocides and kill microbes upon sensing microenvironmental changes. While the nanoparticles alone exhibit excellent biocompatibility, the controlled-release of delafloxacin from the metallodrug complexes contribute to their antimicrobial activity. These strategies have the potential to lead to disruptive technologies and devices for eradicating drug-resistant infections.

### **COLL 833**

#### **Super-resolution imaging of nanoscale chemical heterogeneity on zymosan particles**

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Zymosan particles, mainly composed of layers of mannan,  $\beta$ -glucan and chitin, are the insoluble cell walls extracted from *Saccharomyces cerevisiae*. The different chemical structures can be recognized by different receptors on innate immune cells and subsequently stimulate inflammatory responses. Zymosan particles have been widely used for understanding anti-fungal immunity and treating cancer as immune-potentiator adjuvant. Therefore, understanding the physiochemical properties of the zymosan particles and the correlation between their properties and functions has significant implications. However, even though the topography and composition of zymosan have been investigated previously, little is known about the chemical and surface properties of zymosan particles in nanoscale. Combining scanning electron microscopy and peak force infrared microscopy (PFIR), we revealed the nanoscale heterogeneous distribution of glycans and amide bonds on zymosan particle surface, and more importantly, how such chemical heterogeneity correlates with the surface morphology of the zymosan particles. We also observed the heterogeneous recruitment of Dectin-1 to zymosan phagosomes using structured illumination microscopy indicating that the nanoscale chemical inhomogeneity gives rise to the non-uniform distribution of receptors on phagosome membranes that encapsulate the zymosan particles. Thus, combining different super-resolution techniques, we revealed the chemical heterogeneity on zymosan surface and its correlation with biological functions.

### **COLL 834**

## **Blood-brain barrier penetrating nanoparticle delivery of siRNA for glioblastoma multiforme**

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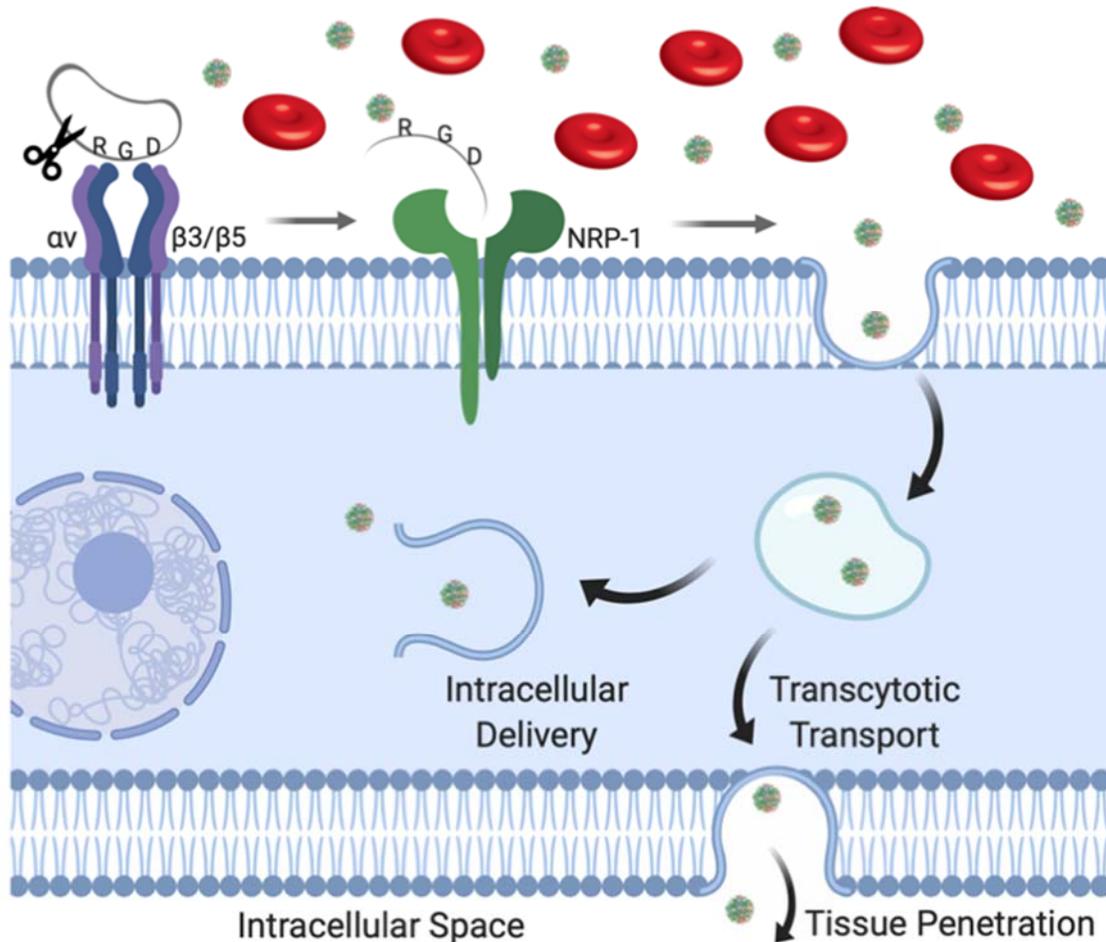
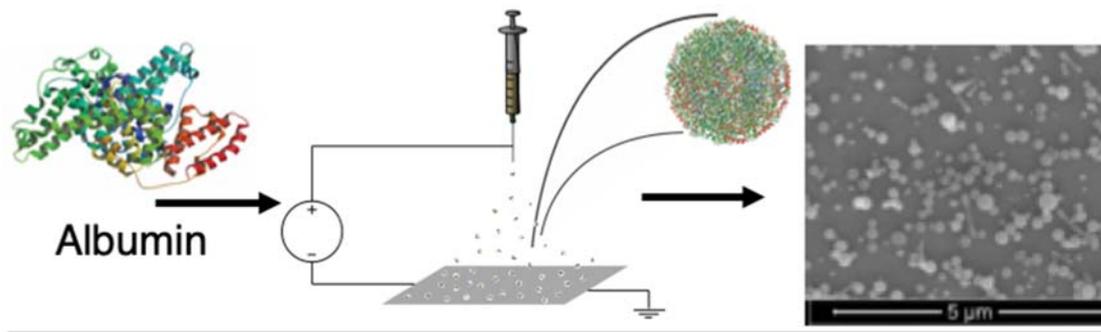
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The treatment of glioblastoma multiforme (GBM) has shown limited efficacy and remains the most lethal form of brain cancer despite therapeutic advancements in recent decades. As a standard-of-care, the combination of surgery and radio-chemotherapy regimens show only moderate benefits with a median survival of just 12-15 months and 5-year survival of less than 5%. Surrounded by functional brain tissue and protected by the blood-brain barrier (BBB), the limited success in treating GBM can be attributed to the pathological hallmarks of the disease, including rapid tumor growth, extensive infiltration, prevalent vascularization and developed resistance to chemotherapeutic agents. Here, we develop a novel type of tumor-targeting, tissue-penetrating nanoparticle capable of effectively interacting with, and traversing the BBB to deliver therapeutic siRNA.

Human serum albumin (HSA) nanoparticles loaded with siRNA and the tumor-targeting, tissue penetrating peptide, iRGD, were synthesized using electrohydrodynamic (EHD) jetting. Physical characterization of the resulting nanoparticles included measuring size and morphology via dynamic light scattering (DLS) and scanning electron microscopy (SEM). Release of encapsulated siRNA, cellular uptake, and intracellular fate was characterized. The targeted delivery of siRNA from albumin nanoparticles and subsequent protein-specific knockdown was validated in GL26 glioma cells. Finally, biodistribution of the targeted nanoparticles, immunogenicity, and in vivo efficacy of the developed system was validated in an established intracranial murine GBM model following systemic administration. Combined with focused radiation, we observe both long-term survivors and complete tumor regression.



Tumor-targeting, tissue-penetrating protein nanoparticles synthesized via electrohydrodynamic (EHD) jetting actively traverse the blood-brain barrier through peptide-induced transcytotic pathway.

**COLL 835**

**Ionic liquids for oral monoclonal antibody delivery**

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Monoclonal antibodies (mAbs) are currently used for the treatment for numerous conditions including cancer, psoriasis, arthritis, and atopic dermatitis, among others. All mAbs are currently administered by either intravenous or subcutaneous injections. Herein, we report the use of ionic liquids (ILs) as a platform for oral administration of therapeutic antibodies. Our lead ionic liquid maintained the stability and structure of TNF $\alpha$  antibody. ILs significantly enhanced paracellular transport of TNF $\alpha$  antibody *in vitro*. ILs also reduced the viscosity of the intestinal mucus, another key barrier for antibody transport. *In vivo* results in rats demonstrate that IL effectively delivers TNF $\alpha$  antibody into the intestinal mucosa as well as systemic circulation. One week repeat dose study followed by histology and serum biochemistry analysis indicated that IL is well tolerated by rats. Overall, this work illustrates the promise of using choline-based ionic liquids as an oral delivery platform for local as well as systemic delivery of therapeutic antibodies.

## COLL 836

### **Caged surfactants: New class of pH dependent surfactants for the delivery of biotherapeutics**

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Degradation of biotherapeutics, such as nucleic acids and proteins, in lysosomes has been shown to be a major bottleneck in drug delivery. Existing strategies are dominated by polymer and particle based methods that are difficult to implement due to their large size, as well as complicated chemical and physical properties. In this study, we present our work on the development of small molecules that disrupt membranes in acidic environments, termed caged surfactants. The caged surfactants are based on known surfactants, such as Triton X and Tween-20, which contain a hydrophilic polyethylene glycol (PEG) chain, and a hydrophobic hydrocarbon segment, allowing for insertion and resulting disruption of membranes. However, in order to achieve pH dependent membrane disruption, the caged surfactants are modified to contain a PEG group which blocks its hydrophobic segment from entering cell membranes at neutral pH values. This blocking group is designed to hydrolyze at acidic pH values, allowing for release of active surfactants in acidic environments, causing selective membrane disruption. This was demonstrated through the disruption of red blood cells at pH 7.4 and pH 5.5, showing 50% cell lysis down to concentrations of 20 $\mu$ M at pH 5.5, with no detectable membrane disruption at pH 7.4 at concentrations above 1mM. The caged surfactants are synthesized in a way that allows for last-step modifications, enabling multi-functionality in a single synthetic step. This has allowed us to make a caged surfactant tailored to the binding and delivery of nucleotide-based macromolecules such as mRNA and pDNA. Taking advantage of positively charged side chains, the caged surfactant binds the negatively charged nucleic acid. Upon cell uptake of the caged surfactant-nucleic acid complex, acidification of the endosomal compartment induces release of

the free surfactant. This release causes lysis of the endosomal membrane, and release of the nucleic acid into the cytosol. Using this strategy, we have shown delivery of both GFP-expressing mRNA, as well as siRNA to HeLa cells. The caged surfactants are a new class of endosomal disrupting agents which can be tailored due to its flexible late-stage synthetic strategy. The caged surfactants therefore show great potential for enhancing the delivery of biomolecules such as plasmids, mRNA, siRNA and therapeutic proteins.

**COLL 837**

### **Folate-targeted liposomes for rheumatoid arthritis therapy**

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Rheumatoid arthritis is the most common inflammatory rheumatic disease, affecting almost 1% of the world population. Although their cause remains unknown, the complex interaction between immune mediators (cytokines and effector cells) is responsible for the joint damage. Activated macrophages are critical in the pathogenesis of rheumatoid arthritis and showed specifically express a receptor for the vitamin folic acid, folate receptor  $\beta$ . This receptor allows internalization of folate-coupled cargo.

Here we propose the encapsulation of methotrexate in a new liposomal formulation using a hydrophobic fragment of surfactant protein conjugated to a linker and folic acid to enhance their tolerance and efficacy. In this study we aim to evaluate the efficiency of this system to treat rheumatoid arthritis, by targeting folate receptor  $\beta$  present at the surface of activated macrophages. The specificity of our liposomal formulation was investigated both *in vitro* as *in vivo* using a mouse model of arthritis (collagen-induced arthritis).

In both systems, the liposomal constructs were shown to be highly specific and efficient in targeting folate receptor  $\beta$ . These liposomal formulations also significantly increase the clinical benefit of the encapsulated methotrexate *in vivo* in arthritic mice (Figure 1). In conclusion, our formulation might be a promising cost effective way to treat rheumatoid arthritis and delay or reduce methotrexate intolerance.

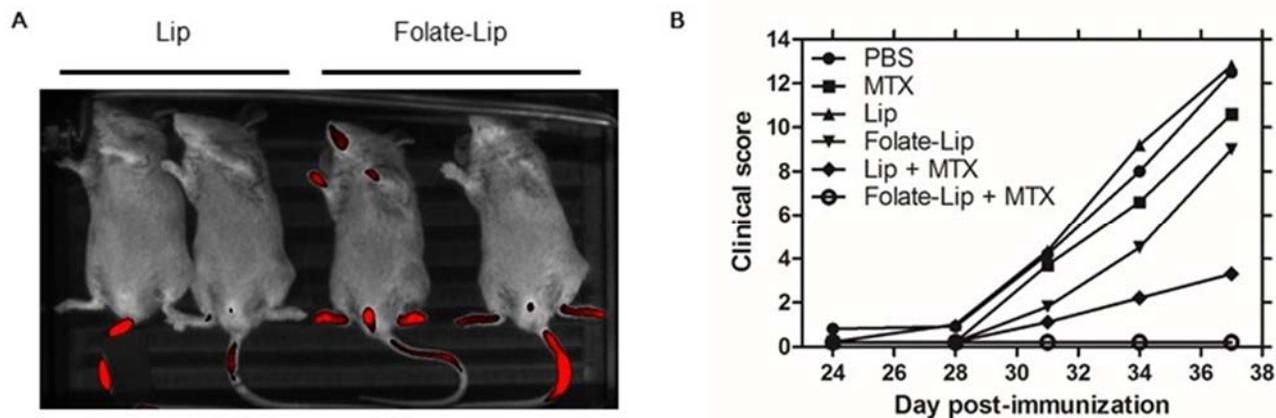


Figure 1. (A) *In vivo* uptake specificity of fluorescently labeled liposomes. (B) Clinical effects of liposomes encapsulating methotrexate on arthritis.

## COLL 838

### Photoswitching liposome surface charge to deliver membrane impermeable cargos *in vivo*

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Surface charge is essential to determine nanoparticle fate *in vivo* and the efficiency of nanoparticle-encapsulated drug delivery to target tissues in the body. In drug delivery, the neutral surface charge required to maximise circulation lifetimes and exposure of nanoparticles within target tissues directly conflict with the cationic surface charges required to maximise nanoparticle cellular uptake (and drug delivery) within target cells. Herein, we describe the switching of liposome surface charge, from neutral to cationic, *in vivo*, using light as an exclusive trigger. Visualising liposome surface charge transition in live zebrafish embryos we show liposomes, freely circulate prior to light activation, but rapidly and non-specifically adhere to all blood vessels upon light triggered activation. Structural integrity of the liposome is not compromised upon light activation leading to the successful intracellular delivery of encapsulated and membrane impermeable payloads within cells.

## COLL 839

### Layer-by-layer nanoparticles for antibiotic delivery and biofilm eradication

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According to the World Health Organization, pulmonary infections rank number four in global mortality, and its effects are compounded with the growing crisis of antibiotic resistance. While free-floating, planktonic bacteria themselves can be toxic in their own right, the issue magnifies as they start to aggregate and work together. When a threshold number of microbes exist, these communities form biofilms, a conglomeration of polymers that confer competitive advantages within the host, including defense against endogenous and exogenous antimicrobial agents. The viscous nature of biofilms works to limit antimicrobial efficacy primarily by inhibiting their infiltration, limiting efficacy to microbes that reside in the outer surface. Therefore, penetrating the biofilm becomes one of the key targets in successfully eradicating the microbes buried deep within. To tackle this challenge, we have synthesized a library of layer-by-layer (LbL) nanoparticles (LbL NPs) with unique surface chemistries to investigate how this enhances penetration into, and antibiotic delivery within biofilms. We constructed this library through layer-by-layer assembly, in which alternately charged polyelectrolytes are electrostatically adsorbed onto a charged colloidal core. This core is comprised of an anionic liposomal carrier loaded with ciprofloxacin, a clinically relevant antibiotic, yielding high encapsulation and loading efficiencies ( $84.8 \pm 8.9\%$  and  $11.7 \pm 1.2\%$ , respectively). Poly-L-lysine (PLK), a polycation that exhibits antimicrobial activity, was adsorbed onto these antibiotic loaded nanoparticles. When administered as a free polymer there is a three-log unit reduction in *Pseudomonas aeruginosa* microbial growth. Furthermore, free PLK decreased the minimum inhibitory concentration of ciprofloxacin four-fold when co-incubated with ciprofloxacin, indicating the potential for combinatorial effects. To complete the LbL NP, a final polyanion from a library of eight bioactive polymers, including natural polysaccharides and homopolypeptides is layered. From our screen we discovered that distinct biopolymers, such as sodium alginate, exhibit two-to-four-fold increased efficacy against planktonic and biofilm associated *P. aeruginosa* as compared to the unlayered liposomal carrier. To characterize how the biopolymer surface increases nanoparticle penetration through biofilms, transwell model and microscopy studies were carried out.

## **COLL 840**

### **Colloidal stability and biodistribution of polymeric nanocarriers encapsulating peptides and proteins produced by inverse Flash NanoPrecipitation**

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Nanoscale carriers can be used to encapsulate peptides, proteins, and nucleotides, imparting beneficial therapeutic properties not exhibited by these biologics alone. For example, encapsulation can alter the biodistribution of the therapeutic or promote internalization by target cells. Lipid formulations and the double emulsion approach to form polymeric nanocarriers have been used for this purpose. However, their clinical use for administration of water-soluble therapeutics has been limited because high process losses pose an economic barrier, among other challenges.

We have developed a process that addresses this limitation using sequential block copolymer assembly steps to encapsulate water-soluble therapeutics in a hydrophilic core, enclosed by a hydrophobic poly(lactic acid) shell. We ionically crosslink this core to stabilize it against osmotic forces and install a dense polymer brush, e.g. PEG, to impart desired surface properties. Called “inverse Flash NanoPrecipitation” (iFNP), the process achieves loadings that are 5-15x higher than liposomes or other polymeric nanocarriers. In the first part of this talk, we describe the processing steps and underlying mechanism of assembly.

Use of these nanocarriers to achieve modified biodistribution or cell internalization demands an understanding of the nanocarrier stability in buffer and in the biological milieu. The properties of the crosslinked core and the hydrophobic shell will dictate the nature and extent of changes to the nanocarrier structure during incubation at physiological conditions. To guide iFNP nanocarrier design, we describe how the composition impacts the stability of size and surface charge on nanocarriers in buffer. Once stable nanocarriers have been produced, well-known surface modifications (charge, ligand conjugation, etc.) can be employed to modify distribution behavior in the desired manner. Finally, we detail the biodistribution of formulations with different surface charges *in vivo* using PET imaging in a mouse model.

## **COLL 841**

### **Polycation-G-DNA binding thermodynamics and complex stability**

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G-DNA is a very stable, four-stranded nucleic acid structure resulting from Hoogsteen hydrogen bonding between guanines to form planar tetrads known as G-quartets. Guanine-rich oligonucleotides (GROs) with at least three consecutive guanines can self-assemble in the presence of monovalent cations into higher order, supramolecular structures called G-wires. Intracellular G-DNA, found in ribosomal sequences, the telomeric regions of chromosomes and promotor regions of proto-oncogenes, has been implicated in gene regulation, which suggests potential therapies are possible through

decoys similar to those using siRNA. Here, we investigated the potential for cellular delivery of G-wires through the formation of complexes with three nonviral agents commonly used in double- and single-stranded nucleic acid delivery: linear polyethylenimine (PEI), generation 5 polyamidoamine (PAMAM) dendrimer and HIV-1 transactivating transcription factor (Tat) peptide. Detailed thermodynamic analysis of the self-assembly between the agents and a model GRO13 G-wire structure was performed, showing that the interactions are electrostatic in nature, entropy-driven with micromolar dissociation constants. Affinity per charge site is stronger for the polymeric agents. All agents condensed the G-DNA into 100-200 nm diameter complexes that aggregated near charge neutrality in water, physiological buffer and serum-containing media into micron-sized particles that would likely trigger rapid RES clearance during circulation. Preliminary intracellular trafficking studies using fluorescently labeled G-DNA and immunocytochemically stained organelles suggests the majority of the G-DNA delivered via these agents gets caught in lysosomes 24 hours post-transfection. This finding identifies a transfection hurdle that could prevent efficient use of the G-DNA for therapeutic gene regulation.

## **COLL 842**

### **Layer-by-layer hydrogen-bonded films of synthetic polymers with antioxidant activity**

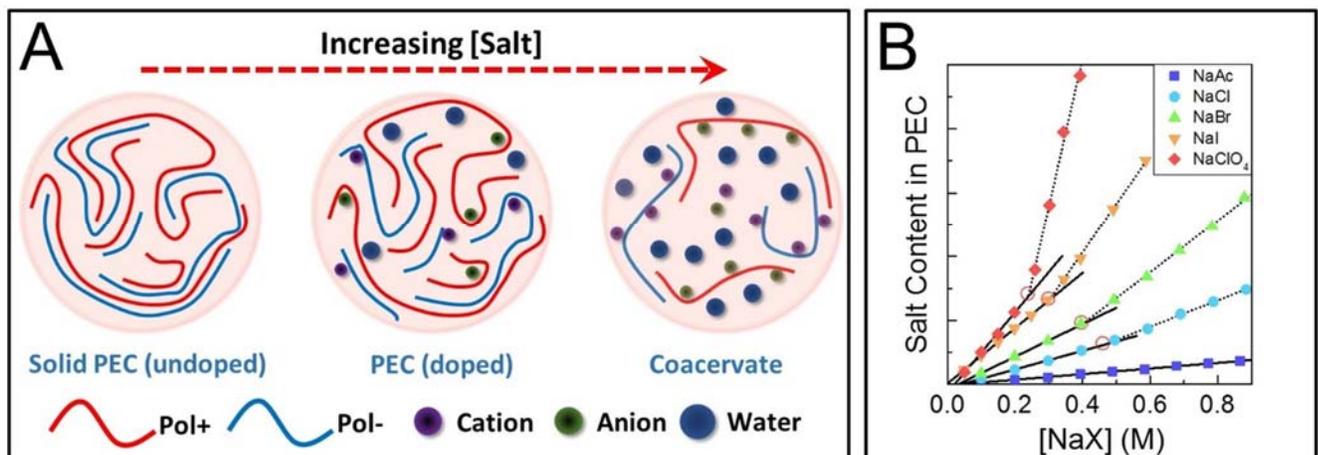
**Raman Hlushko**<sup>1</sup>, [raman.hlushko@tamu.edu](mailto:raman.hlushko@tamu.edu), **John Ankner**<sup>2</sup>, **Svetlana A. Sukhishvili**<sup>1</sup>.  
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Linear synthetic polyphenols, poly(N-(3,4-dihydroxybenzyl) methacrylamide) (P2HMA) and poly(N-(3,4,5-trihydroxybenzyl) methacrylamide) (P3HMA), were used with poly(ethylene oxide) (PEO) for assembly of layer-by-layer films. Film thickness, composition, and internal structure were explored using spectroscopic ellipsometry, Fourier transform infrared spectroscopy, and neutron reflectometry. Because of strong self-association between gallol polymer units, films constructed with P3HMA exhibited exponential growth and were significantly enriched with P3HMA, whereas P2HMA/PEO films demonstrated linear growth. Neutron reflectometry studies employing deuterated PEO showed strong intermixing in P3HMA-containing films, and fussy layering in the P2HMA/PEO system. The internal structure of the films correlated with differences in film swelling and the reduction of the Young's moduli upon exposure of the films to a solvent. The assembled synthetic polyphenols preserved their radical scavenging capability, but the time scale for the radical reaction within the films was significantly longer than that in solution. Recruitment of the assembled units in radical scavenging reactions was also strongly dependent on the film structure, with strongly associated P2HMA/PEO films engaging only the surface region, and weakly associated P3HMA/PEO assemblies being fully available throughout the film to radical species. Importantly, the magnitude of the antioxidant activity could be controlled at the step of film assembly by varying the number of polymer layers within the P3HMA/PEO films.

## Phase behavior and glass transition of polyelectrolyte complexes

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The phase behavior, morphology and mechanical properties of polyelectrolyte complexes (PECs) depend strongly on their compositions, e.g. ion content, which changes the network density by moderating the number of sticky reversible  $\text{Pol}^+\text{Pol}^-$  pairs. Polyelectrolyte complexes are also termed “coacervates” if they are fluid enough to form clear droplets or continuous phases. A glassy PEC can be transformed into a rubbery one if the external salt concentration is high enough. There has been a surge of recent work to rationalize the phase behavior of PECs and how their compositions correlate to glass transition. To address these questions, the compositions of poly(diallyldimethylammonium chloride) (PDADMAC)/poly(4-styrenesulfonic acid, sodium salt) (PSSNa) PEC were investigated with five different salt types: sodium acetate (NaAc), sodium chloride (NaCl), sodium bromide (NaBr), sodium iodide (NaI) and sodium perchlorate (NaClO<sub>4</sub>). A radio-labeling technique was used to precisely determine the salt content of PDADMA/PSS PEC at different salt concentrations. Water and polymer content were obtained by weight. Among the five types of salt, NaClO<sub>4</sub> had the strongest ability to break the  $\text{Pol}^+\text{Pol}^-$  pairs, whereas NaAc was the weakest “doper”. An “inflection” point was observed when plotted salt content in PEC *versus* salt concentration, which might be attributed to the glass transition. To correlate the glass transition behavior of PDADMA/PSS PEC to their compositions, small-amplitude oscillatory shear measurements were carried out to determine the glass transition temperature ( $T_g$ ) of PDADMA/PSS PEC in different solutions. It was found that the water content of PDADMA/PSS PEC dominated their glass transition behavior: at the same ionic strength, the higher the water content, the lower the  $T_g$ .



Panel A: Illustration of the effect of increasing salt concentration on the phase behavior in PEC. Panel B: Salt content in PEC *versus* salt concentration.

## **COLL 844**

### **Self-assembled polymeric micelles with tuned interfaces for docetaxel delivery to triple negative breast cancer**

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Amphiphilic block copolymers such as PEGPLA and PEGPCL can self-assemble in aqueous solutions generating polymeric micelles useful as drug delivery systems. In this study we will present the self-assembling properties, micelle stability, cargo protection, docetaxel loading and release profile of polymeric micelles generated from interfacially-engineered triblock copolymers PEGPBOPCL [1]. We will reveal how the engineered interfaces in these block copolymers selectively stabilize the polymeric micelles in blood vs at tumor site [2,3] and how the same interfaces affect the drug loading and release profile, *in vitro*, as well as *in vivo*, in an orthotopic model of triple negative breast cancer in female SCID mice.

## **COLL 845**

### **Impact of ligand dynamics on thermo-mechanical behavior of self-assembled nanoparticle superlattices**

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Advances in colloidal chemistry techniques have enabled self-assembly of ligand-stabilized nanoparticles (NPs) into highly ordered arrays (termed superlattices) with exotic collective properties that are entirely different from those of bulk phase crystals, isolated nanocrystals and even disordered nanocrystal assemblies. The exceptional thermal, mechanical, electronic, and optical properties of these superlattices (SLs) make them promising for numerous optoelectronics, energy harvesting, and sensing applications. However, precise engineering of SLs to realize their full potential remains challenging due to lack of fundamental understanding of the molecular mechanisms controlling their collective properties. Here, we integrate coarse-grained molecular dynamics simulations with small/wide angle X-ray spectroscopy, and electron

microscopy experiments to identify the crucial role played by ligand coverage density, and surface dynamics of ligands on the structure, thermo-mechanical, and high-pressure behavior of SLs. We find that ligand coverage density dictates (a) the extent of diffusion of ligands over NP surfaces, (b) spatial distribution of the ligands in the interstitial spaces between neighboring NPs, and (c) the fraction of ligands that interdigitate across different nanoparticles. These inter-dependent processes lead to a critical ligand coverage density ( $1.8 \text{ nm}^{-2}$  for 7 nm PbS NPs capped with oleic acid) below which, the SLs collapse via sintering of individual NPs. Above the critical coverage, the SLs can preserve their crystallinity crystalline order even under high applied pressures ( $\sim 40\text{--}55 \text{ GPa}$ ), and show a completely reversible pressure behavior. Such coverage-dependent processes also govern exceptional thermo-mechanical properties, anisotropic crack propagation, and healing in 2D nanoparticle superlattices. These results will be discussed in the context of designing superlattices with prescribed functionality for various energy applications.

## **COLL 846**

### **Kinetically-arrested polymer nanostructures from amphiphilic mikto-grafted bottlebrushes in solution: Simulation study**

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Amphiphilic molecular bottlebrushes are a remarkable class of polymeric materials. Solution self-assembly of these complex polymers has the potential to provide nanostructures unattainable from simple linear block polymers. These nanostructures can be used as smart drug delivery systems, and because of the really small critical micelle concentration of bottlebrushes, single-molecule micelles can be formed and stabilized in solution. In this work, we used a coarse-grained representation of molecular bottlebrushes and performed extensive molecular dynamics simulations to explore the self-assembly behavior of mikto-grafted bottlebrushes when the solvent quality for one of the side blocks is changed by a rapid quench. We have performed a systematic study of the effect of individual structural parameters and the degree of incompatibility between side chains on the final self-assembled nanostructures in the low concentration limit. We found that kinetically-trapped complex nanostructures are prevalent as the number of macromonomers increases. We performed a quantitative analysis of the self-assembled morphologies by computing the radius of gyration tensor and asphericity as the different relevant parameters were varied. Our results are summarized in terms of non-equilibrium phase diagrams.

## **COLL 847**

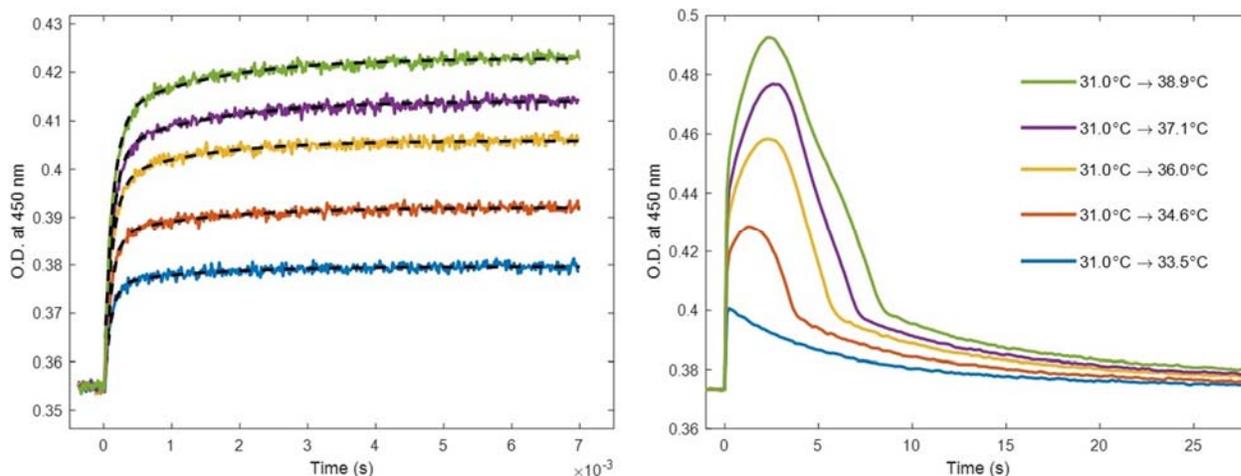
### **Swelling and aggregation dynamics in Au@PNIPAM colloid systems determined by temperature jump spectroscopy**

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Capacitor-based temperature-jump spectroscopy is an extremely useful tool for monitoring dynamics in chemical and biochemical systems that occur on the scale of milliseconds. We have applied this technique to analyse dynamics in a colloid system of PNIPAM-coated Au nanoparticles – which undergo two types of conformational changes upon a very fast change in temperature over the polymer Lower Critical Solution Temperature (LCST).

First: a deswelling transition as the polymer adjusts to a collapsed, more hydrophobic state on the scale of milliseconds. Under certain conditions, the colloid nanoparticles will then aggregate, before coming apart as the solution cools. Both these processes are entirely reversible, reproducible, and the dynamics were measured and modelled based on changes in turbidity of the system (**Fig. 1**).

By carefully designing kinetic models for these phenomena – we have determined how a range of parameters (particle diameter, cross-linker density, particle concentration, [KCl], [SDS], pH etc.) affect the various components of these transitions. These parameters are vital to control the self-assembly of Au@PNIPAM particles into optically active super-structures. The outcome shows the potential of temperature-jump spectroscopy to understanding kinetics for colloidal nanoparticle conformational changes and self-assembly.



**Fig. 1.** Temperature-jump spectra for an Au@PNIPAM system. (Left) 7 ms timescale experiment overlaid

with double-exponential fits represents the particle deswelling dynamics. (Right) 30 s timescale experiment represents aggregation dynamics.

## **COLL 848**

### **Force spectroscopy of a biomimetic polymer in molecular simulations via perturbation theory**

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It has become a common practice of probing various aspects of biological polymers via force spectroscopy. Considering that many proteins exhibit similar phenomena, we are interested in their corresponding universal signatures. For this purpose, we invoke molecular simulations of a biomimetic polymer: Although this homopolymer is solely based on a bead-spring model with a square-well potential, it is capable of universally capturing the protein-like unfolding of any heteropolymer [1]. Foremost, via the Wang-Landau procedure, we calculate at zero force the free energy as a function of the potential energy of the polymer [2]. We continue via perturbation theory, determining the free energy at nonzero force, applying it on different sets of monomeric sites. We in turn find scaling relations for the activation and transition of the biomimetic unfolding, relating these to various polymeric characteristics (e.g. the radius of gyration). Our findings consequently have important ramifications for protein unfolding.

## **COLL 849**

### **Extracellular signaling molecule indole increases permeability of bacterial membranes**

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Indole is a critical bacterial signaling molecule, which is known to influence various cellular processes, including biofilm formation or maintenance and antibiotic resistance. In an effort to better understand and quantify the mechanistic influences of indole, we examined the membrane-specific interactions of indole in various strains of Gram-negative bacteria. Specifically, we employed the surface sensitive nonlinear optical technique, time-resolved second-harmonic light scattering (SHS) to characterize variations in the membrane transport behavior of the cationic dye, malachite green (MG), in the presence of physiologically relevant concentrations of extracellular indole (i.e., 0-1.5 mM). For *E. coli* (which is capable of producing indole), our results reveal a

dramatic increase in the membrane permeability of both the outer membrane (OM) and the inner cytoplasmic membrane (CM). Conversely, for *P. aeruginosa* (which is incapable of producing indole, but needs to uptake indole from the extracellular environment), our results showed absolutely no change in the OM transport behavior, but a slight change in the permeability of the CM. Additionally, a series of control experiments with unilamellar liposomes (composed entirely of lipids isolated from the membranes of *E. coli*) revealed that the MG transport rate was completely independent of the relative presence of indole. Given that the liposomes specifically lacked protein of any kind, suggests that the indole-induced enhancement of membrane permeability observed in bacteria likely stems from an indole-protein interaction.

## **COLL 850**

### **Observation of cell-free synthesized ion channel molecules in artificial lipid bilayer by atomic force microscopy**

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Ion channels are a group of membrane proteins that are essential for the flow of various ions through the plasma membrane, and also take a major part of drug design targets. Artificial lipid bilayers such as black membranes, liposomes and supported lipid bilayers (SLBs) are valuable platforms for the study of membrane proteins at the molecular level. The reconstitution of membrane proteins is a key step in the membrane protein study using the artificial lipid bilayers. Recently, we reported microdomains in a ternary lipid bilayer consisting of phosphatidylcholine (PC), phosphatidylethanolamine (PE) and cholesterol (Chol) promote the fusion of proteoliposomes (PLs). In this study, we aimed to apply the PC+PE+Chol-SLB to reconstitute cell-free synthesized human *ether-a-go-go*-related gene (hERG) channel for investigating the hERG molecular structure. hERG channel is a cardiac voltage-dependent potassium channel that takes part in the action potential. Various medicinal agents block hERG channel as a side effect causing arrhythmia, and thus hERG channel is an important target in biological and medical fields.

In this study, hERG channel proteins were synthesized using a wheat germ cell-free translation system in the presence of liposomes consisting of PC, PE and Chol at 58:9:33 mol% with concentration of liposomes at 5 mg/mL. We prepared SLB by the vesicle fusion method using cell-free synthesized hERG channel-PLs on a freshly cleaved mica substrate. After the SLB preparation, we performed atomic force microscope (AFM) observation in the buffer solution using a Si<sub>3</sub>N<sub>4</sub> cantilever with a spring constant of 0.1 N/m and tip curvature radius of 8 nm.

The AFM topographies showed that SLB that was made from the PC+PE+Chol vesicles without PLs had flat surfaces with microdomains as with our previous study. The SLB

that was made from hERG channel-PLs had many protrusions at the entire surface. Majority of the protrusions had similar area and height, around 110 nm<sup>2</sup> and 2.6 nm, respectively. We attributed these protrusions to hERG channel monomer by considering the effect of AFM tip size. We also found self-associated structures of the monomer that had dimer-, trimer- and tetramer-like arrangement. Statistical analysis of their area showed that their sizes are reasonable for dimer, trimer and tetramer of hERG channel. We have successfully observed molecular images of hERG channel using AFM, and evaluated the association state of the hERG channel monomer.

## **COLL 851**

### **Physicochemical changes arising in zwitterionic phospholipid liposomes with the presence of salt**

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We present the influence of salt on the structure and dynamics of zwitterionic unilamellar liposomes and the phospholipid bilayer. We expect that our study will assist current liposomal drug delivery formulations to look at ionic strength in the range of physiological limits in a new light and to close the knowledge gap in the fundamental understanding of biological membrane structure and dynamics in the widely overlooked saline environment. Several structural changes are revealed by techniques such as cryo-transmission electron microscopy (cryo-TEM), dynamic light scattering (DLS), small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS) with varying NaCl concentration.

We observe a change of the membrane structure and rigidity starting at very small concentrations, leading up to the physiological ionic strength and beyond. We also notice the importance of investigating beyond the established traditional Zilman-Granek analysis with a more advanced model that includes the mobility of fatty acid tails to obtain bending elasticity information.

## **COLL 852**

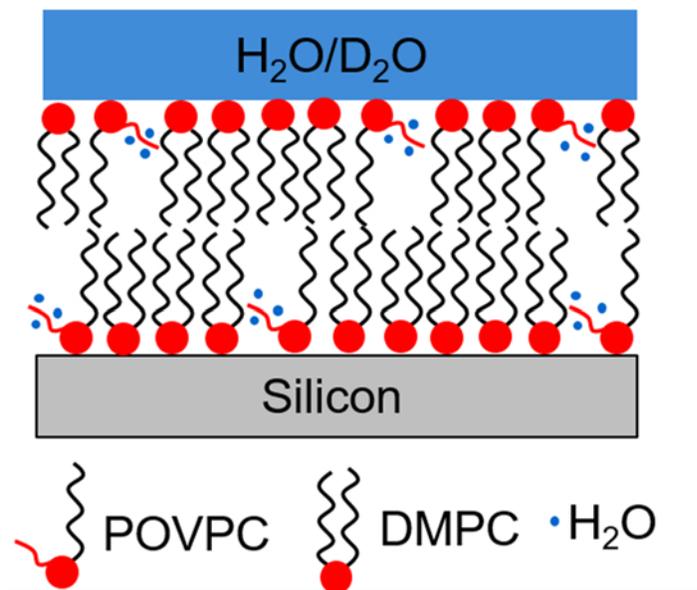
### **Effect of oxidised lipids on bilayer structure and deposition**

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Lipids are found widely in biological systems because of their unique interfacial properties. They are the primary component of cell membranes, which act as barriers containing the contents of the cells and protecting them from external threats. In fulfilling

their function, the lipid membranes are exposed to oxidation processes that change their molecular structure. Such processes occur naturally through the presence of superoxides ( $O_2^-$ ) that are released during inflammatory response, or through environmental pollutants. Oxidation can result in the hydrophobic tail region of lipids becoming more hydrophilic. This alters the physical properties of the lipids and the lipid mixture that in turn can affect their biological function. In this study we used a model system to investigate the changes in structure and physical properties that occur when a portion of the lipid in a bilayer is replaced with a lipid containing a damaged tail group, as found following oxidation.

Mixtures of 1,2-dimyristoyl-sn-glycero-3-phosphocholine (DMPC) that contained a lipid oxidation product, 1-palmitoyl-2-(5'-oxo-valeroyl-sn-glycero-3-phosphocholine (POVPC) have been investigated with a variety of surface and bulk techniques. Neutron reflectivity measured on bilayers revealed an increase in area per headgroup and significantly higher degree of hydration in the tail region when POVPC is present. In contrast, when oxidised lipids with a longer oxidised tail are present, the degree of hydration does not change. Further bilayer characterization with a QCM-D revealed that formation of bilayers containing POVPC is highly sensitive to surface preparation. Surface preparation with basic solutions, which create rough surfaces, inhibit vesicle adsorption and prevents bilayers from forming. Light scattering confirms that vesicles used for QCM-D containing POVPC had similar size to those of pure DMPC. Further, the stability of spread monolayers is reduced when POVPC is present.



Bilayer containing POVPC.

**COLL 853**

## Quantitative membrane partitioning studies of ecologically relevant synthetic organic molecules

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Bioaccumulation describes a biological membrane's ability to concentrate solutes from the surrounding environment and is often correlated with a solutes octanol/water partitioning coefficient (log P). Typically, solutes with log P values between 1 and 5 are thought to be strong candidates for bioaccumulation while still allowed to be used within environmental systems. The log P scale has a long historical legacy and although instructive, fails to describe *chemical* mechanisms responsible for bioaccumulation. Findings presented in this work employ both steady-state and time-resolved fluorescence emission to quantify solute partitioning into lipid vesicle membranes as a function of solute structure and membrane composition. Data illustrate the shortcomings of the log P description as Coumarin-based solutes having closely related structures show dramatically different partitioning behavior. Furthermore, time-resolved fluorescence data imply that solutes experience different environments *within* the lipid bilayer, information that cannot be inferred from log P descriptions of solute partitioning. These data are supported by complementary differential scanning calorimetry measurements that report on how different solute affinities for lipid bilayers change each bilayer's gel-liquid crystalline transition temperature. Together, these discoveries are providing a basis for developing a molecularly-based understanding of bioaccumulation.

### COLL 854

## Highly efficient growth of giant unilamellar vesicles in high salt solutions using nanocellulose paper

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Giant unilamellar vesicles (GUVs) are cell-sized lipid compartments that are of immense interest due to their resemblance to minimal biological cells. Current solvent-free methods used to grow GUVs such as electroformation, gel-assisted hydration, or paper-assisted hydration in aqueous solutions (PAPYRUS), appear to efficiently convert lamellar stacks of phospholipids into vesicular compartments in low ionic strength aqueous solutions. Harvesting high yields of GUVs in high ionic strength solutions that mimic the biological milieu however is still challenging. Using the fractional yield — the molar amount of lipids harvested as GUVs divided by the molar amount of lipids initially deposited on the substrate — as a metric, we show that this reduction in yield can be measured quantitatively for the various solvent-free methods. Further, we show that the PAPYRUS technique produces quantitatively higher fractional yields of GUVs compared

to extant techniques when the ionic strength of the solution is increased in two-steps. The two-step PAPHYRUS technique circumvents the need for osmotic gradients to drive the growth of GUVs in high salt solutions. We also show that PEG-lipids do not promote the formation of GUVs through increased hydration repulsion. PEG modified lipids increase fractional yields of isolated GUVs by preventing flocculation of GUVs in high salt solutions.

## **COLL 855**

### **Myelin figures under stress: Complex morphologies and dynamic instabilities**

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Lipids are known to exhibit variety of complex structural morphologies. One such morphology prevalent in the nature is that of myelin figures. The metastable non-equilibrium membrane assemblies are concentric cylindrical tubules consisting of alternating layers of thousands of smectically ordered lipid bilayers and water. They emerge as closely spaced protrusions, tens of micrometres wide and hundreds of micrometres long, growing from the lipid-water interface during the hydration of dry lipid mass.

Our group aims at studying biogenesis, formation & growth governing mechanisms; elaborate organization & dynamics in addition to structural remodelling of myelin in response to changes in its surroundings. We begin this analysis by subjecting myelin figures to varied external environment such as subjecting them to non-diffusible macromolecules. Here, we report the emergence of novel extended morphology at only the interface of closely juxtaposed myelins—characterized by a well-defined, complementary, and interdigitating undulatory topographical profile (zippering)—when subjected to entropic forces by the macromolecules present in myelin's aqueous environment. Monitoring the dynamics of the growth and propagation suggests that this localized corrugated morphology arises due to a synergistic interplay of osmotically induced compression and excluded volume effects: Former nucleates an undulatory instability and latter synchronizes the undulatory profiles of the opposing myelins. This can be viewed as the first ever observation of highly contained periodic peristaltic corrugated patterning arising purely from physical forces.

Further, we have also incubated myelin figures in an aqueous solution containing diffusible solute (i.e., glycerol), to find that myelins swell. Additionally, such myelin figures tend to maintain their structure over a long duration of time. We see such glycerol permeation as potential way for introducing various molecules inside the myelin lumen. Current ongoing efforts also include the studies of the effects of glycerol-

mediated swelling on zippering and exploitation of myelinic instabilities to induce templated silica mineralization.

Taken together, these observations suggest novel non-equilibrium routes to achieve hierarchical & higher-order self-assembly of otherwise rudimentary molecular building blocks that extend to multiple length scales exhibiting complex dynamic morphologies, far beyond those achievable under equilibrium conditions.

## **COLL 856**

### **Synthetic vesicles encapsulating a macromolecular circadian oscillator viable for days**

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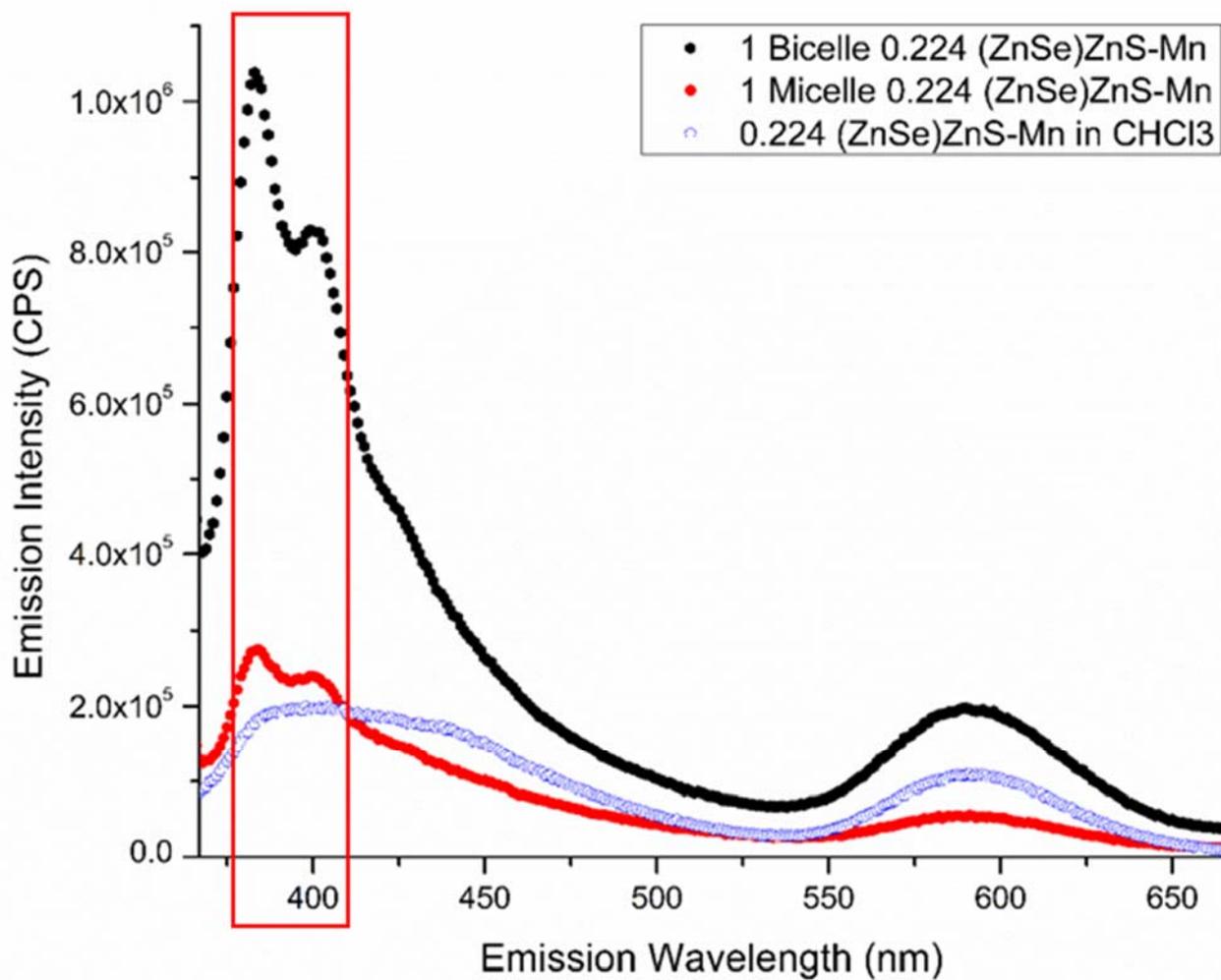
Giant unilamellar vesicles (GUVs) provide an environment that mimics the femtoliter to picoliter volume of biological cells. The micrometer sizes of GUVs further allow for visualization using fluorescence microscopy. Growth of GUVs in high ionic strength buffers using most thin-film hydration techniques is difficult, while functional reconstitution of most proteins requires mimicking physiological ionic strengths and pH. We have recently shown that stepped-Paper-Assisted liPid hYdRation in aqUeous Solutions (stepped-PAPYRUS) produces high yields of GUVs in buffers at physiological ionic strengths. Here we report the successful reconstitution of a circadian oscillator within GUVs grown using stepped-PAPYRUS. The oscillator is stable for at least a week. The circadian oscillator is composed of three proteins, KaiA, KaiB, and KaiC from the cyanobacteria *Synechococcus elongatus*. In an ATP dependent manner, the KaiABC system undergoes a series of conformational changes, phosphorylation and dephosphorylation cycles, and protein-protein complex formation over a 24-hour period. Using fluorescently labeled KaiB, we show that the fluorescence intensity and anisotropy of KaiB oscillates on ~ 24-hour cycle for days in the synthetic oscillators. With thousands of individual synthetic oscillators observed at once, we can examine the significance of variables such as volume, protein copy numbers, and concentration. These results demonstrate the first long term encapsulation of a functional macromolecular oscillator in GUVs and offers an important platform for studying complex protein systems in cell-like environments.

## **COLL 857**

### **Mn doped ZnSe/ZnS quantum dot (QD) species show increased fluorescence emission when encapsulated in a lipid bilayer bicelles**

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Quantum Dots (QD's) are nanoscale-sized semiconducting metals with advantageous fluorescent properties, including resistance to photobleaching, high quantum yield, high emission intensity, and finely tunable excitation and emission wavelengths. We found that when hydrophobic Mn-doped ZnSe/ZnS QDs were encapsulated into a lipid-based bicelle nanostructure, the fluorescence emission intensity increased ~200%+, when compared to the pre-encapsulation QD sample. The absorbance of Mn-doped ZnSe/ZnS QDs post-encapsulation showed 10-fold+ higher absorbance, compared to pre-encapsulation absorbance. When hydrophobic species of non-doped ZnSe/ZnS QDs were encapsulated within the same lipid-based bicelle nanostructure, the emission intensity closely matched pre-encapsulation emission intensities, with some post-encapsulated QDs showing a slight drop in emission intensity. A 10-fold+ higher absorbance was again observed, indicating that higher fluorescence emission was specific to select QD species. When Mn-doped ZnSe/ZnS QDs were packaged in a spherical lipid morphology, micelles, the optical properties did not appreciably change, and showed a similar emission and absorbance intensity as the pre-encapsulation QD sample. In order to further examine how lipid interactions with the QDs may affect the optical properties, a series of bicelles with captured Mn doped ZnSe/ZnS was prepared, with different ratios of lipids to QDs. Results show that emission intensity can be further increased, up to 300%+ emission intensity.



Lipid (mg)	QD (mg)	Emission increase at peak (384nm) emission (%)
1 mg	0.673 mg	228%
3 mg	0.673 mg	246%
6 mg	0.673 mg	276%
15 mg	0.673 mg	338%

Table showing emission intensity increase relative to ratios of lipid material to QD

COLL 858

### Entropic forces mediate topological division and shape instabilities in membrane compartments

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Living systems like cells are often crowded with macromolecules, where a unique non-ideal force called depletion interaction emerges. In aqueous systems where macromolecules and large spatial compartments co-exist, the macromolecules will be excluded from the volume surrounding the compartments. Thus, the system encourages the large compartments to approach each other by exerting this entropic force, minimizing the excluded volume and maximizing the net entropy. Additionally, any disparity in the concentration of molecules across the compartment exerts another entropic force called osmotic stress. Together, these indirect, non-specific, and universal forces, namely osmotic stress and depletion interactions, have been widely found in cells and between biomolecules, affecting their shapes and interactions. We experimentally investigated how the entropic forces influence two typical synthesized biomembrane structures: giant unilamellar vesicles and cylindrically organized multilamellar myelin. We found that the synergistic influence of osmotic stress and depletion interactions drive division of single giant vesicles and induce an extended

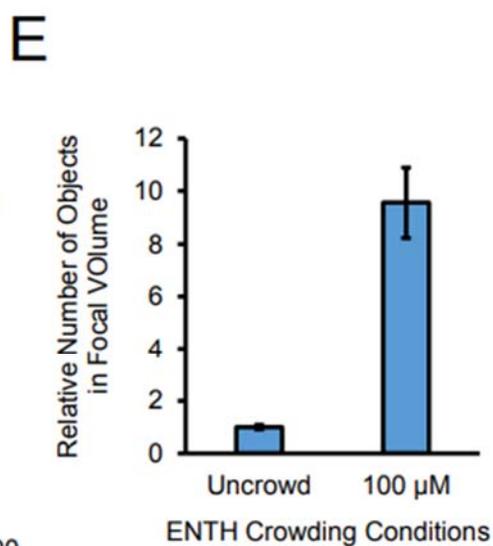
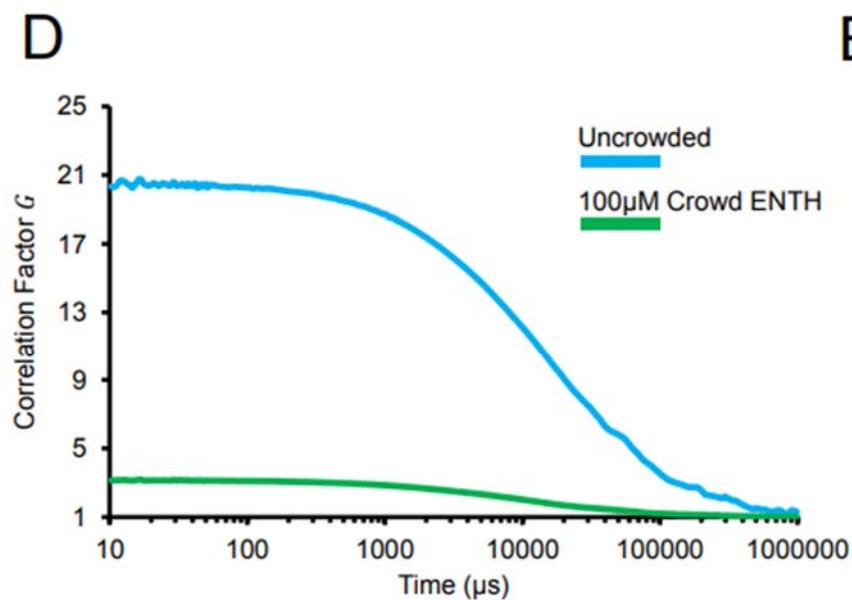
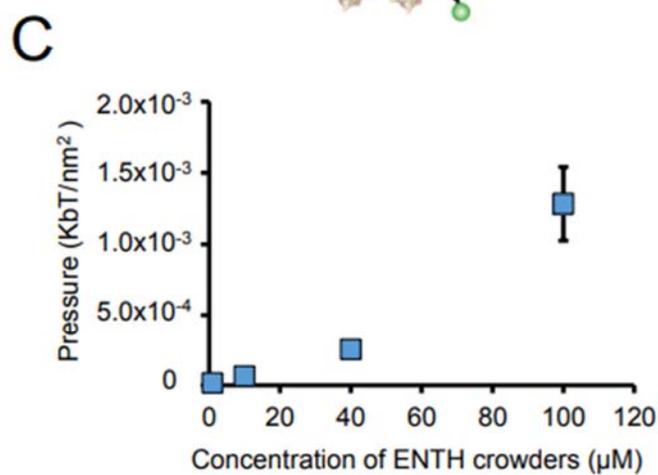
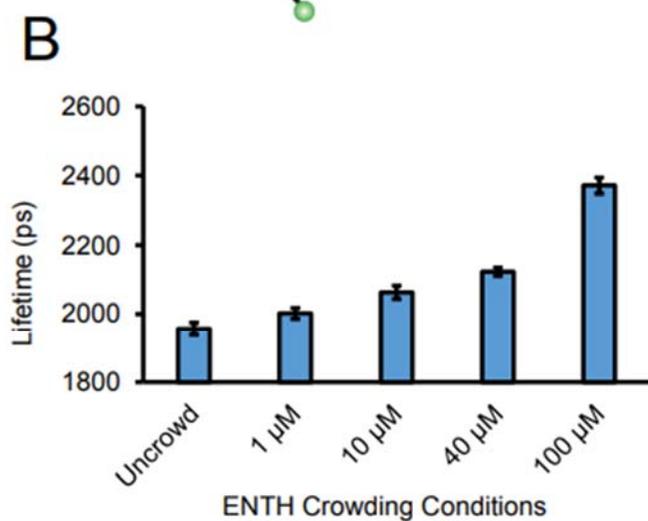
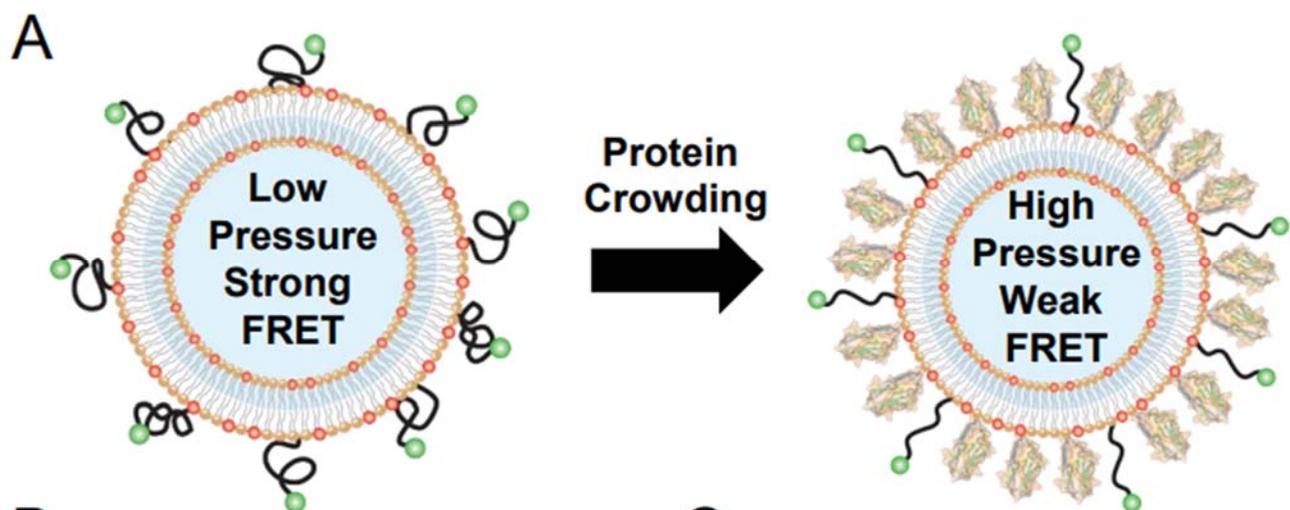
shape instability at the myelin-myelin interface. We propose that these shape, morphological, and topological transitions observed in artificial systems are guided by entropic forces, in a similar way that exists in living systems. Additionally, these synthesized membrane compartments can be developed as models to explain the phenomena observed in biology, and help with the bottom-up synthesis of artificial cells.

## **COLL 859**

### **FRET-based sensor for measuring steric pressure during membrane remodeling**

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Cellular membranes are crowded environments densely packed with proteins and lipids that are constantly remodeled by mechanical forces. Steric pressure generated by these forces is thought to play a significant role in key physiological processes, such as shaping endocytic vesicles and cellular protrusions. However, experimental measurements of steric pressure remain challenging, making it difficult to develop a precise understanding of the role of steric forces during membrane remodeling. To address this gap, we developed a biophysical tool to directly measure steric pressure on crowded membrane surfaces. Using fluorescence lifetime microscopy, we characterized the deformability of polyethylene glycol (PEG) as an entropic spring through Förster Resonance Energy Transfer (FRET). In particular, a membrane-bound PEG chain placed between two fluorophores serves as a molecular sensor for crowding on membranes (Fig. A). Modeling our sensor as an entropic spring, we used changes in fluorescence lifetime to estimate the force required for extension (Fig. B). Here we show that the lifetime of our FRET sensor is modulated by protein coverage on reconstituted vesicle membranes *in vitro*. Specifically, as the membrane surfaces became crowded by the endocytic adaptor protein, epsin1 ENTH, we observed a nonlinear increase in steric pressure with increasing concentration of membrane bound protein (Fig. C). Using fluorescence correlation spectroscopy (FCS) we observed a significant increase in the number of objects diffusing through our laser focal volume as we increased the concentration of bound protein on our vesicles (Fig. D, E). This increase provides a readout of the number of membrane vesiculation events arising from the steric pressure. By combining FCS and FRET, we have developed a tool that can be used to measure steric pressure during membrane remodeling events relevant to endocytic processes in the cell.



## COLL 860

### **Solvent-dependent relaxation of PRODAN: Quantitative simulation and ultrafast spectroscopy**

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Lipophilic dyes such as Laurdan and PRODAN report lipid packing in biomembranes, via a red shift of emission in more polar environments. Disentangling the factors which control the spectral shift is complicated by the stabilization of a charge transfer-like state in more polar environments. Predicting the emission therefore requires modeling both the relaxation of the environment and the corresponding evolution of the excited state. An approach has been developed in which (i) the local environment is sampled by classical molecular dynamics (MD) simulation of the dye and solvent; (ii) prediction of the absorption and excited state of PRODAN by numerical quantum mechanics (QM); (iii) relaxation of the environment around the excited state by MD; (iv) prediction of the emission by QM. The QM steps are computed using GW-BSE (as implemented in Versatile Object oriented Toolkit for Coarse graining Applications: Exciton Transport Simulations(VOTCA-XTP)) with the environment modeled as fixed point charges, sampled in the MD simulation steps. Comparison to ultrafast time resolved transient absorption measurements demonstrates that the iterative MD/QM approach agrees quantitatively with both the polarity dependent shift in emission and the timescale over which the charge transfer state is stabilized.

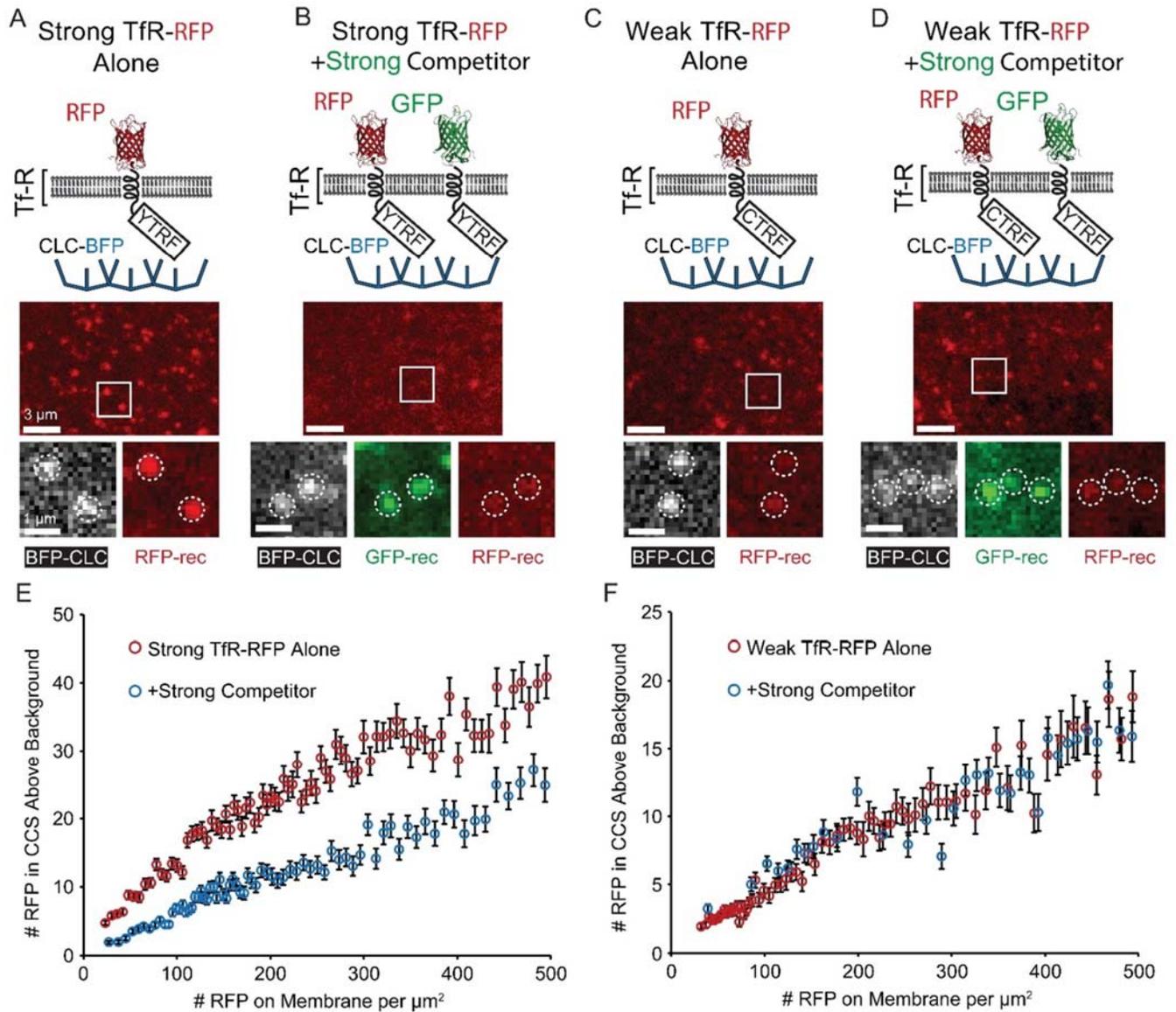
## COLL 861

### **Clathrin-mediated endocytosis of weakly internalized receptors is protected against competition**

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Internalization of receptors from the cell surface regulates diverse physiological processes from the rate of nutrient uptake to the timescale of signaling events. Cells control the number of specific receptors on their surfaces by balancing the rate of receptor delivery with the rate of uptake by endocytosis. The established view is that

internalization of receptors is controlled by specific biochemical binding interactions between receptor internalization motifs and clathrin adaptor proteins. Because many different receptors share recognition motifs for a small set of adaptor proteins, receptors which bind to the same adaptor protein are thought to compete with one another for entry into endocytic structures. However, variants of the same recognition motif have different affinity for the same adaptor protein. How do receptors with different affinities for the same adaptor protein compete with one another for internalization? To address this question, we constructed a series of model receptors with decreasing affinity for the adaptor protein AP2. As expected, internalization of a model receptor with high affinity for AP2 was reduced when co-expressed with a competing receptor of similar affinity for AP2. Surprisingly, internalization of a model receptor with low affinity for AP2 was unaffected by a competing receptor with high affinity for AP2. These findings suggest that weakly internalized receptors are protected against competition with strongly internalized receptors. This protection could arise from the small fraction of the endocytic structure area occupied by the weakly internalized receptor, requiring the competing receptor to saturate nearly all available space within the structure to generate a competitive effect. Given the critical role of internalization in receptor signaling, this effect may serve as a protection mechanism to prevent strongly internalized receptors from interfering with the cell's ability to process signals from weakly internalized receptors.



COLL 862

## Integrating machine-learning and nanomaterial for precision theranostic nanomedicine

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In the field of theragnostic, diagnostic nanoparticles are designed to collect highly patient-selective disease profiles, which is then leveraged by a set of nanotherapeutics to improve the treatment results. Despite their early promise, high inter-patient and intra-tumoral heterogeneities make any rational design and analysis of these theragnostic platforms extremely problematic. Recent advances with the deep learning-based tools may help bridge this gap, using pattern analysis and classification algorithms for better diagnostic precision and therapeutic outcome. Triple-negative breast cancer (TNBC) is a conundrum because of the complex molecular diversity, making its diagnosis and therapy challenging. Currently, there is no FDA-approved targeted therapy for this population of breast cancer. To address these challenges, we designed a high-throughput method to predict the cellular internalization and evaluating nanoparticles (NPs) against different cancer stages using artificial intelligence. Utilizing this approach, we can optimize the nanomaterial properties by quantitatively model the NPs-cellular internalization providing an optimum structure–internalization response against endocytic inhibitors for a given NPs. This methodology could predict the structure–internalization response of the evaluated nanoparticles with  $Q^2=0.9$ . Therefore, it can reduce the effort by minimizing the number of nanoparticles that need to be tested and could be utilized as a screening tool for designing nanotherapeutics. Following this, we have proposed a diagnostic nanomaterial used to assemble a patient-specific cancer profile with the assistant of machine-learning (ML). These nanomaterials comprising eight carbon nanoparticles (CNPs) with multifarious surface chemistries that can differentiate normal breast cells from cancerous cells, then subclassify TNBC cells vs. non-TNBC cells, and within the TNBC group. Here we demonstrate for the first time that a combination of machine learning (ML) algorithm and characteristic cellular uptake responses for individual cancer cell types can be successfully used to classify various cancer cell types. Artificial neural network (AAN) algorithm has also been successfully used in identifying the type of cancer cells from 36 unknown cancer samples with an overall accuracy of >98%, providing potential applications in cancer diagnostics.

## **COLL 863**

### **Design and application of well-defined, anisotropic TiO<sub>2</sub> nanomaterials for rational studies in catalysis**

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Generalized syntheses of TiO<sub>2</sub> nanomaterials are heavily studied due to its earth abundancy, chemical stability, oxygen carrying properties, and its semiconducting properties. As a result, we have access to different phases (anatase, rutile, and brookite), shapes (sheets, bipyramids, rods, etc.), and surface facets in well controlled nanocrystals that allow us to explore many exciting chemistries with a refined knowledge of its active sites. Here, we report an important addition to this class of

materials by reporting a synthesis of transition metal doped, brookite TiO<sub>2</sub> nanorods with exceptional tunability in dopant composition (M = V, Cr, Mn, Fe, Co, Ni, Cu, Mo, etc.). Mono-, bi-, and tri- metallic doped nanorods are all possible in our synthesis. We also elucidate, through Density Functional Theory, why these nanorods develop expressing primarily the (210) facet. Finally, using these materials, we explore ways in which the fine synthetic control expressed in our syntheses may enhance catalytic H<sub>2</sub> production or other catalytic reactions.

## **COLL 864**

### **Electric field-directed particle-based reconfigurable scattering masks for lensless imaging**

*Jennifer R. Miller, jrmiller575@gmail.com, Cheng-Yu Wang, Zhiwen Lui, Christine D. Keating.* Penn State University, State College, Pennsylvania, United States

Light scattering is typically undesired in optical systems as it often introduces defects or otherwise negatively impacts device performance. However, electric-field directed assembly methods can be used to dynamically control particle assemblies and elicit favorable responses from light scattering. Reconfigurable control over particle orientation, location, and number density enables tuning and enhancement of the optical response in a broad array of optical phenomena. One such application, lensless imaging, uses a scattering mask instead of lenses to enable devices with compact construction and a large field of view. Key to this process's efficacy, but also a point of difficulty, is the ability to dynamically tune the scattering pattern produced by the mask as this often results in increased mask complexity and cost. In this study, we utilized electric-field driven particle assembly techniques to design reconfigurable scattering masks which dynamically tune light scattering for lensless imaging, enabling multi-shot image reconstruction. Gold particles are readily tuned by rational application of electric fields, and effectively scatter light without requiring bulky components. Multi-shot reconstruction resulted in enhanced image quality and increased reconstruction resolution. These reconfigurable particle masks are a broadly applicable means of achieving dynamically tunable light scattering.

## **COLL 865**

### **Green synthesis and formation of metal and alloy nanoparticles dispersed in liquid by magnetron sputtering**

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In this research, nanoparticles have been synthesized by putting together a top-down sputtering technique to create atoms/clusters and a liquid medium in the vacuum chamber to capture and manipulate the subsequent particle formation and growth. The generated metal atoms/clusters from the bulk metal targets can collide and grow to form

metal and metal alloy nanoparticles during travelling from the gas to the liquid phase, where they can be trapped and stabilized. The design provides a wide range control of the synthesis parameters such as sputtering head-type, sputtering current, the temperature, composition, and stirring rate of the liquid, etc. for tailoring the size, composition, structure, functionality, and stability of the resulting nanoparticles in the liquid matrix. Our study has demonstrated that particle size can be increased with increasing the sputtering current. In addition, the liquids and their functionalities can also be chosen not only to control the particle size but also to stabilize the formed nanoparticles. Furthermore, co-sputtering of two metal targets allows us to create solid solution nanoparticles of various metal pairs such as Au/Ag, Au/Cu, and Au/Pt, etc. The particle composition can be finely tuned via varying the sputtering currents applied on each target. This, in turn, offers a feasible tool for modifying the optical properties of the alloy nanoparticles. On the other hand, we also study the impact of sputtering parameters on particle size and compositions to shed light on the particle formation and growth. Details of the synthesis, characterization, and formation of metal and alloy nanoparticles with controllable composition, size, and colloidal stability will be addressed in the presentation.

## **COLL 866**

### **Single source precursor route to isolate controlled metal carbide and metal nanocrystals**

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Prussian Blue Analogues (PBAs) have been extensively studied for applications such as gas adsorption, catalysis, Na-ion batteries, etc. Additionally, these PBAs have been employed as single-source precursors in the thermal conversion from PBAs to heterometallic nanoalloys. Recent work in the Strouse group demonstrated that under specific thermal conditions, CoFe-PBAs exhibit a size-dependent conversion behavior. It has been speculated that the conversion follows a templated mechanism, in which the framework and size are motivating factors on the eventual composition and size. In this study, we intend to explore templated nanoparticle growth to the other PBA families, demonstrating a synthetic pathway to controlled mixed metal carbides and alloys for the purpose of materials design. These nanomaterials were characterized using pXRD, SEM, TEM, FT-IR.

## **COLL 867**

### **Development of indium phosphide-based quantum shells**

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Development of brightness matched quantum dots (QDs) is essential to their use in accurate and quantitative sensing and imaging applications. The size dependent emission wavelengths of QDs stemming from the quantum confinement effect, results in inherent differences in brightness values between emitters of different colors, defined as the product of their molar extinction coefficient ( $\epsilon$ ) and quantum yield (QY). The independent tunability of emission wavelengths, extinction coefficients, and quantum yields (QYs) can resolve the widely different brightness values often observed across blue and green to red emitting QDs. This problem is addressed by inverting the structure of traditional type-I InP/ZnSe QDs and synthesizing inverted type-I ZnSe/InP heterostructures with shell thickness dependent emission colors, hence referred to as quantum shells (QShs). ZnSe cores of different sizes were synthesized by taking advantage of the extended LaMer model of growth, using the highly reactive precursor, diethylzinc. Using a continuous drip injection reaction for InP shell deposition and improving the surface ligand dynamics of InP, successful shell deposition can be performed. A secondary ZnS shell is also deposited to render emissive heterostructures. Through the synthesis of QShs with a combination of ZnSe core sizes and InP shell thicknesses, size-matched fluorophores of different colors contributing to similar brightness values can be synthesized. This is essential to broadening the application of these heterostructures in multiplexed imaging and improving the sensitivity of QD-based sensors for biological applications.

## **COLL 868**

### **Different strategies to modulate the optical band gap of semiconducting two-dimensional materials**

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Mono- or few-layers semiconducting two-dimensional materials (S2DM) exhibit exciting optical, electrical, magnetic, and catalytic properties. Due to these properties, S2DM have potential applications in ultrathin electronics, photonics, transistors, light-emitting diodes, touchscreens, energy storage devices, and catalysis. The exciting properties of the S2DM emerge from the formation of localized excitons of a large exciton binding energy when photoexcited. Additionally, the strong spin-orbital coupling (SOC) inside the individual S2DM sheet and the breaking of symmetry inversion induced the splitting of the valence band at the K valley of the Brillouin zone into A and B peaks. The bandgap values and band edge positions of S2DM depend greatly on the strength of SOC. This presentation focus on modifying the bandgap of S2DM by different techniques including: integrating the S2DM with plasmonic nanoparticles of strong electromagnetic field that alters the spin-orbital coupling, thus change the energy of the valence and conduction bands, applying strain that disturbs the bond lengths and the SOC, electron injection, which increase the electron density on the conduction band of

S2DM and induce bandgap renormalization, and change the dielectric function of the surrounding medium.

## **COLL 869**

### **Using metal-organic frameworks to spatially organize quantum dots**

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Advanced integration of colloidal semiconducting nanocrystals, e.g. quantum dots (QDs), into functional materials can benefit from precise control over relative position and orientation of all co-assembled elements. Such geometrically defined assemblies can enhance already existing properties of individual components or provide a platform for cooperative interactions between components, resulting in new emergent functionalities. However, the ability to arrange nanoscale components with precision and over multiple length scales with a desired spacing and geometry remains a significant synthetic challenge. Due to their unprecedented modularity, tunability, and porosity metal-organic frameworks (MOFs) represent a class of materials that can be utilized as a template for arranging nanocrystals in a controllable fashion. Here, we demonstrate the ability of MOFs to assemble nanoscale QDs over a long range through functionalization of their organic linkers and incorporation of QDs as a building block inside the MOF structure. In this way control over the position of optically active components can be achieved through tuning of synthetic parameters. The comprehensive characterization, combining optical imaging, electron microscopy and scattering techniques, of prepared hierarchical assemblies will be discussed. Overall, this work provides a new platform to construct multifunctional hierarchical assemblies, which can lead to development of novel photoactive materials with controlled properties.

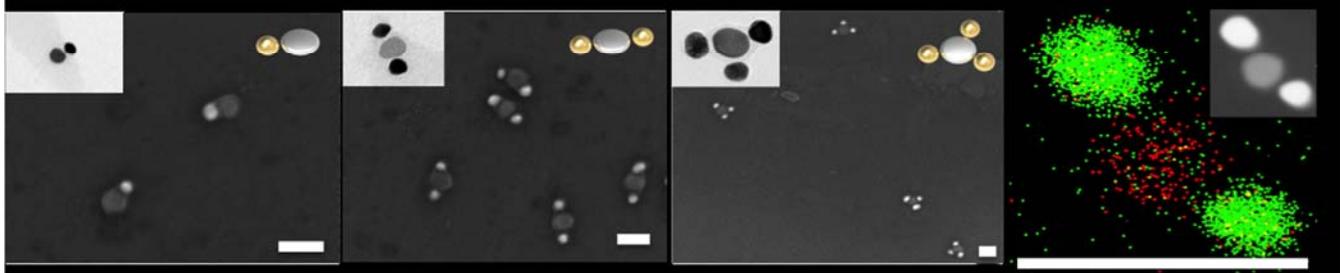
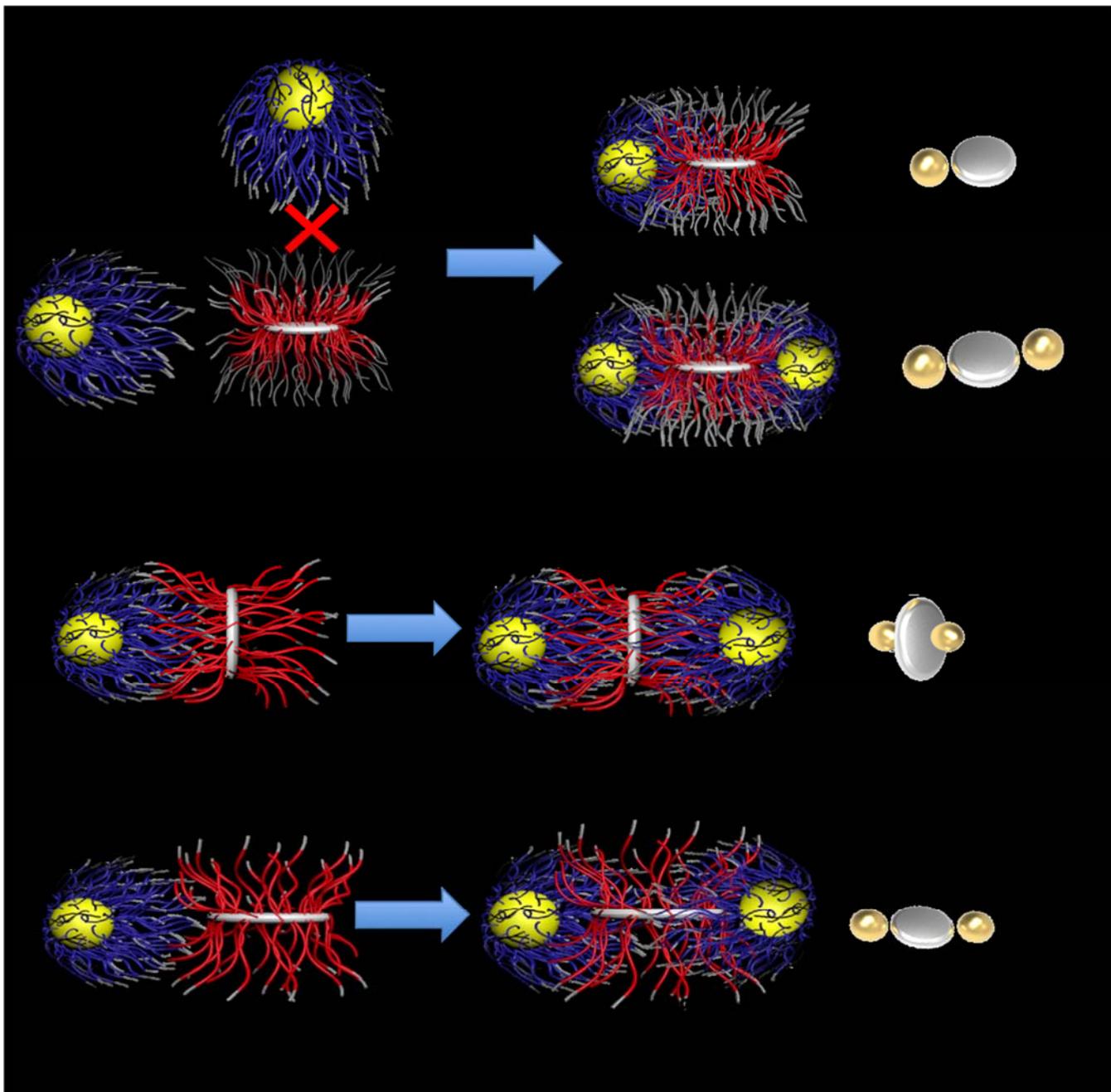
## **COLL 870**

### **Regioselective self-assembly of plasmonic supracolloids modulated by block copolymers with steric effects**

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In the designing of supracolloids, directional interactions play a crucial role in controlling the spatial arrangement and orientation of the building blocks. Sophisticated surface ligands facilitate the formation of directional bindings via specific interactions and encoding of surface. Anisotropic building blocks also attracted much attention with their unique geometries and shape constraints. In this article, we combine the steric

hindrance of polymeric ligands and the anisotropy of nanoparticles to develop a self-assembly system with precise control of the relative orientation of gold nanospheres on silver nanodiscs. The simple yet versatile strategy produces assemblies with ultrahigh regioselectivity and high yields of each well-defined assembly. Plasmonic supracolloids with different orientations have shown different peak shifts and electric field enhancement. This study may provide new insights for designing supracolloids with increased complexity and functionality. Studying the optical properties of the bimetallic assemblies with different orientations of plasmonic building blocks may contribute to the understanding of complex plasmonic coupling phenomena.

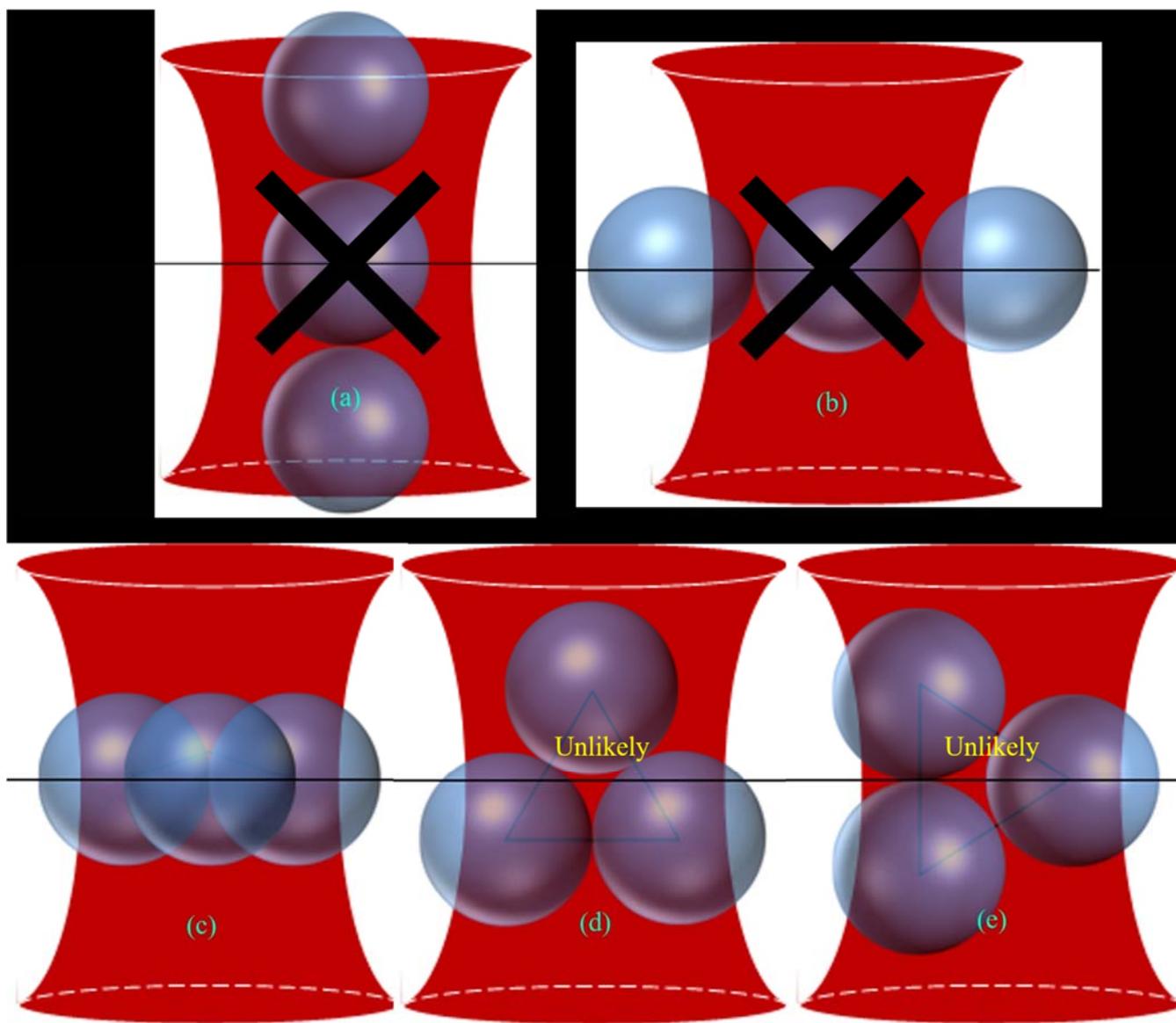


**COLL 871**

**Femtosecond optical tweezers for tracking optically directed self-assembly of nanoclusters *in-situ***

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Fragrance compounding is traditionally considered to be an art, unsullied by science, and often at best used in conjunction with a compounding pyramid for a guideline to accord generation. The current state of scientific understanding of olfaction has not allowed for the predictive modeling of scents. Existing quantitative estimators used in the industry, like the heuristic methodologies based on empirical correlations like the odor value (OV) have to typically account for variations in sociological conditions such as geography, gender and require a large number of trained human specialists. Equation of state methods are not currently scalable or theoretically valid for the complex multi-component mixtures which are used as perfumes. The intractable complexity of multi-component mixture analysis precludes the ability of the equation of state (EOS) methods to aid the industry. We have found that ultrafast optical probing of the precursor compound components of fragrances provides insights into the fragrance industrial process. From the signal generated by the refractive index changes in the solutions of accord primitives due to the heat dissipation processes, we have been able to infer the optimal accord concentration. This signal is generated by the changes in the refractive index due to the various modes of heat dissipation, is known as the thermal lens effect, one of which (convection) was not previously accounted for. The signal in alcohols is notable as it establishes a strong correlation between the TL signal and physical properties, like mobility, steric effects, and hydrogen bonding. We leverage these thermal lens effects as a control parameter for predictive accord generation and to gain insights into the light-matter interactions for industrial use.



Schematic representation of structure determination using our in situ methodology for tracking three-particle colloidal aggregation

**COLL 872**

### **Surfactant-free synthesis and purification of gold nanoprisms**

*Rafael Ramírez-Jiménez*<sup>1,2</sup>, *Álvaro Artiga*<sup>1,2</sup>, *Scott G. Mitchell*<sup>1,2</sup>, ***Rafael Martín-Rapún***<sup>1,2,3</sup>, *martin@unizar.es*, *Jesus M de la Fuente*<sup>1,2</sup>. (1) Institute of Materials Science of Aragon (CSIC-Universidad de Zaragoza), Zaragoza, Spain (2) CIBER de Bioingeniería, Biomateriales y Nanomedicina (CIBER-BBN), Madrid, Spain (3) Institute of Nanoscience of Aragon, University of Zaragoza, Zaragoza, Spain

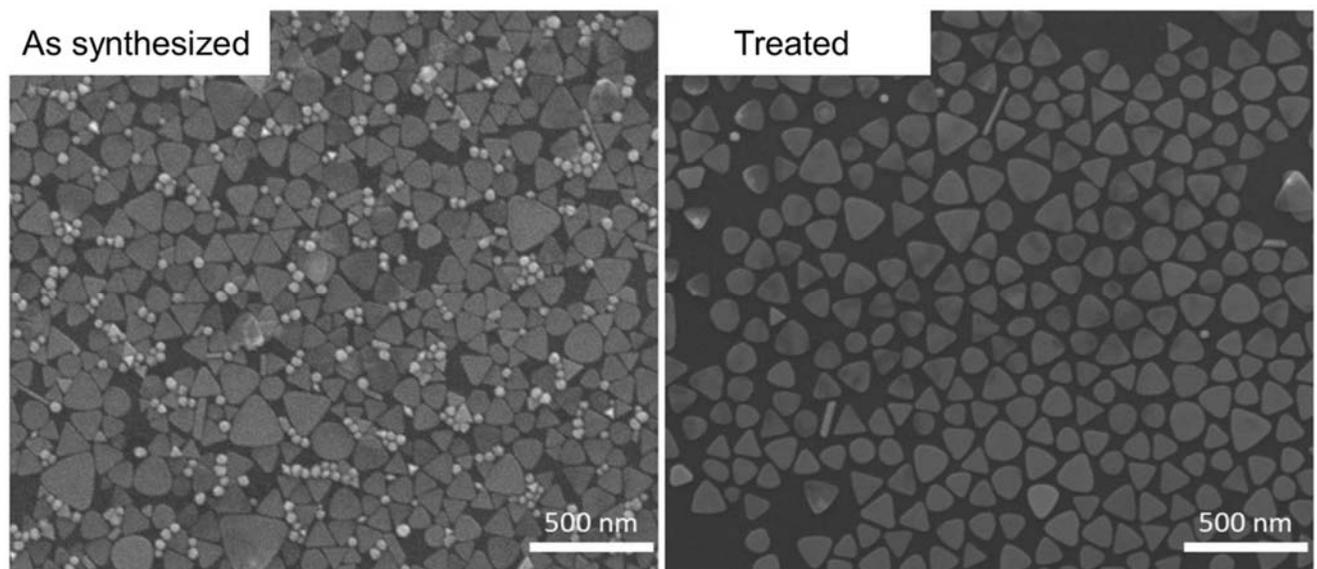
Gold nanoprisms (NPrs) exhibit localized surface plasmon resonance (LSPR) which can be tuned by controlling the size and the aspect ratio of the nanoparticles. Tuning the LSPR of NPrs across the near-infrared region of the spectrum has opened the door for their use as biomedical tools in the so called biological window, the range of wavelength at which the absorbance of biological tissues is highly decreased.

However, the synthesis of anisotropic gold nanoparticles is more challenging than their isotropic counterparts and requires low concentrations with soft reductants. A variety of capping agents or templates are used to favor shape selectivity but the most successful approach involves the toxic surfactants cetyltrimethylammonium bromide (CTAB) or chloride (CTAC) as templates. The toxicity of those additives poses a serious limitation for biomedical applications such as in optoacoustic imaging or in photothermal treatment of tumours.

CTAB-free methods for the preparation of gold NPrs are not easily scalable and provide low selectivity as a large amount of spherical nanoparticles (NSs) is produced too.

Separation methods reported to remove the nanospheres are time consuming and only affordable at very low scale.

Recently we reported a CTAB-free synthetic method of gold NPrs in which a Au(III) solution is treated with sodium thiosulfate and potassium iodide to yield a mixture of NPrs and NSs. In this work we present a scalable separation method in which the addition of glutathione (GSH) leads to the quantitative selective precipitation of gold NPrs. The combination of the synthetic and purification protocols allows tuning the LSPR band of the gold NPrs with good overall yields. The NPrs can be easily redispersed, coated with other stabilizing agents such as poly(ethylene glycol) (PEG) and further functionalized for targeting. Noteworthy, resulting NPrs-GSH-PEG are not internalized by Vero cells as opposed to our previous NPrs-PEG, which paves the way to their use in applications in which selectivity and targeting are crucial.



SEM micrographs of (a) the as synthesized mixture of NPrs and NSs and (b) the purified NPrs obtained by decantation of the mixture treated with glutathione.

## **COLL 873**

### **Susceptibility of superparamagnetic nanoparticles self-assembled in small clusters**

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Monte Carlo simulations were used to study the magnetic susceptibility of 5-10 nm superparamagnetic iron oxides nanoparticles (SPM NPs) self-assembled into clusters of different sizes and post-assembly processing by our experimental collaborators. Both the experiments and simulations have revealed that the cluster susceptibility depend on the sizes and numbers of NPs making the clusters, and their overall arrangement within the clusters. Our simulations clearly illustrate that different interactions between NPs affect the magnetic states of clusters made of them and their susceptibility. In particular, the susceptibility largely changes with the size of the clusters, which can be in mono-domain superparamagnetic or magnetically blocked states.

## **COLL 874**

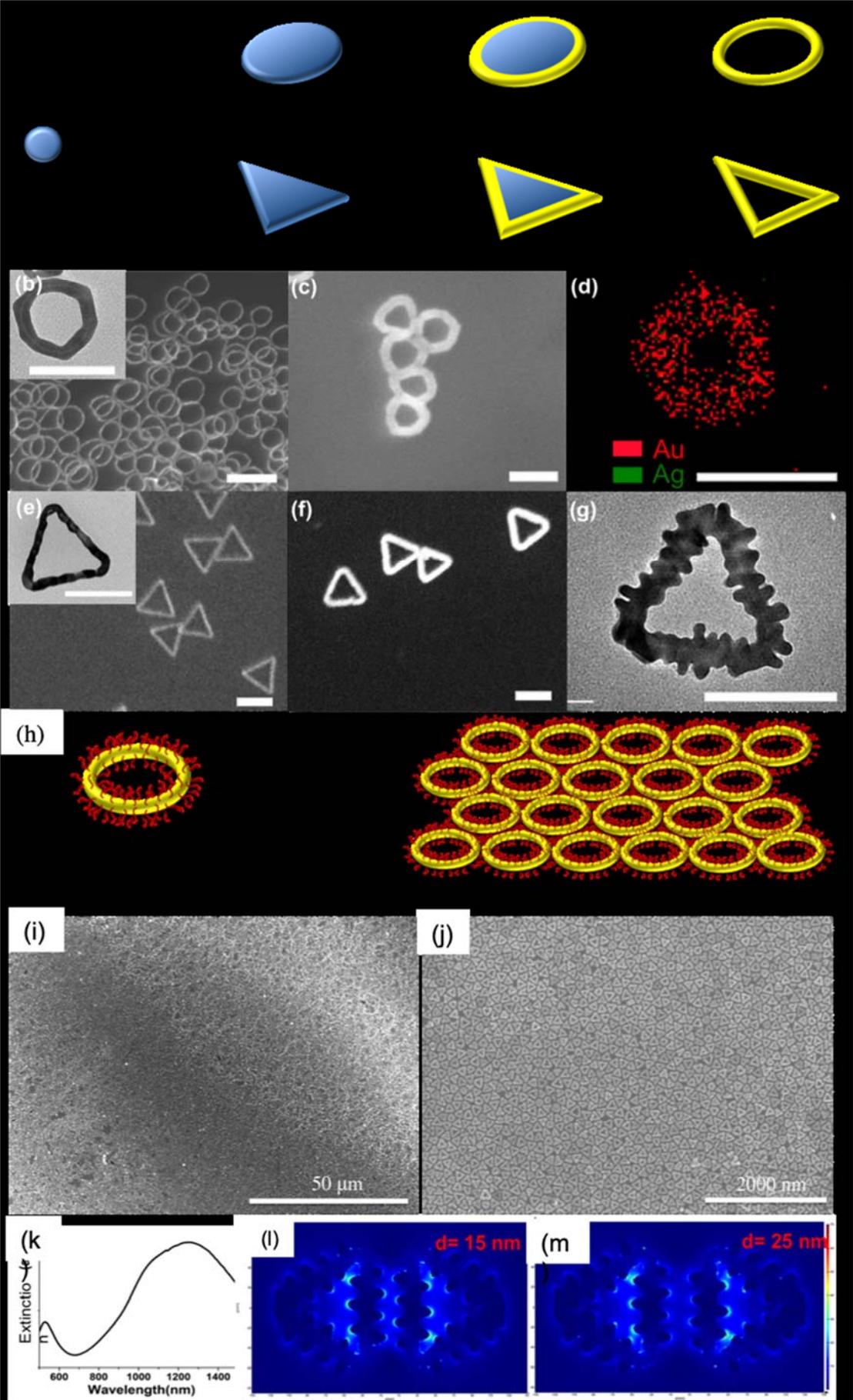
### **Controllable synthesis and two-dimensional self-assembly of gold nanorings with tunable optical properties**

**Xiaoying Lin**, [linxiaoying725@gmail.com](mailto:linxiaoying725@gmail.com), **Zhihong Nie**. Biochemistry and Chemistry, University of Maryland College Park, College Park, Maryland, United States

Gold nanorings (AuNRs) are attractive in photonics, electronics, catalysis, bioimaging, and biosensors, due to their unique geometries and optical properties. Comparing with their isotropic counterparts (*e.g.*, Au nanospheres), such topologically complex nanostructures exhibit localized surface plasmon resonance (LSPR) over a much broader window of wavelengths. Controlling the geometry (*i.e.*, diameter and ridge thickness) and organization (*i.e.*, orientation, symmetry, and spacing) of AuNRs in assemblies is highly desirable for tailoring the plasmonic couplings and hence the optical response of resulting materials. However, to date synthesis and optical study of AuNRs are still in their infancy, mainly due to current challenge in the synthesis of high-quality anisotropic nanoparticles at large quantity with precise control. Although existing top-down techniques (*e.g.*, e-beam lithography) provide high precision and reasonable resolution in fabrication of AuNRs, these methods are limited by their high cost, low yield of production, and the requirement of special equipment.

Herein, we present a facile wet-chemistry synthesis of circular and triangular AuNRs

with tunable surface roughness, dimension, and hence optical properties. The synthesis approach includes the epitaxial Au deposition on sacrificial templates of shaped Ag nanoplates, chemical etching to remove Ag, and further Au deposition to achieve desired ridge thickness. Furthermore, the freestanding AuNRs are ready to be used as building blocks for multi-dimensional self-assembly experiments. We demonstrated the 2-dimensional self-assembled monolayers (SAMs) of AuNRs fabricated at liquid-liquid interfaces. The SAMs can be transferred to flexible substrate and be used for tensile sensors. This research may provide new insights on plasmonic coupling of metallic nanostructures and open avenues to advanced optical devices at micro- and nanoscale.



## COLL 875

### **Poly(*N*-vinylpyrrolidone) end-groups influence shape-control of Ag nanocubes through Ag<sup>+</sup> reduction kinetics**

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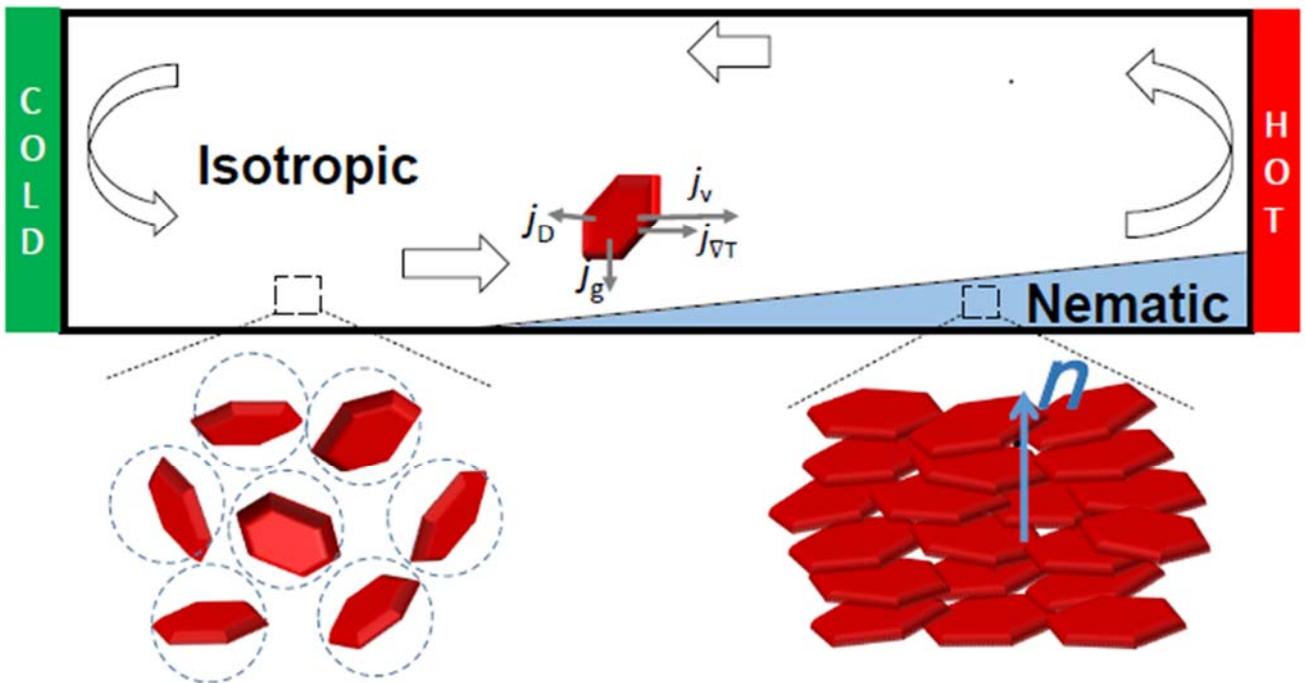
PVP is ubiquitously used in shape-controlled synthesis of Ag nanocubes (NCs). While previous studies considered PVP as the structure-directing agent, recent reports demonstrate Cl<sup>-</sup>, added as HCl, is the dominant structure-directing agent. However, PVP influences the final shape of Ag NPs beyond simple stabilization since changes in monomer concentration ( $C_m$ ) or molecular weight ( $M_w$ ) impact shape. This suggests the concentration and potentially the identity of end groups impact the final shape. We demonstrate PVP acts as the dominant reducing agent, where the end groups influence the rate of Ag<sup>+</sup> reduction leading to kinetically preferred shapes even in the presence of Cl<sup>-</sup>. We constructed an experimental phase diagram for the formation of Ag NCs by varying the PVP  $C_m$  and  $M_w$  at constant [H<sup>+</sup>] and [Cl<sup>-</sup>]. Between the upper (related to the role of PVP in Ag<sup>+</sup> reduction) and lower (related to a required minimum amount of PVP for stabilization) boundary of the phase diagram, any combination of PVP  $C_m$  and  $M_w$  can yield Ag NCs. Optical studies show direct dependence of Ag<sup>+</sup> reduction to the molar ratio of PVP/Ag and a decreased rate with higher  $M_w$  at constant  $C_m$ . These results suggest PVP dominates Ag<sup>+</sup> reduction and the reducing power is enhanced with increased PVP end-groups concentration. Although the end-group/Ag<sup>+</sup> ratio is well below stoichiometric, we demonstrate PVP end-groups induce the reduction (nucleation) of Ag<sup>+</sup>, followed by an autocatalytic reduction at a rate commensurate with AgCl dissolution. The impact of PVP end-groups is further demonstrated by synthesizing Ag NCs using end-group specific PVP synthesized with precise control over the average  $M_w$ . Experimental results reveal PVP with –OH end groups generate kinetically-preferred Ag nanorods while those with –CHO end groups form thermodynamically preferred Ag NCs. Overall this work provides key insights into understanding the role of PVP in influencing Ag<sup>+</sup> reduction kinetics and begins to shed light on why PVP is an effective polymer in shape-controlled growth.

## COLL 876

### **Controlled growth of colloidal nanoplate liquid crystals using temperature gradients**

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Controlling colloidal self-assemblies using external forces is essential to develop modern electro-optical and biomedical devices. Importantly, shape anisotropic colloids can provide optical properties such as birefringence. Here we demonstrate that external temperature gradients can be effective in controlling nematic liquid crystalline (LC) order in suspensions of plate-like colloids also known as nanoplates. Nanoplates, in an isotropic suspension, wherein their orientations are random, could be effectively moved using a temperature gradient environment causing a phase transition to LC nematic phase. Such controllably formed nematic phase featured large nematic monodomains and enabled topologically more stable structures that were evident from the absence of hedgehog-type defects which are typically found in nematics formed spontaneously via nucleation and growth mechanism in a sufficiently high concentration suspension of nanoplates. Due to their high surface area-to-volume ratio and excellent thermophoretic properties, nanoplates can prove to be ideal candidates for transport of biomolecules through temperature varying environments.



## **Laser-based synthesis of functionalized gold nanoparticles in organic environments**

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Pulsed Laser Ablation in Liquids (PLAL) has proven to be an excellent method for the production of highly pure and stable gold nanoparticles in aqueous environments; the factors governing particle size resulting from ablation in water have been elucidated through extensive experimental and computational studies. However, there exist many applications that require gold nanoparticles to be dispersed in organic, and in particular, non-polar environments. Work in this area is far behind that in water and presents a unique set of challenges in terms of particle size, stability, and purity. To further our knowledge in this area, our study looking at pulsed laser ablation of a gold target in n-decane will be presented. This will include a discussion on the addition of various chain length alkanethiols and the influence they have on particle size and stability. Additional considerations, such as the link between dissolved gases, radical formation, and the presence of photothermal oxidation, will also be examined.

### **COLL 878**

## **Synthesis of reduced graphene oxide/carbon nanotubes composites and their colloidal behavior**

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This is a study of colloidal behavior of four different Graphene Oxide and Carbon nanotube composites. Oxygen containing groups in Graphene oxide was removed in presence of carbon nanotubes at three different levels. GO-CNT composites containing 22 to 1% oxygen was studied by SEM, Raman, FTIR and TGA. Colloidal behavior was studied in detail by measuring hydrophobicity, dispersibility, solubility and critical coagulation concentration (ccc value). Solubility, dispersibility and of GO-CNT composite decreased significantly after removing of oxygen containing groups from 6.2 to ~0 µg/ml and 7.1 to 0.5 µg/ml respectively. CCC value also decreased from 16 to 6 in presence of NaCl and it decreased from 3 to 1 in presence of MgCl<sub>2</sub>. It was investigated that hydrophobicity was highly related to oxygen content and the highly hydrophilic composites with hydrophobicity index of -3.2% became highly hydrophobic with hydrophobicity index of 7.4%.

### **COLL 879**

## **Engineering rheological response in water-in-oil emulsions through mixtures of rhamnolipid and sophorolipid biosurfactants with silica particles**

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Sustainable formulations are gaining increasing importance in a wide range of industrial sectors including cosmetics, homecare etc. This need for sustainability is causing a shift in the industry in potentially moving away from synthetic surfactants and replacing them with more sustainable alternatives. One possible route to this has been through the potential utilization of biosurfactants such as rhamnolipids and sophorolipids as emulsifiers. The challenge however has been adequate rheology build in these emulsion systems. In this study we illustrate that the addition of silica particles to biosurfactant stabilized water-in-oil emulsions significantly enhances the viscosity and impacts the viscoelastic response remarkably. The concentration of silica particles and the size of the particles was significantly seen to impact the rheological response. In addition to mechanical rheometry, optical microrheology through Diffusing Wave Spectroscopy (DWS) was carried out to gain insights into the high frequency (short time) dynamics in the system.

### **COLL 880**

#### **Aggregated colloidal suspensions under extensional flows**

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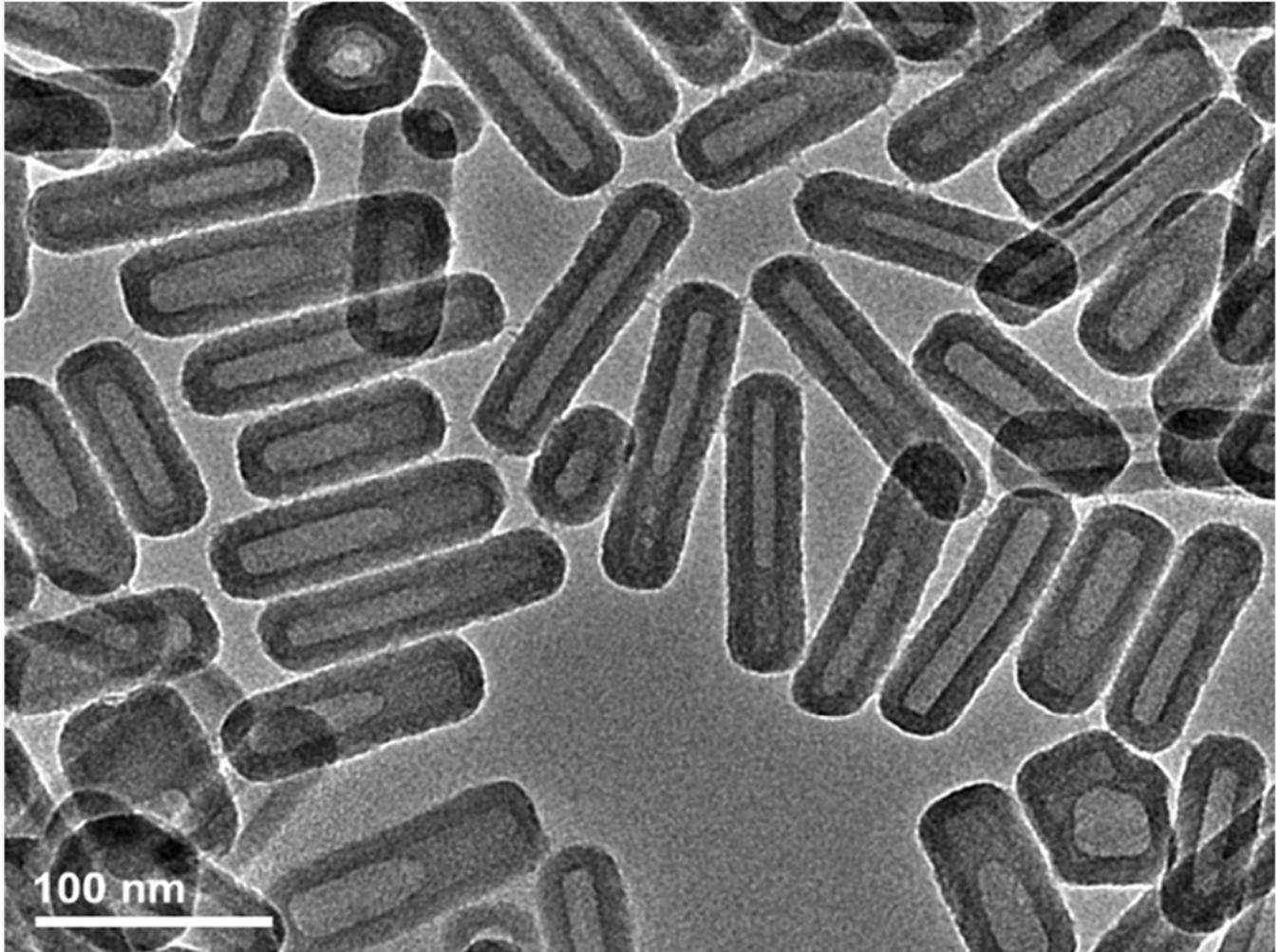
Design of colloidal suspensions for damping and energy absorption applications requires a thorough understanding of the flow fields as a function of the imposed shear rate. In this work, we characterize the rheological properties of amorphous fumed silica suspensions under steady shear and extensional flows to map the location of discontinuous shear thickening and jamming behavior. In the case of extensional flow, we use ultrasound imaging to visualize the evolution of the flow field with increasing shear rate and identify a jamming front. We also assess the tunability of this suspension by imposing an orthogonal superposition flow to control the dethickening process upon the thickened state.

### **COLL 881**

#### **Gelation in colloidal suspensions of rod-like particles of low to moderate aspect ratio**

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Colloidal suspensions of anisotropic particles are widely utilized in consumer products. Homogeneous, physical gelation and vitrification follows rigidity percolation, providing a universal view of dynamical arrest in suspensions of spherical particles (Valadez-Perez et al. PRE, 2013). However, the effect of particle shape on the gel and glass transition boundaries is not well-understood for anisotropic particle suspensions, particularly for colloids with lower aspect ratios (AR,  $L/D \sim 1-10$ ). The key aim of this study is to clarify the effects of particle shape by combining neutron, X-Ray and light scattering measurements of microstructure with rheology and dynamic light scattering measurements of the dynamics. While prior work in our group identified the conditions for gel formation in model silica rod systems, questions remain about the effects of gravity (Murphy et al., Langmuir 32 2016, 8424-8435) A new thermoreversible colloidal system has been developed, which is composed of hollow, octadecyl-coated silica rods with dimensions of 30-200 nm, tunable aspect ratios, and short-range attractions. Importantly, the gravitational Peclet number is sufficiently low so gravitational settling is unimportant except at the lowest volume fractions (Kim et al. PRL, 2013). SAOS measurements confirm the thermoreversibility of the microstructure and its transition from fluid-state to gel-state. SANS characterizes the form factor of primary particles (shape, core and shell dimensions, brush conformation, size dispersity) as well as the interparticle attraction strength and fractal dimension ( $D_f$ ) of the fluid and gel microstructure. Complementary simulations show congruence of dynamical arrest with rigidity percolation, providing a unified view of homogeneous gelation in suspensions of low aspect ratio colloids.



Octadecyl-coated hollow silica rods of dimensions  $D \sim 30$  nm and  $L \sim 120$  nm

## **COLL 882**

### **Rheo-MAGIK: Instrument development for investigating 2D soft materials via interfacial rheology and neutron reflectivity**

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Interfacial structure and rheological properties play a significant role in the behavior of many biological (e.g. membranes) and synthetic systems (e.g. emulsions). Understanding structure-property relationships between the molecular structure of the

interface and interfacial elasticity and shear moduli can guide formulation of surfaces with desired interfacial properties. Langmuir trough experiments are typically used to study interfacial isotherms, but the mixed shear and compression/dilatational flow field generated in the trough create issues with studying complex interfaces. For such systems, both surface shear and dilatational moduli are important. Attempts have been made to resolve the anisotropic state of stress into their pure force, through multiple measurements in the Langmuir trough or radial trough; however, the morphology necessary to fully comprehend the rheological behavior of these systems remains elusive. In this presentation, we describe the design and implementation of the new “Quadrotrough,” a modified Langmuir trough, to better approximate pure interfacial dilation or shear kinematics. The rheological capabilities of this interfacial trough are demonstrated through proof-of-concept experiments on widely studied model systems, stearic acid with and without added multivalent salts. Importantly, this trough enables a more direct way to understand how processing affects the rheological behavior of these interfacial materials. We critically test the hypothesis that anisotropic compression will only significantly affect the dilatational rheology for interfaces with finite surface shear moduli. This is important because convolution of mixed flow fields greatly complicates data interpretation. Combining the new Quadrotrough with both Brewster angle microscopy and neutron reflectivity provides detailed structural measurements of the interface at the microscale and nanoscale that elucidates the source of this path dependence. The potential for rheo-MAGIK, will be discussed and future investigations are reflected on for instrument development.

## **COLL 883**

### **Interactions between colloidal particles mediated by nonadsorbing polymers: Casimir and anti-Casimir effects**

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Using a lattice self-consistent field (SCF) theory and the corresponding lattice Monte Carlo (MC) simulations combined with our recently proposed Z method (Zhang, P.; Wang, Q. *Soft Matter*, 2015, 11, 862), we examined homopolymer solutions confined between two parallel and nonabsorbing surfaces and in equilibrium with a bulk solution, and accurately calculated the effective interaction between the two surfaces. Close to the critical point of the solution, we found for the first time, by using the SCF theory, the Casimir effect with long-range attractive intersurface potential  $W < 0$  extending to  $D/R_e \approx 10$ , where  $D$  denotes the intersurface separation and  $R_e$  the root-mean-square chain end-to-end distance in the bulk solution. On the other hand, by directly comparing our MC results with SCF predictions based on the same model system, we were able to quantitatively and unambiguously distinguish the mean-field and the fluctuation contributions to  $W$ , and found for the first time the fluctuation-induced repulsion  $W > 0$  between the two confining surfaces at intermediate  $D \approx R_e$  (i.e., the anti-Casimir effect)

predicted by Semenov and Obukhov (Obukhov, S. P.; Semenov, A. N. Phys. Rev. Lett. 2005, 95, 038305), which is about one order of magnitude stronger than that due solely to the finite chain length as predicted by the SCF theory. The repulsion strength decreases with decreasing solvent quality and vanishes near the critical point.

## **COLL 884**

### **Application of colloidal functionalized layered silicates in drilling fluids**

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Drilling fluids play a significant role in the successful completion of oil and gas well. The properties of drilling fluids — rheology, density, lubricity, viscosity, yield point — are the governing parameters in oil well construction process for efficient production of crude oil and gas. There are mainly three types of drilling fluids have applied for drilling operation — water-based, oil-based and pneumatic fluids. Among them, oil-based drilling fluids have considered as well-established fluids, owing to their inherent advantages over other fluids. The rheological properties of the drilling fluids can be tailored through different additives. In the present research, we have developed colloidal, layered silicates with covalently-linked organic functionalities and employed as viscosifier in drilling fluids. The nanometer-thick platelets of synthetic layered silicates facilitate formation of stable colloidal dispersion and it allow the suspension of high-density particles in the drilling fluids. The rheological properties of drilling fluids are measured under extreme conditions, up to 10,000 psi and 200 °C. Viscoelastic properties of this novel additive have excelled the conventional viscosifiers. Colloidal functionalized layered silicates have demonstrated exceptional rheological properties under these conditions. Strong Si-C linkages in the colloidal platelets provide excellent thermal stability and steadiness in alkaline or acidic conditions.

## **COLL 885**

### **Unifying framework for testing frictional contact model and shear thickening in industrially relevant systems**

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Shear thickening describes the phenomena where the shear stress increases faster than linear than shear rate, causing an apparent increase in viscosity. It is especially pronounced for high concentration slurries, widely processed in many industries. Several mechanisms have been proposed, including contact friction and hydrodynamic friction, such that surface friction, nanoscale particle interactions, particle shape and

size distribution all contribute to determining the jamming fraction, the volume fraction at which the suspension ceases to flow. Recent simulations provide testable models linking the jamming point for shear thickening to particle surface or lubrication friction. However, many industrially relevant suspensions are aqueous-based, and have more complex interaction potentials, such as the repulsive electrostatic forces and attractive dispersion forces, and thus require the incorporation of additional forces to existing models.

Surface chemistries govern interparticle interaction and the rheology of the slurry. Silica-coated titania and monodispersed silica particles are grafted with a lubricating, short-chain, polymer layer, and dispersed in aqueous and index-matched solvent, respectively. In both systems, significant reduction in shear thickening are achieved with the grafting of the polymer. The contact friction model is fit to flow curves, and appear to be a suitable semi-empirical model for predicting shear thickening for both systems. These findings are complemented by direct friction measurements by atomic force microscopy, and simultaneous measurements of rheology and small angle neutron scattering.

While traditional rheometry relies on measuring the flow curves to extrapolate to a jamming point, this process is time-consuming and prone to error from individual measurements. Thus, methods for rapid, accurate determination of the jamming points are needed for testing and validating results for a wide range of systems. We innovate a way to obtain jamming point through a one-step process for aqueous suspensions. The procedure monitors the shear stress under constant shear stress or shear rate as the sample is dewatered by evaporation using immobilization cell rheometry, until the system physically jams. These jamming point measurements are validated by methods measuring steady state rheology. The procedure allows for the rapid determination of critical suspension properties for a large sample space and at the point of manufacture.

## **COLL 886**

### **Teaching the old mesoporous silica nanospheres (MSN) new tricks: Sensing capabilities**

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In the past three decades mesoporous silica nanomaterials proved to be one of the most versatile platforms in the realms of solid supported catalysis, biomedical applications, sensing (in both gas and liquid) and more recently, optoelectronics. The recent studies on naturally occurring silica materials from glass sponges and diatoms, have pointed out very interesting optical properties, such as light waveguiding, diffraction, focusing, and photoluminescence, owed to both their intricate geometries, as well as low refractive index and a very low absorption coefficient in the visible range.

The presentation will elaborate on the potential of highly ordered mesoporous silica-as a synthetic system-to replicate a similar behavior with the ordered silica-based marine organisms in the interaction with light and the benefits for MSN in novel sensing mechanisms. Specifically, significant (more than one order of magnitude) surface-enhanced Raman scattering (SERS) is observed when using MSN in combination with plasmonic nanoparticles. Surface modifications and the ability to tuning optical properties of MSNs will be also discussed.

## **COLL 887**

### **Lipid corona acquisition by engineered gold nanoparticles**

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Gold nanoparticles (AuNPs) with tunable shape- and size-dependent plasmonic properties and surface chemistry are engineered for potential diagnostic and therapeutic applications, e.g. as sensing, imaging, and drug-delivering agents. However once released into biological environments, AuNPs acquire biomolecular coronas, such as protein coronas, leading to unintended off-target toxic effects. We earlier found that thiol ligands can assemble heterogeneously into ligand islands at small to intermediate NP diameters. We show through simulation that the resulting voids between islands can fill with lipids as the AuNPs acquire them when exposed to lipid-bilayer interfaces. Complementary experiments confirm the acquisition of lipids by engineered AuNPs flowed over supported lipid bilayers. Together, the simulations and experiments reveal (1) characteristic AuNP surface chemistries that drive lipid corona formation and (2) the potential molecular-level basis for the onset of AuNP toxicity.

## **COLL 888**

### **Enhancement of flocculation and dewaterability of MBR activated sludge using a hybrid system**

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This study investigates the influence of hybrid coagulation-flocculation system on the flocculation and dewaterability efficiency of a real highly stable membrane bioreactor (MBR) sludge. Two organic coagulants, polyDADMAC (FL 4440) and polyamine (FL 2949) coupled with different structured polyacrylamides (PAMs) are used. Residual turbidity, zeta potential ( $\zeta$ ), flocs size and capillary suction time (CST) are used to assess the impact of the hybrid system on the degree of flocculation and dewaterability

of MBR sludge. Addition of FL 4440 and FL 2949 prior to PAM has greatly reduced the turbidity and  $\zeta$  of the sludge suspension by decreasing the required doses of PAMs 67% to 80% depending on the type of the PAMs used. Polyamine coagulant was more efficient in coagulation and hybrid coagulation-flocculation for MBR activated sludge. The impact of FL 2949 and FL 4440 was more significant on the linear structured PAMs with 71 and 80% reduction in the required PAM's dose for 40% CD (FO 4490 SSH) and 60% CD (FO 4690 SSH), respectively followed by slightly and highly branched structured PAMs. Similar observations were observed for flocs size and dewaterability (CST) measurements of the flocculated MBR sludge. The results showed a maximum reduction of 58% in the flocs size for sludge conditioned with PAMs in the presence of FL 2949 and FL 4440. Nevertheless, comparable results were obtained for the dewaterability of the flocs produced by PAMs individually and hybrid system. Overall, this study successfully determines the effect of hybrid coagulation-flocculation on the flocculation performance of the MBR sludge.

## **COLL 889**

### **Linear-nonlinear dichotomy rheological behavior of carbon black-filled polybutadiene/tetradecane solutions**

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When dynamic shears are applied in sinusoidal waves on a colloidal gel, the stress responses are usually non-sinusoidal due to the nonlinear viscoelastic behavior of the material. However, for many polymeric rubbers filled with nano-sized solid particles, their dynamic stress shows surprisingly sinusoidal responses even though the stress amplitude decreases as the strain amplitude increases. In literatures, it has been called the "linear-nonlinear dichotomy" of the Payne effect. This unusual paradox behavior has drawn much attention recently. In order to understand this paradox, two monodispersed polybutadienes were prepared and dissolved in tetradecane with the polymer concentration  $\Phi$  ranging from the coil overlapping state ( $\Phi = \Phi^*$ ) to the melt state ( $\Phi = 1$ ). On this basis, we made mixtures by mixing 1 part of carbon black and 2 parts of polybutadiene/tetradecane solutions. Systematic rheometrical measurements were carried out to study the mechanical responses of these particle-filled polymer solutions. Our results show that there is a transition to the linear-nonlinear dichotomy rheology at a specific entanglement molecular weight  $M_e$ . Below  $M_e$ , the carbon black-filled polybutadiene/tetradecane solution displays an anomalous behavior, where the ratio of the third to the first harmonic responses  $I_3/I_1$  decline to zero independent of the drop of modulus  $G'$ , and the stress response shows surprisingly quasi-sinusoidal. The results show that the mesh size of the entangled polymer network may play an important role in this anomalous rheological behavior.

## **COLL 890**

## **Tuning the dielectrophoretic assembly of dielectric particles through surface functionalization**

**Nathan D. Burrows**<sup>1</sup>, *nub90@psu.edu*, **Christine D. Keating**<sup>2</sup>. (1) Department of Chemistry, Pennsylvania State University, State College, Pennsylvania, United States (2) Penn State University, University Park, Pennsylvania, United States

The directed self-assembly of particles in a non-uniform electric field can be achieved due to the phenomenon of dielectrophoresis resulting in an applied force. The strength of this force depends on the polarizability of both the particles & suspending medium, the particles' size and shape, and the frequency of the electric field. The Clausius-Mossotti Factor, a frequency-dependent function of both the particle and medium complex dielectric permittivity, determines the direction and magnitude of particle response to applied AC fields and changes with charge carrier density. Surface functionalization can alter the mobility of the charges associated with the particle surface electrical double-layer and presents an opportunity to further tune the dielectrophoretic (DEP) response. Herein we present the characterization of the DEP response of particles tuned by various surface chemistries and demonstrate the importance of surface charge mobility in DEP assembly.

### **COLL 891**

#### **Nano-additive manufacturing**

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For decades, a staggering amount of research has focused on the creation of novel nanomaterials and the elucidation of their unique property-structure correlations. Highly reliable bottom-up and top-down synthetic routes that produce increasingly complex nanomaterials with highly ordered and complex geometries have been developed. Complications in scaling up and uniformity have hampered widespread application of nanomaterials. In this talk, I will describe the construction and operation of a simple automated flow-throughput domain process that enables a uniform reaction environment for production of high-quality materials in large quantities. Nanomaterials can be subsequently printed on various surfaces through reliable surface functionalization approaches.

### **COLL 892**

#### **Enhanced antioxidant activity of cerium oxide nanoparticles by surface modification and their applications**

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Reactive oxygen species (ROS) generated in vivo from immune responses are generally linked to aging, cancer, and nervous system diseases. Several kinds of antioxidant nanoparticles have been developed by chemists and biologists to reduce the ROS levels in vivo. Cerium oxide nanoparticles exhibit recyclable antioxidant properties due to facile electron transfer between Cerium (III) and Cerium (IV). Recent studies reveal that ceria nanoparticles with diameters of 5 nm are non-toxic and efficient for quenching ROS in vivo. We developed a PEGylated polymeric ceria nanoparticle which is stable and biocompatible. We also observed that the antioxidant activity of cerium oxide nanoparticle is enhanced by this PEGylated surface modification which can be widely used in vivo to control the ROS levels induced by immune responses.

### **COLL 893**

#### **Effects of pH on the synthesis of TiO<sub>2</sub> brookite nanoparticles**

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Titanium dioxide, TiO<sub>2</sub>, nanoparticles are a commonly used material in industry in particular with applications in the photocatalysis of organic compounds. Since the material acts as a heterogeneous catalyst, both surface and crystalline structure play an integral part in photocatalytic activity. This project will be looking at the unexplored brookite morphology of TiO<sub>2</sub> and in particular, methods to optimize the shape and size of the nanoscale particles. Particles were synthesized using hydrothermal method with different pH, and analyzed using scanning electron microscopy and powder x-ray diffraction.

### **COLL 894**

#### **Attenuation length versus packing density: Nitrogen based self-assembled small molecule film on copper with thermal treatment**

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We focus on the phenomenon of thermal treatment of nitrogen based self-assembled small molecule films fabricated on copper, which utilize nitrogen-containing group as anchoring group, investigated by X-ray photoelectron spectroscopy (XPS) quantitative characterization. The interesting result is that the ratio of Cu2p signal intensity decreased after annealing which is opposite to the general theory because the molecules would normally be decayed or removed after annealing and the ratio of Cu2p signal intensity should be increased. We demonstrate that the phenomenon is related to the intermolecular distance variation (e.g. packing density) in multilayers. The small

molecule films on copper will rearrange after thermal treatment and become the denser and thinner layers characterized by water contact angle, ellipsometry and IR. Moreover, the packing density also obviously affects the photoelectron attenuation lengths (AL) of XPS which makes Cu2p signal intensity decreased after annealing.

materials	Cu/ 280°C		TT/ 280°C		TTT/ 280°C	
Contact angle	48.2°	77.7°	35.7°	78.6°	33.2°	82.4°
N area (10 <sup>3</sup> )	2.6	2.8	<b>6.8</b>	<b>3.9</b>	2.9	6.9
Cu area (10 <sup>3</sup> )	590.5	365.7	<b>109.7</b>	<b>140.5</b>	320.9	95.8
N*/(N*+Cu*)%	4.7	7.8	41.1	23.7	9.0	44.4
Thickness (nm)	0.00	0.00	9.1 ± 0.6	4.0 ± 0.6	7.9 ± 0.4	5.1 ± 0.4
materials	DMT/ 280°C		DDT/ 280°C		C8CN/ 280°C	
Contact angle	63.6°	70.7°	104°	98°	62.7°	98.6°
N area (10 <sup>3</sup> )	<b>6.0</b>	<b>6.1</b>	2.4	2.3	2.2	3.7
Cu area (10 <sup>3</sup> )	<b>419.5</b>	<b>454.9</b>	503.6	561.9	578.8	517.1
N*/(N*+Cu*)%	<b>13.9</b>	<b>13.1</b>	5.1	4.4	4.1	7.5
Thickness (nm)	7.3 ± 0.6	7.0 ± 0.6	2.0 ± 0.6	1.9 ± 0.6	2.7 ± 0.4	0.5 ± 0.2
materials	Pt/ 280°C		Gn/ 280°C		Gno/ 280°C	
Contact angle	52.0°	73.4°	55.2°	76.9°	23.0°	90.4°
N area (10 <sup>3</sup> )	3.1	3.1	2.1	6.8	<b>3.9</b>	<b>6.2</b>
Cu area (10 <sup>3</sup> )	558.8	403.6	267.4	264.8	<b>487.5</b>	<b>339.0</b>
N*/(N*+Cu*)%	5.7	7.8	8.2	22.3	8.2	16.9
Thickness (nm)	4.4 ± 0.2	4.3 ± 0.2	-	-	2.2	0.6

Quantitative results of N1s and Cu2p intensity calculated by Relative sensitive factor methodology.

## COLL 895

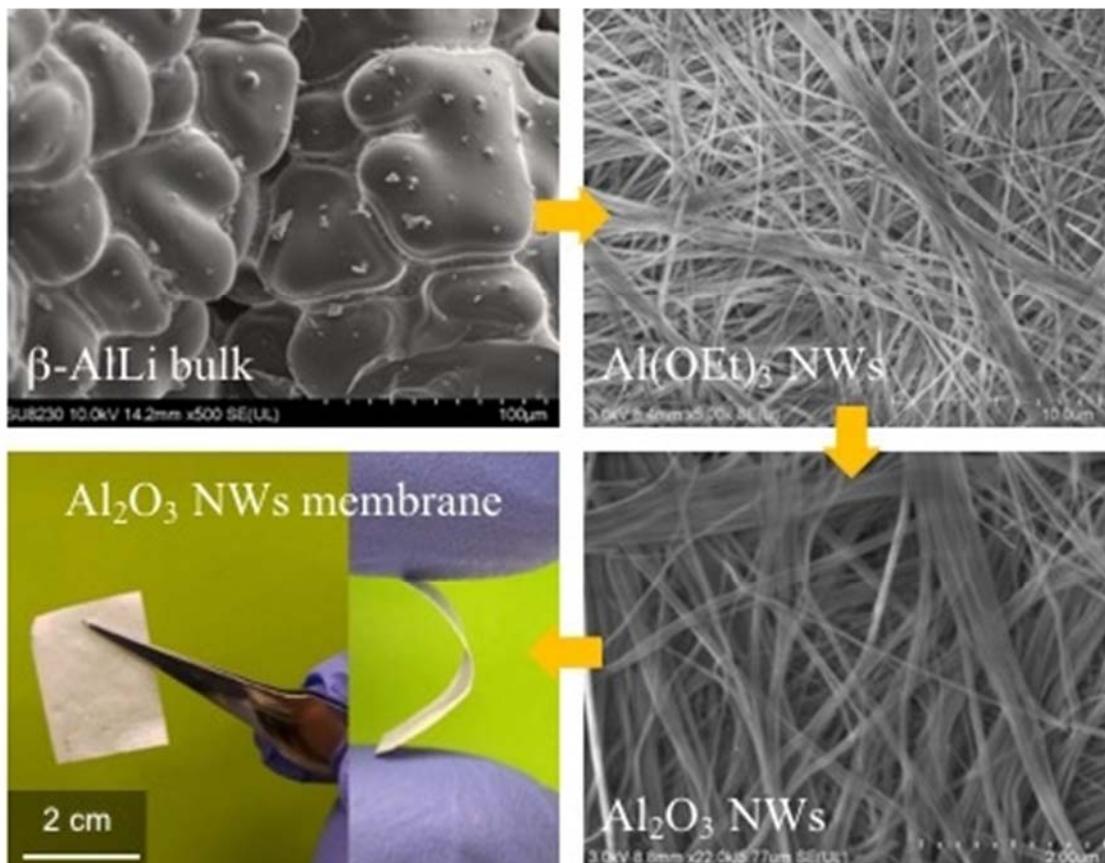
### Transformation of bulk alloys to inorganic nanowires

**Kostiantyn Turcheniuk**, [k.turcheniuk@gatech.edu](mailto:k.turcheniuk@gatech.edu), *Fujia Wang, Shunrui Luo, Alexandre Magasinski, Ah-Young Song, Danni Lei, Jim Benson, Gleb Yushin*. Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States

The reduction of the diameter of the 1D materials from 1000 nm by the factor of 10-100 can dramatically increase their mechanical properties. In particular, the Al<sub>2</sub>O<sub>3</sub> 1D materials with the diameters of the sub 50 nm are believed to exhibit superior tensile strength and modulus, as predicted theoretically (tensile strength 20 GPa), which is of

tremendous importance to the field of engineered composites, especially taking into account availability of alumina, its lightweight and low cost. However, the synthesis of ceramic 1D materials embraces outstanding challenges with the use of complicated reaction techniques.

Here, we demonstrate an unexpected discovery of the synthesis of metal-organic Al and Mg alkoxide NWs with tunable diameters (40-1000 nm) and high aspect ratios (1,000+) upon exposure of bulk bimetallic Al-Li or Mg-Li alloys to alcohols at ambient temperatures and pressures without the use of any catalysts, porous templates, corrosive chemicals or external stimuli. We demonstrate the conversion of metal-organic Al and Mg alkoxide NWs to the corresponding ceramic  $\text{Al}_2\text{O}_3$  and MgO NWs upon heating. We demonstrate the crucial parameters of the controllable growth of the metal-organic NWs, such as the composition of the alloy, molecular structure of the NWs, and the strain energy minimization of alloy grains at the reactive interface. By utilizing the solution and solid-state nuclear magnetic resonance, we provide sufficient characterization rigor of the molecular structure of the metal-organic NWs. We will also demonstrate the technology of the replacement of conventional polymer separators for Li-ion batteries (LIBs) by thermally stable, flexible, and wettable binder-free  $\text{Al}_2\text{O}_3$  NWs fabric.



## COLL 896

### How different polymer structures interact with *in-situ* formed metal sulfide particles in aqueous media

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Understanding the influence of polymer supported in-situ particle formation enables designing special functionalities. Metal sulfide particles like copper and iron sulfide are studied to functionalize their surface for controllable interactions.

The interaction of different functionalities on the polymer backbone with sulfide particles are investigated. This includes studying different chemical compositions, molecular weights and polymer structures. Therefore, different co-polymers are synthesized as random, block (AB) and tri-block (BAB) structures for evaluating the influence of polymer constitution on the interaction with sulfide particles in aqueous media. The polymer consists out of a hydrophilic, anionic part (A) for functionalization and stabilization of particles in water and anchor units (B) for interaction with the sulfide surface. Furthermore, different morphologies of metal sulfide particles are investigated. The synthesized polymers are evaluated by studying the functionalization efficiency. To define the interacting behavior of these polymers with sulfide particles the binding energy with isothermal titration calorimetry (ITC) and the kinetic model of affinity of polymers to sulfide surfaces with quartz crystal microbalance with dissipation monitoring (QCM-D) are determined.

The evaluation of the functionalization efficiency enables a definition of lead structures for polymer supported formation and stabilization of metal sulfide particles in aqueous media. According to these results the functionality units could be clearly distinguished which show strong interaction with sulfide particles. The molecular architecture has a strong influence unattached to the investigated functionalities. Through the selection of the most active anchor group the amount of polymer affects only the stability of the functionalization and not the functionalization itself. In presence of polymer significantly smaller and more homogenous particles are formed. The determination of binding interactions enables a comprehensive understanding of particle formation and dispersion.

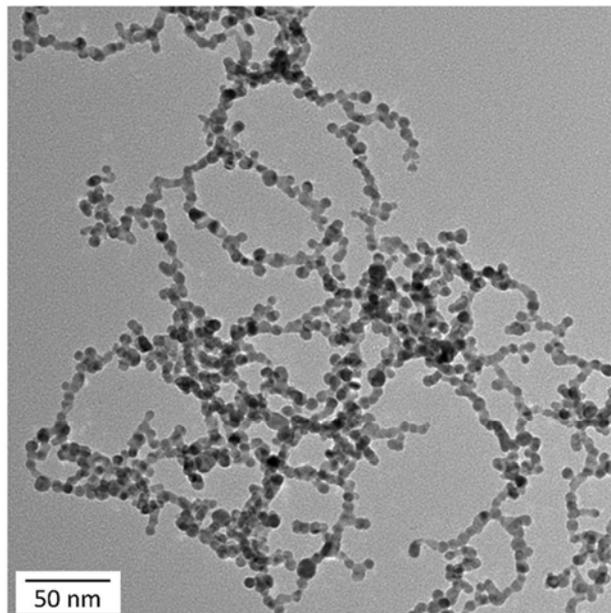
## COLL 897

### Mechanistic studies on metal aerogels

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Some ten years ago we fabricated the first aerogels based on metal nanoparticles. The

gels are formed either via preformed colloidal nanocrystals (two step approach) or directly from the respective metal salt solutions (two step approach). Both synthetic procedures yield similar structures as gels and as aerogels providing finely interconnected three-dimensional metal meshes displaying densities of about 1000<sup>th</sup> of the respective bulk materials. Currently, the materials space covers eight noble metals, a number of less noble metals and a multitude of mixtures of those (two, three or more components) with tunable compositions. While those materials find interest in various fields of applications (so far predominantly in (electro)-catalysis and sensing) the mechanisms of their aggregation and structure formation are still barely understood. In this presentation we will first touch upon theoretical considerations which will conclude in the operational function of diffusion-limited cluster aggregation with a certain contribution of diffusional rotation. From the experimental side we will report on the effects specific ions play in the aggregation of Gold nanoparticles, we will elucidate the various roles a single chemical may play, namely as reducing agent, stabilizing ligand and salt with its influence on the ionic strength, and we will tell about the recently observed self-healing of metal gels.



TEM image of a Au/Pd bi-metallic aerogel

**COLL 898**

## **Preparation porphyrin-based MOF cross nanosheet array films by electrochemistry for electrocatalysis**

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Porphyrin-based metal-organic framework cross nanosheet array (MOF CNSA) films with perfect orientation and excellent crystallinity have been controllably synthesized by the environmentally friendly electrochemical reduction method. With this method at ambient temperature, the uniform Zn-TCPP MOF CNSA films can easily be grown in situ on various conductive substrates with controllable thickness. The construction of Zn-TCPP MOF CNSA film is endowed with highly crystalline order, spatial network structure and hierarchical three-dimensional pore structure, which is conducive to charge transfer and material transmission and suitable for use as an electrochemical catalyst. Importantly this is the first reported that the ab plane of the porphyrin-based MOF is perpendicular to the substrate. As an example of model catalysis, electrocatalytic oxidation of  $\text{NaNO}_2$  shows that the Zn-TCPP MOF CNSA film on conductive substrate can be used directly as an electrochemical sensor, and shows wide linear range, low limit of detection high sensitivity and good anti-interference performance. This work reports a new method of preparing porphyrin MOF thin film electrode, which is expected to be extended to other porphyrin MOF thin film electrodes and study their photocatalytic, electrocatalytic and photoelectrochemical catalytic properties.

**COLL 899**

## **Theoretical framework to describe traveling waves of bacteria in porous media**

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How bacteria move in porous media like tissues and soil underlies processes like infection and bioremediation. However, existing models of how bacteria coordinate their motion at the population scale cannot fully explain collective migration inside porous media. To address this gap in knowledge, we use confocal microscopy to directly track bacteria deep inside transparent porous media. Similar to the case of free liquid, we find that the cells move together in directed, traveling waves following self-generated nutrient gradients. However, unlike the case of free liquid, the wave speed and shape are also regulated by the structure of the porous medium itself. By analyzing the single cell tracks, we characterize how biased “hopping and trapping” of the individual cells generates traveling waves; surprisingly, in stark contrast to the case of chemotaxis in free liquid, we find that hop length bias is not the dominant contributor to this mode of collective migration. Further, we show how the statistical features of single cell motion can be used to develop a continuum model that can describe collective migration in a

porous medium over large length and time scales. Together, our work provides new principles to predict and possibly control bacterial migration in complex environments.

## **COLL 900**

### **High(er) throughput screening for the design and testing of antifouling surfaces**

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The fouling of surfaces by microorganisms is a costly problem in many industries including manufacturing and infrastructure, shipping, and health care. A major stumbling block in the design of anti-fouling surfaces that reduce the adhesion of bacteria is the large parameter design space. Even within the narrower field of polymer-modified surfaces, several parameters including the charge of the substrate and the coating, the Debye length, the molecular weight of polymer, and solvent quality have important influence on mitigating bacterial adhesion onto soft surfaces. Moreover, studying the anti-fouling effectiveness of polymer-coated surfaces is extremely time-consuming and material intensive. To overcome these challenges, we have developed two microfluidic devices to greatly speed up conventional testing methods and allow for the rapid optimization of coating properties as well as observation of the earliest stages of biofilm growth in real time. The first device allows for the simultaneous deposition of polyelectrolyte coatings at different conditions pH and ionic strength conditions and subsequent characterization of the coatings in both the hydrated and dried state. We demonstrate the use of this device by studying the adhesion of chitosan on glass substrates. The second device allows for the tracking and observation of early biofilm growth on anti-fouling surfaces. Unlike conventional techniques our device allows for the observation of biofilm growth on a single cell level without disrupting the growth. We demonstrate the use of this device in observing the growth of bacteria on glass and a model antifouling surface.

## **COLL 901**

### **Nanocultures: Controlled microbial communities in sessile drops**

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Microbes self-organize at various interfaces while transitioning to a sessile form within a protective biofilm matrix. While the biological implications of biofilms for the environment, health, and industry are widely appreciated, the earlier developmental

stage of microbes as microcolonies has received scant attention. This presentation elucidates two new approaches to investigate microbial dynamics in spatially confined microsystems. We describe a novel approach to studying microcolony formation and community dynamics. Using microfluidics-enabled fabrication, a nanoliter-scale sessile culture system (*the nanoculture*) is designed to grow synthetic microbial communities. Each nanoculture begins as a several nanoliter droplets of suspended cells, encapsulated by a polydimethylsiloxane (PDMS) membrane. The physicochemical properties of the encapsulation materials allow the diffusion of functional probes to interrogate cell physiology under chemical insults, allowing microbial interactions to be probed within or across the confining vessel. Alternatively, multiple species of microbes can be co-cultured within a nanoculture. Because chemical communication across the membrane occurs, this system can be used to decouple the effects of the physical and chemical interactions between cells, and investigate microbial pathophysiology or bacterial-fungal (inter-kingdom) dynamics that play a central role in early childhood dental caries and many infections. Such a culture system now provides unique opportunities to assess their therapeutic use for personalized medicine, or for high throughput screening of unculturable microbial species relevant to biotechnology and drug discovery.

## **COLL 902**

### **Migration of bacteria in disordered media**

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While bacterial motility is well-studied on flat surfaces or in unconfined liquid media, most bacteria are found in disordered porous media, such as biological gels and tissues, soils, sediments, and subsurface formations. Understanding how porous confinement alters bacterial motility is therefore critical to modeling the progression of infections, applying beneficial bacteria for drug delivery, and bioremediation. By directly visualizing individual cells, we find a new mode of motility in which individual cells of *E. coli* are intermittently and transiently trapped as they navigate the pore space; analysis of these dynamics enables prediction of bacterial transport over large length and time scales. Additionally, we use direct visualization and 3D bioprinting to show how concentrated populations can collectively migrate through a porous medium—despite being strongly confined. We find that cellular chemotaxis drives collective migration—and that this process depends sensitively on pore-scale confinement, colony density, and differential metabolism of nutrients. This work thus provides a revised picture of bacterial migration in complex media, with implications for healthcare, agriculture, and bioremediation.

## **COLL 903**

## **Heterogeneous diffusion dynamics of micro-particles in pseudomonas aeruginosa biofilms**

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The matrix of extracellular polymeric substances (EPS) secreted by bacteria protects biofilms against external mechanical stress; it also provides a semi-permeable structure that allows the exchange of oxygen and nutrients but blocks some anti-bacteria chemicals. Many methods to remove biofilms from rigid surfaces involve disintegrating the EPS by mechanical rubbing or delivering biocides into the biofilms. The efficacy of these treatments strongly depends upon the micro-structure and mechanical properties of the biofilms. In this study, we investigate the biofilms of *Pseudomonas aeruginosa* on glass substrates in a multi-well plate. Combining scanning laser confocal microscopy and single particle tracking technique, we characterize both the micro-structure of the biofilms and the diffusion dynamics of micron-size tracer particles within the biofilms. Preliminary results confirm that the shear flow generated by shaking the plate during the biofilm growth significantly influence the biofilm micro-structure: stronger shear flows lead to more heterogeneous three-dimensional structures with larger gaps inside the EPS. To quantify the diffusion dynamics of the tracer particles, we compute the mean square displacements, probability distribution function of particle displacements, and radius of gyration of individual particle trajectories from more than a thousand particle trajectories. These results show that some tracer particles attach to the EPS (immobile) while the other diffuse within the EPS at hindered diffusion coefficients (mobile). The dynamics of the mobile particles reveals a continuous distribution of local viscosities within the biofilms. These measurements provide a rigorous standard for comparing properties of biofilms grown on surfaces with anti-fouling coatings.

**COLL 904**

## **Structuring microbial communities using 3D printing**

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Most microbial cells exist in surface-associated communities known as biofilms. Biofilms are densely concentrated communities of microorganisms that are resistant to external

stresses and invasion by competing microorganisms. Biofilms are implicated in a wide variety of intractable medical and industrial problems, but also have beneficial environmental roles. Within a biofilm, microbes have complex interactions that are strongly influenced by community structure. Our goal is to push the frontier of knowledge on the relationship between community structure and function and to elucidate microbial assembly rules for multiple biofilm systems. Progress towards this goal requires control over biofilm structure, which is challenging because biofilms self-assemble under complex and dynamic environmental constraints. 3D printing offers exquisite spatial control, and technologies have already been developed to assemble multicomponent human tissues; however, printing technologies for assembling multicomponent microbial communities are lacking. The ability to print microbial cells in biocompatible materials would enable biofilm researchers to control and manipulate microbial system structure and function. Here, I will present our recent work to develop light-based 3D printing techniques to assemble microbe-loaded hydrogels into microbial communities with well-defined structures, which we use to explore the structure-function relationships that exist in biofilms.

## **COLL 905**

### **Spatial organization and 3D architecture of oral biofilms**

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Biofilms develop from initial bacterial colonizers bound on surfaces that evolves into structured communities that are embedded in an extracellular polymeric matrix. We have applied multiscale population growth and 3D morphometric analyses with multiple imaging modalities to assess the spatiotemporal evolution of colonizers (either single-species or mixed-species) towards the formation of structured communities from sub-micron to submillimeter scale. We found that a subset of initial colonizers displayed clustering behavior and expanded three-dimensionally forming densely populated communities, which were dependent on exopolysaccharides matrices produced *in situ*. The polymeric matrix provided an adhesive scaffold conferring cohesion, inter-species interactions and firm adhesion on the surface. Disruption of the production and assembly of the polymeric matrices markedly altered the clustering behavior, structuring and the 3D architecture of the biofilm, demonstrating the importance of a biophysical scaffold to maintain a spatially organized microbial community

## **COLL 906**

### **Spatio-temporal evolution of micromechanics of pathogenic biofilms**

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The mechanical structure and rheology of bacterial biofilms at the microscale and mesoscale has a critical role in the lifecycles of biofilms. For example, surface-grown bacteria and production of an extracellular polymeric matrix modulate the assembly of highly cohesive and firmly attached biofilms, making them difficult to remove from solid surfaces. This era of antibiotic resistance has driven research to find effective alternatives to conventional antibiotics. The search has turned towards methods that inhibit bacteria from surface colonization and subsequent biofilm formation, or that disrupt the mechanical stability of pathogenic mature biofilms. Such strategies require improved understanding of biofilm structure and mechanics at various stages of growth. We use confocal microscopy, particle tracking, and two-point microrheology to probe and map the local viscoelastic and heterogeneous structure of the biofilm matrix. *Streptococcus mutans* UA159, a virulent cariogenic pathogen and a well-characterized EPS-matrix producing and biofilm-forming strain was used as a model organism. We characterize the spatio-temporal evolution of the biofilm rheology using tracers probes in different regions of interest of the biofilm including microcolonies and EPS matrix.

## **COLL 907**

### **Switchable surfactants: Molecular insights into carboxylate functionalized nanoemulsions**

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Nanoemulsions, kinetically stable oil droplets dispersed in water, are used in oil spill remediation and drug delivery through stabilization of the hydrophobic cargo via surfactants. The efficacy of nanoemulsions lies in the controlled stability of the droplet. Carboxylate-containing surfactants provide high control of nanoemulsion stability due to the switchable nature of the headgroup through diverse bonding interactions with changing environmental conditions. Spectroscopic investigations at planar model systems have provided molecular insights into the structure of these surfactants at the oil-water interface. However, there is a lack of carboxylate-containing surfactant structural data at the curved nanoemulsion interface, which has been shown to observe different adsorptive properties compared to the extended planar interface. This study employs a nonlinear, surface-specific technique, Vibrational Sum-Frequency Scattering Spectroscopy, which directly probes surfactant population and orientation at the curved oil-water interface. Nanoemulsions stabilized with carboxylate-containing surfactants are found to have unique interfacial structural properties with changing environmental conditions, which has significant implications for the informed rational design of more effective nanoemulsion technology. This is correlated with stability data to give a robust molecular level picture of the factors affecting stability and functionality of these droplets.

## COLL 908

### Monodisperse platonic micelles part 6: Its kinetics and thermodynamics

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The concept of micelles was first proposed in 1913 by McBain and has rationalized numerous experimental results of the self-aggregation of surfactants. It is generally agreed that the aggregation number (Nagg) for spherical micelles has no exact value and a certain distribution. However, our studies showed that some amphiphilic molecules form a monodisperse micelle with a defined Nagg whose values are chosen from 4, 6, 8, 12, 20, and 32. Interestingly, the observed Nagg values are related to Platonic solids, thus we named them "platonic micelles". The preferred Nagg values were explained in relation to the mathematical Tammes problem: how to obtain the best coverage of a sphere surface with multiple identical circles. When a transition from dodecamer to icosamer was induced by a rapid increase of the NaCl concentration, Nagg was unchanged at all during 60 s after CNaCl increased, and then abruptly increased to 20. We are now constructing a mathematical model to explain why this strange transition occurs for the platonic micelles.

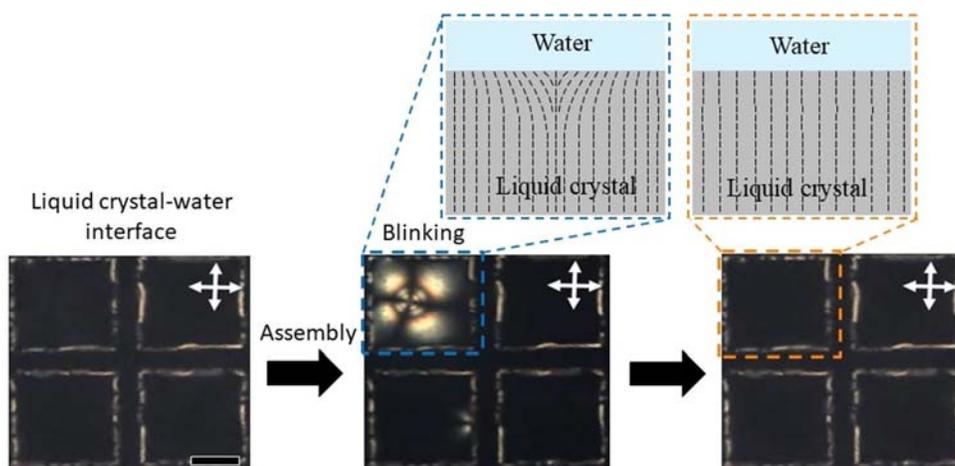
## COLL 909

### Optical "blinking" event triggered by amphiphilic assemblies at liquid crystal interface

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The massive cooperative reorientations at the liquid crystal interfaces have been widely utilized as sensors to identify fine structural changes in supramolecular amphiphiles. The ordering of molecules inside liquid crystals gives rise to anisotropic properties, which enables them to amplify microscopic events to a macroscopic readout. We investigated the structure-property relationship between various amphiphiles and their organizations at the liquid crystal-water interface. This provided us with a deeper understanding of the role of hydrophobic tail length, hydrophilic head group and linker rigidity of the amphiphile on the area occupied by each molecule and thus governing the liquid crystal organization. During our exploration, interestingly we observed spatially localized and transient flashes of light (blinking) through the liquid crystal interfaces. Further mechanistic investigations revealed that this non-equilibrium "blinking" phenomenon was induced by the dynamic interaction of amphiphilic assembly with the liquid crystal interface at a single event level. Each optical "blinking" event results from the introduction of a single supramolecular assembly of amphiphiles with the liquid crystal interface and associated surface pressure-driven flow. This concept of a

responsive blinking system can be further adapted for the design of stimuli-responsive fusion events, such that rates of amphiphilic assembly fusion can be controlled by a trigger. This can potentially serve as a basis for the future development of simple economical assays for protein sensing.



## COLL 910

### Simulation study of polymer CORALs: Densely packed tethered polymer nanoislands

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We report on the simulation study of the configuration of densely packed tethered polymer nanoislands, which constitute of polymer CORALs (CoOrdinated Responsive Arrays of Surface Linked polymers islands, [ACS Applied Materials & Interfaces, 10(8), 7459–7468. (2018)]). The key features of polymer CORALs are uniformly distributed islands of densely grafted polymer chains with lateral sizes and separation distances

comparable to the polymer chains. Here we characterize the structural features of the isolated islands that make up these polymer CORALs. Our studies use three different systems to explore the solvent effects on CORALs. We find that different grafted polymer characteristics are observed within an island depending on the polymer island's size and distance from the center of the island. Specifically, the characteristics of the chains at the island periphery are similar to isolated tethered polymer chains, while chains in the center of the island experience the neighbor effect such as chains in the classic polymer brush. These results can be used in the rational design of CORALs with the specific interfacial characteristics and predictable responses to external stimuli.

## **COLL 911**

### **Surfactant-polymer association modulated by hydrophobicity of surfactant, polymer, or aqueous solvent**

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Mixtures of surfactants and polymers afford great flexibility in conferring structure and function in waterborne formulations applied to coatings, home and personal care products, food and drinks, pharmaceuticals, and enhanced oil recovery. Underlying such structure and function are inter- and intra-molecular interactions that depend on the (i) polymer chemistry, architecture and concentration, (ii) surfactant type and concentration, (iii) solvent conditions (e.g., pH, ionic strength, presence of cosolvents or cosolutes), (iv) interfaces and surfaces (e.g., presence of colloidal particles), and (v) external stimuli (e.g., temperature, shear). The presentation will highlight examples from our research on the formation and structure of complexes by commercially available anionic surfactants and nonionic poly(ethylene oxide)-based polymers in water, as affected by the ability of the polymer to associate upon incorporation of hydrophobic poly(propylene oxide) segments, the hydrophobicity of the surfactant (aliphatic hydrocarbon vs fluorocarbon chain), and the hydrophobicity of the solvent (added ethanol, salt or ionic liquids).

## **COLL 912**

### **Link between chemistry and properties for $C_iE_j$ surfactants**

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Polyethylene glycol mono alkyl ethers are the most commonly used non-ionic surfactants found in a variety of processes. Additionally, they represent a model chemistry which is easily varied in terms of only two structural parameters: length of hydrophobe and length of hydrophil. Predicting the fundamental surfactant performance characteristics based solely on the chemical structure is desirable for all chemistries.

Using this model family of surfactants, we show that simple, thermodynamically driven scaling arguments can be used to create master empirical relationships that are able to predict the key properties of surfactants at the air-water interfaces with a single parameter derived from the surfactant chemistry. We show that the critical micelle concentration (CMC) is a strong function of the length of the hydrophobe, however the adsorption isotherm parameters are dependent on both the hydrophil and hydrophobe.

### **COLL 913**

#### **Surfactant performance at the pressurized CO<sub>2</sub>-water interface**

**Zachary Hinton**, *zrh29@drexel.edu*, **Nicolas Alvarez**. Department of Chemical and Biological Engineering, Drexel University, Philadelphia, Pennsylvania, United States

The use of surfactants in processes at elevated pressure is critical to many fields ranging from oil recovery and extraction to manufacturing and textiles. For the majority of these processes, only an empirical understanding of the role of pressure on surfactant performance exists. While thermodynamics describe surfactant adsorption as a function of pressure, experimental measurements are required to relate surfactant chemistry to performance in extreme conditions. In this work, we describe a novel high-pressure microstensiometer capable of measuring surfactant dynamics as a function of pressure. We use our apparatus to measure the effect of pressure on surfactant isotherms and dynamics for non-ionic surfactants. We show that the effect of pressure is surfactant dependent and, in fact, lowers the effectiveness of surfactants at higher pressures. With these results, we will guide the design of more effective surfactants for high pressure applications.

### **COLL 914**

#### **Low temperature interfacial solvation and morphology of marine hydrogels in sea spray aerosol proxy films**

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Saccharides comprise one of the largest mass fractions of organic matter in sea spray aerosol (SSA), and it is possible that anionic polysaccharide aggregates in the form of marine hydrogels contribute to this enrichment. Polysaccharides larger than 100 kDa bearing carboxylate moieties have been observed to nucleate ice, suggesting that marine gels could contribute to ice and mixed-phase cloud formation within the marine boundary layer. We probed interfacial solvation and morphology of marine hydrogels embedded in sea spray aerosol proxy films at low temperatures to better understand the molecular mechanisms responsible for heterogeneous ice nucleation in SSA. Alginate, an anionic polysaccharide rich in carboxylate moieties that gels in the presence of calcium cations, was used to model marine hydrogels in SSA. A palmitic acid monolayer was spread onto an artificial seawater solution containing alginate hydrogels at

temperatures between 0°C and 21°C. Infrared reflection-absorption spectroscopy and surface tensiometry revealed that alginate exhibits greater adsorption to a palmitic acid monolayer at warmer temperatures. Alginate hydrogels likely disrupt the monolayer solvation structure and interact with the palmitic acid carboxylate headgroups. Additionally, signal enhancement between 3000 and 3200 cm<sup>-1</sup> in the presence of alginate at low temperatures suggests ice-like ordering of the interfacial water molecules. Further investigation is underway to examine the effects of pH on alginate solvation and organization in SSA proxy films.

## **COLL 915**

### **Polysaccharide extract from peanut sediment of aqueous extraction process as a novel Pickering stabilizer for oil-in-water emulsion**

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Aqueous extraction process (AEP) was successfully employed to simultaneously obtain oil and protein of peanut at industrial level. Consequently, the peanut sediment from AEP was produced and mainly comprised carbohydrate (79%, dry basis). In present study, the peanut sediment was used to obtain soluble polysaccharide extract (SPE) under pH8.0 combining with high temperature cooking. The total sugar and protein content of SPE were 65.6% and 12.8%, respectively. Gel exclusion chromatography coupled to RI-UV detectors analysis indicated that a major component with comparatively small size was mixture of polysaccharide-protein and another large-size component mainly contained polysaccharide. SPE possessed average size of 398 nm and strong surface charge. SPE particles mainly exhibited a core-shell structure (protein as core) shown in Confocal laser scanning microscope (CLSM) image. Three-phase contact angle ( $\theta_{o/w}$ ) of SPE was approximately 94.2° closing to neutral wettability, suggesting that SPE could be developed as an effective Pickering emulsifier. Thus, the Pickering emulsion were successfully stabilized by 4.0% of SPE solution at the oil volume fraction ( $\phi$ ) ranging from 0.4 to 0.7, which all exhibited long-term storage stability. CLSM images evidenced that SPE particles formed a packed layer at surface of oil droplet, which provided barriers for coalescence of droplets. Meanwhile the particles dispersed in continuous phase caused viscosity to increase, probably facilitating droplets against creaming. Furthermore, rheological properties analysis illustrated that emulsion freshly prepared exhibited viscoelastic or weak gel structure. However, the extension of storage time contributed to enhancement of emulsion structure. These results were useful to develop SPE as a kind of novel food grade Pickering stabilizer. Additionally, the method for simultaneously obtaining polysaccharide and protein provided an insight into preparing the complexes applied in stabilizers of Pickering emulsion.

## **COLL 916**

## Surface adsorption, aggregate structure and antibacterial activity of Gemini quaternary ammonium surfactants with carboxylic counterions

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A group of gemini quaternary ammonium surfactants with the formula  $C_nH_{2n+1}CONH(CH_2)_2N^+(CH_3)_2(CH_2)_2N^+(CH_3)_2(CH_2)_2NHCOC_nH_{2n+1}2Y$  ( $n=11, 13$  and  $15$ ,  $Y=HCOO^-$ ,  $CH_3COO^-$  and  $CH_3CHOHCOO^-$ ) have been synthesized by a counterion conversion process and characterized by Fourier transform infrared spectroscopy and mass spectroscopy. Their adsorption and self-aggregation properties are investigated by surface tension, conductivity, dynamic light scattering and transmission electron microscopy measurements (TEM). The results show that these synthesized surfactants reduce the surface tension of water to a minimum value of 26.51 mN/m at a concentration of  $5.72 \times 10^{-2}$  mmol/L. Furthermore, the increased alkyl chain length of the carboxylic counterions leads to the increased critical micelle concentration (CMC), the decreased degree of counterion binding ( $\beta$ ), and the decreased self-assembly tendency, but the minimum area per surfactant molecule ( $A_{min}$ ) adsorbed at the air-aqueous solution are similar. TEM images reveal that these surfactants self-assemble spontaneously into aggregates with vesicles or bilayers structure. It is also found that they have superior antibacterial activity at a concentration of 0.1g/L. The high surface activity and high antibacterial activity of the gemini quaternary ammonium salt surfactant containing different carboxylic counterions bring more possibilities for the application in the field of biomedicine.

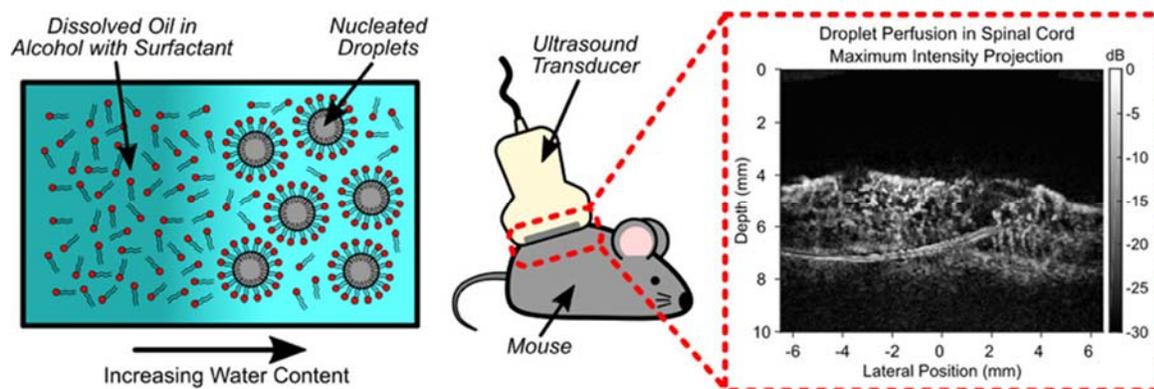
### COLL 917

## Design and synthesis of phase-change contrast agents for ultrasound-based imaging

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Phase-change contrast agents for medical ultrasound are an alternative to currently approved (FDA) microbubbles. While gaseous microbubbles are restricted to intravascular applications due to their large size, phase-change contrast agents are delivered as liquid nanodroplets (<200 nm in diameter), small enough to freely diffuse past the vessel wall or into diseased tissues. To produce ultrasound contrast, the agents are locally activated using either an acoustic or laser pulse to form transient microbubbles. As a result of their small size, interfacial forces may play a significant role in stabilizing droplets, suppressing spontaneous vaporization. Consequently, methods

for producing monodisperse liquid nanodroplets from volatile perfluorocarbons (PFCs) are needed to enable new medical imaging and therapeutic technologies. Spontaneous emulsification or the 'ouzo effect' is a new and efficient method of generating droplet contrast agents. The process begins with dissolving a perfluorocarbon liquid or gas in a good solvent such as ethanol. Once a poor solvent, such as water, is added to the saturated alcohol the solvent quality reduces and leads to the formation of monodisperse nanodroplets. The size of the nanodroplets can range from approximately 100 nm up to several  $>2$   $\mu$ m in diameter. Furthermore, activation thresholds can be modulated by varying the PFC volatility. Moreover, photoacoustic agents can also be designed by coating the interface with a near-infrared light absorbing material. By combining the effects of photothermal heating with the tensile load from the acoustic wave, the activation threshold of agents can be reduced by as much as two orders of magnitude. We demonstrate that a clinical ultrasound imaging array fitted with an optical fiber bundle can be used to electronically steer and selectively activate the agents within phantom materials. These features can be beneficial in precision droplet cavitation for therapeutic applications, such as the mechanical breakdown of blood clots and tumors.



## COLL 918

### Intravital microscopy of the ultrasound-triggered size conversion of microbubbles to nanobubbles

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We recently reported development of high payload porphyrin-encapsulated microbubbles, and their ultrasound-triggered conversion to nanobubbles with actively

increased accumulation in targeted tumor tissue (Huynh et al, *Nature Nano* 2015). We further demonstrated the first direct evidence that nanobubbles can initiate persistent pressure-dependent nonlinear acoustic scattering in vessel- and tissue-mimicking environments at clinically relevant low frequencies and concentrations (Pellow *et al*, *PMB* 2018). This platform holds significant implications for nanomedicine delivery, optical and ultrasound imaging, and photo/sonodynamic therapeutic applications, but remains constrained by a lack of mechanistic and biophysical understanding as well as limited sensitivity to nanobubble signatures. Here we integrate custom ultrasound transmitters and receivers into a two-photon dorsal window chamber setup for simultaneous real-time visual and acoustic monitoring within tumour-affected, functional microcirculation. We further investigate multipulse modulation schemes to improve sensitivity to nanobubble nonlinearities for high resolution imaging applications and begin to explore the therapeutic potential of these porphyrin nanobubbles, with implications of extending the utility of ultrasound contrast agents both within and beyond the vascular compartment.

## **COLL 919**

### **Ultrasound-responsive biomaterials for optical tumor characterization and tissue engineering applications**

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The significant tissue penetration and localization of focused ultrasound enables the design of biomaterials that respond to this energy in tissue with precise spatiotemporal control. One such application of these materials is the development of ultrasound-responsive fluorescent contrast agents for optical tumor characterization. Early-stage tumors are difficult to detect and treat due to their small size. Localized light generation within a small tissue volume can yield spatially-resolved chemical information about the immediate tissue microenvironment to help differentiate small cancerous lesions from benign masses. The detection of this locally-generated light is made difficult by the highly-scattering nature of biological tissue which confounds the spatial information in the signal. In comparison, ultrasound waves scatter less in tissue providing higher spatial resolution. Combining optical and acoustic imaging modalities presents an avenue for obtaining high-contrast, physiologically-relevant optical information with improved spatial resolution.

Our work presented here develops a technique using fluorescent microbubbles that generate light in the precise focal zone of an ultrasound beam by consistently modulating their fluorescence intensity. These contrast agent particles were designed with the nanoscale surface pattern necessary to generate a consistently blinking fluorescent light in response to focused ultrasound. By amplifying these characteristic intensity modulations with a lock-in amplifier, the fluorescence from these locally-activated microbubbles was detected for the first time in an optically-scattering

environment and at significant depth. Using a spectral analysis program it was shown that these microbubbles also displayed harmonic oscillations beyond the ultrasound driving frequency which could be used to further improve the signal-to-noise ratio for detection. This technique could enable sensitive optical imaging with ultrasound-scale millimeter-level spatial resolution, providing an important tool to address the challenge of fluorescence imaging in deep tissue. Beyond this, additional work includes the application of these ultrasound-responsive colloids to hydrogels with relevance to tissue engineering.

## **COLL 920**

### **Recombinant protein-stabilized microbubbles prepared using microfluidics for theranostic applications**

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Microbubbles are used as contrast agents in ultrasound sonography and more recently as therapeutic agents in cancer treatment. The efficacy of microbubbles as theranostic (i.e., therapy + diagnostics) agents depends critically on their size and mechanical properties. Few conventional bubble preparation methods allow for precise control over these two critical factors. In this presentation, I will describe our recent efforts in preparing highly uniform microbubbles with tunable size and mechanical properties by using a mixture of recombinant protein, oleosin. We use a microfluidic device with an air-actuated membrane valve to produce monodisperse microbubbles with narrow size distribution and to control the size of microbubbles by dynamically changing the dimension of the channel using the valve. We demonstrate that the mechanical properties of microbubbles can be tuned by using poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) PEO-PPO-PEO triblock copolymers of different compositions. Microbubbles stabilized with oleosin and triblock copolymers show high stability and excellent echogenicity under ultrasound insonation. Moreover, the echogenicity of microbubbles show strong correlation with the mechanical properties of the bubble shell. We also show that these microbubbles can be functionalized with photoacoustic dye to enable photoacoustic-ultrasound dual mode imaging. The combination of microfluidics and recombinant protein technology affords unprecedented versatility in engineering microbubbles for ultrasound theranostics applications.

## **COLL 921**

### **Direct emulsification of low boiling point perfluorocarbons nanodroplets with improved properties**

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Contrast-enhanced ultrasound imaging provides advantages over conventional ultrasound techniques by increasing image contrast and improving diagnostic accuracy. Existing strategies for contrast-enhanced ultrasound imaging are based on intravenous injection or the introduction of perfluorocarbon (PFC) microbubbles (MBs) into tissue to achieve increased contrast. However, their relatively large size confines them to the intravascular space, and if targeted, their few minutes of circulation time, severely limits their ability to interact with receptors of interest. When used for molecular imaging applications, recent investigations have focused on the development of phase-change contrast agents (PCCAs), including liquid PFC nanodroplets (NDs) that can seek extravascular targets and be acoustically activated *in vivo* to form MBs and enhance contrast.

However, the use of PCCAs has been severely limited by the large particle size of existing NDs and their spontaneous vaporization into MBs in the case of low-boiling point fluorocarbon nanodroplets, as well as unfavorable increases in the boiling points of the liquid perfluorocarbon core as ND size decreases. There is therefore a need for low-boiling point NDs that exhibit small particle size and improved stability.

We recently described a novel, facile and robust method of emulsifying PFC liquids whose boiling point is below 0°C to produce high quality sub-300 nm ND emulsions through direct high pressure homogenization. The resulting ultrasound-activatable NDs were characterized using tunable resistive pulse sensing and dynamic light scattering and their acoustic response investigated with a Siemens Acuson Sequoia S512 ultrasound system with a 15L8 transducer.

The major differences between our work and the published methods is that we use direct emulsification of low-boiling point PFC, whereas others produce microbubbles first that are then condensed into droplets. When duplicating the published method, we confirmed that our emulsions: 1) have a higher ND concentration ( $10^{12}$  vs.  $10^9 - 10^{10}$  ND/mL); 2) presents less batch to batch variability; 3) do not produce non-echogenic liposomes; and 4) have better thermal stability and longer shelf life. More important, our direct emulsification method produced NDs that withstood processing and purification steps to allow conjugation of targeting ligands and/or the addition of payload.

## **COLL 922**

### **Controlled microbubble inflation and drug release using perfluorocarbon nanodroplets**

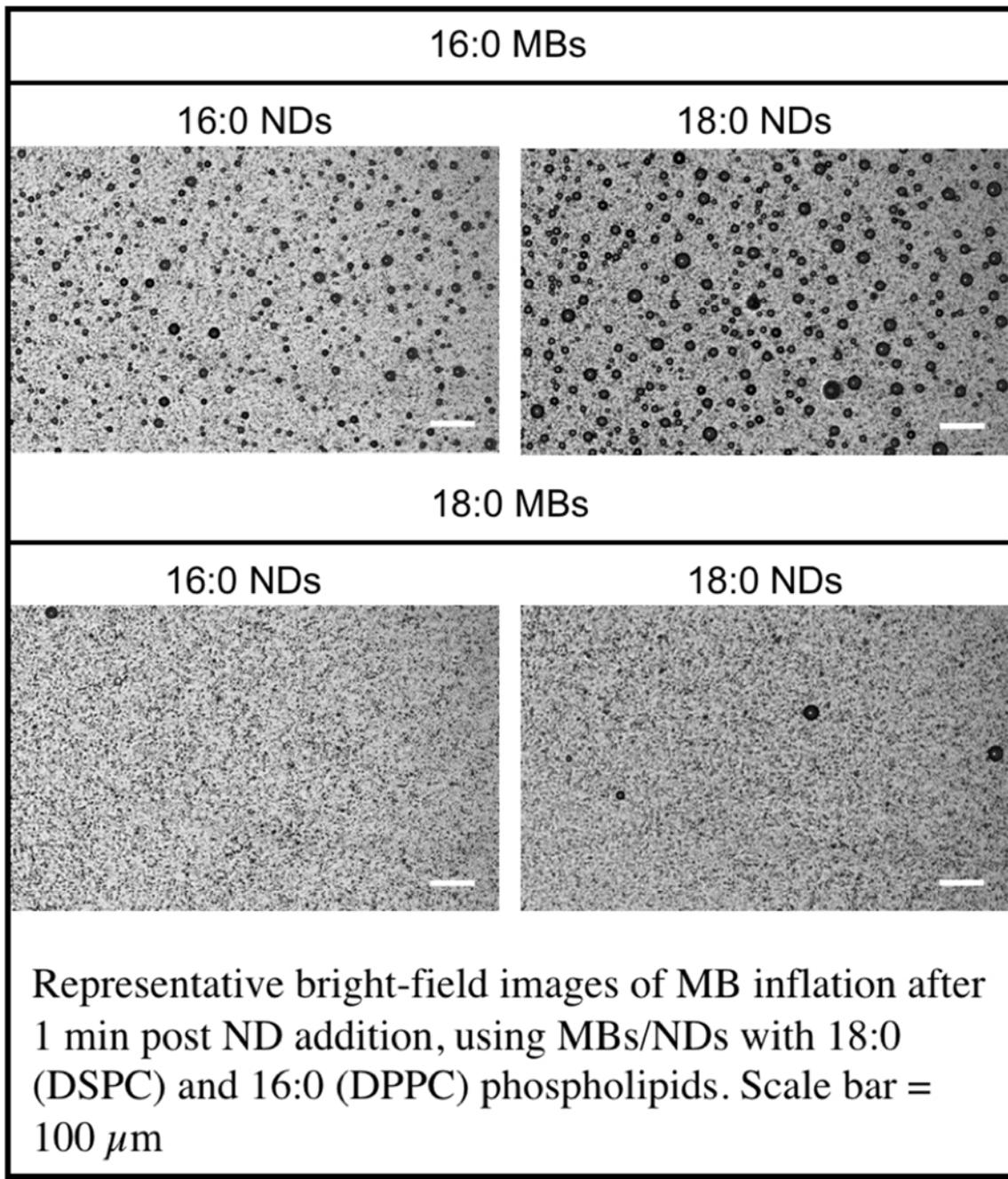
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Inflation of perfluorocarbon (PFC) nanobubbles (NBs) and microbubbles (MBs) when exposed to liquid PFC nanodroplets (NDs) was recently discovered by our group. While preliminary experiments demonstrated the feasibility of our novel approach *in vitro* and *in vivo*, its translational success will rely on our ability to control bubble inflation. Limiting the extent of inflation is critical to safely improve either tumor detection using NBs or to occlude tumor microvasculature with high specificity using MBs. This presentation will describe the impact of different formulation parameters on the extent and rate of MB growth as well as translational opportunities.

We demonstrated that both rate and degree of expansion are affected by the type of PFC used, ND and NB/MB size and the type of lipid emulsifier. Interestingly, limiting the ultimate size of inflated MBs was only possible when using a polymeric MB shell as opposed to phospholipids. We believe that these accomplishments show promises and potential to translate our novel approach to the clinic while creating new paradigms for early detection and treatment of cancer.

As this non-invasive platform can be used to perform chemoembolization as is currently done to treat liver tumors, one of our current goals is to load chemotherapeutics in NDs or MBs and promote drug release specifically in tissues expressing the receptor of interest, analogous to trans-arterial chemoembolization. Furthermore, since this approach is not image guided, tumors will not need to be visible pre-treatment.



**COLL 923**

**Multi-cavity polymer particles for ultrasound-enhanced contrast and drug delivery**

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Microbubbles are conventionally used to provide enhanced contrast in ultrasound images as well as improve the targeted release and delivery of drugs and genes. However, for a number of applications, these gaseous colloids are limited by their size and inability to sustain drug delivery for extended periods of time. It may therefore be desirable to utilise acoustically-active solid degradable polymer particles for therapy and potentially imaging. Here we will report on the development of multi-cavity particles capable of trapping gas pockets that enable acoustic activation with both therapeutic and imaging ultrasound transducers. Depending on the formulation, these particles range from 1 micrometre to 6 micrometres in average diameter, and exhibit a broad range of structures (from hollow porous to multiple well-defined surface cavities). We show that these particles are able to nucleate and sustain cavitation at relatively low peak negative acoustic pressure amplitudes for nearly 10 minutes using pulsed ultrasound from a focused ultrasound transducer. Additionally, these particles may also be remotely implanted into ex vivo tissue and 3D cell cultures using high intensity focused ultrasound without inducing acute cell damage. If loaded with a payload, we show that these particles will release the payload across several days. Similarly, we have demonstrated that multi-cavity polymer particles will also provide contrast enhancement using a conventional ultrasound imaging probe. Considering the enhanced and sustained drug delivery and contrast enhancements, multi-cavity polymer particles may have potential for theranostic applications.

## **COLL 924**

### **Nanoscale organization of ligand-receptor interactions modulates macrophage activation**

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The innate immune system recognizes pathogens by simultaneous detection of and binding to different types of ligands. Up to now, the individual role of receptors in innate immune responses has been studied extensively. In contrast, much less has been done to understand the synergistic activation of different receptor-ligand pairs. For example, the possible connection between receptor cross-talk and their spatial organization remains poorly understood. To tackle this grand question, in this study, we investigated the role of lateral positioning of membrane receptors in the innate immune regulation. We demonstrate that, by using nanolithographical patterning and bioconjugate techniques, how two types of ligands are organized on the array platforms with a series of defined spacing. The nanoarrays of patterned ligands modulate the inflammatory immune responses of macrophages via cascades of the intracellular signal transmissions.

## **COLL 925**

### **Simple construction of electronic structures and their transfer to biological substrates using graphene oxide and commercial off-the-shelf inkjet printing**

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Techniques for interfacing electronic structures with biological systems are a critical capability required for advanced biological engineering. In most cases, biological entities cannot withstand the harsh processing required by electronics fabrication; thus, a method for transferring pre-built electronics onto cells is essential to overcome this roadblock. We recently demonstrated transfer of electronic structures to cells using single layer hydrogenated graphene (SLHG) as a support. However, in addition to its nontrivial synthesis, SLHG is just one atomic layer thick and therefore can only support electronic structures of limited mass before breaking apart. Also, adhesion of SLHG to a biological target substrate requires exposure to chemicals, such as bromine gas, that are incompatible with biological systems. To address these issues, we have now developed a transfer technique based on films of partially reduced graphene oxide (rGO) as the support layer. Graphene oxide (GO) is cheap, abundant, and simple to prepare and manipulate. We have prepared 1-50 nm thick GO films on glass or plastic and reduced the films via chemical or thermal pathways. We have shown that the rGO films delaminate readily in water, with dimensions up to 8 ½" x 11". Concurrently, we have modified a commercial off-the-shelf inkjet printer to print metallic structures onto GO films and demonstrated their subsequent reduction and transfer. Finally, we have optimized the water-based rGO transfer to stem cells for film adhesion and cell viability. Our new methodology comprises a simple and inexpensive system for constructing on-demand electronic elements and transferring them to cells for use in biological engineering.

## **COLL 926**

### **Design of spherical nucleic acids as vaccines against triple negative breast cancer**

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Herein, we describe the synthesis and development of nanoscale vaccines against triple negative breast cancer (TNBC), using spherical nucleic acids (SNAs) that carry oligonucleotide Toll-like receptor 9 (TLR9) agonists as adjuvants on their shell and contain tumor cell lysates as antigens in their core. These lysate-loaded SNAs

demonstrate high encapsulation efficiency, rapid cellular uptake, and enhanced immunostimulation relative to simple mixtures of adjuvant and antigen. Further, oxidation of the lysates prior to incorporation into the vaccine significantly enhances their potency as antigens, resulting in dramatic differences both *in vitro* and *in vivo*. In xenograft mouse models of TNBC, SNAs that encapsulate oxidized lysates show remarkable antitumor efficacy and significantly extend overall survival, relative to SNAs prepared with non-oxidized lysates and simple mixtures of oxidized lysates with adjuvant DNA. This work provides critical insight on the design of biomaterials as cancer vaccines; namely, how incorporation of lysates into nanomaterials improves overall vaccine function, and how the preparation of antigens affects their observed immunogenicity.

## **COLL 927**

### **Molecular mechanisms of the foreign body response: From scars on our skin to the foreign body capsule**

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Any material that is implanted within the body is going to elicit a foreign body response. This process is characterized by protein deposition followed by macrophage and monocyte recruitment, macrophage fusion to form foreign body giant cells, then deposition of a dense collagen matrix by macrophages and fibroblasts. These responses can result in the destruction of the device or render it non-functional while causing damage to surrounding tissue. Much research has focused on the role of macrophages in this response; however, detail is still missing regarding how our body recognizes these materials as foreign. We identified a class of proteins that are adsorbed to the surface of implanted materials that is also present during injury. If we implanted materials in mouse that lacked these proteins, there was a strong and significant decrease in the number of macrophages recruited to the material, and more importantly the amount of fibrosis around the material also decreased. If we implant a device that slowly releases small molecule inhibitors of these proteins, we are able to manage and inhibit fibrosis in wild type mice. These studies have described a bottom-up approach to understand the basic biology behind immune responses to biomaterials, identifying putative therapeutic targets, and subsequently developing a modified material to mitigate fibrosis.

## **COLL 928**

### **Gelatin coated mesenchymal stem cells improve recovery post infarct**

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The pro-inflammatory response to acute myocardial infarction (AMI) spreads the damage beyond the initial infarct region and drives tissue remodeling and loss of function. While mesenchymal stem cells (MSCs) are effective in limiting inflammation to preserve healthy tissues, over 99% of these therapeutic cells are rapidly damaged by the inflammatory environment<sup>1</sup> or washed out with fluids escaping the injection site<sup>2</sup>. Larger injections are prohibited due to the potential for these escaping cells to occlude downstream blood flow. We developed protective, adhesive cellular coatings as a strategy to protect and retain therapeutic MSCs at the site of injection. Our working hypothesis is that greater numbers of healthy, retained cells will limit infarct expansion and improve functional outcomes.

Wild type non-GFP mice were given AMI and treated with coated or uncoated GFP+ MSCs, or buffer, and sacrificed on day 7. The heart was digested, and the retention of the injected GFP+ MSCs was determined by flow cytometry. GFP MSCs are implanted into a non GFP mouse to distinguish the injected cells. The retention of MSCs in animals injected with the GelMA coated MSCs was three-fold higher than that of animals with uncoated MSCs. Histological analysis the peri-infarct and remote areas showed a comparable increase in cell retention for the coated group. The isolated GFP+ cells from the coated cell groups were significantly more proliferative than those of the uncoated MSC group. On day 30, mice treated with coated cells significantly smaller scar versus uncoated mice and buffer injected mice. LV ejection fraction was significantly increased for mice treated with coated cells than other groups. The gelatin coating of MSCs has a significant impact on the retention of healthy MSCs post-AMI. This retention is positively correlated with improved functional outcomes 30 days post-AMI.

## **COLL 929**

### **Fabrication of silk fibroin with tunable hydrophobicity**

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Silk fibroin is a robust protein-polymer with myriad applications as a biomaterial. Diverse processing methods allow silk to be transformed into morphologies such as fibers, sponges, films and microspheres, thus aiding in its translation into biological use. It is important to regulate interactions between biological systems and corresponding biomaterials, frequently, the ability to minimize or prevent these interactions may extend the lifetime and improve the quality of a biomaterial. This can be accomplished by chemical modification to employ the hydrophobic and “omniphobic” characteristics of perfluorocarbon functionalities. We report here a recently developed method by which we can append perfluorocarbon moieties to silk fibroin thus enhancing its hydrophobicity. In addition to presenting our methodology, we will discuss a battery of quantitative and qualitative techniques used to characterize the resulting material.

Targeting specific amino acid residues within the silk fibroin, we use trivalent iodonium salts to form covalent bonds between perfluorocarbon chains and silk. Water contact angles assessed by goniometry correlate with fluorocarbon chain length and perfluorocarbon coverage, indicating that as the fluorocarbon chain length increases, the resulting material becomes more hydrophobic. Some modified silk samples exhibit contact angles greater than that of Teflon<sup>®</sup>. These observations were further corroborated via X-ray photoelectron spectroscopy of the modified silk films. The data reveal substantial total fluorine content within the silk and binding energies that correspond to unique difluoromethylene and trifluoromethyl groups. This method yields tunable physiochemical properties within the silk, a critical component of biomaterial fabrication for a variety of applications.

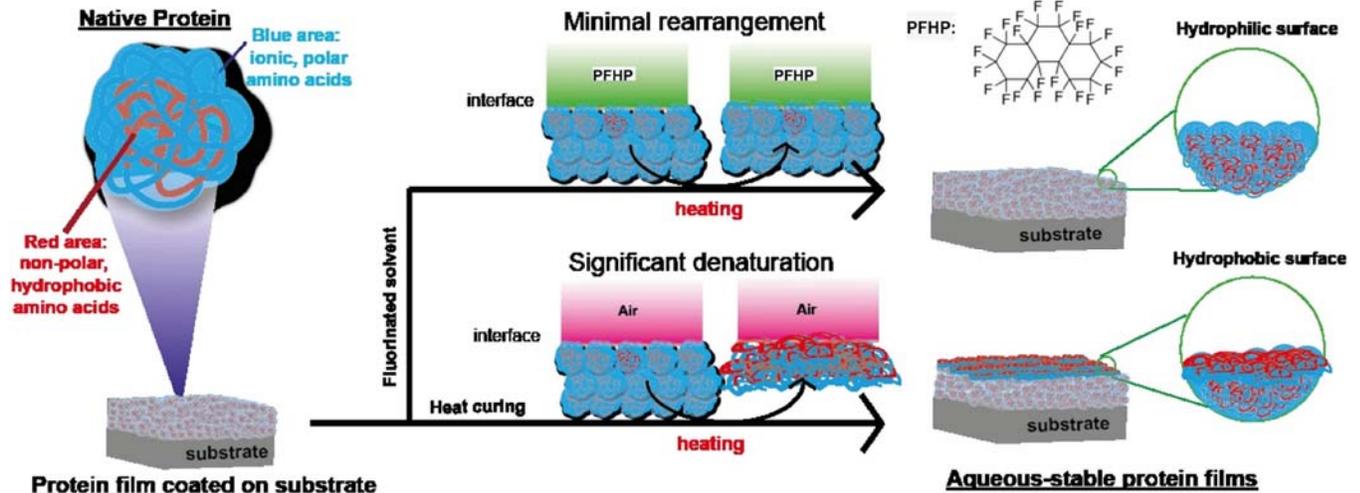
## **COLL 930**

### **Fabrication of protein-based coatings for biomaterial applications**

***Sanjana Gopalakrishnan***<sup>1</sup>, *sgopalakrish@chem.umass.edu*, *Li-sheng Wang*<sup>1</sup>, *Lan Zhang*<sup>1,4</sup>, *Shuting Pan*<sup>1,6</sup>, *Ann Fernandez*<sup>2</sup>, *Jonathan Lee*<sup>1</sup>, *Yi-Wei Lee*<sup>1</sup>, *David C. Luther*<sup>3</sup>, *Kai Li*<sup>4</sup>, *Sankaran Thayumanavan*<sup>5</sup>, *Xuexin Duan*<sup>6</sup>, *Yong Han*<sup>4</sup>, *Vincent M. Rotello*<sup>7</sup>. (1) Chemistry, University of Massachusetts Amherst, Amherst, Massachusetts, United States (2) Chemistry, University of Massachusetts, Amherst, Massachusetts, United States (3) Chemistry, University of MA, Amherst, Amherst, Massachusetts, United States (4) Mechanical Behavior of Materials, Xi'an Jiaotong Univeristy, Xi'an, China (5) Department of Chemistry, University of Massachusetts, Amherst, Massachusetts, United States (6) Precision Instrument Engineering, Tianjin University, Tianjin, China (7) Univ of Massachusetts, Amherst, Massachusetts, United States

Proteins are biocompatible, biodegradable and sustainable building blocks for designing functional materials. Additionally, they naturally occur with a variety of properties that can be harnessed for biomaterial applications such as antimicrobial strategies, tissue engineering, drug delivery etc. One major challenge with the fabrication of protein-based materials is their aqueous stability. Current strategies to design stable protein films are limited due to use of toxic crosslinkers or heat-induced denaturation.

Therefore, a generalizable technique that can be applied to a wide variety of protein precursors to enhance stability while retaining native protein properties, is attractive for biomaterial applications. We have developed a scalable and additive-free thermal treatment for the fabrication of stable, hydrophilic protein films through thermal treatment in fluoruous media. Protein building blocks retain most of their secondary structure and surface properties, enabling us to create protein-based coatings. We demonstrate the versatility of this strategy by studying a variety of proteins for applications such as anti-fouling coatings, drug-eluting coatings, tissue engineering scaffolds and microfluidic systems.



Treatment strategy for stabilization of protein-based coatings

## COLL 931

### Self-assembly of glycine-histidine-glycine hydrogels

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We have discovered a unique series of tripeptides that form strong hydrogels. Previous studies found that the tripeptide Glycine-Histidine-Glycine forms a hydrogel at low concentration and neutral pH. The peptide aggregates into oligomers which ultimately form a gel network of micron-size, crystalline fibrils that are highly entangled and volume spanning. These hydrogels have shown potential in biomedical applications such as drug-delivery and cell scaffolds with the advantage of low-cost and biocompatibility. This study seeks to understand the solubility conditions that favor the fibril phase and to investigate the mechanical properties of the gel using rheology. We explored the tunability of the material for future developments by screening formation conditions. We show that the gel strength, microstructure, and formation kinetics can be tuned by adjusting the pH and peptide concentration. We aim with this work to improve aggregation models and develop this novel material for biomedical applications.

## COLL 932

**Context matters: Investigating the role of culture geometry and microenvironment cues in cell activation using innovative biomaterials-based tools**

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The microenvironment of cells in the human body is increasingly recognized as a driver of cell function and fate, including the differentiation of stem cells and the activation of cancer cells and wound healing fibroblasts. For studying these complex interactions, a variety of tools have been and are being created for controlling the properties of the cell microenvironment in multiple dimensions, particularly the extracellular matrix, and for probing relevant cell responses. These studies have led to the observation that many cell responses are significantly affected by the geometry in which the cells are cultured, where which geometry from two- to three-dimensional (2D to 3D) culture is appropriate for probing a specific cell function and mimicking native microenvironments remains unclear. Toward addressing this, we have established an approach utilizing photopolymerizable biomimetic hydrogels to create a 2.5D culture geometry that enables initial cell spreading while reducing polarization to bridge between and allow comparison to 2D and 3D geometries. With this platform, we examined the effects of cell culture geometry on the activation of primary human lung fibroblasts, a cell response that is mediated by mechanotransduction and relevant in fibrotic disease. We observed that fibroblast responses were more similar between 2D and 2.5D culture than 3D culture at the cellular, protein, and gene levels at early times in these cultures, where cell-cell interactions were identified as key. Despite these new insights, a persistent challenge remains in quantitatively assessing cellular responses within such temporally and spatially regulated microenvironments, owing to the inherent heterogeneity of the cell population. To enable the further parsing of cell response, we have established an approach for assessing individual and collective fibroblast activation in real-time using of lentiviral-based fluorescent reporters. Collectively, these innovative tools enable unique investigations of fibroblast activation in complex and dynamical microenvironments with relevance to the study of other cell functions and types where context matters.

