Meeting Location:
Patrick G. and Shirley W. Ryan Hall
Room 4003
# 2016 Poster Session Presenters

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Liposomal Spherical Nucleic Acids for Gene Regulation and Immunomodulation

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Spherical nucleic acids (SNAs), consisting of densely packed, highly oriented oligonucleotide strands attached to the surface of nanoparticles, are able to overcome the typical challenges of nucleic acid delivery. SNAs have been shown to effectively enter 50 different cell types without the use of auxiliary transfection agents and exhibit minimal cytotoxicity. Typically, SNAs are synthesized from inorganic nanoparticle templates and shells of nucleic acid ligands immobilized on the surface of such particles. Recently, a variety of different templates (gold, silver, silica) and nucleic acids (DNA, RNA, LNA) combinations have been explored by different research groups.

We report here a novel class of biocompatible, metal-free SNA nanoconjugate that can be synthesized from FDA-approved, readily available starting components. The SNAs are composed of 30 nm liposomal templates that were synthesized from 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC) lipid monomer and functionalized with DNA strands modified with a tocopherol tail that intercalates into the phospholipid layer of the liposomal core via hydrophobic interactions. Remarkably, the inherently unstable liposomal template was stabilized due to the negatively charged spherical nucleic acid architecture. This morphology facilitates cellular internalization and gene regulation in cancer cells. Additionally, the liposomal template is ideal for delivery of drug payload and ideal for dual targeting. As such, these nanoconjugates have shown excellent immunomodulatory properties and are now being developed as vaccines for different forms of cancer.
The active layer morphology of organic photovoltaics (OPVs) is critical in the optimization of device efficiencies. Most strategies aimed at improving morphology are focused mainly on annealing methods and more recently in the use of solvent additives. This project uses chemical principles of self-assembly to impart self-recognition capability to molecules by incorporating hydrogen-bonding groups on high performance dyes for solar cells. We recently reported and compared the performance of two pairs of molecules, symmetric and asymmetric, and in each case, one able to hydrogen bond, to one without that capability. The optoelectronic properties of each pair are similar in solution, but studies on the films by grazing incidence x-ray diffraction reveal major differences in crystallinity. Whereas non-hydrogen bonding molecules exhibit commonly seen π-π stacking, hydrogen bonding impedes strong stacking and causes formation of much smaller domain sizes, which interestingly, lead to enhanced power conversion efficiency (PCE) compared to devices with non-hydrogen bonding molecules (see Figure 1). This project is currently exploring designs aimed at avoiding competition between intermolecular forces.

Figure 1. Depiction of stacking in non hydrogen bonding (top left) vs. hydrogen bonded assemblies (bottom left) and resulting current vs. voltage graph (right).
Designing effective cell-based assays that allow cell culture preparation and protein analysis on the same chip would facilitate quantification of molecular activities, significantly reduce the number of cells required for an assay, and enable the discovery of novel drug candidates. Achieving these goals remain challenging for current methods used to measure enzyme activities, which often rely on time-consuming sample preparation steps, lead to loss of enzymatic activity and therefore limit the validity of the readout. We have been successful in developing a cell-based assay whereby a monolayer presenting both an RGD ligand and a peptide substrate for an enzyme can be used for the simultaneous culture of cells and analysis of enzyme activity and have successfully applied this methodology to identify a novel inhibitor of phosphatases from screening a library of 10,000 molecules. We have also expanded the capabilities of our previous design to introduce extracellular matrix (ECM) attachment proteins, such as fibronectin, laminin and collagen, which would allow culture of a wide range of cell types. We first a nanopatterning methodology to template a small linker on a surface that would direct ECM protein attachment to discreet locations in an arrangement that is commensurate with the dimensions of a cell. The remaining surface was then functionalized to display short peptide ligands that would act as substrates for a desired enzyme reaction. In this manner, we combined surface chemistry amenable for cell culture, along with self-assembled monolayer laser desorption/ionization mass spectrometry (SAMDI-MS), thus enabling cell culture and analysis on the same monolayer-coated surface (Scheme). Our results revealed that cell attachment is directed toward the patterned regions while the phosphatase reporter ligand displayed in the unpatterned area showed conversion to the dephosphorylated product following lysis and analysis with SAMDI-MS. We envision to use these capabilities to probe enzyme reactions within cells and carry out single cell measurements.
Development of stable and non-toxic perovskites for high efficiency solar cells

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The introduction of semiconducting halide perovskite compounds, AMX₃ (A = Cs⁺, CH₃NH₃⁺ or HC(NH₂)₂⁺; M = Ge²⁺, Sn²⁺, Pb²⁺; X = Cl, Br, I), in solid-state solar cells has received enormous attention from the photovoltaic community and others in the last three years. Within a short period, the power conversion efficiency has been raised from ~6% in 2012 to ~20% up to date. Among the light absorber candidates, methylammonium lead iodide (CH₃NH₃PbI₃) is the most prominent choice owing to its outstanding properties for a solar cell absorber, such as high extinction coefficient, low band gap, and small exciton binding energy.¹,² However, this compound suffers from two major drawbacks: toxicity of Pb and instability when exposed to moisture. In order to make this perovskite-based technology viable, the two issues need to be resolved.

My research focuses on the lead-free ASnX₃ analogues, ranging from the synthesis, characterization of the bulk materials and subsequent use of them as light absorbing materials in solid-state solar cells. Several synthetic routes, solar cell fabrication techniques and photovoltaic performances will be presented in this poster.³⁴⁵ Additionally, the low moisture resistance of CH₃NH₃MI₃ perovskite, as it decomposes to PbI₂ salt upon exposure to ambient condition, is addressed by introducing a bulkier and more hydrophobic n-C₄H₉NH₃⁺ cation into the 3D network of CH₃NH₃MI₃. By doing so, we were able to improve the moisture resistance of the materials as well as opening up a new class of 2D perovskite materials with many interesting properties.⁶

Spherical Nucleic Acids (SNAs) are a unique class of nanoparticles (NPs) featuring a NP core that is densely functionalized with highly oriented oligonucleotides. The architecture of the SNA imparts novel properties, including high cellular uptake without the use of additional transfection reagents, resistance to nuclease degradation, and increased affinity for complementary nucleic acids compared to linear strands of the same sequence. These features enable the use of SNAs in gene regulation therapies and diagnostics based upon the detection of nucleic acids. In order to expand the utility of SNAs within the context of these applications, the SNA’s surface chemistry may be rationally designed to impart varying functional interactions with biomolecules, ranging in size from proteins to nucleic acids and small molecules. For example, utilizing poly(ethylene glycol) modifications to prevent the formation of a protein corona on SNAs in the presence of serum proteins results in enhanced blood circulation times in mice, which is advantageous for their delivery in vivo. In addition, the use of oligonucleotide sequences that form secondary structures, such as G-quadruplexes, significantly increases their interactions with serum proteins, resulting in enhanced accumulation in the liver and spleen due to recognition of the protein corona by macrophage cells. Lastly, by functionalizing NPs with aptamer oligonucleotides, SNAs may be used to detect small molecule biomarkers, including steroidal hormones.

Modern chemical biology and drug discovery each seek to identify new small molecules that potently and selectively modulate the functions of target proteins. The research presented herein utilizes three unique methods for chemical probe development and discovery. First, a traditional target-based approach has lead to key structural insights into the selectivity of mitogen-activated protein kinase kinase 4 (MEK4), which is suspected to play a key role in prostate cancer metastasis. Second, a novel structure-driven approach has yielded a unique non-toxic, anti-melanoma small molecule which has been optimized to understand this molecule’s role in cancer. Thirdly, through the use of natural products as our chemical starting point, we seek to complete the first total synthesis of an unpublished class of new natural products shown to act as antagonists for a subset of 5-hydroxytryptamine (5-HT, serotonin) receptors. Through chemical synthesis, computational modeling, biochemical and cellular-based experiments, these projects aim to develop small molecule probes to study biological pathways.
Development of small-molecule modulators of E3 ubiquitin ligases using the ubiquitin thioester probe UbFluor

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The ubiquitin-proteasome system controls the degradation of individual proteins, including the protein components of signaling pathways involved in a variety of diseases. Previously, we have shown that it is possible to bypass the E1 and E2 enzymes of the ubiquitination cascade using an activated ubiquitin thioester. This unnatural transfer of ubiquitin directly to the catalytic cysteine of a HECT or RBR E3 ligase has been shown to recapitulate the native function of these E3 enzymes. To refine this concept, we have developed a fluorescent ubiquitin thioester probe, UbFluor, which quantitatively measures E3 enzyme activity in real time using fluorescence polarization. We have confirmed the validity of this assay through mutagenic analysis of the model HECT and RBR ligases Rsp5 and PARKIN, respectively. Further studies of Parkin revealed insights into multiple PARKIN activation states. These results provided a framework for designing appropriate drug-screening conditions for Parkin.

Given the simplicity of the UbFluor assay and the considerable links between E3 ligases and various cancers and neurodegenerative disorders, we screened for small-molecule modulators of WWP1, Nedd4, and PARKIN using UbFluor. This screen demonstrates the utility of the UbFluor assay for high-throughput drug discovery. We have identified selective hit compounds, which we have validated in native in vitro ubiquitination assays. We aim to characterize the mechanisms of our hits and demonstrate their utility in modulating the disease pathways controlled by these E3 ligases using cellular models. These studies will show the effectiveness of targeting E3 ubiquitin ligases as a method for treating cancers and neurodegenerative disorders.
The activation of ubiquitous small molecules, such as H$_2$O, O$_2$, N$_2$, CH$_4$, and CO$_2$, and their subsequent transformation into useful chemical fuels, is among the most important challenges facing science. In Nature, these processes are carried out within metalloproteins, whose active sites are embedded within a protein superstructure, prohibiting the highly-reactive intermediates from engaging in side reactions. Many of these metalloprotein based enzymes feature a metalloporphyrin active sites that help to facilitate the catalytic conversion of these small molecules in useful chemicals. While there have been a large number of advancements in the development of synthetic systems that mimic the function of these metalloporphyrin based enzymes, molecular systems suffer from deleterious bimolecular condensation that arrest catalytic activity. In the absence of a protein superstructure, we have sought to embed reaction centers within metal-organic frameworks (MOFs). Using a porphyrin-based MOF, we have isolated and thoroughly characterized a new class of five coordinate metalloporphyrin dioxygen adducts. From these studies, we have been able to obtain the first crystallographically characterized five coordinate Fe, Co, and Mn porphyrin O$_2$ adducts, ascertain key information regarding the electronic structure of these rare species, as well as examine the thermodynamics of O$_2$ binding to the metal centers. In addition, we have discovered that the strength of O$_2$ binding to four coordinate, metalloporphyrin centers is considerably lower than what has been observe for substituted proteins and model complexes that feature axial ligands, further highlighting the importance of axial ligation in biological O$_2$ transport and storage. These results demonstrate the ability of a MOF, by virtue of its rigid solid-state structure, to enable isolation and thorough characterization of a species that have only be observed transiently in molecular form.
Electron Hopping through Double-Exchange Coupling in a Mixed-Valence Diiminobenzoquinone-Bridged Fe₂ Complex

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The ability of a benzoquinonoid bridging ligand to mediate double-exchange coupling in a mixed-valence Fe₂ complex is demonstrated. Metalation of the bridging ligand 2,5-di(2,6-dimethylanilino)-3,6-dibromo-1,4-benzoquinone (LH₂) with FeII in the presence of the capping ligand tris(2-(6-methyl)pyridylmethyl)amine (Me₃TPyA) affords the dinuclear complex [(Me₃TPyA)₂FeII₂(L)]²⁺. Dc magnetic measurements, in conjunction with X-ray diffraction and Mössbauer spectroscopy, reveal the presence of weak ferromagnetic superexchange coupling between FeII centers through the diamagnetic bridging ligand to give an $S = 4$ ground state. Ac magnetic susceptibility measurements, collected in a small dc field, show this complex to behave as a single-molecule magnet with a relaxation barrier of $U_{\text{eff}} = 14(1)$ cm$^{-1}$. The slow magnetic relaxation in the FeII₂ complex can be switched off through one-electron oxidation to the mixed-valence congener [(Me₃TPyA)₂Fe₂(L)]³⁺, where X-ray diffraction and Mössbauer spectroscopy indicate a metal-centered oxidation. Dc magnetic measurements show an $S = 9/2$ ground state for the mixed-valence complex, stemming from strong ferromagnetic exchange coupling that is best described considering electron hopping through a double-exchange coupling mechanism, with a double-exchange parameter of $B = 69(4)$ cm$^{-1}$. In accordance with double-exchange, an intense feature is observed in the near infrared region and is assigned as an intervalence charge-transfer band. The rate of intervalence electron hopping is comparable to that of the Mössbauer timescale, such that variable-temperature Mössbauer spectra reveal a thermally-activated transition from a valence-trapped to detrapped state. These results demonstrate the ability of quinonoid ligands to mediate electron hopping between high-spin metal centers, by providing the first example of an Fe complex that exhibits double-exchange through an organic bridging ligand and the largest metal-metal separation yet observed in any metal complex with double-exchange coupling.
Synthetic Examination of Decoherence in Molecular Electronic-Spin Qubits

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The construction of a quantum computer is an enormous challenge, the successful accomplishment of which will have profound implications in fields as diverse as cryptography, protein structure elucidation, and the exact simulation of quantum systems. Electronic spins in coordination complexes provide a promising and underexplored approach to the creation of quantum bits (qubits), the fundamental units of information in a quantum computer. However, the short coherence lifetimes of electronic spin qubits currently stand as a significant obstacle their use.

Though there are many factors which influence electronic coherence times, three of the most important to understand are electronic spin magnitude, spin-orbit coupling, and nuclear spin proximity. The effect of each of these parameters on coherence defines the synthetic toolbox that can be employed in the construction of qubit complexes, yet the effects of varying each property within a system are not known.

To explore the effects of spin and spin-orbit coupling, we synthesized two series of molecules. In the first, spin varied within the series \([\text{Ru(C}_2\text{O}_4\text{)}_3]^{3-}\), \([\text{Cr(C}_2\text{O}_4\text{)}_3]^{3-}\), and \([\text{Fe(C}_2\text{O}_4\text{)}_3]^{3-}\) \((S = \frac{1}{2}, \frac{3}{2}, \text{and} \frac{5}{2}, \text{respectively})\); in the second, the series \([\text{Fe(CN)}_6]^{3-}\), \([\text{Ru(CN)}_6]^{3-}\), and \([\text{Os(CN)}_6]^{3-}\) exhibited increasing spin-orbit coupling constants of 464, 880, and 3100 cm\(^{-1}\). We then subjected the complexes to pulsed electron paramagnetic resonance (EPR) spectroscopic experiments to determine their coherence times, and found a small decrease of coherence time with increasing spin, and an increase in coherence time with increasing spin-orbit coupling, both contrary to expectations based on previous theory.\(^1\)

We then studied the impact of changing nuclear spin proximity to a paramagnetic center by synthesizing three novel V(IV) complexes in 5–8 synthetic steps each. This series varied the distance between a propylene moiety (containing spin-bearing protons) and the paramagnetic vanadium center via a scaffold comprised solely of the nuclear spin-free elements carbon and sulfur (see Fig. 1).

Experiments are in progress to determine the coherence properties of the complexes which, once completed, will serve as an invaluable tool for the rational design of long-coherence complexes.

Our work has additionally focused on the synthetic tuning of an additional parameter, known as the spin-lattice relaxation time. This characteristic time serves as both an upper limit to the coherence time and as a lower limit to the operating speed of a future quantum processor, and is therefore a parameter over which exerting synthetic control is extremely important. We conducted a detailed study on a complex, \([\text{Fe(C}_5\text{O}_5\text{)}_3]^{3+}\), which exhibits an abnormally short spin-lattice time, then correlated the relaxation properties with specific vibrational modes in the complex. This allowed us to determine which chemical moieties contributed to relaxation most significantly.

One Electron Changes Everything: a Multi-species Copper Redox Shuttle for Dye-sensitized Solar Cells.


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Dye-sensitized solar cells (DSCs) are an established alternative photovoltaic technology that offers numerous potential advantages in solar energy applications. However, this technology has been limited by the availability of molecular redox couples that are both non-corrosive/non-toxic and do not diminish the performance of the device. In an effort to overcome these shortcomings, a copper-containing redox shuttle derived from 1,8-bis(2′-pyridyl)-3,6-dithiaoctane (PDTO) ligand was investigated. Electrochemical measurements, single-crystal x-ray diffraction, and absorption and electron paramagnetic resonance spectroscopies reveal that, when the common DSC additive 4-tert-butylpyridine (TBP) is present, removal of one metal-centered electron results in PDTO-enshrouded copper ions completely shedding the tetradentate PDTO ligand and replacing it with four or more TBP ligands (see below). Thus, the reduced and oxidized halves of the redox shuttle system, the Cu(I) and Cu(II) complexes, respectively, have completely different coordination spheres with widely differing Cu(II/I) formal potentials and reactivities for electron transfer. Notably, the coordination-sphere replacement process is fully reversed upon converting Cu(II) back to Cu(I). These characteristics are exploited to control the rates of desirable and non-desirable electron transfer processes in DSCs featuring an adsorbed organic dye and a nanoparticulate, TiO₂-based, photo-electrode. In these devices, this dual species redox shuttle system engenders performance superior to that obtained with shuttles based on the (II/I) forms of either of the coordination complexes in isolation.
Directed Assembly of Nucleic Acid-Based Polymeric Nanoparticles from Molecular Tetravalent Cores

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Just as a basic brick can be used to build an intricate cathedral or a much simpler backyard barbeque pit, DNA can be the building block of life or a tool for human invention. Not surprisingly, researchers have exploited DNA’s base-pairing interactions to create precisely controlled molecular structures, from complex DNA origami to high-dimensional structures such as rings, tubes, and boxes. Small molecule-DNA hybrids (SMDHs), which contain organic cores with multiple attached DNA strands, have become popular as starting materials for nanotechnology applications. Frustratingly, SMDHs bearing more than three DNA strands have a tendency to clump, forming ill-defined products. Our research group has capitalized upon this clumping tendency by forming spherical nanoparticles out of four-stranded SMDHs. The size of these small particles can be easily tuned by varying assembly time and salt and nucleic acid concentrations. In experiments, these particles are more resistant to enzymes that cleave DNA, and cells internalize them more quickly than the individual synthetic nucleic acid components. Moreover, the particle surfaces can be further functionalized for applications including sensing, tracing, or capture-release. These attributes make the nanoparticles attractive new molecular vehicles to deliver therapeutic molecules, flag cancer cells or other diseases, follow tracer species through the body, and much more.

Figure 1. The assembly of nucleic acid-based polymeric nanoparticles from SMDH4 and its complementary partner. The size of the particles can be easily tuned by varying assembly time and salt and nucleic acid concentrations.

Reference
Picosecond Control of Photogenerated Radical Pair Lifetimes using a Stable Third Radical

Noah E. Horwitz, Brian T. Phelan, Jordan N. Nelson, Matthew D. Krzyaniak, and Michael R. Wasielewski

Photoinduced electron transfer reactions in organic donor-acceptor systems leading to long-lived radical ion pairs (RPs) have attracted broad interest for their potential applications in fields as diverse as solar energy conversion and spintronics. We present the photophysics and spin dynamics of an electron donor - electron acceptor - stable radical system consisting of a meta-phenylenediamine (mPD) donor covalently linked to a 4-aminonaphthalene-1,8-dicarboximide (ANI) electron-accepting chromophore as well as an α,γ-bisdiphenylene-β-phenylallyl (BDPA) stable radical. Selective photoexcitation of ANI produces the BDPA-mPD−-ANI− triradical in which the mPD+−ANI− RP spins are strongly exchange coupled. The presence of BDPA is found to greatly increase the RP intersystem crossing rate from the initially photogenerated BDPA-1(mPD+−ANI−) to BDPA-3(mPD+−ANI−), resulting in accelerated RP recombination via the triplet channel to produce BDPA-mPD-3∗ANI as compared to a reference molecule lacking the BDPA radical. The RP recombination rates observed are much faster than those previously reported for weakly coupled triradical systems. Time-resolved EPR spectroscopy shows that this process is also associated with strong spin polarization of the stable radical. Overall, these results show that RP intersystem crossing rates can be strongly influenced by stable radicals nearby strongly coupled RP systems, making it possible to use a third spin to control of RP lifetimes down to a picosecond timescale.
Electron Ratchets

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The motion of biological molecules and charge carriers in certain materials is random due to strong interactions with the surrounding environment. In the absence of high source-drain biases, such as in a cellular environment or low-power electronic devices, a ratchet can be used to rectify the random motion of these particles. Ratchets use energy, in the form of an oscillating, periodic potential, to break the symmetries of motion in space and time. Ratchets are a cornerstone of molecular machinery, including the kinesin walker and ATP synthase.

Our research focuses on applying the principles of ratchets to electrons in highly damped environments such as organic electronics, low-power devices, and infrared sensors. We model electron ratchets in the quantum and semiclassical limit. We find that the shape of the ratchet potential and its oscillation frequency play a strong role in controlling the direction and magnitude of the current, respectively. Additionally, we propose that ratchets can be realized in semiconductors through gradients of defects or composition. The goal is the demonstration of an electron ratchet that can improve the efficiency of photovoltaic, logic, or sensing devices, with the possibility of powering itself through wasted thermal power or unabsorbed light.
Development of Fluorinated Diketopyrrolopyrrole as a Building Block for Organic Semiconducting Materials

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Organic semiconducting materials present a low cost alternative to inorganic materials for use in field-effect transistors (FET). Low processing cost and structural tunability give these materials potential for broad applicability in electronic devices. In order to realize broad applications for organic semiconductors, charge carrier mobility values in FET devices must be improved beyond their current maximum values (~1 cm² V⁻¹ s⁻¹). Polymeric materials due to their compatibility with mass produced technologies are the most attractive among organic semiconductors. The synthetic tunability of semiconducting polymers allows for alteration of existing polymer structures, creating new materials to study and evaluate. Synthesis and study of new polymers sheds light on structure-property relationships and broadens the scope of semiconductors available for study in FET devices. Towards this end, we have developed a new fluorinated diketopyrrolopyrrole (FDPP) monomer for use in semiconducting polymers. This monomer is based on the previously developed diketopyrrolopyrrole (DPP) motif, which has been used in many high mobility polymers to date. Incorporation of fluorine into organic semiconductors has been shown to increase crystallinity and planarity in the conjugated backbone and to stabilize the frontier molecular orbitals. This has the effect of increasing the material mobility and stability compared to the unfluorinated counterpart. We have developed a straightforward and scalable synthesis of the FDPP monomer and incorporated it into polymer structures. These polymers exhibit high crystallinity, low frontier molecular orbital energies, and small optical bandgaps. Preliminary results of FET device testing using the new polymer as an active layer semiconductor revealed hole mobilities approaching 1 cm² V⁻¹ s⁻¹, which is an exceptional result for a new polymer based on unprecedented monomer (FDPP). Through further study of the FDPP monomer in new polymer structures, we hope to further broaden the scope of possible structures for semiconducting polymers and further increase the mobility of polymer FET devices.
Singlet Fission in Molecular Dimers and Thin Films of Terrylene Diimide

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Organic semiconductor materials are being increasingly adopted in a variety of high tech products, including light-emitting diodes and organic photovoltaic (OPV) devices. These organic materials offer not only functional advantages, in their synthetic tailorability and amenable optical and electronic properties, but are also economically viable. While much work has been done to characterize and understand the physical properties of organic materials, many of the optical and excitonic properties of organic semiconductors are still not well understood. My research aims to elucidate the excitonic processes available in organic semiconductors by studying the photophysics of aggregated chromophore samples. Of particular interest is the process of singlet fission (SF), whereby a singlet excited state is energetically down-converted to two separate triplet excited states. This process offers a method to dramatically increase the efficiency of OPV. We aim to understand how intermolecular coupling affects the exciton dynamics of a series of terrylene diimide (TDI) derivatives. To this end, I have prepared a covalently bound molecular dimer, which includes the bare minimum number of chromophores for SF, to study the mechanism of SF and direct further research. I have also prepared a series of monomeric TDI derivatives in order to examine its propensity to undergo SF in solid state samples. The first aim of my research is to synthesize and structurally characterize these novel TDI chromophores by structural modelling and single crystal X-ray diffraction to quantify differing π-π stacking motifs in each derivative. In the case of the film samples, I then correlate these structural differences to thin film samples through grazing incidence X-ray diffraction experiments. Finally, with this knowledge of inter-chromophore geometries, I explore the photophysics of these solution and thin film samples via ultrafast pump-probe transient optical techniques in order to determine the role the coupling geometries play in excited state dynamics, specifically as they relate to singlet fission. Ultimately, we are able to correlate structural analysis with optical analysis to more completely understand the photophysics of these chromophore aggregates.
Selective and Reversible Molecular Encapsulation via Allosterically-Regulated Coordination Capsules

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Molecular capsules assembled through coordination chemistry have long been used as scaffolds to explore new types of molecular interactions in constrained geometries and have potential applications in catalysis, drug delivery and separations. However, these assemblies are rigid, usually trapping guests within the cavity or are effective only in a limited set of conditions. These systems can be greatly enhanced by introducing principles from biology such as allosteric regulation to expand the capabilities and reduce the shortcomings of such assemblies. Herein, we introduce a new class of biomimetic, ion-regulated molecular receptors synthesized and assembled via the Weak-Link Approach (WLA). These structures feature both a cavitand (calix[4]arene, resorcin[4]arene or cyclodextrin) moiety which serves as a molecular recognition unit, and an activity regulator composed of hemilabile phosphine alkyl thioether ligands (P,S) or N-heterocyclic carbene alkyl thioether (NHC,S) ligands chelated to a Pt(II) metal. The host-guest properties of the ion-regulated receptors were found to be highly dependent upon the coordination environment of the Pt(II) metal center, which is controlled through the reversible coordination of small molecule effectors. The coordination environment at the regulatory site dictates the charge and the structural conformation of the entire assembly resulting in three accessible binding configurations: a closed, inactive state and two open, active states. $^{31}$P NMR, DOSY NMR, Job plots, $^1$H NMR spectroscopy titrations were used to study the formation of these inclusion complexes, the receptor binding modes, and the receptor binding affinities ($K_a$) in solution. Single crystal X-ray diffraction studies provided insight into the solid-state structures of the receptor when complexed with each guest molecule. DFT calculations were used to understand the nature of the selectivity of the molecular receptor. Finally, we describe the reversible capture and release of guests by switching the receptor between the closed and semiopen configurations via small molecule effectors (Cl$^-$ and CN$^-$). Taken together, this work introduces the use of the WLA as a platform for the synthesis and allosteric regulation of host-guest properties in molecular capsules by utilizing the mechanisms for allosteric control of binding sites that are found in biological machinery, and offers a promising strategy for the development of biomimetic supramolecular assemblies with potential applications in small molecule separations, drug delivery and catalysis.

Motivated increasingly by global energy demands, a wide-variety of redox-active materials such as small molecules, polymers and salts, have been investigated extensively as components in rechargeable lithium-ion batteries (LIBs). Designing small-molecule organic redox-active materials, with potential applications in energy storage, has received considerable attention in the recent past. Here, we report the facile synthesis, characterization and application of two rigid chiral triangles (Figure 1), each of which consist of non-identical pyromellitic diimide (PMDI) and naphthalene diimide (NDI)-based redox active units. Single-crystal X-ray diffraction analyses reveal their rigid triangular prism-like geometries. Unlike previously investigated equilateral triangles containing three identical PMDI or NDI subunits, both isosceles triangles do not choose to form one-dimensional supramolecular nanotubes by dint of \([C-H\cdots O]\) interaction-driven columnar stacking as do the equilateral triangles. The rigid isosceles triangle, composed of one NDI and two PMDI subunits, forms — in the presence of \(N,N\)-dimethylformamide (DMF) — two different types of intermolecular NDI-NDI and NDI-PMDI \(\pi\)-\(\pi\) stacked dimers with opposite helicities in the solid-state. Cyclic voltammetry in \(CH_2Cl_2\) reveals that both isosceles triangles can accept reversibly up to six electrons. Continuous-wave electron paramagnetic resonance (EPR) and electron-nuclear double resonance (ENDOR) spectroscopic investigations, supported by DFT calculations, on the single-electron reduced radical anions of the isosceles triangles confirm the selective sharing of the unpaired electrons among the adjacent redox-active NDI subunit(s) within both molecules. Both the isosceles triangles have been employed as electrode-active materials in organic rechargeable LIBs. The evaluation of the structure-performance relationships of this series of diimide-based triangles reveals that as the number of NDI subunits in the molecules are increased at the expense of the PMDI subunits, the electrochemical cell performance of the organic redox-active materials in batteries experiences a marked improvement.
A SAMDI-based Assay for Profiling of Protein Interaction Domains

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Adaptor domains are protein domains that recognize and bind to specific post translational modifications. They often occur as a domain in larger multi-domain proteins. When they are present in proteins containing enzymatic subunits, they can localize the enzyme to specific locations within multi-protein complexes in the cell, and when present in proteins lacking catalytic domains, they can serve scaffolding purposes. Adaptor domains are very relevant in epigenetic gene expression, where they bind to modified forms of histone proteins and are involved in chromatin maintenance and remodeling. In recent years they have been explored as possible druggable targets.

Commonly used techniques for measuring these interactions all come with limitations, especially when compared to the range of assays available for profiling enzymes. Calorimetry can be used to precisely measure the affinity, but it has a very low throughput and requires restrictively large amounts of protein. Fluorescence polarization can be used for increased throughput, but requires labelled, non-native substrates. Peptide binding arrays such as SPOT allow for the hundreds of interactions to be profiled but only at a qualitative level.

We have developed an enzyme linked assay which uses self-assembled monolayers (SAM) in combination with MALDI-TOF mass spectrometry (SAMDI) for direct quantification. We can generate arrays of ligand peptides of interest immobilized on SAM’s along with substrate for a reporter enzyme. Adaptor domains fused to a reporter enzyme will recruit the enzyme to the surface in a manner dependent on the affinity for the ligand of interest and leave a permanent covalent record of the transient interaction (see figure below). The reporter will show limited activity in the absence of a ligand interaction, but the observed activity will increase when an adaptor domain binds a ligand and brings the enzyme to the surface-bound substrate. In this way, we can profile the affinity of these adaptor domains for possible ligands in a high throughput format that is also compatible with small molecule inhibitor screening.
The nano-bio interface is becoming increasingly important as the amount and prevalence of engineered nanomaterials rise. A key question concerns the assessment of structural changes in lipid membranes once they are brought into contact with nanoparticles. Here, we use supported lipid bilayers (SLBs) as idealized model systems for cell membranes and discuss how to probe SLBs using the interface-specific nonlinear optical technique sum frequency generation (SFG) spectroscopy, as well as fluorescence microscopy, X-ray photoelectron spectroscopy, and quartz crystal microbalance with dissipation monitoring in the context of the nano-bio interface. Our combined study sheds light on how SFG responses produced in the C-H stretching region from symmetric SLBs under isothermal ($T = 22\pm2^\circ C$) conditions co-vary with the transition temperatures of the lipids from which the SLB is formed. The specific lipids studied here are 1,2-dioleoyl-sn-glycero-3-phosphocholine (18:1 $\Delta 9$-Cis, DOPC), 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (16:0-18:1, POPC), 1,2-dilauroyl-sn-glycero-3-phosphocholine (12:0, DLPC), 1,2-dimyristoyl-sn-glycero-3-phosphocholine (14:0, DMPC), 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (16:0, DPPC), and 1,2-distearoyl-sn-glycero-3-phosphocholine (18:0, DSPC) in 100 mM NaCl, 10 mM Tris buffer, pH 7.4. We find that the intensity of the SFG signal at 2870 cm$^{-1}$ ($\pm15$ cm$^{-1}$), which has been attributed by others to the methyl symmetric stretch arising from the lipid tail, co-varies positively with the transition temperature ($T_m$) of the lipid: when the lipid $T_m$ is below the laboratory temperature, the intensity of the peak near 2870 cm$^{-1}$ is low. These results are consistent with temperature-dependent measurements reported by Liu and Conboy (JPCC 2007, 11, 8988). The implications of our work for engineering environmentally safe nanomaterials are discussed.
Desorption of Hydrogen from Corrugated Graphene and Light-driven Electron Transport: Theory, Simulations, and Experiments

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Research on sources of clean energy has received a tremendous thrust for the last few decades due to the ever-diminishing stock of fossil fuels. In this regard, hydrogen-based fuel cells are promising candidates for portable clean energy. Scientists have been looking for novel means of hydrogen storage, which is beyond compressing hydrogen gas inside robust containers. To this end, it has been established experimentally that atomic hydrogen chemisorbs into graphene or any graphitic surface. The hydrogen atoms can be subsequently made to desorb by applying an electrostatic field through scanning tunneling microscopic (STM) tip. Our experimental collaborators observed that this desorption yield follows a sigmoidal increase with applied bias which is the signature of a single electron process. Further, in the presence of corrugations in graphene, the yields at the concave sites were more than that at the convex ones. To explain these results, we perform first principles density functional theory (DFT) simulations to unravel the desorption mechanism and the origin of the substantial yield difference between concave and convex surfaces. Our calculations indicate that charge localization around the concave sites lead to a large equilibrium displacement of the ionic resonance with respect to the neutral state, which leads to a rather efficient desorption yield. However, this mechanism is only relevant for tunneling electrons at a low bias and is inefficient at a convex site. This work furthers our understanding of the hydrogen-graphene system, which has important implications for graphene-based applications in electronics and energy conversion.

In a joint effort with another experimental group we study the light-induced enhanced electron transport characteristics of a molecular-scale junction. The experimental data show a nonlinear increase in electronic current perturbation when the focus of a chopped laser beam moves laterally toward the tip–sample junction. To understand this behavior and generalize it, we apply a combined theory of the electronic nonequilibrium formed upon decoherence of an optically triggered plasmon and first-principles transport calculations. Our calculations indicate that the enhancement in the electronic current is directly proportional to the magnitude of plasmonic excitations only in the presence of a molecular linker, which is in excellent agreement with the experimental results. This occurs due to the increasing availability of virtual molecular orbital channels for transporting electrons with higher injection energies. Our results thus illustrate light-triggered, plasmon-enhanced tunneling current in the presence of a molecular linker.
Unprecedented High Temperature CO$_2$ Selectivity in N$_2$-phobic Nanoporous Covalent Organic Polymers

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The pursuit of synthetic routes for design and preparation of nanoporous polymeric networks with inherent permanent porosity and functionality through bottom-up methodologies remains a driving force in developing materials for energy and the environment applications. We reported a series of nanoporous polymeric networks, Covalent Organic Polymers (COPs) for various applications — gas adsorption & separation, catalysis, water treatment and charge carrier. Post-combustion CO$_2$ capture and air separation are integral parts of the energy industry, although the available technologies remain inefficient, resulting in costly energy penalties. We demonstrated azo-bridged, nitrogen-rich, aromatic, water stable, nanoporous covalent organic polymers, which can be synthesized by catalyst-free direct coupling of aromatic nitro and amine moieties under basic conditions. Unlike other porous materials, azo-covalent organic polymers exhibit an unprecedented increase in CO$_2$/N$_2$ selectivity with increasing temperature, reaching the highest value (288 at 323 K) reported to date. Here we observe that azo groups reject N$_2$, thus making the framework N$_2$-phobic. Monte Carlo simulations suggest that the origin of the N$_2$ phobicity of the azo-group is the entropic loss of N$_2$ gas molecules upon binding, although the adsorption is enthalpically favorable. Any gas separations that require the efficient exclusion of N$_2$ gas would do well to employ azo units in the sorbent chemistry.
Towards quantum teleportation via photo-induced electron transfer

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The ability to manipulate quantum information within a system is necessary if that system is to be utilized for quantum computation and communication. Quantum teleportation, the instantaneous transmission of a quantum state from one place to another through quantum entanglement, has already been realized in various physical systems such as photons and nuclear spins. So far, this phenomenon has not been realized for electron spin states in molecular systems. Following the scheme put forth by Salikhov, et al., it should be possible to teleport electron spin states within an electron donor-acceptor-radical (D-A-R•) system through the reduction of a stable radical by a spin-correlated radical pair. To summarize: a quantum state will be prepared on R• using a π/2 microwave (m.w.) turning pulse. Reduction of R• will then occur by a member of a photo-generated spin-correlated radical pair; this reduction acts as the “measurement step” of the teleportation procedure. Successful teleportation of the initial state to the remaining spin on D will be detected by the spin echo resulting from a π-pulse on resonance with D•+ and off-resonance with R• (Scheme 1). A successful performance of this procedure will demonstrate the viability of using molecular electron spins for quantum information applications.

After several iterations, a candidate for the teleportation experiment, consisting of a covalently-attached tetrathiafulvalene (TTF) donor, naphthalene imide acceptor, and a α,γ-bisdiphenylene-β-phenylallyl radical (BDPA•), was synthesized. Preliminary characterization by transient absorption spectroscopy and X-band and Q-band electron paramagnetic resonance spectroscopy show the successful, long-lived reduction of the BDPA radical in a frozen solvent glass. Spin-echo detection experiments following photoexcitation show evidence of BDPA• depletion and polarized TTF•+. As the timescale of this experiment is much shorter than the typical time for spins localized on an organic molecule to align with a magnet field (T1), this result implies some form of spin information transfer occurring during radical reduction. Recent work has involved re-synthesizing the relevant molecule with BDPA•-d16 (which will allow the selective excitation of D•+ and R•) and establishing the phase-coherence of the two separate m.w. sources necessary for the full teleportation experiment.
Solid-state superstructures, resulting from assemblies programmed by homochirality have attracted a lot of attention. In addition, artificial double-helical architectures have been investigated for the ways they can be controlled to yield helical forms as a result of chiral induction. Herein, we report (Figure 1) the highly specific self-assembly of double-helical superstructures from enantiopure macrocycles composed of two benzophenone-3,3′,4,4′-tetracarboxylic diimide (BTDI) units. Equimolar amounts of two conformational diastereoisomers derived from the configurational enantiomers of this flexible BTDI macrocycle self-organize in the crystalline phase to form two single-handed helices which are complementary to each other giving rise to a double helix by dint of intermolecular \([\text{C–H} \cdots \text{O}]\) and \(\pi\)-\(\pi\) stacking interactions. The helical sense of the double helices depends on the nature of the stereogenic centers present in the macrocycles. The interconversion of the two diastereoisomeric conformations in solution was investigated by variable-temperature \(^1\)H NMR and circular dichroism spectroscopies. The observation of such helical superstructures in the solid state is unprecedented to the best of our knowledge. These findings establish a novel approach to the design of supramolecular architectures and show that highly ordered helical systems are achievable in the crystalline state with equimolar amounts of two conformational diastereoisomers derived from configurationally enantiomeric macrocycles. This approach provides access to highly ordered assemblies of chiral BTDIs which exhibit higher electronic communication when compared with their monomeric analogues.

Single-Face/All-cis Arene Hydrogenation by a Supported Single-Site d⁰ Organozirconium Catalyst

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The stereo-controlled hydrogenation of substituted aromatic molecules is of great interest for pharmaceutical, agrochemical, and fine chemical applications, where the required function is ultimately determined by the molecular stereochemistry.¹ Alkyl-substituted arenes such as xylene have been the subject of extensive studies, as building blocks for more complex systems. Single-site, molecule derived supported catalysts have attracted interest due to their hybrid character combining the complementary features of traditional heterogeneous and homogeneous systems.² In particular, electrophilic d⁰ catalysts supported on “super” Brønsted acids exhibit large percentages of catalytically significant sites (70-90%) with high activity for technologically relevant olefin polymerization and hydrogenation processes.³ The single-site supported organozirconium catalyst Cp*ZrBz₂/ZrS (Cp* = Me₅C₅, Bz = benzyl, ZrS = sulfated zirconia) catalyzes the single-face/all-cis hydrogenation of a large series of alkylated and fused arene derivatives to the corresponding all-cis-cyclohexanes. For o-xylene hydrogenation, kinetic data obey the rate law Nₜ = kobs[arene]₀[PH₂]¹ with Eₐ = 5.3 ± 0.1 kcal/mol and the catalyst demonstrates maintained stereo-control over repeated uses. Kinetic/mechanistic and DFT analysis argue that stereoselection involves rapid, sequential H₂ delivery to a single catalys-bound arene face, versus any competing intramolecular arene pi-face interchange.

References:
Chromium containing selenophosphaes: ACrP₂Se₆ (where A = K, Rb, and Cs)

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The family of compounds ACrP₂Se₆ (where A = K, Rb and Cs) were synthesized via direct combination at 600 °C. These compounds all contain one dimensional chains of $\frac{1}{\alpha}[\text{CrP}_2\text{Se}_6]^{-}$ separated by their respective alkali cations. The Cr center has an oxidation state of 3+ in order to charge balance and, as a result, has three unpaired electrons. This leads to possibly interesting magnetic properties between Cr centers within the chains and between chains themselves. Magnetic measurements have been done on all analogs and preliminary results show that they are all antiferromagnetic below 50 K. The band gap of the analogs are all around 1.2 eV and the compounds do not undergo photoluminescence. The series of materials are all soluble in dimethylsulfoxide yielding a thick brown slurry when concentrated and a light brown solution when dilute. This is exciting as the solutions provide easy processing of the compounds into films. The K analog crystallizes in the space group $P21/c$ and the Rb and Cs analogs crystallize in the space group $P-1$. The K analog forms in two phases: the alpha and beta phase, with the beta phase having disorder of the $\text{K}^+$ cations in between the chains. This disorder changes the dimensions and beta angle of the unit cell, giving rise to a slightly different powder x-ray diffraction pattern.
A New Assay for Profiling Endogenous Phosphatase Activity

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Phosphorylation is a ubiquitous post-translational modification with important roles in regulating many cellular processes including differentiation and metabolism. Phosphorylation of serine, threonine, and tyrosine residues occurs on more than 30% of cellular proteins, and is regulated by a kinetic balance of both kinases and phosphatases. Dysregulation of kinases and/or phosphatases plays a role in the pathogenesis of many diseases such as cancers, diabetes, and neurodegenerative disorders. While extensive research has focused on developing pharmacological agents that regulate kinase activity, comparatively little work has been conducted on phosphatases, as they have proven more challenging to study.

Current methods for studying phosphatase activity include 1) non-specific and indirect radioactive and colorimetric assays that are incompatible with cell lysates, and 2) fluorescent assays that are prone to false positives, low signal-to-noise ratios, and are limited by antibody availability.

We are proposing a new, high-throughput, label-free assay capable of measuring endogenous phosphatase activity using self-assembled monolayers (SAMs) of alkanethiolates on gold with matrix-assisted laser desorption ionization– time of flight mass spectrometry (SAMDI-TOF MS) (Figure 1). With a technique to directly profile phosphatases, our goal is to monitor phosphatase activity during differentiation of human mesenchymal stem cells (hMSCs). We have synthesized three 361-member peptide libraries containing the sequence Ac-CKGXTp/Sp/YpZA (where X and Z represent all amino acids except cysteine). Using SAMDI, we can immobilize all 361 peptides in a library to a steel plate patterned with 384 spots of SAMs on gold, and then treat the surface with hMSC lysates from different stages of cell differentiation. MALDI-TOF mass spectrometry is used to measure the amount of dephosphorylation on each of the 361 peptides, generating a phosphatase activity profile from an array of diverse peptide substrates (Figure 1). We have completed all phosphatase experiments on the Tp SAMDI array and are working on collecting data from the last two arrays. This is the first high-throughput, label-free assay to study and compare endogenous phosphatase activity.

These arrays provide enzymatic fingerprints of phosphatases in different cell types in a way that is comparable to profiling gene expression through early DNA chip arrays. In the future, we hope to identify the active phosphatases in specific cellular conditions and uncover specificity and activity profiles of individual phosphatases in cell lysates, using bottom-up proteomics, inhibitors and overexpression cell lines. This new assay has the potential to offer a better understanding of the mechanisms underlying phosphatase activity and their roles in mesenchymal stem cell differentiation.

Figure 1.
Schematic diagram of profiling global cellular activity of phosphatases by SAMDI

Enhancing the performance of organic photovoltaic devices via synthesis of new small molecules and polymers

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Organic photovoltaic (OPV) devices offer several advantages over inorganic ones. The use of rare and expensive or toxic inorganic semiconductors can be minimized or eliminated entirely and the devices can be made lightweight and fabricated over a large area at low cost. They can also be inkjet printed on flexible substrates, which is suitable for niche applications. The chemistry of organic molecules and polymers can be tailored to obtain desirable physical properties including the bandgap, solubility and crystallinity.

Performances of small molecule based solar cells are rapidly approaching that of polymer based devices. The power conversion efficiency (PCE) of small molecule devices are, however, often limited by their low fill factors (FF). We hypothesized that FF can be enhanced by endcapping molecules with alkyl chains since endcapping has been shown to improve charge carrying behavior in organic semiconductors. Four \( \pi \)-isoelectronic donor molecules based on the diketopyrrolopyrrole (DPP) dye were synthesized. Relationship between the structure of the molecules and their optoelectrical properties were investigated. The alkyl endcapping groups improved the mobility of the donor molecules and that resulted in increased FF and consequently higher PCE in solar cells.

Fullerenes are widely used as the acceptor in OPVs but they suffer from drawbacks including low light absorptivity, high cost and poor stability. Perylenediimide (PDI)s have been employed as a substitute with encouraging results. We hypothesized that slip-stacked PDIs can used to fabricate high performing solar cells because 1) they form crystalline films and 2) unlike in unmodified PDIs, they don’t have eximeric traps states that consume singlet excitons. Slip stacked PDIs are unique in that they are retain an advantageous feature of unsubstituted PDIs – their high crystallinity, but are devoid of their key drawback - the eximeric trap states. A family of slip-stacked PDIs with differing crystallinity and slip angles was successfully employed as acceptors in solar cells. Relationship between slip-angles and performance was established.

A novel fluorinated polymer was synthesized and was used to fabricate fullerene-free solar cells with high PCE. When blended with a twisted PDI dimer, photon absorption was enhanced and geminate recombination was suppressed, which led to devices with a high current. As compared to its under-fluorinated analogue, the fluorinated polymer displayed enhanced crystallinity and preferential packing. These factors contributed to significant enhancement in the OPV performance.
Synthesis and Surface-Specific Analyses of Constituents Relevant for Secondary Organic Aerosols

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Prediction of future changes in climate is challenging due to uncertainties associated with aerosol related processes in the atmosphere. Secondary organic aerosol (SOA) particles are of particular importance as they make up a substantial fraction of tropospheric aerosols and are known to lead to atmospheric cooling. However, SOA particle formation ranks among the least understood chemical processes in the atmosphere, due in part to a lack of information regarding chemical composition at the gas/aerosol interface. This work seeks to identify and characterize molecular species at the SOA particle surface through the synthesis of oxidation products and isotopologues of biogenic volatile organic compounds (BVOCs). BVOCs are released into the atmosphere by forest ecosystems and can react in the troposphere with ozone, hydroxyl radicals, and other oxidants to form lower volatility products with higher O/C ratios that may ultimately partition into the condensed phase and lead to the formation of SOA particles (Figure 1). The combination of surface-selective nonlinear vibrational spectroscopy with organic synthesis allows us to gain molecular-level insight into the structure and orientation of BVOCs and their oxidation products, enhancing our understanding of SOA formation and surface composition. More specifically, generation of SOA material derived from isotopologues of BVOCs has led to the identification of important surface-active groups present in oxidation products of SOA material. The observed surface activity of these products may have important implications for cloud condensation nuclei (CCN) activity and aerosol growth. Generation of deuterated SOA material from BVOC isotopologues also allows for the study of dynamic processes occurring between the gas and aerosol phases.

Figure 1. Products with increasing O/C ratios derived from the oxidation of BVOCs. Products with lower volatilities partition into the aerosol phase leading to the formation of SOA particles.
Lanthanide-catalyzed hydroboration of carbon-heteroatom double bonds

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Lanthanides, despite their nickname as the rare earths, are relatively cheap and abundant and can be utilized as catalysts in some reactions in place of rarer, platinum-group metals. The precedent of lanthanide-catalyzed olefin hydroelementation has been expanded to include carbon-heteroatom multiple bonds, specifically hydroboration of pyridines and carbonyls.

Pyridines were efficiently dearomatized/hydroborated with 1% \([\text{Cp}^*\text{LaH}]_2\) and pinacolborane at 35°C. The kinetics and mechanism were fully investigated and a broad scope of pyridines was tolerated.

\[
\begin{align*}
\text{N} & \quad \text{O} \\
\text{H} & \quad \text{B} \\
\text{O} & \quad \text{R} \\
\end{align*}
\text{R}
\]

\[
\begin{align*}
\text{C}_6\text{D}_{12}, 35 \text{ C} \\
\end{align*}
\]

A commercially available and more air-stable source of lanthanum was used as catalyst for the hydroboration of carbonyls. Ketones, aldehydes, and esters can be almost instantaneously reduced and hydroborated, and then converted to an alcohol. Lanthanum serves as the fastest catalyst, but other lanthanides (samarium, yttrium) can achieve these transformations. An investigation of kinetics and mechanism is ongoing.

\[
\begin{align*}
\text{R} & \quad \text{R'} \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{B} \\
\text{O} & \quad \text{O} \\
\end{align*}
\text{R}
\]

\[
\begin{align*}
\text{La}[\text{N(TMS)}_2]\text{LaH} & \quad \text{25}\text{C} \\
\end{align*}
\]
The heterogeneity of the nanoscale can significantly influence the path of a chemical reaction. The ensemble averaging of a large number of molecules, however, obscures the complexity of molecular interactions. Information on site-specific behavior is consequently lost, which is beneficial in catalysis, electrochemistry, photochemistry, and more. By combining the rich chemical information of vibrational spectroscopy with the single-molecule (SM) sensitivity of surface-enhanced Raman spectroscopy (SERS), we are striving to probe the influence of nanoscale heterogeneity on chemical reactions. To monitor SM chemistry, a strong fundamental understanding of SM-SERS and reliable detection of single molecules is crucial.

I have contributed to the growing understanding and reliability of SM-SERS through three separate research studies: first, I proved the SM capability of lithographically-prepared Ag nanoparticle arrays. These nanoparticle arrays are a reproducible alternative to the commonly used, chemically-synthesized nanoparticles which are inherently polydisperse in shape, size, and aggregation state. Second, I investigated the validity of the bianalyte approach, a common strategy used for proving SM detection. I demonstrated how this approach can provide misleading evidence for SM detection and proposed more rigorous standards for future SM proofs. Third, I explored the potential use of SM-SERS as a nanoscale temperature probe, where I demonstrated how heterogeneity in the nanoscale complicates SM temperature measurements. All of the aforementioned research studies contributed to the central goal of transitioning SERS into a robust technique for studying SM chemistry, allowing us to resolve the complexity of molecular interactions.