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Characterizing the protein corona on perfluorocarbon nanoemulsions stabilized by polymer surfactants

Carolyn Wu¹, Rachael A. Day¹, Ellen M. Sletten*¹

Nanoparticles have been extensively investigated as advanced methods of targeted drug delivery. Their limited success in clinical trials has been attributed to the rapid formation of a surface layer of proteins, called the protein corona, upon contact with biological fluids. This nanoparticle-protein interaction has been shown to control the biological responses of nanoparticles and the selectivity of targeted drug delivery. Nonspecific delivery can be reduced by adding poly(ethylene glycol) (PEG) or alternatives such as, poly(2-oxazoline) (POx). We study perfluorocarbon nanoemulsion-protein interactions by varying the surfactants that stabilize nanoemulsions. These surfactants consist of different hydrophilic blocks of either PEG or POx which can affect the binding affinities of protein. Through polyacrylamide gel electrophoresis, we are able to visualize the adsorbed proteins on nanoemulsions using human serum. We are also able to quantify the amount of protein adsorbed on the nanoemulsions using specific proteins, such as bovine serum albumin (BSA) and lysozyme. With these results, we hope to understand the protein adsorption properties of perfluorocarbon nanoemulsions such that we can predict their performance in vivo.

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Optimization of Peptide Inhibitors of Transthyretin Amyloid Aggregation

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Transthyretin (TTR) is a tetrameric protein that transports thyroxine and retinol in blood and cerebrospinal fluid. It is synthesized in liver, choroid plexus, and retina. Systemic Transthyretin Amyloidosis (ATTR) is caused by the aggregation of TTR, which results from the dissociation of TTR tetramer and monomer unfolding. Liver transplantation has been the traditional way of treating TTR amyloidosis. Other aggregation-preventing strategies use ligands like tafamidis and diflunisal to stabilize the tetramer conformation of TTR, reducing its dissociation rate. However, these treatments have been proven to be not as effective at late stages of ATTR. Our laboratory has made a discovery that explains these clinical observations. We found that preexisting fibril fragments can template amyloid aggregation, thereby accelerating fibril deposition (Saelices et al., 2018, PNAS). This process is kinetically favorable because of its irreversibility, regardless of the presence of stabilizing compounds (Saelices et al., 2019, JBC).

Our approach toward treating ATTR involves the attempts to prevent the fibril fragments from self-association and stop the amyloidogenic process. So far, we have successfully identified the amyloid-driving segments of TTR to be F and H strands using electron microscopy, cross-β x-ray diffraction, and proline substitutions to pinpoint the segments important for fibril formation (Saelices et al., 2015, JBC). Both F and H β-strands are more exposed in the TTR monomer than in the tetramer, which explains how the identical segments can bind and stack when tetramers dissociate, leading to protein aggregation. Then, we were able to determine the structures of segments in their amyloid form (Saelices et al., 2015, JBC; Saelices et al., 2018, Prot. Sci.). Through the identification of these amyloidogenic segments, we had a better understanding of the mechanism of TTR aggregation. Hence, through numerous aggregation assays and computational models, we designed two peptides that specifically target and interact with the F and H segments. These peptide inhibitors (Tab F2 and Tab H2, together called Tab FH2) can cap the tip of the amyloidogenic segments, and the methyl groups on the inhibitors stop other monomers from further aggregating onto the fibril fragments, which halts the process of amyloid fibrils formation. Tab FH2 was then tested in vitro through seeding assays with wild-type TTR and monomeric TTR seeded by ex vivo fibrils extracted from patients’ hearts. In vivo testing of Tab FH2 was performed in fruits flies and mice (Saelices et al., 2018, Neurobio. Dis.). The efficiency of peptide inhibitors in stopping the cascade of amyloidosis was repeatedly proven to be outstanding.

However, the challenge of pushing this peptide inhibitor Tab FH2 onto the next level of clinical trials is that it consists of two separate peptide strands, which means that the difficulty of making it into a potential drug to treat human ATTR is doubled. Thus, we are now optimizing our inhibitors by combining the two peptides while maintaining the properties from both Tab F2 and Tab H2. We have designed a variety of single-peptide inhibitors based on Tab FH2, and we have performed inhibition assays testing the efficiency of all the new peptide inhibitors. Thioflavin T is a fluorescent dye used to detect the fibrils because of its affinity to β sheets. Immuno dot blot and electron microscopy confirm the presence of TTR fibrils in the assays. Evaluation and optimization of these inhibitors as potential drugs could lead to clinical trials and even promising therapeutics for ATTR patients.
Exploiting structure and solvation to control supramolecular aggregation of amphiphilic cyanine dyes

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Realizing molecules with robust near/shortwave infrared (NIR/SWIR, 700-2000 nm) photophysics is a limiting step in the development of high-resolution in vivo fluorescence imaging as well as other advances in telecom technologies. As an alternative to toxic materials such as carbon nanotubes or quantum dots, we utilize the toolkit of self-assembly to build SWIR-active materials from aggregates of amphiphilic cyanine dyes. These molecular aggregates offer many advantages such as exceptional absorbance coefficients (10^5 M^{-1}cm^{-1}), narrow linewidths, as well as tunable absorption based on aggregation.

Our efforts are centered around synthesizing new tetrachlorobenzimidazole dyes, particularly those derived from the scaffold of a well-known tubular J-aggregate from the literature. By extending the polymethine chains in these compounds, we are able to access new colors, stabilities, and morphologies of aggregates active in the NIR/SWIR. By multiplexing the photophysics of this family of aggregates with a FRET pair such as PbS quantum dots, we hope to demonstrate a proof of principle for a LiFi technology—the transmission of information over infrared light.
Fast charging lithium-ion batteries are needed for personal electronics such as cell phones or larger electronics such as electric cars, to allow for charging on the order of minutes instead of hours. Intercalation pseudocapacitance is a key solution to this issue because it allows for intrinsically fast charging/discharging. Some materials can transition from battery-like to pseudocapacitive upon nanostructuring, which decreases the particle size, therefore decreasing the lithium-ion diffusion length and increasing the rate of diffusion. Here we are studying NCA (LiNi$_{0.80}$Co$_{0.15}$Al$_{0.05}$O$_2$), a layered transition metal oxide cathode material, that already shows promising fast cycling in the bulk due to suppression of intercalation induced phase transitions. By nanostructuring NCA, we can shorten the lithium-ion diffusion length for faster charging/discharging. Nanostructured NCA was synthesized using a colloidal polymer templating technique followed by either a traditional heating ramp or a rapid thermal annealing type method, which resulted in either medium particle sizes (~300 nm) or small particle sizes (~150 nm), respectively, both of which are smaller than commercial bulk NCA. The sample with medium sized particles has six times higher specific capacity than the bulk material at a C-rate of 64 C (charge/discharge in ~1 min). While we would expect the smallest sized particles to have even faster cycling, they are instead intermediate between the medium sized sample and the bulk. We found that the short heating times required to obtain the small particle size material resulted in a less perfect crystal structure, which was more detrimental to the rate capabilities than larger sized particles. These results help illustrate how to find the optimal balance between lithium-ion diffusion rate and total diffusion distance for fast charging lithium-ion pseudocapacitors.
Abstract Title:
Targeted Nanoparticles for Boron Neutron Capture Therapy (BNCT)

Abstract:
Boron neutron capture therapy (BNCT) is a treatment primarily applied to cancer therapy that involves the delivery of boron-10-containing molecules in close proximity to cancer cells. After successful delivery of boron to target cells, patients can be exposed to neutron radiation. Low energy (thermal) neutrons are harmless to healthy tissue, however, when boron-10 comes into contact with a thermal neutron, it undergoes nuclear fission to produce a lithium-7 nucleus and one α-particle. The α-particles generated from BNCT cause enough cellular damage to kill cells and are high linear energy transfer particles with a path length of approximately 1-2 cells. Attempts to make BNCT successful in the 1970’s and 1980’s predated neutron sources capable
of producing neutron radiation at the proper flux and energy which led to many research groups abandoning the task. However, advancements in particle physics and technology have made available more practical neutron sources for BNCT and generated a renewed interest in BNCT as an additional treatment for cancer and other diseases. We have been developing two chemical systems for our effort on BNCT. The first system employs ferumoxytol, an FDA approved drug to treat anemia made up of an iron oxide core with a dextran polymer coating. Ferumoxytol has been shown to encapsulate various drugs and can be surface modified to incorporate targeting groups. The second system we have developed is based on a boron oxide nanoparticle where the nanoparticle core will supply all of the necessary boron content for BNCT. Ligands on the boron oxide core can be exchanged to change the size and targeting of these nanoparticles. We have carefully chosen both a more flexible, non-covalent system to incorporate various boron-rich molecules as well as a boron-based nanoparticle system with easily exchanged capping groups. We present the development of these systems including toxicity studies, kinetic experiments, and preliminary biodistribution results.
Poster Title: An Aryne Annulation Strategy for the Synthesis of Conjugated Heterocycles and $\pi$-Expanded Metal–Ligand Complexes

Authors: Jason V. Chari, Katie A. Spence, Robert B. Susick, and Neil K. Garg*

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Abstract: The discovery of new methodologies to synthesize conjugated small molecules is crucial in the development of organic electronics such as organic light-emitting diodes (OLEDs), field-effect transistors (OFETs), and photovoltaic devices (OPVs). In particular, synthetic strategies that incorporate heterocycles into these materials offer the potential for modulation of their electronic properties and potential applications. This presentation will focus on a strategy to access conjugated heterocycles by harnessing a Pd-catalyzed annulation of in-situ generated, strained heterocyclic arynes. In addition, an extension of this strategy for the direct annulation of Ru- and Ir-complexes will be described. The latter methodology demonstrates the capacity for arynes to engage with multiple metal complexes in the same reaction vessel in order to forge new carbon–carbon bonds. These studies seek to demonstrate that strained intermediates can be strategically employed in catalytic reactions to access valuable organic and inorganic materials.

Funding: These studies were supported by the National Institutes of Health, the Christopher S. Foote Graduate Fellowship and the Saul Winstein Fellowship.
Chemical lift-off lithography (CLL) is a subtractive soft-lithographic technique used to pattern self-assembled monolayers (SAMs) containing functional alkanethiolates on Au surfaces. Alkanethiolate molecules, along with a single monolayer of Au, are removed in this process by oxygen-plasma activated polydimethylsiloxane (PDMS) stamps. Monolayers patterned via CLL are robust, in contrast to conventional soft-lithography, enabling high-fidelity patterning over a dynamic range of feature sizes (millimeter to nanometer). This process has a wide range of applications, including patterning of supported Au monolayers, as well as the simple, convenient fabrication of field-effect transistors. Recently, we have advanced CLL to pattern additional surfaces, including other coinage metals (e.g., Pt, Pd, Ag, Cu), reactive transition metals (e.g., Ni, Ti, Al), and semiconductors (e.g., Ge). In all cases, high-fidelity patterns were achieved. X-ray photoelectron spectroscopy analysis of PDMS stamps post-CLL revealed lift-off of corresponding metals or semiconductors, demonstrating that (mono)layers of substrate atoms, along with alkanethiolates, were removed in the process. Additionally, by using bifunctional cage molecules (i.e., isomers of carboxylic-acid-functionalized carboranethiolates), which form more pristine and defect-free monolayers, in comparison to conventional alkanethiolates, we hypothesize the yield of molecules removed by CLL can be increased. Patterning of different carboranethiolate isomers that are functionally identical, but with dipole moments of different magnitude and direction, will enable tuning of the local substrate work function in patterned regions. These advances in metal and semiconductor patterning using CLL demonstrate the versatility of CLL in high-resolution, high-throughput, low-cost fabrication, and for tailoring interfacial surface interactions towards creating precise chemical, physical, and electronic nanoscale contacts.
Multiplexed *in vivo* optical imaging with shortwave infrared polymethine dyes

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Organic fluorophores developed for the visible (400-700 nm) and NIR (700-1000 nm) regions of the electromagnetic spectrum have enabled multiplexed experiments to study live cells and simple organisms with high resolution. In more complex systems such as mammals, limitations in contrast and resolution result from diffuse light originating from background and scattering at visible and near-infrared (NIR) wavelengths. By moving to detection in the shortwave infrared region (1000-2000 nm), high resolution images can be obtained non-invasively at video-rate speeds. While the optical properties of tissue are ideal for SWIR imaging, non-toxic organic small molecules with bright emission > 1000 nm are necessary to obtain high signal with minimal biological perturbation. Polymethine dyes are a prime scaffold for creating SWIR probes, as they can be red-shifted with predictable structural changes. We hypothesized that a flavylum heterocycle, containing no heavy atoms and with an electron donating group, would impart red-shifted photophysical properties without diminished ΦF. With absorbance and emission in the SWIR, the 7-dimethylamino flavylum heptamethine dye is approximately 200 nm red-shifted from heptamethine cyanine dyes traditionally employed for optical imaging at NIR wavelengths. Building on this scaffold, we investigated systematic changes to the flavylum heterocycle to reveal insight into relationships between structure and photophysical properties. By accessing a library of SWIR dyes with consistent brightness, we demonstrated a method which improves the spatial and temporal resolution attainable for non-invasive multicolor imaging in mice.

**Acknowledgments:** This work was supported by grants to E.D.C (NSF GRFP DGE-1144087, Foote Fellowship), O.T.B. (Emmy-Noether-Programme of DRG BR 5355/2-1, Helmholtz Pioneer Campus Institute for Biomedical Engineering), E.M.S. (UCLA, NIH 1R01EB027172-01, Sloan Research Award FG-2018-10855), and by shared instrumentation grants from the NSF (CHE-1048804) and NIH (1S10OD016387-01).

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Evidence for a Critical Electronic Effect in the Second Coordination Sphere of an Artificial Metalloenzyme

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Artificial metalloenzyme design has the potential to improve catalysis. This has been accomplished primarily through steric interactions or electronic interactions in the first coordination sphere. Rovis and co-workers recently used biotin to tether a rhodium(III) catalyst to monomeric streptavidin, improving the reactivity in piperidine synthesis. We computationally examined this system, including several mutants, using the hybrid QM/DMD method to identify factors influencing reactivity. We found the π-stacking interaction between the Cp* ligand and the phenol ring of Y112 in the second coordination sphere to be critical. Our calculations evidence a strong electronic effect from this interaction and show that the distribution of the metal-phenol distance in each mutant correlates with reactivity.
Mechanistic Studies of Adamantylacetophenones with Competing Reaction Pathways in Solution and in the Crystalline Solid State

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Photochemical reactions in crystals occur under conditions of highly restricted molecular mobility such that only one product is generally obtained, even when there are many others that can be observed in the gas phase or in solution. A series of 2-(1-adamantyl)-o-alkyl-acetophenones with γ-hydrogen atoms on both the adamantyl and ortho aromatic groups was selected to determine whether one can engineer and observe competing Norrish type II reaction pathways in the crystalline state. It was shown that excited state competition for hydrogen abstraction between secondary adamantyl and benzylic hydrogens is affected not only by the relative bond dissociation energies but also by the molecular conformation in the crystal. The subsequent fate of the resulting biradical species is determined by competition between radical recombination to form the photoproduct and reverse hydrogen atom transfer to regenerate the starting ketone. Crystallographic information, photoproduct distributions in solution and in the solid state, and the results of multiple mechanistic experiments, including transient absorption spectroscopy in acetonitrile and with nanocrystals suspended in water, are reported. The results demonstrate that it is possible to engineer competing reactions in crystals and that consideration of all of the aforementioned factors is necessary to account for the observed photoproduct selectivity.

This work was supported by National Science Foundation Grants CHE-1855342, MRI-1532232 (solid state NMR), and CHE-1048804 (solution NMR).
**Poster Title:** Progress toward the Total Synthesis of Lissodendoric Acid A

**Authors:** Francesca M. Ippoliti, Evan R. Darzi, Joyann S. Barber, Laura G. Wonilowicz, and Neil K. Garg

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**Abstract:** Members of the manzamine alkaloid family of natural products display a variety of biological activities and contain a distinguishing azadecalin core. Lissodendoric acid A is a manzamine alkaloid that has promising bioactivity against Parkinson’s disease, making it a compelling synthetic target. This presentation will describe our ongoing efforts toward the synthesis of lissodendoric acid A. The development of a key inverse electron-demand Diels–Alder cycloaddition using a strained azacyclic allene, as well as a late-stage reduction and Negishi cross-coupling, will be described.

**Funding:** These studies were supported by the National Science Foundation, the National Institutes of Health, and the Christopher S. Foote Graduate Fellowship.
Examining the effect of nanoscale architecture on the thermal conductivity of mesoporous SiO$_2$ thin films

Sophia C. King, Vivian Wall, Yan Yan, Man Li, Tiphaine Galy, Joon Sang Kang, Michal Marszewski, Yolanda Li, Laurent Pilon, Yongie Hu, Sarah H. Tolbert

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Transparent, thermally insulating coatings can be used for energy saving architectural glass or in solar thermal applications. By increasing phonon scattering in a material, its thermal conductivity can be lowered. The most common way that this is done is by adding porosity to a material which increases interfacial scattering and reduces the total material density. These ideas are used in highly porous silica aerogels with ultra-low thermal conductivities. Unfortunately, these materials significantly scatter light making them unsuitable for applications that require high optical transparency. In this work we will build on these ideas in silica based films by using porosity to reduce thermal conductivity. Importantly, we keep all structural features less than 20 nm to maintain high optical transparency. Using a polymer templating and removal process, highly transparent, mesoporous thin films of SiO$_2$ or SiO$_2$:TiO$_2$ with porosities up to 70% were studied to identify structural parameters that minimize thermal conductivity. Overall, porosity was the dominant parameter affecting the thermal conductivity, but the type of framework precursor, wall thickness between pores and heteroatom incorporation in the mesoporous films also significantly affected the thermal conductivity. Films made from sol-gel or nanoparticle-based SiO$_2$ precursors had similar thermal conductivities when the wall thicknesses were comparable, as well as similar mechanical properties. For films made of sol-gel precursors, there was a strong dependence of the thermal conductivity on the overall wall thickness, while for the nanoparticle-based system, nanoparticle size dominated the thermal conductivity. The addition of TiO$_2$ to the mesoporous SiO$_2$ system decreased the thermal conductivity. Overall we now have a general understanding of how tune the thermal conductivity of mesoporous SiO$_2$ films while retaining the high transparency of the system.
Authors: Rachel R. Knapp, Michael M. Yamano, Aurapat Ngamnithiporn, Melissa Ramirez, K. N. Houk, Brian M. Stoltz, and Neil K. Garg*

Title: Harnessing the reactivity of strained oxacyclic allenes for heterocycle synthesis.

Abstract: Strained organic compounds have captivated the scientific community for over a century. Whereas strained cyclic alkynes have seen a renaissance in the synthetic community over the past few decades, a related intermediate, the cyclic allene has still remained underdeveloped. This presentation will describe the synthesis of precursors for the mild generation of the strained oxacyclic allene and the trapping of the reactive intermediate in (4+2), (3+2), and (2+2) cycloadditions. In addition, the asymmetric synthesis of a silyl triflate allene precursor and its ability to transfer stereochemical information in a Diels–Alder cycloaddition will be described. These studies demonstrate the ability of strained cyclic allenes, despite being highly reactive intermediates, to be utilized in the synthesis of densely functionalized heterocycles.

Funding: These studies were supported by the National Institutes of Health, the National Science Foundation, and the Christopher S. Foote Graduate Fellowship.
Non-covalent interactions involving aromatic rings are responsible for a wide array of phenomena in chemistry and biology. An interesting, yet underexplored non-covalent interaction is the arene-perfluoroarene interaction. Aromatic and perfluoroaromatic compounds have opposite quadrupoles and this electrostatic complementarity results in their stacking interaction.

Theoretical studies of arene-perfluoroarene interactions in the gas phase indicate high binding energies. Furthermore, these interactions have been utilized in solid-state chemistry, supramolecular chemistry, and bioengineering. Despite their ubiquitous applications and growing interests, the strengths of arene-perfluoroarene interactions in aqueous solution have not been studied theoretically or experimentally.

Here, we designed a systematic and quantitative study of these interactions with both experimental data and computational modeling. Prior to the experimental work, we computationally studied the nature of arene-perfluoroarene interactions and built initial theoretical models. Then by synthesizing a small library of model compounds, we quantified these interactions in various media and further validated the trends in several physical organic phenomena such as the effects of fluorination, solvent, and ring size. Lastly, using this large set of experimentally determined data, we performed a thorough computational benchmark study to determine the most accurate and efficient DFT method for modeling arene-perfluoroarene interactions.

From this comprehensive experimental and computational study, it was observed that fluorination, extension of the π systems, and enhancement of solvent polarity greatly stabilizes the stacking energy up to 16-fold and the highest $K_a$ is achieve in H$_2$O. By interplaying computation and experiment synergistically, we promote the fundamental understanding and reliable modeling, and thus, rational design of arene-perfluoroarene interactions in various biological applications.
Probing the Local Nanoscale Heating Mechanism of a Magnetic Core in Mesoporous Silica Drug-delivery Nanoparticles Using Fluorescence Depolarization

Fang-Chu Lin$^{1,2}$ and Jeffrey I. Zink$^{1,2}$

ABSTRACT

In the presence of an alternating magnetic field (AMF), a superparamagnetic iron oxide nanoparticle (SPION) generates heat. Understanding the local heating mechanism of a SPION in a mesoporous silica nanoparticle (MSN) will advance the design of hyperthermia-based nanotheranostics and AMF-stimulated drug delivery in biomedical applications. The AMF-induced heating of single-domain SPION can be explained by the Néel relaxation (reorientation of the magnetization) or the Brownian relaxation (motion of the particle). The latter is investigated using fluorescence depolarization based on detecting the mobility-dependent polarization anisotropy ($r$) of two luminescence emission bands at different wavelengths corresponded to the europium-doped luminescent SPION (FSPION) core and the silica-based intrinsically emitting shell of the novel synthesized core-shell MSN. The fluorescence depolarization experiments are carried out with the free and the silica-encapsulated with and without application of the AMF. The $r$ value of a FSPION core-mesoporous silica shell in the presence of AMF does not change, indicating no additional rotational motion of the core-shell nanoparticles is induced by the AMF, disproving contribution of Brownian heating and thus supporting Néel relaxation as the dominant heating mechanism.

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Functionalization of Boron Clusters Using Two and One Electron Chemistry

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Our laboratory has been interested in developing routes for versatile functionalization of three-dimensional boron clusters. This presentation will highlight our recent work on icosahedral carboranes, and specifically, the chemistry pertaining to boron vertex functionalization of these clusters.

Similar to benzene, and other aromatic carbon-rich molecules, carboranes can be derivatized via electrophilic halogenation at the electron-rich boron-based vertices. These halogenated carboranes can subsequently undergo well-defined two electron chemistry in the presence of catalytic amounts of palladium. We have discovered several unique transformations where these halocarboranes can be efficiently cross-coupled with a wide range of nucleophiles to generate exopolyhedral B−O, B−N, B−C, and B−B bonds.

Unexpectedly, the cross-coupling of sterically hindered O- and N-based nucleophiles has been observed to undergo an off-cycle isomerization pathway, herein referred to as “cage-walking”, that can promote substitution at B(2), B(4), B(5), and B(9) vertices. Importantly, cage-walking can be rationally controlled through solvent choice and additives that permit cage-walking with sterically unhindered nucleophiles, such as CN−.

To further understand the reactivity scope of carboranes, we recently hypothesized that one should be able to oxidatively generate boron vertex-centered carboranyl radicals, thereby providing a platform to conduct one electron transformations. To address this hypothesis, we treated functionalized carboranes containing exopolyhedral B−[B] bonds ([B]: B(OH)2, BF3K) to oxidizing conditions in the presence of various substrates. Conveniently, the in situ formed carboranyl radical intermediates undergo the expected radical coupling with radical traps, yielding exopolyhedral B−O, B−S, B−Se, B−Te, or B−C bonds.

In summary, our work has demonstrated the diverse array of chemistry accessible with carboranes that continues to advance novel carborane substitutions.
Finding harmony among incompatibility in the selective oxidation of CH₄ to CH₃OH with atmospheric O₂

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The conversion of light hydrocarbons, such as methane, to commodity chemicals under ambient conditions with atmospheric O₂ is attractive yet challenging. Homogeneous, low-valent organometallic complexes can activate methane, but their electron-rich nature is incompatible with O₂. Thus, an ambient oxidation process with O₂ as the oxidant poses a clear challenge. Here, we report the use of an O₂-sensitive metalloradical catalyst for the selective oxidation of CH₄ to CH₃OH at room temperature and ambient pressure with air as the terminal oxidant. The inherent incompatibility between the subsequent steps of C‒H activation and O₂ oxidation is resolved through the marriage of electrochemistry and nanomaterials. Within the nanowire array, an O₂ concentration gradient is established such that the incompatible reaction steps of CH₄ activation and ambient air oxidation are spatially segregated. Serendipitously, the observed reaction rate within the wire array electrode increased by a factor of 220,000 which leads to a turnover number up to 52,000 in 24 h. These results promote future work on the synergistic effects between nanomaterials and organometallic catalysts that results in new or enhanced reactivity.
Abstract: A facile method of nanostructuring MoO₃ to study its pseudocapacitive properties

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Nanoarchitectured metal transition oxides have been studied as pseudocapacitors to optimize both energy density and power density in a single material. Pseudocapacitive redox reactions occur when cations reduce a metal through an electrochemical charge-transfer reaction that occurs within tens of nanometers from the surface. This short-range process is kinetically more facile than other processes such as intercalation redox processes. Pseudocapacitive reactions can be induced by nanosizing, increasing surface area and improving the electrical conductivity of the material.

In this study, a mesoporous alloy with a surface MoO₃ was made from partially and fully selectively etching Al from Mo-Al alloys. Furthermore, different annealing methods were performed to crystallize the MoO₃. The crystallization of MoO₃ on the surface along with the mesoporous alloy at the core enhance improves the pseudocapacitive properties of MoO₃. The redox reactions and the capacities of these materials were compared. This one-pot method of selective etching along with annealing is a simple and inexpensive method to make mesoporous with tunable properties which can be used to study pseudocapacitive properties of materials.
Cell processes like growth and division are tightly regulated. One such mechanism of regulation is ubiquitination. Ubiquitination can change a protein’s localization or activity, or it can mark the protein for degradation by the ubiquitin proteasome system. The final step of ubiquitination, transferring ubiquitin to the target protein, is mediated by E3 ligases and their substrate adaptors, proteins that allow E3 ligases to be selective in choosing their targets. Understanding the targets of E3 ligases and substrate adaptors, then, is crucial to understanding cell regulation and disease mechanisms linked to misregulation of protein levels and activity. SPOP is a Cul3 E3 ligase substrate adaptor whose targets, such as c-Myc, PD-L1, and ERG, are crucial for cell cycle progression and cancer proliferation. Through a mass spectrometry screen, we identified SPOP as a potential regulator of NupJ, a nuclear pore protein. Knockdown of SPOP via siRNA in HeLa cells leads to increased protein levels of NupJ via immunoblotting, and SPOP and NupJ both co-localize at the nuclear envelope via immunofluorescence microscopy. Moreover, co-immunoprecipitation assays demonstrate that SPOP and NupJ bind to each other in vitro. Similar to overexpression of NupJ, siRNA against SPOP leads to an increase in the number of nuclear envelope defects. Overexpressed NupJ leads to defects in cell division. Our results suggest that SPOP targets NupJ for ubiquitin-mediated proteasomal degradation.
A quantum computer uses quantum states to store and process information, able to tackle questions that are intractable in classical computers. As modern day computers use bits to represent information, quantum computers use qubits (quantum bits) that can achieve a “mixed state” and become entangled with one another. Trapped ions (gas phase atoms trapped in an external magnetic field) make an effective qubit because they can optically cycle (i.e. be excited by laser radiation and de-excited back to the ground state multiple times). However, the stability of the gas phase atoms relies on cryogenic cooling, electric field traps, and complex interfaces, rendering ionic qubits unscalable in their current paradigm. While cycling transitions in trapped atoms have been crucial for early works in quantum information, the extension of this idea to molecular substrates has been hindered by the lack of systems that have cycling transitions. Alkaline earth (AE) metal atoms are known to optically cycle in gas phase and to bond with fluorine, hydroxyl, and even alkoxyl groups while retaining their cycling properties. This project aims to tether the AE atoms to molecular substrates as OCCs. The OCC will then be activated by resonant, narrow-band light, and the presence or absence of laser induced fluorescence will enable projective measurements of the system’s quantum state. This design combines the efficiency of trapped ions and the stability of room-temperature surface chemistry, essentially creating a network of molecular qubits on a surface.

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We describe and implement an interferometric approach to decay-associated photoluminescence spectroscopy, which we term decay-associated Fourier spectroscopy (DAFS). Using DAFS a stream of emitted photons from the substrate passes through a variable path length Mach–Zehnder interferometer prior to detection and timing. The interferometer encodes spectral information in the intensity measured at each detector enabling simultaneous spectral and temporal resolution. DAFS provides several advantages including wavelength-range insensitivity, drift-noise cancellation, and optical mode retention. DAFS allows us to direct the photon stream into an optical fiber, enabling the implementation of superconducting nanowire single photon detectors for energy-resolved spectroscopy in the shortwave infrared spectral window (λ = 1–2 μm). The broad applicability of DAFS is demonstrated in both the visible and shortwave infrared, using two Förster resonance energy transfer (FRET) pairs: a pair operating with conventional visible wavelengths and a pair showing concurrent acquisition in the visible and the shortwave infrared regime. Balance detection in DAFS is then demonstrated through the use of a third FRET pair.
Synthesis of shortwave infrared flavylium polymethine dyes with improved photophysics

The shortwave infrared region (SWIR; 1000 – 2000 nm) has been of interest for biomedical imaging due to advantageous properties such as reduced light scattering and decrease in autofluorescence of endogenous chromophores. The challenge of the SWIR region is that contrast agents are weakly emissive. Our lab has discovered the brightest small molecule fluorophore that absorbs and emits SWIR light. This molecule is a flavylium-based polymethine fluorophore, deemed Flav7. Here we look to further enhance the photophysical properties of Flav7 through the synthesis of a panel of derivatives functionalizing the 2 position of the flavylium heterocycle. We have found that aryl groups with electron donating substituents (MeO, NMe2) redshift up to 25 nm. Surprisingly, we found that aryl groups with electron withdrawing substituents (NO2, CF3, X = F, Cl, Br) also redshift to a similar degree. Preliminary results suggest that this may be due to a change in electronic delocalization within the fluorophore. Additionally, we have shown that placing more rigid substituents such as a tBu or an adamantyl group can boost fluorescent quantum yield up to 3 fold. Thus far, we have shown that the 2 position plays an important role in the electronics of the scaffold and could be further explored as an avenue towards brighter and more red-shifted flavylium polymethine dyes by adding bulky or electron donating/withdrawing groups respectively.
Mercury Chalcogenide Mid-Gap States as a New Class of Continuously Tunable Bright Shortwave Infrared Emitter.

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The short-wave infrared (SWIR, 1000-2000 nm or 1.24-0.62 eV) is the spectral region that is utilized for imaging, energy conversion, and telecommunications. Semiconductor nanoplatelets (NPLs) have emerged as a recent class of two-dimensional quantum confined nanocrystals with applications in infrared detection. Their thickness defines the charge carrier confinement and a high degree of monodispersity in this dimension results in narrow absorption and emission from the visible to near-IR with high quantum yields. We show that HgX NPLs with narrow bandgaps (700-900 nm) can exhibit tuneable emission beyond the NIR and across the SWIR (from 1000-1500+ nm) by synthetic control of mid-gap states. Furthermore, the quantum yield of these states are high (>30%) making them competitive with other SWIR emitting nanocrystals. Spectroscopic characterization suggests that the mid-gap state is related to a change in stoichiometry on the surface of the NPLs. Their tuneable optical properties and large surface areas make HgX NPLs promising materials for infrared optoelectronics.
Ultrafast photophysics of polarons and bipolarons in doped semiconducting polymers

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Doping semiconducting polymers with the introduction of small molecules can create steady-state free-carriers enhancing the polymers’ otherwise low carrier mobilities. Understanding the nature of the steady-state carriers is essential to maximizing the conductivity and exploiting these materials for electronic device applications. We probe chemically-doped polymer films with ultrafast transient absorption spectroscopy, exciting low energy polaron and bipolaron transitions. Because the dynamics and optical transitions differ between 2D-delocalized polarons, localized polarons, and bipolarons, we can use the corresponding bleaches and transient absorption peaks to assign the doped species to free and trapped polarons and bipolarons. We assign the electronic transitions of the inter-bandgap states to determine the type of quasiparticle species arising from doping the polymers and show that some polymers form principally polarons while other form bipolarons primarily. By understanding the roles polarons and bipolarons play in conducting polymer films, one can better tailor doping of polymers for specific applications.

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Surface-supported cluster catalysis: 
Breaking the rules of conventional models in catalysis

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It has recently been shown that supported nanocluster catalysts in realistic reaction conditions do not follow the conventional models used in catalysis due to their dynamic nature. This opens new doors in catalysis by giving more leverage in catalyst design, but also requires a major revision of the understanding of how dynamic heterogeneous catalytic interfaces operate. We use Pt supported on alumina catalyzing the reaction of dehydrogenation, characterized jointly by theory and experiment. We demonstrate that the statistical ensemble of many thermally-accessible cluster geometries in reaction conditions rather than the single global minimum structure gives a more accurate and comprehensive picture of the catalytic system. Once the description is expanded toward the ensemble, size-dependent catalytic activity is easily explained. We then propose and confirm several doping strategies to control the selectivity of dehydrogenation, yet again, the agreement with experiment is only possible when multiple catalyst states are included in the description. The catalytic activity and selectivity of such dynamic catalysts are driven by rare and metastable catalyst states, and thus, reaction thermodynamics and kinetics are controlled by different states of the catalyst. Therefore, the catalyst state(s) that might not be present in the as-prepared catalyst, and rather would develop in the reaction conditions and would have the desired activity should be considered in the calculations. For instance, while Pt7 and Pt8 on alumina have very similar prismatic global minimum geometries, Pt7 at higher temperatures also has access to more active single-layer isomers, which makes Pt7 much more active than Pt8 toward ethylene dehydrogenation reaction. This highly fluxional behavior, ensemble nature, and rule-breaking is commonplace for clusters and contrasts them to extended surfaces.

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Implantable Metal Oxide Transistor Nanobiosensors: Towards *in Vivo* Neurotransmitter Monitoring

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Monitoring neurotransmitters in vivo necessitates sensors that approach the spatiotemporal resolution of neuronal communication, while differentiating similarly structured neurochemicals with high selectivity. We have developed biosensors based on aptamers, coupled to ultra-thin In₂O₃ (~3-nm thick) field-effect transistors (FETs). These biosensors show high sensitivity and selectivity for serotonin and dopamine with femtomolar detection limits *in vitro*. To enable *in vivo* measurements, we miniaturized our sensor architecture to fabricate neuroprobes with arrays of aptamer-field-effect transistors. The initial prototype for an implantable microprobe is fabricated using micro-electro-mechanical systems (MEMS) technologies on silicon (150-μm thick). Each neuroprobe has lithographically patterned interdigitated gold electrodes deposited atop ultrathin, semiconducting indium oxide channels, where the shank is of 150-μm wide and 150-μm thick. Functionalization of the exposed semiconducting surfaces with neurotransmitter-specific aptamers facilitated electronic neurotransmitter sensing. Reducing individual FET footprints leads to an increase in the numbers independent transistors on a single neuroprobe for multi-site/multi-target detection capabilities. We characterized target sensitivity ranges, detection limits, and sensor stabilities *in vitro* prior to conducting *in vivo* measurements. We assessed biofouling of neuroprobes using *ex vivo* measurements in brain tissue homogenates. We also fabricated flexible neuroprobes using polyimide as substrates instead of rigid Si to reduce immunological responses. Implantable aptamer-field-effect transistor-neuroprobes, including additional designs on flexible substrates, will enable *in vivo* detection of neurotransmitters in the brain with high spatial resolution and selectivity.

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The ability of molecules to form ordered assemblies is a crucial first step in interrogating their structures with atomic-level detail. For many molecules, the length scales to which this order extends can be limited, thus hampering efforts to solve their structures. Nanocrystallography has opened the door to many new molecular structures by reducing the sizes of crystals being interrogated to 10s to 100s of nm. Here we demonstrate that using electron nanobeams, we can extract atomic-level information from ordered regions of crystals 10s of nm in size. By scanning the beam, we can collect diffraction from a wide field-of-view and digitally recombine the diffraction for later analysis. This method obviates the need for capturing diffraction from large portions of one or more crystals with a selected area aperture. Using a direct electron detector, we capture 1000s of sparse diffractions over multiple crystal orientations mapped to specific locations within a single crystal: a scanning nanobeam diffraction tomogram. We then extract this intensity data, representing an angular wedge of reciprocal space, and use it to compute the structure of a segment from the OsPYL/RCAR5 protein at atomic resolution using fragment-based phasing methods. In allowing atomic structures to now be determined from digitally outlined regions of a nanocrystal, scanning nanobeam diffraction tomography breaks new ground in nanocrystallography.
Semiconductor nanorods for membrane potential imaging
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In order to make headways in quantitatively understanding how cells communicate within communities, improved tools are needed that are able to map bioelectrical circuits in real-time, out in the field, and with high spatial and temporal resolutions. This will require developing optical probes that are specific, bright, ratiometric (noise immune) and that specifically localize to the desired subcellular location. Existing tools for reading membrane potential (Δψ) in cells are limited. Some established tools for Δψ measurements of mammalian (mostly excitable) cells are very invasive, such as electrophysiological recordings by patch-clamp electrodes, extracellular recording by ion-selective extracellular probes, and microelectrode arrays. The less invasive fluorescent probes, such as reporters of individual ions, voltage sensing dyes (VSDs), and genetically encoded voltage indicators (GEVI s), however suffer from problems such as photobleaching, toxicity, alteration of membrane capacitance, and/or slow kinetics. Moreover, these existing tools are often only partly applicable to bacteria and archaea, not always compatible with imaging or cumbersome to use and therefore of limited value for practical and applied studies.

We have recently demonstrated theoretically and experimentally that carefully engineered quantum dots (QDs) and nanorods (NRs) display large quantum confined Stark effect (QCSE). The QCSE is observable through the change in fluorescence emission, even at room temperature and at single-particle level. These nanoparticles could be used as efficient nanoscale membrane potential nanosensors by monitoring changes in fluorescence quantum yield, fluorescence lifetime and/or emission spectrum in response to local electric field perturbation.

In this work, we synthesized, characterized, and optimized QDs and NRs to exhibit enhanced QCSE using a dedicated high-throughput single-particle screening approach. Type-II ZnSe-seeded CdS NRs were found to have the best performance among the different nanosensors evaluated in this work. An upper limit for the temporal response of individual ZnSe/CdS NRs to voltage modulation was characterized by high-throughput, high temporal resolution intensity measurements using a novel photoncounting camera. The measured 3.5 µs response time is limited by the voltage modulation electronics and represents ~30 times higher bandwidth than needed for recording an action potential in a neuron. Using a single NR to record electric field modulation at 1 kHz frame rate was also demonstrated. For membrane insertion, the NRs were functionalized with α-helical peptides and zwitterionic-decorated lipoic acids. Specific membrane targeting with high loading efficiency and minimal nonspecific binding was achieved. These NRs display large fluorescence changes in correlation with Δψ in both lipid vesicles and wild-type human embryonic kidney cells.
Solution-Processable Van der Waals Thin Films for Large-Area Electronics

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With emerging flexible and wearable electronics for next-generation display, electronic paper, and health monitoring, high-performance large-area electronics are required to be integrated on flexible plastic substrates with sufficient performance for necessary computation, storage and communication functions. Solution-dispersible inorganic nanostructures (e.g., 0D quantum dots or 1D nanowires/nanotubes) have emerged as a unique class of materials that may be solution processed like organic materials while simultaneously retaining the excellent electronic performance and structural stability of crystalline inorganic materials for high-performance electronics. However, conventional 0D and 1D nanostructures are typically plagued by surface dangling bonds, local chemical disorders, and associated trapping states at the interface, which remain severe challenges to high-performance thin-film electronics.

Here we discuss a new concept of van der Waals (vdW) thin film assembled from solution-processable 2D nanosheets for constructing high-performance large-area electronics. The clean vdW interfaces are free of unsaturated dangling bonds and associated trapping states at grain boundaries that seriously plague the 0D quantum dot or 1D nanowire thin films, and thus promise excellent charge transport for thin-film electronics. In specific, we have successfully assembled vdW thin films with superior electronic performance from 2D Bi2Se3, MoS2, and others. For example, the solution-processable Bi2Se3 thin film exhibits an electrical conductivity approaching that in the high-temperature CVD grown sample. Besides, high-quality 2D MoS2 nanosheets based vdW thin films were readily processed into large-area TFT arrays with high carrier mobility (~ 10 cm²·V⁻¹·s⁻¹) and on/off ratio (~ 10⁶), which, for the first time, enable integrated computational circuits (a series of logic gates and half adder).
A Chemical Bonding Model for Understanding Lanthanide Hexaborides

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Quantum Materials, which feature strong electron-phonon coupling, are an active topic in chemical research due to their exotic properties that derive from them having d- and/or f-active orbitals. Among them, the lanthanide hexaborides family (LnB$_6$) has attached special attention, as a consequence of the number of anomalous and seemingly contradictory properties they bear. For example, SmB$_6$ is mixed-valent and has a Fermi surface despite being an insulator, both EuB$_6$ and SmB$_6$ have an anomalous peak in the specific heat as a function of the temperature, but they take place at different temperatures. Moreover, EuB$_6$ is ferromagnetic, while GdB$_6$ is antiferromagnetic and SmB$_6$ is not magnetic.$^1$

The main obstacle in the study of these systems is that their electronic structure is a formidable challenge for modern computational methods. They exhibit an enormously complex electronic structure as a consequence of the wave-function multi-reference and relativistic character.$^2$ This behavior is beyond current DFT-based approaches, making necessary the use of high level \textit{ab initio} calculations. However, such calculations are restricted to a few atoms, not being applicable to periodic systems.

Within this context, our approach involves the reduction of the system complexity to that of the smallest fragments required to reproduce the essential interactions that take place in the material. This way, we could apply high level \textit{ab initio} methods (Multi-Reference Configurations Interactions). On the basis of these calculations, we were able to build a dynamic bonding model that accounts for many of the disparate properties of SmB$_6$, EuB$_6$, and GdB$_6$, and even allowed to predict new ones that were then tested experimentally.$^3$

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$^2$ Robinson, P. J.; Zhang, X.; McQueen, T. \textit{et al.} \textit{J. Phys. Chem. A 2017, 121, 1849.}

$^3$ Munarriz, J.; Alexandrova, A. \textit{In preparation}