WRM 1

Development of bioluminescent probes for in Vivo Imaging of Metals

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Metals play an important role in normal biological function, and increasing research over the past few decades suggests connections between metal dysregulation and a range of diseases including diabetes, obesity, and various cancers. It is therefore critical to develop new tools to monitor the concentration, flux, and storage of metals in biological systems. We aim to develop molecular imaging probes to achieve this goal using an optical modality known as bioluminescence. Bioluminescence refers to a biological reaction between an enzyme and substrate to produce light. These reactions typically occur through oxidation of the chemical substrate to yield an excited state intermediate that emits photons upon relaxation to ground state. We seek to develop derivatives of these substrates that are blocked from light emission via protecting groups that are chemoselectively cleaved by specific metal analytes. In this regime, the native substrate would be restored only upon reaction with the metal of interest and allowed to interact with the enzyme for light production. Our target system utilizes the substrate coelenterazine, found in many deep-sea organisms, and the luciferase, Gaussia, specifically found in a deep-sea copepod. We chose this system as opposed to the heavily studied firefly luciferase system as its reaction is not dependent on ATP, unlike firefly luciferase. Gaussia luciferase is naturally secreted making it an ideal system for studying extracellular metal pools. This project will add to the toolbox of bioluminescent probes for in vivo monitoring of labile metal pools and offer innovative strategies for tracking extracellular metal pools in living animals.

WRM 2

Incorporation of core-shell quantum dots into coatings for non-destructive evaluation

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In industrial settings, downtime spent on maintenance and repair of assets should be minimized, but not to the detriment of safe operation. Maintaining assets, especially those that are harmed by severe service environments, can be inefficient and costly. A solution we are exploring is the use of core-shell quantum dots incorporated into organic coatings to be used in the early onset detection of metallic substrate corrosion. Core-shell quantum dots (CSQD) are nanocrystals composed of a semiconducting material, which is subsequently shelled with another distinct semiconducting material. When

exposed to proper external stimuli, the dots fluoresce. As the thickness of the CSQD increases, there is a red shift in wavelengths emitted. Quantum dots undergo an aging process as substrate corrosion products and natural weathering or service cycles degrade the dots and decrease their fluorescence.
By incorporating these CSQD into protective surface coatings, the health of the substrate may be interrogated by probing the fluorescent response of the CSQDs. Here we explore the use of CSQDs as internal monitors of accumulated chemical exposure stress, as coatings are exposed to accelerated ultraviolet and corrosive weathering cycles.

WRM 3

Automated chemical perception for force field parameterization

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The Open Force Field Initiative is developing a machinery to automatically parameterize force fields. An important part of this process will be automating chemical perception -- the way force field parameters are assigned to a molecule based on chemical environment. We created the SMIRKS Native Open Force Field (SMIRNOFF) format which allows for changes to easily be made in both the chemical perception and quantitative parameter space. Here, we present a pipeline for creating those SMIRKS patterns which will remove the necessity for a chemical expert to spend countless human hours assigning a force field's chemical perception. Here, we introduce ChemPer, a new tool for chemical perception that takes a systematic approach to learning chemical perception by extracting SMIRKS decorators from molecules. Others in the Open Force Initiative are creating tools using Bayesian Inference to generate ensembles of force field parameter sets. Our final machinery will lead to improved force field science and therefore more accurate and reliable simulation results.

WRM 4

Transition metal-free siladifluoromethylation and trifluoromethylation of P^{V}-H compounds with $TMSCF_3$: novel synthesis of perfluoroalkyl phosphorus compounds

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An operationally simple, transition metal-free method for the fluorofunctionali-zation of phosphonates and secondary phosphine oxides with $TMSCF_3$ is disclosed. Siladifluoromethylation to produce P^V-CF_2TMS and P^V-CF_2H compounds was performed, with multi-gram scale reactions included. An unexpected trifluoromethylation-deoxygenation of secondary phosphine oxides was observed, which offers a novel route to obtain trifluoromethyl-phosphines without costly electrophilic trifluoromethylation reagents.

WRM 5

Applications of nonequilbrium candidate Monte Carlo in molecular dynamics simulations

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Binding modes of ligands using enhanced sampling (BLUES) is a novel method that combines MD simulations with a non-equilibrium candidate Monte Carlo framework to accelerate the exploration of ligand binding modes. BLUES has previously been shown to work well for toluene bound to a model binding site in T4 lysozyme. Here we show that this methodology can A) be applied beyond a model binding system to a pharmaceutically relevant target that is implicated in cardiovascular disease, and B) that it can be repurposed to dart waters for enhancing the sampling of water rearrangement as ligands bind and/or change binding modes, thus alleviating sampling and convergence problems that arise from slow water rearrangements during typical MD simulations.

WRM 6

Assessing protein-ligand binding modes via ensemble molecular dynamics

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It is well known that molecular dynamics (MD) simulations of biomolecular phenomena require extensive sampling to adequately capture thermodynamic properties. Fortunately, advances in computational hardware and algorithmic efficiency now

facilitate the acquisition of ensemble-sized datasets. Correspondingly, there is a growing need for analytical approaches to assess and interpret massive datasets of this nature. In this study, we distinguish and characterize conformations of the enzyme butyrylcholinesterase (BChE), the overactivity of which has been correlated with a number of human health conditions, in complex with a small library of competitive inhibitors. The Folding@Home distributed computing network allowed for the acquisition of over 100 μs of all-atom, explicit solvent MD sampling time for each of thirteen BChE-inhibitor complexes and the enzyme *sans* inhibitor, yielding a total simulation time of approximately 1.5 ms. For each of these systems, post-equilibration structures were characterized by the magnitude and type of contact between inhibitor functional groups and BChE active site residues. The resulting structural descriptors were then clustered using a K-means algorithm and the resulting clusters were described via contact tables, which convey the ensemble-level results of these massive conformational datasets in a comprehensive, concise manner that is accessible to our collaborators, who have provided experimentally measured K_I values for the studied inhibitor. This approach to evaluating the results of modeling enzyme-inhibitor complexes, in tandem with the reported ensemble-level sampling, provides structural insight into inhibitor potency as well as a novel picture of interactions at the atomic level, thus improving our capacity to propose more efficacious inhibitors.

WRM 7

Derivatization and detection of efavirenz metabolites using gas chromatography-mass spectrometry

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Background: Cytochrome P450 2B6 (CYP2B6) and Cytochrome P450 2A6 (CYP2A6) participate in the metabolism of many clinically relevant drugs, including the anti-HIV drug efavirenz (EFV). EFV is metabolized by CYP2B6 to form 8-hydroxyefavirenz, whereas EFV is metabolized by CYP2A6, an enzyme very similar to CYP2B6, to form 7-hydroxyefavirenz. Structural rationale for this differential metabolism is unknown. Prior to further exploring differences in enzyme activity towards EFV, a sensitive and reproducible analytical method must be developed for detection of EFV metabolites. Here we present our efforts towards optimization of chemical derivatization and a gas chromatography-mass spectrometry method for EFV metabolite detection. **Methods:** An Agilent 7690A gas chromatograph coupled to a 5975C mass-selective detector was used in conjunction with various chemical derivatizing agents, including Bis(trimethylsilyl)trifluoroacetamide (BSTFA) + 10% Trimethylchlorosilane (TMCS). **Results:** Optimal detection of both 7-hydroxyefavirenz and 8-hydroxyefavirenz occurred after chemical derivatization using BSTFA +10% TMCS for one hour at 50C. Using pure metabolite standards, approximate lower limits of detection of 7- and 8-hydroxyefavirenz are 33.2 ng/mL and 132.67 ng/mL, respectively. Detection of 7-hydroxyefavirenz is linear from 33.2 ng/mL to 8490.88 ng/mL, whereas 8-hydroxyefavirenz had an inflection point around 132.67 ng/mL and was not linear.

Future work will focus on the discrepancies between 7- and 8-hydroxyefavirenz and further optimization to increase sensitivity.

WRM 8

Compound A, the elusive degradate

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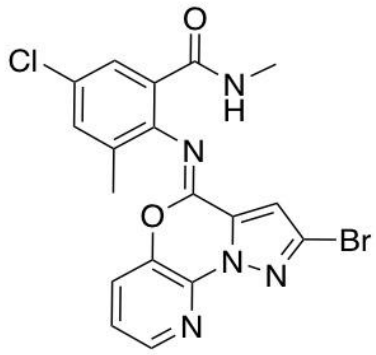
Chlorantraniliprole (CAP), an insecticide pertaining to the anthranilic diamide class, has been of great academic interest to the Tjeerdema group at UC Davis for potential use in California rice fields. In order to study the environmental fate of CAP, degradation products of this insecticide must be synthesized for use as standards in HPLC analysis. Compound A, is one of the degradates of CAP. A synthetic scheme to obtain Compound A is proposed. The initial step of this reaction scheme involves the amination of a 2-halopyridine moiety with 2-*1H*-bromopyrazole. Attempts included a Buchwald-Hartwig Amination cross coupling reaction and nucleophilic aromatic substitution reactions (S_NAr). The S_NAr was further examined in efforts to find a pyridine derivative from which substantial enough yields can be obtained. A 2-fluoro-3-nitropyridine provided the highest yield for the S_NAr coupled with 2-1H-bromopyrazole. Further work will involve eventually replacing the nitro group on the coupled product with a hydroxy group providing an immediate precursor to Compound A.



Compound A

WRM 9

Developing a drug displacement assay for the undergraduate laboratory

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The pharmaceutical industry has a major impact on society and the job market for chemists. Students with enthusiasm for drug design, or occupational interests in pharmacy or medicine, need hands-on laboratory experience in medicinal chemistry. Our goal is to provide this experience through the implementation of a drug synthesis and assessment experiment into the undergraduate chemistry laboratory. To that end, we have developed a novel small molecule binding assay involving the displacement of ANS (anilinonaphthalene-1-sulfonic acid) from the heme-binding active site of AHb (apohemoglobin). We have also examined the binding affinity of several different drug scaffolds for the AHb active site. Our new laboratory experiment thus consists of undergraduate students synthesizing a small molecule, assessing the molecule's binding affinity to AHb via the displacement assay, and then analyzing collective results. The experiment will be launched this semester in the undergraduate organic lab for majors. Assay development, drug scaffold syntheses and AHb binding data, and methods for implementing the experiment in the undergraduate lab will be presented.

WRM 10

Molecular modeling of choline-containing butyrylcholinesterase inhibitors

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In an attempt to mimic the natural substrate of butyrylcholinesterase (BChE), alkyl phenyl phosphate inhibitors containing choline groups were synthesized *in silico* to evaluate how well they would bind to, and thereby inhibit, the enzyme in comparison to their dialkyl phenyl phosphate (DAPP) analogs. Numerous inhibitor structures were created by varying the alkyl chain length and making chemical substitutions on the phenyl ring and alkyl chains. Using the Molsoft ICM-Pro software, 10,000 docking trials of each inhibitor were performed and the 200 trials resulting in the most optimal docking scores were examined. Three subsites within the active site were identified as accommodating the three phosphate substituents. As observed previously for DAPP compounds, choline-containing derivatives with longer alkyl chains were predicted to exhibit greater inhibition, with the cationic choline substituents commonly interacting with the anionic omega loop region, thereby stabilizing the enzyme-inhibitor complex. Some derivatives with additional substitutions at the phenyl ring further stabilized interactions between the enzyme and inhibitor, while others impeded the inhibitor from strongly binding in the BChE active site. For both types of inhibitors, however, r-enantiomers generally achieved more optimal docking poses than their s-enantiomer analogs due to steric restrictions inherent to binding pocket subsites. Modeling the binding of these inhibitors provides an initial glimpse into, and fundamental understanding of, key regions of the BChE active site gorge and provides a starting

point for employing more sophisticated modeling techniques, which will aid in efforts to design more effective BChE inhibitors.

WRM 11

Aggregation of amyloidogenic Tau peptides: To cap, or not to cap, that is the question

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Tau is a protein that binds to and stabilizes microtubules. In Alzheimer's Disease and Tauopathies, Tau can deviate from its normal physiological function and aggregate to form insoluble fibrils. The fibrils are found in abnormally large amounts in intracellular environments in the brain. To study Tau's aggregation, peptides within the R3 region of Tau were used. The N-terminal and C-terminal capping was varied to determine the influence of peptide capping on aggregation. Thioflavin T fluorescence and circular dichroism were used to compare the aggregation propensity between the peptides. Any aggregates formed by the peptides were imaged using electron microscopy. In general, the data show that the fully capped peptides have a greater aggregation propensity than the uncapped peptides. The addition of an anionic cofactor such as heparin was not necessary to induce aggregation since the peptides aggregated in the presence of NaCl alone.

WRM 12

Interactions of ascorbic acid stereoisomers with copper

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Most fuel cells are supplied with hydrogen, but some fuel cells are supplied with alternative fuels that are hydrogen rich such as ascorbic acid. With alternative fuels, different types of catalysts are necessary. It has been reported that the catalytic activity of palladium-copper alloys was shown to have faster oxidation rates of polyalcohols when the copper concentration increased. With that discovery, this research computationally explores the intermolecular interactions of ascorbic acid with copper. The adsorption potential energy of each ascorbic acid stereoisomer adsorbed onto copper were calculated using density functional theory. L-ascorbic acid had the highest adsorption potential energy of -1.34 eV followed by Isoascorbic acid, D-ascorbic acid, and lastly Erythorbic acid with the lowest adsorption potential energy of -1.056 eV. This study will report on how ascorbic acid adsorbs to copper which will lead to more efficient catalyst designs for ascorbic acid fuel cells.

WRM 13

Physiochemical properties of biodiesel monolayers

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Fatty acid methyl esters (FAMEs) can be used to form monolayers at the air-water interface. Biodiesel is a partially renewable fuel composed of a mixture of FAMEs, and is synthesized by transesterifying fats with methanol. We present surface-pressure/area isotherm data for biodiesel and for pure FAMEs. Images taken using Brewster Angle Microscopy (BAM) are also presented. Here we compare the physiochemical properties of biodiesel monolayers with that of a weighted average of the properties of pure FAMEs.

WRM 14

Synthesis and structure of a twisted, alkyne-linked *meta*-quaterphenyl

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A strained molecular cycle comprising an alkyne-linked *meta*-quaterphenyl has been synthesized, and its structural properties have been investigated. DFT calcuations (B3LYP/6-31G*) suggest that the C_2, twisted structure is the lowest energy ground state, and X-ray crystallographic analysis reveals that the twisted structure is present in the solid state. Upon exposure to heat, the molecule undergoes an intramolecular alkynebenzannulation/oxidation to form an extended polyaromatic hydrocarbon. Synthesis, structural features, and properties will be presented.

WRM 15

Improving force fields by identifying small molecules with parameter inconsistencies

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Computer-aided drug design utilizes force fields to simulate chemical structures. Force fields are sets of parameters and functions which return the potential energy of a chemical system. Force fields are widely used, but their inadequacies are often thought to contribute to systematic errors in molecular simulations. Furthermore, different force fields tend to give varying results on the same systems with the same simulation settings. We aim to pinpoint the source of these differences by identifying molecular features that are inconsistently parameterized. Here, we present a pipeline for comparing molecules minimized with a variety of force fields. We apply this pipeline to the DrugBank and eMolecules databases, and highlight outlying functional groups. This project is a subset of the Open Force Field Initiative, which is working to automate force field parameterization. Molecules identified by our pipeline will be used to parameterize future force fields.

WRM 16

Investigation of the effects of C-peptide on metal micronutrients

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C-peptide is a 31-residue bioactive peptide that is co-secreted with insulin in equimolar amounts after cleavage from the A- and B-chains of proinsulin in the beta cells of the pancreas. While initially believed to be biologically inert, recent studies have indicated that C-peptide may have therapeutic effects on diseases such as diabetes and kidney disease. After its release from the pancreas, C-peptide elicits beneficial effects by increasing glucose transport and ATP release from erythrocytes and stimulating blood flow. The signalling mode of C-peptide is still unknown, but one hypothesis states that it may be internalized into cells and interact directly with cytosolic proteins. Interestingly, the beneficial therapeutic effects of C-peptide on diabetic patients have been associated with the presence of metal ions such as Zn(II), Fe(II) and Cr(III). Our lab seeks to elucidate the metal-mediated effects of C-peptide. Using spectroscopic techniques such as circular dichroism and UV-Vis, we are elucidating the effects that these metals ions have on C-peptide secondary structure with the ultimate goal of relating the structure to function. In addition, we are investigating the effects of metal ions on C-peptide internalization using immunofluorescence. Our results support the notion that metal ions affect C-peptide structure and its internalization into cells.

WRM 17

Observation of resonance energy transfer from methyl substituted benzenes to naphthalene on Al_2O_3

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An adlayer of a methyl substituted benzene was vacuum deposited onto a cryogenically cooled Al_2O_3 surface. A bilayer was formed by the deposition of an adlayer of naphthalene on top. The temperature of the Al_2O_3 was linearly ramped in a TPD experiment during which time the fluorescence from the bilayer molecules was monitored. Since the substituted benzenes desorbed at a lower temperature, these molecules percolated through the upper naphthalene adlayer as desorption occurred. This percolation caused the molecules to be sufficiently close to undergo resonance energy transfer and the result was an increase in the fluorescence intensity of naphthalene. The naphthalene fluorescence spectrum during the TPD varied for different methyl substituted benzenes and these will be presented.

WRM 18

Experimental and computational study of the excited-state dynamics of isoguanine in the gas-phase

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Isoguanine-isocytosine has been proposed as a plausible alternative base pair for DNA. Following our recent study of isocytosine, we have now studied the dynamics of isoguanine (isoG) experimentally in the gas-phase with supporting computations. We present the resonance-enhanced multiphoton ionization (REMPI) spectrum of two tautomers of isoG. We found origin transitions at 30807 and 34340 cm^{-1}, respectively. We determined the structures using IR-UV double resonance spectroscopy coupled with anharmonic vibrational frequency calculations at the B2PLYP/def2-TZVP level, finding the *keto*-N3,7 and *enol*-N7 tautomers. We report pump-probe spectra on three peaks of the *keto* tautomer. We found single exponential decay with lifetimes forthe *keto* tautomer around 950 ps. The inability to pump-probe the *enol* tautomer may be due to an ultrafast excited state lifetime. Excited state dynamics calculated at the NEVPT2/SA-2-CASSCF level support the experimentally observed long lifetime of the *keto* and presumably ultrafast lifetime of the *enol* tautomer.

WRM 19

Enhancing sampling of ligand binding modes in molecular simulations with nonequilbrium candidate Monte Carlo

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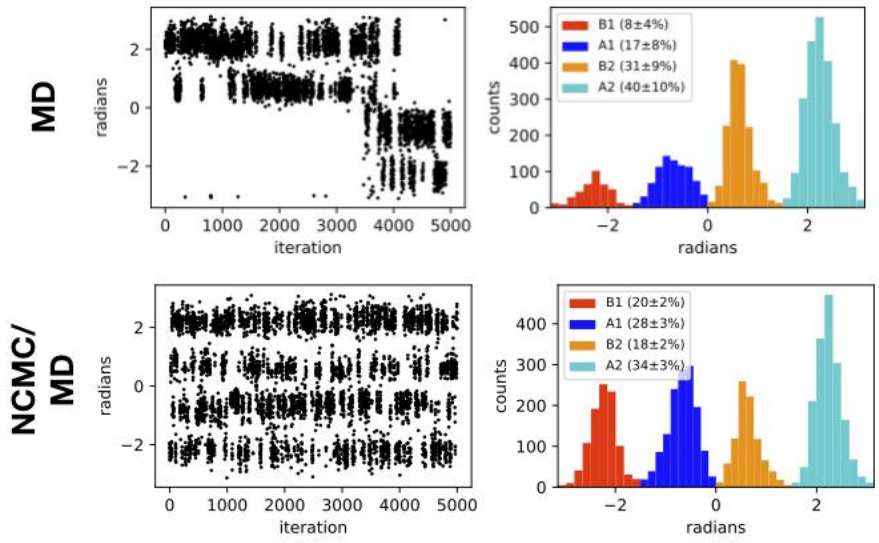
Molecular simulation, or molecular dynamics (MD) is a powerful tool to both understand processes and make predictions, such as relevant physical properties, about a given system. However one limitation of MD is that the timescales it accesses can be magnitudes lower than that of the physical system it attempts to model, which can lead to improper sampling, and thus interpretations of the simulation. One instance in which these sampling issues occur is in the prediction of binding affinities. There are many different simulation-based techniques to predict binding affinities of a given ligand to some target. These methods, however, are all dependent on the ligand starting near the most favorable binding mode which is difficult to predictÂ *a priori, and s*ince binding modes are often kinetically separated from each other on simulation timescales the choice of binding mode greatly impacts the resulting affinity predictions.
Here, we describe our enhanced sampling method to allow proper sampling between different binding modes. Our method applies nonequilibrium candidate Monte Carlo (NCMC) moves, in which the rest of the system is slowly allowed to respond to the ligand being alchemically deleted and then reinserted in a new binding mode. We applied this methodology to a toluene/T4 lysozyme system and show that it correctly recapitulates the different toluene binding mode populations significantly faster than just MD alone.



Comparision of the perfomance of plain MD vs NCMC/MD for sampling the four binding modes

of toluene in T4 lysozyme over a comparable number of iterations. The dihedral angle plotted (on the vertical axis in the left column) is an order parameter that discriminates between binding modes. The right column contains histogram plots of the left column, showing the total population of each binding mode. The MD/NCMC approach improves sampling between binding modes much faster than just MD alone.

WRM 20

Excited state intramolecular proton transfer helps preserve indigo blue

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Indigo is a blue dye molecule that has been used from antiquity, although it is better known today for its use in blue jeans. Indigo has previously been shown to exhibit remarkable photostability due to fast excited state dynamics mediated by an excited state intramolecular proton transfer (ESIPT). Study of this process is complicated by how sensitive ESIPT is to the environment. In order to disentangle the intrinsic photodynamics of indigo from those contributed by the environment, we studied indigo in a molecular beam using resonance enhanced multiphoton ionization. We obtained excited state lifetimes of individual vibronic bands with pump-probe spectroscopy. The results indicate that there is mode-specific relaxation with certain vibronic bands near the origin relaxing much faster than others. In addition to this, we have mapped a barrier to relaxation, beyond which fast excited state dynamics dominate. These data provide a very sensitive probe of the potential energy landscape, responsible for the excited state dynamics. The results may help in understanding the photostability that preserves the blue color of indigo dyes.

WRM 21

Vapor performance testing of filter materials and filter canisters

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Filters protect the first responder and warfighter from toxic vapors. It is necessary to test filters with toxic vapor to prove that deployed filters will protect personnel. Results must be relatable to human toxic effects and to realistic threats.
Collective protection equipment, to include gas masks, cannot be field-tested with toxic chemical agents against human participants. Agent field test performance has been predicted by combining simulant field test data with the results of laboratory component tests using toxic agents.
To address this shortcoming, DPG developed the Swatch Including Filter Test (SWIFT),

a modular near real-time permeation apparatus [1]. Liquid and vapor permeation and off-gassing of filter materials and components can be measured. Simulants or chemical warfare agents (CWAs) may be disseminated in either vapor or liquid states. Pliable and rigid materials as well as small filters may be tested. Only filter testing with vapor is discussed here.

WRM 22

Breeze tunnel testing of collective protection tent systems

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First responders and warfighters must be protected against chemical warfare agents (CWAs) and biological warfare agents (BWAs). Groups are protected in collective protection (CP) areas such as a tent, vehicle, building, or ship. Passive CP structures are protected by barrier materials, filter materials, and closures. Active CP structures feature additional protection by drawing air in through a filter and using overpressure of filtered air to exclude agent.
Due to surety safety and cost, CP structures may not be tested outdoors with agent. Simulants, however, may be used. The results of simulant tests may be combined with agent-simulant relationships (discussed in the companion poster), to predict how the CP structure would behave if challenged with agent on the battlefield.
A US Department of Defense (DoD) program funded testing of five tent systems at Dugway Proving Ground (DPG). Active and passive systems were tested. Each system under test (SUT) was tested at different orientations.
There were three types of trials. In an airflow trial, no simulant was disseminated, but the airflow around the SUT was profiled in detail. In a biological simulant (bio) trial, the SUT was challenged with an aerosol of viable Bacillus atrophaeus (BG) spores. In a chemical simulant trial, the SUT was challenged with vapor of a simulant.

WRM 23

Reproduction of microbial fuel cells: Applications and effectiveness

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A microbial fuel cell (MFC) is an apparatus that converts organic material into energy using microorganisms, primarily the methane-producing (methanogen) Geobacter, as catalysts that facilitate the movement of electrons to produce a substantial electrical differential. During this process, methanogens are also producing combustible gases in abundance. These microbes, supplied by waste material, attach themselves to the

anode where they break down organic material, transporting electrons to the electron acceptor and sending hydrogen protons through an ion exchange membrane. The subatomic particles meet once again in the cathode compartment, where they will react with oxygen to produce water. A prototype cell was designed and assembled using common household items to produce the highest, stable voltage output possible for this system. The purpose of this research is to demonstrate the reproducibility of 0.35V under anaerobic conditions. Implications of these experiments entail scaled-up commercial and industrial applications that can advance knowledge of sustainable sources of energy. Though the expected minimum voltage output on small scales is at least 0.35V, enough to power an led light, the prototype managed to sustain around 0.25V before encountering mechanical issues.

WRM 24

Association preference for phospholipid membrane and propensity for aggregation for luminescent ruthenium(II) bipyridine complexes in mammalian cellular environments.

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In 2013, we reported a class of synthetic nanophotoswitches that respond to light of visible wavelengths by creating an electrical dipole sufficient to alter cell membrane potential. The lead compound is an inherently luminescent ruthenium polypyridyl complex, [Ru(bpy)2(bpy-C17)]2+ where bpy is 2,2'-bipyridine and bpy-C17 is 4-heptadecyl-4'-methyl-2,2'-bipyridine. Ruthenium polypyridyl complexes possess highly desirable properties upon binding to DNA that may potentially be exploited for anticancer applications. Over the past two decades, studies of the many ruthenium polypyridyl complexes designed to preferentially bind to DNA revealed greater lipophilicity and net positive charge are critical for facile cellular uptake and nuclear penetration. Therefore, the lipophilic nature and 2+ overall charge of the Ru(bpy)2(bpy-C17)]2+ complex may be detremental to the ultimate goal using this molecule for the restoration of high-resolution sight to patients suffering blindness due to retinal photoreceptor-degenerative diseases. The propensity to aggregate, the interaction with the phospholipid membrane and any association with organelles were investigated through processing images of various mammalian cells after exposure to the Ru(bpy)2(bpy-C17)]2+ complex.

WRM 25

Hacking electrochemistry: Building a low-cost potentiostat for the undergraduate chemistry lab

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According to the American Chemical Society, undergraduate analytical chemistry labs should include electrochemical methods. This is easier said than done, because the devices used for most electrochemical methods are quite costly and fragile, and not available to most lower division teaching labs. Our research group develops cost effective and robust electroanalytical experiments by hacking or modifying existing equipment, or by utilizing components typically utilized by the Maker Community. Students learn a little about how the instruments work by assembling the device themselves, then learn about the chemistry concepts by calibrating the instrument and making measurements. This particular presentation highlights our latest project, The Teensystat, a low cost potentiostat used to study electrochemical reactions that create currents. The device contains a Teensy microcontroller (cousin to the popular Arduino microcontroller) that controls a programmable Texas Instruments op-amp chip coupled to a Pine Research screen printed electrode, used for a cyclic voltammetry experiment. This potentiostat probes the chemical solution with a voltage that sweeps over a specific range at a specific rate, while monitoring the current that develops as a result of the sweep. The resulting voltammogram is used to characterize the oxidation reduction chemistry of the test solution, as well as quantify the amount of analyte in the solution. While the focus is chemical education, this multi-disciplinary approach promotes student learning about computers and electronic interfacing.

WRM 26

Ultrasensitive detection of cancer biomarker CEA using multi-photon nonlinear laser wave-mixing spectroscopy

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Nonlinear laser wave-mixing spectroscopy integrated to capillary electrophoresis has been demonstrated as a label-free, antibody-free sensitive method for detection of cancer biomarker carcinoembryonic antigen (CEA). Wave mixing offers advantages over current methods including zeptomole-level detection and high spatial resolution suitable for single-cell analysis. Asingle laser is used to generate two input beams that are then focused and mixed inside the sample cell. The input beams created interference gratings, which in turn, diffract incoming photons to produce two coherent laser-like signal beams. The stronger signal beam is collected by a photodetector with high optical collection efficiency and an excellent S/N. Since CEA absorbs in the UV wavelength range, a 20 mW 266 nm UV solid-state laser can be used to excite the analyte in its natural form without the use of labels. The wave-mixing signal has a cubic

dependence on laser power and a quadratic dependence on analyte concentration, and hence, small changes in the analyte can be monitored efficiently. Our preliminary CEA detection limit is comparable or better than those of ELISA or fluorescence-based techniques. Wave-mixing identification can be used for both fluorescing (labeled) and non-fluorescing (label-free) samples; it can also be easily adapted to a battery-powered portable detector that is suitable for use in the field. Potential applications include a reliable detection method for numerous biomarkers, cancer cells, single cells, and viruses for early diagnosis of diseases.

WRM 27

Facile synthesis of Chevrel-phase molybdenum selenides with applications in energy conversion and storage

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Through previous work in our group, Chevrel-phase (CP) molybdenum chalcogenides have been identified as selective catalysts for the electrochemical reduction of CO_2 to methanol. We describe herein the facile, microwave-assisted synthesis of a range of CP molybdenum selenides ($M_xMo_6Se_8$, M = Cu, Cr, Ni, Fe; x = 0-2). Characterization of as-synthesized materials via Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), and Energy-Dispersive X-Ray Spectroscopy (EDX) confirmed successful synthesis of high-quality CP materials.

Further, the CPs synthesized here were evaluated as CO_2 reduction electrocatalysts, where controlled-potential electrolysis experiments were performed in CO_2-saturated aqueous electrolytes. Preliminary testing suggests that when compared to its sulfide analogue ($Cu_2Mo_6S_8$), $Cu_2Mo_6Se_8$ is more active and selective toward methanol production. Hence, compositional tuning of this new class of electrocatalyst may offer a route toward an economically viable, carbon-neutral fuel production system.

WRM 28

Testing of solar cells for satellite applications in suborbital environments using high altitude balloon

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High altitude balloons are a promising low-cost method of testing solar cells in suborbital environments. In partnership with Aerospace, Corp., CSUCI chemistry undergraduates have engineered an automated solar-orienting solar cell platform,

tethered to a latex balloon capabale of reaching the target height of 100,000 feet above the surface of the earth. The purpose is to characterize the performance of novel solar cell materials at a high altitude to determine their appropriateness for future satellite missions. The solar exposure on Earth is not representative of that in space, yet launching test solar cells on $10 million - $400 million satellites is cost and time prohibitive. A helium-filled balloon is a much less expensive and faster way to mimic the desired environment.

WRM 29

Detecting lead in a 3-electrode glass cell by square wave anodic stripping voltammetry

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Lead is a highly toxic heavy metal that is carcinogenic to humans. Because lead can easily leach through the drinking water supply, water test kits have been made readily available for the public to test their water at home to detect any traces of lead. The main disadvantage is that majority of these kits cannot measure the amount of lead in water; they only show whether the water does contain lead or not. One of the most analytical ways to quantify lead is by square wave anodic stripping voltammetry (SWASV). SWASV has the advantage over other voltammetry methods in that it has very high sensitivity and rapid data aquisition. SWASV was applied in this 3-electrode glass cell experiment in order to detect lead in an aqueous solution. To further improve the detection of lead, the platinum working electrode was modified with activated carbon and bismuth, so that more lead ions can get oxidized, hence increasing the detection signal. With the modified working electrode and optimal SWASV settings, the limit of detection (LOD) and limit of quantification (LOQ) were determined to be 0.09 ppm and 0.31 ppm, respectively. In addition, the lowest concentration that can be visually detected was 0.5 ppm. Becasue 0.5 ppm is higher than the LOD and LOQ values, any lead concentration that is 0.31 ppm or higher can be assigned with high level of confidence.

WRM 30

Synthesis of linked chalcones as nematocides

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Nematodes annually cause 80 billion dollars' worth of damage to the agricultural industry worldwide, however, there has yet to be a nematocide which is both safe for the environment and humans.In pursuit of developing new pesticides to counter

nematodes, we previously discovered a library of chalcone small molecules that were effective in exterminating *Caenorhabditis elegans*(a free living nematode) and *Meloidogyne incognita* (the so called Root Knot Nematode, a plant parasitic nematode) nematodes, and that combining the chalcones resulted in a synergistic effect. We then set out to link two different chalcones in one molecule to test the idea that these linked chalcones can be a more potent single-treatment nematocide. We have thus developed a linear four-step synthesis that is modular and accommodating of various linkers, and we successfully prepared a small library of linked chalcones that is currently being assessed for their nemoatocidal activity. We are also currently pursuing other libraries that differ in linker length and in position of linkage. Project motivation, synthesis design, troubleshooting, our library of final compounds, and some preliminary biological data will be presented.

WRM 31

Ruthenium (II) polypyridyls: The effect of an aliphatic chain on cell membrane affinity, cellular and subcellular localization, membrane residence times and binding preferences to biomolecules

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In 2013, we reported a class of synthetic nanophotoswitches that respond to light of visible wavelengths by creating an electrical dipole sufficient to alter cell membrane potential. The lead compound is an inherently luminescent ruthenium polypyridyl complex, [Ru(bpy)2(bpy-C17)]2+ where bpy is 2,2'-bipyridine and bpy-C17 is 4-heptadecyl-4'-methyl-2,2'-bipyridine. The addition of a 17-carbon aliphatic chain (C17) to one of the three bipyridine (bpy) ligands in [Ru(bpy)2(bpy-C17)]2+ serves to anchor the compound in the cellular plasma membrane. Our principle aim of the study is to test the efficacy of the transition metal based nanophotoswitches (NPSs) in conferring light-induced electrical activity in the retinas and the toxicity of the molecules in the ocular environment. To better understand the biological activity of Rubpy-C17, all experiments reported here included a model complex, the well-studied tris(2,2'-bipyridine)ruthenium(II) complex.
Ru(bpy)3 is a structural analogue to Rubpy-C17, yet it does not have the membrane-anchoring hydrophobic C17 tail; this difference between the two molecules may reveal the effect of the C17 tail on cell membrane affinity, cellular and subcellular localization, membrane residence times and binding preferences to biomolecules. These properties were investigated through processing images of various mammalian cells after exposure to the two ruthenium complexes.

WRM 32

Insights on small molecule binding of the Hv1 proton channel from molecular dynamics simulations

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Hv1 is a voltage-gated proton channel whose main function is to extrude excess protons from the cell. It appears to be involved in a variety of maladies (e.g., breast cancer metastasis, brain damage in ischemic stroke). Despite extensive recent research, details of the gating mechanism, proton permeation pathway, and exquisite selectivity of Hv1 remain elusive. We have previously developed an atomistic model of human Hv1 in its open state using molecular dynamics simulations on the microsecond timescale. This model has been validated by comparison with electrophysiology data. Further investigation of the model with respect to small molecule inhibitor binding may further support the structure and lead to the design and development of effective channel blockers. The objective of this work is to understand and improve the binding of small molecules that have been experimentally shown to block Hv1. Our approach utilizes the docking of these inhibitors to our open state model, atomistic molecular dynamics simulations, and alchemical free energy calculations. Here, we present results on the relative binding free energies of these Hv1 inhibitors with comparison to experimental mutagenesis and electrophysiology data.

WRM 33

Characterizing a synthetic promoter toolbox for fine-tuning gene expression in *Vibrio natriegens* using a multiplexed reporter assay

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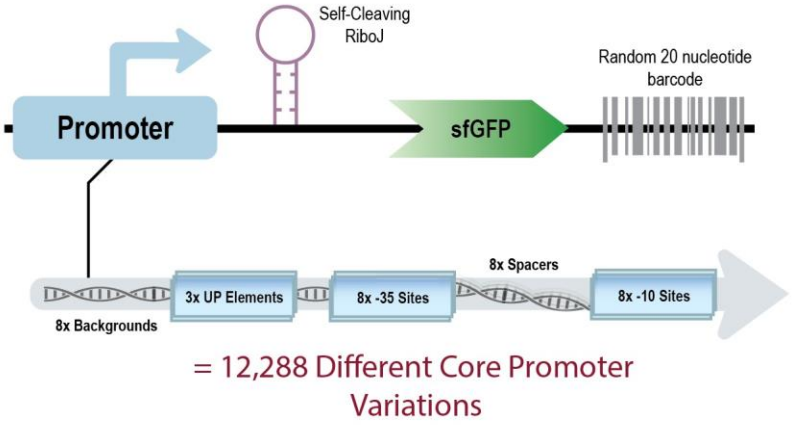
The fast-growing, salt marsh bacterium *Vibrio natriegens* has recently emerged as an exciting new molecular chassis for metabolic engineering owing to its remarkably impressive doubling time of < 10 min, natural ability to secrete proteins, and enhanced protein production rate in comparison to that of *Escherichia coli*. While *E. coli* carries with it decades of research and standardized practices, developing a foundational set of characterized genetic elements in *V. natriegens* will open the doors to new advances in metabolic engineering and industrial biotechnology. However, there are currently no well-established high-throughput techniques for fine-tuning gene expression in *V.*

natriegens. Here, we adopt a massively parallel reporter assay for simultaneously testing the expression of tens of thousands of promoters in *V. natriegens*. We use RNA-seq to quantify expression of a library of nearly 11,000 σ70 promoter variants containing unique combinations of regulatory elements that facilitate RNA polymerase binding. These components include -10 elements, -35 elements, UP elements, and surrounding sequence background, covering a wide spectrum of binding affinities or GC content. We demonstrate that the library yields a dynamic range of expression that allows for selection of a toolbox of promoter sequences that vary in strength, which can potentially be applied for a variety of applications from expediting bench work to optimizing biosynthetic pathways. We also demonstrate that this multiplexed reporter assay can be easily utilized in bacterial systems beyond *E. coli* for rapid characterization of genetic elements, allowing for comprehensive control over promoter selection in any host.



WRM 34

Investigation of the ligand properties necessary for effective cobalt-based nitrate reduction

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Experimental investigations have led to the discovery of a cobalt complex, $[Co(DIM)]^+$, that acts as an electrocatalyst for the selective reduction of nitrate to ammonia in aqueous solution. Other potential Co-based catalysts such as $[Co(cyclam)]^+$ and $[Co(TIM)]^+$ have also been studied. $[Co(cyclam)]^+$ can catalyze nitrate reduction but is not selective and stops at harmful intermediates, such as nitrite and hydroxylamine. $[Co(TIM)]^+$ is inactive for the reduction of nitrate. In order to understand the differences between cyclam, DIM, and TIM ligands, density functional theory (DFT) calculations

were employed to investigate the mechanism for initial reduction of nitrate to nitrite. All calculations utilized the B3LYP functional with D2 dispersion correction, and SDD pseudopotential and accompanying basis set on cobalt. The 6-31G* basis set was used on non-cobalt atoms for structure optimizations, while single point energy calculations employed 6-311+G* on non-cobalt atoms. All complexes were optimized in water using the SMD model to account for the solvent effects. Three mechanisms for nitrate reduction were obtained and analyzed to determine the structural and electronic features that make $[Co(DIM)]^+$ more successful catalyst. This study reveals how a combination of redox non-innocence, hydrogen bonding, and ligand flexibility dictates Co-catalyzed nitrate reduction.

WRM 35

Behavior of microogranisms under elevated g-forces

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The purpose of this study is to examine the effects of high gravity, by hyperacceleration, on the growth of microorganisms. *Saccharomyces cerevisiae*was utilized to develop a UV/Vis based growth assay to determine to monitor growth rates when cultures were exposed to high gravity. An analytical ultracentrifuge was used to subject *S. cerevisiae* to the effects of high gravity. In near real-time, spectrophotometric measurements of cultures containing WST-8 were recorded to track the growth rate of the cultures. It was found that *S. cerevisiae*did grow in a g-force dependent manner—higher g-forces resulted in slower growth . The study was then extended to evaluate how other microorganisms behave in centrifugal fields. Two archaea, *Halobacetrium salinarum* and *Haloquadratum walsbyi,* thrive in hyper-saline conditions and contain gas vesicles within their cells. The primary purpose of gas vesicles is to regulate both organisms buoyancy of both organisms in an aqueous environment. We examined the g-forces necessary to prevent planktonic growth (i.e. floating throughout a water column) for the microorganisms. We have determined that upon exposing cultures to g-forces of between100 – 725 x g, *HalobacteriumH. salinarum* sedimented while *Haloquadratum H.walsbyi* floated under these conditions. Results of the study did demonstrate that microorganisms could survive in very extreme conditions such as high gravity. This could mean that life, in a form of at least at the cellular level (e.g. microorganisms), is possible in an environment in which gravity is much higher than that of Earth.

WRM 36

Adsorption of ADH on gold nanoparticle surface: A Comparison among thermodynamic parameters extracted from second harmonic light scattering, dynamic light scattering and fluorescence measurements

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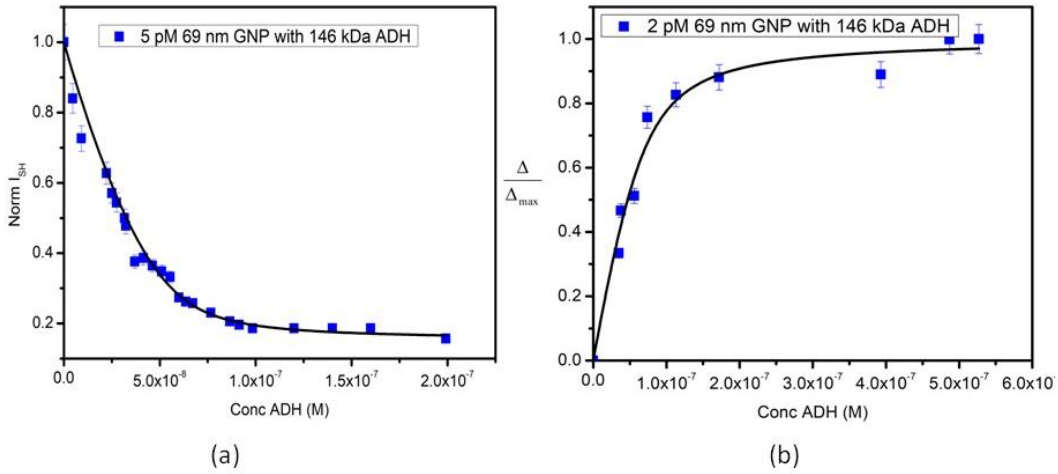
The interaction of nanoparticles (NPs) and biomolecules is of major importance in many areas of modern biomedical research. Understanding the adsorption of proteins and peptides on nanoparticle surface is important to assess the biological viability of NP based delivery of drugs and probes for diagnostics in human systems. Here, we have studied the interaction of four different size citrate capped gold nanoparticles (GNPs) with tetrameric protein, alcohol dehydrogenase (ADH, 146 kDa) in phosphate buffer solution at pH 7. We have used three independent techniques to evaluate the adsorption parameters and to determine the stoichiometry of GNP-ADH conjugate. We have used second harmonic light scattering (SHLS), dynamic light scattering (DLS) and fluorescence spectroscopy to obtain the number of protein molecules in the corona. We have followed the decrease in SHLS intensity and increase in the size of GNPs after adsorption of ADH. Modified Langmuir model (MLM) was used to extract the thermodynamic parameters by fitting the experimental data obtained from SHLS (Figure 1a) and DLS titrations (Figure 1b). Furthermore, decrease in the fluorescence intensity of fluorescein isothiocyanate (FITC) labelled ADH was used to determine the binding stoichiometry. We found that the equilibrium binding (K_b) constant obtained from SHLS and DLS are in the order of 10^9 M^{-1} and increases with increase in the size of GNPs. But the binding constant obtained from fluorescence spectroscopy was two orders of magnitude lower (~10^7 M^{-1}). The free energy change in adsorption measured by SHLS and DLS techniques is ~ -53 kJ/mol. Further, by using variable temperature SHLS measurements, we found that the adsorption of ADH on GNP is an endothermic and entropicaly driven process. The values of enthalpy and entropy of adsorption are ~ +38.7 ± 5 $kJmol^{-1}$ and ~ +318 ± 16.6 $Jmol^{-1}K^{-1}$. We believe that SHLS and DLS techniques are more reliable for quantitative estimation of NP-PC on metallic nanoparticles.



WRM 37

Asymmetric cobaltocenium molecules for mediated electrochemical biocatalysis

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Cytochrome P450 is a class of hemeproteins found in nearly all known life. This enzyme is critical to detoxification and bioactivation of most known pharmaceuticals. Its use in industry could lead to the ability to manufacture powerful new drug derivatives. Moreover, P450 has the potential to create a safer, more economic method for the testing of new drugs. Current laboratory uses of the enzyme are inefficient and require the use of an expensive mediator molecule called NAD(P)H. NAD(P)H serves as a source of electrons to reduce P450 so that it may function, but cost prohibits its use in many research laboratories. In contrast, cobaltocenium molecules that have the potential to act in place of NAD(P)H can be synthesized cheaply and in large quantities. This research project investigates the synthesis and use of an asymmetric, bifunctional cobaltocenium molecule to serve as an electron relay between an electrode and the enzyme, thus eliminating the need for NAD(P)H. We will employ a variety of spectroscopic techniques, such as ^{1}H-NMR and mass spectroscopy, as well as electrochemical methods to characterize the molecule. Once confirmed, we will begin testing its redox characteristics, as well as its potential as a mediator in P450 biocatalysis.

WRM 38

Casimir-Polder size consistency: Case for RPA

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For years, quantum chemical approaches have aimed to accurately and efficiently predict noncovalent interactions (NIs) between atoms and molecules. These include dispersion interactions, π-π stacking, or hydrogen and halogen bonding that play an important role in structural biology and supramolecular chemistry. Here we assess the performance of the random phase approximation (RPA), which has evolved from a semi-analytical technique for model Hamiltonians to a powerful tool for ab initio electronic structure calculations in chemistry and materials science. The accuracy of RPA for weakly interacting systems from the L7, S66, and S30L benchmarks illustrates the critical importance of beyond the pairwise additivity of NIs in moderately large sized molecules with 100 - 200 atoms. Comparison to the second order Møller-Plesset perturbation theory (MP2) and semilocal density functional approximations (DFAs) with dispersion correction reveals that RPA performs better than MP2 and on par with dispersion corrected-DFAs.

WRM 39

Inexpensive metal-free aqueous organic redox flow battery for grid-scale energy storage

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The use of water-soluble organic redox couples is a new and attractive pathway to a sustainable electrical energy storage system with the potential to be inexpensive and environmentally-friendly. Further, several modifications of this type of redox flow battery arrangement using inorganic materials in combination with organic redox couples have also become the subject of research. We have demonstrated the repeated cycling of a redox flow cell based on water-soluble organic redox couples (ORBAT) at high voltage efficiency, coulombic efficiency, and power density. Recently, we reported the synthesis, characterization, and properties of 3,6-dihydroxy-2,4-dimethylbenzenesulfonic acid (DHDMBS) as a new positive side electrolyte material for aqueous organic redox flow batteries (ORBAT). DHDMBS overcame the major issue of the Michael reaction with water faced with previously reported positive electrolyte materials such as 4,5-dihydroxybenzene-1,3-disulfonic acid (BQDS) and other unsubstituted benzoquinones.
The various capacity fade mechanisms were identified and addressed through the

design of specifically tailored organic molecules, use of low permeation membranes and manipulation of operating parameters. The most recent significant advance has been a large-scale demonstration of a 350 W/1 KWh system with our corporate partners ITN Energy Systems. This is the first ever scaled up test on an aqueous organic redox flow battery.
These advances have shown the practical viability and potential commercial value of ORBATs. Our future work is to continue towards the development of stable, high potential positive side molecules, while also working on the optimization of flow fields, electrode structures, and electrolyte separation membranes.

WRM 40

Nickel-catalyzed, carbon dioxide mediated, reductive couplings of imines

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Nickel oxazolidones formed by the oxidative coupling of an imine and carbon dioxide at Ni(0) are used in the reducitve homocoupling of imines to make vicinal diamines. Preliminary results show that this can be accomplished with catalyst loading at or below 10 mol% in near quantitative yield when the imine is *N*-benzylideneaniline. Additionally, the nickel oxazolidones, when paired with a cobalt co-catalyst, are capable of catalyzing the reductive cross-coupling of *N*-benzylideneaniline with an alkyl mesylate in moderate yeild.

WRM 41

Liposome-encapsulated hydrophobic palladium nanoparticles: Applications in biphasic catalysis of olefins in water

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Despite the availability of many water-soluble organometallic and nanoparticulate catalysts, the direct application of water-soluble catalysts for the reaction of immiscible and hydrophobic substrates has been hindered by the low solubility of nonpolar reactants in water. Our research group has shown that alkanethiolate-capped palladium nanoparticles (PdNP) exhibit excellent catalytic activity and selectivity for hydrogenation of unsaturated compounds in organic solvents. This PdNP was synthesized using the thiosulfate protocol using sodium S-dodecylthiosulfate as ligand precursor. The purpose of this study is to examine the catalytic activity of PdNP encapsulated in phosphatidylcholine (PC) lipids in water. After the liposome assembly of PdNP with PC in chloroform, the solvent was removed under vacuum and the hybrid was hydrated with phosphate buffered saline (PBS) solution. The resulting liposome- PdNP hybrids

dissolved in water were characterized by UV-vis spectroscopy, inductively coupled plasma atomic emission spectroscopy (ICP-AES), dynamic light scattering (DLS), and transmission electron microscopy (TEM). During the catalysis reaction, the micellar characteristics of liposome-PdNP hybrid would allow the hydrophobic substrate such as 1-octene to momentarily enter the hydrophobic region of the catalysts with adequate stirring force. After the reaction, the resulting products from bi-phasic system were subsequently extracted with organic solvents and analyzed using ^{1}H NMR spectroscopy. The results suggested that the transformation of 1-octene to octane could be completed within 1 h of catalysis reaction under atmospheric pressure and at room temperature. Liposome catalysis results are then compared to control experiments without PC. The recycling tests of catalysts indicated that the aqueous phase containing the liposome-PdNP hybrids could be reused multiple times with only small decreases in the overall reaction rate.

WRM 42

Optimized growth conditions of MoS_2 nanoflowers for hydrogen evolution reaction (HER) catalyzation

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Fuel cells and metal-air batteries are two of the most promising renewable energy sources currently being researched. However, the latter is restricted in its practical application due to debilitating hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR) kinetics requiring expensive catalysts for their use. MoS_2 is an inexpensive transition metal dichalcogenide (TMD) with catalytic capabilities owing to its exposed edge sites. In this project, vertical MoS_2 nanoflower growth conditions were optimized for integration into metal-air battery systems. These structures were further functionalized with heteroatoms (N and O) to increase the HER catalyzation. Raman spectroscopy and FESEM were utilized to characterize the physical structure and surface, respectively, of these nanoflower structures. Optimal growth conditions were found to be between 200 and 250 sccm of argon flow. This project has developed fundamental understanding of practical applications of 2D materials for sustainable energy uses.

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Spectroscopic studies of DNA binding to ruthenium bipyridyl complexes to determine potential toxicity for retinal applications

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In 2013, we reported a class of synthetic nanophotoswitches that respond to light of visible wavelengths by creating an electrical dipole sufficient to alter cell membrane potential. The lead compound is an inherently luminescent ruthenium polypyridyl complex, [Ru(bpy)2(bpy-C17)]2+ where bpy is 2,2'-bipyridine and bpy-C17 is 4-heptadecyl-4'-methyl-2,2'-bipyridine. The addition of a 17-carbon aliphatic chain (C17) to one of the three bipyridine (bpy) ligands in [Ru(bpy)2(bpy-C17)]2+ serves to anchor the compound in the cellular plasma membrane. Our principle aim of the study is to test the efficacy of the transition metal based nanophotoswitches (NPSs) in conferring light-induced electrical activity in the retinas and the toxicity of the molecules in the ocular environment. To better understand the biological activity of Rubpy-C17, all experiments reported here included a model complex, the well-studied tris(2,2'-bipyridine)ruthenium(II) complex. Calf thymus deoxyribonucleic acid (ctDNA) is used to study the interactions of metal complexes with DNA (binding and/or intercalation) because it is readily accessible and closely resembles mammalian DNA. In order to determine possible mechanisms for ruthenium bipyridyl toxicity, a series of ctDNA concentrations and ruthenium complex concentrations were screened to observe different activities.

WRM 44

Plasmonic photoelectrochemical CO_2 reduction over tunable, ordered gold nanostructures.

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Photoelectrochemical CO_2 reduction uses energy from sunlight and electricity to convert waste CO_2 into fuels or chemical precursors. Challenges to this process include low selectivity for valuable products and high overpotential. Plasmonic catalysts have been shown to selectively lower the overpotential in other reactions, but there is not a well-developed method to predict whether a plasmonic structure will promote a given reaction over another. In this work, we explore the application of plasmonic catalysts to CO_2 reduction to illuminate relationships between the plasmonic nanostructure of the catalyst and the promotion of specific reaction pathways. We have developed a process to pattern gold electrodes with tunable plasmonic nanostructures with resonances in the visible spectrum. These electrodes can then be tested in a photoelectrochemical cell, and CO_2 reduction products can be analyzed. Finite difference time domain modelling is employed to predict absorption maxima and plasmonic electric field enhancement of different structures which can be compared to the distribution of reduction products to provide insight into the plasmonic reduction process.

WRM 45

Synthesis of new donor molecules for organic photovoltaics

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The goal of this work is to synthesize new electron rich organic molecules and polymers. These electron rich molecules have applications in organic photovoltaics and other organic optioelectronic devices. The two primary synthetic targets include a rubrene-like molecule that incorporates a negatively charged aromatic ring, and an organic polymer based on a disubstituted furo[3,2]furan repeat unit. Progress toward each target is reported, which includes yields and characterization of new compounds.

WRM 46

Immobilization of glucose oxidase onto silicon-on-insulator wafer for glucose sensing

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We immobilized glucose oxidase (GOx) onto a silicon-on-insulator (SOI) wafer via amine derivatization to create a working electrode for glucose sensing with immobilized GOx. Electrochemical analysis was employed to evaluate the sensitivity and stability of these SOI-based glucose sensors. Cyclic voltammograms revealed that the height of redox peaks increased monotonically with the increase of glucose concentration, in the range of 1 mM – 15 mM. Moreover, a reasonable stability was maintained after running these electrodes for more than 20 cycles, indicating that the immobilization of GOx onto the SOI wafer was successful. Further experimental evidence on GOx immobilization will be presented. Our studies suggest that these SOI-based GOx working electrodes might be a promising candidate for implantable glucose biosensors.

WRM 47

Exploring prebiotic chemistry on silica nanostructured surfaces

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Many questions surrounding the “origin of life” remain elusive even after decades of research, in part because much is still unknown of environmental conditions of Archean Earth. However, it is generally accepted that amino acids were present during prebiotic conditions and that mineral catalysts played an important role in these reactions, providing a plausible route towards increasing the complexity of life. Research

presented here seeks to investigate novel routes of chemical evolution that may have been responsible for increasing biological complexity. Silicon dioxide, or silica, composes roughly 60% of Earth's crust and likely hosted some of these prebiotic chemical reactions. Many different silica morphologies exist and we acknowledge the importance of geological complexity and diversity by selecting three distinct silica surfaces to represent various naturally occurring silica morphologies. We will investigate and characterize the possible variation that could arise from environmental diversity by comparing results of amino acid adsorption and the self-assembly of peptides on three distinct silica surfaces. Preliminary results indicate that the structural differences among morphologies impact ligand behavior and organization. Surface reactivity will be measured using Brunauer-Emmett-Teller (BET) and morphology analyzed using transmission electron microscopy (TEM) direct imaging techniques. Adsorption and thermal condensation of amino acids at these silica interfaces will be probed by thermal analytical techniques; catalytic potential for polymerization of each surface will be assessed using thermogravimetric analysis (TGA). We hypothesize that fumed silica will exhibit enhanced catalytic activity compared to the other surfaces due to the inherently unique surface chemistry of this nanostructure. The purity or favorability of the peptide product(s) will be investigated using high pressure liquid chromatography (HPLC) and the structure characterized by solution state nuclear magnetic resonance (NMR). Deepening our understanding of chemical evolution will aid astrobiologists as the search for life and assessment of habitability beyond our Solar System continues.

WRM 48

Water dynamics in $CaSO_4.2D_2O$ investigated by deuterium nuclear magnetic resonance

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Deuterium with a spin quantum of one, has a non-spherically symmetrical nuclear charge distribution. It possesses a quadrupole moment that interacts with the electrical field gradients around the nucleus giving rise to a quadrupolar interaction, which dominates its solid state NMR spectrum. Deuterium line shapes are very sensitive to molecular motion and provide valuable information through line shape simulations. We are investigating the molecular motion of D_2O in perdeuterated Gypsum using variable temperature deuterium NMR line shape analysis and deuterium T_1 relaxation time simulations. At 295K the results indicate that the deuterium nuclei of D_2O in Gypsum undergo two-site $C_2$180 degree jumps about the D-O-D bisector angle of 54.8^0 at a rate of $>10^7 sec^{-1}$. The jump rate stays in the fast motion regime down to 198K. At 198K and 173K the motion is in the intermediate motion regime where the line intensities drop and k varies from $1x10^6$ to $5x10^5 s^{-1}$. The best fit quadrupole coupling constants for the range of temperatures (qcc's) vary between 216 kHz and 235kHz and the asymmetry parameters between 0.10 to 0.15. We calculated activation parameters of $\Delta H^{\ddagger}$= 15.12kJ/mol, and $\Delta S^{\ddagger}$= -42.30 J/mol.K and an activation energy of E_a= 16.93 kJ/mol for the C_2 jumps.

WRM 49

Adsorption of a 2,2,2-Trifluoro-1-phenylethanol dimer on Pt(111)

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Chiral modifiers are important in fields such as pharmaceuticals because the stereoisomer of a molecule has the ability to affect its function. 2,2,2-trifluroacetophenone (TFAP) serves as a template molecule for chiral modification when undergoing asymmetric hydrogenation to test for these chiral modifiers. However, the enantioselectivity of TFAP only reaches high amounts when it interacts with a chiral modifier on an achiral metallic catalytic surface, allowing the hydrogenation at the chiral sites to exceed the hydrogenation at the achiral sites. 2,2,2-Trifluoro-1-phenylethanol (TFPE) is formed as a result, and therefore its behavior must also be studied in order to understand its role, if any, in the symmetry breaking process. Using a combination of the PBE and van der Waals (optB88-vdW) density functional theory (DFT), we will present the results from the density functional theory calculations of the most favorable TFPE/TFPE dimer as well as discuss their role in achiral heterogeneous hydrogenation.

WRM 50

Reversed alkyl thiosulfate addition synthesis of ligand-capped palladium nanoparticles: Isolating the catalytic influence of surface ligand density

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Ligand-capped metal nanoparticles exhibit promising properties as catalysts. Its large surface to volume ratio allows for high catalytic activity, while its ligands dictate the immediate environment around the catalytic surface, allowing for directed catalytic selectivity. Alkanethiolate-capped palladium nanoparticles (PdNPs) have previously been synthesized using a modified Brust-Schiffrin synthesis (using alkyl thiosulfate instead of alkanethiol), in which the nanoparticle core size is established during alkyl thiosulfate ligand passivation of the nanoparticle nucleation-growth initiated by borohydride reduction. Due to the dependence of core size on amount of ligand present, surface ligand density decreases with increasing core size. Herein we present a method in which core size is established independent to ligand addition, allowing the formation of PdNPs with similar core sizes, yet different surface ligand density. In this method, core size is established during the temporary passivation of growing nanoparticles by borohydride and tetraoctylammonium bromide (TOAB), allowing nucleation to reach completion. Various molar equivalents of alkyl thiosulfate are then added, prompting the replacement of borohydride and TOAB and the formation of alkanethiolate-capped PdNP. The resulting PdNPs were characterized via ^{1}H NMR, UV-Vis spectroscopy,

thermogravimetric analysis (TGA), transmission electron microscopy (TEM), FT-IR, and inductively coupled plasma atomic emission spectroscopy (ICP-AES). Enhanced catalytic activity was observed for hydrogenation/isomerization of dienes and alkenes using PdNPs with lower surface ligand density proving the isolated effect of surface ligand density from other parameters such as core size and shape. PdNPs with lower surface ligand density demonstrated decreased selectivity for isomerization of alkenes possibly due to less steric hindrance and ligand-induced poisoning of the di-σ-bonded intermediate formation needed for hydrogenation.

WRM 51

Computational research in chemistry: Amino acid enantiomeric interactions in zeolites

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In the past years, we studied zeolites as a possible medium for enriching the enantiomeric excess of solutions. Zeolite lattices being achiral, do not prefer one enantiomer over the other, and adsorb both enantiomers equally well. However, if the D- and L- enantiomers adsorb together as a heterodimer, the enantiomeric excess of the solution they leave behind is augmented. The goal of this project is to complement the experimental results in finding a new avenue to enantiomeric enrichment in an achiral medium provided by zeolites which are aluminosilicate cages with adsorption capabilities. The separation of one enantiomer from the other is a very important practical issue in medicine today because the incorrect enantiomer is either useless or may cause detrimental side effects. Our research efforts are towards making a significant and fundamental contribution to our knowledge about the repertoire of processes leading to enantiomeric purity which is also a very important unresolved question in the prebiotic processes leading to the emergence of life.
We use Material Studio Software from Accelrys Biovia to investigate the enantiomeric interactions of Alanine, Methionine, Leucine, Proline, Tryptophan, and Phenylalanine in the zeolite NaY. We have used geometry optimization as well as simulated annealing to generate the lowest energy conformers for the amino acids. The energetics of the amino acids adsorbed onto NaY were studied by the Sorption algorithm as well as Molecular Dynamics. We will be presenting our findings and show videos of the D- and L-enantiomers adsorbed in zeolites.

WRM 52

Tandem oxidation and dehydrogenative-coupling for the rapid synthesis of 1,3-diones

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The oxidation of alcohols into aldehydes and ketones is a fundamental transformation in synthetic organic chemistry, as these products serve as versatile functional handles for further functionalization of organic molecules. This makes oxidation reactions extremely useful in organic synthesis of either reactive intermediates or target products. However, forming more reactive carbonyl moieties such as 1,3-diones has proven difficult through oxidation alone. It is shown here that through the tandem oxidation and nucleophilic coupling of two alcohol starting materials, 1,3-diketone functionalities can be synthesized in a one-pot method through the oxidation of a reactive intermediate. By coupling multiple transformations, we can capture and functionalize reaction components too sensitive to be isolated, allowing for the conversion of simple functional groups to more useful moieties in a single step. The utility and efficiency of this transformation is highlighted by the ready availability of the starting materials, including the oxidant which is generated *in situ* from ambient oxygen. The development of this method shows potential for future expansion of substrate scope as well as the elucidation and understanding of the mechanism through which this transformation occurs.

WRM 53

High-throughput characterization of inducible-promoter architectures in *Escherichia coli*

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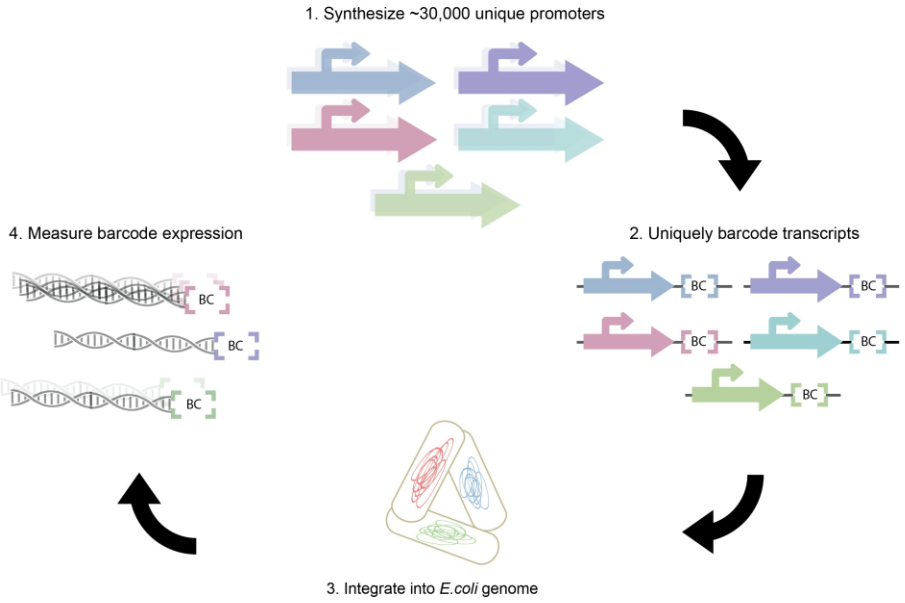
Current inducible promoters are often leaky and limited in their individual ranges of expression, hindering exploration of protein function, metabolic pathway optimization, and ordered gene expression. This shortcoming stems from our incomplete understanding of the exact relationship between the architecture of an inducible system and its corresponding expression level. As such, there is a need for more comprehensive analyses in order to explore and characterize this relationship. Here, we simultaneously test the expression levels of ~30,000 unique LacI inducible promoter variants encompassing a wide spectrum of binding affinities through different combinations of -10 elements, -35 elements, and UP elements by utilizing a massively parallel reporter assay. These variants contain LacI repression loops composed of various permutations of operator distance, strength, and quantity. Additionally, we will determine whether these promoter architectures exhibit similar behaviors with the alternative inducible system, AraC. These design criteria were strategically developed to evaluate whether the architectures of tightly-regulatable LacI promoters yield consistency when replaced with AraC binding sites, whether additional local LacI/AraC binding sites contribute to repression, and whether hybrid LacI/AraC promoters are feasible. The library is expected to yield a large set of inducible promoters whose expression span a dynamic range and can be finely titrated using a molecular stimulant. Furthermore, we hope to discover new insights regarding how each of these regulatory

elements behave at the molecular stage and deconstruct the design rules of transcriptional repression systems.



WRM 54

Measuring the unfolding and ligand-binding of CusF, a copper chaperone

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Although a protein's stability derives from its structure, ligands can also affect structure and stability. The bacterial copper chaperone CusF is stabilized via ligand binding of silver or copper ion, showing increased stability to thermal and chemical denaturation. We are investigating the thermodynamic mechanism of this stabilization through tryptophan fluorescence measurements of CusF unfolding behavior in the absence (apo) and presence (holo) of its ligand Ag(I). Stability curve analysis shows the temperature- and ligand dependence of enthalpy, entropy, and heat capacity of unfolding. We show that ligand binding increases CusF's unfolding enthalpy (ΔH) by approximately 5kcal-mol, its heat capacity (ΔCp) by 0.5kcal-mol, and its entropy (ΔS) by 30 cal-mol. Though the enthalpy change is the most obvious determinant of CusF's ligand-dependent stabilization, the mixed mechanism - particularly the heat capacity change - leaves open the possibility that CusF might show residual structure in the unfolded state of its holo-structure. Such residual structure would narrow the difference between folded and unfolded state heat capacities, resulting in a smaller ΔCp and a wider range of apparent thermal stability.