DEPARTMENT OF CHEMISTRY

30th APRIL
Undergraduate Research Symposium

WHERE: STRONG HALL
WHEN: 12:00 PM - 7:30 PM

mark your calendar

chem.utk.edu/undergraduate-research-symposium/
Undergraduate Research Symposium
Saturday April 30th, 2022

12:00 PM – Kickoff lunch (Strong Hall)
1:00 PM – Poster session I (Strong Hall Atrium)
2:00 PM – Oral presentations session I (Strong Hall 103-104)
2:45 PM – Coffee and cookie break
3:15 PM – Oral presentations session II (Strong Hall 103-104)
4:00 PM – Poster session II (Strong Hall Atrium)
5:00 PM – Move to Geier Hall
5:30 PM – Dinner and awards ceremony (Geier Hall G033/034)
6:00 PM – Keynote address: Dr. Eugene DePrince (Geier Hall G033/034)
7:30 PM – Closing remarks (Geier Hall G033/034)

https://chem.utk.edu/undergraduate-research-symposium/
<table>
<thead>
<tr>
<th>Name</th>
<th>Session</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ghaeath</td>
<td>Poster 1</td>
<td>The Effects on Expression Levels of Heterologous Gene BpsA in Streptomyces Albus Based on Genomic Loci</td>
<td>6</td>
</tr>
<tr>
<td>Tarek</td>
<td>Poster 2</td>
<td>Spectroelectrochemical Detection of Redox-Active Neurotransmitters</td>
<td>7</td>
</tr>
<tr>
<td>Malcom</td>
<td>Poster 1</td>
<td>Tethered, Axial Coordination for Diruthenium Paddlewheel Complexes</td>
<td>8</td>
</tr>
<tr>
<td>Sarah</td>
<td>Poster 2</td>
<td>Quantum Chemical Study on the Interactions between CO₂ and Functionalized Norbornenes</td>
<td>9</td>
</tr>
<tr>
<td>Will</td>
<td>Poster 1</td>
<td>Using Non-Ribosomal Peptide Synthetases to Develop a Heterologous Expression Platform</td>
<td>10</td>
</tr>
<tr>
<td>Rowan</td>
<td>Oral 2</td>
<td>Synthesis and Characterization of Novel N-Heterocyclic Carbene Ligands for Use in Biological Gold Nanoparticle Applications</td>
<td>11</td>
</tr>
<tr>
<td>Henry</td>
<td>Poster 2</td>
<td>Synthesis of C2-symmetric chiral dimidazoles for NHC macrocycle construction for catalytic applications</td>
<td>12</td>
</tr>
<tr>
<td>Carmen</td>
<td>Poster 1</td>
<td>Exploring Noncovalent Interactions of Molecular Models of Van der Waals Heterostructures</td>
<td>13</td>
</tr>
<tr>
<td>Isabelle</td>
<td>Oral 1</td>
<td>Raman Spectroscopic Characterization of UV Degraded Emulsion Lotions with and without Protective Additives</td>
<td>14</td>
</tr>
<tr>
<td>Zoe</td>
<td>Poster 2</td>
<td>Exploring Drug Compound Space with Persistence Images (PharmPIs)</td>
<td>15</td>
</tr>
<tr>
<td>Hayden</td>
<td>Poster 1</td>
<td>Molecular Weight Effect on Associating Behavior of PDMS Based Multi-OH System</td>
<td>16</td>
</tr>
<tr>
<td>Hannah</td>
<td>Oral 2</td>
<td>The Synthesis of Boronic Acid Lipids and Analysis of Their Carbohydrate Binding Properties</td>
<td>17</td>
</tr>
<tr>
<td>Makayla</td>
<td>Poster 2</td>
<td>Discovery and characterization of novel palmitic acid-derived lipids through physical enrichment</td>
<td>18</td>
</tr>
<tr>
<td>Elijah</td>
<td>Oral 1</td>
<td>Modeling Amino Acid Stereoselectivity Using a Type-1 Polyketide Synthase Ketoreductase</td>
<td>19</td>
</tr>
<tr>
<td>Ellie</td>
<td>Poster 1</td>
<td>Molten Ferrofluid</td>
<td>20</td>
</tr>
<tr>
<td>Harper</td>
<td>Poster 2</td>
<td>Synthesis of Alkyl Substituted NHCs for Application on Electrochemical Aptamer-based Sensors</td>
<td>21</td>
</tr>
<tr>
<td>Ellie</td>
<td>Oral 2</td>
<td>Insight into the Formation, Desorption, and Structural Effects of Subsurface Oxygen on Ag(111) Using a Lattice-gas Model and Monte Carlo Simulations</td>
<td>22</td>
</tr>
<tr>
<td>Name</td>
<td>Institution</td>
<td>Poster</td>
<td>Title</td>
</tr>
<tr>
<td>------------------</td>
<td>-------------</td>
<td>--------</td>
<td>----------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Dakota Landrie</td>
<td></td>
<td>Poster 1</td>
<td>Electron tunneling models of junctions containing aromatic heterocyclic molecules with gold or silver electrodes</td>
</tr>
<tr>
<td>Bryce Lane</td>
<td></td>
<td>Poster 1</td>
<td>Synthesis of a C2 Symmetric Chiral Cobalt Centered N-Heterocyclic Carbene Macrocyle Complex</td>
</tr>
<tr>
<td>Christopher Lane</td>
<td></td>
<td>Poster 2</td>
<td>Investigation into the inactive Acryltransferase (AT) domains in Mod 2 and Mod 4 of the Gephyronic acid Biosynthesis</td>
</tr>
<tr>
<td>Nicholas Legaux</td>
<td></td>
<td>Poster 2</td>
<td>Impact of Conformational Restriction on Tetraazacyclododecene Ligands for Atom Transfer Radical Polymerization (ATRP)</td>
</tr>
<tr>
<td>Connor Long</td>
<td></td>
<td>Poster 1</td>
<td>The Effects of Corticosterone on Pancreatic Peptide Hormones: A Single-Islet Analysis</td>
</tr>
<tr>
<td>Kaitlyn Mastrangeli</td>
<td></td>
<td>Poster 2</td>
<td>Phase Diagram of an Asymmetric Lipid Bilayer</td>
</tr>
<tr>
<td>Rahul Nandwani</td>
<td></td>
<td>Poster 1</td>
<td>Codon Optimization of BpsA in E.Coli modeling for PKS and NRPS.</td>
</tr>
<tr>
<td>Dianna Nguyen</td>
<td></td>
<td>Poster 1</td>
<td>Molten Ferrofluid</td>
</tr>
<tr>
<td>Mandy Pham</td>
<td></td>
<td>Poster 1</td>
<td>Exploiting Ion-Mobility Spectrometry-Mass Spectrometry to understand β-amyloid-Homocysteine cross-seeding in Alzheimer's disease</td>
</tr>
<tr>
<td>Justin Phillips</td>
<td></td>
<td>Poster 2</td>
<td>Investigation of the Non-Covalent Interactions Between Carbon Dioxide and Pyridine Using Data-Driven Coupled-Cluster Singles and Doubles</td>
</tr>
<tr>
<td>Paul Pitcher</td>
<td></td>
<td>Poster 1</td>
<td>Synthesis of Selenium Ligands for Dirhodium Paddlewheel Complexes</td>
</tr>
<tr>
<td>Thaddeus Puzdrakiewicz</td>
<td></td>
<td>Poster 2</td>
<td>Cost-effective synthesis of a functionalized trans-cyclooctene (TCO) for selective protein isolation after bioorthogonal labelling</td>
</tr>
<tr>
<td>Nicholas Robins</td>
<td></td>
<td>Poster 1</td>
<td>Deep Tissue Detection of N-Heterocyclic Carbene Gold Nanoparticle Probes with SESORS</td>
</tr>
<tr>
<td>Grace Shelton</td>
<td></td>
<td>Poster 1</td>
<td>Synthesis of a Dirhodium Paddlewheel Complex for Selective Electrochemical Detection</td>
</tr>
<tr>
<td>Rachel Sparks</td>
<td></td>
<td>Poster 2</td>
<td>Identifying Organic Dietary Compounds in Ancient Greek Pottery</td>
</tr>
<tr>
<td>Jacob Steeley</td>
<td></td>
<td>Poster 1</td>
<td>Encoding Angular Information in Persistent Images for Machine Learning Algorithms</td>
</tr>
<tr>
<td>Cass Stover</td>
<td></td>
<td>Poster 2</td>
<td>Benchmarking C2+N1 Aziridination Catalysts</td>
</tr>
<tr>
<td>Name</td>
<td>Last Name</td>
<td>Presentation Type</td>
<td>Title</td>
</tr>
<tr>
<td>------------</td>
<td>-----------</td>
<td>--------------------</td>
<td>----------------------------------------------------------------------</td>
</tr>
<tr>
<td>Andrew</td>
<td>Thayer</td>
<td>Poster 1</td>
<td>Synthesis and Characterization of Cobalt MB-DIPYs</td>
</tr>
<tr>
<td>Wilson</td>
<td>Wang</td>
<td>Oral 1</td>
<td>Studies of Chlorination of Metals and Metal Oxides with S₂Cl₂ and SOCl₂ and the Binding Strength of ZrCl₄ and SOCl₂</td>
</tr>
<tr>
<td>Eddie</td>
<td>Zhang</td>
<td>Poster 2</td>
<td>Synthesis and Characterization of (R)/(S)-BINOL Substituted Phthalocyanine Dimers</td>
</tr>
</tbody>
</table>
The Effects on Expression Levels of Heterologous Gene BpsA in Streptomyces Albus Based on Genomic Loci

Ghaeath Abbas, Tien Sword, Constance Bailey

Important natural products and useful medicinal drugs have been developed from working with the enzymatic pathways polyketide synthase (PKS) and non-ribosomal synthetase (NRPS) found in bacteria, plants, fungi, and a few animals. Many of these products have been created through heterologous expression by integrating a gene in a host organism that does not naturally have that gene. Previous studies have suggested that the location of the integrated heterologous gene at different sites in the genome of Escherichia coli showed significant differences in expression levels from one location to another. Therefore, if the location of the gene matters in the genome of E. coli in terms of expression, then it may also matter when integrating heterologous genes in the genome of Streptomyces albus. Unlike E. coli’s circular DNA, Streptomyces has linear DNA, so it is unknown how the same concept applies to it. Yet, it has also been previously shown that a gene’s genomic loci on S. albus DNA can affect its expression depending on how close it is to the center.

The goal of this research aims to analyze the effects on the levels of expression of heterologous NRPS gene BpsA based on its genomic loci in S. albus. This will be done using two methods. First, BpsA will be integrated into the fixed phage site PhiC31 on S. albus using conjugation from E. coli to develop a reliable conjugation protocol. If this is successful, then the CRISPR-Cas9 system will be used to selectively integrate BpsA into many different sites on the S. albus genome using the same conjugation protocol to examine changes in expression levels. The success of this project will be valuable for efficient drug making that uses heterologous expression. This is an ongoing research project at its early stages.
Spectroelectrochemical Detection of Redox-Active Neurotransmitters

Tarek Atyia, Bhavya Sharma

Neurological disorders (NDs), such as Parkinson’s disease (PD) and Alzheimer’s disease, are diagnosed primarily based on the presence of symptoms. In PD, for example, symptoms arise when 70% of dopamine (DA) producing neurons have degraded, resulting in decreased dopamine production, which then gives rise to symptoms. Once these neurons have degraded, they cannot be repaired, and new neurons will not grow in their place. Current detection methods fail to detect early-onset disease, are invasive, require multi-step sample preparation, and long experimental times. The work presented here focuses on the development of a spectroelectrochemical technique that combines surface-enhanced Raman spectroscopy (SERS) and cyclic voltammetry (CV) for highly sensitive, highly specific, rapid, and ultralow concentration detection of DA and of 4 of its major metabolites - 3,4-dihydroxyphenylacetic acid (DOPAC), 3-methoxytyramine (3-MT), 3-O-methyldopamine (3-OMD), and homovallinic acid (HVA), which are correlated with PD. We have characterized and established detection of dopamine and its metabolites at physiologically relevant concentrations (nM) with SERS in cerebrospinal fluid, urine, and phosphate buffered saline in combination with multivariate analysis, specifically principal component analysis. Additionally, we have successfully established cyclic voltammograms for DA and its metabolites using commercially available gold ceramic electrodes. Pyridine, a strong redox active Raman scatterer has been used to optimize the spectroelectrochemical method, which uses the gold working electrode and simultaneously as the SERS substrate. DA has been successfully detected in vitro at physiologically relevant concentrations using spectroelectrochemistry.
Tethered, Axial Coordination for Diruthenium Paddlewheel Complexes

Malcolm Bailey, Ampofo Darko

Dirhodium paddlewheel complexes are well known for their phenomenal activity and selectivity as carbene transfer catalysts. Research in their use has received intense attention for several decades, but a significant drawback is their cost. Currently, the average cost of rhodium is $19,000 per troy/oz. Efforts to replicate the versatility of dirhodium paddlewheel complexes have included replacing the rhodium center with ruthenium. While much less expensive ($625 per troy/oz), synthesis and characterization of ruthenium paddlewheel complexes are less straightforward and they suffer from selectivity issues as carbene transfer catalysts — metathesis reactions are a competitive pathway. The selectivity of diruthenium paddlewheel complexes may be controlled by axial coordination, and the Darko group is experienced in the synthesis of novel ligands for dirhodium complexes that incorporate axial coordination. This poster describes the synthesis of a thioether functionalized pyrrolidinone ligand that will be used as a ligand for ruthenium paddlewheel complexes. It is anticipated that the incorporation of axial coordination will affect the selectivity of carbene transfer products in competition with metathesis products.
Quantum Chemical Study on the Interactions between CO$_2$ and Functionalized Norbornenes

Sarah Barber, Jeffrey A. Laub, Konstantinos D. Vogiatzis

Global warming due to the presence of greenhouse gases such as CO$_2$, CH$_4$, and NO$_2$ is an ever-pressing issue and new-innovative chemical techniques are needed to mitigate such immense productions. Using non-porous and dense polynorbornenes instead of amine absorption for gas separation are at the forefront of these alternative techniques due to its cost-efficient and mechanically simple nature. Polynorbornenes’ rigid interchain structure create a highly selective but permeable membrane that captures CO$_2$ and other greenhouse gases like N$_2$ through its noncovalent interactions between its functional group and respective gases. The purpose of this study is the performance of quantum chemical calculations for the determination of the CO$_2$-philicity of functionalized norbornenes. A molecular database of more than 50 functionalized norbornenes was created and density functional theory (DFT) computations were performed for the estimation of their CO$_2$ interaction energies. Thus far, our results have revealed that various functional groups (e.g. carboxylic acids) yield interaction energies at approximately -5 kcal/mol due to favorable intermolecular forces. Moreover, their energies are further lowered if S, F, and other halogens are introduced in the functional groups which align with the electronegative trend to CO$_2$ affinity. These results can be applied during industrial processes by engineering norbornene-based membranes to aid in removing harmful greenhouse gases from entering the atmosphere. We hope to evaluate more norbornene structures, analyze them with CO$_2$, as well as broaden our greenhouse gas database to SO$_2$ and NO$_2$ which are prominent sources of acid rain, and determine ways to mitigate the copious amount of gas output.
As one of the fundamental cornerstones of modern medicine, antibiotics have helped save countless lives by making many infections treatable where once they guaranteed mortality. Many antibiotics are natural products derived from microorganisms known as polyketides. Microorganisms manufacture these compounds via Polyketide Synthases (PKS), multi domain enzymes that biosynthesis polyketides. These PKSs and their related class of proteins, Non-Ribosomal Peptide Synthetases (NRPS), work like assembly lines, with each module in the enzymatic complex adding another piece to the primary substrate. Given their status as natural products, many medically relevant compounds can be found in poorly characterized organisms, or organisms that aren’t able to be cultured efficiently. The present study works to provide a model in heterologously expressing PKSs and NRPSs in Escherichia coli. This is done specifically by editing the original gene sequence for the blue pigment synthesizing NRPS, BPSA, according to the codon usage bias in E.coli. BPSA is an ideal model protein as its product is directly observable and it is relatively simple compared to other NRPSs. By expressing both the original DNA sequence and the codon optimized sequence in E.coli, we can observe and compare the differences between the two products. Furthermore, this codon optimization can give us insight into how more clinically relevant PKSs and NRPSs can be heterologously expressed in the future.
Synthesis and Characterization of Novel N-Heterocyclic Carbene Ligands for Use in Biological Gold Nanoparticle Applications

Rowan Borsari, Isabel Jensen, Shelby Strausser, David Jenkins

N-Heterocyclic carbenes (NHCs) are an emerging alternative to thiols in gold nanoparticle and surface chemistry due to their increased stability in thermal and oxidative conditions. While this surface stability of NHCs is critical for nanoparticle functionalization, their hydrophobic nature often leads to unwanted aggregation of nanoparticles. To reduce nanoparticle aggregation, asymmetric, water-soluble imidazole substituents with triethylene glycol (TEG) pendant arms have been synthesized. These ligands are of discreet mass, making them more useful for mass spectrometry (MS) applications than afforded previously in NHC ligands with polyethylene glycol (PEG) arms. They are also symmetric, making them more effective for surface-enhanced Raman spectroscopy (SERS), which gives detailed conformational chemical information. The novel syntheses of these ligands and their gold complexes are presented.
Synthesis of C2-symmetric chiral diimidazoles for NHC macrocycle construction for catalytic applications

Henry Brothers, Jerred J. Russell, David M. Jenkins

A series of chiral N-heterocyclic carbene (NHC) macrocycles have been designed by our group for oxidation catalysis. When ligated to first-row transition metals, these macrocyclic tetra-NHC complexes may be useful in cyclopropanation, epoxidation, and aziridination of both conjugated and aliphatic alkenes. Recently, we have focused on the synthesis of macrocyclic tetra-NHC ligands bearing chiral aliphatic substituents specifically for aziridination. Upon ligation to an iron center, these macrocyclic tetra-NHC complexes are hypothesized to be effective in stereoselective C2+N1 aziridination. However, chiral diimidazole precursors are crucial to the synthesis of chiral tetra-NHC ligands. A comparison of different synthetic routes to various chiral diimidazoles as well as their impact on the chemistry of catalytic aziridination will be presented.
Exploring Noncovalent Interactions of Molecular Models of Van der Waals Heterostructures

Carmen Brown, Grier Jones, Konstantinos D. Vogiatzis

Van der Waals (VdW) heterostructures are layered 2D materials with potential applications for ultrathin dielectrics, selectively permeable membranes, and composite materials. While covalent bonds hold monolayers together, noncovalent interactions, such as Van der Waals forces, allow monolayers to stack to form 2D materials. In this study, a database of potential energy surfaces (PESs) of molecular models will be generated using density functional theory (DFT) to study noncovalent interactions of VdW heterostructures. DFT has been utilized to generate potential energy surfaces of stacked benzene in the t-shape and parallel conformations. Additional PESs will be generated by varying the stacking confirmations, number of layers, and molecular composition of each layer.
Raman Spectroscopic Characterization of UV Degraded Emulsion Lotions with and without Protective Additives

Isabelle Dancer, Avery Wood, Bhavya Sharma

In the cosmetics industry, formulating products that withstand the harmful UV radiation that people are exposed to daily is crucial. Lotions formulated with additives, such as Vitamin C and silver nanoparticles (AgNPs), have been shown to protect against UV exposure. In addition to protecting against UV radiation, these additives display other qualities that are desirable to consumers and formulators. Vitamin C plays an important role in stimulating collagen synthesis, which makes the skin appear younger. AgNPs exhibit antibacterial and antifungal properties that aid in extending the shelf life of lotions. Here we present research on the formulation of an optimized emulsion lotion and the effects of adding Vitamin C and AgNPs in the optimized lotion to determine the lotion’s resistance to change after UVA/UVB/UVC degradation via Raman Spectroscopy (RS). RS is a non-destructive, highly specific and rapid vibrational light scattering technique. Raman spectra of the lotion were measured before and after degrading lotion samples with UVA/UVB/UVC light, allowing for the extent of degradation to be spectroscopically characterized. Four lotions were formulated and analyzed – the optimized base lotion with no additives, the base lotion formula with Vitamin C, the base lotion formula with AgNPs, and the base lotion formula with Vitamin C and AgNPs. Through a comparison of these four lotions, we will present a further optimized lotion formulation demonstrates resistance to UV degradation.
Exploring Drug Compound Space with Persistence Images (PharmPIs)

Zoe Edge, Grier M. Jones, Konstantinos D. Vogiatzis

Pharmacophores are a type of molecular descriptor commonly utilized in computer aided drug design. These molecules can be specific depending on which type of disease that is being treated. Experimenters run into the problem of trying to find which pharmacophore could be most useful in treating a specific disease. This problem can be solved by using machine learning (ML). In this study, we seek to apply a novel molecular representation, called persistence images (PIs), to determine their applicability for classifying drug activity. We will also compare PIs with state-of-the-art representations such as Pharmacoprint, Bag of Bonds, Coulomb Matrices, and the molecular access system (MACCS).
Molecular Weight Effect on Associating Behavior of PDMS Based Multi-OH System

Hayden Garza, Bingrui Li, Alexei Sokolov

Associating Polymers are characterized by the transient properties of their reversible bonds. These polymers contain a similar backbone to conventional polymers but with associating functional groups. Their particular structure enables structural rearrangements and recovery of broken reversible bonds. This results in self-healing properties, specific viscoelastic properties, and unique material recyclability. Previous studies conducted in our group analyzed the macroscopic properties and dynamics of associating polymers. These studies explored the viscoelastic properties and associating interaction dynamics of the Polydimethylsiloxane (PDMS)-based systems. Our research interest is in the molecular weight effect on the associating behavior of PDMS-based multi-OH systems. Research will be conducted by analyzing the NMR, Rheology, and BDS of the polymer in order to explore the effect that molecular weight has on the dynamic and viscoelastic properties. For future research, the combination of molecular weight effect with polymer associative properties may be explored for the optimization of self-healing materials.
Liposomes are microscopic vesicles composed of lipids in aqueous media which are used to deliver both hydrophobic and hydrophilic drug cargo to targeted cells. Because variation in cell surface glycosylation is prevalent on cancerous cells, carbohydrates exhibit strong potential as targeting groups for delivery of these therapeutic liposomes. Boronic acid moieties form favorable interactions with the cis-diols present in carbohydrates, and thus we are developing boronic acid liposomes for cellular delivery. For the first step in this research project, mono- and bis-boronic acid lipids were synthesized. The bis-boronic acid lipids differ in the linker between their phenylboronic acid groups, allowing for the optimization of steric properties and spacing between these moieties. After this, these bis-boronic acid lipids were incorporated into liposomes, and their binding affinities to various carbohydrates and glycoproteins were assessed using microplate binding assays. Lastly, the hydrophilic cargo release of liposomes containing boronic acid polymer lipids was also analyzed using fluorescent dye release assays, and various lipid formulations were attempted within these liposomes to allow for the optimization of hydrophilic cargo release.
Lipids serve as important biomarkers that are a valuable source of information regarding physiological health, and routine analysis of lipid content is often done through liquid chromatography coupled with high-resolution mass spectrometry (LC-HRMS). However, LC-HRMS analysis of lipids is complicated by a remarkable degree of structural complexity that arises from similar biosynthetic building blocks. This complicates interpretation of chromatography and spectral data, as several species with similar masses and fragmentation patterns can co-elute at the same retention time. As a direct consequence the identification and characterization of trace lipids remains difficult, which suggests that there exists a strong possibility that rare lipids have remained undetected. To address this challenge, we propose to apply a click-chemistry based strategy to investigate lipids that are derived from palmitic acid, a straight-chain fatty acid that is particularly abundant in mammalian cells and is used for the construction of a wide variety of more complex lipids. By using previously synthesized bioorthogonally labeled palmitic acid analogues, palmitic acid-derived lipids can subsequently be tagged and captured via clickable solid-phases. Together, physical enrichment and tagging has great potential to simplify analysis of lipids and allow for more thorough investigation of palmitic acid metabolism, potentially leading to the discovery of novel lipids and lipid modifications.
Modeling Amino Acid Stereoselectivity Using a Type-1 Polyketide Synthase Ketoreductase

Elijah Hix, Constance Bailey

Antibiotics are one of the most powerful medical tools in the modern world. As such, understanding how they are made is a vital step in discovering and designing new antibiotics. Polyketide synthases are one of the most common sources of these molecules and are an excellent target for engineering. Ketoreductase modules in polyketide synthases are of particular interest because they can set the stereochemistry of 2 stereocenters with greater than 99% conversion.

This work focuses on the second ketoreductase module of the amphotericin polyketide synthase (AmpKR2) and understanding how it controls stereochemistry. It is a modular type-1 ketoreductase with high levels of homology with other ketoreductases so what we learn about AmpKR2 can be applied to a wide range of other enzymes. We investigated stereo control by replacing residues that are near the active site and have lots of steric or electronic bulk with alanine. When then performed turnover assays on all mutants to screen for activity and we are ready to run the products on a chiral GC/MS system to determine the stereochemical distributions of the products. In addition to the experimental work, we developed a machine learning method that can predict activities of mutants with 68.6% accuracy.
**Molten Ferrofluid**

Ellie Kim, Dianna Nguyen, Phillip Halstenberg, Sheng Dai

The first-time investigation into the properties of molten chloride ferrofluid was accomplished through the synthesis of magnetic nanoparticle containing eutectic mixtures of molten NaCl-MgCl2. Demonstrating the formation high temperature ferrofluid with the use of magnetic nanoparticles, specifically iron and cobalt compositions. Colloidal stability was qualitatively confirmed through visual light scattering via the Tyndall Effect. A novel experimental apparatus was then used to examine magnetic susceptibility of the solutions as a function of temperature. Experimental results demonstrate the ability of molten chloride ferrofluid to maintain magnetic susceptibility at temperatures higher than any previously studied ferrofluid, 750 oC (Fe particles) and 1000 oC (Co particles). Reproducibility of results confirm that ferrofluid maintains magnetism over multiple heating/cooling cycles, implying chemical stability of nanoparticles in solution for the duration of all experiments. These findings create a unique application opportunity to advance the engineering controls of high temperature molten chloride salts as heat transfer fluids (HTF) on the microscopic level.
Synthesis of Alkyl Substituted NHCs for Application on Electrochemical Aptamer-based Sensors

Harper L. Kirby, Isabel M. Jensen, David M. Jenkins

Current electrochemical aptamer-based sensors utilize a thiol-based monolayer to combine a gold electrode surface with a redox aptamer to detect in vivo biological markers. Due to sensor failure as a result of thiol monolayer decomposition, an interest in more robust self-assembled monolayers has led researchers to investigate alternatives like N-heterocyclic carbenes. These strong σ-donors bond to gold to form robust SAMs and are a potential candidate to replace thiols for E-AB sensors. Preliminary data shows NHCs exhibit different behavior from benchmark thiol mercaptohexanol after prolonged cycling, suggesting that NHCs arrange into stronger monolayers that can outlast standard thiol protected electrodes. Although this finding highlights the potential to enable multiday E-AB sensing with NHCs, additional properties such as monolayer packing and molecular orientation on the gold electrode must first be elucidated, which are highly dependent on NHC structure. The determination of wingtip influence on monolayer packing and stability is the primary motivation of my research under Dr. Jenkins for which the synthesis and isolation of N,N-dimethyl benzimidazolium triflate (29.2%) and N,N-diethyl benzimidazolium triflate (72.4%) have been accomplished.
Insight into the Formation, Desorption, and Structural Effects of Subsurface Oxygen on Ag(111) Using a Lattice-gas Model and Monte Carlo Simulations

Ellie Lander, Carson Mize, Lonnie Crosby, Sharani Roy

Theoretical gas-surface models are commonly utilized to compute elementary steps of surface chemistry. Adsorption, for example, is crucial in processes such as heterogeneous catalysis, chemical separations, protein denaturation, and nanoelectronics. To this end, we have developed a fully parametrizable lattice-gas model using electronic structure theory, which includes both surface and subsurface adsorption. Utilizing density functional theory (DFT), we have applied this model to investigate atomic oxygen adsorption on Ag(111). Our previous results on an unreconstructed surface show a high population of oxygen adsorbed in the second subsurface, the region between the second and third silver layers, at coverages more than 0.375 ML. Canonical Monte Carlo simulations indicate a similar distribution at 300 K that remains more or less unchanged up to 600 K. However, simulations of grand canonical Monte Carlo performed in the industrially relevant temperature range of 450 K to 550 K and pressure range 1.00 bar to 2.00 bar show highly temperature-sensitive oxygen distributions with subsurface oxygen forming below 475 K and increasing from 1.00 bar to 2.00 bar. These results suggest that subsurface oxygen is present in catalytic oxidation reactions on silver surfaces. To extend this model, we have introduced silver-silver and silver-oxygen pairwise interactions on and within the surface to allow for lattice distortion and reconstruction due to accumulation of atomic oxygen on the surface and in the subsurface. Through the addition of these interactions, our goal is to study the role of surface and subsurface oxygen in inducing well-known surface reconstructions of Ag(111), such as $p(4 \times 4)$ and $c(4 \times 8)$, as a function of surface temperature and oxygen pressure using Monte Carlo simulations.
Electron tunneling models of junctions containing aromatic heterocyclic molecules with gold or silver electrodes

Dakota Landrie, Matthew R. Curry, Sharani Roy

Theoretical work in molecular electronics looks to produce a model that can accurately describe experimental data for unimolecular rectifiers. Factors that influence the conductance of these metal-molecule-metal motifs include binding site, tunneling height, applied bias voltage, intertip distance and orbital energies. In this work, we seek to gain an inherent understanding of how these factors influence conductance. This was done using density functional theory (DFT) and tunnelling based models. Conductance varied linearly with intertip distance; the general trend shows conductance increasing as the junction is compressed from the DFT calculated optimized geometry. All molecules were placed in face centered cubic (FCC) and on-top sites between both Ag and Au electrodes, respectively. As expected, regardless of junction all molecules showed an increase in conductance as the intertip distance was decreased. Though still in its nascent stages similar work is being conducted with Ag electrodes and the general trends from Au are manifested in Ag junctions. Namely, a linear relationship between intertip distance and conductance. Conductance increases as intertip distance decreases, but the orbital energies increase as intertip distance decreases, and the junction becomes less stable. This indicates the subtle interplay between intertip distance, conductance and stability in Au and Ag junctions containing sulphur or nitrogen terminated aromatic molecules and heterocycles.
Synthesis of a C2 Symmetric Chiral Cobalt Centered N-Heterocyclic Carbene Macrocycle Complex

Bryce Lane, Kevin Blatchford, David Jenkins

C2-symmetric N-heterocyclic carbene (NHC) macrocycle complexes have recently been shown as promising systems for asymmetric oxidative transfer reactions. I have focused on the synthesis of a chiral 18-atom tetracarbene macrocycle, ((S,S)-1,2-Ph2-Et, MeTCH)(PF6)4, centered around first row transition metals for their use in catalyzation of oxaziridination. Computational studies point to the result that a cobalt centered macrocycle would demonstrate success for stereoselective N1C1+O1 oxaziridination catalysis with imines. The successful synthesis of the macrocyclic complex ((S,S)-1,2-Ph2-Et, MeTCH)(PF6)4 was performed and then confirmed through 1H,13C, and 19F NMR, HR-ESI-MS, and SCXRD. A silver dimer of this macrocycle was synthesized, after which a transmetallation reaction was done to create the cobalt centered tetracarbene macrocycle, [((S,S)-1,2-Ph2-Et,MeTCH)Co(Solvnet)2](PF6)2. Successful synthesis of this cobalt complex was confirmed through high resolution (<5ppm error) mass spectrometry along with other spectroscopic techniques. Future works will involve the catalytic testing of this cobalt NHC macrocycle for oxaziridination of imines as well as investigating the precise mechanism for the system.
Gephyronic acid is a polyketide natural product that is produced by the myxobacterium Archangium gephra strain Ar3895. Gephyronic acid exhibits biological properties that shows potential as a strong candidate in the treatment of cancer, and it also exhibits antibiotic effect against yeast and mold. The biosynthesis of gephyronic acid is carried out by a Type I polyketide synthase (PKS) complex which has an inactive acyl transferase (AT) domain in module 2 and module 4. This is interesting as these domains are required to select the appropriate extender unit and load it onto the acetyl carrier protein (ACP) for chain elongation to take place. The question then is: how is gephyronic acid being produced if the AT domains in modules 2 and 4 are inactive? Hence, this research aims to investigate how the extender unit transfers are being mediated to the ACP in modules 2 and 4. We believe that the type II fatty acid synthase malonyl acyl transferase enzyme, FabD, is responsible for providing the extender unit to the ACPs in modules 2 and 4. To investigate this, module 2 and the entire Gephf gene will be recreated in vitro to uncover extender unit transfer. A photo-crosslinking probe will be used to study if there is crosslinking between FabD and the ACPs in modules 2 and 4. Lastly, we will also explore the overexpression of FabD to see if it produces more gephyronic acid.
Atom transfer radical polymerization (ATRP) is an advanced polymerization technique that enables the synthesis of polymers with bespoke properties that are otherwise difficult, if not impossible, to access using conventional free radical polymerization. Examples include polymers with well-defined architectures, controlled molecular weights, and narrow dispersities. This impressive control is facilitated by a reversible deactivation step between the growing radical chain end and a transition metal complex, typically copper, resulting in the in-situ formation of a “dormant” polymer chain. A high rate of chain deactivation (kdeact) is desirable to limit the number of actively growing chains and suppress termination events. Simultaneously, the equilibrium constant of this process (KATRP) should be a relatively large value to achieve a high overall rate of polymerization. Although ATRP has become a mature polymerization technique with significant commercial and academic applications, further studies are necessary to probe the intimate relationship between ligand structure and metal complex performance. In this study, we will describe our efforts to evaluate the impact that conformational restriction has on a series of 1,3,5,7-tetraazacyclododecane-derived ligands has on KATRP and kact when conducting copper-based ATRP polymerizations. Conformational restriction is achieved through two techniques - first by introducing pyridyl-substitutions into the ligand backbone and second by introducing bridging functionalities between ligand nitrogens. The catalytic performance of each ligand-metal combination is probed using UV/Vis spectroscopy techniques. The results of these studies indicate that conformation has an important impact on kact and KATRP.
The Effects of Corticosterone on Pancreatic Peptide Hormones: A Single-Islet Analysis

Connor Long, Aleksandra Antevska, Thanh D. Do

Corticosterone (CORT) is the main stress hormone in mice and rats. CORT acutely inhibits the hypothalamo-pituitary-adrenal axis for the regulation of blood pressure, inflammation, and blood glucose levels. Chronic exposure to CORT leads to depressive-like behavior, increased body weight, and decreased insulin sensitivity which can lead to type II diabetes. In the present study, we investigate the effects of acute CORT exposure on the mouse islet environment using liquid chromatography-ion mobility spectrometry-mass spectrometry (LC-IMS-MS).

We have recently developed a robust and viable workflow to assess mouse insulin 1 (Ins1) and insulin 2 (Ins2) levels in single mouse islets. In addition to Ins1 and Ins2 detection, our workflow can also detect amylin, glucagon, and truncated forms of Ins1 and Ins2 from single islets with high mass accuracy. This method was applied to observe the effects of CORT on insulin and amylin co-secretion.

LC-IMS-MS analysis shows that Ins2 is more prone to degradation than Ins1. In this study, the enzymatic cleavage patterns of Ins1 and Ins2 were assessed for the first time. Furthermore, the effects of CORT on Ins1 and Ins2 clearance were explored.

Results show that intact Ins2 levels decreased significantly in CORT-treated samples compared to control samples. This was coupled with increases in the levels of amylin, as well as truncated Ins1 and Ins2. Due to the differential degradation tendencies of Ins1 and Ins2, we propose that 1) insulin may not be a viable biomarker for β-cell proliferation in mice, and 2) amylin may fill the role of a biomarker as it is co-secreted with insulin and does not experience the same degradation that insulin does. Our results also show that CORT increases enzymatic activity within mouse islets that disproportionally affect Ins2 compared to Ins1 due to structural differences between the two.
Phase Diagram of an Asymmetric Lipid Bilayer

Kaitlyn M. Mastrangeli, Kristen B. Kennison, Frederick A. Heberle

The plasma membranes of living eukaryotic cells have a different lipid composition in their two bilayer leaflets. Physical chemistry studies of simple model membranes consistently find that lipid mixtures mimicking the outer leaflet tend to separate into coexisting liquid phases in symmetric bilayers, while inner leaflet mixtures do not. How the phase behavior of the two leaflets is coupled in an asymmetric bilayer is a major open question. Asymmetric phase diagrams calculated from regular solution theory predict unique phase behavior that depends on the relative strength of in-plane and out-of-plane lipid interaction energies [1]. My project aims to experimentally determine an asymmetric phase diagram for the binary mixture 16:0-PC/16:1-PC. I will use calcium-induced hemifusion between giant unilamellar vesicles (GUVs) and supported lipid bilayers to generate asymmetric GUVs which I will then examine with confocal fluorescence microscopy. The extent of outer leaflet lipid exchange can be determined by a quantitative analysis of fluorescent probe intensities. The hemifusion method produces a wide range of exchange efficiencies in individual vesicles within the same sample preparation, which aids in the construction of phase diagrams. My preliminary experiments have defined the region of gel-fluid coexistence in symmetric GUVs composed of 16:0-PC and 16:1-PC, paving the way for determining the phase boundaries in asymmetric GUVs.
Codon Optimization of BpsA in E.Coli modeling for PKS and NRPS.

Rahul Nandwani, Tien Sword, John Barker, Constance Bailey

Medicine, especially in the last two years with the Coronavirus pandemic has been an important subject of advancement in the modern world. Polyketides are Secondary Metabolites found in nature that can make a host of natural products such as antibiotics and other molecules with medicinal properties. Microorganisms in nature construct these compounds using Polyketide Synthases (PKS). PKS is a process involving multidomain enzyme complexes that use a repeated iterative Claisen Condensation reaction to derive polyketides. This, along with a similar process called Non-Ribosomal Peptide Synthetase (NRPS) which is a function that can occur without the need for the cell ribosomal machinery and mRNAs are processes where each module adds another piece consecutively. This study is conducted to probe codon dependence for the heterologous host expression with blue pigment synthetase A (BpsA) to understand the functionality of PKS and NRPS. BpsA is a NRPS, and the goal is to express both the original DNA sequence and the codon optimized sequence in E.Coli, and observe any changes. Specifically, to observe and analyze how the difference in G/C content might affect protein stability, function, and expression. Furthermore, this study can be used as a benchmark to further study heterologous expression and functionality of PKS and NRPS.
Exploiting Ion-Mobility Spectrometry-Mass Spectrometry to understand β-amyloid-Homocysteine cross-seeding in Alzheimer's disease

Mandy Pham, Damilola Oluwatoba, Thanh D. Do

In America alone, the case of Alzheimer’s disease (AD) is continually on the rise with over 6 million cases. AD is a neurodegenerative disease that negatively impacts the brain leading to behavioral changes such as memory loss, impaired speech, delusion and incoherence. Previous studies have established that the formation and deposition of β-amyloid peptide (Aβ) trigger the onset of AD. Recently, in-vitro studies have shown that high levels of homocysteine can instigate the deposition of Aβ thus making it a risk factor for AD. In this study, we employed ion-mobility spectrometry-mass spectrometry (IMS-MS) to elucidate the interactions between homocysteine and amyloid beta in gas phase. We varied the concentration of Aβ and homocysteine and observed that the detected Aβ peaks differ in an interesting manner. In addition, the presence of Aβ in the nebulizer during the data collection of homocysteine indicated more features than those reported earlier.
A CO₂-pyridine supersystem was investigated to better understand various aspects of the performance of the Data-Driven Coupled-Cluster Singles and Doubles (DDCCSD) model on systems that contain non-covalent interactions. The DDCCSD model was trained and tested using CO₂-pyridine configurations in which the distance between the carbon of the CO₂ and the nitrogen of the pyridine was varied, with all the atoms lying in the same plane. Initial DDCCSD calculations were completed, revealing a large mean absolute error between DDCCSD and conventional CCSD calculations. A novel algorithm which eliminates excess coupled-cluster amplitudes, responsible for biasing machine learning algorithms, was developed. The algorithm was implemented into the DDCCSD model and tested on the CO₂-pyridine supersystem. The resulting mean absolute error of the DDCCSD calculations was reduced. The frozen core approximation was implemented to eliminate two-electron excitations that provide a small amount of correlation energy. This further reduced the mean absolute error of the DDCCSD calculations of the CO₂-pyridine supersystem and lowered the computational cost of the DDCCSD model. A set of novel algorithms which rank amplitudes based on the uniqueness of their corresponding features was developed, allowing for the reverse bias of overpopulated regions of feature space, thusly ensuring the trained DDCCSD model contained a robust feature-space. The set of algorithms were implemented into the DDCCSD model and tested on the CO₂-pyridine supersystem. The resulting mean absolute error of the DDCCSD calculations was reduced. The transferability of the trained DDCCSD model was determined by performing calculations with CO₂-pyridine systems with orientations not introduced during the training of the model. The errors of the calculations done with orientations not introduced during the training of the model were much greater than the errors of the calculations done with orientations similar to those used during the training of the model. In the future, effective sampling of molecular configurations will be used for training the DDCC scheme in order to eliminate such errors.
Synthesis of Selenium Ligands for Dirhodium Paddlewheel Complexes

Paul Pitcher, Ampofo Kwame Darko

The Darko lab has been researching lately on novel ligands for dirhodium paddlewheel complexes. A defining feature of the ligand design is a hemilabile system in which tethered thioethers are coordinated to the axial (or apical) site of the rhodium center. This has resulted in improved yields for carbene transfer reactions such as cyclopropanation and Si-H insertion. Due to the potential lability of the axial thioether ligand, a persistent question remains about the nature of coordination in solution. Is the axial coordination on or off? Selenium variants of the ligands could be useful in this regard so that we can track coordination dynamics in solution with 77Se NMR. This poster outlines our ongoing efforts towards the synthesis of one of these selenium variants and plans for future experiments.
Cost-effective synthesis of a functionalized trans-cyclooctene (TCO) for selective protein isolation after bioorthogonal labelling

Thaddeus Puzdrakiewicz, Dillon McBee, Joshua Baccile

This study demonstrates a cost-effective synthesis of trans-cyclooct-4-enol, a functionalized trans-cyclooctene (TCO). TCO molecules are a common click chemistry tool due to their highly selective and rapid reaction with tetrazines through an inverse electron demand Diels-Alder (IEDDA) mechanism that can occur in physiologic conditions at high yields. The functionalized TCO produced by this synthesis is intended to be attached to a resin through a rink amide linker that is cleavable in mildly acidic conditions, allowing for the conservation of the primary structures of E. coli proteins that had previously integrated a tetrazine-phenylalanine derivative through the work of Dillon McBee. This synthesis is intended to provide the starting material for this method of selective protein isolation at a significantly lower cost than purchasing from an online supplier. This was accomplished through three relatively inexpensive reactions. First, cyclooctadiene was epoxidized by meta-chloroperoxybenzoic acid (mCPBA). Di-epoxidation of the diene was limited by conducting the reaction at -78°C. The resulting epoxide was reduced by LiAlH₄. The product of this reaction was purified by normal phase column chromatography with a mobile phase of 100% DCM. A more common mobile phase of ethyl acetate and hexanes was avoided, as it would complicate solvent removal due to the low boiling point of the alcohol, 86-90°C. Lastly, the cis double bond was isomerized to trans by photoisomerization with a Rayonette photoreactor with bulbs emitting a wavelength of 254nm. Methyl benzoate was added to act as a singlet sensitizer. With a traditional, no-flow setup, the trans isomer appeared at a yield of <10%. A flow setup was modeled after that of Darko et al1, in which the reaction mixture was continuously passed through a column of AgNO₃ impregnated silica gel. 1H NMR spectroscopy was used to analyze the product(s) of each reaction.
N-heterocyclic carbenes (NHCs) display superior deep-tissue detection when compared to thiol-based probes for off-resonance Raman sensing when conjugated with gold nanoparticles (AuNPs). Harsh environmental conditions, such as increased pH and changes in temperature, as well as unwanted aggregation and degradation of thiols results in instability, especially under conditions necessary for in vivo applications. NHCs are more robust than thiols, do not undergo changes due to pH and temperature, and form a stronger chemical bond with the AuNPs than thiols, which prevents dissociation of the molecule from the nanoparticle. We utilize surface-enhanced spatially-offset Raman spectroscopy (SESORS), which combines the high sensitivity and specificity of Raman spectroscopy with the enhancing power of surface-enhanced Raman spectroscopy (SERS) and the depth detection capabilities of spatially offset Raman spectroscopy (SORS). Here we present detection of NHC-AuNP probes to greater than 25 mm depths in porcine tissue. Additionally, we were able to detect the NHC-AuNP Raman signal immediately upon injection in tissue and over an extended period. In comparison to thiols, the NHC-AuNP probes were detected quicker and to greater depths in tissue. Our results demonstrate great promise for the use of NHC-AuNPs in biosensing and imaging applications at biomedically relevant time scales and depths.
Glucocorticoids (GCs) are commonly used as anti-inflammatory and immunosuppressant medications for the treatment of a variety of diseases such as rheumatoid arthritis, certain types of cancer, and organ/tissue transplantation through transrepression activities. Chronic GC use has been linked with untoward complications such as Steroid Induced Diabetes Mellitus (SIDM) potentially through dimerization of the Glucocorticoid Receptor (GR) and subsequent transactivation. Unpublished data in the Campagna lab has demonstrated the ability of 2-mercaptobenzothiazole modified GCs show reduced transactivation with continued immunosuppressive properties across a series of GC backbones. In particular, the dexamethasone derivative with 2-mercaptobenzothiazole showed 87% reduced transactivation activity when compared to commercial dexamethasone. While these compounds show promising therapeutic potential, the underlying structure-activity-relationship (SAR) behind this response is not well understood. In order to further investigate this relationship, a series of dexamethasone derivatives with multiple mercapto groups have been synthesized and computationally analyzed for unique binding interactions. This work aims to identify what structural component is responsible for the improved activity of dexamethasone which may lead to the development of an optimized compound.
Synthesis of a Dirhodium Paddlewheel Complex for Selective Electrochemical Detection

Grace Shelton, Ampofo Darko

It is an understatement to say that selective detection is important in the biological system. In the biological milieu, there are a variety of interactions possible when probing a specific process. This is especially important when trying to monitoring neurotransmitters, where it is a challenge to obtain high sensitivity and selectivity. To potentially address selectivity, we sought to use dirhodium paddlewheel complexes with ligands that can be used to modulate the detection behavior of the rhodium sites. In collaboration with researchers at the University of Vermont, the rhodium complexes we synthesize will then be attached to carbon fiber electrodes for sensitive and selective detection of bioreceptors and other recognition elements. This poster describes efforts to synthesize a rhodium complex for these studies and some of the issues encountered along the way.
Identifying Organic Dietary Compounds in Ancient Greek Pottery

Rachel Sparks, Vernon H. Stafford III, David. M. Jenkins

This project employs instrumental and synthetic organic techniques for the identification of organic compounds inside ancient Greek pottery that are related to dietary substances, such as oil and wine. Chemistry has recently taken on an important role in the study of ancient civilizations through analysis of archaeological artifacts, which has led to the development of the field of archaeochemistry. Through the utilization of Gas Chromatography/Mass Spectrometry (GC/MS) we were able to detect esterified organic acids for the identification of lipids and wine. For lipid identification the target fatty acids—palmitic acid, stearic acid, and oleic acid—were derivatized to fatty acid methyl esters (FAMEs) using acidified methanol. The results of FAME analysis on ancient pottery samples from two archeological excavations in Greece showed a significant presence of the target FAMEs, indicating that the ancient ceramics were used for storage, preparation, or consumption of foods containing lipids. For wine identification, we investigated several sterically hindered alcohols for the selective esterification of the free acid component of ethyl hydrogen succinate, a key organic biomarker of wine, while avoiding transesterification of the existing ethyl ester. The results from the esterification of ethyl hydrogen succinate found that neopentanol was the ideal alcohol for esterification, producing the highest yield of the desired product. This research demonstrates how the application of analytical techniques on archeological samples has potential to yield valuable information regarding the way of life for ancient civilizations.
As the technology of machine learning advances, new and exciting applications for it are frequently found for it. In chemistry, one such application is identifying and classifying molecules based on their substituent parts and the shape they take. To do this, some work must be done to transform relevant data from the molecule into data that is readable by machine learning algorithms. Previous work in this subject has led to the creation of persistent images (PI) created using the center of the atomic nuclei of the molecule. Building on this work, we are seeking to utilize the previous method to develop PIs describing the bond angles found within a molecule. This is done by placing a point at the midpoint of each of the bonds within a molecule and expanding it until holes are formed and die. The resulting persistent diagram (PD) shows the birth vs the persistence of the holes created by the expanding ball centered around the midpoint. This PD is then pixelized to be converted into a PI for the machine learning algorithms. Eventually, the PIs from both the atomic nuclei and the angular PIs will be concatenated into one “super-PI.” This methodology is robust enough to create a PI out of many types of molecules by severing the reliance on geometric representations. This technology could eventually be used to train machine learning algorithms to identify molecules with homologous structures that could react in similar ways to a known molecule.
C2+N1 aziridination catalysis is an area of chemistry that is receiving increasing attention. The C2+N1 catalytic can mitigate unwanted carbon biproducts with the use of azides in the formation of iron imide. As the Jacob’s ladder of density functionals demonstrates, the broadest goal of computational chemistry is to provide systematic improvement in accuracy up to chemical accuracy. The goal, specifically, of this project is to provide accuracy in the calculations of potential molecular catalysts for C2 + N1 aziridination. Benchmarking is way for computational chemists to evaluate different methods and their accuracies against a “known” standard/reference value. This allows us to conclude which methods will be most reliable in exploring the chemical space. In this case, a benchmark entailed testing five different density functionals to ascertain the most accurate and efficient. BLYP was revealed to be the most efficient and accurate density functional of the five tested, based on the mean absolute error (MAE) of the iron-ligand bond lengths. Although M06L was more accurate, it was the least efficient. The data revealed that two of the five catalysts, named 18W-Fe-EM-2 and 18W-Fe-EB-0, that were used in this study were candidates for a full aziridination profile in the future.
Synthesis and Characterization of Cobalt MB-DIPYs

AJ Thayer, Briana Schrage, Laurel Harrison, Viktor Nemykin

Reported herein is an adapted synthetic strategy for the scalable preparation of isoindolin-1-imine derivatives from aromatic ketones and phthalonitrile. These isoindolines undergo self-condensation reactions in mild conditions, generating sodium salts which can be coordinated to a metal center. Previously, these MB-DIPYs have been coordinated to zinc and sodium metal centers, forming benzo-fused, highly electron-deficient core-extended azadipyromethene chromophores known as MB-DIPYs. We explored the synthesis of a series of novel cobalt MB-DIPYs and characterized them by various spectroscopic methods.
Nuclear energy is being pursued as an avenue toward clean energy that is both energy dense and has the capacity to replace traditional combustion-based fuels. A main factor impeding widespread use of nuclear power is the large amount of hazardous waste generated as byproducts of producing nuclear energy. This hazardous waste often exists as spent nuclear fuel rods, which accumulate on site at nuclear power plants with no way forward to easily recycle them. This research specifically seeks to recycle the nuclear grade zirconium in the Zircaloy™ cladding of many spent nuclear fuel rods through use of sulfur-chlorine reagents, such as thionyl chloride and sulfur monochloride. Research in the Barnes lab has found that thionyl chloride can efficiently chlorinate the zirconium metal found in Zircaloy™ forming [ZrCl₄·SOCl₂]₂ adducts, which can be transformed into pure ZrCl₄ through simple heating in vacuum. This study will focus on studying the thermodynamics of chlorination reactions between thionyl chloride and sulfur monochloride with the metals and metal oxides present in spent nuclear fuel to evaluate if it is thermodynamically favorable to chlorinate metals and metal oxides using these chlorinating reagents. In addition, we seek to determine the equilibrium vapor pressure of SOCl₂ over the [ZrCl₄·SOCl₂]₂ as a function of temperature because this can provide the thermodynamic parameters of the vaporization of SOCl₂, which is the final step of the proposed recycling strategy.
Synthesis and Characterization of (R)/(S)-BINOL Substituted Phthalocyanine Dimers

Eddie Zhang, Tanner Blesener, Viktor Nemykin

Phthalocyanines are dyes known for their deep colors, their high thermal and chemical stability, and unique optical properties. Due to their optical properties, they have been investigated for use in nonlinear optics, optical recording media, cancer therapies, semiconductors, chemical sensors, and solar panels. We have synthesized chiral (R)/(S)BINOL substituted phthalocyanine dimers; the BINOL is used to impart chirality to the phthalocyanine dimer. After the dimer was synthesized, extensive chromatography was done to separate the dimer. The optical properties of the dimer were investigated using absorption, circular dichroism, and magnetic circular dichroism, along with mass spectroscopy.