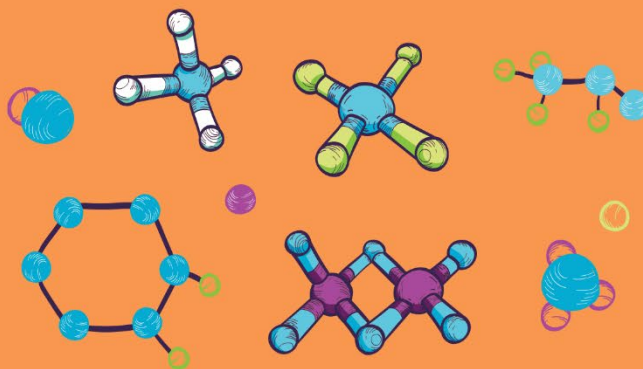




CHEMISTRY



29th APRIL

**U n d e r g r a d u a t e
R e s e a r c h**

SYMPOSIUM

WHERE: MOSSMAN HALL

WHEN: 12:00 - 5:00 PM

**Keynote Speaker
Prof. William Grover
(UC Riverside)**

mark your calendar

www.chem.utk.edu/undergraduate-symposium

Abstract Deadline: Wednesday, April 21st, 2023

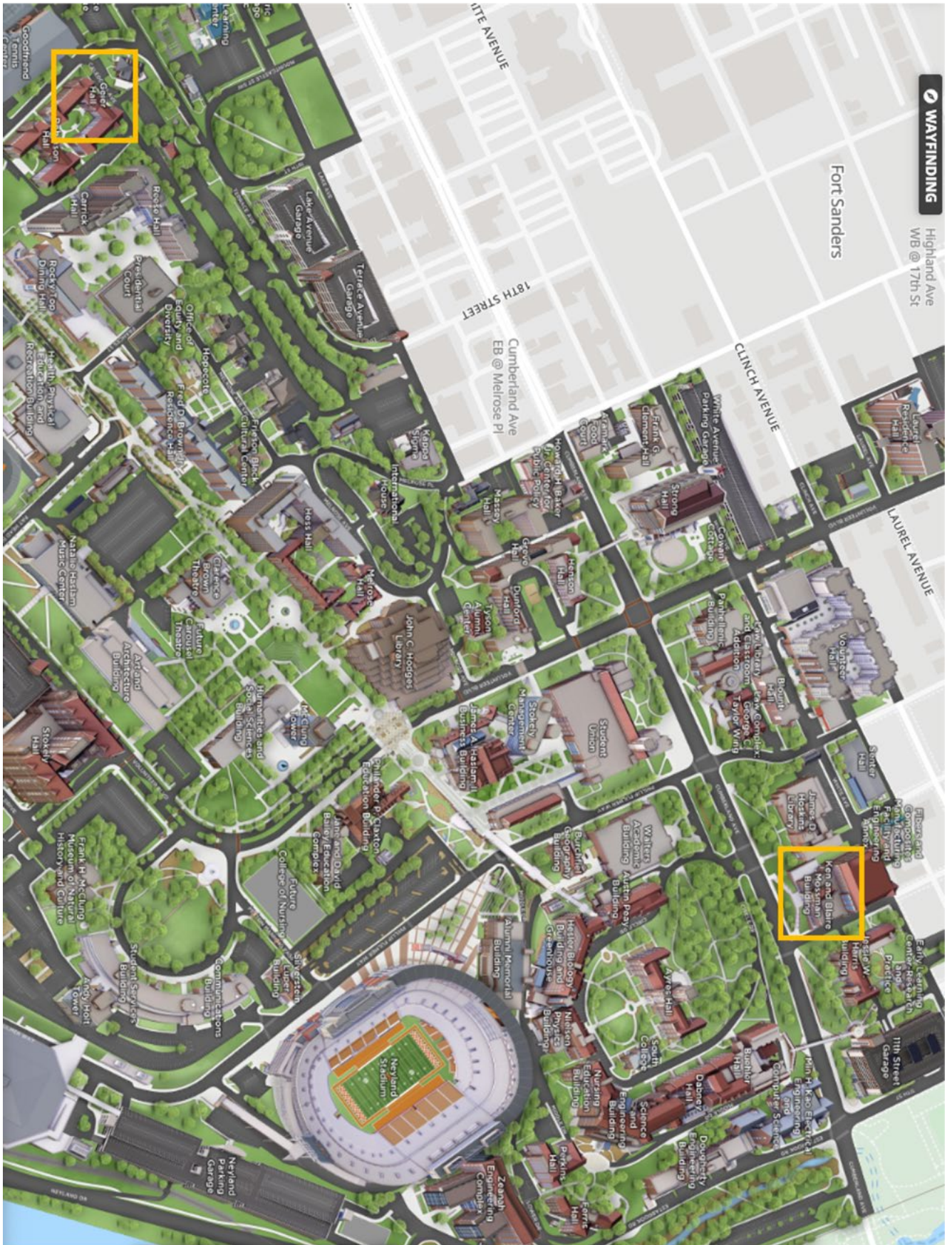
Undergraduate Research Symposium
Saturday April 29th, 2023



DEPARTMENT OF CHEMISTRY

- 12:00 PM** – Kickoff Lunch (Mossman Lobby)
- 1:00 PM** – Poster Session I (Mossman Lobby)
- 2:00 PM** – Student Presentations Session I (Mossman 102)
- 2:45 PM** – Coffee and Cookie Break
- 3:15 PM** – Student Presentations Session II (Mossman 102)
- 4:00 PM** – Poster Session II (Mossman Lobby)
- 5:00 PM** – Move to Geier Hall
- 5:30 PM** – Keynote Address: Dr. William H. Grover (Geier Hall G033/034)
- 6:00 PM** – Dinner and Awards Ceremony (Geier Hall G033/034)
- 7:30 PM** – Closing Remarks (Geier Hall G033/034)

<https://chem.utk.edu/undergraduate-research-symposium/>



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Investigating the Phase Behavior of Lipid Bilayers that Mimic Mammalian Plasma Membranes

Maryam Ahmed, Deeksha Mehta, Emily Chaisson, Frederick A. Heberle

The mammalian plasma membrane is one of the most active and complex cellular membranes. In addition to its role as a barrier and structural support for the cell, the plasma membrane regulates the entry and exit of substances needed or produced by the cell and participates in cell-to-cell communication. The remarkable structural diversity of lipids in the plasma membrane contributes to its functional versatility, making it a fascinating structure for biophysical studies. Model membranes mimicking the outer leaflet composition of the plasma membrane show coexisting liquid phases when imaged with confocal fluorescence microscopy. This is primarily due to unfavorable interactions between saturated and unsaturated lipid chains, with cholesterol ensuring the overall fluidity of the membrane. The outer and inner leaflets of the plasma membrane are also asymmetric in their lipid composition, an aspect of biomembrane architecture that has yet to be fully explored. Using simplified model membranes of 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC), chain asymmetric phosphocholine and cholesterol, we can investigate the biophysical properties of the outer leaflet of the PM. Chain asymmetric lipids in particular are thought to contribute to structural coupling of the two leaflets. Using confocal fluorescence microscopy, we will determine compositional phase diagrams for these lipid mixtures to establish phase coexistence regions and their boundaries.

Thermal Analysis of Quantum Materials

Dylan Andrews, Luther Langston, Janice L. Musfeldt

Quantum materials have emerged as a key area of interest in next-generation electronics, photovoltaics, and even quantum computing, owing to their unique thermal and magnetic properties. One such material is Mn₁₂-Acetate (Mn₁₂-Ac), the first single-molecule magnet, which holds potential for magnetic memory devices. To date, little information has been available on its thermal characteristics. A thermal investigation of Mn₁₂-Ac has revealed three distinct features at 100°C, 230°C, and 300°C, corresponding to water evolution, ligand detachment, and decomposition, respectively. Upcoming studies on other quantum materials are scheduled for this summer, utilizing near-field infrared spectroscopy at the Advanced Light Source at Lawrence Berkeley National Lab.

Synthesis of Pyrrolidinone Dirhodium Paddlewheel Complexes

Malcolm Bailey, Ampofo Darko

Rhodium is well known for its catalytic ability. Specifically, dirhodium paddlewheel complexes are particularly useful for cyclopropanation and carbene insertion reactions. It is known that monosubstitution of a thioether ligand can improve catalytic ability, but it is unknown whether or not this holds true for a similar selenoether compound. By synthesizing both a thioether and selenoether ligand-paddlewheel complex, analysis can be conducted to determine their relative catalytic efficacy. This poster will report on the synthesis of pyrrolidinone ligands that are functionalized with thioether or selenoether groups, and efforts towards their ligand exchange with dirhodium paddlewheel compounds.

Investigating and Optimizing the Cell-Free Expression of Nonribosomal Peptide Synthetases

Will Barker, Jaime Lorenzo N. Dinglasan, Tien T. Sword, Mitchel J. Doktycz, Constance B. Bailey

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 secondary metabolites called Non-ribosomal peptides. Microorganisms manufacture these compounds via Non-ribosomal peptide synthetases (NRPS), multi-domain enzyme complexes that biosynthesize these peptides independently of mRNA. These NRPSs work like assembly lines, with each module in the complex adding another piece to the initial substrate. This means that by mutating the sequence of DNA encoding these proteins, we can change the manner in which these pathways synthesize the peptides, and thus change the final structure of the peptide itself.

As natural products, many medically relevant compounds synthesized by NRPSs can be found in poorly characterized organisms or produce compounds that can be toxic to a heterologous host. Expressing these proteins in a Cell-Free system can address these problems. Cell-Free Protein Synthesis (CFPS) is the expression of a protein *in vivo*, via the addition of all the enzymes, co-factors, and substrates necessary for a plasmid to undergo transcription and translation. By doing so the system can be optimized one factor at a time without the need to worry about impacting the metabolic activities that would be present in a cell.

Development of a C₂-Symmetric Chromium Complex for Asymmetric Aziridination

Connor W. Belcher, Kevin M. Blatchford, David M. Jenkins

Three-membered rings in chemistry, such as epoxides, cyclopropanes, and aziridines, are powerful reagents. The ring strain (nearly 30 kcal/mol!) of a three-membered ring allows for nucleophilic attack to readily occur. Moreover, the synthesis of these rings can create new chiral centers and produce an asymmetric molecule. As a result, stereocontrol in these reactions is critical. One such three-membered ring crucial in both medicinal and synthetic chemistry is the aziridine. An aziridine, a three-membered heterocyclic ring containing two carbons and one nitrogen, is used both in synthetic chemistry as a synthetic precursor and as the active functional group in certain pharmaceutical drugs, such as Mitomycin C. Despite the medicinal and synthetic potential of aziridines, no commercial catalyst is available for asymmetric aziridination. To address this problem, the Jenkins Group has previously synthesized Iron and Chromium systems for catalytic aziridination; these systems have successfully performed aziridination. While these catalysts have had success in aziridination catalysis, a new class of catalysts in the Jenkins Group is being developed – catalysts with a C₂-symmetric ligand scaffold with the capability of doing catalytic asymmetric aziridination. This research focuses on the synthesis, purification, and testing of chromium (III) tetra-NHC complexes for use as catalysts for asymmetric aziridination.

Development of multiplexed surface-enhanced Raman spectroscopy (SERS) sensors for biomarkers of mild traumatic brain injury (TBI)

Megan Byrd, Michael Lenahan, Kevin Ledford, Bhavya Sharma

In the U.S., 1.5-2 million people suffer from TBIs annually. Current diagnosis of TBI is based on cognitive performance and neurological screenings. This subjective analysis often results in misdiagnosis of mild TBIs (mTBI) and can lead to potential harmful health impacts. Imaging techniques, such as CTs, MRIs, or PET, show little to no evidence of brain trauma for patients with acute mTBIs, but do present evidence of long-term abnormalities. New sensing technologies that are sensitive, selective, rapid, have multiplexing capabilities, and require little to no sample processing is an area of need in mTBI diagnostics. Our ultrasensitive sensor platform for mTBI uses plasmonic noble metal nanoparticles, which generates an oscillating electric field, the localized surface plasmon resonance (LSPR), on their surface when excited with an electromagnetic radiation (laser). The LSPR amplifies the Raman scattered light from molecules absorbed to the surface of the nanoparticles, referred to as surface-enhanced Raman spectroscopy (SERS), SERS is a highly sensitive, vibrational spectroscopy that requires little to no sample processing, is rapid, label-free, and SERS sensors can be designed to include multiplexing capabilities. We will present recent results from our group on the development of SERS-based biosensors for mTBI.

Impact of Flake Size on Depolymerization Process of PET by Glycolysis

Kendra Day, Shelby Watson-Sanders, Mark Dadmun

Polyethylene Terephthalate (PET) is one of the most commercially utilized and mechanically recycled polymers, making it a promising candidate for industrial chemical recycling. The heterogeneous depolymerization of PET via glycolysis is often characterized as a surface reaction in which the surface area of PET flakes affects the reaction rate. By altering flake size, the available surface area can be modified, and the hypothesis that the depolymerization is controlled by the amount of surface area can be evaluated. Our research seeks to understand the evolution of chain structure during the depolymerization process to intercept useful intermediates. Our results show that the heterogeneous reaction is controlled by the diffusion of ethylene glycol into the polymer, not the surface area of the PET flake. NMR and DSC data illustrate a decrease in M_n with reaction time while maintaining high yields of highly crystalline polymer throughout the depolymerization. The diffusion of ethylene glycol into the amorphous phase of the polymer causes chain scission of inter-crystalline tie chains. Increasing PET flake length increases the time required for successful diffusion and depolymerization to occur. The catalyzed depolymerization of longer PET flakes via glycolysis produces oligomers with higher molecular weights and similar crystallinity than are produced from shorter flakes. Understanding the stages of depolymerization and the effects of flake surface area provides an opportunity to control the chain length of intermediates that can be used in the production of value-added materials through less energy intensive methods than depolymerization to monomer.

Expression of RppA in a Cell-Free System

Damian Gooden, Will Barker, Tien Sword, Constance Bailey

Using biological engineering to manipulate modular, multi-domain megasynthases such as non-ribosomal peptide synthases (NRPSs) and polyketide synthases (PKSs) affords the ability to design new clinically relevant natural product analogs. To maximize the titer of NRPSs, heterologous expression in host cells has become a research focus. Because of the metabolic burden on host cells brought on by the large size (100 to 10,000 kDa) and complexity of these enzymes, there are difficulties when expressing NRPSs *in vivo*. Cell-free systems are a promising method to bypass the time-consuming and error-prone nature of cell-based synthesis. Cell-free expression shows potential for providing a better understanding of NRPSs and their optimum conditions without needing to undergo multiple design-build-test-cycles. Post-translational modifications differ from protein to protein, and the reaction conditions are likely to differ depending on the size of the protein. The cell-free expression of RppA will be used as a reporter system which will better the understanding of observed truncations and optimal conditions for *in vitro* NRPS expression and provide a prototype for future experimentation for *in vivo* NRPS production.

In-vivo Isotopic Labeling in the Mevalonic Acid Pathway

Makayla Hedges, Zackary Hulseley, Joshua Baccile

In all organisms, the structurally related five-carbon metabolites, isopentenyl pyrophosphate (IPP) and dimethylallyl pyrophosphate (DMAPP) are the central precursors to all isoprenoids. The ability to chemically differentiate the metabolic fate of IPP and DMAPP in cells requires isotopically distinguishing the two structurally related precursors and creating cell permeant analogs. For this reason, we have sought to synthesize ^{13}C labeled IPP and DMAPP with a known and distinct heavy isotope pattern. Here we present the synthesis of the cell-permeant IPP and DMAPP isotopologues. The synthesis of 3- ^{13}C DMAPP has been successfully completed through a 5-step route beginning with ethyl bromoacetate and [$^{13}\text{C}_3$] acetone. Its cell-permeant analog has been made using a cleavable esterase chain for in-vivo application. The synthesis of 4- ^{13}C IPP has now been completed as well through an 8-step route starting from [1,2,3,4- $^{13}\text{C}_4$] ethyl acetoacetate, which will be converted into the cell-permeant analog in the same manner as the DMAPP analogs. These will soon be utilized in metabolic incorporation experiments with U-87 and MB-231 cell lines and *Mycobacterium smegmatis*. This is in order to identify novel isoprenoids and to distinguish their metabolic origins between IPP and DMAPP.

Synthesis of Novel Benzimidazolium Triflate Salts for Applications in Biosensing

Harper Kirby, Isabel Jensen, David Jenkins

Electrochemical sensors have proven to be highly successful platforms for achieving continuous molecular monitoring *in vivo*. Due to the limited set of redox active biomarkers, however, researchers are looking into an alternative sensor technology that takes advantage of reversible affinity interactions in nucleic acid aptamers to widen the scope of biological targets. Currently, this technology utilizes thiol self-assembled monolayers to bridge a gold electrode surface to the aptamer containing a redox reporter, which communicates the concentration of biological targets based on electron transfer rates. However, thiol-based sensors have limited operational lifetimes, preventing long-term stability of the sensors. To increase monolayer stability, a new attachment chemistry is proposed in N-heterocyclic carbenes (NHCs). Varying the alkyl substituents on the nitrogen atoms has been shown to affect NHC orientation and monolayer packing on the gold surface. To this end, NHC triflate salts with methyl, ethyl, hexyl and tert-butyl wingtips were synthesized and characterized to explore the effects of surface coverage and electrode performance.

Developing Synthesis Methods for ^{13}C Labeled NHC Wingtips Towards Dissociation Kinetics Studies of Functionalized Gold Nanoparticles

Grace Miller, Isabel Jensen, David Jenkins

N-heterocyclic carbenes (NHCs) are a new ligand for the functionalization of gold nanoparticles and their association and dissociation kinetics on nanoparticles are not well understood. We seek to apply solution state NMR to study ligand dissociation kinetics of NHCs on nanoparticles. To achieve this goal, we need ^{13}C isotopically labelled NHCs where the ^{13}C is placed at multiple positions on the ligand. Thus, methods for synthesizing labelled NHC wingtips have been explored. As the labelled carbon starting material is the ^{13}C -isopropanol, conditions for synthesis are constrained by the need for our labelled material to be the limiting reagent, as well as the small scale on which the labelled material can be utilized. We have explored the synthesis methods targeting various functional groups such as tosylate, nosylate, and bromide to act as leaving groups for the attachment of the wingtip to the base benzimidazole.

Computational Investigation of CO₂ Activation with Transition Metals

Ryan Millsaps, Virginia White, Konstantinos D. Vogiatzis

In recent decades, growing concern regarding the rising levels of gaseous carbon dioxide in the atmosphere has increased significantly. The purpose of this study is to investigate potential routes and mechanistic details for CO₂ conversion to a more useful and less impactful molecules. Here, we have explored with quantum chemical methods the CO₂ conversion to a carboxylic group with the help of transition metals in the gaseous phase. Through the use of computational methods, we have studied the role of iron and its potential to accelerate this reaction at the lowest activation energy possible. The current focus of our work is the identification of the proper molecular space that is used as “active space” in correlated methods such as the complete-active-space-self-consistent-field (CASSCF) calculations and its extension through second-order perturbation theory (CASPT2).

Synthesis and Spectroscopic Investigation of Axially Coordinated Ruthenium Phthalocyanines

Annabelle Mitchell, Dustin Nevonen, Victor Nemykin

Phthalocyanine (29H,31H-tetrabenzob[b,g,l,q]-5,10,15,20-tetraazaporphine) is a vibrant blue/green pigment that has been commonly used in colorants for decades. It is a macrocyclic compound that strongly binds to metals, such as iron or copper. A less commonly used and understood metal phthalocyanine complex is ruthenium phthalocyanine (PcRu). Substantial synthetic and spectroscopical research is needed to fully evaluate and understand its characteristics and potential uses. To further expand our knowledge of this compound, we used quantitative UV-Vis and MCD spectra analysis to understand the electronic structure of ruthenium phthalocyanine complexes. We subjected ruthenium phthalocyanine to a variety of basic and reductive conditions using triethylamine (TEA) and sodium borohydride (NaBH₄) and evaluated the resultant products using spectrometry. We found good correlation when comparing our experimental results to theoretical values, suggesting good predictive value of our model, which assesses relationship of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) relationships. This research represents a small but significant analysis into the physical, synthetic and spectroscopical properties of the ruthenium phthalocyanines molecules and provides preliminary data suggesting that further research on these compounds would be of interest.

Elucidation of the Epoxidation Reaction Mechanism Promoted by Winged Tetracarbene Complexes

Elokin K. Pate-Geames, Brett Smith, Konstantinos D. Vogiatzis

Epoxidation is an important chemical reaction, particularly in pharmaceutical and biological processes. In vivo, this reaction is catalyzed using enzymes. Outside of biological systems, chemical catalysts are used to facilitate this reaction in high yield and efficiency. Two series of proposed catalysts that can promote epoxidation reactions are winged tetracarbene iron and chromium complexes synthesized by the Jenkins group (University of Tennessee). In order to provide mechanistic insights into the epoxidation reaction, we have performed density functional theory (DFT) calculations to determine the stability and the spin states of the reaction intermediates of the proposed mechanism. The key step in this reaction is the formation of a metal-oxo intermediate, which further forms an epoxide with an alkene. This leaves a carbon radical on the second carbon, which then consequently binds to the oxygen for the formation of the desired product. The epoxide then dissociates from the complex, and the catalyst is recovered.

Investigation of the Performance of Data-Driven Coupled-Cluster Singles and Doubles on Systems with Large Amplitude Spaces

Justin T. Phillips, P. D. Varuna S. Pathirage, Konstantinos D. Vogiatzis

The ability to accelerate the calculation of the energies of molecular systems is integral to modern computational chemistry. One such method of accelerating quantum chemical calculations is Data-Driven Coupled-Cluster Singles and Doubles (DDCCSD), which uses machine learning algorithms to predict coupled-cluster amplitudes using information from less expensive quantum chemical methods, namely Hartree-Fock (HF) and second-order Møller-Plesset Perturbation Theory (MP2). The performance of the DDCCSD model on systems with large amplitude spaces was investigated using a set of five small molecules. Initial DDCCSD calculations revealed a large mean absolute error between DDCCSD and conventional CCSD calculations. In hopes of reducing the error, novel algorithms that eliminate excess coupled-cluster amplitudes, responsible for biasing machine learning algorithms, were developed. The algorithms reduced the number of amplitudes used to train the machine learning model by selecting a subsection of the amplitudes in accordance with assigned weights, based on quantum chemical information from HF and MP2. The algorithms were implemented into the DDCCSD scheme and tested on the small molecules, resulting in a reduction of the mean absolute error of the DDCCSD calculations.

Solvatochromism of Cupric Chloride and Its Conversion to Copper Oxide

Miranda Phillips, Michael J. Jenkins, Zi-Ling Xue

Solvatochromism is observed as a result of solvent polarity effects on a polarizable solute, leading to a difference in the electronic ground and excited states of the solute, shifting the energy gap, which is often observed as a color change. By mixing copper(II) chloride dihydrate in different solvents a change in absorbance be explored, based on the polarity of the solvent. The process of making CuO through the reaction of CuCl_2 and NaOH can be conducted both in the solid state and in several solutions via the sol-gel process involving copper(II) hydroxide, gradually forming CuO. Completing this experiment using the solvents, acetone, isopropanol, and water, it was found copper chloride exhibits negative solvatochromism; wherein as the polarity of the solvent increases, the energy gap also increases. Conducting this experiment provided an opportunity to learn the following: (1) how the effects of solvent polarity change the color of solutions, (2) the advancement of green chemistry through solid-state reactions, (3) the formation of CuO from solution through the sol-gel process, and (4) how to interpret information derived from the characterization of such chemical compounds by UV-visible, infrared, and powder x-ray diffraction.

Optimization of Reaction Conditions for Ligand Exchange of Axial Coordinating Ligands onto Dirhodium Paddlewheel Complexes

Paul Pitcher, Ampofo Darko

The Darko Lab has been researching novel ligands for heteroleptic 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 feature has resulted in improved yields for carbene transfer reactions such as cyclopropanation and Si-H insertion. While these dirhodium complexes are useful in applications, their synthesis has proven to be a challenge due to low yields and the presence of mixtures of products. Using fluorinated ligands, reaction conditions are being optimized in order to give the best yields of desired complexes. The features of this approach include low amounts of side products, quick reaction times, and high selectivity of desired isomers.

Selective Transformations of Isopropanol on the Strontium Titanate (100) Surface

Graci Sexton, Carson Mize, Sharani Roy

Perovskite crystals, with the form ABX_3 , are widely used in heterogeneous catalysis applications due to their versatility in chemical transformations and reactions. These types of materials have numerous forms, with some of the more common consisting of alternate layers of transition metal-oxides. A TiO_2 surface, a metal-oxide example, is used as a catalyst to reduce a variety of atmospheric pollutants and as a non-carbon nanotube for their many chemical properties. However, some molecular transformations performed by these crystals and surfaces directly compete with others, and which transformation is favored is unsettled. To better understand these systems and any tunability for these transformations, we study the competing isopropanol dehydration (forms water and propylene) and dehydrogenation (forms H_2 and acetone)

transformations on a TiO_2 -terminated $SrTiO_3$ crystal. We chose this system since various experimental results contradict which pathway is kinetically favored, and our past studies suggest interfacial acidity could affect this chemical preference. Our calculations suggest that acetone is the more favorable product, however, we hypothesize increased interfacial acidity drives the chemical transformation towards propylene formation by lowering its required kinetic barrier. Understanding chemical tunability involving properties like interfacial acidity could lead to better design of a wide range of catalysts.

Investigating the Second Harmonic Generation and General Polarization of Laurdan in Gram-Positive Bacterial Membranes

Brandon Shaw, Marea Blake, Tessa R. Calhoun

The growing threat of antibiotic resistance in bacteria has prompted research into the complexity of bacterial membranes and their interactions with small molecules. Of particular interest is how bacteria modulate their fluidity and formation of rigid domains as this has been shown to be responsible for many cellular processes including signal transduction. A popular approach to monitor membrane domains is to use a fluorescent probe that exhibits distinct spectral properties when it resides in fluid or rigid regions, such as laurdan. By monitoring these spectral shifts, a generalized polarization (GP) value can be extracted to inform on the overall fluidity of the membranes of interest. Here, we aim to correlate second harmonic generation (SHG) signals to changes in the GP of laurdan in living *Staphylococcus aureus* cell membranes. SHG is a nonlinear spectroscopic technique sensitive to the orientation and polarizabilities of small molecules arranged along an interface, such as that of cell membranes. By correlating GP and SHG signals, we show that SHG is a technique capable of detecting changes in fluidity of living cells in real time. Further, we can use this method to monitor how small molecules, such as antibiotics and drug adjuvants, influence the formation and disruption of domains in living bacterial membranes.

Synthesis of a Dirhodium Paddlewheel Complex for Selective Electrochemical Detection

Grace Shelton, Ampofo Darko

The catalytic centers of rhodium are capable of an extensive number of chemical transformations which has made the inorganic compound popular for chemical research. The synthesis of rhodium for new catalytic applications has also been proven to make the compound more efficient and selective. Thus, the ability to manipulate the configuration of rhodium catalysis centers is of great interest as it can have beneficial properties in medical and industrial chemistry. Techniques such as the asymmetric synthesis have become increasingly popular as they are used to produce a single enantiomer of a chiral center. The application of chiral ligand can be used to transfer chirality on metal groups such as rhodium in order to help produce these highly stereoisomeric products.

Therefore, the Darko Lab decided to produce a chiral ligand that can provide axial coordination to a rhodium paddlewheel complex in order to control the stereochemical outcome of carbene transfer reactions. The project began with the synthesis of the amino-thioether compound from Evan's oxazolidinone chiral auxiliary. We then used this in a reaction with phthalic anhydride in order to make the chiral ligand for the rhodium paddlewheel complex. Once we had our ligand, we then used it in ligand exchange reactions in order to produce our desired dirhodium paddlewheel complexes in "mono" or "bis" form.

Exploring Structure-Property Relationships in Bicyclic Terpenoid Polymers

Jonathan Shepherd, Nick Galan, Chase Chromer, Jonathan Brantley

Biomass-derived monomers are rapidly advancing the field of sustainable polymer synthesis. Camphene, a Fir sourced terpenoid, is a particularly attractive petrochemical substitute as the retention of its sterically hindered bicyclic core helps elucidate the relationship between form and polymer properties. Recent reports have demonstrated that β -Pinene, a constitutional isomer of camphene, can undergo Nickel-catalyzed living vinyl-addition polymerization. This has led to further exploration of camphene as a potential monomer for block copolymer addition.

To accomplish polymerization, camphene must be cyclopropanated via chloroform. The dichlorocarbene undergoes a Skattebøl rearrangement utilizing *n*-Butyl Lithium to yield an allene. Treating the allene with the same nickel catalyst used in the β -pinene reaction results in a polymer possessing distinctive traits such as high conversion and temperature sensitivity. These promising results have led to further inquiry into establishing better control over the polymerization process.

Biomass-derived monomers such as camphene hold great promise for the sustainable production of polymers. Recent findings have demonstrated the potential of camphene as a substitute for petrochemicals in polymer synthesis, and its unique structure offers insights into the relationship between form and polymer properties. Further investigation of the polymerization process and control over the resulting properties could lead to the development of even more advanced and sustainable soft materials in the future.

A Study on Conformations and Dynamics of Entangled Ring Polymers using Persistent Homology

Jacob D. Steeley, Grier M. Jones, Ting Ge, Konstantinos D. Vogiatzis

The prevalence of polymers in modern life necessitates the development of tools to characterize them at the molecular level. Molecular dynamics (MD) simulations are a common computational tool used to study polymers by providing comprehensive microscopic information with a tunable model. The bulk of MD trajectories can be post-examined using persistent homology (PH), a tool from topological data analysis (TDA), that measures the topological features of data. While the conformations and dynamics of conventional linear polymers are well understood, topologically non-trivial polymers such as non-concatenated yet entangled ring polymers have remained elusive. Previous studies have shown that PH can be used to describe the conformations of ring polymers in a melt. One method of utilizing PH in this manner has been to describe the topological constraints on a system using non-traditionally defined threading events, known as homological threading (H-threading). H-threading events are characterized by changes in a polymer's homological features, which are related to the presence of loops of neighboring ring polymers. The variation of H-threading along the MD trajectory is anticipated to further elucidate the dynamic environment of a polymer melt and thus benefit the processing and application of ring polymers as novel building blocks of polymeric materials.

Synthesis of Potential Oxidative Catalytic Tetra-NHC Cobalt Complexes

Joseph Tepper, Jerred Russell, David Jenkins

N-Heterocyclic Carbenes (NHCs) are strong σ -donor ligands, allowing them to stabilize atypical high oxidation states of first-row transition metals. Species such as oxos and imides are intermediates for catalytic oxidation reactions such as epoxidation and aziridination, respectively. Our group has studied catalytic aziridination with first-row transition metal complexes, including iron and chromium. We have recently transferred to investigating catalytic epoxidation as well on iron. My research focuses on shifting this catalytic reaction to cobalt. In this poster, I showcase the cobalt complexes that have been synthesized thus far by our group. These include a carbon-backboned ligand in addition to both chiral and achiral borate-backboned ligands, with special focus on the chiral ligands due to their proven ability to perform asymmetric oxidation catalysis (1).

1. Blatchford, K. M.; Mize, C. J.; Roy, S.; Jenkins, D. M. Toward Asymmetric Aziridination with an Iron Complex Supported by a D₂-Symmetric Tetra-NHC. *Dalton Transactions* 2022, 51 (16), 6153–6156.

Synthesis of Desonide Derivatives Using Aromatic Mercaptan Moieties to Improve Therapeutic Efficacy of Glucocorticoids

Clay West, Wesley Seaton, Shawn Campagna

Glucocorticoids are an important class of therapeutic steroids that have been utilized in the treatment of a large number of diseases due to their anti-inflammatory effects through binding to the glucocorticoid receptor (GR). Despite their utility as medicines, their prolonged use has also been shown to cause a whole host of undesirable side effects including steroid-induced diabetes. Due to the presence of these undesirable effects, there has been a lot of interest in synthesizing glucocorticoids that retain anti-inflammatory properties and minimize these negative side effects. Recent studies have found that the addition of a thiobenzothiazole moiety to the C22 carbon of hydrocortisone causes a large decrease in insulin impairment while retaining anti-inflammatory effects. This study expands on that finding through the synthesis of desonide derivatives with aromatic mercaptan moieties at the C22 position, which have slight differences in heteroatoms and size. Four derivatives were synthesized first by mesylation of the C22 alcohol on desonide followed by nucleophilic substitution of the appropriate mercapto group. The derivatives were subsequently characterized by NMR and IR spectroscopy as well as mass spectrometry. Finally, interactions with the GR binding pocket for each of the ligands were investigated by docking each ligand with the GR using computational modeling. It was found that all of the recorded spectra accurately represent the structures of each product, while docking studies with the GR showed that the mercaptan moieties strengthen interactions overall with the binding pocket, largely due to the size of the ring structures.

Exploring Conductance Behavior of Amine-mediated Aromatic Molecular Junctions

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The study of single molecule junctions has been a topic of great interest recently due to its importance in the emerging field of nanoelectronics. Despite a large body and theoretical work, reported models often overestimate the conductance by orders of magnitude. In experiment, conductance distributions are obtained via many single measurements, portraying the changes in conductance as the molecule adopts different geometries and occupies different electrode sites in the system. To elucidate the molecular and dynamical mechanisms underlying the observed variations in conductance, we have studied the internal motion of molecular junctions, using a combination of atomistic electrode-molecule-electrode models, density functional theory, and ab initio molecular dynamics. Working in the microcanonical ensemble, conductance is computed along a trajectory to construct conductance histograms. Specifically, systems with sulphur and nitrogen-terminated aromatic molecules bound between two gold electrodes have been investigated. Fourier transforms of conductance trajectories, illuminates the normal vibrational modes contributing the most to the calculated distributions. Our results highlight the chemical-dynamical properties that control conductance, and may offer potential targets for tailoring the conductance distribution.

Using Magnetic Circular Dichroism, Nuclear Magnetic Resonance, and Single Crystal-X Ray Diffraction to Investigate Diamine Ligand Interactions With Iron Phthalocyanine

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Phthalocyanine based molecules are one of the most promising electron donor/acceptor compounds that are being investigated for quantum computing purposes. These molecules show increased absorptivity, higher solubility, and higher potential for modification compared to fullerene-based donor/acceptors. These factors may result in higher power conversion ratios for phthalocyanine based donor/acceptors. Diamine based ligands have interesting curling interactions with the iron core of iron phthalocyanines that alter the molecular energy orbitals of the molecule and decrease the HOMO-LUMO gap.