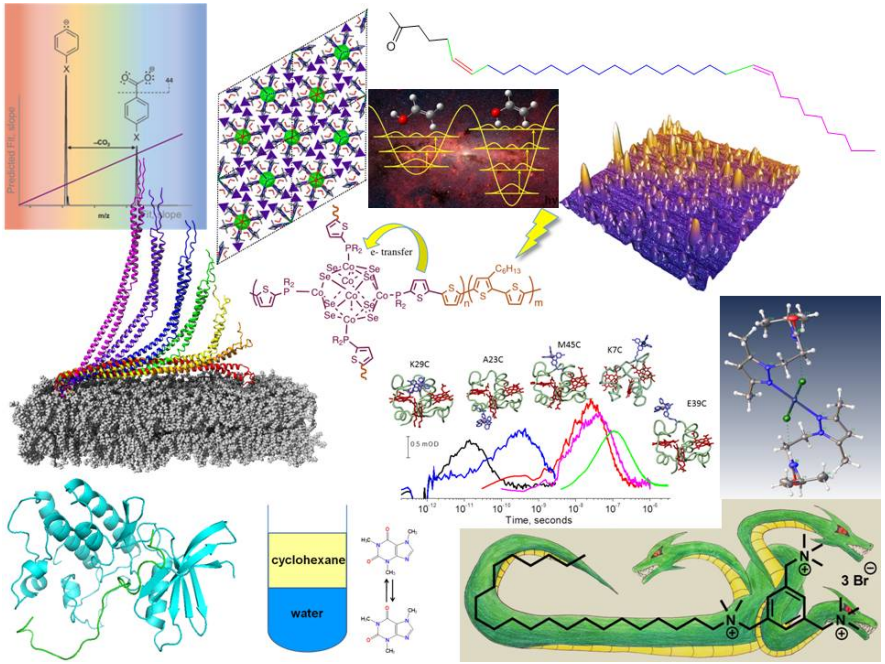
JAMES MADISON UNIVERSITY®

DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY



42ND ANNUAL SPRING UNDERGRADUATE RESEARCH SYMPOSIUM

THURSDAY MARCH 23, 2017

ORAL SESSION I: 1:00 – 4:15 PM (PCB 3216)

POSTER SESSION: 4:30 – 5:30 PM (PCB LOBBY)

FRIDAY MARCH 24, 2017

ORAL SESSION II: 1:15 – 3:30 PM (ISAT 259)

SPECIAL ANNOUNCEMENTS: 3:40PM (ISAT 159)

KEYNOTE ADDRESS: 3:45 – 4:45 PM (ISAT 159)

See back cover for image description.

42nd Annual Department of Chemistry and Biochemistry
Spring Undergraduate Research Symposium

Keynote Speaker

Dr. Zeric Hulvey, PhD

(JMU Class of 2004)

United States Department of Energy

Washington, DC

Zeric Hulvey received his B.S. in chemistry from James Madison University in 2004. His undergraduate research, under the direction of Prof. Barbara Reisner, focused on the synthesis of hybrid-inorganic organic frameworks. Zeric then received his Ph.D. in Inorganic Chemistry in 2010 from the University of California, Santa Barbara under the supervision of Prof. Anthony Cheetham. His doctoral work involved the synthetic and structural studies of metal-organic frameworks (MOFs) containing fluorinated ligands, primarily for gas adsorption applications. Dr. Hulvey then carried out postdoctoral work at the University of Nevada, Las Vegas with Prof. Paul Forster on the evaluation of MOFs for krypton/xenon separations. This was followed by a postdoctoral appointment at the University of Maryland, College Park from 2012-2015, where he carried out neutron diffraction and scattering experiments on gas adsorption in porous materials at the National Institute of Standards and Technology Center for Neutron Research under the direction of Dr. Craig Brown. Since 2015, Dr. Hulvey has been a fellow at the U.S. Department of Energy in Washington, DC, in the Office of Energy Efficiency and Renewable Energy's Fuel Cell Technologies Office (EERE-FCTO). His work supports FCTO's efforts to improve the range and cost of Hydrogen Fuel Cell Electric Vehicles by developing solid-state hydrogen storage materials as an alternative to high pressure compressed gas tanks.

Past Keynote Speakers

Each year we feature a keynote speaker for the Department's annual Spring Undergraduate Research Symposium. We are honored to have had speakers who are alumni of the department and are willing to come back and share with our students their experiences of "life after JMU". We thank each of these speakers and look forward to future alumni participation in Spring Symposium.

Year	JMU Class	Speaker	Affiliation
2017	2004	**Dr. Zeric Hulvey**	*United States Department of Energy*
2016	2007	**Dr. Reid Gadziala**	*Cleveland Clinic*
2015	1994	**Dr. Michael Leopold**	*University of Richmond*
2014	1996	**Dr. Dana McGraw Dattelbaum**	*Los Alamos National Laboratory*
2013	1999	**Dr. Christy Vestal Martin**	*Vorbeck Materials*
2012	1994 N/A	**Dr. Melissa C. Rhoten** **Dr. Orde Q. Monro**	*Longwood University* *University of KwaZulu-Natal*
2011	1992	**Dr. Morgan S. Sibbald**	*The Sherwin-Williams Company*
2010	1988	**Dr. Kevin Morris**	*Carthage College*
2009	1988	**Dr. Chris E. Holmes**	*The University of Vermont College of Medicine*
2008	1995	**Dr. Jonathan Dattlebaum**	*University of Richmond*
2007	1987	**Dr. Elizabeth Perry (M.D.)**	*Signature Healthcare, Inc.*
2006	1967	**Dr. Carolyn Abitbol (M.D.)**	*University of Miami (FL) School of Medicine*
2005	1975 1976	**Dr. Daniel Downey** **Dr. Gary Rice**	*James Madison University* *College of William and Mary*
2004	1987	**Dr. James (Dusty) Baber**	*National Institutes of Health*
2003	1984	**Dr. Fred King**	*West Virginia University*
2002	1977	**Dr. Roger Bertholf**	*University of Florida School of Medicine*
2001	1979	**Mrs. Katheryn Lam**	*International Business Machines*
1999	1987	**Dr. Jose Madalengoitia**	*University of Vermont*
1997	1986	**Dr. Fred R. Kinder**	*Novartis Research Institute*
1996	1976	**Dr. Terry O. Trask**	*DuPont Chemicals*
1995	1973	**Dr. Carl Lentz**	*Eastman Fine Chemicals*
1994	1990	**Dr. Michele A. Kelly**	*University of Maryland Baltimore County*
1993	1985	**Dr. Cynthia K. Fallon**	*DuPont Chemicals*
1992	1983	**Dr. Laurie Locascio**	*National Institute of Standards and Technology*
1991	1983	**Dr. Noreen Naiman**	*North Carolina School of Science and Mathematics*
1990	1982	**Dr. Matthew T. Stershic**	*Atomchem North Amercia*
1989	1982	**Dr. Michael Kinter**	*Cleveland Clinic Lerner Research Institure*
1988	N/A	**Dr. Thomas J. Meyer**	*Los Alamos National Laboratory*
1987	1980	**Dr. Steven Davis**	*Naval Research Laboratory*
1986	1980	**Dr. Steven A. Hackney**	*Michigan Technological University*
1983	1978	**Dr. Richard B. Lam**	
1982	1975	**Dr. Daniel Downey**	*West Virginia University*
1981	1959	**Mr. Ronald E. Ney**	*Environmental Protection Agency*
1980	N/A	**Dr. Stanley G. Sunderwirth**	*Metropolitan State College (Denver, CO)*
1979	1973	**Dr. Carl Lentz**	*Eastman Fine Chemicals*

Oral Session I: Thursday March 23, 2017 (PCB 3216)		
1:00 pm	Kortnie E. Holton and Dr. Linette M. Watkins	Identification of Novel Folate-binding Proteins
1:15 pm	R. Hunter Wilson and Dr. Isaiah Sumner	A Computational Investigation into the Mechanism of the Histone Acetyltransferase, Gcn5
1:30 pm	Tye S. Thompson, Anthony P. Allsbrook and Dr. Yanjie Zhang	Effects of Osmolytes on Caffeine Partitioning Thermodynamics
1:45 pm	David T. Boyle, Jeremy A. Wilke, Vivian H. Lam, Daniel A. Schlosser, Wil J. Andahazy, Cameron Z. Stopak and Dr. Ashleigh E. Baber	Elucidation of Active Sites for the Reaction of Ethanol on TiO_2/Au(111)
2:00 pm	Moira Lauer, Elizabeth Rogers, Christopher Kubow, Kyle Seifert and Dr. Kevin L. Caran	A Study of Fluorescent Quaternary Ammonium Amphiphiles to Gain Insight into the Mechanism of Antibacterial Activity
2:15 pm	Elijah T. Roberts and Dr. Barbara A. Reisner	Synthesis and Characterization of New Metal-Organic Materials Incorporating the Hydrotris(3,5-dimethyl-1,2,4-triazolyl)borate Ligand
2:30 pm	Break	
2:45 pm	Austin Miller and Dr. Isaiah Sumner	Comparing Force Fields with Density Functional Theory in Small, Solvated Peptides
3:00 pm	Walker M. Jones, Aaron G. Davis, Serban G Zamfir, and Dr. Isaiah C. Sumner	Computational Analysis of the Mechanism of the Ubiquitin Conjugating Enzyme UBC13
3:15 pm	Daniel R. Marzolf, Coleman Swaim, Aidan M. McKenzie, C. Alexander Hudson, Dr. Nathan T. Wright, and Dr. Oleksandr Kokhan	Porphyrin Induced Multimerization of Solution-State Proteins
3:30 pm	Jeremy A. Wilke, David Boyle, Daniel Schlosser, Vivian Lam, Wil Andahazy and Dr. Ashleigh E. Baber	Stabilization and Reaction of Small Molecules on TiO_2/Au(111) Inverse Model Catalysts
3:45 pm	Aidan M. Willey, Tracy A. Caldwell, Dr. Nathan T. Wright, and Dr. Isaiah C. Sumner	Obscurin Acts as a Variable Force Resistor
4:00 pm	Ryan T. Kelly and Dr. Christopher E. Berndsen	Conformational locking of Ufm1 upon binding to Uba5 UIS

(Student presenters underlined)

(See next page for Thursday poster presentations.)

Poster Session: Thursday March 23, 2017, 4:30 – 5:30 pm *(PCB lobby)*	
Kolin J. Kulzer, S. J. Johnston, T. Teears, and Dr. Daniel. M. Downey	Water Quality Improvement Plan for Montebello Fish Cultural Station
Austin B. Kilgore, Annie Lin, Dr. Debbie Mohler	Synthesis of Antisense Nucleic Acid Monomers
Rachel A. Policke and Dr. Nathan T. Wright	Examination of the Possible Auto-inhibitory Nature of Obscurin Kinase KII
Reafa A. Hossain and Dr. Christopher E. Berndsen	Structure of CRX and Epigenetic Regulation of DNA Binding
Killian Hull and Dr. Richard D. Foust	Changes to As, Cu, Fe, Mn and Zn Concentrations in Soil Resulting from the Application of Poultry Manure
NIthesh P Chandrasekharan and Dr. Christopher E. Berndsen	Proteolytic Activity of Ubiquitin C-Terminal Hydrolases (UCHs) on Pro-ubiquitin
Renna L. Nouwairi, Matthew D. Davisson, and Dr. Debbie L. Mohler	Synthesis of Antisense Nucleic Acid Monomers
Allyn G. Letourneau and Dr. Nathan T. Wright	High Resolution Structure of Titin ZIg10
Ty W. Faulkner, Dr. Gary Douberly and Dr. Paul Raston	Infrared Spectroscopic Investigation of Ozone Hydration in Superfluid Helium Nanodroplets
Coleman Swaim and Dr. Oleksandr Kokhan	Biological Semiconductors: Structural Control of Heme Redox Potentials in PpcA, a 3-Heme Cytochrome
Casey Noll and Dr. Isaiah Sumner	A Computational Study of the Interactions between the Histone Acetyltransferase, Gcn5, and a Histone Tail
Taylor N. Norman and Dr. Oleksandr Kokhan	Expression and Preliminary Characterization of OmcM
Tyler Palombo, Dr. Donna Amenta and Dr. John Gilje	Preparation of Palladium Complexes of N-pyrazolylpropanamide Derivatives
Annie Lin and Dr. Debbie Mohler	Synthesis of Antisense Oligonucleotide Analogues
Cassidy E. Jackson, Dr. Donna S. Amenta, and Dr. John W. Gilje	The Synthesis of Propanamide Derivatives of 1H-1,2,3-Triazole and their Reaction with Palladium Complexes
Vivian H. Lam, David T. Boyle, Jeremy A. Wilke, Nicholas L. Tosti, Maxwell Z. Gillum, and Dr. Ashleigh E. Baber	Unraveling the Relationship Between Nanoscale Morphology and Reactivity of TiO_2/Au(111) for Ethanol Conversion
Max E. Henderson and Dr. Christopher E. Berndsen	Computational Identification of Small-Molecule Ligands of Human and Leishmania Donovani Ufm1
Keid Idrizi, Dr. Linette Watkins, Dylan Hoang and Jacob Gumpf	Expression, Purification, and Characterization of Codon Optimized DszB from N. asteroides
Dylan Hoang, Emily Smith and Dr. Linette Watkins	Specificity Studies of the Aromatic Desulfinase, 2-(2'-hydroxyphenyl)Benzenesulfinate Desulfinase (DszB) from Nocardia Asteroides A3H1
Kearney M. Foss, Karen Fortmann and Dr. Christine A. Hughey	Targeted and Untargeted Metabolomic Profiling of a Pale Ale Brewed with Genetically Different Yeast Strains
Rebekah M. Soliday, Dr. Isaiah C. Sumner and Dr. Paul L. Raston.	Computational Analysis of the Geometry and Vibrational Frequencies of Syn- and Anti-Vinyl Alcohol
Jacob John Gumpf, Keid Idrizi and Dr. Linette Watkins	Expression, Purification, and Characterization of Codon Optimized and Mutant Variations of DszB from N. asteroides
Dr. Debra L. Mohler, Madelaine W. Fritsche and Ashley L. Creighton	Synthesis of Antisense Nucleic Acid Monomers for Therapeutic Benefit
Matthew O'Malley, Coleman Swaim, Daniel Marzolf, Aidan McKenzie and Dr. Oleksandr Kokhan	Exploring Ultrafast Charge Transfer in ppca-$Ru(bpy)_3$ Complexes
Michael Khafaji Zadeh, Andrew Nguyen, Bashir Noor and Dr. Kevin Caran	The Synthesis of Tetracationic Amphiphilic Viologens

(Student presenters underlined)

Oral Session II: Friday March 24, 2017 *(ISAT 259)*		
1:15 pm	Leanna C. Carter, Karen Fortmann, and Dr. Christine Hughey	Effect of yeast strain on the volatile profile of beer as determined by solid phase microextraction (SPME) GC/MS
1:30 pm	Daniel A. Corbin and Dr. Brycelyn M. Boardman	Recent Advances in the Optical and Structural Characterization of Organic-Inorganic Copolymers with Photovoltaic Applications
1:45 pm	Kenna Salvatore and Dr. Barbara Reisner	Synthesis of Metal Coordination Compounds Derived from 3-5-dimethyl-1,2,4-triazole
2:00 pm	Alexis Johnston, Dr. Scott B. Lewis, and Dr. Debra L. Mohler	Synthesis of 6,24-tritriacontene-2-one, a Brown Tree Snake Pheromone
2:15 pm	Wil J. Andahazy, Dr. Ashleigh E. Baber and Dr. Costel Constantin	Optical and Electrical Properties Investigation of 10-Minute Acid Treated PEDOT-PSS Thin Films
2:30 pm	Benjamin Ashamole, Elizabeth Rodgers, Emmanuel Ogunjirin, Dr. Kyle Seifert, Dr. Kevin Caran	Antimicrobial and Colloidal Properties of Novel Polycationic Amphiphiles
2:45 pm	Perrin Godbold, Dr. Samuel A. Morton, Dr. Thomas C. DeVore, and Dr. David J. Lawrence	Real Time Monitoring of Photocatalysis with TiO_2 Coated QCM Crystals
3:00 pm	Kevin Pyszka and Dr. Dan Downey	Atmospheric Acid Deposition Reduction and Stream Water Chemistry Response in Three Virginia Trout Stream
3:15 pm	Melanie T. Odenkirk, Ren T. Blackart, James M. Matilla, Michael L. Poltash, and Dr. Christine A. Hughey	Predictive Models of Negative Ion Electrospray Response Explored through Machine Learning Applications

(Student presenters underlined)

Special Announcements *(ISAT 159)*	
3:40pm	Announcement of Chemistry and Biochemistry Student Award Winners

Keynote Address: Friday March 24, 2017 *(ISAT 159)*		
3:45 - 4:45 pm	Dr. Zeric Hulvey JMU Class of 2004	Hydrogen Storage Materials for Vehicular Applications

Keynote Address

Friday, March 24, 2017 at 3:45pm
ISAT Room 159

Hydrogen Storage Materials for Vehicular Applications

Dr. Zeric Hulvey, PhD
(JMU Class of 2004)
United States Department of Energy
Washington, DC

The U.S. Department of Energy's Fuel Cell Technologies Office covers a comprehensive portfolio of activities that address the full range of barriers facing the development and deployment of hydrogen and fuel cells with the ultimate goals of decreasing our dependence on oil, reducing carbon emissions, and enabling clean, reliable power generation. Over the past two decades, the most significant of these efforts has been aimed at the eventual widespread introduction of Hydrogen Fuel Cell Electric Vehicles (FCEVs). A few car companies have begun selling FCEVs; however, several hurdles still must be overcome before they can be more widely introduced. One of the most challenging technical hurdles involves the method in which sufficient hydrogen is stored on the vehicle to allow for a driving range of 300 or more miles, with similar cost, safety, reliability, and performance to gasoline vehicles. Current commercially available FCEVs utilize onboard 700 bar compressed gas storage in relatively large, expensive, and heavy carbon fiber overwrapped pressure vessels. Certain solid-state materials, such as metal hydrides or porous adsorbents, have the potential to store greater volumes and masses of hydrogen than can be stored even at elevated pressures due to the very low density of hydrogen gas. These materials do so either through a chemical interaction with hydrogen where the molecules are dissociated and absorbed into a medium and then released by heating, or through simpler physisorptive interactions with porous surfaces where hydrogen molecules can achieve short intramolecular distances and high densities. This presentation will cover past and current efforts to develop hydrogen storage materials, focusing on the chemical challenges facing the optimization of hydrogen-material interactions for practical applications.

STUDENT ABSTRACTS

(Student presenters underlined)

Optical and Electrical Properties Investigation of 10-Minute Acid Treated PEDOT-PSS Thin Films

Wil J. Andahazy[1], Dr. Ashleigh E. Baber[1] and Dr. Costel Constantin[2]
[1]Department of Chemistry and Biochemistry, James Madison University, Harrisonburg, VA 22807
[2]Department of Physics and Astronomy, James Madison University, Harrisonburg, VA 22807

Poly(3,4-ethylenedioxythiophene) poly(4-styrenesulfonate) (PEDOT-PSS) is one of the most promising transparent conductors which has applications in flexible electronics including organic light emitting diodes (OLEDs), organic photovoltaics (OPVs), and organic field transistors (OFETs). Recently, scientists discovered that post-treatment with sulfuric acid of PEDOT-PSS thin films result in electrical conductivity increase and a UV absorption decrease due to the replacement of majority of PSS with sulfate ions (SO_4^{2-}). However, the optical properties of this material are not very well understood. In this report, we prepare PEDOT-PSS thin films by spin-coating and drop-casting onto microscopic slides, and then we submerge these films into 18-molar sulfuric acid for 10 minutes. In order to measure optical properties we used a HS-190 variable angle spectroscopic ellipsometer with a wavelength range of 200-2500 nm, and for the electrical properties we used a homemade van der Pauw set up. This investigation provides a clearer picture of the correlation between optical dielectric constants and electrical conductivity.

Antimicrobial and Colloidal Properties of Novel Polycationic Amphiphiles

Benjamin Ashamole[1], Elizabeth Rodgers[2], Emmanuel Ogunjirin[1], Dr. Kyle Seifert[2] & Dr. Kevin Caran[1]
[1]Department of Chemistry and Biochemistry, James Madison University, Harrisonburg, VA 22807
[2]Department of Biology, James Madison University, Harrisonburg, VA 22807

Four novel series of amphiphiles with six heads and three tails, or four heads and two tails were synthesized and minimum inhibitory concentration (MIC) against seven bacterial strains (including two Gram negative strains) were tested. Critical aggregation concentrations (CAC) were also measured through conductivity analysis for these amphiphiles. Amphiphiles in this study have either a mesitylene or a xylene core. The amphiphiles with a mesitylene core have three benzylic diammonium groups, each of which has an alkyl chain (8, 10 or 12 carbons in length). The amphiphiles with a xylene core have two benzylic diammonium groups, each having an alkyl chain (8, 10, or 12 carbons in length), substituted *ortho*, *meta*, and *para*. Based on data collected thus far, antibacterial activity appears to decrease with increasing tail length. One representative compound was able to inhibit growth in Escherichia coli which has developed resistance to some antibiotics, at concentrations as low as 2 µM. With MIC values this low, these amphiphiles show promise as future antibacterial agents that could be used in various fields. CAC values follow an expected trend with longer chain lengths having lower values due to decreased solubility in water.

Elucidation of Active Sites for the Reaction of Ethanol on TiO_2/Au(111)

David T. Boyle, Jeremy A. Wilke, Vivian H. Lam, Daniel A. Schlosser, Wil J. Andahazy, Cameron Z. Stopak and Dr. Ashleigh E. Baber
Department of Chemistry and Biochemistry, James Madison University, Harrisonburg, VA 22807

Obtaining a molecular-level understanding of the reaction of alcohols with heterogeneous model catalysts is critical for improving industrial catalytic processes, such as the production of H_2 from alcohols. Gold has been shown to be an excellent oxidation catalyst once oxygen is added to it. The use of reducible oxides provides a source of oxygen on Au(111) for the reaction of ethanol, which is easily regenerated in the presence of an oxygen background. In this work, ethanol operates as a probe molecule to investigate the role of Au(111), TiO_2 nanoparticles, and TiO_2/Au interfacial surface sites on the catalytic properties of TiO_2/Au(111). Ultrahigh vacuum temperature programmed desorption (TPD) studies with ethanol/Au(111) elucidate previously unreported adsorption sites for ethanol. Ethanol molecularly adsorbs to Au terrace sites, step edges, and under-coordinated kink sites with adsorption energies of -51.7 kJ/mol, -55.8 kJ/mol, and -65.1 kJ/mol, respectively. A TPD coverage study of ethanol on TiO_2/Au(111) indicates ethanol undergoes dissociative adsorption to form H*(a) and CH_3CH_2O*(a) on the inverse model catalyst surface. The desorption temperature of low coverages of ethanol from TiO_2/Au(111) (T_{des}= ~235 K) is at an intermediate temperature between the desorption temperatures from bulk Au(111) and TiO_2(110), indicating both Au and TiO_2 play a role in the adsorption of ethanol. Both low temperature adsorption and high temperature reactions are studied, and indicate that ethanol-derived products, acetaldehyde and ethylene, desorb from TiO_2/Au(111) at ~500 K.

Effect of yeast strain on the volatile profile of beer as determined by solid phase microextraction (SPME) GC/MS

Leanna C. Carter[1], Karen Fortmann[2] and Dr. Christine Hughey[1]
[1]Department of Chemistry and Biochemistry, James Madison University, Harrisonburg, VA 22807
[2]White Labs, San Diego, CA

Headspace solid phase microextraction (HS-SPME) is a method used to adsorb and concentrate volatiles from the headspace of a sample. The analytes are desorbed from the SPME fiber into the GC inlet, then separated by GC and quantified by MS. Eighteen standard compounds suggested by New Belgium Brewery and White Labs were used to optimize a previously developed SPME method. The optimized method decreased variability between SPME fibers and replicate samples through consistent incubations, extractions, desorptions, GC conditions and MS peak integration. In addition, several compounds were evaluated for use as an internal standard. 2-ethyl-1-butanol was selected. Overall RSDs were reduced from 30% to less than 10% for most compounds by controlling SPME incubation times and temperatures. The optimized method was used to compare the volatile metabolites in a simple pale ale fermented with four genetically different yeast strains. Twenty three compounds (all with NIST scores >70) were putatively identified across the different yeast strains. These compounds include 13 esters, four alcohols, one ketone, two acids, two terpenes and styrene. Fifteen of these compounds were present in all beer samples, regardless of yeast type. Presently, only two compounds appear unique to a particular yeast. Amyl acetate was unique to the California ale yeast and isoamyl octanoate was unique to the Belgium saison. Some of these compounds have been confirmed by matching to standards, other confirmations are in progress. Furthermore, the number of compounds identified will continue to increase as we work to improve extraction of EI mass spectra and sample alignment in Mass Profiler Professional. Preliminary statistical analysis and hierarchical clustering show that while many of the same compounds are observed in the headspace, the abundance varies with yeast strain. Upon further investigation these differences may serve as a fingerprint for that particular yeast.

Proteolytic Activity of Ubiquitin C-Terminal Hydrolases (UCHs) on Pro-ubiquitin

Nithesh P. Chandrasekharan and Dr. Christopher E. Berndsen
Department of Chemistry and Biochemistry, James Madison University, Harrisonburg, VA 22807

Ubiquitin is a 76 amino acid protein that marks proteins for degradation in a cell. However, before ubiquitin can be used to modify proteins, the polypeptide must be cleaved from the raw form that is made from ribosomes called pro-ubiquitin. Pro-ubiquitin consists of a ubiquitin fused in-frame to either an amino acid, a ribosomal protein, or another ubiquitin. Ubiquitin C-terminal Hydrolases (UCHs) are the de-ubiquitinases that break the peptide bond between ubiquitin and the C-terminal fusion. In humans, there are 5 UCHs that are proposed to cleave pro-ubiquitin substrates, however in S. cerevisiae there is only 1 known UCH, YUH1. Our goals are to determine if YUH1 does cleave pro-ubiquitin substrates and to identify any other UCH enzymes in yeast that could cleave the pro-ubiquitin substrates. We have purified pro-ubiquitin cleaving activity from yeast cells and are moving towards identifying the UCH that has this activity. Future work will include refinement of the purification process, purifications based on other pro-ubiquitin substrates and in vitro activity assays.

Recent Advances in the Optical and Structural Characterization of Organic-Inorganic Copolymers with Photovoltaic Applications

Daniel A. Corbin and Dr. Brycelyn M. Boardman
Department of Chemistry and Biochemistry, James Madison University, Harrisonburg, VA 22807

Hybrid organic-inorganic materials have recently gained interest in the scientific community due to their potential to offer more efficient, solution processable photovoltaics. However, these materials are often simple mixtures of organic and inorganic materials, which suffer from phase separation due to the components' orthogonal properties. To investigate the impact of covalent attachment of the organic and inorganic components in these systems, we synthesized a new series of copolymers via Stille coupling with a constant amount of $(Me_3Sn)_2(C_4H_2S)$ and varying ratios of $Co_6Se_8(Br(C_4H_2S)P(Ph)_2)$ (**1**) to $Br_2(C_4HS)(CH_2)_5CH_3$; these copolymers have been named poly(cluster-co-thiophene-co-hexylthiophene)a-c (**PCLTHTa-c**). To date, we have demonstrated successful attachment of the organic and inorganic components, as well as shown increased charge transfer in the hybrid copolymers when compared to representative simple mixtures of the donor and acceptor materials. However, two issues have remained unsolved: 1) comprehensive structural characterization of the copolymers, which has failed through traditional characterization techniques due to their complex nature, and 2) complete characterization of the copolymers' thin films. Herein, we present recent advances in each of these areas. Using ligand exchange reactions in conjunction with UV-visible, fluorescence, and NMR spectroscopy, the polymers' components were separated and the organic portions analyzed. In addition, several techniques were used to study the copolymers' thin film properties, including UV-visible and fluorescence spectroscopy as well as cyclic voltammetry.

Infrared Spectroscopic Investigation of Ozone Hydration in Superfluid Helium Nanodroplets

Ty W. Faulkner[1], Dr. Gary Douberly[2] and Dr. Paul Raston[1]
[1]Department of Chemistry and Biochemistry, James Madison University, Harrisonburg, VA 22807
[2]Department of Chemistry, University of Georgia, Athens, GA 30602

Helium is unique amongst the chemical substances in that it remains liquid down to the lowest possible temperatures. Upon cooling to below 2.2 K helium becomes superfluid, possessing strange properties such as zero viscosity and frictionless flow. Superfluid helium nanodroplets have been referred to as the ultimate spectroscopic "matrix" because of their low temperature (T = 0.4 K) and weakly interacting nature, which leads to greatly simplified spectra relative to the gas phase [1]. They are particularly useful for synthesizing molecular complexes, and several previous investigations have focused on investigating the hydration of atmospherically important molecules, such as the hydroxyl radical [2]. While ozone-water complexes are of significance to atmospheric chemistry, little is known experimentally beyond the ozone-water dimer. In this study we focus on isolating O_3-$(H_2O)N$ complexes in helium nanodroplets, and on uncovering their infrared signatures using laser spectroscopy.

[1] K.K. Lehmann and G. Scoles. Science 279, 2065 (1998).
[2] F. J. Hernandez et al. The Journal of Chemical Physics 143, 164304 (2015).

Targeted and Untargeted Metabolomic Profiling of a Pale Ale Brewed with Genetically Different Yeast Strains

Kearney M. Foss[1], Karen Fortmann[2] and Dr. Christine A. Hughey[1]
[1]Department of Chemistry and Biochemistry, James Madison University, Harrisonburg, VA 22807
[2]White Labs, San Diego, CA

A pale ale was brewed by White Labs (San Diego, CA) and fermented with four genetically yeasts: a California ale yeast, an English ale yeast, a neutral grain yeast, and a Belgium saison yeast. The Belgium saison yeast was contaminated during fermentation, so it was excluded from the analysis. Beer samples were collected during and at the end of fermentation. Each sample was profiled with both positive and negative ion ESI LC q-TOF MS. After molecular feature extraction, metabolites were matched to metabolites in known Saccharomyces cerevisiae pathways. Only a few metabolites in the final beer samples were matched. These include malic acid, 5-methylthioadenosine (5-MTA), tryptophan, and phenylalanine (all confirmed by matching retention times to standards). Malic acid is part of the TCA cycle and 5- MTA is part of polyamine biosynthesis pathway. Both tryptophan and phenylalanine were matched to multiple pathways. The abundance of malic and tryptophan varied little across the samples, with RSDs of 7% and 3%, respectively. More differentiation was observed for phenylalanine (20%) and 5-MTA (48%). Samples collected during fermentation yielded more matches to the S. cerevisiae library. We are currently analyzing this data. The limited success of the targeted experiments led us to simultaneously pursue untargeted experiments. Hierarchical clustering, PCA plots and Venn diagrams were used to globally compare the composition of the final samples and to identify unique molecular features (3-12%), in hopes of identifying chemical signatures characteristic of each yeast type.

Synthesis of Antisense Nucleic Acid Monomers for Therapeutic Benefit

Dr. Debra L. Mohler, Madelaine W. Fritsche and Ashley L. Creighton
Department of Chemistry and Biochemistry, James Madison University, Harrisonburg, VA 22807

RNA can act naturally as a therapeutic agent due to its gene silencing capabilities. Antisense oligonucleotides (ASOs) are short sequences of RNA that run 3' → 5' (hence "antisense") that bind to a complementary segment of mRNA to prevent translation of mRNA into proteins. ASOs can be used therapeutically to prevent the expression of sequences of DNA into harmful proteins, which may become phenotypically evident. Naturally occurring antisense oligonucleotides, generated by RNAi, face the risk of degradation due to the structure of the sugar-phosphate backbone. Therefore, synthetic oligonucleotide analogs are being developed to artificially silence gene expression while avoiding degradation. Assuming the sequence of the target mRNA is known, complementary sequences of synthetic ASOs can be designed to hybridize with the sense mRNA to inhibit translation. Our goal is to synthesize cyclic nucleic acid monomers that can be used in a ring-opening metathesis reaction to form oligonucleotide analogues. This strategy differs from previous work because rather than using a stepwise approach (protecting each base, linking it, deprotecting it, protecting the next base, linking it, deprotecting it, etc.), we are using a templated ring-opening metathesis polymerization to link the bases in one step. These synthetic ASOs may have potential use in a variety of human diseases, including cancers and viral infections.

Real Time Monitoring of Photocatalysis with TiO_2 Coated QCM Crystals

Perrin Godbold[1], Dr. Samuel A. Morton[2], Dr. Thomas C. DeVore[1], and Dr. David J. Lawrence[3]
[1]Department of Chemistry and Biochemistry, James Madison University, Harrisonburg, VA 22807
[2]Department of Engineering, James Madison University, Harrisonburg, VA 22807
[3]Department of Integrated Science and Technology, James Madison University, Harrisonburg, VA 22807

The quartz crystal microbalance (QCM) is a well-used analytical tool, capable of detecting mass changes on the nanogram scale. Titanium dioxide (TiO_2) is a much studied photocatalyst. This project attempts to combine these to investigate the capabilities of the QCM as a real-time mass sensor to monitor catalytic reactions. Theoretically, this application would allow for the elucidation of any reaction able to be photolyzed by TiO_2. TiO_2 is well studied and modified but for simplicity this project does not enhance the photocatalyst. Two common reactions undertaken with TiO_2 are the degradation of organics for waste water remediation and water splitting for the production of hydrogen fuel. TiO_2 suspended in a PAA solution was deposited onto QCM crystals by spin coating. Simple organics were tested for the development of this sensor, and their photochemical degradation was confirmed with Fourier transform infrared spectroscopy.

Expression, Purification, and Characterization of Codon Optimized and Mutant Variations of DszB from N. asteroides

Jacob John Gumpf[1], Keid Idrizi[2] and Dr. Linette Watkins[2]
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2-(2'-hydroxyphenyl)benzenesulfinate desulfinase (DszB) catalyzes the final carbon-sulfur bond cleavage reaction in the rate-limiting step in the biodesulfurization of dibenzothiophene, a recalcitrant organosulfur compound found in fossil fuels. The dszb gene from Nocardia asteroides (A3H1) was codon-optimized and overexpressed in E. coli. Expression was examined by FT-IR and activity assays. His-tagged DszB expressed from a codon-optimized gene requires co-expression with GroEL and GroES to fold properly. The DszB enzyme was purified using a Ni^{2+} column, and a k_{cat} of 52.8 ± 5.49 hr^{-1} and a K_m of 3.71 ± 0.60 μM was determined. Enzyme stored in aliquots containing 15% DMSO was stable at -80 °C for several weeks. DszB has optimal activity at 35 °C but is not stable for longer than 30 minutes at room temperature. Three mutated enzymes were expressed, purified and characterized. The A195R, A200R, and A195R/A200R DszB mutant altered kinetic parameters, increased temperature optimum, and increased temperature stability.

Computational Identification of Small-Molecule Ligands of Human and Leishmania Donovani Ufm1

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Ubiquitin-fold modifier 1 (Ufm1) is a widely conserved ubiquitin-like protein that is transferred to protein lysine amines in a process called ufmylation. Ufmylation regulates blood cell differentiation and promotes cell survival during stressed states such as following heart attacks. Here we studied the structure of the Ufm1 homologs found in humans and the intracellular parasite *Leishmania donovani* and identified small molecules that bind to each homolog. First, we virtually screened four small-molecule libraries, totaling 20,775 compounds, against hUfm1. We identified 16 ligands that bind with a predicted affinity below 2 μM. Molecular dynamics simulations were then run on the top hits to determine the stability of the ligand interactions. We next screened the *L. donovani* homolog of Ufm1 to compare small molecule binding and specificity. In order to screen LdUfm1, we first homology modeled the structure and equilibrated the structure to improve model quality. The four libraries were then screened against the equilibrated structure of LdUfm1 which led to 15 hits. Analyses of the final hits determined that of the 31 total ligands below the cutoff for each Ufm1 homolog, only 4 bound to both homologs within the given limits. We next aim to measure the binding energies for the molecules *in vitro* to verify the *in silico* results. The data provided by these studies will assist in elucidating the mechanics of Ufm1 binding events and may shed light on molecules of therapeutic interest.

Specificity Studies of the Aromatic Desulfinase, 2-(2'-hydroxyphenyl)Benzenesulfinate Desulfinase (DszB) from Nocardia Asteroides A3H1

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2-(2'-hydroxyphenyl)benzenesulfinate desulfinase (DszB) is a desulfinating enzyme that catalyzes the final carbon- sulfur bond cleavage reaction in the biodesulfurization (BDS) of dibenzothiophene (DBT), a major organosulfur compound in fossil fuels. Homology studies suggest that Alanine 195 and Alanine 200 are important in determining the specificity of the active site. Point mutations were created to determine the effect of switching A200 to an Arginine (A200R), as well as switching A195 to an Arginine (A195R) and switching both A195 and A200 to Arginine (A195/200R). By altering amino acids in the active site of DszB, the effects of amino acid A195 and A200 on the active site specificity can be determined. Codon optimized DszB was cloned into pTAC-MAT-Tag-2, overexpressed in E. coli, and purified using a Ni2+ column. Enzyme stored in aliquots containing 15% DMSO was stable at -80 Â°C for several weeks. The natural substrate 2-(2'-hydroxyphenyl)benzenesulfinate (HPBS) was tested, along with the smaller ring analogs 2-(2'-hydroxyphenyl)enthen-1-sulfinate (HPES) and benzenesulfinate (BS), in order to test whether the active site prefers one, two or three rings. The kinetic data of the codon optimized DszB showed a K_m of 3.71 ± 0.60 μM and k_{cat} of 52.8 ± 5.49 hr^{-1}. The specificity of DszB-A3H1-A200R showed a change in specificity, preferring HPES over BS.

Identification of Novel Folate-binding Proteins

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Folic acid is a critical nutrient that serves as a cofactor in many metabolic pathways. Food testing assays detect only one form of folic acid. In an effort to identify enzymes that could be used to develop assays that detect multiple forms of folate in food, soil samples were screened for a bacterium capable of using folic acid as a single carbon source. A gram-negative bacterium capable of growing on folic acid as a sole-carbon source was isolated and characterized. 16S rRNA sequencing identified the organism as a strain of Stenotrophomonas maltophilia. Cells were harvested, lysed, and the cell lysate was passed through a folate affinity column. Protein eluted off the column with a folate solution was quantitated, concentrated, and isolated by SDS-PAGE. The resulting bands were excised, digested with trypsin, and sequenced by LC-MS. The sequenced protein was not identified in any sequencing database. NGS analysis of isolated chromosomal DNA will be used to identify the gene that codes for the novel folate binding protein.

Structure of CRX and Epigenetic Regulation of DNA Binding

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The process of synthesizing a strand of RNA from DNA or transcription is controlled by proteins that regulate RNA polymerase activity by binding to specific gene regulatory sequences. One such protein is the cone-rod homeobox (CRX), a mammalian transcription factor that controls photoreceptor gene expression.Homeodomain proteins, such as CRX, bind to DNA through hydrogen bonding and van der Waals interactions typically in the major groove of DNA. Methylation of DNA within the CRX binding site on DNA is thought to block CRX binding and therefore regulate gene transcription. While much is known about the functions and DNA binding specificity of CRX, less is known about the structure including how methylation might block DNA binding. Therefore we used molecular modeling to propose a structure of CRX and study how DNA modification would affect DNA binding. Using the model, we can explain how CRX mutations associated with retinal dystrophy and retinitis pigmentosa (RP) induce altered protein function. These data support that the modeled structure reflects the actual structure of CRX. Docking of CRX to the consensus CRX motif produces complexes that are comparable DNA-protein complexes of sequence related proteins. Molecular dynamics simulations of the DNA binding site with and without methylation suggest changes in the flexibility and groove widths upon modification. These structural alterations may be the basis for the regulation of CRX DNA binding by DNA methylation.

Changes to As, Cu, Fe, Mn and Zn Concentrations in Soil Resulting from the Application of Poultry Manure

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The objective of this study was to determine the how quickly fields that have been treated with poultry manure containing arsenic residue from Roxarsone return to background arsenic levels. Samples were taken from a field that had been treated with poultry manure and a control site directly adjacent to the treated field. The farm where samples were collected is located approximately 20 miles north of Harrisonburg, in the Shenandoah Valley. Soil was sampled with a soil auger. Twelve samples were taken from the treated field, 12 samples were taken from the control, and each sample was divided into two portions representing the top soil layer and a lower soil layer. Soils were extracted with a solution of acetic acid for iron, manganese, copper and zinc determinations, and digested with nitric acid, hydrogen peroxide and hydrofluoric acid for arsenic determinations. Arsenic concentrations were determined using Graphite Furnace Atomic Absorption (GFAA) with Zeeman background correction. Zinc, copper, manganese, and iron concentrations were determined using Flame Atomic Absorption (FAA). The data were analyzed with a one-way Analysis of Variance test (95% confidence level). There was no notable difference between the arsenic levels in the control (4900-25000 μg/kg) and the samples (4200-29000 μg/kg).

Expression, Purification, and Characterization of Codon Optimized DszB from N. asteroids

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2-(2'-hydroxyphenyl)benzenesulfinate desulfinase (DszB) catalyzes the final carbon-sulfur bond cleavage reaction in the rate-limiting step in the biodesulfurization of dibenzothiophene, a recalcitrant organosulfur compound found in fossil fuels. The dszb gene from Nocardia asteroides (A3H1) was codon-optimized and overexpressed in E. coli. Expression was examined by FT-IR and activity assays. His-tagged DszB expressed from a codon-optimized gene requires co-expression with GroEL and GroES to fold properly. The DszB enzyme was purified using a Ni^{2+} column, and kinetic constants were determined. Enzyme stored in aliquots containing 15% DMSO was stable at -80 °C for several weeks. DszB has optimal activity at 35 °C but is not stable for longer than 30 minutes at room temperature. Three mutated enzymes were expressed, purified and characterized. The A195R, A200R, and A195R/A200R DszB mutant altered kinetic parameters, temperature optimum, and temperature stability.

The Synthesis of Propanamide Derivatives of 1H-1,2,3-Triazole and their Reaction with Palladium Complexes

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A propanamide derivative of 1H-1,2,3-triazole was successfully synthesized from the reaction between 1H-1,2,3-triazole and acrylamide with Triton B as a catalyst. Two isomers formed: 3-(1H-1,2,3-triazol-1-yl) propanamide (**1**) and 3-(2H-1,2,3-triazol-2-yl) propanamide (**2**). These were separated by fractional crystallization. The two isomers were characterized by NMR and IR spectroscopy. Bis(benzonitrile)dichloropalladium(II) and potassium tetrachloropalladate(II) appear to react with **1** but not with **2**. These reactions are still being characterized.

Synthesis of 6,24-tritriacontene-2-one, a Brown Tree Snake Pheromone

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Boiga irregularis, the brown tree snake unintentionally transported to Guam during World War II, has greatly reduced the native biodiversity on the island of Guam. The use of snake pheromones to control and eventually eliminate the snake population on Guam will be tested upon the successful synthesis of the six identified organic compounds present in the brown tree snake pheromone. These identified compounds are methyl ketones ranging from 33 to 39-long carbon chains. The synthesis of the titled compound, will be completed using alkyne nucleophiles to produce the 33-long carbon chain methyl ketone. The five other synthetically similar organic compounds will be synthesized in a similar manner.

Computational Analysis of the Mechanism of the Ubiquitin Conjugating Enzyme UBC13

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Post translational modification (PTM) is a process by which proteins are chemically altered after they have been assembled. In one such PTM, lysine ubiquitination, the small protein ubiquitin is added to the lysine of a target protein via a thioester aminolysis reaction. This reaction is catalyzed by a series of enzymes. The second enzyme in this cascade, E2, which is covalently linked to ubiquitin, transfers ubiquitin to the target lysine. The accepted mechanism for ubiquitination is a stepwise mechanism that creates an oxyanion intermediate. This intermediate is hypothesized to be stabilized by an "oxyanion hole." In Ubc13, the E2 enzyme under investigation here, there is an asparagine sidechain that is hypothesized to serve as the oxyanion hole. However, the validity of the accepted mechanism has come into question and because recent studies have suggested a structural role for this residue. In our study, molecular dynamics was used to examine the hydrogen bonding environment of the active site in two structures of Ubc13 and determine the likelihood for the formation of the oxyanion hole. Furthermore, a combination of metadynamics, a rare-events sampling method, and hybrid quantum mechanics/molecular mechanics (QM/MM) was used to find potential reaction pathways and to then calculate their relative barrier heights.

Conformational locking of Ufm1 upon binding to Uba5 UIS

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Ubiquitin fold modifier 1 (UFM1) is an ubiquitin-like protein (UBL) found in eukaryotic organisms which plays a crucial role in cell cycle regulation, signal transduction, and more. A three step enzymatic pathway composed of enzymes E1, E2, and E3 is utilized to attach UFM1 to its target protein. This conjugation pathway is common to Ubiquitin and other UBL proteins such as UFM1, ATG8, and SUMO. The crystal structure of UFM1 and its E1 (UBA5) in complex shows that UFM1 binds to the adenylation domain of UBA5 and interacts with a separate ubiquitin interacting sequence (UIS) in the C-terminus of UBA5. The UIS interacts with UFM1 on the opposite side of the UBL protein from the adenylation domain. The reason for this second interaction site is unclear. Through molecular dynamics simulations, we analyzed UFM1 bound to the UIS sequence in the absence of the UBA5 adenylation domain. The residues in the adenylation interaction site of UFM1 have less movement when the UIS peptide was bound to UFM1 and formed a structure that aligns well with UFM1 bound to the UBA5 adenylation domain. These data suggest the UIS induces formation of the proper structure for interacting with UBA5 and may enhance the affinity by locking the conformation of UFM1. The “locked” conformation of UFM1 is observed in the absence of the peptide, but less frequently. Through additional simulations on Ubiquitin and Ubiquitin-like proteins, we show that similar allosteric trends exist for ATG8 which like UFM1 uses a non-canonical E1 enzyme while Ubiquitin and SUMO do not show this behavior. Ubiquitin and SUMO, instead show increased motion (“unlocking”) upon binding to known interacting partners. Non-canonical E1 enzymes lack of some substrate binding domains found in the canonical E1 enzymes suggesting this locking mechanism may compensate for the lack of these domains.

Synthesis of Antisense Nucleic Acid Monomers

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Antisense oligonucleotides (ASOs) are important because of their ability to selectively hinder or silence the expression of genes. The sugar-phosphate backbone of natural oligonucleotides degrades relatively quickly within the body, which has led to the study of synthetic analogues lacking this feature. Progress towards the synthesis of monomers leading to a more stable glycidyl backbone will be discussed.

Water Quality Improvement Plan for Montebello Fish Cultural Station

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Montebello Fish Culture Station in Nelson County Virginia operated by Virginia Department of Game and Inland Fisheries (VDGIF) is the oldest state owned facility in the Commonwealth for trout production. Initially constructed in 1929, the fish production facility consists of thirty four concrete ponds in a raceway that utilizes a large spring as the main water source. The spring originates from a granite rock formation and discharges water that is low in pH, calcium and alkalinity. To improve water quality and increase trout production at the hatchery, it is hypothesized that the addition of limestone could increase the pH and enhances other water quality parameters. Preliminary tests were conducted in the laboratory to study the dissolution rate of limestone in de-ionized and tap water. These trial experiments were conducted with old rain gutters filled with limestone of varying sizes and qualities. Metrics included particle size, geometry, temperature, flow rate, bed length and depth. Assays included measurement of pH, alkalinity, dissolved calcium, conductivity, and other components of water discharged from the troughs. Results showed that Frazier # 8 (0.625, 35.6% calcium) limestone was the best quality product based on dissolution rate. The second stage of this research (currently in progress) is pilot scale tests at Montebello using spring water fed into a 30’ trough, then into a 350 gallon tub with rainbow trout. If successful the treatment will be put in place as an integral part of the operation of the facility. Phase I of this project was funded with a JMU environmental sustainability grant. Phase II is being funded by the 4VA program.

Unraveling the Relationship Between Nanoscale Morphology and Reactivity of TiO_2/Au(111) for Ethanol Conversion

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Understanding the relationship between surface structure and reactivity can help guide the design of more efficient catalysts. Inverse model catalysts (oxide nanoparticles supported on metal substrates) have shown high reactivity for industrial catalytic reactions. In particular, TiO_2 nanoparticles supported on Au(111) have shown promise for alcohol (methanol, ethanol, and propanol) decomposition, the water gas shift, and hydrogen dissociation reactions. The growth and reactivity of TiO_2/Au(111) inverse model catalysts were characterized in an effort to elucidate the relationship between the surface morphology and its reactivity for ethanol conversion. The effect of surface preparation on morphology was studied using atomic force microscopy (AFM). AFM imaging showed a lower density of particles after high temperature anneals, indicating sintering occurs at higher temperatures. Temperature programmed desorption was used to study the reactivity of the model catalyst surfaces. High temperature surface preparation yields a different desorption trace for ethanol derived products in comparison to the low temperature surface preparation.

A Study of Fluorescent Quaternary Ammonium Amphiphiles to Gain Insight into the Mechanism of Antibacterial Activity

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The ever-pressing issue of antibacterial resistance necessitates the development and synthesis of novel antibacterials. By understanding the mode of attack for these antibacterial compounds, their effectiveness can be maximized. The arena of synthetic amphiphilic antibacterial compounds is continuously expanding as their proposed mechanism may prevent the rapid onset of resistance traits seen with previous antibacterials. We have synthesized and purified several amphiphilic antibacterial compounds in which we have incorporated a fluorescent head group. The inclusion of the fluorophore acridine orange in the underlying amphiphiles’ structures may allow us to visualize their interaction with bacteria. Fluorescence spectroscopy reveals an interesting characteristic of the selected fluorophore: an intensity shift accompanying a change in the polarity of its surroundings. Ongoing work includes biological activity studies, isolation and visualization of our antibacterial compounds with live bacterial cultures utilizing the confocal microscope, and further syntheses to prepare more effective derivatives.

High Resolution Structure of Titin ZIg10

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Titin domains ZIg9/10 bind to obscurin domains Ig58/59 during myofibrillogenisis. Mutations in this region lead to hypertrophic cardiomyopathy (HCM) in humans. While the cellular consequences of this interaction are well characterized, the molecular determinants governing this structure are unknown. Previous work from our lab has solved the high-resolution structure of the obscurin domains of the complex. Here, we describe the purification and complete structure characterization of titin domain ZIg10.

Synthesis of Antisense Oligonucleotide Analogues

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Due to antisense oligonucleotides' (ASO) gene silencing capabilities, the clinical application of ASO as systemic drugs have been widely studied. However, natural oligonucleotides’ sugar-phosphate backbones are highly susceptible to degradation, rendering them unacceptable as therapeutic drugs. To avoid problems with backbone degradation, synthetic oligonucleotides analogs that lack traditional ribose-phosphate backbone are being developed and will be studied to assess their ability to silence or suppress gene expression.

Porphyrin Induced Multimerization of Solution-State Proteins

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Interactions between charged porphyrins and complimentary or similarly charged proteins provide important models systems for studies of electron transfer processes, artificial photosynthesis, and control of protein-protein interactions. Typically, the experimental results are analyzed and discussed assuming that the proteins exist in a monodisperse state. Here, we explored interaction of four solution-state proteins (horse heart cytochrome c, hen egg-white lysozyme, 3-heme c-type cytochrome PpcA from Geobacter sulfurreducens, 2-heme cyt c4 from Pseudomonas stutzeri) with several cationic and anionic water-soluble derivatives of tetraphenylporphyrin. Combined small- and wide-angle X-ray scattering experiments revealed formation of multimers with a wide range of complex sizes. Thermodynamic interaction parameters and complex binding stoichiometries were established with isothermal calorimetry. Locations of porphyrin binding sites were determined with heteronuclear single quantum coherence (HSQC) and total correlation spectroscopy (TOCSY) NMRs for PpcA and cytochrome c, while covalent labeling shielding experiments followed by LC-MS analysis of tryptic digests were used to map ligand binding sites on cyt c4 and lysozyme surfaces. The obtained results demonstrate that multimerization of solution-state proteins by large water-soluble ligands appears to be a wide-spread phenomenon controlled by a delicate interplay of electrostatic and hydrophobic forces. Molecular level mapping of the binding sites allows us to build a theory explaining the size of the formed complexes and provides opportunities for targeted design and assembly of multi-subunit protein complexes.

Comparing Force Fields with Density Functional Theory in Small, Solvated Peptides

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It is well known that a protein's structure is related to its function and that misfolded proteins can cause diseases. Therefore, understanding how proteins fold or misfold is an important topic of research. Simulations often provide critical insight into this process. However, when studying protein folding/misfolding in silico, it is critical that the simulation is reliable. The purpose of this research is to test the reliability of molecular mechanics force fields (a common technique used to study protein structure) by comparing force field calculations to density functional theory (DFT). Ultimately, this information will be used to predict the effect of force field errors in the computational determination of protein folding mechanisms. Being able to detect and correct for force field bias before a simulation can make molecular dynamics (MD) a more powerful tool for determining protein-folding mechanisms. Specifically, we use force fields and DFT to calculate the energies of a small, solvated peptide (ACE-ALA-GLY-ALA-NME) in one of five different secondary structures of α_L, α_R, β, β_R and PP-II. The solvation environment for each secondary structure was equilibrated at room temperature while the peptides were held fixed. Five frames were then chosen from each equilibration and the energies of the peptides plus solvation were calculated with the Amber force field (ff12SB), the CHARMM27/CMAP force field, and the M06-2X density functional. M06-2X was performed in combination with various basis sets including: dgdzvp, aug-cc-pvtz, and jun-cc-pvqz. Preliminary results indicate that the solvation environment mitigates the effect of basis set size seen in gas phase calculations.

A Computational Study of the Interactions between the Histone Acetyltransferase, Gcn5, and a Histone Tail

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Post-translational modifications (PTMs) can have a profound effect on protein structure and function. One such PTM involves the acetylation of free lysine residues. An essential acetylation reaction involves the transfer of the acetyl group from acetyl CoA to a histone (a protein involved in DNA binding). This transfer neutralizes the positively charged lysine, which allows for the DNA to be exposed for transcription. The histone acetyltransferase our study focuses on is Gcn5. The first step in the reaction is the deprotonation of a lysine on the histone tail by a glutamate in Gcn5. This glutamate is ~15 Å away from the transferring acetyl group. Thus, after deprotonation, the Gcn5/histone/acetylCoA complex must reorganize and the lysine must swing back towards the active site. We use molecular dynamics (MD) simulations to probe the interactions between the histone and Gcn5 before and after lysine deprotonation to understand which contacts must be broken before the final acetylation step can occur.

Expression and Preliminary Characterization of OmcM

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Outer membrane cytochromes (Omc) play an important role in respiration of dissimilatory iron-reducing bacteria. They form extended conduits for charge transfer between cellular metabolism and external electron acceptors such as particles of iron oxide, metal ions, and humic substances. However, very little is known about biophysical, biochemical, and structural properties of this large and diverse family of proteins. Out of more than 20 members of Omc family in Geobacter sulfurreducens, only the smallest single-heme OmcF have been successfully expressed and characterized. To get a better insight into structure-function relationships in this family of proteins, we successfully cloned a gene responsible for OmcM, a 6-heme cytochrome with the expected mature size of ~170 amino acids. The protein was expressed in E.coli and demonstrated an unexpected propensity to form inclusion bodies. We successfully isolated the recombinant protein under denaturating conditions using a combination of ion exchange and metal affinity chromatographies. The purity, mass, and correct attachment of all 6 hemes were verified with LC-MS. The protein was characterized with UV-Vis and CD spectroscopy. They demonstrated the expected spectral peak positions. We are currently pursuing redox titrations and further optimizing expression and isolation conditions to accumulate sufficient amount of protein crystallization trials.

Synthesis of Antisense Nucleic Acid Monomers

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Antisense oligonucleotides are capable of silencing genes, making them a promising method of gene therapy; however, natural oligonucleotides are subject to degradation in a cell. Therefore, antisense oligonucleotide analogs, with modifications to the backbone or nucleotide, are an important area of research. Progress towards the synthesis of antisense oligonucleotide analogs with a glycidol backbone in place of the typical sugar-phosphate backbone will be discussed.

Predictive Models of Negative Ion Electrospray Response Explored through Machine Learning Applications

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Numerous studies have used physiochemical properties to predict positive ion electrospray response. Less work has been done to predict negative ion response. Most notably, Kruve et al. (Anal. Chem. 2014, 86, 4822-4830) developed a multiple linear regression model with 48 phenols and benzoic acids that correlated ionization efficiency with physiochemical properties, such as WAPS (a measure of charge delocalization in anions), pKa, and degree of ionization in solution. We present a predictive model using over 70 small acidic compounds that range in pKa from -1.3 to 18 and span more than eight different compound classes with systematically selected functional group substitutions ranging from strong electron-donating to strong electron-withdrawing groups. This model was constructed by investigating negative ion response of ~110 compounds measured by flow-injection experiments (Agilent 6460 QqQ) over two years. Compounds or replicates that did not meet metrics for precision, accuracy, and linearity were not included in the model building process. Predictive models were explored with both logistic regression and support vector machines, having the final model's input parameters sub-selected from 34 pre-computed physiochemical properties ranked from thousands of models. The aim was to determine if models built with the systematically substituted compounds could be used to predict response (e.g. the slope of the normalized instrument response between the estimated linear range) of compounds within, and outside of, the original five classes. Preliminary data suggest that a conserved set of physiochemical properties routinely assist in generating models with the highest performance. Furthermore, we observed differences in physiochemical properties influencing the top models built within a given compound class, such as benzoic acids or phenols. This observation suggests that while it is possible to construct a universal model with decent performance, defining compound class-specific models may offer better performance when predicting instrument response

Exploring Ultrafast Charge Transfer in ppca-ru(bpy)$_3$ Complexes

Matthew O'Malley, Coleman Swaim, Daniel Marzolf, Aidan McKenzie and Dr. Oleksandr Kokhan

Converting light energy into its electrochemical equivalent requires precise control and fine tuning of relevant kinetic and thermodynamic parameters, including primary charge separation. To this end, we developed a series of 22 cysteine mutants of PpcA, a 3-heme cytochrome from Geobacter sulfurreducens as a model system to study short distance photo-induced electron transfer. These proteins were successfully expressed in E.coli and isolated for covalent labeling with Ru(bpy)$_2$(bpy-Br). Protein purity and successful posttranslational modifications were confirmed with HPLC-MS. Time-resolved nanosecond and ultrafast transient absorbance characterization was performed at Argonne National Laboratory (ANL) and identified 6 constructs with apparent photo-induced charge transfer time constants of 20 ps or faster, including 2 constructs with 1-2 ps time constants. The latter is a significant result as up to this point only natural photosynthetic systems demonstrated such a fast initial charge separation, while all artificial covalent constructs exhibited charge transfer rates 3 or more orders of magnitude slower. To understand molecular principles responsible for such a dramatic acceleration of electron transfer rates, we conducted small- and wide angle X-ray scattering data collection at the Advanced Photon Source at ANL. Further, we are currently attempting to obtain X-ray crystallographic and NMR structures of the ultrafast constructs. Finally, we performed triplicate 250-300 ns all-atom molecular dynamics simulations of all 6 ultrafast constructs. Based on the obtained results we conclude that that photo-induced ultrafast charge transfer requires van der Waals contact between heme vinyl groups and photosensitizers while contacts with propionates or short covalent donor-acceptor distances play a much less significant role.

Preparation of Palladium Complexes of N-pyrazolylpropanamide Derivatives

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3,5-Dimethylpyrazolyl-*N*-isopropylpropanamide (I) has been successfully synthesized through the reaction of 3,5-dimethylpyrazole and *N*-isopropylacrylamide in the presence of triton B. The product has been characterized by NMR and I.R. spectroscopy, single crystal X-Ray diffraction, and is awaiting elemental analysis. The reaction of I with dichloro(1,5-cyclooctadiene)palladium(II) displaced the cyclooctadiene and formed a dichloropalladium complex containing two I ligands. This complex has been characterized by NMR and IR spectroscopy and single crystal X-Ray diffraction. It is composed of a square planar Pd with trans I ligands bonded through a pyrazolyl nitrogen. The I ligands also form intramolecular N-H hydrogen bonds with the chlorides that coordinate to the Pd. NMR spectroscopy indicates that a change occurs when the complex is in solution over a period of days. This change is being investigated. The reactions of several other related ligands with dichloro(1,5-cyclooctadiene)palladium(II) are under investigation.

Examination of the Possible Auto-inhibitory Nature of Obscurin Kinase KII

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Obscurin and titin are two closely related, giant muscle proteins. Both contain multiple, highly-conserved kinase domains with N-terminal and C-terminal tails. Recently, the kinases of titin- and twitchin-like proteins were found to be auto-inhibited, with the N- and C-terminal tails playing a part in activation and inhibition. To investigate whether obscurin kinases also behave this way, we modeled a possible structure for the second kinase domain of obscurin, KII. After computationally validating this structure, the binding affinity of the ATP-binding site and the N-terminal tail was tested, as well as that of the ATP-binding site and the C-terminal tail. It was found that the N-terminal tail was too short to bind to the ATP-binding site, and tests are still being run to determine the affinity for the C-terminal tail.

Atmospheric Acid Deposition Reduction and Stream Water Chemistry Response in Three Virginia Trout Stream

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Fossil fuel combustion has delivered large amounts of SOx and NOx gases into the atmosphere where sulfuric and nitric acids have formed. These acids have been delivered to the landscape in precipitation and have caused acidification of streams that drain base poor watersheds. The decreased stream pH and acid neutralizing capacity (ANC) have resulted in loss of acid sensitive aquatic life. To address this problem, the U. S. Congress passed the Clean Air Act to reduce power plant emissions. Between the years 1990 and 2015, SOx and NOx gases have been reduced by 86% and 70%, respectively. During the period, 1996-2015, the deposition of sulfate and nitrate at Big Meadows Air Quality Monitoring Station have decreased by X and Y% respectively. We have intensively collected water chemistry data on three acid sensitive streams in the George Washington National Forest: Little Stony Creek, Mill Creek, and Mountain Run monthly since 1987. In the period, 1987-1995, there was no change in stream water chemistry for these streams; however in the period 1996-2015, all three streams have experienced a positive response to the reductions in atmospheric acid deposition but have not yet returned to pre-industrial age values. Little Stony Creek has 25% reduction in sulfate with a corresponding decrease in hydronium ion of 58% (4.07 µeq/L to 1.70 µeq/L) and an ANC increase of 400% (-2.0 µeq/L to 6.0 µeq/L). For Mill Creek there is a 26% reduction in sulfate with a corresponding decrease in hydronium ion of 52% (14.45 µeq/L to 6.92 µeq/L) and an ANC increase of 54% (-14.2 µeq/L to -6.6 µeq/L). Mountain Run has a 39% reduction in sulfate and a corresponding decrease of hydronium ion of 17% (26.92 µeq/L to 22.39 µeq/L) and 20% (-33.7 µeq/L to -27.0 µeq/L). Differences in response are dependent on watershed geology and soils.

Synthesis and Characterization of New Metal-Organic Materials Incorporating the Hydrotris(3,5-dimethyl-1,2,4-triazolyl)borate Ligand

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Six coordination complexes have been synthesized using the hydrotris(3,5-dimethyl-1,2,4-triazolyl)borate anion, ([BH(dmtrz)$_3$]$^-$, dmtris). A(dmtris) (A = Li, Na, K) were synthesized from the reaction between ABH_4 and excess 3,5-dimethyl-1,2,4-triazole (Hdmtrz) under flux conditions. Powder X-ray diffraction showed that each had a unique structure. The morphology of K(dmtris) crystals changed depending on the solvent used for crystallization. The morphology Na(dmtris) was not sensitive to the solvent used for crystallization. Thermalgravimetric analysis (TGA) of K(dmtris) crystallized from methanol showed a mass loss at 150 ºC that did not correspond to decomposition of the material or methanol. Evolved gas analysis (EGA) of K(dmtris) showed evolution of CO_2 at 176 ºC, possibly due to prior absorption from the atmosphere. M(dmtis)$_2$ (M = Co, Ni, Zn) compounds were synthesized by the reaction of Na(dmtris) and M(NO$_3$)$_2$ in methanol. Yellow-orange Co(dmtris)$_2$, lavender Ni(dmtris)$_2$, and colorless Zn(dmtris)$_2$ prisms were isolated from the reaction mixtures after one hour to three days. Powder X-ray diffraction data showed that Co(dmtris)$_2$, Ni(dmtris)$_2$, and Zn(dmtris)$_2$ were isostructural.

Synthesis of Metal Coordination Compounds Derived from 3-5-dimethyl-1,2,4-triazole

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In an effort to explore the coordination chemistry of the 3,5-dimethyl-1,2,4-triazolate anion ($C_4H_6N_3^-$, dmtrz$^-$), its reaction chemistry was explored with metal ions including Mg^{2+}, Sr^{2+}, Cr^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^{+}, Pr^{3+}, Nd^{3+}, Gd^{3+}, and Er^{3+}. Evaporation, solvothermal synthesis, and diffusion were used in an effort to crystallize new materials that incorporate this ligand. Single crystal X-ray diffraction (SCXRD) data indicate that two novel coordination compounds, $[M_3(Hdmtrz)_6(H_2O)_6](NO_3)_6(H_2O)_6$ (M=Co, Ni), were synthesized by solvent evaporation of solutions of $M(NO_3)_2 \cdot 6H_2O$ and Hdmtrz from ethanol and methanol. Both contain an $[M_3(azole)_6(H_2O)_6]^{6+}$ trimer, which has been previously observed in divalent metal-azolate systems. The trimer units are held together in the solid state by hydrogen bonding. Upon heating, both the coordinating and outer sphere water molecules are lost by 100 °C. The synthesis and structure and thermal behavior of these compounds will be discussed.

Computational Analysis of the Geometry and Vibrational Frequencies of Syn- and Anti-Vinyl Alcohol

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Ro-Vibrational spectroscopy has been an indispensable tool in discovering the presence of organic molecules in the interstellar medium and in planetary atmospheres. Vinyl alcohol is of particular interest since it is an intermediate in many organic reactions. Its high-resolution ro-vibrational spectrum is complex and is further complicated by the presence of both a syn and anti structural isomer. High accuracy electronic structure calculations, therefore, are an invaluable tool for analyzing this spectrum. The CFOUR software package was utilized to calculate the geometry, harmonic and anharmonic ro-vibrational frequencies of syn- and anti-vinyl alcohol at the CCSD(T)/ccPVTZ level of theory.

Biological Semiconductors: Structural Control of Heme Redox Potentials in PpcA, a 3-Heme Cytochrome

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In an effort to tune and optimize relative bandgap potentials found in biological nanowires that form from multiheme domains of members of the cytochrome c7 family, we developed and extensively characterized 12 point mutations of PpcA, a 3-heme member of the cytochrome c7 family native to Geobacter sulfurreducens. These mutations were engineered to influence the redox potential (Em) of the middle heme (heme III) in PpcA by using four different strategies: performing charge reversal mutations, decreasing solvent access to the heme plane with bulky residues, altering the native bis-histidine axial ligation of the heme, and by attempting to form hydrogen bonds with the propionates of the heme. The latter strategy is expected not only to increase Em but also to introduce a redox Bohr effect. Out of 12 mutants, 11 were expressed in E.coli in sufficient quantities and show thermal stability in temperature-dependent CD experiments comparable to wild-type protein (Tm > 90Â°C). HPLC-ESI-MS was used to confirm both the purity and the mass of the expressed mutants. Small-angle X-ray scattering confirmed that the mutant proteins were folded correctly and formed the expected compact globular structures. In addition to ongoing attempts to obtain good quality protein crystals for X-ray crystallography, we performed extensive all-atom molecular dynamics simulations for all mutant forms. Formation of propionate hydrogen bonds is supported for A19R and A23R, while increased solvent access is supported for A19I, A19R, A23R, H20M, and K60E. UV/Vis and NMR redox titrations will be performed in order to measure the effect of the mutations on the electrochemical properties of all 3 hemes and to understand the underlying principles and viable approaches in tuning relative heme redox potentials. Successful development of this project may lead to biological semiconductors with much smaller footprints and selectively tunable bandgap properties.

Effects of Osmolytes on Caffeine Partitioning Thermodynamics

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This project illustrates the effects of nine osmolytes on the partitioning thermodynamics of caffeine between aqueous and cyclohexane phases. The stabilizers such as betaine and sarcosine decrease the Gibbs free energy for caffeine transfer and enhance caffeine transfer from the aqueous to cyclohexane phase. On the other hand, the denaturants such as urea and guanidinium salts behave the opposite to hinder the caffeine transfer. Gibbs free energy for caffeine transfer was measured at different temperatures to obtain the enthalpy and entropy for caffeine transfer. Caffeine transfer from the aqueous to cyclohexane is entropically driven, though the differences between osmolytes arise primarily from the enthalpy of caffeine transfer. ^{13}C and ^{1}H NMR spectroscopy were employed to determine the specific interactions of each osmolyte with caffeine molecule.

Stabilization and Reaction of Small Molecules on TiO_2/Au(111) Inverse Model Catalysts

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The adsorption of CO_2, CO, and H_2O, components of important industrial reactions including the water gas shift (WSG) reaction ($CO + H_2O \rightarrow CO_2 + H_2$), were utilized to investigate the catalytic activity of TiO_2 nanoparticles supported on Au(111). Systematic studies of TiO_2 nanoparticle coverage were conducted using temperature programmed desorption to understand the adsorption and reaction of these molecules over the inverse model catalyst. Increasing the coverage of TiO_2 nanoparticles led to an increased desorption temperature of CO_2. The stabilization of CO_2 by the presence of TiO_2 nanoparticles indicates the potential of the material to act as a low temperature hydrogenation catalyst. A coverage study of D_2O was done on the TiO_2/Au surface that showed D_2O exhibiting second order kinetics at lower coverages then switching to first order kinetics at higher coverages. It was expected that adsorption of CO and H_2O on TiO_2 nanoparticles supported on Au(111) would exhibit WGS chemistry, however, the formation of formaldehyde was observed. The production of formaldehyde is likely a result of the reduced state of the surface which promoted the hydrogenation of CO.

Obscurin Acts as a Variable Force Resistor

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Obscurin (800-900 kDa) is a giant cytoskeletal protein important to muscle cell maintenance and organization. One of its functions is to connect distal regions within the cell. The protein architecture suggests this role; obscurin consists of dozens of individually-folded domains linked together. Given obscurin's shape and position in the cell, it likely responds to cell motion and stretch by itself stretching and compressing. One outstanding question is how obscurin accomplishes this. Here, we begin to probe the molecular mechanism and outcomes of obscurin stretch resistance. We hypothesize that obscurin could either act like a rope, only resisting stretch when fully extended, or it could act as a spring, resisting stretch regardless of how extended it is. By studying a collection of representative obscurin domains and tandem domains, using NMR and SAXS techniques, we gain insight into obscurin's shape and self interactions. Using computational techniques, we supplement our wet lab data and gain increased understanding of how obscurin resists external force. Our data suggest that different tandem domains, with unique linker sequences (but not lengths) variably react to stretch. As all of these domains are within one obscurin molecule, these results show obscurin to be a nonuniform force resistor; different regions resist force to different magnitudes.

A Computational Investigation into the Mechanism of the Histone Acetyltransferase, Gcn5

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Post-translational modifications (PTMs) have a profound effect on protein structure and function. One such PTM is the acetylation of histone (a protein involved in DNA binding). In this reaction, an enzyme catalyzes the transfer of the acetyl group from acetyl CoA to a free lysine on the histone. This transfer neutralizes the positively charged lysine, which ultimately allows the DNA to be exposed for transcription. In our study, we focus on the acetyltransferase, Gcn5. Details regarding the reaction mechanism used by Gcn5 remain obscure. However, current mechanistic hypotheses suggest that the reaction occurs through a tetrahedral oxyanion intermediate, which is stabilized by a hydrogen bond to a nearby residue, i.e. an oxyanion hole. We utilize several computational methods (Quantum Mechanics/Molecular Mechanics, Metadynamics, etc.) to further probe possible mechanistic schemes of this reaction.

The Synthesis of Tetracationic Amphiphilic Viologens

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With a rise in antibiotic resistant bacterial strains, the demand for novel antimicrobial compounds has increased. The goal of this study is to produce a series of tetracationic amphiphilic viologen derivatives and to determine their antimicrobial properties. The synthesis of these compounds consists of two steps to produce a polycationic amphiphile. Progress toward the synthesis of the target compounds will be presented, as will the results of solubility and reactivity studies. Further research needs to be done to produce and analyze the properties of all mono- and polycationic compounds.

2017 Department of Chemistry and Biochemistry Student Award Winners

Amenta Award	Kearney Foss
R.D. Cool Award	Tyler Palombo
J.W. Chappell Scholarship	Coleman Swaim
Palocsay Award in Undergraduate Research	Ryan Hunter Wilson
Service Award	Leanna Carter & Austin Miller
J. W. Chappell Award	Casey Ramirez Cortes & Lindsey Thompson
American Institute of Chemists	Aidan Willey
Degesch America Award	David Boyle
ACS-Award	Daniel Corbin
Hypercube Scholar	Walker Jones
Casali Scholarship (May, 2016)	Lindsey Thompson
CRC First Year Student Award (April 2016)	Amy Fox
Outstanding Student Researcher Award	*to be announced*

American Chemical Society Divisional Awards

ACS Analytical	Melanie Odenkirk
ACS Environmental	Kevin Pyszka
ACS Inorganic	Daniel Corbin
ACS Organic	Moira Kelly Lauer
ACS POLYED Organic Award	Coleman Swaim

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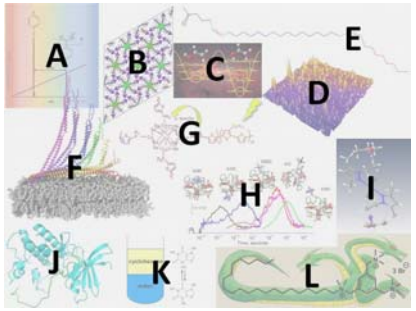

F. Berndsen

G. Boardman

H. Kokhan

I. Amenta / Gilje

J. Wright

K. Zhang

L. Caran

We gratefully acknowledge the following for their support:

American Chemical Society – Petroleum Research Fund
Argonne National Lab
Camille and Henry Dreyfus Foundation
Department of Defense – ASSURE
Department of Energy – Office of Science
The Extreme Science and Engineering Discovery Environment (XSEDE)
Huntsman Corporation
Institute for Infrastructure Assurance
International Society for Chemical Ecology
Jeffress Memorial Trust
James Madison University Center for Materials Science
James Madison University College of Integrated Science and Engineering
James Madison University College of Science and Mathematics
National Institute of Standards and Technology
National Science Foundation – OCI, REU, RUI
Research Corporation for Scientific Advancement
Tickle Summer Research Scholarship
US Forest Service – George Washington & Jefferson National Forests
US-Israel Binational Science Foundation
4-VA
Virginia Department of Game & Inland Fisheries
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