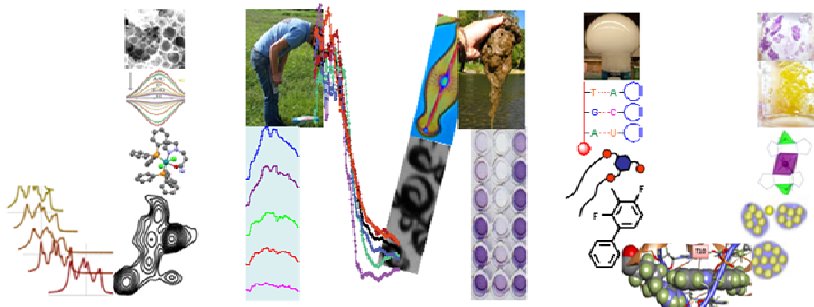


DEPARTMENT OF CHEMISTRY & BIOCHEMISTRY



Spring Undergraduate Research Symposium

THURSDAY MARCH 22, 2012

ORAL SESSION I: 1:15 – 3:45 PM (ISAT 259)

KEYNOTE ADDRESS: 4:00 – 5:00 PM (ISAT 159)

POSTER SESSION: 5:00 – 6:00 PM (PHYS/CHEM LOBBY)

FRIDAY MARCH 23, 2012

ORAL SESSION II: 1:15 – 3:45 PM (ISAT 159)

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

See back cover for image description.

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 the Department of Chemistry Spring Undergraduate Research Symposium.

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

37th Annual Department of Chemistry and Biochemistry
Spring Undergraduate Research Symposium
Thursday Keynote Address

Thursday, March 22, 2012 at 4:00pm
ISAT Room 159

**“From Here to There and Back Again: The
Journey of a Mid-Career Academic Chemist”**



Melissa C. Rhoten (JMU Class of 1994), Ph.D.

Associate Professor and Chair
Department of Chemistry and Physics
Longwood University
Farmville, VA

Melissa C. Rhoten received her B.S. in chemistry from James Madison University in 1994, having completed research under the direction of Dr. Thomas DeVore. Melissa received her Ph.D. in Analytical Chemistry in 2000 from Virginia Commonwealth University. In 2000 Melissa joined the faculty at Longwood University. She was tenured and promoted to the rank of Associate Professor in 2007 and was subsequently promoted to Full Professor in 2012. Her research focuses on the construction of biologically-modified electrode surfaces for both fundamental and applied studies. Professor Rhoten's research interests and experience are in the areas of metalloenzymes, biological electron transfer, and chemically modified electrodes. She is involved in two main areas of biosensor research: the immobilization of enzymes in electrode-supported lipid bilayer membranes and the immobilization of other biologically relevant species (i.e., DNA, proteins, antibodies) for sensing applications. Enzymes of interest include cytochrome c oxidase, monoamine oxidases, and drug metabolizing cytochrome P450. Dr. Rhoten has also been involved in pedagogical activities focused on the implementation of inquiry-based learning into Longwood's chemistry curriculum. She is currently working on an NSF sponsored project (POGIL-PCL) focused on the development and implementation of inquiry-based experiments for the physical chemistry laboratory. Professor Rhoten is an active member of her department and university. She currently serves as the Chair of the Department of Chemistry & Physics. She is also faculty advisor for the Gamma Chi chapter of Alpha Chi Sigma. Melissa has received several honors and has authored numerous publications/presentations.

37th Annual Department of Chemistry and Biochemistry
Spring Undergraduate Research Symposium
Friday Keynote Address

Friday, March 23, 2012 at 3:45pm
ISAT Room 159

**“Bis(Pyrrole-Imine) Gold(III) Macrocycles:
Nucleotide-Specific Catalytic Inhibitors of
Human Topoisomerase I”**



Orde Munro, Ph.D.

Fulbright Scholar, College of Medicine
University of Central Florida
School of Chemistry and Physics
University of KwaZulu-Natal
South Africa

Professor Munro received his BS degree in Chemistry in 1990 from WITS University (University of the Witwatersrand, Johannesburg, South Africa). He completed his Ph.D. in the Department of Chemistry at WITS in 1995 (graduating in April 1996), where his thesis work focused on physical and computational studies of heme-peptide model systems for heme proteins and other metalloporphyrins. He joined Professor Robert Scheidt's laboratory at the University of Notre Dame in Indiana (Department of Chemistry & Biochemistry) in November 1995 and spent 18 months as a post-doctoral researcher working on the synthesis, characterization, X-ray structures, and molecular simulations of iron porphyrins and related macrocycles with unusual conformations. In 1997 he joined the Department of Chemistry at the University of Natal (South Africa), where he continued to work on porphyrin and other pyrrole compounds as well as luminescent complexes of Pt(II). He has received numerous awards over the years at this institution, including the National Research Foundation (NRF) President's Award (2000), the Vice Chancellor's Research Award (2007), and the Raikes Medal of the South African Chemical Institute in 2008. Professor Munro is currently a Visiting Fulbright Scholar at the University of Central Florida (College of Medicine, Biomolecular Research Annex) working with Prof. Mark Muller on delineating the mechanism of action of a new class of anticancer metallodrug compounds invented in his laboratory in South Africa. Several companies (De Beers, Avitronics, SASOL, AuTEK BioMed) and the NRF have supported his research. His current work is also indirectly supported by the NIH (USA) through their Developmental Therapeutics Program (DTP).

Oral Session I: Thursday March 22 nd (ISAT 259)		
1:15 – 1:30	Heidi M. Campbell and Colin J. Wallace	Impact of Water-Broadening on Atmospheric Remote Sensing of Carbon Dioxide
1:30 – 1:45	Skylar White	Real-Time Micro-Phase Separation Kinetic Analysis of POSS-MA Thin Films Using Atomic Force Microscopy
1:45 – 2:00	Allison Wickham	Improved Method of Nitrate-Nitrogen Determination in Soils and Sediments by Instrumental Ion Chromatography
2:00 – 2:15	Jenny Phung	Beer-omics: Molecular fingerprinting of craft beers by high resolution mass spectrometry
2:15 – 2:30	Brian Reeves	Investigation of N-Sulfide Bond Formation in Soluble Precursors for Metal Chalcogenide Thin Films
2:30 – 2:45	----- break -----	
2:45 – 3:00	Justin Hagerman	Amino Acid-Amino Acid Interactions at the Air/Water Interface
3:00 – 3:15	Brian Huffman	Effect of protic and aprotic solvents on negative ion electrospray ionization of small acidic molecules
3:15 – 3:30	Gregory Berman	Thermal Decomposition of 2-Propanol using a molybdenum trioxide catalyst
3:30 – 3:45	Karen Corbett	Monitoring the Effect of Salts on the Aggregation and Unfolding of the <i>Escherichia Coli</i> DNA Repair Protein, RecA, Utilizing Attenuated Total Reflectance Infrared Spectroscopy
3:45 – 4:00	----- break -----	
Keynote Address: Thursday March 22 nd (ISAT 159)		
4:00 – 5:00	Dr. Melissa C. Rhoten (JMU Class of 1994)	From Here to There and Back Again: The Journey of a Mid-Career Academic Chemist

Poster Session: Thursday March 22 nd 5:00 – 6:00 pm (Ph/Ch lobby)	
Nikita Cherednichenko and Zak Bartley	Synthesis and Design of Conjugated Polymers for Photovoltaic Applications
Duane Bock	Synthesis of Ruthenium Dinitrosyl Compounds with Phosphine/Phosphine Oxide Ligands; Potential NO Releasing Drugs
Caroline Campbell	Synthesis and characterization of hybrid organic-inorganic frameworks using the hydrotris(triazolyl)borate ligand
Andrew Evangelista	The Synthesis of Tripod Molecules for Ultrafast Photolysis Studies
Jindong Kang	The Synthesis of Tripodal Sensitizer for the Study of Long-Range Electron Transfer across Molecule-Nanocrystalline Semiconductor Interfaces As model solar cells
Ivan Liapin	Gelation of Ethanol-Water Mixtures by a Novel Propargylic Alcohol
Kent McQueen & Charles Smith	Synthesis of Ruthenium Complex Containing N-pyrazolylpropanamide
Jarvis Mitchum	Quantitating Neurotransmitters and their Metabolites in Urine
Daniel Moon	Polycationic Polycephalic (and other) Amphiphiles
Michael Morris	A "Snapshot" Study of Water Chemistry for Three Streams in the Shenandoah Valley
Michelle Rudman	The Synthesis of Tripod Molecules for Ultrafast Photolysis Studies
Scott Steehler	The synthesis and coordination chemistry of $K[BH_2(C_2H_2N_3)_2]$
Brooke N Stevens	Synthesis of siRNA Analogues
Emigdio Turner	Effects of Osmolytes on the Phase Behaviors of PEO-PPO-PEO

Oral Session II: Friday March 23 rd (ISAT 159)		
1:15 – 1:30	Arlie Bagley	Thermal Decomposition of $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ and $\text{Cu}(\text{OH})_2$
1:30 – 1:45	Matt Dent	Synthesis and Characterization of $\text{Li}[\text{BH}(\text{C}_2\text{H}_2\text{N}_3)_3]$ Frameworks
1:45 – 2:00	Justin Sims	Formation of assymmetric 1,3-difluorobenzenes
2:00 – 2:15	Casey Rogers	Developing an Infrastructure for Chemical Demonstration Outreach
2:15 - 2:30	Brittany Danzig	Infrared and Circular Dichroism Studies on the Effects of Salts on RecA
2:30 – 2:45	----- break -----	
2:45 – 3:00	Rima Januszewicz	Effect of temperature on phenolics and proanthocyanidins during the blanching of almonds
3:00 – 3:15	Jhosdyn Barragan	The Synthesis of Novel Polycephalic and Gemini Amphiphilic Derivitives of Mesitylene.
3:15 – 3:30	Alan Mo	Improving the Adhesion of Au Thin Films Onto PMMA Substrates Using Organic Solvents
3:30 – 3:45	Waleed Ahmad and Philip Chambers	Elemental Composition of <i>Didymosphenia geminata</i> "Didymo" In The Jackson River, Virginia
Keynote Address: Friday March 23 rd (ISAT 159)		
3:45 – 4:45	Dr. Orde Munro	Bis(Pyrrole-Imine) Gold(III) Macrocycles: Nucleotide-Specific Catalytic Inhibitors of Human Topoisomerase I

Thursday Keynote Address

Thursday, March 22, 2012 at 4:00pm
ISAT Room 159

“From Here to There and Back Again: The Journey of a Mid-Career Academic Chemist”

Melissa C. Rhoten (JMU Class of 1994), Ph.D.
Department of Chemistry and Physics
Longwood University
Farmville, VA

This talk will focus on my development as a chemist from 1991 to the present. It was during my undergraduate years at JMU that I discovered my true passion - a love of learning and scientific discovery. I will share details of my journey, both personal and professional. The research aspects of this talk are varied and will include brief discussions of my undergraduate work with Tom DeVore, my doctoral work at VCU with Fred Hawkridge, and my current interests at Longwood.

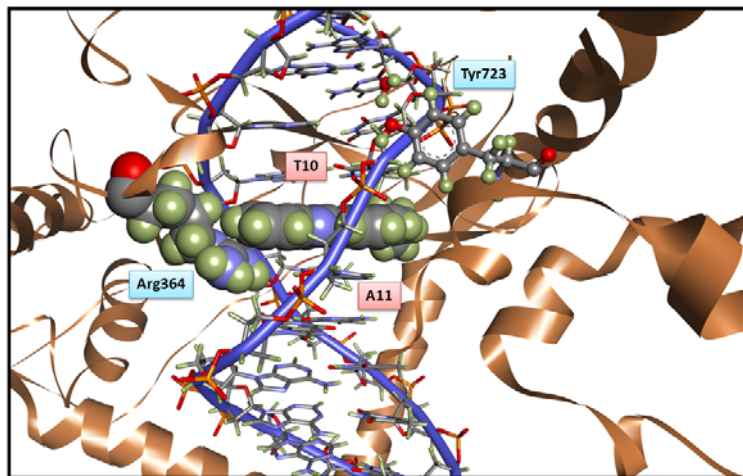
Friday Keynote Address

Friday, March 23, 2012 at 3:45pm
ISAT Room 159

“Bis(Pyrrole-Imine) Gold(III) Macrocycles: Nucleotide-Specific Catalytic Inhibitors of Human Topoisomerase I”

Kate J. Akerman¹, Alexander M. Fagenson², Vidusha Cyril², Michael Taylor,² Mark T. Muller^{2*},
Matthew P. Akerman¹, and Orde O. Munro^{1,†*}

Topoisomerase IB (TOP1) is an essential eukaryotic nuclear enzyme that regulates the topology of DNA by making transient single-strand breaks to guide torque-driven relaxation of the positively or negatively supercoiled double helix during DNA replication and gene transcription. Anticancer drugs that block TOP1 are divided into two classes: well-characterized interfacial poisons (IFPs, e.g camptothecin) and a smaller group of catalytic inhibitor compounds (CICs). Here we describe a new class of cytotoxic cationic Au³⁺ macrocycles that are unconventional competitive catalytic inhibitors of the enzyme. The talk will focus on the synthesis, cytotoxicity, and mechanism of action of the new patented anticancer compounds.



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STUDENT ABSTRACTS

Elemental Composition of *Didymosphenia geminata* “Didymo” In The Jackson River, Virginia

Phillip C. Chambers,¹ Waleed Ahmad,¹ Daniel M. Downey¹ and Joline McNece²

¹Department of Chemistry and Biochemistry, James Madison University

²National Technical Institute for the Deaf, Rochester Institute of Technology

Didymosphenia geminata (Didymo) is a fresh water diatom invasive algal species that produces large mats in rivers that may adversely affect the stream habitat and sources of food for fish. Initially restricted to Northern Hemispheric climates in Europe, it has spread to New Zealand, Canada, and nine states in the United States. As a diatom, it is characterized by a silica (SiO₂) cell wall that also produces a polysaccharide strand. The elemental composition of *Didymo* is not well established. We believe that a better understanding of its elemental makeup and its relation to the water chemistry of the streams in which it is found may aid control and eradication efforts. The combination of both inorganic and organic components makes the organism difficult to analyze. We have developed a three stage method to determine the elemental fingerprint of *Didymo* that involves cleaning/drying, acid and base digestion and elemental analysis by Ion Coupled Plasmas - Mass Spectrometry (ICP-MS). Samples collected from the Jackson River in Bath County, Virginia were evaluated for this project. Digestions were accomplished with a Microwave Accelerated Reaction System (MARS) in order to produce completely dissolved samples necessary for the trace elemental analysis. By performing an acid and base digestion, we were able to dissolve both the silica and organic matter. Water chemistry was also determined for the reach of the river where *Didymo* was found. Twenty nine elements in the *didymo* and water samples were evaluated for this project. It was found that Cd, Sb, Bi, Ti, In and Ag were below ICP-MS detection limits. Elements that were detected by ICP-MS in the *didymo* with high concentration (>1000 ppb) were Mg, Al, K, Ca, Mn, Fe and Ni. Elements that were found in moderate concentration (>10 ppm) were Li, B, P, Cr, Co, Zn, Ga, Sr, Ba and Pb. Trace element analysis of the stream water showed that *Didymo* was present in locations where Mg, P, K and Ca were at high concentration values.

Thermal Decomposition of CuCO₃•Cu(OH)₂ and Cu(OH)₂

Arlie Bagley and Thomas C. Devore

Department of Chemistry and Biochemistry, James Madison University

CuCO₃•Cu(OH)₂ and Cu(OH)₂ decomposed when they were heated to approximately 600 K. The TGA for CuCO₃•Cu(OH)₂ showed only one mass loss step. Since the ATR-IR showed the loss of the peaks at 3000-3600 cm⁻¹ and 600-1500 cm⁻¹ indicating that both water and CO₂ were lost. Cu(OH)₂ also decomposed in one step. The kinetics for the decomposition of each compound has been determined using the Ozawa method.

The Synthesis of Novel Polycephalic and Gemini Amphiphilic Derivatives of Mesitylene

Jhosdyn Barragan and Kevin L. Caran

Department of Chemistry and Biochemistry, James Madison University

Derivatives of mesitylene were synthesized in order to prepare a series of amphiphiles with *n* benzylic quaternary ammonium headgroups and 3-*n* benzylic pyridinium headgroups, where *n* = 0-3. The series includes compounds with tail lengths from 8 – 16 carbons. Eleven compounds in this series have been prepared, including derivatives where *n* = 0, 2 and 3. The preparation of compounds in the remaining subset (*n* = 1) are still in progress. Reaction temperature, water content, and solvent polarity were found to be key factors in controlling the synthesis of various derivatives. Preliminary studies, in collaboration with JMU Biology, suggest that antibacterial activity was inversely proportional to tail length for compounds where *n* = 2.

Thermal Decomposition of 2-Propanol using a molybdenum trioxide catalyst

Gregory Berman and Thomas C. DeVore
Department of Chemistry and Biochemistry James Madison University

Evolved Gas Analysis FT-IR (EGA-FTIR), Attenuated Total Reflectance FT-IR (ATR-FTIR), and X-Ray Diffraction Analysis was used to investigate the properties of molybdenum trioxide as a catalyst. 2-Propanol was streamed over the catalyst to produce propene and acetone in an approximate 3:1 ratio in the temperature range between 380 K and 570 K. The Propene indicates that there are acid sites on the catalyst and the acetone indicates that there are base sites on the surface indicating there is a 3:1 ratio of acid to base sites on the catalyst surface. While the molybdenum trioxide turned dark, ATR - FTIR indicated no significant composition change was detected. Heating to 653K deactivated the catalyst. CO₂ was observed in the products and ATR-FTIR indicated there was a change in composition of the surface of the catalyst. These results indicated that a chemical reaction with the surface had occurred leaving MoO_x where x was less than 3.

Synthesis of Ruthenium Dinitrosyl Compounds with Phosphine/Phosphine Oxide Ligands; Potential NO Releasing Drugs

Duane Bock, Donna S. Amenta and John W. Gilje
Department of Chemistry and Biochemistry James Madison University

NO is an important cellular messenger molecule involved in many physiological and pathological processes. Low levels of NO production are important in protecting an organ such as the liver from ischemic damage.¹ Chronic expression of NO is associated with various carcinomas and inflammatory conditions including juvenile diabetes, multiple sclerosis, arthritis and ulcerative colitis.¹ A number of ruthenium nitric oxide complexes are of interest as drugs as they are known to release NO under certain conditions. In our lab, we have evidence that NO is released from Ru(NO)Cl₃[P(Ph)₂CH₂CH₂P(O)Ph₂]₂ during a reaction with AgBF₄. We postulate that this reaction is aided by the ability of the P(Ph)₂CH₂CH₂P(O)Ph₂ ligand to convert from mono to bidentate coordination. In this project we have looked into the preparation of ruthenium dinitrosyl complexes with P(Ph)₂CH₂P(O)Ph₂, P(Ph)₂CH₂CH₂P(O)Ph₂, and P(Ph)₂CH₂CH₂CH₂P(O)Ph₂ ligands. Reactions similar to those used to prepare Ru(NO)₂(PPh₃)₂ failed.² From there, the reactions of Ru(NO)₂(PPh₃)₂ with P(Ph)₂CH₂P(O)Ph₂, P(Ph)₂CH₂CH₂P(O)Ph₂, and P(Ph)₂CH₂CH₂CH₂P(O)Ph₂ were investigated. In NMR tube experiments using P(Ph)₂CH₂CH₂P(O)Ph₂, mixtures of Ru(NO)₂(PPh₃)₂, Ru(NO)₂(PPh₃)(P(Ph)₂CH₂P(O)Ph₂) and Ru(NO)₂(P(Ph)₂CH₂P(O)Ph₂)₂ were observed. However, pure samples could not be obtained from bulk scale reactions. With P(Ph)₂CH₂CH₂P(O)Ph₂ similar NMR tube results were obtained, but through careful manipulation of solvents and other conditions relatively pure Ru(NO)₂(PPh₃)(P(Ph)₂CH₂CH₂P(O)Ph₂) or Ru(NO)₂(P(Ph)₂CH₂CH₂P(O)Ph₂)₂ can be isolated. Experiments using P(Ph)₂CH₂CH₂CH₂P(O)Ph₂ are in very initial stages. Details of these experiments will be discussed.

¹Wikipedia contributors. Nitric Oxide [Internet]. Wikipedia, The Free Encyclopedia; 2011 Jul 23, 16:48 EST [cited 2011 Jul 26]. Available from: http://en.wikipedia.org/wiki/Nitric_oxide.

²Ahmad, N.; Levison, J.J.; Robinson, S.D.; Uttley, M.F. "Triphenylphosphine Complexes of Transition Metals." *Inorg. Synthesis* 1977, 15, 52-53

Synthesis and characterization of hybrid organic-inorganic frameworks using the hydrotris(triazolyl)borate ligand

Caroline Campbell and Barbara A. Reisner
Department of Chemistry and Biochemistry James Madison University

Zeolitic imidazolate frameworks have captured a great deal of attention because of their potential for gas storage, separations, and catalysis. A new material, K[BH(trz)₃], (trz=1,2,4-triazolate) was synthesized from the reaction between potassium borohydride (KBH₄) and excess triazole (Htrz). K[BH(trz)₃] (KL) was crystallized from acetonitrile, producing clear, transparent hexagonal rods about 0.2 mm in length. The FTIR and NMR spectra confirmed that the compound was present without excess triazole or solvent. TGA data indicated that the compound is stable to 250 °C. Single crystals have been grown for elemental analysis and single crystal structure determination. Three new frameworks containing transition metals (M = Co, Ni, Cu) were synthesized by layering. Yellow plates of Co[BH(trz)₃]₂ were synthesized by the slow diffusion of CoCl₂·6H₂O and KL in DMF and hexanes. Purple plates of Ni[BH(trz)₃]₂ were synthesized by the slow diffusion of NiCl₂·6H₂O and KL in DMF and hexanes. Blue rods of Cu[BH(trz)₃]₂ were synthesized by the slow diffusion of CuCl₂·2H₂O and KL in DMF and hexanes. Analyses of these materials will be reported.

Impact of Water-Broadening on Atmospheric Remote Sensing of Carbon Dioxide

Heidi M. Campbell, Colin J. Wallace, Eric M. Vess, Chae yeun Jeon, Courtney N. Anderson and Daniel K. Havey
Department of Chemistry and Biochemistry, James Madison University

CO₂ is an important greenhouse gas in the atmosphere. Political pressures driven by climate change require precise and accurate measurements of CO₂ concentration in order to determine its atmospheric sources and sinks. High-fidelity reference data of spectral line parameters are required to successfully measure small changes in CO₂ on top of the large atmospheric background of approximately 390 ppm. Currently satellite missions rely on optical spectra of both CO₂ and O₂ to accurately determine atmospheric concentrations of CO₂. Measurements of O₂ are important because its concentration is uniform and well-mixed in the atmosphere. Thus, measuring O₂ remotely allows determination of atmospheric path lengths. Since H₂O makes up approximately 1-4% of the Earth's atmosphere, it can potentially be a source of error in spectra of O₂ and CO₂ by acting as a foreign broadener for CO₂ and/or O₂ lines. Recent work by our group will be discussed which quantifies water-broadening of CO₂ and O₂ with modest uncertainty. Neglecting to include our results in retrieval algorithms will result in a geographically and temporally varying measurement bias.

Synthesis and Design of Conjugated Polymers for Photovoltaic Applications

Nikita Cherednichenko,¹ M. Alex Carpenter,² Zak Bartley¹ and Brycelyn M. Boardman¹
¹Department of Chemistry and Biochemistry, James Madison University
²Department of Chemistry, University of Mary Washington

Poly(3-hexylthiophene) (P3HT) and poly[2,1,3-benzothiadiazole-4,7-diyl[4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2,6-diyl]] (PCPDTBT) are commonly used donor materials in bulk heterojunction solar cells. P3HT forms ordered domains producing efficient cells but are plagued by a small range of absorption; PCPDTBT however suffers from the reverse. Functionalization of the alkyl chains of PCPDTBT with phenyl groups was investigated, to probe whether pi-pi stacking of the phenyl groups would increase the ordering of the polymer domains. The synthesis of the model monomer 3-(6-phenylhexyl)thiophene (**1**) was used to determine the most efficient reaction pathway. The synthesis of **1** was performed in a one-pot reaction by sequential addition of 3-bromothiophene and bromobenzene to an in-situ generated alkyl bisgrignard. GC-MS was used to monitor the progress and to identify the side products of the reaction. Separation of **1** from 1,6-dithienylhexane, the main side product, has proven to be a significant challenge due to similar polarity. Optimizing reaction conditions are currently being investigated. Additionally the interaction of P3HT with semiconducting cobalt clusters Co₆Se₈(PEt₃)₆ was also investigated. Various molecular weights of P3HT have been obtained and were characterized by NMR and gel permeations chromatography (GPC). UV-visible spectroscopy and fluorescence measurements were used to probe the optical and electronic interactions of the polymer and the semiconducting cluster. Quenching of the polymers fluorescence is an indication of charge transfer between the two materials, making the blend a candidate for photovoltaic devices.

Monitoring the Effect of Salts on the Aggregation and Unfolding of the *Escherichia coli* DNA Repair Protein, RecA, Utilizing Attenuated Total Reflectance Infrared Spectroscopy

Karen Corbett,¹ Vince LiCata,² and Gina MacDonald¹
¹Department of Chemistry and Biochemistry, James Madison University
²Department of Biological Sciences, Louisiana State University

RecA is an essential DNA-repair protein in *Escherichia coli* that has homologous sequences present in nearly every species. Previous Circular Dichroism (CD) studies in our lab revealed that salts affect the secondary structure, stability, and unfolding transitions of RecA. How salts influence RecA stability does not follow the direct Hofmeister series, a general guideline to protein solubility and stability. Attenuated total reflectance infrared (ATR-IR) spectroscopy was used to study a variety of changes in RecA-salt solutions as temperature was increased. We observed significant changes in the secondary structure and aggregation behavior of RecA, as well as the water structure, in the presence of different Hofmeister salts. Second derivatives of the infrared spectra were utilized to help identify and isolate structural changes.

Infrared and Circular Dichroism Studies on the Effects of Salts on RecA

Brittany Danzig and Gina MacDonald

Department of Chemistry and Biochemistry, James Madison University

The Escherichia coli RecA protein is a multifunctional enzyme that performs a DNA strand exchange reaction and is typically a DNA-dependent ATPase. However, high salt concentrations are known to activate RecA mediated ATP hydrolysis in the absence of DNA. Previous experiments in our lab found that RecA stability is dependent on the concentration and nature of the salt ions present in solution. In order to better understand the nature of the salt ion-RecA interactions, this study continues to monitor RecA using Fourier Transform Infrared Spectroscopy (FTIR) and Circular Dichroism (CD). Difference FTIR was used to study the effects of buffer salts on the nucleotide binding to RecA. The presence of salts results in altered difference FTIR spectra associated with ADP binding to RecA. Complementary CD studies were used to monitor the unfolding of RecA in the presence of single stranded DNA and various salts. RecA-ssDNA complexes in low salt concentrations have different thermal transitions than RecA complexes in high salt concentrations used in previous studies. Future studies of RecA are required to determine how lower salt concentrations and ssDNA influence RecA secondary structure, unfolding transitions, and nucleotide binding.

Synthesis and Characterization of Li[BH(C₂H₂N₃)₃] Frameworks

Matthew R. Dent and Barbara A. Reisner

Department of Chemistry and Biochemistry, James Madison University

In order to expand the class of metal-organic frameworks possessing zeolytic topologies, lithium hydrotris(1,2,4-triazolyl)borate, Li[BH(trz)₃], was synthesized by reacting LiBH₄ in a triazole flux under inert atmosphere. The crude, white Li[BH(trz)₃] solid was crystallized under solvothermal conditions, and several resulting crystalline phases were identified by powder X-ray diffraction. Colorless, pseudo-hexagonal plates of a compound that is likely Li[BH(trz)₃]-CH₃CH(OH)CH₃ were crystallized from IPA and further characterized by elemental analysis, ¹H NMR spectroscopy, thermogravimetric analysis, and single crystal X-ray diffraction. A 2-D layered material with the formula Li[BH(trz)₃] was previously crystallized from acetonitrile. The structure of Li[BH(trz)₃]-CH₃CH(OH)CH₃ will be discussed and compared to other materials containing the hydrotris(1,2,4-triazolyl)borate ligand.

The Synthesis of Tripod Molecules for Ultrafast Photolysis Studies

Andrew Evangelista, Michelle Rudman, Jin Kang and Debra L. Mohler

Department of Chemistry and Biochemistry, James Madison University

To better understand the influence of anchoring groups on the rate of interfacial electron transfer, adamantane tripod derivatives with carboxy methyl anchoring groups were synthesized and bonded to a perylene compound. The specific goal is to create an anchoring complex for later study by femtosecond IR spectroscopy.

Amino Acid-Amino Acid Interactions at the Air/Water Interface

Justin Hagerman,¹ Melissa Palmer,¹ Leigh Matano² and Yanjie Zhang¹

¹Department of Chemistry and Biochemistry, James Madison University

²Department of Chemistry, The College of New Jersey

Amino acid surfactants were synthesized and employed as a model system to investigate the amino acid-amino acid interactions at the air-water interface. *N*-stearoyl-glutamic acids with different chirality (L- and D-) were spread at the air-water interface on subphases containing varying concentrations of L-arginine at pH 3 and pH 5. The pressure-area (*P*-*A*) isotherms of *N*-stearoyl-glutamic acid monolayer at the air-water interface were used to study the interactions between amino acids. A fluorescence microscope was used to observe the domain formation of these chiral molecules at the air-water interface. The correlation between the amino acid-amino acid binding affinities and the surface morphology is being explored.

Effect of protic and aprotic solvents on negative ion electrospray ionization of small acidic molecules

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Negative ion electrospray (ESI) is used to selectively ionize acidic molecules for mass spectrometric detection. The negative ion ESI response of 50 physicochemically diverse molecules was measured in protic (water and methanol) and aprotic (acetonitrile and acetone) solvents to evaluate ionization efficiency. In order to attribute analyte response to solvent selection and to reduce the effects of changes in instrument response, a rigorous quality control program was implemented. In addition, the UV response was compared to ESI response over three orders of concentration, thus providing another means to evaluate ionization efficiency and monitor data quality. Figures of merit, such as sensitivity and limit of detection (LOD), were also determined. This data set represents 4200 data points (50 compounds x 7 concentrations x 4 solvents x triplicate measurements) and is, to date, the most comprehensive study on the effects of solvent selection on negative ion ESI ionization.

The majority of compounds exhibited the highest response in protic solvents, with methanol yielding higher ionization efficiencies than water. Interestingly, *n*-carboxylic acids with six to 14 carbons exhibited a greater response in water while hexadecanoic and stearic acids ionized better in methanol. LODs were also generally lower in methanol. Comparison of each analyte's MS and UV calibration curves provided valuable information regarding solvent selection and ionization. The slope for UV-active compounds was statistically equivalent in water, methanol and acetonitrile (acetone absorbs UV). However, the MS slopes (a measure of sensitivity) varied greatly with solvent selection (generally, methanol > water > acetonitrile > acetone). The UV data was also verified poor ionization. For example, compounds 1,3,5-trihydroxybenzoic acid, gallic acid, *p*-cresol and 4-acetamidophenol exhibited a linear UV-response but no detectable MS response. UV detection prior to ESI offers a level of validation that has not been previously employed in fundamental ESI ionization studies.

Effect of temperature on phenolics and proanthocyanidins during the blanching of almonds

Ryann Diehl and Christine A. Hughey

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The distribution of polyphenols in blanched almond skins and blanch water as a function of time and temperature was quantified in Summer 2011 using negative ion electrospray time-of-flight mass spectrometry (ESI TOF-MS). Almonds were blanched in 25 °C (RT) and 100°C (HW) water for up to 10 min. At 10 min. ~30% (25 °C) and 90% (100°C) of the polyphenols quantified had leached from the skins into the blanch water. Many of the compounds precipitated from the blanch water due to limited water solubility as evidenced by a logarithmic fit to kinetic data (1st order kinetics). The rate of procyanidin degradation into smaller polymeric units (e.g., catechin and epicatechin) also increased as a function of time as temperature. This work will appear in the April 2012 issue of Food Chemistry (doi:10.1016/j.foodchem.2011.09.093).

In Fall 2011, we began a more extensive investigation into the thermal degradation of proanthocyanidin compounds during blanching. Data collected in the summer demonstrated that mass balances were not obtained in the 100 °C treatment for catechin and epicatechin. For instance, catechin decreased in the skins by 37% but increased in the 100 °C water by 90%. We hypothesized that the increased concentration of (epi)catechin in the blanch water was due to thermal degradation of polymerized proanthocyanidins. To test this hypothesis, we monitored the change in concentration of select procyanidins in the skins and blanch water as a function of time and temperature. MS/MS experiments on an ESI q-TOF MS were used to verify the identity of the procyanidins. A few dimeric compounds exhibited trends similar to (epi)catechin in that their concentration increased in the blanch water and decreased in the skins. For larger polymeric compounds (trimers and tetramers) the percent lost from the skins was significantly higher than the percent gained by the water, thus providing further evidence that polymers do thermally degrade into their monomeric units.

The Synthesis of Tripodal Sensitizer for the Study of Long-Range Electron Transfer Across Molecule-Nanocrystalline Semiconductor Interfaces as Model Solar Cells

Jindong Kang and Debra L. Mohler

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A series of a compound of 1-(ethynylphenyl)-3,5,7-tris(4-carbomethoxyphenyl)adamantane have been synthesized to study the relationship between molecular structure and electron transfer (ET) rate in ultrafast interfacial processes occurring between semiconductor nanoparticles and molecular adsorbates. Interfacial ET from molecular adsorbates and semiconductor nanoparticles is an important step in the function of solar cells, photocatalysis, and many other molecular devices. Since the rate of ET plays a significant role in determining the efficiency in these systems, significant efforts have focused on this phenomenon. It has been found that rigid linkers between semiconductor and sensitizer modulate efficiency; the compounds that we have made contain rigid tripods, having a tetrahedral core made of 1,3,5,7-tetraphenyladamantane, three COOR surface binding groups, and a rigid rod arm carrying the sensitizer. These rigid tripods are also able to position the linker perpendicular to the surface. Characterization of the compound was accomplished by ¹H and ¹³C NMR.

Gelation of Ethanol-Water Mixtures by a Novel Propargylic Alcohol

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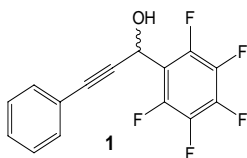
The design and control of self-assembly of low molecular weight gelators offers a powerful tool for the development of functional supramolecular nanostructures. In this study, novel gels were prepared using a ternary mixture of a propargylic alcohol gelator (**1**), a good solvent (EtOH), and a poor solvent (H₂O). This allowed the gelator to spread throughout the solvent prior to gelation.

A closer investigation of this system showed that the optimum percentage of ethanol is between 20% and 40%. Minimum concentrations of gelator were determined for a range of EtOH/H₂O ratios.

Robust gels were prepared at gelator concentrations as low as 2 mg gelator per mL of liquid.

A scanning electron microscopy (SEM) study confirmed that the gel is composed of long fibers.

Preliminary powder XRD experiments suggest the presence of competing phases during gel formation. The results of an ATR-IR study suggest that a phase transition occurs between 25 and 35 °C.



Quantitating Neurotransmitters and their Metabolites in Urine

Jarvis Mitchum, Gina MacDonald and Christine Hughey

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Serotonin (5HT) is a heterocyclic amine that is synthesized from the amino acid tryptophan and is metabolized by monoamine oxidase (MAO). One product of serotonin breakdown is 5-Hydroxyindoleacetic acid (5-HIAA) that is excreted in urine. Quantitation of serotonin levels have been studied in relation to many physiological and behavioral functions including: carcinoid tumors, aggression, depression, and appetite. Many studies have shown the links between increased aggression and differing levels of neurotransmitters/metabolites in body fluids. Our studies use ELISA (Enzyme-Linked Immunosorbent Assay) to quantitate serotonin levels in urine. In addition, the LC-MS (Liquid Chromatography–Mass Spectrometry) was used for serotonin and metabolite quantitation. LC-MS has the potential to measure the concentrations of many different neurotransmitters and their metabolites of interest. These measurements were used to determine if we were able to observe differences in serotonin and metabolite levels between animals.

Improving the Adhesion of Au Thin Films Onto PMMA Substrates Using Organic Solvents

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One of the recent trends in microfabrication technologies is to produce devices such as flat panel displays, sensors, photovoltaic cells and lab-on-a-chip devices using polymeric substrates. The deposition of Au thin films is a critical component in many of these devices. The properties that make Au useful are its corrosion resistance, high infrared reflectivity, and outstanding electrical and thermal conductivity. Unfortunately, Au is an inert metal that has notoriously poor adhesion to polymers. The conventional techniques to improve Au thin film adhesion have resulted in limited success. In this study, Au thin film adhesion onto poly(methyl methacrylate) (PMMA) was improved by a factor of four when samples were either spun-cast with chloroform or exposed to a saturated gaseous environment prior to metal deposition. Scotch-tape tests and corresponding image analyses showed that strong Lewis acids, such as chloroform and dichloromethane, were most consistent in improving Au thin film adhesion. The solvent pre-treated PMMA surfaces were characterized through atomic force microscopy (AFM), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), evolved gas analysis FTIR (EGA-FTIR), and X-ray photoelectron spectroscopy (XPS). Then, the interaction between PMMA ester groups, solvent molecules, and metals were modeled through density functional theory (DFT). DFT modeling showed that the adhesion of other metals to PMMA could be improved by using organic pre-treatment.

Polycationic Polycephalic (and other) Amphiphiles

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Polycationic polycephalic amphiphiles have two or more cationic head groups and one non-polar tail group. Previous studies have shown that cationic amphiphiles exhibit antimicrobial properties on both gram-positive and gram-negative bacteria. The goal of the experiments was to study the antimicrobial activities of amphiphiles and to relate this activity to molecular structure. Variations in amphiphile structure include the number and relative position of cationic head groups and as well as the number of carbons in the tail. For comparison, gemini amphiphiles (with multiple heads and multiple tails) having analogous core structures were also prepared. Dr. Seifert's group (JMU Biology) tested the aqueous amphiphile samples for antimicrobial activity. From these data, we have begun to develop an understanding of the trends of antimicrobial activities based on the structure of the amphiphile for two Gram-positive and two Gram-negative bacteria.

A "Snapshot" Study of Water Chemistry for Three Streams in the Shenandoah Valley

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²Rochester Institute of Technology/NTID

There are two ways to collect stream water samples for water chemistry and environmental evaluation: grab samples taken from select sites at regular intervals for a long period of time, or grab samples taken at many sites in a short period of time. The latter approach is known as a snapshot or synoptic sampling. For most of our projects monthly water quality samples have been collected for a number of streams to support research on acid deposition, liming and non-point source pollution. However due to time, effort and budget limitations only a few sites for each stream are regularly sampled. To better understand the changes in water chemistry as a stream moves downgrade, synoptic samples were collected during the summer of 2011 for three streams we sample on a monthly basis. Little Stony Creek in Shenandoah County and Mountain Run in Rockingham County are acid sensitive streams that have been treated with limestone. Mountain Run discharges into Smith Creek, a meandering stream that flows through agricultural land. For Little Stony Creek on two days in June 2011 we sampled 4,800 meters from the downstream US Forest Service boundary to upstream of the limestone treatment site. In a three day period in July 2011 we sampled Mountain Run and Smith Creek for 8,420 meters. In the field physical measurements of pH, temperature, turbidity and conductivity were made at each site. Samples were returned to the lab for determination of acid neutralization capacity (ANC) and the concentrations of sodium, potassium, magnesium, calcium, chloride, sulfate, nitrate and aluminum. These parameters and on-site physical observations were used to evaluate geology, soils, land use and pollution on the water quality of the above streams, and to provide data for evaluation of the effectiveness of limestone treatment for acidic streams.

Beer-omics: Molecular fingerprinting of craft beers by high resolution mass spectrometry

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The number of craft breweries, brewpubs and microbreweries has grown to meet consumer demand for unique brews. According to the Brewer's Association, there were 1,753 breweries in operation in 2010 and 1,927 in 2011. In appreciation of craft beers around the globe, we present one of the first applications of beer-omics. Metabolomic techniques were utilized to fingerprint 18 single-hop beers produced by the Mikkeller brewery in Denmark. The brewer, who takes a scientific approach to brewing, kept all parameters the same and only varied the hop used in each beer. The beers were analyzed by UHPLC q-TOF MS in both positive and negative ion modes.

An algorithm in Agilent's MassHunter Qualitative Analysis software was utilized to find molecular features (unique m/z and retention time) in the QC beer (Green Flash West Coast IPA) and Mikkeller beers. Approximately ~3500+ features were reproducibility extracted from each sample. Mass Profiler Professional software was used to conduct differential analysis of the samples. Hierarchical clustering and principle component analysis revealed, for example, that Nelson Sauvin, Warrior, Nugget and Simcoe were similar in composition. The "fingerprint" of each hop, was then used in a class prediction model to identify the hops used in the West Coast IPA. The model, which is still under development, correctly identified the most abundance hop, Simcoe. Other hops used in the beer include Columbus, Cascade, Amarillo and Centennial. Finally, we evaluated the concentration of alpha-acids, compounds largely responsible for the bitterness in IPAs, and correlated the concentration to the known IBUs (International Bitterness Units) for each beer. The West Coast IPA, with an IBU of 99 (out of 100), had the highest concentration of alpha acids, thus indicating that beer-omics must ultimately be correlated to sensory attributes of the "sample."

Investigation of N-Sulfide Bond Formation in Soluble Precursors for Metal Chalcogenide Thin Films

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Developing soluble inorganic precursors for metal chalcogenide thin films requires fundamental knowledge and control of the precursor's ligand chemistry. This study involves the investigation of the formation of pyridine N-sulfide (S-Py) from elemental sulfur and pyridine in a range of solvents with increasing polarity. Chemical shifts in variable temperature nuclear magnetic resonance (VT-NMR) spectra and an increase in molar absorptivity seen through UV-Visible spectroscopy suggest the formation of the N-sulfide bond. Modeling of the UV data with the SIVVU software reveals an increase in the Gibbs free energy and equilibrium constants with increasing solvent polarity, suggesting the N-sulfide bond exists as a charged species. Finally the formation of S-Py was confirmed by gas chromatography-mass spectrometry (GC-MS) with a M+ of 111 m/z, corresponding to a single sulfur bonded to a single pyridine.

Developing an Infrastructure for Chemical Demonstration Outreach

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This project aims to aid and provide resources to people interested in using chemistry demonstrations in a variety of venues. Specifically, we are targeting college professors, college students and K-12 teachers, largely within the state of Virginia. We have made significant progress over the last year. A new website was developed (Summer 2011), with improved functionality and appearance compared to the original site. This website includes over 50 demonstrations with instructions on how to perform them, including downloadable and editable Word formats. In addition the website contains lesson plans and problem sets corresponding to selected demos for ease of use in the classroom. The Second Annual Chemistry Demonstration Workshop for High School Teachers was held for 20 participants on July, 15th, 2011. The workshop (9am-3pm) included hands-on demonstration instruction, a presentation on the importance of demos, and opportunities to discuss demos with other high school teachers. Seven chemical demonstration videos were recorded and produced in collaboration with JMU's Center for Instructional Technology (CIT). These videos were incorporated into the website. Finally a number of demos have been prepared and delivered for JMU instructors to use in class.

The Synthesis of Tripod Molecules for Ultrafast Photolysis Studies

Michelle Rudman, Andrew Evangelista and Debra L. Mohler
Department of Chemistry and Biochemistry, James Madison University

A 1,3,5,7-tetraphenyladamantane tripod with carboxymethyl anchoring groups and a photoactive perylene complex was synthesized according to literature. The purpose of this system is to keep the light-sensitive perylene complex perpendicular to the semiconductor surface in order to study the effects of distance on solar cell efficiency. By varying the distance between the perylene "dye" and the molecular anchoring groups, improvements may be made in solar cell technology. Further studies of this molecule via femtosecond IR spectroscopy will be conducted at Emory University.

Formation of asymmetric 1,3-difluorobenzenes

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In an effort to produce a variety of substituted cyclobutenes as starting material for the one-pot synthesis of difluoroaromatic compounds, the synthesis of asymmetric 1-isopropylcyclobutene (1) and 1-hexanecyclobutene (2) was accomplished. The preparation of 1 and 2 were achieved through a 4-step synthesis. The intermediates were purified and characterized through column chromatography, GCMS, and NMR. Further purification of 1 was accomplished via bromination across the double bond, however, compound 2 has not yet been brominated. The 1,3-difluoro-2-isopropyl benzene final product was accomplished for 1 through a reaction with a 2:1 mole ratio of carbene reagent to starting material, the compound was confirmed with NMR and GCMS.

Synthesis of Ruthenium Complex Containing N-pyrazolylpropanamide

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Department of Chemistry and Biochemistry, James Madison University

The synthesis of RuCl₂(PPh₃)₂N-ppa (1) was accomplished via the addition of N-pyrazolylpropanamide (N-ppa) (2) to Cl₂Ru(PPh₃)₃ (3). The crystal structure of 1 was determined by X-ray crystallography. Variable temperature NMR spectroscopy has been employed to study a solution phase equilibrium that exists for 1 in dimethylformamide.

The synthesis and coordination chemistry of K[BH₂(C₂H₂N₂)₂]

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Potassium dihydrobis(1,2,4-triazolyl)borate, K[BH₂(trz)₂], has been synthesized as a potential linker for making metal organic frameworks. K[BH₂(trz)₂] was synthesized by reacting KBH₄ with a triazole flux under a nitrogen atmosphere. K[BH₂(trz)₂] was reacted with transition metal ions (Ag⁺, Co²⁺, Cu²⁺, Zn²⁺, and Ni²⁺) via solvothermal reactions and slow layer diffusion in an attempt to form frameworks. Results of ligand synthesis, characterization and attempts to understand the coordination chemistry of this ligand will be presented.

Synthesis of siRNA Analogues

Brooke N. Stevens and Debra L. Mohler
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The synthesis of stable RNA analogues that can bind via Watson-Crick base pairing is a goal of therapeutic siRNA treatments. One method of synthesis of the RNA analogues is using a single step polymerization. Individual monomers are first synthesized by protecting deoxynucleosides then forming a ring. The monomers are polymerized using a ring opening metathesis polymerization (ROMP). Due to the method of constructing the monomers and the method of polymerization, the siRNA strand can be constructed to target a specific gene.

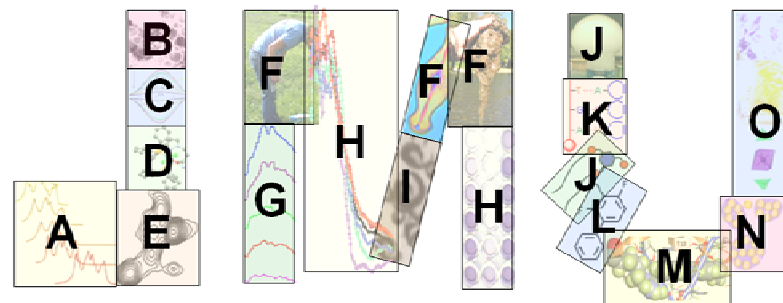
Effects of Osmolytes on the Phase Behaviors of PEO-PPO-PEO

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The phase behavior of triblock copolymers in the presence of osmolytes was employed as a model system to investigate the mechanisms of osmolyte-protein interactions. Specifically, the phase transition temperatures of PEO-PPO-PEO in the presence of 12 osmolytes were measured by using an automated melting point system. It was found that the polymer undergoes a two-step phase transition in solutions containing all the protein stabilizers used in this study. On the other hand, protein denaturants showed an interesting trend in affecting the phase transition of the polymer. The polymer shows a two-step phase transition in solutions containing urea up to 6 M. When the hydrophobicity of the denaturant increases, switching from urea to 1,3-diethylurea, the polymer shows only one step in phase transition. The molecular level interactions of triblock copolymers with osmolytes will be explored.



Real-Time Micro-Phase Separation Kinetic Analysis of POSS-MA Thin Films Using Atomic Force Microscopy

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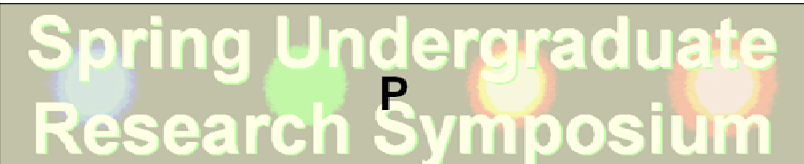
Poly(propylmethacrylisobutyl POSS co-methylmethacrylate) (POSS-MA) is a co-polymer that contains polyhedral oligomeric silsesquioxane (POSS) cages co-polymerized to a poly(methyl methacrylate) (PMMA) backbone. 2 mg/mL solutions of 20 – 70 wt% POSS-MA are dissolved in chloroform and deposited onto samples of oxidized Si wafers using spin casting. Immediately after spin casting, these samples are analyzed using atomic force microscopy (AFM) while being heated in a range of 25-90° C. Typical 30 – 70 wt% POSS-MA thin films exhibit varying rates of micro-phase separation. Once this micro-phase separation is complete, the pixel areas of the dendritic structures are measured using the AFM software on the complete time-series of AFM scans. These varying area determinations are normalized and then fit to the Avrami plot by graphing $\ln(-\ln(1-f))$ vs. $\ln(\text{time})$ with "f" being the normalized area and the time being time after deposition. From this graph, the resulting slope is the dimensionality of growth constant and the y-intercept is the natural logarithm of the rate constant ($\ln k$). Data shows the dimensionality of growth constant to vary from 1.72 to 2.15 and the $\ln(k)$ to vary from -9.02 to -14.14 when the scan is conducted at 35° C for 30 wt% POSS-MA thin films. This data is consistent with the literature values of two dimension micro-phase separation in polymer thin films. Current work involves characterization of the silicon composition of the dendritic structures present on the POSS-MA thin films.

Improved Method of Nitrate-Nitrogen Determination in Soils and Sediments by Instrumental Ion Chromatography

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The standard determination of nitrate-N in soil samples requires extraction into potassium chloride solution, nitrate to nitrite reduction with a cadmium column, and a colorimetric analytical finish with sulfanilamide. The reduction and colorimetry steps are difficult and time consuming and are prone to contamination and matrix interferences. Instrumental ion chromatography (IC) is a less complicated and more rapid procedure for nitrate determination in aqueous samples. However, the high concentration of chloride (2M) necessary for extraction has precluded the use of IC due to column and detector saturation. Recently, the development of a silver extraction column (Dionex OnGuard® II Ag) has provided means of removing chloride ion prior to IC determination of nitrogen-nitrate. We have found that more than 99.9% of the chloride can be removed from solution by the silver cartridges. Calibration standards were assayed and nitrate was recovered with no loss in the silver cartridges ($p < 0.001$). Nitrate-N was determined by both the colorimetric and IC methods in samples collected from farm fields in the Shenandoah Valley for method comparison.



The image on the front cover is a collage of images from the research labs of:

A	Dr. Brycelyn M. Boardman	I	Dr. Yanjie Zhang
B	Dr. Brian H. Augustine	J	Dr. Kevin L. Caran
C	Dr. Melissa C. Rhoten	K	Dr. Debbie L. Mohler
D	Dr. John W. Gilje & Dr. Donna S. Amenta	L	Dr. Scott B. Lewis
E	Dr. Nathan T. Wright	M	Dr. Orde Munro
F	Dr. Daniel M. Downey	N	Dr. Christine A. Hughey
G	Dr. Thomas C. DeVore	O	Dr. Barbara A. Reisner
H	Dr. Gina MacDonald	P	Dr. Daniel K. Havey

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