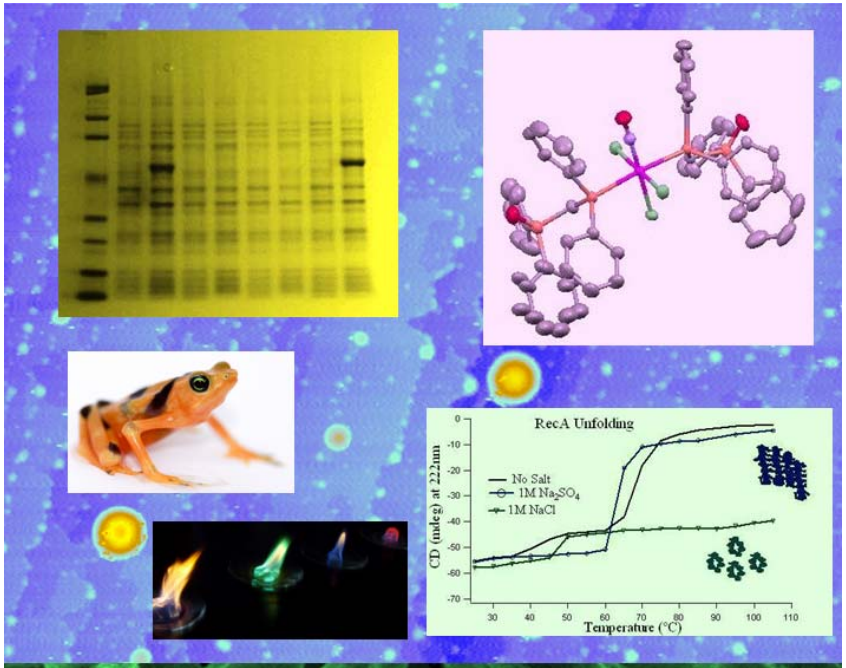
JAMES MADISON UNIVERSITY

DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY

35th Annual



SPRING UNDERGRADUATE RESEARCH SYMPOSIUM

THURSDAY APRIL 8, 2010

POSTER SESSION: 1:30 – 3:00 PM (PH/CH 3348)
ORAL SESSION I: 3:15 – 4:45 PM (ISAT 259)

FRIDAY APRIL 9, 2010

ORAL SESSION II: 2:15 – 3:15 PM (ISAT 159)
KEYNOTE ADDRESS: 3:45 – 4:45 PM (ISAT 159)

See back cover for description of images.

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 AND AFFILIATION
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	**Dr. Daniel Downey** *James Madison University*
	1976	**Dr. Gary Rice** *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*

35th Annual Department of Chemistry and Biochemistry

Spring Undergraduate Research Symposium Keynote Address

Friday, April 9, 2010 at 3:45pm
ISAT Room 159

"Using NMR Spectroscopy to Probe the Intermolecular Interactions in Chiral Chromatography"

Kevin Morris (JMU Class of 1988), Ph.D.
Klingenmeyer Distinguished Professor of Chemistry
Carthage College
Kenosha, WI

Dr. Morris received his BS degree in Chemistry in 1988 from James Madison University. He obtained his Ph.D. from the University of North Carolina Chapel Hill Department of Chemistry in 1993 where his thesis work focused on the development of new two-dimensional NMR experiments. After graduation, he was a Camille and Henry Dreyfus Fellow and then Assistant Professor at Grinnell College before joining the chemistry department at Carthage College in 1996. In 2006, he was appointed Carthage's first Ralph E. Klingenmeyer Distinguished Professor of Chemistry. He also served as chemistry department chair from 2002-2008. At Carthage he teaches Physical and General Chemistry and conducts NMR research on the binding of chiral drugs to molecular micelles. The Camille and Henry Dreyfus Foundation and the American Chemical Society Petroleum Research Fund have supported his research.

Poster Session: Thursday April 8th 1:30 – 3:00 pm *(Ph/Ch 3348)*	
Anne Battalia and Daniel Downey	Nutrient and Sediment Loading in Lake Shenandoah, Rockingham County, Virginia
Courtney Braxton, Jillian Stanton and Victoria Mariani	Cloning and Expression of Inosine 5-Monophosphate Dehydrogenase (IMPDH) from Extremophiles
Adam Colbert and Gina MacDonald	Using Difference Infrared Spectroscopy to Investigate the Effects of pH on PGK-Substrate Complexes
Brittany Danzig, Nathaniel Talley, William Cannon and Gina MacDonald	The Effect of Salt and DNA on RecA Stability and Unfolding
Alexa DeLuca, Donna S. Amenta and John W. Gilje	Monohydride and Dihydride Ruthenium Complexes of Bis(diphenylphosphine) Ligands
James Dillon and Scott Lewis	Synthesis and Characterization of 1-isopropylcyclobutene
Robert East and Victoria Mariani	Cloning and Expression of 5-Enolpyruvylshikimate-3-phosphate Synthase From Thermus Thermophilus HB27
Seth Ensign, Amanda Hoffman, Puja Mody and Debra L. Mohler	Synthesis of a chlorotricarbonylrhenium (I) complex of [4, 4'- bis(aminomethyl)-2,2'-bipyridine] for rate of interfacial electron transfer study
Kelly George, Georgia Stoyanov and Kevin P. C. Minbiole	The Synthesis of Nitrogen- and Sulfur-Containing Heterocycles from Cyclopropanol Fragmentation
Alan Mo, Brian H. Augustine and W. Christopher Hughes	Au Thin Film Adhesion to PMMA Substrates Through Spin-Coated POSS-MA
Jennifer Phillips, Holly Tuck and Daniel Downey	Update of Long Term Results for Liming a "Sinking" Stream Versus a Perennial Surface Stream
Casey Rogers and Kevin L. Caran	Chemistry Demonstrations at JMU
Michael Salim, Yanita Boayue, Paris Hamilton, Kevin L. Caran, Lin Pu and Michal Sabat	Dimeric Propargylic Alcohols
Cameron Straughn and Debra L. Mohler	Synthesis of Stable RNA Analogs
Lindsay Walton, Sadie Knight, Donna S. Amenta and John W. Gilje	Synthesis and characterization of the products from the reaction of $RuCl_3NO(PPh_3)_2$ with $Ph_2PCH_2P(O)Ph_2$ and $Ph_2P(CH_2)_2P(O)Ph_2$.
Curtis White and Thomas DeVore	Proton Chemical Shifts for Alcohols in the Vapor Phase and Dilute Solutions

Oral Session I: Thursday April 8th *(ISAT 259)*		
3:15 – 3:30	Jacob Smith and Daniel Downey	Trace Metal Analysis in Fish Tissue by Laser Ablation Inductively Coupled Plasma Mass Spectrometry
3:30 – 3:45	Christian Schwantes, Kevin P. C. Minbiole, Reid N. Harris	The Antifungal Bacterium, *Janthinobacterium lividum*, Does Not Protect the Extinct Panamanian Golden Frog from Chytridiomycosis in Vitro
3:45 – 4:00	Samuel Moore and Katherine Layman	Catalytic Oxidation of p-Cresol on Aluminum Oxide-Supported Cobalt Catalysts
4:00 – 4:15	David Warnock, Kaitlin Simmons, Kristina Hamill and Kevin L. Caran	Bicephalic (Double-Headed) Amphiphiles
4:15 – 4:30	Nicole Ando, Donna S. Amenta, John W. Gilje, Glenn P. A. Yap	Ruthenium Complexes Containing $PPh_2(CH_2)_nP(O)Ph_2$ Ligands
4:30 – 4:45	Megan Woods and Thomas DeVore	The Thermal Decomposition of 2-Propanol Using a Zinc Sulfide Catalyst

Oral Session II: Friday April 9th *(ISAT 159)*		
2:15 - 2:30	Matthew J. Bradley, Brian H. Augustine, W. Christopher Hughes	Analysis of the Time Evolution Of Structures in POSS-MA Thin Films Deposited by Spin Casting
2:30 – 2:45	Patrick J. Wiggins, Christian R. Schwantes, Kevin P. C. Minbiole and Reid N. Harris	Antimicrobial Chemical Defense: Identification and Application of Antifungal Metabolites from *Janthinobacterium lividum* and *Pedobacter cryoconitis*
2:45 – 3:00	Kevin Kindley, Hollins Kitt, Allyson Jones and Kathryn Layman	Characterization of Magnetic Iron Oxide Composites
3:00 – 3:15	Georgia Stoyanov, Kelly L. George and Kevin P. C. Minbiole	The Synthesis of Nitrogen- and Sulfur-Containing Heterocycles from Cyclopropanol Fragmentation
3:15 – 3:45	**---------- break ----------**	
Keynote Address: Friday April 9th *(ISAT 159)*		
3:45 – 4:45	**Dr. Kevin Morris** *(JMU Class of 1988)*	**Using NMR Spectroscopy to Probe the Intermolecular Interactions in Chiral Chromatography**

Keynote Address

Friday, April 9, 2010 at 3:45pm
ISAT Room 159

Using NMR Spectroscopy to Probe the Intermolecular Interactions in Chiral Chromatography

Dr. Kevin Morris
Carthage College

Chiral separations are necessary in drug discovery and medicinal chemistry because chiral drug enantiomers often have different physiologic properties. Electrokinetic chromatography (EKC) is an analytical method that efficiently separates the enantiomers in racemic mixtures based upon differences in their interactions with chiral polymers. This presentation will focus on how NMR spectroscopy has been used to probe the intermolecular interactions, thermodynamics, and motional dynamics associated with the binding of analyte enantiomers to polymers used in chiral EKC separations. The polymers investigated are made of surfactant or soap molecules that are covalently attached to one another at the end of each molecule's hydrocarbon chain. Each surfactant monomer also contains a chiral amino acid or dipeptide head group. The structures of the intermolecular complexes formed between the chiral polymers and analyte enantiomers were investigated with two-dimensional NOESY experiments. NOESY spectra provide information about interactions between nuclei that are within ~5 Å but not necessarily connected through chemical bonds. The thermodynamics of the analyte:polymer interactions were investigated with NMR diffusion experiments. These experiments probe the rate of diffusion or translational motion when analyte enantiomers are in free solution and bound to the chiral polymers. Diffusion experiments were used to measure analyte:polymer association constants. These binding constants were then correlated with and compared to the chiral resolution achieved in EKC. Finally, NMR relaxation experiments were used to study the rotational or reorientational motion of the analyte enantiomers. These experiments revealed which analyte atoms became constrained or immobilized when the analyte bound to the chiral polymer.

STUDENT ABSTRACTS

Ruthenium Complexes Containing $PPh_2(CH_2)_nP(O)Ph_2$ Ligands

Nicole Ando,[1] Donna S. Amenta,[1] John W. Gilje[1] and Glenn P. A. Yap[2]
[1] Department of Chemistry and Biochemistry, James Madison University
[2] Department of Chemistry and Biochemistry, University of Delaware

The reactions of $Cl_2Ru(PPh_3)_3$ with 1 or 2 equivalents of $PPh_2CH_2CH_2P(O)Ph_2$ or $PPh_2CH_2P(O)Ph_2$ were run in toluene at room temperature. From the reaction of $Cl_2Ru(PPh_3)_3$ with 1 equivalent of $PPh_2CH_2P(O)Ph_2$, $Cl_2Ru(PPh_3)_2(PPh_2CH_2P(O)Ph_2)$ was characterized by ^{31}P NMR spectroscopy and by a crystal structure. When the reaction is run in acetonitrile or with benzonitrile as a reagent, $Cl_2Ru(PPh_3)(PPh_2CH_2P(O)Ph_2)(NCR)$ is observed. The chemical shifts of the PPh_2 and P(O) moieties and the crystal structure show that both the phosphino phosphorus and phosphoryl oxygen are bonded to the ruthenium. We postulate that the basicity of acetonitrile or benzonitrile facilitates the dissociation of the second PPh_3. The reaction of $Cl_2Ru(PPh_3)_3$ with 2 equivalents of $PPh_2CH_2P(O)Ph_2$ and excess acetonitrile or benzonitrile produces $Cl_2Ru(PPh_2CH_2P(O)Ph_2)_2(NCR)_x$. The ^{31}P NMR spectrum contains two peaks, one due to the phosphine and the other to the phosphoryl phosphorus of the ligands. Chemical shifts indicate both coordinate to the ruthenium.

Nutrient and Sediment Loading in Lake Shenandoah, Rockingham County, Virginia

Anne Battaglia and Daniel Downey
Department of Chemistry and Biochemistry, James Madison University

Lake Shenandoah, a VDGIF recreational reservoir that supports a sport fishery for warm water fish species, is located in Rockingham County, Virginia near the city of Harrisonburg. The lake experiences chronic fishery and aesthetic management problems due to macrophyte growth, sedimentation and eutrophication. In 1996-97, a study was conducted that measured nutrient loading and found that sedimentation and eutrophication problem had occurred due to agricultural practices and recent land development in the watershed. The purpose of this study was to determine if sediment and nutrient loading have changed since the watershed land use has changed from agriculture to suburban development in the last ten years. Water quality parameters include pH, ANC, Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, NO_3^-, SO_4^{2-}, ammonia (NH_3/NH_4^+), turbidity, conductivity and total phosphorus (P_T) were measured for each of the two streams entering the reservoir. The average values for nutrient and turbidity (sediment) loading from Massanetta Spring Run (north) were 51.6 ppb P_T, 1.94 ppm NO_3-N, 0.32 ppm NH_3/NH_4^+-N and 12.1 NTU. The average values for nutrient and turbidity (sediment) loading from Congers Creek (west) were 67.9 ppb P_T, 4.09 ppm NO_3-N, 0.14 ppm NH_3/NH_4^+-N and 10.1 NTU. Phosphorus values exceeded the federal criterion of 50 ppb for streams entering lakes. We found that nutrient and turbidity increased during runoff from episodic events. Sediment samples collected from the west and north reaches of the lake contained average values of 33 mg/kg P_T, 9.5 mg/kg NO_3-N and 9.3 mg/kg NH_3/NH_4^+-N. These data should provide information useful for management directives for mitigation and restoration of Lake Shenandoah.

Analysis of the Time Evolution Of Structures in POSS-MA Thin Films Deposited by Spin Casting

Matthew Bradley,[1] Brian Augustine[1] and Chris Hughes[2]
[1] Department of Chemistry and Biochemistry, James Madison University
[2] Department of Physics and Astronomy, James Madison University

Poly(methacrylisobutyl POSS-co-methylmethacrylate) (POSS-MA) is a nanocomposite co-polymer that is capable of exhibiting properties of both organic polymers and nanometer scale silica. POSS-MA may be readily deposited as a thin film by spin casting using a solution of POSS-MA in chloroform. Previous work had shown that dendridic crystalline structures form on 45wt% POSS-MA as soon as deposited on to the substrate (real-time and in-situ observations were made using AFM). Atomic force microscopy (AFM) analysis of these spin cast films show these dendritic structures forming on 30wt% POSS-MA thin films in as little as 5 hours after deposition at room temperature. Analysis work has been performed in an attempt to measure the morphological changes of the films of the structures as a function of time. The growth rate was also measured at varying temperatures. Increasing temperature resulted in an increase in both the number of nucleation sites and in the rate of growth of the dendridic structures. The crystallization has been modeled using the classic Avrami growth kinetics model. This resulted in an Avrami exponent n=1.84 and rate constant k=11.3 at 23 C which is consistent with literature values for the isothermal crystallization of POSS-MA films. X-ray diffraction studies have also been initiated to better understand the crystallization process. Comparisons will be made with differing POSS-MA compositions to suggest a POSS-MA crystallization phase diagram across the 0-70 wt% composition range.

Cloning and Expression of Inosine 5-Monophosphate Dehydrogenase (IMPDH) from Extremophiles

Courtney Braxton, Jillian Stanton and Victoria Mariani
Department of Chemistry and Biochemistry, James Madison University

Inosine 5-monophosphate dehydrogenase (IMPDH) is a critical enzyme in the synthesis of DNA nucleotide purines, adenine and guanine. IMPDH catalyzes the oxidation of xanthosine monophosphate (XMP) which is a precursor for guanosine monophosphate (GMP). GMP, which is readily converted to guanosine-5'-triphosphate (GTP) and guanosine 5'-diphosphate (GDP), is a necessary cofactor for the synthesis of adenosine monophosphate (AMP). An isoform of IMPDH, type II IMPDH, is linked to both cancer and RNA viruses. DNA encoding for IMPDH from extremophilic bacteria Colwellia pyscherythaea 34H and Thermus thermophilus HB27 was successfully isolated via a high fidelity polymerase chain reaction (PCR). This PCR product, along with expression vector, pET-19b, will be restriction digested in preparation for a ligation reaction to create a means to purify the corresponding recombinant IMPDH enzymes. These enzymes will be compared to their mesophilic counterpart from Escherichia coli K12, in which we hope to determine which second tier amino acids are pivotal in the structure and function of the IMPDH.

Using Difference Infrared Spectroscopy to Investigate the Effects of pH on PGK-Substrate Complexes

Adam Colbert and Gina MacDonald
Department of Chemistry and Biochemistry, James Madison University

Yeast phosphoglycerate kinase catalyzes the reversible phosphate transfer in the reaction: ADP +1,3-bis-phosphoglycerate $\rightleftharpoons$ ATP + 3-phosphoglycerate. Prior research indicates a hinge-bending mechanism occurs during catalysis to bring the substrates into closer proximity. Domain closure is only initiated in ternary complexes, in which both substrates are simultaneously bound to the enzyme. The activity and conformation of PGK is directly influenced by substrate and salt concentrations as well as pH. Activity assays confirm that PGK activity increases from pH 5.5 to 7.5. We used difference Fourier transform infrared spectroscopy (FTIR) in conjunction with caged nucleotides to determine the effects of pH and buffer salts on the conformational changes of PGK. Difference infrared data associated with nucleotide (ATP or ADP) binding to PGK or PGK-3PG complexes was compared at pH 5.5, 6.5 and 7.5. Circular dichroism was also used to study PGK secondary structure at the aforementioned pH conditions. Comparison of the difference FTIR data allowed the isolation of pH dependent vibrations that arise from protein conformational changes induced by substrate binding. Considerable differences were observed in the difference spectra between samples using HEPES and MES buffer salts. We have identified multiple vibrations that are associated with the PGK ternary complex and are influenced by pH. Difference FTIR studies resulted in the identification of specific changes within amino acid side chains and protein secondary structures associated with ternary complex formation that are altered by pH and buffer salt.

The Effect of Salt and DNA on RecA Stability and Unfolding

Brittany Danzig, Nathaniel Talley, William Cannon and Gina MacDonald
Department of Chemistry and Biochemistry, James Madison University

The RecA protein of Escherichia coli is a multifunctional enzyme involved in homologous recombination, DNA repair, and SOS gene induction. Although RecA is typically a DNA-dependent ATPase, high salt concentrations have been shown to activate RecA mediated ATP hydrolysis in the absence of DNA. Previous experiments in our lab involving the thermally induced unfolding of RecA in various salt conditions determined that RecA stability is dependent on the concentration and nature of the salt ions present in solution. The current study continues this examination of RecA unfolding while in the presence of single stranded DNA. Circular Dichroism (CD) studies have shown that the presence of single stranded DNA do not significantly influence the melting temperature of RecA at high salt concentrations. However, RecA-ssDNA complexes at low concentrations are dependent upon solution conditions. Future studies of RecA in the presence of multiple low salt concentrations are required to determine how ssDNA influences the secondary structure of the RecA protein.

Monohydride and Dihydride Ruthenium Complexes of Bis(diphenylphosphine) Ligands

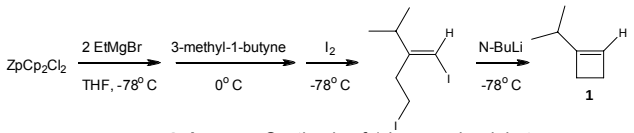
Alexa DeLuca, Donna S. Amenta and John W. Gilje
Department of Chemistry and Biochemistry, James Madison University

Transition metal complexes of *bis* phosphinomonoxide ligands ($R_2P(CH_2)_nP(O)R_2$) play important roles in catalytic reactions. We are interested in synthesizing Ru (II) hydride complexes of $Ph_2P(CH_2)_nP(O)Ph_2$. The reaction of $RuHCl(CO)(PPh_3)_3$ with $Ph_2PCH_2P(O)Ph_2$ in THF produces $RuHCl(CO)(PPh_3)(PPh_2CH_2P(O)Ph_2)$. This compound has been characterized by ^1H NMR, ^{31}P NMR, and IR Spectroscopy. The two PPh_3 ligands that are removed in the reaction were *cis* to each other and *trans* to the hydride and carbonyl ligands respectfully. The $Ph_2PCH_2P(O)Ph_2$ ligand chelates to the ruthenium through the phosphorus and oxygen of the ligand and the PPh_2 group is *trans* to the PPh_3 ligand that remains on the compound. In solution $RuHCl(CO)(PPh_3)(PPh_2CH_2P(O)Ph_2)$ slowly isomerizes to two new compounds. While these two compounds have not yet been completely identified, one has two *trans* phosphino phosphorus atoms and one phosphoryl phosphorus that is *cis* to the other two. The reaction of $RuH_2(CO)(PPh_3)_3$ with $Ph_2PCH_2P(O)Ph_2$ in THF produces $RuH_2(CO)(PPh_3)(PPh_2CH_2P(O)Ph_2)$. This compound has also been characterized by ^1H NMR, ^{31}P NMR, and IR Spectroscopy. After the two PPh_3 ligands are removed the $Ph_2PCH_2P(O)Ph_2$ ligand chelates to the ruthenium through both phosphorus and oxygen. The PPh_2 is *trans* to the PPh_3 ligand that remains on the compound and the two hydride ligands which were *cis* to each other in $RuH_2(CO)(PPh_3)_3$, have moved to a *trans* conformation.

Synthesis and Characterization of 1-isopropylcyclobutene

James Dillon and Scott Lewis
Department of Chemistry and Biochemistry, James Madison University

In the ongoing effort to produce a variety of substituted cyclobutenes as starting material for the one-pot synthesis of difluoroaromatic compounds[1], the synthesis of the asymmetric 1-isopropylcyclobutene (**1**) was accomplished. The preparation of **1** was achieved through a 4-step synthesis (Scheme 1) via a two-pot reaction. A di-iodo alkene intermediate and its isomer were isolated via column chromatography and characterized using NMR. The di-iodo alkene was cyclized using n-BuLi and confirmed via GC-MS. Purification of **1** was accomplished via bromination of the olefin and isolated through column chromatography. Purified **1** was characterized using NMR and IR spectroscopy.



Scheme 1. Synthesis of 1-isopropylcyclobutene.

1. Lewis, S. B.; Borden, W. T. Tetrahedron Lett., 1994, 35, 1357.

Cloning and Expression of 5-Enolpyruvylshikimate-3-phosphate Synthase From Thermus Thermophilus HB27

Robert East and Victoria Mariani
Department of Chemistry and Biochemistry, James Madison University

The aroA gene encodes for the expression of 5-Enolpyruvylshikimate-3-phosphate (EPSP) synthase which catalyzes the reversible reaction forming EPSP from shikimate-3-phosphate (S3P) and phosphoenolypyruvate (PEP) in the sixth step of the shikimate pathway. The shikimate pathway, which links the metabolism of carbohydrates to aromatic amino acid biosynthesis, is found in plants, fungi, and bacteria. Because of this aforementioned exclusivity, EPSP synthase is a promising target for antibiotic, antiparasitic, and herbicide development. Through structural characterization of thermophilic, mesophilic, and psychrophilic EPSP synthases, we also hope to elucidate which particular moieties outside of the active site are pivotal to function. Here we report successful amplification of the aroA gene from cDNA libraries of Thermus thermophilus, Colwellia pyscherythaea and *Escherichia coli* via a high fidelity polymerase chain reaction. Restriction enzyme digestion of aroA as well as the expression vectors pET-31b and pET19b are being attempted so as to enable a subsequent ligation of the aroA gene into the vectors. Upon successful ligation, the recombinant plasmids will be transformed into *E. coli* JM109 strain which will amplify the recombinant plasmid so that it may be extracted and sequenced. The clone will then be transformed into *E. coli* BL21 pLysS strain which will express the EPSP synthase. All actions proceed towards the ultimate goal of performing structural and kinetic analysis on the various EPSP synthases.

Synthesis of a chlorotricarbonylrhenium (I) complex of [4, 4'- bis(aminomethyl)-2,2'-bipyridine] for rate of interfacial electron transfer study

Seth Ensign, Amanda Hoffman, Puja Mody 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, chlorotricarbonylrhenium complexes of bipyridines with varying anchoring groups were synthesized and bonded to the rhenium complex. The specific goal of this work is to create a chlorotricarbonylrhenium (I) complex of [4,4'-bis(aminomethyl)-2,2'-bipyridine] for later study by femtosecond IR spectroscopy.

The Synthesis of Nitrogen- and Sulfur-Containing Heterocycles from Cyclopropanol Fragmentation

Kelly George, Georgia Stoyanov and Kevin Minbiole
Department of Chemistry and Biochemistry, James Madison University

The prevalence of heterocycles as the backbone of common pharmaceutical entities has created a demand for simple reactions to prepare them. Our research aimed to create six-and seven-membered heterocycles containing both a carbonyl group and either sulfur or nitrogen in the ring. A cyclopropanol fragmentation approach to the formation of oxepanes was developed in previous work done by Minbiole lab. Using a similar approach, our current endeavor is to synthesize nitrogenous heterocycles, particularly piperidines and azepines, as well as sulfur-containing thiepanes. The nitrogenous approach begins with either N-benzyl-protected alpha- or beta-amino acid ethyl esters which were transformed by cyclopropanols via the Kulinkovich reaction. The resulting alpha- or beta-amino cyclopropanols were then reacted with various aldehydes to form an aminal. Subsequently, various Lewis acids were used to promote the rearrangement of the aminal into the piperidine or azepine formation. This rearrangement is still under investigation. Analogously, a seven-membered sulfur-containing heterocycle was formed by sequential addition of aluminum (III) triflate and bismuth (III) triflate as Lewis acids to a mercaptocyclopropanol/benzaldehyde mixture, though heterocycle was only produced in low yields(<20%).

Characterization of Magnetic Iron Oxide Composites

Kevin Kindley, Hollins Kitts, Allyson Jones and Kathryn Layman
Department of Chemistry and Biochemistry, James Madison University

In order to remove metal cations from contaminated ground water, magnetic iron oxide composites are being investigated. These composites can be supported on various ratios of NaY zeolites, aluminum oxide, and silica. A previously published procedure to synthesize these composites was varied in order to create a more effective and practical adsorbent. The composites were then characterized using IR spectroscopy, the magnetic susceptibility balance, and the x-ray power diffractometer (XRD). In order to determine the amount of Cu^{2+} uptake by the composite, atomic absorption (AA) was used. Prior research has shown that 25°C is the optimal temperature for the synthesis of these composites. The amount of Cu^{2+} uptake and the magnetic susceptibility were influenced by six factors: 1) whether or not the support was added prior to the formation of the iron oxide particles; 2) the support to iron oxide mass ratio; 3) the type support used; 4) the source of iron; 5) the stirring time; and 6) the amount of time it took to add the NaOH. The type of support used determines the degree of correlation between the amount of Cu^{2+} uptake and the magnetic susceptibility. XRD data shows that the zeolite support with the SiO_2: Al_2O_3 ratio equal to 4.9 was best able to maintain its structure. These metal composites have also shown unselective reactivity in the oxidation of *p*-cresol.

Au Thin Film Adhesion to PMMA Substrates Through Spin-Coated POSS-MA

Alan Mo, Brian H. Augustine and W. Christopher Hughes
Department of Chemistry and Biochemistry, James Madison University

Nanotechnology has been beneficial in shrinking existing processes, such as those related to computer architecture. Currently, there is another goal of miniaturizing processes in the field of bioanalytical chemistry. The shrinking of common laboratory techniques, such as polymerase chain reaction (PCR), can allow for faster reactions and require less reagents and analytes. One essential component in many such devices is metal electrodes, in particular gold. Some properties that make gold widely chosen are its resistance to corrosion, high reflection, and electrical conductance. Yet production in miniaturized devices is often difficult because Au only binds well to inorganic materials rather than plastics. But through a thin layer of POSS-MA, a nanocomposite polymer that contains glassy-like properties, we demonstrate that Au thin films can bind well to plastics. Experiments have been conducted where POSS-MA has been spin-coated onto 1"x1" squares of PMMA. These were then plasma treated to expose the glassy-like properties of POSS-MA and Au thin films were sputter deposited. Acetone was added while the chemical adhesion of gold to PMMA was observed through light microscopy. By video analysis, the effect of plasma treated POSS-MA was compared to the controls: these controls were the effect of non-plasma treated POSS-MA, the effect of no POSS-MA, and the effect of plasma-treatment on PMMA. Preliminary data shows that non-plasma treated POSS-MA provides the best adhesion at the PMMA-Au interface.

Catalytic Oxidation of p-Cresol on Aluminum Oxide-Supported Cobalt Catalysts

Samuel A. Moore and Kathryn Layman
Department of Chemistry and Biochemistry, James Madison University

p-Hydroxybenzaldehyde (PHBA) is an important starting material and intermediate for the synthesis of many polymers, pharmaceuticals, fragrances, and flavoring agents. *p*-Cresol oxidation may reduce the cost, simplify synthesis, and decrease the environmental hazards associated with the current industrial processes used to synthesize PHBA. Metal oxide catalysts have been demonstrated to oxidize *p*-cresol to PHBA in the presence of NaOH, gaseous O_2 and solvent methanol. Cobalt catalysts prepared by impregnation onto aluminum oxide and subsequent calcinations are shown to be effective catalysts in the oxidation of *p*-cresol. Calcination temperature is shown to have a direct influence on catalytic ability of the product catalyst, which reaches a maximum of 95.7% conversion of *p*-cresol and 92.4% selectivity to PHBA using a 30 wt% Co/Al_2O_3 catalyst calcined at 900°C for 3 hours. Cobalt aluminate ($CoAl_2O_4$) is shown to preferentially form over cobalt (III) oxide (Co_2O_3) at calcination temperatures ≥ 700°C and accounts for the downward trend of catalytic ability concurrent with calcinations temperature. Sad *et al.* recently reported that methanol reacts with phenol, the internal standard, indicating the need to develop a new calibration methodology. To this end, recent research has focused on creating calibration plots based on the ratio of PHBA to *p*-cresol.

Update of Long Term Results for Liming a "Sinking" Stream Versus a Perennial Surface Stream

Jennifer Phillips, Holly Tuck and Daniel Downey
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Mountain Run (Fridley Gap Run) is located in the Massanutten Mountain Range of Virginia in the George Washington National Forest. Brook trout and other fish species historically found in this stream suffered severe losses due to the decrease in pH caused by atmospheric acid injection (acid rain). To improve water quality and enable fish survival Mountain Run has been treated with limestone at various times from 1993 to 2008. Initial treatments in 1993 and 1997 were done at a location in a lower reach that flows perennially. This site was only accessible by helicopter. To save costs, later liming (1999, 2002, 2005, and 2008) was done by front end loader in an upper reach at a trail/road. Under normal flow conditions the upper reach of the stream sinks into the channel substrate several times before the stream is remains surficial. Water quality parameters (WQP) have been assessed for samples collected monthly at six (or more) locations from 1992 to 2010. Key WQP values were catalogued as follows for four locations: upstream of the perennial site, 1.25 km downstream of the perennial site, upstream of the sinking site and 1.25 km downstream of the sinking site. Average values found were pH = 4.64, 5.73, 4.59, 5.05; ANC = -22.2, 20.1, -28.2, -6.9 (μeq/L); Ca:H = 1.3, 265.1, 0.87, 9.0; AlT = 303, 108, 409, 184 (ppb) for these four locations, respectively. This study compared the effectiveness of liming Mountain Run in the two locations, and showed that the response to liming the upper reach is less effective due to the sinks in the stream and the acidic nature of the soil. A model has been developed for the upper reach that predicts soil saturation should occur 19 years from the initial liming.

Chemistry Demonstrations at JMU

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The chemistry demonstrations done by student organizations were inventoried and are in the process of being written into handouts explaining the details of each demonstration in an effort to improve upon, and bring more organization to the demonstrations. New demonstrations are also being researched, tested, and developed into handouts in a similar fashion as the existing demonstrations. This modular approach allows flexibility for presenters to organize the demonstrations in various ways. For example, they may be organized into themes or areas of interest for a particular presentation. One major goal is to incorporate stronger explanations of the chemistry occurring in the demonstrations. Ultimately we plan to develop a website detailing the demonstrations for use in the department as well as externally. In the future we plan to develop demonstrations that instructors could use in lecture as examples of various chemical phenomena; this will likely include implementation of a system to request, prepare, and transport the demonstrations for use by the instructor.

Dimeric Propargylic Alcohols

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Our group previously studied a family of novel low molecular weight organogelators based on a racemic propargylic alcohol (Langmuir, 2008, 24, 7421). These compounds possess a pentafluoroarene group (connected to the alcohol carbon) and a second non-fluorinated arene (connected by an alkyne). Through hydrogen bonding and π-π stacking, the compounds self-assemble in a highly organized fashion to gel nonpolar liquids. We report the synthesis and preliminary study of a series of dimeric derivatives, in which two of the propargylic alcohols are joined by a linear hydrocarbon chain (six, ten, or twelve carbons long) on the nonfluorinated aromatic ring. The bis-propargylic alcohols were prepared in reasonable yield in four steps from commercially available compounds. Based on structural similarities to molecules that assemble into supramolecular polymers, we hypothesize that the bis-propargylic alcohols will form materials of greater strength than the previously studied gels. Self-assembling behavior will be studied with the neat compounds and in various liquids. Preliminary studies including solubility testing, differential scanning calorimetry, infrared spectroscopy, x-ray diffraction, and scanning electron microscopy imaging are underway.

The Antifungal Bacterium, *Janthinobacterium lividum*, Does Not Protect the Wild-Extinct Panamanian Golden Frog from Chytridiomycosis

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Amphibian populations worldwide are in a rapid decline. This is due to a number of issues including, deforestation, pollution, global climate change, and emerging diseases. Chytridiomycosis is an emerging disease caused by the fungus *Batrachochytrium dendrobatidis*. This fungus has caused the extinction of the Panamanian golden frog, *Atelopus zeteki*, in the wild. Some salamander and frog species are able to survive the fungal infection, however. These species have been linked to symbiotic antifungal bacteria as well as antimicrobial peptides. In particular, *Janthinobacterium lividum* is an antifungal bacterium that produces two antifungal metabolites, indole-3-carboxaldehyde and violacein. *J. lividum* has previously been shown to be an effective treatment for the disease on the mountain yellow legged frog, *Rana muscosa*. A population of captive *A. zeteki* was used in a treatment study with *J. lividum*. The bacterium was unable to protect individuals from the fungus. In addition, the bacterium did not persist on the individuals as it had previously on *R. muscosa*. The levels of violacein were below the noise seen in a UV-vis spectrum. Therefore, *J. lividum* is not been shown to be an effective treatment on *A. zeteki*, however other bacteria may be able to protect *A. zeteki* better than *J. lividum*.

Trace Metal Analysis in Fish Tissue by Laser Ablation Inductively Coupled Plasma Mass Spectrometry

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Inductively coupled plasma mass spectroscopy (ICP-MS) is a tool for elemental analysis of liquid or gaseous samples with sensitivity in the ppb to ppt range. Solution mode ICP-MS allows for effective sample introduction but is not time efficient. The standard method for solution analysis by ICP-MS involves sample uptake time of 30 seconds and stabilization time of 300 seconds prior to a 2-second analysis with a volume consumption of several milliliters. Previous research by our group involved that use of laser ablation to aerosolize solid samples from fish otoliths for analysis by ICP-MS. Current research has focused on the use of laser ablation to vaporize liquid samples for introduction into the ICP-MS. LA-ICP-MS does not require the uptake or stabilization periods needed in solution mode ICP-MS, so it should be possible to directly analyze microliter volumes of aqueous samples or water-rich biologicial tissue. To date we have studied the analysis of solutions in wells in a plate and capillary tubes. Standard solutions of 0.500, 1.00, 1.50, and 2.00 ppm Mg, Mn, and Ca were produced with 1.0 ppm Ba as an internal standard. Ablation of solutions in capillary tubes yielded very low signal even from solutions with concentrations in the ppm range. Solution ablation rates of samples in wells were found to be orders of magnitude higher but inconsistent. However, ratioing the analyte signal to the Ba internal standard yielded consistent results. This method has allowed for production of calibration curves with regression values typically exceeding r=0.9800 from the standard solutions. Direct ablation of fresh and dried samples of fish tissue has indicated that trace elemental signals are low but detectable. However, significant signal gradients have been observed between different regions of tissue samples. Homogenizing samples to reduce gradient error is currently being studied.

The Synthesis of Nitrogen- and Sulfur-Containing Heterocycles from Cyclopropanol Fragmentation

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The prevalence of heterocycles as the backbone of common pharmaceutical entities has created a demand for simple reactions to prepare them. Our research aimed to create six-and seven-membered heterocycles containing both a carbonyl group and either sulfur or nitrogen in the ring. A cyclopropanol fragmentation approach to the formation of oxepanes was developed in the Minbiole lab's previous work. Using a similar approach, our current endeavor is to synthesize nitrogenous heterocycles, particularly piperidines and azepines, as well as sulfur-containing thiepanes. The nitrogenous approach begins with either N-benzyl-protected α- or β-amino acid ethyl esters which were transformed by cyclopropanols via the Kulinkovich reaction. The resulting α- or β-amino cyclopropanols were then reacted with various aldehydes to form an aminal. Subsequently, various Lewis acids were used to promote the rearrangement of the aminal into the piperidine or azepine formation. This rearrangement is still under investigation. Analogously, a seven-membered sulfur-containing heterocycle was formed by sequential addition of aluminum (III) triflate and bismuth (III) triflate as Lewis acids to a mercaptocyclopropanol / benzaldehyde mixture, though heterocycle was only produced in low yields (<20%).

Synthesis of Stable RNA Analogs

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The synthesis of stable RNA analogs that can effectively bind via base pairing and that can be prepared by a highly convergent in a single step polymerization is a desired goal in therapeutic treatments using siRNA. Therefore, this paper describes recent synthetic advances towards producing stable analogs via ring opening metathesis polymerization using synthetic monomers.

Antimicrobial Chemical Defense: Identification and Application of Antifungal Metabolites from *Janthinobacterium lividum* and *Pedobacter cryoconitis*

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For many years, amphibians worldwide have fallen prey to deforestation, global climate change, and pollution. In 1998, it was discovered that a fungus, *Batrachochytrium dendrobatidis*, has plagued lake and mountainside habitats of frogs and salamanders. With previous skin extraction, cutaneous bacteria revealed a mutualistic relationship between bacteria and amphibians in defending against the deadly fungus. To develop a probiotic antifungal treatment against the deadly fungus, *Batrachochytrium dendrobatidis*, anti-fungal metabolites from bacteria on the amphibians' skin were identified. As a preliminary step, metabolites from *Pedobacter cryoconitis* separated through High Performance Liquid Chromatography are currently being tested against *B.d.* Inhibition of *B.d.* zoospores in a 96-well plate signifies that certain secondary metabolites are anti-fungal. A previous study of the mountain yellow-legged frog (Rana muscosa), infected with B.d., provides a model for the probiotic treatment of amphibian populations with *Janthinobacterium lividum*. Using the model set by the Rana muscosa trials, a study is underway to measure the effects of *Janthinobacterium lividum* against Chytridiomycosis on the now extinct in nature Panamanian golden frog (Atelopus zeteki). A soil extraction protocol to detect violacein, an anti-fungal secondary metabolite, currently under development, will allow for the identification of *J. lividum* in soil samples. If successful, this could simplify the transition from the lab to the wild, thus catalyzing conservation efforts.

The Thermal Decomposition of 2-Propanol Using a Zinc Sulfide Catalyst

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In an effort to create a hydrogen source the thermal decomposition of 2-propanol over zinc sulfide catalyst was investigated. The reaction produced hydrogen gas and acetone at temperatures between 500K and 600K. The data was fit using a mechanism found in a paper by Rioux et al [1]. The findings indicate an activation energy of 117 kJ/mol. While mass of the catalyst did not affect the activation energy it lowered the temperature at which the sample converted entirely to acetone.

1. Rioux, R. M.; Vannice, M. A. Hydrogenation/dehydrogenation reactions: Isopropanol dehydrogenation over copper catalysts *Journal of Catalysis* **2003**, *216*, 362-376.

Synthesis and characterization of the products from the reaction of $RuCl_3NO(PPh_3)_2$ with $Ph_2PCH_2P(O)Ph_2$ and $Ph_2P(CH_2)_2P(O)Ph_2$

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$RuCl_3NO(PPh_3)_2$ reacts with $Ph_2PCH_2P(O)Ph_2$ (dppmO) or $Ph_2P(CH_2)_2P(O)Ph_2$ (dppeO) to form $RuCl_3NO[Ph_2PCH_2P(O)Ph_2]_2$ or $RuCl_3NO[Ph_2P(CH_2)_2P(O)Ph_2]_2$, respectively. $RuCl_3NO[Ph_2PCH_2P(O)Ph_2]_2$ is a light orange solid, which was characterized with IR and NMR spectroscopy, along with x-ray crystallography. The compound is octahedral with the two dppmO ligands *trans* to each other. With $RuCl_3NO[Ph_2P(CH_2)_2P(O)Ph_2]_2$, another light orange product was obtained and characterized through use of IR and NMR spectroscopy. The IR spectrum indicates the presence of a coordinated NO group, and the ^{31}P NMR spectrum indicates an AA'XX' spin system with coupling constants characteristic of phosphine ligands coordinated to ruthenium in a *trans* fashion, as expected for a structure analogous to that of $RuCl_3NO[Ph_2PCH_2P(O)Ph_2]_2$. Preliminary data indicates that one chloride can be removed from $RuCl_3NO[Ph_2PCH_2P(O)Ph_2]_2$ by reaction with $AgBF_4$.

Bicephalic (Double-Headed) Amphiphiles

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A series of bicephalic (double-headed) biscationic amphiphiles with two trimethylammonium heads, an aromatic spacer, and a single 14 carbon hydrophobic tail were synthesized. The orientation of the hydrocarbon tail relative to the normal of the interface was altered by changing the location of the head groups on the aromatic ring. The head groups were located in the 2,3-, 2,4-, 2,6-, 3,4-, and 3,5-positions. The Krafft temperature (T_K) of the 2,3- derivative was determined using conductivity and differential scanning calorimetry (DSC). The critical micelle concentration (CMC) was determined using conductivity and proton nuclear magnetic resonance spectroscopy (^{1}H NMR). NMR experiments demonstrate that dynamic processes within the colloidal aggregates range between slow and fast, relative to the NMR timescale. Results show that the relative positions of the head groups affect the T_K, CMC, and exchange rate of the monomers into micelle.

Proton Chemical Shifts for Alcohols in the Vapor Phase and Dilute Solutions

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Alcohol molecules form hydrogen bonded clusters in solution and the chemical shift observed for the OH proton is known to depend on the concentration of the alcohol and provides an indication of the amount of cluster formation. Quantitative information can be obtained if the chemical shifts for the pure species can be established, for instance by using high level Hartree-Fock or density functional theory calculations. Calculations at various levels of theory are compared to the measured chemical shifts in the proton NMR spectrum of methanol, ethanol, 2-propanol, and 2-methyl 2-propanol in the vapor phase and 2-methyl 2-propanol in dilute toluene, chloroform, and acetone solutions. While the relative chemical shifts agree well with the measurements made for the vapor molecules, the absolute chemical shifts differ by ~2 ppm, suggesting that the air introduces an absolute shift to the spectrum. The high level calculations for methanol are fast enough for use in a laboratory.

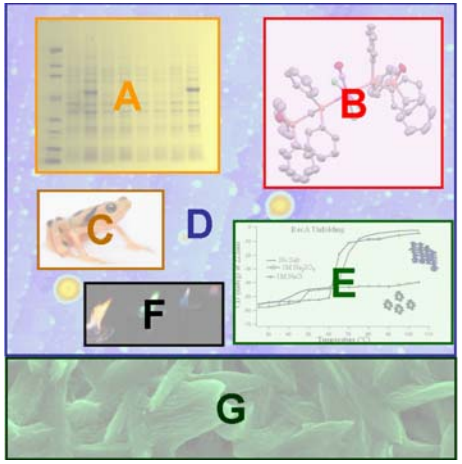

Image descriptions (from front cover)

A The Mariani lab used this SDS-PAGE analysis to determine if a DNA plasmid clone created expresses the protein IMPDH in *E. coli* cells.

B Crystal structure of a ruthenium nitrosyl complex of a phosphine / phosphine oxide ligand from the Amenta/Gilje lab.

C Protection strategies for the Panamanian golden frog, driven to extinction in the wild by fungal disease, are being investigated by the Minbiole lab using antifungal metabolites produced by skin bacteria.

D (Background image) Small molecule organic ligand self-assembled into a high aspect ratio crystal imaged using AFM from a collaboration between Dr. Augustine and Prof. Orde Munro from the School of Chemistry at the University of KwaZulu-Natal, South Africa.

E Circular dichroism studies of RecA unfolding transitions and stability in the presence of salts performed by the MacDonald lab.

F Colored flames from the ACS/AXΣ chemical demonstrations, courtesy of Casey Rogers and Kelly Clouston.

G Scanning electron microscopy (SEM) image of an aggregate formed from a dimeric propargylic alcohol, from the Caran lab.

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