The Sixth Annual
Undergraduate Research Symposium

Sponsored by the Western New York Section
of the American Chemical Society

Saturday April 13, 2013

Niagara University, NY
Welcome Message From The Organizing Committee

Welcome to the 6th annual Undergraduate Research Symposium sponsored by the Western New York Section of the American Chemical Society! During the past 6 years, this Symposium has evolved into a valuable experience for area students and an inspiration to research mentors. A strength of the WNY local section's Undergraduate Research Symposium is our ability to cross regional and international boundaries to increase appreciation for our students' work, and we are delighted to again have representatives here from colleges and universities in western New York and surrounding regions, including southern Ontario.

I hope that today you will learn, you will share, and you will meet new people who will become friends and colleagues in your own network. I also hope that you have some fun!

Thanks go to all of our student presenters and especially to our keynote speaker, Emma Master, Ph.D. of the University of Toronto. I would also like to extend my appreciation to the volunteers from the Niagara University Student Affiliates of the ACS, to the members of the Organizing Committee and to our generous sponsors.

Sincerely,
Robyn Goacher, Ph.D.
Chair, 2013 Symposium Committee

2013 Symposium Organizing Committee

Chair: Dr. Robyn Goacher
Department of Biochemistry, Chemistry and Physics, Niagara University

Dr. Timothy M. Gregg
Department of Chemistry and Biochemistry, Canisius College

Dr. Sarbajit Banerjee
Department of Chemistry, University at Buffalo, SUNY

Dr. Valerie A. Frerichs
Department of Chemistry, University at Buffalo, SUNY
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2013 Undergraduate Research Symposium

Pearson Education

The Student Affiliates of the ACS, Niagara University

The Department of Biochemistry, Chemistry and Physics, Niagara University
Dr. Emma Master earned a B.Sc. in Microbiology from McGill University in 1995, and a Ph.D. in Environmental Biochemistry from UBC in 2002. She then joined the Royal Institute of Technology in Stockholm, Sweden (KTH) as a Post-doctoral Fellow. There, she studied wood fibre biosynthesis and modification by carbohydrate-active enzymes and led the enzyme discovery and characterization group of KTH’s wood biotechnology division. In 2004, she joined the Fungal Genomics Project at Concordia University, before she became a faculty member in the Department of Chemical Engineering and Applied Chemistry at the University of Toronto in 2005.

Emma Master received a Finnish Distinguished Fellowship (FiDiPro) in 2010 and an Early Researcher Award from the Ontario Ministry of Research and Innovation in 2009. She is a theme leader in the Canadian NSERC Bioconversion Network, and the Genome Canada project “BEEM: Bioproducts and Enzymes from Environmental Metagenomes”; she also leads “Forest FAB: Applied Genomics for Functionalized Fibre and Biochemicals”, a 4-year collaborative research program funded by the Ontario Ministry for Economic Development and Innovation.
Schedule of Events

April 13, 2013
Dunleavy Hall, room 127
Niagara University, Niagara University, NY

9:00 – 9:50 am  Registration and Poster set-up
9:50 – 10:00 am  Introductory Remarks
10:00 – 12:00 pm  Student Oral Presentations
12:00 – 1:00 pm  Lunch  (St. Vincent’s Hall, 4th floor)
1:00 – 2:00 pm  Student Poster Session (St. Vincent’s Hall, 4th floor)
2:00 – 3:00 pm  Keynote presentation by Prof. Emma Master, Dept. of Chemical Engineering & Applied Chemistry, University of Toronto

“Enzymatic modification of plant fibre chemistry:
From outside in to inside out”

3:00 pm  Symposium Awards and Closing remarks
Oral Presentations
Time: 10:00AM - 12:00 PM  (Dunleavy Hall, room 127)

1. 10:00 am  Allison Roberts  Syracuse University
   *Synthesizing a Vitamin B12 Based Radio Copper64 Probe for Detection of Cancer Cells*

2. 10:20 am  Michael Molnar  College at Brockport, SUNY
   *Denaturing of Bovine Albumin Serum By Different Surfactants*

3. 10:40 am  Jessica Spellane  Niagara University
   *ATR and Transmission FTIR Analysis of the Enzymatic Breakdown of Lignocellulosic Material*

4. 11:00 am  Shivanthi Sriskandha  McMaster University
   *Thin Polymer Films as Cellular Matrices*

5. 11:20 am  Catherine Downey  Hobart and William Smith Colleges
   *Synthesis and Oxidative Cyclization of 3,4-Diaryl-3-pyrrolin-2-ones*

6. 11:40 am  John DeBackere  McMaster University
   *Towards the Syntheses of Mercury(IV) Compounds*

Keynote Address
2:00 pm  Emma Master  University of Toronto
*Enzymatic Modification of Plant Fibre Chemistry: From Outside In to Inside Out*
Oral Presentation Abstracts

Talk 1

**Synthesizing a Vitamin B\textsubscript{12} Based Radio Copper\textsuperscript{64} Probe for Detection of Cancer Cells**

*Allison M. Roberts\textsuperscript{a}, Anna R. Kahkoska\textsuperscript{a}, Oluwatayo F. Ikotun\textsuperscript{b}, Suzanne Lapi\textsuperscript{b*} and Robert P. Doyle\textsuperscript{a*}*

\textsuperscript{a}Department of Chemistry, Syracuse University, Syracuse, NY
\textsuperscript{b}Division of Radiological Sciences, Washington University School of Medicine, St. Louis, MO

The field of medicine, especially oncology, is centered on the quality of imaging technology. Positron emission tomography (PET) and single photon emission computed tomography are two forms of nuclear medicine imaging technology that utilize isotopic emissions to create three dimensional images of a patient. These images are then utilized for diagnosis and tracking tumor growth or remission. Many current isotopes used in medical imaging are not readily accessible and also expose otherwise healthy tissues to radiation or have a long half-life, resulting in exposing the body to damaging radiation for a longer period of time than necessary for the scan. These current problems with isotopes used for medical imaging makes the development or expansion of new imaging probes even more necessary. The hypothesis of this work is that a vitamin B\textsubscript{12} (B\textsubscript{12}) copper\textsuperscript{64} (Cu\textsuperscript{64}) probe can be utilized to target the increased exogenous uptake of B\textsubscript{12} characteristic of cancerous cells. The NOTA and DOTA ligands were successfully conjugated off of the 5' -ribose moiety of B\textsubscript{12} and sent to Washington University for coupling with Cu\textsuperscript{64} and \textit{in vivo} studies.
Talk 2

Denaturing of Bovine Albumin Serum By Different Surfactants

*Michael Molnar and Mark Heitz*

Department of Chemistry, College at Brockport, SUNY, Brockport, NY

Protein denaturing plays an important role in the biological world. By understanding how proteins unfold allows scientists to understand structure alignment, bond forming/breaking, and even how the protein moves within a solution. Bovine serum albumin (BSA) is a plasma protein that has three domains. Acrylodan was covalently attached to BSA on Cysteine-34, which is located in the first domain. Sodium dodecyl sulfate (SDS) and trihexyl (tetradecyl) phosphonium chloride were used as different denaturants. SDS was added with quantifying increments up to 2 mM. The data showed that trihexyl (tetradecyl) phosphonium chloride had the same denaturing effect as SDS but with a 10 fold decrease in concentration in order to denature BSA. Both SDS and trihexyl (tetradecyl) phosphonium chloride showed an increasing blue shift. This presentation will focus on details of the denaturing process of BSA in denaturant solutions.
Lignocellulosic material (plant biomass) has garnered attention over the past few years for its potential as a biofuel. Plant biomass is mainly composed of cellulose, hemicellulose, lignin and pectin. Cellulose and hemicellulose can be hydrolyzed by enzymes into glucose and other sugars, which can then be converted to ethanol through a fermentation process. Cellulosic ethanol would be a beneficial alternative to the burning of fossil fuels because it would greatly cut down on the amount of greenhouse gases produced. Furthermore, cellulosic ethanol would not require the use of land that is needed to produce food crops. The goal of this research project is to analyze the enzymatic breakdown of lignocellulosic material into fermentable sugars. Specifically, extracted and un-extracted red spruce and trembling aspen wood are used as sources of biomass. Cellulase and xylanase are the enzymes employed to determine how this material can most effectively be broken down. Transmission Fourier Transform Infrared Spectroscopy (FTIR) and Attenuated-Total-Reflectance (ATR) FTIR are utilized to quantify the results; additionally Principle Component Analysis (PCA) software is being used to further evaluate the infrared spectroscopy data. Particular attention is paid to comparing the information depth of transmission and ATR-FTIR and to the enzyme dosage required to detect enzyme activity. The ultimate goal of the project is to form conclusions on what instrumental methods are most effective at characterizing plant biomass before and after it is subjected to enzymatic degradation, with potential applications to screening for new active enzymes from environmental protein libraries.
Thin Polymer Films as Cellular Matrices

Shivanthi E. Sriskandha, Nicholas A. D. Burke and Harald D. H. Stöver*.

Department of Chemistry and Chemical Biology, McMaster University, Hamilton, ON

There is great interest in using synthetic polymers as matrices for cell growth and stem cell differentiation, in particular, polymers that can form films with a broader range of chemical and mechanical properties than traditional biological supports. This study focuses on the use of reactive hydrophilic polymers to prepare two-dimensional thin films for cell growth (Fig. 1). A water soluble anionic copolymer poly(methacrylic acid–co–2-vinyl-4,4-dimethylazlactone) (PMV) was prepared through batch photopolymerization with 98 weight percent purity. The azlactone group of PMV can rapidly react with amines to form crosslinked or functionalized films. In aqueous environments, hydrolysis of azlactones limits this crosslinking ability. The rate of azlactone hydrolysis is therefore of importance during PMV dissolution in aqueous media for the preparation of thin films. Hydrolysis experiments revealed that the half-life of PMV55 was 70±10 min at pH 6. Thin films were prepared through a layer-by-layer deposition technique of PMV and cationic poly(aminopropylmethacrylamide) (p(APM)) copolymers of varying APM content. Films were characterized to demonstrate crosslinking, and to determine the thickness, roughness and hydrophilicity. Film thicknesses determined by ellipsometry and optical profilometry are comparable with the thickest films having the largest cationic charge on the p(APM) copolymer. Contact angle measurements established that the surface hydrophilicity was approximately 55±5° for all film compositions due to diffusion of polyelectrolyte multilayers. C2C12 myoblast cells were then seeded onto the thin films to test for cell attachment, viability and proliferation as a function of film properties.

Talk 5

Synthesis and Oxidative Cyclization of 3,4-Diaryl-3-pyrrolin-2-ones

*Catherine R. Downey and Erin T. Pelkey*

Department of Chemistry, Hobart and William Smith Colleges, Geneva, NY

The synthesis of phenanthrene-fused 3-pyrrolin-2-ones (dibenzo[\textit{e,g}]isoindol-1-ones) via phenyliodine(III) bis(trifluoroacetate) (PIFA) mediated oxidative cyclization of polymethoxyphenyl 3,4-diaryl-3-pyrrolin-2-ones was investigated. Dibenzo[\textit{e,g}]isoindol-1-ones are compounds of interest as they represent simplified indolo[2,3-\textit{a}]pyrrolo[3,4-\textit{c}]carbazol-5-ones (indolocarbazoles), a class of compounds with a wide range of biologically activity. While there have been many reports on the oxidative cyclization of indole containing compounds, there are no reports on the cyclization of simpler polymethoxyphenyl compounds. Our interest in simplified phenanthrenes stems from the lack of information about the biological activity of these compounds and their potential to act as more selective inhibitors or enhancers of enzymes involved in cancer and some neurodegenerative diseases.
Towards the Syntheses of Mercury(IV) Compounds

John R. DeBackere, Hélène P.A. Mercier and Gary J. Schrobilgen*

Department of Chemistry, McMaster University, Hamilton, ON

Among the group-12 elements, mercury appears to be the best candidate for the synthesis of Hg(IV) species as a result of relativistic and spin-orbit coupling effects. A recent matrix-isolation study has provided evidence for the formation of Hg(IV) as HgF₄.¹ The latter compound proved to be unstable, decomposing to HgF₂ and F₂ upon warming the matrix. Quantum-chemical calculations indicate that derivatives of the highly electronegative –OChF₅ (Ch = Se, Te) groups could provide avenues to the bulk syntheses of Hg(IV) compounds, e.g., Hg(OChF₅)₄ and F₂Hg(OChF₅)₂.² In the present work, the synthetic precursor, Hg(OTeF₅)₂, has been synthesized in high purity and high yield and structurally characterized along with its coordination complexes, cis-, trans-(F₅TeO)₂Hg(NCCH₃)₄ and (F₅TeO)₂Hg⋅1.5XeF₂ (Figure 1). The latter compounds were characterized by low-temperature single-crystal X-ray diffraction, Raman spectroscopy and quantum-chemical calculations. The (F₅TeO)₂Hg⋅1.5XeF₂ complex is the first example reported in the literature in which XeF₂ is coordinated to a mercury center. Preliminary Raman spectroscopic studies indicate that a KrF₂ coordination complex with Hg(OTeF₅)₂ is formed. Structural characterization of the latter complex would represent the first Lewis acid-base complex in which KrF₂ is coordinated to other than a group 6 transition metal center, e.g., FKrF---MOF₄ (M = Cr, Mo, W).³

Student Poster Presentations
Time: 1:00-2:00 PM (St. Vincent’s Hall, 4th floor)

Poster 1. Aditya G. Rao, Kirsten Norrell, David Samuel and David G. Hilmey*
Department of Chemistry, St. Bonaventure University, St. Bonaventure, NY
A Conserved [3+2] Cycloaddition of Singlet Oxygen (1O2) to Vitamers of Vitamin B6

Poster 2. Alyssa M. Blake, Rebecca A. Wheeling and Clinton D. Jones*
Department of Chemistry and Biochemistry, Mercyhurst University, Erie, PA
The Synthesis and Characterization of Hydrogel Nanoparticles with Varying Crosslinker Type and Concentration

Poster 3. Amanda Oldacre, AnneMarie Laurri, and Christopher S. Stoj*
Department of Biochemistry, Chemistry and Physics Niagara University, Lewiston, NY
Purification and Characterization of the Vacuolar Multicopper Oxidase Fet5 Protein from Saccharomyces cerevisiae

Poster 4. Justin P. Younga, Phillip M. Sheridan*a, Matthew P. Bucchino b and Lucy M. Ziurys b
aDepartment of Chemistry and Biochemistry, Canisius College, Buffalo, NY
bDepartment of Chemistry, The University of Arizona, Tucson, AZ
Millimeter-Wave Spectroscopy of IZnCH3

Poster 5. Yusuke Nakano, Kevin E. Sitters and Janet R Morrow*
Department of Chemistry, University at Buffalo, SUNY, Buffalo, NY
Fluorescent Properties and Selective Binding of Metal ions to Macrocyces

Poster 6. Kelly Morrison, Umar Asif, Brian Shultz, Sarbajit Banerjee and David G. Hilmey*
Department of Chemistry, St. Bonaventure University, St. Bonaventure, NY
Synthesis of Dihalogenated Precursors for the Bottom-Up Fabrication of Graphene Nanoribbons

Poster 7. Robert W. Kubiak II and Dominic L. Ventura*
Math and Natural Sciences Department, D’Youville College, Buffalo, NY
Metallophthalocyanine Catalyzed Carbenoid Reactions

Poster 8. Stephen R. Bruening, Guanquin Li, Taryn M. White, Catherine R. Downey, Amy A. van Loon, Maeve K. Holton and Erin T. Pelkey*
Department of Chemistry, Hobart and William Smith Colleges, Geneva, NY
Oxidative Cyclization of 3,4-Diaryl-3-pyrrolin-2-ones
Poster 9. Ashley Hobson, Matthew Waldron and Fehmi Damkaci*

*Department of Chemistry, SUNY Oswego, Oswego, NY

Ligand Development for Ullman Type N-Arylation

Poster 10. Connor Kinslow, Kamalika Mukherjee and Susan Bane*

*Department of Chemistry, Binghamton University, SUNY, Binghamton, NY

Cytotoxicity of Tubulin Tyrosine Ligase Substrates

Poster 11. Jeffrey P. Aldinger, Brian J. Schultz and Sarbjit Banerjee*

*Department of Chemistry, University at Buffalo, SUNY, Buffalo, NY

Synthesis, Investigation, and Applications of Single Layer Graphene

Poster 12. Cory R. Clugston and Robyn E. Goacher*

*Department of Biochemistry, Chemistry and Physics Niagara University, Lewiston, NY

Effects of Accelerated Freeze-Thaw Cycling on the Physical and Chemical Properties of HPDE-Based Wood-Polymer Composites

Poster 13. David R. Anthony, Matthew J. Moschitto and Chad A. Lewis*

*Department of Chemistry, Cornell University, Ithaca, NY

Concise Total Synthesis of Arnottin I.

Poster 14. David J. Fortman, Russell F. Algera and Timothy M. Gregg*

*Department of Chemistry and Biochemistry, Canisius College, Buffalo, NY

Cyclopropanation-Cross-Coupling Strategy Employing Novel Protected Allenyl Boronic Acids

Poster 15. Daye Kim, Stephanie A. Gardina and Janet R. Morrow*

*Department of Chemistry, University at Buffalo, SUNY, Buffalo, NY

Selective Recognition of Thymine by Zn(II) Complexes

Poster 16. Eric G. Stoutenburg and Robyn E. Goacher*

*Department of Biochemistry, Chemistry and Physics, Niagara University, Lewiston, NY

Analysis of Wood-Polymer Composites After UV and water Exposure Using Time-of-Flight Secondary Ion Mass Spectrometry
Poster 17. Amy A. van Loon, Taryn M. White, Catherine R. Downey, Maeve K. Holton, and Erin T. Pelkey
Department of Chemistry, Hobart and William Smith Colleges Geneva, NY
Regiocontrolled Synthesis of 3,4-Diaryl-3-pyrrolin-2-ones

Poster 18. Juliana Sledziewski, Erik Boldt, and Christopher S. Stoj*
Department of Chemistry, Biochemistry and Physics, Niagara University, Lewiston, NY
Expression of Human Pyruvate Kinase in Pichia pastoris

Poster 19. Forest S. Blanchard, Robert V. Dennis, Gregory A. Horrocks, Peter M. Marley and Sarbajit Banerjee*
Department of Chemistry, University at Buffalo, SUNY, Buffalo, NY
VO₂ Nanostructured Coatings with Applications in “Smart” Windows

Poster 20. Jesse V. Vanucchi and Webe C. Kadima*
Department of Chemistry, SUNY Oswego, Oswego, NY
Investigating Inhibition of the Enzyme Glucose-6-Phosphatase by Musanga cecropioides

Department of Chemistry and Biochemistry, Canisius College, Buffalo, NY
Stimuli-Responsive Linkers for Use in Silica Theranostic Materials and Application to ¹⁹F MRI “Switch-On” Imaging

Poster 22. Marie E. Albano and Robyn E. Goacher*
Department of Chemistry, Biochemistry and Physics, Niagara University, Lewiston, NY
Differential Scanning Calorimetry of Hard Wood and Soft Wood Samples Treated with Biodegradable Enzymes

Poster 23. Christina Wong and Sherry Chemler*
Department of Chemistry, University at Buffalo, SUNY, Buffalo, NY
Synthesis of Isoxazolidines via Copper (II) Promoted Intra/Intermolecular Diamination of Hydroxylamine Olefins

Poster 24. Jason Biasini, Stuart Bates and Fehmi Damkaci*
Departmen of Chemistry, SUNY Oswego, Oswego, NY
Synthesis of Thiazolidinedione Derivative Library
**Poster Abstracts**

**Poster 1**

**A Conserved [3+2] Cycloaddition of Singlet Oxygen (\(^1\)O\(_2\)) to Vitamers of Vitamin B\(_6\).**

*Aditya G. Rao, Kirsten Norrell, David Samuel and David G. Hilmey*

Department of Chemistry, St. Bonaventure University, St. Bonaventure, NY

During times of high light intensity, plants can experience photo-oxidative stress, such as lipid peroxidation. In order to maintain cellular integrity, vitamin B\(_6\) has been documented to display an antioxidant property in *A. thaliana*. The focus of this study was to mechanistically understand how vitamin B\(_6\) quenches singlet oxygen (\(^1\)O\(_2\)), a type of reactive oxygen species, to function as an antioxidant. The primary focus was to determine the product(s) yielded by subjecting aqueous, phosphate-buffered solutions of the studied B\(_6\) vitamers to exogenous \(^1\)O\(_2\). The secondary focus was to conduct low-temperature oxidation studies to identify a transient intermediate whose presence would support the reaction between \(^1\)O\(_2\) and the B\(_6\) vitamer. Of the various vitamers of B\(_6\), this study investigated the oxidation of pyridoxine, pyridoxamine, and pyridoxal. Oxidation of pyridoxine, a structural model for other B\(_6\) vitamers, yielded a unique, ring-contracted product. More interestingly, low-temperature oxidation of pyridoxine presented a bicyclic endoperoxide intermediate, suggesting a [3+2] cycloaddition of \(^1\)O\(_2\) to the pyridine ring. Furthermore, oxidation of pyridoxamine and pyridoxal generated fused bicyclic compounds that similarly presented a [3+2] cycloaddition of singlet oxygen.
Poster 2

The Synthesis and Characterization of Hydrogel Nanoparticles with Varying Crosslinker Type and Concentration

Alyssa M. Blake, Rebecca A. Wheeling and Clinton D. Jones*

Department of Chemistry and Biochemistry, Mercyhurst University, Erie, PA

Hydrogels are crosslinked polymer networks that can range in size from macroscopic bulk gels to nanometer-sized colloids. Common applications of hydrogel nanoparticles include drug delivery, tissue regeneration, biosensors, and chemical separations. The hydrogel nanoparticles synthesized and characterized in this work are composed primarily of N-isopropylacrylamide (NIPAm) polymer, which is popular due to its temperature responsive nature and its ability to interact favorably in aqueous environments. The inherent lower critical solution temperature (LCST) of pNIPAm is 31 °C, across which the nanoparticles undergo a phase transition from a hydrophilic swollen state to a hydrophobic collapsed state. A comparison was conducted between nanoparticles containing N,N′-methylenebis(acrylamide) (BIS) and nanoparticles containing ethylene glycol dimethacrylate (EGDMA) as the crosslinker to determine how crosslinker type and concentration affect the temperature responsive nature of pNIPAm nanoparticles. Each crosslinker was varied from 5, 10, and 20% relative to the total monomer concentration. Once purified via dialysis, all samples were characterized with temperature-programmed dynamic light scattering in aqueous conditions from 21 – 47 °C. For all three crosslinker concentrations, it was determined that the EGDMA samples produced a more dramatic volume phase transition across the LCST; the largest volume change was 180%. In addition, all EGDMA samples exhibited approximately the same LCST value of ~ 31 °C. The BIS crosslinked particles showed a lower overall volume change and variable LCST temperatures. Both sets of crosslinked particles showed a definitive correlation between total volume change and crosslinker concentration.
Purification and Characterization of the Vacuolar Multicopper Oxidase Fet5 Protein from *Saccharomyces cerevisiae*

*Amanda Oldacre, AnneMarie Laurri, and Christopher S. Stoj*

Department of Biochemistry, Chemistry, and Physics, Niagara University, Lewiston, NY

A significant link has been established between the regulation of iron homeostasis and a class of metalloenzymes known as multicopper oxidases. This research seeks to develop a deeper understanding of metallobiochemistry through the purification and characterization of the multicopper oxidase Fet5p from the baker’s yeast *Saccharomyces cerevisiae*. Fet5p is directly involved in the oxidation of iron(II) and thereby the mobilization of iron stores from the yeast vacuole. A new strategy has been implemented incorporating the plasma membrane ferroxidase Fet3p, a paralog to Fet5p, which has been truncated to secrete from the yeast cell. An expression vector containing an inactive form of *FET3* fused to *FET5* allowed for the successful secretion of functional Fet5p. Currently, attempts to separate the fusion and obtain purified Fet5p are underway as well as kinetic characterization of the intact chimera.
Millimeter-Wave Spectroscopy of IZnCH$_3$

Justin P. Young$^a$, Phillip M. Sheridan$^{*a}$, Matthew P. Buchino$^b$ and Lucy M. Ziurys$^b$

$^a$Department of Chemistry and Biochemistry, Canisius College, Buffalo, NY  
$^b$Department of Chemistry, The University of Arizona, Tucson, AZ

Millimeter-wave direct absorption techniques were used to record the pure rotational spectrum of IZnCH$_3$ (X$^1$A$_1$). This work represents the first experimental observation of this molecule in the gas phase. IZnCH$_3$ was produced by the reaction of zinc vapor with ICH$_3$ in the presence of a DC discharge. Rotational transitions ranging from J = 109 $\leftrightarrow$ 108 to J = 122 $\leftrightarrow$ 121 were recorded for the $^{164}$ZnCH$_3$ and $^{166}$ZnCH$_3$ isotopologues in the frequency range of 250 – 290 GHz. The K = 0 – 3 components were measured for each transition, with the K-ladder structure and nuclear spin statistics indicative of a symmetric top. Geometric parameters determined from the rotational constants will be presented. As with HZnCH$_3$ (X$^1$A$_1$), the detection of IZnCH$_3$ provides further evidence for a zinc insertion process.
Fluorescent Properties and Selective Binding of Metal ions to Macrocycles

Yusuke Nakano, Kevin E. Siters and Janet R Morrow*

Department of Chemistry, University at Buffalo, SUNY, Buffalo, NY

The cause of many diseases has been elucidated at the genetic level. Although senile dementia, diabetes and osteoporosis are called geriatric diseases or lifestyle-related diseases, transition metals such as iron have been implicated as contributing to these disease states. Metal ions are significant in cell homeostasis; however, unregulated serious defects can occur. Iron, when not properly regulated, can generate reactive oxygen species that can harm cells. Also, the lack of iron causes anemia. Dansyl-Cyclen (DSC) is a fluorescent macrocycle that detects metal ions under physiologically relevant conditions. Our study involves the search for macrocycles that bind selectively to biologically relevant metal ions. It was found that DSC binds Zn(II) well, but not Fe(II). A second generation sensor, Dansyl Cyclen-3OH (DSC_3OH), is promising. In this macrocycle the -OH donors are predicted to be more selective for Fe(II) over Zn(II). Iron binds to DSC_3OH and then turns fluorescence off. The development of a turn-on sensor would be very beneficial for the detection of Fe(II). A turn-on sensor could be developed using RNA or DNA. When these complexes bind to to certain spots of DNA or RNA, a change of geometry or rotation between the metal and dansyl fluorophore might allow for the restoration of fluorescence.
Nanotechnology is becoming increasingly important in scientific applications, especially in electronics. Despite many advances, there is still need to increase the efficiency of production and determine nanoochemical physical properties and how they affect function. A graphene nanoribbon (GNR) is an extremely thin, single layer of graphite less than 10 nm wide which can have properties ranging from metallic to semiconducting depending on the edge pattern. These differences define each nanoribbon. In studying the bottom-up fabrication of graphene nanoribbons, several dibrominated precursors have been prepared through electrophilic aromatic substitution and Suzuki coupling reactions. The synthetic strategies used are flexible to prepare a variety of monomers. These polyaromatics give rise to a variety of potential nanoribbons of different widths and edge properties. The dihalo monomers can be linked using surface-assisted coupling followed by subsequent cyclohydrogenation to generate the desired nanoribbons. Future directions will focus on continuing the synthesis of precursors, the fabrication of various GNRs, and the synthesis of zigzag GNR precursors. Other research has been conducted to evaluate the possibility of forming a claw-like molecule to assist with solubilizing carbon nanotubes (CNTs). With molecules such as these, it will be possible to dissolve CNTs \textit{in vivo} for probing and labeling biological molecules, as well as delivering nanogram amounts of medicine directly into the infected area.
Metallophthalocyanine Catalyzed Carbenoid Reactions

Robert W. Kubiak II and Dominic L. Ventura*

Math and Natural Sciences Department, D’Youville College, Buffalo, NY

Metallophthalocyanine (MPc) catalyzed carbenoid reactions have had little attention to date. Recently these metal complexes have been found to catalyze cyclopropanation reactions. We have investigated these metallophthalo cyanines in reactions to catalyze cyclopropanation reactions from donor-acceptor carbenoids. The yields and diastereoselectivity of these reactions are influenced by the nature of the styrene as well as the aryldiazoacetate and catalyst. The products have been synthesized in good yields (up to 74%) with high diastereoselectivity (up to 20:1 ratio cis:trans products). In addition, we investigated substrates that contain the possibility to yield both cyclopropane and C-H insertion products. We began to study the effects of a variety of substrates as well as catalyst and the diazo compound. Initial results (example shown below) have shown that both products are formed, but much in favor of the cyclopropane compound. The products herein have been synthesized in good yields and up to 7:1 ratio cyclopropane : C-H insertion products.

\[ \begin{align*}
\text{R} & = \text{H, Me, OMe, Br, Cl, CF}_3 \\
M & = \text{Cu, Co, Zn, Ni, Ag, Fe}
\end{align*} \]
Oxidative Cyclization of 3,4-Diaryl-3-pyrrolin-2-ones

Stephen R. Bruening, Guanqun Li, Taryn M. White, Catherine R. Downey, Amy A. van Loon, Maeve K. Holton and Erin T. Pelkey*

Department of Chemistry, Hobart and William Smith Colleges, Geneva, NY

3-Pyrrolin-2-ones are an important class of nitrogen heterocycles proven to have biological activity as anticancer, anti-inflammatory, and pain reduction agents. Our research is focused on the development of these analogs through the synthesis of 3,4-diaryl-3-pyrrolin-2-ones by Suzuki-Miyaura cross-coupling of 3-aryl triflates with boronic acids. Next, cyclization of these products was investigated using a Scholl oxidation in which a C3-C4 aryl bond is formed in the presence of phenyliodine(III) bis(trifluoroacetate) (PIFA) and boron trifluoride etherate (BF$_3$•OEt$_2$). In our studies, different combinations of methoxy-substituted 3,4-diaryl-3-pyrrolin-2-ones underwent Scholl reactions to produce phenanthrene-fused 3-pyrrolin-2-ones.
Ligand Development for Ullman Type N-Arylation

Ashley Hobson, Matthew Waldron and Fehmi Damkaci*

Department of Chemistry, SUNY Oswego, Oswego, NY

The rediscovery of the Ullmann reaction using ligands has led to it becoming a central method of aryl-aryl C-C coupling, diaryl amine C-N formation, and ether C-O formation. In our previous work, we showed that phenylpicolinic amide acts as a ligand to achieve Ullmann type aryl-aryl homocoupling of aryl iodides and bromides at room temperature in high yields. Here, we would like to report the results of Ullmann coupling using phenylpicolinic amide N-Oxides as ligands in Ullman type C-N bond formation in high yields will be discussed. The results of coupling of several aryl halides with pyrazole, imidazole, and pyrrole will be discussed.
Microtubules are commonly targeted in cancer chemotherapy due to their active role in cell division. These dynamic proteins undergo a natural posttranslational modification in which a tyrosine residue is added to the carboxy terminus of \( \alpha \)-tubulin by the enzyme tubulin tyrosine ligase (TTL). Low expression of TTL has been associated with cancer. Therefore, effector molecules that activate TTL may prove to be useful as anti-cancer agents. Our lab has synthesized several tyrosine derivatives and demonstrated in vitro that they are substrates of TTL. We are now exploring if these substrate derivatives are also modulators of TTL. Modulators of TTL may exhibit cytotoxic effects on cancer cells. We have therefore determined cytotoxicity of these TTL substrates. Human prostate cancer (PC3) cells were treated with the derivatives and their viability was recorded via Sulforhodamine B (SRB) assay 96 hours later. Taxol and tyrosine were used as controls. IC50 values are listed below. 3-formyl tyrosine showed toxicity at moderate to high concentrations. Interestingly, the corresponding methyl ketone, 3-acetyl tyrosine, showed toxicity only at very high concentrations. 3-amino tyrosine showed toxicity only at higher concentrations as well. Our next step is to determine if cytotoxicity of 3-formyl tyrosine is due to its effect on TTL or by another mechanism involving the reactive aldehyde group.

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<th>Molecule</th>
<th>IC50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Taxol</td>
<td>5.7 nm +/- 0.70</td>
</tr>
<tr>
<td>3-formyl tyrosine</td>
<td>25uM +/- 2.5</td>
</tr>
<tr>
<td>3-amino tyrosine</td>
<td>840uM +/- 20</td>
</tr>
<tr>
<td>3-acetyl tyrosine</td>
<td>&gt;5mM</td>
</tr>
<tr>
<td>tyrosine</td>
<td>&gt;1mM</td>
</tr>
</tbody>
</table>

PC3 Cells, 1000 cells/well in 96 well plate
Graphene, a system of carbon atoms arranged in a honeycomb crystal lattice, is renowned for its incredible electronic properties. These include itinerant massless Dirac fermions, a high mobility of its charge carriers, and ballistic conduction. As a result, graphene is a sought after nanomaterial for applications in spintronics, integrated circuits, ultra-fast field effect transistors, and transparent conducting electrodes. One route of graphene synthesis is through chemical vapor deposition (CVD), where a carbon source, generally a gas such as methane or acetylene, is flown over a substrate (generally a transition metal foil acting as a catalyst) at high temperatures. The gaseous carbons interact with the substrate surface and, after a reorganization and crystallization, form graphene. Subsequently after synthesis graphene is then characterized via Raman spectroscopy. Raman is useful for identifying graphene as single, bi, or multilayer graphene stacks as controllably grown by CVD. In the past, we have successfully grown graphene on both copper and nickel substrates with good control over the thickness of the number of layers. We also have taken the aforementioned graphene and transferred it onto 300 nm SiO$_2$/Si substrates by use of a polymer support. Currently, we are attempting to grow graphene onto cold-rolled steel foils using acetylene, a waste gas at most steel plants. Successful results would lead to applications in many categories; one of particular interest is as an anticorrosion coating.
Effects of Accelerated Freeze-Thaw Cycling on the Physical and Chemical Properties of HPDE-Based Wood-Polymer Composites

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Wood-polymer composites (WPCs) have proven to be suitable substitutes for wood and plastic lumber, offering greater dimensional stability than wood lumber and greater tensile and flexural stiffness than plastic lumber. Additionally, they require little maintenance. Despite these advantages, WPCs have been shown to degrade upon exposure outdoor weathering conditions such as UV/light, exposure, and freeze-thaw cycles. Degradation causes decreased mechanical performance as well as a yellowing and fading of the surface and results in an aesthetically unappealing product, according to consumer reports. Little research has been published in relation to the effects of freeze-thaw cycling on WPCs and to our knowledge no research has been published using Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) to analyze WPCs. ToF-SIMS uses a primary ion source to bombard a solid sample, releasing secondary ions from the surface of the sample, which are then mass analyzed. ToF-SIMS is a powerful technique because it combines mass spectrometry with the ability to map the chemical properties at the sample surface by moving the primary ion beam across the sample. The purpose of this study was to characterize the physical and chemical changes occurring during freeze-thaw weathering of WPCs. The experimental samples were exposed to 0, 6, or 12 freeze-thaw cycles. In addition to ToF-SIMS analysis, flexural strength testing, SEM imaging, and light microscopy were used to characterize the samples and as a method of comparison with literature previously published. Principle Component Analysis was used to process the ToF-SIMS spectra due to the high volume of data obtained.
Concise Total Synthesis of Arnottin I.

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The present work is focused on the synthesis of Arnottin I, with the key step of the current route being a benzyne Diels-Alder reaction between the two molecules shown at the top-left of Figure 1. From this product, cleavage of the ether bond and lactonization is proposed to result in Arnottin I. From a derivative of Arnottin I, an enantioselective lactonization using a novel hypervalent iodide oxidant is proposed to lead to Arnottin II. The current synthetic route of Arnottin I is notable for its brevity, with the longest linear sequence of only four reactions from commercially available starting materials.

Figure 1: Proposed synthetic route to Arnottin I and II.
Cyclopropanation-cross-coupling Strategy Employing Novel Protected Allenyl Boronic Acids

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We are investigating new methodology for enantioselective cyclopropanation of boron-substituted allenes. Recent reports describe protected boronic acid groups that are stable to multiple synthetic steps and yet are still useful in palladium-catalyzed cross-coupling. Our efforts have led to two novel N-alkyl iminodiacetic acids applied as protecting groups for aryl- and allenylboronic acids. These boronate esters exhibit solubility appropriate for use in rhodium-carbenoid mediated cyclopropanation reactions, where solvents of low Lewis basicity are required. We demonstrate that a tandem cyclopropanation/Suzuki-Miyaura cross-coupling sequence using such groups has promise for constructing densely-functionalized chiral alkylidene cyclopropanes.
Selective Recognition of Thymine by Zn(II) Complexes

Daye Kim, Stephanie A. Gardina and Janet R. Morrow*

Department of Chemistry, University at Buffalo, SUNY, Buffalo, NY

Studying sequence-specific recognition of DNA is critical for understanding drug mechanisms, monitoring cellular metabolism and controlling gene therapy. Work done in the Morrow group focuses on selective thymine recognition with Zn(II) macrocycles containing different aromatic pendants. The Zn(II) macrocycle is able to selectively and effectively bind to the base-pairing face of thymine. This is done through the Zn(II) center forming a coordination bond to the deprotonated N3 imide of thymine. The aromatic pendant then provides a flat surface which is favorable for stacking on the nucleobase, increasing the binding strength. Previous studies have shown that Zn(II) complexes bind to bulge DNA containing an extrahelical thymine. An NMR structure was solved and showed that a Zn(II) tetraazamacrocycle appended with a quinoline pendant was able to flip into a binding pocket formed in the bulge, increasing specificity. Further studies are being done to better understand pendant design. Methylene linkers and sulfone linkers are being compared to understand the importance of the flexibility of the pendant groups in the complexes. Studies are also being done to better understand the importance of a heteroatom in the pendant. Preliminary studies show that a Zn(II) complex containing a naphthalene pendant binds less strongly than a quinoline pendant which contains a nitrogen atom.
Analysis of Wood-Polymer Composites After UV and water Exposure Using Time-of-Flight Secondary Ion Mass Spectrometry

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Over the past decade, wood-polymer composites (WPCs) have become a popular alternative to traditional wood decking. Their properties surpass those of natural wood in terms of strength and resistance to the natural elements. However, recent evidence suggests these composites are decomposing at a faster rate than initially hypothesized. To test this, wood-polymer composites were subjected to accelerated weathering using Ultraviolet light, heat and water over the course of four months. The samples were then analyzed using Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) in order to characterize the changes in chemistry of the samples for different treatment conditions. ToF-SIMS has not previously been used for the analysis of WPC but the technique has unique abilities to produce chemical images of solid samples. The main goal of this research was to assess whether ToF-SIMS can detect changes in WPC chemistry due to weathering. Future work will focus on the spatial distribution of compounds in the composites and how such distribution changes with weathering. This work should expand our knowledge of the deterioration of the wood-plastic interface. Future studies hope to gain insight into how this interface is decomposing and how this can be prevented.
Regiocontrolled Synthesis of 3,4-Diaryl-3-pyrrolin-2-ones

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Department of Chemistry, Hobart and William Smith Colleges Geneva, NY

3-Pyrrolin-2-ones are an important class of nitrogen heterocycles proven to have biological activity as anticancer, anti-inflammatory, and pain reduction agents. These biologically active compounds often have aryl substituents at the C-3 and C-4 positions. Our research is focused on developing a flexible synthesis toward 3,4-diaryl-3-pyrrolin-2-ones that will allow for the integration of a wide variety of aryl groups at the C-3 and C-4 positions. Starting with a free amine, the 3-aryl tetramic acid can be obtained in three steps. From the 3-aryl tetramic acid, 3-aryl triflates can be obtained and cross-coupled in a Suzuki-Miyaura fashion with a variety of commercially available boronic acids to easily obtain the 3,4-diaryl-3-pyrrolin-2-one. Through this synthetic strategy we have successfully obtained a variety of 3-aryl tetramic acids and cross-coupled them to expand our 3,4-diaryl-3-pyrrolin-2-one library.
Expression of Human Pyruvate Kinase in

*Pichia pastoris*

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Pyruvate kinase is a highly regulated enzyme that catalyzes the final step of glycolysis, turning phosphoenol pyruvate into pyruvate while producing an ATP. Recent studies have indicated that increased temperature inactivates pyruvate kinase and thus limits muscular recovery potential leading to muscular fatigue. To further investigate the temperature dependence and regulatory properties of pyruvate kinase, plasmids containing genes for the human isoform M2 were obtained from AddGene and isolated from kanamycin resistant bacterial strains. PCR primers were constructed to allow for subsequent cloning and heterologous expression in the methylotrophic yeast *Pichia pastoris*. Upon successful expression and purification of pyruvate kinase from *Pichia*, functional studies and further characterization will begin.
VO₂ Nanostructured Coatings with Applications in “Smart” Windows

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Nanostructured vanadium(IV) oxide (VO₂) has shown remarkable potential in applications for infrared (IR) heat reflective coatings on windows. These “smart” windows would allow transmission of IR radiation on cold days to help warm interiors but reflect IR radiation on hot summer days, thereby significantly lowering space cooling costs. The spectrally selective switchability of these nanostructured coatings is predicated on one of the most remarkable properties of VO₂: VO₂ undergoes a sharp metal-insulator phase transition, which is accompanied by a solid—solid structural phase transition between a tetragonal and a monoclinic phase. The critical transition temperatures can be tuned via the introduction of dopant atoms during hydrothermal synthesis of VO₂ from the abundant and inexpensive precursor V₂O₅. Tungsten has been used as a dopant in varying concentrations to produce WₓV₁₋ₓO₂ nanowires. Herein we present the synthesis and characterization of VO₂ nanowires with controlled transition temperatures. The nanowires have been further integrated onto clear window glass using a facile coating process. Characterization of the VO₂ nanowires was carried out by X-ray diffraction (XRD), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM) while VO₂ glass coatings were additionally characterized by Fourier transform infrared spectroscopy above and below the transition temperatures and temperature differential IR heating experiments. DSC was used to identify the critical temperatures of the VO₂ and SEM was used to determine the morphology and size distribution of VO₂ nanowires. Several different coating methods will be contrasted in terms of their efficacy of deposition and adhesion to the window glass substrates.
Poster 20

Investigating Inhibition of the Enzyme Glucose-6-Phosphatase by *Musanga cecropioides*

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Department of Chemistry, SUNY Oswego, Oswego, NY

Defects in ability of the human body to convert glucose into energy causes diabetes. A target of anti-diabetes drug development involves insulin signaling pathways. Gluconeogenesis is one of the pathways, which leads to the production of glucose from pyruvate. The aim of my research was to investigate whether an aqueous plant extract of *Musanga cecropioides* inhibits the activity of glucose-6-phosphatase, the enzyme that catalyzes the last step in the production of glucose via gluconeogenesis, thereby preventing hyperglycemia. A spectrophotometric method was used to determine activity of glucose-6-phosphatase in absence and in presence of both a known inhibitor and the *Musanga cecropioides* extract. It was determined that *Musanga cecropioides*, in fact, shows inhibitory activity upon glucose-6-phosphatase in comparison to a known inhibitor, which can possibly contribute to a lower blood-glucose level in diabetics.
Stimuli-Responsive Linkers for Use in Silica Theranostic Materials and Application to $^{19}$F MRI “Switch-On” Imaging

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Many theranostic systems depend on triggers from biologically-relevant stimuli, e.g. pH or reducing environments, to effect the release of a payload or the activation of imaging modalities. We present progress toward a set of universal, stimuli-responsive organoalkyoxysilanes cleaved under either acidic or reducing conditions for use with silica theranostic agents. These silanes contain either an azide or a terminal alkyne, making them reactive in the azide/alkyne “click” reaction with many potential payloads.

Moreover, we are interested in fluorine-containing groups for use in $^{19}$F MRI with “switch-on” imaging triggered by biological stimuli. Thus, we have additionally developed cleavable and non-cleavable fluorine-containing alkoxy silanes for modifying silica particles with fluorine atoms. Here, we present proof-of-principle studies showing that $^{19}$F NMR can be used to detect fluorine atoms immobilized to mesoporous silica nanoparticles.
Due to the repercussions of using fossil fuels, wood is one alternative being explored to increase the use of renewable resources and move away from non-renewable fuels. In order to make this transition successful, the structure of wood and how chemical and biological treatments affect the composition of wood-based products are important pieces of the puzzle. Since the structure of wood is well understood, the current research in this field is focusing on the effects of enzymes, or other biological or chemical treatments, on wood components such as cellulose and hemicellulose. Our research focuses on assessing instruments to directly determine the composition of the wood samples and follow enzyme treatments of wood, with the ultimate goal of screening enzymes for activity on wood. Wood is tough to analyze since it is a solid, complex and not water soluble. For rapid enzyme screening, it will be ideal to use a technique that does not require dissolution of the wood. One instrument that permits analysis without pretreating samples is Differential Scanning Calorimetry (DSC) which is studied here to determine whether or not lignocellulose degradation by enzymes can be seen using the DSC. The enzymes being investigated are xylanase and cellulase (Celluclast), which degrade wood components xylan and cellulose, respectively. In order to better understand the effect of the enzymes, both hardwood (Aspen) and softwood (Red Spruce) samples were studied. Preliminary DSC data acquired on extracted and unextracted samples of these woods will be discussed, with an emphasis on whether it will be possible to quantify the amount of cellulose and hemicelluloses degraded in each type of wood by the enzymes.
Synthesis of Isoxazolidines via Copper (II) Promoted Intra/Intermolecular Diamination of Hydroxylamine Olefins

Christina Wong and Sherry Chemler*

Department of Chemistry, University at Buffalo, SUNY, Buffalo, NY

Copper promoted diamination reaction of hydroxylamine olefin substrates with various nitrogen nucleophiles. This reaction can be used to synthesize isoxazolidines, which are found in biologically active compounds. This scaffold is important to the pharmaceutical industry as it has displayed possible therapeutic uses. An advantage of this chemistry over existing methods is that it utilizes readily available and non-toxic copper (II) salts as opposed to expensive and/or toxic metals. Currently, studies are underway to improve the efficiency and the diastereoselectivity of the copper promoted reaction and ultimately to render the process catalytic.

\[
\begin{align*}
\text{Nu} &= p\text{-chlorobenzenesulfonamide, Sodium Azide, Methanesulfonamide} \\
\text{solvent} &= 1,2\text{-dichloroethane, trifluorotoluene}
\end{align*}
\]
Thiazolidinediones, also known as glitazones, are a class of medications used in the treatment of diabetes mellitus type II, which are utilized in drugs such as Rosiglitazone and Pioglitazone. A library of glitazone derivatives has been synthesized using microwave irradiation over two steps, with optional hydrogenation for select compounds and increased diversity. Numerous aromatic aldehydes and heterocyclic aromatic electrophiles have been tested and used in the construction of the library. Approximately 14, 24 and 20 compounds have been synthesized from each step respectively, and will soon be sent for medicinal testing.