

*2011 WNYACS Undergraduate Research Symposium*



The Fourth Annual  
**Undergraduate Research Symposium**

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

*Saturday April 16, 2011*

*University at Buffalo, SUNY*



**University at Buffalo** *The State University of New York*

***Welcome Message From The Organizers***

Welcome to the 4<sup>th</sup> Annual Western New York American Chemical Society Undergraduate Research Symposium! Sharing your research findings to your peers and communicating your results to a broader scientific community is as important as conducting a successful research program. This symposium will provide an invaluable opportunity to undergraduate students to present their research, learn about other exciting science going on in the area and interact with scientific peers and faculty members from neighboring institutions. More than 11 colleges and universities from New York and Ontario will be represented at the symposium. The keynote address will be presented by a member of the National Academy of Sciences, Professor Timothy M. Swager from Massachusetts Institute of Technology. We are looking forward to continuing the tradition of excellence of WNY ACS Undergraduate Research Symposia.

Sincerely,

Javid Rzayev

Chair, 2011 Symposium Committee

***2011 Symposium Organizing Committee***

Chair: Dr. Javid Rzayev

Department of Chemistry, University at Buffalo, SUNY

Dr. Sarbajit Banerjee

Department of Chemistry, University at Buffalo, SUNY

Dr. Valerie A. Frerichs

Department of Chemistry, University at Buffalo, SUNY

Dr. Timothy M. Gregg

Department of Chemistry and Biochemistry, Canisius College

Dr. Ronny Priefer

Department of Biochemistry, Chemistry and Physics, Niagara University

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2011 Undergraduate Research Symposium

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

## Our Keynote Speaker



### **Prof. Timothy M. Swager**

John D. MacArthur Professor of Chemistry

Department of Chemistry

Massachusetts Institute of Technology

#### ***EDUCATION:***

Ph.D., Chemistry, *California Institute of Technology* 1988

Research Advisor: Professor Robert H. Grubbs

B.S., Chemistry, With Highest Honors, *Montana State University* 1983

#### ***PRINCIPAL RESEARCH INTERESTS:***

Electronic Materials, Chemical Sensors, Supramolecular Science, Polymer Science, Liquid Crystals, Synthetic Conductors, Molecular Recognition, Molecular Electronics, Photonics

39 patents

Over 250 journal articles

#### ***SELECTED HONORS AND AWARDS:***

Elected to the National Academy of Sciences 2008

Elected to the American Academy of Arts and Sciences 2006

The Carl S. Marvel Creative Polymer Chemistry Award (ACS-Polymer Div) 2005

Cope Scholar Award (ACS) 2000

## Schedule of Events

April 16, 2011

Natural Sciences Complex (NSC)

University at Buffalo, SUNY, North Campus

8:30 - 9:50 am	Registration/ Poster Setup	
9:50 - 10:00 am	Introductory Remarks	(NSC Room 210)
10:00 - 11:00 am	Keynote Presentation by Dr. Timothy M. Swager, Department of Chemistry, Mass. Institute of Technology <i>Molecular- and Nano-wires for Chemical Sensing</i>	
11:00 - 12:15 pm	Student Presentations	
12:15 - 1:30 pm	Lunch	(NSC Room 222)
1:30 - 3:00 pm	Student Poster Presentations	(NSC 2 <sup>nd</sup> floor)
3:00 pm	Awards and Closing Remarks	(NSC Room 210)

## Oral Presentations

Room: NSC 210, Sarbajit Banerjee presiding

Time 10:00 AM - 12:15 PM

## Keynote Address

1. 10:00 am **Timothy M. Swager** *Massachusetts Institute of Technology*  
"Molecular- and Nano-wires for Chemical Sensing"

## Student Presentations

2. 11:00 am **Gene M. Nolis** *Binghamton University, SUNY*  
"Structure, Defects and Thermal Stability of Delithiated Olivine Phosphates"
3. 11:15 am **Onintza Ros Bengoetxea** *McMaster University*  
"Reactive Polymers for Crosslinked Cell Encapsulation"
4. 11:30 am **Christopher Dietz** *Niagara University*  
"Vinyl Cubane Derivatives: Cage Opening/Rearrangements"
5. 11:45 am **Talena Rambarran** *McMaster University*  
"Reactive Silicone Elastomers: Synthesis and Applications"
6. 12:00 pm **Anthony J. Chipre** *University at Buffalo, SUNY*  
"Progress Towards the Total Synthesis of the Strychnos Alkaloid Strychnofoline"

*Oral Session*

**Talk 2**

**Structure, defects and thermal stability of delithiated olivine phosphates**

*Gene M. Nolis, Shailesh Upreti, Natasha A. Chernova, and M. Stanley Whittingham\**

Department of Chemistry, Institute for Materials Research,  
State University of New York at Binghamton

Commercialized electrode materials must demonstrate the ability to maintain their chemical structure over the course of hundreds of charge/discharge cycles and range of climate conditions. Olivine phosphates,  $\text{Li}_x\text{FePO}_4$  (*o*- $\text{Li}_x\text{FePO}_4$ ), are commercialized cathode materials used in rechargeable lithium battery systems; however, the thermodynamics and stability data for their delithiated forms are scarce and contradictory. In this work we have synthesized *o*- $\text{LiFePO}_4$  by solid-state synthesis methods. To obtain *o*- $\text{FePO}_4$ , chemical delithiation was performed using various concentrations of  $\text{NO}_2\text{BF}_4$  or  $\text{Br}_2$  in acetonitrile. Powder x-ray diffraction (PXRD) and magnetic susceptibility data analysis indicate that complete delithiation of micron-sized particles can hardly be achieved without introducing antisite defects, such as iron ions on lithium sites. Differential scanning calorimetry, performed under inert atmospheric conditions, and PXRD results indicate exothermic phase transition from *o*- $\text{FePO}_4$  to *t*- $\text{FePO}_4$  during heating from room temperature to  $725^\circ\text{C}$ . The effect of particle size on the structure of *o*- $\text{FePO}_4$ , its thermal stability and thermodynamic characteristics will be discussed.

Talk 3

## Reactive polymers for crosslinked cell encapsulation

*Onintza Ros Bengoetxea, Nicholas D. Burke, Harald D. H. Stöver\**

Department of Chemistry, McMaster University

Immunoisolation by cell encapsulation is an effort to solve many hormone and enzyme deficiency disorders such as, hemophilia, neurological disorders, Parkinson's, Alzheimer's and diabetes. The basic idea for cell encapsulation is to entrap therapeutic cells in semipermeable polymeric hydrogel beads to provide them a comfortable media to live in.

Many hydrogel beads will not be able to resist the immune response and must be coated with different polymer layers creating a protective microcapsule. These capsules consist of a calcium alginate hydrogel core coated with a polycation (poly-L-lysine, PLL) and a polyanion. These polyelectrolytes form a shell around the core that protects the cells from the immune response after implantation. Furthermore, the outer polyanion layer is thought to neutralize remaining positive charges from PLL on the surface and avoid immune system reaction to the positively charged surface.

However, this type of microcapsule still presents several challenges and further research has been done changing the last polyanion layer. New polyanion layers provide covalent crosslinking to the capsule, increasing the long-term stability of the shell. In this study, two new polymers are suggested as polyanions for microcapsule crosslinking: poly(itaconic anhydride) and poly(itaconic anhydride-co-poly((ethylene glycol) methyl ether methacrylate)), and their properties will be studied for their application in cell encapsulation.

Talk 4

## **Vinyl cubane derivatives: Cage opening/rearrangements**

*Christopher Dietz, Danielle M. Raymond, Ronny Priefer\**

Department of Chemistry and Biochemistry, Niagara University

Based on previous studies of cubane, and its ultimate successful incorporation into polymers, it was found that vinylcubane has a tendency to undergo cage opening/rearrangement. It was in this finding that a cubyl styrene derivative is proposed in order to deter the cage opening of the cubane and thus perform polymerization from a vinylcubane-based monomer. The goal of this research is to perform a novel synthesis of this cubyl styrene derivative and attempt polymerization of the molecule in order to study the cage opening/rearrangement due to the initial a radical formation.

Talk 5

## Reactive silicone elastomers: Synthesis and applications

*Talena Rambarran, Ferdinand Gonzaga and Michael A. Brook\**

Department of Chemistry, McMaster University

Silicone (polysiloxane) elastomers are a class of hydrophobic polymers with a broad range of applications. Traditional methods to cure silicones involve platinum-catalyzed addition cure, radical cure, and tin- or titanium-catalyzed room temperature vulcanization. Post curing modification of such elastomers has proven difficult, but can be accomplished utilizing plasma treatment, acid or base equilibration or inclusion of excess reactive groups during the curing process. Recently, we have shown that the thermal Huisgen 1,3-dipolar cycloaddition ('click' chemistry) can be used to crosslink mixtures of alkyne- and azido-functionalized polysiloxanes.<sup>1</sup> This new methodology allows extensive control over the curing time and temperature, and avoids the use of precious metal catalysts.

We have prepared a series of alkyne- and azido-functionalized polysiloxanes of different reactivities, including activated propiolates- and less reactive propargylic-terminated polydimethylsiloxanes; subsequent crosslinking using different ratios results in elastomers that contain excess reactive groups available for successive modification. Molecules or polymers of various polarities and properties – such as hydrophilic poly(ethylene oxide) or fluorescent pyrenes- can then readily be tethered to the elastomers, allowing their properties to be fine-tuned.

Moreover, this methodology allows the synthesis of multi-layered elastomers: a first strategy involves a second cure-process on top of a pre-formed reactive elastomer; more importantly, adhesive elastomers resulted from the chemical welding of separately cross-linked alkyne- and azido-containing elastomers as a second strategy.

The synthesis of the precursor molecules, crosslinking, post curing modification and the resultant properties of the various elastomers will be discussed.

1. Gonzaga, F.; Yu, G.; Brook, M.A.; *Macromolecules*, **2009**, 42, 9220-9224.

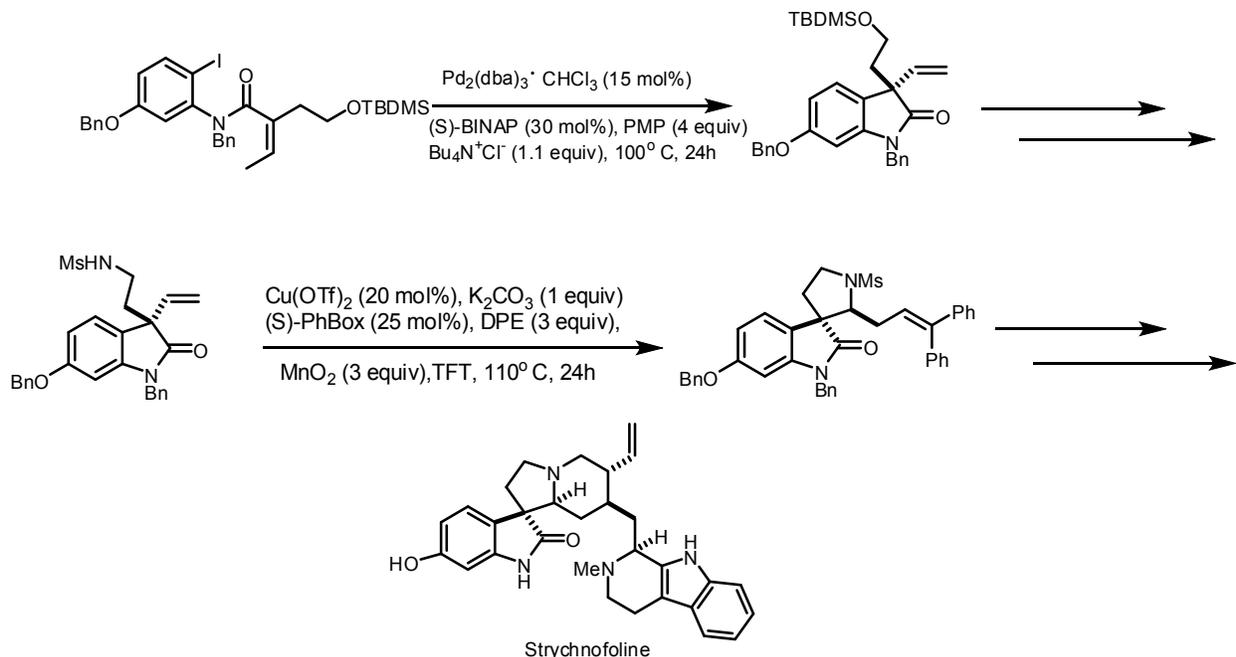
## Talk 6

# Progress towards the enantioselective synthesis of the strychnos alkaloid strychnofoline

*Anthony J. Chipre and Sherry R. Chemler\**

Department of Chemistry, University of Buffalo, SUNY

The family of 3,3'-pyrrolidinyl-spirooxindole natural product alkaloids are a structurally diverse group and exist as a formidable synthetic challenge. Strychnofoline is a challenging target and has exhibited anti-mitotic activity in cancer cells. The only reported synthesis of Strychnofoline is racemic. It is our goal to achieve the first chiral synthesis of this natural product. The methodologies we utilize may allow for an efficient and stereoselective approach to this alkaloid. We will employ a  $\text{Cu}^{\text{II}}$ -catalyzed enantioselective intramolecular carboamination as a key reaction for the installation of the core pyrrolidinyl-spirooxindole. Judicious choice of substrate and catalyst may permit the stereoselective synthesis of the naturally occurring C(7)-epimer, Isostrychnofoline.



## Poster Presentations

NSC 2<sup>nd</sup> Floor

Time: 1:30-3:00 PM

Poster #	Presented by	Institution
1	Jessica Stachowski	Canisius College
2	Greggory J. Martinez	University at Buffalo, SUNY
3	Nicholas D. Cultrara	University at Buffalo, SUNY
4	Robert J. Stewart	Canisius College
5	Peter Thayer and Charles Fennie	Monroe Community College
6	Thomas P. Smith	University at Buffalo, SUNY
7	Melissa L. Rosenburg	Houghton College
8	Yun Zheng	University at Buffalo, SUNY
9	Vivian Yaci Yu	Syracuse University
10	Michael Sennett	Canisius College
11	Joshua S. Wallace	Houghton College
12	S. Alison Stewart	McMaster University
13	Mansu Shim	University at Buffalo, SUNY
14	Makaia Papasergi	SUNY Geneseo
15	Bryce Paolella	Niagara University
16	Daniel Murphy	Niagara University
17	Jasmine L. May	University at Buffalo, SUNY
18	Joonyeob Lee	University at Buffalo, SUNY
19	Nicole E. Kendel	University at Buffalo, SUNY
20	Patrick J. Heaphy	Niagara University
21	Philip M. Farha	Brock University
22	Soreen Cyphers	Syracuse University
23	Marshall K. L. Binns	Canisius College
24	Nicholas J. Azzarelli	Syracuse University
25	Nicolas A. McLeod	Brock University
26	Mark P. Ghassibi	St. Bonaventure University

*Poster Session*

Poster 1.

**Direct NMR evidence for dimer formation by  
transition metal substituted polyoxometalates in  
nonpolar solvents**

*Jessica Stachowski, Derek Zemla, David Fortman, Matthew DiStasio, Steven H.  
Szczepankiewicz\*, Mariusz Kozik\**

Department of Chemistry and Biochemistry, Canisius College

Our recent work demonstrated that structures of Transition Metal Substituted Heteropoly Tungstates, TMSHT, in nonpolar solvents are more complex than published in the literature. Phase transfer of TMSHTs, which is accomplished by mixing the potassium salt of TMSHT in water with tetraheptylammonium bromide in toluene, also causes some KBr to be transferred into the toluene phase, as indicated by elemental and extracted ion analysis. Characteristic  $^{31}\text{P}$  NMR signals are attributed to the presence of the  $\text{K}^+$  and  $\text{Br}^-$  ions interacting with TMSHTs in toluene solution. However, even after the quantitative removal of potassium and bromide ions, new  $^{31}\text{P}$  NMR data at low temperature (low water content) indicate that another phenomenon takes place. In a nonpolar solvent two TMSHT anions join together through oxide bridges, and more NMR signals appear. Theoretical calculations show preference for certain isomeric structures.

Poster 2.

## Chemical sensors based on xerogels and reflective Bragg gratings

Greggory J. Martinez,<sup>1</sup> Ka Yi Yung<sup>1</sup>, Huina Xu<sup>2</sup>, Ke Liu<sup>2</sup>, Frank V. Bright<sup>1</sup>, and Alexander N. Cartwright<sup>2</sup>

<sup>1</sup>Department of Chemistry, University at Buffalo, SUNY

<sup>2</sup>Department of Electrical Engineering, University at Buffalo, SUNY

Throughout the last decade, xerogel-based optical sensors have been widely developed and implemented. They are popular because they are tunable and optically transparent. Thanks to advancements in light sources (e.g. light emitting diodes (LEDs)) and detectors (e.g. photodiodes), xerogel-based optical sensors can be designed into inexpensive, efficient and mobile devices. However, the use of LEDs and photodiodes comes at a cost: poor signal to noise ratio (S/N). In the past, members in our laboratories developed an O<sub>2</sub>-responsive xerogel-based sensor<sup>1</sup>. In concert, other team members have developed holographically-ordered porous polymer (HOPP) gratings<sup>2</sup>. Xerogel-grating integration is an exciting concept for improving overall S/N. In this presentation, we describe our integrated system and compare its performance characteristics.

1. Tang, Y.; Tehan, E. C.; Tao, Z.; Bright, F. V., Sol-Gel-Derived Sensor Materials That Yield Linear Calibration Plots, High Sensitivity, and Long-Term Stability. *Analytical Chemistry* **2003**, 75 (10), 2407-2413.
2. Kim, S. J.; Chodavarapu, V. P.; Cartwright, A. N.; Swihart, M. T.; Bunning, T. J., Enhanced oxygen detection using porous polymeric gratings with integrated recognition elements. *Sensors and Actuators B: Chemical* **2008**, 130 (2), 758-764.

Poster 3.

## Non-hydrolytic sol-gel synthesis and characterization of $\text{Ce}_x\text{Hf}_{1-x}\text{O}_2$ nanocrystals

*Nicholas D. Cultrara, Sean W. Depner, and Sarbajit Banerjee\**

Department of Chemistry, University at Buffalo, SUNY

Mixed ceria ( $\text{CeO}_2$ ) and hafnia ( $\text{HfO}_2$ ) solid solutions have shown promise in applications for nuclear control rods, oxygen gas sensors, and solid electrolytes for fuel cells. In the bulk, pure  $\text{CeO}_2$  crystallizes in the cubic phase and pure  $\text{HfO}_2$  crystallizes in the monoclinic phase at room temperature. As  $\text{CeO}_2$  is incorporated into the  $\text{HfO}_2$  lattice, the phase changes from a monoclinic structure to a tetragonal structure ( $t'$ ); as the concentration of  $\text{CeO}_2$  is further increased, transformation to a second ( $t''$ ) tetragonal phase is evidenced. When the solid-solution stoichiometry approaches a pure  $\text{CeO}_2$  lattice, the cubic phase is observed. Scaling to finite size can alter the phase stabilities of transition metal oxides. Consequently, we have attempted to elucidate the nanoscale phase diagram of the  $\text{CeO}_2$ - $\text{HfO}_2$  system.  $\text{Ce}_x\text{Hf}_{1-x}\text{O}_2$  nanocrystals have been synthesized using the non-hydrolytic sol-gel method, involving the condensation reaction of a metal halide and a metal alkoxide through a  $\text{S}_\text{N}^1$  mechanism. Tri-*n*-octylphosphine oxide is used as a high-boiling solvent, leading to the formation of monodisperse, high-crystalline-quality nanoparticles. The prepared nanocrystals have been characterized using X-ray diffraction, Raman spectroscopy, and transmission electron microscopy.

Poster 4.

## Electronic control of intermolecular allene cyclopropanation

*Furqan Hassan, Robert J. Stewart, John R. Frost, Timothy M. Gregg*

Department of Chemistry and Biochemistry, Canisius College

Intermolecular cyclopropanation of monosubstituted allenes is a powerful method for preparing chiral alkylidene cyclopropanes. This efficient rhodium-catalyzed reaction is subject to electronic effects of substituents, which can accelerate or retard the reaction rate. To improve the usefulness of the reaction, we are investigating electronic effects of aryl substitution on the rate of phenylallene cyclopropanation. Cyclopropanation of a series of para-substituted phenylallene substrates in competition with the unsubstituted analog indicated that reaction rates correlate with Hammett substituent coefficients. This is consistent with a mechanism involving buildup of positive charge at the central carbon of the allene substrate. We have demonstrated that electron-releasing substituents accelerate the rate of cyclopropanation, and electron-withdrawing substituents decrease the rate of cyclopropanation thus aiding the development of enantiomerically enriched alkylidene cyclopropanes for use in the synthesis of complex targets.

Poster 5.

## Synthesis of 2,4,6-tris(trifluoromethyl)aniline as a precursor to fluorinated $\beta$ -diketiminato ligands

*Peter Thayer,<sup>1</sup> Charles Fennie,<sup>1</sup> Brian Edelbach,<sup>1</sup> Patrick Holland,\*<sup>2</sup> Sarina Bellows,<sup>2</sup> Ryan Cowley<sup>2</sup>*

<sup>1</sup>Department of Chemistry and Geosciences, Monroe Community College

<sup>2</sup>Department of Chemistry, University of Rochester

The desired compound 2,4,6-tris(trifluoromethyl)aniline was synthesized from 1,3,5-trifluoromethyl benzene through two reaction schemes. Both schemes used 2,2,6,6-tetramethylpiperidinyllithium for deprotonation of the starting material. One method reacts the resulting 2,4,6-tris(trifluoromethyl)phenyllithium with imidazole-1-sulfonyl azide, followed by a reduction of the azide to an amine using Pd/C and H<sub>2</sub> gas in an 11% yield. The second method quenches the deprotonated starting material in iodine followed by a copper coupling reaction involving NaN<sub>3</sub>, Cu<sub>2</sub>O, and proline to yield 45% 2,4,6-tris(trifluoromethyl)aniline.

Poster 6.

## **Copper (II) catalyzed intramolecular aminooxygenation of hydroxylamine olefins**

*Thomas P. Smith and Sherry R. Chemler\**

Department of Chemistry, University at Buffalo, SUNY

Isoxazolidines are a class of biologically active compounds defined broadly as containing a five member heterocyclic ring with adjacent oxygen and nitrogen atoms. These types of compounds are gaining scientific attention as having potent antiviral and antibacterial activity comparable to compounds containing  $\beta$ -lactam structures as well as showing anti-inflammatory and antitumor activity. This hydroxylamine-containing motif is not only synthetically useful for its role in isoxazolidines but also for its easy access to the weakly held N-O bond, which can be reduced to  $\beta$ -amino alcohols as well as being a precursor to larger natural products. We have shown that these important heterocycles can be accessed via a single step synthetic process utilizing copper (II) catalyzed intramolecular aminooxygenation chemistry with high yield and good diastereoselectivity. Work on further functionalization is currently being performed.

Poster 7.

## **Palladium catalyzed reactions: A search for a greener oxidation pathway**

*Melissa L. Rosenberg, Scott A. MacBeth, and Karen E. Torraca\**

Department of Chemistry, Houghton College

One of the standard reactions used to generate aldehydes and ketones is the direct oxidation of alcohols. Although there are many current synthetic organic methods for completing this oxidation, several of them have significant disadvantages for large-scale manufacture: the use of stoichiometric amounts of heavy metals, the use of hazardous reagents, the use of molecular oxygen in the presence of highly flammable organic reagents, and the use of solvent-intense extractive work-ups. In light of this, our research is focused on the development of a mild and green oxidation method that would be amenable to implementation at large scale. Our initial efforts have focused on the use of palladium catalysis to complete this oxidation. Reagents we examined included various palladium sources, bases, and temperatures. The highest conversion obtained at the conclusion of this summer's research oxidized 1-phenylethanol to 1-phenylethanone using 0.10 equivalents of palladium acetate, 1.0 equivalent of sodium fumarate as the base, and 2.0 mL of dioxane as the solvent at 85°C for 24 hours, with no additional additives or oxidants. The reaction was kept under argon gas for one hour before the argon hose was removed and the contents of the reaction flask were left open to air, allowing volatile components to escape. The resulting percent conversion of the reaction was 97.5% according to HPLC. Future research will focus on understanding the mechanism of this reaction, application of the method to several types of alcohols and development of a simple extractive work-up method.

Poster 8.

## **Analysis of anions in local water bodies**

*Yun Zheng, Valerie Frerichs\*, Kenton M. Stewart\**

Department of Chemistry, University at Buffalo, SUNY

The sustainability of a healthy ecosystem received greater attention due to recognized climate and industry-related changes. Ion content can serve as a marker of industrial and climate changes, as well as ecosystem health, therefore it is critical to analyze the ion contents in targeted lakes. With enhanced analysis techniques, lower levels of critical ions can be monitored. A new ion-exchange chromatographic method has been developed and validated for the simultaneous analysis of inorganic anions from fresh water samples from lakes and streams throughout WNY mostly from 2008 to present. Concentration of two critical markers, chloride and sulfate will be presented from four of these samples sites. Results indicate that even lakes within close proximity have markedly different anion content over a period of three years, indicating different chemistries in these waters that can affect biological and sedimentary changes. With this information, we can begin to determine the local factors that have caused differences in the dynamics and chemical conductivity of these local waters.

Poster 9.

## **Expression and purification of recombinant saposin B for coenzyme Q10 purification**

*Vivian Yaci Yu, David Dixson, Robert Doyle\**

Department of Chemistry, Syracuse University

Coenzyme Q10 (CoQ10) plays a critical role in energy production in humans. Low levels of CoQ10 have been linked to diseases such as Parkinson's and Huntington's disease. CoQ10 levels decrease as we age, and use of statin drugs also lowers CoQ10 levels. Oral supplementation however increases CoQ10 levels. Current purification methods for Coq10 are difficult and expensive. A protein based purification method may alleviate the current problems associated with typical LC purification. Saposin B (SapB) has been shown to bind with CoQ10 at selective pH's. We hypothesized that utilizing a SapB coated support resin that an affinity purification method for CoQ10 could be produced. To this end, SapB was recombinantly expressed and bound via a His-Tag to a sepharose IMAC bead. This work demonstrates that CoQ10 can be bound by a SapB based affinity resin.

Poster 10.

## **Linker-assisted attachment of quantum dots to TiO<sub>2</sub> through a "one-pot" in-situ method and using a novel bifunctional organic linker molecule.**

*Mike Sennett<sup>1</sup> and David Watson<sup>2\*</sup>*

<sup>1</sup>Department of Chemistry and Biochemistry, Canisius College

<sup>2</sup>Department of Chemistry, University at Buffalo, SUNY

The linker-assisted attachment of Quantum Dots (QD) to TiO<sub>2</sub> is currently plagued by irreproducibility and low coverages. Two methods to approach these problems are currently being investigated. The first possible solution is a "one-pot" synthesis of QD in the presence of a substrate (TiO<sub>2</sub>). Depending on the nature of the capping group the substrate is either functionalized or not. Coverage has been achieved utilizing "one-pot" methods. The second proposed solution is the synthesis of a novel bifunctional organic linker. Current bifunctional linkers consist of varying lengths of mercaptoalkanoic acids. Phosphonic acids bind with greater affinity to TiO<sub>2</sub> than carboxylic acids and would possibly lead to increased reproducibility and surface coverage. A sulfur protecting group has been successfully attached to the alkyl phosphonate and the alkyl phosphonate has been successfully converted to an acid.

Poster 11.

## **Towards the synthesis of biodegradable glycopolymers**

*Joshua S. Wallace,<sup>1</sup> Marilyn E. Holt,<sup>1</sup> Alan Stier,<sup>1</sup> Kelly Harty,<sup>1</sup>  
Geoffrey W. Coates,<sup>2</sup> John M. Rowley<sup>1\*</sup>*

<sup>1</sup>Department of Chemistry, Houghton College

<sup>2</sup>Department of Chemistry and Chemical Biology, Cornell University

Synthetic glycopolymers, polymers containing sugar moieties as pendant groups, have become targets in an increasingly active field of research, and are most notable for their ability to act as cell surface mimics. Most research on glycopolymers has focused on acrylate- and styrene-based polymerizations. For biomedical applications, biodegradable polymers could have a significant advantage over these polymers, but this area remains largely unexplored. The goal of our research is to develop a method for the synthesis of a new class of biodegradable polymers.

Poster 12.

## Two-dimensional hydrogel arrays

*S. Alison Stewart, Nicholas D. Burke, Harald D. H. Stöver\**

Department of Chemistry, McMaster University

Encapsulating enzyme-secreting cells within a semi-permeable hydrogel matrix is a promising approach for the treatment of enzyme deficiency disorders such as diabetes and Tay-Sachs Syndrome. The Stöver research group is working on semi-permeable polymer coatings that might be applied to hydrogel beads. In addition to allowing in/out diffusion of nutrients and therapeutic enzymes while limiting the in-diffusion of immune modulators (e.g., immunoglobulins), the polymer coating must provide mechanical protection and be biocompatible such that there is not an immune response to the capsule surface resulting in loss of the encapsulated cells. A wide variety of coating materials have been investigated and there are many steps involved in creating and coating these capsules, leading to a large number of variables that must be optimized. This variable optimization can be a time consuming process and there is need for a more rapid screening process.

In this project, a rapid screening process based on thin films or arrays of dots of calcium alginate hydrogel were investigated. Slow immersion into a polycation solution followed by immersion at right angles into a polyanion solution gave a film or array with varied exposures to each of the two polyelectrolytes. Sulfonated polystyrene, polyester, glass and glass silanized with aminopropyltrimethoxysilane were investigated as potential substrates for the films or dots. Fluorescein- or rhodamine-labelled polyelectrolytes, including those capable of cross-linking, were employed so that the polymer binding could be probed and the coatings could be tracked during subsequent chemical challenges.

Poster 13.

## Selective binding of zinc complexes to DNA

*Mansu Shim, Kevin Sifers, Janet R. Morrow\**

Department of Chemistry, University at Buffalo, SUNY

Our studies focus on Zn(II) macrocyclic complexes that contain both a 1,4,7,10-tetraazacyclododecane and an aromatic pendent group. These complexes bind to unpaired thymidines in DNA including bulged structures. The Zn(II) center binds to the N3 of thymidine and the aromatic group stacks on the thymidine. Binding of the Zn(II) complex to thymidine in a bulge does not disrupt the DNA structure. However, binding of the Zn(II) complex to thymidine in a duplex will destabilize the structure. Once the nucleic acid changes conformation, it loses its original function and cannot be a template for the production of the malfunctioning enzymes (proteins) anymore. Whether the complexes successfully bound to and changed the conformation of the duplex DNA was checked by performing two tests. The first test was gel electrophoresis of the nucleic acids with the Zn(II) macrocycles bound to them and a control. The solution containing the Zn(II) complex bound to the nucleic acid moved a shorter distance in the gel than the control did because the control had a more compact shape. The second test was performed with a fluorescence displacement assay, which involved a fluorescent compound called ZnDSC that bound to the DNA. Binding of the ZnDSC displaces ethidium bromide resulting in a change in the fluorescence of the solution. This data was analyzed to determine the magnitude of the binding constant of the Zn(II) complex for the DNA.

Poster 14.

## **Electron microscopy study of the amyloid beta protein on the surface of gold colloidal nanoparticles**

*Kazushige Yokoyama, \*Makaia Papasergi, Jeffery Ma, Marissa Evarts, Songwoung Hong*

Department of Chemistry, SUNY Geneseo

Our research involves the investigation of the nanoscale aggregation of the Amyloid Beta Protein ( $A\text{-}\beta_{1-40}$ ) under interfacial conditions.  $A\text{-}\beta_{1-40}$  is involved in the process of fibrillogenesis, a known characteristic of Alzheimer's disease. Through research of the reversibility of the  $A\text{-}\beta_{1-40}$  aggregated conformation, it may be possible to find a process to reverse Alzheimer's disease in its early stages. We succeeded in characterizing microscale properties of  $A\text{-}\beta_{1-40}$  coated 20 nm gold colloids by using Transmission Electron Spectroscopy (TEM) for various pH conditions. This study enabled us to determine the behavior of  $A\text{-}\beta_{1-40}$  as seen through its interaction with gold colloid nanoparticles.

Poster 15.

## Novel dimerization of benzylamine

*Bryce Paolella, Ronny Priefer\**

Department of Chemistry and Biochemistry, Niagara University

The dimerization of primary amines to form secondary amines has yet to be reported. We have developed a novel process by which benzylamine reacts with sulfur monochloride to initially form the dibenzylamino disulfide, which subsequently fragments and dimerizes to form *N*-benzylidenebenzylamine. Reacting the imine with  $\text{NaBH}_4$  yields the dibenzylamine final product. In addition, we have begun to react the imine with various carbanions to make unsymmetrical disubstituted amines.

Poster 16.

## **Evaluation and comparison of organic extracts from the leaves and the flowers of *Salidago canadensis* (golden rod)**

*Daniel Murphy, Paul Pisarski, Ronny Priefer\**

Department of Chemistry and Biochemistry, Niagara University

Natural product extraction has yielded many beneficial compounds. Taxol, which is extracted from the bark of the Pacific Yew tree, is used as a treatment of breast cancer. Salicylic acid is another form of natural extract that comes from a willow tree. In our study of natural extracts, a combination of the leaves and the flowers of *Salidago canadensis* were used and extracted by the means of hexanes, ethyl acetate, dichloromethane, ethanol and water. Very few studies have been done on this plant, however through Chinese culture this plant has been used as a tea for the treatment of kidney stones, though no one has been able to ascertain whether there a particular compound that is beneficial for removal of stones.

Poster 17.

## Luminescent biocompatible silicon quantum dots for imaging applications.

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Quantum dots (QDs) have size-dependent optical properties that make them uniquely advantageous for *in vivo* targeted fluorescence imaging, traceable delivery, and therapy. The use of group II-VI (*e.g.* CdSe) QDs for these applications is advancing rapidly. However, group II-VI QDs contain toxic heavy metals that may limit their *in vivo* applications. Thus, replacing these with biocompatible QDs, such as silicon (Si), is desirable. *This study was done to test the hypothesis that drug delivery methods can be used for delivering biocompatible QDs made from silicon in vivo for bioimaging purposes.* This work reported here evaluates 5 water soluble biocompatible silicon quantum dot nanoformulations, for imaging applications. The formulations include (1) lysine modified, (2) chitosan coated, (3) DSPE-PEG encapsulated, (4) pluronic block copolymer modified, and (5) mPEG PLA modified silicon quantum dots. The benefits and disadvantages of each formulation are evaluated at physiological conditions. Temperature and pH stability tests are carried out and all of the formulations used maintained above 50%, ranging from 79-96%, of the initial photoluminescence but only the pluronic, DSPE-PEG, and the chitosan formulations maintained over 50% of the initial photoluminescence of the quantum dots after encapsulation, pluronic showing no decrease in photoluminescence intensity. Overall, the formulations are demonstrated to be useful for targeted cancer cell imaging and some *in vivo* cancer imaging applications. Based upon these demonstrations, we anticipate that Si QDs can play an important role in more sophisticated *in vivo* models, by alleviating QD toxicity concerns while maintaining the key advantages of QD-based imaging methods.

Poster 18.

## **The mechanism of citrate effects on apatite nanocrystal stability and size control**

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Nanocrystals of apatitic calcium phosphate participate in the organic-inorganic nanocomposite in bone to provide favorable mechanical properties. So far, the mechanisms of crystal size and morphology control have not been fully identified. Here we show citrate concentration effects on crystal growth rate and crystal morphology development by the Constant Composition (CC) method at hydroxyapatite (HAP) relative supersaturation of 9.0 at pH 7.40. In the presence of citrate, HAP crystal growth was markedly reduced by strong citrate binding on the crystal surface. However, the change of crystal growth rate with the citrate concentration is not monotonic, which means that there exists a maximum inhibition at a specific concentration of citrate. At lower concentration, the crystal growth rate decreases with increasing citrate concentration; whereas at higher concentration, the crystal growth rate increases with concentration. SEM images show that at high citrate concentration the crystal morphology changes from nanorods to aggregated ribbons, suggesting nucleation also involves this mechanism. By increasing the citrate concentration, the crystal growth model can change from classic step growth to a nucleation growth model. CC data also show that at lower citrate concentration, the presence of this ion decreases the density of crystal growth sites and surface steps as crystal growth proceeds, by which the apatite crystal is stabilized.

Poster 19.

## **Transannular enantioselective intramolecular carboamination using copper(II) catalyst**

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Carboamination is the simultaneous formation of carbon-nitrogen and carbon-carbon bonds from an alkene. The transannular intramolecular carboamination reaction studied involves the formation of these two bonds across a ring driven by a copper (II) catalyst. The syn-aminocupration transition state that is formed through the course of the reaction leads to high enantioselectivity. This methodology is an attractive and easy way to produce bond formations leading to 3-benzazepines, which are core structures found in biologically active compounds and natural products. Using a *gem*-diphenyl, mesyl-protected substrate, we were able to optimize previously determined conditions by lowering the temperature, the time necessary, and also the copper loading. These adjustments still provided the same yields and high enantioselectivity. Currently, we are expanding the scope of this reaction by introducing substituents at the para- position of the phenyl rings. We are also trying other electron-rich aliphatic substrates involving some substituted alkenes. In the future, we plan on trying substitution at the ortho- and meta- positions on the phenyl rings and also creating substrates with heterocycles, where we introduce an oxygen or sulfur into the ring.

Poster 20.

## **Cage opening/rearrangement of cubanes and surfactant synthesis**

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Cubane is a highly strained unsaturated tetrahedral molecule that was synthesized in 1964 by Eaton and Cole. Since cubane's synthesis, it has been researched in pharmaceuticals, explosives and polymers. Octanitrocubane is considered the most powerful non-nuclear explosive. Dipivaloylcubane has been known to have antiviral effects, specifically against HIV. However, 4-Iodo-1-vinylcubane has shown to have rearrangement properties in the presence of heat and Lewis acids. Due to its range of uses, we have explored the thermo-stability of a number of cubane derivatives, which have revealed the propensity to undergo cage opening/rearrangement. We focused on 1-iodocubane-4-carboxaldehyde due to the unique results it presented.

Furthermore, we have expanded our research into the synthesis of a cubane-based surfactant. This approach involves a four-step synthesis concerning a base hydrolysis of dimethyl-1,4-cubane dicarboxylate, followed by a combination of Vilsmeier with amide synthesis and then synthesis is completed by another base hydrolysis.

Poster 21.

## Catalytic hydroboration of unsaturated organic substrates by imido hydrido complexes of Mo(IV)

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Catalytic hydroboration of alkenes and alkynes has been known for decades, but catalytic hydroboration of carbonyls and nitriles has yet to be reported. We have recently disclosed the application of molybdenum (IV) imido hydrido complexes to catalytic hydrosilylation of carbonyls.<sup>1</sup> Herein, we report an extension of these studies to catalytic hydroboration. Three imido hydrido complexes of Mo(IV) were found to be potent catalysts for a variety of hydroboration reactions, including the addition of HBCat to carbonyls, alkenes, alkynes and nitriles. Stoichiometric reactivity towards these substrates and catecholborane presents some evidence for a non-classical M---H-B intermediate; albeit the exact mechanism remains unknown.

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Poster 22.

## Using a K159D mutated intrinsic factor protein as an oral delivery agent to the small intestine

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Although both the  $\alpha$ - and  $\beta$ -domains of intrinsic factor, a key protein in intestinal uptake of vitamin B<sub>12</sub> (B12), have been previously expressed, the full crystal structure of the protein has yet to be completed. The purpose of this research is (1) to express intrinsic factor in order to obtain a complete crystal structure and (2) to utilize a mutant form of it in order to orally deliver antigens to the ileum. The first goal of this research is to express intrinsic factor in the yeast *Pichia pastoris*. The second goal is to express a K159D intrinsic factor mutant protein. Lys 159 of intrinsic factor plays a role in salt bridge formation between intrinsic factor and the CUB<sub>6</sub> domain of cubilin, vital for enterocyte passage of IF-B12. We hypothesize the mutant will either prohibit binding to cubilin or allow binding, but not allow for receptor-mediated endocytosis. Utilizing the vitamin B<sub>12</sub> pathway with the K159D mutated intrinsic factor will allow oral delivery of drugs to the ileum where it can trigger an IgA immune response.

Poster 23.

## **Optimization of a laser ablation/molecular jet spectrometer system**

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Spectroscopic studies of small metal-containing molecules in the gas phase offer insight into metal-ligand bonding. A laser ablation/ molecular jet spectrometer system has been constructed in order to study these species using laser excitation spectroscopy. Low-resolution laser excitation spectra of previously observed calcium-containing molecules, CaCl, CaOH, CaNC, CaCCH and CaNH<sub>2</sub> were measured in order to optimize molecular synthesis conditions and increase detection sensitivity in this instrument. The spectrometer system was then used to observe a new electronic transition of the deuterium isotopologue CaND<sub>2</sub>. The design and optimization of the spectrometer system, as well as planned high-resolution laser excitation spectroscopic studies of isotopologues, will be discussed.

Poster 24.

## **Acridine orange staining to increase sensitivity of gel electrophoresis of DNA capped gold nanoparticles**

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DNA-functionalized gold nanoparticles (DNA-AuNP) have exhibited the potential for application within the medical field, such as drug delivery. Gel electrophoresis is a powerful analytical tool that can be used to quantify and separate AuNPs based on size and charge. However, due to the high concentration (1-5  $\mu\text{M}$ ) of DNA-AuNP needed per lane to perform gel electrophoresis experiments, DNA-AuNP electrophoresis is relatively expensive and inconvenient. Due to this constraint, a more sensitive method for gel electrophoresis is necessary. Using low percentage agarose gels (0.2%) to increase band intensity, and a common nucleic acid stain, acridine orange, in a negative staining technique, bands of DNA-AuNP with concentrations in the nanomolar range can be analyzed with gel electrophoresis image software. This staining technique allows gel electrophoresis to be performed with increased sensitivity and minimal usage of nanoparticle materials.

## Poster 25.

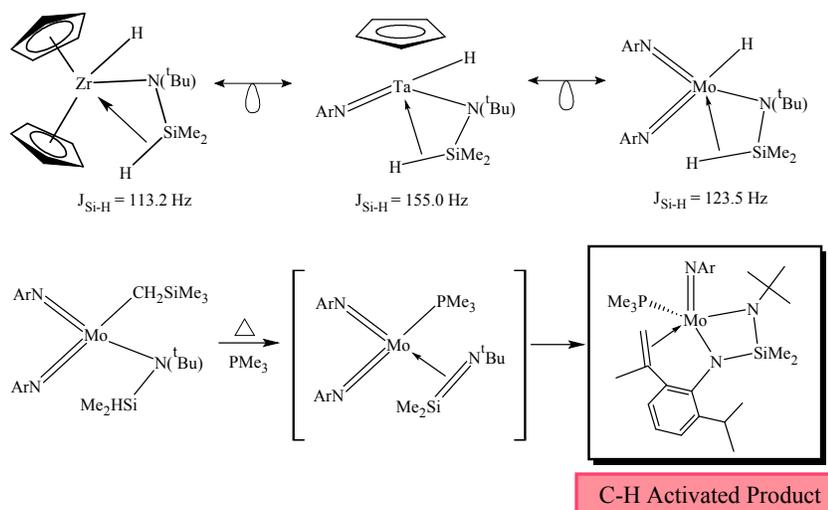
## $\beta$ -Agostic silylamido and silanimine complexes of tantalum and molybdenum

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$\beta$ -Agostic silylamido  $\text{SiH}\cdots\text{M}$  interactions are poorly studied for group 5 and group 6 metals.<sup>1</sup> We chose to study the possibility of such interactions in the Ta(V) complexes  $\text{Cp}(\text{ArN}=\text{Ta}(\text{N}(\text{tBu})\text{SiMe}_2\text{H}\cdots)(\text{X}))$  ( $\text{X} = \text{Cl}$  (**1**),  $\text{H}$  (**2**),  $\text{I}$  (**3**);  $\text{Ar} = 2,6$ -diisopropylphenyl) and Mo(VI) complexes  $(\text{ArN}=\text{Mo}(\text{N}(\text{tBu})\text{SiMe}_2\text{H}\cdots)(\text{X}))$  ( $\text{X} = \text{Cl}$  (**4**),  $\text{H}$  (**5**),  $\text{I}$  (**6**)), which are isolobal to the previously reported agostic complexes  $\text{Cp}_2\text{Zr}(\text{N}(\text{tBu})\text{SiMe}_2\text{H}\cdots)(\text{H})$ .<sup>2</sup> Compounds **2** and **5** exhibited strong  $\beta$ -agostic  $\text{NSiH}\cdots\text{M}$  interactions characterised by the reduced  $J_{\text{Si-H}}$  values of 155.0 Hz and 123.5 Hz respectively, as deduced from NMR analysis. Complexes **1**, **3**, **4**, **6** are classical.

Upon an attempt to prepare the silanimine complex  $(\text{ArN}=\text{Mo}(\eta^2\text{-N}(\text{tBu})=\text{SiMe}_2)(\text{PMe}_3))$ , an unusual C-H activation product was obtained upon intensive heating ( $100^\circ\text{C}$  for 20 days) of  $(\text{ArN}=\text{Mo}(\text{N}(\text{tBu})\text{SiHMe}_2)(\text{CH}_2\text{SiMe}_3))$ . The resulting product was the olefinic metalocyclic derivative  $(\text{ArN}=\text{Mo}\{\eta^2\text{-(C,C)}, \kappa^2\text{-N}(\text{tBu})\text{-Si}(\text{Me})_2\text{-N}(\text{Ar}'')\})(\text{PMe}_3)$ , where  $\text{Ar}''$  is a phenyl ring with an isopropyl group in one ortho position and a coordinated 2-propenyl group in the other ortho position.



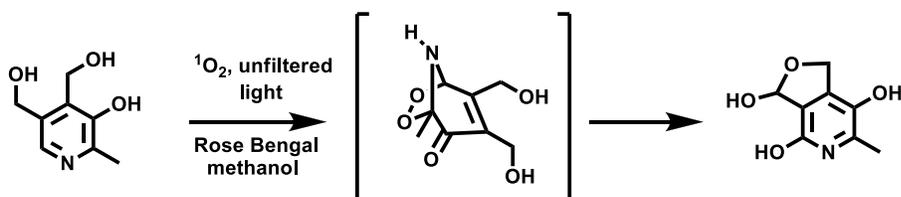
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2. Procopio, L. J.; Carroll, P. J.; Berry, D. H. *J. Am. Chem. Soc.* **1991**, 113, 1870.

Poster 26.

## A unifying mechanistic hypothesis for the oxidation of vitamin B<sub>6</sub> by singlet oxygen

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Vitamin B<sub>6</sub> has been shown to have antioxidant properties in both plants and humans. It specifically has a protective affect against singlet oxygen. Studying the reaction between singlet oxygen and various vitamin B<sub>6</sub> derivatives may reveal more about the mechanism of its function as an antioxidant. In a series of experiments modeled after research performed by Christopher Foote, pyridoxine was reacted with singlet oxygen under two conditions, 0.25 M phosphate buffer and methanol. Two different light sources were used to for this process, unfiltered light and a green filtered CFL. Three products were identified from these reactions. Under aqueous conditions the same product was formed using either light source. When the experiment was performed in methanol, a second product was formed using the green filtered LED while the third product was formed after using unfiltered light. All new products were characterized by proton and carbon NMR, 2D NMR, and mass spectrometry (University at Buffalo). Pyridoxal and pyridoxal-5'-phosphate were also reacted under these conditions, but the products proved too difficult to purify by normal phase chromatography. The product of the reaction of singlet oxygen with pyridoxal-5'-phosphate could potentially be purified by HPLC in the future. Since vitamin B<sub>6</sub> is primarily a bound cofactor for numerous enzymes, its ability to quench singlet oxygen in the blood and in tissues is relevant to understanding its role as an antioxidant.

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