

Poster Number	Title & Authors
1	Oxidation, The New Sensation Ellie Roberts and Peyton O'Brien
2	Red Cabbage Juice as a pH Indicator Roi Bein
3	Turn Down for White Duncan Bowen, Sam Hendricks, and Trey Bartels
4	Utilization of Ordinary Differential Equations for Estimating Metastasis in Breast Cancer Hannah Dille, Jonathan Low, Dr. Diana Ivankovic, Dr. David Prager and Dr. D.W. Weinbrenner
5	Retinoic Acid-Induced Mitotic Cell Death in the Leukemia Cell Line KG1-A Jonathan Low, Hannah Dille, Dr. David Prager, Dr. Donna Weinbrenner and Dr. Diana Ivankovic
6	Analysis of Phytoestrogens Found in the Symbiotic Relationship Between Sea Anemone and Algae Using HPLC UV-VIS and MS S. Kathleen Mowery and Nicholas J Kuklinski
7	Effects of Solvent on Electrochemistry of Biogenic Amines in Non-Mammalian Systems Sydney M Wright and Nicholas J Kuklinski
8.	A Hydraulic Sensor to Measure Tibial Plate Bending via X-Ray Radiography Apeksha Rajamanthrilage

Poster Number	Title & Authors
9.	Toward Imaging Radiopharmaceuticals Near Surfaces of Radioluminescent Medical Devices Gretchen B. Schober
10.	Non-Invasive Detection of Local pH Change on Implant Surfaces by Using Hydrogel Swelling Based Sensor in Standard Radiography Md. Arifuzzaman
11.	Towards the Development of a Smart Device Surface to Noninvasively Image and Monitor Implant Associated Infection In-Situ Unaiza Uzair
12.	Understanding Cellular Mechanisms for Prevention of Iron-Mediated Oxidative Stress by Sulfur and Selenium Antioxidants Craig Goodman
13.	Synthesis, Characterization, and Structures of Ruthenium(II) and Ruthenium(IV) Complexes with Multiple Solvato Ligands Mohammed A. Abbas
14.	Detection of Small Molecules Binding with Nanoparticles by Using Saturation Transfer Difference-Nuclear Magnetic Resonance(STD-NMR) Yunzhi Zhang
15.	Thick Silica Shell used as a Scaffold for Modification of Silver Nanoparticles Dallas Estepp
16.	Bipolymer Strips for Organic Vapor Sensing Emay Wen

Poster Number	Title & Authors
17.	Synthesis of Electrolyte Materials for Fuel Cell and Electrolysis Applications Kyle Beard
18.	High-Energy & High-Power Li-Ion Batteries Lakshman K. Ventrappagada
19.	A Novel Miniaturized Electrochemical Cell for Electrolysis and Fuel Cells Applications Saheed Bukola
20.	Regioselective 1,4-Conjugate Addition of Grignard Reagents to $\alpha,\beta\text{-}\gamma,\delta$ -Dienones and $\alpha,\beta\text{-}\gamma,\delta$ -Dienyl Thiol Esters Katherine Youmans
21.	Studying Chemically Modified Amphiphilic Tripeptide Catalysis by Molecular Dynamics Simulation Lisi Wang
22.	Human Insulin Adsorption to Monolayer Graphene. A Molecular Dynamics Study Richard Overstreet
23.	Analytical Applications of Cellulose-Derived Fluorescent Compounds Kaylee Clark
24.	Immobilization of Proteins onto Cellulose to Minimize Signal Gradient in Paper-Based Microfluidic Devices (μ PADs) Laura McCann

Poster Number	Title & Authors
25.	Development of an Electrochemical Paper-Based Microfluidic Device Paige A. Reed
26.	Protein Adsorption onto Optically Transparent Carbon Electrodes under AC Stimulation Tomas Benavidez
27.	Inorganic-Organic Hybrids – Crystal Assembly via Non-Conventional Bonding Yu Shen
28.	Crystal Growth Analysis of Simple and Complex Ionic Salts Justin Talbert
29.	Using Heat Capacity to Improve the Simulated Annealing Algorithm Mariia Karabin
30.	Mining New Sulfates from Classical Solution Chemistry Ashley Dickey
31.	Structural Characterization of Novel Lanthanide Containing Ruthenium and Rhenium Complexes Muditha Kolambage
32.	Hydrothermal Crystal Growth of Tridymite Framework Materials Rylan Terry

Poster Number	Title & Authors
33.	Enhanced Isotope Ratio Accuracy and Precision Using the Liquid Sampling Atmospheric Pressure Glow Discharge with a Quadrupole Exactive Orbitrap Instrument Edward Hoegg
34.	Parametric Dependence of Ambient Desorption Optical Emission Spectroscopy utilizing a Liquid Sampling-Atmospheric Pressure Glow Discharge (AD-OES-LS-APGD) Microplasma Htoo W. Paing
35.	Investigating the Application of Protein A Modified Capillary-Channel Polymer (C-CP) Polypropylene (PP) Fibers to the Quantitation of Immunoglobulin (IgG) in Complicated Matrices Hung K. Trang
36.	Development of Liquid Sampling-Atmospheric Pressure Glow Discharge as a Field-Deployable Source for Elemental Analysis via Optical Emission Spectroscopy Katja Hall
37.	Studying of Hydrodynamic and Loading Characteristics in Analytical Protein Separations on Polypropylene Capillary-Channeled Polymer (C-CP) Phases Lei Wang
38.	X-Panded Polyiodides and Triiodide Asymmetry in Organoiodine Hybrid Salts Khadijatul Kobra
39.	Tuning the Assembly of Multifunctional Copolymers by Solvent Quality Anuradhi Wickramasinghe
40.	Structure and Dynamics of Ionic Block co-Polymer Melts: Computational Study Dipak Aryal

Poster Number	Title & Authors
41.	Solvent Tuning of Structure of Ionic Block Copolymers in Solutions Manjula Senanayake
42.	Molecular Dynamics Simulation Study of Confined Conjugated Polymers: Charge Effects on Stability Sidath Wijesinghe
43.	Confined Rigid Conjugated Polymers at Interface Supun S. Mohottalalage
44.	Stimuli-Responsive Functional Materials Sourav Saha
45.	Convenient Synthetic Route to Tetraarylphosphonium Polyelectrolytes via Palladium-Catalyzed P–C Coupling of Aryl Triflates and Diphenylphosphine Wang Wan
46.	Functionalization of Carbon Nanoparticles and Defunctionalization Fan Yang
47.	Steady-State and Time-Resolved Fluorescence Studies on Interactions of Carbon "Quantum" Dots with Nitrotoluenes Gregory Lecroy
48.	Preparation of TiO ₂ /C Nanocomposite Dots and Their Photophysical Properties Yamin Liu

Poster Number	Title & Authors
49.	Optical and Magnetic Properties of Polymer Functionalized Carbon/Iron Oxide Nanoparticles Yin Hu
50.	New Perfluoroalkoxyl Co- and Ter-Polymers with Tetrafluoroethylene (TFE) Cameron A. Parrish
51.	New Polyfluorinated Polyethers and Synthesis of Their Hypothetic Epoxide Intermediates Chen Liu
52.	Synthesis and Chemistry of SF ₅ N- and SF ₅ CF ₂ - Containing Heterocycles Steven P. Belina
53.	Precise Control of Polyhydroxamate Ligand Topology for Selective Actinide Coordination Kirstin Sockwell
54.	Trifluorotoluenesulfonyl as a New Nitrogen Protecting Group Megan Sibley
55.	Facile Synthesis of PEGylated Vasopressin, Lypressin, and Oxytocin Analogs Victoria Haberman
56.	Non-Lethal Small Molecule Inhibition of the Starch Utilization System in Select <i>Bacteroides</i> Species Anthony Santilli

Poster Number	Title & Authors
57.	Vicinal Diamines Synthesis Using Azodicarboxylates and Electron-Rich Alkenes and Alkynes Chandima J. Narangoda
58.	Evaluation of Substituted Ebselen and Benzamidobenzoic Acid Peptide Conjugates as Potent Trypanocidal Agents Heeren Gordhan
59.	Development and Applications of Iodoarene Peptide Catalysts for Asymmetric Organic Transformations Maria Swasy
60.	Guanidinium Sulfation Crystallization: Strategy for Enantiomeric Resolution and Identification Beau R. Brummel

8.A hydraulic sensor to measure Tibial Plate bending via X-ray radiography

Apeksha Rajamanthrilage¹, Hunter Pelham²; Md. Arifuzzaman¹, Paul W Millhouse¹, Nathan Carrington², Bryce Kunkle², John D. DesJardins², Caleb J. Behrend³, Jeffrey N. Anker¹

¹Department of Chemistry, Clemson University, Clemson, SC

²Department of BioEngineering, Clemson University, Clemson, SC

³Department of Orthopaedic Surgery, Virginia Tech Carilion School of Medicine, Roanoke, VA

Abstract:

We describe a sensor to non-invasively measure orthopedic plate bending, read using in plain X-ray radiography. Bending the plate under load presses upon a sensor bulb which pushes a radiopaque fluid through a channel, such that fluid height within the channel indicates the degree of plate bending. Fracture healing can be monitored by measuring plate bending under load (which decreases as the fracture heals and callus stiffens) in order to determine when a patient can safely bear weight. The hydraulic action amplifies the signal from the plate bending motion, and the radiopaque fluid level is easily observed using standard X-ray imaging already employed in routine patient workups. In addition, the approach is generalizable to detecting pressure from analyte-specific gel swelling for in vivo non-invasive chemical measurements using standard X-ray imaging.

9.Toward Imaging Radiopharmaceuticals near Surfaces of Radioluminescent Medical Devices

Gretchen B. Schober¹, Donald Benza¹, Unaiza Uzair¹, Yash Raval², Tzuen-Rong J. Tzeng², Jeffrey N. Anker^{1,3}

¹Department of Chemistry, Clemson University, Clemson, SC

²Department of biological Sciences, Clemson University, Clemson, SC

³SCBioCRAFT Center for Biomedical Research Excellence (COBRE)

Abstract:

We describe a method to measure the proximity of radiolabelled antibiotics to the surface of implanted medical devices. Radioluminescent phosphor particles, such as europium doped gadolinium oxysulfide ($Gd_2O_2S:Eu^{3+}$), emit light with narrow spectral peaks when excited by blue light, X-Rays, or alpha/beta radiation. Our method uses alpha/beta radiation from radiolabeled analytes to excite a film of $Gd_2O_2S:Eu^{3+}$ particles, which only occurs when the radionuclide is in close proximity. The signal intensity and location are recorded using a CCD camera. Interaction between antibiotics and implant associated biofilms is difficult to investigate *in vivo*, which hinders understanding of reduced susceptibility of biofilms to antibiotic treatment. In application, we will image radiolabeled antibiotic localization at the surface of radioluminescent phosphor coated medical devices

in vivo. Our novel approach will permit further interrogation of the interaction between bacterial biofilms and antibiotics.

Acknowledgements:

This work was supported by National Science Foundation (NSF) CAREER award CHE1255535 and South Carolina Bioengineering Center of Regeneration and Formation of Tissues (SCBioCRAFT) funded under NIH grant 5P20GM103444-07

10. Hydrogel swelling based sensor detects local pH change on implant surfaces noninvasively in standard radiography

Md. Arifuzzaman¹, Yash Raval², Paul Millhouse¹, Caleb Behrend^{3, 5}, John D DesJardins³, Tzuen-Rong J Tzeng², and Jeffrey N Anker^{1,3,4}

¹Department of Chemistry, Clemson University, Clemson, SC

²Department of Biological Sciences, Clemson University, Clemson, SC

³Department of Bioengineering, Clemson University, Clemson, SC

⁴Center for Optical Materials Science and Engineering Technology (COMSET), Clemson University, Clemson, SC

⁵Virginia Tech Carilion School of Medicine and Research Institute, Roanoke, VA

Abstract:

A well responsive sensor was constructed to detect local pH changes on implanted device surfaces using Rontgen invented standard X-ray. The sensor comprised of a hydrogel film which exhibits pH dependent swelling/deswelling and facilitates the displacement of an indicator-dial relative to an internal scale. The sensor was calibrated in a series of standard pH buffers, and tested in a bacteria growth culture. Radiographic measurements were also performed with the sensor attached to a human cadaver tibia implant. Hydrogel swelling based sensor is a really simple approach to obtain chemical information from standard X-ray, a technique routinely used in patient follow-up.

11. Towards the development of a smart device surface to noninvasively image and monitor implant associated infection in-situ

Unaiza Uzair¹, Donald Benza^{1,2}, Fenglin Wang¹, Yash Raval³, Tzuen-Rong J. Tzeng³, Caleb Behrend⁴ and Jeffrey N. Anker¹

¹Department of Chemistry, Center for Optical Materials Science and Engineering (COMSET) and Environmental Toxicology Program, Clemson University, Clemson SC

²Department of Biological Sciences, Clemson University, Clemson SC

³Department of Electrical and Computer Engineering, Clemson University, Clemson SC

⁴Virginia Tech Carilion School of Medicine, Roanoke, VA

Abstract:

To noninvasively detect and monitor bacterial colonization of implanted medical devices, a 'smart' device surface is developed to track changes in pH at device surface using X-ray Excited Luminescence Chemical Imaging (XELCI) which allows high spatial and pH resolution while minimizing tissue scattering effects. The smart surface uses combination of X-ray excited optical luminescence and pH-dependent optical absorption to detect pH changes and it is characterized for reversibility, sensitivity and resolution. Bacteria and inflammatory responses cause a pH drop in affected area which can indicate infection. We imaged pH on device surface through tissue in-vitro, in cadaver and in animal models.

Acknowledgements:

This research was supported in part by National Science Foundation (NSF) CAREER award CHE1255535, a Fulbright Scholarship award to Unaiza Uzair, and animal studies funded through the South Carolina Bioengineering Center of Regeneration and Formation of Tissues (SCBioCRAFT) funded under NIH grant R15EB014560-01A1.

12. Understanding cellular mechanisms for prevention of iron-mediated oxidative stress by sulfur and selenium antioxidants

Craig Goodman¹, Julia L. Brumaghim¹

¹Department of Chemistry, Clemson University, Clemson, SC

Abstract:

Hydroxyl radical generation by Fe(II) reduction of hydrogen peroxide is the primary cause of cell death in both prokaryotes and eukaryotes. This hydroxyl radical generation is made catalytic by cellular reductants such as NADH, and NADH reduction of Fe(III) to radical-generating Fe(II) is the rate-limiting step for iron-mediated oxidative stress in cells. Using wild-type and NADH-dehydrogenase-mutant *E. coli* strains, we examined the role of NADH levels on sulfur and selenium antioxidant prevention of cell death. We found that NADH-dehydrogenase mutant *E. coli* have significantly higher NADH levels than wild-type cells, and are much more susceptible to cell death upon oxidative challenge. The sulfur-containing anti-thyroid drug methimazole prevented 53% cell death upon hydrogen peroxide challenge in the NADH-dehydrogenase mutant, slightly more than observed for the wild-type strain. Comparison of these results with those of the selenium analog, selenomethimazole, and the oxidized methimazole disulfide also will be discussed. Adding these sulfur and selenium antioxidants slows the rate of Fe(III) reduction by NADH, likely by binding and stabilizing Fe(II) over Fe(III). Thus, the iron-binding properties of these sulfur and selenium compounds may not only prevent cellular oxidative damage by hydroxyl radical but also slow iron redox cycling.

Acknowledgements:

The authors thank NASA, the South Carolina Space Grant, NSF (CHE 1213912), and Clemson University for funding this work.

References:

1. Imlay, J. A.; Linn, S. *Science*. 1988, 240, 1302-1309.
 2. Brumaghim, J.L.; Li, Y.; Henle, E.; Linn, S. *J. Biol. Chem.* 2003, 278, 42495-42504.
 3. Perron, N.R.; Hodges, J.N.; Jenkins, M.; Brumaghim, J.L. 2008, 47, 6153-6161.
 4. Angelé-Martínez, C.; Goodman, C.; Brumaghim, J.L. 2014, 6, 1358-1381.
 5. Woodmansee, A.N., Imlay, J.A. *J. Biol. Chem.* 2002, 277, 34055-34066.
-

13.Synthesis, characterization, and structures of ruthenium(II) and ruthenium(IV) complexes with multiple solvato ligands

Mohammed A. Abbas¹, Colin D. McMillen¹, and Julia L. Brumaghim¹

¹Department of Chemistry, Clemson University, Clemson, SC

Abstract:

Ru(II) solvato complexes are excellent starting materials for entry into Ru(II) synthetic chemistry. $[\text{Ru}(\text{NCCH}_3)_6]^{2+}$ is an ideal choice as a synthon, since it is homoleptic and doesn't retain chloride ligands as does $\text{RuCl}_2(\text{DMSO})_4$, and it is also aprotic and soluble in organic solvents, unlike $[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$. However, synthesis of $[\text{Ru}(\text{NCCH}_3)_6]^{2+}$ is challenging because the $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, $\text{RuCl}_2(\text{PPh}_3)_3$, and $\text{RuCl}_2(\text{DMSO})_4$ starting materials retain chloride, phenyl phosphate, and dimethyl sulfoxide ligands, respectively. We report an improved synthesis for $[\text{Ru}(\text{NCCH}_3)_6][\text{BF}_4]_2$ from $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ as well as a novel synthesis for Ru(IV) analog $[\text{Ru}(\text{NCCH}_3)_6][\text{ZnCl}_4]_2$. We have also synthesized two Ru(II) heteroleptic solvato species: $[\text{RuCl}(\text{NCCH}_3)_2(\text{DMSO})_3]^{2+}$ and $[\text{Ru}(\text{NCCH}_3)_5(\text{DMSO})]^{2+}$. Modifications for synthesis of $[\text{Ru}(\text{NCCH}_3)_6][\text{BF}_4]_2$ improved its yield from 60% to 75% and reduced the reaction time from 13 to 8 h with better control compared to previous synthetic methods. Similarly, yields of the heteroleptic Ru(II) solvato complexes were between 65% to 79% with reaction times around 4 h. These solvato complexes will be useful and convenient starting materials to synthesize both homoleptic and heteroleptic complexes of ruthenium.

Acknowledgements:

The authors would like to thank NSF grant CHE 1213912 for funding this work. M. A. A. also thanks the Higher Committee for Education Development in Iraq (HCED) for a graduate fellowship

References

1. Palmer, A. M.; Pena, B.; Sears, R. B.; Chen, O.; El Ojaimi, M.; Thummel, R. P.; Dunbar, K. R.; Turro, C. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* 2013, 371, 1-10.
 2. Brindell, M.; Kuliš, E.; Elmroth, S. K. C.; Urbańska, K.; Stochel, G. J. *Med. Chem.* 2005, 48, 7298–7304
 3. Derrah, E. J.; Giesbrecht, K. E.; McDonald, R.; Rosenberg, L. *Organometallics* 2008, 27, 5025–5032.
 4. Schrock, R. R.; Johnson, B. F. G.; Lewis, J. J. *Chem. Soc. Dalton Trans.* 1974, 9, 951–959.
 5. Underwood, C. C.; Stadelman, B. S.; Sleeper, M. L.; Brumaghim, J. L. *Inorg. Chim. Acta* 2013, 405, 470–476.
 6. Anzellotti, A.; Briceño, A. *Acta Crystallogr.* 2001, E57, 538–540.
 7. Tu, Y.-J.; Mazumder, S.; Endicott, J. F.; Turro, C.; Kodanko, J. J.; Schlegel, H. B. *Inorg. Chem.* 2015, 54, 8003–8011.
 8. Chen, C.; Lu, C.; Zheng, Q.; Ni, S.; Zhang, M.; Chen, W. *Beilstein J. Org. Chem.* 2015, 11, 1786–1795.
 9. Sharma, R.; Knoll, J. D.; Ancona, N.; Martin, P. D.; Turro, C.; Kodanko, J. J. *Inorg. Chem.* 2015, 54, 1901–1911.
 10. Evans, I. P.; Spencer, A.; Wilkinson, G. J. *Chem. Soc. Dalton Trans.* 1973, 2, 204–209.
-

14. Synthesis, characterization, and structures of ruthenium(II) and ruthenium(IV) complexes with multiple solvato ligands

Mohammed A. Abbas¹, Colin D. McMillen¹, and Julia L. Brumaghim¹

¹Department of Chemistry, Clemson University, Clemson, SC

Abstract:

Ru(II) solvato complexes are excellent starting materials for entry into Ru(II) synthetic chemistry. $[\text{Ru}(\text{NCCH}_3)_6]^{2+}$ is an ideal choice as a synthon, since it is homoleptic and doesn't retain chloride ligands as does $\text{RuCl}_2(\text{DMSO})_4$, and it is also aprotic and soluble in organic solvents, unlike $[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$. However, synthesis of $[\text{Ru}(\text{NCCH}_3)_6]^{2+}$ is challenging because the $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, $\text{RuCl}_2(\text{PPh}_3)_3$, and $\text{RuCl}_2(\text{DMSO})_4$ starting materials retain chloride, phenyl phosphate, and dimethyl sulfoxide ligands, respectively. We report an improved synthesis for $[\text{Ru}(\text{NCCH}_3)_6][\text{BF}_4]_2$ from $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ as well as a novel synthesis for Ru(IV) analog $[\text{Ru}(\text{NCCH}_3)_6][\text{ZnCl}_4]_2$. We have also synthesized two Ru(II) heteroleptic solvato species: $[\text{RuCl}(\text{NCCH}_3)_2(\text{DMSO})_3]^{2+}$ and $[\text{Ru}(\text{NCCH}_3)_5(\text{DMSO})]^{2+}$. Modifications for synthesis of $[\text{Ru}(\text{NCCH}_3)_6][\text{BF}_4]_2$ improved its yield from 60% to 75% and reduced the reaction time from 13 to 8 h with better control compared to previous synthetic methods. Similarly, yields of the heteroleptic Ru(II) solvato complexes were between 65% to 79% with reaction times around 4 h. These

solvato complexes will be useful and convenient starting materials to synthesize both homoleptic and heteroleptic complexes of ruthenium.

Acknowledgements:

The authors would like to thank NSF grant CHE 1213912 for funding this work. M. A. A. also thanks the Higher Committee for Education Development in Iraq (HCED) for a graduate fellowship

References:

1. Palmer, A. M.; Pena, B.; Sears, R. B.; Chen, O.; El Ojaimi, M.; Thummel, R. P.; Dunbar, K. R.; Turro, C. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* 2013, 371, 1-10.
 2. Brindell, M.; Kuliš, E.; Elmroth, S. K. C.; Urbańska, K.; Stochel, G. J. *Med. Chem.* 2005, 48, 7298–7304
 3. Derrah, E. J.; Giesbrecht, K. E.; McDonald, R.; Rosenberg, L. *Organometallics* 2008, 27, 5025–5032.
 4. Schrock, R. R.; Johnson, B. F. G.; Lewis, J. J. *Chem. Soc. Dalton Trans.* 1974, 9, 951–959.
 5. Underwood, C. C.; Stadelman, B. S.; Sleeper, M. L.; Brumaghim, J. L. *Inorg. Chim. Acta* 2013, 405, 470–476.
 6. Anzellotti, A.; Briceño, A. *Acta Crystallogr.* 2001, E57, 538–540.
 7. Tu, Y.-J.; Mazumder, S.; Endicott, J. F.; Turro, C.; Kodanko, J. J.; Schlegel, H. B. *Inorg. Chem.* 2015, 54, 8003–8011.
 8. Chen, C.; Lu, C.; Zheng, Q.; Ni, S.; Zhang, M.; Chen, W. *Beilstein J. Org. Chem.* 2015, 11, 1786–1795.
 9. Sharma, R.; Knoll, J. D.; Ancona, N.; Martin, P. D.; Turro, C.; Kodanko, J. J. *Inorg. Chem.* 2015, 54, 1901–1911.
 10. Evans, I. P.; Spencer, A.; Wilkinson, G. J. *Chem. Soc. Dalton Trans.* 1973, 2, 204–209.
-

15. Thick Silica Shell used as a Scaffold for Modification of Silver Nanoparticles

Dallas Estep¹, George Chumanov¹

¹Department of Chemistry, Clemson University, Clemson, SC

Abstract:

Silver nanoparticles are used for many imaging techniques. Stability of these silver nanoparticles is important. Silver nanoparticles made with addition of sodium silicate have a silica shell surrounding the nanoparticle, which allows the particles to be more stable. This shell can be made thicker by condensing more silica via the ethanol precipitation. The thick silica shell around the nanoparticles acts as a scaffold for further modifications including with other ions. The process for synthesizing these modified silver nanoparticles is being developed with the possibility of many applications in imaging, where silver nanoparticles can be used as a universal modifier.

16. Bipolymer Strips for Organic Vapor Sensing

Yimei Wen¹, George Chumanov¹

¹Department of Chemistry, Clemson University, Clemson, SC

Abstract:

Bimetallic strips are widely used to convert temperature changes into mechanical displacements. Two metals with different thermal expansion coefficient are fused together. When being heated, bimetallic strips bent in the direction of the metal with the smaller coefficient. Inspired by this principle, we made bipolymer strips with two polymers capable of absorbing organic vapors. When exposing the bipolymer stripes to organic vapors, the two polymers swell to different degrees because they absorb different amounts of the vapors. Different polymer were investigated for sensing methanol, acetone, toluene, formaldehyde, benzene, etc. The vapor response was reversible. The morphology of bipolymer strips was determined using atomic force microscopy. An intended application of the bipolymer strips is in “electronic nose” systems.

References:

1. Topham, P. D.; Howse, J. R.; Crook, C. J.; Armes, S. P.; Jones, R. A. L.; Ryan, A. J., Antagonistic Triblock Polymer Gels Powered by pH Oscillations. *Macromolecules* 2007, 40 (13), 4393-4395.
 2. Stadermann, M.; Baxamusa, S. H.; Aracne-Ruddle, C.; Chea, M.; Li, S.; Youngblood, K.; Suratwala, T., Fabrication of Large-area Free-standing Ultrathin Polymer Films. 2015, (100), e52832.
-

17.Synthesis of electrolyte materials for fuel cell and electrolysis applications

Kyle Bear¹, Dr. Stephen Creager¹

¹Department of Chemistry, Clemson University, Clemson, SC

Abstract:

This work will present the current synthetic methods being implemented in the synthesis of quaternary ammonium phosphonates for the application of anion-exchange membrane fuel cells (AEMFCs), as well as the synthesis, functionalization, and characterization of perfluorocyclobutyl (PFCB) aryl ether copolymers as acid ionomers, for applications in proton exchange membrane fuel cells (PEMFCs).

18.High-Energy & High-Power Li-Ion Batteries

Lakshman K. Ventrpragada^{1,2} Stephen E. Creager¹, Apparao M. Rao^{2,3}, Ramakrishna Podila^{2,3}.

¹Department of Chemistry, Clemson University, Clemson, SC

²Clemson Nanomaterials Institute, Clemson, SC, 29634 USA.

³Department of Physics and Astronomy, Clemson University, Clemson, SC 29634 USA.

Abstract:

Li-ion rechargeable batteries are the most promising candidates for use in electric vehicles. We are using a scalable approach to modify the current collector and active material interfacial (CCAMI) resistance with carbon nanotubes^{1,2}. We tested LiFePO₄ and NMC based cathodes and achieved an enhancement in capacities. Moreover, the improved CCAMI resulted in gravimetric energy densities up to 360 Wh/kg and power densities up to 200 W/kg with much higher power capability with LiFePO₄ and 750 Wh/kg at 1C-rate with NMC based cathode. We successfully made a silicon-CNT composite with ~1100 mAh/g capacity.

References:

1. M. R. Arcila-Velez et al., Nano Energy. 8 (2014) 9–16. doi:10.1016/j.nanoen.2014.05.004.
 2. M. Karakaya et al., Appl. Phys. Lett. 105 (2014). doi:10.1063/1.4905153.
-

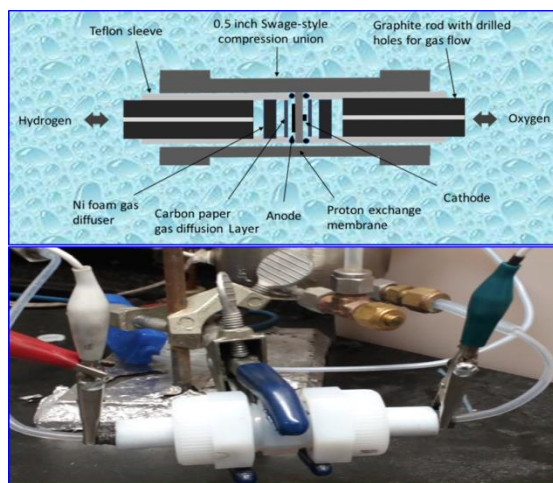
19.A Novel Miniaturized Electrochemical Cell for Electrolysis and Fuel Cells Applications

Saheed Bukola¹, Kyle Beard¹, and Stephen E. Creager¹

¹Department of Chemistry, Clemson University, Clemson, SC

Abstract:

The test platform for both proton-exchange membrane (PEM) electrolysis cells and fuel cells is often construed to be time consuming and intricate as a result of membrane electrode assembly on a large active and total membrane areas. Existing test protocol, such as rotating disc electrode, that utilizes small materials is often conducted in an environment that differs significantly from the real application testing. We present here a miniature PEM fuel cell test platform that may be used to conduct tests on catalyst layers containing just a few tens of micrograms of supported catalyst over an area less than 0.1 cm².



Acknowledgements:

The authors gratefully acknowledge the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences of the U.S. Department of Energy through Grant DE-FG02-05ER15718 for financial support of the work

References:

1. M. Carmo, D.L. Fritz, J. Merge, D. Stolten, A comprehensive review on PEM water electrolysis, *International Journal of Hydrogen Energy* 38(12) (2013) 4901-4934.
 2. Y. Jiao, Y. Zheng, M.T. Jaroniec, S.Z. Qiao, Design of electrocatalysts for oxygen- and hydrogen - involving energy conversion reactions, *Chemical Society Reviews* 44(8) (2015) 2060-2086.
 3. Y. Wang, K.S. Chen, J. Mishler, S.C. Cho, X.C. Adroher, A review of polymer electrolyte membrane fuel cells: Technology, applications, and needs on fundamental research, *Applied Energy* 88(4) (2011) 981-1007.
 4. H.A. Gasteiger, S.S. Kocha, B. Sompalli, F.T. Wagner, Activity benchmarks and requirements for Pt, Pt-alloy, and non-Pt oxygen reduction catalysts for PEMFCs, *Applied Catalysis B Environmental* 56(1-2) (2005) 9-35
-

20.Regioselective 1,4-Conjugate Addition of Grignard Reagents to $\alpha,\beta,\gamma,\delta$ -Dienones and $\alpha,\beta,\gamma,\delta$ -Dienyl Thiol Esters

Katherine Youmans¹, Emmanuel Amoah¹, Dr. R. Karl Dieter¹

¹Department of Chemistry, Clemson University, Clemson, SC

Abstract:

Alkyl Grignard reagents (Et, ⁿBu, ⁱPr, cyclohexyl), with the exception of ^tBuMgCl, undergo exceptionally highly regioselective 1,4-addition reactions to $\alpha,\beta,\gamma,\delta$ -unsaturated ketones, while aryl and heteroaryl Grignard reagents give mixed results ranging from exclusive 1,4-addition to regioselective 1,2-addition. All alkyl, aryl, and heteroaryl Grignard reagents examined gave exclusive 1,4-addition reactions with $\alpha,\beta,\gamma,\delta$ unsaturated thioesters, with the exception of ^tBuMgCl which gave an 80:20 mixture of 1,4-:1,6-addition products. The high chemo- and regioselectivity observed for these reactions is attributed to a radical or radical-like pathway for the alkyl Grignard reagents and possibly a carbanion pathway for aryl Grignard reagents.

21.Studying Chemically Modified Amphiphilic Tripeptide Catalysis by Molecular Dynamics Simulation

Lisi Wang¹, Brian Dominy¹

¹Department of Chemistry, Clemson University, Clemson, SC

Abstract:

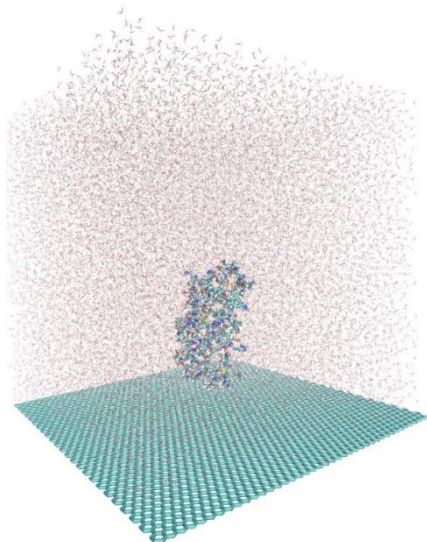
The recent development of a chemically modified H-D-Pro-Pro-Glu-NH₂ tripeptide capable of catalyzing conjugate addition reactions in an aqueous environment presents an opportunity to better understand the catalytic mechanisms shared with modern enzymes, and explore the evolutionary origins of biocatalysis. A hypothesis was proposed that the amphiphilic nature of the modified tripeptides drives the formation of an emulsion, which dehydrates the catalytic region of the peptide and contributes to the experimentally observed high yields and stereoselectivities. To test this hypothesis, classical molecular dynamics simulations were used to investigate the role of aggregation on the catalytic function of the tripeptides in water.

22. Human Insulin Adsorption to monolayer graphene. A molecular dynamics study

Richard Overstreet¹, Dr. Brian Dominy¹

¹Department of Chemistry, Clemson University, Clemson, SC

Abstract:



Molecular dynamics simulations were conducted using the CHARMM22 potential and TIP3P solvent to model human insulin adsorption to graphene. TIP3P explicit solvent was used to capture the hydrophobic effect, the mechanism responsible for the adsorption of proteins to hydrophobic surfaces. This water model was originally parameterized for the CHARMM22 potential and proteins thus it was required to develop Lennard-Jones graphene carbon parameters to reproduce the empirical water graphite contact angle of 86 degrees. Adsorption was modeled with five different orientations about graphene. Insulin shows varying degrees of adsorption surface area and correlated binding affinity due to limited solvent exposure.

23. Analytical Applications of Cellulose-Derived Fluorescent Compounds

Kaylee Clark¹, Tomas Benavidez¹, Dr. Carlos D. Garcia¹

¹Department of Chemistry, Clemson University, Clemson, SC

Abstract:

While extreme thermal treatment of cellulose (such as pyrolysis) can be used to produce graphite and a number of other nanostructured materials, mild conditions lead to the formation of low-MW compounds with aromatic structures. To determine the most relevant variables of this process, 3MM chromatography paper was treated using a standard 15W CO₂ laser engraver. Upon this step, a blue fluorescent pattern was observed when the substrate was irradiated with a handheld UV lamp (365 nm). The experimental conditions leading to maximum intensity (speed, power, and number of engraving steps) were first optimized. Next, the resulting cellulose-derived fluorescent compounds were characterized using fluorescence spectroscopy, HPLC (coupled to both UV and fluorescence detection), and ESI-MS.

24. Immobilization of Proteins onto Cellulose to Minimize Signal Gradient in Paper-Based Microfluidic Devices (μ PADs)

Laura McCann¹, Tomas Benavidez¹, Dr. Carlos D. Garcia¹

¹Department of Chemistry, Clemson University, Clemson, SC

Abstract:

Heterogeneity of the color distribution in the detection zones is the most remarkable drawback in μ PADs. This issue, attributed to the mobility of enzymes and reagents towards the edge of the detection zone, can result in increased variability and poor judgment of the final color by the user. In this regard, a rational selection of the conditions selected for the immobilization process could help controlling the adsorption of proteins to cellulose substrates (Chromatography paper). Protein concentration, adsorption time, solution pH, and ionic strength of the buffer solution, and the number of times the protein (BSA) was spotted were investigated.

25. Development of an electrochemical paper-based microfluidic device

Paige A. Reed¹, Tomas E. Benavidez¹, Dr. Carlos D. Garcia¹

¹Department of Chemistry, Clemson University, Clemson, SC

Abstract:

In recent years, there has been an overwhelming interest in small, inexpensive, and effective analytical devices for the detection of biomolecules. To address this need, we have developed an electrochemical paper-based microfluidic device (ePAD) using simple materials such as paper, tape, wires, and super glue. Carbon electrodes were constructed out of pyrolyzed chromatography paper and then modified with Prussian blue to be selective toward hydrogen peroxide. The selectivity towards hydrogen peroxide is desirable as many oxidative enzymatic reactions produce hydrogen peroxide. In this manner the Prussian blue carbon electrodes can be used to detect biomolecules that undergo redox reactions.

26. Protein Adsorption onto Optically Transparent Carbon Electrodes under AC Stimulation

Tomas E. Benavidez¹, L.M.S. Silva¹, Dr. Carlos D. Garcia¹

¹Department of Chemistry, Clemson University, Clemson, SC

Abstract:

Adsorption of Lysozyme (LSZ), Myoglobin (Mb), and Bovine Serum Albumin (BSA) onto Optically Transparent Carbon Electrodes (OTCE) was investigated by applying an alternating current (AC) potential. The AC potential was set at +800 mV, the amplitude at 100 mV, and the frequency investigated in the 0.1-10,000 Hz range. Protein adsorption under direct current (DC) potential (amperometry at +800 mV) was recorded as a control. AC potentials induced higher protein adsorption than the corresponding DC experiments. The maximum adsorption behavior was observed at the lower frequencies (0.1, 0.5, and 1 Hz) and LSZ (a hard protein) displayed the highest accumulation on the OTCE.

27. Inorganic-Organic Hybrids – Crystal Assembly *via* Non-conventional Bonding

Yu Shen¹, Qiuying Zhang¹, Shiou-Jyh Hwu¹

¹Department of Chemistry, Clemson University, Clemson, SC

Abstract:

Hybrid solids made of water-soluble POM (polyoxometalate)-based inorganic clusters as building blocks and organic molecules as linkers are typically synthesized under hydrothermal conditions. Our goal is to understand the structural principles through which desired frameworks of technological importance can be designed and synthesized. Water-soluble POM salts can be chemically manipulated *via* co-crystallization with organic salts to render the POMs soluble in organic solvents. Soluble POM salts can further be manipulated with respect to synthesis in organic solvents. In addition, soluble POMs can be used in homogenous oxidative catalysis of, for example, secondary alcohols.

References:

1. Queen, W. L.; West, J. P.; Hwu, S-J.; Tran, T. T.; Halasymani, P. S.; VanDerveer, D. Chem. Commun. 2012, 48, 1665-1667.
 2. Campbell, M. L.; Sulejmanovic, D.; Schiller, J. B.; Turner, E. M.; Hwu, S-J.; Whitehead, D. C. Catal. Sci. Technol., 2016, Advance Article.
 3. Inoue, M.; Suzuki, T.; Fujita, Y.; Oda, M.; Matsumoto, N.; Yamase, T. Journal of Inorganic Biochemistry, 2006, 100, 1225–1233.
-

28. Crystal Growth Analysis of Simple and Complex Ionic Salts

Justin Talbert¹, Dr. Shiou-Jyh Hwu¹, Dr. Brian Dominy¹

¹Department of Chemistry, Clemson University, Clemson, SC

Abstract:

Traditionally, ionic salts are analyzed as point charge compounds. Though this is fine for simple ionic salts, like NaCl and CsCl, this approach is not the best way to represent more complex ionic salts, like polyoxometallates (POMs), which contain polyatomic, covalent clusters. We introduce a method that performs classical electrostatic interaction calculations in a CHARMM suite software package to create an interaction energy grid-map. From this grid-map, we can determine the most thermodynamically stable positions for ions to locate as the crystal system grows. Our method is successful in determining ion positions, when compared to crystallographic positions, for point charge analysis and when assigning charge to individual atoms.

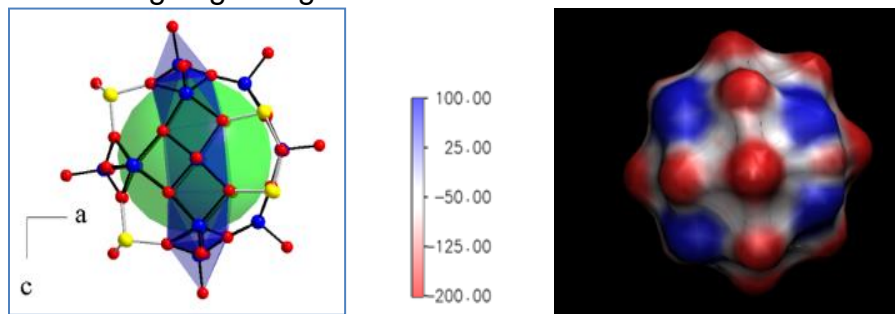


Figure One: Electrostatic potential surface energy mapping of polyoxovanadate cluster, POV₁₄.

References:

1. Wendy L. Queen, J. Palmer West, Shiou-Jyh Hwu, Thanh Thao Tran, P. Shiv Halasyamani, and Don VanDerveer. Symmetry preservation in a new noncentrosymmetric lattice comprised of acentric POM cluster residing in bowls of Cs⁺-based half SOD β -cage. *Chem. Commun.* 2012, 48 1665-1667.
 2. Li L, Li C, Sarkar S, Zhang J, Witham S, Zhang Z, Wang L, Smith N, Petukh M, Alexov E. "DelPhi: a comprehensive suite for DelPhi software and associated resources." *BMC Biophys.* (2012) May14;4(1):9.
-

29.Using Heat Capacity to Improve the Simulated Annealing Algorithm

Mariia Karabin¹, Mariia Karabin¹, Steven Stuart¹, Arkady Kholodenko¹

¹Department of Chemistry, Clemson University, Clemson, SC

Abstract:

The simulated annealing is popular optimization method for finding the global optimum of a function. Our modification to this algorithm, suitable for atomistic simulations, changes the cooling rate on the fly, based on the heat capacity, which is calculated from the fluctuations in the system energy. The system is cooled slowly when the heat capacity suggests that the system is near a phase transition, but cooled more quickly at other times. That way, the system has a smaller probability of getting trapped in a local minimum, and the simulation runs with lower computational cost.

30.Mining New Sulfates from Classical Solution Chemistry

Ashley Dickey¹, Colin D. McMillen¹, Joseph W. Kolis¹

¹Department of Chemistry, Clemson University, Clemson, SC

Abstract:

Metal sulfates represent a broad class of interesting materials with applications ranging from mineral supplements to their recent implementation in energy storage. The study of such systems might seem a topic of the past, but many of these minerals have been overlooked or poorly characterized, and there remain a number of unanswered questions. Our group is interested in a systematic exploration of synthetic routes, chemistry, and structural characterization of metal sulfates. Many complex sulfate minerals occur naturally and we look to use these minerals as templates and mirror their environments by using ambient conditions and classical solution chemistry. Initial experiments have led to the synthesis of several new alkali-iron sulfate compounds containing intriguing iron clusters.

Acknowledgements:

The authors thank the National Science Foundation Grant # DMR-1410727 for financial support.

31. Structural Characterization of Novel Lanthanide containing Ruthenium and Rhenium Complexes

Muditha Kolambage¹, J.W.Kolis¹, Colin McMillen¹

¹Department of Chemistry, Clemson University, Clemson, SC

Abstract:

The chemistry of ruthenium and rhenium are interesting due to their stability in a wide variety of oxidation states and coordination geometries. Single crystals of $\text{Ln}_5\text{Ru}_2\text{O}_{12}$ (Ln = Yb, Ho, Y), LnReO_4 (Ln = Pr, Nd) and $\text{Ln}_4\text{Re}_2\text{O}_{11}$ (Ln = Tb, Gd) were hydrothermally prepared at 650 °C. The structures feature greatly different Ru and Re units – edge-sharing $[\text{RuO}_6]$ chains in $\text{Ln}_5\text{Ru}_2\text{O}_{12}$, $[\text{Re}_4\text{O}_{16}]$ clusters in LnReO_4 , and $[\text{Re}_2\text{O}_{10}]$ dimers in $\text{Ln}_4\text{Re}_2\text{O}_{11}$. The Ru-Ru and Re-Re distances also vary across the structure types. The growth of well-formed single crystals not only enables structural characterization, but also future spectroscopic and magnetic studies.

32. Hydrothermal Crystal Growth of Tridymite Framework Materials

Rylan Terry¹, Daniel Vinton¹, Colin McMillen¹, Joseph Kolis¹

¹Department of Chemistry, Clemson University, Clemson, SC

Abstract:

A series with the general formula ABCO_4 (A = alkali ion, B = trivalent metal and C = tetravalent metal) featuring a stuffed tridymite, framework has been synthesized through hydrothermal methods. Tridymite is high temperature variant of quartz that forms six-membered rings propagating through the structure, creating vacant channels. In a stuffed variation of this structure type, rings having negative charge are balanced by the "stuffing" of an alkali or alkali earth cation into the vacant channels. Interest has grown due to the prevalence of these structures crystallizing in noncentrosymmetric space groups, as well as displaying transparencies down to 200 nm.

33.Enhanced Isotope Ratio Accuracy and Precision Using the Liquid Sampling Atmospheric Pressure Glow Discharge with a Quadrupole Exactive Orbitrap Instrument

Edward Hoegg^{1,2}, George Hager², David Koppenaal², Garret Hart², Kenneth Marcus¹

¹Department of Chemistry, Clemson University, Clemson, SC

²Pacific Northwest National Lab, Richland Wa, 99354

Abstract:

In order to meet the needs of the international nonproliferation and safeguards communities for a field deployable ionization source capable of highly accurate and precise isotope ratio (IR) measurements, the liquid sampling-atmospheric pressure glow discharge (LS-APGD) ion source is being developed. As part of the evaluation of IR qualities, the microplasma has been interfaced with Orbitrap mass analyzers. It has previously been shown that the LS-APGD is capable of producing a plasma with a higher energy density than found in ICP sources, all while requiring fewer consumables for operation making it an ideal candidate as a field deployable ion source. The LS-APGD /Orbitrap combination has been shown to measure a natural U sample ($^{235}\text{U}/^{238}\text{U} = 0.0072$), as 0.007003, with a relative standard deviation of 0.41%. This value is close to the International Target Values expressed by the IAEA for destructive analysis, making this a promising system for uranium IR measurements in general. The performance to date, on par with commercial quadrupole ICP-MS, was not anticipated. This work hopes to improve upon those characteristics by replacing the baseline Exactive instrument with a Q-Exactive Orbitrap mass analyzer. The Q-Exactive employs a quadrupole mass analyzer that can be used to pre-select the ions that are injected into the Orbitrap for high resolution analysis. It is expected that this added functionality will limit the number of interfering ions as well as any present matrix ions from entering the trap, thus extending the dynamic range and improving the accuracy and precision of the measurements.

34.Parametric Dependence of Ambient Desorption Optical Emission Spectroscopy utilizing a Liquid Sampling-Atmospheric Pressure Glow Discharge (AD-OES-LS-APGD) Microplasma

Htoo W. Paing¹, R. Kenneth Marcus¹

¹Department of Chemistry, Clemson University, Clemson, SC

Abstract:

The operating parameters for liquid sampling-atmospheric pressure glow discharge (LS-APGD) microplasma have been evaluated as an ambient desorption optical emission source for the purpose of elemental analysis. The use of optical (atomic) emission is being pursued due to its greater flexibility than mass spectrometry for field-based measurements. Use of the the microplasma in an ambient desorption (AD) mode allows

for direct solids analysis of diverse materials in their native state. Parameters that were evaluated include discharge current, electrolyte liquid flow rate, sheath gas flow rate, counter gas flow rate, and angle of liquid electrode. Furthermore, varying metals, electrolyte solution identity, and different matrix forms of copper substrate were evaluated in order to better understand the precise mechanisms of operation. The intensity of the atomic emission, standard deviation, and signal-to-noise ratios were analyzed to gather understanding of how the LS-APGD operates and how the volatilization of the metal substrates occurs. The results indicate that the identity of acid has little effect on the volatilization of different metals, however the intensity of emission is still heavily dependent on the type of metal. Different matrix forms also showed a small but notable effect on the intensity. Increasing flow rate not only increases the intensity of emission (logarithmically) but also decreases the standard deviation of the emission signal. Other key parameters that determine the intensity of the signal were the counter gas flow rate and angle of incidence of the plasma onto the solid sample.

35. Investigating the application of protein A modified capillary-channel polymer (C-CP) polypropylene (PP) fibers to the quantitation of Immunoglobulin (IgG) in complicated matrices

Hung K. Trang¹, R. Kenneth Marcus¹

¹Department of Chemistry, Clemson University, Clemson, SC

Abstract:

Widely known for its high affinity for the Fc region of IgG, of recombinant *Staphylococcus aureus* protein A (rSPA) has long been utilized to capture IgG from complex biological matrices such as cell culture supernatant. Combining the attributes of both separation and immunoassay techniques, affinity chromatography employing protein A is typically the first chromatographic step in the downstream processing of therapeutic monoclonal antibody (mAb). Moreover, at the analytical scale, this technique is also used in the early development phase of mAb production when a great number of high titer harvest cell culture samples need to be screened and monitored for IgG expression.

This study investigated the potential application of the rSPA-modified C-CP PP column to the quantification of IgG in complex biological matrices. Optimization of the chromatographic method regarding mobile phase components and loading/eluting conditions was investigated. The six-minute analysis, including a loading step with 12mM phosphate pH 7.4, an eluting step with 0.025% phosphoric acid and a re-equilibration step, was optimal for quantitation of IgG1 from 0.075 to 3.00 mg mL⁻¹. The inter-day and intra-day precision of the method were 3.1% and 3.5% respectively. Column performance was decently reproducible across columns prepared from different batches. The method reported proved to be potentially suited for high IgG titer analysis in complex harvest cell culture.

36. Development of Liquid Sampling-Atmospheric Pressure Glow Discharge as a Field-Deployable Source for Elemental Analysis via Optical Emission Spectroscopy

Katja Hall¹, R. Kenneth Marcus¹

¹Department of Chemistry, Clemson University, Clemson, SC

Abstract:

Liquid sampling-atmospheric pressure glow discharge (LS-APGD) microplasma methods of analysis require less sample and power while producing less waste than current industrial instrumentation like the ICP-OES. These advantages as well as the compact design of the LS-APGD source give it potential in field deployability. Assessments of optical spectra, electrolytic solution composition and flow rate, carrier gas flow rate, and inter-electrode separation distance were performed in order to characterize the instrument. Final parameters include a 5% HNO₃ electrolytic solution at a flow rate of 45 uL/min, sheath gas flow rate of 0.500 L/min, and an inter-electrode distance of 2 mm. Single-element and multi-element solutions were used to perform the studies.

37. Studying of Hydrodynamic and Loading Characteristics in Analytical Protein Separations on Polypropylene Capillary-Channeled Polymer (C-CP) Phases

Lei Wang¹, R. Kenneth Marcus¹

¹Department of Chemistry, Clemson University, Clemson, SC

Abstract:

In the field of protein analytics, the coupling of liquid chromatography separations, especially reversed phase (RP), and electrospray ionization mass spectrometry (ESI-MS) provides a great deal of information. Capillary-channeled polymer (C-CP) fibers have been employed for fast protein separations on both the analytical and preparative scales, explicitly for the capability to operate at high linear velocities (>50 mm s⁻¹), without van Deemter C-term penalties. Because of the high hydrophobicity and salt matrix removal functionality, polypropylene (PP) has been used for protein separation through RP mode. In order to maintain the preferred high linear velocities, while also using volume flow rates compatible with standard ESI-MS, smaller column diameters (i.d. = 0.5 mm) are evaluated with the intention to achieve high chromatographic throughput. In order to study the hydrodynamic characteristics in C-CP fiber protein separations, different operational parameters required evaluation, including gradient rate (elution volume) and flow rate etc. Their effects on peak shape, resolution, and efficiency were correlated. In addition, volume and mass loading effects were studied on the C-CP fiber stationary phase as a function of pH variance using bovine serum albumin (BSA) as the model protein. For the ultimate LC-ESI-MS applications, mixtures of ribonuclease A, cytochrome c, myoglobin and lysozyme were prepared in phosphate buffered saline (PBS) and urine matrices. The

efficiency of the matrix removal is reflected in the near-identical qualitative and quantitative responses. It is considered that C-CP fiber columns can provide the comparably high throughput and recoveries desired in top-down proteomics applications.

38.X-panded Polyiodides and Triiodide Asymmetry in Organoiodine Hybrid Salts

Khadijatul Kobra¹, Khadijatul Kobra¹, Austin Miller³, Adam M. Siegfried³, Timothy W. Hanks², William T. Pennington¹

¹Department of Chemistry, Clemson University, Clemson, SC

²Furman University, Greenville, SC.

³Science, Math, and Health, Spartanburg Methodist College, Spartanburg, SC.

Abstract:

Polyiodides, anionic arrays composed of iodide, triiodide, and diiodine building blocks, display enormous structural diversity and have attracted extensive experimental and theoretical interest. Replacement of diiodine with an organoiodine, such as tetraiodoethylene, results in a similar class of anionic arrays, which we have labeled as “X-panded polyiodides.” With the choice of organoiodine, and of I⁻, I₃⁻, or higher I^{x-}, even greater structural diversity is observed. The role of the cation on structure in [cat]I_n•x RI, will be discussed, as will factors leading to a significant preference for asymmetric triiodides in these crystal structures.

39.Tuning the Assembly of Multifunctional Copolymers by Solvent Quality

Anuradhi Wickramasinghe¹, Manjula Senanayake¹, Sidath Wijesinghe¹, Supun S. Mohottalalage¹, Lilin He², Dipak Aryal¹, Gary S. Grest³, Dvora Perahia¹

¹Department of Chemistry, Clemson University, Clemson, SC

²HFIR, Oak Ridge National Laboratory, Oak Ridge, TN, 37831

³Sandia National Laboratories, Albuquerque, NM

Abstract:

Tunability of multifunctional copolymers under different conditions make them suitable for current and potential applications. These polymers have tendency to self-assemble into variety of structures. Here we probed the structure of non-ionic pentablock copolymer (A-B-C-B-A), where C is polystyrene, B is poly (ethylene-r-propylene), and A is poly (t-butyl styrene) in cyclohexane propanol mixed solvent using Small Angle Neutron Scattering. We find that in cyclohexane fractal like aggregates are formed. However, with increasing solvent polarity these aggregates rearrange into spherical structures.

Acknowledgements:

NSF DMR-1611136 is kindly acknowledged. This research used resources at the High Flux Isotope Reactor, a DOE Office of Science User Facility operated by the Oak Ridge National Laboratory.

40. Structure and Dynamics of Ionic Block co-Polymer Melts: Computational Study

Dipak Aryal¹, Dvora Perahia¹, Gary S. Grest²

¹Department of Chemistry, Clemson University, Clemson, SC

²Sandia National Laboratories, Albuquerque, NM 87185

Abstract:

Tethering ionomer block into co-polymers enables engineering of polymeric systems designed to encompass transport while controlling structure. Here the structure and dynamics of symmetric pentablock copolymers melts are probed by fully atomistic molecular dynamics simulations. The center block consists of randomly sulfonated polystyrene with sulfonation fractions $f = 0$ to 0.55 tethered to a hydrogenated polyisoprene (PI), end capped with poly(*t*-butyl styrene). We find that the ionic blocks segregates into domains whose structure depends on the sulfonation fraction. The dynamics is constrained by these ionic domains.

Acknowledgements (as necessary):

NSF DMR-1611136; NERSC; Palmetto Cluster Clemson University; CINT Sandia National Laboratory; Kraton Polymers US, LLC

41. Solvent Tuning of structure of Ionic Block Copolymers in Solutions

Manjula Senanayake¹, Anuradhi Wickramasinghe¹, Sidath Wijesinghe¹, Supun S. Mohottalalage¹, Lilin He², Dvora Perahia¹

¹Department of Chemistry, Clemson University, Clemson, SC

²HFIR, Oak Ridge National Laboratory, Oak Ridge, TN, 37831

Abstract:

Ionic block copolymers find broad uses in transport-controlled applications. Tuning ionic clusters formed in solutions that can propagate into membranes offers a path to tailor performance. Here micellar structures of a symmetric ABCBA co-polymer resolved by SANS, as the polarity of the solvent is changed by adding propanol to cyclohexane, are reported. C is a randomly sulfonated polystyrene, B is hydrogenated polyisoprene, and A is poly(*t*-butyl styrene) using Small angle neutron scattering. We find that core-shell

aggregates dominate the solutions where their shape is controllable using the dielectric constant of the solvent.

Acknowledgements (as necessary):

NSF DMR-1611136 is kindly acknowledged.

This research used resources at the High Flux Isotope Reactor a DOE Office of Science User Facility operated by the Oak Ridge National Laboratory.

**42.Molecular Dynamics Simulation Study of Confined Conjugated Polymers:
Charge effects on stability.**

Sidath Wijesinghe¹, Dvora Perahia¹, Gary S. Grest²

¹Department of Chemistry, Clemson University, Clemson, SC

²Sandia National Laboratories, Albuquerque, NM 87185

Abstract:

Luminescent rigid polymers confined into nanoparticles, or polydots, are emerging as a promising tool for nano medicine. The constrained architecture of a rigid backbone trapped in nanodimensions results in photophysics that differs from that of spontaneously assembled rigid polymers. Here using fully atomistic molecular dynamics simulations we investigate the structure of dialkyl p-phenylene ethynylene confined into polydots. We find that the structure and thermal stability of polydots are sensitive to both the molecular weight n and to the carboxylation fraction f .

Acknowledgements (as necessary):

NSF CHE 1308298 and Palmetto Cluster Clemson University is kindly acknowledged

43.Confined Rigid Conjugated Polymers at Interface

Supun S. Mohottalalage¹, Dvora Perahia¹

¹Department of Chemistry, Clemson University, Clemson, SC

Abstract:

Confinement of conjugated polymers to spontaneously formed aggregates and nanoparticles is strongly affected by their rigid architecture and determines their photophysics through conformational constraints. Here X-ray of highly rigid dialkyl poly (para-phenylene ethynylene)s (PPEs) at an interface as the films are solvent annealed in presence of toluene vapor are compared with thermal annealing. With increasing

annealing time, larger aggregates are formed for both, dictated by the inherent polymer architecture. Solvent annealing affects selectively the backbone and the substituting size chains impact the internal packing at early exposure times. Solvents unlock the interfacial interactions, forming architecture dominated assemblies.

Acknowledgements (as necessary):

NSF CHE 1308298 is kindly acknowledged

44. Stimuli-Responsive Functional Materials

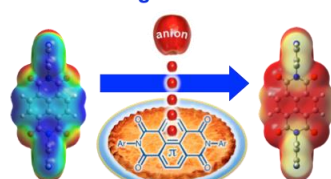
Sourav Saha¹, Krishnendu Maity¹, Amina Khatun¹, Monica Varela¹, Dillip Panda¹, Jonathan Gallup¹

¹Department of Chemistry, Clemson University, Clemson, SC

Abstract:

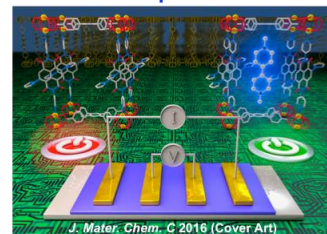
The skyrocketing energy demand and growing urgency to limit anthropogenic strains on our health and environment have created a need for smart materials that can generate energy from clean renewable sources, capture and detect pollutants and toxic chemicals, improve energy efficiency of modern electronic devices, deliver drugs in our bodies in a controlled fashion, and help sustain a myriad of other technological advances. To meet these demands, we are developing functional materials that can carry out these functions by interacting with various chemical and physical stimuli, such as guest molecules and ions, applied electric field, and light. This poster will highlight our efforts toward (i) detection and remedy of toxic anions using π -acidic anion receptors,¹⁻⁴ (ii) conversion of light into electricity using multi-chromophoric supramolecular solar cells,⁵ (iii) construction of electrically conducting metal-organic frameworks⁶ that can be used in chemiresistive sensors, capacitors, field-effect transistors, and rechargeable batteries, and (iv) development of controlled drug-delivery systems based on pH-responsive self-assembled vesicles.⁷

Discriminating Anions w/ π -Acids



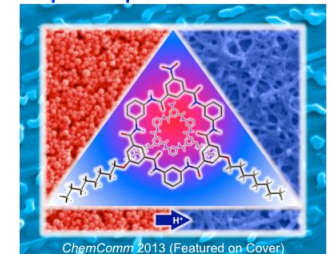
JACS (2010, 2011, 2012, 2015), CrystEngComm 2012, OrgBiomolChem 2013, ChemComm 2013

Stimuli-Responsive MOFs



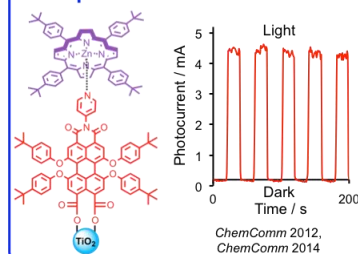
J. Mater. Chem. C 2016 (Cover Art)

pH-Responsive Vesicles



ChemComm 2013 (Featured on Cover)

Supramolecular Solar Cells



Photocurrent / mA
Dark Time / s

ChemComm 2012, ChemComm 2014

References (as necessary):

1. Saha, S. et al. *J. Am. Chem. Soc.* 2012, 134, 13679.
 2. Saha, S. et al. *Org. Biomol. Chem.* 2013, 11, 4797.
 3. Saha, S. et al. *Chem. Commun.* 2013, 49, 6629.
 4. Saha, S. et al. *J. Am. Chem. Soc.* 2015, 137, 2812.
 5. Saha, S. et al. *Chem. Commun.* 2014, 50, 5358.
 6. Saha, S. et al. *J. Mater. Chem. C* 2016, 4, 894.
 7. Saha et al. *Chem. Commun.* 2013, 49, 4601.
-

45. Convenient synthetic route to tetraarylphosphonium polyelectrolytes via palladium-catalyzed P–C coupling of aryl triflates and diphenylphosphine

Wang Wan¹, Rhett Smith¹

¹Department of Chemistry, Clemson University, Clemson, SC

Abstract:

A new polymerization method has been investigated, and a series of eight tetraarylphosphonium polyelectrolytes have been successfully synthesized by starting from diols. The palladium catalyst is effective in polymerizing with high degree of polymerization up to 65. All triflates polymers have good thermal stability in the range of 350-450 °C. The properties of tetraarylphosphonium polymers are investigated that strongly depend on the spacer between adjacent phosphonium sites as well as counterions. Success of this synthetic method provides a new way to use more commercial available precursors, so that more tetraarylphosphonium polymers can be prepared and their properties can be investigated systematically.

46. Functionalization of Carbon Nanoparticles and Defunctionalization

Fan Yang¹, Ya-Ping Sun¹

¹Department of Chemistry, Clemson University, Clemson, SC

Abstract:

Small carbon nanoparticles were functionalized by 3-ethoxypropylamine (EPA) for carbon dots of bright fluorescence emissions. The optical properties of the EPA-carbon dots share many features with those found in carbon dots of other surface functionalities. The EPA-carbon dots were defunctionalized by removing the EPA species from the carbon nanoparticles, along with spectroscopic characterizations on the samples of different degrees of defunctionalization. The outcomes confirm the critical role of surface functionalization to the superior optical properties of carbon dots. Results from systematic

measurements of fluorescence quantum yields at different excitation wavelengths for the EPA-carbon dots and their defunctionalized samples are presented.

47. Steady-State and Time-Resolved Fluorescence Studies on Interactions of Carbon "Quantum" Dots with Nitrotoluenes

Gregory Lecroy¹, Ya-Ping Sun¹

¹Department of Chemistry, Clemson University, Clemson, SC

Abstract:

Structurally compact and brightly fluorescent carbon dots were used in steady-state and time-resolved measurements of fluorescence quenching by 4-nitrotoluene and 2,4-dinitrotoluene, which are commonly used as signature compounds for nitroaromatic explosives. The observed fluorescence quenching behaviors reflecting mechanistically interactions of the photoexcited carbon dots with the quenchers in different concentration regions are understood as being primarily dynamic in nature, whose implications on the use of the carbon dots as fluorescence sensors for nitroaromatics and related explosives are discussed.

48. Preparation of TiO₂/C Nanocomposite Dots and Their Photophysical Properties

Yamin Liu¹, Ya-Ping Sun¹

Department of Chemistry and Laboratory for Emerging Materials and Technology,
Clemson University, Clemson, SC 29634

Abstract:

Carbon dots have generated much attention since the original discovery, and the research and development on carbon dots have become a rapidly expanding field. Beyond the currently widely carbon dots and their various applications, the coupling of nanoscale carbon with other functional materials for composite dots can provide opportunities for enhanced and/or unique applications that take advantage of the combined merits of multiple materials. In this reported work we prepared nanoscale TiO₂/C nanoparticles with polyethylene glycol as both the carbon source and surface functional groups. The TiO₂/C nanocomposite dots were characterized on their structures and compositions, along with a study of their optical properties.

49. Optical and Magnetic Properties of Polymer Functionalized Carbon/Iron Oxide Nanoparticles

Yin Hu¹, Ya-Ping Sun¹

¹Department of Chemistry, Clemson University, Clemson, SC

Abstract:

A facile thermal/microwave method was developed to synthesize Fe₃O₄-carbon magnetic-fluorescent nanoparticles. Ferric ammonium citrate was used as both iron and carbon sources, and polyethylenimine polymers as surface functional groups of the resulting nanoparticles. The structures of the nanoparticles were characterized, and their optical properties were studied by using a series of instrumental techniques including thermal gravimetric analysis, electron microscopy, FT-IR, UV/vis, and fluorescence spectroscopy. Potential applications of the nanoparticles and the broad applicability of the synthetic method are highlighted and discussed.

50. New Perfluoroalkoxyl Co- and Ter-polymers with Tetrafluoroethylene (TFE)

Cameron A. Parrish¹, Daniel A. Hercules¹, Anthony R. Scavuzzo¹, Emory G. Burns¹, Andrej V. Matsnev¹, Joseph S. Thrasher¹

¹Department of Chemistry, Clemson University, Clemson, SC

Abstract:

Tetrafluoroethylene is a well-known and widely used monomer in the fluoropolymer industry. We have previously reported, through our use of a combination of expired patent technologies by 3M¹ and DuPont², our ability to safely prepare and handle tetrafluoroethylene on the kilogram scale. I have thus undertaken a program aimed at the preparation and characterization of PFA resins with the goal of either incorporating termonomers or new perfluoroalkoxy trifluorovinyl ethers for more desirable properties. This includes the synthesis of aliphatic and olefinic trifluorovinyl-terminal olefins^{3,4} and the novel synthesis of a pentafluorosulfanyl substituted perfluoroalkyl vinyl ether⁵ and its copolymerization with tetrafluoroethylene

References:

1. Hals, L. J.; Reid, T. S.; Smith, G. H. "Process of Making Perfluoro Olefins," U.S. Patent 2,668,864, Feb. 9, 1954.
2. Van Bramer, D. J.; Shiflett, M. B.; Yokozeki, A. "Safe Handling of Tetrafluoroethylene," U.S. Patent 5,345,013, Sept. 6, 1994.
3. Dixon, S. Elimination Reactions of Fluoroolefins with Organolithium Compounds. J. Org. Chem. 1956, 21, 400-403.

4. Ohashi, M.; Kamura, R.; Doi, R.; Ogoshi, S. Preparation of Trifluorovinyl Compounds by Lithium Salt-promoted Monoalkylation of Tetrafluoroethylene. *Chem. Lett.* 2013, 42, 933-935.
 5. Du, L; Elliott, B; Echegoyen, L; DesMarteau, D. D. Synthesis of Pentafluorosulfanyl Trifluorovinyl Ether and Its Facile Rearrangement to Difluoro(pentafluoro-sulfanyl)acetyl Fluoride. *Angew. Chem. Int. Ed.* 2007, 46, 6626-6628.
-

51. New polyfluorinated polyethers and synthesis of their hypothetical epoxide intermediates

Chen Liu¹, Xiaolin Liu¹, Andrej V. Matsnev¹, Joseph S. Thrasher¹

Department of Chemistry, Clemson University, Advanced Materials Research
Laboratory, Anderson, SC 29625 USA

Abstract:

In this work, we reinvestigate the thermal decomposition of alkali metal hexafluoroisopropoxide $\{M[\text{OCH}(\text{CF}_3)_2]\}$ salts in sealed vessels, and after aqueous workup, polymeric materials were found. After some characterization by multinuclear NMR spectroscopy and MALDI-TOF mass spectrometry, we proposed a possible repeat unit for these polymers, namely $[(\text{CF}_3)\text{C}(\text{H})\text{CF}_2\text{O}]_n$, based in part on the spacing of 148 mass units between peaks in the MALDI mass spectra. Presumably, the polyfluorinated polyether is formed from the ring-opening polymerization of the intermediate epoxide $c\text{-}[(\text{CF}_3)\text{C}(\text{H})\text{CF}_2\text{O}]$. Furthermore, we will overview our efforts to directly prepare this epoxide starting from either 1,1,3,3,3- pentafluoropropene, $\text{CF}_3\text{CH}=\text{CF}_2$, or bromopentafluoroacetone, $\text{BrCF}_2\text{C}(\text{O})\text{CF}_3$.

References (as necessary):

1. Ligg, L. J.; Berry, A. D.; Purdy, A. P.; Ewing, K. J. Sodium fluoride thin films by chemical vapor deposition. *Thin Solid Films* 1992, 209, 9-16.
 2. Trischler, F. D.; Hollander, J. Highly Fluorinated Polymers. U.S. Patent 3,577,356 (assigned to Whittaker Corp., Los Angeles, CA), May 4, 1971.
 3. Bardin, V. V.; Frohn, H.-J. Perfluoroorganylxenonium(II) salts from reactions of XeF_2 or $[\text{FXe}][\text{SbF}_6]$ with selected perfluorinated alk-1-yn-1yl and alk-1-en-1-yltrifluoroborate salts in aHF. *J. Fluorine Chem.* 2012, 138, 28-33.
-

52.Synthesis and Chemistry of SF₅N- and SF₅CF₂- Containing Heterocycles

Steven P. Belina¹, Andrej V. Matsnev¹, Joseph S. Thrasher¹

¹Advanced Materials Research Laboratory, 91 Technology Drive, Anderson SC, 29625

Abstract:

The chemistry of the pentafluorosulfanyl functional group has been expanding over the past several years, due in part to the availability of pentafluorosulfanyl substituted benzene rings.¹ This presentation will focus on the synthesis and chemistry of SF₅N- and SF₅CF₂- containing compounds. Heterocycles featuring the SF₅N- moiety, substituted at the 2 position will be shown. These compounds were formed by the nucleophilic substitution of pentafluorosulfanyldichloroimine.² Subsequent reactions were performed with these heterocycles. In addition, several quinazolines containing the SF₅CF₂- functional group will be displayed.³ Finally, characterization of SF₅CF₂H will be shown, including mass spectral data as well as Raman spectroscopic data.

References (as necessary):

1. Umemoto, T.; Garrick, L.M.; Saito, N. *Beilstein J. Org. Chem.* 2012, 8, 461-471.
 2. Sitzmann, M.E.; Gilardi, R.D. *J. Fluorine Chem.* 1993, 63, 203-215.
 3. Matsnev, A.V.; Qing, S.-Y.; Stanton, M.A.; Berger, K.A.; Haufe, G.; Thrasher, J.S. *Org. Lett.* 2014, 16, 2402-2405.
-

53.Precise control of polyhydroxamate ligand topology for selective actinide coordination

Kirstin Sockwell¹, Modi Wetzler¹

¹Department of Chemistry, Clemson University, Clemson, SC

Abstract:

The hydroxamate-containing siderophore ferrichrome was used as basis for selective actinide ligand design. Two categories of polyhydroxamate ligands, cyclic peptoids and EDTA derivatives, were tuned toward selective metal binding through precise control of their geometries. Peptoids allow for a straightforward, modular synthesis of close ferrichrome analogs, which incorporate hydroxamate-containing residues into a cyclic backbone. Due to limited peptoid characterization methods, synthesis of several hydroxamate-EDTA derivatives was carried out to study the impact of sidechain length and rigidity on metal binding affinity. These findings will be applied toward the synthesis of ferrichrome-inspired cyclic peptoids designed for selective coordination of tetravalent actinides.

54. Trifluorotoluenesulfonyl as a New Nitrogen Protecting Group

Sibley, Megan;¹ North, Alexandra;² Harris, William;³ Bein, Omri;⁴ Wasilewski, Matthew;¹ McMillen, Colin;¹ and Wetzler, Modi.¹

¹Department of Chemistry, Clemson University, Clemson, SC

²Department of Genetics and Biochemistry, Clemson University, Clemson, SC 29634

³Department of Bioengineering, Clemson University, Clemson, SC 29634

⁴Daniel High School, Central, SC 29630

Abstract:

Benzenesulfonyls are one of the most common protecting groups for amines, but historically suffer from great difficulty in deprotection, particularly for aliphatic amines¹. Deprotection of the common toluenesulfonyl, for example, is often conducted in 70-96% sulfuric acid at temperatures ranging from 100-180 degrees over 1-7 days². Clearly such conditions are incompatible with many functional groups and therefore limit the applicability of this class of protecting groups. The great electron-withdrawing ability of the nitro group in the Fukuyama base, nitrobenzenesulfonyl (Ns), enables a new and facile mechanism of deprotection proceeding through a nucleophilic aromatic substitution³⁻⁴. Aromatic nitro groups, however, have a well-known susceptibility to photochemistry⁵, and Ns in particular often imparts poor solubility upon the amines it is used to protect. Therefore, we investigated the use of trifluorotoluenesulfonyl as a protecting group for aliphatic amines. The fluorine substituents provide a convenient NMR handle as well as potential solubility in a fluoruous solvent. We hereby demonstrate facile protection of a wide range of aliphatic amines with trifluorotoluenesulfonyl, subsequent monoalkylations of the protected amines, and deprotection of the trifluorotoluenesulfonyl.

References (as necessary):

1. Searles, S.; Nukina, S. *Chem Rev.* 1959, 1077-1103.
 2. Brady, O. L.; Day, J. N. E.; Reynolds, C. V. *J Chem Soc* 1929, 2264
 3. Fukuyama, T.; Jow, C. K.; Cheung, M. *Tet. Lett.* 1995, 36, 6373.
 4. Kan, T.; Fukuyama, T. *Chem. Commun.* 2004, 353.
 5. Ho, T.-I.; Chow, Y. L. John Wiley & Sons, Ltd, Chicester, UK 1996.
-

55. Facile synthesis of PEGylated vasopressin, lyspressin, and oxytocin analogs

Victoria Haberman¹, Jessica Cannon¹, Paris Hamilton¹, Modi Wetzler¹

¹Department of Chemistry, Clemson University, Clemson, SC

Abstract:

Vasopressin, its mammalian analog lyspressin, and oxytocin are cyclic peptide nonamers that are critical in governing social behavior and development. They play critical roles in pathologies ranging from autism spectrum disorders to neurodegenerative diseases to sexual function and mental health, yet are surprisingly not the subjects of significant pharmaceutical focus in the U.S. This oversight is likely due to their lack of oral bioavailability and vanishingly short lifetimes in plasma which would complicate dosing. Modification of proteins and peptides with poly-ethylene glycol (PEGylation) is a proven method to increase their lifetimes and prevent degradation, but site-specific post-synthetic PEGylation of peptides is cumbersome, requiring juggling of orthogonal protecting groups. Instead, by utilizing pre-PEGylated Fmoc-glutamine and lysine with 1-3 PEG chains each, we readily synthesized a small library of PEGylated vasopressin, lyspressin, and oxytocin analogs. The branched nature of the PEGylation represents a novel approach to peptide PEGylation and demonstrates a new approach to fine-tuning the pharmacokinetics of these potential drug candidates.

Acknowledgements:

Clemson University Research Foundation, Technology Maturation Fund: "PEGylated Peptides: From the Lab Bench to the Masses" (PI Wetzler)

References:

1. Holmes, C. L. *Critical Care*. 2003. 19-21.
 2. De Weid, D. *British Journal of Pharmacology*. 1972. 118.
 3. Lethagen, S. *European Journal of Anaesthesiology*. 1997. 1-9.
 4. Delmas, A. *Critical Care*. 2004. 212-219.
-

56. Non-Lethal Small Molecule Inhibition of the Starch Utilization System in Select *Bacteroides* Species

Anthony D. Santilli¹, Elizabeth M. Dawson¹, Kristi J. Whitehead², Daniel C. Whitehead¹

¹Department of Chemistry, Clemson University, Clemson, SC

²Clemson University Department of Biological Sciences, Clemson SC, 29634

Abstract:

Alterations to the human gut microbiota have been linked to various diseases and health complications.¹⁻³ Therapies that selectively modulate community members, via a non-

microbicidal mechanism, offer a tantalizing avenue for treatment of such disorders.⁴ Studies presented aimed to show that the starch utilization system (Sus) of *Bacteroides* species can be selectively inhibited with the use of the amylase inhibitor acarbose. Investigations found that acarbose can selectively disrupt this system in *Bacteroides thetaiotaomicron* and *Bacteroides fragilis*, suggesting potential therapeutic applications for regulation of the gut microbial community.

Acknowledgements:

We gratefully acknowledge the JDRF (Project 1-INO-2015-131-A-N), the Clemson University Creative Inquiry Program, and the Clemson University Departments of Chemistry and Biological Sciences for financial support. We also thank Prof. Eric Martens, Dr. Nicole Koropatkin, and Nick Pudlo (University of Michigan) for gifts of the bacterial strains, growth protocols, and many helpful discussions and suggestions.

References:

1. Round, J. L.; Mazmanian, S. K. *Nat. Rev. Immunol.* 2009, 9, 313-323.
 2. Ohata, A.; Usami, M. *Nutrition* 2005, 21, 838-847.
 3. Peng, L.; Li, Z.; Green, R. S.; Holzman, I. R.; Lin, J. J. *Nutr.* 2009, 139, 1619-1625.
 4. Ng, K. M.; Ferreyra, J. A.; Higginbottom, S. K.; Lynch, J. B.; Kashyap, P. C.; Gopinath, S.; Naidu, N.; Choudunry, B.; Weimer, B. C.; Monack, D. M.; Sonnenburg, J. L. *Nature* 2013, 502, 96-99.
-

57. Vicinal diamines synthesis using azodicarboxylates and electron-rich alkenes and alkynes

Chandima J. Narangoda¹, Daniel C. Whitehead¹, Emma M. Frank¹

¹Department of Chemistry, Clemson University, Clemson, SC

Abstract:

Vicinal diamines are a significant functionality that can be found in numerous pharmaceutical and drug directing candidates. For instance, the diamine motif can be seen in many leading clinical drugs such as penicillin and cephalosporins. Currently used methods for preparation of diamines fail to access a broad substrate scope. Our approach is to synthesize vicinal diamines from electron-rich alkenes and alkynes to access valuable vicinal diamine products. In this work, we have examined the reactivity of various azodicarboxylates as our main nitrogen source for the vicinal diamination of the electron-rich alkenes and alkynes.

Acknowledgements:

Daniel C. Whitehead, John A. Weller, Emma M. Frank, Colin McMillen, Clemson Chemistry Department

References:

1. Moriarty, R. M.; Prakash, I. The Reaction of Silyl Enol Ethers With Ethyl Azodicarboxylate and 4-Phenyl-1,2,4-Triazoline-3,5-Dione. *Synthetic Communications* 1985, 15 (7), 649-655.
 2. Yamashita, Y.; Ishitani, H.; Kobayashi, S. Silver-catalyzed asymmetric amination of silyl enol ethers. *Canadian Journal of Chemistry* 2000, 78 (6), 666-672.
 3. Sweis, R. F.; Schramm, M. P.; Kozmin, S. A. Silver-Catalyzed [2 + 2] Cycloadditions of Siloxy Alkynes. *Journal of the American Chemical Society* 2004, 126 (24), 7442-7443.
 4. Mamone, M.; Morvan, E.; Milcent, T.; Onger, S.; Crousse, B. Electrophilic Amination of Fluoroalkyl Groups on Azodicarboxylate Derivatives. *The Journal of Organic Chemistry* 2015, 80 (3), 1964-1971.
-

58. Evaluation of substituted ebselen and benzamidobenzoic acid peptide conjugates as potent trypanocidal agents

Heeren Gordhan¹; Stephen L. Patrick²; Maria I. Swasy¹; Jim Morris²; Daniel C. Whitehead¹

¹Department of Chemistry, Clemson University, Clemson, SC

²Department of Biochemistry and Genetics, Clemson University, Clemson, SC 29634

Abstract:

Human African Trypanosomiasis (HAT), commonly called African Sleeping Sickness, is caused by bloodstream form *Trypanosoma brucei*, also called trypanosomes, and has the potential to affect millions of people in sub-Saharan Africa.¹ Treatments have existed for the past fifty years, but they are characterized by severe adverse side-effects and poor efficacy prior to the crossing of the trypanosomes across the blood-brain barrier.² Trypanosomes generate energy via the metabolism of glucose. This process, called glycolysis, is catalyzed by enzymes called hexokinases. In trypanosomes, the two major hexokinases involved in glycolysis are TbHK1 and TbHK2. Through high throughput screenings (HTS), it was determined that both hexokinases can be targeted with small molecules to inhibit the first step in the glycolytic pathway of trypanosomes. Of the two hexokinases, TbHK1 has shown promise as a target for the development of trypanocidal therapeutics.

The first half of the presentation will report the syntheses of several derivatives of the potent TbHK1 inhibitors, Ebselen and Benzamidobenzoic Acid (BABA). Ebselen, or 2-phenyl-1, 2-benzisoselenazol-3(2*H*)-one, is a drug that is currently in trials for patients suffering from hearing loss or bipolar disorder that has also demonstrated potency against trypanosomes with an IC₅₀ of 0.05 ± 0.03 mM.¹ BABA is a novel therapeutic derivative that was revealed to be a hit through our HTS efforts. The final aim of these syntheses is coupling of the inhibitor derivatives to a peptidic scaffold via Solid Phase Peptide Synthesis (SPPS).³⁻⁵ The results of the bioassays conducted on these conjugates will be

described and presented with future aims at expanding the role of these inhibitors toward other tropical diseases.⁶

Acknowledgements:

Clemson University Department of Chemistry and Department of Biochemistry and Genetics for funding.

References:

1. Joice, A.C.; Harris, M.T.; Kahney, E.W.; Dodson, H.C.; Maselli, A.G.; Whitehead, D.C.; Morris, J.C. *International Journal for Parasitology: Drugs and Drug Resistance*. 2013, 3, 154-160.
 2. Sharlow, E.R.; Lyda, T.A.; Dodson, H.C.; Mustata, G.; Morris, M.T.; Leimgruber, S.S.; Lee, K.H.; Kashiwada, Y.; Close, D.; Lazo, J.S.; Morris, J.C. *PLoS Neglected Tropical Diseases*. 2010, 4 (4), e659.
 3. Park, C.; Burgess, K. J. *Comb. Chem.* 2001, 3, 257-266; Hoogerhout, P.; Stittelaar, K.J.; Brugghe, H.F.; Timmermans, J.A.M.; ten Hove, G.J.; Jiskoot, W.; Hoekman, J.H.G.; Roholl, P.J.M. *J. Peptide Res.* 1999, 54, 436-443.
 4. Zheng, Y.; Huo, Q.; Kele, P.; Andreopoulos, F.M.; Pham, S.M.; Leblanc, R.M. *Org. Lett.* 2001, 3 (21), 3277-3280.
 5. Li, D.; Elbert, D.L. *J. Peptide Res.* 2002, 60, 300-303.
 6. Gordhan, H.M.; Patrick, S.L.; Swasy, M.I.; Hackler, A.L.; Anayee, M.; Golden, J.E.; Morris, J.C.; Whitehead, D.C. *Bioorg. Med. Chem. Lett.* 2017, 27, 537-541.
-

59. Development and Applications of Iodoarene Peptide Catalysts for Asymmetric Organic Transformations

Maria I. Swasy¹, Jacob Garber¹, Daniel C. Whitehead¹

¹Department of Chemistry, Clemson University, Clemson, SC

Abstract:

Hypervalent iodine reagents (HIR) have been shown to serve as attractive alternatives to transition metals due to their mild reactivity, high selectivity, and commercial availability as oxidants and electrophiles. In particular, the emergence of catalytic and enantioselective processes with iodine (III) species is starting to make these compounds competitive with metal catalysis. One way to impart enantiocontrol is to attach the active iodoarene site to chiral information, such as a short peptide sequence consisting of 5 to 6 amino acids. Peptides can serve as an advantageous source of ligands and organocatalysts for a variety of organic transformations. Their modularity and facile preparation following standard Fmoc-Solid-Phase Peptide Synthesis techniques facilitates the synthesis and evaluation of numerous catalyst structures in a timely manner. The overall goal of this research is to merge the fields of hypervalent iodine chemistry with peptide-mediated asymmetric catalysis to facilitate the synthesis and

implementation of hypervalent aryl-iodo peptides for catalytic asymmetric organic transformations.

60. Guanidinium Sulfation Crystallization: Strategy for Enantiomeric Resolution and Identification

Beau R. Brummel¹, Kinsey G. Lee¹, Colin D. McMillen¹, Joseph W. Kolis¹,
Daniel C. Whitehead¹

¹Department of Chemistry, Clemson University, Clemson, SC

Abstract:

The presented research focuses on using a simple protocol to sulfate different functional groups followed by crystallizing the sulfated product with guanidinium. A guanidinium-sulfate network has been proven to be a sound strategy for material design, due to the highly directing hydrogen-bonding and ionic character of the guanidinium-sulfate network. In this work, we propose that one can take advantage of this network allowing for the crystallization and separation/identification of substrates that otherwise might be difficult to crystallize. The ultimate goal would be to employ this strategy for enantiomeric resolution and identification.