DEPARTMENT of CHEMISTRY

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ANNUAL MEETING
STUDENTS POSTER COMPETITION

Nov. 11th, 2016

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### Table of Content

**Analytical**

1. Casto - Using Diagonal Capillary Electrophoresis for Developing a Rapid and Selective Assay for Oxytocin
3. Lincoln - Retention in Porous Layer Pillar Array Planar Separation Platforms
5. Ogburn - Microalgae as Embedded Environmental Monitors
6. Schott - Supported Bicyclic Amidine Ionic Liquids as a Potential CO$_2$/N$_2$ Separation Medium

**Inorganic**

7. Powell - α-RuCl$_3$ an Excellent Model Compound for Testing Metal Chlorides as Anode Materials for Li-ion Batteries

**Organic**

8. Mattern-Schain - A Novel Liposomal Affinity Based Protein Profiling Technique

**Physical**

10. Dutra - In silico Studies of Silver-Doped Helium Droplets
11. Strange - Neutron Imaging Studies of In Situ Growth of Neutron and Gamma Detector Materials

**Polymer**

12. Anderson - Controlling Polyolefin Microstructure through Redox-Active Olefin Polymerization Catalysis
13. Hong & Xing - Tuning CO$_2$-philicity in Highly Permeable Polymeric Membranes for Gas Separation
14. Lu - All Acrylic Multigraft Copolymer Superelastomer
Using diagonal capillary electrophoresis for developing a rapid and selective assay for oxytocin

Laura D. Casto and Christopher A. Baker
Department of Chemistry, University of Tennessee, Knoxville, TN 37996

Abstract

Oxytocin, a neuropeptide found in the hypothalamus and pituitary gland, is a key hormone involved in development and expression of social bonding behavior. While dysregulation of oxytocin is hypothesized to play a role in autism spectrum disorders (ASD), studies to determine the nature of the dysregulation have been inconclusive. Therefore, tools for measuring oxytocin secretion profiles in real-time with high spatial and temporal resolution are needed to gain insight into the role of oxytocin dysregulation in ASD. This work aims to develop a rapid and selective assay for oxytocin using capillary electrophoresis on a microfluidic device. Capillary electrophoresis enables quick assays using small sample volumes. High selectivity is generally achieved using immunoassays which require expensive antibodies and fluorescent labels that could sterically hinder small molecules from forming an immunocomplex. We propose an alternative approach for selectively measuring oxytocin in complex biological samples based on diagonal capillary electrophoresis (DCE), a pseudo-two-dimensional electrophoresis method in which a reaction step is conducted following an initial CE separation and prior to an identical second stage of CE separation. DCE resolves species based on reaction-induced changes in electrophoretic mobility, therefore initial experiments demonstrate the ability to modify the migration time of oxytocin with a single thiol reduction reaction. Because oxytocin is cyclized by a disulfide bond, reduction of this bond creates a linearized peptide with significantly reduced electrophoretic mobility. This proof-of-concept is illustrated in Figure 1.

Figure 1. Modification of the migration time of oxytocin illustrates a proof-of-concept for realizing oxytocin assays using diagonal capillary electrophoresis.
Label Free Imaging of the Amphotericin B – Membrane Interaction using Transient Absorption Microscopy

Kevin Higgins, Tessa R. Calhoun
Department of Chemistry, University of Tennessee

Abstract

Despite being in clinical use for over five decades, Amphotericin B (AmB), has shown limited microbial resistance, while the resistance of other, less toxic alternatives is increasing. Even with its high toxicity, AmB has become a standard for treatment of systemic fungal infections. The mechanism of action in which AmB leads to cell death is still largely debated, as there have been three separate mechanisms proposed. Due to its low quantum yield, imaging of AmB with conventional fluorescent microscopies has been limited. In this study we use transient absorption microscopy (TAM) to image native AmB and its interaction with live yeast cells for the first time. Our preliminary results indicate that yeast cells are internalizing AmB in aggregate form in direct contradiction to all three mechanisms previously proposed. These results show the possibility for TAM to provide new insight into AmB’s mechanism of action while unveiling a possible new drug target for antifungal agents in the future.
Retention in Porous Layer Pillar Array
Planar Separation Platforms

Danielle R. Lincoln,† Nickolay V. Lavrik,† Ivan I. Kravchenko,‡ and Michael J. Sepaniak†
†Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996, United States
‡Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, United States

Abstract

This work presents the retention capabilities and surface area enhancement of highly ordered, high-aspect-ratio, open-platform, two-dimensional (2D) pillar arrays when coated with a thin layer of porous silicon oxide (PSO). Photolithographically prepared pillar arrays were coated with 50–250 nm of PSO via plasma-enhanced chemical vapor deposition and then functionalized with either octadecyltrichlorosilane or n-butyldimethylchlorosilane. Theoretical calculations indicate that a 50 nm layer of PSO increases the surface area of a pillar nearly 120-fold. Retention capabilities were tested by observing capillary-action-driven development under various conditions, as well as by running one-dimensional separations on varying thicknesses of PSO. Increasing the thickness of PSO on an array clearly resulted in greater retention of the analyte(s) in question in both experiments. In culmination, a two-dimensional separation of fluorescently derivatized amines was performed to further demonstrate the capabilities of these fabricated platforms.
Bioanalytical Sensor Development for Detection of Neurotransmitters in vivo and in biofluids

Amber Moody, Kelsey Webb, Peymon Baghernejad, Bhavya Sharma
University of Tennessee Knoxville, Department of Chemistry, 37996, Knoxville, TN, USA

Abstract

Many diseases are difficult to diagnose in the early stages where treatment would be most beneficial. Various neurological diseases can be detected through studying changes in neurotransmitter concentration. Generally, neurotransmitter concentration is probed in vivo by drilling holes in the skull. Neurotransmitters can also be detected in biofluids, however this involves copious amounts of sample processing and long measurement times. There is a need for the development of sensors for the detection of neurotransmitters in a selective, rapid, label-free, non-invasive manner with little to no sample processing. Our group focuses on the detection of biomarkers for neurological activity in non-invasively collected biofluids and through the skull.

Our approach is to apply surface enhanced Raman spectroscopy (SERS), which provides greatly enhanced Raman signals from very low concentration analytes that have been adsorbed to metal nanoparticles, for the detection of neurotransmitters. The metal nanoparticles create an oscillating electric field called the localized surface plasmon resonance (LSPR) when excited with a laser, which results in the enhancement of the weak Raman signal. SERS is surface selective, highly sensitive, rapid, label-free and requires little to no sample processing. By collecting Raman scattered light at a location that is spatially offset from the incident illumination point signal can be obtained from subsurface layers of turbid media. This technique, known as spatially offset Raman spectroscopy (SORS) is combined with SERS to develop the technique termed as surface enhanced spatially offset Raman spectroscopy (SEORS). SEORS can be used to obtain signal from metal nanoparticles coated with various neurotransmitters through the skull. We present results on the SERS detection of neurotransmitters in the micromolar (µM) to nanomolar (nM) concentration range in aqueous solution and artificial urine and SEORS measurements of neurotransmitters through a cat skull.
Microalgae as Embedded Environmental Monitors

Zachary L. Ogburn, Frank Vogt *
University of Tennessee, Knoxville

Abstract
In marine ecosystems, microalgae are important as they transform large quantities of inorganic compounds into biomass thereby impacting environmental chemistry. Of particular relevance is phytoplankton’s sequestration of atmospheric CO$_2$, a greenhouse gas, and nitrate, one cause of algae blooms. On the other hand, microalgae sensitively respond to changes in their chemical environment initiating an adaptation of their chemical composition. Analytical methodologies were developed in this study that utilize microalgae’s adaptation as a novel approach for in-situ environmental monitoring. Longterm applications of these novel methods are investigations of environmental impacts on phytoplankton’s sequestration performance and their nutritional value to higher organisms.

In order to analyze the chemical composition of live microalgae cells (Nannochloropsis oculata), FTIR-ATR spectroscopy was employed. From time-series of IR spectra, the formation of bio-sediment can be monitored and it has been shown that nutrient availability has a small but observable impact. Since bio-sediment formation is governed by several biological parameters such as cellular growth rate, size, buoyancy, etc., this enables studies of impacts of chemical environments on biomass formation and these physical parameters.

Moreover, spectroscopic signatures of these microalgae have been determined from cultures grown under 25 different CO$_2$ and NO$_3^-$ mixtures (200ppm-600ppm CO$_2$, 0.35mM-0.75mM NO$_3^-$). A novel, nonlinear modeling methodology, ‘Predictor Surfaces’, is being presented by means of which the nonlinear responses of the cells to their chemical environment could reliably be described. This approach has been utilized to measure concentrations of atmospheric CO$_2$ over the phytoplankton culture as well as dissolved nitrate in their growing environment. The achieved precision of concentration predictions were a few percent of the measurement range. Moreover, the Predictor Surface itself allows for chemical interpretations of cells’ responses to shifts in their chemical environment. This opens new approaches to study the link between concentration levels in an ecosystem and the biological consequences.

Novel Predictor Surfaces describe how the IR signature of e.g. the marine microalgae Nannochloropsis oculata changes as a function of their chemical environment. By means of these nonlinear calibration models, for instance atmospheric CO$_2$ can be quantified accurately.

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Supported Bicyclic Amidine Ionic Liquids as a Potential CO$_2$/N$_2$ Separation Medium

Jennifer A. Schott$^1$, Chi-Linh Do-Thanh$^1$, Shannon Mahurin$^2$, De-en Jiang$^3$, Sheng Dai$^{1,2}$

$^1$Department of Chemistry, University of Tennessee, Knoxville, TN 37996
$^2$Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831
$^3$Department of Chemistry, University of California, Riverside, CA 92521

Abstract

Due to rising CO$_2$ levels there is a need for more efficient, cost effective, and less energy intensive carbon capture techniques, all of which can be achieved via a passive membrane separation. While membranes allow for the selective separation of light gases through a solution diffusion process mediated by the solubility of each gas, it is necessary that the materials maintain high permeability for efficient throughput. Extensive analysis of traditional polymer membranes has shown an inherent tradeoff between a membrane’s permeability and selectivity, therefore the ideal membrane remains somewhat elusive. However, advances can be made by transitioning to supported ionic liquids (ILs) which allows new opportunities to tailor the anion and cation to optimize both solubility and diffusivity.

Our goal is to develop new ILs with greater permeability by increasing the free volume through decreased cation–anion interactions. To examine the relationship between free volume and permeability, a new series of ILs containing cations of bicyclic amidines 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) with varying alkyl chain substituents have been paired with two different anions tetracyanoborate and bis(trifluoromethanesulfonfyl)imide. Eight bicyclic ionic liquids have been examined for their physical and chemical properties, and of those, the five room temperature ionic liquids were tested as supported ionic liquid membranes (SILMs), two of which were found to exceed Robeson’s upper bound for CO$_2$/N$_2$ separations.

This research was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division.
α-RuCl₃, an excellent model compound for testing metal chlorides as anode materials for Li-ion batteries

Jonathan M. Powell, Sheng Dai, Gabriel M. Veith, Craig A. Bridges

a Department of Chemistry, University of Tennessee Knoxville, Knoxville, Tennessee
b Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831,
c Materials Science & Technology Division, Oak Ridge National Laboratory

Abstract

There continues to be a need for new battery chemistry that combines high capacity and reversible cycling, to enable advances in areas such as renewable energy and portable electronics. Very few reports of metal chlorides being used as electrodes for Li-ion batteries exist due primarily to solubility issues. Due to its highly insoluble nature, layered honeycomb α-RuCl₃ makes an excellent model compound to study the reactions of metal chlorides in Li-ion batteries. A novel synthesis technique for α-RuCl₃ was implemented using direct chlorination via HCl gas and the associated electrochemical properties of the powders formed from this approach are reported. Having a graphite like layered structure and being a metal chloride means that α-RuCl₃ can react with lithium ions by both intercalation and conversion type mechanisms. α-RuCl₃ shows a high specific capacity on its first discharge of 748.6 mAh g⁻¹ and still retains a reversible specific capacity of 291.6 mAh g⁻¹ at 100 cycles, which is over 75 % of its theoretical capacity of 387 mAh g⁻¹. It has been shown via ex situ XRD that this material undergoes both intercalation and conversion type reactions during the first lithiation cycle. RuCl₃ exhibits the best reversible cycling, with good reversible specific capacity, of any reported bulk metal chloride electrode material.
A novel liposomal affinity based protein profiling technique

Samuel Mattern-Schain, Adam Carr and Michael Best
University of Tennessee, Knoxville

Abstract

The recruitment and activation of membrane binding proteins by phospholipids is a fundamental aspect of cellular behavior. Signaling lipids such as diacylglycerol, phosphatidic acid and phosphatidylserine drive these interactions and thus are the keystones of cellular activities including oncogenesis, tumor suppression and apoptosis. Understanding protein-lipid interactions and identifying new protein binding partners for lipids implicated in important cellular phenomena is a crucial part of drug development. Here, we present a biomimetic assay for characterizing these interactions. Using liposomes and synthetic lipid probes we are able to assess variations in protein recruitment to membranes based on the presence of particular lipids. In this way, we may identify new protein binding partners for signaling lipids as well as characterize the binding affinities of proteins of interest. Furthermore, this assay may be used in nanodrug optimization by tailoring membrane composition to maximize affinities for target proteomes and also selecting individual protein targets to increase the selectivity of liposomal nanocarriers. We confirmed efficacy and repeatability by observing predictable labeling increases using known protein-lipid interactions and have shown that our liposomal probes label membrane proteins exclusively over cytosolic proteins. Lipid-specific probes have been synthesized and tested as well as generic lipid probes which are less discriminate and allow for the study of virtually any combination of natural lipids.

Figure 1: A liposome with a small percentage of generic probe in the membrane. The probe has both a photoactivatable cross linker (fish hook) to covalently bind membrane-bound proteins and a click tail for enrichment. The chase lipid in this example is phosphatidylserine (PS, red dots).
Effect of Electrode Surface Structure on Electron Transport in Molecular Junctions: A Computational Study

Andrea N. Becker and Sharani Roy
Department of Chemistry, University of Tennessee, Knoxville, TN 37996

Abstract

Molecular junctions are the smallest form of nanoelectronic circuits, consisting of one molecule bound between two electrodes. The properties of these junctions have been of great interest to the scientific community for decades; however, there is still much unknown about the transport of electrons through the junction, and how it is affected by various electronic and geometric properties of the bridging molecule. Our research uses density functional theory to computationally examine the effect of binding site and terminal group on the binding properties, electronic structure, ground-state geometry, and resulting conductance of the molecular junction. The electrode tips are modeled using the (111) face of a gold crystal, and the conducting molecules of interest consist of a benzene ring with either thiol or amine terminal groups (i.e., benzenedithiol or benzenediamine). The Simmons’ model has been applied to these systems to gather preliminary conductance values, while more rigorous calculations are currently being performed using non-equilibrium Green’s functions in conjunction with density functional theory (NEGF-DFT) to yield transmission spectra. Future studies will include detailed investigations into how nuclear dynamics of the junction affect its conductance.
In Silico Studies of Silver-Doped Helium Droplets

Matthew Dutra, R. J. Hinde

University of Tennessee

Abstract

The world of quantum fluids has garnered increased attention over the past few decades, particularly with respect to condensed-phase helium systems. Much of this interest is due to advances in helium droplet spectroscopies, in which atoms or molecules under scrutiny are collected by helium droplets and analyzed via helium depletion. Because of the ultracold boiling point of helium, changes in internal energy of the embedded system cause evaporation of helium atoms from the droplets, which then returns information on the probed excitation. However, a more complete understanding of the nature of the superfluid helium droplets used in such techniques is required. With this in mind, we utilize a theoretical approach to calculate energetic properties of both homogeneous and Ag-doped superfluid helium droplets. Our calculations employ a density functional scheme paired with imaginary time propagation to self-consistently calculate the chemical potentials and per-atom energies of a variety of droplet sizes. Structural information is also gained from the associated density profiles, again determined self-consistently. In the case of silver-doped droplets, we are able to benchmark our density functional results against quantum Monte Carlo data available in the literature. Also of interest to theorists is the mathematical description of the helium-helium interactions; thus, we explore and assess multiple popular helium functionals. Current endeavors focus on developing a computationally efficient method for modelling droplets with lower-symmetry dopants using the best available helium functionals.

Figure: Helium density profile of a 100 atom droplet in the presence of a silver atom. The red and green peaks indicate the first and second solvation shells, respectively.
Neutron Imaging Studies of In Situ Growth of Neutron and Gamma Detector Materials

Nicholas Strange, Christopher Crain, J.Z. Larese

University of Tennessee

Abstract

The studies described here are aimed at addressing the critical need to develop dependable crystal growth techniques of solid-state materials used as radiation detectors for both national security and medical applications. We present the results of our pulsed neutron radiographic and resonant imaging studies aimed at optimizing the synthesis of CZT (CdZnTe), CLYC (CsLiYCl), and CHC (CsHfCl). Our goal is to identify the conditions that favor the production of defect free materials in large quantity. The likely outcome of these studies is to identify: (1) the thermodynamic and convective conditions that exist at the furnace wall, within the melt and at the crystal melt interface, (2) the nature and creation of solute segregation, voids, and crystal dislocation networks (3) the variations in crystal stoichiometry and (4) the formation of multi-crystalline domains.

Using a pulsed neutron beam and a time/energy resolved detection method we employ the penetrating power and wavelength dependence of neutron absorption and resonances (of Cd, Cs, & Hf) to perform our measurements during crystal growth in situ (i.e. with the materials contained in quartz ampoules inside industrial scale furnace in the liquid state and at the liquid solid interface). Furthermore, solid boules can be examined (nondestructively and without cutting or segmenting) either inside the furnace or free standing. Another objective of these studies include: the validation/improvement of the modeling studies of CLYC, CHC and CZT growth behavior, the development of new/improved furnace design and the identification of optimum growth techniques that enable the production of large boules of defect free, single crystalline materials in a timely and cost effective manner. We provide our recent results including: a description of the experiential setup at LANSCE, sample time/temperature resolved neutron radiographic images and synchrotron based IR images of CZT flat solid plates. Selected results of MCNP (Monte Carlo) calculations that illustrate the neutron absorption and scattering cross section variation with energy and sample isotopic composition to understand the contrast contribution of the various elemental components of the materials will also be included.
Controlling Polyolefin Microstructure through Redox-Active Olefin Polymerization Catalysis

W. Curtis Anderson Jr., Jesse Kern, Sharani Roy, and Brian K. Long*
Department of Chemistry, University of Tennessee, Knoxville, TN 37996, United States

Abstract

The ability to control catalytic activity, selectivity, and reactivity via in situ changes in a catalyst’s oxidation-state represents a promising tool for enhanced polymerization control. Herein, we will provide fundamental evidence that olefin polymerization catalysts bearing redox-active ligands may be used to effectively modulate polymer microstructure via simple oscillations in their electronic structure facilitated by ligand-based redox chemistry. Furthermore, we will demonstrate that comonomer incorporation percentages can also be tailored via these redox events. Detailed GPC and NMR analyses are provided to support these changes in both branching density and branching identity as a function of ligand oxidation-state. EPR analyses and computational studies are included as evidence for the identity of the reduced catalytic species.
Tuning CO$_2$-philicity in highly permeable polymeric membranes for gas separation

Tao Hong$^1$, Kunyue Xing$^1$, Shannon Mahurin$^2$, De-en Jiang$^2$, Brian Long$^1$, Jimmy Mays$^{1,2}$, Alexei Sokolov$^{1,2}$, Tomonori Saito$^2$

$^1$Department of Chemistry, University of Tennessee, Knoxville, Tennessee, United States, $^2$Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee

Abstract

A climate change caused by a greenhouse effect is one of the most challenging problems we face today, and the development of high performance materials for CO$_2$ separation and capture will significantly contribute to solution of the problem. Passive membranes present one of the promising and energy efficient solutions. However, materials with high CO$_2$ permeability and good gas selectivity are needed for use in these membranes, and no one current materials can meet these requirements. Traditional gas separation membranes work on size-sieving principles. This approach, however, is not efficient for separation of CO$_2$, because this molecule has size comparable to other molecules in the flue gas, e.g. N$_2$ and O$_2$. Our work is focused on a different approach, tuning of solubility selectivity. It is based on the incorporation of CO$_2$-philic groups, e.g. amidoxime (AO) and polyethylene oxide (PEO), into high permeable polymer matrix, e.g. polydimethylsiloxane (PDMS) and poly (1-trimethylsilyl-1-propyne) (PTMSP), to achieve a better gas solubility selectivity in order to increase the overall gas separation performance. Fine-tuning of the degree of functionalization in our membrane with CO$_2$-philic groups resulted in a controlled gas separation performance, and some representative membranes demonstrated performance above the Robeson upper bound line (Figure 1). The latter is considered as an empirical limit of the current technologies. A variety of characterization techniques, e.g. gas sorption, rheology, quartz crystal microbalance and broadband dielectric spectroscopy measurements are performed to elucidate the key parameters necessary for achieving their excellent performance. Moreover, the performed theoretical calculation of CO$_2$-polymer interactions provides a guidance to further improvements of the polymeric membranes, as well as ways of farther membranes

Figure 1. Representative data of developed polymeric membranes in Robeson plot.
All Acrylic Multigraft Copolymer Superelastomer

Wei Lu1, Andrew Goodwin1, Yangyang Wang2, Xinyi Lu1, Panchao Yin2, Kunlun Hong2, Nam-Goo Kang1, Jimmy Mays1

Department of Chemistry, University of Tennessee, Knoxville, TN 37996, United States
Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States

Abstract

Thermoplastic elastomers (TPEs) have been widely studied in academia and industry because of their recyclability, good processability, low production cost and unique performance. Compared to the widely used styrenic TPEs, all acrylic TPEs have potential advantages including exceptional chemical, heat, oxygen and UV resistance, optical transparence, and oil resistance. However, the high entanglement molecular weight (Mₑ) of polyacrylates lead to “disappointing” mechanical performance as compared to styrenic TPEs. In this study, single-tailed and double-tailed graft copolymers composed of poly(methyl methacrylate) (PMMA) and poly(n-butyl acrylate) (PnBA) were synthesized through a grafting-through methodology. (Figure 1) The single-tailed and double-tailed macromonomers of poly(methyl methacrylate) (PMMA) were synthesized with the initiator system of either N-isopropyl-4-vinylbenzylamide (PVBA)/sec-BuLi or 3,5-bis(isopropylaminomethyl)styrene/sec-BuLi in THF at -78 °C via living anionic polymerization using glass-blowing and high vacuum techniques. RAFT polymerization was carried out to copolymerize the macromonomers with n-butyl acrylate to make multigraft copolymers. The combination of multigraft architecture and high molecular weight endows the resulting materials with strong microphase separation behavior, which was demonstrated by atomic-force microscopy (AFM) and small angle X-ray scattering (SAXS). Surprisingly, the multigraft copolymers exhibit extremely high strain at break as compared to not only conventional acrylic triblock copolymers but also styrenic TPEs. This innovative synthetic approach greatly expands the potential application range of all-acrylic TPEs.

![Scheme 1. Synthetic routes on all acrylic multigraft copolymer superelastomers](image-url)