

Department of Chemistry & Biochemistry

FIU Sensing, Monitoring and Detection NSF-REU Program

2016 REU Research Symposium Book of Abstracts



REU Participants:

Maria Ferrer
Alvio Dominguez
Carlos Valenzuela
Joennis Rosado
Rebecca Marshall
Rachel Colvin
Suzanne Wilson
Genique Nicholas
Eugenia Vasileiadou
Zachary Gregg
Stephanie Spence
Ramon Gutierrez
Aurora Burkus-Matesevac

Paine College Participants:

Sierra Harris
Kai Chambers
Bemsi Nabi Ajoff

The REU participants were supported by the NSF-REU Site grant No: CHE-1156886 and CHE-1560375 to FIU (PI: K. Kavallieratos)

The Paine College participants were supported by a Savannah River Nuclear Solutions LLC award to FIU No: SRNS:0000217393 (PI: K. Kavallieratos)

The REU program and the Department of Chemistry and Biochemistry kindly acknowledge the generous support of FIU-University Graduate School (Dean Lakshmi Reddi) and the SISH/College of Arts & Sciences (Deans Michael Heithaus and Walter Van Hamme).

Study of Self-assembly behavior of flexible Poly(p-phenylene butadiynylene) polymer in Hyaluronic Acid

Maria-Jose Ferrer^{1,2}, Prakash Manandhar¹ and Joong Ho Moon^{1,*}

¹Department of Chemistry and Biochemistry, Florida International University, Miami, FL 33155, USA

²Department of Chemistry, University of Hartford, West Hartford, CT 06117, USA

Positively charged, poly(p-phenylene butadiynylenes) (PPBs) were synthesized by varying the amount of flexible non-conjugated linker in polymer backbone to modulate aggregation structures of PPBs upon polyionic complexation with hyaluronic acid. Modulated aggregation of PPBs exhibits distinctive absorption and emission profiles, which the analysis of the profiling can lead to developing new sensory materials for detection of glycosaminoglycan in biological fluids. In this paper, synthesis of PPB containing various amount of flexible linker and photophysical characterization of PPB/HA complexes are described. The structure-property relationship obtained from the study will lead to rational design of highly sensitive sensory materials for GAG detection.

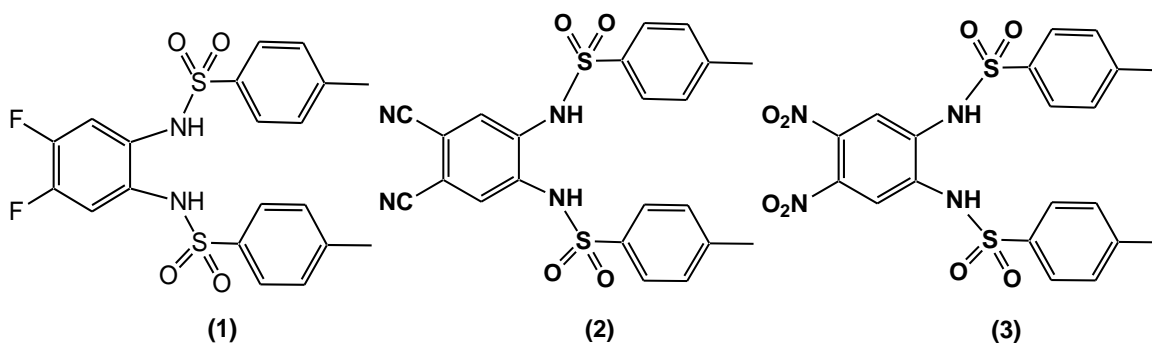
Disulfonamide Ligands for selective sensing of Pb(II) and other toxic metals

Alvio J. Dominguez^{1,2}, Ingrid Lehman-Andino¹ and Konstantinos Kavallieratos^{1*}

¹Florida International University, Department of Chemistry and Biochemistry, 11200 SW 8th St., Miami, Florida 33199.

²Miami Dade College, Wolfson Campus, NE 2nd Ave, Miami, FL 33132.

Lead contamination is a serious public health issue in the US and worldwide. Pb(II) which is the most environmentally mobile form of lead can be sensed by selective extraction and complexation. This newly introduced technique can address the challenging problem of toxic metal detection. Thus, it is important to design selective sensors and extractants that can complex and extract Pb(II) and other toxic metal species from water into an organic phase, providing an opportunity for selective extraction-based sensing via a change in fluorescent or UV-Vis spectroscopic properties. This project aims to study the Pb(II) coordination, extraction, and sensing properties of new disulfonamide ion-exchangers such as *N,N*-(4,5-difluoro-1,2-phenylene)bis(4-methylbenzenesulfonamide) (1), and *N,N'*-(4,5-dicyano-1,2-phenylene)bis(4-methylbenzenesulfonamide) (2). These ligands were synthesized with yields of 68% and 10%, respectively, and characterized by ¹H-NMR, UV-Vis, and FT-IR spectroscopic methods. Attempts to extract Pb(II) from water into dichloromethane with 1 using UV-analysis show changes in the UV-Vis spectra, in the 300-320 nm range, indicating complexation between 1 and Pb(II) after deprotonation of ligand with trimethylamine. Extraction-based sensing experiments using different concentrations of Ca(II), Zn(II) and Pb(II) with 1 show no optical response, in the visible light, with or without base. Thus extraction-based optical sensing with 1 is not as successful as the previously studied ligand *N,N*-(4,5-dinitro-1,2-phenylene)bis(4-methylbenzenesulfonamide) (3).



Screening for Novel Leads Towards Antibacterial Compounds Targeting Topoisomerase I

Carlos A. Valenzuela^{1,2}, Thirunavukkarasu Annamalai¹, Rachid Skouta², Yukching Tse-Dinh¹

¹Department of Chemistry and Biochemistry, Florida International University, Miami, FL, 33199

²Department of Chemistry, Border Biochemical Research Center, University of Texas at El Paso, El Paso, TX, 79968, USA

Bacterial topoisomerase I (topo I) represents a potential therapeutic target for a novel class of antibacterial inhibitors. Topoisomerases are essential for the regulation of DNA supercoiling and overcoming topological barriers that are encountered during vital cellular processes. Topo I regulates the supercoiling of the DNA helix through a single strand cleavage and religation. Natural products (crude extracts from dessert flora), as well as synthetic small molecules (arylakylamine, thiophenes) were screened in order to identify topoisomerase I inhibitors, as part of a larger effort to identify new antibacterial compounds. Antibacterial screening was performed on *E. coli* strains, ASI7 and ASI7 tolc (decreased efflux pump) and *M. smegmatis*, containing recombinant plasmids capable of expressing *E. coli* topoisomerase I or *M. tuberculosis* topoisomerase. Chosen hit compounds were then assayed for enzymatic inhibitory activity. Out of the 101 plant extracts (PE) and 89 small molecules (SM), 19 PE and 10 SM showed antibacterial activity in the primary screening. Enzyme-based assays show that at least 2 SM and 9 PE have supercoiled DNA relaxation inhibition activity against Mtb topoisomerase I. These compounds will be further studied in similar assays to determine bactericidal activity. Promising leads will be studied in mammalian cell cytotoxicity assays to determine their specificity towards prokaryotic topoisomerases.

Assessment of Hydroxyl Radicals Production During Ultrasonic Irradiation for Potential Treatment of Diphenhydramine Pollution

Joénisse M. Rosado^{1,2}, Danni Cui¹ and Kevin O'Shea^{1,*}

¹Department of Chemistry and Biochemistry Florida International University, 11200 SW 8thST, Miami, FL, 33199.

²Department of Natural Science Universidad del Sagrado Corazón, CllSagrado Corazón De Jesús, San Juan, Puerto Rico, 00912

Recent studies have shown that drinking water contains up to 0.1 µg/L of prescribed drugs and are a health risk to humans. Typical water purification methods are often not effective or too costly to remove pharmaceuticals. Ultrasonic irradiation is an attractive alternative to purify contaminated water since it can be applied to a range of water qualities and it does not require the addition chemicals or adsorbents. Diphenhydramine (DPH), the active ingredient Benadryl and other antihistamines, has been found in drinking waters. The presence of DPH even at low concentrations can be a threat to environmental and human health. Ultrasonic induced degradation is the result direct pyrolysis and hydroxyl radical induced oxidation. Our preliminary results demonstrate DPH is readily degraded by hydroxyl radicals during the ultrasound process. Within this mind, two hydroxyl radical trapping agents were used in an attempt to quantitate the amount of hydroxyl radicals produced during ultrasonic irradiation. The trapping agents produce specific hydroxyl radical products that can be readily detected using fluorescence techniques. Specifically, coumarin, a hydrophobic compound, reacts with the hydroxyl radicals to produce 7-hydroxycoumarin. Terephthalic acid, a hydrophilic compound, forms the fluorophore 2-hydroxyterephthalic acid upon reaction with hydroxyl radical. Ongoing competition experiments of DPH and each of the hydroxyl traps over a range of concentrations will provide insight about the localization of hydroxyl radical generation during ultrasonic treatment. The rates of hydroxyl radical generation determined herein will be useful for predicting treatment times for hydrophobic and hydrophilic pollutants. Our results show the rapid degradation of DPH by ultrasound is quite effective and suggest it can be used for remediation of a variety of polluted water sources.

A Study of the Lipid Profile of *Escherichia coli* Strains in Response to Antibiotic Stress

C. Ray Marshall^{1,2}, Alyssa Garabedian¹ and Francisco Fernandez-Lima¹

¹Department of Chemistry, Florida International University, Miami, FL

²Department of Chemistry, Fort Lewis College, Durango, CO

In the present work, a new method for discovery and targeted monitoring of lipid profiles in three strains of *E. coli* was developed based on LC-ESI-TIMS-MS. Changes in the lipid profiles were studied for a wild type, MG1655; and the isogenic pair of DPB635 and DPB636 as a function of the antibiotic (norfloxacin) treatment. Two liquid-liquid extraction methods were evaluated. Preliminary results showed that LC-TIMS-MS platform is capable of detecting a large number of lipid species in a single analysis and that separation of lipid class identification can be performed based on accurate mass and mobility measurements. Ongoing efforts are focus on the study of lipid expression levels as a function of the antibiotic treatment.

Making Predictions and Constructing Explanations: An investigation into introductory chemistry students' understanding of structure-property relationships

Rachel A. Colvin^{1,2} and Sonia M. Underwood^{2,3}

¹Department of Chemistry, Adelphi University, Garden City, NY USA

²Department of Chemistry & Biochemistry, Florida International University, Miami, FL USA

³STEM Transformation Institute, Florida International University, Miami, FL USA

The relationship between a chemical structure and its physical and chemical properties is a core idea for chemistry. Previous studies have shown that students have much difficulty with the relationship between structure and properties particularly due to the multiple pieces of information that must be concatenated (e.g. drawing a Lewis structure, determining molecular shape, and identifying molecular polarity). The goal of this research is to determine (i) when do students self-report their ability to predict structure-property relationships and (ii) how do students predict and explain structure-property relationships for a familiar boiling point ranking task. Second-semester general chemistry students were administered an assessment online using beSocratic, a free-form structure drawing program which allows students to submit written and drawn responses. The first half of the assessment consisted of multiple answer questions that examined students' self-report on what information could be predicted using a Lewis structure. The second half of the assessment consisted of open-ended questions (both text and drawings) aimed to scaffold student explanations of the relationship between a chemical structure and its boiling point, in terms of strength of intermolecular forces. The results from this study will be presented.

Development of a Supercoiled DNA Molecule into a Ultrasensitive Nuclease Sensor

Suzanne F. Wilson^{1,2} and Fenfei Leng^{1,*}

¹Department of Chemistry and Biochemistry, Florida International University, 11200 SW 8th Street, Miami, Florida 33199.

²Department of Chemistry, Biochemistry, and Physics, Florida Southern College, 111 Lake Hollingsworth Dr, Lakeland, FL 33801

Nucleases are a type of enzyme that cleaves phosphodiester bonds of nucleic acids. They are associated with various metabolic reactions and are vital in programmed cell death. Due to their association with metabolic reactions, nuclease imbalances are associated with cancer and autoimmune diseases. Their detection is significant as nuclease can be used as disease markers and cause contamination issues in laboratory settings. In this study, a supercoiled DNA molecule is developed and tested against different nuclease with the end objective to produce a more sensitive and versatile nuclease sensor. The supercoil DNA molecule, pABI_FL918, was produced via a four-day method that included cleaving, annealing, ligating, and purifying. The molecule was produced from a fluorescent component, FL918, and a plasmid isolated from *E. coli* cells that contains the specific nuclease cleavage site of Nt.Bbvcl. The supercoiled DNA molecule was tested against four types of nucleases to see if detection could occur. These nucleases are as followed: Nt. Bbvcl, DNase I, Mung. bean, T2 endo. The limit was estimated through a titration method using DNase I. It was concluded that pABI_FL918 could detect the four types of nucleases. When testing against DNase I, the detection at the lower levels became less quantifiable as the trend no longer represented a best fit line. However, the fluorescence signal was distinguishable from no nuclease reaction and rivaled the limit of DNase Alert (0.002 U/mL).

Bioavailability of Methylmercury in Rice Cereal and Fish

Genique Nicholas^{1,2} and Yong Cai^{1,*}

¹Department of Chemistry and Biochemistry, Florida International University, 11200 SW 8th Street, Miami, Florida 33199.

²Department of Chemistry, University of the Virgin Islands

Methylmercury (MeHg) is known as a contaminant worldwide and a potent neurotoxin that is harmful to the neurodevelopment in infants. MeHg is formed from inorganic mercury by the action of microbes that live in aquatic systems and then bioaccumulated through the food chain. Traditionally, consumption of fish or fish based food was considered as the major pathway of MeHg exposure to human. A lot of effort has been made to study the concentration, bioaccessibility, and bioavailability of MeHg in fish. However, the recent finding that rice could also accumulate MeHg in its grain prompted our interest in studying the MeHg level and bioavailability in rice and rice product due to the high consumption of rice product around the world, especially for human infants. Infants do not directly consume fish or rice, however, could still expose to MeHg due to the consumption of breast milk and rice or fish based baby food such as rice cereal. There is a very limited information available regarding MeHg in rice cereal and the potential exposure of infants to MeHg. Therefore, the main objectives for this research are to: 1) determine the amount of MeHg in rice cereals, 2) estimate the bioaccessibility of MeHg in rice cereals, and 3) compare the bioaccessibility of MeHg in rice cereal and fish. To achieve these goals, experiments have been designed and conducted. Twelve commercially available rice samples were purchased from a market and tested. Preliminary experiments have shown that rice cereals do contain considerable level of MeHg. To evaluate the bioaccessibility of MeHg in rice cereals, in vitro gastrointestinal digestion procedure was used to simulate the digestion process followed by acidic KBr extraction and analysis using cold-vapor atomic fluorescence spectrometry. The MeHg concentrations were recorded in ng/g. The results showed that the MeHg concentrations were lower than that of recorded concentrations for fish (ranging from 14.3±13.9 ng/g to 527.4±84.1 ng/g in sea food samples). The results show that out of the samples we tested the average MeHg concentration was 5.6±4.19 ng/g, and the average bioaccessibility was approximately 50 %. Considering the great amounts of rice cereal consumed by infants, the MeHg intake through rice cereal may post potential health risk to infants. MeHg bioavailability in the rice cereal samples and also fish samples will be conducted in order to compare the bioavailability between MeHg in rice and in fish.

Survey of the Coordination Chemistry of N,N-Diphenyl-1,2-Benzenedisulfonamide: Synthesis, Spectroscopic Characterization and Structural Studies

Eugenia Vasileiadou^{1,2}, Logesh Mathivathanan¹, Konstantinos Kavallieratos¹ and Raphael G. Raptis^{1,*}

¹Department of Chemistry and Biochemistry, Florida International University, 11200 SW 8th Street, Miami, Florida 33199

²Department of Chemistry, Aristotle University of Thessaloniki, University Campus, Thessaloniki, Greece 54124.

We are investigating the coordination plasticity of N,N-diphenyl-1,2-benzenedisulfonamide with transition metals and f series metals in order to establish the complexation mode(s) of this ligand. Two new complexes have been structurally characterized by single crystal X-ray diffraction: [Cu(1,2-C₆H₄(NSO₂C₇H₉)₂)(C₁₀H₈N₂)] and [Zn(1,2-C₆H₄(NSO₂C₇H₉)₂)(C₁₀H₈N₂)]. The compounds have also been fully characterized by 1H NMR, FT-IR, UV-Vis absorption and fluorescence spectroscopic methods. New complexes of Co²⁺, Ni²⁺, Mn²⁺, Pd²⁺, Cr²⁺ have been prepared and their spectroscopic and structural characterization is in progress. X-ray characterization shows the formation of ternary metal-sulfonamido-bipy complexes with distorted tetrahedral geometry, which have been formed through the sulfonamide nitrogen atoms of the coordination reagent, for both Cu²⁺ and Zn²⁺ ions. In an effort to evaluate potential applications in the treatment of radioactive High Level Waste (HLW), complexation studies of lanthanide ions are being carried out, as well.

The role of porphyrins in chemical education: Aesthetically appealing and informative experiments

Zachary J. Gregg^{1,2}, Jonathan C. K. Quirke^{1,3} and J. Martin E. Quirke^{1,*}

¹Florida International University, Department of Chemistry and Biochemistry, Miami, Florida 33199

²University of Tampa, Department of Chemistry, Biochemistry, and Physics, Tampa, Florida 33606

³Oberlin College, Department of Chemistry and Biochemistry, Oberlin, OH 44074

Porphyrins are large aromatic macrocycles that are brilliantly colored. These factors coupled with their well-known importance in biological processes, such as oxygen and electron transport, make the porphyrins potentially valuable for teaching concepts in core Organic Chemistry courses. Surprisingly, this pedagogical potential has been largely untapped. Herein we present several demonstrations that illustrate the value of this pedagogical tool. Specifically the porphyrins are used to demonstrate the existence of antibonding orbitals by discussion of their highly fluorescent natures. In addition, the metallation of porphyrins is used to illustrate both Brønsted acid-base and Lewis acid-base reactions in a one-pot reaction. The visual impact of the experiment was maximized by the use of a divided U tube. Electrophilic aromatic substitution reactions are illustrated by nitration of octaethylporphyrin. The existence of π cation radicals is illustrated by means of another nitration process involving the reaction of Mg(II)OEP with iodine, followed by NaNO₂. The pedagogical potential use of porphyrins in microfluidic experiments is currently being explored. Finally, the relationship between fluorescence and occupancy of d orbitals is explored.

Caffeine Analysis of Wastewater Using Online SPE-HPLC High Resolution Mass Spectrometry

Stephanie Spence^{1,2} and Piero Gardinali^{1,*}

¹Department of Chemistry and Biochemistry, Florida International University, 11200 SW 8th Street, Miami, Florida 33199.

²Department of Chemistry, Rollins College, 1000 Holt Ave, Winter Park, Florida, 32789.

A novel online solid phase extraction (SPE) high pressure liquid chromatography (HPLC) high resolution mass spectrometry method was developed to analyze caffeine concentrations in wastewater and natural waters in order to evaluate caffeine's usefulness as an environmental tracer. Caffeine is a universally used substance present in beverages and foods and is regularly detected in wastewaters even after chemical treatment. Traces of caffeine in water samples may indicate the presence of wastewater along with additional, more harmful compounds that may have also been left untreated. In this study, samples of reclaimed water and natural waters were analyzed using Equan MAX Plus SPE pre-concentration system coupled to a high pressure liquid chromatography system and Q Exactive Hybrid Quadrupole-Orbitrap HRMS in full scan, positive identification mode. Fluorescence excitation emission matrices parallel factor analysis (EEM-PARAFAC) was also performed on the samples as an additional method of characterization. Caffeine was found to have a concentration ranging between 76 and 1425 ng/L in reclaimed water samples and a concentration ranging between 10 and 664 ng/L in natural waters. The higher concentration in reclaimed water suggests caffeine may be a useful tracer of the presence of wastewater and its associated compounds.

Fluorescence study of the allosteric modulators in hemoglobin

Ramón A Gutierrez^{1,2}, David Butcher¹ and Jaroslava Miksovska^{1,*}

¹Department of Chemistry and Biochemistry, Florida International University, 11200 SW 8th Street, Miami, Florida 33199.

²Department of Physical Sciences, Barry University, 11300 NW 2nd Ave, Miami, Florida 33161.

WT human hemoglobin (Hb) is found abundantly in vertebrate blood. It's an iron containing heme protein responsible for delivering oxygen from the respiratory organs to the rest of the body. Distinct structural changes (in term of volume and enthalpy) in hemoglobin upon dissociation of O₂ at high and low temperatures were determined using photoacoustic calorimetry, which has not been previously observed. Here we aim to use a fluorescent probe 8-hydroxypyrene-1,3,6-trisulfonate (HPTS) to monitor temperature dependent structural changes. Precious studies have shown that HPTS binds in the $\beta 1/\beta 2$ cleft in Hb and mimics physiological effectors such as 2,3-bisphosphoglycerate (2,3-BPG). The dissociation constants (K_d) for the met-, oxy-, and deoxy-Hb were determined by steady state fluorescence measurements. The binding affinity of met-Hb to HPTS is much higher than that of oxy-Hb due to the structural transition between the different forms. In addition, the impact of bezafibrate (BZF) on the binding affinity of HPTS was determined.

Cocaine-Specific Field Test Using Aptamer-Fluorophore Assembly

Aurora Burkus-Matasevac^{1,2}, Juan Canoura¹ and Yi Xiao^{1,*}

¹Department of Chemistry and Biochemistry, Florida International University, 11200 SW 8th Street, Miami, FL, 33199

²Department of Physical Sciences, Barry University, 11300 NE 2nd Avenue, Miami Shores, FL, 33161

The plausibility of using a cocaine-specific aptamer-fluorophore biosensor assembly in place of the current chemical detection method was analyzed. The chemical method, known as the Scott's test, is a three-step process and is renowned for its false positives and false negatives. In contrast, aptamers are well-known for their binding specificity. While aptamer based biosensors are known for specificity, the most common cocaine aptamer is not as specific as other aptamers due to versatility in ligand binding. In this study, a one-step fluorophore assembly based on the binding ability of the fluorescent molecule 2-amino-5,6,7-trimethyl-1,8-naphthyridine (ATMND) was used to test the specificity of three cocaine-specific aptamers in both desalted and HPLC purified configuration. Eight common cutting agents of cocaine were tested in each aptamer assay to determine the level of interference experienced. It was determined that there was no significant difference between the desalted and HPLC purified aptamers, but there was significant interference from the cutting agents. This indicates that neither of the pre-folded aptamer assays are completely cocaine specific, but the aptamer-fluorophore assembly may be more cost and time effective than the Scott's test.

Synthesis of 1,3,5-tris(chlorosulfonylmethyl)benzene as a precursor for trisulfonamide actinide(III) extractants

Sierra R. Harris^{1,2}, Evgen V. Govor¹, Konstantinos Kavallieratos^{1,*}

¹Florida International University, Department of Chemistry and Biochemistry, 11200 SW 8th St., Miami, FL 33199

²Paine College, Department of Mathematics, Science, and Technology, 1235 15th St., Augusta, GA 30901

Nuclear weapons production has resulted in almost 100 Mgal of high-level waste (HLW), currently stored in underground tanks at Hanford and Savannah River (SRS) sites. Actinides and ⁹⁰Sr are removed from HLW by sorption on monosodium titanate and then ¹³⁷Cs is extracted by a calixarene extractant during the Caustic-Side Solvent Extraction process (CSSX), invented at Oak Ridge National Laboratory (ORNL). Modification of the CSSX process by adding trisulfonamides with soft N-donor sites for combined Cs and actinide separation from alkaline HLW streams into the organic phase could potentially make the HLW separation process more economical. Alkylaromatic moieties are promising linkers of sulfonamide groups, because they can lead to preorganized N-binding site orientation, thus providing a versatile and robust platform for An(III) complexation. Accordingly we have developed a synthetic pathway of obtaining of 1,3,5-tris(chlorosulfonylmethyl)benzenes (Scheme 1), which are precursors for synthesis of trisulfonamides by coupling with various anilines. All compounds were characterized via FT-IR and ¹H NMR.

Synthesis of Tripodal Pyrazole Ligands for Combined Cesium, Strontium, and Actinides Complexation and Separation from High Level Waste

Kai Chambers^{1,2}, Raphael G. Raptis² and Shambhu Kandel²

¹Department of Biochemistry and Chemistry at Florida International University

²Department of Mathematics, Technology, and Science at Paine College

High-level waste (HLW) are highly radioactive materials that are stored in both the Savannah River Site (SRS), located in the Upper Coastal Plain of South Carolina along the Savannah River, and Hanford Site (HR), located in state of Washington in the Columbian River. The presence of strontium (Sr) and actinides (Ac) in the tank supernatants and saltcake, present in both the SRS and HS sites, makes the removal of HLW difficult to accomplish. Pyrazoles with different substitutions and coordinating ability were synthesized. Their solubilities were tested and found that they are readily soluble in lipophilic solvents like dichloromethane and insoluble in water, as desired in order. To extract cesium, strontium, and actinide from the HLW present in SRS and HS, lipophilic ligands are needed. We successfully synthesized: i) of 3,5-(ditert butyl)-1H-pyrazole ($N_2C_{11}H_{20}$); ii) trispyrazole of 4-(phenyl)-1H-pyrazole ($N_6C_{42}H_{42}$); iii) trispyrazole of 3,5-(diphenyl)-1H-pyrazole ($N_6C_{60}H_{54}$); iv) trispyrazole of 4-(bromo)-1H-pyrazole ($Br_3N_6C_{24}H_{27}$); and v) trispyrazole of 4-(iodo)-1H-pyrazole ($N_6C_{27}H_{36}$). Synthesis of trispyrazole of 3,5-(ditertbutyl)-1H-pyrazole failed. Complexation studies of tripodal pyrazoles with lanthanides as model compounds for HLW treatment are in progress. Currently, we are trying to coordinate different lanthanide salts, such as samarium nitrate, erbium chloride, samarium chloride and neodymium chloride, with the trispyrazoles synthesized. Among the pyrazoles that were synthesized, trispyrazole with 4-(phenyl)-1H-pyrazole, trispyrazole with 3,5-(diphenyl)-1H-pyrazole and trispyrazole with 4-(iodo)-1H-pyrazole are new compounds, while the rest were already synthesized and reported. All the trispyrazoles were characterized by ¹H-NMR and IR, but trispyrazole with 4-(phenyl)-1H-pyrazole was also structurally characterized by single crystal X-ray defraction (SCXD) methods.

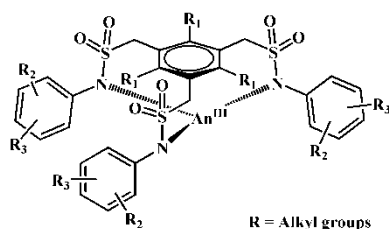
Synthesis of aniline-derived trisulfonamides for actinide complexation and extraction from alkaline solutions

Bemsi Nabi Ajoff^{1,2}, Evgen V. Govor¹ and Konstantinos Kavallieratos^{1,*}

¹Department of Chemistry and Biochemistry, Florida International University, 11200 SW 8th Street, Miami, Florida 33199.

²Department of Mathematics Sciences and Technology, Paine College, 15th Street, Augusta Georgia 30901

Various approaches of treatment of alkaline radioactive high-level waste (HLW), which has been generated and stored at the Savannah River (SRS) and Hanford Sites for over 50 years, have been proposed or applied, such as sorption on elutable and non-elutable ion-exchange columns (zeolites, resins), in-tank precipitation (NaBPh₄), selective dissolution, fractional crystallization, and solvent extraction via various organic extractants. The currently used processes for separation of TRU and fission products (primarily Cs and Sr) from HLW at SRS are: i) the Actinide Removal Process (ARP), which involves sorption of ⁹⁰Sr and TRU on monosodium titanate followed by ii) Caustic Side Solvent Extraction (CSSX); invented at Oak Ridge National Laboratory (ORNL) for Cs separation. Combined extraction of Cs and Actinides in the CSSX step using new soft N-donor ligands for An extraction could potentially lead to economic advantages due to decreased amount of sorbent needed during ARP and faster ARP process. In this context, trisulfonamides based on alkylaromatic frameworks (scheme 1) are promising because: i) their moderate pK_a (9-11) can allow reversible An extraction-stripping at different pH; ii) they have suitable N-donor site orientation for selective binding of An(III) and iii) there are possibilities of tuning their lipophilicity by introducing aliphatic substituents in various positions. Synthesis of 1,3,5-tris(4-isopropyl-phenylsulfamoylmethyl)-benzene and 1,3,5-tris-(3,5-di-tert-butyl-phenylsulfamoylmethyl)benzene were performed by reaction of 1,3,5-tris(chlorosulfonylmethyl) benzene and corresponding anilines in DMF. All compounds were characterized spectroscopically by FT-IR and ¹H/¹³C NMR.



Scheme 1. Trisulfonamide frameworks for An(III) complexation and extraction.