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AMERICAN CHEMICAL SOCIETY
Dallas - Fort Worth Section



55th Annual
Meeting-in-Miniature
April 22, 2023



TARLETON STATE UNIVERSITY

CHEMISTRY

Dallas – Fort Worth Local Section
American Chemical Society
55th Annual Meeting-in-Miniature

Saturday, April 22, 2023

Tarleton State University, Stephenville Campus

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Schedule

BC - Biochemistry/Biological Chemistry

IA – Inorganic/Analytical

M – Materials

O - Organic Chemistry

PC - Physical/Computational Chemistry

P - Polymer Chemistry

U - Undergraduate

| Time | Sci 102 | Sci 105 | Sci 109 | Sci 110 | Sci 111 | Sci 112 |
|-------|------------------|--------------|---------------|---------------|---------------|--------------|
| 9:20 | Greetings | | | | | |
| 9:30 | | U – 1 | | PC – 1 | BC – 1 | |
| 9:45 | | | IA – 1 | | | P – 1 |
| 10:00 | | | | | | |
| 10:15 | Break | Break | Break | Break | Break | Break |
| 10:30 | | U – 2 | IA – 2 | PC – 2 | BC – 2 | P - 2 |
| 11:00 | | | | | | |
| 11:15 | Keynote | | | | | |
| 12:15 | Lunch | Lunch | Lunch | Lunch | Lunch | Lunch |
| 12:30 | | | | | | |
| 1:00 | | | | | | |
| 1:30 | | U – 3 | IA – 3 | PC – 3 | O – 1 | M – 1 |
| 2:00 | | | | | Break | |
| 2:30 | | | | | | |
| 2:45 | Break | Break | Break | Break | O - 2 | Break |
| 3:00 | | U – 4 | IA – 4 | PC – 4 | | M - 2 |
| 3:30 | | | | | | |
| 4:00 | | | | | | |

Keynote Speaker



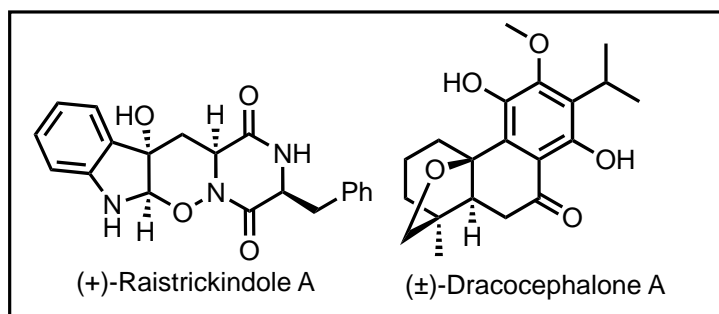
Science 102 at 11:15

Recent Efforts in the Synthesis of Complex Natural Products

John L. Wood

Department of Chemistry and Biochemistry, Baylor University, One Bear Place
97348, Waco, Texas 76798, U.S.A.

Recent efforts in our laboratories culminated in a completed synthesis of Raistrickindole A as well as Dracocephalone A. The evolution of our synthetic approaches to these molecules will be discussed.



Session: U-1 **Room: Science 105** **Moderators: McAfee and Merkel**

9:30 Tanner Taylor, Tarleton, “Titrimetric Measurement of Urinary Sulfate and Interfering Ions in Horses and Swine”, TA-55

9:45 Caryn Lawrence, McMurry, “Breast Cancer Cell Viability in Cyrene and Hydroxamic Acid Derivatives”, TA-2

10:00 Samuel Rodriguez, Tarleton, “Preparation of Osage Orange Isoflavones for Co-Transfection with Fenugreek Carbohydrate Polymer in Pancreatic Tumor Cell Proliferation Assays”, TA-63

Session: IA-1 **Room: Science 109** **Moderators: Matthews and Whaley**

9:30 Greetings

9:45 Muhammad Abbas, UT-Dallas, “Transformation of a Copper Metal-Organic Polyhedron into Metal-Organic Frameworks for CO₂ Capture”, TA-38

10:00 Joseph Adebajo, North Texas, “The Computational Investigation of the Photophysical Properties of Fac-Rhenium Complex of 4-[4,6-bis(3,5-dimethyl-1H-pyrazol-1-yl)-1,3,5-triazin-2-yl]-N,N-diethyl-benzenamine”, TA-34

Session: PC-1 **Room: Science 110** **Moderators: Low and J. McAfee**

9:30 Ishna Satyarth, Southern Methodist, “Machine Learning Approaches for Tensor Hypercontraction”, TA-78

9:45 Alexis Delgado, Southern Methodist, “Elucidating Upon the Role of Hydrogen Bonding Networks in X-Ray Absorption Spectra”, TA-6

10:00 Mojgan Gharee, North Texas, “Computational Study of Metal Oxynitride Thin-Film Electrocatalysts for Nitrogen Reduction”, TA-19

Session: BC-1 **Room: Science 111** **Moderators: Anderson and Rathburn**

9:30 Prabavi Dias, UT-Dallas, “Hydrogen-Deuterium Exchange of Isotopically Labeled Protein Mixtures”, TA-52

9:45 Evan Bonnard, UT-Dallas, “Mapping Allosteric Regulation of Pyruvate Kinases by Native and Synthetic Ligands”, TA-36

10:00 Katayoun Morakabi, UT-Dallas, “The Acidic Domain of Asf1 Contributes to Binding Histones H3-H4 and Modulates Histone Acetyltransferase Rtt109”, TA-62

Session: P-1 **Room: Science 112** **Moderators: Bell and Williams**

9:30 Greetings

9:45 Abhi Bhadran, UT-Dallas, "Reversible Cross-linked Thermoresponsive Polymeric Micelles for Enhanced Stability and Controlled Release", TA-51

10:00 Himanshu Polara, UT-Dallas, "Synthesis of Disubstituted γ -Amide ϵ -Caprolactone Monomers for the Amphiphilic Diblock Copolymers in Drug Delivery Applications", TA-28

Session: U-2 **Room: Science 105** **Moderators: McAfee and Merkel**

10:30 Aubry Hutson, Tarleton, "Measurement of Non-elevated Sulfate Levels in West Texas Groundwater", TA-79

10:45 Dax Hildebrand, UT-Dallas, "Synthesis and Characterization of Several Copper-Lanthanide Mixed-Metal Organic Frameworks Containing a Fluoro-bridged Hexacluster", TA-67

11:00 Emad Siddiki, UT-Dallas, "Formation of Fluoro-bridged Rare-earth-based Metal-Organic-Frameworks", TA-46

Session: IA-2 **Room: Science 109** **Moderators: Matthews and Whaley**

10:30 Emily Buchanan, UT-Southwestern, "Development of Novel diaCEST Agents for PH Sensing", TA-23

10:45 Fahad Danladi, UT-Arlington, "Tuning the Electronic, Optical and Photoelectrochemical Properties of Copper Metavanadate Via Alkaline Earth Metal Substitution", TA-50

11:00 Hamid Reza Firouzi, UT-Dallas, "Mechanistic Study of Direct Extraction of Fluorine from 2-Fluorobenzoic Acid and 2,6-difluorobenzoic Acid by Holmium Ion and the effect of fluorine extraction on tri-, hexa- and nona- cluster MOFs' Properties", TA-66

Session: PC-2 **Room: Science 110** **Moderators: Low and J. McAfee**

10:30 Bibek Sapkota, North Texas, "Small-Molecule Perturbation of Phospholipid Bilayer as a Possible Cause and Remedy of High-Pressure Neurological Syndrome", TA-26

10:45 Alireza Haji Seyed Javadi, North Texas, "Computational Study of N-Fused Co-Porphyrins as Electrocatalysts for Nitrogen Reduction Reaction", TA-22

11:00 Duc Anh Lai, Southern Methodist, "The Electric Field-induced Second Energy Minima of Carbon Monoxide", TA-35

Session: BC-2 **Room: Science 111** **Moderators: Anderson and Rathburn**

- 10:30 Joy Shaffer, UT-Dallas, "Molecular basis of RanGTP-activated release of Histones H2A-H2B from Importin-9", TA-45
- 10:45 Duc Ngu, UT-Arlington, "Biogenesis of U1 Small Nuclear RNA Mutations in Pan-Cancer Patients Reveals a Key Regulation of U1 snRNP Abundance", TA-42
- 11:00 Isaiah Odeyemi, UT-Dallas, "Optimized Enzymatic Synthesis and Purification Protocol of S-Adenosyl-L-Methionine (SAM) for Infrared Spectroscopic Studies", TA-60
- 11:15 Sanat Myti, UT-Arlington, "The Role of Diadenosine Tetraphosphate in the Formation of RNA: Protein Complexes in Innate Immunity", TA-68

Session: P-2 **Room: Science 112** **Moderators: Bell and Williams**

- 10:30 Tejas Shah, UT-Dallas, "Molecular Dynamics Simulation Study of the Biodegradable Amphiphilic Polymers for their Potential Application in Anticancer Drug Delivery", TA-61
- 10:45 Somayeh Taslimy, UT-Dallas, "Design and Synthesize of Lanthanide Phosphate Catalysts", TA-32

Session: U-3 **Room: Science 105** **Moderators: McAfee and Merkel**

- 1:30 Andrew Vu, UT-Dallas, "Europium Oxide-Catalyzed Formation of Electrically-Conductive Carbon for Hybrid Supercapacitors", TA-24
- 1:45 Chaney Kelley, Tarleton, "Cultured Pancreatic Tumor Cell Growth Is Inhibited by Co-Transfections with Osage Orange Isoflavones and Fenugreek Carbohydrate Polymer", TA-64
- 2:00 Murtaza Degani, UT-Dallas, "Synthesis and Characterization of Holmium Based Metal-Organic Framework", TA-41
- 2:15 Logan Estridge, North Texas, "The Prevention of Corrosion and Oxidation Related Failures in Cu-Al and Cu-Cu Wire-Bonded Devices", TA-71
- 2:30 Clayton Smithhart, UT-Dallas, "Synthesis and Magnetic Properties of Gadolinium Metal-Organic Frameworks", TA-40

Session: IA-3 **Room: Science 109** **Moderators: Matthews and Whaley**

- 1:30 Manan Guragain, North Texas, "Photoinduced Electron Transfer in the Self-Assembled Metal-Ligand Axial Coordination of Donor-Acceptor Conjugates", TA-76
- 1:45 Sheikh Mohammad Sirajul Islam, North Texas, "Highly Porous Metal-Organic Framework Based on a Texas-sized tri-Carboxylate Linker and its Application on Selective C₂H₂/CH₄ and C₂H₂/CO₂ Separation at Ambient Conditions", TA-18

- 2:00 Marie Mortensen, UT-Dallas, "Several New Lanthanide Containing Metal Organic Frameworks Exhibiting Fluoro-Bridged Triclusters and Their Structural and Luminescence Properties", TA-48
- 2:15 Jatan Kumar Sharma, "Intramolecular Charge Transfer (ICT) in Hypervalent Antimony(V) and Phosphorus(V) Porphyrin-Based Push-Pull Systems", TA-75
- 2:30 Simin Sheybani, "Synthesis of Fluoro-Bridged Ho³⁺ and Gd³⁺ 1,3,5-Tris(4-carboxyphenyl) benzene Metal-Organic Frameworks from Perfluoroalkyl Substances", TA-13

Session: PC-3 **Room: Science 110** **Moderators: Low and J. McAfee**

- 1:30 Mauricio Martil de la Garza, UT-Dallas, "Computational Characterization of Cancer-Associated Mutations on POT1", TA-69
- 1:45 George Rawling, North Texas, "New Reactions of Diazene and Related Species for Modeling Combustion of Amine Fuels", TA-77
- 2:00 Arkanil Xiao, UT-Dallas, "Computational Investigation of the Effects of a Single Point Mutation on the Structural and Dynamical Properties of DNA Polymerase γ ", TA-54
- 2:15 Sian Xiao, Southern Methodist, "Iterative Expansion of Protein Conformational Space with Variational Autoencoder", TA-27
- 2:30 Shubham Chatterjee, "Catalysis by Horse Radish Peroxidase in aqueous [emim][EtSO₄]: A Molecular Dynamics and Quantum Mechanics/Molecular Mechanics investigation", TA-70

Session: O-1 **Room: Science 111** **Moderators: Donney and Fennimore**

- 1:30 Nilakshi Dey, UT-Arlington, "Studies Toward a Total Synthesis of the Bioactive Pyrrole-Imidazole Alkaloid Ageliferin- a Marine Origin Metabolite", TA-43
- 1:45 Anasuya Ghorai, UT-Arlington, "Development of Concise Asymmetric Total Synthesis of Imidazolyl-quinolone Ceratinadin B", TA-20
- 2:00 Sachin Giri, UT-Dallas, "One-Pot Formal Carboradiofluorination of Alkenes: A Toolkit for Positron Emission Tomography Imaging Probe Development", TA-58
- 2:15 Nazamee Parveen, UT-Arlington, "Synthetic Studies on Dearomatizing Cyclization of Ureas", TA-30

Session: M-1 **Room: Science 112** **Moderators: Rajani and Rackov**

- 1:30 Kevin Antony Jesu Durai, North Texas, "Improving the Reliability of Solder Bonding in IC Packaging Devices with a Cu Passivation Coating", TA-73

- 1:45 Haritha Asokan Sheeja, UT-Arlington, "Self-Assembling Peptides with Internal Ionizable Non-Natural Amino Acids: A New Approach to PH-Responsive Peptide Materials", TA-56
- 2:00 Kabirat Balogun, North Texas, "Surface Changes and Stability of Vanadium Oxide Thin Film at Ambient and Electrochemical Conditions for Nitrogen Reduction; Surface Science Approach", TA-25
- 2:15 Precious Chukwunye, North Texas', "Stability, Selectivity and NRR Activity of Magnetron Sputtered Titanium Oxynitride at Different PH Values", TA-17
- 2:30 Oluchukwu Igboenyasi, UT-Arlington, "Superhydrophobic Surface Modification with Perfluoro-Hydrocarbons: Preparation and Characterization", TA-29

Session: U-4 **Room: Science 105** **Moderators: McAfee and Merkel**

- 3:00 Luke Reynolds, Tarleton, "Preparation of Pure Osajin Suitable for Cell Proliferation Assays with Pancreatic Tumor Cells", TA-72
- 3:15 Trang Nguyen, North Texas, "Study of Reactivity of $CF_2=CFCH_2CH_2Cl$ with Cl and OH Radicals", TA-12
- 3:30 Addison Anderson, Tarleton, "Hydrogels and Determination of Correct Concentration and Methods", TA-44

Session: IA-4 **Room: Science 109** **Moderators: Matthews and Whaley**

- 3:00 Katherine Smith, Texas Christian, "Effects of a Secondary Pyridine Ring Substitution on Electronics and SOD Activity of Pyridinophanes", TA-4
- 3:15 Arslan Umer, UT-Dallas, "Rare Earth Metal Oxide Templated-Conductive Carbon for Energy Storage Application", TA-37

Session: PC-4 **Room: Science 110** **Moderators: Low and J. McAfee**

- 3:00 Yazdan Maghsoud, UT-Dallas, "Investigation of a Series of Small Molecules as Lead Compounds for Lysyl hydroxylase-2 (LH2) Inhibition", TA-33
- 3:15 Dogukan Yazici, UT-Arlington, "CO₂ Capture Using Nanomaterials: A Density Functional Theory Study", TA-47
- 3:30 Chao Yin, Southern Methodist, "Recurrence Relation Schemes for Electron Repulsion Integral Computation on GPUs", TA-21
- 3:45 Tingting Zhao, Southern Methodist, "Rank-Reduced Representations of the Connected Triples in Coupled Cluster Theory", TA-5
- 4:00 Upeksha Dissanayake, UT-Dallas, "Computational Study of Acyl Chain Hydrolysis in Trans-AT Polyketide Synthase Enzyme", TA-65

Session: O-2 **Room: Science 111** **Moderators: Donney and Fennimore**

2:45 Saad Shaikh, North Texas, “Cyclooctatetraene Attached π Conjugated Porphyrins and Optoelectronic Studies on Their Conformational Planarization State”, TA-10

3:00 Muhammad Abbas, UT-Dallas, “Breaking-Down PFAS During Rare-Earth Metal-Organic Frameworks Synthesis”, TA-39

Session: M-2 **Room: Science 112** **Moderators: Rajani and Rackov**

3:00 Dinesh Kumar Kumaravel, North Texas, “Development of an Operando Fourier Transform Infrared Electrochemical Analysis for Mechanistic Insights into Nitrogen Reduction Reaction”, TA-74

3:15 Hoa Nguyen, UT-Arlington, “Probing Lone Pairs and Vacancies Effects on Optoelectronic Properties of TeO₂ Polymorphs from First Principles”, TA-8

3:30 Melissa Orr, UT-Arlington, “Establishing Synthetic Strategies and Structure-Property Relationships for Oxytellurides”, TA-9

3:45 A. K. M. Nur Alam Siddiki, UT-Dallas, “Unlocking the Potential of Wrinkled Mesoporous Silica through SPIONs Encapsulation: A Promising Path to Advanced Materials”, TA-14

Biochemistry and Biological Chemistry Abstracts

Sponsors

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Biochemistry



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Mapping Allosteric Regulation of Pyruvate Kinases by Native and Synthetic Ligands

Evan Bonnand

Department of Chemistry and Biochemistry

The University of Texas at Dallas

Email: efb200000@utdallas.edu

Classification: Graduate

Category: Biochemistry/Biological Chemistry

Abstract:

Pyruvate Kinase (PK) catalyzes the final and energetic payoff step of glycolysis, converting Phosphoenolpyruvate and ADP to pyruvate and ATP. PK is allosterically regulated by the product of step three, fructose 1,6-bisphosphate (FBP). FBP stabilizes the homotetramer interfaces of PK, thus increasing enzymatic activity. At high concentrations, ATP product inhibition occurs. There are four PK isoforms in humans, PKL, PKR, PKM1 and PKM2. Mutations in regions of PKR required for FBP binding result in destabilization of the tetramer and loss of activity, causing hemolytic anemia. The drug Mitapivat targets PKR by binding at a site distinct from that of FBP but similarly activates enzyme activity. In this work, we explore ligand binding and allosteric effects with PKL and PKM2. Bottom-up Hydrogen-Deuterium Exchange coupled with Mass Spectrometry (HDX-MS) was performed to compare five conditions, PK, PK+ATP, PK+FBP, PK+ATP+FBP and PK+Mitapivat for both enzymes. Samples were prepared in quadruplicate with saturating concentrations of ligand. Labeling was carried out over a time course at 25°C and quenched at 10¹, 10², 10³, 10⁴ and 10⁵ seconds. Samples were digested using an online pepsin column, followed by separation and analysis by LC/MS. Enzyme stability was verified by comparing D-uptake with samples that were incubated in parallel and labeled for 10 seconds at the end of the time course. Non-deuterated samples, prepared in parallel, were analyzed by tandem MS for peptide identification in deuterated samples. We demonstrate how HDX can be used to probe the interaction of small molecules

Biogenesis of U1 small nuclear RNA mutations in Pan-cancer patients reveals a key regulation of U1 snRNP abundance

Duc Ngu, Ayesha Khan, Sanat Myti, and Byung Ran So

Department of Chemistry & Biochemistry

University of Texas at Arlington

Email: duc.ngu@mavs.uta.edu

Classification: Graduate

Category: Biochemistry/Biological Chemistry

Abstract:

In eukaryotes, newly synthesized pre-messenger RNAs undergo post-transcriptional processing including 5'-capping, splicing of introns, and 3'-end cleavage and polyadenylation to produce full-length protein-coding mRNAs. Small nuclear ribonucleoproteins (snRNPs) are non-coding RNA-protein complexes and major components of spliceosomes in splicing. U1 snRNP, the most abundant RNP particle among the spliceosomal snRNPs, plays a key role in splicing as well as telescripting, which prevents premature termination of nascent transcripts. Both activities are ensured by RNA:RNA base-pairing between U1 snRNA and 5' splice site (5'ss) on pre-messenger RNA (pre-mRNA). Previous study showed that frequent mutations in U1 small nuclear RNA (snRNA) were found in pan-cancer patients. However, how those U1 snRNA mutations exist as U1 snRNPs and the function of U1 snRNP in cells remain unknown. The cellular abundance and stability of snRNP relies on the formation of Sm core, a heptameric Sm ring protein surrounding a uridine-rich Sm sequence. This is chaperoned by a multi-subunit RNP complex, survival of motor neuron (SMN) complex. Here, we found that the formation of Sm core on U1 snRNA mutants significantly decreased in vitro, suggesting that U1 snRNAs in pan-cancers cannot form stable U1 snRNPs. This finding provides insight into the regulation of U1 snRNPs abundance, linking snRNP biogenesis and U1 snRNP-dependent protein-coding gene expression.

Molecular basis of RanGTP-activated release of Histones H2A-H2B from Importin-9

Joy Shaffer

Department of Chemistry and Biochemistry

University of Texas at Dallas

Email: joy.shaffer@utdallas.edu

Classification: Graduate

Category: Biochemistry/Biological Chemistry

Abstract:

Padavannil et al. 2019 show that Importin-9 (Imp9) transports Histones H2A-H2B from the cytoplasm to the nucleus using a non-canonical mechanism whereby binding of a GTP-bound Ran GTPase (RanGTP) fails to evict the H2A-H2B cargo. Instead, a stable complex forms, comprised of equimolar RanGTP, Imp9, and H2A-H2B. Unlike the binary Imp9•H2A-H2B complex, this RanGTP•Imp9•H2A-H2B ternary complex can release H2A-H2B to an assembling nucleosome. Here, we define the molecular basis for this RanGTP-activated nucleosome assembly by Imp9. We use hydrogen-deuterium exchange coupled with mass spectrometry and compare the dynamics and interfaces of the RanGTP•Imp9•H2A-H2B ternary complex to those in the Imp9•H2A-H2B or Imp9•RanGTP binary complexes. Our data are consistent with the Imp9•H2A-H2B structure by Padavannil et al. 2019 showing that Imp9 HEAT repeats 4-5 and 18-19 contact H2A-H2B, as well as many homologous importin•RanGTP structures showing that importin HEAT repeats 1 and 3, and the h8 loop, contact RanGTP. We show that Imp9 stabilizes H2A-H2B beyond the direct binding site, similar to other histone chaperones. Importantly, we reveal that binding of RanGTP releases H2A-H2B interaction at Imp9 HEAT repeats 4-5, but not 18-19. This exposes DNA- and histone-binding surfaces of H2A-H2B, thereby facilitating nucleosome assembly. We also reveal that RanGTP has a weaker affinity for Imp9 when H2A-H2B is bound. We delineate the molecular link between the nuclear import of H2A-H2B and its deposition into chromatin by Imp9.

Hydrogen-Deuterium Exchange of Isotopically Labeled Protein Mixtures

Prabavi S Dias, Darby J Ball, Oladimeji S Olaluwoye, Javier Flores, Sheena D'Arcy
Department of Chemistry and Biochemistry

University of Texas at Dallas

Email: prabavishayana.dias@utdallas.edu, darby.ball@utdallas.edu, oladimeji.olaluwoye@utdallas.edu,
javier.flores@utdallas.edu, sheena.darcy@utdallas.edu

Classification: Graduate

Category: Biochemistry/Biological Chemistry

Abstract:

Hydrogen-deuterium exchange coupled with mass spectrometry (HDX-MS) experiments as comparative analyses are technically challenging. In these experiments, all samples must be in the same conditions with regard to pH, temperature, and time. HDX-MS also imposes limitations in monitoring multiple, non-interchanging populations of a protein in a single sample. A novel workflow using mixtures of proteins distinguished by isotopic labeling with ^{12}C , ^{13}C , or ^{15}N can address these limitations. Such a workflow also provides biologically interesting analysis for oligomeric systems in which different copies of the same protein are in unique environments. We are using histone proteins as a system to test the feasibility of an isotopically labeled HDX-MS workflow. We performed HDX-MS time course experiments on a mixture of wild type, ^{15}N , ^{13}C H2A, and H2B in their unfolded state and on a mixture of wild type, ^{15}N , ^{13}C folded H2A-H2B. Results for both experiments showed no significant difference between the deuterium uptake of ^{13}C or ^{15}N with the wild type of histone. The results for unfolded histones and refolded histones suggest that there is no considerable influence on the chemical exchange rate and hydrogen bonding, respectively, by stable isotopic labeling. These results validate the feasibility of using stable isotopic labeled proteins in HDX-MS workflow.

Optimized enzymatic synthesis and purification protocol of S-adenosyl-L-methionine (SAM) for infrared spectroscopic studies.

Isaiah O. Odeyemi¹, Robert J. Fick¹, Teri A. Douglas¹, Nosakhare F. Igie¹, Drew Hargrove¹, Grace Hamilton¹, Brianna Bradley¹, Cathy Thai¹, Brendan Le¹, Maitri Unjia¹, Dylan Wicherts¹, Zackery Ferneyhough¹, Anjali Pillai¹, Raymond C. Trievel², Allison L. Stelling*¹

1. The University of Texas at Dallas, 800W Campbell Rd, Richardson, TX, 75080, U.S.A.

2. University of Michigan, 503 Thompson Street, Ann Arbor, MI 48109, U.S.A.

Supervisor: Allison L. Stelling (UTD)

Department of Chemistry and Biochemistry

The University of Texas at Dallas

Email: isaiah.odeyemi@utdallas.edu

Classification: Graduate

Category: Biochemistry/Biological Chemistry

Abstract:

S-adenosyl-L-methionine (SAM) is a cofactor used by methyltransferases, a class of important drug targets, to regulate a wide range of essential cellular processes. Yet, drugging these targets remains challenging due to specificity issues resulting in off-target effects in this large class of enzymes. NMR evidence suggests that SAM is multi-conformeric when free in solution. If present in methyltransferase active sites, alternate conformers of SAM can provide new structural leads to be used to increase compound specificity as different enzymes may possess unique alternate conformers. Vibrations of SAM can be used as probes to detect any druggable alternate conformers that may be present in methyltransferase active sites. This information can be incorporated into a design strategy to improve specificity, but first signals in SAM's Raman and IR spectra must be assigned to specific functional groups in the molecule. The established purification protocols result in SAM with interfering counterions, which produce large interfering IR signals. We report a new purification that removes the excess salts and present the first IR and Raman spectra of isotopically labeled SAM. These results will provide a foundation for employing specific vibrations of SAM for label-free diagnosis of specific molecular conformations and noncovalent interactions to the cofactor.

The Acidic Domain of Asf1 Contributes to Binding Histones H3-H4 and Modulates Histone Acetyltransferase Rtt109

Katayoun Morakabi, Noushin Akhavantabib, Darby J Ball, Sheena D'Arcy

Department of Chemistry and Biochemistry

The University of Texas at Dallas

Email: big_bunny@tarleton.edu

Classification: Graduate

Category: Biochemistry/Biological Chemistry

Abstract:

Anti-Silencing Factor1 (Asf1) is a conserved histone H3-H4 chaperone that is integral for genome stability due to its role in promoting the acetylation of H3K56. The histone acetyltransferase Rtt109 is the sole enzyme in yeast responsible for H3K56Ac and is strongly activated by Asf1, as well as another histone chaperone Vacuolar protein sorting 75 (Vps75). Asf1 contains a well-structured core domain that mediates binding to histone H3-H4, and a C-terminal domain (CTD) that is acidic and natively unfolded. We set out to characterize the functional role of the Asf1 CTD and how it modulates Rtt109 using solution and activity assays. We performed bottom-up HDX-MS using recombinant full-length (1-279) ScAsf1^{FL} and a C-terminal deletion (1-169) Asf1^{ΔCTD}. We reconstituted each protein in complexes with (H3-H4)₂ (histone-bound complex) and (H3-H4)₂-Rtt109-Vps75₂ (acetyltransferase complex) using SEC. We also employed *in vitro* histone acetyltransferase (HAT) assays using LC/MS to monitor acetylation over time on intact H3-H4. Our results show that the CTD does not stably interact with the Asf1 core in the apo state. However, we find that the core domain is altered by the CTD when in the histone bound and acetyltransferase complex. Our HDX data also reveal that histones are globally stabilized when the Asf1 CTD is included in the histone-bound complex. We find that H3-H4 binds Asf1^{FL} with a 6-fold tighter binding affinity than Asf1^{ΔCTD}. Additionally, we find that the Asf1 CTD influences Rtt109 and Vps75₂, weakening interfaces in the acetyltransferase complex. Our *in vitro* HAT assays reveal that the Asf1 CTD improves Rtt109 catalytic activity on H3 with higher abundance acetyl groups over time compared to conditions without the CTD. Our study highlights how acidic domains play a role in mediating histone interactions and regulating the incorporation of PTMs.

The role of diadenosine tetraphosphate in the formation of RNA: Protein complexes in innate immunity

Sanat Myti, Ayesha Khan, Duc Ngu, and Byung Ran So

Department of Chemistry and Biochemistry

University of Texas at Arlington, Arlington, TX 76019

Email: sxm5562@mavs.uta.edu

Classification: Graduate

Category: Biochemistry/Biological Chemistry

Abstract:

The modulation of gene expression, through co-transcriptional or post-transcriptional process, plays a key role in the development and function of innate immunity. Protein-coding messenger RNA (mRNA) is produced by associating a myriad of RNA:Protein complexes on precursor mRNA (pre-mRNA), including spliceosomes in splicing of introns and 3'-end termination factors. Diadenosine tetraphosphate (Ap₄A), a nucleotide derivative ubiquitously exists as an alarmone conserved from bacteria to human cells. Upon inflammatory stimulation, Ap₄A is synthesized by the lysyl-tRNA synthetase (LysRS), which gains a non-canonical function by post-translational modifications. Moreover, ubiquitin and ubiquitin-like enzymes produce Ap₄A. In addition, the elevation of Ap₄A concentrations triggers stress adaptive processes in response to inflammation, such as activation of the transcription factor MITF, suppression of STING-activated inflammation, and autocrine activation of purinoceptors through known mechanisms. Recent studies by Marx group and ours have revealed that Ap₄A associates with several pre-mRNA processing machineries such as hnRNPC, hnRNPL, CPSF6, and ELAVL1, known to regulate alternative splicing and 3'-end termination. However, the precise role of the interaction between Ap₄A and its interacting proteins in response to cellular stress remains unclear. To understand the role of Ap₄A in the formation of RNA:Protein complexes to regulate co- and post-transcriptional gene expressions, we are investigating the interactomes of Ap₄A in immune and cancer cell types. Our study will uncover the role of Ap₄A as a secondary signaling molecule that alters RNA:Protein complexes in innate immunity.

Inorganic and Analytical Chemistry Abstracts

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University of Texas Dallas – Department of Chemistry and
Biochemistry



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Effects of a Secondary Pyridine Ring Substitution on Electronics and SOD Activity of Pyridinophanes

Katherine J Smith

Department of Chemistry and Biochemistry

Texas Christian University

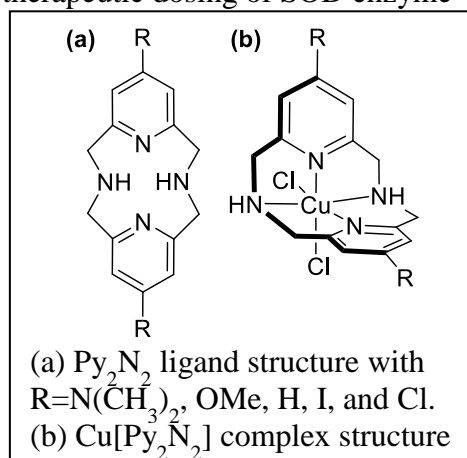
Email: k.j.whiteside@tcu.edu

Classification: Graduate

Category: Inorganic/Analytical

Abstract:

Oxidative stress is caused by the accumulation of reactive oxygen species (ROS) in the body and is a key player in many maladies, including neurological diseases like Parkinson's and Alzheimer's disease. Superoxide dismutase (SOD) enzymes are capable of transforming the common ROS molecule superoxide (O_2^-) into less toxic species such as H_2O_2 or O_2 , thus protecting the body from harmful reactions of superoxide. Synthetic metal complexes show promise as SOD mimics and can be effective alternatives to therapeutic dosing of SOD enzyme for oxidative stress. In this work, we present a series of 12-membered tetra-aza pyridinophanes (Py_2N_2) and the corresponding copper complexes with substitutions on the 4-position of the pyridine ring. The SOD mimic capabilities of the $Cu[Py_2N_2]$ series were explored using a UV-Visible spectrophotometric assay. Spectroscopic, potentiometric, and crystallographic methods were used to explore how the electronic nature of the 4-position substitution affects the electronics of the overall complex, and the complex's activity as a SOD mimic. This work is an initial step toward developing these $Cu[Py_2N_2]$ complexes as potential therapeutics for neurological diseases by mimicking SOD's capabilities and protecting the body from oxidative stress.



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Exp. Neurobiol. 2013, 22(1), 11-17

Int. J. Biochem. Cell Biol. 39 (1), 44-84.

Highly Porous Metal-Organic Framework Based on a Texas-sized tri-Carboxylate Linker and its Application on Selective C₂H₂/CH₄ and C₂H₂/CO₂ Separation at Ambient Conditions

Sheikh M. S. Islam, Rashida Yasmeen, Mohammad A. Omary
Department of Chemistry
University of North Texas

Email: sheikhmohamislam@my.unt.edu

Classification: Graduate

Category: Inorganic/Analytical

ABSTRACT:

A new metal-organic framework (MOF), UNT-22 [UNT = University of North Texas] has been successfully synthesized and structurally characterized. The activated UNT-22a displays a BET surface area of 3009 m²/g and a pore volume of 1.19 cm³/g. Owing to the combined features of high porosity and suitable pore sizes the resulting MOF material exhibits moderate C₂H₂ uptake and shows high selectivity for C₂H₂/CH₄ and C₂H₂/CO₂ separation at ambient conditions.

Development of novel diaCEST agents for pH sensing

Emily Buchanan, Mai Huynh, Sara Chirayil, and Zoltan Kovacs

Advanced Imaging Research Center

University of Texas Southwestern Medical Center

Email: emily.buchanan@utsouthwestern.edu

Classification: Graduate

Category: Inorganic/Analytical

Abstract:

Magnetic resonance imaging (MRI) is one of the most important clinical imaging modalities because it can provide high resolution images of soft tissues in a non-invasive manner. While conventional MR image contrast is generated based on differences in the T1 and/or T2 relaxation of water protons, it can also be generated via the chemical exchange saturation transfer (CEST) mechanism. CEST image contrast is generated by transferring saturated proton spins to the bulk water pool from a small molecule with labile protons via chemical exchange. CEST has a built-in signal amplifying mechanism since proton exchange occurs many times on the time scale of relaxation. This allows for the observation of the agent through the bulk water signal at concentrations below the direct detection limit while also delivering richer, more varied information about molecular interactions. However, clinical translation of CEST imaging is currently limited by a lack of selectivity since the chemical shifts of exchanging protons in sugars and proteins overlap and are close to the bulk water signal. The aim of this project was to synthesize a novel CEST probe which uses intramolecular hydrogen bonding to increase the chemical shift of the exchanging proton, thereby enhancing efficiency and selectivity. The CEST agent (2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-ene-1-carboxamide) was synthesized and characterized by ^1H , ^{13}C , mass spectrometry, and X-ray crystallography. CEST spectra collected at 600MHz confirmed that hydrogen bonding increases the chemical shift of the exchanging OH proton (12.0 ppm) far beyond the bulk water signal (0.0 ppm). Titration studies were performed to elucidate the protonation mechanism and characterize the pH dependency of the CEST effect. The large chemical shift and pH dependency of this agent demonstrate the exciting potential for use as a pH sensitive MRI probe.

The computational investigation of the photophysical properties of *fac*- Rhenium complex of 4-[4,6-bis(3,5-dimethyl-1H-pyrazol-1-yl)-1,3,5-triazin-2-yl]-N,N-diethyl-benzenamine)

Joseph O. Adebanjo, Mohammed A. Omary

Department of Chemistry
University of North Texas

Email: josephadebanjo@my.unt.edu

Classification: Graduate

Category: Inorganic/Analytical

Abstract

We have previously synthesized *fac*-[ReL(CO)₃Cl₂] using microwave-assisted synthesis, and the photoluminescence properties have been evaluated. Herein, results from the computational investigation are discussed. Optimization was done at the singlet and triplet state of the complex using its crystal coordinates as a starting point. The differences in the optimized triplet compared to the optimized singlet point shows possible oxidation in the metallic center with a decreased distance between the metal and neighboring groups. HOMO, LUMO, and EDD maps were plotted, and simulated absorption spectra with five different solvents agreed with the experimental data. The absorption depicts the ¹MLCT transition, while the emission transition shows ³MC/³LLCT.

Transformation of a Copper Metal-Organic Polyhedron into Metal-Organic Frameworks for CO₂ Capture

Muhammad Abbas, Kenneth J. Balkus Jr.

Department of Chemistry and Biochemistry

The University of Texas at Dallas

Email: Abbas@utdallas.edu

Classification: Graduate

Category: Inorganic/Analytical

Abstract:

Metal-organic frameworks (MOFs) are porous crystalline materials with surface areas ranging up to 10,000 m²/g, better than traditional porous materials such as carbons or zeolites. These materials can possess open compartments for guest substrates, functional linkers, active catalytic sites, and tunable metal nodes. These characteristics allow MOFs to be used for gas storage, gas separation, catalysis, sensing, drug delivery, radiotherapy, and other biological applications. Synthesis of possible theoretical structures is not always straightforward and may need multiple routes to reach the target. Metal-organic polyhedra (MOPs), also called nanoballs, are porous zero-dimensional high symmetry discrete units. These are composed of metal paddlewheel clusters M₂(RCO₂) and organic linker. MOPs could serve as high connectivity supramolecular building blocks for 2D and 3D MOFs synthesis. A copper-based MOP is modified to get a new MOF. The newly synthesized MOF is a microporous structure with zig-zag channels. The MOF is characterized by XRD, TGA, and surface area analyzer. The gas adsorption results show it is selective for CO₂ adsorption over N₂.

Several New Lanthanide Containing Metal Organic Frameworks exhibiting fluoro-bridged triclusters and their structural and luminescence properties.

Marie L. Mortensen, Muhammad Abbas, Gregory T. McCandless, Kenneth J. Balkus Jr.

Department of Biochemistry and Chemistry

University of Texas at Dallas

Email: mlm140430@utdallas.edu

Classification: Graduate

Category: Inorganic/Analytical

Abstract:

Lanthanide containing metal organic frameworks or MOFs have unique magnetic and luminescent properties. To improve their stability and further increase the number of topologies formed, the modulator, 2-fluorobenzoic acid, was added to the synthesis to create lanthanide clusters. Recently, it was determined that the lanthanides are reacting with the modulator and extracting the fluorine from the compound. This results in lanthanide clusters that are fluoro-bridged instead of hydroxy-bridged. Using this method, a series of lanthanide containing MOFs were synthesized from a N,N-dimethylformamide/water solution containing 2, 2'-bipyridine 4, 4'-dicarboxylic acid, a fluorinated modulator, and lanthanide nitrate (Ho^{3+} , Eu^{3+} , Tb^{3+} , and Gd^{3+}). The synthesis of two different MOFs, containing either Ho^{3+} , Eu^{3+} , Tb^{3+} , or Gd^{3+} will be described. The presence of the fluorinated clusters, as demonstrated in Figure 1, is shown through single crystal X-ray diffraction, energy dispersion X-ray spectroscopy, and X-ray photoelectron spectroscopy. The luminescence of the Eu^{3+} , Gd^{3+} , and Tb^{3+} MOFs will also be described.

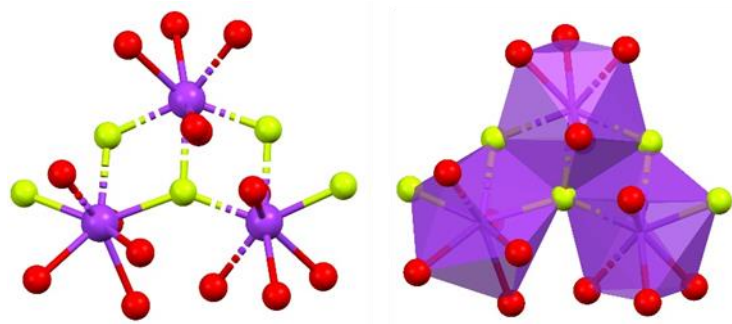


Figure 1: The fluoro-bridged tricluster of Eu 4,4'-BPDC MOF.

Tuning the electronic, optical and photoelectrochemical properties of copper metavanadate via alkaline earth metal substitution

Fahad Ibrahim Danladi, Ana Lucia Ledesma, Krishnan Rajeshwar
Department of Chemistry and Biochemistry
University of Texas at Arlington

Email: fahadibrahim.danladi@mavs.uta.edu

Classification: Graduate

Category: Inorganic/Analytical

Abstract:

Here, we present a fundamental understanding of the effect of alkaline earth metal substitution on optical, electronic, and photoelectrochemical properties of copper metavanadate. Mixed compositions of $A_{0.1}Ca_{0.9}V_2O_6$ ($A = Mg, Ca, Sr$) photoanodes were synthesized via time and energy-efficient solution combustion (SCS) method. The effect of introducing alkaline earth metals on crystal structure, microstructure, electronic, and optical properties of copper metavanadates was investigated by powder x-ray diffraction (PXRD), scanning electron microscopy (SEM), diffuse reflectance spectroscopy (DRS), transmission electron microscopy (TEM) and Raman spectroscopy. PXRD patterns, TEM, and Raman results showed that the polycrystalline powder samples were solid solutions of copper and alkaline earth metal metavanadates. DRS showed a decrease in the optical bandgap with Cu incorporation. In addition, the photoelectrochemical properties exhibited a strong dependence on the alloy composition. These semiconductor samples are potential candidates for photoelectrochemical water splitting, photocatalysis, phosphors, or photovoltaic devices.

Acknowledgements. This work was primarily supported by the National Science Foundation UTA/NU Partnership for Research and Education in Materials (NSF DMR-2122128).

Mechanistic Study of Direct Extraction of Fluorine from 2-Fluorobenzoic Acid and 2,6-difluorobenzoic Acid by Holmium Ion and the effect of fluorine extraction on tri-, hexa- and nona- cluster MOFs' Properties.

Hamid Reza Firouzi

Department of Chemistry

University of Texas at Dallas

Email: hxf180003@utdallas.edu

Classification: Graduate

Category: Inorganic/Analytical

Abstract:

Metal organic frameworks (MOFs) containing rare-earth elements are highly interesting and attractive due to their diverse coordination environments that allow for the formation of a variety of topologies. These materials have potential applications in optics, magnetism, and gas separation. Recently, 2-fluorobenzoic acid and 2,6-difluorobenzoic acid have been used as modulators to synthesize tri-, hexa-, and nona-clusters of lanthanides in MOFs. While these clusters were previously identified in Zr-MOFs like Zr-UIO-66, it was recently discovered that holmium ions can extract fluorine directly from these fluorinated modulators to form μ_3 -fluorine-bridging tri- and hexanuclear cluster MOFs using 2,2'-bipyridine-4,4'-dicarboxylic acid and terephthalic acid, respectively. The presence of these modulators also led to the formation of holmium fluoride precipitation. This study investigates the mechanism of direct fluorine extraction by holmium ions from these modulators, and possible change in magnetic, fluorescent, and CO₂ absorption properties of MOFs by easily changing the reaction condition.

Photoinduced electron transfer in the self-assembled metal-ligand axial coordination of Donor-Acceptor conjugates

Manan Guragain

Department of Chemistry, University of North Texas, Denton, TX

Email: mananguragain@my.unt.edu

Classification : Graduate

Category: Inorganic/Analytical

Abstract:

The electron transfer in the self-assembled via axial coordination of zinc tetraphenylporphyrin (ZnP), zinc phthalocyanine (ZnPC), and zinc naphthalocyanine (ZnNC) to highly electron deficient tetracyanobutadiene (TCBD) and dicyanodiquinodimethane (DCNQ) derivatives are investigated in a non-coordinating solvent, dichlorobenzene, using both steady state and time-resolved transient absorption technique. The formed donor-acceptor conjugates were fully characterized by spectroscopic, computational, and electrochemical methods. The binding constants measured for the 1:1 complex from optical absorption spectra data were found to be in a range of $1.28 * 10^4 \text{ M}^{-1}$ - $8.75 * 10^4 \text{ M}^{-1}$ suggesting the fairly stable complex formation. The established energy level diagrams suggested that the photoinduced electron transfer process is thermodynamically favorable. The photoinduced electron transfer was possible to establish from femtosecond transient absorption studies where as the cation and anion radicals were spectrally identified and the kinetics of photo events were determined.

Intramolecular Charge Transfer (ICT) in Hypervalent Antimony(V) and Phosphorus(V) Porphyrin-Based Push-Pull Systems

Jatan K. Sharma

Department of Chemistry, University of North Texas, Denton, TX 76203-5017, USA

Email:

Classification: Graduate

Category: Inorganic/Analytical

Abstract:

Donor-acceptor (D-A) constructs with “push–pull” architecture have gained a lot of attention in recent years because of their impressive properties in a variety of applications. For instance, a porphyrin comprised of a push-pull system with an electron-donating group at the peripheral position and an electron-withdrawing group at the opposite led to remarkably improved solar energy conversion efficiencies in dye-sensitized solar cells. This property not only minimizes the energy-wasting electron recombination in electron transfer reactions but also provides directionality to electron flow thus increasing the efficiencies of the photoinduced processes.

In the present presentation, push-pull style intramolecular charge transfer (ICT) in an elegantly designed antimony(V) and phosphorous (V) porphyrins peripherally decorated with electron-rich methoxy substituents will be demonstrated.^{1,2} While the +5 oxidation state of the central metal/nonmetal makes the porphyrin ring electron-poor (pull), the methoxy groups induce the opposite electron-rich (push) property ultimately promoting ICT. We demonstrate that the ICT is strongly dependent on the position of the methoxy groups on the phenyl ring and the polarity of the employed solvent. Steady-state and time-resolved emission, and transient absorption spectroscopic techniques have been employed to establish the tunable ICT in the studied systems. Furthermore, time-dependent density functional theory (TD-DFT) calculations have been performed to complement the experimental results. The systematic study of hypervalent porphyrins, especially the observed tunable ICT is expected to play an important role in prompting high-yield charge-separated states in multi-modular donor-acceptor systems comprised of hypervalent porphyrins for solar energy conversion and molecular electronic and photonic applications.

1. Jatan K. Sharma, Brandon J. Bayard, Nick Zosel, Syeda Ali, Noah Holzer, Vladimir N. Nesterov, Paul A. Karr, Francis D’Souza, Prashanth K. Poddutoori, ‘Hypervalent Phosphorus(V) Porphyrins with meso-Methoxyphenyl Substituents: Significance of Number and Position of Methoxy Groups in Promoting Intramolecular Charge Transfer.’ *Inorg. Chem.* **2022**, *61*, 16573-16585.
2. Noah Holzer, Jatan K. Sharma, Steven Peterson, Brandon J. Bayard, Vladimir N. Nesterov, Paul A. Karr, Francis D’Souza and Prashanth K. Poddutoori, Antimony(+5) ion-induced tunable intramolecular charge transfer in hypervalent antimony(V) porphyrins, *Dalton, Trans.* **2022**, *51*, 5890-5903.

Synthesis of Fluoro-Bridged Ho^{3+} and Gd^{3+} 1,3,5-Tris(4-carboxyphenyl)benzene Metal-Organic Frameworks from Perfluoroalkyl Substances

Simin Sheybani,¹ Muhammad Abbas,¹ Hamid R. Firouzi,¹ Zhifeng Xiao,² Hong-Cai Zhou,² Kenneth J. Balkus, Jr.^{1,*}

¹ Department of Chemistry and Biochemistry, The University of Texas at Dallas, Richardson, Texas 75080-3021, United States

² Department of Chemistry, Texas A&M University, College Station, Texas, 77843, United States

Email: simin.sheybani@utdallas.edu

Classification: Graduate

Category: Inorganic/Analytic

Abstract:

Rare-earth metal organic frameworks with their unique optical and electronic properties have gained interest in recent years. Previously, the synthesis of fluoro-bridged RE metal organic frameworks with the use of fluorinated modulators such as 2-fluorobenzoic acid or 2,6-difluorobenzoic acid have been reported. This research shows the cleavage of the C-F bond of perfluoroalkyl substances with rare-earth ions. Perfluoroalkyl substances (PFAS) as a large, complex, and ever-expanding group of manufactured compounds are used in a wide array of industrial and commercial products to make them more resistant to stains, grease, and water. Because the carbon-fluorine (C-F) bond is among the most chemically robust bonds; the degradation of fluorinated hydrocarbons in the environment is exceptionally difficult. Multiple fluorine atoms from perfluorooctanoic acid (PFOA) and perfluorohexanoic acid (PFHxA) can be removed and bridge the lanthanide atoms in the lanthanide fluoride structure. A new fluoro-bridged rare-earth (RE) metal-organic framework consisting of 15-connected nonanuclear and 9-connected trinuclear clusters $\{[\text{RE}_9-(\mu_3\text{-F})_{14}(\text{H}_2\text{O})_6][\text{RE}_3(\mu_3\text{-F})(\text{H}_2\text{O})_3](\text{HCO}_2)_3\text{-}(\text{BTB})_6\} \cdot (\text{solvent})_x$ (RE = Ho^{3+} and Gd^{3+}) was synthesized through the transformation of a dimeric complex formulated as bis(2,2'-bipyridine)tetrakis(μ -2-fluorobenzoato-O,O')-bis(2-fluorobenzoato)diRE(III) with the bridging linker 1,3,5-tri(4-carboxyphenyl)benzene (H_3BTB). The rare-earth metal ions Ho^{3+} and Gd^{3+} were also found to remove fluorine from other organo-fluorine compounds such as perfluorohexanoic acid (PFHxA) and perfluorooctanoic acid (PFOA) resulting in the new fluoro-bridged RE-MOFs.

Rare Earth metal oxide templated-conductive carbon for energy storage application.

Arslan Umer

Department of Chemistry and Biochemistry

The University of Texas at Dallas

Email: arslan.umer@utdallas.edu

Classification: Graduate

Category: Inorganic/Analytical

Abstract:

Increased energy consumption triggered the development of various energy storage devices. Supercapacitors have gained much attention as important energy storage devices due to their high-power density and long cycle life. The energy stored in a supercapacitor relies on two fundamental working principles, electric double layer capacitance (EDLC) and pseudocapacitance (PC). Meeting both characteristics within a single material has been a hot research topic, but intrinsic materials limitations have severely hindered it. Here we present an approach to design a hybrid material that combines both EDLC and PC within the same material for better performance than conventional material based on individual mechanisms. For this, the synthesis of highly conductive carbon by using rare-earth metal hydroxide as a template followed by its coupling with redox-active material to get the synergetic effects between EDLC from conductive carbon and PC from the redox-active compound. This work paves the door to develop novel hybrid supercapacitors.

Materials Abstracts

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Biochemistry



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Probing lone pairs and vacancies effects on optoelectronic properties of TeO₂ polymorphs from first principles

Hoa H. Nguyen¹, Robin T. Macaluso¹, Muhammad N. Huda²

¹Department of Chemistry & Biochemistry

²Department of Physics

University of Texas at Arlington

Email: hoa.nguyen2@mavs.uta.edu

Classification: Graduate

Category: Materials

Abstract:

With high refractive index and third order optical susceptibility that is 50 times larger than silica glass, tellurium dioxide-based glasses have attracted a lot of attention on their optoelectronic properties and technological applications. Three known tellurium dioxide phases are α -TeO₂, β -TeO₂ and γ -TeO₂. First-principles density functional theory calculations on the structural, electronic, and optical properties of all three TeO₂ polymorphs were performed to investigate the effects of Te⁴⁺ 5s² lone pairs and oxygen defects on the local atomic structure and optoelectronic properties with the focus on α -TeO₂. Hybrid functionals were employed with generalized gradient approximation (GGA) to emphasize the localization of the lone pairs. All three crystalline TeO₂ phases are wide-gap semiconductors and have Te⁴⁺ 5s² lone pairs contribution near the Fermi level, affecting the optical properties. Due to presence of the lone pairs and the favorable oxygen defects, the local symmetry of α -TeO₂ is broken. Thus, creating asymmetric electron density, which contributes to the cause of nonlinear optical effect.

Establishing Synthetic Strategies and Structure-Property Relationships for Oxytellurides

Melissa Orr

Department of Chemistry and Biochemistry

The University of Texas at Arlington

Email: melissa.orr@mavs.uta.edu

Classification: Graduate

Category: Materials

Abstract:

Heteroanionic compounds have recently gained significant attention as exploration of anion composition presents an exciting opportunity to strategically target new materials and modify physical properties. Among heteroanionic materials, oxytellurides are highlighted as promising candidates in various green energy applications such as transparent semiconductors and thermoelectrics; yet they remain relatively underexplored. In this work, the series $\text{Ln}_2\text{O}_2\text{Te}$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}$), featuring oxide and telluride anions, was synthesized by two different solid-state methods. Powder X-ray diffraction and Rietveld analyses were used for structural determination and reveal a layered structure with segregated hard and soft anions. Optical properties were characterized by diffuse reflectance spectroscopy and band gaps are estimated in the semiconducting range $\sim 2.1\text{-}2.7$ eV. Differential scanning calorimetry and thermogravimetric analyses, coupled with *in situ* diffraction experiments indicate phase transformations that showcase the broad range of tellurium oxidation states, as well as its unique reactivity. We find $\text{Ce}_2\text{O}_2\text{Te}$ to be air sensitive and demonstrate instability in ambient conditions by timelapse X-ray diffraction and diffuse reflectance spectroscopy experiments.

Unlocking the Potential of Wrinkled Mesoporous Silica through SPIONs Encapsulation: A Promising Path to Advanced Materials

A. K. M. Nur Alam Siddiki, Kenneth J Balkus Jr.

Department of Chemistry and Biochemistry, The University of Texas at Dallas, TX 75080, USA

Email: siddiki@utdallas.edu

Classification: Graduate

Category: Materials

Abstract:

Wrinkled mesoporous silica is a unique porous material with cone-shaped pores formed by a wrinkled structure, which can be fabricated with various morphologies and pore structures. This study reports a convenient method of encapsulating superparamagnetic iron oxide nanoparticles (SPIONs) within the core of wrinkled mesoporous silica, unlocking its potential for imaging, plasmonic, and photothermal applications. SPIONs were synthesized via a reduction-precipitation method and encapsulated in the core of wrinkled mesoporous silica using a surfactant template during synthesis. The resulting mesoporous silica particles were characterized using transmission electron microscopy (TEM), scanning electron microscopy (SEM), Physical Property Measurement System (PPMS), and X-ray diffraction (XRD). TEM images show that the wrinkled structure effectively encapsulates the SPIONs within the core, while SEM images reveal the conical shape and wide openings of the pores. The encapsulation of SPIONs within wrinkled mesoporous silica provides several advantages, including protection against oxidation, improved dispersibility and colloidal stability, as well as a surface for targeted delivery and drug molecule conjugation.

Stability, Selectivity and NRR Activity of Magnetron Sputtered Titanium Oxynitride at Different pH Values

Precious Chukwunenye, Ashwin Ganesan, Mojgan Gharaee, Kabirat Balogun, Qasim Adesope, Stella Chinelo Amagbor, Teresa D. Golden, Francis D'Souza, Thomas R. Cundari, and Jeffry A. Kelber

Department of Chemistry

University of North Texas

Email: PreciousChukwunenye@my.unt.edu

Classification: Graduate

Category: Materials

Abstract:

The development of electrocatalysts for the nitrogen reduction reaction (NRR) is of broad interest. An important but often ignored factor in the design of electrocatalysts is their long-term electrochemical stability. Titanium oxynitride films were deposited using DC magnetron sputter deposition and tested for NRR activity and stability, using electrocatalytic current–potential measurements, fluorescence, absorption, and GC measurements of NH_3 production, *ex-situ* X-ray photoelectron spectroscopy (XPS) and *in-situ* XPS with controlled transfer between ultrahigh vacuum combined with electrochemistry environments (UHV-EC). In acidic pH, there is the continued formation and slow dissolution of a Ti (IV) overlayer. At neutral or basic pH, however, a Ti (IV) overlayer also develops, but is stable in solution, inhibiting NRR activity. DFT calculations showed that Ti (IV) would not bind to N_2 consistent with results of inactivity at neutral and basic pH. GC mass spectrometry studies indicate an absence of hydrogen evolution at acidic, neutral and basic pH. The absence of hydrogen evolution is consistent with DFT calculations indicating that N_2/Ti (III) binding is energetically favored over $\text{H}_2\text{O}/\text{Ti}$ (III) binding.

Surface changes and stability of Vanadium oxide thin film at ambient and electrochemical conditions for nitrogen reduction; Surface science approach

Kabirat Balogun, Precious Chukwunenye, Ashwin Ganesan, Qasim Adesope, Stella Chinelo Amagbor, Dominic Willadsen, Slavomir Nemšák, Paul S. Bagus, Thomas R. Cundari, Francis D'Souza, and Jeffry A. Kelber

Department of Chemistry

University of North Texas

Email: KabiratBalogun@my.unt.edu

Classification: Graduate

Category: Materials

Abstract:

The electrocatalytic reduction of N_2 to NH_3 (the nitrogen reduction reaction—NRR) is an environmentally and energy-friendly alternative to the Haber-Bosch process, which accounts for ~ 2% of world energy consumption.

Understanding which catalyst oxidation states are most catalytically active for NRR and yet stable under relevant conditions is of importance in understanding and predicting catalyst effectiveness. We have demonstrated vanadium oxide to be NRR active at pH 7 [1]. Near ambient pressure XPS (NAP-XPS) was used to monitor N_2 interaction at the solid/vapor interface of a polycrystalline VO_x thin film at room temperature and up to 10^{-1} Torr pressure with less than a monolayer N_2 coverage in the presence and absence of water vapor [2]. XPS spectra acquired showed N_2 adsorption at 10^{-5} Torr with features at 396 eV and 401 eV, these features remained after pump down indicating a strong interaction. DFT calculation results show N_2 preferential bonding to V(III) even in the presence of water vapor. Hartree-Fock-based calculations explained the two N 1s features as normal and Shake-up configuration for N_2 bound end-on to a V(III) center, with binding energy difference in agreement with experimental data [2]. XPS data obtained after controlled transfer of vanadium oxide samples between electrochemical and UHV/XPS environments demonstrate the stability of V(III) state under relevant electrochemical conditions.

ACKNOWLEDGEMENTS

Work at UNT was supported by NSF under grant DMR 2112864, by Grant CHE-1531468 for the CASCaM HPC cluster, by NSF-REU grant CHE-1757946 (DW) and by the DOE Geosciences Program at Pacific Northwest National Laboratories (PSB). NAP-XPS studies were performed at the Advanced Light Source, supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences and Materials Sciences Division of the U.S. Department of Energy at the Lawrence Berkeley National Laboratory under Contract No. DE-AC02-05CH11231

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Superhydrophobic surface modification with perfluoro-hydrocarbons: preparation and characterization

Oluchukwu Virginia Igboenyasi, Bootpakdeetam Pawarat, Brian Dennis and Frederick MacDonnell

Department of Chemistry and Biochemistry

The University of Texas at Arlington

Email: oluchukwuvirgin.igboenyasi@mavs.uta.edu

Classification: Graduate

Category: Materials

Abstract:

Hydrophobicity is the ability to repel water. Superhydrophobic surfaces with high water repulsion have diverse applications in textile, automotive, medical, marine, and aerospace industries. The peculiar ability of these surfaces to exclude and highly repel water have increased their use in protective and self-cleaning coatings, automobiles, corrosion resistant coatings, biosensors, and protection of electronic devices in wet or humid environment. This study involves modification of alumina and silica surfaces with perfluoro carbons which can alter the hydrophilicity of the surface and potentially work to exclude water from the modified surfaces, even at high water partial pressures. We explored the best method of modification, hydrophobic properties, thermal stability of three different perfluoro surface modifying agents (Perfluorooctanesulfonic acid, perfluorobutanesulfonic acid and perfluorooctyltriethoxysilane) and the effect of the superhydrophobic modification on the stability and textural properties of the modified alumina and silica monoliths. The minimum amount of loading of the perfluorocarbons was established to be 10% by mass of the monolith. Perfluorobutanesulfonic acid was the least hydrophobic with a contact angle of 143° and a sliding angle of 11° while the other two perfluorocarbons show superhydrophobicity with contact angle above 150° and sliding angle of 5° for perfluorooctanesulfonic acid and 0° for perfluorooctyltriethoxysilane. Perfluorooctyltriethoxysilane maintains thermal stability and hydrophobicity up to 400°C on silica and 300°C on alumina. The high thermal stability on silica could be attributed to the silane head group on the perfluorocarbon forming a stronger bond with the silica monolith which requires higher temperature and thermal stress to dissociate. Perfluorooctanesulfonic acid maintained thermal stability and hydrophobicity up to 320°C on alumina surface and 200°C for silica surface.

Self-assembling peptides with internal ionizable non-natural amino acids: A new approach to pH-responsive peptide materials

Haritha Asokan-Sheeja, Su Yang, Ashley Adones, Weike Chen, He Dong*

Department of Chemistry and Biochemistry

The University of Texas at Arlington

Email: hxa8189@mavs.uta.edu

Classification: Graduate

Category: Materials

Abstract:

The recent developments in self-assembling peptide materials have led to a growing interest in their potential biomedical and biotechnological applications, particularly in targeted therapy and cancer therapy. To enhance the biological functions of these materials, it is desirable to introduce and control their pH responsiveness. Taking inspiration from proteins containing internal ionizable residues, we present a straightforward approach to construct pH-responsive peptide assemblies containing unnatural ionic amino acids with an aliphatic tertiary butyl amine side chain denoted X_b . To demonstrate this concept, we incorporated X_b into a multidomain peptide (MDP) that self-assembles into a sandwich-like β -sheet nanofiber, in which hydrophobic residues are embedded within the core of the assembly. By replacing some hydrophobic residues with X_b , we obtained nanofibers with a proton-ionizable hydrophobic core, enabling self-assembly under pH-induced conditions. We observed that a local hydrophobic environment can shift the pK_a of X_b from its typical basic range for free amines to a biologically relevant weakly acidic range. Our biophysical analyses, including CD, NMR, and AUC, confirmed pH-dependent self-assembly. Furthermore, our preliminary antimicrobial studies showed that the acidity-triggered properties of these nanofibers could combat bacterial growth. These findings offer valuable insights into the fundamental understanding of pH-triggered peptide self-assembly and hold significant promise for bacterial cell-targeted therapeutic delivery. Future studies will focus on creating a library of non-natural amino acids with tertiary amine groups, abbreviated as X. As part of this research, non-natural amino acids

containing a tertiary amine group can be used as tunable hydrophobic groups at various pH levels to create pH-responsive nanomaterials.

Improving the Reliability of Solder Bonding in IC Packaging Devices with a Cu Passivation Coating

Kevin Antony Jesu Durai

Department of Chemistry

University of North Texas

Email: kevinantony@my.unt.edu

Classification: Graduate

Category: Materials

Abstract:

Solder bonding is a critical process for the miniaturization of high-density input/output (I/O) devices. However, the process poses significant challenges due to the quick oxidation of copper bonding substrate at high temperatures needed for solder reflow. While the industry uses solder flux to dissolve copper oxides and organic contaminants, this method can cause corrosion and electrical leakage at the bonded interface, ultimately leading to a decrease in device reliability. To overcome these challenges, we have been exploring a low-cost copper-selective passivation process that aim to increase the reliability of solder bonding for copper bonding pads during IC packaging manufacturing process. Typical lead-free solder like SAC305 is a lead-free Tin/Silver/Copper alloys that contain 96.5% Tin (Sn), 3% Silver (Ag), and 0.5% Copper (Cu) with a melting range of 217°C – 219°C. To form a strong Cu/solder bond, the devices undergo either mass reflow or thermal compression bonding processes which use elevated temperature of 220-260°C. In this work, we report the analytical metrology development effort to monitor both nanometer growth of passivation coating and oxide growth on Cu substrate. With careful interfacial chemistry control on Cu surface, the passivation layers (<10 nm) have shown good protection against thermal oxidation of Cu substrate. SAC305 solder balls was used to bond on passivated Cu substrate with and without N₂ purging conditions and no chemically-loaded fluxes were used. We utilized SEM and cross section polishing to explore intermetallic formation between SAC305 solder and Cu bonding substrate with the protection of passivating layer. Our data suggest that the proposed passivation coating process is a simple, cost-effective, and potentially a reliable solution for protecting the copper interface during solder bonding.

Development of an Operando Fourier Transform Infrared Electrochemical Analysis for Mechanistic Insights into Nitrogen Reduction Reaction

Dinesh Kumar Kumaravel, Oliver Chyan*

Department of Chemistry

University of North Texas

Email: dineshkumarkumaravel@my.unt.edu

Classification: Graduate

Category: Materials

Abstract:

The electrochemical reduction of nitrogen (N_2) to ammonia (NH_3) is a promising alternative to the energy-intensive Haber-Bosch process for sustainable ammonia production. However, the mechanistic understanding of this complex reaction remains limited, hindering the rational design of efficient electrocatalysts. Here, we report the development of an Operando Fourier Transform Infrared (FT-IR) electrochemical cell for the real-time investigation of the nitrogen reduction reaction (NRR) and identifying key intermediates and reaction pathways. After Constructing the cell, initial Optimization of the incidence angle and catalyst thickness is done with Potassium ferricyanide experiments over 10 nm and 20nm Cu (Copper) films. The Results showed a change in the 2093 cm^{-1} $C \equiv N$ stretching peak for a corresponding increase in Copper thickness which helped us determine the catalyst's thickness without affecting the signal-to-noise (S/N) ratio.

Further the results from the FT-IR spectroelectrochemical investigation of Acetate buffer with (Cu) Copper film showed an increase in 1451 cm^{-1} ($Cu-COO^-$ stretch) peak when sweeping the potential anodically from 0.06V to 0.26 with a scan rate of 10mV/sec even when it is scanned only once, thereby confirming the sensitivity of this Operando Cell. The initial Mechanistic study has been done with Vanadium Oxy Nitride as an electrocatalyst for NRR. The first results showed a severe delamination of Vanadium Oxynitride films over Si- Hemisphere. On Further investigation, it is found that a few nm of Titanium would serve as an adhesion layer without affecting much of the S/N ratio. The Operando FT-IR with VO_xN_y films, when they are cathodically polarized with -0.8V vs Ag/AgCl under Nitrogen saturated solutions has been observed. The results from the Macro experiment showed an increase in peaks of 3467 cm^{-1} , 1652 cm^{-1} , 1451 cm^{-1} , 1225 cm^{-1} , and 1110 cm^{-1} , corresponding to various intermediates and water absorption in the catalyst layer. Furthermore, we observed an irreversible surface hydration over the catalyst. This work demonstrates the potential of operando FT-IR electrochemical analysis as a powerful tool for elucidating the mechanistic aspects of complex electrochemical reactions and accelerating the progress towards sustainable ammonia production.

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Cyclooctatetraene attached π conjugated porphyrins and optoelectronic studies on their conformational planarization state

Saad Shaikh

Department of Chemistry,
University of North Texas

Email: Saadshaikh@my.unt.edu

Classification: Graduate

Category: Organic

Abstract:

Cyclooctatetraene with 8π electron system is non-aromatic failing to satisfy the important Hückel's criteria. The energetically favored tub-shaped conformation allows this molecule to avoid conjugation with the alternate double bonds within the ring. Upon excitation, cyclooctatetraene will be planarized due to aromatization, and it is thus of interest in fundamental research because of their $4n+2$ excited-state aromaticity relevant to extended Baird's rule¹. Baird's rules suggest that annulenes that follow $4n$ and $4n+2$ criteria in their ground state switches their aromaticity in their excited state. There have been growing interests to study aromaticity reversal phenomena using aromatic and antiaromatic annulene systems and the non-aromatic cyclooctatetraene molecule. In this work, cyclooctatetraene moieties were incorporated into porphyrins to construct cyclooctatetraene-porphyrin fused π -systems. The impact of the exotic cycles on the electronic, optical, and aromatic properties of porphyrins were investigated using UV-Vis spectroscopy, fluorescence, transient absorption spectroscopy and spectroelectrochemistry.

Development of Concise Asymmetric Total Synthesis of Imidazolyl-quinolone Ceratinadin B

Anasuya Ghorai

Department of Chemistry and Biochemistry

The University of Texas at Arlington

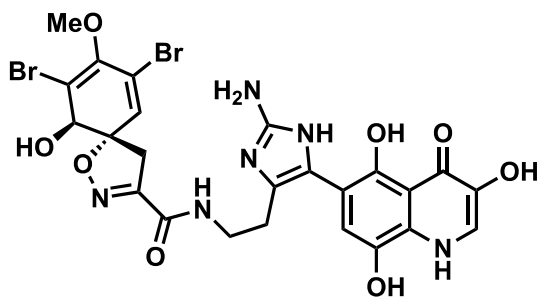
Email: axg7274@mavs.uta.edu

Classification: Graduate

Category: Organic

Abstract:

Natural products synthesis has inspired incredible advances in the development of new synthetic methods and strategies for the construction of heterocycles. Marine sponges of the order *Verongida* are rich source of dibromotyrosine alkaloids possessing three common structure elements: a central amide bond, an oxyamine on the carboxy side of the amide, and polar substituents on the amino side. In this study, we propose an asymmetric total synthesis of ceratinadin B, a dibromotyrosine natural product centered around the union of two key fragments: an unusual bis heterocycle **imidazolyl-quinolone** framework and a more common **spiroisoxazoline** moiety. Quinolone-imidazole-containing alkaloids are of great importance due to their special structural properties and potent bioactivities. Ceratinadin B is an attractive target for the treatment of drug-resistant strains of *Mycobacterium tuberculosis*, the causative agent of TB - a leading pathogenic cause of death worldwide. The natural product was screened using a fluorescence-detected assay for MCA inhibition and it exhibited potent activity against mycothiol S-amidase ($IC_{50} = 3\mu M$). The connection between the imidazole and the quinolone is quite unique in natural products and its construction is a key step in the total synthesis. Sonogashira cross-coupling reaction, a key step for the synthesis of 2-amino imidazolyl quinolone was achieved and further hydration of alkyne followed by alpha bromination/iodination will set the stage to install the 2-aminoimidazole. Encouraging prior preliminary data have been secured for an asymmetric Pd/Cu co-catalyzed dearomatizing spirocyclization to afford the enantioenriched spiroisoxazoline framework but requires confirmation and optimization. Our plan is to investigate the key reactions involved in the development of spirobicyclic molecule and finally unite the two fragments to obtain the target natural product ceratinadin B in the shortest possible routes.



Ceratinadin B

Synthetic studies on dearomatizing cyclization of ureas

Nazmee Parveen

Department of Chemistry and Biochemistry

The University of Texas at Arlington

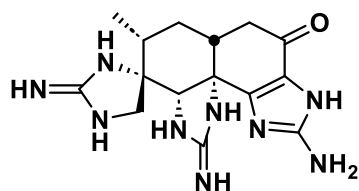
Email: nazmee.parveen@mavs.uta.edu

Classification: Graduate

Category: Organic

Abstract:

Dearomatization of aromatic compounds is a powerful synthetic tool for construction of highly functionalized frameworks primed for further elaboration. Loss of aromaticity in benzene derivatives have garnered a lot of interest in recent years as it results in chemical scaffolds that can be useful in total synthesis of natural products. In particular, oxidative methods have been used effectively to disrupt aromaticity. When these oxidative dearomatization reactions occur intramolecularly, it may give rise to spirocyclic systems. These chemical transformations result in formation of an electron deficient system from an electron rich aromatic system which can react readily with nucleophiles or act as a dienophile. Hence, these reactions are attractive owing to their ability to build up spirocyclic systems rapidly which can undergo further functionalization to form a broad range of derivatives. Our research group is interested in studying the oxidative dearomatizing cyclization of ureas and guanidines using hypervalent iodine reagents and investigate functionalization of dearomatized products to form building blocks of marine natural product KB343 which was isolated from the aqueous extract of zoantharian, *Epizoanthus illoricatus* from the Republic of Palau in 2018 by Sakai's group. Our initial attempts to develop oxidative dearomatizing conditions to target the spirocyclization of N-methoxy tri-substituted ureas have resulted in formation of spiro imidazolinones in moderate to good yield whereas di-substituted urea derivatives do not follow the oxidative dearomatization pathways but undergo net nucleophilic attack by the fluorinated alcohol solvent. Our plan is to apply the developed oxidative dearomatization conditions to study the spirocyclization of guanidines and to utilize this chemistry to target the total synthesis of KB343 which consists of three cyclic guanidines in one ring system.



KB343

Breaking-Down PFAS During Rare-Earth Metal-Organic Frameworks Synthesis

Muhammad Abbas, Kenneth J. Balkus Jr.

Department of Chemistry and Biochemistry

The University of Texas at Dallas

Email: Abbas@utdallas.edu

Classification: Graduate

Category: Organic

Abstract:

Per, and Polyfluoroalkyl substances (PFAS), are a group of more than 9000 thousand human-made chemicals. The carbon and Fluorine atoms form among the strongest chemical bond in organic chemistry. They are used in various consumer and industrial products, including protective and non-stick coatings, waterproof fabrics, and firefighting foams. PFAS contaminations have the potential to affect growth, learning and behavior of children. They can also lead to other adverse health effects, such as increased cholesterol levels, cancer, liver damage, and weakened immune responsiveness. Metal-organic frameworks (MOFs) are porous crystalline materials constructed from organic linkers and metal ions (or clusters). We recently discovered rare-earth (RE) metals can break highly stable carbon-fluorine bonds in aromatic and aliphatic fluorinated compounds. RE metals make fluoro-bridged rare-earth (RE) clusters in MOFs. A series of RE MOFs (RE= Y, Eu, Gd, Tb, Dy, Ho, and Yb) will be discussed. The formation and role of fluoro-bridged rigid metal clusters will also be discussed. The presence of fluorine in hexaclusters was verified by XRD, EDS and XPS analysis. These MOFs are selective for CO₂ capture. The Eu-MOFs are fluorescent, their fluorescence can be tuned using mixed metals for thermo or host-guest based sensing applications. This study will also help to explore how presence of μ_3 -F bridging could increase the fluorescence intensity in hexacluster MOFs.

Studies toward a total synthesis of the bioactive pyrrole-imidazole alkaloid Ageliferin- a marine origin metabolite

Nilakshi Dey, Moumita Singha Roy, and Carl J. Lovely*

Department of Chemistry and Biochemistry

University of Texas at Arlington

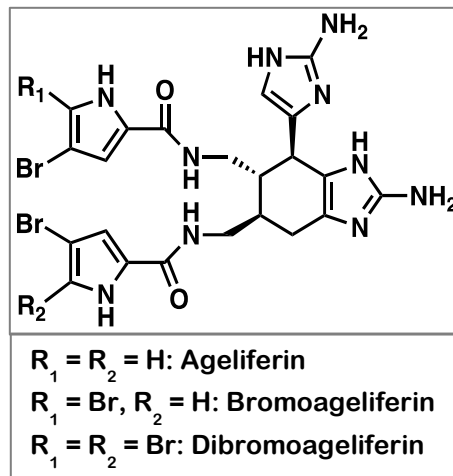
Email: nxd7569@mavs.uta.edu

Classification: Graduate

Category: Organic

Abstract :

In the marine environment, sponges (porifera) synthesize fascinating natural products which can be an attractive resource for novel drug candidates due to their rich chemodiversity and wide spectrum bio-activities. Among other collections of natural products, derivatives of pyrrole imidazole alkaloids (PIA), first reported in 1969, have emerged as a family of great interest. This study aims to achieve a total synthesis of ageliferin, which is a bromopyrrole imidazole alkaloids isolated initially from a Caribbean sponge and later from an Okinawan marine sponge in 1990. Our proposed strategy seeks to develop to a total synthesis of ageliferin by the shortest route desired to date. Ageliferin contains a tetrahydrobenzimidazole moiety, and to construct such type of building block, we explored the Tsuji-trost reaction between an activated vinylimidazole and N-phenyl urazole to form a bisvinylimidazole intermediate and a N-N bond framework. This advanced intermediate bisvinylimidazole will be further subjected to intramolecular Diels-Alder reaction followed by N-N bond cleavage to generate the cyclic framework of ageliferin. Reduction of nonactivated N-N bond is less explored, and our final focus is to investigate the best conditions for the reduction which may be helpful to other pyrrole-imidazole alkaloids synthesis as well.



One-Pot Formal Carboradiofluorination of Alkenes: A Toolkit for Positron Emission Tomography Imaging Probe Development

Mónica Rivas, Sashi Debnath[‡], Sachin Giri[‡], Yusuf M. Noffel, Xiankai Sun,^{*} and Vladimir Gevorgyan^{*}

Department of Chemistry and Biochemistry

The University of Texas at Dallas

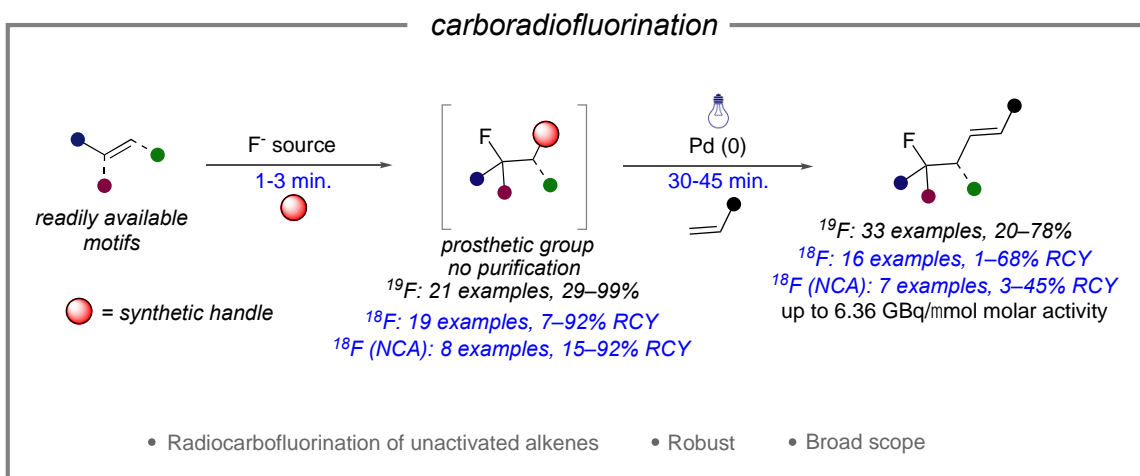
Email: sachin.giri@utdallas.edu

Classification: Graduate

Category: Organic

Abstract:

We have developed a method for the formal carboradiofluorination of alkenes, with the alkenes serving as both prosthetic group precursors and coupling partners. This one-pot-two-step approach involves a Markovnikov-selective iodofluorination followed by a visible light induced palladium-catalyzed Heck reaction, producing over thirty fluorine-labeled analogues of various bioactive molecules. The method was then successfully translated to radiofluorination for positron emission tomography (PET) imaging probe development. The iodofluorinated intermediates, which represent a new class of prosthetic groups for PET radiotracer synthesis, were obtained in moderate to excellent radiochemical conversion and the method was automated in a radiosynthesis module, with simple filtration affording >99% pure product. These intermediates were then used for alkenylfluorination reaction in a one-pot fashion, with generally good radiochemical conversion. Moreover, molar activities up to 6.3 GBq were obtained when the protocol was further optimized for no-carrier added (NCA) conditions. We report the first case of direct alkyfluorination of electron rich alkenes to produce α -fluoroethers in good to excellent yield and radiochemical conversion. This method is anticipated to stimulate the development of new radiotracers for PET imaging probe development.



Physical and Computational Chemistry Abstracts

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Rank-Reduced representations of the connected triples in Coupled Cluster theory

Tingting Zhao, Dr. Devin Matthews

Department of Chemistry

Southern Methodist University

Email: zhaot@smu.edu Classification:

Classification: Graduate

Category: Physical/Computational

Abstract:

Coupled cluster (CC) has proven to be one of the most successful quantum chemical methods, however, it is plagued by the presence of high-rank tensors: the two-electron integrals and the T (cluster) amplitudes. This high dimensionality leads to steep polynomial scaling. Reducing the scaling via rankreduction presents two main difficulties: the lack of a clear prescription for the factorized (rank-reduced) form of the T amplitudes, and the complexity and extreme non-linearity of the rank-reduced coupled cluster equations. Despite these difficulties, many methods have been proposed, such as the singularvalue decomposition coupled cluster with triple excitations (SVD-CCSDT) of Lesiuk, and the rank-reduced coupled cluster method of Parrish et al. (RR-CCSD and related methods). We discuss recent developments connecting rank-reducing factorizations of the integrals and doubles amplitudes (as in density fitting/resolution-of-the-identity and RR-CCSD), a Tucker-decomposed form of the triple amplitudes (as in SVD-CCSDT). We also explore graph-based diagrammatic techniques and knowledge-based algorithmic search through the Design-by-Transformation methodology to produce optimal working equations. Such automated techniques also enable new methods beyond the complexity of hand-derivation such as rankreduced CCSD(T), SVD-CCSDTQ, etc. Reduced-scaling implementations of such methods will enable new model chemistries suitable for accurate thermochemistry (at the ~ 1 kJ/mol scale) of molecules with as many as 12 first- or second-row atoms.

Elucidating Upon the Role of Hydrogen Bonding Networks in X-Ray Absorption Spectra

Alexis Antoinette Ann Delgado, Devin A. Matthews

Department of Chemistry

Southern Methodist University

Email: aadelgado@smu.edu

Classification: Postdoctoral

Category: Physical/Computational

Abstract:

The abnormal properties of water, governed by hydrogen-bonded networks, give way to different phases of disordered and ordered microstructures. Though x-ray based (core-hole) spectroscopies provide details on the local structure of water, some spectral features observed in experimental spectra have yet to be reproduced theoretically. For small gas-phase systems the coupled cluster (CC) and equation-of-motion CC (EOM-CC) methods have shown exceptional success in describing molecular properties and spectra. However, in core-hole spectroscopies, the occurrence of orbital relaxation upon the excitation of core electrons is an obstacle even for EOM-CC. Recently developed transition-potential coupled cluster (TP-CC) and core-triples similaritytransform equation-of-motion (STEOM-CCSD+cT) methods nearly eliminate the orbital relaxation error and produce accurate x-ray absorption spectra (XAS) for molecules with first-row atoms. In this work we compute oxygen K-edge XAS spectra for the water dimer using CCSD, STEOM-CCSD+cT, and TP-CCSD with contracted and uncontracted Pople basis sets. From our results we will understand, in greater detail, the effect of basis sets in CC calculations of core-level states of (H₂O)₂ dimer, we will create a protocol to establish the best theoretical estimates from XAS, and we will determine the most cost-effective strategy. This work will further applied in correlating XAS findings of small water clusters ((H₂O)_n, n = 3-8) with our dimer-based investigation in order to isolate cooperative effects and deviations from ideal additive behavior and to correlate spectral features with the hydrogen bond network topology.

Computational Study of Metal Oxynitride Thin-Film Electrocatalysts for Nitrogen Reduction

Mojgan Gharaee Prof.

Thomas R. Cundari

Department of Chemistry

University of North Texas

Email: Mojgangharaee@my.unt.edu

Classification: Graduate

Category: Physical/Computational

Abstract:

The Haber-Bosch process is a crucial method for reducing dinitrogen to ammonia, playing a vital role in agriculture, and consuming approximately 2% of global energy. However, this process also generates a significant amount of CO₂. To address this issue, researchers are investigating electrocatalytic reduction of N₂, or the nitrogen reduction reaction (NRR), as a more environmentally friendly approach for ammonia production. Many types of electrocatalysts, including noble and non-noble metal oxides and nitrides, are under study for this purpose.

Recently, there has been growing interest in Earth-abundant oxynitrides for NRR, although the catalytic mechanism is not yet fully understood. Through DFT calculations integrated with experiment, we have found that both lattice N and solvated N₂ can be reduced to ammonia by cathodic polarization of cobalt oxynitride films. The formation of CoN, Co-N=N-H, and other proposed reaction intermediates occurs preferentially on [Co]_O versus [Co]_N surface sites. Furthermore, the preferred pathway for this reaction (distal and alternating mechanism) varies among different metal oxynitrides, with CoO_xN_y and TiO_xN_y favoring alternating and distal mechanisms, respectively. Preliminary studies on different MO_xN_y catalysts suggest that the Volmer step (the first step in HER) may be favorable, but more research is under way to confirm this finding.

Recurrence Relation Schemes for Electron Repulsion Integral Computation on GPUs

Chao Yin, David Jiang, Alexis A.A. Delgado, Devin A. Matthews

Department of Chemistry

Southern Methodist University

Email: chaoy@smu.edu

Classification: Graduate

Category: Physical/Computational

Abstract:

The evaluation of electron repulsion integrals is the most common bottleneck in quantum chemistry. Integral evaluation algorithm development in coordination with computational hardware enhancement enables the application of computational chemistry on large chemical systems. In this work, the Obara-Saika (OS) and Head-Gordon-Pople (HGP) algorithms, based on recurrence relations, are implemented using a code-generation approach on both NVIDIA and AMD graphical processing units (GPUs) to accelerate the evaluation of electron repulsion integrals. We illustrate the interplay between algorithmic concerns and the parallel characteristics of GPUs which allow for efficient computations using these algorithms.

Computational Study of N-Fused Co-Porphyrins as Electrocatalysts for Nitrogen Reduction Reaction

Alireza Haji Seyed Javadi

Dr. Thomas R. Cundari

Department of Chemistry

University of North Texas

Email: SeyedAlirezaHajiseyedJavadi@my.unt.edu

Classification: Graduate

Category: Physical/Computational

Abstract (300 words or less):

The electrocatalytic reduction of nitrogen to ammonia using N-fused cobalt porphyrins (CoNHF) as a molecular catalyst was investigated in this study. Density functional theory (DFT) methods were employed to simulate the nitrogen reduction reaction (NRR), and different spin states were considered for both distal and alternating N₂ reduction pathways as well as a Mars-van-Krevelen (MVK) mechanism. It was indicated by our results that the alternating pathway was more favorable, as the CoNHF catalyst had a lower energy barrier for this pathway than the distal and MVK pathways. Furthermore, all first-row transition metals were studied and compared with cobalt. In general, apart from cobalt, which has the lowest energy pathway among all the first-row metals, NHF complexes of the early 2+ transition metal ions seem to have better performance for NRR than the late metals. It is suggested from our findings that N-fused porphyrins can be a promising candidate for the electrocatalytic reduction of nitrogen to ammonia under mild conditions.

Small-molecule perturbation of phospholipid bilayer as a possible cause and remedy of high-pressure neurological syndrome

Bibek Sapkota and Dr. Hao Yan

Department of Chemistry

University of North Texas

Email: bibeksapkota@my.unt.edu

Classification: Graduate

Category: Physical/Computational

Abstract:

Malfunction of the central nervous system experienced by deep divers, known as the high-pressure neurological syndrome (HPNS), poses a significant barrier to human exploration of the deep sea. While HPNS is pathologically connected with the inhalation of helium under high pressure, its molecular foundation remains unknown. Most current research focuses on understanding the interaction between helium and the neurotransmitter receptors, while its effect on the cell membrane has received far less attention. Here I show, using Raman spectroscopy and small-angle X-ray scattering, that gas molecules selectively disrupt the conformational order while retaining the long-range order of phospholipid bilayers under high pressure. Different inert gases (He, Ar, and Xe) exhibit distinctive effects on the phospholipid bilayer. Lastly, osmolytes such as trimethyl amine-N-oxide (TMAO) partially restore the conformational order. These results highlight the complexity of phospholipid-small-molecule interactions, and point to possible causes and remedies of HPNS.

Iterative Expansion of Protein Conformational Space with Variational Autoencoder

Hao Tian^a, Xi Jiang^b, Sian Xiao^a, Hunter La Force^a, Eric C. Larson^c, and Peng Tao^a

Department of Chemistry^a, Statistical Science^b, and Computer Science^c

Southern Methodist University

Email: sxiao@smu.edu

Classification: Graduate

Category: Physical/Computational

Abstract:

Molecular dynamics (MD) simulation is widely used to study protein conformations and dynamics. However, conventional simulation suffers from being trapped in some local energy minima that are hard to escape. Thus, most of the computational time is spent sampling in the already visited regions. This leads to an inefficient sampling process and further hinders the exploration of protein movements in affordable simulation time. The advancement of deep learning provides new opportunities for protein sampling. Variational autoencoders are a class of deep learning models to learn a low-dimensional representation (referred to as the latent space) that can capture the key features of the input data. Based on this characteristic, we proposed a new adaptive sampling method, latent space-assisted adaptive sampling for protein trajectories (LAST), to accelerate the exploration of protein conformational space. This method comprises cycles of (i) variational autoencoder training, (ii) seed structure selection on the latent space, and (iii) conformational sampling through additional MD simulations. The proposed approach is validated through the sampling of four structures of two protein systems: two metastable states of Escherichia coli adenosine kinase (ADK) and two native states of Vivid (VVD). In all four conformations, seed structures were shown to lie on the boundary of conformation distributions. Moreover, large conformational changes were observed in a shorter simulation time when compared with structural dissimilarity sampling (SDS) and conventional MD (cMD) simulations in both systems. In metastable ADK simulations, LAST explored two transition paths toward two stable states, while SDS explored only one and cMD neither. In VVD light state simulations, LAST was three times faster than cMD simulation with a similar conformational space. Overall, LAST is comparable to SDS and is a promising tool in adaptive sampling. The LAST method is publicly available at <https://github.com/smu-tao-group/LAST> to facilitate related research.

Investigation of a Series of Small Molecules as Lead Compounds for Lysyl hydroxylase-2 (LH2) Inhibition

Yazdan Maghsoud,¹ Erik Antonio Vázquez-Montelongo,² Xudong Yang,³ Juhoon Lee,⁴ Kevin N. Dalby,^{*4} Pengyu Ren,^{*3} and G. Andrés Cisneros^{*1,5}

¹ *Department of Chemistry and Biochemistry, The University of Texas at Dallas, Richardson, Texas 75080, USA*

² *Department of Physical Medicine and Rehabilitation, University of Texas Southwestern Medical Center, Dallas, Texas 75390, USA*

³ *Department of Biomedical Engineering, The University of Texas at Austin, Austin, Texas 78712, USA*

⁴ *Division of Chemical Biology and Medicinal Chemistry, College of Pharmacy, The University of Texas at Austin, Austin, Texas 78712, USA*

⁵ *Department of Physics, The University of Texas at Dallas, Richardson, Texas 75080, USA*

Email: YXM210021@utdallas.edu

Classification: Graduate

Category: Physical/Computational

Abstract:

Lysyl hydroxylase-2 (LH2) is a member of the Fe(II)/ α KG-dependent oxygenase superfamily. This enzyme catalyzes the hydroxylation of lysine to hydroxylysine in collagen, which results in stable hydroxylysine aldehyde-derived collagen cross-links (HLCCs). Accumulation of HLCCs due to the high amounts of LH2 leads to fibrosis and other types of cancer metastasis. Therefore, inhibiting this enzyme can be an effective way to confront these diseases. However, efficacious inhibitors of LH2 are still lacking. Intra-molecular tunnels for O₂ transport have also been reported in some members of the Fe(II)/ α KG-dependent superfamily. In this study, we have employed molecular docking and molecular dynamics (MD) in tandem with quantum mechanics/molecular mechanics (QM/MM) to study a series of forty-four small molecules as lead compounds to inhibit the LH2 activity. We have also investigated the existence of intramolecular tunnels for O₂ transport (a required co-substrate) into the LH2 active site and the possible impact of the ligands on these tunnels. Our tunneling analysis suggested the existence of several intra-molecular tunnels in both the apo- and holoenzyme. Three sets of molecules were investigated, starting with a series of structures having diketone, enol, or enolate ligand skeletons branched with aromatic rings and various electron-donating and electron-withdrawing groups. Our results suggest that the enolate form of diketone compounds makes strong interactions with the active site of LH2, and branching the enolate compounds with pyridinyl or phenyl groups increases the non-covalent interactions between the inhibitor and the residues of the binding pocket. Several of the tested ligands are seen to affect the enzyme's structure and possibly block (at least partially) the tunnels. Based on this, we designed a final set of compounds consisting of a series of enolate-based structures with morpholine/piperazine rings, several of which have been experimentally synthesized and tested. Two candidates have been identified as competitive inhibitors of α KG with IC₅₀ < 300 nM and < 500 nM, respectively, show a 9–10 fold selectivity for LH2 over LH1 and LH3, and one of them also exhibits anti-migration activity in 344SQ lung adenocarcinoma cell line.

The Electric Field-induced Second Energy Minima of Carbon Monoxide

Duc Anh Laj, Devin A. Matthews*

Department of Chemistry

Southern Methodist University

Email: damatthews@smu.edu

Classification: Graduate

Category: Physical/Computational

Abstract:

Potential energy surfaces (PES) play a foundational role in reaction dynamics analysis and molecular structure studies. Typically, the stable states and the transition states of a molecule occupy the stationary points on the PES, which is a function of the relative positions of the atoms. Some systems possess two stable isomeric forms that are under equilibrium and can be reversibly isomerized via chemical or photochemical activation, resulting in differing molecular properties such as polarity, optical properties, and steric hindrance. Alternatively, oriented external electric fields (OEFs) have in recent years been demonstrated as a feasible and powerful tool to modify the electronic transitions of molecules. We hypothesize that under the effect of an oriented electric field, some stable, uniconformational molecules can exhibit another energy minima on the molecular PES defined by external field orientation. We initially conduct a study of carbon monoxide molecule showing that the second energy minimum is created separately with an adequate strength of the applied electric field. With the same idea, it may be possible to convert many molecules into electric field-induced two-state molecules.

CO₂ Capture Using Nanomaterials: A Density Functional Theory Study

Dogukan Yazici, Emily Williams, Robin Macaluso¹, Michael Bozlar²

¹Department of Chemistry and Biochemistry

²Department of Mechanical and Aerospace Engineering

University of Texas at Arlington

Email: bozlar@uta.edu; robin.macaluso@uta.edu

Classification: Graduate

Category: Physical/Computational

Abstract:

Intensive human activities in recent decades have led to increased environmental concerns, including alarming levels of carbon dioxide (CO₂) emissions. CO₂ is a major anthropogenic greenhouse gas, mainly produced from excessive combustion of fossil fuels, which exacerbates greenhouse effect. In this work, we carry out numerical simulations to study the interaction of CO₂ molecules with Graphene; Graphene Oxide (GO); and Amino-functionalized GO structures based on adsorption energy values. First-Principle calculations are performed via Quantum ESPRESSO open-source simulation package with plane-wave basis set based on Density Functional Theory (DFT). The Projector Augmented-Wave (PAW) type pseudo-potentials are chosen to describe the electron-ion interactions. Perdew-Burke-Ernzerhof (PBE) functional with the Generalized Gradient Approximation (GGA) is used to define exchange-correlation energy of the electronic system. Convergence tests are performed to determine system parameters such as degauss, kinetic energy cut-off for wavefunctions - charge density and k-point set. Emphasis is put on surface simulations to determine the detailed electronic structures of the compounds studied. The position of functional groups, including Hydroxyl and Epoxide on the surface of GO is systematically calculated in accordance with the Carbon/Oxygen (C/O) ratio. Effects of functional groups on the structure of GO are determined by comparing their respective Density of States (DOS).

Computational investigation of the effects of a single point mutation on the structural and dynamical properties of DNA polymerase γ

Arkanil Roy¹, G Andrés Cisneros^{1,2}

1. Department of Chemistry and Biochemistry, University of Texas at Dallas

2. Department of Physics, University of Texas at Dallas

Email: arkanil.roy@utdallas.edu

Classification: Graduate

Category: Physical/Computational

Abstract:

DNA polymerase γ (pol γ) is the only polymerase present in the mitochondria and is responsible for the replication and maintenance of the mitochondrial DNA. Mutations in pol γ has been linked to various diseases and cancer. Clinical mutations at the R853 site have been shown to be related to diseases such as Alpers, Myocerebrohepatopathy and other Infantile Hepatocerebral Syndromes with mtDNA depletion (R853Q) and Progressive External Ophthalmoplegia (PEO) (R853W). This study aims to investigate the effect of a mutation on the same site, R853A, on the structure and function of the polymerase. Experimentally it has been observed that the mutation causes a change in the rate of DNA polymerization. We have carried out long time-scale Molecular Dynamics simulations on the wild type and mutant. Various structural and dynamical analyses have been done to understand better the atomic level differences between the systems. The results of these analyses will be discussed and will be compared and contrasted to experimental outcomes.

Computational Study of acyl chain hydrolysis in trans-AT Polyketide Synthase Enzyme

Upeksha C. Dissanayake¹, Christopher D. Fage², Matthew Jenner², G. Andrés Cisneros^{1,3*}

1. Department of Chemistry and Biochemistry, University of Texas at Dallas
2. Department of Chemistry, University of Warwick, UK
3. Department of Physics, University of Texas at Dallas

Email: upekshad@utdallas.edu

Classification: Graduate

Category: Physical/Computational

Abstract:

Polyketide synthases (PKSs) are a type of complex and large enzymes that play an important role in the biosynthesis of various bioactive natural products, that have applications in agriculture and medicine. Within PKSs, there is a class of trans-acting acyl transferase-like domains that have hydrolytic activity with acyl chains from Acyl Carrier Protein (ACP) domains. These domains are classified as acyl hydrolases (AH) because they differ from acyl transferase (AT) domains at the sequence level. Based on experimental findings, AH domains serve as proofreading enzymes for PKSs, hydrolyzing short acyl chain intermediates while having a trace hydrolysis with malonyl chain. This hydrolysis reaction occurs when acyl chains are transferred to Ser99 residue. This study was carried out to investigate why the hydrolysis reaction only occurs with acyl units and not malonyl, and to understand how these reactions work in Polyketide synthase enzyme. Molecular dynamics (MD) and quantum mechanics/molecular mechanics simulations were conducted on three different systems: apo AT, AT with acetylated Ser99 (acSer99), and AT with malonylated Ser99 (malSer99). Our simulation analysis reveals significant differences among the systems, indicating that the hydrolysis reaction considerably more favorable in acSer98 compared to malSer99.

Computational Characterization of Cancer-Associated Mutations on POT1

Mauricio Gerardo Martil de la Garza¹, Emmett Leddin¹, Carla Daniela Robles-Espinoza, David J. Adams, G. Andrés Cisneros^{1,4}

¹Department of Chemistry and Biochemistry, University of Texas at Dallas

²International Laboratory for Human Genome Research, UNAM

³Wellcome Sanger Institute

⁴Department of Physics, University of Texas at Dallas

Email: mauricio.martil@utdallas.edu

Classification: Graduate

Category: Physical/Computational

Abstract:

Mutations caused by single nucleotide polymorphisms (SNPs) have been associated with the development of cancer cells. Mutations on the protection of telomeres 1 (POT1) have been shown to increase the length of telomeres and facilitate the development of melanoma. POT1 plays an important role in the shelterin complex for the binding to the telomere and signals the end of the chromosomes. In this project, we explored three different mutations (K39N, C59Y and D224N) that have been experimentally shown to affect POT1. We used classical MD simulations to investigate changes in binding affinity, structural and dynamic behavior of the three POT1 variants compared to the wild type. Our results provide insights on the effects of each melanoma-associated mutation by observing changes in the first and second normal mode, as well as a decrease in the trend of the binding affinities and differences in the pattern for the hydrogen bonding. Our results are in agreement with the experimental data.

Catalysis by Horse Radish Peroxidase in aqueous [emim][EtSO₄]: A Molecular Dynamics and Quantum Mechanics/Molecular Mechanics investigation

Shubham Chatterjee¹, G. Andrés Cisneros^{1,2*}

¹Department of Chemistry and Biochemistry, University of Texas at Dallas, Richardson, Texas, 75080, United States

²Department of Physics, University of Texas at Dallas, Richardson, Texas, 75080, United States

Email:

Classification: Graduate

Category: Physical/Computational

Abstract:

Studies by Aqvist. et al. revealed that in specific homologs, the flexibility of surface residues affected the activation energies of catalysis. We hypothesize that solvents can affect the activation energy associated with enzymatic catalysis by affecting the flexibility of the surface residues. To test our hypothesis, we are investigating the catalysis by Horse Radish Peroxidase (HRP) in aqueous [emim][EtSO₄]. We have investigated the effects of the solvent on the structure of HRP via molecular dynamics (MD) simulations for 20 ns with Atomic Multipole Optimized Energetics for Biomolecular Applications (AMOEBA) polarizable force field, followed by structural and dynamic studies. The Root Mean Square Deviation (RMSD), Root Mean Square Fluctuation (RMSF), and potential energy analysis studies suggest an equilibrated system. Quantum Mechanics/Molecular Mechanics (QM/MM) modeling with Layered Interacting Chemical Models (LICHEM) indicates that a 17 kcal/mol activation energy is required for the catalytic reaction. The effects of residues around the active site of HRP are studied using Non-Covalent Interaction (NCI) analysis. This presentation will describe a comparative study of HRP catalysis by HRP in aqueous [emim][EtSO₄] and water, with further discussing about the effects of surface residues on reaction barrier associated with both the solutions.

New Reactions of Diazene and Related Species for Modeling Combustion of Amine Fuels

George Rawling, Paul Marshall, and Peter Glarborg

Department of Chemistry

University of North Texas

Email: georgerawling@my.unt.edu

Classification: Graduate

Category: Physical/Computational

Abstract:

There is increasing interest in investigating ammonia as a potential carbon-free fuel, which involves high concentrations of NH_3 in a high-pressure system. These conditions favor formation of N_2 -amines, which are formed from the recombination of amine radicals.

Potential energy surfaces for reactions involving N_2H_2 isomers of diazene (diimide) have been explored using density functional theory at the M06-2X/6-311++G(2df,2p) level, with single-point energies computed with the CBS-APNO method, which extrapolates CCSD(T) theory to the complete basis set limit with an RMS deviation of 0.7 kJ/mol from the ATcT data. As a check, CBS extrapolation of CCSD(T) data with the aug-cc-pVQZ and aug-cc-pV5Z basis set yields an RMS deviation of 1.0 kJ/mol from the ATcT data.

A focus is on processes that create or consume these species, and isomerization between the E (trans) and Z (cis) forms of HNNH and the importance of the diazene isomers. These include isomerization and dissociation pathways for HNNH [$\text{E-HNNH (+M)} \rightarrow \text{Z-HNNH (+M)}$], addition of H atoms to form N_2H_3 [$\text{H + HNNH (+M)} \rightarrow \text{N}_2\text{H}_3 (+\text{M})$], abstraction by H atoms yielding short-lived NNH [$\text{H + HNNH} \rightarrow \text{H}_2 + \text{NNH}$], and abstraction reactions of H with N_2H_3 [$\text{H + N}_2\text{H}_3 \rightarrow \text{H}_2 + \text{HNNH}$].

Transition state and capture theories are applied for high-pressure-limiting behavior, while low-pressure and falloff regions are characterized via the methods of Troe and coworkers. Rate constants and thermochemistry are computed to improve models of diamine chemistry, relevant to the combustion of NH_3 and N_2H_4 , especially at high concentrations, high pressures or under reducing conditions.

Results indicate that amine radical recombination mainly yields the E-HNNH isomer, while H-abstraction from N_2H_3 results in E-HNNH and H_2NN . However, at elevated temperature $\text{E} \rightarrow \text{Z}$ isomerization becomes competitive, and Z-HNNH, being more reactive, acts to enhance the diazene consumption rate.

Machine Learning Approaches for Tensor Hypercontraction

Ishna Satyarth, Gabriel Mongaras, Devin A. Matthews

Department of Chemistry

Southern Methodist University

Email: isatyarth@smu.edu

Classification: Graduate

Category: Physical/Computational

Abstract:

Wavefunction Wavefunction-based quantum methods are some of the most accurate tools for predicting and analyzing the electronic structure of molecules, in particular for accounting for dynamical electron correlation. However, most methods of including dynamical correlation, beyond the simple second-order Møller-Plesset perturbation theory (MP2) level, are too computationally expensive to apply to large molecules. Approximations which reduce scaling with system size are a potential remedy, such as the tensor hypercontraction (THC) technique of Hohenstein et al., but also result in additional sources of error.

Our goal is to automatically correct errors in THC-approximated methods using machine learning (ML). Specifically, we apply THC to third-order Møller-Plesset theory (MP3) as a simplified model for full coupled cluster with single and double excitations (CCSD), and train several machine learning models on observed THC errors from the Main Group Chemistry Database (MGCDB84). We have tested simple multiple linear regression (MLR) models, as well as more complex multi-layer perceptron neural network architectures. Potential systematic error cancellation is examined by comparing and cross-validating models trained on absolute and relative (e.g. reaction and interaction) energies. We discuss the potential for ML to correct THC-MP3, and potentially THC-CCSD errors compared to the "canonical" MP3 and CCSD reference values, as well as the practical aspects of training and deploying machine learning models in quantum chemistry calculations.

Additionally, we discuss initial work on training graph-based ML models for automating the determination of optimal contraction order for the kinds of complex contraction networks encountered in THC-MP and THC-CCSD theories.

Polymer Chemistry Abstracts

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Biochemistry



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Synthesis of disubstituted γ -amide ϵ -caprolactone monomers for the amphiphilic diblock copolymers in drug delivery applications

Himanshu Polara, Hanghang Wang, Abhi Bhadran, Tejas Shah, Godwin Babanyinah, Michael C. Biewer, Mihaela C. Stefan*

Department of Chemistry and Biochemistry
The University of Texas at Dallas, Richardson, Texas 75080

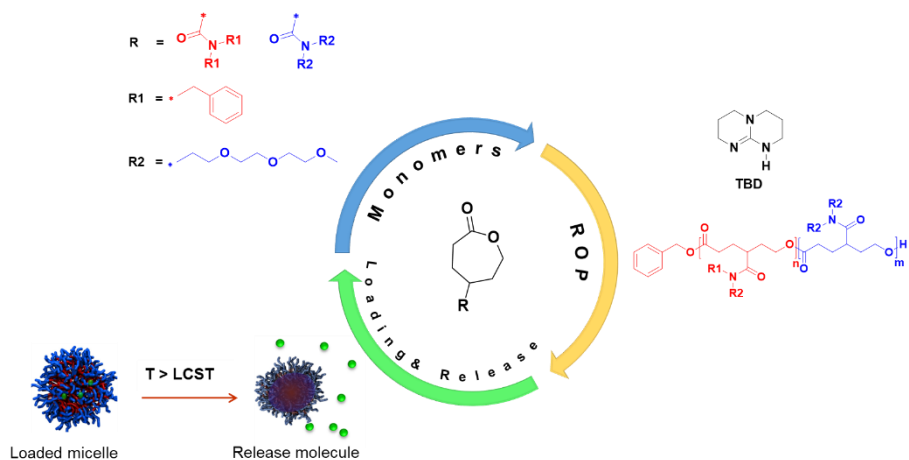
Email: Himanshu.Polara@UTDallas.edu

Classification: Graduate

Category: Polymer

Abstract:

Polycaprolactones (PCLs) are essential aliphatic polyesters for drug delivery due to their biodegradability, biocompatibility, and synthetic versatility. Introducing different substituents at γ -position of ϵ -caprolactone (ϵ -CL) monomers can easily tune the properties of synthetic polymers. Most studies involve single substituent at the γ -position of ϵ -CL monomers due to ease of functionalization. This is a drawback since the side chain significantly affects the polymer's properties. Disubstituted γ -amide ϵ -CL monomers can double the density of substituents on a single polymer chain, which directly affects the properties of polymeric micelles, such as load capacity (LC) and thermodynamic stability.



Our research aims to synthesize disubstituted amphiphilic block copolymers (AmBCs) from the novel disubstituted γ -amide ϵ -CL monomers and investigate their properties. The amide functionality allows two substituents to generate both hydrophobic and hydrophilic monomers. The hydrophobic substituents are comprised of aryl functional groups to explore the DLC via π - π stacking and hydrogen bonding with the hydrophobic drug molecule, Doxorubicin (DOX), and release of the drug. The chosen hydrophilic substituent contains thermoresponsive tri(ethylene glycol), which can increase the micelles' thermodynamic stability. AmBCs were prepared by ring-opening polymerization (ROP) of each monomer using Triazabicyclodecene (TBD) catalysts to generate living polymerization behavior. Self-assembly, thermoresponsive behavior, and DLC of the AmBCs were analyzed. The *in vitro* biocompatibility and cellular uptake of the AmBCs will be thoroughly investigated for breast cancer treatment using MCF-7 cells.

Design and Synthesis of Lanthanide Phosphate Catalysts

Somayeh Taslimy, Ruvanthi N. Kularatne, Ren Yixin, Abhi Bhadran, Michael C Biewer, Mihaela C. Stefan*

Department of Chemistry and Biochemistry

The University of Texas at Dallas, Richardson, TX 75080

Email: sxt163130@utdallas.edu

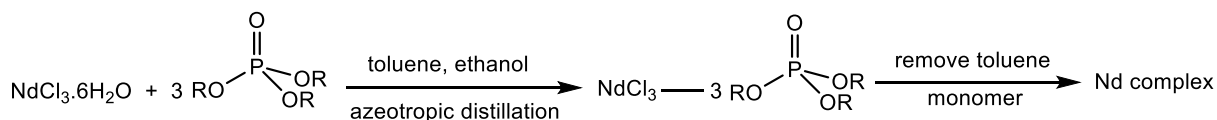
Classification: Graduate

Category: Polymer

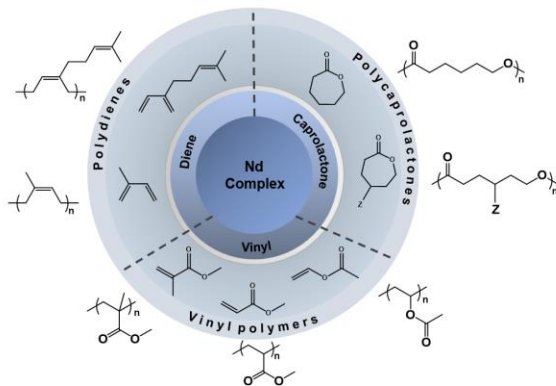
Abstract:

Lanthanide Ziegler-Natta (ZN) catalysts polymerize dienes in enormous quantities. However, they fail to polymerize polar vinyl monomers. Therefore, neodymium-based ZN catalysts, [Nd(μ -DEP)₃]_x (DEP=diethyl phosphate) (1), NdCl₃.3TEP (TEP=triethyl phosphate) (2), NdCl₃.3TIBP (TIBP=triisobutylphosphate) (3), and NdCl₃.3TEHP (TEHP=tris(2-ethylhexyl) phosphate) (4) were developed in our group for polymerization of dienes and polar vinyl monomers such as methyl methacrylate (MMA), methyl acrylate (MA), and vinyl acetate (VA) in combination with triisobutylaluminum as a cocatalyst. These complexes were created by azeotropic distillation.

Previous studies have shown that a halide or pseudohalide is necessary for the polymerization in ZN catalysts. To the contrary, (1), a novel halide-free Nd catalyst, polymerized β -myrcene with high *cis*-1,4 content (96%) and a narrow PDI (1.8). Additionally, (2) and (3) polymerized isoprene and β -myrcene, with PDI=1.6 and high *cis* content (92% and 96%), respectively. Comparing anionic, cationic, and radical polymerization techniques, these catalysts were employed to polymerize epsilon-caprolactone (CL) and gamma-functionalized CL with less sensitivity to substituents. (2) and (4) synthesized both PCL and poly gamma-functionalized CL with a variety of linkages at the gamma-position, including benzyl, 4-phenyl butyrate, acetate, and bromo with PDI=1.22-1.84. Based on kinetic studies and synthesized block copolymers like poly (β -myrcene)-*b*-poly (isoprene) and poly (β -myrcene)-*b*-PMMA, all our catalytic systems demonstrated the quasi-*living* behavior.



R = TEP (triethyl phosphate), TIBP (triisobutylphosphate), and TEHP (tris(2-ethylhexyl) phosphate)



Z = Benzyl, 4-Phenyl butyrate, Acetate, Bromo, gamma-2-[2-(2-methoxyethoxy)ethoxy]ethoxy

Reversible Cross-linked Thermoresponsive Polymeric Micelles for Enhanced Stability and Controlled Release

Abhi Bhadran, Himanshu Polara, Godwin Babaniyah, Tejas Shah, Michael C Biewer, Mihaela C Stefan

Department of Chemistry and Biochemistry

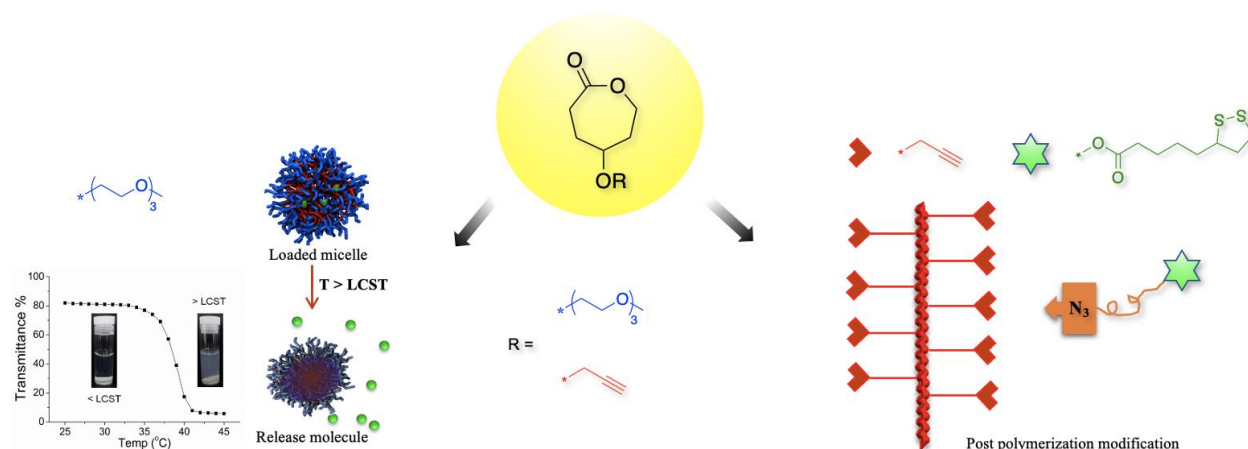
The University of Texas at Dallas

Email: abhi.bhadran@utdallas.edu

Classification: Graduate

Category: Polymer

Abstract :



Poly(ϵ -caprolactone)s (PCL)s are among the most important classes of aliphatic polyesters for biomedical application due to their biodegradability, biocompatibility and synthetic versatility. The properties of this synthetic polymer can be easily tuned by introducing different functionalities. However, the difficulty in polymerizing functionalized ϵ -caprolactone (CL) monomers limits further applications. A major issue is the involvement of these functionalities in the polymerization process which results in unwanted side reactions. Herein, we utilized post-polymerization reactions as an alternative to introduce redox responsive lipoic acid to the side chain of PCL. We developed an ether linked γ -propargyl substituted PCL as the hydrophobic block of an amphiphilic diblock copolymer (AmDC). The propargyl group is used to couple the lipoic acid via click chemistry. The hydrophilic block is composed of an ether linked, thermo-responsive γ -tri(ethylene glycol) substituted PCL. The final AmDC can self-assemble in aqueous solution to form polymeric micelles with lipoic acid functionalized hydrophobic core and tri(ethylene glycol) functionalized hydrophilic shell. These polymeric micelles can be used as a drug delivery system for delivering the anticancer drug doxorubicin. The tri(ethylene glycol) containing hydrophilic shell is used to enhance the solubility of micelles, their circulation in the bloodstream, as well as thermo-responsive properties for triggering drug release. While the lipoic acid containing hydrophobic core can undergo reversible cross-linking to enhance the stability of the micelle and to prevent premature drug leakage.

Molecular dynamics simulation study of the biodegradable amphiphilic polymers for their potential application in anticancer drug delivery

Tejas Shah, Mihaela Stefan*, Hedieh Torabifard*

Department of Chemistry and Biochemistry, University of Texas at Dallas, Richardson, TX 75080, USA.

E-mail: Tejas.Shah@UTDallas.edu

Classification: Graduate

Category: Polymer

Abstract:

Micelles obtained from biodegradable amphiphilic diblock copolymers are one of the widely investigated materials for anticancer drug delivery systems. The hydrophobic nucleus of the micelles provides a solubilizing medium for the hydrophobic drugs, whereas the hydrophilic shell protect them and provides colloidal stability. Additionally, micelles smaller than 100nm diameter can passively target tumors via enhanced permeability and retention (EPR) effect- improving selectivity of the drug. However, synthesizing and characterizing polymeric micelles is an extraneous and cost-demanding task, often leading to suboptimal properties for drug delivery carriers. Moreover, existing experimental methods provide limited insights to molecular-level interactions, hindering the possibility of improving these carriers' performance. To this end, we have utilized the molecular dynamics (MD) simulations approach to gain mechanistic insights into the intermolecular interactions of these polymeric micelles. We subjected micelles comprising biodegradable amphiphilic polycaprolactones to MD simulation, determining transition temperature and drug-polymer interaction, and compared it with experimental data. We foresight our approach to expedite the development of micellar drug delivery carriers for their potential application in doxorubicin drug delivery.

Undergraduate Chemistry Abstracts

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Biochemistry



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Breast Cancer Cell Viability in Cyrene and Hydroxamic Acid Derivatives

Lawrence, Caryn J¹, Shin, Hyunshun², Pyenta, Paul³

1. Department of Chemistry and Biochemistry, McMurry University, Abilene, TX.
2. Department of Chemistry and Biochemistry, McMurry University, Abilene, TX.
3. Department of Chemistry and Biochemistry, McMurry University, Abilene, TX.

Email:

Classification: Undergraduate

Category: Biochemistry/Biological Chemistry

Abstract:

One of the most common types of cancer in females is breast cancer. The American Breast Cancer society expects that 43,250 women will die of breast cancer in 2022. Due to the uses of Class I Histone deacetylases' inhibitors as anticancer agents, we synthesized HDAC new inhibitors using microwaveassisted methods, including N-hydroxy-1H-indole-2-carboxamide and 1H-indole-2-carboxylic acid. These products and the reactant were tested to be used as an HDAC Class I inhibitor in mammalian breast cancer cells. Two synthesized compounds and ethyl indole-2-carboxylate were tested using WST-1 for cell viability in MDA-MB-231 and MCF-7 breast cancer cells: The MDA-MB-231 cells are triple negative cells that lack estrogen receptors (ER), progesterone receptors (PR), and HER2 proteins. The MCF-7 breast cancer cells have ER, PR, and HER2 proteins. Based on the viability test there is cell death that occurs at a higher micromolar dosage than desired. The half maximal effective concentration (EC50) for ethyl indole-2-carboxylate for the MDA-MB-231 was 335 μ M and 315 μ M for the MCF-7. The EC50 for N-hydroxy-1H-indole-2-carboxamide was 340 μ M for the MDA-MB-231 and 300 μ M for the MCF-7. The EC50 for 1H-indole-2-carboxylic acid was 800 μ M for the MDA-MB-231 and was not effective on the MCF-7 cells. Adjustments can be made to increase the toxicity of the compounds so the micromolar dosage is within the recommended range to proceed with further testing.

The common solvent, dimethyl sulfoxide (DMSO) used in pharmacology discovery is toxic to the cells and reacts with compounds in cell viability tests. Therefore, we investigated the toxicity of Cyrene® advertised as a green solvent, compared to DMSO using WST-1 cell viability test in MDA-MB-231 and MCF-7 breast cancer cells. We discovered that Cyrene® is significantly more toxic to these cells than DMSO.

Acknowledgement – This work was funded by The Welch Foundation Z-0036.

Study of reactivity of $\text{CF}_2=\text{CFCH}_2\text{CH}_2\text{Cl}$ with Cl and OH radicals

Trang Nguyen

Department of Chemistry

University of North Texas

Email: trangnguyen9@my.unt.edu

Classification: Undergraduate

Category: Physical/Computational

Abstract:

Chlorofluorocarbon (CFCs) gases are made of carbon, chlorine, and fluorine. They are widely used for air conditioners, refrigerators, manufacturing foam, aerosol propellants, etc. They are very useful in industry and are widely used. Besides their benefits, there are consequences for the inconsiderate uses of these CFCs. They create ozone depletion, and they also trap the heat from earth's radiation which led to global warming potentials. The possibility of mitigating climate change by substituting materials that have low global warming potentials and ozone-friendly materials motivates a study of the spectroscopic and kinetic properties of chlorinated olefins and fluorinated olefins. The relative rate method was used to find the rate constant for the reaction of 4-chloro-1,1,2-trifluoro but-1-ene ($\text{CF}_2=\text{CFCH}_2\text{CH}_2\text{Cl}$) or CFCs. We make a mixture of gasses that mimic the environment. We add CFCs gas, reference, chlorine, and argon together. We use a mercury UV lamp to shine the light through our mixture as the earth's radiation shine through in the atmosphere. The FTIR spectroscopy which is an instrument in our lab is used to monitor the reaction of our mixture and obtain its infrared spectroscopy. The measured infrared spectroscopy of the reaction and estimated lifetime were used to calculate the global warming potential. The reaction creates mostly carbonyl difluoride and 3-chloropropanoyl fluoride ($\text{CF}_2=\text{CFCH}_2\text{CH}_2\text{Cl}$) as the major products. Even it absorbs the radiation, our CFCs's lifetime is short, it is safe to use, and it does not contribute to the climate change and global warming potential.

Europium Oxide-Catalyzed Formation of Electrically-Conductive Carbon for Hybrid Supercapacitors

Andrew Vu

Department of Chemistry and Biochemistry

The University of Texas at Dallas

Email: adv180004@utdallas.edu

Classification: Undergraduate

Category: Inorganic/Analytical

Abstract:

Supercapacitors are known for their rapid ability to charge and discharge with long cycle lifetimes. Supercapacitors could be the future of energy storage because they balance power density and energy density. The goal of this project is to create redox-active, electrically conductive carbon as a supercapacitor that has an energy density comparable to batteries and a power density comparable to conventional capacitors. Europium oxide (Eu_2O_3) will be used to create a special type of capacitor called a pseudocapacitor because europium is known to be redox active. Europium can cycle between the +3 and +2 oxidation states, which allows for the storage of additional charge. The incorporation of redox-active europium will provide a solution to the drawbacks of current supercapacitors.

The electrically conductive carbon was created and had a nanorod morphology that was confirmed by Transmission Electron Microscopy as can be seen in Figure 1. Electrochemical characterization yielded promising results. The resultant material showed that there was pseudocapacitance present, allowing for additional charge to be stored.

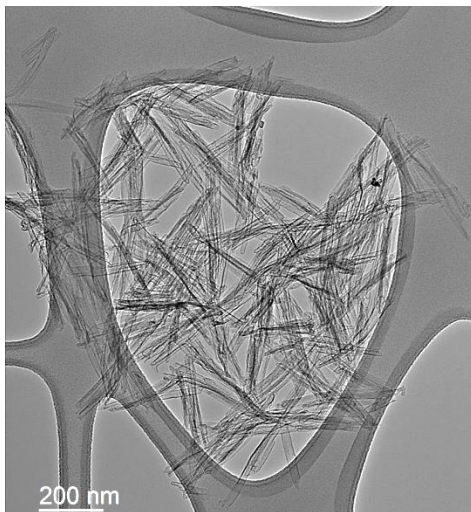


Figure 1: Transmission Electron Microscopy Image of Fully-Washed Carbon-Coated Europium Oxide Nanorods

Synthesis and Magnetic Properties of Gadolinium Metal-Organic Frameworks

Clayton Smithhart, Muhammad Abbas, Kenneth J. Balkus Jr.

Department of Chemistry and Biochemistry

The University of Texas at Dallas

Email: clayton.smithhart@utdallas.edu

Classification: Undergraduate

Category: Materials

Abstract:

Metal-organic frameworks (MOFs) are microporous crystalline materials formed through the connection of metallic ions or nodes with organic linkers and can generate extended 3D structures. These materials provide a high surface area by housing large cavities and various openings in the structure. The permeability of MOFs combined with their tunability merits utilization for various applications such as gas separation, water harvesting, drug delivery, sensors, catalysis, and gas storage. We have recently discovered a new methodology for the preparation of fluoro-bridged rare-earth (RE) clusters in MOFs. Two new Gd-MOFs have been prepared using using bichinchonic acid (BCA). In the absence of a modulator, binuclear Gd-nodes nodes are formed resulting in a 2D coordination polymer. With the use of fluorinating agents, e.g., 2-fluorobenzoic acid (2-fba), 2,6-difluorobenzoic acid (2,6-dfba), and perfluorohexanoic acid, fluoro-bridged hexaclusters are formed resulting in porous 3D MOF. The presence of fluorine is also verified by EDS and XPS analysis. The magnetic properties of the new MOFs will be discussed.

Synthesis and Characterization of Holmium Based Metal-Organic Framework

Murtaza Degani, Muhammad Abbas, Kenneth J. Balkus Jr.

Department of Chemistry and Biochemistry

The University of Texas at Dallas

Email: murtaza.degani@utdallas.edu

Classification: Undergraduate

Category: Materials

Abstract:

Metal-organic frameworks (MOFs) are porous crystalline materials constructed from organic linkers and metal ions (or clusters). Advances in MOFs applications include gas storage and separation, drug delivery, sensors, water capture, and catalysis, depends in part on new structures. In this presentation holmium and 3,3',5,5'-azobenzene-tetracarboxylic acid (abtc) based new MOFs will be discussed. The Ho-abtc Mofs have been charactrized using XRD, TGA and gas adsorption. These MOFs will be evaluated for their radiotherapeutic applications.

Hydrogels and Determination of Correct Concentration and Methods

Addison Anderson

Department of Chemistry, Geoscience, and Physics

Tarleton State University

Email: addison.anderson@go.tarleton.edu

Classification: Undergraduate

Category: Polymer

Abstract:

Hydrogels are three-dimensional network structures able to imbibe large amounts of water. Hydrogels do not typically dissolve due to chemical or physical cross-links and chain entanglements. The research's primary goal was to develop plant-based delivery systems for the therapeutic use of bacteriophages. The research includes synthesis of the delivery systems and the characterization followed by studying their toxicity/safety on biological systems through a series of tissue culture experiments. As well as the experiments done throughout the semester have been trying to see the best concentration of substrates and how they will react when heated and introduced to bacteriophages. The bacteriophages being a part of the gel and being able to move within the gel freely is one of the most important aspects; as needed, the formation of plaques is necessary to show that the bacteriophage can move and kill the bacteria. The gel used for research is currently a 10:10 Tamarind Powder, Green Tea Extract with 20mL of DI water, and more research is needed on the highest temperature range the gel can take. Lastly, research is required on whether when the bacteriophage enters the bacteria cell, and the cell lyses, the cell releases water, and that's why there is water in the agar plate or what is causing that issue.

Formation of Fluoro-bridged Rare-earth-based Metal-Organic Frameworks

Emad Siddiki¹, Simin Sheybani¹, Kenneth J. Balkus, Jr.*

¹Department of Chemistry and Biochemistry

University of Texas at Dallas

Email: emadsiddiki@gmail.com

Classification: Undergraduate

Category: Inorganic/Analytical Abstract:

Metal-organic frameworks (MOFs) are crystalline and structurally diverse materials composed of both inorganic and organic components. MOFs self-assemble by forming coordination bonds between inorganic metal ions or clusters and multidentate organic linkers. The porosity of MOFs leads to many applications including separations, chemical sensing, and drug delivery. Rare-earth metal ions have high coordination numbers and form clusters. MOF crystal growth can be regulated by utilizing modulators. Modulators are small organic molecules that coordinate to the metal ions slowing crystallization. It was recently discovered that RE metal ions can extract fluorine from various organo-fluorine molecules resulting in fluoro-bridged RE clusters. PFAS are extensively used as a surfactant in industrial applications and consumer products. Due to their strong carbon-fluorine bonds they are persistent in the environment. In this research, organo-fluorine modulators such as perfluorohexanoic acid were utilized to synthesize fluoro-bridged RE-based MOFs. The extraction of fluorine from PFAs by RE metal ions results in formation of fluorobridged metal-organic frameworks. Three different linkers 1,2,4,5-Tetrakis(4-carboxyphenyl)benzene (TCPB), Tetrakis(4-carboxyphenyl) porphyrin, (TCPP), and 1,3,5-Tris(4-carboxyphenylethynyl)benzene (BTE) were combined with RE metal as well as the perfluorohexanoic acid modulator to form these MOFs. These MOFs were characterized by single crystal X-ray diffraction crystallography, powder X-ray diffraction and energy dispersive X-ray spectroscopy.

**Titrimetric Measurement of Urinary Sulfate and Interfering Ions
in Horses and Swine**

Tanner J. Taylor and Dr. Linda D. Schultz

Department of Chemistry, Geoscience, and Physics

Tarleton State University

Email: tanner.taylor@go.tarleton.edu

Classification: Undergraduate

Category: Inorganic/Analytical

Abstract:

Urinalysis is a valuable tool for diagnosis and evaluation of many disease states in both livestock and humans and is a noninvasive technique. However, urine is a complex mixture containing a variety of potentially interfering substances which complicate analysis of urinary ions by many methods. Classical techniques have been largely supplanted by modern instrumental methods in today's clinical laboratories because they have advantages in accuracy, precision, suitability for automation, and speed. Unfortunately, many of these methods require expensive equipment and highly trained technical personnel to operate them, which largely limits their availability to large metropolitan areas and reference labs. These factors can be an obstacle to routine testing for some physiological species for veterinarians and physicians in isolated regions. This study reports results of an adaptation of classical titrimetric methods from water chemistry analysis to urinalysis of equine and swine samples. Urine samples from a small group of quarter horses were analyzed for sulfate and carbonate content by conductometric titration and potentiometric titration respectively. Urine samples from a small group of crossbred domestic pigs were analyzed for sulfate and phosphate content by conductometric titration. Results were compared to those obtained by ion chromatography. Inconsistencies in the results were noted, but were primarily due to procedural problems. Urinary sulfate is seldom studied in horses and pigs, and very sparse reference values are available. Such information could be of clinical significance, so we consider the continuation of this study to be a worthwhile endeavor.

Preparation of Osage orange isoflavones for co-transfection with Fenugreek carbohydrate polymer in pancreatic tumor cell proliferation assays.

Samuel Rodriguez, Anne M. Wood, Luke Reynolds, Rajani Srinivasan,
William L. Whaley, Department of Chemistry, Geoscience and Physics
Tarleton State University

Email: samuel.rodriguez@go.tarleton.edu

Classification: Undergraduate

Category: Biochemistry/Biological Chemistry

Abstract:

The Osage orange (*Maclura pomifera*) is a species that is native to the Bosque River Valley in Erath County, TX. The mature fruit tissue of this species contains two prenylated isoflavones, osajin and pomiferin, that together account for about 5% of the dried tissue mass. Osajin has been reported to inhibit the growth of cultured prostate cancer cells, while pomiferin has been reported to inhibit the growth of cultured breast cancer cells. Pancreatic cancer tends to be resistant to many currently used chemotherapy agents. Osajin and pomiferin were obtained from Osage orange fruit in a diethyl ether fraction using a Soxhlett extractor. The isoflavones were separated by normal phase column chromatography using silica adsorbent and a step-gradient elution with hexane and ethyl acetate. The preparations of osajin and pomiferin were assessed to be 98% pure by an assay based on ¹H-NMR spectroscopy. Each compound was separately dissolved in dimethyl sulfoxide, with and without conjugation to Fenugreek carbohydrate (microwave technique) and diluted to a concentration of 5 μM in the culture media of actively growing Panc5 cells. After 48 hours, the cultures treated with only pomiferin exhibited 50% dead cells; whereas, cultures treated with pomiferin conjugated to carbohydrate polymer exhibited 98% dead cells. These results demonstrate an effective method for delivery of very hydrophobic anti-tumor agents into aqueous cultures of tumor cells. Many flavonoids have been reported to have anti-tumor activity; however, low water solubility has limited their delivery to target cells and their utility as chemo-therapeutic agents. The isoflavones and carbohydrate polymer have very low toxicity and may represent a novel future approach for treatment of some cancer types. (This research was financially supported by the Welch Foundation Departmental Research Grant #AS-0012 and the Tarleton Presidential Excellence in Research Scholar Program.)

Cultured pancreatic tumor cell growth is inhibited by co-transfections with Osage orange isoflavones and Fenugreek carbohydrate polymer.

Chaney Kelly and Anne Marie Wood

Department of Chemistry, Geoscience, and Physics

Tarleton State University

Email: chaney.kelly@go.tarleton.edu

Classification: Undergraduate

Category: Polymer Abstract:

The Osage orange (*Maclura pomifera*) is a species that is native to the Bosque River Valley in Erath County. The mature fruit of this species contains significant amounts of two isoflavones called osajin and pomiferin. Osajin has been demonstrated to inhibit the growth of prostate cancer cells while pomiferin has been demonstrated to inhibit the growth of breast cancer cells in culture. The fruit of Osage orange was obtained from trees growing in Stephenville, TX, and was processed by solvent extraction using diethyl ether or ethanol. These compounds were then dissolved in dimethyl sulfoxide and the solution was added to the media for cultured panc cells (human pancreatic tumor cells). At a concentration of 5×10^{-6} M (5 micromolar), osajin exhibited very little efficacy in killing panc cells; however, with the added carbohydrate copolymer (obtained from fenugreek) there was a significant increase in cell death. Pomiferin (at 5 micromolar) exhibited some tendency to kill cultured panc cells; however, the efficacy was greatly improved when the carbohydrate copolymer (from fenugreek) was added. The use of these isoflavones together with the carbohydrate co-polymer derived from fenugreek may offer a low-toxicity approach for inhibiting the growth of pancreatic tumor cells in culture. Pancreatic tumors are particularly difficult to treat with conventional chemotherapeutic agents. There is a need for anti-tumor compounds that have low toxicity to normal human cells but are effective at destroying pancreatic tumor cells.

Synthesis and Characterization of Several Copper-Lanthanide Mixed-Metal Organic Frameworks Containing a Fluoro-bridged Hexacluster

Dax J. Hildebrand, Marie L. Mortensen, Gregory T. McCandless, Yihao Yang, Hongcai Zhou, Kenneth J. Balkus Jr.**

Department of Chemistry and Biochemistry

The University of Texas at Dallas

Email: djh180005@utdallas.edu

Classification: Undergraduate

Category: Inorganic/Analytical

Abstract:

Metal-organic frameworks (MOFs) are a class of crystalline coordination polymers composed of organic linkers and metal centers, which can be either single ions or clusters. MOFs are notable for their permanent porosity and often have interesting magnetic properties especially when they are made with lanthanides. These properties are further influenced by the presence of copper in conjunction with these rare earth elements due to the possibility for coupling effects. This further enables the tuning properties such as magnetism, fluorescence, and overall topography. The modulator 2-fluorobenzoic acid (2-Fba), was discovered to create lanthanide clusters rather than dimers, which commonly occur in lanthanide-containing MOFs. It was recently determined in our lab that lanthanide ions extract fluorine from 2-Fba to form clusters.

In this research, the reaction of 2-Fba, the organic linker, 2,2' bipyridine 4,4' dicarboxylic acid (BPDC), with lanthanide ions (holmium, gadolinium, or dysprosium) and copper ions formed two different fluoro-bridged hexacluster containing mixed-metal MOFs. The two structures of this MOF that can form depend on if benzoic acid is included as a modulator, each has unique properties. Interestingly, both structures contain fluorine-bridged hexaclusters that contribute to numerous properties such as fluorescence intensity, selectivity for CO₂ and affects hydrophilicity. Small changes in the topography generated by the inclusion of a non-participatory modulator creates vastly different properties. Gadolinium and dysprosium were selected because they offer unique magnetic properties. Holmium was chosen for this research due to its potential to be neutron activated, which is important in medical applications. Single-crystal x-ray diffraction and powder x-ray diffraction were used to determine the structure and bulk purity. Energy dispersive x-ray spectroscopy was used to verify fluorine content. Thermal stability was determined using thermalgravimetric analysis.

The Prevention of Corrosion and Oxidation Related Failures in Cu-Al and Cu-Cu Wire-Bonded Devices

Logan Robert Estridge

Department of Chemistry

University of North Texas

Email: LoganEstridge@my.unt.edu

Classification: Undergraduate

Category: Materials

Abstract:

Advancements in the fabrication of microelectronic devices are oriented towards decreasing size and cost, and maximizing product reliability. To these ends, the metal of choice for many circuit elements in wire-bonded devices (WBDs) has traditionally been gold. However, in the past few decades the more popular choice is copper (Cu), which has several advantages such as low cost, superior solder-joint reliability, and greater electrical and thermal conductivities. The major concern for typical copper-aluminum (Cu-Al) WBDs is the prevention of corrosion-related failures. In addition, the oxidation of copper during the bonding process can lead to non-stick on pad (NSOP) failures, particularly in Cu-Cu wire-bonding applications. Currently, the industry is demanding failure rates to be near zero ppb for several important applications including automotive and smart-wear microchips, which are subjected to harsh temperatures and contaminating environments.

Our key research innovation is real-time corrosion micro-screening, where exposed Cu-Al WBDs are subjected to an accelerated chloride contaminated environment and investigated via an optical microscope in situ. The catalyst for corrosion was determined to be the contaminating halide species, which attacks the native aluminum oxide exposing the vulnerable AlO underlayer and increasing the local acidity. The exposed aluminum is then oxidized, shuffling its electrons to the copper wire where the reduction of local protons leads to the evolution of hydrogen gas, as verified by headspace GC analysis. Using this better understanding of the interfacial chemistry, our group was able to develop and optimize a passivator that stops the cathodic half reaction, ceasing corrosion entirely and preventing wire-bond lift off / device failure. The developed passivator is a thin-film coating that is low cost, copper-selective, hydrophobic, thickness tunable down to the low nanometers range, and a suppressor of copper oxidation, which is critical for avoiding NSOP failures in Cu-Cu WBDs.

Preparation of Pure Osajin Suitable for Cell Proliferation Assays with Pancreatic Tumor Cells.

Luke Reynolds, Sam Rodriguez, Anne M. Wood, Rajani Srinivasan, William L. Whaley

Department of Chemistry, Geoscience, and Physics

Tarleton State University

Stephenville, Texas, 76402

Email: luke.reynolds@go.tarleton.edu

Classification: Undergraduate

Category: Organic

Abstract:

Osajin and pomiferin are two prenylated isoflavones present in the mature fruit of Osage orange (*Maclura pomifera*), a species native to central Texas. These two isoflavones account for 5 to 7 percent of the mass of the dried fruit tissue. When processed using a Soxhlet extractor, a diethyl ether fraction containing osajin and pomiferin in a 1 to 2 molar ratio was obtained. These isoflavones have nearly identical structures with pomiferin (MW=420 amu) containing a single oxygen atom that is not present in osajin (MW=404 amu). These compounds were separated by normal phase column chromatography with silica adsorbent using a step gradient of hexane and ethyl acetate. A fraction containing 85% osajin (15% pomiferin) was subjected to a second separation by column chromatography. A fraction containing nearly pure osajin (>95%) was obtained. Osajin has been reported to inhibit prostate cancer cell growth; however, it has been reported to be inactive against breast cancer cells and other tumor cell types. Results from this laboratory indicate that preparations of osajin inhibited proliferation of pancreatic tumor cells; however, contamination of the preparation with traces of pomiferin could account for the observed activity. In order to determine the true activity of osajin, traces of pomiferin must be removed. Thin-layer chromatography with basic alumina (alumina-B) indicated that pomiferin bound tightly to this adsorbent while osajin was eluted with 80/20 hexane/ethyl acetate. A cartridge column containing alumina-B was tested and found to bind pomiferin very tightly while allowing osajin to be eluted. An increase in the scale of this separation should provide milligram quantities of very pure osajin for use in cell proliferation assays. (This research was supported by the Tarleton Presidential Excellence in Research Scholar Program and by the Welch Foundation Departmental Research Program, Grant #AS-0012.)

Measurement of Non-elevated Sulfate Levels in West Texas Groundwater

Aubry L. Hutson and Dr. Linda D. Schultz

Department of Chemistry, Geosciences, and Physics, Tarleton State University, Stephenville,
TX 76402

Email: aubrylee@gmail.com

Classification: Inorganic/Analytical Category:

Undergraduate

Abstract:

The most reliable technique for measuring sulfate in dilute aqueous solutions is ion chromatography. However, this method is very expensive and requires highly trained personnel. Our laboratory has been investigating conductometric titration as an alternative method which is simple and inexpensive. Previous results have indicated that it works well for elevated sulfate concentrations but does not give reliable results below approximately 5 mM (500 mg/L). The goal of this study was to see if improved results could be obtained using a lower range (more sensitive) instrument. Three groundwater samples obtained from the High Plains Water Development Board from the Dockum Aquifer near Lubbock, Texas were analyzed using both high and low range conductivity meters and differing concentrations of titrant. Inconsistent data were obtained, and the ion chromatograph was unavailable over the time period of this study. The conclusion was reached that benefits of the increased sensitivity of the low range conductivity meter were generally offset by dilutions necessitated by elevated concentrations of other ions in individual samples. These conclusions will be verified by ion chromatography using fresh samples.