



102nd Florida Annual Meeting and Exposition

Book of Abstracts

Cover design by Stefanie Habenicht and Lukasz Dobrzycki depicting a copper(II) tetrachloride layer from an organic-inorganic hybrid perovskite prepared by Tanzina Akter (Daniel Talham lab, Department of Chemistry, University of Florida)

Contents

Contents	3
Oral Sessions	12
Plenary Lecture	12
Ru three ways with a side of Pt	12
Showcase Symposium	12
Exploring the Carboxylato-Pyrazolato Structural Parallel and Accessing New Redox-Modified States of Multinuclear Transition Metal Complexes	12
Sulfur as a Source of Dark Matter in Proteomics: Roles of Mass Accuracy and Fragmentation Pathways	13
Laser-Based Nanoscale 3D Printing	14
Additive Manufacturing	15
3D Printing and Laser Annealing of Strain Sensors for Structural Health Monitoring	15
Coupled Physics-Informed Neural Network for Multi-Physics Modeling in Additive Friction Stir Deposition	16
Organosilane nanostructure fabrication on semiconductor substrates using particle lithography	16
Direct Ink Written Membranes with Aligned 2D Channels for Application in Selective Extraction of Lithium via Electrodialysis	17
Analytical and Environmental Chemistry	18
Photocatalytic Degradation of Ibuprofen Using Methylene Blue-Sensitized TiO ₂ -Coated 3D-Printed PLA Plates	18
Towards Reliable DNA Extraction from Granular Activated Carbon in Drinking Water Treatment Plants	18
Tracking Long-Term Petroleum Weathering Using Molecular Markers: Lessons from the Deepwater Horizon Oil Spill	19
MIP-based electrochemical sensing for health and environmental management	19
Coaxial electrospun nanofibers for oil spill bioremediation	20
Observing Chloride Concentrations in Southwest Florida using Ion-Selective Electrodes	20
The Evolving Landscape of Ion Mobility Spectrometry	21
Synthesis and Photophysical Characterization of Methylene Blue Stearate	21
Rapid Characterization of Microplastics in Beverages Using Automated Laser Direct Infrared (LDIR) Chemical Imaging	22
Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Meat, Seafood, Eggs, and Milk following AOAC 2023.003	23
Integrated evaluation of oxidative potential and antioxidant activity of ambient PM _{2.5} in Lahore: Decoupling between mass concentration and redox reactivity	23
Exploring the mechanisms of radical directed dissociation enabled by novel cupric lipid ion types	24

Zwitterionic Self-Assembled Monolayer Modification of Lithium Niobate for Enhanced Surface Acoustic Wave Nebulization Mass Spectrometry	25
Development of Focused Surface Acoustic Wave Nebulization Mass Spectrometry.....	26
Sediment Microbiome Dynamics Across a Northern Gulf of Mexico Salinity Gradient	26
Biochemistry and Chemical Biology	27
Computational insights into arginine side chain activation and post-translational modification.	27
Discovery of a Sub-Femtomolar Modulator of the Human STING Receptor	27
Development of a synthetic biology platform for natural product chemistry	28
Targeted Protein Degradation: From PROTACs to Molecular Glues.....	28
Structural Mechanisms of the Constitutive Activity in Ion Channel TRPM1	29
Beyond Four Letters: Expanding the Chemical and Functional Space of Nucleic Acids	30
Characterization of the Hsp70 and J-Domain Protein Chaperone System in the Tardigrade <i>Hypsibius exemplaris</i>	31
The Mechanism of Oxalate Decarboxylase and How to Improve its Catalytic Efficiency.....	31
Host-factor phase separation properties transport the HIV-1 core to vDNA integration sites	32
Leveraging anaerobic HDX-MS to decipher RiPP-rSAM substrate recognition ..	33
Exploring the NO peroxidase pathway of <i>Mycobacterium kansasii</i> (Mka) HLP...	33
Evolutionary Emergence of a Non-Native Metabolite in Response to Loss of an Essential Enzyme.....	34
Chemistry Education	35
Mastery Paths for Metacognitive Engagement in an Introductory Chemistry Course	35
AI Tutor, AI Media, or Human Instructor? Student Use, Trust, and Confidence in a Flipped Analytical Chemistry Module	35
Beyond 2D: Visualizing Molecular Orbitals through Virtual Reality	36
Investigating the Efficacy of Self-Selected Weekly Peer-Mediated Study Groups for At-Risk Students Across the General Chemistry Sequence	37
Empowering Students, Strengthening Skills: Developing an Internship Program in Teaching Labs.....	38
Turning Assessment into Learning	38
Academic pathways: Exploring the Relationship Between STEM Identity and Factors That Influence a Student to Consider Changing Their Majors	39
Identifying resources that engineering students use to explore their academic pathways	39
Principle of Chemistry Course: Investigating Factors that can Influence Students' Relationship to their Major	40

Picturing the Future: How Visualizing Graduation Shapes STEM Student Confidence	40
Outreach Initiatives and Resources by the ACS Student Chapter at the University of Florida	41
Computational Chemistry	41
Computational Design of Aptamers for Targeted Cancer Therapy: Advances, Applications, and Future Perspectives	41
Determining Protein Structure Ensembles from NMR Exchange Format (NEF) Data Using MELD	42
Beyond Classical Force Fields: Physics-Driven Assessment of the Grappa Machine-Learned Force Field on the FoldBind Dataset	43
Toward Robust Solutions of the Projected Schrödinger Equation	43
Direct C(sp ³)-H Activation Through Ni-Catalyzed Cascading Hydrogen Atom Activation.....	44
Embedded cluster density approximation for scalable high-level exchange-correlation calculations in periodic systems	44
Inorganic Chemistry	45
Structural and Spectroscopic Investigation of Trinuclear Oxovanadium Pyrazolato Complexes	45
Generating Porosity in Metal Halide Semiconductors	46
Synthetic Analogues of the Photosynthetic Oxygen-Evolving Complex (OEC) near Photosystem II of Cyanobacteria and Plants.....	46
Design, synthesis, and characterization of a small molecule inorganic photoresist candidate for EUV lithography	47
Separation of Rare Earth Elements: Traditional Methods and Emerging Approaches	47
Covalently-linked Metalloporphyrins for the Design of Quantum Systems: Methods, Characterization, and Device Integration	48
Sulfonamide Ligands for Sensing Lanthanides in High-Level Waste	49
Strain-Promoted and New Inorganic Click Strategies for Porous Organometallic Polymers	50
Towards photo-switchable magnetic exchange interactions in dihydropyrene-based copper complexes.....	50
Mixed-Anion Design for Enhanced Lithium-Ion Transport in Solid Electrolytes...	51
Synthesis, characterization, and electrochemical study of redox-active cyclic polyacetylenes.....	51
Synthesis and characterization of redox active Fe _n (μ _n -O) pyrazolates: X-ray crystal structures, spectroscopy, and electrochemistry	52
Dipicolinamide Ligands for Binding and Sensing of Uranyl and Perrhenate: The Effect of <i>p</i> -Phenolic Substitution on the Central Pyridinyl Ring.....	52
Molecular Clusters as Models of the Repeating Unit of the LnMnO ₃ Lanthanide Manganites with the Perovskite Structure	53
Porous Metal Halide Semiconductors for K. brevis Mitigation: Understanding Structure-Property Relationships that Guide HAB Control	53

Direct Synthesis of High-Surface-Area Perovskites for Enhanced CO Production in Reverse-Water Gas-Shift Chemical Looping (RWGS-CL).....	54
Oxo/ hydroxo -bridged dinuclear copper pyrazolate complex as efficient catalyst for hydrocarbon oxidation: redox and oxygen-atom transfer studies.	55
B-Site Ti Engineering of $\text{LaNi}_{1-x}\text{Ti}_x\text{O}_3$ /MCF Perovskite-Silica Catalysts for Enhanced Ni Active-Site Formation and CO_2 Methanation.....	56
Green Synthesis of Metal Oxides Nanoparticles by Using Aloe Vera Leaves Extract for Efficient Electrocatalytic Water Splitting	56
Organic Chemistry	57
Oxidative Dearomatization and Formal Arylation of Carbonyl Derivatives	57
Multivalent DBCO-Based Building Blocks as a Route to Porous Organometallic Polymers	57
Synthesis of 3,4-Dihydroxyphenylacetaldehyde (DOPAL): A toxic dopamine metabolite in Parkinson's disease pathogenesis	58
Mechanistic investigation of catalyst-free amide to ester conversion (ATEC).....	59
Optimization of P7C3-Derived NAMPT Activators for Treatment of Cardiac Injury	59
Physical and Biophysical Chemistry	60
Accelerating rare events in biomolecular simulations with Continually Adaptive Local Memory sampling.....	60
Molecular simulations reveal paralog-specific recognition of peptides in BET ET-domains	61
Unlocking Long-Range Quantum Transport Through Single Molecules	62
Nuclear Hyperfine Effect and an Astonishingly Large Primary Kinetic Isotope Effect in Anthracene-9- ^{13}C Photodimerization.....	62
Transient absorption spectroscopy of the stilbenes in methanol – adiabatic cis to trans photoisomerization by sequential two-photon excitation.....	63
Optically Steering Ultrafast Carrier Scattering, Cooling, and Trapping Pathways in Nanoscale Semiconductors	63
Thermodynamic Behavior of Hydrocarbons Confined in Mesoporous Silica Investigated by Differential Scanning Calorimetry.....	64
Zero- to Ultralow-Field NMR: From Hyperpolarized Spin Networks to Molecular J -Oscillators	65
Defect engineering in nanomaterials and their implications for sensing and heterogeneous catalysis	65
PMSE/POLY and Materials Chemistry	66
Approaches for generating crosslinked networks by metal-free ring opening metathesis polymerization	66
Glutathione-Responsive Polyhomocysteine Derivatives with Ultralow Toxicity toward Therapeutic Delivery	67
Enzyme-Mediated Photoiniferter Polymerization Enables Ultrahigh Molecular Weight Polymers with Tunable Adhesive and Frictional Properties	68
Preceramic Polymer-Grafted MXene Hybrids for Enhanced Thermo-Oxidative Stability	69

Supramolecular arene-perfluoroarene assembly enhances photoiniferter polymerization kinetics.....	70
Depolymerization of Commercial Polymethacrylates	71
Poster Presentations	72
Friday Posters	72
F1: Cysteine-Directed Synthesis of Chiral CoMn_2O_4 Spinel Nanoparticles for Spin-Selective Electrochemical Oxygen Evolution	72
F2: Boronic Acid Copolymers for Substantive Skin Hydration and Topical Delivery	73
F3: Precursor-Directed Growth of Molybdenum Disulfide Thin Films by Aerosol-Assisted Chemical Vapor Deposition	73
F4: Adhesive Polyelectrolyte Complex Coacervates with Structural Antibiotics ..	74
F5: Precision Engineering of $\text{Cd}_{32}\text{Te}_{14}$ Semiconductor Nanocluster via Cation Exchange	75
F6: Printing Yttria Stabilized Zirconia (YSZ) for High Dielectric Breakdown Structures for High Voltage Applications.....	76
F7: Stoichiometric Liquid-ALD Synthesis of High-Surface-Area LaAlO_3 Thin Films with Controlled Surface Chemistry.....	77
F8: Designing and Investigating the Properties of Ultra-Long Acrylic Bottlebrush Polymers	77
F9: Synthesis optimization of Ruddlesden-Popper metal halide semiconductors	78
F10: Depolymerization of silicon-methacrylate materials.....	78
F11: Pomegranate peel-derived activated carbon as a sustainable electrochemical platform for future biosensor development.....	79
F12: Evaluating Plasmonic Behavior of Semiconducting Nanocrystals via SQUID	79
F13: Phase evolution and functional properties of Bi-In-Sn oxides.....	80
F14: Order from Chaos: Unsupervised Learning of Conformational Landscapes	80
F15: Metal Halide Semiconductors with Engineered Porosity	80
F17: Photoassisted chemical vapor deposition of ruthenium on functionalized self-assembled monolayers using $(\eta^2\text{-olefin})\text{Ru}(\text{CO})_4$ precursors	81
F18: High flux X-ray scintillation of FAPbI_3 halide perovskite/Polymer Composite Scintillators: Polylactic acid (PLA) versus Polyimide (PI) Matrices	81
F19: A Combined Experimental and Computational Approach to CO_2 Capture in Nanoparticle-Metal-Organic Framework Composite Catalysts	82
F20: Membrane-dependent transport of linear and cyclic polymers	83
F21: nanoGUMBOS: tunable organic nanomaterials for biomedical applications	83
F22: Ultra-High Molecular Weight (UHMW) Triblock SLIPs as Synthetic Mucins	84
F23: Comparison of Linkers in Hybrid Metal Halide Semiconductors for Selective CO_2 Photoreduction.....	84
F24: Stoichiometry-Driven Optical Tuning and Thiophene-Induced Photoluminescence Enhancement in WS_2 Quantum Dots.....	85

F25: Design of DHS-Molybdenum hybrid halide semiconductors	85
F26: High Fracture Toughness in Ultra-High Molecular Weight Thermoplastics with Strain-Induced Crystallization	86
F27: Novel Precursors for Extreme Ultraviolet (EUV) and Beyond-EUV Lithography	86
F28: Visible-light-curable fluorescent underwater adhesives	87
F29: Molecular Clusters as Models of the Repeating Unit of the LnMnO_3 Lanthanide Manganites with the Perovskite Structure	88
F30: Effect of Barium Titanate particle size on the rheology of BaTiO_3 -PVDF composites inks	89
F31: HIV Therapy: Synthetic and Computational analysis of Ring-modified Efavirenz analogs	90
F32: Post-Synthetic Trigger Installation Facilitates Efficient PMMA Depolymerization	90
F33: Point-of-Care Electrochemical Sensing of Microplastic	91
F34: <i>In-situ</i> analyses of Crystallization kinetics and Stress Relaxation in 3D Printed Polymer Nanocomposites	92
F35: Family of Iron-Oxo 'Molecular Nanoparticles' Related to $\gamma\text{-Fe}_2\text{O}_3$: Structural Characterization and Magnetic Properties	93
F36: Effect of chain length on the thermodynamic behavior of hydrocarbons confined within nanopores	93
F37: 30-Minute Materials: A Green Route to Sulfonium-Based Metal Halide Semiconductors	94
F38: Tandem Upcycling Drives Rapid and Near-Quantitative Depolymerization of RAFT-Derived PMMA	94
F39: Long-Range Magnetic Exchange Coupling in Ce/Mn-oxo Clusters	95
F40: pH-responsive copolymer micelles for targeted endosomal release and enhanced antiviral efficacy of Ribavirin against Zika virus	95
F41: The Oxygen-Evolving Complex (OEC) of Photosystem II: Strontium-based Synthetic Analogues	96
F42: 3D Printed Barium Titanate High Voltage Capacitors	97
F43: MIP-Assisted Electrochemical Sensing of L-thyroxine (T4) for Thyroid Diagnostics	98
F44: Effects of Preceramic Polymer Chemistry on Crosslinking, Ceramic Yield, and PIP Densification of Binder Jetted ZrB_2 UHTCs	99
F45: Distinguishable Molecular Spin Qubits in Asymmetric Meso-Substituted Metalloporphyrins	99
F46: Collagen Inspired Trivalent Crosslinking of Epoxy Functional Methacrylate Copolymers for Tough Polymer Networks	100
F47: Aerosol-assisted CVD of NbN using novel niobium imido single-source precursors	100
F48: Oxidation-Induced Chemical Interface Damping in Au–Ag Alloy Nanoparticles for Plasmon-Assisted Photocatalysis	101

F49: Hg(II) Liquid-Liquid Extraction into Dichloromethane by a Simple Nitropyrazole	101
F50: Optimization of Polysulfone-based Adsorptive Membranes for Heavy Metal Ion Removal from Water	102
F51: Lipophilic o-(Sulfonamido)phenol ligands as f-element extractants for combined Cs and actinide separations in High-Level Waste	103
F52: Performance analysis of Sr ₃ SbI ₃ -based perovskite solar cell using SCAPS-1D software	103
F53: Diglycolyl- and Dipicolino-Sulfonamide Ligands for Ln(III) Complexation and Selective Separation	104
F54: Observing Chloride Concentrations in Southwest Florida Using Ion-Selective Electrodes	104
F55: Integrated Process Optimization of Printed Silver Composite Strain Sensors through Direct Ink Writing and Laser Processing	105
Saturday Posters	106
S1: Rhodium-catalyzed divergent silylation of styrene derivatives using alkoxysilanes	106
S2: Exploring the Role of Molecular Chaperones in Carcinogenesis	106
S3: Designing β -barrel Membrane Protein using Distributed Structure-to-Sequence Adapters.	107
S4: Tuning polymer nanoparticle morphologies via photochemical decarboxylation	107
S5: Synthesis of Peptoid-based Inhibitors of Protein Arginine Methyl Transferases (PRMTs) for Application in the Treatment of Cancer	108
S6: Yeast <i>S. cerevisiae</i> as a model to study human molecular chaperones <i>in vivo</i>	108
S7: Catalyst Development for Enantioselective Ritter-Type Amidation of Benzylic Alcohols.....	109
S8: Stimulation of Hsp70 ATPase activity by tardigrade DNAJB1	109
S9: Designing Haloalkane Dehalogenase Variants With Generative AI: Accelerating the SN2 Reaction	109
S10: Regulating Dimerization of Human J-Domain Protein	110
S11: Synthesis of Substituted 4,4'-dihydroxyazobenznes based Analogs of a Novel Jak2 Inhibitor	110
S12: Role of the DNAJB1 Gly-rich helix in Hsp70 interaction	111
S13: Receptor-State-Aware Virtual Screening for Discovery of Novel Apo-IDO1 Inhibitor Candidates.....	112
S14: Functional Characterization of Molecular Chaperone DNAJA1 in Tardigrades	113
S15: Improvements in the design and synthesis of sensor heterocyclophanes	113
S16: Initiation of nemamide biosynthesis in <i>Caenorhabditis elegans</i>	114
S17: Structure-Guided Identification of Small-Molecule CFTR Activators for Cystic Fibrosis Using Pharmacophore Modeling	115

S18: Investigating the structures and antiproliferative properties of secondary metabolites produced by different species of the freshwater algae <i>Euglena</i>	115
S19: Investigating Amide Substitution Effects on Transannular H-bonding in Heterofunctionalized [2.2]Paracyclophanes	116
S20: Kinetic and Structural Basis of the Inhibition Mechanism of Human Asparagine Synthetase by ASX-173.....	116
S21: Total Synthesis and Biological Evaluation of Nemamide Analogs	117
S22: Biochemical Characterization of <i>Moraxella catarrhalis</i> HemW	117
S24: Fisetin as a fluorescent probe of different DNA architectures.....	118
S25: Photo-Driven Photocatalyst-Dependent Radical Cascade Cyclizations of Simple N-Acryloyl Indoles for the Selective Synthesis of Sulfonylated Dihydropyrido[1,2-a]-indolones	118
S26: Investigating the molecular mechanisms driving immune evasion in bronchial premalignant lesions	119
S27: Providing Visual Support for the Concepts of Kinetic vs. Thermodynamic control and Trapping Singlet Oxygen.....	120
S28: Uncertainty-Aware Multi-Objective Computational Prioritization of Pancreatic Cancer Molecular Candidates with Convergent NF- κ B1 Target Hypotheses.....	121
S29: Dapoxyl-10 split light-up aptameric sensor used as fluorescent probe for LAMP amplicons of <i>MalB</i> gene of <i>E. coli</i> in PURED system	122
S30: Stereochemistry in Disulfide-Bond Disrupting Agents: Synthesis of Novel <i>cis</i> -Disubstituted Derivatives	123
S31: Analysis and Quantification of Point Mutations in Cancer DNA Biomarkers using Multicomponent Hybridization Probes	124
S32: Cyclophanes and their Ring-Opened Isosteres: The Interplay between Folding and Self-Assembly.....	125
S33: Investigation of the trans-acting enzymes involved in non-canonical intermediate trafficking in nemamide biosynthesis	126
S34: Structure-Guided Design of De Novo Protein Binders Targeting Interleukin-2 Receptor α in Leukemia Using a Deep Learning-Based Method	127
S35: Discovery and characterization of one eunicellane diterpene synthase homolog from <i>Chitinophaga solisilvae</i>	128
S36: Visible-Light-Induced Radical Cascade [4 + 2]/[4 + 2] Cycloaddition of Underexplored N-Acryloyl Indoles to Access Dihydropyrido[1,2a]-Indolones ...	128
S37: A DNA Cephalopod Nanostructure for Rapid Detection of Human Thrombin	129
S38: Less Sugar, All Sweet: Structure-Based Computational Design of Peptide Binders Targeting the Sweet Taste Receptor.....	130
S39: Functional characterization of hexokinase 2 from <i>Callorhinchus milli</i> (ghost shark).....	130
S40: Synthesis of SCN-Containing Indole-Fused Polycycles through an Oxidant-Mediated Dearomative Electrophilic Thiocyanation/Cyclization Cascade	131
S41: Effect of Organic Waste Feedstock Selection on Biogas Production During Anaerobic Digestion	131

S42: Physics-Guided Digital Twin Framework for Performance Prediction and Design Optimization of Organic Solar Cells.	132
S43: Investigating the nitration pathway of pyrrolomycins in <i>Streptomyces sp.</i>	132
S44: Rhodium(II)-catalyzed hydrosilylation of styrene derivatives: Reactivity and regioselectivity	133
S45: Biosynthesis of a putative isothiocyanate indole-like natural product	133
S46: Synthesis of CF ₃ -Containing Dihydropyrido[1,2-a]indolones via a Visible-Light-Promoted Radical Cascade [4 + 2]/[4 + 2] Cycloaddition.....	133
S47: An outer-sphere threonine residue is critical for NO-dependent tryptophan nitration by the cytochrome P450, TxtE	134
S48: Beyond Classical Force Fields: Physics-Driven Assessment of the Grappa Machine-Learned Force Field on the FoldBind Dataset	135
S49: Double crossover DX tile facilitated the cyclization of small-sized DNA oligomers by phosphodiester linkage	136
S51: Lyso-PCTP: A Reengineered Lipid Biosensor for Early PDAC Diagnosis and Monitoring	137
S53: Effect of sodium bicarbonate concentration and PLGA composition on degradation and release of magnesium ions from PLGA microspheres.	137
S54: Computational Design of COMT-Targeting PROTACs for Parkinson's Disease Using Cereblon-Mediated Targeted Protein Degradation	138

Oral Sessions

Plenary Lecture

Ru three ways with a side of Pt

Lisa McElwee-White

University of Florida

Techniques for fabrication of Ru-containing thin films and nanostructures have been of recent interest due to applications in building interconnect wires in semiconductor devices, repair of photomasks for extreme ultraviolet lithography, and area selective deposition of metal on thermally sensitive substrates. This talk will present mechanism-based design of organometallic precursors for deposition of Ru thin films and nanostructures by three different methods: Photo-Assisted Chemical Vapor Deposition (PACVD), Focused Electron Beam-Induced Deposition (FEBID) and Focused Ion Beam-Induced Deposition (FIBID). Precursor choice for any deposition method requires consideration of the reaction conditions and possible decomposition mechanisms for the particular method. Synthesis of candidate precursor complexes, evaluation of their reactivity with photons, electrons and ions, deposition of Ru-containing material by the three techniques, and simpler experimental models will be discussed.

Showcase Symposium

Exploring the Carboxylato-Pyrazolato Structural Parallel and Accessing New Redox-Modified States of Multinuclear Transition Metal Complexes

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The recognition of a structural parallel between (widely explored) carboxylato and (less common) pyrazolato multinuclear oxo complexes has led to the synthesis of several homo- and heterometallic examples of the latter. In contrast to labile carboxylates, the more robust pyrazolato analogues allow access to new redox-modified species, including charge-localized and -delocalized mixed valence species. Electrochemical, spectroscopic and magnetic susceptibility studies have revealed spin crossover and spin isomerization cases. The discussion will focus primarily on the $M_3(\mu_3-O)$ and $M_8(\mu_4-O)_4$ motifs, but other polynuclear structures will also be discussed.

Sulfur as a Source of Dark Matter in Proteomics: Roles of Mass Accuracy and Fragmentation Pathways

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Proteolytic peptide tandem mass spectra show lower complexity than top-down spectra from intact protein fragmentation. However, proteoform-level information is often lost in bottom-up workflows. Bottom-up proteomics still requires high mass accuracy due to isobaric interferences, e.g., tyrosine phosphorylation vs. sulfation. Due to this challenge and the extreme sulfate gas-phase lability, tyrosine O-sulfation, an important PTM in extracellular proteins, is understudied, has been misassigned as phosphorylation (or vice versa), or is often unidentified in typical informatics workflows [1]. Cysteine thiols constitute another complication due to their high reactivity. While alkylation is the gold standard for quenching reactivity in bottom-up proteomics, thiols are typically unmodified in top-down protocols. Free thiols undergo a high degree of radical thiol loss to form w-type ions in electron capture/transfer dissociation (ECD/ETD) when backbone cleavage occurs N-terminal to cysteine [2]. Here, we explore approaches to improve sulfate retention and annotation of sulfopeptide MS/MS spectra. We also examine radical thiol loss in top-down ECD/ETD.

Reanalysis of published higher energy collision dissociation (HCD) data refuted histone H3 sulfation [3]. By contrast, despite partial SO₃ loss, bottom-up EThcD (Orbitrap Fusion Lumos) revealed previously unreported autosulfation of tyrosylprotein sulfotransferases. A naturally occurring leech sulfopeptide with multiple arginines [4] showed sulfate retention in collision induced dissociation (CID; Orbitrap Elite), a surprising result hypothesized to be due to salt bridging that stabilizes the anionic form of sulfate, consistent with lower than expected cross-sections measured with gated trapped ion mobility spectrometry (TIMS) on a 9.4 T FT-ICR instrument. Top-down ETD combined with proton transfer reaction (Eclipse Tribrid coupled with 21 T FT-ICR MS) of reduced bovine fibrinogen proceeds without SO₃ loss. Such top-down ETD analysis identified several gamma chain proteoforms with differential glycosylation, sulfation, and C-termina, complementing previous bottom-up data.

A sulfopeptide proposed by MSFragger based on accurate mass revealed isobaricity with an alkylation artifact [5]. Radical thiol loss is prevalent in top-down ECD/ETD (9.4 T gTIMS-MRMS/21 T FT-ICR) of NIST mAb, particularly upon backbone cleavage N-terminal to cysteine. However, long (z - SH) fragment ion series reveal that such losses can occur from cysteine at any position within a primary fragment ion. These (z - SH) ions can be isobaric with calculated masses for internal fragment ions corresponding to two backbone bond cleavages and thus have important implications for spectral annotation and sequence coverage determination. MS³ experiments (Orbitrap Eclipse) and cysteine alkylation were used to identify thiol loss as the correct assignment.

1. Kweon et al. *J. Proteome Res.* **2024**, 23, 71-83.
2. Kempkes, et al. *J. Mass Spectrom.* **2018**, 53, 1207-1213.
3. Youssef, et. al. *Nat. Chem. Biol.* **2025**, 21, 1667-1670.
4. Hsu, et al. *Anal. Chem.* **2017**, 89, 8251-82583.
5. Youssef, et al. *J. Proteome Res.* **2024**, 23, 2386-2396.

Laser-Based Nanoscale 3D Printing

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Nanophotonics is the development of fundamental science, materials, and devices that leverage the interaction of light and matter on nanometer to micrometer length scales. This growing and highly interdisciplinary field involves chemistry, materials science, physics, engineering, and bio-science. In this presentation we will explore the field of nanophotonics, learn how nature does it, and discover ways that we can leverage chemistry to create ultra-small nanophotonic devices with unusual and useful optical properties.

Additive Manufacturing

3D Printing and Laser Annealing of Strain Sensors for Structural Health Monitoring

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Strain sensors are essential to structural health monitoring (SHM) systems that track fatigue, vibration, deformation, and localized stress in aerospace and space structures subjected to severe mechanical and thermal loads. Conventional strain gauges remain the standard in SHM systems, but their relatively low sensitivity limits their ability to resolve fine structural changes. This work presents an alternative fabrication route based on Direct Ink Writing (DIW), a high-resolution additive manufacturing technique capable of producing customizable, high-performance strain sensors directly on target substrates. Printing inks directly onto substrates avoids many of the interfacial issues associated with transferred sensors and enables the incorporation of functional nanomaterials during ink formulation to improve sensitivity, durability, and reliability. A series of conductive inks was formulated from a commercial silver-flake ink (CB028) modified with varying concentrations of ethyl cellulose (EC) and polyolefin (PO) as cohesion and adhesion modifiers, respectively. Rheological characterization of the resulting inks guided ink selection for extrusion, producing uniform printed lines (~120 μm wide, ~25 μm tall) with consistent structural integrity across substrates, including flexible polyethylene terephthalate (PET) film and high-pressure fiberglass laminate (G-10). For these structures, laser curing offers a practical alternative to conventional oven-based thermal curing, reducing processing time and energy consumption while overcoming the geometric limitations of oven curing. Using a 1064 nm infrared laser, we systematically varied laser power (0.2–1.5 W), number of passes (1–7), and scan speed (1–10 mm/s) to determine their effects on the resistivity and strain sensitivity of the cured sensors. Laser power had the strongest effect on both properties, followed by the number of scans and scan speed. Laser-annealed sensors also showed excellent electrical stability, with resistivity varying by less than 2% over 48 hours under ambient conditions (25°C, 50% RH). Because laser curing is localized and precisely controllable, it enables fine-tuning of a sensor's electrical and mechanical properties for specific applications, offering a scalable, substrate-flexible manufacturing route for next-generation SHM systems operating in demanding environmental and mechanical conditions.

Keywords: Conformal Printing, Direct Ink Writing, 3D printing, Conductive Ink, Strain Sensors, printed electronics, laser annealing.

Coupled Physics-Informed Neural Network for Multi-Physics Modeling in Additive Friction Stir Deposition

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Additive Friction Stir Deposition (AFSD) is an emerging metal additive manufacturing process gaining attention for its solid-state processing, which yields desirable mechanical properties and enables the fabrication of large parts. To understand the multiphysics nature of the process, modeling of thermal distribution and material deformation during processing is imperative and can be addressed by solving the associated partial differential equations (PDEs). However, complex coupled PDEs entail inaccuracies and slowness in utilizing the existing numerical methods, such as the Finite Volume Method (FVM). This work proposes a neural network-based method, coupled Physics Informed Neural Network (coPINN), as a fast and accurate mesh-free solution for predicting the thermomechanical states during the AFSD process. In the case studies, the proposed coPINN accurately predicts the velocity and temperature distribution for a steady-state non-linear coupled fluid dynamics-heat transfer model of the AFSD process faster than the existing FVM. Comprehensive comparisons with residual errors show the proposed method's trustworthiness in handling coupled physics, non-linearity, and mixed boundary conditions. In addition, the solutions from our approach show better agreement with the experimental data than those from the FVM-based solver. Overall, this is one of the first works to show more efficient neural network-based solutions of a PDEs-based model than a traditional numerical method.

Organosilane nanostructure fabrication on semiconductor substrates using particle lithography

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Patterned organosilane monolayers serve as molecular platforms for electronic, optical, and sensing applications. Among the strategies to pattern organosilane monolayers, particle lithography offers a high throughput means to fabricate organosilane nanopatterns across large areas. However, the size, spacing, and features of the organosilane nanopatterns created via particle lithography are closely coupled to the size of the mesospheres. Herein, the utility of particle lithography for generating organosilane nanostructures is enhanced by disintermediating the organosilane nanopattern features and mesosphere size by tailoring sample preparation conditions. Specifically, the influence of solvent, surface water, and humidity in the formation various types of organosilane nanopatterns are investigated. These insights lead to additional levels of hierarchical control over organosilane nanostructure formation on semiconductor substrates and enables a broader range of nanostructures that can be manufactured.

Direct Ink Written Membranes with Aligned 2D Channels for Application in Selective Extraction of Lithium via Electrodialysis

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Lithium remains a critical mineral due to its limited availability and rapidly increasing demand for electric vehicle batteries and energy storage systems. Consequently, scalable technologies for lithium recovery from unconventional sources, including wastewater and natural brines, are receiving significant attention. While solvent extraction and nanofiltration have shown promise, electrodialysis offers a potentially more scalable and energy-efficient route for lithium separation. In this context, nanocomposite membranes incorporating two-dimensional (2D) materials have emerged as attractive candidates for selective ion transport. However, conventional fabrication methods often rely on expensive raw materials, hazardous solvents, and complex processing steps, while achieving precise alignment of layered materials remains a major challenge. Here, we present a direct ink writing (DIW)-based additive manufacturing approach to fabricate aligned 2D-material-enabled ceramic membranes for selective lithium separation. A printable nanocomposite feedstock was prepared by directly exfoliating layered materials within a commercial silicone polymer using a three-roll mill. The resulting composite was extruded through DIW to induce vertical alignment of the 2D layers, forming interconnected sub-nanometer transport channels. Subsequent thermal treatment converted the printed structures into ceramic membranes. Scanning electron microscopy confirmed the successful alignment of the layered materials during the printing process. When evaluated in an electrodialysis system using a simulated brine solution, the fabricated membrane demonstrated high lithium flux and promising selectivity. This work establishes a simple and scalable pathway for producing aligned 2D-channel ceramic membranes and highlights their potential for lithium recovery and the separation of other critical minerals.

Analytical and Environmental Chemistry

Photocatalytic Degradation of Ibuprofen Using Methylene Blue-Sensitized TiO₂-Coated 3D-Printed PLA Plates

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Florida Institute of Technology

The widespread presence of pharmaceuticals and dyes in wastewater has become a significant environmental concern because conventional wastewater treatment processes often fail to remove these contaminants completely. Although photocatalytic degradation of individual pollutants has been extensively investigated, studies addressing the simultaneous removal of pharmaceuticals and dyes under environmentally relevant conditions remain limited. In this study, the simultaneous photocatalytic removal of ibuprofen (IBP) and methylene blue (MB) was evaluated using TiO₂ immobilized on a polylactic acid (PLA) plate under simulated solar irradiation. MB was pre-adsorbed onto the TiO₂ surface to function as a visible-light sensitizer, and its influence on IBP degradation was investigated. Removal efficiencies were quantified using liquid chromatography–mass spectrometry (LC–MS) for IBP and UV–Vis spectroscopy for MB. The results demonstrated that the presence of MB enhanced the photocatalytic degradation of IBP by approximately 10% during the first hour of irradiation. The enhancement likely results from electron transfer from excited MB to the TiO₂ conduction band, improving visible-light utilization and promoting IBP degradation. Accordingly, MB removal was slightly reduced in the presence of IBP. The enhancement in IBP degradation gradually diminished after the first hour, likely because of the depletion of MB adsorbed on the TiO₂ surface.

Towards Reliable DNA Extraction from Granular Activated Carbon in Drinking Water Treatment Plants

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Granular activated carbon (GAC) is a high-surface-area adsorbent widely used in drinking water treatment plants (DWTPs) for the removal of organic contaminants and the improvement of water quality. Over time, GAC surfaces can be colonized by microorganisms that contribute to treatment performance through biodegradation processes. Characterizing these microbial communities is therefore important for advancing biologically active filtration systems. However, DNA extraction from GAC remains challenging due to its strong adsorptive properties, which can compromise DNA recovery and quality, thereby limiting downstream analyses.

The objective of this study is to develop a reproducible DNA extraction method for GAC materials used in water treatment. Spent GAC samples (Calgon Carbon®) were collected from the Polk County Central Region Water Treatment Facility, while virgin GAC served as a control matrix. To better understand factors influencing DNA recovery, physicochemical properties of the materials were characterized using Brunauer-Emmett-Teller (BET) surface area analysis, point of zero charge (PZC), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and methylene blue adsorption measurements. Experimental DNA extraction approaches were evaluated and compared with the commercial DNeasyPowerSoil Pro Kit (QIAGEN®) using DNA yield (Qubit fluorometry) and purity metrics (NanoDrop UV–Vis spectrophotometry).

This ongoing work seeks to support more reliable microbial community characterization of biologically active carbon filters and facilitate the application of DNA-based approaches in drinking water treatment research and monitoring.

Tracking Long-Term Petroleum Weathering Using Molecular Markers: Lessons from the Deepwater Horizon Oil Spill

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Environmental weathering progressively alters the chemical composition of spilled petroleum residues and complicates the forensic oil spill fingerprinting long after a spill. The 2010 *Deepwater Horizon* (DWH) oil spill provided a unique opportunity to examine these transformations under natural coastal-marine environmental conditions. In this study, over 17,00 surface sediment samples collected from coastal Louisiana between 2010 and 2016 were analyzed for n-alkanes, polycyclic aromatic hydrocarbons (PAHs), and petroleum biomarkers using gas chromatography–mass spectrometry (GC-MS). The DWH (Macondo MC252) oil residues were identified using hopane and sterane biomarkers, and biomarker-positive samples were classified into three progressive weathering patterns: A, AB, and B, representing relatively less weathered, intermediate, and more extensively weathered residues, respectively. A pronounced temporal transition in biomarker profiles was observed over the seven-year period. Pattern A represented >90% of biomarker-positive samples in 2010 but declined substantially over time, whereas the more weathered Pattern B increased from 90% by 2016. This progressive alteration of petroleum biomarker fingerprints was accompanied by changes in the molecular composition of PAHs—widely used for source diagnostics following petroleum spills. Multivariate analysis demonstrated significant effects of sampling year, biomarker-defined weathering pattern, and their interaction on the overall PAH molecular-ratio profile. Several individual PAH ratios also varied significantly with time and weathering stage, indicating that commonly applied molecular signatures are not necessarily conserved during long-term environmental weathering. These results provide a field-scale record of the progressive chemical transformation of petroleum residues and highlight the importance of accounting for weathering when applying biomarkers and molecular indicators to aged oil residues in environmental monitoring and petroleum forensics.

MIP-based electrochemical sensing for health and environmental management

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Florida Polytechnic University

Our laboratory is exploring molecularly imprinted polymer (MIP)-based electrochemical sensing for health and environmental management. To be specific, the MIP-based sensing approach emerged as suitable for direct sensing of a targeted marker, even in the setting of point-of-care applications. Recently, we have detected microplastics (MPs, long-lasting pollutants) and per- and polyfluoroalkyl substances (PFAS, forever chemicals) in aquatic systems using MIP-based electrochemical sensing streams. Such proposed electrochemical sensors can detect MPs (ppb) and PFAS (ppt) selectively. On the same track, the MIP-based sensing has also been optimized for the detection of thyroid-specific markers (pM), needed for the efficient diagnostics of thyroid disorders, in a personalized manner. Our approach consists of customized electrodes interfaced with the smart electrochemical analyzer that can be operated using a smartphone.

Our developed MIPs-based electrochemical sensing system can detect microplastics (polystyrene and polyethylene) and PFAS in water samples at a low concentration. At the same time, several biomarkers of thyroid disorder can be detected using an engineered MIP-based electrochemical sensor. Altogether, MIP-based electrochemical sensing can be optimized for POC testing for health and environmental management.

Coaxial electrospun nanofibers for oil spill bioremediation

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Oil contamination poses major environmental risks to both freshwater and marine ecosystems. Over the ocean, large volumes of crude oil are spilled during errors in the drilling and transportation processes – poisoning and fouling native organisms and impacting the area for years. Freshwater sources such as rivers, lakes, and wetlands are contaminated with oil at lesser volumes, but at greater frequencies than marine sites as these spills are closer linked to the transportation of smaller oil shipments; these spills more directly impact human activities by polluting water supplies and infrastructure. Current remediation strategies for these harmful releases often involve adding chemical dispersants to the environment or physically removing oil using heavy machinery, both of which have drawbacks in effectiveness and environmentalism. We propose a more natural alternative, in which oil-metabolizing bacteria stored within core-shell nanofibers (CSNs) are utilized via bioaugmentation to clean polluted aquatic ecosystems.

Our current work focuses on developing CSNs with inorganic and biological cores, wrapped in a porous shell spun from natural polymers. CSNs are synthesized with coaxial electrospinning, a technique for nanofiber generation achieved by applying a high-voltage charge to polymer solutions within two syringes joined by a coaxial needle tip. This allows for the two solutions to be extruded as a uniform core (inner layer) and shell (outer layer).

We have successfully developed the inorganic half of a two-part blend of CSNs for oil contamination remediation – a nanofiber containing a CaO_2 core wrapped in a marine collagen-based shell. During remediation, CaO_2 will act to oxygenate the aquatic system to support aerobic, oil-metabolizing bacteria that will be present in the second CSN, currently under method development. Scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR) are used to confirm nanofiber morphology and structure.

Observing Chloride Concentrations in Southwest Florida using Ion-Selective Electrodes

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Water is essential for life, thus understanding, analyzing, and monitoring ion concentrations is essential to ensure the health and safety of both humans and wildlife. Particularly chloride concentration in the tropical region of southwest Florida is important due to recent storm surges. This symposium will connect the analytical techniques of ion selective electrodes (ISE) to the chloride concentrations in local canals and lakes/ivers. Using the voltage measured by the ISE in chloride standard solutions, a calibration curve between the voltage and the logarithm of known chloride concentration was created. This relationship is consistent with the Nernst equation in which the voltage is linearly proportional to the logarithm of chloride concentration. The analyzed water samples collected from local canals and lakes/ivers were all prepared with a total ionic strength buffer (TISAB) to keep the ionic strength consistent during all voltage measurements, so that their chloride concentrations can be calculated using the chloride calibration curve mentioned above. Chloride concentrations were calculated and they varied significantly from a few tens mg/L to nine thousand mg/L. These results were further incorporated into the Google map, and we found that the chloride concentration was incredibly related to hurricane-prone regions and this promotes interdisciplinary discussion of water monitoring and possible hurricane impact on the southwest Florida area.

The Evolving Landscape of Ion Mobility Spectrometry

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Ion Mobility Spectrometry (IMS) was discovered in the late 1960s. When IMS was introduced to the scientific community, the technology demonstrated a unique ability to measure a compound's shape/size/charge. One of the first benefits this technology offered investigators was its ability to interface with other instruments, thereby creating a hyphenated instrumental technique. We will discuss the capabilities of IMS technology when interfaced with techniques, such as mass spectrometry, and comment on what the technology can offer to the analytical, bioanalytical, and forensic communities. Ion mobility mass spectrometry (IMMS) provides confirmatory data with added advantages not usually available to other hyphenated instrumental methods. These advantages include the separation of isomers, isobars, and conformers, the reduction of chemical noise, and the measurement of ion size. In addition, structurally similar ions and ions of the same charge state separate into family ions, which appear along a unique mass-mobility correlation line. The presentation will briefly discuss the history of IMS, how IMS technology works, and present some applications our research has developed using IMS technology. IMS has many applications, and I plan to comment on the future strategic directions.

Synthesis and Photophysical Characterization of Methylene Blue Stearate

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Methylene blue (MB) is a versatile dye with multifaceted clinical applications, including the treatment of methemoglobinemia, photodynamic therapy, and diagnostic imaging. There has been increased interest in modulating the photophysical properties of MB through structural modification and counterion exchange. Ion exchange, followed by photophysical characterization, provides a promising approach to expanding the chemical and biomedical utility of MB. Here, methylene blue stearate was synthesized via metathesis from methylene blue chloride to alter the dye's solubility and photophysical behavior. Unlike the parent compound, methylene blue stearate exhibited marked solvent-dependent color changes (solvatochromism). Fluorescence spectroscopic characterization of MB stearate in dimethyl sulfoxide (DMSO) revealed distinct emission properties, with excitation spectra that differ substantially from the UV-Vis absorption spectra. These differences between the absorption and excitation spectra may arise from several factors, including ion-ion interactions, molecular aggregation, and variations in fluorescence quantum yields among the molecular species present. Given a low MB concentration used in these measurements, significant inner-filter effects are unlikely. Further investigations are underway to determine the relative contributions of these mechanisms and to explore potential sensing applications of MB stearate.

Rapid Characterization of Microplastics in Beverages Using Automated Laser Direct Infrared (LDIR) Chemical Imaging

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Microplastic contamination in beverages has become an emerging concern due to the widespread use of plastic materials in manufacturing, packaging, and distribution. Analytical approaches commonly used for microplastics characterization, such as μ FTIR and Raman microscopy, often require time-consuming sample preparation and lengthy analysis times, limiting routine monitoring capabilities. This study presents a rapid and automated workflow for the detection and characterization of microplastics in commercially available carbonated beverages and apple juice using an Agilent 8700 Laser Direct Infrared (LDIR) Chemical Imaging System.

Carbonated beverages packaged in recycled polyethylene terephthalate (PET), glass bottles, and aluminum cans, as well as apple juice packaged in PET bottles and multilayer cartons, were analyzed. Beverage samples were processed using direct filtration onto aluminum-coated polyester membranes, eliminating digestion and density separation steps. Apple juice samples were subjected to a two-stage filtration workflow to address matrix-related filter clogging. Procedural blanks were included throughout the study to assess background contamination. Automated particle detection, sizing, and polymer identification were performed using the Agilent Clarity Particle Analysis workflow and a dedicated microplastics spectral library. Particles were classified based on infrared spectral matching with a Hit Quality Index threshold >0.85 .

Microplastics were detected in all beverage samples analyzed. In carbonated beverages, particle counts ranged from 39 to 384 particles per sample and particle sizes ranged from 20 to 500 μm . Polyvinyl chloride and PET were identified as the predominant polymers. In apple juice, 66 microplastic particles were detected in the multilayer carton product and 20 particles in the PET-bottled product. Polyethylene was the dominant polymer detected in the carton-packaged juice, while PET was the primary polymer identified in the PET-bottled juice, suggesting a relationship between packaging composition and observed microplastic profiles.

The automated LDIR workflow provides rapid, low-handling microplastics analysis with particle count, size, and polymer data, supporting routine beverage monitoring, packaging assessment, and contamination source investigations.

Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Meat, Seafood, Eggs, and Milk following AOAC 2023.003

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Per- and polyfluoroalkyl substances (PFAS) comprise a large group of synthetic chemicals used in industrial and consumer products. The dietary exposure to PFAS substances through foods draws more and more attention, calling for the reliable analytical methods for PFAS determination in food. AOAC released performance criteria 2023.003 with the limits of quantification (LOQ) at lower to mid part per trillion level for typical animal-origin food matrices. The ultra-low LOQs and high complexity of animal-origin food matrices pose challenges on the PFAS testing workflow, from sample preparation to LC/MS/MS detection.

In this study, we developed a method using QuEChERS extraction, enhanced matrix removal (EMR) mixed-mode passthrough cleanup using Captiva EMR PFAS Food II cartridges, and LC/MS/MS detection for PFAS analysis in typical animal-origin food matrices. Pre-homogenized food sample was extracted using QuEChERS followed by pass through clean on the EMR PFAS Food II cartridges. Sample analysis was performed using an Agilent 6495D LC-MS system, with the modified LC system using a PFC-free conversion kit. Method calibration was based on neat calibration curve standards with the use of isotopic internal standards. The method was demonstrated to provide below or equal LOQs and acceptable method recovery and reproducibility according to AOAC 2023.003. The sample preparation method demonstrated a simplified but reliable workflow saving time and effort, and improved lab productivity for food sample analysis.

Integrated evaluation of oxidative potential and antioxidant activity of ambient PM2.5 in Lahore: Decoupling between mass concentration and redox reactivity

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Ambient fine particulate matter (PM2.5) can induce oxidative stress, yet mass concentration alone does not capture particle reactivity. We conducted a nine-month field investigation (August 2024–April 2025; $n = 68$) in Lahore, Pakistan, using an integrated redox framework combining the dithiothreitol (DTT) assay for oxidative potential with DPPH and ABTS assays for antioxidant capacity. PM2.5 concentrations increased from $166.14 \pm 5.24 \mu\text{g m}^{-3}$ in August to $400.23 \pm 63.82 \mu\text{g m}^{-3}$ in November. Volume-normalized oxidative potential (DTTv) ranged from $6.71\text{--}20.22 \text{ nmol min}^{-1} \text{ m}^{-3}$ and correlated positively with PM2.5 mass ($r = 0.518$, $p < 0.001$), indicating greater oxidative burden during high-pollution episodes. In contrast, mass-normalized oxidative potential (DTTm; $0.02\text{--}0.13 \text{ nmol min}^{-1} \mu\text{g}^{-1}$) was inversely associated with PM2.5 ($r = -0.714$, $p < 0.001$), revealing greater intrinsic particle reactivity during lower-mass periods. DPPH antioxidant capacity reached $133.57 \mu\text{g AAE mg}^{-1}$ in aqueous and $144.64 \mu\text{g AAE mg}^{-1}$ in ethanolic extracts, while ABTS capacity reached $205.49 \mu\text{g TE mg}^{-1}$; all increased with PM2.5 loading. Together, the divergence between DTTv and DTTm and concurrent antioxidant responses reveals a composition-dependent redox regime in which high particle loadings increase total oxidative burden while lower-mass aerosols can be intrinsically more reactive. These findings challenge reliance on PM2.5 mass alone and support integrated redox metrics for chemically informed assessment of aerosol reactivity and potential health relevance.

Exploring the mechanisms of radical directed dissociation enabled by novel cupric lipid ion types

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Introduction

The type of fragmentation observed, and thus the structural information obtained, from a tandem mass spectrometry (MS/MS) experiments is a function of how energy is imparted and the type of ion studied. We have used novel $[M+Cu^{II}Cl]^+$ ($M=Lipid$) ion types to efficiently generate $[M-H+Cu]^{+•}$ radical cations upon collision induced dissociation (CID), eliminating the need for photocaged radical initiators and photodissociation required in most radical-directed dissociation (RDD) MS/MS workflows. $[M-H+Cu]^{+•}$ radical cations undergo subsequent RDD, enabling improved lipid structural characterization. However, the mechanism of radical formation and RDD has not been fully deciphered. Herein, we investigate the gas-phase ion chemistry of these novel $[M+Cu^{II}Cl]^+$ ion types formed with different lipids to elucidate the reaction mechanisms of $[M-H+Cu]^{+•}$ radical cation formation and RDD.

Methods

Experiments were performed on a 7T Solarix FT-ICR MS (Bruker Daltonics) in positive ion mode. Standard solutions were prepared by mixing 0.02 mg/mL of PC standards and 0.02 mg/mL of $Cu^{II}Cl_2$ in a 1:1 (v/v) ratio in 100% methanol. Standard PC 16:0/18:1, PC 18:0/18:2, PC 18:3/18:3, PC 16:0/20:4, PC 18:0/20:5, PC 18:0/22:6, PE 16:0/18:1, LPC 18:1, d18:1 SM, and C18:1 carnitine were studied using $Cu^{II}Cl_2$. Complexes were generated using electrospray ionization (ESI) and isolated using a quadrupole mass filter (2 Da isolation window) and subjected to CID in a hexapole collision cell using collision energies ranging from 16-30 eV. Mass spectra were collected using two average scans.

Preliminary Data

Briefly, $[PC+Cu^{II}Cl]^+$, $[LPC+Cu^{II}Cl]^+$, $[SM+Cu^{II}Cl]^+$, $[AC+Cu^{II}Cl]^+$, and $[PE+Cu^{II}Cl]^+$ (PC=phosphatidylcholine, LPC=lysophosphatidylcholine, SM=sphingomyelin, AC=acyl carnitine, and PE=phosphatidylethanolamine) complexes were generated via electrospray ionization and subjected to CID. CID of $[PC+Cu^{II}Cl]^+$, $[LPC+Cu^{II}Cl]^+$, $[SM+Cu^{II}Cl]^+$, and $[AC+Cu^{II}Cl]^+$ complexes results in a net loss of an HCl molecule and reduction of Cu^{II} to Cu^I , generating an odd-electron $[M-H+Cu]^{+•}$ radical cation. CID of $[PC-H+Cu]^{+•}$ and $[LPC-H+Cu]^{+•}$ radical cations induces highly efficient radical-driven intrachain C-C bond cleavages along the fatty acyl chain, producing abundant fragment ions that are used to locate the double bond position. In contrast, CID of $[SM-H+Cu]^{+•}$ and $[AC-H+Cu]^{+•}$ radical cations instead produces RDD cleavage of the trimethylamine moiety from the lipid headgroup. CID of $[PE+Cu^{II}Cl]^+$ complexes doesn't result in radical formation and instead promotes cleavage of PE headgroup. These observations suggest alternative reaction mechanisms for radical formation and RDD in the gas-phase for $[M+Cu^{II}Cl]^+$ complexes. We propose that the distorted d^9 coordination sphere of Cu^{II} ion with PC and LPC allows for the abstraction of an activated allylic hydrogen, resulting in the formation of the radical cation on the fatty acyl chain. Conversely, with SM and AC, the hydrogen abstraction necessary for the radical formation occurs at the methylene adjacent to the trimethylamine, forming a radical on the lipid headgroup. The absence of radical formation with PE indicates that deprotonation from the lipid headgroup occurs more readily than H-abstraction for radical formation. DFT calculations are performed on the optimized $[M+Cu^{II}Cl]^+$ systems to locate the site of hydrogen abstraction. The results are largely consistent with the hypothesis that hydrogen abstraction indeed occurs at the allylic hydrogen in PCs and the headgroup in ACs.

Zwitterionic Self-Assembled Monolayer Modification of Lithium Niobate for Enhanced Surface Acoustic Wave Nebulization Mass Spectrometry

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Surface acoustic wave nebulization mass spectrometry (SAWN-MS) is an emerging sample introduction technique capable of generating fine aerosol particles from microliter-scale samples without the high temperatures, auxiliary gases, or matrix compounds required by many conventional ionization methods. The technique has demonstrated utility for the analysis of compounds spanning a wide range of chemical polarities while minimizing sample degradation during introduction. However, broader adoption of SAWN-MS is hindered by limited reproducibility arising from surface fouling of lithium niobate (LiNbO_3) devices. Accumulation of adventitious carbon on the delay-line region increases droplet contact angles, alters nebulization behavior, and necessitates frequent plasma cleaning to restore performance.

Here, we investigate the use of a superhydrophilic zwitterionic self-assembled monolayer (SAM) of 3-[[dimethyl(3-trimethoxysilyl)propyl]ammonio]propane-1-sulfonate (SBSi) to stabilize surface wetting behavior on 128° YX-cut LiNbO_3 SAWN devices. The SBSi-modified surfaces resist fouling and maintain sub-10° water contact angles during repeated operation, providing cleaning-free superhydrophilic performance. By preserving consistent droplet spreading, the SAM improves the reproducibility and robustness of aerosol generation while enabling systematic investigation of the relationships between operating conditions and particle formation. These results demonstrate that zwitterionic surface modification is an effective strategy for improving SAWN-MS reliability and accessibility, supporting the continued development of SAWN-MS as a practical platform for soft, sensitive, and high-throughput mass spectrometric analysis.

Development of Focused Surface Acoustic Wave Nebulization Mass Spectrometry

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University of South Florida

Focused surface acoustic wave (FSAW) devices offer a promising approach for microscale aerosol generation and sample introduction in mass spectrometry (MS) by concentrating acoustic energy into a confined focal region. In this work, we investigated the effect of FSAW operating frequency and focusing geometry on aerosol generation and MS performance. Six FSAW devices with resonant frequencies of 10 and 20 MHz and arc angles of 45°, 90° and 120° were fabricated and evaluated. Device performance was characterized through thermal analysis, aerosol particle size measurements and MS analysis of caffeine as a model analyte. Higher-frequency devices generated larger populations of submicron droplets, while increasing arc angle promoted stronger acoustic focusing and enhanced atomization efficiency. These trends were accompanied by improved MS response, with signal intensity increasing consistently with both operating frequency and arc angle. Device with 120° arc angle produced the highest signal intensities compared to smaller arc angle configurations. The correlation between droplet size distribution and MS response highlights the importance of acoustic focusing in controlling nebulization behavior and ion generation. These results demonstrate that optimizing FSAW device geometry can significantly improve aerosol production and analytical sensitivity, establishing FSAW nebulization as a promising platform for low volume sample introduction and ionization in mass spectrometry.

Sediment Microbiome Dynamics Across a Northern Gulf of Mexico Salinity Gradient

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Estuarine and coastal ecosystems provide essential ecological and economic services, including biodiversity support, carbon sequestration, flood protection, and shoreline stabilization. The microorganisms inhabiting these systems are exposed to strong environmental gradients and stressors, including shifts in salinity and nutrient loading, emerging contaminants, sea-level rise, extreme weather events, and coastal development. Despite their importance to ecosystem function, sediment microbial communities in estuarine environments remain relatively understudied.

This study characterizes sediment microbial community structure across a salinity gradient in Econfina River State Park, located along the eastern Northern Gulf of Mexico. Surface sediments (0–10 cm) were collected from 25 sites spanning upstream freshwater habitats to downstream coastal seagrass beds. DNA was extracted from sediment samples and analyzed using 16S rRNA gene amplicon sequencing to assess microbial community composition across the gradient. The results will strengthen understanding of how salinity-associated habitat variation structures sediment microbial communities in Northern Gulf of Mexico coastal ecosystems.

Biochemistry and Chemical Biology

Computational insights into arginine side chain activation and post-translational modification.

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A variety of important biological processes are underpinned by the enzyme-catalyzed modification of arginine side chains, including the regulation of gene expression, subversion of the immune system by bacterial pathogens, and a method of buffering ATP concentration in cells. This lecture will outline recent insights, obtained by DFT analyses of quantum chemical cluster models for arginine kinase and protein arginine methyltransferase (PRMT), into how arginine side chains are activated for reaction. Our findings, when taken together with recent work by Rovira and co-workers on arginine *N*-glycosylation, suggest that arginine-modifying enzymes employ similar strategies for activating the cationic guanidinium moiety despite being evolutionarily unrelated.

Discovery of a Sub-Femtomolar Modulator of the Human STING Receptor

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Stimulator of Interferon Genes (STING) has been a target of medical interest for some time, prompting considerable interest in both the pharmaceutical industry and academia to find molecules capable of modulating the transmembrane endoplasmic reticulum receptor. We have found a series of molecules with remarkable activity that are capable of serving as both agonists and antagonists, and some of the results of these efforts to date will be presented.

Development of a synthetic biology platform for natural product chemistry

Edward Kalkreuter

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Biosynthetic gene clusters (BGCs) are the genetic blueprints for the diverse natural products (NPs) that have evolved over hundreds of millions of years. These compounds are foundational to modern chemistry and medicine, underpinning the development of antibiotics, anticancer agents, agrochemicals, and other therapeutics and chemical agents. Genome sequencing has revealed that prolific NP producers, including Actinobacteria, encode 30 or more BGCs per strain and are responsible for 60% of known bacterial NPs. However, up to 90% of these BGCs remain cryptic, regulated by complex global and BGC-specific mechanisms that restrict their expression to specific and often unknown environmental conditions. Traditional approaches to accessing these cryptic BGCs have relied on random elicitor screenings, media optimization, or heterologous expression in model organisms. While these strategies have been and remain exceptionally valuable, they often bypass native regulatory systems, leaving substantial gaps in our understanding of BGC regulation. The Kalkreuter lab focuses on addressing these gaps by leveraging synthetic biology, with a focus on native regulation. By systematically decoding and rationally rewiring these regulatory networks, our lab aims to unlock cryptic BGCs, leading to the discovery of novel NPs (with a focus on drug-like molecules) and insights into their biosynthetic pathways. This approach not only enhances our ability to access hidden chemical diversity but also establishes a foundation for the rational production of NPs to address pressing challenges in medicine and biotechnology.

Targeted Protein Degradation: From PROTACs to Molecular Glues

Xingui Liu

University of Florida

Targeted protein degradation (TPD) is reshaping drug discovery by enabling small molecules to eliminate disease-causing proteins rather than simply inhibiting their functions. This presentation will highlight our efforts to advance TPD through proteolysis-targeting chimeras (PROTACs) and molecular glue degraders (MGDs).

Leucine-rich repeat kinase 2 (LRRK2) is a genetically validated therapeutic target for Parkinson's disease. Through systematic optimization of LRRK2-targeting PROTACs, we discovered XL01126, a potent, selective, and blood-brain barrier-penetrant LRRK2 degrader, demonstrating the potential of PROTACs for targeting proteins in the central nervous system.

Moving beyond bifunctional degraders, my laboratory is developing monovalent MGDs through an integrated platform combining fragment-based drug discovery, artificial intelligence, and medicinal chemistry. Our efforts have identified novel E3 ligase ligands that provide new starting points for molecular glue discovery. We are exploring how these ligands can be evolved into functional degraders, with the broader goal of expanding the druggable proteome through TPD.

Structural Mechanisms of the Constitutive Activity in Ion Channel TRPM1

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Transient receptor potential melastatin 1 (TRPM1) is a membrane protein essential for vision in dim light, and mutations in TRPM1 cause complete congenital stationary night blindness. Although TRPM1 shares sequence similarity to other TRPM ion channels such as TRPM3, whether it independently functions as an ion channel remains controversial. This controversy is largely caused by TRPM1's challenging biochemical behaviors that prevent detailed molecular characterization. In this work, we isolate TRPM1 and determine its structures using cryogenic electron microscopy (cryo-EM). The structures reveal a canonical tetrameric fold in the intracellular domain, consistent with other TRPM family members that are ion channels. Surprisingly, in the transmembrane domain, despite the presence of the conserved voltage sensor-like domain (VSLD) and pore domain (PD) in a domain-swapped fashion, the VSLD and PD are arranged with an opposite handedness compared to other related channels. This inverted transmembrane domain allows the formation of a large pore-like structure that supports the role of TRPM1 as an ion channel. This non-canonical architecture of TRPM1 may also confer unique permeation and pharmacological properties.

Beyond Four Letters: Expanding the Chemical and Functional Space of Nucleic Acids

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Standard DNA and RNA are informationally and chemically constrained polymers. With only four canonical nucleobases, they encode a comparatively narrow range of chemical functionality, limiting the molecular solutions available for binding, catalysis, and evolution.

Artificially Expanded Genetic Information Systems (AEGIS) overcome these limitations by increasing both the information density and chemical diversity of nucleic acids while retaining the base pairing, replication, and molecular recognition properties required for Darwinian evolution.

Across multiple in-vitro evolution experiments, we have found that this additional information and chemical functionality translate into substantially improved molecular performance. AEGIS libraries have yielded high-affinity aptamers against cellular and protein targets, with selected molecules exploiting functionalities unavailable to standard DNA. Expanded alphabets can also support catalysis: RNA-cleaving AEGISzymes evolved under low-magnesium conditions directly exploit the acid-base chemistry of the noncanonical nucleobase Z, demonstrating that alphabet expansion can provide catalytic strategies inaccessible to standard nucleic acids.

More strikingly, our recent comparative evolution experiments indicate that alphabet expansion changes not only what nucleic acids can do, but how efficiently they evolve function. Parallel selections of standard four-letter DNA and six-letter AEGIS libraries, varying in random region length, reproducibly show that expanded alphabet populations generate functional catalysts more rapidly and with higher apparent activity than their four-letter counterparts, despite sampling a dramatically smaller fraction of their available sequence space.

These studies illustrate how expanding the chemistry encoded within nucleic acids can reshape their functional landscape, providing both a tool for experimentally studying molecular evolution and a platform for developing nucleic acid molecules with enhanced binding and catalytic properties.

Characterization of the Hsp70 and J-Domain Protein Chaperone System in the Tardigrade *Hypsibius exemplaris*

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Molecular chaperones are proteins dedicated to maintaining protein homeostasis and cellular stress response. The Hsp70 molecular chaperone, with its obligatory co-chaperones, J-domain proteins (JDPs), plays a central role in facilitating these cellular processes. Unique organisms, such as tardigrades, exhibit astonishing resilience to extreme environmental stresses, including dehydration, low temperature, and even conditions in space. Very little is known about the Hsp70/JDP systems in tardigrades and their contribution to resilience at the molecular level. Here we focused on identifying and characterizing the main cytosolic Hsp70/JDP system in tardigrade *Hypsibius exemplaris*. Using genomic, phylogenetic, and structural analyses, we identified candidate cytosolic class A and class B JDPs and the Hsp70 proteins. Comparative sequence and structural analyses revealed conservation of hallmark features of eukaryotic Hsp70/JDP systems, including the J-domain HPD motif, zinc-binding regions characteristic of class A JDPs, and the C-terminal EEVD motif of Hsp70. Biochemical analyses of both wild-type proteins and altered variants showed that tardigrade JDPs stimulate Hsp70 ATPase activity, which depends on conserved features of this system. This work provides the first comprehensive experimental characterization of the Hsp70/JDP chaperone system in *H. exemplaris*. These findings establish a foundation for investigating the molecular basis of tardigrade stress tolerance.

The Mechanism of Oxalate Decarboxylase and How to Improve its Catalytic Efficiency

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Oxalate decarboxylase (OxDC) is a manganese-dependent enzyme belonging to the cupin superfamily, commonly found in fungi and soil bacteria. As a bicupin, it contains two Mn ions per protein subunit, one bound to each cupin domain by one glutamate and three histidine residues. The primary enzymatic function of OxDC is the redox-neutral disproportionation of the environmental toxin oxalate, resulting in the generation of carbon dioxide and formate, while concurrently increasing solvent pH. Current insights into the enzymatic mechanism of OxDC, involving a long-range electron transfer pathway between neighboring protein subunits in its hexameric quaternary structure, will be reviewed. The enzyme has shown promise for applications in medicine, agriculture, and industry. It has been commercially produced for over two decades. Our study focuses on the use of rational protein engineering to improve the catalytic efficiency of the enzyme. We worked with two paralogous isozymes from *Bacillus subtilis* (gene names *oxdc* and *oxdd*) and explored several different strategies. We report on mutant isozymes with up to 3-fold enhanced catalytic efficiencies compared with their respective wild-type forms. Specifically, we report on the C383A mutant, which reduces non-specific aggregation of the protein; the use of Strep-tag II technology, which leads to higher Mn retention after protein purification; and modification of the auxiliary tryptophans W171 and W348, all of which lead to higher catalytic efficiencies. We also report on mutations testing the active site loops (SENST161-165 in OxDC) of OxDC and OxDD and the effect of residues near a small channel leading to the C-terminal Mn binding site.

Host-factor phase separation properties transport the HIV-1 core to vDNA integration sites

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Following its nuclear entry the HIV-1 capsid core is transported to phase-separated membraneless organelles of the nucleus called nuclear speckles. The localization of HIV-1 to nuclear speckles is driven by interactions between the viral capsid and its host-cellular polyadenylation specific factor CPSF6. Three functional domains within CPSF6's structure, namely: an N-terminal RNA recognition (RRM)-motif, a central low-complexity prion-like (PrLD)-domain, and the C-terminal mixed-charge domain (MCD) have all been implicated in viral replications. Here, we combined biochemical reconstitution, capsid-binding analyses, and live-cell single-virus imaging to determine how CPSF6 drives HIV-1 trafficking within the nucleus. Using recombinant CPSF6 purified from a newly established bacterial expression system, we show that the MCD is required for robust liquid-liquid phase separation (LLPS) of CPSF6 proteins, while MCD deletion abolishes condensate formation and yields protein aggregates. Single virus binding assays showed that, although wild-type and MCD-deficient CPSF6 bind HIV-1 capsids with comparable affinity at low-nM concentrations, only wild-type CPSF6 exhibits a non-saturable high-avidity binding phase that depends on LLPS activity and is disrupted by 1,6-hexanediol. To determine how these biochemical properties influence viral behavior in cells, we performed high-temporal-resolution live-cell imaging of fluorescent HIV-1 cores together with fluorescent CPSF6 and nuclear speckle markers. We found that capsid-CPSF6 interactions trigger the *de novo* formation of small nuclear speckle droplets at sites of viral nuclear entry. In the absence of CPSF6 interactions, HIV-1 cores remained associated with the nuclear lamina and speckle droplet formation was rarely detected. Once formed, these CPSF6-dependent speckle droplets facilitated viral entry into the nucleoplasm, where cohesive speckle-speckle fusion, a hallmark of LLPS behavior, and rapid directional movement transported viral cores to integration compartments. By contrast, disruption of CPSF6-phase separation by MCD deletion resulted in viral retention at the nuclear lamina or random intranuclear distribution. Together, these findings identify CPSF6 MCD-mediated phase separation as a key driver of high-avidity capsid binding, nuclear speckle remodeling, intranuclear transport, and reveal a previously unrecognized mechanism by which host condensate biology directs HIV-1 genome positioning and integration site selection within the nucleus.

Leveraging anaerobic HDX-MS to decipher RiPP-rSAM substrate recognition

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Unlocking the potential of substrate-controlled catalysis by Radical S-adenosylmethionine (SAM) enzymes for the generation of novel drug candidates within the class of ribosomally synthesized and post-translationally modified peptides (RiPPs) has recently garnered interest and traction in the field. Although significant progress has been made in understanding the chemical reactions catalyzed by this intriguing class of enzymes, the structural and biophysical mechanism behind peptide substrate recognition remains relatively obscure. We utilized anaerobic hydrogen-deuterium mass spectrometry (HDX-MS) to probe substrate engagement of RiPP-rSAM enzymes. By comparing the apo enzyme with the binary and ternary enzyme-substrate complexes formed before catalysis, we have identified substrate-binding pockets, including regions responsible for peptide recognition. This work furthers our understanding of peptide engagement by rSAM enzymes, specifically those lacking the canonical RiPP recognition element (RRE) typically responsible for peptide binding and provides another example of employing HDX-MS for the study of peptide-modifying rSAM enzymes.

Exploring the NO peroxidase pathway of *Mycobacterium kansasii* (Mka) HLP

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Mycobacteria virulence is associated with hemerythrin-like proteins (HLPs) which exhibit unique nitric oxide (NO) peroxidase activity, but little is known about the mechanism of this activity.¹⁻³ Investigating the mechanism associated with this unique activity could lend valuable information regarding mycobacteria virulence.³ When engulfed by a macrophage, mycobacteria are exposed to a toxic combination of NO and superoxide.² The NO peroxidase activity of HLPs involves peroxide (H₂O₂) as an oxidant to convert NO to less harmful nitrite. Studies have validated that *Mka* HLP contains a highly conserved diiron active site with a coordinated tyrosine ligand that is critical for catalase and NO peroxidase activities.^{3,4} NO peroxidase activity typically associated with heme enzymes but never non-heme diiron enzymes. Our work focuses on the unique *Mka* HLP NO peroxidase pathway through study of the wild-type and a tyrosine mutant protein, Y54F. Results include characterization of resting states and trapped intermediates through EPR and Mössbauer spectra. Furthermore, stopped flow studies allow for understanding of the role of the mixed-valent species with H₂O₂ and O₂ as co-substrates.

Evolutionary Emergence of a Non-Native Metabolite in Response to Loss of an Essential Enzyme

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Enzyme recruitment is the process whereby existing promiscuous enzymes are repurposed to perform new functions.¹ The biochemical literature is replete with examples in which enzymes are recruited to provide a weak, but direct replacement of a lost essential enzyme. Much less is known about the extent to which enzymes can be recruited to expand metabolism via the synthesis and utilization of new metabolites. Recently, we discovered that aspartate transcarbamoylase (PyrB) can be recruited to restore growth to a bacterium lacking the essential enzyme *N*-acetyl-glutamate synthase (ArgA) in arginine biosynthesis.² PyrB natively produces *N*-carbamoyl-L-aspartate in the second step of pyrimidine biosynthesis. Here, we report that PyrB can also utilize L-glutamate as an alternative substrate to produce a non-native metabolite, *N*-carbamoyl-L-glutamate, that is readily accepted by downstream arginine biosynthetic enzymes. We discover that supplementation with *N*-carbamoyl-L-glutamate restores growth in an ArgA-deficient strain upon acquisition of a small number of spontaneous mutations. Following adaptive laboratory evolution of these isolates, we identify ArgA-deficient strains that are capable of growth without *N*-carbamoyl-L-glutamate supplementation, suggesting the emergence of endogenous *N*-carbamoyl-L-glutamate production. Whole-genome sequencing, transcriptomics and biochemical assays support the postulate that these cells have evolved to use a set of promiscuous enzymes to actively synthesize and subsequently process *N*-carbamoyl-L-glutamate. Our findings demonstrate how promiscuous side reactions can be leveraged to circumvent traditional, highly conserved metabolic pathways. Our results also uncover specific details of the evolutionary events facilitating the emergence and expansion of new metabolic capabilities.

This study was supported by grant GM157172 and GM133843 (B.G.M.) from the NIH.

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Chemistry Education

Mastery Paths for Metacognitive Engagement in an Introductory Chemistry Course

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This project examines the pilot implementation of mastery paths for a complete 16-week introductory online chemistry course (CHM1030). Mastery paths conditionally release instructional materials, practice sets, and assessments based on student performance on formative checkpoints. Short, timed low-stakes diagnostic assessments were delivered frequently, providing students with opportunities to identify conceptual gaps and to revisit content before summative evaluations. The mastery path structure was intentionally designed to promote metacognitive engagement by requiring students to evaluate their understanding before progressing. Frequent low-stakes diagnostics served as structured reflection points, prompting learners to identify conceptual gaps and decide whether to revisit instructional materials. By embedding these reflection cycles into the course architecture, the design encourages active self-regulation and greater ownership of learning in an asynchronous online environment.

AI Tutor, AI Media, or Human Instructor? Student Use, Trust, and Confidence in a Flipped Analytical Chemistry Module

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Generative artificial intelligence (AI) is often evaluated as a single instructional intervention, although students may respond differently to passive AI-generated media, a dialogic tutor, and human-guided activities. This convergent mixed-methods case study examined how students used and evaluated these roles within a three-part AI-supported flipped acid–base module in CHM3120 Analytical Chemistry at the University of Florida. The module combined instructor-prepared slides, NotebookLM-generated audio and video, a course-grounded conversational tutor (ChemGPT), readiness quizzes, instructor-curated AI-generated worksheets, group problem solving, and instructor/teaching-assistant feedback. Data included 47 valid pre-module surveys, 39 valid post-module surveys, 20 unambiguous pre/post matches, open-response comments, and 157 quiz-linked ChemGPT learning logs.

Among matched respondents, mean self-rated confidence across 11 acid–base problem-solving tasks increased from 3.21 to 3.99 on a five-point scale. Instructor slides (37/38 ratings of 4–5) and guided worksheets (32/39) were rated more useful than AI-generated podcast/audio (3/37) or short overview media (2/37). ChemGPT was used by 29/39 respondents, while 34/39 expressed high concern about inaccurate information and 35/39 about dependency; 27/39 both used ChemGPT and retained at least one of these concerns. A chemistry question or actionable request for class appeared in 111/157 learning logs.

These findings show that students evaluated each instructional tool separately rather than accepting or rejecting AI as a whole. They used the course-specific ChemGPT for clarification and reasoning support but rated the AI-generated audio and video poorly. Instructor explanations and guided practice received the strongest ratings. Because the study did not include an equivalent pre/post measure of achievement, it cannot show that AI improved examination performance. Instead, the results suggest a practical division of responsibilities: instructors should provide the central explanations, monitor accuracy, and give feedback, while AI should serve as an optional resource for clarification and reasoning checks. Learning logs can also help instructors identify what students still find confusing and address those difficulties during class.

Beyond 2D: Visualizing Molecular Orbitals through Virtual Reality

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Understanding abstract chemical concepts can be challenging for students, particularly when it requires visualization of intangible constructs, such as molecular orbitals (MOs). Traditionally, students have relied on mental visualization and two-dimensional representations such as those in textbooks, and computer-based images and/or animations. Emerging immersive technologies, including augmented reality (AR) and virtual reality (VR), provide an opportunity to move beyond these conventional representations by allowing students to visualize and directly interact with molecular structures in three-dimensional space.

We developed a VR-compatible application featuring the MOs of small molecules to support teaching concepts that require visualization. Rather than viewing static representations, students can “see” and interact with MOs in real time by grabbing, rotating, translating, and examining them from different perspectives. We incorporated the application into classroom activities that connect MO theory with fundamental chemical concepts. In one activity, students use orbital interactions to learn the MO basis of a reaction between a Lewis acid and a Lewis base. In another, students interact with MOs in three-dimensional space to identify symmetry and assign Mulliken symbols.

These immersive activities transform MOs from abstract representations into interactive objects that students can directly explore and manipulate. Student feedback and instructor observations indicate a positive perception of the VR activities and increased participation during instruction, highlighting the potential of immersive visualization as an engaging approach for supporting the teaching and learning of abstract concepts in chemistry.

Investigating the Efficacy of Self-Selected Weekly Peer-Mediated Study Groups for At-Risk Students Across the General Chemistry Sequence

Martina Sumner, Steven Harris, Ashlyn R. E. Hale, and Robert Bailey

University of Florida, Dept. of Chemistry (Sumner, Harris, Hale) 2. University of Florida, College of Liberal Arts and Sciences (Bailey)

Students may self-select to participate in weekly study groups that provide additional academic support and promote peer-to-peer connections. This work examines the use of small, peer-mediated study groups as a supplemental support mechanism within the General Chemistry sequence, specifically General Chemistry I (CHM2045) and General Chemistry II (CHM2046).

Initially implemented in CHM2045, the program was later expanded to include CHM2046 to explore how participation across one or both courses relates to student outcomes. The initiative is administered by the Academic Resources department in collaboration with General Chemistry I and II instructors and undergraduate teaching assistants (UGTAs) from the College of Liberal Arts and Sciences at the University of Florida.

This study focuses on understanding patterns of student participation, particularly among those who may be at greater academic risk, as well as how students engage with available academic support resources. Ongoing evaluation informs the development of UGTA training practices to ensure effective peer support. Using longitudinal data and predictive indicators of course success, this work explores factors influencing students' decisions to engage in peer-mediated study groups.

Additionally, the study examines relationships between study group participation, attendance patterns, and course performance. Together, these findings aim to contribute to a broader understanding of the role of peer-mediated academic support in student success within foundational chemistry coursework.

Empowering Students, Strengthening Skills: Developing an Internship Program in Teaching Labs

Jhon J Figueroa

University of South Florida

Teaching labs are crucial in scientific education, providing hands-on experience and fostering critical thinking skills. However, opportunities for students to delve deeper into lab operations and gain valuable professional insights are often limited. Teaching labs often face a shortage of personnel dedicated to curriculum development, leading to outdated materials and missed opportunities for innovative learning experiences. This presentation explores the solution implemented by the University of South Florida's chemistry department: an internship program specifically designed to address this challenge. This presentation will show the use of an internship program to help in the curriculum development within teaching labs, offering students a unique and enriching learning experience. This internship program is believed to become a cornerstone of experiential learning at USF, empowering students, enriching the lab experience, and preparing graduates for successful careers. This initiative aims to provide undergraduate students with an invaluable opportunity to gain hands-on experience in the educational setting while developing essential skills sought by future chemists. This internship program not only empowers students to explore their passion for chemistry but also contributes to developing future educators who are well-equipped to meet the evolving needs of diverse learning environments.

Turning Assessment into Learning

Jack Huang

Jacksonville University

Quizzes and exams are generally considered assessment tools. The advancement of online courseware can turn these assessment tools into learning tools.

In this talk, I will demonstrate how the learning tools are used in the teaching/learning process. Using classroom tools within online courseware can help instructors collect, analyze, and share student data effectively. The courseware also provides correlation charts generated after an exam, showing the relationship between grades on quizzes, homework, and exams. Instructors can help students develop metacognitive skills based on these correlation charts. The "Make Me Exam Ready" tool within the courseware can help students discover deficiencies and use their time efficiently — focusing their efforts on concepts and skills that have not yet been mastered.

Academic pathways: Exploring the Relationship Between STEM Identity and Factors That Influence a Student to Consider Changing Their Majors

Massimiliano Scorpio,¹ Adam John,¹ Hannah Barrineau,¹ Cameron Bechard,² Nicole Lapeyrouse¹

1. University of Central Florida,

2. Landmark College

Understanding the reasons behind students' doubts about their chosen field is crucial to better understanding how these reservations affect their connection to their major and their persistence in their major. This study aims to connect and relate students' identity to their consideration of alternative academic paths, focusing on a Principles of Chemistry course that is aimed at engineering students. For this study, a survey was administered at the beginning and end of the Spring 2022 and Fall 2023 semesters. The survey contains various types of questions, including open-response and Likert-scale questions, regarding how students develop their STEM identity throughout their undergraduate degree. The students' responses were analyzed using thematic analysis to find shared patterns in responses. Preliminary results show that the most prominent codes among students' responses were a sense of commitment to their current major, personal opinions on their courses, and various or changing interests. The following presentation will explore the reasons students consider leaving engineering for another major and how these doubts relate to their sense of identity and belonging within the field. The information presented can be used to inform retention efforts and tailor students' learning experience, creating an improved environment that enables them to excel throughout their major.

Identifying resources that engineering students use to explore their academic pathways

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Gaining insight into student resource utilization is essential for fostering career readiness and supporting successful transition into professional roles. While many resources are provided to undergraduate students, less is known about which resources students prioritize. This study examines the various resources utilized by undergraduate students enrolled in a Principles of Chemistry course. Data were collected through an open-ended survey administered to students enrolled in a Principles of Chemistry course, a curriculum designed for engineering students. Using qualitative content analysis, the responses were analyzed and categorized based on the type and intended purpose of the described resource. Student responses revealed a spectrum of formal and informal support systems used to enhance their undergraduate experience. The resources identified in this study are organized into four distinct categories: media, networking, occupational, and academic resource types. By examining student resource use through these categories, the findings highlight text-based media as the most frequently utilized code, driven by students' strong preference for easily accessible, self-guided formats. Consequently, because students heavily gravitate toward these low-barrier options while other critical supports remain underutilized, the results suggest room for further integration of resources, allowing institutions to focus on those with higher impact. Quantifying the frequency of student resource use can be used to streamline support systems, foster stronger career identity, and optimize communication with students about their academics and available opportunities.

Principle of Chemistry Course: Investigating Factors that can Influence Students' Relationship to their Major

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Previous research has shown that students who develop and maintain a strong relationship with their major and future profession are more likely to continue in their field. This study aims to analyze factors influencing students' feelings toward their major and profession. Students enrolled in a Concepts in Chemistry course aimed at engineering received a mixed-methods survey. There were 20 Likert-scale questions, along with five open-ended response questions. This survey aims to better students' perspectives on their major. The following study will focus on one of the open-ended questions of the survey, which asked, "How do you feel at this moment about being a future graduate in your major?" Thematic analysis was used to analyze the open-response question. Students have reported being overall positive toward their major, with some reporting feeling self-assured in their major. In the current study, students have given a wide variety of justifications for their current feelings toward their major, including academic performance, academic progress, and comments about their future in the workforce. The results from this project can help create a broader understanding of the influences affecting a student's relationship with their major.

Picturing the Future: How Visualizing Graduation Shapes STEM Student Confidence

Ashley Vargas, Abigail Castillo, Cameron Bechard, Dr. Nicole Lapeyrouse, PhD

University of Central Florida

Student persistence in STEM remains a national challenge, with many undergraduates leaving their majors before degree completion. While academic performance is often emphasized, students' confidence is also shaped by how they envision themselves as future professionals. Professional identity theory highlights the importance of future-oriented self-reflection, yet little is known about how students feel when imagining themselves as graduates or how they justify those feelings. This study examines undergraduates' confidence in envisioning themselves as future professionals and the justifications underlying these perspectives, situating responses within three professional identity statuses: achievement, diffusion, and moratorium. Students enrolled in chemistry courses completed an open-response survey to address this question, and responses were analyzed using thematic analysis. Results revealed distinct patterns across groups, with achievement students demonstrating the highest levels of confidence, diffusion students reporting moderate confidence, and moratorium students showing the lowest confidence, each supported by unique forms of justification. These findings highlight how differences in identity development may influence students' outlook on their academic and professional futures. They also lay the groundwork for future research aimed at developing targeted advising and counseling strategies for students with lower confidence levels, helping make professional pathways more visible, prevent academic disengagement, and support persistence in STEM.

Outreach Initiatives and Resources by the ACS Student Chapter at the University of Florida

Lily Carlson, Kate Parr, Harold Bishop, Ashlyn Hale

University of Florida

The University of Florida Student Chapter of the American Chemical Society has developed a broad community outreach program designed to make chemistry accessible, engaging, and relevant to students throughout Gainesville and the surrounding communities. Through hands-on demonstrations, school visits, community events, and collaborations with local organizations, undergraduate volunteers introduce participants to chemical concepts while encouraging curiosity and interest in STEM.

This presentation will highlight the outreach initiatives developed and implemented by the UF ACS Student Chapter, with particular emphasis on strategies for creating engaging demonstrations, training undergraduate volunteers, adapting scientific concepts for different age groups, and coordinating partnerships with schools and community organizations. Examples of successful activities and event formats will be discussed alongside practical considerations including safety, volunteer organization, materials preparation, and communicating complex chemistry in an approachable way.

In addition to showcasing UF's outreach efforts, this presentation will share adaptable resources and organizational strategies that other ACS student chapters can use to establish or expand their own outreach programs. By sharing activities, lessons learned, and approaches to program development, we hope to encourage greater collaboration among ACS student chapters and increase the impact of chemistry outreach throughout Florida.

Computational Chemistry

Computational Design of Aptamers for Targeted Cancer Therapy: Advances, Applications, and Future Perspectives

Gaurav Sharma

Eigen Sciences

Cancer treatment remains challenging because of drug resistance, systemic toxicity, and limited tumor selectivity. Aptamers are short DNA or RNA molecules that bind cancer-associated proteins and receptors with high specificity. In this presentation, I will discuss different computational methods and techniques used in aptamer design, including sequence analysis, secondary- and tertiary-structure prediction, molecular docking, molecular dynamics simulations, and binding-energy calculations. These approaches help predict aptamer folding, evaluate aptamer–target interactions, identify key binding nucleotides, and select promising candidates for experimental validation. The therapeutic applications of aptamers as receptor inhibitors, diagnostic probes, and targeted drug-delivery agents will also be reviewed. Finally, major challenges, including nuclease degradation, off-target binding, in vivo instability, and limited experimental validation, will be discussed. Overall, computational modeling provides an efficient and cost-effective approach for developing selective aptamers for cancer diagnosis and treatment.

Determining Protein Structure Ensembles from NMR Exchange Format (NEF) Data Using MELD

Binod L. Perera, Mondal, A., Perez, A.

University of Florida

NMR raw data represents ensemble average information about biomolecular systems. However, this data is often modeled in some way to represent assignments, and interpretations about distances between pairs of atoms. A major bottleneck in the field has been the lack of homogenous standards for NMR data sharing. The PDB NMR task force converged on the NEF standard for data sharing. However, that means that buy-in is required from all the computational software that has been used to determine NMR structures (or ensembles) based on this NMR data. We have developed MELD (Modeling Employing Limited Data) as an integrative approach to structural biology and adapted it to read/write NEF data. With the information from this data, we present a novel two stage protocol to determine protein structure ensembles directly from NEF NMR data using MELD. We developed a custom MELD restraints parser to extract out Nuclear Overhauser Effect (NOE) distances directly from NEF files and use them as distance restraints and TALOS torsion angles where available as torsional restraints. With H,T-REMD using MELD, we were able to fold the proteins from extended primary sequence under 50 ns simulation time using our protocols. To improve the accuracy and refining the structures we used another 20 ns short simulation cycle. We validated our method on the established NEF challenge dataset consisting of 15 protein systems both blindly and referring the existing native structures. Our blind, restraint based selection strategy successfully isolated native like structural ensembles with RMSD below 2 Å relative to the experimental reference for 11 out of 15 targets. And the non-blind selection showed RMSD below 1 Å for 13 out of 15 system. Our physics based protocols eliminate the use of current traditional NMR structure prediction methods, enabling generation of physically plausible, thermodynamic ensembles while significantly reducing computational cost.

Beyond Classical Force Fields: Physics-Driven Assessment of the Grappa Machine-Learned Force Field on the FoldBind Dataset

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Molecular dynamics has long relied on force fields built from empirically fitted, manually curated atom types. Machine-learned force fields now offer an alternative, chemically adaptive, data-driven parameterization without hand-tuned atom typing. Yet their performance under demanding conformational sampling, rather than near-native refinement, remains largely untested. We address this gap by integrating the Grappa machine-learned force field into MELD (Modeling Employing Limited Data), a Bayesian framework that combines replica-exchange molecular dynamics with ambiguous or noisy physical restraints to drive efficient exploration of conformational space. Grappa's neural-network-predicted bonded parameters replaced those of the classical force field while nonbonded terms were held fixed, isolating the contribution of the learned bonded potential. To stress-test this MELD-Grappa hybrid, we developed the FoldBind Benchmark, 18 systems comprising 14 protein-folding targets and 4 fold-upon-binding peptide-protein complexes, extending well beyond typical near-native validation.

MELD-Grappa recovered native experimental structures across the full benchmark set. Nine systems under standard MELD and ten under MELD-Adapt achieved sub-angstrom accuracy in their best-sampled conformations, with marked improvement on previously intractable cases (2HBA, 1POU, ubiquitin) relative to classical force fields. Clustering analysis confirmed this was not incidental sampling luck; the native basin was the most populated cluster in 12/14 systems with MELD and 13/14 with MELD-Adapt. For peptide binding, native-like interfaces emerged for MDM2-p53, MDM2-PDIQ, and BRD3-ET-TP, with funnel-plot analysis showing sharper convergence for higher-affinity binders. Analysis of N and C-terminal hairpin formation further showed MELD-Adapt-Grappa correctly reproduced experimentally established folding pathways, including registry-shifted intermediates for protein G, protein L, and their mutants. Critically, these gains came without added computational cost relative to classical force fields. Together, these results demonstrate that machine-learned bonded parameters integrate seamlessly into physics-based Bayesian sampling, establishing FoldBind as a rigorous testbed for future force-field development.

Toward Robust Solutions of the Projected Schrödinger Equation

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Finding the optimal energy and wavefunction parameters to the Schrödinger equation is at the heart of theoretical chemistry. Employing the variational principle is a common approach, since a lower energy always means better results. However, this is not always feasible for every chemical system and wavefunction. In these cases, solving the projected Schrödinger equation is a better strategy. For this, one needs a reasonable initial guess, which can be challenging. Our group has previously proposed a perturbation theory framework called FANPT, which provides stable numerical results for various systems and wavefunctions. In that framework, the energy was an active parameter. Here, we present a modification to FANPT, where the energy is no longer an active parameter. We demonstrate the stability of this approach on systems with static and dynamic correlation and various wavefunction methods.

Direct C(sp³)-H Activation Through Ni-Catalyzed Cascading Hydrogen Atom Activation

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Alkyl halides, particularly alkyl chlorides, are a crucial chemical motif seen in pharmaceuticals, agrochemicals, and as valuable organic intermediates. Due to their wide use, exploring alternative synthesis methods such as without pre-functionalized reagents, strong oxidants, and external energy sources are attractive. This work will report on the direct chlorination of γ -C(sp³)-H enabled using Ni (II) catalysis. By selectively tuning a nickel catalytic system, a pathway for direct C-H activation on an inert amino acid was discovered which would significantly assist organic chemists. The thermodynamically preferred pathway for a series of elementary steps proposes the favorable formation of an internal γ -C-Cl bond. The rate determining step (RDS) was shown energetically be the activation of leucine's γ -C(sp³)-H with a calculated activation energy of 26.44 kcal/mol in comparison to a literature result of 39.4 kcal/mol. Elementary steps showed the formation of an intermediate γ,δ -dehydroamino acid, which is stabilized by the presence of the nickel catalyst. Through the addition of aqueous HCl through the Markovnikov addition, the catalyst has been shown to readily be regenerated.

Embedded cluster density approximation for scalable high-level exchange-correlation calculations in periodic systems

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Accurate prediction of electronic properties in extended materials often requires high-level exchange-correlation (XC) methods whose computational cost limits their application to large systems. We present an extension of the Embedded Cluster Density Approximation (ECDA), a density partitioning framework that enables high-level XC calculations for periodic systems while maintaining computational efficiency. In ECDA, local cluster electron densities are constructed using density functional embedding theory to ensure seamless embedding within the periodic environment. High-level XC energy densities are evaluated for each cluster and projected onto central atoms, allowing the total XC energy of the system to be assembled from atom-centered contributions. Using hybrid density functionals as the reference high-level method, we demonstrate that ECDA provides a robust and nearly black-box approach for periodic materials with diverse bonding characteristics. Accurate total energies and energy differences are obtained using relatively small cluster sizes while producing smooth potential energy surfaces. We also analyze the influence of density partitioning on convergence behavior and discuss the role of unsaturated boundary bonds in covalent materials. These results establish ECDA as an efficient and broadly applicable framework for extending high-level electronic structure methods to large periodic systems.

Inorganic Chemistry

Structural and Spectroscopic Investigation of Trinuclear Oxovanadium Pyrazolato Complexes

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Vanadium compounds are capable of accessing multiple oxidation states, most commonly V^{IV} and V^V ; the V^{IV}/V^V couple is often employed in the development of redox flow batteries.^{1,2} The V^{IV} species exhibits well-defined EPR spectra in which the $S = 1/2$ electronic spin couples with the nuclear spin ($I = 7/2$) of ^{51}V (abundance of 99.75%), generating molecular spin qubits with long coherence times (T_m).³ These characteristics give rise to properties that are highly desirable for the design of molecular charge/energy storage and transfer systems, as well as in electrochemical catalysis for small-molecule activation.⁴ The goal of our research group is to synthesize multinuclear redox-active transition-metal pyrazolato complexes and provide their comprehensive structural, spectroscopic, and electrochemical fingerprints. Recent efforts have focused on the preparation of trinuclear oxovanadium-pyrazolato compounds with a $[V_3(\mu_3-O)(\mu-4-R-pz)_6O_3]^{z-}$ motif ($R = NO_2$ and CN ; $z =$ charge). These compounds have been structurally characterized by single-crystal X-ray diffraction (SCXRD) and further analyzed by UV-Vis-NIR, FTIR, cyclic voltammetry, magnetic susceptibility, and EPR. Electrochemical studies revealed three quasi-reversible oxidation events, involving the $[V_3]^{+}$ (d^0), $[V_2V^{IV}]^0$ (d^1), $[V^VV_2^{IV}]^-$ (d^2), and $[V^{IV}_3]^{2-}$ (d^3) species.

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Generating Porosity in Metal Halide Semiconductors

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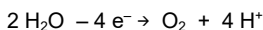
Porous Metal Halide Semiconductors (PMHS), an emerging class of Hybrid Metal Halide materials, has attracted attention for combining porosity, permanent water stability, and notable optoelectronic properties. The organic part of the PMHS serves not only as a structure-directing agent, but also as a porosity-attributing factor in the material. Building on this concept and using a molecular engineering approach, we designed and synthesized a new molecular cage to serve as a counter-cation and incorporated it into PMHS to further tune their porous properties. Tailoring the pore characteristics of these materials will open new avenues for applications such as solid-state batteries, rare-earth metal capture, or water remediation.

Synthetic Analogues of the Photosynthetic Oxygen-Evolving Complex (OEC) near Photosystem II of Cyanobacteria and Plants

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Photosystem II (PS II), found in cyanobacteria, algae, and plants, is a macromolecular complex consisting of twenty protein subunits and 80 cofactors. It contains the water-splitting catalyst, a Mn_4CaO_5 cluster consisting of a Mn_3CaO_4 cubane with the fifth, external manganese attached to a cubane oxide ion and an external oxide/hydroxide ion, with peripheral ligands provided primarily by aspartate and glutamate carboxylate side-chains. This catalyst is responsible for producing essentially all the oxygen gas in our atmosphere on which respiring life on Earth depends. In the presence of light, the OEC undergoes four one-electron oxidations driven by the PS II reaction center, and then the accumulated four oxidizing equivalents result in the four-electron oxidation of two water molecules to generate O_2 gas and four H^+ .



Efforts to study the magnetic properties of the biological catalyst and characterize the interactions between its metal ions have been challenging due to its location within the protein environment of Photosystem II. However, synthetic analogues would provide an opportunity to investigate these properties in the absence of the surrounding protein environment. This presentation will describe the status of our work targeting the preparation of synthetic analogues of the OEC, and the structural and magnetic properties of some of the obtained compounds.

Design, synthesis, and characterization of a small molecule inorganic photoresist candidate for EUV lithography

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Further advances in extreme ultraviolet lithography (EUVL) require new photoresist materials that combine high EUV absorption and functional groups that promote electron-stimulated solubility switching. Here, we investigate bis(N-vinylimidazole)zinc diiodide as a single-component metal-containing resist designed to exploit the complementary functions of its constituent ligands. The ZnI_2 center provides enhanced EUV absorption, while the vinylimidazole ligands provide chemically active vinyl groups capable of electron-induced polymerization and subsequent crosslinking to produce negative-tone behavior. Single-crystal X-ray diffraction has confirmed the molecular structure and indicates a spatial proximity of the vinyl groups that may facilitate intermolecular crosslinking in the condensed phase. An EUV absorption coefficient was estimated from elemental absorption cross-sections and the crystallographic density of the complex, indicating greater EUV absorption than metal-oxo photoresists. The material formed uniform thin films from cyclohexanone and exhibited negative-tone behavior following 15 keV electron exposure. X-ray photoelectron spectroscopy was used to measure the impact of electron exposure on chemical composition while thermogravimetric analysis demonstrates that the resist exhibits thermal stability compatible with typical pre-bake requirements. These results establish (N-vinylimidazole)₂ZnI₂ as a promising molecular platform for further investigation as a high absorption, negative-tone EUV resist.

Separation of Rare Earth Elements: Traditional Methods and Emerging Approaches

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Rare earth element (REE) separation remains a significant challenge and represents a major cost in producing purified REEs from ore. The current industrial standard relies on solvent extraction using phosphonic acids, a process characterized by excessive chemical consumption, large volumes of wastewater, and hundreds of processing steps to isolate individual REEs. This project aims to advance domestic REE production by developing a two-ligand separation technology that leverages the complementary selectivity of lipophilic and hydrophilic neutral ligands. This presentation will explore the distinctions between acidic and neutral extractants, outline the step-by-step design of the two-neutral ligand solvent extraction process, discuss pathways for recycling all chemicals, and detail the system's separation efficiency and flowsheet design.

Covalently-linked Metalloporphyrins for the Design of Quantum Systems: Methods, Characterization, and Device Integration

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Over the last decade, research in our group has focused on the design of covalently-linked oligomers of magnetic molecules that possess the properties needed for spin-based quantum technologies. Our previous work utilizing tetranuclear Mn(III,IV) and trinuclear Mn(III) clusters with $S = 9/2$ and $S = 6$ ground states, respectively, successfully showed that weak exchange-coupling between two single-molecule magnets (SMMs) in a linked dimer generates quantum superposition and entanglement states, as well as exchange-biased quantum tunneling of magnetization.^{1,2} These observations have more recently led to the pursuit of spin-based quantum bit (qubit) systems realized through the exchange interactions between two transition metal ions. Porphyrins are attractive candidates as the complexing agents for these ions due to their rigid structure and tunable functionality for constructing molecular systems with the higher quantum coherence times necessary for quantum applications. In this work, cofacial bis-porphyrins were metalated with oxo-vanadium(IV), giving two weakly interacting, $S = 1/2$ qubit centers within the individual porphyrin architectures. The syntheses of these vanadyl porphyrins will be described, as well as DFT calculations, UV-Vis spectra, and electron paramagnetic resonance (EPR) spectroscopic studies used to understand the structure and magnetic exchange couplings of the resulting dimeric porphyrin product. In addition, our recent efforts in integrating the metalloporphyrins onto silicon surfaces towards quantum device fabrication will be introduced.

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Sulfonamide Ligands for Sensing Lanthanides in High-Level Waste

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Separation of transuranic f-elements from highly alkaline, high-level nuclear waste remains a significant challenge, driven by the need to minimize waste volume and limit radionuclide mobility. Fluorescence sensing presents a promising approach for monitoring these elements. Previous work from our group demonstrated that both disulfonamide and picolinamide ligands can extract and sense lanthanides, which are actinide surrogates for HLW. These ligands showed strong binding and “turn-on” fluorescence when modified with fluorophores. We furthered these studies by utilizing a previously reported bis-naphthyl disulfonamide. Our studies show this ligand can detect trace Ln(III) in CH₃CN:CH₃OH (99:1 v/v) solution, showing a tenfold increase in fluorescence due to chelation-enhanced fluorescence (CHEF). UV-Vis and fluorescence titrations were carried out at constant ligand and NaOH concentrations, with sole variable the concentration of the Ln(III). Upon the addition of Ln(III) nitrate salts (5.0×10^{-4} M) to the naphthyl-sulfonamide (5×10^{-5} M) in acetonitrile with 2.2 equivalents of NaOH spectroscopic changes were observed with Sm(III), Eu(III), and Lu(III). The binding data by non-linear regression analysis using the HypSpec® program was consistent with predominant formation of 1:2 metal ligand ML₂ complexes. UV-Vis data showed large binding constants, $\text{Log}\beta_2 = 11.60 \pm 0.50$ for Sm(III), $\text{Log}\beta_2 = 10.75 \pm 1.15$ for Eu(III), and $\text{Log}\beta_2 = 13.47 \pm 1.48$ for Ln(III). Analysis of fluorescence data showed similar binding constants $\text{Log}\beta_2 = 10.70 \pm 1.91$, $\text{Log}\beta_2 = 10.70 \pm 0.98$, and $\text{Log}\beta_2 = 14.45 \pm 1.17$ for each metal, respectively. A novel bisdansyl dipicolinamide has also been synthesized which can sense trace Ln(III) within THF. UV-Vis and fluorescence titrations were carried out at constant ligand and diisopropylethylamine (DIPEA) concentrations, with sole variable the Ln(III) concentration. Upon gradual addition of Ln(NO₃)₃·6H₂O (5.0×10^{-4} M) to the ligand (5×10^{-5} M) in THF with 10 equivalents of DIPEA a large decrease in fluorescence intensity was observed due to chelation-enhanced quenching (CHEQ). UV-Vis titrations showed changes in absorbance with multiple isosbestic points confirming complexation. Non-linear regression analysis of the binding data using HypSpec, and Job Plots provided insight into Ln(III) binding affinities and complexation stoichiometry.

Strain-Promoted and New Inorganic Click Strategies for Porous Organometallic Polymers

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University of Florida

UT San Antonio

Click chemistry offers a powerful strategy for constructing complex molecular architectures with exceptional efficiency and selectivity. This seminar will highlight recent advances in inorganic click (iClick) chemistry and its integration with strain-promoted azide–alkyne cycloaddition (SPAAC) to synthesize porous organometallic polymers (POMPs). A new high-yield route to multivalent dibenzocyclooctyne (DBCO) building blocks enables the preparation of hyperbranched and three-dimensional polymer networks under mild, catalyst-free conditions. In parallel, a complementary cyano–azide strategy expands iClick chemistry through the synthesis of tetrazolate-based organometallic materials. Together, these approaches establish a versatile platform for incorporating metal centers directly into porous polymer frameworks with applications in catalysis, gas separation, and energy storage.

Towards photo-switchable magnetic exchange interactions in dihydropyrene-based copper complexes

Besarion Dgebuadze, Alexander Diodati, Zain Becerra, Ion Ghiviriga, and George Christou

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Magnetic exchange interactions govern communication between spin centers and underpin the behavior of molecular magnetic materials being investigated for applications in spin-based electronics and quantum information processing. Developing strategies for reversibly modulating exchange coupling is a major goal in molecular magnetism, with light offering a particularly attractive, non-invasive handle. Modulation of exchange coupling with light has been achieved using organic radicals bound to diarylethene photoswitches [1] and in a limited number of other photoresponsive systems [2,3]. However, achieving such control within a well-defined, synthetically tunable scaffold that supports systematic binding of metal centers remains challenging. Dihydropyrenes offer a promising platform for addressing this challenge because they are robust, highly conjugated photoswitches that can be chemically modified at multiple positions and undergo a pronounced change in planarity between their closed and open forms. This presentation will describe our efforts towards the synthesis of terpyridine-functionalized dihydropyrene systems coordinated to copper centers, along with characterization by NMR and EPR spectroscopy.

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Mixed-Anion Design for Enhanced Lithium-Ion Transport in Solid Electrolytes

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Mixed-anion chemistry has emerged as a promising approach for enhancing lithium-ion transport in halide solid electrolytes by tuning the local structural environment and ionic diffusion pathways. In this work, we report the synthesis and characterization of a new mixed-anion lithium halide solid electrolyte exhibiting a room-temperature ionic conductivity of 1.52 mS cm^{-1} and a low activation energy of 0.32 eV . Structural characterization reveals retention of the parent crystal framework accompanied by increased local structural disorder. Raman spectroscopy and solid-state NMR provide evidence of modifications to the local coordination environment and lithium-ion distribution following anion substitution. Electrochemical characterization demonstrates a wide electrochemical stability window and favorable compatibility with all-solid-state battery configurations. These findings highlight the potential of mixed-anion chemistry as an effective strategy for developing high-performance halide solid electrolytes for next-generation all-solid-state batteries.

Synthesis, characterization, and electrochemical study of redox-active cyclic polyacetylenes

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A consistently growing global economy has fueled a continuous increase in global energetic needs. Materials that can store potential energy are resultantly invaluable, and critical in ensuring this energetic demand is met. One class of energy storage materials, namely redox-flow batteries (RFBs), has attracted considerable attention as they possess the inherent capability to store energy in the redox potential of their active materials. The main problem affecting the scalability of this battery technology is the cost associated with their development. Specifically, the ion-exclusion membranes currently used to separate the metal-ion active materials used in present technologies are very costly. In contrast, development of RFBs where redox-active polymers are the active materials, represent a value-added approach to modern technologies. Their simpler, size-exclusion method of separation allows for cheaper membranes to be employed and thus presents a viable alternative to the technology. In the scope of this size-exclusion approach, topology is a key property that has been considerably underexplored in this field. Cyclic polymers, with the absence of chain-ends compared to their linear counterparts, are topologically better suited to prevent membrane permeation, and thus represent a viable class of active materials. To this end, our group's history with preparing cyclic polyacetylenes has led to a focus on redox-active cyclic polymers. Herein, cyclic polyacetylenes with redox-active pendant groups have been prepared, characterized, and electrochemically studied.

Synthesis and characterization of redox active $\text{Fe}_n(\mu_n\text{-O})$ pyrazolates: X-ray crystal structures, spectroscopy, and electrochemistry

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Two redox active $\text{Fe}_n(\mu_n\text{-O})$ pyrazolato motifs (for $n = 2$ and 3) for complexes of formulae $[\text{Fe}_3(\mu_3\text{-O})(\mu\text{-4-R-pz})_6\text{X}_3]^z$ and $[\text{Fe}_2(\mu\text{-OH})(\mu\text{-4-CN-pz})_6\text{CN}_6]^z$ (Figure 1), have been studied by FT-IR, UV-Vis, UV-Vis-NIR, Single Crystal X-Ray Diffraction (SCXRD), RT-Magnetic Susceptibility, ^{57}Fe -Mössbauer spectroscopic and electrochemical methods. For the Fe_3 , where $\text{R} = \text{NO}_2$, CN , Cl , Br , and I ; $\text{X} = \text{Cl}$, Br , CN , NCO , NCS , N_3 and Py . All-ferric $[\text{Fe}_3(\mu_3\text{-O})]^{9+}$ as well as mixed-valent $[\text{Fe}_3(\mu_3\text{-O})]^{8+/10+}$, formally $\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}$ and $\text{Fe}^{\text{III}}_2\text{Fe}^{\text{IV}}$ species, have been accessed allowing an evaluation of the effect of **R**- and **X**-substitution on physicochemical properties, revealing relationships between electrochemical properties and electronic structure. The nature of **R** and **X** determine the high-spin or low-spin electronic structure, while spin crossover events have also been identified.

Dipicolinamide Ligands for Binding and Sensing of Uranyl and Perrhenate: The Effect of *p*-Phenolic Substitution on the Central Pyridinyl Ring

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Evaluating potential environmental contamination with UO_2^{2+} and TcO_4^- rapidly and accurately is increasingly relevant as the possibility of leaking tanks containing high-level waste (HLW) in the US remains. Although recent technologies are proposed to detect these species, synthetic organic ligands remain at their core. Herein, we synthesized and characterized two modified dipicolinamide ligands (**L3OH** and **L3naphthOH**) and studied their binding affinity toward UO_2^{2+} . The *p*-phenolic hydroxy moiety on the ligands allows for their subsequent incorporation into norbornene monomers, which can then be polymerized and used for liquid-liquid or solid-liquid extraction and sensing. The binding affinity of these new ligands was investigated via UV-Vis titrations in CH_3CN and 9:1 $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ (v/v). When compared to simple dipicolinamide versions of the ligands (*i.e.*, **L3** and **L3naphth**) that contain no phenolic -OH, **L3OH** and **L3naphthOH** retain almost identically their affinity toward UO_2^{2+} . However, the OH-modified ligands also displayed a larger spectroscopic response toward anions, particularly larger ones like I^- . Furthermore, we evaluated the binding affinity of both ligand families toward I^- and ReO_4^- (surrogate for TcO_4^-) via UV-Vis, in CH_3CN and 9:1 $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ (v/v), and via $^1\text{H-NMR}$ in DMSO-d_6 . Our results suggest that the *p*-phenolic OH- modification also has a negligible effect on the binding affinity toward anions, but that binding may occur via H-bonding from the phenolic -OH rather than the amide -NH.

Molecular Clusters as Models of the Repeating Unit of the LnMnO_3 Lanthanide Manganites with the Perovskite Structure

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The AMnO_3 manganites with the perovskite structure and their doped $\text{A}_{1-x}\text{B}_x\text{MnO}_3$ (A and B are main group or lanthanide metal ions) are extremely important magnetic oxides renowned for their remarkable properties such as ferromagnetism, multiferroicity, and colossal magnetoresistance. DFT calculations on LaMnO_3 have predicted its ground state spin vector configuration to be sensitive to the sign and magnitude of the exchange interactions between Mn^{3+} ions but attempts to demonstrate this experimentally with pressure have been unsuccessful. Previous studies in our group led to the $[\text{Ce}_3\text{Mn}_8\text{O}_8(\text{PhCO}_2)_{18}(\text{PhCO}_2\text{H})_2]$ molecular cluster,¹ which is the repeating unit of the manganite perovskite structure plus two additional Ce^{3+} ions, and shown that “chemical pressure” from bulkier substituted-benzoate ligands can change the ground state as predicted by DFT for the bulk solids. Building on this success, we have more recently targeted variation of the lanthanide ions in this perovskite structures and have successfully synthesized Gd_3Mn_8 , Nd_3Mn_8 , Pr_3Mn_8 , and Ce-doped derivatives of general formula $[\text{Ln}_3\text{Mn}_8\text{O}_8(\text{RCO}_2)_{18}(\text{RCO}_2\text{H})(\text{MeCN})]$. We shall give an overview of this work, including syntheses, crystal structures, magnetic studies, and EPR analyses.

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Porous Metal Halide Semiconductors for *K. brevis* Mitigation: Understanding Structure-Property Relationships that Guide HAB Control

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Harmful algal blooms (HABs) have emerged as a critical environmental threat in recent years, largely due to increasing water temperatures and pollution. Red tide is caused by the HAB *Karenia Brevis* (*K. brevis*) that releases brevetoxins which kill marine life and negatively impact public health due to contamination and air-borne toxins. Many attempts to mitigate this issue have been made with little success, highlighting the need to address this growing problem. Porous metal halide semiconductors (PMHS) have recently been reported as potential candidates for HAB mitigation as a result of their highly tunable optoelectronic properties, and composition consisting of cheap, biocompatible elements with attributes superior for mitigating *K. Brevis* over other traditionally used compounds such as hydrogen peroxide or copper. Four members of the PMHS family were analyzed, and when irradiated with visible light, the compounds generated ROS that can selectively inhibit *K. brevis* to varying degrees. By comparing the structural properties and pore size, optoelectronic behavior, ROS generation kinetics/speciation, and algicidal activity, we identify key structure–property relationships associated with effective HAB mitigation. These results provide insight into the rational design of PMHS materials for selective, light-driven control of harmful algal blooms.

Direct Synthesis of High-Surface-Area Perovskites for Enhanced CO Production in Reverse-Water Gas-Shift Chemical Looping (RWGS-CL)

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Direct synthesis of high-surface-area complex oxides with controlled cation organization remains challenging, despite their importance in catalytic and energy-conversion processes. In reverse water-gas shift chemical looping (RWGS-CL), iron-based perovskites are promising oxygen carriers, but their activity is strongly influenced by active-site accessibility, near-surface cation distribution, and lattice oxygen transport. Conventional synthesis methods such as sol-gel typically produce low-surface-area perovskites and provide limited control over near-surface composition, which can restrict redox activity and CO production. Here, we report a stoichiometric liquid atomic layer deposition (LALD) approach for the direct synthesis of high-surface-area perovskite materials with controlled cation organization. Metal precursors were introduced sequentially in repeated deposition cycles, with precursor quantities determined from GC-FID analysis of ligand release to achieve stoichiometric growth. This surface-limited synthesis produced a conformal perovskite phase with uniform elemental distribution and a surface area of $88 \text{ m}^2 \text{ g}^{-1}$. The LALD-derived material exhibited a six-fold increase in CO yield and a higher maximum CO production rate compared with a compositionally comparable sol-gel-derived perovskite. Spectroscopic, kinetic, and physicochemical characterization showed increased turnover frequency, higher basic-site density, enhanced Fe–O redox participation, and lower barriers for oxygen transport. These results indicate that improved near-surface cation organization and greater accessibility of redox-active sites facilitate faster lattice oxygen exchange and more efficient redox cycling during RWGS-CL. This work demonstrates how surface-controlled synthesis can directly influence cation organization, oxygen mobility, and catalytic redox behavior in complex oxides, providing a route toward the rational design of high-surface-area perovskites for chemical looping and related catalytic applications.

Oxo/ hydroxo -bridged dinuclear copper pyrazolate complex as efficient catalyst for hydrocarbon oxidation: redox and oxygen-atom transfer studies.

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The transformation of alkanes into value-added products by oxidation of C-H bonds remains as one of the most significant challenges in chemistry. The development of catalysts based on earth-abundant metals that operate under mild and energy-efficient conditions is a major research goal. This work addresses the synthesis, structural characterization, and catalytic evaluation of a dinuclear copper(II) pyrazolate complex $[\text{Cu}_2\mu\text{-OH})(\mu\text{-pnpz})_2(\text{bipy})_2](\text{pnpz})^-$, where $\text{pnpzH} = \text{bis}(2,4\text{-dinitrophenyl})\text{-4-nitropyrzazole}$ (pentanitropyrzazole). The complex cycles between the Cu^{II}_2 and Cu^{I}_2 states while mediating oxygen-atom transfer reactions. Qualitative investigations revealed that both the pnpz^- counterion and the pentanitro substitution of the bridging pyrazolato ligands are essential for catalytic activity and oxidative reactivity. Reactivity of the complexes are moderated by interactions with the secondary coordination sphere; either by hydrogen bonding which can impart partial stability towards the complex, while also being liable enough to not be detrimental, or by interactions with cationic/ionic species. The copper(II) dimer oxidizes alkanes such as dihydroanthracene (DHA), THF, toluene and cyclohexane. Complete characterization of the dinuclear copper-pyrazolate complex was achieved using FT-IR, UV-Vis, elemental analysis and single crystal X-ray diffraction, magnetic measurements, confirming its molecular structure and supporting its promising potential as an earth-abundant catalyst for selective C-H bond oxidation. The turnover number (TON) and turnover frequency (TOF) of the catalyst are determined by monitoring the conversion of substrate to product(s) by GCMS.

B-Site Ti Engineering of $\text{LaNi}_{1-x}\text{Ti}_x\text{O}_3$ /MCF Perovskite-Silica Catalysts for Enhanced Ni Active-Site Formation and CO_2 Methanation

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Engineering the composition and architecture of inorganic oxide materials provides an effective strategy for tailoring metal-oxygen interactions, redox properties, and catalytically active sites. Perovskite oxides offer particular versatility because their B-site composition can be systematically modified, while integration with mesostructured cellular foam (MCF) silica provides a high-surface-area mesoporous architecture for improved dispersion and accessibility of the active phase. In this work, a series of $\text{LaNi}_{1-x}\text{Ti}_x\text{O}_3$ /MCF perovskite-silica catalysts ($x = 0, 0.2, 0.6, 0.8, \text{ and } 1.0$) was developed to investigate how B-site Ti substitution and MCF integration influence the structural and surface properties of Ni-based inorganic catalysts for CO_2 methanation.

The catalysts were synthesized using a modified Pechini sol-gel method with in situ incorporation of MCF silica. XRD revealed systematic structural evolution with Ti substitution, while N_2 physisorption confirmed the retention of the mesoporous MCF architecture. Ti incorporation modified the reducibility and surface chemistry of the perovskite catalysts, as demonstrated by H_2 -TPR, CO_2 -TPD, CO_2 adsorption, and XPS. Reduction of the Ti-containing catalysts promoted the formation of accessible metallic Ni species, providing favorable active sites for CO_2 hydrogenation. Among the investigated compositions, $\text{LaNi}_{0.2}\text{Ti}_{0.8}\text{O}_3$ /MCF exhibited the highest CO_2 adsorption capacity ($224.17 \mu\text{mol g}^{-1}$) and delivered 61% CO_2 conversion, 85% CH_4 selectivity, ~4% CO selectivity, a CO_2 consumption rate of $86.98 \text{ mmol g}^{-1} \text{ h}^{-1}$, and a CH_4 formation rate of $74.49 \text{ mmol g}^{-1} \text{ h}^{-1}$, with stable performance over 60 h. In situ DRIFTS further provided insight into the surface intermediates involved in CO_2 hydrogenation.

Overall, the results demonstrate that coupling B-site Ti substitution with MCF-supported perovskite architecture provides a materials-based approach for tuning the structure, reducibility, and surface chemistry of Ni-containing oxide catalysts, enabling improved CO_2 conversion and selective methane formation.

Green Synthesis of Metal Oxides Nanoparticles by Using Aloe Vera Leaves Extract for Efficient Electrocatalytic Water Splitting

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The development of efficient and cost-effective electrocatalysts is important for advancing sustainable hydrogen production through water splitting. In this work, transition-metal oxide nanoparticles and their composites with reduced graphene oxide (rGO) were synthesized using *Aloe vera* leaf extract as a green reducing agent. CuO/rGO , ZnO/rGO , and NiO/rGO nanocomposites were prepared and characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), and Fourier-transform infrared spectroscopy (FTIR). Their electrochemical performance toward water splitting was evaluated using cyclic voltammetry and Tafel analysis. The CuO/rGO , ZnO/rGO , and NiO/rGO nanocomposites exhibited overpotentials of 0.47, 0.30, and 0.32 V, respectively, with corresponding Tafel slopes of 67, 53, and 66 mV dec^{-1} . Among the investigated materials, ZnO/rGO showed the lowest overpotential and Tafel slope, indicating more favorable electrocatalytic kinetics. These results demonstrate that coupling transition-metal oxides with rGO through a green synthetic approach can provide promising electrocatalytic materials for water-splitting applications.

Organic Chemistry

Oxidative Dearomatization and Formal Arylation of Carbonyl Derivatives

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Synthetic methodologies featuring oxidative dearomatization and one-pot formal enantioselective α -arylation of carbonyls will be presented. The oxidative dearomatization enables streamlined access to densely functionalized spirocycles, while the arylation demonstrates formal Umpolung reactivity at the indole C3 site. The utility of these methods is demonstrated in the total synthesis of natural products, including acremoauxin A and oxazinin 3.

Multivalent DBCO-Based Building Blocks as a Route to Porous Organometallic Polymers

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Building on a foundation of inorganic click (iClick) chemistry, significant recent progress has been made toward the synthesis of porous organometallic polymers (POMPs) that incorporate metal ions directly into the polymer backbone. Central to this effort is the development of key multivalent building blocks that enable strain-promoted azide-alkyne cycloaddition (SPAAC) polymerization, with optimized synthetic routes now providing these components in high yield. Coupling these scaffolds with diazide linkers has opened access to hyperbranched polymer architectures. These advances represent critical steps toward well-defined, high-molecular-weight POMP networks, with ongoing work targeting the integration of metal nodes and the expansion into three-dimensional porous architectures for applications in carbon capture, catalysis, and energy storage.

Synthesis of 3,4-Dihydroxyphenylacetaldehyde (DOPAL): A toxic dopamine metabolite in Parkinson's disease pathogenesis

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Parkinson's Disease (PD) is a prevalent neurodegenerative disorder that impacts nearly 2% of individuals above 65 years of age. The etiology of PD is idiopathic, though its primary trigger is the degeneration of dopaminergic neurons within the substantia nigra. This brain region regulates motor coordination and skeletal smoothness. When it is lost, patients experience the characteristic symptoms of PD, including tremors, bradykinesia, and postural stiffness. Although the precise cause of PD remains elusive, one hypothesis suggests that catechol metabolites act as "steppingstones" in disease progression. DOPAL (3,4-dihydroxyphenylacetaldehyde), a by-product of dopamine, has been directly associated with neurotoxicity and PD. It damages nigrostriatal dopamine terminals and contributes to dopamine depletion, the defining feature of PD. A previously reported synthesis obtained DOPAL in four steps, involving three chromatographic purifications, with an overall yield close to 4%. To investigate further efficient and high-yielding DOPAL synthesis, three different routes were performed using 3,4-dihydroxybenzaldehyde, vanillin, and DOPAC respectively as a starting compound. This is an innovative technique in biochemical research. The first route applied a THP protecting group followed by a Wittig reaction. THP was essential to stabilize the intermediate, allowing reduction to the aldehyde. The second route emphasized vanillin, reduced in good yield to vanillyl alcohol using NaBH₄ in MeOH (0–5 °C; rapid workup), then homologated to homovanillin (4-hydroxy-3-methoxyphenylacetaldehyde). This intermediate served as a stable, oxidizable precursor to DOPAL. The third route began with DOPAC which was protected and then reduced using DIBAL-H in anhydrous THF to yield the aldehyde, and then finally deprotected. The synthesized DOPAL showed the decomposition with air and the results were obtained using NMR. The overall yield is expected to be higher than our past results. IR and NMR analysis were carried out to elucidate the structure of the intermediates and the synthesized DOPAL. Overall, this research project shows promise for an efficient synthesis of DOPAL using innovative techniques to further the field of PD research.

Mechanistic investigation of catalyst-free amide to ester conversion (ATEC)

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Amides are found in a variety of organic compounds but are often considered to have low reactivity because the carbonyl group is stabilized by resonance donation from the nitrogen. Numerous groups have investigated the conversion of amides to esters; however, these methods often require the use of transition metal catalysts, harsh reaction conditions, organic solvents, hazardous reagents, or a combination thereof. Herein, we present a mechanistic investigation of catalyst-free amide to ester conversion (ATEC). Computational analysis of the ATEC transition state (DFT/B3LYP/6-31G*) indicated that *N*-hydroxyalkyl amides containing two methylene units provide a low-energy pathway while using commercially accessible reagents. ¹H NMR kinetic studies monitoring ester formation at 200 °C determined a second-order rate law for ATEC of *bis*-hydroxyethyl-*N,N*-dimethyladipamide (BHEDMAA). Analogous studies with *bis*-hydroxyethyl-*N,N*-dimethylterephthalamide (HEDMTP) revealed an unexpected kinetic result: first-order with respect to the amide and negative half-order with respect to the alcohol. Reaction coordinate diagrams (DFT/B3LYP/6-31G*) for ATEC of *N*-(2-hydroxyethyl)-*N*-methylacetamide (HEMAA) and *N*-(2-hydroxyethyl)-*N*-methylbenzamide (HEMBA) revealed similar activation barriers for the two transformations but different thermodynamic favorability. The ester/amide equilibrium constants (K_{eq}) were measured by alcoholysis of the amide (BHEDMAA or HEDMTP) and aminolysis of the ester (dinonyl adipate or dinonylterephthalate). The K_{eq} values of BHEDMAA and HEDMTP revealed that the thermodynamic favorability of ATEC is dependent on the amide substrate, corroborating the computational results. At 200 °C, the equilibrium of aliphatic BHEDMAA favored the amide ($K_{eq} = 0.45\text{--}0.55$), while aromatic HEDMTP favored the ester ($K_{eq} = 4.8\text{--}7.1$). Additional calculations and equilibrium studies confirmed the hydroxyethyl moiety acts as a kinetic accelerant.

Optimization of P7C3-Derived NAMPT Activators for Treatment of Cardiac Injury

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Heart failure remains a major contributor to cardiac injury and human mortality, underscoring the need for therapeutic strategies that preserve cellular energy metabolism during cardiac stress. Nicotinamide phosphoribosyltransferase (NAMPT), the rate-limiting enzyme in the nicotinamide adenine dinucleotide (NAD⁺) salvage pathway, is critical for maintaining NAD⁺ homeostasis and cardiomyocyte function. Pharmacological activation of NAMPT is therefore a promising approach to enhance cardiac metabolic resilience.

Here, we describe a structure–activity relationship (SAR)-guided medicinal chemistry campaign based on the P7C3 scaffold to identify and optimize small-molecule NAMPT activators with potential cardioprotective activity. P7C3-derived analogs were designed and synthesized, with optimization focused on structural modifications, stereochemical configurations, salt forms, and physicochemical properties. Several optimized analogs exhibited enhanced NAMPT activation relative to the parent P7C3 scaffold. Salt-form optimization was undertaken to improve the aqueous solubility of selected compounds, facilitating the evaluation of their biological properties. Collectively, these findings demonstrate that systematic structural and stereochemical optimization of the P7C3 scaffold can generate more effective NAMPT activators with improved physicochemical properties and cardioprotective activity.

Physical and Biophysical Chemistry

Accelerating rare events in biomolecular simulations with Continually Adaptive Local Memory sampling

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Over the last decades molecular dynamics practitioners have utilized and developed enhanced sampling methods that apply a biasing potential along a collective variable (CV) to accelerate transitions associated with rare events. The extended adaptive biasing force method (eABF) is effective at accelerating CV transitions, but it is well known that eABF can have diminished sampling capabilities over time when transitions become stalled. This stalling is, in part, because the eABF biasing potential becomes unable to adapt to changes in the CV environment. The loss of adaptivity can result in biasing forces that are not synchronized with the current state of the CV, causing delayed transitions and sampling diminishment. The Continually Adaptive Local Memory (CALM) sampling method is designed to maintain adaptivity of the eABF biasing force to promote sustained transitions along the CV. The modification of eABF to CALM is presented along with several applications of CALM to biomolecular systems, including folding/unfolding of small peptides in water, membrane permeation of small solutes, and conformational sampling of proteins.

Molecular simulations reveal paralog-specific recognition of peptides in BET ET-domains

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The bromodomain and extra-terminal (BET) protein family plays a fundamental role in regulating gene expression during immune responses, and its dysregulation is directly implicated in various cancers and inflammatory diseases. The extra-terminal (ET) domain functions as a key protein-protein interaction hub, binding transcription factors, chromatin regulators, and viral proteins through short linear peptide motifs. Consequently, the ET domain represents a promising target for paralog-selective peptide therapeutics. Despite sharing high sequence identity and tertiary structure, the BRD3 and BRD4 paralogs exhibit distinct peptide-binding preferences through mechanisms that remain poorly understood.

In this study, we employed extensive all-atom molecular dynamics (MD) simulations to investigate the recognition mechanisms of BRD3 and BRD4 ET domains bound to two distinct peptide motifs: the host regulatory protein NSD3 and the murine leukemia virus integrase terminal peptide (TP). Our simulations revealed that paralog-specific recognition is driven by subtle variations in loop dynamics—encompassing two divergent sequence sites—which directly modulate the secondary structure propensity of adjacent regions. Notably, the dynamical characteristics persist across each paralog regardless of the bound peptide. Furthermore, regions that present larger changes upon binding in our simulations are in good agreement with experimental NMR chemical shift perturbation (CSP) data observed for BRD3.

These findings exhibit how localized sequence divergence shapes the global conformational landscape of BET ET-domains. By revealing mechanistic basis of paralog discrimination, this work provides a rationale for designing selective peptide-based inhibitors and underscores the power of molecular simulations to capture subtle dynamical features in closely related biomolecular systems.

Unlocking Long-Range Quantum Transport Through Single Molecules

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Controlling and manipulating quantum properties of molecular-scale materials is central to the development of a new generation of miniaturized electronic, spintronic, sensing, and quantum information technologies. However, designing highly conductive molecular materials that transmit electrons efficiently over long distances remains a major challenge. Conventional molecular designs typically exhibit off-resonant transport behaviors, resulting in low electron transmission that decays exponentially with molecular length. In this talk, I will discuss our efforts to overcome this fundamental bottleneck by harnessing the interplay of electron and spin at the single-molecule level. I will first provide a brief introduction to molecular quantum electronics and the experimental techniques used to probe quantum transport through single molecules. I will then discuss different design strategies we have developed to enable long-range quantum transport, including the use of quantum interference effects, the formation of spin topological states, and incorporation of π - π conjugation. Finally, I will highlight emerging opportunities and discuss the challenges that remain.

Nuclear Hyperfine Effect and an Astonishingly Large Primary Kinetic Isotope Effect in Anthracene-9- ^{13}C Photodimerization

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We present here the effects of 9- ^{13}C substitution on anthracene photodimerization induced by direct and triplet sensitized excitation. This study parallels our work on 9-D substituted anthracene, A_D . A modest ^{13}C nuclear hyperfine effect (NFE) is revealed by the comparison of the photodimerization rates of ordinary anthracene, $\text{A}_{12\text{C}}$, and anthracene-9- ^{13}C , $\text{A}_{13\text{C}}$, under direct, ($k_{12\text{C}}^{\text{S}}/k_{13\text{C}}^{\text{S}} = 1.23 \pm 0.02$) and triplet sensitized ($k_{12\text{C}}^{\text{T}}/k_{13\text{C}}^{\text{T}} = 1.05$ and 1.04 for fluorenone in C_6D_6 and for $\text{Ru}(\text{dmb})_3$ in CD_3CN , respectively) conditions. $\text{A}_{13\text{C}}$ photodimerized 17% faster from the triplet state because the ^{13}C NFE increases the population of singlet anthracene excimers. The ratio of $\text{A}_{13\text{C}}/\text{A}_{12\text{C}}$ second order decay rate constants, 1.10, supports the conclusion that the ^{13}C NFE increases the singlet excimer concentration by promoting $^3(\text{AA})^{**}$ to $^1(\text{AA})^*$ intersystem crossing. Astonishingly large head to tail (HT) to head to head (HH) photodimer ratios ($\text{D}_{\text{HT}}/\text{D}_{\text{HH}}$) are solvent independent, but depend strongly on the T , ranging from 1.71 to 2.32 in C_6D_6 , CD_2Cl_2 , and CD_3CN , as the T is raised from 4.6 to 60.1 °C. Although reminiscent of our observations with A_D , they do not mainly reflect changes in the ratios of precursor excimer concentrations, as in that case. Known ^{13}C kinetic isotope effects for bond formation to C_{12} are too small ($k_{12\text{C}12\text{C}}/k_{12\text{C}13\text{C}} = 1.025 \pm 0.005$) to account for this regioselectivity. However, kinetic analysis reveals a large primary kinetic isotope effect for ^{13}C - ^{13}C bond formation ($k_{12\text{C}12\text{C}}/k_{13\text{C}13\text{C}} = 1.81$ at 21 °C), marking the first time for the measurement of such an isotope effect. van't Hoff analysis of the $\text{D}_{\text{HT}}/\text{D}_{\text{HH}}$ T dependence yields $\Delta H = 1.00 \pm 0.03$ kcal/mol favoring D_{HH} , with ΔS favoring D_{HT} .

Transient absorption spectroscopy of the stilbenes in methanol – adiabatic *cis* to *trans* photoisomerization by sequential two-photon excitation.

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Femtosecond pulse excitation gave the time evolution of the transient absorption spectra (TAS) of *trans*- and *cis*-stilbene (*t*- and *c*-St) in methanol. Global analysis of *t*-St TAS gives the spectrum of the singlet excited state of *t*-St, $^1t^*$, with a lifetime, 46 ps, consistent with previous measurements. The spectrum of the singlet excited state of *c*-St, $^1c^*$, has bands at 360 and 630 nm in agreement with early literature spectra in other solvents. However, the $^1c^*$ spectrum obtained on multiexponential global analysis of *c*-St TAS is much more intense in the UV relative to the visible in disagreement with the observed TAS. Although the lifetime of the 630 nm band, 0.47 ps, agrees with the reported lifetimes, monoexponential fits in the UV region yield lifetimes that are significantly longer. We attribute this discrepancy to interference by the twisted phantom singlet, $^1p^*$, whose growth and decay occur in the same UV region. The 360 nm band rises together with a weak 405 nm band that decays faster and may be the Franck-Condon $^1c^*$ transient or a $^1c^*$ transient on the way to dihydrophenanthrene formation. Also observed on exciting *c*-St is the TAS of $^1t^*$. A mechanism involving two photon sequential excitation of *c*-St accounts for this result.

Optically Steering Ultrafast Carrier Scattering, Cooling, and Trapping Pathways in Nanoscale Semiconductors

Tom Hopper

University of Central Florida

The performance of semiconductors in energy-harvesting and light-emitting technologies is driven by the behavior of charge carriers, particularly at the point of carrier injection via light or electrical excitation. Here I will present how multi-pulse optical control spectroscopies, such as pump-push-probe techniques, can be used to parse out the real-time interactions of carriers with phonons, defects and other carriers in emerging semiconductor materials. Drawing on examples from colloidal quantum dots and transition metal dichalcogenide monolayers, we will examine distinct but complementary aspects of hot carrier phenomena in low-dimensional semiconductors which can be used to not only explain the unique photophysics of these materials, but guide the design of more efficient optoelectronic devices.

Thermodynamic Behavior of Hydrocarbons Confined in Mesoporous Silica Investigated by Differential Scanning Calorimetry

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Phase behavior of hydrocarbons under nanoscale confinement plays an important role in fluid recovery from tight-oil reservoirs, where a significant portion of hydrocarbons resides in nanoporous media. However, direct experimental measurements of phase transitions under confinement remain limited.

In this work, the boiling behavior of heptane and toluene confined in mesoporous silica is investigated using differential scanning calorimetry (DSC) at pressures of 101, 700, and 1300 kPa. A well-defined mesoporous material (SBA-15, ~4 nm pore size) is used to isolate the effect of nanoscale confinement.

The DSC measurements show clear shifts in phase-transition temperatures relative to the bulk fluids, corresponding to lower apparent vapor pressures for the confined hydrocarbons. This shift is consistently observed across all pressures tested, indicating that confinement-induced deviations persist under varying thermodynamic conditions.

These results provide direct experimental evidence of nanoconfinement effects on hydrocarbon phase behavior and improve the understanding of confined-fluid thermodynamics in nanoporous materials.

Zero- to Ultralow-Field NMR: From Hyperpolarized Spin Networks to Molecular J -Oscillators

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Zero- and ultralow-field nuclear magnetic resonance (ZULF NMR) provides access to spin dynamics governed primarily by spin-spin couplings (also known as J -couplings) rather than Zeeman interactions, enabling chemically specific spectroscopy without a conventional superconducting magnets. I will discuss recent developments that extend ZULF NMR from passive spectroscopy toward active molecular sensing, magnetic field amplification, and coherent signal generation. Hyperpolarization using parahydrogen gas, combined with magnetic-field measurements via optically pumped atomic magnetometers, enables the detection and manipulation of nuclear-spin signals at nanotesla-to-microtesla magnetic fields. I will also describe quadrature-detected ZULF NMR, in which orthogonal magnetometers recover the direction of nuclear-spin precession, separate positive and negative frequencies, and simplify spectral interpretation.

A central focus will be recent work on hyperpolarization-enabled molecular magnetic amplifiers and J -oscillators [1-2]. Under continuous SABRE (Signal Amplification by Reversible Exchange) hyperpolarization, solution-phase molecules form an active gain medium capable of amplifying weak oscillating magnetic fields near their zero-field J -transitions. Digital feedback converts this molecular amplifier into a self-sustained oscillator/clock whose frequency is determined by an intrinsic molecular J -coupling. Below threshold, picotesla-scale inputs are amplified; above threshold, coherent oscillations emerge with sub-millihertz linewidths over long measurements. Together, these advances establish ZULF NMR as a platform not only for magnet-free chemical spectroscopy, but also for precision sensing, quantum control, and molecularly encoded signal generation.

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Defect engineering in nanomaterials and their implications for sensing and heterogeneous catalysis

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Defects in nanomaterials offer opportunities to tune the local environment and chemical properties of the nanomaterial. Here we present our recent work investigating the photophysical changes in alloy metal nanoparticles and transition metal dichalcogenide quantum dots. We use a combination of single-particle and ensemble spectroscopy to quantify the effects of the defects and relate them to utility in sensing and catalysis.

PMSE/POLY and Materials Chemistry

Approaches for generating crosslinked networks by metal-free ring opening metathesis polymerization

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MF-ROMP, introduced by the Boydston group, is a novel photopolymerization method driven by ring opening of high-strain monomers such as norbornene (NB). Eliminating the metal catalyst by using an organic initiator and photosensitizer makes this reaction compatible with bio-related applications. Extending MF-ROMP to the formation of crosslinked polymer networks could open paths to new photo-patternable materials with tunable chemical functionality and mechanical properties.

We explored MF-ROMP for developing crosslinked networks by synthesizing and evaluating different norbornene-substituted crosslinkers. The crosslinkers were investigated through homopolymerization and copolymerization with NB under ambient conditions. Our preliminary results showed limited polymerization efficiency with synthesized crosslinkers, possibly due to the sensitivity of MF-ROMP toward nucleophilic functionalities, particularly oxygen-containing groups. Employing HFIP as a co-solvent improved conversion efficiency and promoted network formation. Results suggest that propagation and cross-linking are promoted by the unique properties of HFIP, which include low nucleophilicity and, the ability to stabilize cations, and the ability to suppress unwanted nucleophilic attack through hydrogen bonding.

The ring opening mechanism was confirmed by monitoring the reaction prior to gelation using proton nuclear magnetic resonance (¹H NMR) and fourier transform infrared spectroscopy (FTIR). Swelling studies of cross-linked gels indicate that increasing the crosslinker content leads to higher crosslink density and reduced swelling.

Glutathione-Responsive Polyhomocysteine Derivatives with Ultralow Toxicity toward Therapeutic Delivery

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Many therapeutic agents, either small-molecule drugs or biologic agents, have been challenged by their lack of specificity, short half-life, low therapeutic efficiency, increased risk of undesired side effects, and requirements of higher-dose and frequent administration. There is a pressing need for biocompatible and degradable smart drug delivery systems (SDDSs) that can preferentially accumulate and bind to diseased sites with controlled drug release. Glutathione-responsive synthetic polypeptides hold significant promise as biodegradable and biocompatible carriers for controlled drug and gene delivery. The addition of disulfide bonds into the pendant side chains enables triggered nucleic acid release while reducing cytotoxicity. However, achieving this remains challenging, whether through direct polymerization of disulfide-containing monomers or post-polymerization modification. In this work, we present an innovative and simple strategy to incorporate disulfide bonds into polypeptides using the ring-opening polymerization of N-carboxyanhydride derived from homocysteine, a thiol-containing amino acid. The polymerization was well-controlled, yielding repeating units up to 100 with narrow dispersity. The pendant side chains could be easily converted into a range of GSH-responsive moieties, including anionic, neutral, zwitterionic, cationic groups, and therapeutic agents toward a wide range of biomedical applications. The incorporation of disulfide bonds in the side chains facilitates the cleavage of pendant groups, triggering the release of cargos in the targeted environment. The drug-loaded amphiphilic polymer-drug conjugates displayed responsive release of intact drug and potent anticancer activities. Furthermore, we demonstrated cationic polyhomocysteine derivatives could effectively deliver siRNA, eGFP mRNA, and more complex CRISPR components with extremely low cytotoxicity and excellent transfection efficiency.

Enzyme-Mediated Photoiniferter Polymerization Enables Ultrahigh Molecular Weight Polymers with Tunable Adhesive and Frictional Properties

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Ultrahigh molecular weight (UHMW) synthetic polymers are essential to the development of high-performance biomaterials, coatings, adhesives, and structural materials, owing to material properties that emerge specifically at high chain lengths. Conventional UHMW polymers, such as polyethylene and polytetrafluoroethylene, are typically synthesized via Ziegler-Natta catalysis, which is effective primarily for nonpolar vinyl monomers. Consequently, there is strong demand for polymerization techniques capable of producing UHMW polymers from chemically diverse, functional monomers. Photoiniferter polymerization addresses this need by offering fine control over molecular weight, dispersity, and reaction kinetics while tolerating a broad range of functional groups. However, its radical mechanism remains highly oxygen-sensitive, requiring rigorous degassing and sealed reaction conditions that limit throughput and scalability. Here, we introduce an enzyme-assisted, degassing-free photoiniferter polymerization (Enz-PI) strategy that couples direct photolysis of dithiocarbonate-based chain transfer agents with enzymatic, in situ oxygen scavenging. This metal-free, light-controlled process enables the synthesis of well-defined UHMW polymers ($M_w > 1$ MDa) under ambient, aqueous, open-air conditions, while maintaining narrow dispersity and high end-group fidelity. Because Enz-PI requires no specialized deoxygenation setup, it is directly compatible with microliter-scale reactions in multiwell formats, enabling the rapid construction and screening of chemically diverse UHMW polymer libraries. Using this platform, we show that the resulting UHMW polymers exhibit tunable, composition-dependent adhesion and frictional behavior, with synergistic effects arising from the interplay between interfacial interactions and bulk energy dissipation. Together, these results establish Enz-PI as a sustainable, oxygen-tolerant, and high-throughput platform for engineering advanced functional materials, offering a practical route toward the accelerated design of next-generation polymer adhesives and coatings.

Preceramic Polymer-Grafted MXene Hybrids for Enhanced Thermo-Oxidative Stability

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MXenes are two-dimensional transition-metal carbides with exceptional electrical, mechanical, and thermal properties, but their use in high-temperature environments is limited by poor thermo-oxidative stability. Here, we report a surface-engineering strategy using preceramic polymer grafting to improve the thermal stability of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene for high-temperature ceramic applications. Phase-pure $\text{Ti}_3\text{C}_2\text{T}_x$ MAX phase was synthesized by optimizing the Ti:Al:C molar ratio and confirmed by X-ray diffraction (XRD). Selective Al etching using HCl/LiF produced layered $\text{Ti}_3\text{C}_2\text{T}_x$, evidenced by a shift of the (002) peak toward lower angles and confirmed by SEM and TEM. The MXene surface was functionalized using allyl dimethyl silane, followed by covalent preceramic polymer grafting at monomer-to-MXene weight ratios of 1:1, 1:2, and 1:3. Fourier Transform Infrared Spectroscopy (FTIR) confirmed successful grafting, while XRD indicated changes in the interlayer structure associated with polymer incorporation. Thermogravimetric analysis demonstrated improved thermal stability, with the 1:1 formulation achieving the highest ceramic yield of 52.6 wt%. Post-pyrolysis XRD revealed suppressed TiO_2 formation and enhanced SiC formation, demonstrating improved thermo-oxidative resistance. These results establish preceramic polymer grafting as a promising strategy for developing thermally durable MXene nanofillers for ceramic matrix composites and other extreme-temperature applications.

Supramolecular arene-perfluoroarene assembly enhances photoiniferter polymerization kinetics

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Accessing ultra-high molecular weight (UHMW) polystyrene remains challenging because of its prohibitively slow homopolymerization kinetics. This can be circumvented by—among other methods—copolymerization with pentafluorostyrene (PFS). Given the electronic similarities to prototypical arene-hexafluorobenzene supramolecular heterodimers, we were inspired to investigate the effect of arene-perfluoroarene interactions on photoiniferter crosspropagation rate constants (k_p). Thus, we designed additional styrenic comonomers bearing increasing numbers of methoxy substituents (*i.e.*, 4-mono-, 3,4-di-, and 3,4,5-trimethoxystyrene) aimed to strengthen AP interactions with PFS during copolymerization. Copolymerization kinetics, rheological and thermomechanical properties, and density functional theory (DFT) computational analysis will be discussed that support a mechanism in which strengthened supramolecular AP interactions promote monomer assembly and afford up to a 2000% increase in experimental k_p relative to styrene homopolymerization. These correlative trends enabled the use of 3,4,5-tri(*n*-decyloxy)styrene comonomer that, leveraging enhanced propagation kinetics, provided ultra-soft UHMW materials despite its high steric bulk. Overall, this work suggests that supramolecular interactions can circumvent the slow propagation rates inherent to some radical-based polymerizations and provide access to UHMW materials that remain difficult to achieve via conventional methods alone.

Depolymerization of Commercial Polymethacrylates

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University of Florida

The current recycling methods lag behind the rate at which the polymeric materials are produced, which drives the researcher to develop novel upcycling and recycling methodologies. The current industrial production of PMMA is over 4 million tons per year and expected to increase rapidly in future. Conventional thermomechanical methods of depolymerizing PMMA uses high temperature ($>400\text{ }^{\circ}\text{C}$) induced C–C bond cleavage, leading to the high amount of degradation to lower molecular weight compared to depolymerizing back to MMA. Earlier work in this field demonstrated that the bulk depolymerization of polymethacrylates synthesized using reversible-deactivation radical polymerization (RDRP) methods via chain end initiation using external stimuli like heat. Although we can achieve high extent of depolymerization under solvent free bulk state, however, the polymers made by these methods are often colored and in some cases it also uses catalysts. Recent work on the bulk depolymerization of polymethacrylates derived from via conventional radical polymerization demonstrates the use of low mol % incorporation of thermolytically labile group like phthalimide ester that could give $>95\%$ reversion to methyl methacrylate (MMA) at considerably low temperature like $290\text{ }^{\circ}\text{C}$. Despite the current reports on the depolymerization of PMMA providing great advances in the field, the approaches require premade PMMA copolymers to trigger the depolymerization. In our work, we are focusing on the depolymerization of pristine PMMA synthesized by conventional radical polymerization via post-polymerization modification. Our approach relies on the low extent of hydrolysis ($< 15\%$) of PMMA and subsequent use of Photo/thermal trigger or incorporation of thermolabile group to depolymerize it. Methodology would open a novel way to efficiently depolymerize commercially available PMMA of different molecular weights.

Poster Presentations

Friday Posters

F1: Cysteine-Directed Synthesis of Chiral CoMn_2O_4 Spinel Nanoparticles for Spin-Selective Electrochemical Oxygen Evolution

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The oxygen evolution reaction (OER) is the anodic half-cell reaction for many electrochemical systems, including electrolyzers, metal-air batteries, and fuel cells. A recent approach to improving the efficiency of materials for this reaction involves the spin-selective oxidation of singlet reactants (H_2O or OH^-) to triplet O_2 . Traditionally, this has been approached through the synthesis of metal oxides incorporating chiral ligands to induce asymmetric spin polarization through an effect known as chiral-induced spin selectivity (CISS). However, incorporating chiral ligands into mixed-metal oxide nanomaterials remains challenging. This project utilizes $\beta\text{-MnOOH}$ nanosheets functionalized with cysteine ligands to facilitate the incorporation of $\text{Co}(\text{NH}_3)_6^{2+}$ between the layers. Increasing the reaction temperature under ambient conditions promotes the removal of interlayer water and the formation of $\text{t-CoMn}_2\text{O}_4$ spinel nanoparticles. Cysteine is subsequently removed through a series of washing steps. Materials synthesized using enantiomerically pure L- and D-cysteine, as well as a racemic mixture, exhibit indistinguishable XRD, UV-Vis, Raman, and TEM characterization and similar Co: Mn ratios. In contrast, circular dichroism spectroscopy reveals opposite optical activity for the L- and D- CoMn_2O_4 materials, while the racemic CoMn_2O_4 exhibits minimal optical activity. Notably, a corresponding difference in catalytic activity is observed, with L- and D- CoMn_2O_4 exhibiting approximately 1.5-fold higher OER activity than racemic CoMn_2O_4 at 1.70 V vs. RHE in 0.1 M KOH. Overall, this work demonstrates a synthetic approach for incorporating chirality into mixed-metal spinel oxide nanomaterials through a cysteine-functionalized layered precursor, providing a route to prepare structurally similar materials for enhancing spin-selective reactions.

F2: Boronic Acid Copolymers for Substantive Skin Hydration and Topical Delivery

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University of Florida

Substantivity in dermal delivery presents significant challenges. Conventional humectants such as hyaluronic acid hydrate through water retention but lack specific interactions with the skin's outer layer, resulting in the loss of hydration and active compounds upon washing. We are developing dimethylacrylamide copolymers bearing pendant boronic acids that form reversible boronate esters with skin glycoproteins, glycolipids, and sugars, thereby providing sustained hydration and controlled cargo release. The primary obstacle is a pH mismatch: boronic acids effectively bind diols only when converted to their anionic form; however, the commonly used monomer 3-acrylamidophenylboronic acid ($pK_a \approx 8.5$) remains non-binding at skin pH levels (4.5–5.5). Rheological studies on diol-free copolymers reveal a loss of elastic behavior from pH 7 to 5, indicating that boronic acid ionization governs network dynamics. To enhance binding under acidic conditions, we synthesized two monomers: 2-acrylamidophenylboronic acid, which stabilizes the tetrahedral form without pH-dependent switching issues, and a benzoxaborole ring with destabilizing strain. Copolymerization with DMA is in progress, and NMR titrations will evaluate diol affinity to establish design principles for stable boronate networks on the skin.

F3: Precursor-Directed Growth of Molybdenum Disulfide Thin Films by Aerosol-Assisted Chemical Vapor Deposition

Delawar Ashraf, Lisa McElwee-White

University of Florida

Transition metal dichalcogenides, including molybdenum disulfide (MoS_2) are promising two-dimensional materials and have distinct electronic, optical and catalytic properties and can be used energy storage devices, sensors, nanoelectronics, and catalytic applications. Various molybdenum-based single-source precursors, including molybdenum(IV) dithiocarboxylate, molybdenum(IV) dithiocarbamate, and molybdenum(IV) dithioxanthate, were synthesized and characterized for AACVD of MoS_2 materials. Effects of various precursor ligands on the growth and morphology of MoS_2 thin films will be discussed.

F4: Adhesive Polyelectrolyte Complex Coacervates with Structural Antibiotics

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Florida State University

Rapid-setting adhesives capable of functioning in aqueous environments are highly desirable for a wide range of applications. Complex coacervates dense, hydrated, phase-separated materials have recently emerged as promising candidates for such uses due to their inherent compatibility with wet conditions. In this study, negatively charged polyelectrolytes, poly(styrenesulfonate) (PSS) and poly(acrylamidomethylpropanesulfonate) (PAMPS), were combined with cationic antibiotics, including neomycin and streptomycin. Electrostatic interactions between oppositely charged species led to the formation of coacervate materials exhibiting viscoelastic properties well-suited for pressure-sensitive, rapid adhesion in water.

Under physiological conditions (0.15 M NaCl, 37 °C), PSS-based coacervates with neomycin, or with mixtures of neomycin and streptomycin, remained approximately 20 °C above their glass transition temperature. These materials demonstrated adhesive strengths up to 100 kPa and adhesion energies approaching 80 J m⁻² at low strain rates. Effective underwater adhesion was achieved across a variety of substrates, including hydrophilic surfaces such as glass and metals, as well as hydrophobic materials like rubber.

Despite the relatively low charge density of the antibiotic components (3+ to 6+), strong interactions between their protonated amine groups and the aromatic sulfonate moieties of PSS contributed to notable salt tolerance, with stability maintained in NaCl concentrations as high as 1.7 M. Investigation of equilibrium complexation behavior (liquid–liquid phase separation) between small-molecule ligands and high-molecular-weight polyelectrolytes revealed that salt resistance is influenced by ligand concentration. This behavior also enables a sustained release profile, allowing gradual diffusion of the antibiotics while maintaining structural integrity of the coacervate.

Quantitative NMR analysis of buffered saline solutions (0.15 M NaCl) in contact with the coacervates confirmed the controlled release of antibiotic species, with minimal loss of the polymer component. Overall, this work demonstrates a strategy for designing bioactive, underwater, instant adhesives based on polyelectrolyte–small molecule coacervate systems with competitive mechanical and functional performance.

F5: Precision Engineering of Cd₃₂Te₁₄ Semiconductor Nanocluster via Cation Exchange

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Atomically precise semiconductor nanoclusters provide an excellent platform for understanding the relationship between composition, structure, and optoelectronic properties at the nanoscale due to their well-defined inorganic cores and organic ligand frameworks. Cation exchange (CE) offers a versatile approach for modifying the composition of precursor nanoclusters while retaining their anionic structural framework. Here, we investigate the cation exchange of the atomically precise semiconductor nanocluster Cd₃₂Te₁₄(TBBT)₃₆(PPh₃)₄ (TBBT= 4-tert-butylbenzenethiolate) using precise thiolate complexes of Hg²⁺ and Ag⁺ as cation sources. The exchange reactions were studied to evaluate the feasibility, kinetics, and final product of replacing Cd²⁺ with cations of different chemical and electronic character. Cation exchange with Hg²⁺ produces an ultrasmall, single-sized HgTe nanocluster exhibiting consistent and prominent absorption features compared to the parent Cd₃₂Te₁₄ cluster, while retaining the anionic lattice similar to that of the zinc-blende precursor cluster. In contrast, exposure to Ag⁺ ions results in rapid exchange along with pronounced changes in absorption features of the parent cluster. The obtained monoclinic Ag₂Te cluster indicates transformation of the anion lattice accompanied by cation exchange. The resulting CE products were characterized using UV–visible spectroscopy, NMR spectroscopy, mass spectrometry, thermogravimetric analysis, and diffraction analyses such as SCXRD and PXRD. In contrast to conventional semiconductor syntheses, which are often lengthy and intricate, this CE approach provides a straightforward and accessible method for studying molecular-level nanoscale transformations, thereby facilitating the highly controlled synthesis of precise semiconductor nanoclusters.

F6: Printing Yttria Stabilized Zirconia (YSZ) for High Dielectric Breakdown Structures for High Voltage Applications

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Reliable dielectric insulation is essential for high-voltage components across power transmission, electric vehicle, pulsed power, and aerospace applications, where materials must withstand extreme electric fields without mechanical or dielectric failure. Yttria-stabilized zirconia (YSZ) is an attractive candidate material for these applications, offering high dielectric breakdown strength, thermal stability, and mechanical durability. However, a significant challenge in manufacturing high voltage ceramics is how brittle those materials are, which makes it difficult to machine desired structures, and limits the geometries achievable for components that must contain or shield high-voltage fields, particularly as devices trend toward more compact, complex, and conformal designs. This work explores direct ink writing (DIW) as an alternative manufacturing route for producing detailed, customizable green-body ceramic structures that better protect and contain electric fields. Using a commercial high-loading YSZ ceramic ink (3 mol %), continuous ink deposition was achieved with a 20-gauge (610-micron) tip on a 3DFlexible tabletop printer. Structures were printed successfully onto a curved substrate, demonstrating the in-house capability to produce custom high-voltage insulation and protection across a variety of geometries. These results highlight the versatility of DIW for producing complex ceramic structures beyond the reach of conventional machining. These initial results establish a foundation for future work, including sintering and characterization of printed structures to evaluate dielectric performance, as well as expanding the range of substrate geometries and print resolutions achievable with this approach.

Key Words: Additive manufacturing, Direct Ink Writing, 3D Printing, Yttria Stabilized Zirconia (YSZ)

F7: Stoichiometric Liquid-ALD Synthesis of High-Surface-Area LaAlO₃ Thin Films with Controlled Surface Chemistry

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Metal oxide thin films are important in heterogeneous catalysis because catalytic activity can depend strongly on surface composition, cation distribution, and accessibility of active sites. Conventional atomic layer deposition provides excellent control over film thickness and composition but is often limited by low deposition rates, high precursor consumption, and process complexity. Here, an acid-catalyzed liquid atomic layer deposition (L-ALD) approach was developed for the controlled synthesis of lanthanum oxide and lanthanum aluminate thin films on high-surface-area alumina. Vacuum-dried nano-alumina was used as the support, and the surface hydroxyl density was determined to be approximately 13 OH nm⁻². Stoichiometric precursor requirements were established by GC-FID monitoring of ligand release, enabling controlled sequential deposition. Hydrolysis conditions were optimized by varying acid identity, concentration, and temperature, with nitric acid providing up to 99% hydrolysis efficiency at 40 °C. Repeated deposition cycles showed reproducible hydroxyl consumption and regeneration, allowing uniform layer-by-layer growth over multiple cycles. XRD confirmed the formation of La₂O₃ and LaAlO₃ phases after calcination, while STEM-EDS demonstrated uniform elemental distribution and minimal aggregation. XPS further confirmed the expected La-containing oxide environments. Increasing the number of L-ALD cycles resulted in a modest decrease in BET surface area, consistent with progressive pore filling, while CO₂ chemisorption increased, indicating a greater density of accessible basic surface sites. Catalytic testing for oxidative methane coupling showed improved CH₄ conversion, C₂ selectivity, C₂ yield, and turnover frequency with increasing L-ALD deposition cycles. These results demonstrate that stoichiometric, surface-limited liquid deposition enables control over oxide composition, surface coverage, and catalytic site density while retaining the high surface area of the support. The approach provides a versatile route for synthesizing conformal complex oxide films with tunable surface chemistry for heterogeneous catalysis and related functional-material applications.

F8: Designing and Investigating the Properties of Ultra-Long Acrylic Bottlebrush Polymers

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Bottlebrush polymers are defined by their densely grafted side chains that create steric repulsion and suppress chain entanglements, producing unique mechanical and structural properties. The exploitation of this architecture allows for the access of super-soft, ultra-long, one dimensional (1D) nanorods. Using controlled radical polymerization, including photoiniferter (PI) polymerization and atom transfer radical polymerization (ATRP), ultra-long bottlebrush polymers with acrylic side chains and a styrenic backbone were synthesized via a "grafting-from" strategy. The synthesized polymers exhibit an ultra-soft character, pronounced tackiness, and high ductility, highlighting their potential as super-soft adhesive materials for advanced applications, including flexible electronics and biomimetic tissue interfaces.

F9: Synthesis optimization of Ruddlesden-Popper metal halide semiconductors

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2D metal halide semiconductors are of great interest for increasing photovoltaic efficiency in solar cells and light emitting diodes. Here, we synthesized materials to investigate the mechanical and thermal stability of Metal Halide Perovskites (MHPs) as a function of the Pb—X bond, *n*-layer thickness, and carbon chain length of the organic linkers, which are known to affect the in- and out-of-plane mechanical properties of 2D materials.

To assess the mechanical properties of 2D MHPs at differing thicknesses and linker lengths, we synthesized pure-phase (BA)₂(MA)₂Pb₃Br₁₀, (HA)₂(MA)₂Pb₂Br₇, and (OA)₂(MA)₂Pb₂Br₇ for single crystal Brillouin scattering spectroscopy. Optimization of reaction conditions was necessary, because existing literature protocols gave mixed-phases or no yield. We observed that annealing to lower temperatures resulted in increasing extraneous peaks on the Powder X-Ray Diffractometer (PXRD), indicating the formation of undesired lower *n*-value phase crystals. By optimizing synthesis protocols, we established reproducible procedures for the isolation of pure-phase (BA)₂(MA)₂Pb₃Br₁₀, (HA)₂(MA)₂Pb₂Br₇, and (OA)₂(MA)₂Pb₂Br₇. Ongoing single crystal Brillouin scattering spectroscopy will determine properties of 2D metal halide semiconductors that affect their mechanical robustness and overall stability.

F10: Depolymerization of silicon-methacrylate materials

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Properties such as hydrophobicity, gas diffusivity, chemical inertness, and flexibility of polysiloxanes have traditionally made them promising candidates for a variety of commercial applications (contact lenses and biomedical materials, caulks and sealants, flexible bakeware). The most common of the polysiloxanes, polydimethylsiloxane (PDMS), is frequently employed in copolymer networks and blends with petro-based plastics to yield the final commercial materials. However, existing chemical, and mechanical, recycling strategies can be impeded by chemical stability and frequent covalent crosslinking inherent to these materials, respectively. Recently-discovered comonomer depolymerization triggers, such as phthalimide ester methacrylates, have been shown to readily reveal backbone carbon radicals, through pendent group homolysis and subsequent decarboxylation events, that unzip styrenic and methacrylic polymer backbones, achieving monomer reversion. Using strategic incorporation of comonomer depolymerization triggers to PDMS-methacrylate networks, recyclability of siloxane-methacrylate networks is enhanced.

F11: Pomegranate peel-derived activated carbon as a sustainable electrochemical platform for future biosensor development

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Activated carbon materials derived from agro-industrial waste have attracted increasing interest as sustainable substrates for electrochemical sensors because of their high specific surface area, tunable porosity, surface functionality, chemical stability, and low production cost. In this study, activated carbon was synthesized from pomegranate peel (*Punica granatum*) through chemical activation with KOH. Two synthesis routes were evaluated: a direct one-step route using raw biomass and a two-step route involving precarbonization of the precursor at 450 °C to obtain biochar. Activation temperatures of 700, 800, and 900 °C were investigated to determine their influence on product yield, textural properties, structural characteristics, surface morphology, and electrochemical behavior.

The two-step route resulted in higher activated carbon yields, with the material produced at 900 °C achieving the highest yield of 31%. In contrast, the one-step route exhibited a progressive decrease in yield as the activation temperature increased. Thermogravimetric analysis showed that the biochar had greater thermal stability than the raw biomass, with approximate mass losses of 30% and 70%, respectively. Nitrogen physisorption analysis confirmed the formation of highly porous materials, with BET specific surface areas of approximately 1000 m² g⁻¹ for all synthesized samples. Complementary FTIR, Raman, and SEM analyses revealed the presence of surface functional groups, defective carbon domains, graphitic contributions, and irregular porous morphologies, all of which are relevant to interfacial electrochemical processes.

The electrochemical evaluation of activated carbon inks deposited onto glassy carbon electrodes revealed predominantly capacitive behavior in 1 mol L⁻¹ KCl, associated with the formation of an electrical double layer. These findings indicate that activated carbon derived from pomegranate peel—particularly CA2-800—represents a promising sustainable platform for the subsequent immobilization of gold nanoparticles and the future development of electrochemical biosensors.

F12: Evaluating Plasmonic Behavior of Semiconducting Nanocrystals via SQUID

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The oscillation of free carriers in a nanocrystal when irradiated with light of a specific frequency is called a localized surface plasmon resonance (LSPR). Plasmonic semiconducting nanocrystals hold great potential for exhibition of magneto-optical effects which are required for the development of future nanophotonic technologies. This phenomenon is governed by the material's dielectric function, and in semiconductors, it can be tuned by modification of carrier density (*n*) and carrier effective mass (*m*^{*}). Standard analysis of nanocrystals' plasmonic behavior is accomplished by fitting a UV/VIS/NIR spectrum to a variation of the Drude model, however, a full analysis of optoelectronic properties at the nanoscale is a challenge. A different approach to understand plasmonic behavior may be to analyze carriers through the lens of magnetism. A series of metal oxide nanocrystals will be characterized using UV/VIS/NIR spectroscopy, pXRD, XRF, TEM, and SQUID measurements.

F13: Phase evolution and functional properties of Bi-In-Sn oxides

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Bismuth-containing mixed-metal oxides exhibit useful dielectric, electrical, optical, and catalytic properties. The properties can be tuned through targeted chemical substitutions within the limits of the formation of solid solutions. In this study, the extent of substitution and its structural effects were investigated in the Bi₂O₃-In₂O₃-SnO₂ system. Phase evolution and crystal structures were characterized using powder X-ray diffraction and Rietveld refinement, establishing the phase diagram and identification of stable phases and extent of solid solution formation. Detailed structural, electrical, optical, and photocatalytic analyses were performed for selected Sillénite and pyrochlore compositions. The tunability of the dielectric and optical properties in this system highlights the potential for photocatalytic applications and for use in low-temperature cofired ceramics.

F14: Order from Chaos: Unsupervised Learning of Conformational Landscapes

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Molecular dynamics (MD) simulations are a popular way to understand chemical reactions and behaviors. To gain insight from the data generated by MD simulations, efficient analysis tools are needed. We have previously introduced MDance, a Python package that houses ultra-fast clustering tools, including k-means N-Ary Natural Initiation (NANI) and the Hierarchical Extended Linkage Method (HELM). NANI addresses a key challenge in k-means clustering: how to choose the seeds for the initial clusters. Additionally, it is deterministic and scales linearly with the number of frames. While k-means is popular for its low memory and time requirements, hierarchical clustering methods allow molecules to be grouped more flexibly. HELM significantly improves on the memory requirements of traditional hierarchical clustering. Here we present MDance C++, in which we have reimplemented both NANI and HELM to increase their accessibility and take advantage of performance features available in C++ but not in Python.

F15: Metal Halide Semiconductors with Engineered Porosity

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Hybrid Metal Halide Semiconductors have recently gained traction for numerous reasons, including their thermal stability, water stability, and tunable optoelectronic properties. Attempting to broaden their application potential, we introduced a new family of materials, namely Porous Metal Halide Semiconductors (PMHS), where the organic linker serves a dual role as both a counter cation and a structural component that imparts permanent porosity to the material. We develop custom-made molecular cages to fine-tune the porosity, while unlocking new possibilities for applications such as energy storage, catalysis, and sensing.

F17: Photoassisted chemical vapor deposition of ruthenium on functionalized self-assembled monolayers using (η^2 -olefin)Ru(CO)₄ precursors

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Metallized organic substrates are critical for applications in fine pitch interconnects, multilayer integration, and low temperature device fabrication. Chemical vapor deposition (CVD) is a versatile method for metal film growth, but its high processing temperatures limit compatibility with thermally sensitive organic materials. Here, the Ru(0) carbonyl olefin complexes, (η^2 -dimethylfumarate)Ru(CO)₄ and (η^2 -dimethylmaleate)Ru(CO)₄, were synthesized as precursors for low temperature deposition by photoassisted chemical vapor deposition (PACVD). Their excited states are assigned as metal to ligand charge transfer (MCT) or ligand field (LF) based on solvatochromism and DFT analysis, and their photochemical quantum yields exhibit wavelength dependence. Deposition on functionalized alkanethiolate self-assembled monolayers (SAMs) shows selective Ru growth on -COOH and -OH terminations, with no deposition on -CH₃ surfaces, as confirmed by XPS.

Notably, Ru deposition occurs even without UV irradiation, indicating that these complexes can also function as room temperature thermal CVD precursors. The characterization results and the influence of stereochemistry on photoassisted chemical deposition will be discussed.

F18: High flux X-ray scintillation of FAPbI₃ halide perovskite/Polymer Composite Scintillators: Poly(lactic acid) (PLA) versus Polyimide (PI) Matrices

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Solution-processed halide perovskite/polymer composites are attractive candidates for flexible, low-cost X-ray scintillators, but their radiation hardness and imaging performance remain poorly understood relative to conventional inorganic scintillators. Here, we compare two FAPbI₃-based composite films: FAPbI₃/polyimide (FAPI) and FAPbI₃/poly(lactic acid) (FAPLA) under continuous high-flux radioluminescence (RL) monitoring, time-resolved RL (TRRL), and modulation transfer function (MTF) imaging. Both composites showed a blue shift of the RL emission maximum, which might be attributed to X-ray-induced ion migration and defect accumulation. RL intensity trends diverged sharply. However, FAPLA showed a net intensity gain (+34%) that increased under continuous dosing for 25 minutes, while FAPI lost ~61% of its peak intensity over 5 minutes of continuous dosing. TRRL revealed an order-of-magnitude longer excited-state lifetime for FAPI ($\tau = 15.3$ ns) compared to fast, sub-nanosecond, band-edge-like kinetics for FAPLA, implicating a trap-mediated radiative pathway as the shared origin of FAPI's brightness and instability. This same trap population correlated with degraded spatial resolution: FAPI reached only 6.8 LP/mm, compared with 12.6 LP/mm for FAPLA. These results revealed the importance of polymer matrix selection as a critical design lever governing the trade-off among brightness, radiation stability, and imaging resolution in FAPbI₃-based scintillator composites, with FAPLA favored for radiation-hard, high-resolution imaging and FAPI for applications that prioritize peak light yield.

F19: A Combined Experimental and Computational Approach to CO₂ Capture in Nanoparticle-Metal-Organic Framework Composite Catalysts

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This work seeks to define structure-function relationships for the rational design of nanoparticle-metal-organic framework (NP-MOF) composite catalysts. Here, we focus on Pd NPs integrated into MUF-16 (Pd@MUF-16) for CO₂ capture and reduction. CO₂ is produced as a waste product in many industrial processes and converting it to higher value chemicals could have significant economic and environmental impact. Metal-organic frameworks (MOFs) offer a promising route to selective CO₂ capture, increasing the local concentration at the Pd NP catalyst surface. Preliminary experimental work includes shape-selective Pd NP synthesis, composite fabrication, and materials characterization via scanning electron microscopy, energy dispersive x-ray spectroscopy, and x-ray diffraction. Density functional theory (DFT) calculations are used to predict the binding energies governing CO₂ adsorption within isolated MUF-16 unit cells. These computational predictions complement experimental characterization to build a more complete picture of CO₂-binding behavior within MUF-16. Work is ongoing to apply Pd@MUF-16 for thermal CO₂ reduction. Together, this combined experimental and computational approach aims to establish structure-function design principles for pairing MOF-based CO₂ capture with NP catalysis. We expect the generated knowledge can be extended to inform future optimization of composite catalysts for industrial carbon reduction applications.

F20: Membrane-dependent transport of linear and cyclic polymers

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Cyclic polymers lacking chain ends exhibit unique properties, including smaller hydrodynamic radii, lower intrinsic viscosity, and slower elution times on GPC columns than linear polymers of comparable molar mass, making them useful for applications ranging from drug delivery to advanced lubricant performance. Another interesting feature of these topological analogs is that they cannot exhibit end-first motion in solution, thereby altering their diffusion in confined environments compared with linear polymers, which could be useful for reducing the crossover of redox-active species in a polymer redox-flow battery. Therefore, in this study, the transport behavior of a model linear and cyclic polymer, poly(phenylacetylene) (l-PPA and c-PPA), was quantified through two different membranes: a 0.1 μm hydrophilic PTFE membrane and a 6-8 kDa MWCO (molecular weight cut-off) RC (regenerated cellulose) dialysis membrane. Both polymers were dissolved in THF and allowed to diffuse through the membranes in a 2-compartment diffusion cell. The polymer concentration in the receiver compartment was determined by UV-Vis spectroscopy. The concentration vs time data were utilized to calculate percent rejection and permeability values. In the case of the PTFE membrane, c-PPA exhibited an order-of-magnitude higher permeability than l-PPA, with respective values of 5.1×10^{-8} and $5.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. The trend in polymer permeability reversed with the RC dialysis membrane. Replicate measurements yielded values of $3.55 \pm 0.57 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for l-PPA and $2.01 \pm 0.05 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for c-PPA, with approximately 80% and 86% rejection, respectively. The results suggest that compact cyclic chains move efficiently through less-restrictive pathways, whereas chain-end-associated motion may favor linear chains under strong confinement. Because MWCO is an operational retention specification rather than an absolute pore size, this mechanistic interpretation remains tentative. To further validate it, ongoing studies are using a linear telechelic polystyrene (PS) precursor and its ring-closed cyclic analog to evaluate the topological effect in polymers derived from the same molecular weight distributions.

F21: nanoGUMBOS: tunable organic nanomaterials for biomedical applications

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NanoGUMBOS are nanomaterials derived from GUMBOS—*Group of Uniform Materials Based on Organic Salts*—a class of compounds that combine the tunable properties of ionic liquids with the structural versatility of solid-state materials. With melting points ranging from 25°C to 250°C, GUMBOS can be engineered to exhibit diverse functionalities, including fluorescence, magnetism, hydrophobicity, and bioactivities such as antibacterial, antifungal, and anticancer effects. These properties have enabled their integration into a wide range of biomedical applications. At the nanoscale, nanoGUMBOS demonstrate enhanced bioactivity and physicochemical characteristics tailored for targeted therapeutic and diagnostic use. They have been successfully applied in selective cancer cell targeting, hemoglobin isolation from whole blood, and molecular recognition of amino acids. Furthermore, nanoGUMBOS have been developed as multifunctional theranostic agents—magnetic, fluorescent, and pH-sensitive—as well as imaging probes, owing to their dynamic spectroscopic behavior. This poster will highlight the development and biomedical potential of nanoGUMBOS, showcasing key studies and emerging directions that position them as a versatile platform for next-generation nanomedicine.

F22: Ultra-High Molecular Weight (UHMW) Triblock SLIPs as Synthetic Mucins

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Mucus derives its viscoelastic, network-forming, and protective properties from mucins, ultra-high-molecular-weight (UHMW) ($>10^6$ g mol⁻¹) glycoproteins that reversibly associate with one another and biological surfaces. Reproducing these properties synthetically without complex glycosylation requires combining ultra-high molecular weight, aqueous solubility, and reversible interactions. Here, we report ultra-high-molecular-weight ABA triblock shear-labile interaction polymers (SLIPs) designed to mimic key mucin properties through a property-based approach. A hydrophilic poly(*N,N*-dimethylacrylamide) central block is flanked by blocks containing phenylboronic acid for reversible, pH-responsive diol binding and acrylic acid for charge and potential divalent-cation bridging. Photoiniferter polymerization produced triblocks with molecular weight in the UHMW region. Outer block chemistry strongly influenced physiological pH solubility: 3-acrylamidophenylboronic acid rendered the polymers insoluble, whereas amphoteric 2-acrylamidophenylboronic acid restored solubility toward neutral pH. Rheology revealed that chain architecture, rather than boronic-acid content, governs interchain association. At comparable molecular weight and composition, complex viscosity increased from random $\approx$ water $\ll$ diblock $<$ triblock, demonstrating that end localized binding groups promote a percolating associative network. Preliminary probe tack measurements confirmed mucosal adhesion. These results establish triblock SLIPs as a modular, glycan free platform for reproducing key mucus properties.

F23: Comparison of Linkers in Hybrid Metal Halide Semiconductors for Selective CO₂ Photoreduction

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Transition metals display marked catalytic activity in metal halide semiconductor applications. The electronic configuration of transition metals allows for tunability of optoelectronic properties, enhanced photocatalytic efficiency, and viable alternatives to lead-based materials when used in hybrid organic inorganic perovskites. In the exploration of CO₂ photoreduction using transition metal hybrid semiconductors, examining the band structure of metal centers and interacting reaction species is essential for understanding and optimizing photocatalytic performance.

In this work, three hybrid copper bromide semiconductors were synthesized using Cu metal centers alongside [2.2.2] cryptand(C₁₈N₂H₃₆O₆)(DHS), CRB (C₅₄H₆₆N₈) and CRT(C₃₆N₈H₅₄) as counter cations with bromide (Br⁻) acting as a counter anion in the corresponding copper halide structure. The electronic structures, optical properties, and photoluminescence behavior of these materials were investigated through experimental and theoretical approaches.

The results demonstrate that these copper-based materials possess promising optical and electronic characteristics that enable light absorption and facilitate the photoreduction of CO₂ into CO and CH₄. Differences in the organic counter cation composition influence the materials' electronic structures and photocatalytic behavior, providing insight into structure-property relationships within this class of hybrid semiconductors. These findings highlight the potential of copper-based hybrid metal halide materials in developing tunable and selective photocatalysts for CO₂ reduction and future sustainable-energy applications.

F24: Stoichiometry-Driven Optical Tuning and Thiophene-Induced Photoluminescence Enhancement in WS₂ Quantum Dots

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WS₂ quantum dots (QDs) provide a platform in which quantum confinement and surface chemistry converge, coupling size-dependent optical properties to molecular interactions. Here, we investigate the effect of W:S precursor stoichiometry on the optical properties of bottom-up synthesized WS₂ QDs and examine how these changes influence their interaction with thiophene. WS₂ QDs were synthesized hydrothermally using W:S precursor ratios of 1:0.5, 1:1, and 1:2, yielding a systematic decrease in average particle size from 9.2 to 2.8 nm as determined by TEM. Optical characterization revealed pronounced stoichiometry-dependent changes in absorption, Tauc-estimated optical band gap (2.79-3.28 eV), photoluminescence, quantum yield (1.8-4.16%), and excited-state lifetime. Excitation-dependent emission and wavelength-dependent spectral shifts indicate multiple emissive states, consistent with contributions from both quantum confinement and surface-related electronic states. Upon thiophene addition, all three QDs exhibited enhanced photoluminescence accompanied by changes in excited-state dynamics, with the magnitude of enhancement strongly dependent on precursor stoichiometry. DFT calculations were used to explore possible thiophene binding configurations at the QD edge, offering a computational framework for interpreting the observed optical response. Given that thiophene is a classic probe molecule in hydrodesulfurization catalysis, these results point to potential applications of precursor-tuned WS₂ QDs as optical probes and catalytic materials for sulfur-containing aromatic compounds.

F25: Design of DHS-Molybdenum hybrid halide semiconductors

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Organic-inorganic hybrid transition-metal halides provide a structurally versatile platform for developing materials with tunable optical, electronic, and magnetic properties. This work is motivated by introducing molybdenum into hybrid metal halides to harness its catalytic and optoelectronic properties. Previous reports show that structurally isolated Mo(V)-oxyhalide units can exhibit multiple ligand-field and ligand-to-metal charge-transfer transitions, as well as near-infrared luminescence. In this work, we used the double-protonated [2.2.2] cryptand (DHS) cage as an organic structure-directing agent and counter-cation to prepare new porous molybdenum-based hybrid halide materials with enhanced stability. Thus, we report the synthesis and crystal structures of the isostructural X = (Cl, Br) and (DHS)MoI₅(H₂O) to investigate how halide tunability can modify the metal environment and underlying optoelectronic properties.

F26: High Fracture Toughness in Ultra-High Molecular Weight Thermoplastics with Strain-Induced Crystallization

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Highly fracture-resistant materials traditionally require covalent crosslinking, a feature that prevents them from being melt-reprocessed or recycled. To overcome this trade-off, a strategy was developed using linear, ultra-high molecular weight (UHMW) alternating styrenic copolymers that combine high topological entanglement densities with strain-induced side-chain crystallization. By utilizing bulk photoiniferter polymerization and subsequent quantitative post-polymerization modification, a series of UHMW poly(styrene-alt-pentafluorostyrene) derivatives functionalized with various alkyl thiol lengths (Sty-PFSX) were synthesized. This method produces polymers featuring uniform degrees of polymerization, highly tunable glass transition temperatures (2°C to 35°C), interdigitation and crystallization of the alkyl side-chains. This structural arrangement triggers a two-stage failure resistance mechanism that halts crack propagation. As a result, the linear Sty-PFS8 copolymers achieve an exceptional fracture toughness exceeding 13kJ/m². They outperform high-density polyethylene (6 kJ/m²) and natural rubber (10kJ/m²)—while retaining full melt-(re)processability. This combined entanglement-engineering and pendant-crystallization approach offers a design framework for sustainable, high-performance structural materials across various polymer chemistries.

F27: Novel Precursors for Extreme Ultraviolet (EUV) and Beyond-EUV Lithography

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Extreme ultraviolet lithography is a patterning method used in the semiconductor industry to produce feature sizes down to 20 nm. During EUV exposure with 13.5 nm light, high-energy photons generate secondary electrons, causing an electron cascade within the resist film and inducing the solubility switching that forms the pattern. Beyond EUV is a next-generation approach that uses a 6.7 nm wavelength to achieve even smaller feature sizes. One of the key challenges in designing novel resists is ensuring that they are sufficiently EUV or BEUV sensitive. Molecular resists containing elements with high absorption cross-section have been demonstrated to have better lithographic performance than the traditional C, H, O-based polymer resists. A novel class of zinc- and cobalt-based precursors has been designed to combine halides (I and Br), and an organic ligand containing a cross-linking vinyl group that can promote the formation of an insoluble polymer network upon EUV/BEUV exposure. Estimated absorption coefficients suggest these complexes will be promising EUV resist candidates.

F28: Visible-light-curable fluorescent underwater adhesives

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Underwater adhesives with strong interfacial bonding and rapid curing are of significant interest for applications ranging from marine engineering and aquatic infrastructure to biomedical, dental, and underwater robotic technologies. Recently, light-responsive underwater adhesives have attracted considerable attention as they enable rapid and spatially controlled curing with tunable parameters, including wavelength, intensity, and irradiation time. In this study, we developed two classes of visible-light-curable fluorescent polymers based on coumarin. The first polymer incorporates soybean oil and coumarin diol to combine hydrophobic interactions with light-triggered network formation. The second system consists of butyl acrylate and coumarin acrylate random copolymers, allowing the mechanical and adhesive properties to be tuned by composition. Upon visible irradiation at ~ 440 nm, coumarin groups undergo [2+2] photocycloaddition, generating crosslinked networks capable of forming robust adhesive interfaces underwater. Both polymer systems exhibited molecular weights ranging from 10 to 30 kDa, with PDIs between 1.4 and 2.1, and lap shear stresses of approximately 0.13 MPa, forming cohesive networks suitable for underwater applications. Additionally, incorporating fluorescent functionality allowed visualization and monitoring of the adhesive during and after application. These results demonstrate the potential of coumarin-based fluorescent polymers as visible-light-curable underwater adhesives that combine rapid photocrosslinking, cohesive network formation, and robust interfacial adhesion. These multifunctional materials therefore represent a promising platform for the development of next-generation underwater adhesives for marine, biomedical, and other aqueous-environment applications.

Keywords: coumarin-based polymers, underwater adhesives, fluorescent polymers, visible-light curing, interfacial adhesion.

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F29: Molecular Clusters as Models of the Repeating Unit of the LnMnO_3 Lanthanide Manganites with the Perovskite Structure

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The AMnO_3 manganites with the perovskite structure and their doped $\text{A}_{1-x}\text{B}_x\text{MnO}_3$ (A and B are main group or lanthanide metal ions) are extremely important magnetic oxides renowned for their remarkable properties such as ferromagnetism, multiferroicity, and colossal magnetoresistance. DFT calculations on LaMnO_3 have predicted its ground state spin vector configuration to be sensitive to the sign and magnitude of the exchange interactions between Mn^{3+} ions but attempts to demonstrate this experimentally with pressure have been unsuccessful. Previous studies in our group led to the $[\text{Ce}_3\text{Mn}_8\text{O}_8(\text{PhCO}_2)_{18}(\text{PhCO}_2\text{H})_2]$ molecular cluster,¹ which is the repeating unit of the manganite perovskite structure plus two additional Ce^{3+} ions, and shown that “chemical pressure” from bulkier substituted-benzoate ligands can change the ground state as predicted by DFT for the bulk solids. Building on this success, we have more recently targeted variation of the lanthanide ions in this perovskite structures and have successfully synthesized Gd_3Mn_8 , Nd_3Mn_8 , Pr_3Mn_8 , and Ce-doped derivatives of general formula $[\text{Ln}_3\text{Mn}_8\text{O}_8(\text{RCO}_2)_{18}(\text{RCO}_2\text{H})(\text{MeCN})]$. We shall give an overview of this work, including syntheses, crystal structures, magnetic studies, and EPR analyses.

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F30: Effect of Barium Titanate particle size on the rheology of BaTiO₃-PVDF composites inks

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Advances in Additive Manufacturing (AM), specifically Direct Ink Writing (DIW), offer the potential to fabricate functional devices, such as electrical circuit components, with complex geometries and tunable architectures. In this process, viscoelastic ink is extruded through a deposition nozzle in a sequential, layer-by-layer pattern to construct scaffolds and various 3D shapes. Barium titanate (BaTiO₃), an important ferroelectric material, combines several remarkable properties within a single system: a high dielectric constant ($\epsilon \approx 1500$), and piezoelectric activity. Polyvinylidene fluoride (PVDF) is a polymer widely recognized for its excellent piezoelectric properties, thermal stability, and mechanical strength, while also exhibiting remarkable physical properties such as a high dielectric constant, chemical resistance, UV resistance, nuclear radiation resistance, and weatherability. The combination of PVDF and BaTiO₃ has therefore emerged as a promising route for the development of lightweight, flexible, and printable dielectric systems for capacitors, electronics, energy storage devices, and spacecraft engineering. Despite the large number of studies involving PVDF/BaTiO₃ composites, most investigations remain focused primarily on increasing dielectric permittivity through the modification of ceramic filler concentration, surface functionalization, or morphological alterations. For this reason, it is crucial to study the relationship between the barium titanate particle size and the molecular weight of the PVDF to identify the optimal formulation that ensures reliable printability. This study presents the rheological results of changing BaTiO₃ particle size and concentration, using 200 nm and 500 nm BaTiO₃ nanoparticles, at four targeted weight percentages; 50 wt%, 57 wt%, 67 wt%, and 77 wt%, which correspond to volume fractions (ϕ) of 0.14, 0.18, 0.25, and 0.35, respectively. Trends such as shear-thinning and a higher storage modulus (G') than loss modulus (G'') are observed across all inks. The 200 nm particles exhibited a higher elastic modulus and yield stress, with the 77 wt% sample for 200 nm having a modulus of 1.18×10^7 Pa (three orders of magnitude) and a yield stress two orders higher than 50 wt%. Rheological data is then correlated with printing experiments to determine the optimal window of the rheological parameters required for direct ink writing.

Keywords: Rheology. Additive Manufacturing. Direct Ink Writing. Barium titanate. Polyvinylidene fluoride.

F31: HIV Therapy: Synthetic and Computational analysis of Ring-modified Efavirenz analogs

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Acquired immunodeficiency syndrome (AIDS) is a disease caused by the human immunodeficiency virus (HIV), which affects individuals worldwide. Effective therapy for the treatment of HIV-1 infection requires a combination of antiviral drugs. One common therapy is the drug, Efavirenz (EFV), a non-nucleoside reverse transcriptase inhibitor (NNRTI) that binds to allosteric sites on reverse transcriptase, resulting in the inhibition of DNA synthesis. Although EFV has demonstrated efficacy in reducing viral load, cases of drug resistance and adverse side effects have motivated the development of modified analogs. While dolutegravir-based regimens are widely used, EFV remains clinically relevant in many developing countries. Cyclopropylacetylene (CA) is a key intermediate in the synthesis of EFV; however, CA is prone to ring strain-induced instability. To address this limitation, alternative ring-containing side chains, including cyclohexylacetylene and the compact bicyclo[1.1.0]butane motif, were explored as replacements.

esium bases present themselves as potential alternatives to *n*-butyllithium, enabling controlled access to conformationally constrained ring systems with improved chemical stability. These modifications aim to improve synthetic efficiency and cost-effectiveness, which is critical for the development of therapeutics accessible to low-resource communities. Computational docking and structure-based analyses were employed to evaluate the binding interactions of cyclohexylacetylene and bicyclo[1.1.0]butane–analogs within the reverse transcriptase NNRTI binding pocket. Computational results were used to assess binding orientation and predicted inhibitory activity relative to EFV. Together, this synthetic and computational approach aims to identify structurally accessible EFV analogs that retain antiviral activity while enhancing chemical stability, improving synthetic feasibility, and develop more affordable treatment options.

F32: Post-Synthetic Trigger Installation Facilitates Efficient PMMA Depolymerization

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This work reports an efficient closed-loop bulk depolymerization method applicable to commercially available PMMA. Acid hydrolysis (<10%) and subsequent esterification with *N*-hydroxyphthalimide are used to incorporate a thermally sensitive trigger that allows efficient depolymerization of PMMA at a temperature lower than conventionally employed. We showed that this strategy is applicable to model PMMA homopolymers with molecular weights ranging from 28 to 1140 kg/mol. The same method was used for efficient bulk depolymerization (~70%) of commercially available PMMA ($M_n = 439$ kg/mol), supporting the efficacy of this work for practical applications. Furthermore, we demonstrate that this method can be leveraged to generate depolymerizable polymer networks. The depolymerization approach reported here holds potential to mitigate polymethacrylate waste and maintain a sustainable polymer economy.

F33: Point-of-Care Electrochemical Sensing of Microplastic

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The rapid expansion of plastic waste breakdown into micro/nano-plastics (M/N-Ps) poses significant environmental and bioaccumulative health risks, requiring sensitive detection platforms to replace costly, complex analytical methods. Here, we present a point-of-care (PoC) electrochemical sensor utilizing molecularly imprinted polymers (MIP) for the sensitive detection of polystyrene (PS) nanoparticles (nPS). Screen-printed carbon electrodes (SPCE) were modified via electro-polymerization of poly-o-phenylenediamine (PoPD) around 100 nm and 500 nm nPS templates. Target template elution was carried out using a 50/50 methanol and deionized (DI) water solution for 30 min to generate selective imprinted recognition cavities. Following a 10 min analyte incubation and DI water rinse, sensor performance was evaluated using cyclic voltammetry (CV), differential pulse voltammetry (DPV), and chronoamperometry (CA) interfaced with portable potentiostats. The MIP@PoPD@SPCE sensor demonstrated rapid detection within 15 min, exhibiting a linear dynamic range from to across both 100 nm and 500 nm particle sizes. Furthermore, the platform achieved an ultra-low limit of detection (LOD) down to 4 parts per billion (ppb). This MIP-assisted electrochemical sensing strategy provides a scalable, affordable, and portable alternative for point-of-need environmental surveillance of microplastics, with ongoing work directed toward selectivity testing in complex real-world matrices.

F34: *In-situ* analyses of Crystallization kinetics and Stress Relaxation in 3D Printed Polymer Nanocomposites

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Polymer nanocomposites (PNCs) have received significant attention due to their enhanced material properties compared to neat polymers, making them indispensable in numerous industrial applications. The interactions between structure and properties in PNCs, particularly during non-equilibrium processing, are crucial for optimizing their performance in advanced manufacturing techniques such as 3D printing. Fused filament fabrication (FFF) is an emerging fabrication method for prototyping, tooling, and fabrication of unique parts in fields such as aerospace, robotics, and biomedical applications. While FFF offers several advantages over traditional manufacturing techniques, its potential for large-scale production is limited by structural imperfections. These imperfections, including residual stresses within printed parts, can result in issues like warping and layer delamination, ultimately reducing the mechanical performance of the final product. The objective of this study is to obtain a more complete understanding of the processes involved in the structure formation during FFF of polymer composites by combining time-resolved WAXS, which is sensitive to ordered structures on Angstrom length scales, with time-resolved coherent small angle scattering (c-SAXS), which provides information about structural processes on nano- to micrometer length scales. Understanding these unique elements is essential for analyzing the effects of individual processing steps on the final structures, properties, and performance of the materials. Isotactic polypropylene (iPP) was selected as a model material for this work due to its semicrystalline nature, which enables effective monitoring of structural evolution, along with its strong mechanical properties and excellent resistance to moisture, heat, and chemicals. Additionally, iPP-based composites have been widely used in high-performance applications. Specifically, this work focuses on a model system of monodisperse spherical silica nanoparticles (Si-NPs) dispersed within an iPP matrix. The NPs were synthesized by the Stober method and surface functionalized to facilitate dispersion in the iPP matrix. A twin-screw extruder was used to fabricate filaments with a diameter of 1.75 mm for 3D printing using commercial FFF printheads. Si-NPs with sizes of approximately 40 nm were incorporated to create different loadings, ranging from 0.5% to 5% by volume. The impact of shear profiles, influenced by nozzle sizes and print speeds, and temperature profiles, determined by the gradient of printbed and nozzle temperatures, on the crystallization of the extruded filaments were systematically examined. Structure formation during the 3D printing process is largely determined by spatially heterogeneous shear and temperature profiles, along with external stimuli. Spatially resolved measurements with micrometer-sized X-ray beams allow for the investigation of spatial heterogeneities, such as high-shear regions near the top surface or at filament interfaces. Preliminary results reveal the presence of the iPP β -phase in the polymer composite matrix, primarily influenced by shear, with its formation depending on the shear profiles applied. In addition to time- and spatially resolved crystallization kinetics, simultaneous time-resolved coherent X-ray scattering (c-SAXS/XPCS) permits following structural relaxation processes, driven by residual stresses, even minutes after the molecular structure (as probed by WAXS) became static. Combining the results from simultaneous, time-resolved WAXS and c-SAXS enables the creation of scattering-based 'imaging' of the extruded filaments in terms of structure and mesoscale dynamics. This study demonstrates how combining different X-ray scattering techniques within the same in-situ experiment provides a more comprehensive understanding of the various processes that determine the structure-property

relationships and their dependence on material and processing parameters in polymer FFF.

Keywords: Isotactic Polypropylene (iPP), Polymer Nanocomposites (PNCs), Silica, 3D Printing, Structure–Property relations, time-resolved coherent X-ray scattering, X-ray photon correlation spectroscopy.

F35: Family of Iron-Oxo ‘Molecular Nanoparticles’ Related to γ -Fe₂O₃: Structural Characterization and Magnetic Properties

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University of Florida

Nanosized magnetic iron oxides have attracted significant research interest because of their high Curie temperatures, chemical stability, low toxicity, superparamagnetic behavior, and biocompatibility.¹ These properties make iron oxide nanomaterials important in diverse fields, including biomedicine², magnetism, catalysis³, and materials science. Their properties strongly depend on particle size and size distribution, which influence their structural, chemical, and magnetic characteristics. From a nanoscience perspective, molecular iron/oxo clusters with the γ -Fe₂O₃ structure and dimensions in the 1-3 nm range can be considered “molecular nanoparticles”, bridging the molecular and nanoparticle regimes.

Although numerous Fe/oxo clusters and iron oxide nanoparticles have been reported, atomically precise molecular species that possess the structural features of γ -Fe₂O₃ remain largely unexplored. This study focuses on developing synthetic approaches to atomically precise iron oxide ‘molecular nanoparticles’ that possess the same structure as bulk γ -Fe₂O₃, together with their detailed structural and magnetic characterization. Three large iron-oxo molecular clusters have been synthesized through a molecular bottom-up approach using Fe³⁺ salts in combination with Nd³⁺, Ho³⁺, or Y³⁺ salts. Incorporation of different lanthanide or yttrium ions into the Fe/oxo framework results in distinct magnetic properties, demonstrating the important influence of metal composition on overall magnetic behavior. These molecular clusters provide atomically precise models for investigating structure-property relationships of γ -Fe₂O₃ nanoparticles and their potential single-molecule magnet behavior.

F36: Effect of chain length on the thermodynamic behavior of hydrocarbons confined within nanopores.

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ZIF-8 is a nanoporous material that belongs to a class of materials known as metal–organic frameworks (MOFs). Nanoporous materials have a wide range of industrial applications, including gas separation, water purification, emissions control, and hydrocarbon recovery. ZIF-8 acts as a nanoscale porous structure whose pore environment can be tailored for the capture and confinement of selected molecules. In this research, ZIF-8 is used as a model nanoporous material to study the thermodynamic properties of confined hydrocarbons. ZIF-8 is synthesized through two routes: a room-temperature method using methanol as the solvent and a solvothermal method using DMF. X-ray diffraction (XRD) will be used to confirm successful synthesis, while N₂ adsorption–desorption measurements and BET analysis will be used to determine surface area, pore volume, and pore-size distribution. Differential scanning calorimetry (DSC) will then be used to investigate how molecular structure and chain length influence the thermodynamic behavior of hydrocarbons confined within nanopores.

F37: 30-Minute Materials: A Green Route to Sulfonium-Based Metal Halide Semiconductors

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Metal halide semiconductors (MHS) offer tunable electronic and optical properties; however, their environmental instability is a hindrance to their use in many practical applications. Here, we showcase an efficient and rapid synthetic route, via microwave-assisted synthesis, to grow a two-dimensional lead bromide MHS with benzyl dimethyl sulfonium (BDMS⁺), a relatively unexplored class of counter-cation. The synthesis of the BDMS⁺ and the hybrid material is entirely achieved by microwave heating in under 30 minutes, showcasing a rapid and greener approach to accessing these materials. Notably, the addition of the sulfonium cations yields materials with remarkable water stability while maintaining favorable optical properties. Moreover, electrochemical measurements further reveal redox-active behavior and hydrogen generation through water splitting. This work demonstrates how microwave-assisted synthesis and counter-cation engineering can be leveraged to efficiently design and generate water-stable MHS for emerging photo- and electrochemical applications.

F38: Tandem Upcycling Drives Rapid and Near-Quantitative Depolymerization of RAFT-Derived PMMA

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This work reports a one-pot tandem strategy in which the depolymerization of RAFT-derived PMMA is coupled with irreversible consumption of the regenerated monomer, extending conversion well beyond the thermal limit while delivering a value-added aromatic product. Liberated methyl methacrylate is rapidly intercepted in situ by 2,5-dimethylfuran through a BBr₃-promoted Diels–Alder aromatization sequence, affording 1,2,4-trimethylbenzene without the need to isolate the monomer. We showed that this strategy results in near-quantitative depolymerization with kinetic analysis across a series of controls establishing that the enhancement arises from the irreversibility of the trapping step rather than from cycloaddition alone. The same method afforded ~ 58% depolymerization at 500 mM RUC, a concentration at which thermal RAFT depolymerization alone is inefficient, thereby supporting the efficacy of this work at practical loadings. The tandem approach reported here establishes monomer fate, rather than chain-end chemistry, as a lever for depolymerization that complements existing activation strategies and remains effective at concentrations where those strategies become inefficient.

F39: Long-Range Magnetic Exchange Coupling in Ce/Mn-oxo Clusters

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Bulk Ce/Mn oxides have attracted significant interest because of the redox, electronic and magnetic properties of Ce and Mn, leading to a wide range of applications including catalysis and environmental remediation. Ce/Mn-oxo molecular clusters have also shown interesting magnetic properties, such as unusual structural topologies, similarity to the repeating unit of the LnMnO_3 manganites with the perovskite structure, single-molecule magnetism and even unusual long-range ferromagnetic interactions. Various synthetic procedures have been developed over the years by our group and others to synthesize Ce/Mn clusters with a wide range of nuclearities and Ce-to-Mn ratios, including comproportionation, oxidation of Mn^{II} by Ce^{IV} , and reductive aggregation procedures. In this presentation we will describe the synthesis and structures of some new Ce/Mn clusters recently prepared using comproportionation procedures. Their structures suggested long-range exchange couplings might be present, and we shall describe the results of a detailed analysis of this possibility.

F40: pH-responsive copolymer micelles for targeted endosomal release and enhanced antiviral efficacy of Ribavirin against Zika virus

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Zika virus (ZIKV) presents a severe global health threat due to its vertical transmission risk and neurological complications, yet no targeted antivirals exist. The broad-spectrum analog ribavirin is potent but limited by dose-dependent toxicity and poor systemic bioavailability. Because ZIKV utilizes receptor-mediated endocytosis for cell entry, targeting the acidic endosomal environment offers a precise pathway for localized drug delivery. This study evaluated two biocompatible nanocarriers: an ABA triblock polymer (mPEG-PCL-mPEG) and an AB diblock polymer (mPEG-PCL). Synthesized via ring-opening polymerization of ϵ -caprolactone and validated by FTIR/¹H NMR, both systems self-assembled into micellar nanoparticles (MNPs). Ribavirin was encapsulated via sonication through hydrophilic interfacial interactions. Triblock MNPs exhibited a mean diameter of 63.4 nm with 62.3% encapsulation efficiency (EE), while diblock MNPs measured 34.9 nm with 87.1% EE. Both maintained a near-neutral surface charge (−3.3 to −3.7 mV) to evade immune clearance. In vitro profiles showed accelerated, pH-dependent release under simulated endosomal conditions (~88% at pH 5.5 vs. ~20% at pH 7.4). In ZIKV-infected choriocarcinoma (JEG-3) cells, MNPs dramatically enhanced antiviral potency, shifting the effective dose from micromolar to nanomolar thresholds. Triblock and diblock formulations achieved half-maximal effective concentrations (EC_{50}) of 0.15 nM and 0.20 nM, respectively, reducing the required drug volume by up to 90%. Consequently, targeted delivery eliminated severe cytotoxicity, preserving 80% to 95% host cell viability. Intracellular uptake and complete viral suppression were confirmed via laser scanning confocal microscopy and the absence of detectable vRNA through RT-qPCR. Exploiting endosomal acidification pathways with biodegradable copolymer matrices significantly expands the therapeutic index of hydrophilic antivirals. These platforms offer a scalable, highly efficient nanomedicine framework to combat emerging viral pathogens.

F41: The Oxygen-Evolving Complex (OEC) of Photosystem II: Strontium-based Synthetic Analogues

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The oxygen-evolving complex (OEC) of Photosystem II is a Mn_4CaO_5 cluster found in the thylakoid membranes of photosynthetic organisms such as plants, algae, and cyanobacteria. The OEC catalyzes the light-induced oxidation of water to molecular oxygen and protons, providing the electrons needed for the photosynthetic electron transport chain [1,2]. Researchers have long been interested in developing synthetic analogues of the OEC to study the spectroscopic, magnetic, and catalytic properties that are difficult to characterize within the native protein environment. Although the exact role of Ca^{2+} within the complex is not fully understood, it has been found to be necessary for oxygen-evolution. In Ca^{2+} -substituted cell cultures, Sr^{2+} was the only metal found to retain oxygen evolution activity [3]. This retention of functionality creates interest in strontium-based synthetic analogues to investigate how metal substitution influences the properties of the cluster and in turn to provide insight into the role of Ca^{2+} in oxygen evolution. This presentation will describe our progress towards achieving strontium-based analogues of the OEC and their electrochemical, structural, and magnetic properties.

1. Umena, Y., Kawakami, K., Shen, JR., *Nature*, **2011**, 473, 55-60
2. Barber, J., *Philos Trans R Soc Lond B Biol Sci*, **2008**, 363, 2665-2674
3. Koua, F.H.M., Umena, Y., Kawakami, K. *et al.*, *Proc. Natl. Acad. Sci. U.S.A.*, **2013**, 110 (10) 3889-3894

F42: 3D Printed Barium Titanate High Voltage Capacitors

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High Voltage in space travel and exploration is a great workaround, allowing for the use of lighter, narrower cabling to save weight while still providing sufficient power throughout a space craft. Other uses for high voltage include: the regulation of power for electrically propelled spacecraft, heightened performance in various detectors, and the movement of power over long distances like transmission cables used on earth. To regulate power systems at high voltages, capacitors are a useful tool. Capacitors can also be used as an alternative power source to batteries. 3D printing high voltage capacitors can serve as a means of expediting spacecraft manufacturing and testing. For high voltage, printed capacitors need to utilize a high dielectric constant (ϵ_r) material in order to perform within the dictated capacitance of 100 pF to 1000 pF and operate at voltages higher than 200 V. Barium titanate (BaTiO_3) is promising material with a potential ϵ_r greater than 10000. Direct ink write (DIW) syringe printing using proprietary barium titanate ink, capacitors were manufactured and tested. A basic, parallel plate design achieved a capacitance of ~300 pF. After partial discharge (PD) testing of the manufactured capacitors, PDs were conceived at 750 V – hence the parallel plate capacitor could be rated for ~500 V (70% of PD conception voltage). Further evaluation determined that the ϵ_r was around 30 for the parallel plate design using the commercial ink, meaning that the ink was perceived to have low concentrations of barium titanate. Future studies will improve upon the current ink and explore custom ink formulation to further improve electrical properties and printability. Coupled with laser post-processing, the goal is to optimize the manufacturing process for on-demand high voltage capacitors.

F43: MIP-Assisted Electrochemical Sensing of L-thyroxine (T4) for Thyroid Diagnostics

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Florida Polytechnic University

Monitoring L-thyroxine (T4) levels is critical for managing hypothyroidism, a condition affecting millions of individuals annually. Traditional monitoring relies on ELISA-based (Enzyme-Linked Immunosorbent Assay) blood serum assays, which are highly accurate but unsuitable for rapid point-of-care (POC) testing. To address this limitation, this work demonstrates a molecularly imprinted polymer (MIP)-assisted electrochemical sensor designed for non-invasive, rapid, and selective detection of T4 at concentrations relevant to human saliva.

The sensor was fabricated by electropolymerizing *o*-phenylenediamine (oPD) monomer onto a screen-printed carbon electrode (SPCE) in the presence of T4. After template elution, the sensor was characterized and tested across real-world concentration ranges using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) on a multi-channel potentiostat platform.

The developed sensor achieved reliable, parts-per-billion (ppb) level detection of T4 within 15 minutes of exposure. Calibration plots showed a strong linear relationship between peak amperage and the logarithm of T4 concentration.

These results confirm the successful application of MIP-based electrochemical sensing for T4 diagnostics. Future efforts will focus on evaluating sensor performance in human saliva samples, integrating reduced graphene oxide nanoparticles to enhance sensitivity, and adapting the platform for smartphone-based potentiostat systems to enable field-deployable POC applications.

F44: Effects of Preceramic Polymer Chemistry on Crosslinking, Ceramic Yield, and PIP Densification of Binder Jetted ZrB₂ UHTCs

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Polymer infiltration and pyrolysis (PIP) is an effective post-processing method for densifying porous ultra-high-temperature ceramic (UHTC) components with complex geometries. However, uncontrolled preceramic polymer flow, early mass loss, and shrinkage during heat treatment reduce precursor retention, limit densification efficiency, and increase the number of PIP cycles required. To address this issue, this study compares three preceramic polymer chemistries: polycarbosilane (SMP-10), polycarbosilazane, and polycarbosiloxane, each mixed with 5 wt% crosslinker. TGA analysis demonstrated that the addition of a crosslinker cured at room temperature for about 12 hr substantially reduced precursor mass loss at 250 °C, decreasing from 20.23% to ~2% for SMP-10, 11.67% to 4.5% for polycarbosilazane, and 28% to 4.5% for polycarbosiloxane. Final char yield also improved, with polycarbosilazane reaching the highest yield of 90.87%, followed by SMP-10 at 86.54% and polycarbosiloxane at 85.73%. FTIR confirmed crosslinking through changes in reactive C=C and Si-H groups, with additional N-H changes for polycarbosilazane. Following pyrolysis at 1600 °C, XRD revealed crystalline β-SiC from SMP-10, amorphous SiCN-based ceramic with Si₃N₄- and SiC-related phases from polycarbosilazane, and amorphous SiOC-based ceramic with SiC from polycarbosiloxane. These differences in precursor stabilization and ceramic conversion influenced subsequent densification. After five PIP cycles, relative density increased to 79.97% for polycarbosilazane, compared with 74.64% for SMP-10 and 74.97% for polycarbosiloxane, demonstrating the superior effectiveness of polycarbosilazane for crosslinker-assisted PIP densification of binder-jetted ZrB₂ UHTCs.

F45: Distinguishable Molecular Spin Qubits in Asymmetric Meso-Substituted Metalloporphyrins

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Recent research in our group has included the synthesis and study of covalently-linked oligomers of metal-oxo clusters that exhibit magnetic and quantum properties that make them potential spin-based molecular components of new 21st century technologies such as spintronics and quantum information systems of various types. In previous work, a family of covalently-linked cofacial bis-metalloporphyrin complexes were synthesized that are structurally rigid and allow variation of the metal ions incorporated. In the present work, we have targeted covalent linkage of two paramagnetic metal ions in differing environments as a potential 2-qubit system. This presentation shall describe the organic synthesis of the targeted porphyrins and the preparation of representative metalloporphyrin derivatives, as well as their DFT computational results, magnetic properties, and electron paramagnetic resonance spectral studies.

F46: Collagen Inspired Trivalent Crosslinking of Epoxy Functional Methacrylate Copolymers for Tough Polymer Networks

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Crosslinked polymer networks offer dimensional stability and mechanical strength but often exhibit limited toughness and energy dispersion capacity¹. Collagen addresses this trade-off through trivalent crosslinks containing one weaker sacrificial arm. Under stress, this arm can break preferentially and disperse energy, while the two remaining arms preserve network connectivity, stability, and durability². Inspired by this mechanism, mechanically responsive tricarboxylic acids are investigated as crosslinkers for epoxy-functional polymer networks³.

Here, poly(2-ethylhexyl methacrylate-co-glycidyl methacrylate), poly(EHMA-co-GMA), is reacted with cyclobutane containing acid acting as crosslinker. Preliminary mechanical testing indicated toughening without losing stiffness. Additionally, we envision that our easily synthesized cyclobutane mechanophore crosslinker can be readily integrated to enhance mechanical properties of commercial polymers such as epoxidized natural rubber, thereby extending use life for sustainability efforts.

F47: Aerosol-assisted CVD of NbN using novel niobium imido single-source precursors

Hao-Hung Chen, Narender Kumar, Tatsuya Kasai, Lisa McElwee-White

University of Florida

Niobium nitride (NbN) is an important material due to its potential to act as a diffusion barrier for copper in microelectronics. However, achieving high-quality NbN thin films with precise stoichiometry and conformal coverage remains a persistent challenge. Here, we report a new class of thermally robust niobium imido single-source precursors designed for low-temperature aerosol-assisted chemical vapor deposition (AACVD). The strong Nb–N imido bond enables incorporation of nitrogen into the films. The precursors were fully characterized by multinuclear NMR spectroscopy and single-crystal X-ray diffraction, and their thermal stability was evaluated using thermogravimetric analysis, confirming their structural integrity and favorable thermal decomposition pathway. Preliminary AACVD experiments demonstrate efficient precursor transport and the formation of NbN thin films, which were analyzed using SEM and XRD.

F48: Oxidation-Induced Chemical Interface Damping in Au–Ag Alloy Nanoparticles for Plasmon-Assisted Photocatalysis

Ashfia Tasnim, Stephen A. Lee

University of Miami

Gold–silver (Au–Ag) alloy nanoparticles are promising plasmonic materials for photocatalysis because they combine the strong plasmonic response of Ag with the chemical stability of Au. Despite their widespread use, the role of native metal-oxide formation as a charge acceptor to extend the hot carrier lifetime and the influence of alloy composition on this process remain poorly understood. Here, we investigate the spectroscopic evolution of individual Au–Ag alloy nanoparticles with varying alloy compositions during ambient aging using correlated single-particle spectroscopy, complemented by electron microscopy.

Oxide formation progressively modifies the plasmonic response of the nanoparticles, producing resonance-energy shifts and linewidth broadening characteristic of increased plasmon damping, a phenomenon known as chemical interface damping (CID). These effects are most pronounced in Ag-rich nanoparticles and decrease systematically with increasing Au content, demonstrating that alloy composition regulates the extent of native oxide formation and the resulting CID. Controlled oxidation experiments further establish oxide formation as the origin of the observed spectroscopic evolution, while structural characterization confirms that increasing Au concentration suppresses oxidation-induced surface modification.

This work identifies oxide formation as an intrinsic mechanism governing CID in Au–Ag alloy nanoparticles and demonstrates that alloy composition provides an effective means to control this process. These findings offer fundamental insight into the relationship between oxidation and plasmon damping and establish practical design principles for developing stable Au–Ag nanostructures for plasmon-assisted photocatalytic applications.

F49: Hg(II) Liquid-Liquid Extraction into Dichloromethane by a Simple Nitropyrazole

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Mercury is a naturally occurring toxic post-transition metal that presents a global environmental and public health concern and is tracked by the Environmental Protection Agency (EPA) in its Toxic Release Inventory (TRI) as a chemical of special concern. Mercury and its compounds are considered persistent, bioaccumulative, and toxic, which emphasizes the importance of Hg remediation efforts, especially at Hg waste sites, where concentrated Hg waste may leach into the environment. Pyrazoles (pz) are versatile soft-donor ligands with a high affinity for Hg(II), which may be tuned via addition of substituents at the 3-, 4-, and 5- ring positions. They have been used for extraction and adsorption of divalent metals, including Cd(II), Hg(II), and Pb(II), and immobilized on polysiloxane, used as macrocyclic chelators, and as tripodal extractants. However, there is scant literature where simpler pyrazole ligands are used for liquid-liquid extraction of Hg(II). Rapid formation of mono- and polynuclear Hg(II)-pyrazolato complexes in those cases often results in precipitation which prevents the recovery of Hg. Herein we report complexation and liquid-liquid extraction of Hg(II) from water into dichloromethane with 3,5-dimethyl-4-nitropyrazole in near quantitative efficiency after a single loading/stripping cycle due to what is likely the formation of a uniquely soluble 2:3 Hg(II):pz complex. We are also reporting the X-ray crystal structures of $[(\text{Hg}_2\text{Cl}_2(\mu\text{-}3,5\text{-Me}_2\text{-}4\text{-NO}_2\text{pz})_3)(\text{Et}_3\text{NH})]$ and $[\text{Hg}(\mu\text{-Cl})(\mu\text{-}3,5\text{-Me}_2\text{-}4\text{-NO}_2\text{pz})]_n$.

F50: Optimization of Polysulfone-based Adsorptive Membranes for Heavy Metal Ion Removal from Water

Brandee Jones, Redemption Edegbe, Annabelle Li, Shukun Zhong, William A. Phillip
Florida A&M University, University of Notre Dame

Access to clean and safe water is paramount as the global population increases. However, industrial and agricultural runoff introduce heavy metals into water sources. Adsorptive membranes have been investigated as a potential water treatment method to remove these ions from drinking water. Compared to traditional separation methods such as nanofiltration and packed beds, absorptive membranes offer low energy requirements, high permeability, and high selectivity advantages. This study explores the impact of fabrication conditions on membrane structure and heavy metal ion removal. Membrane fabrication occurs via surface-segregation and vapor-induced phase separation (SVIPS), and utilizes the interaction of the polymer, solvent, and non-solvent. Polysulfone (PSF) and polystyrene-*b*-poly(acrylic acid) (PS/PAA) are dissolved in 2-pyrrolidone (2P), the solution is cast on a glass substrate, and humid air intrudes into the membrane. The intrusion stage leads to the formation of the membrane's porous structure and facilitates water flow across the membrane. The membrane is placed in a DI water bath to vitrify. The fabrication conditions, such as polymer concentration, casting time, humidity, and annealing, can influence the nanostructure, throughput, and adsorption efficiency of the membranes. Scanning electron microscopy (SEM) and hydraulic permeability testing are used to characterize membranes. The membrane's copper adsorption capacity is measured using ICP-OES. Preliminary results show that either annealing the membrane or increasing the PS/PAA concentration decreases permeability. These modifications to the casting process present an opportunity to optimize the performance of polysulfone-based membranes based on target contaminants and functionalized ligands such as terpyridine (TeRP) and polyethylenimine (PEI).

F51: Lipophilic o-(Sulfonamido)phenol ligands as f-element extractants for combined Cs and actinide separations in High-Level Waste

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Florida International University

During the cold war nuclear weapons development led to generation of large volumes of alkaline High Level Waste (HLW) stored at the Hanford and Savannah River Sites (SRS). Processing of HLW at SRS consists of a two-step process the Actinide Removal Process (ARP) for sorption of Sr-90 and actinides with monosodium titanate sorbent followed by the Next-Generation Caustic Side Solvent Extraction (NG-CSSX) for Cs-137 removal. Improvement to this process could be achieved by the incorporation of actinide chelators that are compatible with NG-CSSX in order to reduce sorbent quantity and contact times resulting in more efficient processing and less secondary waste. Our group has recently identified four lipophilic o-sulfonamidophenols as Ln chelators, due to electron rich O- and N- sites in the deprotonated form of the ligand under alkaline pH. N-(5-(tert-butyl)-2-hydroxyphenyl)-4-(dodecan-3-yl) benzenesulfonamide (**msa6**), N-(5-(tert-butyl)-2-hydroxyphenyl)dodecane-1-sulfonamide (**msa7**), N-(5-(tert-butyl)-2-hydroxyphenyl)-2-ethylhexane-1-sulfonamide (**mm1**), and N-(5-(tert-butyl)-2-hydroxyphenyl)-3-methylbutane-1-sulfonamide (**mm2**) were synthesized and evaluated for extraction and Ln binding by UV-Vis titrations. The ligands exhibited promising extraction performance, maintaining significant Sm(III) recoveries from simulated HLW solutions, as recently reported from our group (*Journal of Radioanalytical and Nuclear Chemistry*, **2026**, 335, 2403-2414). In extension of this work, compounds **msa6** and **msa7** demonstrated up to 30% Sm (III) recovery under modified Next-Generation Caustic-Side Solvent Extraction (NG-CSSX) conditions, while branched analogs **mm1** and **mm2** achieved over 45% recovery of Sm(III) in modified CSSX with major ions including NaNO₃ (2.5 M), Na₂SO₄ (0.2 M), NaNO₂ (2.5 M), NaOH (2.0 M), Na₂CO₃ (0.2 M), KCl (0.02 M), NaCl (0.01 M). UV-Vis titrations with **mm1** and **mm2** showed 1:1 binding with LogK= 5.74 ± 0.08 and LogK= 6.26 ± 0.15 respectively in 96:4 (v/v) CH₃CN:CH₃OH.

F52: Performance analysis of Sr₃SbI₃-based perovskite solar cell using SCAPS-1D software

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2. Prime University

Perovskite solar cells, as a potential renewable energy technology, could improve the efficiency of traditional photovoltaic cells. Their high efficiency and relatively low material and processing costs make them promising alternatives to commercial silicon and other organic and inorganic solar cells. In this research, we investigated inorganic Sr₃SbI₃ as an absorber material for perovskite solar cells using SCAPS-1D software. Strontium antimony iodide (Sr₃SbI₃) holds promise as an absorber material due to its potential for high light absorption and suitable electronic properties. This study utilized abundant and environmentally friendly tungsten trioxide (WO₃) as the electron transport layer to improve device efficiency. Copper antimony sulfide (CuSbS₂) was used as the hole transport material for the Sr₃SbI₃-based perovskite solar cell. To further improve device performance, we investigated the effects of absorber and buffer layer thickness, acceptor density, Sr₃SbI₃ defect density, and interfacial defect densities at the WO₃/Sr₃SbI₃ and Sr₃SbI₃/CuSbS₂ interfaces. We also explored the effects of operating temperature, series resistance, and shunt resistance on the optimized device performance, along with capacitance-voltage, current density-voltage (J-V), and quantum efficiency (QE) characteristics. The optimized Sr₃SbI₃-based solar cell achieved a simulated power conversion efficiency (PCE) of 30.51%, with a Voc of 1.078 V, Jsc of 35.03 mA/cm², and FF of 80.81%. These simulation results demonstrate the potential of Sr₃SbI₃ as an absorber material for high-efficiency perovskite solar cells.

F53: Diglycolyl- and Dipicolino-Sulfonamide Ligands for Ln(III) Complexation and Selective Separation

Yolanda C. Rodriguez, Shadrach J. Waugh, and Konstantinos Kavallieratos*

Florida International University

Lanthanides (Ln), have become vital components of many advanced technologies. Currently, worldwide supply of Ln is highly dependent on PR of China. Due to their strategic importance, and to decrease the need for foreign supply, the US Department of Energy (DOE) has deemed Ln as critical elements and has called for increased efforts into mining from domestic mineral deposits or recovering them from spent technology. However, due to their similar chemical and physical properties, Ln are notoriously difficult to separate. The current practices pose an economic and environmental strain due to the need for various extraction steps and large volumes of toxic eluents.

To aid in this domestic effort, and encouraged by recent success with our *p*-nitrophenol-sulfonamide ligands, which have shown selective Dy(III) separation over Sm(III) and Nd(III), our group is now exploring other ligand frameworks that could be used to efficiently extract and separate these metals, such as diglycolamides and dipicolinamides, which have shown excellent binding and separation of trivalent f-elements. For example, the ligands N,N,N',N'- tetraoctyl-diglycolamide (TODGA) and N,N-diethyl-N,N-ditolyl-dipicolinamide (EtTDPA) have been studied extensively as powerful extractants for Ln(III) and minor actinides from high level nuclear waste solutions. Combining these frameworks with sulfonyl groups is expected to create stronger binding sites of Ln(III) complexation, and potentially introduce unique selectivity for specific Ln. Herein, we have synthesized two new diglycolylsulfonamide ligands (**DGSA-1** and **DGSA-2**) and a new dipicolinosulfonamide ligand (**DPSA-1**) and studied their binding with Ln(III), including Ln separation experiments. UV-Vis spectroscopic titrations of **DGSA-1** (4.0×10^{-4} M) with several Ln(III) have shown formation of ML_2 complexes ($\log \beta_2 = 7.69$ for Nd(**DGSA-1**)₂).

F54: Observing Chloride Concentrations in Southwest Florida Using Ion-Selective Electrodes

Julia Jurca, Tara Buis, Ju Chou

Florida Gulf Coast University

Water is essential for life; thus, understanding, analyzing, and monitoring ion concentrations is essential to ensure the health and safety of both humans and wildlife. Particularly, monitoring chloride concentration in the tropical region of southwest Florida is important due to recent storm surges. This symposium will connect the analytical techniques of ion-selective electrodes (ISE) to the chloride concentrations in local canals and lakes/ivers. Using the voltage measured by the ISE in chloride standard solutions, a calibration curve between the voltage and the logarithm of known chloride concentration was created. This relationship is consistent with the Nernst equation, in which the voltage is linearly proportional to the logarithm of chloride concentration. The analyzed water samples collected from local canals and lakes/ivers were all prepared with a total ionic strength buffer (TISAB) to keep the ionic strength consistent during all voltage measurements, so that their chloride concentrations can be calculated using the chloride calibration curve mentioned above. Chloride concentrations were calculated, and they varied significantly from a few tens of mg/L to nine thousand mg/L. These results were incorporated into a [Google Map List](#), and it was discovered that the chloride concentration was strongly related to hurricane-prone regions. This promotes interdisciplinary discussion of water monitoring and possible hurricane impact on the southwest Florida area.

F55: Integrated Process Optimization of Printed Silver Composite Strain Sensors through Direct Ink Writing and Laser Processing

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Strain sensors are essential devices for monitoring materials and structures that are subjected to dimensional variations due to different forces and mechanical stresses. They are widely used in structural engineering, materials testing, and structural integrity monitoring. In particular, in the aerospace sector, these sensors are extensively used for real-time monitoring of structural fatigue, vibrations, deformations, and localized mechanical stresses, ensuring the integrity of these aircraft, which are often subjected to extreme environmental conditions and variations. Among the numerous technologies employed in these devices, 3D printing, specifically Direct Ink Writing (DIW), has emerged as an effective alternative for manufacturing strain sensors due to its customization capabilities, including the ability to print complex geometries, high precision, and simplicity of production. In this work, a flexible resistive strain sensor based on a Direct Ink Written silver composite ink was developed for enhanced sensitivity and long-term electromechanical stability. The ink formulation incorporated chlorinated polyolefin and ethyl cellulose to improve adhesion, mechanical robustness, and conductive network integrity. The influence of printing parameters, including nozzle diameter, printing temperature, and printing height, was systematically investigated to optimize line morphology and conductive network homogeneity. Following printing, near-infrared laser curing was employed to enable rapid localized curing and controllable conductive network densification. A multifactorial Design of Experiments (DOE) combined with ANOVA and multi-response optimization was used to investigate the effects of laser power (0.4–0.8 W), scanning speed (2.5–7.5 mm s⁻¹), and number of passes (1–5) on electrical resistivity, gauge factor (GF), and calibration curve linearity (R²). Laser power was identified as the dominant parameter controlling electromechanical performance. The electrical resistance of the sensors could be tuned from approximately 180 kΩ to 49 Ω through laser processing, demonstrating the transition from connectivity-limited to post-percolation conductive regimes. Lower laser powers promoted higher sensitivity through percolative and electron tunneling conductive pathways, achieving GF values up to 6.7, while higher powers improved conductive network stability and calibration curve linearity up to R² ≈ 0.99. Multi-response optimization identified the condition of 0.8 W, 7.5 mm s⁻¹, and 5 passes as the best compromise between sensitivity, linearity, and electrical stability. The optimized sensors exhibited signal fluctuations below 5% after 1000 loading–unloading cycles, operational stability for up to 180 days, and the ability to detect strains on the order of 10⁻⁵. These results demonstrate that ink engineering, DIW, and laser processing can serve as complementary tools for tailoring the microstructure, conductive network topology, and piezoresistive behavior of high-performance flexible strain sensors. This represents a promising alternative for the development of more effective, simple and low-cost sensors in additive manufacturing.

Saturday Posters

S1: Rhodium-catalyzed divergent silylation of styrene derivatives using alkoxysilanes

Calla Marco, Yosthinn Cuitiva, and Niroshani S. Abeynayake

Barry University

Hydrosilylation and dehydrogenative silylation are valuable methods for the synthesis of organosilicon compounds from readily available alkenes and silanes. In this study, we investigate the silylation of styrene derivatives with tertiary alkoxysilanes catalyzed by $\text{Rh}_2(\text{OAc})_4$. A key challenge in these transformations is controlling regioselectivity, which governs the site of silyl-group incorporation across the carbon-carbon double bond. We therefore evaluate the ability of $\text{Rh}_2(\text{OAc})_4$ to promote both hydrosilylation and dehydrogenative silylation of aromatic alkenes and examine its catalytic efficiency, product distribution, and regioselectivity. The results provide insight into the reactivity of tertiary alkoxysilanes in rhodium-catalyzed silylation reactions and contribute to the development of selective methods for the preparation of organosilicon compounds.

S2: Exploring the Role of Molecular Chaperones in Carcinogenesis

Angie Ordoñez, Donieliza Munford, Szymon Ciesielski

University of North Florida

Cancer refers to a group of diseases distinguished by the uncontrolled growth of abnormal cells, often driven by an accumulation of genomic mutations that disrupt normal protein function and create cellular stress. A defense mechanism cells employ to cope with this stress is the molecular chaperone network, proteins that help maintain protein stability and proper folding. A category of molecular chaperones relevant to this study is human Hsp70 proteins and their obligatory partners, particularly DNAJB1. While Hsp70 is essential under normal conditions, it is frequently upregulated in cancer cells, where it can inhibit apoptosis and support tumor progression. This project aims to investigate whether DNAJB1 mutations alter its interaction with Hsp70, potentially increasing chaperone activity in ways that help cancer cells survive. Using bioinformatics tools and genomic databases, we identified several DNAJB1 point mutations predicted to affect protein structure and function. We expressed these DNAJB1 variants in *E. coli* and purified them to test their effects on Hsp70 activity through biochemical assays. By studying how cancer-related DNAJB1 mutations affect Hsp70 function, this work aims to provide insight into the role of chaperone systems in cancer biology and inform future therapeutic strategies targeting chaperone pathways.

S3: Designing β -barrel Membrane Protein using Distributed Structure-to-Sequence Adapters.

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Membrane proteins, particularly β -barrel membrane proteins, play essential roles in cellular processes and have growing applications in biotechnology, biosensing, and sequencing technologies. However, de novo design of membrane proteins remains underexplored because current inverse folding models are primarily trained on soluble proteins and have limited exposure to membrane protein structures. The scarcity of experimentally determined membrane protein structures further limits the development of deep learning models for membrane protein design.

In this work, we investigate strategies to retrain ProteinMPNN for membrane protein sequence design by retraining the model on a number of membrane protein datasets consisting of α -helical and β -barrel membrane protein complexes. Model performance is evaluated using blind-test set composing of natural and de-novo backbones, on sequence recovery, hydropathy, and β -sheet propensity, with particular emphasis on β -barrel proteins.

To complement structure-based sequence generation with membrane-specific sequence information, we integrate ProteinMPNN with MemDLM, a protein language model trained on large-scale membrane protein sequence data. We introduce a distributed adapter architecture that injects ProteinMPNN-derived structural embeddings into different layers of MemDLM, enabling backbone information to shape sequence representations throughout the language model. By leveraging structural features and membrane-specific sequence representations, we hypothesize that the model will improve sequence recovery and better reproduce membrane-associated sequences, particularly for β -barrel proteins. More broadly, this framework provides a general strategy for combining inverse-folding models with domain-specific protein language models for de novo membrane protein design. At the end, we will test these new models on our blind test set to determine its accuracy, hydropathy and β -sheet propensity.

S4: Tuning polymer nanoparticle morphologies via photochemical decarboxylation

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Polymerization-induced self-assembly (PISA) is a versatile synthetic strategy for the facile generation uniform polymer nanoparticles with high yield. Conventional PISA chain-extends a solvophilic macro chain transfer agent (mCTA) with a solvophobic block, inducing solubility-driven self-assembly and morphological transition. The final morphology is determined by the ratio between the two blocks, known as the packing parameter P , and is observed to retain its structure after polymerization.

Herein, we separate the morphology transformation step from the polymerization through solvophilic block cleavage. Previous work has shown that incorporating N-(methacryloyloxy)phthalimide (PhthMA) monomers allows polymers to undergo photocatalytic degradation. By tuning the amount of PhthMA within the solvophilic block, we show that different final morphologies can be targeted. This strategy affords a new possibility for nanomaterial processing, as different morphologies impart different properties to the solution and particles.

S5: Synthesis of Peptoid-based Inhibitors of Protein Arginine Methyl Transferases (PRMTs) for Application in the Treatment of Cancer

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Protein arginine methyl transferases (PRMTs) are a family of enzymes that catalyze the transfer of methyl groups from S-adenosylmethionine (SAM) to the guanidinium nitrogens arginine residues within protein substrates. These methylation events can yield mono-methylarginine (MMA), symmetric dimethylarginine (SDMA), or asymmetric dimethylarginine (ADMA) residues. Histone proteins are well known substrates for PRMTs, and their post-translational methylation can act as signaling events that affect gene transcription. Evidence suggests that dysregulated activity of these enzymes may have deleterious effects that result in cancer etiology. Peptoids are a class of peptide mimics that differ structurally by a shift of the sidechain from the alpha-carbon to the nitrogen of the amide bond. These structures maintain the functional diversity of the peptide side chains, along with the polyamide backbone, but are less susceptible to hydrolytic degradation by peptidases/proteases and should therefore have longer *in vivo* utility. Herein, we describe the synthesis of a peptoid-based inhibitor that is designed to target PRMTs and study the potential as a cancer therapeutic.

S6: Yeast *S. cerevisiae* as a model to study human molecular chaperones *in vivo*

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Molecular chaperones are critical for maintaining cellular homeostasis by facilitating proper protein folding. Interruptions to this process can lead to protein misfolding and cytotoxic aggregation. Furthermore, specific types of protein aggregates, such as amyloid-like fibrils, have been associated with human neurodegenerative disorders. This includes amyloid- β , tau, and α -synuclein proteins associated with Alzheimer's and Parkinson's diseases, respectively. The molecular chaperone system composed of Hsp70 and its obligatory co-chaperone, a J-domain protein (JDP), can target and fragment amyloid-like fibrils. However, its underlying mechanism is not well understood. Our recent *in vitro* results suggest that a specific short helical region present in class B JDPs may be a key mechanistic element that enables Hsp70 to fragment amyloid-like fibrils. This project focuses on investigating the importance of this helical region in the human JDP DNAJB1 for its co-chaperone function. Following *in vitro* investigation of purified components using structural and functional methods, we utilized baker's yeast, *Saccharomyces cerevisiae*, to perform *in vivo* studies. We took advantage of previous results revealing that human chaperone proteins can functionally substitute for their yeast counterparts and tested the ability of different DNAJB1 variants to maintain yeast cell viability. We verified the biological relevance of the introduced alterations in human proteins for their chaperone activity. This approach revealed that the helical region, together with selected conserved amino acids, is necessary for DNAJB1 activity and functional cooperation with Hsp70. These results significantly enhance our understanding of Hsp70/JDP activity and highlight the yeast model as an effective approach for investigating the biological activity of human proteins.

S7: Catalyst Development for Enantioselective Ritter-Type Amidation of Benzylic Alcohols

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Amide substructures are highly prevalent in pharmaceuticals and bioactive molecules, yet the enantioselective introduction of amides bearing α -chiral centers remains challenging because of the difficulty of stereochemistry control. We aim to develop a metal-free, enantioselective Ritter-type amidation that converts racemic benzylic alcohols directly into α -chiral amides using simple nitrile and amide feedstocks. The strategy employs chiral phosphoric acid (CPA) catalysts to promote alcohol activation and stabilize carbocation intermediates through cation- π interactions, providing a potentially milder and more sustainable alternative to conventional amide-coupling and transition-metal-catalyzed C–H amination methods.

S8: Stimulation of Hsp70 ATPase activity by tardigrade DNAJB1

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Tardigrades survive extreme environmental stress by entering a state of cryptobiosis, during which gel-like structures form within their cells. Molecular chaperones such as Hsp70 and its co-chaperones, J-domain proteins (JDPs), play important roles in cellular stress responses. However, although these chaperone systems are well characterized in humans, their functions in tardigrades remain poorly understood. The purpose of this study is to evaluate a candidate tardigrade DNAJB1 homolog by examining its ability to stimulate Hsp70 ATPase activity. A defining feature of JDPs is the J-domain, which contains a highly conserved His-Pro-Asp (HPD) motif that is essential for stimulating Hsp70 ATP hydrolysis. To determine whether this conserved function is present in the candidate tardigrade DNAJB1 homolog, we generated a variant with an alteration in the HPD motif. ATPase assays were performed to compare Hsp70 activation by wild-type and altered DNAJB1. The obtained results provided functional evidence supporting the candidate protein as a potential tardigrade DNAJB1 homolog. Continued investigation of these molecular chaperones may provide insight into their potential contribution to the remarkable stress tolerance of tardigrades.

S9: Designing Haloalkane Dehalogenase Variants With Generative AI: Accelerating the SN2 Reaction

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Generative Artificial Intelligence (AI) models trained on natural protein sequences have been used to design functional enzymes. However, their ability to predict individual reaction steps in enzyme catalysis remains unclear, limiting the potential use of sequence information for enzyme engineering. In this study, we demonstrated that sequence information can predict the SN2 step of a haloalkane dehalogenase using a generative maximum-entropy (MaxEnt) model. We then designed lower-order protein variants of haloalkane dehalogenase using the model. Kinetic measurements confirmed the successful design of protein variants that enhance catalytic activity, above that of the wild type, in the overall reaction and in particular in the SN2 step. Metadynamics simulations emphasize the importance of substrate positioning in enzyme catalysis. Overall, our AI-guided approach successfully enabled the design of a variant with a faster rate for the SN2 step than the wild-type enzyme, despite haloalkane dehalogenase being extensively optimized through natural evolution.

S10: Regulating Dimerization of Human J-Domain Protein

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Molecular chaperones maintain cellular protein homeostasis by promoting protein folding, preventing protein aggregation, and facilitating the refolding or degradation of damaged proteins. Among various chaperone families, the Hsp70/J-domain protein (JDP) system acts as a central system for protein quality control. Class B JDPs have been implicated in facilitating Hsp70-mediated disaggregation of β -amyloid fibrils associated with neurodegenerative disease. The human class B JDP DNAJB1 exists as a stable homodimer, with each monomer containing functional domains involved in substrate recognition and Hsp70 interaction. This raises the question of how individual monomers contribute to DNAJB1 dimer function. To address this, we engineered DNAJB1 variants with alterations that prevent homodimerization; however, the introduced complementary charges allow the two monomer variants to form a heterodimer. This heterodimer enables selective manipulation of individual monomers while preserving native dimer architecture, allowing analysis of monomer-specific contributions to DNAJB1 function. To assess whether the designed monomeric variants interact, we developed a pull-down assay that immobilizes one monomer on beads. We also evaluated the functionality of each monomer variant using ATPase assays to examine its ability to stimulate Hsp70 activity. Together, this work establishes a controlled heterodimer model for investigating DNAJB1 dimer function and provides a foundation for future studies examining the molecular mechanisms of Class B JDPs and their regulation of Hsp70.

S11: Synthesis of Substituted 4,4'-dihydroxyazobenzenes based Analogs of a Novel Jak2 Inhibitor

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The JAK2-V617F mutation in the Janus kinase 2 (JAK2) gene is present in the majority of myeloproliferative disorders (MPDs), including polycythemia vera (PV), primary myelofibrosis (PMF), and essential thrombocythemia (ET). In response to the need for targeted therapies, the Bisht laboratory previously developed G6, a small-molecule JAK2 inhibitor. Structure-activity relationship (SAR) studies of G6 demonstrated that its stilbene core and Mannich base functionality constitute the key structural features responsible for JAK2 inhibition. A series of Mannich base analogs incorporating different amine substituents were subsequently synthesized and evaluated for their inhibitory effects on JAK2 activity. In this study, we describe the synthesis of 4,4'-dihydroxyazobenzene-based analogs, which possess significant structural similarities to the stilbenoid scaffold of G6. These compounds were designed to investigate 4,4'-dihydroxyazobenzene as a promising alternative scaffold for the development of novel JAK2 inhibitors. The synthesis of ortho-substituted 4,4'-dihydroxyazobenzene Mannich base analogs, along with their chemical characterization, is presented and discussed.

S12: Role of the DNAJB1 Gly-rich helix in Hsp70 interaction

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Molecular chaperone systems, composed of Hsp70 and J-domain proteins (JDPs), are fundamental for the quality control of virtually all other cellular proteins. Hsp70 can be recruited by diverse JDP co-chaperones to support various biological activities. Among the three classes of JDPs, class B proteins are unique due to their essential yet poorly understood function and ability to fragment amyloid-like fibrils associated with neurodegenerative diseases. Previously published NMR studies of the human class B JDP, DNAJB1, revealed the importance of a short helix in the class B JDPs' glycine-rich region (Gly-rich) for autoinhibitory regulation of DNAJB1-Hsp70 interactions. Our recently published study of yeast Hsp70/JDP systems indicates that the Gly-rich helix might serve as an additional binding site for Hsp70 beyond the known mode of Hsp70-JDP interactions. To explore this phenomenon further, we first asked whether the same interaction occurs in human Hsp70/JDP systems. Our NMR analysis of DNAJB1 structural features indicated that autoinhibitory regulation is stronger than in its yeast counterpart. To investigate whether the DNAJB1 Gly-rich helix serves as an Hsp70-binding site, we introduced alterations designed to alleviate autoinhibition and prevent canonical JDP activity. We utilized *in vivo* testing using a yeast model to identify whether candidate alterations unlocked the ability of DNAJB1 variants to support the viability of cells lacking the essential yeast class B JDP Sis1. Next, we purified the identified DNAJB1 variants to test Gly-rich helix-Hsp70 interactions using NMR. Results from these studies suggest that some variants can alleviate autoinhibitory regulation. To further investigate the interaction between DNAJB1 and Hsp70, we utilized an ATPase assay to measure the functional activity of the molecular chaperone system with different DNAJB1 variants. These findings not only provide insights into a potential new mode of regulation of Hsp70/JDP systems but also improve our understanding of the unique functions of class B JDPs and their relevance to human neurodegenerative disease.

S13: Receptor-State-Aware Virtual Screening for Discovery of Novel Apo-IDO1 Inhibitor Candidates

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L-Tryptophan (Trp) is an essential amino acid, and most dietary Trp is metabolized through the kynurenine pathway (KP). The first and rate-limiting step of this pathway is catalyzed by three heme-dependent enzymes: tryptophan 2,3-dioxygenase (TDO), indoleamine 2,3-dioxygenase 1 (IDO1), and IDO2. Increased KP activity can deplete local Trp and increase immunoregulatory kynurenine metabolites, suppressing effector T-cell proliferation and function and promoting tumor immune escape. IDO1 is particularly responsive to inflammatory signals and is expressed in antigen-presenting cells and tumor microenvironments, making IDO-dependent Trp metabolism an attractive target for anticancer drug discovery.

In this study, we developed an experimental receptor-state-aware virtual-screening strategy to identify apo-IDO1 inhibitor candidates. Eight experimental inhibitor-bound apo-IDO1 X-ray structures were used to define the binding pocket, benchmark native-pose recovery, and establish a validated experimental receptor model. A de novo-prepared library of 1,380 FDA-approved compounds was docked using GNINA, generating 13,800 poses. Application of a benchmark-calibrated pocket-geometry filter retained 5,628 contact-valid poses, and 1,145 compounds contained at least one valid binding pose. Importantly, contact-based pose selection changed the preferred pose for 557 of the 1,145 retained compounds, demonstrating that docking score alone was insufficient for reliable pose selection.

A score-based threshold advanced 39 compounds to structurally visual inspection. Integrated evaluation of binding-pocket occupancy, interaction geometry, docking metrics, and physicochemical properties identified eight chemically diverse primary FDA-approved candidates for further study. These results establish a geometry-first virtual-screening framework that incorporates experimental structural information and receptor conformational behavior to prioritize apo-IDO1 binding hypotheses for subsequent receptor-ensemble analysis and experimental validation.

S14: Functional Characterization of Molecular Chaperone DNAJA1 in Tardigrades

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Tardigrades are microscopic, multicellular eukaryotes known for their resilience to extreme environmental conditions; however, little is known about the molecular mechanisms underlying this phenomenon. Molecular chaperones are a subset of cellular proteins dedicated to the cellular stress response and proteome quality control. Specifically, Hsp70 and its co-chaperones, J-domain proteins (JDPs), play a key role in the chaperone network and the cellular stress response. This study investigates whether DNAJA1, the most abundant JDP, contributes to tardigrade resilience. We used *Hypsibius exemplaris* as the tardigrade species for this experiment and began by performing bioinformatic analyses using full-length human and *H. exemplaris* DNAJA1 sequences as references. To verify whether the newly identified tardigrade DNAJA1 possesses the characteristics of a canonical class A JDP, we focused on a truncated variant of DNAJA1 containing only the N-terminal J-domain and adjacent glycine-rich (Gly-rich) region. The J-domain is the fundamental structural element responsible for Hsp70 binding and stimulation. In class B JDPs, the Gly-rich region can interact with the J-domain and inhibit Hsp70 engagement. Class A JDPs should not exhibit this autoinhibition. We constructed and purified a truncated variant of DNAJA1 in *Escherichia coli* with a His-SUMO purification tag and tested its ability to stimulate Hsp70 activity using *in vitro* assays. These results provide the first evidence of tardigrade DNAJA1 activity, an important step toward understanding the role of class A JDPs in tardigrade stress resilience and the activity of the Hsp70/DNAJA1 system.

S15: Improvements in the design and synthesis of sensor heterocyclophanes

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The use of heterocyclic emitter-quencher pairs for the detection of primary amines such as hydrazine has great potential, but the synthesis of these compounds has several key issues. Historically, the synthesis of such sensors was expensive, produced low yield, and the sensors themselves were not fully optimized structurally. The cost has been lowered significantly by optimizing the reaction conditions and through the use of palladium recycling techniques. The sensor's performance is also improved by strengthening the hydrogen bond through the addition of activating groups in the para position and allowing the heterocycles to achieve the optimal twist angle by increasing the bridge length.

S16: Initiation of nemamide biosynthesis in *Caenorhabditis elegans*

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The nematode *Caenorhabditis elegans* exhibits distinct developmental arrest programs in response to environmental stress, entering L1 arrest under starvation conditions and dauer diapause under crowding conditions. The nemamides are hybrid polyketide-nonribosomal peptides and function as important chemical signals that regulate the growth and development of nematodes. The nemamides are biosynthesized by a hybrid polyketide synthetase (PKS)-nonribosomal peptide synthetase (NRPS) that is conserved across many nematode species, including parasitic ones. Hence, studying the nemamide biosynthetic pathway could provide potential insights into the regulation of development in parasitic nematodes. *C. elegans* produce two nemamides: nemamide A, which contains a triene in its polyketide side chain, and nemamide B, which contains a tetraene. Previously, by doing comparative metabolomics, we determined that the peroxisomal carnitine O-octanoyl transferase (CROT-1), is required for the biosynthesis of nemamide A, and the enoyl-CoA hydratase (ECH-7), is required for the biosynthesis of nemamide B. Using comparative metabolomics, enzymatic assays, and genome editing, we are investigating the role of CROT-1 and ECH-7 in the initiation of nemamide biosynthesis to determine how these enzymes control the biosynthesis of nemamide A versus B. We performed comparative metabolomic analyses of wild-type and the *crot-1* and *ech-7* mutant strains and are currently analyzing the data to identify metabolic intermediates that accumulate because of the disrupted enzymatic activity. To characterize the preferred substrates of the ECH-7 enzyme, we are expressing and purifying ECH-7 for subsequent biochemical assays. To further investigate the roles of the initial domains of the PKS in processing the initiation unit provided by ECH-7, we are using CRISPR to mutate an active-site residue in the second ketosynthase (KS) domain. This work will allow us to assess whether this KS domain is involved in extending substrates provided by ECH-7 or simply passing them along the assembly line. By understanding the possible initiation mechanism of nemamide biosynthesis, we may be able to predict the structures of other potential nemamides produced by other nematode species. Studies of the initiation mechanisms will give an idea about how nematodes regulate the biosynthesis and production of distinct nemamides.

S17: Structure-Guided Identification of Small-Molecule CFTR Activators for Cystic Fibrosis Using Pharmacophore Modeling

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Cystic fibrosis (CF) is an inherited disorder caused by mutations in the cystic fibrosis transmembrane conductance regulator (CFTR) gene, resulting in impaired chloride and bicarbonate transport and the accumulation of thick mucus in the lungs, pancreas, and digestive tract. Activating CFTR restores chloride and water transport, thinning mucus and improving lung function in cystic fibrosis. This study identifies potential small-molecule modulators targeting the closed conformation of the CFTR protein. We obtained the human CFTR amino acid sequence from UniProt and collected open- and closed-state structures from the Protein Data Bank, then comparatively modeled them using AlphaFold 3 and Boltz-2. CFTR membrane topology and transmembrane helices were characterized using Protter and TMHMM. Potential ligand-binding pockets in the open and closed conformations were identified using P2Rank and PocketFlow. We then used Pharmit to define essential molecular features, including hydrogen-bond donors, hydrogen-bond acceptors, and hydrophobic regions. Pharmacophore modeling identified four (P1-P4) compounds as promising matches, with RMSD values of 0.688-0.825 Å, indicating strong alignment with the pharmacophore features. We performed molecular docking against selected CFTR binding residues to evaluate ligand orientation, structural compatibility, and potential interactions. The analysis identified four promising binding regions, with P3 forming the strongest interaction (-302.6 kcal/mol) with the CFTR binding site. These findings demonstrate the value of integrating structural modeling, pocket prediction, pharmacophore screening, and molecular docking for discovering potential CFTR modulators.

S18: Investigating the structures and antiproliferative properties of secondary metabolites produced by different species of the freshwater algae *Euglena*

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The green freshwater algae *Euglena gracilis* has not only been used for decades in the laboratory as a model organism but has also recently been reported to produce secondary metabolites known as euglenatides with cytotoxic properties against human cancer cell lines. These secondary metabolites are hypothesized to be produced by a hybrid pathway whose framework is conserved across many domains of life. A similarly structured metabolite with a polyketide side chain and a peptide head, known to be synthesized by a PKS and NRPS, respectively, has been previously reported in the model nematode *Caenorhabditis elegans*. By studying other species in the genus *Euglena*, we hope to uncover more novel metabolites and understand their biological role. Indeed, our preliminary data suggests that other species of *Euglena* produce novel metabolites different from that of *E. gracilis*. Using liquid chromatography coupled with ultraviolet spectroscopy and mass spectrometry (LC-UV-MS), we were able to observe key UV peaks known to be present that correlate to the polyketide side chain containing a conjugated triene and significant masses like those in the previously reported euglenatides. Using tandem mass spectrometry (MS-MS), structures were proposed based on the fragmentation patterns of the known euglenatides. To characterize the antiproliferative qualities, we will isolate and purify these novel metabolites and use them in mammalian cytotoxicity assays. To confirm their structures, we will use techniques such as NMR spectroscopy. By investigating these novel metabolites, we hope to uncover more potent euglenatides, learn about their structure-activity relationships, and perhaps identify new therapeutics.

S19: Investigating Amide Substitution Effects on Transannular H-bonding in Heterofunctionalized [2.2]Paracyclophanes

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[2.2]Paracyclophanes (**[2.2]pCps**) are organic molecules in which two aromatic rings are co-facially stacked and connected by ethylene bridges, resulting in strong transannular π - π interactions. **[2.2]pCp** is the smallest member of the paracyclophane family, and its strain, through-space conjugation, and planar chirality have led to their application within chiral ligands, optoelectronic materials, and conjugated polymers. For the past decade, our group has exploited the unique properties of **[2.2]pCp** to synthesize tetra-amide supramolecular monomers (**[2.2]pCpTAs**) that undergo self-assembly facilitated by both intra- and intermolecular H-bonding and π - π interactions. Further studies have shown that self-assembly strength can be tuned according to amide connectivity and, consequently, H-bonding geometry and preorganization. Our most recent report on mixed-amide **[2.2]pCps** bearing both C- and N-centered amides demonstrated that asymmetric intramolecular (transannular) amide pairs can program the directionality of intermolecular H-bonding. Expanding on this work, we hypothesize that if transannular amide pairs are further desymmetrized both sterically and electronically, supramolecular polymerization can be further strengthened without disrupting the established H-bonding geometry. To probe this idea, we targeted ditopic amide mixed-deck pseudo-*ortho* **[2.2]pCpBAs** monomers, furnished with C- and N-centered amides bearing noncanonical R-groups. NMR studies and density functional theory (DFT) will be applied to investigate how new amide functionalities control the strength and directionality of intramolecular H-bonding. Guided by our results, we hope to transfer these motifs to self-assembling tetrafunctionalized **[2.2]pCpTA** monomers and realize more sophisticated programmability in new supramolecular polymers.

S20: Kinetic and Structural Basis of the Inhibition Mechanism of Human Asparagine Synthetase by ASX-173

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Cancer cells with limited access to extracellular asparagine must rely on asparagine synthetase (ASNS) to maintain intra-cellular asparagine levels and support continued growth. Consequently, direct inhibition of ASNS may offer a therapeutic strategy for malignancies that resist asparagine-depleting treatments. In this study, we define the inhibitory mechanism of ASX-173, a cell-permeable small molecule targeting human ASNS. Using a combination of steady-state kinetics assays, biophysical measurements, and structural biology, we demonstrate the inhibition mechanism of ASX-173 *in vitro*. These results provide the molecular basis of this high-affinity ASNS inhibitor and establish a framework for developing selective inhibitors that exploit transient catalytic states of the enzyme.

S21: Total Synthesis and Biological Evaluation of Nemamide Analogs

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University of Florida

The nemamides are hybrid polyketide–nonribosomal peptides that are produced in two neurons of the nematode *Caenorhabditis elegans* and promote recovery from starvation-induced early larval stage arrest. Because the worm produces the nemamides in minute quantities and no total synthesis of these molecules has been reported, it has been difficult to study their mechanism of action. Here, by using a miniaturized assay, we demonstrate that nemamides purified from the worm exhibit antiproliferative activity against mammalian cancer cells. Moreover, we present the stereoselective synthesis of two nemamide analogs and evaluate their biological activity in the proliferation assay. While the nemamides exhibit significant biological activity, the analogs have reduced potency, indicating that the lipid tail, polyene group, and methoxy group all play crucial roles in the antiproliferative properties of the nemamides. These findings offer valuable insights into the structure–activity relationships of the nemamides and lay the groundwork for future synthetic and mechanistic investigations of this unique class of natural products.

S22: Biochemical Characterization of *Moraxella catarrhalis* HemW

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Moraxella catarrhalis is a bacterial pathogen that requires the conserved *hemW* gene for growth under iron-limiting conditions. The *hemW* gene encodes a putative radical S-adenosylmethionine (SAM) enzyme in the HemN-like subfamily. Its biochemical properties, however, remains unclear. Here, we report the first experimental characterization of *M. catarrhalis* HemW (*McHemW*). Bioinformatic analysis established its evolutionary relationship with the putative heme-binding HemW from *Escherichia coli*. Biochemical and spectroscopic analyses demonstrate that *McHemW* contains a catalytically active [4Fe-4S] cluster and binds heme. Hydrogen-deuterium exchange mass spectrometry (HDX-MS) localized the heme-binding site to the C-terminal auxiliary domain unique to HemW homologues. These findings provide insight into heme recognition by *McHemW* and establish a foundation for understanding its role in *M. catarrhalis* under iron-limiting conditions.

S24: Fisetin as a fluorescent probe of different DNA architectures

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Fisetin is a naturally occurring flavonoid that exhibits a distinct dual-emission phenomenon when tautomerized in favorable environments, producing a red-shifted excited-state proton transfer (ESPT) signal: free fisetin predominantly exists as the enol tautomer and displays an emission maximum near 485 nm, whereas the keto tautomer resulted from the intramolecular proton transfer in the excited state emits near 540 nm. This behavior makes fisetin a promising probe for investigating structural motifs in DNA. Although fisetin has been reported to interact with both triplex and G-quadruplex (G4) DNA, the environmental conditions that determine its specificity for either structure have not been systematically explored. In this work, we characterized fisetin's ESPT fluorescence across G4 and triplex DNA environments and identify how ionic conditions modulate its emissive states. Specifically, we demonstrated that across almost all conditions tested, fisetin exhibits a stronger red shift in the presence of triplex DNA than with G4 structures. The exception from this trend was shown to be DAP-10-42, a DNA light-up aptamer proposed to fold into a G4-duplex architecture. In the presence of DAP-10-42, fisetin exhibits the keto tautomer-specific emission at ~540 nm with the intensity greater than that for fisetin in the presence of triplex DNA under specific ionic conditions. The DAP-10-42-induced emission shift of fisetin appears to be dependent on the presence of both monovalent ions and magnesium ions, while triplex-induced fluorescence of fisetin's keto tautomer is inhibited by the presence of magnesium ions. These results indicate a unique interaction between fisetin and DAP-10-42 that differs from other G4 sequences and may be explained by "sandwiching" the flavonoid structure between a base pair and a G-tetrad to enable continuity of pi-pi stacking and stabilization of the excited keto tautomer.

S25: Photo-Driven Photocatalyst-Dependent Radical Cascade Cyclizations of Simple N-Acryloyl Indoles for the Selective Synthesis of Sulfonfylated Dihydropyrido[1,2-a]-indolones

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Dihydropyrido[1,2-a]-indolone (DHPI) is a prominent scaffold in natural products and drug molecules, exhibiting broad pharmacological and biological activities. Therefore, it is of great significance to develop novel protocols for its synthesis. Specifically, we use photoredox catalysis as our method because it represents an environmentally friendly approach due to the ready availability and sustainability of visible light. In this project, we aim to develop a visible-light-driven photocatalyst-dependent radical cascade cyclizations between simple N-acryloyl indoles and tosyl chloride. On one hand, when NaH₂PO₄ was employed as the base and the reaction was conducted in MeCN under blue light without a photocatalyst, the [4 + 2]/[4 + 2] product was obtained in 50% yield as the major product. On the other hand, the [4 + 2] product was delivered in 56% yield as the major product when fac-Ir(ppy)₃ was used as the photoredox catalyst by carrying out the reaction in MeCN under blue light in the presence of NaH₂PO₄. Therefore, we have demonstrated the feasibility of the development of visible-light-driven photocatalyst-dependent radical cascade cyclizations for the selective synthesis of sulfonfylated [4 + 2]/[4 + 2] DHPIs and [4 + 2] DHPIs. Future directions of this project include evaluation of substrate scope, the scale-up reaction, downstream transformations, and mechanistic studies.

S26: Investigating the molecular mechanisms driving immune evasion in bronchial premalignant lesions

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Lung squamous cell carcinoma (LUSC) arises from bronchial premalignant lesions (PMLs) that progress through grades of dysplasia to invasive carcinoma. However, many PMLs spontaneously regress, suggesting that molecular mechanism within lesions influence their clinical outcome. Previous studies from our group showed that progressive PMLs exhibit decreased antigen presentation and immune surveillance, suggesting that immune evasion emerges early during lung carcinogenesis. However, the molecular mechanisms underlying these changes remain unclear. Based on previous profiling of PMLs we have identified increased expression of miR-149-5p and alterations in YAP/TAZ signaling that we hypothesize contribute to immune evasion by suppressing antigen presentation and CD8+ T cell function. To directly test the role of miR-149-5p over-expression and increased YAP/TAZ nuclear localization, SW900 LUSC cell lines were subject to a transfection of miR-149-5p mimic, and to modulate YAP/TAZ via siRNA knockdown of LATS1/2. We examined MHC-I surface expression by flow cytometry, and measured antigen presentation-related genes by qPCR. To test the functional suppression of MHC-I, CD8+ T cell co-culture and cytotoxicity assays were performed to examine impacts to T-cell mediated killing. miR-149-5p overexpression significantly decreased MHC-I surface expression ($p = 0.0317$) and reduced CD8+ T cell-mediated cytotoxicity ($p = 0.0126$). LATS1/2 knockdown also significantly reduced CD8+ T cell-mediated cytotoxicity ($p = 0.00923$), although preliminary flow cytometry analyses did not detect significant changes in MHC-I or MHC-II surface expression. Together these findings implicated miR-149-5p and YAP/TAZ signaling in tumor cell resistance to CD8+ T cell-mediated killing, while suggesting that their effects on immune evasion may occur through distinct mechanisms. Defining these mechanisms may reveal targets for restoring immune surveillance and intercepting LUSC before invasive disease develops.

S27: Providing Visual Support for the Concepts of Kinetic vs. Thermodynamic control and Trapping Singlet Oxygen

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Most reactions and concepts in core Organic Chemistry rely on drawings and line art, with little visual-evidence-based material available. This probably contributes to students' difficulties in translating their classroom material into real life chemistry. Furthermore, it relates to the students' struggles in retaining information from core Organic Chemistry to advanced classes. Our long-term goal is to provide visual-evidence-based methodology to assist instructors in teaching reaction outcomes, reaction mechanisms, and key concepts in Organic Chemistry. When designing experiments, we require that all the visual material fulfill strict guidelines. The experiments must: a) maximize visual impact, b) be layered, c) have additional value such as historical impact or real-world applications. Herein we present two examples of visual-evidence-based experiments. Both have been used in lectures, and each reaction provides the potential for additional interactive teaching. Experiment one illustrates the concept of kinetic vs. thermodynamic control using competitive chelation of octaethylporphyrin, which is treated with equimolar concentrations of Zn(II) and Ni(II) acetate. Initially, the kinetically favored Zn is inserted to form an orange fluorescing solution. Upon heating, the thermodynamically favored Ni is inserted, which does not fluoresce. The experiment fulfills our requirements: the chelation reactions illustrate both Brønsted and Lewis acid-base reactions. Analogous transmetallation of Ni(II) porphyrins to V=O (IV) porphyrins plays a valuable role in crude oil exploration. Experiment 2 illustrates a novel Diels-Alder reaction and the concept of photosensitizers. When protoporphyrin-IX dimethyl ester (PIXDME) is exposed to sunlight, it acts as a photosensitizer that transforms the diradical triplet oxygen into singlet oxygen, which acts as a dienophile and reacts with PIXDME. The two isomeric green products and the starting material are separated by TLC. This mixture is also used in our Rogues' Gallery for TLC.

S28: Uncertainty-Aware Multi-Objective Computational Prioritization of Pancreatic Cancer Molecular Candidates with Convergent NF- κ B1 Target Hypotheses

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Pancreatic ductal adenocarcinoma (PDAC) presents a difficult molecular-prioritization problem because predicted response, target relevance, systemic exposure, intracellular accessibility, and model uncertainty need not agree for the same compound. We evaluated an evidence-gated computational oncology workflow using 75 post-training molecular candidates generated across PANC-1 pancreatic, HT29 colorectal, and SW1271 lung contexts, with focused analysis of 25 PANC-1 candidates. SuperPred 3.0 yielded 250 candidate-target predictions. NFKB1, encoding the intracellular p105 precursor of p50, appeared among the top ten predicted targets for 23/25 PANC-1 candidates (92%), with mean probability 0.959 and median within-candidate rank 2; it was top-ranked for 6 candidates. NFKB1 probability was not associated with the locked training reward (Spearman $\rho = -0.07$, $p = 0.768$), supporting a distinct target-prediction layer. External admetSAR3.0 profiling showed broad predicted oral-exposure support: 22/25 candidates were HIA-positive, 21/25 F20-positive, 19/25 F30-positive, 22/25 satisfied Lipinski criteria, and 19/25 were predicted not to inhibit P-glycoprotein. Direct permeability classifiers were more selective (Caco-2 7/25; MDCK 10/25). A transparent descriptive intersection identified six in-domain candidates (1, 2, 3, 8, 23, and 25) that were HIA- and F30-positive, Lipinski-accepted, non-P-gp inhibitors, and positive in at least one Caco-2/MDCK classifier; all six retained NFKB1 in the SuperPred top ten. DiffDock generated pose ensembles for all 25 candidates against the same predicted full-length two-chain p105 receptor. These results support prioritization of exposure-compatible, experimentally testable NFKB1-associated molecular hypotheses while not establishing intracellular concentration, biochemical binding, safety, anticancer efficacy, or clinical utility.

S29: Dapoxyl-10 split light-up aptameric sensor used as fluorescent probe for LAMP amplicons of MalB gene of *E. coli* in PURED system

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The dapoxyl-10 aptamer is a sequence of DNA which non-covalently binds to dye ligands, which exhibit intrinsically low fluorescence in aqueous solutions, but become highly emitting upon aptamer binding. Dap-10 SLAS's are designed by splitting the dapoxyl-10 aptamer and equipping each strand with a stem as well as a binding arm which is complementary to a sequence of target DNA and are a useful tool for DNA analysis. The objective of PURED is to design a device that uses a SLAS to detect LAMP amplified MalB amplicons for usage as a point-of-collection diagnostic tool for environmental water samples. Compared to traditional tools, PURED units can be created at a much lower cost, while maintaining high selectivity, with the added advantage of yielding results within 1 hour of collection. Loop-mediated isothermal amplification (LAMP) can be used to amplify DNA in a point-of-collection setting, the target sequence chosen was the MalB gene in *E. coli* because this sequence is highly conserved across strains and the LAMP primers that target this gene have high selectivity. By designing a SLAS which hybridizes with the target LAMP amplicon, presence of *E. coli* can be determined using a visually observed fluorescent assay. Optimization of SLAS sensors can be performed by adjusting the concentration of sensor components or by changing sequence of the sensor. We ran different assays to determine ideal conditions for visual detection of fluorescence, hybridization kinetics and background fluorescence levels. By continuing sensor and LAMP optimization, we plan to realize the objective of designing an environmental diagnostic tool for *E. coli* and using similar technology, expand diagnostic capabilities to other pathogens and sample types.

S30: Stereochemistry in Disulfide-Bond Disrupting Agents: Synthesis of Novel *cis*-Disubstituted Derivatives

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The American Cancer Society anticipates breast cancer (BC) to have the highest diagnosis frequency in American women, apart from basal and squamous cell skin cancers, and to be the second-most common cause of cancer mortality. The effectiveness of current FDA-approved BC drugs is limited due to drug resistance and harmful side effects. Consequently, developing novel BC therapeutics remains critical and has motivated our research group to establish a novel class of small molecules called Disulfide-Bond Disrupting Agents (DDAs). DDAs possess a cyclic thiosulfonate pharmacophore and have demonstrated potential to treat BC by selectively inducing apoptosis in EGFR-overexpressing BC cell lines *in vitro* and by suppressing breast tumor growth *in vivo*, with no observed toxicity. All bicyclic DDAs synthesized to date exhibit *trans*-disubstitution on the carbons most distant from the pharmacophore, due to synthetic accessibility; other stereochemical configurations have not yet been explored. Stereochemistry can play a significant role in the way a drug interacts with target receptors, as it determines the three-dimensional arrangement of atoms in space. Therefore, altering a drug's stereochemistry can influence its pharmacodynamics and pharmacokinetics.

This poster showcases the synthesis of the first *cis*-disubstituted DDAs structurally derived from one of our most potent DDAs, ($\pm$)-dMtcyDTDO. The synthesis was initiated by oxidation of a commercially available, racemic, disubstituted cyclohexene to yield a *cis*-diol, followed by methylation to establish the desired *cis*-dimethoxy functionalization. The remainder of the synthesis involved constructing the pharmacophore through a series of steps, including reduction, mesylation, thiolation, and oxidation. The final synthetic step yielded two *cis*-disubstituted regioisomers, which were separated and individually evaluated to determine whether *cis*-, as opposed to *trans*-, dimethoxy substitution alters the biological performance, and ultimately the pharmacodynamics and pharmacokinetics, of the DDAs. Overall, this work will expose the consequences of DDA stereochemistry that have yet to be explored.

Ongoing work includes *in silico* molecular docking and molecular dynamics simulations to investigate covalent and noncovalent binding interactions between DDAs and their target proteins, which may help to elucidate why some DDAs exhibit greater biological potency than others. Additionally, we are performing chiral resolution of the DDAs, all of which have thus far existed as racemates, by forming and separating diastereomeric salts. Findings from these studies could provide additional insight into the impact of DDA stereochemistry on biological behavior.

S31: Analysis and Quantification of Point Mutations in Cancer DNA Biomarkers using Multicomponent Hybridization Probes

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Cancer has been linked to point mutations in cancer DNA biomarkers. Therefore, the detection of sequence variations, especially in the presence of wildtype (WT) sequences, is important for accurate diagnostics and monitoring of cancer treatments. Current diagnostics include NGS or allele-specific PCR, which can be costly or time consuming. DNA hybridization probes are effective biosensing tools, and specifically multicomponent probe assays (MPA) provide selectivity down to a single nucleotide polymorphism (SNP). In this work, we tested a split deoxyribozyme multicomponent probe system to selectively detect a point mutation in a Glioblastoma-related biomarker gene, then quantified the SNP in in the presence of WT DNA. We were able to determine the relative abundance of SNP to WT in heterogeneous mixtures, and we found the LOD of target unchanged in the presence of excess WT. MPAs can be tailored to multiple sequence variations in a single assay, surpassing the capability of allele-specific PCR, and can be used to interrogate multiple samples as a more cost-effective option than sequencing.

S32: Cyclophanes and their Ring-Opened Isosteres: The Interplay between Folding and Self-Assembly

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Controlling aromatic stacking is fundamental to the biological and chemical function of molecular systems, yet precise structural control remains elusive. Foldamers provide an attractive platform for addressing this challenge because they can adopt conformationally ordered states in the solution state that are stabilized by noncovalent interactions such as hydrogen bonding (H-bonding) and π - π stacking. They can exist as discrete folded entities or further assemble into higher-order supramolecular assemblies through inter-foldamer noncovalent interactions. New designs in this space are expected to pave the way for increasingly functional molecules and responsive materials. Over the past decade, our group has developed a strategy to direct the self-assembly of [2.2]paracyclophanes (**[2.2]pCps**) into highly ordered 1-D supramolecular assemblies using pre-organized architecture, planar chirality, intra- and intermolecular H-bonding, and π - π stacking interactions. Inspired by dithia[3.3]pCptetracarboxamides (**dt[3.3]pCpTAs**), **pCp** derivatives that can form supramolecular polymer assemblies through self-complementary intermolecular and transannular amide H-bonding, we propose the synthesis and characterization of their 'ring-opened' counterparts. Removing one of the macrocyclic thiobis(methylene) bridges provides a foldamer—"thiobis(methylene)-diterephthalamide (**TMTA**)"—a foldamer capable of intra- and intermolecular H-bonding, whose assembly is uniquely governed by a thermodynamic folding equilibrium, offering a powerful new handle for controlling supramolecular polymer organization. We further expanded the bridge by introducing bis(prop-2-ynyl) linker to arrive at "thiobis(prop-2-ynyl)-diterephthalamide (**TPTA**)" to evaluate how these foldamers could display **pathway-dependent self-assembly**, dictated by the linker geometry. Systematic variation of heteroatoms (O vs. S) within the diterephthalamide linker backbone is used to probe their impact on folding energetics and self-assembled morphologies. In contrast to preorganized cyclophanes that employ two linkers to provide structural constraint, the foldamers contain a single flexible linker and therefore populate condition-dependent conformational ensembles governed by linker geometry, temperature, and concentration. A combination of variable-concentration and -temperature ^1H NMR experiments, variable-temperature UV-Vis studies, and density functional theory (DFT) established the importance of both stereoelectronic and thermodynamic effects to be critical for well-behaved folding (*intramolecular* H-bonds) as well as supramolecular assembly (*intermolecular* H-bonds). Co-assembly studies between pre-organized **dt[3.3]pCpTAs** and the flexible foldamers revealed that intramolecular folding dynamics can indeed be controlled by supramolecular copolymerization. We are hopeful that elucidating the supramolecular assembly of these foldamers in detail will establish a versatile platform for next-generation supramolecular architectures.

S33: Investigation of the trans-acting enzymes involved in non-canonical intermediate trafficking in nemamide biosynthesis

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Nematodes use chemical signaling molecules to regulate their development, behavior, and life cycle. Understanding the biosynthetic pathways of these molecules will uncover new biosynthetic strategies and may enable approaches to interfere with the reproduction and survival of parasitic nematodes, which cause significant agricultural losses and many human diseases worldwide. Nemamides are a family of hybrid polyketide-nonribosomal peptide natural products that are produced by the hybrid megasynthetases PKS-1 and NRPS-1 in the canal-associated neurons of *C. elegans* and regulate the nematode response to starvation. Nemamides have also demonstrated antiproliferative activity against mammalian cancer cell lines. However, it is not clear how their biosynthesis is regulated. Using genome editing, comparative metabolomics, and biochemical studies, we are investigating the roles of several trans-acting enzymes in trafficking intermediates between PKS-1 and NRPS-1.¹ We focus on PKAL-1, a fatty acyl-AMP ligase that loads a polyketide intermediate directly onto a carrier protein domain of NRPS-1, revealing a previously undescribed mechanism for intermediate transfer between the two assembly lines. We also present ongoing work on two additional accessory enzymes in trafficking intermediates and in regulating nemamide biosynthesis.² Further characterization of these accessory enzymes will reveal how they selectively recognize and act on specific intermediates, determining the products generated by the PKS-NRPS assembly line. Together, this work will reveal how trafficking mechanisms expand the biosynthetic potential of hybrid PKS-NRPS systems and advance strategies to target nematode development.

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S34: Structure-Guided Design of De Novo Protein Binders Targeting Interleukin-2 Receptor α in Leukemia Using a Deep Learning-Based Method

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Leukemia is a heterogeneous group of hematologic malignancies characterized by uncontrolled proliferation of abnormal blood-forming cells, highlighting the need for more selective therapeutic strategies that minimize the toxicity and limitations associated with conventional chemotherapy, immunotherapy, and stem cell transplantation. This study investigated interleukin-2 receptor α ; IL-2R α (CD25) as a potential therapeutic target and computationally explored protein binders capable of interacting with CD25. The amino acid sequences of CD25 were from UniProt, and modeled its three-dimensional structure using AlphaFold 3. PROTTER was used to model protein topology and membrane organization, and PASSer to identify potential CD25 binding pockets and interaction regions. BindCraft was used to computationally design candidate protein binders targeting CD25. BindCraft uses deep-learning-based protein structure prediction and sequence optimization to design novel protein binders that are predicted to interact strongly and specifically with a selected target protein. The interface-predicted TM-score (i_pTM) was used to measure the confidence in the predicted interaction and relative positioning between CD25 and the eigen ligand binders; higher values indicate a more reliable binding interface. The binding energy analysis further demonstrated that I-59 exhibited the most favorable interaction profile, with the highest number of hydrogen bonds and hydrophobic interactions among the evaluated candidates. In addition, I-59 showed the strongest predicted binding affinity (-13.8 kcal/mol) and a predicted dissociation constant (Kd) of 7.2×10^{-11} at 25°C , supporting its potential as the most promising candidate. The binding energy analysis further demonstrated that I-59 exhibited the most favorable interaction profile, with the highest number of hydrogen bonds and hydrophobic interactions among the evaluated candidates. In addition, I-59 showed the strongest predicted binding affinity, with a binding energy of approximately -10 kcal/mol, supporting its potential as the most promising candidate. Finally, structural analysis using molecular dynamics (MD) simulations was performed to evaluate the stability and dynamic behavior of the complex. The computational workflow provides a structure-based framework for identifying and evaluating novel CD25-targeting protein binders that could potentially interfere with CD25-associated signaling in leukemia.

Keywords: CD25, Leukemia, IL-2R α , Deep Learning-Based Structure Prediction.

S35: Discovery and characterization of one eunicellane diterpene synthase homolog from *Chitinophaga solisilvae*

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Terpenoids are a vast and diverse group of natural products with intricate structures and unique bioactivities. Because of their properties, terpenoids have found extensive applications in medicine, agriculture, and cosmetics. Although the structures of terpenoids are complex, they originate from acyclic and achiral precursors of various lengths. Terpene synthases (TSs) catalyze the cyclization of these precursors into polycyclic hydrocarbon scaffolds with multiple stereocenters. Tailoring enzymes, such as cytochrome P450s and glycosyltransferases, modify the terpene skeleton to yield the final bioactive natural product. Most terpenoids and their respective TSs are discovered from plants and fungi; terpenoids from bacteria have also been isolated but are rare, especially for the eunicellanes, a class of 6/10-bicyclic diterpenoids typically derived from soft coral. However, genomic sequencing data reveals the presence of biosynthetic gene clusters (BGCs) containing putative eunicellane TSs in various families of bacteria. The presence of these BGCs suggests that bacteria may produce coral-type terpenoids that were previously unreported.

A BGC containing a putative TS from the bacterial strain *Chitinophaga solisilvae* was identified by genome mining. The TS was expressed *in vivo* by an engineered *E. coli* system for terpene production, and its metabolites were screened by GC-MS and HPLC. Positive hits for diterpene skeletons were isolated and purified, and their structures were elucidated by NMR spectroscopy. Thirteen products were determined to be diterpenes by GC-MS, and three structures were characterized by NMR; the eunicellane alcohol chitinol, the 4/9-bicyclic diterpene xeniaphyllene, and a new 6/11-bicyclic diterpene were identified. The 6/11-bicyclic diterpene features a unique ring junction framework, which suggests that its biosynthetic mechanism is distinct from other terpenes. Mechanistic studies and investigations into the remaining diterpene products can provide deeper insight into the enzymology of TSs and expand their capabilities for natural product discovery and biocatalysis.

S36: Visible-Light-Induced Radical Cascade [4 + 2]/[4 + 2] Cycloaddition of Underexplored N-Acryloyl Indoles to Access Dihydropyrido[1,2a]-Indolones

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Dihydropyrido[1,2-*a*]-indolone (DHPI) is a prominent scaffold in many natural products and pharmaceutical compounds with notable medicinal properties and biological activities. Despite its significance, methods that construct this framework directly from simple N-acryloyl indoles are limited. Therefore, developing novel protocols for its synthesis from underexplored simple N-acryloyl indoles is highly desirable, which is the aim of this project. Herein, we develop a visible-light-mediated radical cascade [4 + 2]/[4 + 2] cycloaddition of simple N-acryloyl indoles and N-hydroxyphthalimide esters, providing a streamlined route to structurally complex DHPIs. The reaction features a sequence of four consecutive radical additions involving two N-acryloyl indole molecules, which forges four new C–C bonds and induces dearomatization of one indole ring. The proposed mechanism is supported by observations of [4 + 2] cycloaddition byproducts and additional control experiments. The synthetic utility of this method is demonstrated by the scale-up reaction and downstream derivatizations.

S37: A DNA Cephalopod Nanostructure for Rapid Detection of Human Thrombin

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Introduction:

Rapid and sensitive detection of proteins is essential for biomedical diagnostics and real-time monitoring of biological processes, yet biosensor response rates can be limited by slow analyte transport and diffusion to the sensing interface. Here, we investigate a DNA-based nanostructure, the DNA Cephalopod, as a strategy to enhance analyte delivery to a molecular sensor. The Cephalopod consists of a central DNA nanostructure functionalized with multiple extended DNA “tentacles” strands that contain analyte-binding fragments (ABFs). We hypothesize that the cephalopod will actively capture analyte to increase the local concentration around the sensor, reducing incubation times and achieving lower detection limits.

Methods:

As a model protein target, we selected human thrombin, a well-characterized serine protease with established G-quadruplex-forming DNA aptamers. A thrombin-specific aptamer sensor will be incorporated into the DNA Cephalopod, while additional thrombin-binding aptamer fragments will be positioned along the tentacle strands. The sensor itself is built as a Split Light-up Aptameric Sensor (SLAS), composed of two complementary strands that are held within the cephalopod scaffold. Upon thrombin binding, the two SLAS strands are brought into close proximity and assemble into a functional Dapoxyl aptamer, which binds the fluorogenic dye Auramine O to generate a fluorescent signal. The affinity of the tentacle-associated analyte binding fragments will be adjusted through sequence modifications to establish an affinity gradient that favors transfer of thrombin from the tentacles to the sensing interface. Sensor assembly and optimization will be evaluated using fluorescence-based assays, comparing the kinetics between the Cephalopod and its corresponding sensor lacking tentacle strands.

Results:

We anticipate that the multivalent capture architecture of the DNA Cephalopod will increase the effective local concentration of thrombin at the sensing interface, and consequently improve sensor response rates.

Conclusion:

This work will establish whether a programmable DNA nanostructure can overcome mass-transfer limitations in protein biosensing and provide a general strategy for developing faster and potentially more sensitive sensors for non-nucleic-acid analytes.

S38: Less Sugar, All Sweet: Structure-Based Computational Design of Peptide Binders Targeting the Sweet Taste Receptor

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Overconsumption of dietary sugar is strongly associated with type 2 diabetes and other metabolic diseases, motivating strategies that preserve the perception of sweetness while reducing sugar intake. Sweetness is detected by the heterodimeric class C GPCR TAS1R2–TAS1R3, whose full atomic structure was resolved only recently by cryo-electron microscopy. Building on this structure (PDB: 9UTB), we applied a structure-based computational pipeline using RFdiffusion for backbone generation, ProteinMPNN for sequence design, and AlphaFold2 for structure prediction and scoring in order to design short peptide binders intended to stabilize the active state of the receptor and thereby prolong the sweetness signal. Across the receptor interface, 28 hydrophobic hotspot sites were selected, from which 17,550 backbones were generated. The 3,696 backbones that passed a hotspot-contact filter were carried into sequence design, which yielded 18,480 candidate sequences. Structure prediction with AlphaFold2 and filtering at a predicted aligned error (pAE) threshold of 15 Å retained 20 sequences originating from 8 targets. The five top-ranked designs were evaluated in virtual reality (Nanome) for hydrogen bonds, ionic interactions, and steric clashes, followed by VR-guided point mutation. One candidate, exp1–990_s1 (pAE 8.801 Å), outperformed all others across predicted error, interfacial contact number, and clash count, forming 29 hydrogen bonds and 18 ionic interactions with a clash-free interface after iterative relaxation. These results demonstrate that an RFdiffusion → ProteinMPNN → AlphaFold2 pipeline can identify short-peptide binder candidates with favorable predicted interface properties, providing a promising starting point for experimental validation and, ultimately, for reducing dietary sugar consumption without sacrificing perceived sweetness.

S39: Functional characterization of hexokinase 2 from *Callorhinchus milii* (ghost shark)

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There are four 100kDa hexokinase isozymes composed of two domains that catalyze the conversion of glucose to glucose-6-phosphate, the first step in glycolysis. The two domains likely originated from a duplication and fusion event from an ancestral 50kDa hexokinase. Hexokinase 1 and 3 lack enzymatic activity in the N-domain but are subject to allosteric regulation through binding of G6P or glucose, respectively, to the N-domain. Uniquely, hexokinase 2 in humans maintains catalytic activity in both the N domain and C domain. It also lacks allosteric regulation but remains sensitive to product inhibition. The emergence or conservation of this activity and regulation is yet to be understood. To investigate the evolutionary origins and conservation of enzymatic activity and allosteric regulation in the N-terminal domain, we are investigating the functional properties of diverse vertebrate HKs. We present here the functional characterization of hexokinase 2 (HK2) from *Callorhinchus milii* (ghost shark), a taxonomically distant species of jawed vertebrates. We demonstrate that hexokinase 2 from *C. milii* has functional similarities to human HK2, including inhibition by glucose-6-phosphate. These results provide a framework to understand critical points in hexokinase evolution. Further studies will investigate other hexokinases identified in taxonomically distinct species to understand the evolution of activity and regulation amongst the various 100kDa hexokinase isozymes.

S40: Synthesis of SCN-Containing Indole-Fused Polycycles through an Oxidant-Mediated Dearomative Electrophilic Thiocyanation/Cyclization Cascade

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Indole-fused polycycles are prevalent in a variety of natural products and drug molecules, many of which display notable medicinal properties and biological activities. Among the various synthetic approaches, radical cascade cyclization has emerged as an efficient strategy for their constructions due to its ability to streamline synthetic sequences, reduce costs, and minimize waste generation. The aim of this project is to develop a dearomative electrophilic thiocyanation/cyclization cascade for the synthesis of SCN-containing indole-fused polycycles. By reacting N-Boc-3-(2-hydroxyethyl)indole with potassium thiocyanate in the presence of $K_2S_2O_8$ in acetic acid, the desired SCN-containing indole-fused polycycle product was obtained in 60% isolated yield. It is worth noting that the reaction can be performed under ambient air, making the protocol easy to handle compared to the reported approach. A series of other oxidants have also been screened to obtain better reaction yield. Future work will focus on further optimization of the reaction conditions, expanding the substrate scope, evaluating the scalability of the reaction, exploring downstream product derivatizations, and developing possible photocatalytic approaches.

S41: Effect of Organic Waste Feedstock Selection on Biogas Production During Anaerobic Digestion

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Accumulation of organic waste has become a significant environmental challenge due to inefficient waste management practices. Anaerobic digestion provides a potential solution by converting organic matter into biogas, a renewable energy source. This study investigated how different organic waste feedstocks influenced biogas production during anaerobic digestion. Fruit waste, grass clippings, and cow manure compost were compared under controlled conditions to determine differences in biogas accumulation. Identical anaerobic digesters were constructed, and biogas production was estimated by measuring increases in balloon circumference over a 56-day period. Experimental conditions, including feedstock mass, water addition, temperature, and digestion duration, were maintained as consistently as possible. The fruit-waste digester exhibited the greatest increase in balloon circumference (17.5 cm, which was 52.2% greater than manure compost), followed by manure compost at 11.5 cm (reaching 65.7% of fruit's maximum expansion and exhibited its peak expansion rate during the initial 7-day phase), while plant waste showed no measurable expansion. These results supported the hypothesis that feedstock composition influences biogas production potential. These findings suggest that optimized feedstock selection can improve anaerobic digestion efficiency and contribute to more sustainable approaches for organic waste management and renewable energy production.

S42: Physics-Guided Digital Twin Framework for Performance Prediction and Design Optimization of Organic Solar Cells.

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Organic solar cells (OSCs) offer lightweight, flexible, and solution-processable photovoltaic technologies; however, their performance strongly depends on coupled optical and electrical processes, making device optimization through trial-and-error fabrication challenging. This work develops a physics-guided digital twin framework for investigating thickness-dependent performance in PM6:Y6 organic solar cells under the standard ASTM G173 AM1.5G spectrum. The initial digital-twin implementation incorporates wavelength-dependent optical properties to calculate active-layer absorbance and optical-limit short-circuit current density ($J_{sc,opt}$) over an active-layer thickness range of 50–220 nm. The model predicts increasing photon absorption with thickness and yields $J_{sc,opt}$ values of 18.81, 22.85, 28.66, and 31.20 mA cm⁻² at 53, 75, 135, and 212 nm, respectively, reaching 31.33 mA cm⁻² at 220 nm. In contrast, experimentally reported PM6:Y6 devices exhibit J_{sc} values of 24.99, 27.16, 25.43, and 26.77 mA cm⁻² at the corresponding thicknesses, with the highest experimental J_{sc} occurring at 75 nm. The resulting normalized trend mean absolute error (MAE) of 0.1986 reveals that enhanced optical absorption alone does not explain thickness-dependent device performance. In particular, the experimentally reported charge-collection probability decreases from 87.0% at 75 nm to 80.1% at 212 nm, indicating increasing electrical losses in thicker active layers. These results motivate a coupled optical-electrical digital twin in which photon absorption, charge generation, and charge collection are jointly represented. The proposed framework provides a physics-interpretable pathway toward virtual OSC design and reduced experimental fabrication iterations.

S43: Investigating the nitration pathway of pyrrolomycins in *Streptomyces* sp.

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Nitrate (NO₃⁻), nitrite (NO₂⁻), and nitric oxide (NO) are integral to the nitrogen cycle, but these species also serve in the biosynthesis of bacterial natural products. Nitrated natural products are of special interest as nitro groups are rare among natural products and influence biological activity. Bacteria can enable selective nitration chemistry that is otherwise difficult to perform synthetically. Pyrrolomycins, discovered from *Streptomyces vitaminophilus*, are an example of this chemistry with many featuring a nitro group at position 3 of the pyrrole ring. Bioinformatics of *S. vitaminophilus* elucidated a defined biosynthetic gene cluster (BGC) for pyrrolomycins that indicate the presence of a cytochrome P450 gene (Pyr20) adjacent to nitrate reductase (Pyr18) and nitrite reductase (Pyr19) genes. Emerging literature on natural products thaxtomin A and rufomycin evidences nitration capabilities of P450s. We hypothesize that *S. vitaminophilus* uses nitrogen cycle enzymes Pyr18 and Pyr19 to produce NO or NO₂⁻ for Pyr20 to utilize in nitration. In substrate-screening assays, Pyr20 showed selective binding to pyrrolomycin C, suggesting it is the nitrating substrate. Steady-state and single turnover in-vitro reactions with Pyr20, pyrrolomycin C, and various nitrogen donors have yet to yield a nitrated product. Our latest work examining a range of biochemical assays in the presence of pyrrolomycin C will be discussed.

S44: Rhodium(II)-catalyzed hydrosilylation of styrene derivatives: Reactivity and regioselectivity

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In this study, we investigate the hydrosilylation of styrene derivatives catalyzed by $\text{Rh}_2(\text{OAc})_4$ using tertiary hydrosilanes as the silylating reagents. A major challenge in hydrosilylation reactions is controlling regioselectivity, which determines the position at which the silyl group is incorporated across the alkene. Although many catalytic systems predominantly afford anti-Markovnikov products, achieving high regioselectivity under mild reaction conditions remains an important objective. Here, we evaluate the catalytic activity of $\text{Rh}_2(\text{OAc})_4$ toward the hydrosilylation of aromatic alkenes and examine its efficiency and selectivity for the formation of the desired organosilicon products.

S45: Biosynthesis of a putative isothiocyanate indole-like natural product

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Isothiocyanates are desirable natural products for their bioactivity which ranges from fungicidal activity to cancer cell growth suppression. Most known isothiocyanates are produced by plants, while only four are known to be produced by bacteria. Of those four, only one is produced by Actinobacteria. Genome mining identified a 12 kb putative biosynthetic gene cluster (BGC) in *Actinosynnema* sp. NPDC023815 containing genes likely involved in isothiocyanate indole biosynthesis. The BGC does not follow canonical biosynthetic pathway types, making it especially interesting because it suggests a unique pathway with promiscuous enzymes. To identify the natural product produced by this putative BGC, we will be taking parallel in vivo and in vitro approaches. The in vivo approach involves cloning the BGC and integrating it into a heterologous host for production and isolation. The in vitro approach involves isolating the individual genes and purifying their resulting proteins to build the natural product step-by-step. This two-pronged approach will allow for the identification of novel oxygenases, an isothiocyanate indole natural product, and chemical intermediates.

S46: Synthesis of CF₃-Containing Dihydropyrido[1,2-a]indolones via a Visible-Light-Promoted Radical Cascade [4 + 2]/[4 + 2] Cycloaddition

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Both dihydropyrido[1,2-a]indolones (DHPis) and CF_3 -containing compounds are widely found in natural products and pharmaceutical agents. Therefore, the development of new synthetic methods for the construction of CF_3 -containing dihydropyrido[1,2-a]indolones remains highly significant, which is the aim in this project. Specifically, visible-light-mediated radical cascade cyclization is the synthetic strategy of particular interest to our research because of its operational simplicity, mild reaction conditions, and excellent step economy. In this study, a photo-driven $\text{Ir}(\text{ppy})_3$ -catalyzed radical cascade [4 + 2]/[4 + 2] cycloaddition of simple N-acryloyl indoles and Umemoto Reagent I is reported, which provides a straightforward and efficient route to a range of CF_3 -containing dihydropyrido[1,2-a]indolones (under mild conditions). The protocol exhibits broad functional group tolerance, including various synthetically useful substituents. The reaction proceeds through four sequential radical additions, leading to the dimerization of N-acryloyl indoles along with the formation of four C–C bonds and two fused six-membered rings. The successful scale-up experiment and product derivatization studies further demonstrate its synthetic utility. A plausible reaction mechanism has also been proposed based on mechanistic studies and the isolation of several undesired [4 + 2] cycloaddition byproducts.

S47: An outer-sphere threonine residue is critical for NO-dependent tryptophan nitration by the cytochrome P450, TxtE

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Aromatic nitro compounds serve as crucial building blocks and synthetic intermediates in the development of scaffolds for pharmaceuticals, agrochemicals, dyes, and explosives. Traditional aromatic nitration methods are limited by hazardous reagent use including nitric and sulfuric acids, highly exothermic conditions, and poor regioselectivity, which lead to extensive purification requirements and increased environmental and manufacturing costs. Biocatalysis offers a promising alternative, enabling regioselective nitration under mild reaction conditions. TxtE, a cytochrome P450, catalyzes the direct nitration of L-tryptophan to 4-nitro-L-tryptophan using dioxygen and nitric oxide as co-substrates. While TxtE's nitration mechanism is not fully understood, emerging evidence suggests that hydrogen bond networks play a key role in cytochrome P450 catalysis. To investigate the role of such networks in TxtE function, site-directed mutagenesis was performed at residue Thr250, a position hypothesized to contribute to hydrogen bond stabilization. Mutants TxtE_{T250A}, TxtE_{T250S}, and TxtE_{T250V} were generated and characterized using spectroscopic techniques including stopped-flow spectrophotometry and electron paramagnetic resonance spectrometry to evaluate their effects on the spin-equilibrium of the resting ferric state and the lifetime of the ferric-superoxo intermediate. Furthermore, their nitration activity was assessed using liquid chromatography-mass spectrometry. Our latest results will be discussed and their implications on how proton transfer governs TxtE's catalysis, which can contribute to the rational design of biocatalysts for sustainable aromatic nitration.

S48: Beyond Classical Force Fields: Physics-Driven Assessment of the Grappa Machine-Learned Force Field on the FoldBind Dataset

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Physics-based molecular modeling has traditionally depended on empirically fitted force fields built from manually curated atom types. Recent advances in AI are reshaping this landscape, replacing hand-tuned parameterization with machine-learned models. Here, we integrate the Grappa machine-learned force field into MELD (Modeling Employing Limited Data), a Bayesian inference framework that enhances conformational sampling by incorporating ambiguous or noisy physical restraints within replica-exchange molecular dynamics. Grappa's neural-network-predicted bonded parameters were benchmarked directly against classical force fields (ff14SB and ff14SBside), with nonbonded interactions held fixed to isolate the effect of the learned bonded terms. To rigorously stress-test this hybrid framework, we introduce the FoldBind Benchmark set: 18 systems spanning 14 protein-folding targets and 4 peptide-protein complexes that fold upon binding, extending validation well beyond near-native refinement into large-scale conformational transitions. Across the full FoldBind set, MELD-Grappa consistently recovered native experimental structures. For the folding benchmarks, 9 systems under standard MELD and 10 under MELD-Adapt reached sub-angstrom accuracy in their best-sampled structures, with previously difficult cases - 2HBA, 1POU, and ubiquitin - showing substantial gains over classical force fields. Clustering confirmed this convergence was robust: the native basin was the most populated cluster in 12 of 14 systems with standard MELD and 13 of 14 with MELD-Adapt. For peptide binding, native-like interfacial geometries were recovered for MDM2-p53, MDM2-PDIQ, and BRD3-ET-TP, with funnel-plot analysis showing that higher-affinity binders funneled more sharply toward the native state. End-to-end hairpin distance analysis further showed that MELD-Adapt-Grappa reproduced experimentally established folding pathways for protein G, protein L, and their variants, including registry-shifted folding intermediates. Despite the added neural-network evaluation, MELD-Grappa retained computational efficiency comparable to classical force fields. These results establish that AI-derived bonded parameters can be integrated into physics-based Bayesian sampling without loss of accuracy or speed, and position the FoldBind dataset as a practical, demanding testbed for future force-field development.

S49: Double crossover DX tile facilitated the cyclization of small-sized DNA oligomers by phosphodiester linkage

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Circular DNA (circDNA) has advantages because it lacks free termini, which are targets for many nucleases, enabling practical and in vivo applications. Typical in vitro synthesis techniques include ligating DNA ends using a DNA template to bring them together, followed by ligation with either T4 DNA ligase or a chemical reagent. This is an efficient and well-known method for ligating oligonucleotides over 30 nucleotides (nt) long, but synthesis success is limited for shorter oligonucleotides. To overcome this limitation, we employed a double crossover (DX) tile template to promote the cyclization of 16 – 50 nt long ssDNA by phosphodiester-linkage using 1-cyanoimidazole as a condensing agent. Using this method, we achieve cyclization yields of 12 – 49%. Additionally, phosphoanhydride-linked circDNAs were successfully synthesized with yields of up to 80% without assistance from a DX tile, with sizes ranging from 14 – 50 nt. Finally, using a 12% AA:BA denaturing PAGE, we observed a trend in relative electrophoretic mobility shifts in both linear and circular oligonucleotides. Specifically, circDNAs longer than 30 nt migrate slower than their linear precursors, while circDNAs shorter than 30 nt migrate faster. These results show that a double-crossover DX tile using 1-cyanimidazole ligation techniques is an efficient method for cyclizing DNA oligonucleotides shorter than 50 nt via phosphodiester linkages. Our results indicate that stabilizing the reactive conformation of the ssDNA precursor by forming multisite complexes within the DX tile nanostructure improves the cyclization yield and extends the accessible size range in comparison with other templating methods. Our findings also provide insights into the electrophoretic mobility of short circDNA fragments for further studies on circDNA hydrodynamic behavior.

S51: Lyso-PCTP: A Reengineered Lipid Biosensor for Early PDAC Diagnosis and Monitoring

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Pancreatic ductal adenocarcinoma (PDAC) ranks 10th in US cancer incidence, yet it causes more deaths per year than breast cancer, ranked 1st, a disparity largely driven by complications regarding late diagnosis and a lack of effective early screening. Per recent publications by Peterka et al. and others, lipid panels show significant potential for early diagnosis and monitoring, with sensitivity and specificity >95% across all stages, although current assays for lipid biomarkers remain too costly and impractical for clinical use. To fill this translational gap, Lyso-PCTP presents as the first optical biosensor to leverage the extremely specific lipid-binding properties of phosphatidylcholine transfer protein (PCTP) for robust molecular quantification via Förster resonance energy transfer (FRET). Through 12 systematic mutations, PCTP binding was reengineered from its native ligand, phosphatidylcholine 16:0/18:2 (PLPC), to lysophosphatidylcholine (LPC) 18:2, a significant lipid biomarker for PDAC risk, with selectivity then validated through multiple molecular dynamics simulation in GROMACS against PLPC, 4 common blood phospholipids, and 2 other LPC species. Following per atom fluctuation and distance analyses, residues A24 and K167 were identified as optimal labeling sites with a Cy2/Cy7 Förster Resonance Energy Transfer (FRET) donor-acceptor pair, yielding a change in FRET efficiency of 28%, a value readily detectable with clinical microplate technology widely present in modern hospital infrastructure. Lyso-PCTP thus proposes the first example of transfer protein based lipid biosensing with broader implications in PDAC diagnosis and monitoring, although further validation is necessary in vitro.

S53: Effect of sodium bicarbonate concentration and PLGA composition on degradation and release of magnesium ions from PLGA microspheres.

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Mineral ions, specifically those found in oral supplements, have a crucial role in regulating the functions of many organs. Deficiencies can lead to arrhythmias, heart failure, type 2 diabetes, osteoporosis and more. Although oral supplements are used to ameliorate ion deficiency in patients, alternatives remain underexplored, despite needs of patients who cannot effectively absorb ions through their gastrointestinal (GI) tract. Geriatric patients are particularly affected because age-related changes in the GI tract, decrease ion absorption. In addition, there are several medications, like omeprazole, which suppress transcellular and paracellular magnesium absorption in the small intestine and colon. This study focuses on a strategy for delivering ions transdermally using microspheres. Magnesium ions and sodium bicarbonate are sequestered within PLGA-based hollow microspheres, fabricated using a double emulsion technique. Sodium bicarbonate could then react with protons in the interstitial fluid of the dermis, producing carbon dioxide that accelerates PLGA degradation. The microspheres would be incorporated into poly(vinylpyrrolidone) (PVP) based microneedles. Microneedle patches would enable intradermal administration of mineral ions in a controlled manner, enabling them to quickly enter the systemic circulatory system, bypassing the digestive tract and reducing side effects.

S54: Computational Design of COMT-Targeting PROTACs for Parkinson's Disease Using Cereblon-Mediated Targeted Protein Degradation

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Proteolysis-targeting chimeras (PROTACs) have emerged as a promising therapeutic strategy for selective protein degradation by recruiting E3 ubiquitin ligases. Catechol-O-methyltransferase (COMT), an enzyme involved in dopamine metabolism, represents an attractive therapeutic target because dysregulated dopamine homeostasis contributes to the pathogenesis and progression of Parkinson's disease. In the present study, ten novel PROTAC candidates (P1–P10) were designed to target COMT and evaluated for their binding affinity toward the cereblon (CRBN) receptor using molecular docking analysis. The calculated binding energies ranged from -4.86 to -5.45 kcal/mol, indicating favorable interactions between the designed molecules and the target protein. Among all candidates, P9 exhibited the strongest binding affinity with a binding energy of -5.45 kcal/mol, followed by P8 (-5.24 kcal/mol), P4 (-5.19 kcal/mol), and P10 (-5.18 kcal/mol). Detailed interaction analysis revealed that P9 formed multiple stabilizing interactions, including hydrogen bonds, hydrophobic contacts, and π -cation interactions within the cereblon binding pocket. The enhanced affinity of P9 is likely associated with the presence of a sulfate-containing substituent that promotes additional electrostatic and hydrogen-bonding interactions. Overall, the results demonstrate that structural modifications significantly influence cereblon binding and identify P9 as a promising lead compound for further optimization and experimental validation. These findings provide valuable insights for the rational design of cereblon-recruiting PROTACs with improved therapeutic potential.