

Program and Abstracts for the

**2024 DOE BES Separation Science
Principal Investigators' Meeting**

DoubleTree by Hilton Washington DC North/Gaithersburg
Gaithersburg, Maryland

September 10-12, 2024

Chemical Sciences, Geosciences, and Biosciences Division
Office of Basic Energy Sciences
Office of Science
U.S. Department of Energy

Foreword

The 2024 Separation Science Research PI Meeting was sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences (BES), U.S. Department of Energy (DOE) and held on September 10-12, 2024, at the DoubleTree by Hilton Washington DC North/Gaithersburg in Gaithersburg, Maryland. The purpose of this meeting was to accelerate research progress through collegial interactions by developing a common understanding of present activities, maximizing potential for collaboration, identifying the scientific needs of the research community, and providing an opportunity to discuss future research directions among the BES Separation Science Program PIs. Separation Science research activities within BES emphasize fundamental, hypothesis-driven molecular-level experimental and computational research projects that address questions to discover, understand, predict, and control demixing transitions. The resulting knowledge will enable chemical separation paradigms that may become the basis for solutions to current and long-term energy challenges.

This year's meeting, which contained 22 oral and 45 poster presentations by BES Separation Science PIs, was organized into four themes: Advancing Separations by Exploiting and Predicting Dynamic States and Solvation Effects; Chemically Driven Reactive Separations for Dilute Constituent Removal and Release; Molecular Driven Separation Phenomena: New Phase Formation, Confinement, and/or Intermolecular Interactions; and Non-Thermal Mechanisms for Energy Efficient Separations. Two breakout sessions were held that aimed at helping the community look back to look forward. The first breakout session, entitled "Reflections of Separation Science since the 2019 Report and What Fundamental Science Should Deliver by 2029/2039?" allowed participants to reflect on the progress made since the 2019 NASEM Report, A Research Agenda for Transforming Separation Science and to discuss new opportunities arising from that progress. The second breakout session, entitled "Separation Science and Data Science – Challenges and Future Needs" provided participants an opportunity to discuss overlapping goals of these two fields to identify how fundamental knowledge gaps in separation science might be advanced using data science.

Thank you to the program investigators as well as the students, post-doctoral associates, and collaborators who are involved in this research, for their dedication to the continued success and visibility of the BES Separation Science Program. Thank you to detailees Carrie Farberow and Vanda Glezakou for assisting with the planning and execution of this meeting; meeting co-chairs Santa Jansone-Popova, Ryan Lively, and Michael Tsapatsis for formulating the ideas for, leading the discussion on, and summarizing the outcomes of the two breakout sessions; and Raul Miranda for his support of the program and role as Team Lead for Chemical Transformations. Finally, thank you to Teresa Crocket (BES) and the Oak Ridge Institute for Science and Education staff for their logistical and technical support of this meeting.

Amanda J. Haes, Ph.D.
Program Manager
Separation Science Program, Office of Basic Energy Sciences
U.S. Department of Energy

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Agenda

2024 DOE BES Separation Science Principal Investigators' Meeting

Location: DoubleTree Hotel, 620 Perry Parkway, Gaithersburg, Maryland, 20877

Meeting Co-Chairs: **Santa Jansone-Popova** (Oak Ridge National Laboratory), **Ryan Lively** (Georgia Institute of Technology), **Michael Tsapatsis** (Johns Hopkins University)

Tuesday, September 10, 2024

7:30-8:30 AM Breakfast and Presentation/Poster Setup

8:30 AM Welcome, News from DOE-BES Chemical Sciences, Geosciences, and Biosciences (CSGB) Division

Gail McLean, Director, DOE Office of Basic Energy Sciences, CSGB Division

Session 1 **Advancing Separations by Exploiting and Predicting Dynamic States and Solvation Effects**

Session Chair: **Francesco Paesani**, University of California, San Diego

9:00 AM **Daniel (Dan) Schwartz**, University of Colorado Boulder

Single-molecule Dynamics in Complex and Interface-Rich Separations Environments

9:30 AM **Ngai Yin Yip**, Columbia University

Separation of Lithium Ions from Competing Alkali Metal Cations using Switchable Solvent Selective Extraction

10:00 AM Break

10:30 AM **Vyacheslav (Slava) Bryantsev**, Oak Ridge National Laboratory

Interfacial and Photochemical Control of CO₂ Binding, Transport, and Release in Direct Air Capture

11:00 AM **Daniel Higgins**, Kansas State University

Solvation and Pore Surface Interactions Govern Solute Diffusion in Binary Ethanol/Water Mixtures Confined within Anodic Alumina Nanopores

11:30 AM **Michael Servis**, Argonne National Laboratory

Interplay between Solution Structure and Separations

12:00 PM Working Lunch with Continued Discussion/Presentation Setup

Session 2 **Chemically Driven Reactive Separations for Dilute Constituent Removal and Release**

Session Chair: **Abigail Knight**, University of North Carolina at Chapel Hill

- 1:30 PM Introduction, Overview, and Meeting Charge
Amanda Haes, Program Manager, Separation Science Program
- 1:50 PM **David Heldebrant**, Pacific Northwest National Laboratory
Harnessing Confinement Effects, Stimuli, and Reactive Intermediates in Separations
- 2:20 PM **Jindal Shah**, Oklahoma State University
Ionic Liquids for Direct Air Capture of CO₂ using Electric-Field-Mediated Moisture Gradient Process
- 2:50 PM Break/Presentation/Poster Setup

Breakout Session A Reflections of Separation Science Progress since the Report in 2019, and What Fundamental Science Should the Field Deliver by 2029/2039?
Session Chair(s): **Ryan Lively, Michael Tsapatsis, Santa Jansone-Popova**

- 3:00 PM Topic Introduction and Breakout Session Charge
Ryan Lively, Meeting Co-Chair
- 3:10 PM Breakout Discussion, *See Attachment for Format and Leading Questions*
- 4:15 PM 2-Minute Reports from Table Scribes Back to the Entire Group
Led by **Meeting Co-Chairs**
- 4:45 PM Poster Highlights/Lightning Round I (1 slide/60 sec/poster introduction)
- 5:15 PM Posters (see list)/Continued Discussion
- 7:00 PM Dinner/Continued Discussion (on your own)

Wednesday, September 11, 2024

7:30-8:25 AM Breakfast and Presentation/Poster Setup

8:25 AM Announcements

Amanda Haes

Session 3 **Molecular Driven Separation Phenomena: New Phase Formation, Confinement, and/or Intermolecular Interactions - I**

Session Chair: **Eric Schelter**, University of Pennsylvania

8:30 AM **David Cantu**, University of Nevada, Reno

Identifying Small Circular Peptides for Ln/Ln Selectivity with Yeast Display, Molecular Simulation, and Spectroscopy

9:00 AM **Jovan Kamcev**, University of Michigan

Ion Transport in Highly Charged Polymer Membranes with Subnanometer Free Volume Elements

9:30 AM **Kristin Bowman-James**, University of Kansas

Molecular to Mesoscale Targeting of Oxoanions with Multi-Tasking Hosts

10:00 AM Break

10:30 AM **Jeffrey Long**, Lawrence Berkeley National Laboratory

Interrogating Selective Metal-Adsorbate Interactions in Metal-Organic Frameworks

11:00 AM **Merlin Bruening**, University of Notre Dame

Highly Selective Membrane-Based Ion Separations

11:30 AM **Gangli Wang**, Georgia State University

Memristor Effects for the Selective Ion Enrichment and Entrapment at Asymmetric Nanointerfaces

12:00 PM Working Lunch with Continued Discussion/Presentation Setup

Session 4 **Non-Thermal Mechanisms for Energy Efficient Separations**

Session Chair: **Justin Wilson**, University of California, Santa Barbara

1:30 PM **Revati Kumar**, Louisiana State University

Bridging the Length Scales in Ionic Separations via Data-Driven Machine Learning

2:00 PM **Mark Jensen**, Colorado School of Mines

Driving Selectivity Among Rare Earth Elements through Phase Modifiers

2:30 PM **Chong Liu**, University of Chicago

Probing the Coordination in Confinement for Electrochemical Separation among Rare Earth Elements

2:45 PM Break/Presentation/Poster Setup

Breakout Session B Separation Science and Data Science – Challenges and Future Needs
Session Chair(s): **Santa Jansone-Popova, Ryan Lively, Michael Tsapatsis**

3:00 PM Topic Introduction and Breakout Session Charge

Santa Jansone-Popova, Meeting Co-Chair

3:10 PM Breakout Discussion, *See Attachment for Format and Leading Questions*

4:15 PM 2-Minute Reports from Table Scribes Back to the Entire Group

Led by **Meeting Co-Chairs**

4:45 PM Poster Highlights/Lightning Round II (1 slide/60 sec/poster introduction)

5:15 PM Posters (see list)/Continued Discussion

7:00 PM Dinner/Continued Discussion (on your own)

Thursday, September 12, 2024

7:30-8:25 AM Breakfast and Presentation/Poster Setup

8:25 AM Announcements

Amanda Haes

Session 5 **Molecular Driven Separation Phenomena: New Phase Formation, Confinement, and/or Intermolecular Interactions - II**
Session Chair: **Jerry Lin**, Arizona State University

8:30 AM **Tanya Prozorov**, Ames Laboratory

Geo-Inspired Separation of Rare Earth Elements

9:00 AM **Sameh Elsaïdi**, Illinois Institute of Technology

Controlling Densification-Induced Structural transformations in Metal-Organic Frameworks for Size-Selective Separations

9:15 AM **Bryan Beckingham**, Auburn University

Transport of Complex Mixtures in Ion-Containing Polymer Membranes

9:30 AM **Venkat Ganesan**, University of Texas at Austin

Nanostructured Polymer Membranes with Chemical Structure Selectivity

10:00 AM Break/Presentation Setup

10:30 AM **Amar Flood**, Indiana University

Binding Anions Selectively with Modular Triazolophanes and Releasing Them with Light

11:00 AM **Phillip Milner**, Cornell University

Carbon Capture Beyond Amines using Oxidatively Stable Oxygen-Based Nucleophiles

11:30 AM Briefing by Program Co-Chairs and Discussion

Michael Tsapatsis with assistance from **Santa Jansone-Popova** and **Ryan Lively**

12:00 PM Summary, Outcomes, and Path Forward

Amanda Haes

12:30 PM Adjourn

Breakout Sessions

Breakout Session A (Tuesday at 3 pm) - Reflections of Separation Science Progress since the 2019 Report, and What Fundamental Science Should the Field Deliver by 2029/2039?

We will breakout into small teams and discuss the recent National Academies report on Separations Science. Each table will focus on one of the key themes highlighted by that report. Please assign a scribe at the start of the session and summarize your responses in 1 PowerPoint slide. The scribe will present a PowerPoint slide for 2 minutes upon reconvening and will send it to tsapatsis@jhu.edu.

The tables are tasked with answering the five questions below.

For Questions 1, 2 and 3, see Box 1 for 2019 report research theme(s) assigned to the table. For an Overview of Earthshots, see Box 2.

1. What are the key breakthroughs or achievements in the last 5 years that are aligned with the 2019 report research theme(s) assigned to the table?
2. What knowledge gaps remain between the key research objectives of the 2019 report research theme(s) assigned to the table, and what we have learned in the intervening 5 years?
3. At least four of the eight DOE Earthshots rely on separations. How does the 2019 report research theme(s) assigned to the table intersect with (and hopefully address) key challenges for achieving the Earthshots?
4. What are the key research items that were missed by the 2019 report, and what are the rapidly emerging scientific questions that could be considered if an 'updated' report were to be made today?
5. "Success" for an Earthshot is intrinsically an interdisciplinary endeavor. Identify ways in which the various disciplines supported within separation science (e.g., biology, chemistry, engineering, mathematics, physics) can contribute scientifically to the Earthshots.

Box 1: Themes from the 2019 Report:

Theme 1: Designing Separation Systems That Have High Selectivity, Capacity, and Throughput

1-A. Advance the Understanding of Complex Systems

1-A-i: Development of measurement and simulation techniques for multicomponent mixtures. **(Table 1)**

1-A-ii: Design of separation systems that can handle a large dynamic range. **(Table 2)**

1-A-iii: Trace analysis and multistep processes. **(Table 2)**

1-B. Explore the Entire Array of Thermodynamic and Kinetic Mechanisms

1-B-i: Explore a broader variety of multiple forces, entropic strategies, and cooperative binding mechanisms. **(Table 3)**

1-B-ii: Design for recycle and reuse. **(Table 3)**

1-B-iii: Explore a wide array of chemical transformations to facilitate separations. **(Table 4)**

1-B-iv: Determine and control rates of species transport. **(Table 4)**

1-C. Characterize the Interface and Understand the Interfacial Forces

1-C-i: Controlling interface structure and transport to enhance separations. **(Table 5)**

1-C-ii: Understanding interfaces in separation systems. **(Table 5)**

1-D. Understand the Physical Changes That Result from External Forces (Table 6)

Theme 2: Understanding Temporal Changes That Occur in Separation Systems

2-A. Determine Changes from Nonequilibrium States That Affect the Chemical and Physical Properties of Separation Materials (Table 7)

2-B. Determine the Identity and Rates of Fundamental Chemical Reactions That Can Change Separation Materials and How the Reactions Are Influenced by Operating Conditions (Table 8)

2-C. Understand the Fate of Unwanted Products (Table 9)

2-D. Explore Alternative Strategies to Address Temporal Changes in Separation Systems (Table 10)

Box 2: Overview of DOE Earthshots: “The climate crisis calls for a different kind of moonshot. Energy Earthshots™ will accelerate breakthroughs of more abundant, affordable, and reliable clean energy solutions within the decade. They will drive the major innovation breakthroughs that we know we must achieve to solve the climate crisis, reach our 2050 net-zero carbon goals, and create the jobs of the new clean energy economy. The Energy Earthshots target the remaining solution points of the most challenging technical problems across our energy economy.”

<https://www.energy.gov/sites/default/files/2024-04/energy-earthshots-2024-factsheet.pdf>

Carbon Negative Shot™
Remove CO₂ from the atmosphere and durably store it at meaningful scales for less than \$100/net metric ton of CO₂-equivalent within a decade.

Hydrogen Shot™
Accelerate innovation and spur demand of clean hydrogen by reducing the cost by 80% to \$1 per 1 kilogram of clean hydrogen within 1 decade.

Clean Fuels & Products Shot™
Decarbonize the fuel and chemical industry through alternative sources of carbon to advance cost-effective technologies.

Industrial Heat Shot™
Develop cost-competitive industrial heat decarbonization technologies with at least 85% lower greenhouse gas emissions by 2035.

Enhanced Geothermal Shot™
Reduce the cost of enhanced geothermal systems by 90% to \$45 per megawatt hour by 2035 to unlock Earth's nearly inexhaustible heat resources to provide reliable, clean power for Americans and expand opportunities for a robust domestic geothermal industry.

Long Duration Storage Shot™
Achieve affordable grid storage for clean power—anytime, anywhere—by reducing the cost of grid-scale energy storage by 90% for systems that deliver 10+ hours of duration within the decade.

Floating Offshore Wind Shot™
Drive down costs to \$45 per megawatt hour by 2035 to spur U.S. leadership in floating offshore wind technology, accelerate decarbonization, and deliver benefits for coastal communities.

Affordable Home Energy Shot™
Reduce the cost of energy-efficient retrofits in affordable homes by 50% and decrease residents' energy costs by at least 20% within a decade.

Breakout Session B (Wednesday at 3 pm) - Separation Science and Data Science – Challenges and Future Needs

*Each table will be assigned to respond to all general questions and one specific question. Please assign a scribe at the start of the session and summarize your responses in 1 PowerPoint slide. **The scribe will present one PowerPoint slide for 2 minutes upon reconvening and will send the slide to tsapatsis@jhu.edu***

Specific Questions (two tables will be assigned each of the questions):

1. How can data collection/curation/processing be improved to enhance the utility of data in separation science? Are existing databases sufficient to advance the field? **(Tables 1 and 2)**
2. What steps should be taken to ensure data quality and reproducibility? Is collaborative research across different institutions necessary to address data quality and reproducibility needs? **(Tables 3 and 4)**
3. What are the limitations of current experimental, ML, simulations, and data analytics approaches in accurately predicting separation outcomes? What key factors influence the accuracy of these predictive models? **(Tables 5 and 6)**
4. What are the most exciting opportunities for autonomous discoveries in separation science using data science? **(Tables 7 and 8)**
5. How can data science be leveraged to accelerate the discovery of novel separation processes and to support the development of promising new chemistries for advancing the separations field? **(Tables 9 and 10)**

General Questions (for all tables):

- A. How can interdisciplinary collaboration be fostered to develop next-generation separation technologies? What approaches can improve communication and synergism among the various disciplines supported within separation science ((e.g., biology, chemistry, engineering, mathematics, physics)?
- B. What are best practices for training the next generation of researchers in this synergistic field? What new educational programs are needed or how can existing programs be updated to meet the needs?
- C. Fundamental discoveries and insights drive innovation; what steps might be taken to ensure these breakthroughs lead to practical technologies? What current strategies effectively bridge the gap between basic/early-stage research to applied science to accelerate next-generation technology development?

Poster Sessions

Tuesday, September 10, 2024

Last Name	Board Number	Poster Title
Bandosz	1	<i>Insight into a Full Engagement of Highly Porous Carbon Surfaces in an Effective PFAS Separation</i>
Bara	2	<i>Gas Transport and Separation Mechanisms in Ionic Polymer Membranes</i>
Bollini	3	<i>Controlling CO₂ Solvation and Binding in its Direct Capture from Ambient Air Over Inorganic Sorbents</i>
Carrick	4	<i>Synergistic Approaches to Advanced Minor Actinide Separations</i>
Chan	5	<i>The Rare Earth Project: Using Light and Other Stimuli to Separate Lanthanide Materials</i>
Clark	6	<i>Bespoke Liquid/Liquid Interfaces that Modulate Solute Transport Mechanisms in Solvent Extraction</i>
Cotruvo	7	<i>Probing Lanmodulin's Mechanisms of Rare Earth Selectivity for Protein-Based Bioseparations</i>
Custelcean	8	<i>Reactive Separations of Superhydrophilic Anions and CO₂ from Ultradilute Environments</i>
Dai	9	<i>Fundamental Studies of Novel Separations</i>
Galizia	10	<i>Elucidating the Molecular Mechanisms by which Porous Polymer Networks Affect Structure, Aging Propensity, and Selectivity of Microporous Glassy Polymer Membranes using a Multiscale Approach</i>
Guo	11	<i>Addressing Temporal Changes in Polymer Gas Separation Membranes via Leveraging Free Volume Design</i>
Gurkan	12	<i>From Structured Solvents to Hybrid Materials for Chemically Selective Capture and Electromagnetic Release of CO₂</i>
Hupp	13	<i>Coordination-Chemistry-Derived Materials Featuring Nanoscale Porosity and Selective Chemical Separation Capabilities</i>
Hutchins	14	<i>Extraction of Rare Earth Elements from Waste Streams Using Chemically-Enhanced Electrodialysis (CEED)</i>
Jacobs	15	<i>Leveraging High-throughput Computation and Machine Learning to Discover and Understand Low-Temperature Fast Oxygen Conductors</i>
Jansone Popova	16	<i>Transforming Critical Materials Separation using Precision Control</i>
Johnson	17	<i>Ion Separations with Functionalized Laminate Membranes</i>
Knight	18	<i>A Macromolecular Selection Platform for the Isolation of Lanthanide Ions</i>
Knope	19	<i>Transforming Critical Materials Separations through Metal-Oxo Cluster Chemistry</i>

Koros	20	<i>Fundamental Improvements in Carbon Molecular Sieve Membranes for Energy Intensive Separations</i>
Kuroda	21	<i>Microscopic Insights into the Solvation Properties of Complex Non-Ionic Deep Eutectic Solvents</i>
H. Lin	22	<i>Integrated Direct Air Capture and H₂-Free CO₂ Valorization</i>
Tang	23	<i>Data Science-Enabled Ion Transport in Metallopolymer-Based Anion Exchange Membranes</i>
Shi	24	<i>Integrated Direct Air Capture and H₂-Free CO₂ Valorization</i>

Wednesday, September 11, 2024

Name	Board Number	Poster Title
Abergel	1	<i>The Rare Earth Project</i>
Anderson	2	<i>Ionic Liquids and Deep Eutectic Solvents in Separation Science: An Understanding of Nanoscale Ordering</i>
J. Lin	3	<i>Understanding Lithium-Ion Transport in Micropores Filled with Liquid Electrolyte</i>
Li-Oakey	4	<i>Single-Crystalline and Polycrystalline Covalent Organic Framework Membranes: Experimentally and Theoretically Connecting Formation Conditions to Mass Transfer and Selectivity Performance</i>
Lively	5	<i>Exploring the Potential of "Sorpvection" as a Separation Modality for the Recovery of Dilute High Value Species</i>
McGuirk	6	<i>Building a Scientific Foundation for a New Generation of Low Energy Adsorptive Separations: Probing the Role of Responsive Structural Flexibility Using Synthetic Porous Frameworks</i>
Murad	7	<i>Exploring the Feasibility of Aqua-Mining for Recovery of Critical Metals Using Computational Molecular Modeling</i>
Paesani	8	<i>Reticular Materials and Data-Driven Computer Simulations for Seawater Mining of Valuable Metals</i>
Prabhakaran	9	<i>Electric Field Driven Ionic Liquid Interphase Formation for Separation of Critical Minerals</i>
Schelter	10	<i>Advancing Selective, Reactive Separations of Rare Earth Elements through Tailored Coordination Chemistry and Photochemistry</i>
Schlossman	11	<i>Ion-Extractant Coordination at Liquid Interfaces Relevant to Solvent Extraction</i>
Schulz	12	<i>Polymeric Chelators for Rare-Earth Element Extraction and Separation</i>
Sessler	13	<i>Receptor-based Approaches to Separations</i>
Snoeyink	14	<i>Role of Energy in Continuous Dielectrophoretic Molecular Separations</i>
Su	15	<i>Investigation of Thermodynamic and Kinetic Selectivity Mechanisms in Redox-Mediated Electrochemical Separations</i>
Taylor	16	<i>Long-Range Cooperativity among Rare-Earth Binding Sites in Organic Materials</i>

Tsapatsis	17	<i>Permeation Properties of Disordered Metal-Organic Framework Membranes Made by Vapor Phase Deposition and Irradiation Treatments</i>
Uysal	18	<i>Aqueous Interfaces in Chemical Separations</i>
Wilson	19	<i>Leveraging Macrocyclic Chelators for Rare Earth Element Separations</i>
Xia	20	<i>Understanding the Structure-Property Relationships and Unusual Aging Behavior of Microporous CANAL Polymer Membranes for Gas Separation</i>
Yang	21	<i>Autonomous Discovery of Selective Separation of f-Elements for Clean Energy</i>

Abstracts

From Small-Molecule Chelators to Macromolecular Assemblies: Combining Electronic Structure with Allosteric Effects for Enhanced Rare Earth Selectivity

Rebecca J. Abergel,^{1,2} Polly L. Arnold,^{1,2} Wayne W. Lukens,¹ Michael D. Connolly,¹ Ting Xu,^{1,2} Wibe A. de Jong,¹ Emory M. Chan,¹ Stefan G. Minasian¹

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Key Words: Bioinspired Recognition; Inorganic Chelation; Reactive Separations; Solvation; Rare Earths

FWP CH20CRIMAT: The Rare-Earth Project: Harnessing Differences in Electronic Structure for Multiscale, Multicomponent Separations

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Postdoc(s): Rebecca Hamlyn, Sabari Ghosh, Megan Keener, Daniel Loh, Jia-Ahn Pan, Roger M. Pallares, Amy Price, Xiao Qi, Artom Skripka, Patrick W. Smith

Student(s): Gretchen M. Brown, Elise Eng, David J. Fiszbein, Ivan Jayapurna, Baichuan Na.

Research Project Scope.

The overall goal of this project is to delineate fundamental principles that will guide the incorporation of specific molecular systems into higher order materials, ultimately leading to breakthrough and innovation in rare earth extraction processes. The proposed scope of work include (i) the design, synthesis, and characterization of fundamentally new molecular architectures and biomimetic materials that enable electronic structure manipulation and selective charge- or size-based binding of rare earth metal ions; (ii) the discovery of new separation principles and materials that efficiently discriminate rare earth elements from complex mixtures, including possible cooperative, switch-like mechanisms, and allow for subsequent recovery and reuse of pure rare earth compounds with minimal energy input; and (iii) the use of in situ and in operando physical characterization techniques to directly probe the physical and chemical properties of rare earth systems and can be used to correlate behavior with electronic structure or monitor uptake and transport of rare earth metal ions. Computational methods, including machine learning approaches, are combined with high-throughput screening, to support and accelerate the design of new functional materials and molecules for rare earth separations, as well as the interpretation of the physical characterization techniques required for accelerated discovery and design in this context.

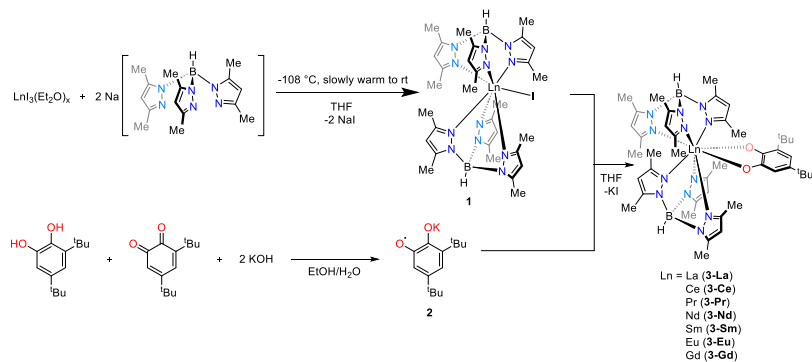


Figure 1. Synthetic scheme for the isolation of LnTp*₂(DTBSQ) complexes.

Recent Progress.

Tuning RE Oxidation State for Easier Separation. We have been exploring orbital use and overlap across a series of isostructural LnTp*₂(DTBSQ) (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tp* = tris(3,5-dimethyl-1-pyrazolyl)borate, DTBSQ = 3,5-di-*tert*-butyl-*o*-semiquinone) complexes that were isolated and

characterized crystallographically (**Fig. 1**). While the Ln-N bonds demonstrate the expected shortening across the Ln series, the C-O and C(O)-C(O) distances in the bound DTBSQ ligand are diagnostic for the redox state of the DTBSQ ligand and show separate trends: (a) C-O bonds decrease in the order Nd > Gd ~ Sm > Eu ~ La > Pr ~ Ce; (b) C(O)-C(O) bonds decrease in the order Ce > Sm > Nd > Pr > La > Eu ~ Gd.

The complexes were also found spectroscopically to retain the Ln³⁺-semiquinone ground state *via* EPR and ¹H NMR spectroscopy. The La^{III}Tp*₂(DTBSQ) shows an organic radical on the DTBSQ while the Ce^{III}Tp*₂(DTBSQ) shows a paramagnetic open-shell singlet ground state. Computations show that f-orbital stabilization drives the differences in the electronic structure and bonding of the complexes, with complexes featuring low-lying empty f-orbitals, such as Pr, or less stabilized filled f-orbitals, such as Sm, were observed to deviate from isolated fⁿ-organic radical systems.

Discovery and Synthesis of Polymeric Macromolecular Platforms. We are investigating the selective incorporation of specific RE-binding moieties within several families of (bio)polymeric platforms: native proteins through selective amino-acid functionalization, chelating peptoids, the well-known styrene maleic anhydride (StyMAAnh, **Fig. 2**) copolymers, through post modification of side chains, and random methacrylate-based heteropolymers (RHPs) where monomer distribution can be statistically controlled. Synthesis was guided by RHP sequence simulation, which determines the side chain distribution along polymer chains. We are transitioning the existing bench-scale workflow to a robotic, high-throughput (HTP) system, to accelerate the development of heteropolymer libraries for rapid binding screening.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. Lukens, W. W.; Booth, C. H.; Walter, M. D. "Experimental Evaluation of the Stabilization of the COT Orbitals by 4f Orbitals in COT₂Ce Using a Hubbard Model." *Dalton Trans.* **2021**, 50, 2530-2535. DOI: 10.1039/D0DT03897K.
2. Pallares, R. M.; Carter, K. P.; Faulkner, D.; Abergel, R. J. "Macromolecular Crystallography for f-Element Complex Characterization." *Meth. Enzymol.* **2021**, 651, 139-155. DOI: 10.1016/bs.mie.2021.01.014.
3. Pallares, R. M.; Hebert, S.; Sturzbecher-Hoehne, M.; Abergel, R. J. "Chelator-Assisted High Performance Liquid Chromatographic Separation of Trivalent Lanthanides and Actinides". *New J. Chem.* **2021**, 45, 14364-14368. DOI: 10.1039/D1NJ01966J.
4. Pallares, R. M.; Charrier, M.; Tejedor-Sanz, S.; Li, D.; Ashby, P. D.; Ajo-Franklin, C. M.; Ralston, C. Y.; Abergel, R. J., Precision Engineering of 2D Protein Layers as Chelating Biogenic Scaffolds for Selective Recovery of Rare-Earth Elements. *J. Am. Chem. Soc.* **2022**, 144 (2), 854-861. DOI: 10.1021/jacs.1c10802.
5. Price, A. N.; Berryman, V.; Ochiai, T.; Shephard, J. J.; Parsons, S.; Kaltsoyannis, N.; Arnold, P. L., Contrasting behaviour under pressure reveals the reasons for pyramidalization in tris(amido)uranium(III) and tris(arylthiolate) uranium(III) molecules. *Nature Communications* **2022**, 13 (1), 3931. DOI: 10.1038/s41467-022-31550-7
6. Price, A.; Gupta, A.; de Jong, W. A.; Arnold, P., Tris(carbene)borates; Alternatives to Cyclopentadienyls in Organolanthanide Chemistry. *Dalton Trans.* **2023**, 52, 5433-5437. DOI:10.1039/D3DT00718A

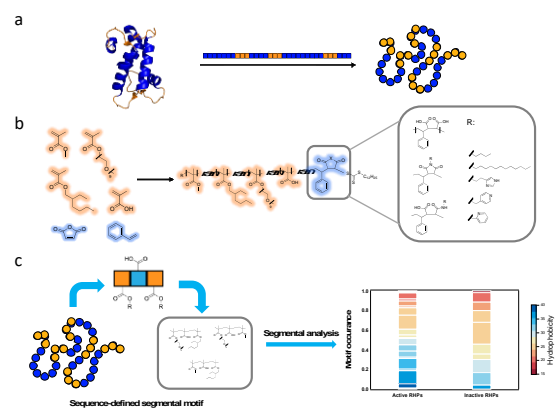


Figure 2. Recapitulating key features in lanthanide binding proteins in random heteropolymers.

7. Pan, J.-A.; Skripka, A.; Lee, C.; Qi, X.; Pham, A. L.; Woods, J. J.; Abergel, R. J.; Schuck, P. J.; Cohen, B. E.; Chan, E. M., Ligand-Assisted Direct Lithography of Upconverting and Avalanching Nanoparticles for Nonlinear Photonics. *J. Am. Chem. Soc.* **2024**, *146* (11), 7487-7497. DOI 10.1021/jacs.3c12850

Grant cited but not intellectually led by this award:

1. Arnedo-Sanchez, L.; Smith, K. F.; Deblonde, G. J.-P.; Carter, K. P.; Moreau, L. M.; Rees, J. A.; Tratnjek, T.; Booth, C. H.; Abergel, R. J. “Combining the Best of Two Chelating Titans: A Hydroxypyridinone-Decorated Macrocyclic Ligand for Efficient and Concomitant Complexation and Sensitized Luminescence of f-Elements.” *ChemPlusChem.* **2021**, *86*, 483-491. DOI: 10.1002/cplu.202100083
2. Cosby, A. G.; Arino, T.; Bailey, T. A.; Buerger, M.; Woods, J. J.; Aguirre Quintana, L. M.; Alvarenga Vasquez, J. V.; Wacker, J. N.; Gaiser, A. N.; Strong, R. K.; Abergel, R. J., Siderocalin Fusion Proteins Enable a New $^{86}\text{Y}/^{90}\text{Y}$ Theranostic Approach. *RSC Chem. Biol.* **2023**. DOI 10.1039/d3cb00050h.
3. Ramanathan, A.; Kaplan, J.; Sergentu, D.-C.; Branson, J. A.; Ozerov, M.; Kolesnikov, A. I.; Minasian, S. G.; Autschbach, J.; Freeland, J. W.; Jiang, Z.; Mourigal, M.; La Pierre, H. S., Chemical Design of Electronic and Magnetic Energy Scales of Tetravalent Praseodymium Materials. *Nat. Commun.*, **2023**, *14*, 3134. DOI: 10.1038/s41467-023-38431-7.
4. Kynman, A. E.; Christodoulou, S.; Ouellette, E. T.; Peterson, A.; Kelly, S. N.; Maron, L.; Arnold, P. L., Photocatalytic Dechlorination of Unactivated Chlorocarbons including PVC using Organolanthanide Complexes. *Chem. Commun.* **2023**, *50*, 10924–10927, DOI 10.1039/D3CC02906A.
5. Skripka, A.; Lee, M.; Qi, X.; Pan, J.-A.; Yang, H.; Lee, C.; Schuck, P. J.; Cohen, B. E.; Jaque, D.; Chan, E. M., A Generalized Approach to Photon Avalanche Upconversion in Luminescent Nanocrystals. *Nano Lett.* **2023**, *23*, 7100–7106. DOI 10.1021/acs.nanolett.3c01955.
6. Peterson, A.; Wacker, J. N. Six Degrees of Actinide Separation. *Nat. Rev. Chem.* **2024**. DOI 10.1038/s41570-024-00610-5.

Ionic Liquids and Deep Eutectic Solvents in Separation Science: An Understanding of Nanoscale Ordering

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Key Words: Assembly/Ordering; Interfaces; Liquid-Liquid Phase; Solvation.

AL-19-380-059: Project Title: Ionic Liquids and Deep Eutectic Solvents in Separation Science: An Understanding of Nanoscale Ordering

PI: Jared L. Anderson; co-PIs: Emily A. Smith, Jacob W. Petrich, Xueyu Song

Research Project Scope

The goal of the work is to understand the role of nanoscale ordering, or "nanodomains," in ionic liquids (IL) and deep eutectic solvents (DES) and their influence on separation systems. These nanodomains, ranging from a few nanometers to hundreds of nanometers, are hypothesized to play a crucial role in molecular transport and partitioning, significantly impacting separation processes. Our aim is to elucidate the nature of these nanodomains and how they contribute to the properties of IL and DES separation media, thereby influencing the underlying separation mechanisms. We hypothesize that tuning IL and DES nanodomains may lead to the development of more efficient, scalable, and energy-saving separation processes using these solvents. Our multidisciplinary team combines separation techniques, optical spectroscopy, and computational studies to achieve our goals of revealing the properties of nanodomains and their effects on chemical separations.

Recent Progress.

Our team has employed two complementary spectroscopic methods, namely, fluorescence correlation spectroscopy (FCS) and single-molecule tracking (SMT) to demonstrate the presence of large (~20 nm) nanodomains in an IL. FCS measurements have been performed on the tetradecyl-(triethyl)phosphonium chloride [P_{66614}^+][Cl⁻] IL using fluorescent probes of varying sizes (ATTO 532, ~2 nm as well as 20- and 40-nm fluorescent beads). The fluorescence correlation function, $G(\tau)$, was analyzed in terms of a distribution of diffusion coefficients using a maximum entropy method (MEM). For ATTO 532 and the 20-nm beads, the fit to $G(\tau)$ yielded two well-defined distributions; for the 40-nm beads, however, only one was obtained (see Figure 1(A)). These results are consistent with the existence of two nanodomains whose size is greater than or equal to 20 nm and less than 40 nm. The origin of such nanodomains is attributed to a liquid-liquid phase transition that the team has investigated. The complementary method of SMT permits the observation of a single probe molecule in the IL, and because of the nature of the experimental setup, also permits the temperature to be varied. The distribution of diffusion coefficients of the ATTO 647N probe were measured in the [P_{66614}^+][Cl⁻] IL at 20°C, 35°C, 45°C, and 50°C. As in the FCS experiments, two distinct populations were observed (see 20°C and 35°C data in Figure 1(B)). The populations of the diffusion coefficients were temperature dependent representing the two liquid phases in the [P_{66614}][Cl⁻] IL at 20°C (4020 cP). However, only a single fast population was measured at 50 °C (439 cP), as observed in Figure 1(B). At a similar viscosity (640 cP), the [P_{66614}^+] bis[(trifluoromethyl)sulfonyl]imide [NTf₂⁻] IL showed only a single diffusing population at 20°C. Results from the FCS and SMT studies allow us to make the following conclusions: (1) We suggest that because

large regions (*i.e.*, greater than 1-2 nm) resulting from the liquid-liquid phase transition would be expected to have different properties, such as viscosity, and because their presence would necessarily increase the number of interfaces in the ionic liquid, these regions provide a possible explanation for the exceptional separation performance of ILs; (2) These temperature-dependent data provide insights and better understanding into nanodomain tunability in ILs. The ability to measure the trajectory of a single probe molecule as a function of temperature supports the conclusions drawn from the FCS measurements, and the temperature dependence of the populations of diffusion coefficients unambiguously assigns this dependence to the viscosity dependence of the structure of the ~20-nm nanodomains.

Our team has developed molecular drivers capable of highly selective olefin/paraffin separations using coordinated silver(I) ions (Ag^+) in nanostructured ILs. Different ligand species (*e.g.*, 4,4'-dimethyl-2,2'-bipyridine (DMBP), bis(pyridine) (Py)₂, bis(2,6-lutidine), and triphenylphosphine (PPh_3), were coordinated to Ag^+ ions to produce separation media with varying interaction strengths to olefins. Inverse gas chromatography was employed to examine the ability to tailor and modulate Ag^+ -olefin π -complexation, impart additional ligand-olefin interactions, and extend the lifetimes of separation media containing Ag^+ ions by varying the type and coordination behavior of the ligand(s). The $[\text{Ag}^+(\text{DMBP})][\text{NTf}_2^-]$ complex offered the highest thermal stability and H_2 reduction stability amongst the tested nitrogen donor ligands. The coordination environment of $[\text{Ag}^+(\text{Py})_2][\text{NTf}_2^-]$ produced the greatest interactions with olefins, amongst the coordinated Ag^+ salts tested, but had the lowest thermal stability and second worst H_2 reduction stability. The $[\text{Ag}^+(\text{PPh}_3)][\text{NTf}_2^-]$ complex exhibited impressive H_2 stability and was the only tested coordination compound that reduced less than the neat $[\text{Ag}^+][\text{NTf}_2^-]$ salt in a reducing environment. It was also observed that some of the coordination complexes can undergo ligand-analyte interactions, indicative of an additional pathway to modulate analyte retention. Findings from this research demonstrate the ability to tailor and modulate Ag^+ -olefin π -complexation, impart additional ligand-olefin interactions, and extend the lifetimes of separation media containing Ag^+ ions by varying the type and coordination behavior of the ligand(s). The results further enhance the viability of Ag^+ ion containing ILs as separation media for complex olefin-paraffin mixtures, ultimately leading to improved and tunable separation performance with lower energy inputs.

Future Plans.

Our team is employing various separation platforms to measure intermolecular interactions between ILs, transition metal ions, and DESs, and will use the data to further understand the connection between the nanoscale ordering of ILs and overall separation characteristics (*i.e.*, separation efficiency, selectivity). Using coordination chemistry, we are developing coordination complexes as molecular drivers to further improve the separation performance of ILs. Using our theory-based classification method, we have obtained a preliminary liquid-liquid phase diagram for the Kob-Andersen model potential. We will use this approach to calculate temperature dependent viscosity data for model systems and ILs used in the separations and structural characterization experiments. Such calculations will be performed in concert with experimental

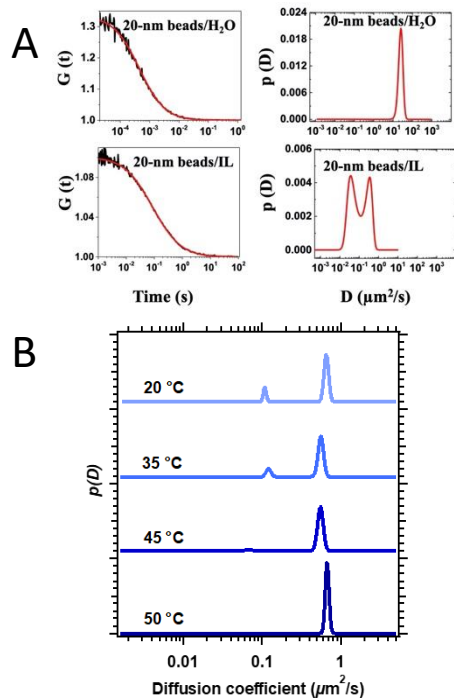


Figure 1. (A) Probability distributions, $p(D)$, of diffusion coefficients obtained from FCS data for 20-nm fluorescent beads in water (control experiment) and $[[\text{P}_{66614}^+][\text{Cl}^-]]$; (B) SMT data revealing the effect of temperature on nanodomains in which only one distribution is observed at 45 and 50 °C.

measurements so that the effect of nanodomains on separations can be further elucidated via iterations between experimental and theoretical analysis. Our team continues to collaborate with other separations projects at Ames National Laboratory to understand rare earth element solvation in ILs and DESs to exploit the tailorability of the solvents in the separation of rare earth elements.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. Farooq, M.Q., Abbasi, N.M., Anderson, J.L. Modulating Solvation Interactions of Deep Eutectic Solvents Formed by Ammonium Salts and Carboxylic Acids Through Varying the Molar Ratio of Hydrogen Bond Donor and Acceptor. *Journal of Chromatography A*, **2021**, 1643, 462011.
2. Farooq, M.Q., Abbasi, N.M., Anderson, J.L. Investigating the Variation in Solvation Interactions of Choline Chloride-Based Deep Eutectic Solvents Formed Using Different Hydrogen Bond Donors. *ACS Sustainable Chemistry and Engineering* **2021**, 9, 11970-11980.
3. Eor, P., Anderson, J.L. Using a Chromatographic Pseudophase Model to Elucidate the Mechanism of Olefin Separation by Silver(I) Ions in Ionic Liquids, *Analytical Chemistry* **2021**, 93, 13284.
4. Farooq, M.Q., Zeger, V.R., Anderson, J.L. Comparing the Extraction Performance of Cyclodextrin containing Supramolecular Deep Eutectic Solvents versus Conventional Deep Eutectic Solvents by Headspace Single Drop Microextraction. *Journal of Chromatography A* **2021**, 1658, 462588.
5. Li, J., Farooq, M.Q., Petrich, J.W., Anderson, J.L., Smith, E.A. Fast and Non-Destructive Determination of Water Content in Ionic Liquids at Varying Temperatures by Raman Spectroscopy and Multivariate Regression Analysis. *Analytica Chimica Acta*, **2021**, 1188, 339164.
6. Farooq, M.Q., Abbasi, N.M., Anderson, J.L. Investigating the Effect of Systematically Modifying the Molar Ratio of Hydrogen Bond Donor and Acceptor on Solvation Characteristics of Deep Eutectic Solvents Formed using Choline Chloride Salts and Polyalcohols. *Journal of Chromatography A*, **2022**, 1667, 462871.
7. Farooq, M.Q., Abbasi, N., Smith, E.A., Petrich, J.W., Anderson, J.L. Characterizing the Solvation Characteristics of Deep Eutectic Solvents Comprised of Active Pharmaceutical Ingredients as Hydrogen Bond Donor and/or Acceptor. *ACS Sustainable Chemistry and Engineering*, **2022**, 10, 3066-3078.
8. Abbasi, N., Zeger, V.R., Biswas, A., Anderson, J.L. Synthesis and Characterization of Magnetic Ionic Liquids Containing Multiple Paramagnetic Metal Centers and Functionalized Diglycolamide Ligands. *Journal of Molecular Liquids*. **2022**, 361, 119530.
9. Farooq, M.Q. Tryon-Tasson, N., Biswas, A., Anderson, J.L. Preparation of Ternary Hydrophobic Magnetic Deep Eutectic Solvents and an Investigation into Their Physicochemical Properties, *Journal of Molecular Liquids* **2022**, 365, 120000.
10. Stephens, N.M., Masching, H.P., Walid, M., Petrich, J.W., Anderson, J.L., Smith, E.A. Temperature-Dependent Constrained Diffusion of Micro-Confined Alkylimidazolium Chloride Ionic Liquids. *The Journal of Physical Chemistry B*, **2022**, 126, 4324.
11. Farooq, M.Q., Ocana, I, Anderson, J.L. Analysis of Persistent Contaminants and Personal Care Products by Dispersive Liquid-liquid Microextraction using Hydrophobic Magnetic Deep Eutectic Solvents. *Journal of Chromatography A*, **2022**, 1681, 463429.
12. Stephens, N.M., Smith, E.A. Structure of Deep Eutectic Solvents (DESs): What We Know, What We Want to Know, and Why We Need to Know It. *Langmuir*, **2022**, 38, 14017-14024.
13. Li, J., Anderson, J.L., Smith, E.A. Determination of Infinite Dilution Activity Coefficients of Molecular Solutes in Ionic Liquids and Deep Eutectic Solvents by Factorization-Machine-Based Neural Networks. *ACS Sustainable Chemistry and Engineering* **2022**, 10, 13927-13935.
14. Eor, P., Tryon-Tasson, N., Kong, S., Smith, E.A., Anderson, J.L. Deconvoluting the Combined Effects of Gas Composition and Temperature on Olefin Selectivity for Separations Using Silver(I) Ions in Ionic Liquids. *ACS Measurement Science Au*, **2023**, 3, 53.

15. Eor, P., Tryon-Tasson, N., Anderson, J.L. Effect of Silver(I) Ion Reduction on the Selectivity of Olefins, Paraffins, and Aromatic compounds by Gas Chromatographic Stationary Phases Consisting of Silver(I) Salts in Ionic Liquids. *Journal of Chromatography A*, **2023**, 1689, 463757.
16. Eor, P. Byington, M., Anderson, J.L. “Comparing π -complexation capabilities of ionic liquids containing silver(I) and copper(I) ions by headspace single drop microextraction in combination with high-performance liquid chromatography” *Journal of Separation Science* **2023**, 46, e2300649.
17. Abbasi, N.M. and Anderson, J.L. “Insights into the Solvation Characteristics of Zwitterionic Deep Eutectic Solvents Using Multiple Polarity Scales” *Industrial and Engineering Chemistry Research* **2023**, 62, 4084-4094.
18. Mastellone, G., Abbasi, N.M. Cagliero, C., Anderson, J.L. “New Class of Tunable Choline Bromide-Based Hydrophobic Deep Eutectic Solvents for the Extraction of Bioactive Compounds of Varying Polarity from a Plant Matrix” *ACS Sustainable Chemistry and Engineering* **2023**, 11, 6665-6675.
19. Tryon-Tasson, N.M., Ryoo, D.; Eor, P. Anderson, J.L. “Silver-mediated separations: A comprehensive review on advancements of argentation chromatography, facilitated transport membranes, and solid-phase extraction techniques and their applications” *Journal of Chromatography A* **2023**, 1705, 464133.
20. Nguyen, V. and Song, X. Automated characterization of spatial and dynamical heterogeneity in supercooled liquids via implementation of Machine Learning, *Journal of Physics and Condensed Matter*. **2023**, 35, 465401.
21. Eor, P. Tryon-Tasson, N., Anderson, J.L. “Elucidating the role of temperature and water on the π -complexation strength of copper(I) ion-containing ionic liquids using inverse gas chromatography” *Analytica Chimica Acta* **2024**, 1287, 342021.
22. Abbasi, N.M. Anderson, J.L., Pellett, J.D., Yehl, P., Barrio, M., Zhong. Q. “Deep eutectic solvents as green and sustainable diluents in headspace gas chromatography for the determination of trace level genotoxic impurities in pharmaceuticals *Journal of Pharmaceutical and Biomedical Analysis* **2024**, 244, 116128.
23. Xiao, T.J. and Song, X. A Gaussian field approach to the solvation of spherical ions in electrolyte solutions, *Journal of Chemical Physics*, **2024**, 160, 034102.
24. Ryoo, D., Bara, J.E., Anderson, J.L. “Polymeric Ionic Liquids Containing Copper (I) and Copper (II) Ions as Gas Chromatographic Stationary Phases for Olefin Separations” *Journal of Chromatography A* **2024**, 1735, 465306.

Grant cited but not intellectually led by this award:

1. Naik, P.J., An, Y., Sedinkin, S.L., Masching, H., Freppon, D., Smith, E.A., Venditti, V., Slowing, I.E. Non-Innocent Role of the Ceria Support in Pd-Catalyzed Halophenol Hydrodehalogenation. *ACS Catalysis* **2021**, 11, 10553–10564.
2. Thomas, D-G., De-Alwis, S., Gupta, S., Pecharsky, V.K., Mendivelso-Perez, D., Montazami, R., Smith, E.A., Hashemi, N.M., Protein-assisted scalable mechanochemical exfoliation of few-layer biocompatible graphene nanosheets, *Royal Society Open Science* **2021**, 8(3) 200911.
3. Xiao, T., Song, X. A systematic way to extend the Debye-Huckel theory beyond dilute electrolyte solutions, *Journal of Physical Chemistry A*, **2021**, 125, 2173.
4. Copeland-Johnson, T.M., Nyamekye, C., Ecker, L., Bowler, N., Smith, E.A., Rebak, R.B. Analysis of Inconel 600 Oxidized Under Loss-of-coolant Accident Conditions: A Multi-Modal Approach. *Corrosion Science*, **2021**, 195, 109950.

Insight into a Full Engagement of Highly Porous Carbon Surfaces in an Effective PFAS Separation from Firefighting Waters: Involving Surface Chemistry and Interface in the Removal, Modification and Degradation

Teresa J. Bandosz

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Key Words : Confinement; Interfaces; Reactive Separations

DE-SC0025258: Insight into a full engagement of highly porous carbon surfaces in an effective PFAS separation from firefighting waters: Involving surface chemistry and interface in the removal, modification and degradation

PI: Teresa J. Bandosz

Research Project Scope/Future Plans

To address the urgent need to efficiently remove PFAS (as “forever chemicals”) from the environment, chemical modifications of carbon surfaces are proposed with an objective to increase the carbon capacity and selectivity to remove short-chain PAFS from firefighting waters. Both groups of interactions, dispersive ones employing carbon hydrophobicity and the full range of PAFS specific interactions or even reactivity, will be targeted, explored and understood. Controlled desorption/reactive desorption in various atmospheres and influenced by heat treatments and the effect of carbon confined spaces are expected not only to destroy PAFS “forever chemicals” but also to lead to new adsorbents of specific and unique properties. We hypothesize that the chemical modifications of carbon surfaces in specific pores are important not only for efficient adsorption and separation of a broad range of PFAS from complex mixtures of organic compounds, but they also govern reactive desorption/regeneration process. The research will focus on answering three distinctive questions: 1) can we specifically modify surface chemistry in large pores (in the mesopores range) with an intent to target/adjust/alter specific adsorption forces/selectivity and reactive desorption? 2) what are the interactions which govern the separation process at various conditions (composition, concentration, temperature)?; 3) how does reactive desorption/regeneration impact the surface chemistry of carbon and adsorption /separation/ destruction of PFAS? The following tasks are planned: 1) carbon modifications by focusing on the introduction of target N and S-groups to specific pore sizes; 2) carbon characterization; 3) PAFAS adsorption/separation from simulated AFFF waters 4) thermal/reactive regeneration of carbons. The collected results will contribute to the answers to the research questions emphasizing the roles of pore size, pore volume, the nature and amounts of functional groups, their location on the surface on the separation of PFAS from firefighting waters. Various performance factors such as adsorption kinetics, amounts adsorbed at equilibrium, efficiency for the PFAS removal and efficiency of separation from the other components will be analyzed. The surface features advancing the separation mechanism and the involvement of the specific forces and interfaces will be emphasized. The analysis of the reactive desorption process will contribute not only to reusability of adsorbents either for PAFS separation or for other separation processes informed by new and specific surface features, but it will lead to the destruction of these “forever” chemicals. The separation process that we explicitly address is very relevant to materials-water-energy nexus.

Gas Transport and Separation Mechanisms in Ionic Polymer Membranes

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Department of Chemical & Biological Engineering, The University of Alabama, Tuscaloosa, AL 35487-0203

Key Words: Membranes; Non-Thermal Separation Mechanisms; Theory/Simulation; Transport Phenomena.

DE-SC0025219: Gas Transport and Separation Mechanisms in Ionic Polymer Membranes

PI: Jason E. Bara; co-PI: C. Heath Turner

Research Project Scope.

This synergistic experimental and computational research studies and understands transport and separation mechanisms in new PIM-TB and PIM-PI ionenes. These materials are built using the highly permeable and selective PIM-TB and PIM-PI backbones and can interact with and support ILs within the polymer matrix. This work will focus on understanding transport of single and mixed gases at relevant temperatures/pressures/concentrations via systematic and rational variation of the polymer membrane structure, with an emphasis on the density and nature of the ionic components. Our highly tailorable materials can be uniquely and systematically varied to understand gas transport separation and separation mechanisms in polymer membranes. The project aligns with the DOE BES Separation Science mission to discover, predict, and ultimately control separation processes through “manipulation of molecular, atomic and electronic factors” via the “design of inorganic and organic membranes and their hybrids”.

Recent Progress.

We have already made great progress in the study of our new ionenes as gas separation membranes. Figure 1 shows the synthesis route to both the neutral polyimide and its corresponding ionic form.

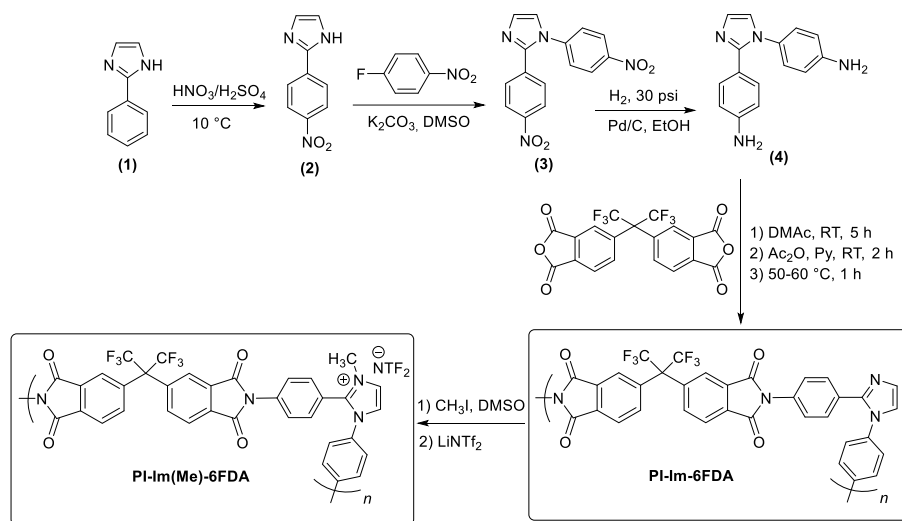


Figure 1. Synthesis of new PI materials in both neutral and ionic forms.

MALDI-TOF MS indicated that a molecular weight of 91 kDa was achieved for PI-Im-6FDA. The materials also exhibit excellent thermal stability as illustrated by TGA (Figure 2).

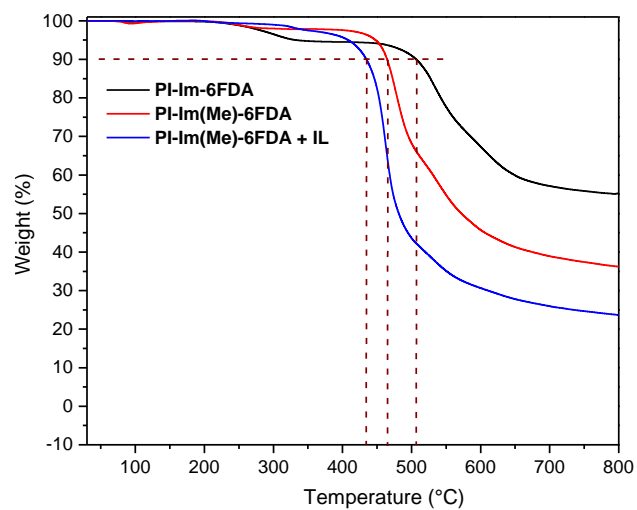


Figure 2. TGA plot for neutral, ionic, and ionic + IL material forms.

We have successfully formed membranes of PI-Im-6FDA and PI-Im(Me)-6FDA + IL (Figure 3).

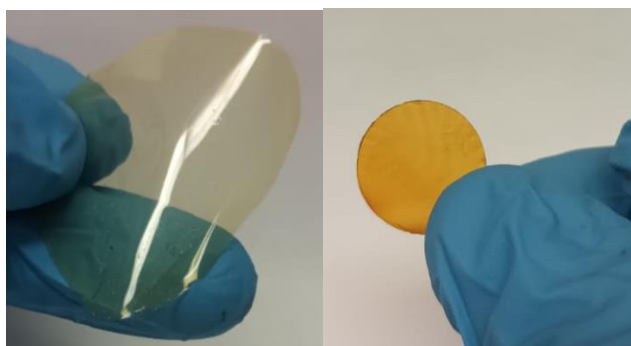


Figure 3. Membranes of PI-Im-6FDA (left) and PI-Im(Me)-6FDA + IL (right).

The membrane permeability results are provided in Table 1.

Table 1. Permeability and selectivity in neutral and ionic + IL polymer membranes.

Membrane	Permeability P_i (barrer)				
	H ₂	O ₂	N ₂	CH ₄	CO ₂
PI-Im-6FDA	20.05	2.83	0.58	0.65	19.62
PI-Im(Me)-6FDA + IL	9.60	2.42	0.77	0.99	17.52
Membrane	Ideal selectivity $\alpha (P_i/P_j)$				
	H ₂ /N ₂	O ₂ /N ₂	CO ₂ /CH ₄	CO ₂ /N ₂	H ₂ /N ₂
PI-Im-6FDA	34.56	4.87	30.18	33.82	34.56
PI-Im(Me)-6FDA + IL	12.22	3.14	17.69	22.75	12.22

We are highly encouraged by the success of our synthetic methods for producing new polymers and their corresponding ionic forms which will allow us to deeply probe the influence of structure and charge on gas transport in polymer membranes. The initial polyimide material we studied here has already revealed that H₂ seems to be particularly influenced by the presence of charge/ionic liquid. Moving forward, we will begin to work with more permeable backbone components associated with higher fractional free volume (e.g., spirobisindane, ethanoanthracene). The versatility of our monomers and post-polymerization functionalization also allows us to probe structure-property-performance relationships related to the nature of the side chain on the imidazolium cation within the polymer backbone, the anion, and the type of polymer backbone connectivity (i.e., imide, amide, Tröger's base, etc.). A manuscript on this study acknowledging BES funding has recently been submitted to *Macromolecules*.

Transport of Complex Mixtures in Ion-Containing Polymer Membranes

Bryan Beckingham,¹ Jung Min Kim¹, Pravin Aravindhan¹, Yi-hung Lin¹, Sarah Gaston¹

¹Auburn University

Key Words: Membranes; Multi-Modal Phenomena; Non-Thermal Separation Mechanisms; Transport Phenomena

DE-SC0021215: Transport of Complex Mixtures in Ion-Containing Polymer Membranes

PI: Bryan Beckingham

Research Project Scope.

Permselective ion-containing membranes are an integral component for many applications from water treatment, fuel cells, and solar fuels devices where the selective transport of molecules and ions is desired. To design and understand membrane behavior in such systems a fundamental understanding of the transport processes occurring is critical. In the case of a mixture of solutes, the presence of a solute in a membrane can affect the diffusion and/or sorption of other solutes, such that we've found significant differences in transport behavior between single and two-solute permeation behavior for several solutes through ion-containing membranes. The objective of this research is to improve our understanding of the complex array of factors that influence transport behavior of multiple solutes within ion-containing polymer membranes. This research is of critical relevance to the Separation Science Program as noted by the NASEM report “*A Research Agenda for Transforming Separation Science*” which stated, ‘*The ability to understand and design for the separation of complex mixtures will be a turning point for the separations community and is a key to transforming separation science and industrial practice.*’ In our work we have focused on the transport and co-transport of solar fuels products as controlling their transport across the membrane in solar fuels devices is critical for improving device efficiency.

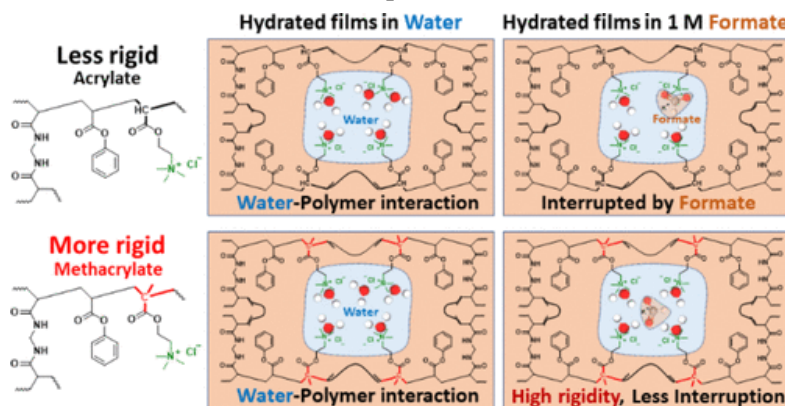


Figure 1. Schematic depicting phenomena where the presence of a methacrylate linkage yields a more rigid backbone than an acrylate linkage and ultimately a difference in the interactions between the polymer membranes, water, and solutes (methanol and formate). Reprinted with permission from *J. Phys. Chem. C* 2023, 127, 22, 10826–10832. Copyright 2023 American Chemical Society.

Recent Progress.

To understand how membrane structure (chemistry) impacts observed transport and cotransport behavior in dense, hydrated polymer membranes, this project has systematically manipulated membrane chemistry and characterized the physiochemical properties, transport and co-transport behavior of a large selection of polymer membranes including uncharged polymer membranes, cation exchange membranes, anion exchange membranes, and zwitterion-containing membranes. One recent example of this work is the comparison of the methacrylate form with the acrylate form of the ionic monomer (in otherwise analogous membranes). In this comparison the differences in polymer rigidity—due to the methacrylate quaternary carbon—impact how the membranes behave. For instance, due to the additional steric hinderance in the

methacrylate-containing membranes, higher water volume fractions but less osmotic deswelling is observed. The difference in water volume fraction leads to anticipated changes in transport behavior (higher permeability for higher water content membranes) but also unexpected transport behavior. Namely, both the sorption coefficients and the relative permittivity of otherwise analogous acrylate and methacrylate membranes were similar for formate-containing solutions. This is unexpected behavior since the presence of formate in the solution should decrease the relative permittivity. Taken together this behavior is an indication that the use of the methacrylate influences the polymer/solvent interactions (likely hydrogen bonding behavior). Characterization of the cotransport behavior (methanol and formate) found that while permeabilities to formate were typically unchanged in cotransport with methanol, solubilities to formate decreased. This indicates that the presence of methanol within the membrane led to increased formate diffusivity likely through flux coupling.

In other recent work we have investigated incorporation of comonomers with different length side chains as a methodology for impacting the cotransport behavior. We synthesized polymer cation exchange membranes using two different neutral comonomers, phenoxyethyl acrylate (PEA) or poly(ethylene glycol) phenyl ether acrylate (PEGPEA), that are chemically analogous except for the number of ethylene glycol repeat units on the side chain and investigated transport and cotransport behavior for methanol and acetate. In this case acetate diffusivities for cation exchange membranes without a neutral comonomer or with the shorter PEA comonomer increased, while those with the longer chain comonomer PEGPEA decreased. Critically, the use of PEGPEA ultimately led to essentially unchanged permeability to acetate in cotransport with methanol for the cation exchange membranes whereas cation exchange membranes without PEGPEA tended to display an increase in the acetate permeability in cotransport. This is a promising result, and additional related work on this topic is ongoing to understand the underlying mechanism towards leveraging this methodology to control transport and co-transport behavior.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. Bachmann, A.L.; Hunter, B.; Beckingham, B.S. Development of Structure–Property Relationships for Ammonium Transport through Charged Organogels. *Membranes* **2024**, *14*, 71. <https://doi.org/10.3390/membranes14030071>
2. Kim, J. M., Lin, Y., Bannon, S. M., Geise, G. M., & Beckingham, B. S. (2023). Improved Structural Stability of Charged Hydrogels under Organic CO₂ Reduction Products: Effect of Acrylate and Methacrylate Backbone Linkages. *Journal of Physical Chemistry C*, **2023**, *127*(22), 10826–10832. <https://doi.org/10.1021/acs.jpcc.3c01854>
 - a. Published as part of *The Journal of Physical Chemistry* virtual special issue “Early-Career and Emerging Researchers in Physical Chemistry Volume 2”.
3. Yi-hung Lin, Jung Min Kim, and Bryan S. Beckingham, "Salt Transport in Dense Crosslinked Hydrogel Membranes Containing Zwitterionic Sulfobetaine Methacrylate and Hydrophobic Phenyl Acrylate", *Polymers*, **2023**, *15*(6), 1387. DOI: 10.3390/polym15061387.
4. Kim, J.M., Lin, Y-h., Aravindhana, P.P., Beckingham B.S., "Impact of hydrophobic pendant phenyl groups on transport and co- transport of methanol and acetate in PEGDA-SPMAK cation exchange membranes", *Chemical Engineering Research and Design*, **2022**, *185*, 418, DOI: 10.1016/j.cherd.2022.07.017.
5. Kim, J.M., Wang, Y., Huang, T., Yoon, J.S., Kim, D.J., Auad, M., Beckingham B.S., "Fabrication and characterization of cross- linked phenyl-acrylate-based ion exchange membranes and performance in a direct urea fuel cell", *Industrial & Engineering Chemistry Research*, **2021**, *60*, 41, 14856–14867. DOI: 10.1021/acs.iecr.1c02798.
6. Kim, J.M.; Lin, Y.-h.; Hunter, B.; Beckingham, B.S., "Transport and Co-Transport of Carboxylate Ions and Ethanol in Anion Exchange Membranes ", *Polymers*, **2021**, *13*(17), 2885. DOI:

10.3390/polym13172885.

Grant cited but not intellectually led by this award:

1. Yoon, Jaesik; Kim, Jung Min; Lin, Yi-hung; Geise, Geoffrey; Kim, Dong-Joo; Beckingham, Bryan "Impact of a novel nickel-based catalyst and phenyl acrylate-based anion exchange membrane in a direct urea fuel cell" *Energy & Fuels*. **2024**, 38, 13, 12274–12281.
<https://doi.org/10.1021/acs.energyfuels.4c00929>

Controlling CO₂ Solvation & Binding in its Direct Capture from Ambient Air over Inorganic Sorbents

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¹University of Houston, ²Johns Hopkins University

Key Words: Confinement; Dilute Species; Solvation; Theory/Simulation.

DE-SC0025264: Project Title: Controlling CO₂ Solvation and Binding in its Direct Capture from Ambient Air over Inorganic Sorbents

PI: Praveen Bollini; co-PI: Brandon C. Bukowski

Research Project Scope.

The goal of this project is to advance direct air capture (DAC) under ambient conditions through an understanding of adsorption and diffusion phenomena occurring within high-performing solid sorbents that are purely inorganic in composition. We seek to use highly porous layered double hydroxide (LDH) nanosheets derived from the exfoliation of Brucite-like LDH crystals as a class of highly tunable metal hydroxides that carry both the requisite porosity as well as the appropriate coordination environment of the hydroxyl moieties for DAC applications. The overarching scientific objective of the proposed project is to combine equilibrium and dynamic sorption experiments and in-situ spectroscopy with ab-initio simulations and theory to unravel binding and solvation mechanisms at play on porous transition metal hydroxide surfaces that could in turn translate to discovering hitherto unidentified classes of DAC sorbents.

Recent Progress.

Carbonate-assisted precipitation under basic conditions were used to produce crystalline Brucite-like hydroxide layers separated by interlayer carbonate anions (Figure). Ethanol redispersion of the crystalline powder resulted in a more than 100-fold increase in nickel hydroxide surface area from 3.3 to 820 m²/g (Figure) with a minimal impact on LDH layer crystallinity, helping us create a sample that carries what is to the best of our knowledge the highest surface area ever reported for a nickel hydroxide material.

In-situ Fourier transform infrared (FTIR) spectroscopy was used to infer the speciation of adsorbed CO₂. Measurements on α-Ni(OH)₂ samples under 400 ppm CO₂ revealed a series of infrared bands between 1000-1700 cm⁻¹ that correspond to carbonate and bicarbonate species. Bands at 1645 and 1680 cm⁻¹ detected in the presence

of 400 ppm CO₂ without any water vapor can be attributed to O-C-O asymmetric modes for HCO₃⁻ species that have been reported previously to appear in the 1600-1680 cm⁻¹ range during CO₂ adsorption over a

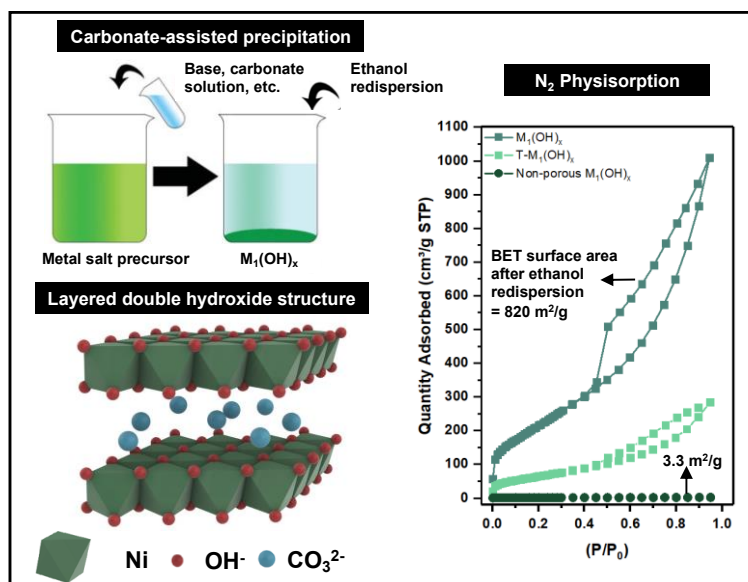


Figure. Top left: carbonate-assisted precipitation method used to synthesize porous metal hydroxides. Bottom left: Layered double hydroxide Brucite-like structure formed with the assistance of intercalated carbonate anions. Right: N₂ physisorption isotherms of porous metal hydroxide samples.

variety of hydroxyl-bearing materials including MOFs, reducible bulk metal oxides, and hydrotalcites. The three bands at lower wavenumbers – 1387, 1435, and 1473 cm^{-1} – can be assigned to symmetric O-C-O bending modes for CO_3^{2-} species. Adding in 2.2 kPa water vapor to the 400 ppm CO_2 -containing stream results in a significant increase in each of the aforementioned carbonate and bicarbonate bands. These data point to carbonate-bicarbonate chemistry as constituting the chemical basis for the facilitative effect of water on CO_2 binding onto nickel surfaces.

Future Plans.

Future work will emphasize combining density functional theory and molecular dynamics simulations with equilibrium and dynamic adsorption measurements to elucidate the nature and effect of solvation spheres in stabilizing adsorbate species on inorganic surfaces. The relationship between local coordination environment and binding configuration and energy will be directly probed through a combination of theory and experiment.

Functional Group Influences on Anion Binding with Heterotopic Hosts

Kristin Bowman-James, Sandeep Kaur, Subhamay Pramanik, Victor W. Day

University of Kansas

Key Words: Anion Coordination; Ion-pair Coordination; Recognition; Solvation

DE-SC0018629: Molecular to Mesoscale Targeting of Oxoanions with Multi-Tasking Hosts

PI: Kristin Bowman-James

Research Project Scope.

Supramolecular-based hosts for anions come in various shapes, sizes, and functional groups. This project has involved heterotopic hosts consisting of pyridine/pyrazine-based frameworks with mixed amide-amine bridges, and *o*-phenylene-based frameworks with mixed urea-amine bridges. The one thing in common for all these hosts is the presence of secondary or tertiary amine groups. The primary targets have been oxo anion guests. Additionally, starting from phenylene-based crown ethers, bis-*o*-phenylene-urea-amine chelates have been synthesized and examined as tritopic K_2A ($A = \text{dianion}$) receptors. Crystallographic and NMR solution studies have also examined the structural influences of solvent on host, guest, and host-guest complex formation, all three of which are crucial aspects of successful separations.

Recent Progress.

Earlier studies revealed that, in terms of the chelate effect, *o*-phenylene-bis-urea-amine-based chelates were superior to pyridine-bis-amide-amine-based chelates.

Expansion of these studies to macrocyclic versions of the *o*-phenylene-based hosts indicated that anion affinity of the *o*-phenylene-based chelate containing four mini-chelate urea groups was just as capable of binding sulfate selectively as a macrocyclic version (Figure – top picture). As in the urea-based chelate, the macrocyclic host was found to be selective for sulfate over other common oxoanions in DMSO. We also found what appears to be a solvent-dependent structural change in macrocycle:sulfate stoichiometries, from 2:1 macrocycle:sulfate (possibly sandwich complex) in DMSO with only small amounts (0.5%) water, to 1:1 macrocycle:sulfate ratios at higher water concentrations (Figure – bottom graph). This would be consistent with the very strong competition of water for the sulfate over the macrocyclic host.

Ion pair hosts were obtained by using crown ether-attached phenylenes to obtain hosts capable of binding two cations with a central dianion. While the tetra-urea chelate showed significant ion pair synergism in binding common anions, a similar enhancement in anion affinity was not observed for the macrocyclic corollary. Given the versatility of these urea chelates and extended chelate systems, higher ratios of cation:anion complexes can be envisioned, including multiple pockets for both cations and anions.

While crystal structures of phosphate, sulfate and perchlorate with the pyridine-based hosts indicated significant similarities, solvent interaction differences were also observed. Similar chemical shift

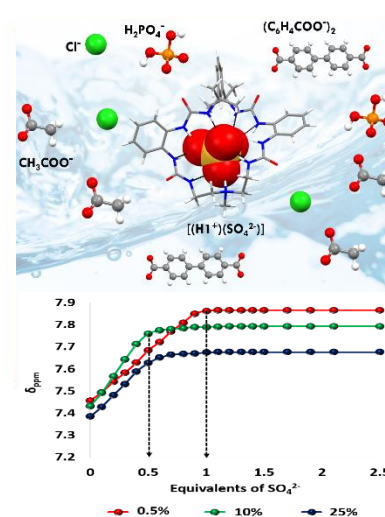


Figure. Top: schematic representation of the urea-based macrocycle for selective sulfate encapsulation; bottom: chemical shift changes as a function of SO_4^{2-} ions in DMSO solutions with different percentages of water.

variations were seen in solution NMR titration studies and are most probably attributed to anion hydrophilicity. These findings, and especially aquation effects seen in other recent crystal structures, are encouraging for future studies of solvation in anion complex formation.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. J. Lohrman, S. Pramanik, S. Kaur, H. Telikepalli, V. W. Day, K. Bowman-James, Hydrophilic and hydrophobic carboxamide pincers as anion hosts, *Org. Biomol. Chem.* **2021**, 8516-8520.
2. S. Pramanik, P. Thordarson, V. W. Day, K. Bowman-James, Oligomeric phosphate clusters in macrocyclic channels, *CrystEngComm.* **2022**, 24, 8047-8051.

Highly Selective Membrane-Based Ion Separations

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¹University of Notre Dame, ²Polytechnic University of Catalonia

Key Words: Field-Driven Separations; Transport Phenomena; Ion Separations

DE-SC0017618: Highly Selective Ion Separations Based on Counterflow Diffusion and Electrically Driven Facilitated Transport

PI: Merlin Bruening

Research Project Scope.

This research aims to develop the principles for new aqueous-based ion separations that in some applications might displace processes such as precipitation and solvent extraction. These ion separations rely on the combination of selective membranes, flow, electromigration, and diffusion. Modelling employs the extended Nernst-Planck equation and rotating membranes that control concentration polarization to accurately determine ion permeances. The research focuses on isolating critical ions including Li^+ and rare-earth ions.

Recent Progress.

Rare earth elements (REEs) are critical materials due to their utilization in high-flux magnets for wind turbines and electric motors. Purification and recycling of REEs are vital for maintaining their supply.

Our recent work explores and models nanofiltration (NF), electrodialysis, and diafiltration (filtration with continuous addition of water) for concentrating REE ions and polishing their concentrated solutions from monovalent ions. The combination of NF and diafiltration provides concentrated La^{3+} with a molar purity of 99% when starting with an equimolar mixture of La^{3+} and Na^+ . Highly negative monovalent-ion rejections (the concentration of the ion in the permeate is greater than in the feed) greatly enhance this polishing step. The negative Na^+ rejection appears because the membrane is much more permeable to Cl^- than to La^{3+} . Thus, NF of LaCl_3 spontaneously creates a transmembrane electrical potential to cause electromigration that decreases the net Cl^- flux and increases the La^{3+} flux to achieve zero current. When Na^+ is also in the mixture, the electrical potential increases its flux and preferentially moves Na^+ ions through the membrane (compared to La^{3+}) because of the high Na^+ permeance. Additionally, proton concentrations in LaCl_3 solutions decrease 3-4 orders of magnitude in 2-3 cell volumes of diafiltration due to the high proton permeance. Controlling the pH of acidic solutions is potentially important when exploiting complexation to separate the metal ions, as complex formation often depends on pH.

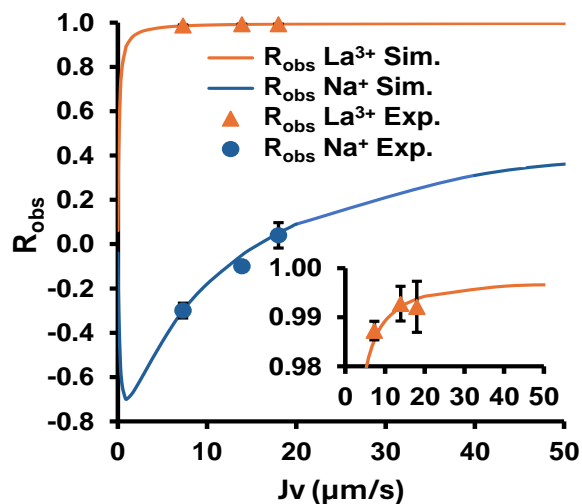


Figure 1. Simulated (lines) and experimental (symbols) observed rejections, R_{obs} , of La^{3+} and Na^+ as a function of the solution velocity, J_v , during filtration of 0.01 M LaCl_3 + 0.01 M NaCl through a NF270 membrane. The inset shows the data for La^{3+} on an expanded y scale.

Simulations of NF and diafiltration using the solution-diffusion-electromigration model agree with

experiments and demonstrate how separations depend on flow rates, boundary layers in solution, and the solution composition. As an example, Figure 1 shows that in a solution containing equimolar LaCl₃ and NaCl, at low flow rates the observed Na⁺ rejection may reach a value of -0.7, meaning that the concentration of Na⁺ is 1.7 times more in the permeate than in the feed. Rejections become even more negative with an increasing ratio of La³⁺/Na⁺ in the feed solution, but concentration polarization hinders the separations. These simulations rely on experiments with a rotating membrane to determine single-ion permeances. The rotating membrane is vital for providing a known and uniform boundary layer thickness to account for concentration polarization at the membrane surface.

Future Plans.

Future work will model and perform electrodialysis for selective concentration of REE ions. Coupling of electrodialysis to complexation should yield very high selectivities due to unusual concentration profiles in the membrane. Additionally, further work aims to exploit ion hydration energies for separating Li⁺ from K⁺ and Na⁺.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. S. Zhang, J. Wang, A. Yaroshchuk, Q. Du, P. Xin, M. L. Bruening, and F. Xia. Addressing Challenges in Ion-Selectivity Characterization in Nanopores. *J. Am. Chem. Soc.* 2024, 146, 11036-11042.
2. D. Ding, L. Yang, J. Wang, A. Yaroshchuk, J. L. Schaefer, and M. L. Bruening. Selective Transport of Trivalent Lanthanide in Electrodialysis: Limitations due to Concentration Polarization. *J. Membrane Sci.* 2023, 685, 121949.
3. C. Tang, A. Yaroshchuk, and M. L. Bruening. Ion Separations Based on Spontaneously Arising Streaming Potentials in Rotating Isoporous Membranes. *Membranes.* 2022, 12, 631.
4. D. Ding, A. Yaroshchuk, and M. L. Bruening. Electrodialysis through Nafion Membranes Coated with Polyelectrolyte Multilayers Yields >99% Pure Monovalent Ions at High Recoveries. *J. Membrane Sci.* 2022, 647, 120294.
5. C. Tang, M. P. Bondarenko, A. Yaroshchuk, and M. L. Bruening. Highly Selective Ion Separations Based on Counter-flow Electromigration in Nanoporous Membranes. *J. Membrane Sci.* 2021, 638, 119684.

Grant cited but not intellectually led by this award:

1. Z.S. Siwy, M.L. Bruening, and S.W. Howorka. Nanopores: Synergy from DNA Sequencing to Industrial Filtration – Small Holes with Big Impact. *Chem. Soc. Rev.* 2023, **52**, 1983-1994.
2. S. Zhang, L. Yang, D. Ding, P. Gao, F. Xia, and M. L. Bruening. Highly Rectifying Fluidic Diodes Based on Asymmetric Layer-by-Layer Nanofilms on Nanochannel Membranes. *Anal. Chem.* 2021, 93, 4291-4298.
3. M.P. Bondarenko, A. Yaroshchuk, and M. L. Bruening. Electro-osmo-dialysis Through Nanoporous Layers Physically Conjugated to Micro-perforated Ion-exchange Membranes: Highly Selective Accumulation of Trace Coions. *J. Membrane Sci.* 2021, 622, 19022.

Interfacial and Photochemical Control of CO₂ Binding, Transport, and Release in Direct Air Capture

Vyacheslav S. Bryantsev,¹ Vera Bocharova,¹ Radu Custelcean,¹ Benjamin Doughty,¹ Yi Liao,² Yingzhong Ma,¹ Uvinduni Premadasa,¹ Santanu Roy,¹ Dengpan Dong,¹ Nitesh Kumar,¹ Xinyou Ma,¹ Zewen Zhu¹

¹Oak Ridge National Laboratory, ²Florida Institute of Technology

Key Words: Assembly/Ordering; Interfaces; Non-Thermal Separation Mechanisms; Theory/Simulation.

DE-SC_ERKCG26: Interfacial and Photochemical Control of CO₂ Binding, Transport, and Release in Direct Air Capture

PI: Vyacheslav S. Bryantsev; co-PIs: Vera Bocharova, Radu Custelcean, Benjamin Doughty, Yi Liao, Yingzhong Ma, Uvinduni Premadasa, Santanu Roy.

Research Project Scope.

This project addresses the major fundamental roadblocks in efficient mass and energy transfer dynamics that limit current-generation direct air capture (DAC) technologies. The overarching goal of this proposal is to understand and control the fundamental factors governing CO₂ transport across the air-aqueous water interface and develop photochemical processes for energy-efficient CO₂ release in DAC systems. To address the overarching goal, two specific aims, will be pursued: 1) How can we understand and control CO₂ transport and reactivity across the air-aqueous interface for more efficient DAC? 2) What are the factors controlling the efficient photochemical release of CO₂ in DAC systems that require no thermal input and avoid degradation of the CO₂-sorption molecules? The proposed work will uncover new mechanistic principles for developing highly efficient DAC systems with improved mass transfer of CO₂ at the air-aqueous interface and energy efficient means for regeneration. The insights gained from this study will provide the necessary knowledge to make DAC energy-efficient, affordable, and environmentally friendly for climate change mitigation.

Recent Progress.

We demonstrated the speed up of DAC using interfacial oligomers. Acting as surfactants, these oligomers lowered the surface tension, increased residence times for CO₂ at the surface to maximize the chances of CO₂ transport through the surface and set up chemical gradients to encourage reactions. We demonstrated that by directing reactions to take place near the interface via ionic interactions, one could speed up the CO₂ capture by ~15%.

We have learned how interfacial amino acids order at the air/aqueous interface in the context of DAC. Through MD simulations and nonlinear vibrational sum-frequency generation (vSFG) spectroscopy, we understand how both reactive anionic species and deactivated zwitterionic species compete for interfacial vacancies and provide some insight into how this would impact DAC.

We explored the fundamental role that the bulk and surface properties of CO₂-permeable polymer membranes play in enhancing the efficiency of the solution sorption process in passive DAC. This work leverages various spectroscopic and computational studies to demonstrate that a hybrid system, comprising a reusable CO₂-permeable polymer layer placed atop an aqueous amino acid (AA) solution, can outperform a bare aqueous AA system. We show how the enhanced solubility of CO₂ in the polymer layer can improve the transport of CO₂ into the aqueous phase, while the chemistry of the polymer can control the interfacial barrier for CO₂ permeation and the interfacial concentration of reactive AAs.

We explored the bulk reaction mechanism and rate limiting steps of CO₂ capture by aqueous anionic AAs via ab initio molecular dynamics (AIMD) simulations, free energy analysis, and reaction rate theory. The overall process was found to follow a zwitterionic mechanism, wherein we find the formation of a thermodynamically stable zwitterion to be the rate-limiting step, followed by the proton release from the zwitterion by overcoming a similar barrier. Due to stronger nonequilibrium solvent effects in the first step, many trajectories recrossed the barrier without stabilizing the zwitterion state, resulting in a slower timescale for zwitterion formation.

Following our first photochemically-driven approach for CO₂ release by exploiting the unique properties of an indazole metastable-state photoacids (mPAH), we unveiled the photoisomerization dynamics of an indazole mPAH using time-resolved fluorescence (TRF) spectroscopy. The integration of experiment with time-dependent density functional theory (TDDFT) calculations enabled us to determine timescales and potential energy barriers associated with photoinduced structural changes.

We developed an effective approach to photochemically-controlled DAC based on a new class of photobases. We demonstrated that upon photoirradiation with UV light, the photobase increases the solution pH by 1.7 units, thereby activating the CO₂ capture agent for DAC. After the solvent is saturated with atmospheric CO₂, leaving it in the dark under ambient conditions leads to a pH drop and CO₂ release. Three consecutive DAC cycles have been demonstrated, with a measured average cyclic capacity of 0.25 mols CO₂ per mol of the capture agent and minimal loss in efficiency from one cycle to another.

Future Plans.

Surface spectroscopy efforts will be directed toward controlling ion pairing interactions between oligomers and amino acids via functionalization of oligomers with different head groups. Mechanistic details on the mechanism of adsorption and dynamics of glycine and CO₂ in the interfacial region will be obtained from classical MD simulations.

We will investigate the effects of the water solvent in terms of reorganization dynamics and structures around the reactant and product species of aqueous amino acid-based DAC by employing MD simulations and modeling of vSFG spectroscopy of the OH stretches in water. The interface-selective computed vSFG spectra of water and detailed spectral density analysis will reveal information on the interfacial speciation (e.g., ion pairs—contacts and solvent separated) mediated by water with distinct orientational ordering, which varies across the systems.

We will explore how to enhance CO₂ capture kinetics using interfaces by reducing the coupling with the solvent and ion pairing interactions. AIMD simulations incorporating enhanced sampling to overcome the sizable free energy barriers will be employed to tease out the differences in the reactivities of amino acids at the surface and in the bulk.

A collective variable to track the proton will be developed and applied to glycinate to track the possible proton positions for the reaction products of CO₂, kinetic analysis will be performed to estimate reaction rates with inclusion of nonequilibrium solvent effects.

We will investigate the recently discovered imidazole photoacids and apply them for photo-regeneration of CO₂ sorbent. This type of photoacid possesses very low dark acidity and could be used with high-basidity amine or amino acid sorbents.

Structure-properties relationship will be established for photoacids and photobases with the goal of maximizing the yields and rates of photoisomerization and shifting the absorption maximum into the visible range for a more sustainable photo-DAC.

We will study the hydrogen-bonding interactions and intermolecular proton transfer reactions of

photoacids and photobases using steady-state, time- and frequency-resolved electronic spectroscopic techniques in various neat solvents or their mixtures. The molecular level understanding about these microscopic interactions and dynamics will be further applied to design photoresponsive materials for the photochemically-driven CO₂ release and solvent regeneration at the macroscopic level.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. Kumar, N.; Premadasa, U. I.; Dong, D.; Roy, S.; Ma, Y.Z.; Doughty, B.; Bryantsev, V. S. Adsorption, Orientation, and Speciation of Amino Acids at Air-Aqueous Interfaces for the Direct Air Capture of CO₂. *Langmuir* **2024**, *40*, 14311-14320.
2. Premadasa; U. I.; Doughty, B.; Custelcean; R.; Ma, Y.-Z. Towards Energy-Efficient Direct Air Capture with Photochemically-Driven CO₂ Release and Solvent Regeneration. *ChemPlusChem* **2024**, e202300713, DOI: 10.1002/cplu.202300713.
3. Premadasa, U. I.; Kumar, N.; Zhu, Z.; Li, T.; Roy, S.; Carrillo, J.-M.; Einkauf, J.; Custelcean, R.; Ma, Y.-Z.; Bocharova, V.; Bryantsev, V. S.; Doughty, B. Synergistic Assembly of Charged Oligomers and Amino Acids at the Air-Water Interface: An Avenue Towards Surface Directed CO₂ Capture. *ACS Appl. Mater. Interfaces* **2024**, *16*, 12052-12061.
4. Ma, Y.-Z.; Premadasa, U. I.; Bryantsev, V. S.; Miles, A. R.; Ivanov, I. N.; Elgattar, A.; Liao, A.; Doughty, B. Unravelling photoisomerization dynamics in a metastable-state photoacid. *Phys. Chem. Chem. Phys.* **2024**, *26*, 4062-4070.
5. Ma, X.; Roy, S.; Bryantsev, V. S. An Ab Initio Free Energy Study of the Reaction Mechanism and Rate Limiting Steps of CO₂ Capture by Aqueous Glycine. *Cell Rep. Phys. Sci.* **2023**, *4*, 101642.
6. Premadasa, U. I.; Bocharova, V.; Miles, A. R.; Stamberg, D.; Belony, S.; Bryantsev, V. S.; Elgattar, A.; Liao, Y.; Damron, J. T.; Kidder, M. K.; Doughty, B.; Custelcean, R.; Ma, Y.-Z. Photochemically-Driven CO₂ Release Using a Metastable-State Photoacid for Energy Efficient Direct Air Capture. *Angew. Chem., Int. Ed.* **2023**, *62*, e202304957.
7. Premadasa, U. I.; Dong, D.; Stamberg, D.; Custelcean, R.; Roy, S.; Ma, Y.-Z.; Bocharova, V.; Bryantsev, V. S.; Doughty, B. The Chemical Feedback in the Self-Assembly and Function of Air-Liquid Interfaces: Insight into the Bottlenecks of CO₂ Direct Air Capture. *ACS Appl. Mater. Interfaces* **2023**, *15*, 19634-19645.
8. Elgattar, A.; Alghazwat, O.; Brown, A.B.; Bryantsev, V. S.; Bocharova, V.; Liao, Y. Photoreaction of indazole metastable-state photoacid. *J. Photochem. Photobiol. A: Chem.* **2023**, *439*, 114599.
9. Alghazwat, O.; Elgattar, A.; Liao, Y. Photoacid for Releasing Carbon Dioxide from Sorbent. *Photochem. Photobiol. Sci.* **2023**, *22*, 2573.
10. Liao, Y. Reversible photo control of proton chemistry. *Phys. Chem. Chem. Phys.* **2022**, *24*, 4116-4124.
11. Ozkan, M.; Custelcean, R. The status and prospects of materials for carbon capture technologies. *MRS Bulletin* **2022**, *47*, 1-5.

Grant cited but not intellectually led by this award:

1. Deka, D. J.; Jang, G. G.; Kasturi, A.; Stamberg, D.; Keum J. K.; Custelcean, R.; Tsouris, C. Pronounced reduction in the regeneration energy of potassium sarcosinate CO₂ capture solvent using TiO₂. *Sep. Purif. Technol.* **2025**, *354*, 128850.
2. Zening Liu, Lu Lin, Tianyu Li, Uvinduni I Premadasa, Kunlun Hong, Ying-Zhong Ma, Robert L Sacci, John Katsaras, Jan-Michael Carrillo, Benjamin Doughty, C Patrick Collier, Physicochemical control of solvation and molecular assembly of charged amphiphilic oligomers at air-aqueous interfaces, *J. Colloid Interface Sci.* **2024**, *669*, 552-560.
3. Xiao, Z.; Drake, H. F.; Day, G. S.; Kuszynski, J. E.; Lin, H.; Xie, H.; Cai, P.; Ryder, M. R.; Zhou, H.

C. Photoinduced Reversible Phase Transition in a Phenothiazine-Based Metal-Organic Framework.
Cell Rep. Phys. Sci. **2022**, 3, 101074.

Identifying Small Circular Peptides for Ln/Ln Selectivity with Yeast Display, Molecular Simulation, and Spectroscopy

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Key Words: Bioinspired Recognition; Inorganic Chelation; Liquid-Liquid Phase; Theory/Simulation

DE-SC0024556: Identifying Small Circular Peptides for Ln/Ln Selectivity with Yeast Display, Molecular Simulation, and Spectroscopy

PI: David C. Cantu; co-PI: Ana de Bettencourt Dias; co-PI: Maryam Raeeszadeh-Sarmazdeh

Research Project Scope.

The aim of this project is to identify small circular peptides with specificity to particular lanthanide (Ln) ions. Extractants with improved specificity to particular Ln ions are needed to make Ln/Ln solvent extraction more efficient. Peptides are expressed on the surface of yeast cells to separate cells with Ln-binding peptides from cells whose peptides do not bind Ln ions with fluorescence-activated cell sorting. The Ln binding affinity of the peptides in solution is being determined with emission and excitation spectroscopy. The Ln coordination structure of the peptides is being resolved with molecular dynamics simulations, computational chemistry calculations, and extended X-ray absorption fine structure spectroscopy.

Recent Progress.

Efforts have focused on developing the computational and experimental capabilities to meet the project aim. We are working with small peptides with a circular structure that results from cysteine residues in both the N- and C-terminal positions.

- We are expressing the peptides on the surfaces of yeast cells to gain the capability of separating cells with Ln-binding peptides from cells without using fluorescence-activated cell sorting. We used both flow cytometry and plate reader assays to show Ln binding to cyclic peptides expressed on yeast cells. We observed signals in the presence of Ln ions in the nanomolar range; however, the yeast cells also showed Ln binding. Ln ions did not affect yeast growth.
- To determine the Ln-peptide binding in solution with emission and excitation spectroscopy, and measure the stability of the complexes, we initiated the synthesis of cyclic peptides and established the protocols to use a high-resolution fluorimeter for the fast assessment of different peptides bound to Eu(III) in solution in a 96-well plate format.
- Using molecular dynamics simulations, we are replicating the structure of a Ln-peptide complex (Figure). Based on the computational protocol, the structure of >50 circular peptides were predicted with molecular dynamics simulations. A quick metric to estimate complex stability is the number of coordinated water molecules, which can also be determined with emission and excitation spectroscopy. Promising peptides were identified for experimental characterization. To quantify Ln-

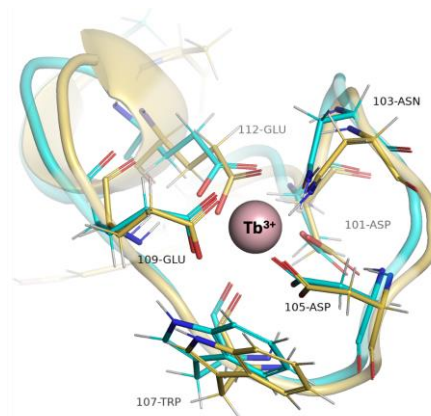


Figure. Structure of a Tb-peptide complex predicted with molecular dynamics simulations (blue) compared with the experimentally resolved crystal structure of the same peptide complexed with Tb (yellow, PDB: 1TJB).

peptide complex binding, umbrella sampling molecular dynamics simulations were performed with a peptide (1TJB) whose binding free energies with Ln ions are known), and the La(III), Eu(III) and Yb(III) ions.

Future Plans.

We will continue developing high throughput methodologies to screen a larger library of cyclic peptide and use fluorescence-activated cell sorting. We will continue efforts to synthesize and isolate peptides for spectroscopic characterization in solution with Eu(III), namely lifetimes in water and D₂O to infer the number of water molecules coordinated to the metal ion and compare with simulation. We will continue working on developing an electronic structure calculations protocol to quantify binding energies. The level of theory required with lanthanides, combined with the large number of atoms in the peptide ligands, makes all-electron calculations for accurate binding energies computationally too expensive. We will use an embedded calculations approach in which the Ln(III) ion and coordinating functional groups are treated with a high level of theory combined with a semi-empirical model for the remaining atoms.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Grant cited but not intellectually led by this award:

1. M. Kalantar, G.A. Hilpert, E.R. Mosca, M. Raeeszadeh-Sarmazdeh. Engineering metalloproteinase inhibitors: tissue inhibitors of metalloproteinases or antibodies, that is the question. *Current Opinion in Biotechnology*. 2024, 86, 103094.

Synergistic Approaches to Advanced Minor Actinide Separations

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Key Words: Inorganic Chelation; Liquid-Liquid Phase; Organic Ligand Recognition; Theory/Simulation

DE-SC0018033: Development of Bipolar Complexants for Minor Actinide Separations

PI: Jesse D. Carrick; co-PI: David A. Dixon

Research Project Scope.

Separation and recycling of the minor actinides from the lanthanides via the partition and transmutation strategy can decrease the volume, radiotoxicity, and heat load of used nuclear fuel destined for storage in a geologic repository. Extraction of the minor actinides from the neutron-poisoning lanthanides presents numerous challenges as physical properties of the f-elements are quite similar. Work in this laboratory has sought to develop molecular constructs which selectively bind to the minor actinides over lanthanides by accentuating metal:complexant interactions of soft-N-donors with the diffuse f orbitals.

Recent Progress.

Achieving high solubility, chemoselectivity, stability, and reversibility are at the forefront of separation method development. Recently, a discovery that solubility of C₂-symmetric BTP complexants, polar molecules, in nonpolar, process-relevant diluents including isooctanol and kerosene, could be effectively modulated by purposeful installation of additional carbon atoms at the 3,3'-positions of dihydroxybenzyl followed by standard condensation to afford the BTP complexant has accelerated momentum of the alkoxy-BTP class of complexants. Reversibility of the metal:complexant binding event by pH modulation without competitive ligand exchange, as well as recyclability of the complexant for subsequent extractions, add further value to the developed approach. Elements of molecular design, separations validation, in addition to spectroscopic and density functional theory data will be presented.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. L. S. Fletcher; M. L. Tedder; S. O. Olayiwola; J. D. Carrick, A Hydrolytically Stable Complexant for Minor An Separation from Ln in Process Relevant Diluents. *Chemical Communications* 2024, 60, 5642–5645. DOI: <https://doi.org/10.1039/D4CC00983E>
2. O. J. Edirin and J. D. Carrick, Synthesis of Fused [1,2,3]-Triazoloheteroarenes via Intramolecular Azo Annulation of *N*-Tosylhydrazones Catalyzed by 1,8-Diazabicyclo[5.4.0]undec-7-ene. *Journal of Organic Chemistry* 2024, 89, 7201–7209. DOI: <https://doi.org/10.1021/acs.joc.4c00627>
3. M. L. Tedder and J. D. Carrick, A Synthetic Strategy for the Preparation of Alkoxy-Functionalized Bis-1,2,4-triazinyl-pyridines. *Journal of Heterocyclic Chemistry* 2024, Early View. DOI: <https://doi.org/10.1002/jhet.4828>
4. E. A. Agyei and J. D. Carrick, Synthetic Approach to the Construction of Unsymmetric Pyridyl-1,2,4-Triazine Complexants. *Tetrahedron* 2024, 155, 133872. DOI: <https://doi.org/10.1016/j.tet.2024.133872>

5. L. S. Fletcher; M. L. Tedder; S. O. Olayiwola; N. A. Joyner; M. M. Mason; A. G. Oliver; D. D. Ensor; D. A. Dixon; J. D. Carrick, Next Generation 3,3'-AlkoxyBTPs as Complexants for Minor Actinide Separation from Lanthanides: A Comprehensive Separations, Spectroscopic, and DFT Study. *Inorganic Chemistry* **2024**, *63*, 4819–4827. DOI: <https://doi.org/10.1021/acs.inorgchem.3c02061>
6. L. S. Fletcher; M. L. Tedder; S. O. Olayiwola; D. D. Ensor; J. D. Carrick, Separation of $^{241}\text{Am}^{3+}$ from $^{154}\text{Eu}^{3+}$ from Simulated Spent Nuclear Fuel in Trifluoromethylphenyl Sulfone using 3,3'-butyloxy-bis-1,2,4-triazinyl-2,6-pyridine as a Potent Receptor. *Solvent Extraction and Ion Exchange* **2024**, *42*, 105–117 DOI: <https://doi.org/10.1080/07366299.2024.2320094>
7. E. A. Agyei and J. D. Carrick, Metal-Free, Oxidative Condensation of Heteroaryl- and Aryl Carbaldehydes towards Functionalized Carbonitriles. *Chemistry Select* **2023**, *8*, e202300866. DOI: [doi/10.1002/slct.202300866](https://doi.org/10.1002/slct.202300866)
8. F. O. Dzeagu and J. D. Carrick, Synthetic Access to Unsymmetric 1,3,4-oxadiazolyl Complexant Scaffolds via Intramolecular Oxidative Annulation of Arylhydrazones with Heteroaryl Carbaldehydes. *Journal of Organic Chemistry* **2023**, *88*, 419–432. DOI: doi.org/10.1021/acs.joc.2c02421

5. Z. Z. Gullledge; C. C. Pinson; A. M. Stovall; F. O. Dzeagu; J. D. Carrick, Chemoselective, Osmium-Free, Dihydroxylation / Oxidative Cleavage of Heteroaryl Isoprenes by a Contemporary Malaprade Reaction. *Organic and Biomolecular Chemistry* **2022**, *20*, 7916–7922. DOI: [10.1039/D2OB01643E](https://doi.org/10.1039/D2OB01643E)
6. Z. Z. Gullledge; D. P. Duda; D. A. Dixon, J. D. Carrick, Microwave-Assisted, Metal- and Azide-Free Synthesis of Functionalized Heteroaryl-1,2,3-triazoles via Oxidative Cyclization of N-Tosylhydrazones and Anilines. *Journal of Organic Chemistry* **2022**, *87*, 12632–12643. DOI: [10.1021/acs.joc.2c01042](https://doi.org/10.1021/acs.joc.2c01042).
7. M. L. Tedder; F. O. Dzeagu; M. M. Mason; D. A. Dixon; J. D. Carrick, Microwave-Assisted C-H Oxidation of Methylpyridylheteroarenes via a Kornblum-type Reaction. *Tetrahedron* **2022**, *116*, 132805. DOI: [10.1016/j.tet.2022.132805](https://doi.org/10.1016/j.tet.2022.132805)
8. M. M. Mason; C. M. Smith; M. Vasiliu; J. D. Carrick; D. A. Dixon, Density Functional Prediction of An(III)/Ln(III) Separation by 1,2,4-Triazinyl-pyridine Derivatives. *Journal of Physical Chemistry A*, **2021**, *125*, 6529-6542. DOI: [10.1021/acs.jpca.1c01854](https://doi.org/10.1021/acs.jpca.1c01854)

The Rare Earth Project: Using Light and Other Stimuli to Separate Lanthanide Materials

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Key Words: Non-Thermal Separation Mechanisms

DE-AC02-05CH11231 (CH20CRIMAT): Rare Earth Project

PI: Rebecca J. Abergel; co-PIs: Polly Arnold, Emory Chan, Ethan Crumlin, Wibe de Jong, Alexei Federov, Wayne Lukens, Stefan Minasian, Ting Xu

Research Project Scope.

The overall goal of the Rare Earth Project is to delineate fundamental principles that will guide the incorporation of specific molecular systems into higher order materials, ultimately leading to breakthrough and innovation in rare earth extraction processes. The scope of work includes (1) the design, synthesis, and characterization of fundamentally new molecular architectures and materials that enable electronic structure manipulation and selective separation of rare earth metal ions; (2) the discovery of new separation principles and materials that efficiently discriminate rare earth elements from complex mixtures; and (3) the use of in situ and in operando physical characterization techniques to directly probe the physical and chemical properties of rare earth systems, correlate behavior with electronic structure, and monitor uptake and transport of rare earth ions.

Recent Progress.

A major component of the Rare Earth project is to leverage photon and electron absorption to augment the selective chemistry of lanthanide ions (Task 1 above) and enable new separation techniques (Task 2). Here, we exploit the ability of selected ligands and lanthanide ions to modulate the solubility of lanthanide-doped nanomaterials when exposed to ultraviolet (UV) photons, near-infrared (NIR) light and electron (e^-) beams. Using lanthanide-doped upconverting nanoparticles (UCNPs) as a model system, we explored ligand chemistries that enable the selective deposition of nanoparticles doped with specific lanthanide compositions onto substrates,

enabling patterning with microscale and even nanoscale resolution. These UCNPs, 6-18 nm in diameter and singly doped with Tm^{3+} or codoped with Yb^{3+}/Tm^{3+} , or Yb^{3+}/Er^{3+} , have distinct absorption lines and nonlinear optical responses owing to the unique $4f^N$ electronic structures of their rare earth dopants and the complex energy transfer interactions between them. To enhance absorption and modulate the solubility of the UCNPs, we developed a library of ligands that form either new ionic linkages or covalent bonds between UCNPs under UV, e-beam, and NIR exposure. We find that 6-nm UCNPs can be deposited and patterned with compact, ionic-based ligands, while larger UCNPs requires long-chain, cross-linkable ligands. This highly localized photo/electron-initiated chemistry enables the fabrication of densely packed UCNP patterns with high resolutions ($\sim 1 \mu m$ with UV and NIR exposure; $< 100 \text{ nm}$ with e-beam). Our upconversion NIR lithography approach demonstrates the potential to use the intrinsic electronic structure of rare earth elements and their unique optical properties as distinguishing characteristics for separating these materials. The deposited UCNP patterns retain their upconverting, photon avalanching, and

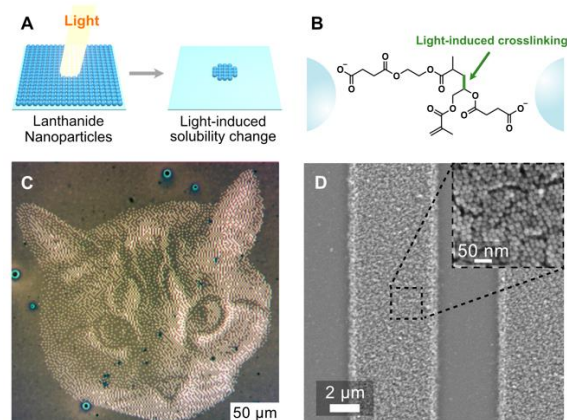


Figure 1. Thin-film-based separation of lanthanide-doped nanoparticles using direct optical lithography.

photoswitching behaviors, which can be exploited in optical devices for next-generation optical applications. This selective lithography potentially enables the on-demand, fine separation of crudely processed critical materials at the site of their integration into high value devices, rather separating lanthanide ions in bulk as raw materials.

Peer Reviewed Publications Acknowledging this Grant (relevant to this abstract)

Intellectually led by this grant:

1. Pan, J.-A.; Skripka, A.; Lee, C.; Qi, X.; Pham, A. L.; Woods, J. J.; Abergel, R. J.; Schuck, P. J.; Cohen, B. E.; Chan, E. M. Ligand-Assisted Direct Lithography of Upconverting and Avalanching Nanoparticles for Nonlinear Photonics. *J. Am. Chem. Soc.* 2024, *146* (11), 7487-7497.

Grant cited but not intellectually led by this award:

1. Skripka, A.; Lee, M.; Qi, X.; Pan, J. A.; Yang, H.; Lee, C.; Schuck, P. J.; Cohen, B. E.; Jaque, D.; Chan, E. M. A Generalized Approach to Photon Avalanche Upconversion in Luminescent Nanocrystals. *Nano Lett.* 2023, *23* (15), 7100–7106.

Surfactant Tuning of Liquid Interfacial Geometries – How to Enhance or Suppress Surface Deformation and Fluctuations

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Key Words: Assembly/Ordering; Data Science; Liquid-Liquid Phase; Theory/Simulation

DE-SC0001815 & DE-SC0023637: Bespoke Liquid/Liquid Interfaces that Modulate Solute Transport Mechanisms in Solvent Extraction

PI: Aurora E Clark

Research Project Scope. Understanding the mechanisms behind solute transport, including the structural features and intermolecular forces that modulate their energetics, represents a strategic and necessary investment to advance separations, and in turn energy technologies within the BES portfolio. At a molecular level, liquid/liquid interfaces naturally feature structural and dynamic heterogeneity across the rough surface that derives from local thermally induced stochastic motion at the instantaneous surface and longer-range capillary waves. This results in a distribution of microenvironments that seems to be highly tunable by surface active molecules (whether they are the solutes or surfactants). The current work seeks to understand the fundamental forces that determine interfacial organization and elucidate the correlating relationship between organization and solute transport processes. We employ multiscale computational methods and recently developed graph theoretical, algebraic, and geometric topology algorithms to characterize interfacial structure, competitive interfacial interactions, and transport energy landscapes.

Recent Progress.

Although liquid/vapor and liquid/liquid interfaces exhibit significant disorder relative to solid and solid/liquid interfaces, the intermolecular interactions of surfactants with surface waters and ions can dramatically change interfacial geometry and its associated fluctuations. In recent work we have: 1) developed two new mathematical approaches for describing and quantifying surfactant adsorption and the changes to geometry that occur in the presence and absence of transport events, and 2) identified large changes to the surface geometry as a function of surfactant structure and whether the surface is a water/vapor interface or a water/organic surface (DOI: 10.1021/acs.jctc.3c00090, DOI: 10.26434/chemrxiv-2023-x66jd-v3). Indeed, water/vapor geometries are distinctly different than analogous surfaces at the water/organic phase boundary. This is particularly important, as water/vapor interfaces are employed as surrogates for understanding water/organic surface organization and properties. Fluctuations of the interface, measured by autocorrelation functions of different geometric metrics additionally show large variability of the oscillations of the interfacial film as a function of surface composition.

Future Plans. These data form the basis for ongoing research into modifications to capillary wave theory and for new phenomenological models that relate surface deformation to dynamic evolution, including the impact upon desorption rates during transport processes with mass transfer.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

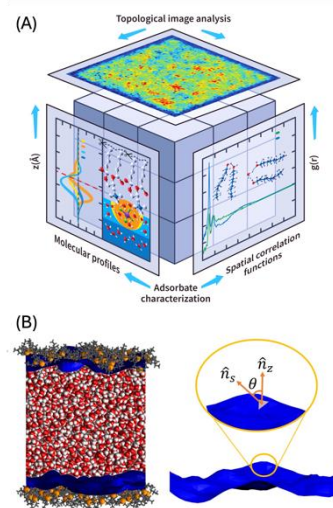


Figure 1. (A) Topological image analysis provides information about density changes of adsorbates. (B) Surface geometric metrics measure extent of surface deformation and relationships with surface tension and transport.

Intellectually led by this grant:

1. Kumar, N.; Clark, A. E. Persistent Homology Descriptors for Surface Image Analysis in Complex Chemical Systems, *Journal of Chemical Theory and Computation*, **2023**, *19*, 3303-3312. DOI: 10.1021/acs.jctc.3c00090
2. Kumar, N.⁺; Clark, A. E. Unexpected Inverse Correlations and Cooperativity in Ion-pair Phase Transfer, *Chemical Science*, **2021**, *12*, 13930-13939. DOI: 10.1039/D1SC04004A
3. Kumar, N.,[#] Servis, M.; Clark, A. E. Uranyl Speciation in the Presence of Ion Gradients at the Electrolyte/Organic Interface, *Solvent Extraction and Ion Exchange*, **2021**, *40*, 165-187. <https://doi.org/10.1080/07366299.2021.1954323>
4. Liu, Z.,⁺ Clark, A. E. An Octanol Hinge Opens the Door to Water Transport, *Chemical Science*, **2021**, *12*, 2294 – 2303. DOI: 10.1039/D0SC04782A.

Grant cited but not intellectually led by this award:

1. Nayak, S.; Kuma, R.; Liu, Z.,[#] Qiao, B.; Clark, A. E.; Uysal, A. Origins of Clustering of Metalate-Extractant Complexes in Liquid-Liquid Extraction. *ACS Applied Materials and Interfaces*, **2021**, *13*, 24194-24206. <https://doi.org/10.1021/acsami.0c23158>
2. Kumar, N., Sadhu, B., Clark, A. E. Essential Aspects of Solvent Effects and Solution Conditions Upon the Modeling and Simulation of Lanthanide and Actinide Complexes. Rare Earth Elements and Actinides: Progress in Computational Science Applications. Penchoff, D. A., Windus, T. L., Peterson, C. C. Eds.; ACS Symposium Series; American Chemical Society: Washington, DC, **2021**; Vol. 1388, Chapter 12, pp (TBD). DOI: 10.1021/bk-2021-1388.ch012.

Probing Lanmodulin's Mechanisms of Rare Earth Selectivity for Protein-Based Bioseparations

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Key Words: Bioinspired Recognition; Dynamics; Inorganic Chelation; Other (Biomolecules)

DE-SC0021007: Probing Lanmodulin's Mechanisms of Rare Earth Selectivity for Protein-Based Bioseparations

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Research Project Scope. The small differences in coordination chemistry and ionic radius within the rare earth elements (REs: the lanthanide series, plus yttrium and scandium) make their separation a long-standing challenge, but one that is critical for the continued use of these metals in myriad technologies. The discovery that certain lanthanides are specifically utilized by biological systems has opened new avenues for development of novel biochemistry-based strategies for highly selective recovery and separation of rare earth elements and actinides. The first family of natural, selective chelators for rare earths is the lanmodulin (LanM) family of lanthanide-binding proteins, discovered by our group in 2018. Lanmodulins possess $>10^{11}$ -fold selectivity for rare earths over other metal ions. The overall goal of this project is to understand the origins of the high RE selectivity of lanmodulins and to use this knowledge to develop methods for intra-RE separations using these proteins and their derivatives. A major area of emphasis is determining the importance of interactions outside of the primary coordination sphere on metal selectivity, in particular selectivity within the lanthanide series.

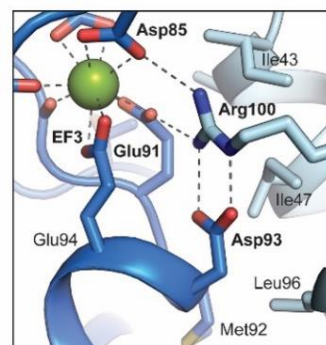


Figure. Detailed view of the dimer interface near *H. quercus* LanM's EF-hand 3, showing the hydrogen bonding network tying lanthanide coordination (La(III), green sphere) in one monomer to Arg100 in the other. By tying multiple interactions at the dimer interface to positioning of the Glu91 residue, subtle differences between REs can be amplified.

Recent Progress. We recently identified and characterized a novel LanM with an oligomeric state that is sensitive to RE ionic radius, the La(III)-induced dimer being >100 -fold tighter than the Dy(III)-induced dimer (Mattocks et al., *Nature* 2023), improving discrimination between La(III) and Dy(III) by ~ 10 -fold versus the prototypal LanM. X-ray crystal structures revealed that the picometer-scale differences between La(III) and Dy(III) result in a reduction in coordination number from 10 to 9 that propagates to the dimer interface via a hydrogen-bonding network conserved in a subset of LanM proteins (**Figure**). Immobilization of this protein yielded a column-based separation of Nd(III) and Dy(III) in a single column stage. We believe that similar differences in global protein structure induced by small differences in coordination at the metal-binding sites also underlie the behavior of the monomeric lanmodulins, and we seek to understand these interactions in order to exploit these effects for enhanced separations.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. J.A. Mattocks, J.A. Cotruvo, Jr., G.J.-P. Deblonde. Engineering lanmodulin's selectivity for actinides over lanthanides by controlling solvent coordination and second-sphere interactions. *Chemical Science*. 2022, 13, 6054-6066.
2. J.A. Mattocks, J.J. Jung, C.-Y. Lin, Z. Dong, N.H. Yennawar, E.R. Featherston, C.S. Kang-Yun, T.A. Hamilton, D.M. Park, A.K. Boal, J.A. Cotruvo, Jr. Enhanced rare-earth separation with a metal-

sensitive lanmodulin dimer. *Nature*. 2023, 618, 87-93.

3. J.A. Cotruvo, Jr., J.A. Mattocks, J.J. Jung, C.-Y. Lin, Z. Dong, E.R. Featherston, C.S. Kang-Yun, D.M. Park, A.K. Boal. Lanmodulin orthologs with improved rare earth separation performance. PCT International Application No. PCT/US2023/074516. Pending.

Grant cited but not intellectually led by this award:

1. G.J.-P. Deblonde, J.A. Mattocks, H. Wang, E.M. Gale, A.B. Kersting, M. Zavarin, J.A. Cotruvo, Jr. Characterization of americium and curium complexes of the protein lanmodulin: a potential macromolecular mechanism for actinide mobility in the environment. *Journal of the American Chemical Society*. 2021, 143, 15769-15783.
2. Z. Dong, J.A. Mattocks, G.J.-P. Deblonde, D. Hu, Y. Jiao, J.A. Cotruvo, Jr., D.M. Park. Bridging hydrometallurgy and biochemistry: A protein-based process for recovery and separation of rare earth elements. *ACS Central Science*. 2021, 7, 1798-1808.
3. G.J.-P. Deblonde, J.A. Mattocks, Z. Dong, T. Woody, J.A. Cotruvo Jr., M. Zavarin, Capturing an elusive but critical element: Natural protein enables actinium chemistry. *Science Advances*. 2021, 7, eabk0273.
4. K.E. Martin, J.A. Mattocks, D. Smilowicz, E. Alucio-Sarduy, J.N. Whetter, J.W. Engle, J.A. Cotruvo, Jr., E. Boros. Radiolabeling and in vivo evaluation of lanmodulin with biomedically relevant lanthanide isotopes. *RSC Chemical Biology*. 2023, 4, 414-421.
5. G.J.-P. Deblonde, K. Morrison, J.A. Mattocks, J.A. Cotruvo, Jr., M. Zavarin, A.B. Kersting. Impact of a biological chelator, lanmodulin, on minor actinide aqueous speciation and transport in the environment. *Environmental Science and Technology*. 2023, 57, 20830-20843.
6. Z. Dong, J.A. Mattocks, J.A. Seidel, J.A. Cotruvo, Jr., D.M. Park. Protein-based approach for high-purity Sc, Y, and grouped lanthanide separation. *Separation and Purification Technology*. 2024, 333, 125919.
7. J.A. Seidel, Z. Dong, P. Diep, J.A. Cotruvo, Jr., D.M. Park. EF-hand battle royale: hetero-ion complexation in lanmodulin. *JACS Au*, in press.

Reactive Separations of Superhydrophilic Anions and CO₂ from Ultradilute Environments

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Key Words: Assembly/Ordering; Dilute Species; Organic Ligand Recognition; Reactive Separations

DE-SC_ERKCC08: Principles of Ion Recognition and Transport in Sustainable Chemical Separations

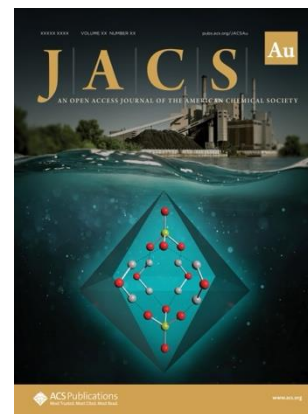
PI: Radu Custelcean; co-PIs: Vyacheslav Bryantsev, Benjamin Doughty, Jeffrey Einkauf, Santa Jansone-Popova, Nikki Thiele,

Research Project Scope.

The overarching goal of this project is to understand the structural, energetic, and mechanistic factors leading to selective, energy-efficient, and sustainable anion separations with reactive, self-organizing receptors, frameworks, and crystals. Toward addressing this goal, we are pursuing three specific aims: 1) Understand how novel switching mechanisms based on physical stimuli can achieve sustainable release of bound anionic species with minimal chemical and energy inputs; 2) Explore reactive crystallization of (bi)carbonate anions for energy-efficient CO₂ capture and release; 3) Understand how self-assembly of anion-binding units into preorganized receptors and materials can lead to enhanced anion-separation functions. To address the overarching goal and the specific aims, we are developing anion receptors and materials based on iminoguanidines (IGs), exploiting their versatility and special ability to selectively separate anions and capture CO₂. Specific separation targets are strongly hydrophilic oxyanions (e.g., sulfate, selenate, chromate, phosphate), PFAS, and atmospheric CO₂ (via carbonate anions), which are extremely challenging to remove selectively and effectively from dilute aqueous environments and air, respectively.

Recent Progress.

Building on our signature chemistry involving bis-iminoguanidinium (BIG) receptors that can effectively remove oxyanions (e.g., sulfate, selenate, chromate, carbonate) from aqueous solutions through crystallization of hydrogen-bonded solids of extremely low aqueous solubilities, we have demonstrated effective separation of selenate anions from dilute and competitive aqueous environments. Here, we took advantage of the similarity between sulfate and selenate oxyanions, leveraging the excess sulfate concentration often found in Se-containing wastewaters, and co-crystallized the two anions through the formation of solid solutions with BIG receptors. This approach allowed the quantitative removal of the two oxyanions, leading to Se concentration reduction in wastewaters generated by coal-burning power plants down to below 5 ppb, the discharge limit imposed by the EPA.



Along a different line of investigation, we demonstrated a new approach to direct air capture by reactive crystallization (RC-DAC) of CO₂ with aqueous amino acid/guanidine. The crystallization was monitored in situ by pH measurements, real-time imaging with a microscope probe, and by Raman spectroscopy, and ex situ by NMR spectroscopy, powder X-ray diffraction, and total inorganic carbonate analysis. The investigation provided a detailed mechanistic picture of the RC-DAC process, involving formation of carbamate and carbonate anions in solution, followed by sequential crystallization of different guanidinium carbonate phases.

In synergy with Bryantsev's BES project on DAC at ORNL, we developed a new class of diiminoguanidinium (DIG) photobases that can regulate the solution pH with light. Upon photoirradiation, pyridine-functionalized DIGs photoisomerize from E,E to Z,Z configuration, leading to a large increase in the pK_a (2.8 units) and solution pH (1.7 units). This new class of photobases is being further explored for photochemically controlled direct air capture.



Future Plans.

1. Mechanistic investigation of CO₂ release in direct air capture via crystallization with bis-iminoguanidines. This includes experimental studies by X-ray and neutron diffraction, solid-state NMR spectroscopy, and Raman spectroscopy, as well as DFT calculations and MD simulations.
2. Understand the structure/properties relationships of iminoguanidinium-based photoswitchable oxyanion receptors using a combination of spectroscopic methods and quantum chemical calculations. Specifically, we will investigate the correlation between the pK_a s of the anions and the receptors and the strength of anion binding, and the effects of substituents on the photochemical properties of the receptors (e.g., absorption wavelength, quantum yield, photostationary equilibrium, kinetics of photoswitching and thermal relaxation).
3. Investigate the interfacial assembly and recognition properties of a series of flexible amphiphilic receptors comprising hydrophilic iminoguanidine anion-binding units in conjunction with lipophilic hydrocarbon tails. These ligands will vary in the length, branching, and placement of their tails as well as in their potential to provide convergent hydrogen-bond donors via increasing numbers of IG groups. We hypothesize that these structural and chemical differences between ligands will lead to variations in their supramolecular organization and solvation at an oil-water interface that can be leveraged to understand, control, and drive the extraction of different anion species.
4. Understand how interfaces can be used to control chemical transport in solvent extraction via SFG measurements with supporting DFT/MD simulations. Specific ion interactions, ion pairing, and transport phenomena will be probed in these systems in the presence of competitive anions for limited surface vacancies. We will probe characteristic spectroscopic reporters for ions and headgroups, as well as OH stretches descriptive of solvation interactions at the interface, which are hypothesized to change based on the solvation of the ligand tails in the neighboring oil phase. This work will shed light on how interfaces can be used in selective, kinetically-controlled ion separations.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. Custelcean, R. Direct Air Capture with Bis-Iminoguanidines (BIGs): *From Discovery to Commercialization*. *Chem* **2021**, *7*, 2848-2852.
2. Custelcean, R. *Direct Air Capture of CO₂ via Crystal Engineering*. *Chem. Sci.* **2021**, *12*, 12518-12528.
3. Li, P.; Damron, J. T.; Veith, G. M.; Bryantsev, V. S.; Mahurin, S. M.; Popovs, I. Jansone-Popova, S. *Bifunctional Ionic Covalent Organic Networks for Enhanced Simultaneous Removal of Chromium(VI) and Arsenic(V) Oxoanions via Synergetic Ion Exchange and Redox Process*. *Small* **2021**, *17*, 2104703 (featured on the cover).
4. Einkauf, J. D.; Bryantsev, V. S.; Moyer, B. A.; Custelcean, R. *A Photoresponsive Receptor with a 10⁵ Magnitude of Reversible Anion-Binding Switching*. *Chem. Eur. J.* **2022**, *28*, e202200719 (featured on the cover).
5. Custelcean, R. *Direct Air Capture of CO₂ Using Solvents*. *Annual Reviews of Chemical and*

- Biomolecular Engineering*, **2022**, *13*, 217-234.
6. Einkauf, J. D.; Bryantsev, V. S.; Custelcean, R. *Anti-Electrostatic Hydrogen-Bonded Tellurate Dimers Captured and Stabilized by Crystallization of a Bis-iminoguanidinium Salt*, *Polyhedron* **2022**, *223*, 115990.
 7. Ozkan, M.; Custelcean, R. *The Status and Prospects of Materials for Carbon Capture Technologies*, *MRS Bulletin* **2022**, *47*, 1-5 (featured on the cover).
 8. Premadasa, U. I.; Ma, Y.; Sacci, R. L.; Bocharova, V.; Thiele, N. A. Doughty, B. *Understanding Self-Assembly and the Stabilization of Liquid/Liquid Interfaces: The Importance of Ligand Tail Branching and Oil-Phase Solvation*. *J. Colloid Interface Sci.* **2022**, *609*, 807-814.
 9. Stamberg, D.; Thiele, N.; Custelcean, R. *Synergistic Direct Air Capture of CO₂ with Aqueous Guanidine/Amino Acid Solvents*. *MRS Advances*, **2022**, *7*, 399-403.
 10. Sharafoddinzadeh, D.; Salehi, M.; Jansone-Popova, S.; Herath, A.; Bhattacharjee, L. *Advance modification of polyacrylonitrile nanofibers for enhanced removal of hexavalent chromium from water*. *J. Appl. Polym. Sci.* **2022**, e52169.
 11. Herath, A.; Salehi, M.; Jansone-Popova, S. *Production of Polyacrylonitrile/Ionic Covalent Organic Framework Hybrid Nanofibers for Effective Removal of Chromium(VI) from Water*. *J. Hazardous Mater.* **2022**, *427*, 128167.
 12. Roy, S.; Bocharova, V.; Stack, A. G.; Bryantsev, V. S. *Nucleation Rate Theory for Coordination Number: Elucidating Water-Mediated Formation of a Zigzag Na₂SO₄ Morphology*. *ACS Applied Materials & Interfaces* **2022**, *47*, 53213-53227.
 13. Custelcean, R. *Reducing Atmospheric Carbon Dioxide through Direct Air Capture*, *ORNL Reviews* **2022**, *55*, 48-51.
 14. Jansone-Popova, S. *Organic Polymer Compositions for Removal of Oxoanions from Aqueous Solutions*. U.S. Patent No. 11,369,944, June 28, **2022**.
 15. Einkauf, J. D.; Williams, N. J.; Seipp, C. A.; Custelcean, R. *Near Quantitative Removal of Selenate and Sulfate Anions from Wastewaters by Cocrystallization with Chelating Hydrogen-Bonding Guanidinium Ligands*. *JACS Au* **2023**, *3*, 879-888.
 16. Premadasa, U. I.; Bocharova, V.; Lin, L.; Genix, A.-C.; Heller, W. T.; Sacci, R. L.; Ma, Y.-Z.; Thiele, N. A.; Doughty, B. *Tracking Molecular Transport Across Oil/Aqueous Interfaces: Insight into "Antagonistic" Binding in Solvent Extraction*. *J. Phys. Chem. B* **2023**, *127*, 4886-4895 (featured on the cover).
 17. Fargher, H. A.; Delmau, L. H.; Bryantsev, V. S.; Haley, M. M.; Johnson, D. W.; Moyer, B. A. *Disrupting the Hofmeister Bias in Salt Liquid-Liquid Extraction with an Arylethynyl Bisurea Anion Receptor*. *Chem. Sci.* **2024**, *15*, 5311-5318.
 18. Moyer, B. A. *Are We Condemned to Repeat History? Solvent Extraction and Ion Exchange*. **2024** DOI: 10.1080/07366299.2024.2358200.
 19. Liu, Z.; Lin, L.; Premadasa, U.I.; Hong, K.; Ma, Y.; Sacci, R. L.; Katsaras, J.; Carrillo, J.M.; Doughty, B.; Collier, P. *Physicochemical Control of Solvation and Molecular Assembly of Charged Amphiphilic Oligomers at Air-Aqueous Interfaces*. *Journal of Colloid and Interface Science* **2024**, *669*, 552-560.
 20. Stamberg, D.; Einkauf, J. D.; Liu, M.; Custelcean, R. *Direct Air Capture of CO₂ via Reactive Crystallization*. *Cryst. Growth Des.* **2024**, *24*, 4556-4562.
 21. John, E. A.; Marie S A.; Wieske, L. H. E.; Ray, D.; Decato, D. A.; Boller, M.; Takacs, Z.; Erdelyj, M.; Bryantsev, V.; Berryman, O. *Taming Molecular Folding: Anion-Templated Foldamers with Tunable Quaternary Structures*. *J. Am. Chem. Soc.* **2024**, *146*, 16419-16427.

Grant cited but not intellectually led by this award:

1. Hwang, I.; Huang, S.-Y.; Smith, S.; Lynch, V.; Custelcean, R.; Moyer, B. A.; Kumar, N.; Bryantsev, V. S.; Sessler, J. L. *Direct Extraction of Sodium Hydroxide by Calix[4]pyrrole-Based Ion-Pair Receptors*. *J. Am. Chem. Soc.* **2023**, *145*, 14387-14394.

2. Du, S.; Huang, J.; Ryder, M. R.; Daemen, L. L.; Yang, C.; Zhang, H.; Yin, P.; Lai, Y.; Xiao, J.; Dai, S.; Chen, B. Probing Sub-5 Angstrom Micropores in Carbon for Precise Light Olefin/Paraffin Separation. *Nature Communications* **2023**, *14*:1197.
3. Sun, J.; Decato, D. A.; Bryantsev, V. S.; John, E. A. Berryman, O. B. The Interplay Between Hydrogen and Halogen Bonding: Substituent Effects and Their Role in the Hydrogen Bond Enhanced Halogen Bond. *Chem. Sci.* **2023**, *14*, 8924-8935.
4. Titov, K.; Ryder, M. R.; Lamaire, A.; Zeng, Z.; Chaudhari, A. K.; Taylor, J.; Mahdi, E. M.; Rogge, S. M. J.; Mukhopadhyay, S.; Rudic, S.; Van Speybroeck, V. V.; Fernandez-Alonso, F.; Tan, J.-C. *Quantum Tunneling Rotor as a Sensitive Atomistic Probe of Guests in a Metal-Organic Framework.* *Phys. Rev. Mater.* **2023**, *7*, 073402.
5. Bracco, J. N.; Camacho Meneses, G.; Colón, O.; Yuan, K.; Stubbs, J. E.; Eng, P. J.; Wanhala, A. K.; Einkauf, J. D.; Boebinger, M. G.; Stack, A. G.; et al. *Reaction Layer Formation on MgO in the Presence of Humidity.* *ACS Applied Materials & Interfaces* **2023**, *16*, 712-722.
6. Wanhala, A. K.; Gibson, L. D.; Subbs, J. E.; Custelcean, R.; Hexel, C.; Eng, P. J.; Bryantsev, V. S.; Stack, A. G. *Structure of the Bastnasite (001) Surface by Crystal Truncation Rod X-ray Diffraction and Ab Initio Molecular Dynamics: Implications for Separation of a Rare Earth Ore Mineral.* *J. Phys. Chem. C* **2023**, *43*, 21150.
7. D. M. Driscoll, F. D. White, S. Pramanik, J. D. Einkauf, B. Ravel, D. Bykov, S. Roy, R. Mayes, L. Delmau, S. Schrell, T. Dyke, A. Miller, M. Silveira, S. v. Cleve, R. Copping, S. Davern, S. Jansone-Popova, I. Popovs, A. S. Ivanov, *Observation of a Promethium Complex in Solution.* *Nature* **2024**, 629 (8013), 819-823.

Fundamental Studies of Novel Separations

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Key Words: Gas Phase; Membranes; Multi-Modal Phenomena; Reactive Separations

FWP ERKCT08: Fundamental Studies of Novel Separations

PI: Sheng Dai; co-PI: Zhenzhen Yang, Shannon Mahurin, De-en Jiang

Research Project Scope.

The overarching goal of this project is to investigate fundamental issues that control the selective binding and transport of target molecular species in nanostructured architectures and unconventional separation media via tailored interactions at multiple length scales. To achieve this overarching goal, we will pursue three integrated specific aims by addressing: (1) Can collective gas transport be developed in ionic liquids? (2) Can collective transport in ionic liquids and free volume-driven transport in porous media be integrated through porous liquids? (3) Can gas transport be controlled via the tailored interaction of porous membranes with ionic liquids? In answering these synergistic research aims, we will be addressing three major challenges of extraordinary importance in separations: selectivity, transport, and their interplay. The central theme of this research is to master the complexity of the ionic structure, interface, free volume, and dynamics that control interactions and transport at multiple length scales, in order to achieve desired separation efficiency, via integrated synthesis, characterization (including neutron scattering), and modeling. The knowledge gained from this project has far-reaching consequences in the way we generate, transform, and store energy and for greenhouse gas mitigation and environmental remediation, in support of the DOE's critical mission as well as recent DOE Energy Earthshots initiatives.

Recent Progress.

1. One of the extensively studied and appealing systems in carbon capture via chemisorption is the Superbase-derived task-specific ionic liquids (STSILs). The capacity to capture CO₂ in these liquids is strongly influenced by the basicity of the anions. However, challenges remain in terms of the high energy required for desorption and the occurrence of side reactions due to the strong basicity of the anions. To address these issues, there is a need for the development of tailored STSILs that utilize a different driving force to achieve efficient CO₂ chemisorption and desorption. We focused on carbanion-derived STSILs, which demonstrated efficient CO₂ chemisorption through the formation of carboxylic acid. Interestingly, the STSIL with the deprotonated malononitrile molecule ([MN]) as the anion exhibited a significantly higher CO₂ uptake capacity compared to the one derived from 2-methylmalononitrile ([MMN]), despite having lower basicity ([MN] < [MMN]). Detailed characterization and theoretical simulations confirmed that carboxylic acid formation occurred in the [MN]-derived STSILs through proton transfer upon reaction with CO₂, while [MMN] lacked the necessary α -H for this process. These findings demonstrate an alternative design principle for STSILs, utilizing extended conjugation in the CO₂-integrated product.
2. Facile approaches capable of constructing stable and structurally diverse porous liquids (PLs) that can deliver high-performance applications are a long-standing, captivating, and challenging research area that requires significant attention. Herein, a facile surface deposition strategy was demonstrated to afford diverse type III-PLs possessing ultra-stable dispersion, external structure modification, and enhanced performance in gas storage and transformation by leveraging the expeditious and uniform precipitation of selected metal salts. The Ag(I) species-modified zeolite nanosheets were deployed as

the porous host to construct type III-PLs with ionic liquids (ILs) containing bromide anion as the liquid phase, leading to stable dispersion driven by the formation of AgBr nanoparticles. The as-afforded type-III PLs displayed promising performance in CO₂ capture/conversion and ethylene/ethane separation. Property and performance of the as-produced PLs could be tuned by the cation structure of the ILs, which can be harnessed to achieve polarity reversal of the porous host via ionic exchange. The surface deposition procedure could be further extended to produce PLs from Ba(II)-functionalized zeolite and ILs containing [SO₄]²⁻ anion driven by the formation and coating of BaSO₄ salts. The as-produced PLs were featured by well-maintained crystallinity of the porous host, good fluidity and stability, enhanced gas uptake capacity, and attractive performance in small gas molecule utilization.

3. Superbase-derived ionic liquids (SILs) are promising sorbents to tackle the carbon challenge featured by tunable interaction strength with CO₂ via structural engineering, particularly the oxygenate-derived counterparts (e.g., phenolate). However, for the widely deployed phenolate-derived SILs, unsolved stability issues severely limited their applications leading to unfavorable and diminished CO₂ chemisorption performance caused by ylide formation-involved side reactions and the phenolate-quinone transformation via auto-oxidation. In this work, robust pyrazolonate-derived SILs possessing anti-oxidation nature were developed by introducing aza-fused rings in the oxygenate-derived anions, which delivered promising and tunable CO₂ uptake capacity surpassing the phenolate-based SIL via a carbonate formation pathway (O–C bond formation), as illustrated by detailed spectroscopy studies. Further theoretical calculations and experimental comparisons demonstrated the more favorable reaction enthalpy and improved anti-oxidation properties of the pyrazolonate-derived SILs compared with phenolate anions. The achievements being made in this work provides a promising approach to achieve efficient carbon capture by combining the benefits of strong interaction strength of oxygenate species with CO₂ and the stability improvement enabled by aza-fused rings introduction.

Future Plans.

Development of next-generation separation media with unparalleled performance will require molecular level understanding and control of interactions of the target gas species with the separations material to achieve high selectivity, fast transport and facile release, allowing the coupling of different separation mechanisms into a single integrated separation medium. we seek to understand in greater detail the interactions that drive gas solubility and diffusivity in IL systems to couple transport to IL structures, thereby overcoming the paradox related to selectivity and transport in separation media. ILs have become an unconventional liquid medium for gas separations because of their extremely low vapor pressure, versatile chemical functionalities, and the electrostatically dominated solvation environment created by their molten-salt nature. Currently, only ILs that can physically absorb gas molecules (e.g., CO₂) have been intensively investigated for liquid-membrane separation. The separation mechanism is purely of physical diffusion with no chemical bond formation and breaking involved. They are like the traditional polymer membrane systems that can only be used in separation of highly concentrated targeted species. Our group and others have developed novel superbase-derived ILs that can chemisorb acidic gas molecules. Even though this class of ILs is highly selective for gas uptake, they are seldom investigated in membrane-based separations because of slow diffusion. To fully leverage the advances in chemisorbing ILs for membrane separations calls for a deeper understanding of how the molecular structure of a liquid medium dictates gas interaction and transport. If a gas is chemically absorbed in a liquid, the key is to tune the molecular structure to achieve fast transport. Can we design ILs for fast CO₂ transport to overcome the constraint of viscosity? Can we balance the physical/chemical sorption mechanisms to control the interaction of ILs with CO₂ for high selectivity and fast transport? The ability to customize the physicochemical properties of ILs through either selection of the ionic constituents that comprise the liquid or addition of specific functionality will enable us to accurately identify and elucidate the key fundamental interactions in ILs, inducing collective diffusive transport of chemically absorbed molecules.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. Li, E.; Li, B.; Ganesan, A.; Qiu, L.; Jiang, D. E.; Mahurin, S. M.; Pramanik, S.; Popovs, I.; Yang, Z.; Dai, S. Supramolecular Complexation-enhanced CO₂ Chemisorption in Amine-derived Sorbents. *Chemistry - A European Journal* **2024**, e202402137. DOI: 10.1002/chem.202402137.
2. Tong, Y. J.; Dai, S.; Jiang, D. E. 2D Carbonaceous Materials for Molecular Transport and Functional Interfaces: Simulations and Insights. *Accounts Chem. Res.* **2024**, 11. 10.1021/acs.accounts.4c00398
3. Qiu, L. Q.; Fu, Y. Q.; Yang, Z. Z.; Johnson, A. C.; Do-Thanh, C. L.; Thapaliya, B. P.; Mahurin, S. M.; He, L. N.; Jiang, D. E.; Dai, S. Surpassing the Performance of Phenolate-derived Ionic Liquids in CO₂ Chemisorption by Harnessing the Robust Nature of Pyrazolonates. *ChemSusChem* **2024**, 17, 7. 10.1002/cssc.202301329
4. Suo, X.; Fu, Y.; Fan, J.; Do-Thanh, C.-L.; Jiang, D.-e.; Mahurin, S. M.; Yang, Z.; Dai, S. Expeditious Coordination-Driven Construction of Hierarchically Nanoporous Barium Salts. *CCS Chemistry* **2023**, DOI:10.31635/ccschem.023.202302774.
5. Suo, X.; Zhang, F.; Yang, Z.; Wang, L.; Lei, M.; Gaugler, J. A.; Li, M.; Fan, J.; Thapaliya, B. P.; Popovs, I.; Ivanov, A. S.; Gallington, L. C.; Jiang, D.-e.; Liu, Z.; Dai, S. Electrochemical CO₂-to-ethylene conversion on metal-free covalent quinazoline network-derived electrodes. *Chem Catal.* **2023**, 3 (2), 100506. DOI: 10.1016/j.checat.2023.100506.
6. Du, S. J.; Huang, J. W.; Ryder, M. R.; Daemen, L. L.; Yang, C. T.; Zhang, H. J.; Yin, P. C.; Lai, Y. Y.; Xiao, J.; Dai, S.; Chen, B. L. Probing sub-5 Angstrom micropores in carbon for precise light olefin/paraffin separation. *Nat. Commun.* **2023**, 14, 9. 10.1038/s41467-023-36890-6.
7. Qiu, L.; Peng, H.; Yang, Z.; Fan, J.; Li, M.; Yang, S.; Driscoll, D. M.; Ren, L.; Mahurin, S. M.; He, L. N.; Dai, S. Revolutionizing Porous Liquids: Stabilization and Structural Engineering Achieved by a Surface Deposition Strategy. *Adv. Mater.* **2023**, 35, e2302525. DOI: 10.1002/adma.202302525.
8. Qiu, L.; Yang, Z.; Dai, S. Covalent Triazine Framework-Derived Membranes: Engineered Sol-Gel Construction and Gas Separation Application. *Acc. Mater. Res.* **2023**, 4, 1020-1032. DOI: 10.1021/accountsmr.3c00054.
9. Suo, X.; Yang, Z. Z.; Fu, Y. Q.; Do-Thanh, C. L.; Maltsev, D.; Luo, H. M.; Mahurin, S. M.; Jiang, D. E.; Xing, H. B.; Dai, S. New-Generation Carbon-Capture Ionic Liquids Regulated by Metal-Ion Coordination. *ChemSusChem* **2022**, 15, e202102136.
10. Suo, X.; Fu, Y.; Do-Thanh, C. L.; Qiu, L. Q.; Jiang, D. E.; Mahurin, S. M.; Yang, Z.; Dai, S. CO₂ Chemisorption Behavior in Conjugated Carbanion-Derived Ionic Liquids via Carboxylic Acid Formation. *J. Am. Chem. Soc.* **2022**, 144 (47), 21658. DOI: 10.1021/jacs.2c09189.
11. Fu, Y.; Suo, X.; Yang, Z.; Mahurin, S.M.; Dai, S.; Jiang, D.E. Computational Insights into Malononitrile-based Carbanions for CO₂ Capture. *J. Phys. Chem. B*, **2022**, 126, 6979–6984. DOI: 10.1021/acs.jpcc.2c03082.
12. Kwon, H.; Jiang, D. E. Tuning Metal–Dihydrogen Interaction in Metal–Organic Frameworks for Hydrogen Storage. *J. Phys. Chem. Lett.* **2022**, 13, 9129–9133. DOI: 10.1021/acs.jpcclett.2c02628.
13. Yang, Z. Z.; Liu, T. Y.; Wang, S.; Chen, H.; Suo, X.; Wang, T.; Thapaliya, B. P.; Jiang, D. E.; Popovs, I.; Dai, S. Fabrication of Ionic Covalent Triazine Framework-Linked Membranes via a Facile Sol-Gel Approach. *Chem. Mat.* **2021**, 33, 3386–3393.
14. Yang, Z. Z.; Guo, W.; Chen, H.; Kobayashi, T.; Suo, X.; Wang, T.; Wang, S.; Cheng, L.; Liu, G. P.; Jin, W. Q.; Mahurin, S. M.; Jiang, D. E.; Popovs, I.; Dai, S. Benchmark CO₂ separation achieved by highly fluorinated nanoporous molecular sieve membranes from nonporous precursor via in situ cross-linking. *J. Membr. Sci.* **2021**, 638, 10, 119698.
15. Wang, Z. Y.; Wang, Y. Y.; Chen, J. H.; Arnould, M.; Popovs, I.; Mahurin, S. M.; Chen, H.; Wang, T.; Dai, S. Synthesis of Poly(ionic Liquid)s-block-poly(methyl Methacrylate) Copolymer-Grafted Silica Particle Brushes with Enhanced CO₂ Permeability and Mechanical Performance. *Langmuir* **2021**, 37, 10875–10881.

16. Wang, Z. Y.; Chen, H.; Wang, Y. Y.; Chen, J. H.; Arnould, M. A.; Hu, B.; Popovs, I.; Mahurin, S. M.; Dai, S. Polymer-Grafted Porous Silica Nanoparticles with Enhanced CO₂ Permeability and Mechanical Performance. *ACS Appl. Mater. Interfaces* **2021**, *13*, 27411-27418.
17. Fu, Y. Q.; Yang, Z. Z.; Mahurin, S. M.; Dai, S.; Jiang, D. E. Ionic liquids for carbon capture. *MRS Bull.* **2022**, *47*, 395-404. 10.1557/s43577-022-00315-4
18. Wang, S.; Mahurin, S. M.; Dai, S.; Jiang, D. E. Design of Graphene/Ionic Liquid Composites for Carbon Capture. *ACS Appl. Mater. Interfaces* **2021**, *13*, 17511-17516.
19. Thapaliya, B. P.; Puskar, N. G.; Slaymaker, S.; Feider, N. O.; Do-Thanh, C. L.; Schott, J. A.; Jiang, D. E.; Teague, C. M.; Mahurin, S. M.; Dai, S. Synthesis and Characterization of Macrocyclic Ionic Liquids for CO₂ Separation. *Ind. Eng. Chem. Res.* **2021**, *60*, 8218-8226.
20. Suo, X.; Zhang, F. T.; Yang, Z. Z.; Chen, H.; Wang, T.; Wang, Z. Y.; Kobayashi, T.; Do-Thanh, C. L.; Maltsev, D.; Liu, Z. M.; Dai, S. Highly Perfluorinated Covalent Triazine Frameworks Derived from a Low-Temperature Ionothermal Approach Towards Enhanced CO₂ Electroreduction. *Angew. Chem.-Int. Edit.* **2021**, *60*, 25688-25694.
21. Suo, X.; Yang, Z. Z.; Fu, Y. Q.; Do-Thanh, C. L.; Chen, H.; Luo, H. M.; Jiang, D. E.; Mahurin, S. M.; Xing, H. B.; Dai, S. CO₂ Chemisorption Behavior of Coordination-Derived Phenolate Sorbents. *ChemSusChem* **2021**, *14*, 2854-2859.
22. Luo, Y. L.; Yang, Z. Z.; Suo, X.; Chen, H.; Wang, T.; Wang, Z. Q.; Liu, Y. F.; Lyu, Y. N.; Popovs, I.; Dai, S. Robust perfluorinated porous organic networks: Succinct synthetic strategy and application in chlorofluorocarbons adsorption. *Nano Res.* **2021**, *14*, 3282-3287.
23. Jie, K. C.; Zhou, Y. J.; Ryan, H. P.; Dai, S.; Nitschke, J. R. Engineering Permanent Porosity into Liquids. *Adv. Mater.* **2021**, *33*, 18, 2005745.
24. Feider, N. O.; Mahurin, S. M.; Do-Thanh, C. L.; Dai, S.; Jiang, D. E. Molecular dynamics simulations of a dicationic ionic liquid for CO₂ capture. *J. Mol. Liq.* **2021**, *335*, 5, 116163.
25. Chen, H.; Fan, J. T.; Fu, Y. Q.; Do-Thanh, C. L.; Suo, X.; Wang, T.; Popovs, I.; Jiang, D. E.; Yuan, Y. T.; Yang, Z. Z.; Dai, S. Benzene Ring Knitting Achieved by Ambient-Temperature Dehalogenation via Mechanochemical Ullmann-Type Reductive Coupling. *Adv. Mater.* **2021**, *33*, 8, 2008685.

Grant cited but not intellectually led by this award:

1. Xu, Y.; Ren, Y.; Zhou, G.; Feng, S.; Yang, Z.; Dai, S.; Lu, Z.; Zhou, T. Amide-Engineered Metal–Organic Porous Liquids Toward Enhanced CO₂ Photoreduction Performance. *Adv. Funct. Mater.* **2024**, *34*, 2313695. DOI: 10.1002/adfm.202313695.
2. Xu, L. X.; Yin, J.; He, J.; Li, H. P.; Zhu, L. H.; Ning, H. L.; Jie, K. C.; Zhu, W. S.; Li, H. M.; Dai, S.; Jiang, W. Completely Inorganic Deep Eutectic Solvents for Efficient and Recyclable Liquid-Liquid Interface Catalysis. *Adv. Mater.* **2024**, *36*, 9. 10.1002/adma.202313853
3. Zhang, R.; Cui, G.; Wang, X.; Chen, Y.; Qiu, X.; Ke, Q.; Deng, D.; Ge, C.; Lu, H.; Dai, S. Ionic liquid-based advanced porous organic hyper-crosslinked polymers (ILHCPs) for CO₂ capture and conversion. *Chem. Eng. J.* **2024**, *489*, 151102. DOI: 10.1016/j.cej.2024.151102.
4. Yang, N.; Yan, W. K.; Zhou, Z. J.; Tian, C. C.; Zhang, P.; Liu, H. L.; Wu, X. P.; Xia, C. G.; Dai, S.; Zhu, X. Synthetic Leaves Based on Crystalline Olefin-Linked Covalent Organic Frameworks for Efficient CO₂ Photoreduction with Water. *Nano Lett.* **2024**, *24*, 5444-5452. 10.1021/acs.nanolett.4c00343
5. Guan, L.; Guo, Z.; Zhou, Q.; Zhang, J.; Cheng, C.; Wang, S.; Zhu, X.; Dai, S.; Jin, S. A highly proton conductive perfluorinated covalent triazine framework via low-temperature synthesis. *Nat. Commun.* **2023**, *14*, 8114. DOI: 10.1038/s41467-023-43829-4.
6. Fleshman, A. M.; Goldman, A. M.; Hetcher, W. J.; Debbert, S. L.; Do-Thanh, C.-L.; Mahurin, S. M.; Dai, S. Effects of Methylating Imidazolium-Based Ionic Liquids on Viscosity: New Insights from the Compensated Arrhenius Formalism. *The Journal of Physical Chemistry B* **2023**. doi.org/10.1021/acs.jpcc.3c02057.

7. Gutierrez, D. B.; Caldon, E. B.; Yang, Z.; Suo, X.; Cheng, X.; Dai, S.; Espiritu, R. D.; Advincula, R. C. 3D-printed PDMS-based membranes for CO₂ separation applications. *MRS Communications* **2022**, DOI: 10.1557/s43579-022-00287-1.
8. Yu, L.; Keffer, D. J.; Hsieh, C. T.; Scroggins, J. R.; Chen, H.; Dai, S.; Harper, D. P. Lignin-Derived Magnetic Activated Carbons for Effective Methylene Blue Removal. *Ind. Eng. Chem. Res.* **2022**, *61*, 11840-11850. 10.1021/acs.iecr.2c02311
9. Lin, W. W.; Chen, H.; Lin, G. B.; Yao, S. Y.; Zhang, Z. H.; Qi, J. Z.; Jing, M. Z.; Song, W. Y.; Li, J.; Liu, X.; Fu, J.; Dai, S. Creating Frustrated Lewis Pairs in Defective Boron Carbon Nitride for Electrocatalytic Nitrogen Reduction to Ammonia. *Angew. Chem.-Int. Edit.* **2022**, *61*, 7. 10.1002/anie.202207807.

Densification-Induced Structural Transformations in Metal-Organic Frameworks for Enhanced Selective Separation Processes

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Key words: Confinement; Gas Separation; Flexibility; Assembly/Ordering

PI: Sameh Elsaïdi, Co-PI: Wenqian Xu

DE-SC0024594: Controlling Densification-Induced Structural Transformations in Metal-Organic Frameworks for Size-Selective Separations

Research Project Scope.

Metal-organic frameworks (MOFs) can dynamically respond to external stimuli, leading to bond rearrangements and/or structural transformations that alter key material properties like porosity, surface area, and guest recognition. In this context, we introduce a universal strategy for MOF densification by modulating nanoparticle interactions at the molecular level, resulting in the stitching of neighboring crystallites. This enhances particle adherence, reduces intergranular voids, and improves volumetric capacity. Additionally, densification can trigger lattice rearrangements that modify pore structure, shape, and size, significantly impacting the material's separation properties.

Recent Progress.

In this project, we introduce a novel approach to controlling structural transformations in the CuBTC MOF through a high degree of MOF densification. The densification of MOF nanocrystals induces shearing of the crystal lattice, resulting in modified pore characteristics.

The structural transformations of the densified MOF were investigated using synchrotron powder X-ray diffraction in collaboration with Argonne National Laboratory. The newly identified deformed phase of the densified MOF exhibits exceptional mechanical strength, radiation resistance, and unprecedented selectivity for krypton (Kr) over xenon (Xe) at ambient conditions. On the other hand, the densification process and the resultant structural changes have led to a remarkable transformation in CO₂/hydrocarbon selectivity, where the originally hydrocarbon-selective CuBTC MOF becomes CO₂-selective. Additionally, the material is highly shapeable, capable of forming monolithic chunks, strands, or self-standing flat sheets. It can also be applied as continuous coatings via spray, knife, or drop-casting onto surfaces such as stainless steel, glass, and plastic. These findings highlight the potential of densified MOFs to revolutionize material design and open up new avenues for scalability of MOFs and its integration in various industries.

Future Plan.

Our future work will focus on inherently flexible MOFs to explore the effects of densification on their pore properties and gas adsorption and separation behavior. The inherent gate-opening behavior exhibited by certain flexible MOFs presents challenges to gas selectivity, as multiple gases may adsorb simultaneously during pore gating. Our goal is to develop new strategies to modulate gas selectivity and gate-opening dynamics in flexible MOFs, providing a promising path for their practical use in advanced gas separation processes.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. Mohamed, M. H.; Elzeny, I.; Samuel, J.; Xu, W.; Malliakas, C. D.; Picard, Y. N.; Pham, T.; Miller, L.; Hogan, A.; Space, B.; Hopkinson, D.; Elsaidi, S. K., Turning Normal to Abnormal: Reversing CO₂ /C₂-Hydrocarbon Selectivity in HKUST-1. *Advanced Functional Materials*, 2024, 34 (19), 2312280.
2. Mohamed, M. H.; Elzeny, I.; Samuel, J.; Huang, Y.; Helal, A. S.; Galanek, M.; Kim, S. Y.; Picard, Y. N.; Xu, W.; Malliakas, C. D.; Pham, T.; Li, J.; Elsaidi, S. K. Trailblazing Kr/Xe Separation: The Birth of the First Kr-Selective Material. *ACS Applied Materials & Interfaces*, 2024, 34 (19), 2312280.

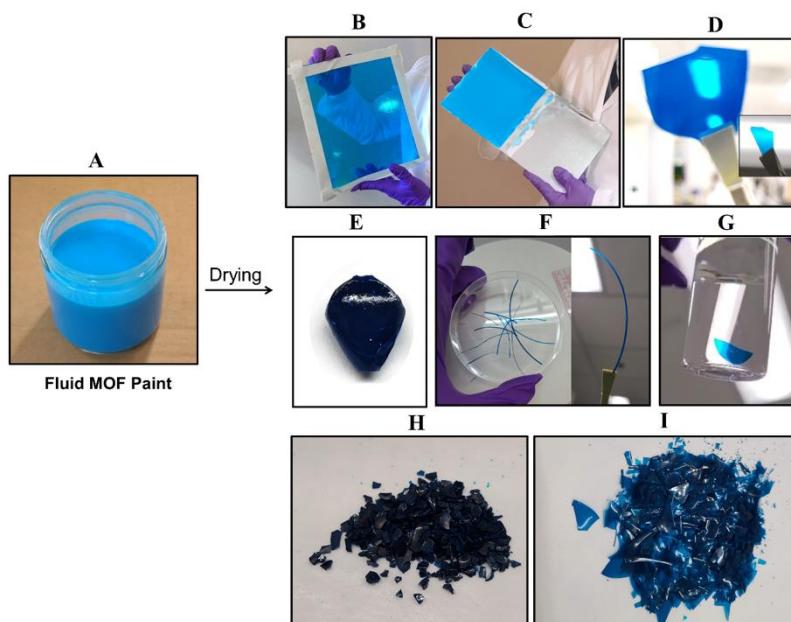


Figure 1. Pictures of the different forms of densified material.

(A) Gel CuBTC in ethanol. (B) Thin film coated on 30 cm glass sheet. (C) Thin film coated on 20 cm stainless steel sheet. (D) Transparent self-standing sheets. (E) A monolithic chunk as a size of a quarter. (F) Self-standing strands after being taken out of silicon molds. (G) Stability of the sheet after shaking and soaking in ethanol for a month. (H and I) Scale-up of Mono-CuBTC and FS-CuBTC, respectively.

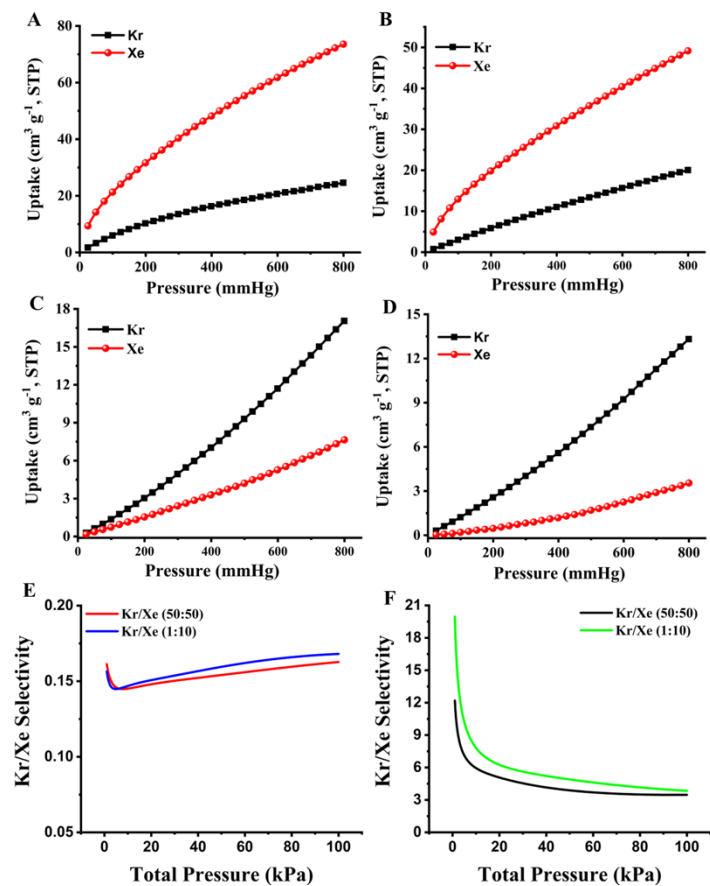


Figure 2. Single Kr and Xe adsorption isotherms and IAST selectivity at 298K.

(A) Kr and Xe isotherms of CuBTC_{TWP}. (B) Kr and Xe isotherms of Mono-CuBTC (769). (C) Kr and Xe isotherms of Mono-CuBTC_{UM}. (D) Kr and Xe isotherms of FS-CuBTC_{UM}. (E) Kr/Xe selectivity of CuBTC_{TWP}. (F) Kr/Xe selectivity of FS-CuBTC_{UM}.

Molecular-Level Understanding of Structures and Solvents for Anion Binding and Photodriven Release

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Indiana University

Key Words: Non-Thermal Separation Mechanisms; Recognition (General); Solvation; Theory/Simulation

DE-SC0002728; Project Title: Binding Anions Selectively with Modular Receptors and Releasing Them with Light

PI: Amar Flood; co-PI: Krishnan Raghavachari

Research Project Scope.

Anions play important roles across many areas of the energy cycle, e.g., bicarbonate intermediate (HCO_3^-) in carbon capture, and the separation of radioactive $^{99}\text{TcO}_4^-$ generated during nuclear power production. Anion recognition and the molecular receptors that modulate anion binding help provide a means for the selective capture of dilute forms of these anions for use in separations. Here we seek to understand deeply and control the binding affinity and selectivity of both rigid and flexible receptors in the form of macrocycles and foldamers using a combination of experiment and theory. Fundamental efforts are focused on creation of modular receptors to test and understand how structure impacts binding, and how solvation modulates affinities and folding preferences of receptors. These efforts are directed towards understanding how to design photoswitchable receptors for use in liquid-liquid extraction, and proof-of-principle demonstrations of the selective and photodriven capture and release of larger anions.

Recent Progress.

Solvent acts to screen electrostatics in anion binding events for cationic and neutral receptors alike

To provide a molecular level understanding of the receptor-anion binding behaviors needed for liquid-liquid extraction (LLE) of anions, we provide the first combined experiment-theory characterization of solvation for cationic receptors. This work showcases a track record of success with a solvation model[1] (see equation in Figure 1a), where the solution-phase binding free energy (ΔG_{sol}) depends on the electrostatic contribution to stability ($\Delta G_{\text{ES,gas}}$) that is screened and reduced in effectiveness by the solvent's dielectric response (ϵ_r). We find that the non-electrostatic contribution ($\Delta G_{\text{non-ES}}$), which stems from polarization, dispersion and charge-transfer, are unaffected by this screening and can buoy up affinity. This model was found to work when extended from rigid to flexible receptors.[2] In our most recent work,[3] we tested the validity of the model with cationic receptors (Figure 1b) with equal success of the model for aprotic solvents spanning polarity (Figure 1c) from chloroform ($\epsilon_r = 4.5$) to DMSO ($\epsilon_r = 47$).

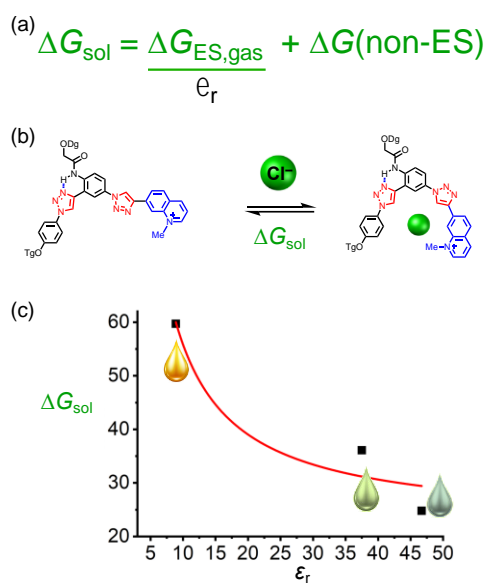


Figure 1. (a) Predictive model of solution phase binding energies based on dielectric-screening of electrostatic and unscreened non-electrostatic contributions. (b) Model was tested for binding Cl^- to cationic receptor and found to hold across (c) three solvents

All these tests rely on detailed thermodynamic analysis, that we are sharing with others.[4] We are also excited by the strong correlations between experiment and theory, suggesting that we are coming closer to an accurate molecule-scale picture of receptor-anion binding in solution. The key to this progress is developing a series of modular receptors and investigating the theoretical basis to make progress towards computer-aided receptor design.

Solvent-driven folding of anion receptors

One key element of anion binding is the geometrical pre-organization of the receptor, and thus the response of the organization to changes in solvent and solvation. To study this factor, we examined the coil-helix folding preferences of an aromatic foldamer. While the folding has been examined extensively by experiment,[2, 5] they have only rarely been examined by theory for the purpose of providing atomic level insights. We conducted all-atom molecular dynamics (MD) simulations to examine the role of solvent polarity on driving the helical folding behavior of aryl-triazole foldamer.[6] The simulation results show that in a low polarity solvent (dichloromethane), the foldamer prefers to stay in the random-coil state. This state has four dipolar triazoles (5 Debye) in their favored all-*anti* geometries favoring *anti*-parallel arrangements. However, an increase in solvent polarity using acetonitrile resulted in solvophobic collapse, yielding the helically folded form as the predominant state. The folded helix has an all-*syn* geometry with triazoles in parallel arrangements.

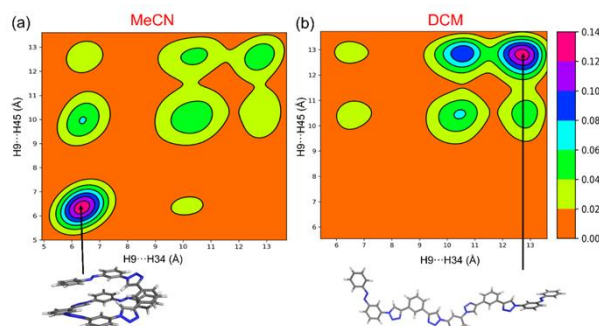


Figure 2. (a) The helix form of the foldameric receptor is favored in MeCN and (b) disfavored in dichloromethane.

Ultimately, the degree of organization boosts the anion-binding affinity,[7] and thus knowledge of the factors dictating receptor folding translate from affinity to efficiency in extraction. This ability to understand the folding preferences, despite the existence of 4096 conformations, lays the groundwork for using modelling to help with computer-guided design of receptors.

Light-driven release of anions for selective and efficient liquid-liquid extraction and anion isolation

Towards use of light as a non-thermal separation mechanism, we are developing photoactive receptors and investigating the molecular-level mechanisms for binding and release of anions. We are using the selectivity of specific macrocycles to form strong complexes with PF_6^- anions to extract them under dilute conditions from a salt solution containing Cl^- . We are using liquid-liquid extraction (LLE) for this purpose. We find that the complex can be subjected to photo-irradiation to enable the release of the anion.

References

1. Liu, Y.; Sengupta, A.; Raghavachari, K.; Flood, A. H., Anion binding in solution: Beyond the electrostatic regime, *Chem* **2017**, *3*, 411-427.
2. Parks, F. C.; Sheetz, E. G.; Stutsman, S. R.; Lutolli, A.; Debnath, S.; Raghavachari, K.; Flood, A. H., Revealing the hidden costs of organization in host-guest chemistry using chloride-binding foldamers and their solvent dependence. *J. Am. Chem. Soc.* **2022**, *144*, 1274-1287.
3. Bhattacharjee, N.; Gao, X.; Nathani, A.; Dobscha, J. R.; Pink, P.; Ito, T.; Flood, A. H., Solvent Acts as the Referee in a Match-up Between Charged and Preorganized Receptors, *Chem. Eur. J.* **2023**, *23*, e202302339
4. Flood, A. H.; Vander Griend, D. A.; Thordarson, P. Driving to K-town: the quest for quality binding constants, *Supramol. Chem.* **2024**, *34*, online

5. Hua, Y.; Flood, A. H., Flipping the switch on chloride concentrations with a light-active foldamer, *J. Am. Chem. Soc.* **2010**, *132*, 12838-12840.
6. Debnath, S.; Flood, A. H.; Raghavachari, K., Solvent-Dependent Folding Behavior of a Helix-forming Aryl-Triazole Foldamer, *J. Phys. Chem. A.* **2024**, *128*, 1586-1594.
7. Parks, F. C.; Sheetz, E. G.; Stutsman, S. R.; Lutolli, A.; Debnath, S.; Raghavachari, K.; Flood, A. H., Revealing the hidden costs of organization in host-guest chemistry using chloride-binding foldamers and their solvent dependence. *J. Am. Chem. Soc.* **2022**, *144*, 1274-1287.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. A. H. Flood, Y. Liu, W. Zhao, Aryl triazole cages, US Patent (11,939,336), Awarded May 26, 2024
2. A. H. Flood, D. A. Vander Griend, P. Thordarson, Driving to K-town: the quest for quality binding constants, *Supramol. Chem.* **2024**, *34*, online <https://doi.org/10.1080/10610278.2024.2359949>
3. S. Debnath, A. H. Flood, K. Raghavachari, Solvent-Dependent Folding Behavior of a Helix-forming Aryl-Triazole Foldamer, *J. Phys. Chem. A.* **2024**, *128*, 1586-1594.
4. Y. Li, H. D. Castillo, J. R. Dobscha, A. R. Morgan, S. L. Tait, A. H. Flood, Breaking radial dipole symmetry in planar macrocycles modulates edge-edge packing and disrupts cofacial stacking, *Chem. Eur. J.* **2023**, *23*, e202302946
5. N. Bhattacharjee, X. Gao, A. Nathani, J. R. Dobscha, M. Pink, T. Ito, A. H. Flood, Solvent Acts as the Referee in a Match-up Between Charged and Preorganized Receptors, *Chem. Eur. J.* **2023**, *23*, e202302339
6. A. Lutolli, M. Che, F. C. Parks, K. Raghavachari, A. H. Flood, Cooperativity in Photofoldamer Chloride Double Helices Turned On with Sequences and Solvents, Around with Guests, and Off with Light, *J. Org. Chem.*, **2023**, *68*, 6791-6804.
7. Y. Li, A. Saha, W. Zhao, J. F. Neil, Y. Chen, A. H. Flood, H. C. Allen, Recognition competes with hydration in anion-triggered monolayer formation of cyanostar supra-amphiphiles at aqueous interfaces. *Chem. Sci.* **2022**, *13*, 4283-4294.
8. F. C. Parks, E. G. Sheetz, S. R. Stutsman, A. Lutolli, S. Debnath, K. Raghavachari, A. H. Flood, Revealing the hidden costs of organization in host-guest chemistry using chloride-binding foldamers and their solvent dependence. *J. Am. Chem. Soc.* **2022**, *144*, 1274-1287.
9. A. Lutolli, A. H. Flood, Photoswitchable Ion Receptors, Book Chapter for “*Molecular Photoswitches – Synthesis, Properties and Applications*,” Ed. Z. Pianowski, Wiley **2022**

Elucidating the Molecular Mechanisms by which Porous Polymer Networks Affect Structure, Aging Propensity, and Selectivity of Microporous Glassy Polymer Membranes using a Multiscale Approach

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Key Words: Membranes; Non-Thermal Separation Mechanisms; Theory/Simulation; Transport Phenomena

DE-SC0024554: Project Title: Discovering the Mechanism by Which Polymer Porous Networks Reduce Physical Aging and Plasticization While Enhancing Permeability and Selectivity in Microporous Polymer Membranes

PI: Michele Galizia; co-PI: Alberto Striolo

Research Project Scope.

The overarching goal of this project is to suppress physical aging in glassy polymer membranes for gas separation, while simultaneously tuning permeability and selectivity. To accomplish this goal, we propose to blend commercial and in-house synthesized microporous polymers with hyper-crosslinked Porous Polymer Networks (PPNs), using molecular simulations as a tool to understand the molecular phenomena leading to improved transport properties and stability.

The overarching hypothesis is that polymer chains can thread through and/or absorb within the PPN porosity. This phenomenon, in synergy with polymer-PPNs-penetrant interactions and the configurational free volume exhibited by PPNs, which eliminates the transient, entropically disordered conformational free volume exhibited by conventional glassy polymers, is expected to regulate penetrant transport rate, selectivity and membrane long-term stability.

Recent Progress.

A model microporous, high free volume glassy polymer, poly(trimethyl silyl propyne) (PTMSP), was blended with a porous polymer network (PPN) synthesized from the hydroxy alkylation reaction between an aromatic substrate, triptycene, and an activated ketone, isatin. The fabrication step was followed by a detailed structural and transport characterization.

While slight reductions or enhancements in gas permeability and either an increase or decrease in selectivity were observed upon blending, depending on the PPN loading and the gas being tested, physical aging resistance significantly improved.

A dedicated physical aging study was run using N₂ as a probe molecule, and a 20 mm thin film. We observed that N₂ permeability in the PTMSP-PPN blend containing 5%wt PPN declines by merely 14% over the course of 500h, in striking contrast with the 41% decline observed in neat PTMSP over the same time frame. A variety of experimental and theoretical approaches, such as Positron Annihilation Lifetime Spectroscopy (PALS), molecular dynamics simulations, ¹³C CP/MAS NMR spectroscopy, as well as modeling with the Struik and dual mode model indicate that the hindered aging rate is ascribed to the adsorption of PTMSP chains in the PPN porosity.

Finally, we demonstrate that, to correctly interpret small molecule transport mechanism in these systems, diffusion coefficients must be carefully corrected for thermodynamic non-idealities.

Ion Selectivities in Random Zwitterionic Copolymer Membranes

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Key Words: Confinement; Interfaces; Membranes; Theory/Simulation

DE-SC0024394: Nanostructured Polymer Membranes with Chemical Structure Selectivity

PI: Venkat Ganesan; co-PI: Ayse Asetkin

Research Project Scope.

The objective of this collaborative project is to elucidate a fundamental understanding of the effect of nanoconfinement and polymer-solute interactions on the permeation of organic molecules in membranes through a combination of experimental and computational analyses. As a test bed to achieve the above objectives, we will use the self-assembly and cross-linking of cross-linkable zwitterionic (ZI) amphiphilic copolymers (X-ZACs) to create membrane selective layers featuring nano-domains/channels of tunable size, filled with ZI functional groups that exhibit interaction selectivity between solutes of interest (e.g. aromatic ZI groups). Ultimately, we aim to leverage our findings to develop membranes capable of chemical-structure-based selectivity for downstream separation of phenolics produced in biorefineries for lignocellulosic biomass valorization for the energy-efficient production of high-value chemicals.

Recent Progress.

We conducted all-atom molecular dynamics (MD) simulations of ZAC membranes with sulfobetaine methacrylate (SBMA) as the zwitterionic moiety and allyl methacrylate (AMA) as the hydrophobic moiety.¹ These simulations revealed the ability of r-ZAC membranes to separate halide ions while evading the solubility-diffusivity tradeoff. Subsequently, we switched to using reduced order models, wherein only the zwitterion-lined nanopores were simulated to save on computational costs.² Our simulations showed that smaller ions preferentially reside near the pore center while larger anions reside closer to the pore walls in these systems. This results in the larger ions being confined in an environment of higher zwitterionic volume fraction and low water mobility, which in conjunction with their smaller affinity towards the zwitterionic moieties results in much faster diffusion. Our results clarified the mechanisms underlying the ability of ZACs to separate a mixture of halide ions from one another, with larger anions being selectively transported over the smaller ones.

We extended our above work to investigate the impact of zwitterionic architecture on the transport of halide ions.³ This was achieved by inverting the positive and negative charge centers of the SBMA zwitterions in our reduced order simulations. Overall, the permselectivity values were significantly higher in the case involving zwitterions with positive charge centers located at the end of the molecule due to the ultra-high partitioning selectivity in these systems. Our study revealed the potential for significant enhancement in ionic selectivity by altering the architecture of the zwitterionic dipoles in r-ZAC membranes.

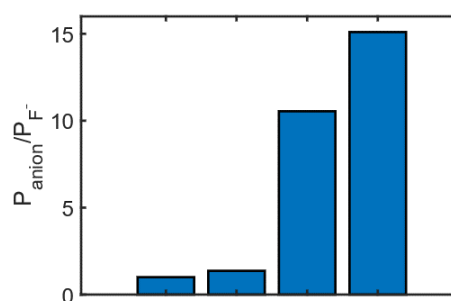


Figure 1. Permselectivity of various halide ions with respect to F⁻ in an SBMA-functionalized nanopore.

Future Plans.

We plan to extend our simulations to the separation of mixtures of organic compounds dissolved in water. Specifically, we plan to study zwitterionic moieties involving aromatic rings with the goal of separating aromatic solutes from non-aromatic solutes in water. The differences in specific interactions (such as pi-pi interactions) between the aromatic zwitterions and the various organic solutes (depending on their aromaticity) will result in selective permeation of one component over another. By leveraging reduced order models, we aim to discern the design principles for r-ZAC membranes involving aromatic zwitterions for aromatic – non-aromatic separations.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. Sachar, H. S., Zofchak, E. S., Marioni, N., Zhang, Z., & Ganesan, V. (2024). Impact of confinement and zwitterionic ligand chemistry on ion-ion selectivity of functionalized nanopores. *Langmuir*, 40(18), 9563-9578.

Addressing Temporal Changes in Polymer Gas Separation Membranes via Leveraging Free Volume Design

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University of Notre Dame

Key Words: Gas Phase; Membranes; Transport Phenomena

DE-SC0024384: Addressing Temporal Changes in Polymer Gas Separation Membranes via Leveraging Free Volume Design

PI: Ruilan Guo

Research Project Scope.

The goals of this new research project are to: 1) examine physical aging behavior of super rigid ladder polymers instilled with configurational free volume using shape-persistent pentiptycene units for gas separations; 2) interrogate the role of free volume architecture enabled by semi-interpenetrating polymer network (sIPN) structure based on PIM-1 ladder polymers in providing physical aging resistance; and 3) evaluate temperature tolerance of configurational free volume introduced in polybenzimidazole (PBI) membranes with iptycene-based structure units, focusing on high temperature (up to 200 °C) H₂/CO₂ separations central to hydrogen fuel production from syngas.

Recent Progress.

We have established fully the synthesis of pentiptycene-containing ladder polymers (PPIM), iptycene-based PBI (PPBI), as well as crosslinkable telechelic iptycene-containing oligomers with controlled molecular weight for the preparation of sIPN membranes. We demonstrated that PPIM ladder copolymers prepared from a mixture of isomeric pentiptycene-based monomers (i.e., S-shaped and C-shaped tetrahydroxyl pentiptycenes) showed comparable gas permeabilities with pure PIM-1 but noticeably higher selectivities for all gas pairs. The enhanced selectivity could be attributed to the presence of configurational free volume microcavities delineated by the configuration of pentiptycene skeleton, which provides better size sieving properties and potentially better aging resistance due to its configuration-based permanent nature. We are making great progress in preparing a series of ladder copolymers with systematically varied pentiptycene molar content to establish the correlation between configurational free volume and transport properties and aging resistance. In exploring the strategy of constructing semi-interpenetrating polymer network (sIPN) structure to improve physical aging resistance of ladder polymers, PIM-1 was chosen as the model system. We successfully synthesized telechelic PIM-1 oligomers with well-controlled molecular weight (4k, 6k and 8k) and crosslinkable end groups. A series of PIM-1 s-IPN membranes were prepared using PIM-1 oligomers and the linear high-molecular-weight PIM-1 in systematically varied weight ratios, with the network content ranging from 10% to 30%. Flexible and defect-free membranes were obtained via solution casting and thermal crosslinking. Insoluble content observed when immersing the s-IPN membranes in organic solvent indicates successful crosslinking. Pure-gas permeation test results demonstrated that PIM-1-based s-IPN membranes exhibit no appreciable loss in permeability after two-week aging, in sharp contrast to the fast-aging behavior of linear PIM-1 reported in the literature. Moreover, two-month aging studies showed CH₄ permeability loss occurring two to three times slower than linear PIM-1. While long-term aging studies are yet to complete, these results demonstrated the great potential of s-IPN design in providing physical aging resistance to glassy ladder polymer membranes. To evaluate temperature tolerance of configurational free volume of iptycene-based polymers, we developed new synthesis strategies to prepare microporous pentiptycene-containing polybenzimidazoles (PPBI) for

high temperature (up to 200 °C) H₂/CO₂ separations. High molecular weight of PPBI product was evidenced by the fibrous precipitation of the polymer solution after the reaction was completed, and the fully cyclized imidazole structure and high thermal stability of the synthesized PPBI were confirmed by ¹H NMR and TGA analysis, respectively. Robust, defect-free and solvent-free PPBI thin films (~20-30 μm) were solution cast following our established thermal protocols, which were subjected to both pure- and mixed-gas permeation tests at temperatures ranging from 35 °C to 180 °C. Compared to commercial *m*-PBI film, PPBI showed much higher H₂ permeability due to its higher free volume fraction instilled by pentyptycene moieties. In mixed-gas permeation tests using a 50:50 mol% H₂/CO₂ mixture at 130 psig, PPBI films showed exceptional separation performance approaching the mixed-gas upper bound with markedly increased H₂/CO₂ selectivity at 180 °C. Work is ongoing to explore several strategies (e.g., acid-doping, physical blending, copolymerization) to further improve overall separation performance at high temperatures as well as to provide fundamental insights regarding the role of configurational free volume in providing high temperature resistance.

From Structured Solvents to Hybrid Materials for Chemically Selective Capture and Electromagnetic Release of CO₂

Burcu Gurkan,¹ Michelle Kidder,² Rachel Getman,³ Emily Pentzer⁴

¹Case Western Reserve University, ²Oak Ridge National Laboratory, ³The Ohio State University, ⁴Texas A&M University

Key Words: Non-Thermal Separation Mechanisms; Interfaces; Reactive Separations; Transport Phenomena

DE-SC0022214: From Structured Solvents to Hybrid Materials (SS2HM) for Chemically Selective Capture and Electromagnetic Release of CO₂: Mechanisms, Stability and Interfaces

PI: Burcu Gurkan; co-PIs: Michelle Kidder, Rachel Getman, Emily Pentzer, Joshua Sangoro

Research Project Scope

The goal of this research program is to develop high-capacity sorbents amenable for alternative regeneration approaches for direct air capture (DAC) of CO₂. In particular, the research aims to develop an understanding of CO₂ binding mechanism, thermal and oxidative stability, and regeneration energetics of functionalized ionic liquids (ILs), deep eutectic solvents (DESs), and porous materials. ILs and DESs are high-dielectric solvents with structural tunability that permits the rational-design for energy-efficient regeneration approaches based on electromagnetic (EM) field and moisture-swing. By further incorporating these solvents into polymeric capsules and other structural supports, multi-scale interfaces for targeted CO₂ and energy transfers are achieved. Aspects related to CO₂ capacity, selectivity, stability, dielectric properties, and binding energies are examined by experiments and computations to identify molecular descriptors through machine learning to inform future design of structured solvents and hybrid materials for DAC.

Recent Progress

An extensive review of CO₂ capture with ILs, DESs, and derivatized composites as well as a perspective on DAC are now available in literature through support from this project.^{2,3} We've shown that the CO₂ absorption and binding energetics in structured solvents are significantly influenced by hydrogen bonding interactions.⁴⁻⁶ As DESs are commonly formed from mixtures of halide salts that act as the hydrogen bond acceptors (HBAs) and alcohols, amines or amides that act as hydrogen bond donors (HBDs), structure and dynamics are primarily governed by the hydrogen bonding network.⁶⁻⁸ In particular, our study contributes to the understanding of how H-bond interactions influence reactive separation of CO₂ using spectroscopy, density functional theory (DFT), and molecular dynamics (MD) simulations where we revealed the mechanism by which the HBD component hindered the proton transfer between two active sites (e.g., choline proline with ethylene glycol), thus eliminating site deactivation and hence increasing the CO₂ capacity.⁵ Our more recent work⁷ underlines the importance of structure-composition-property relations in these solvents as varied trends in physical properties and CO₂ binding affinities are possible via modulation of (i) the number and strength of H-bonding groups in the parent compounds, (ii) proton sharing equilibrium, and (iii) HBA/HBD composition. Encapsulation of these solvents have been demonstrated to enhance thermal stability and gaseous transport.^{9,10} In complement, we developed machine learning (ML) approaches in consideration of the vast design space and non-intuitive correlations among the structure-property-composition parameters that successfully predicted some of the critical solvent parameters such as viscosity and CO₂ capacities;^{11,12} these models will be useful in guiding our future solvent design efforts.¹³⁻¹⁶

Towards our goal of sorbent development amenable to alternative regeneration approaches, we demonstrated the susceptibility of ILs to microwave (MW) irradiation and the utility of MWs for dielectric heating, thus CO₂ release.¹⁷ Further, composites of metal organic framework, ZIF-8, and a functionalized IL were developed for a coupled moisture-swing and EM-based regeneration that demonstrated high CO₂ capacity, selectivity, and rapid CO₂ release (**FIG 1**).¹ The intellectual merit in the demonstrated approach is five-fold: (1) synergizing the high CO₂ solubility and selectivity of the IL with the high porosity of the MOF for improved transport; (2) stability against moisture and maintained selectivity; (3) mild regeneration temperature (e.g., 60 °C) via dielectric heating that acts on the entire volume with minimal MW power; (4) targeted energy transfer to the active IL domain where the chemisorbed CO₂ resides; and (5) suppressed degradation kinetics (e.g., thermal oxidative degradation) due to the instant nature of the EM irradiation. Ongoing work is focused on understanding the dielectric properties of the developed liquids and composites to tune the EM frequency for enhanced dielectric storage and loss that govern energy transfer and efficiency.

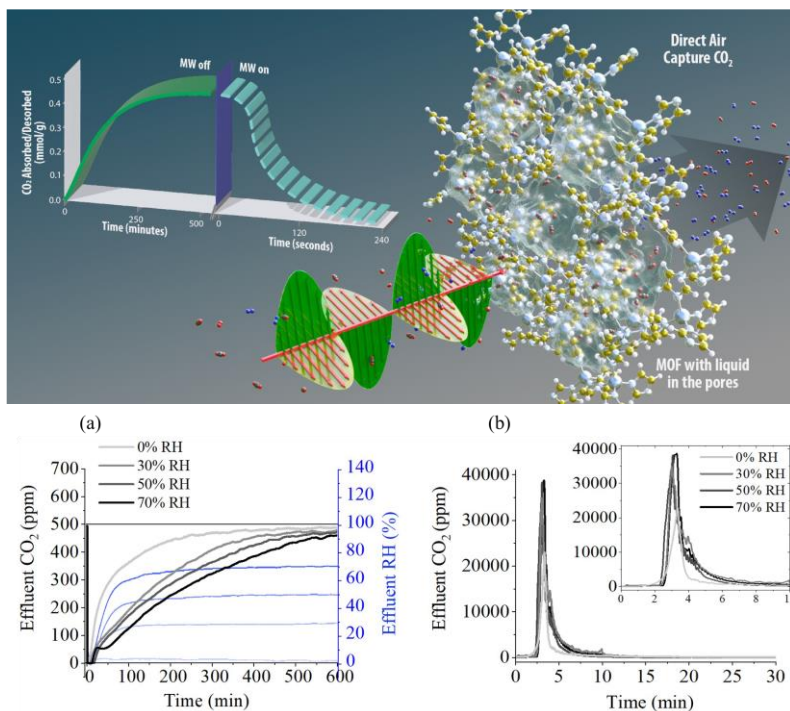


FIG 1. Illustration of the MW assisted regeneration of IL-MOF composites.¹ CO₂ breakthrough curves of IL/ZIF-8 (35 w% IL) under 500 ppm CO₂ at 30 °C with 0 and 50% RH (a) and MW-assisted CO₂ desorption at 60 °C (b). Gray to black lines are the CO₂ breakthrough curves representing the effluent CO₂ concentration relative to the feed and blue lines represent humidity in the effluent. During regeneration, temperature of the samples was held at 60 °C by automatically adjusting the MW input power between 1 to 10 W.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024

Intellectually led by this grant:

1. Zeeshan, M.; Klemm, A.; Damron, J. T.; Unocic, K. A.; Kidder, M. K.; Gurkan, B., Ionic Liquid Functionalizes the Metal Organic Framework for Microwave-Assisted Direct Air Capture of CO₂. *ACS Materials Letters* **2024**, 6 (8), 3854-3861.
2. Zeeshan, M.; Kidder, M. K.; Pentzer, E.; Getman, R. B.; Gurkan, B., Direct air capture of CO₂: from insights into the current and emerging approaches to future opportunities. *Frontiers in Sustainability* **2023**, 4.
3. Dongare, S.; Zeeshan, M.; Aydogdu, A. S.; Dikki, R.; Kurtoğlu-Öztulum, S. F.; Coskun, O. K.; Muñoz, M.; Banerjee, A.; Gautam, M.; Ross, R. D.; Stanley, J. S.; Brower, R. S.; Muchharla, B.; Sacci, R. L.; Velázquez, J. M.; Kumar, B.; Yang, J. Y.; Hahn, C.; Keskin, S.; Morales-Guio, C. G.; Uzun, A.; Spurgeon, J. M.; Gurkan, B., Reactive capture and electrochemical conversion of CO₂ with ionic liquids and deep eutectic solvents. *Chemical Society Reviews* **2024**.
4. Dikki, R.; Cagli, E.; Penley, D.; Karayilan, M.; Gurkan, B., Formation of choline salts and dipolar ions for CO₂ reactive eutectic solvents. *Chemical Communications* **2023**, 59 (80), 12027-12030.

5. Klemm, A.; Vicchio, S. P.; Bhattacharjee, S.; Cagli, E.; Park, Y.; Zeeshan, M.; Dikki, R.; Liu, H.; Kidder, M. K.; Getman, R. B.; Gurkan, B., Impact of Hydrogen Bonds on CO₂ Binding in Eutectic Solvents: An Experimental and Computational Study toward Sorbent Design for CO₂ Capture. *ACS Sustainable Chemistry & Engineering* **2023**, *11* (9), 3740-3749.
6. Cagli, E.; Liu, H.; Khokhar, V.; Klemm, A.; Gurkan, B. E., Thermal and Physical Properties of CO₂-Reactive Binary Mixtures. *Journal of Chemical & Engineering Data* **2024**, *69* (8), 2676-2687.
7. Dikki, R.; Khokhar, V.; Zeeshan, M.; Bhattacharjee, S.; Coskun, O. K.; Getman, R.; Gurkan, B., Composition–property relationships of choline based eutectic solvents: impact of the hydrogen bond donor and CO₂ saturation. *Green Chemistry* **2024**, *26*, 3441.
8. Bhattacharjee, S.; Dikki, R.; Gurkan, B.; Getman, R. B., Effect of water on eutectic solvents: Structural properties and physical interactions with CO₂. *Journal of Molecular Liquids* **2024**, *410*, 125569.
9. Al-Mahbobi, L.; Klemm, A.; Taylor, C.; Gurkan, B.; Pentzer, E., CO₂ Capture with Capsules of Ionic Liquid/Amines. *ACS Applied Engineering Materials* **2024**, *2* (5), 1298-1305.
10. Taylor, C. D. L.; Klemm, A.; Al-Mahbobi, L.; Bradford, B. J.; Gurkan, B.; Pentzer, E. B., Ionic Liquid–Glycol Mixtures for Direct Air Capture of CO₂: Decreased Viscosity and Mitigation of Evaporation Via Encapsulation. *ACS Sustainable Chemistry & Engineering* **2024**, *12* (20), 7882-7893.
11. Mohan, M.; Demerdash, O.; Simmons, B. A.; Smith, J. C.; Kidder, M.; Singh, S., Accurate prediction of carbon dioxide capture by deep eutectic solvents using quantum chemistry and a neural network. *Green Chemistry* **2023**, *25* (9), 3475-3492.
12. Mohan, M.; Demerdash, O. N.; Simmons, B. A.; Singh, S.; Kidder, M. K.; Smith, J. C., Physics-Based Machine Learning Models Predict Carbon Dioxide Solubility in Chemically Reactive Deep Eutectic Solvents. *ACS Omega* **2024**, *9* (17), 19548-19559.
13. Mohan, M.; Smith, M. D.; Demerdash, O. N.; Simmons, B. A.; Singh, S.; Kidder, M. K.; Smith, J. C., Quantum Chemistry-Driven Machine Learning Approach for the Prediction of the Surface Tension and Speed of Sound in Ionic Liquids. *ACS Sustainable Chemistry & Engineering* **2023**, *11* (20), 7809-7821.
14. Mohan, M.; Smith, M. D.; Demerdash, O.; Kidder, M. K.; Smith, J. C., Predictive understanding of the surface tension and velocity of sound in ionic liquids using machine learning. *The Journal of Chemical Physics* **2023**, *158* (21).
15. Mohan, M.; Jetti, K. D.; Guggilam, S.; Smith, M. D.; Kidder, M. K.; Smith, J. C., High-Throughput Screening and Accurate Prediction of Ionic Liquid Viscosities Using Interpretable Machine Learning. *ACS Sustainable Chemistry & Engineering* **2024**, *12* (18), 7040-7054.
16. Mohan, M.; Jetti, K. D.; Smith, M. D.; Demerdash, O. N.; Kidder, M. K.; Smith, J. C., Accurate Machine Learning for Predicting the Viscosities of Deep Eutectic Solvents. *Journal of Chemical Theory and Computation* **2024**, *20* (9), 3911-3926.
17. Lee, Y.-Y.; Cagli, E.; Klemm, A.; Park, Y.; Dikki, R.; Kidder, M. K.; Gurkan, B., Microwave Regeneration and Thermal and Oxidative Stability of Imidazolium Cyanopyrrolide Ionic Liquid for Direct Air Capture of Carbon Dioxide. *ChemSusChem* **2023**, *16* (13), e202300118.
18. Lee, Y.-Y.; Wickramasinghe, N. P.; Dikki, R.; Jan, D. L.; Gurkan, B., Facilitated transport membrane with functionalized ionic liquid carriers for CO₂/N₂, CO₂/O₂, and CO₂/air separations. *Nanoscale* **2022**, *14* (35), 12638-12650.
19. Dongare, S.; Coskun, O. K.; Cagli, E.; Lee, K. Y. C.; Rao, G.; Britt, R. D.; Berben, L. A.; Gurkan, B., A Bifunctional Ionic Liquid for Capture and Electrochemical Conversion of CO₂ to CO over Silver. *ACS Catalysis* **2023**, *13* (12), 7812-7821.
20. Cagli, E.; Klemm, A.; Ali, A.; Gai, Z.; Unocic, K. A.; Kidder, M. K.; Gurkan, B., Tuning Surface, Phase, and Magnetization of Superparamagnetic Magnetite by Ionic Liquids: Single-Step Microwave-Assisted Synthesis. *ACS Applied Materials & Interfaces* **2024**, *16* (16), 20937-20948.
21. Premadasa, U. I.; Bocharova, V.; Miles, A. R.; Stamberg, D.; Belony, S.; Bryantsev, V. S.; Elgattar, A.; Liao, Y.; Damron, J. T.; Kidder, M. K.; Doughty, B.; Custelcean, R.; Ma, Y.-Z., Photochemically-Driven CO₂ Release Using a Metastable-State Photoacid for Energy Efficient Direct Air Capture. *Angewandte Chemie International Edition* **2023**, *62* (29), e202304957.

Assessing the Influence of Confinement in Separations of Carbon Dioxide

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Key Words: Confinement; Reactive Separations; Theory/Simulation; Transport Phenomena.

DE-SC-FWP 81462: Harnessing Confinement Effects, Stimuli, and Reactive Intermediates in Separations

PI: David Heldebrant; co-PI: Grant E. Johnson, co-PI: Jose Leobardo Bañuelos

Research Project Scope.

Efficient and selective separations of acid gases is among the most difficult and essential challenges needed to enable the transition towards a CO₂ negative emissions economy. Solvents, porous materials, and membranes have been used for these separations, yet the design of more advanced materials remains hamstrung due to an antiquated understanding of how molecular level phenomena control macroscale performance. To address this need, these joint experimental and theoretical studies focus on gaining a deep understanding of how we can coax CO₂ into novel behavior by means of introducing precisely controlled confining environments in solvents and porous sorbents.

Recent Progress.

Taking inspiration from respiration and the click MOFs developed by Long's group, we posited that liquid amines could achieve cooperative binding akin to oxygen to the heme groups of hemoglobin. Our studies have discovered the first ever stepwise, albeit negatively cooperative, capture of CO₂ by a single-component water-lean solvents (WLS) occurring *via* self-assembly of reverse micelle-like clusters in solution. This unique hydrogen-bonding environment creates a novel tetrameric binding mechanism of CO₂ fixation as compared to conventional dimeric models used for all amines. This new method of capture enables us to design nanoscale clusters of solvents with double the degrees of freedom of other amines, giving us twice the enthalpies and free energies of CO₂ fixation for us to control the thermodynamics of CO₂ capture. This unique confining environment also promotes the formation and stabilization of the first ever observed carbamic-anhydride, a species with two CO₂ molecules bound in a linear fashion (Figure 1, top). These findings enable us to design novel solvents that may exhibit positively cooperative binding in addition to doubling the CO₂ storage capacity of amines.

The effects of confining environments have also been studied for porous materials and membranes; these materials could become far more efficient if CO₂ diffused directionally through the sorbent without any inefficiencies like a magnetically levitating train or 'hyperloop.' One of the primary inefficiencies of diffusion is Brownian

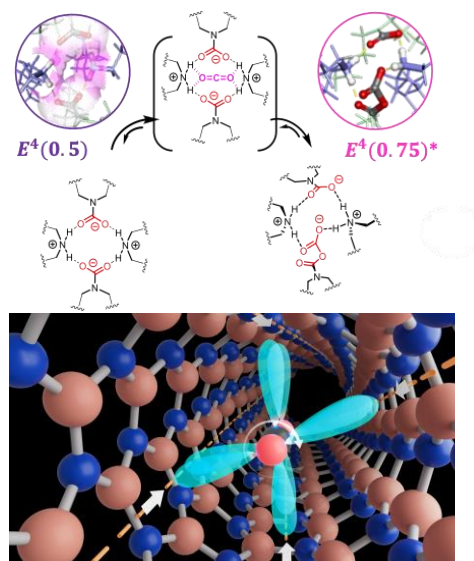


Figure 1. Top) Tetrameric amine cluster activating CO₂ by proximal carbamates enabling double CO₂ fixation as a carbamate-anhydride. Bottom) Direction-specific diffusion of CO₂ augmented by polygonal riffling in chiral hexagonal boron nitride nanotubes.

motion, where CO₂ randomly flips, tumbles, and bounces into interfaces or other molecules, resulting in sporadic changes in direction slowing down diffusion. We have learned how to overcome this challenge by using specifically sized chiral hexagonal boron nitride (h-BN) nanotubes that facilitate directional motion of CO₂ molecules down their axis by imparting a molecular level “spin” like a bullet in a rifled gun barrel (Figure 1, bottom), resulting in minimized Brownian collisions and directional changes. This finding will enable us to exploit these unique chiral confining environments and molecular level spinning to design more efficient separation media that allow nearly 100% of diffusion to occur directionally through a sorbent or membrane, potentially breaking the Robeson upper bound of selectivity and permeability.

Future Plans.

We will continue to investigate the properties of molecular clusters of aminopyridine and diamine WLS. We will evaluate enthalpy/entropy contributions to the stabilization of molecular clusters and provide a more thorough understanding of CO₂ capture processes. A machine learning force field will be developed using *ab initio* molecular dynamics simulations of WLS, enabling us to explore the impact of temperature and speciation on reactive CO₂ capture at a larger dimensional and longer temporal scale than simulations with comparable modeling accuracy. X-ray scattering experiments will be used to probe how molecular structure and water content impact cluster size, shape, and structure to gain a predictive understanding of WLS clustering and active sites.

We will conduct a comparative study of the transport of N₂, O₂, and water molecules in h-BN to obtain insight into the effects of the electronic and atomic structure of small molecules on their diffusion in one-dimensional confinement environments to determine if this phenomenon is more broadly applicable in separations. We will also procure and isolate varied dimensions and chiralities of h-BN tubes and perform high-pressure ¹³C NMR DOSY NMR in high-pressure cells with ¹³C-enriched CO₂ to measure the diffusion coefficients to link diffusion rates to the chirality of the tubes.

Peer Reviewed Publications Acknowledging this Award in 2021-2024.

Intellectually led by this grant:

1. Leclaire, J.; Heldebrant, D.J.; Grubel, K.; Septavaux, J.; Hennenbelle, M.; Walter, E.; Chen, Y.; Leobardo Bañuelos, J.; Zhang, D.; Nguyen, M.T.; Allec, S.; Malhotra, D.; Joo, W.; King, J. Nano-Clustering in Water-Lean Solvents Establishes Novel CO₂ Chemistry *Nature Chemistry* (IF: 22), **2024**, [10.1038/s41557-024-01495-z](https://doi.org/10.1038/s41557-024-01495-z)
2. Kroll, J.O.; Kothandaraman, J.; Grubel, K.; Heldebrant, D.J. “An integrated approach to CO₂ capture and conversion to cyclic carbonates under solvent- and additive-free conditions utilizing the CO₂ capture solvent 2-EEMPA.” *Energy Fuels* (IF: 5), **2024**, [10.1021/acs.energyfuels.3c04993](https://doi.org/10.1021/acs.energyfuels.3c04993) (invited for thematic collection: Recent Advances in CO₂ Conversion to Chemicals and Fuels)

Award cited but not intellectually led by this award:

1. Shaw, W.J.; Autrey, T.; Bare, S.R.; Biddinger, E.J.; Boettcher, S.; Britt, P.F.; Brown, R.C.; Bullock, R.M.; Chen, J.G.; Daniel, C.; Delferro, M.; Dorhout, P.K.; Gaffney, K.G.; Gagliardi, L.; Harper, A.S.; Heldebrant, D.J.; Kidder, M.K.; Luca, O.R.; Lyubovsky, M.; Male, J.L.; Miller, D.; Morris, J.R.; Prozorov, T.; Rallo, R.; Rioux, R.M.; Sadow, A.D.; Schaidle, J.A.; Schulte, L.A.; Senanayake, S.D.; Sholl, D.S.; Tarpeh, W.A.; Toma, F.; Vlachos, D.G.; Vogt, B.D.; Weber, R.S.; Yang, J.Y.; Arenholz, E.; Helms, B.A.; Huang, W.; Jordahl, J.L.; Karakaya, C.; Kian, K.; Kothandaraman, J.; Lercher, J.; Liu, P.; Malhotra, D.; Mueller, K.T.; O'Brien, C.P.; Palomino, R.M.; Qi, L.; Rodriguez, J.A.; Rousseau, R.; Russell, J.C.; Sarazen, M.L.; Smith, E.A.; Burke Stevens, M. Surendranath, Y.; Tassone, C.J.; Tran, B.; Tumas, W.; Walton, K.S. “Closing the Carbon Cycle: Net-Zero Carbon

Emissions for Difficult to Electrify Segments of our Economy.” Nature Reviews Chemistry, 2024,
<https://doi.org/10.1038/s41570-024-00587-1>.

Solvation and Pore Surface Interactions Govern Solute Diffusion in Binary Ethanol/Water Mixtures Confined within Anodic Alumina Nanopores

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Key Words: Confinement; Dynamics; Solvation; Transport Phenomena

DE-SC0002362: Molecular-Level Investigations of Diffusion Behavior within Cylindrical Nanoscale Pores

PI: Takashi Ito; co-PI: Daniel Higgins

Research Project Scope.

The overall goals of this project are to quantitatively and comprehensively understand key molecular-level mechanisms behind energy-relevant chemical separations employing nanoporous membranes. We are systematically investigating solute diffusion dynamics within model solvent-filled cylindrical nanopores using advanced fluorescence microscopic methods including confocal fluorescence correlation spectroscopy (FCS) and super-resolved single molecule tracking (SMT) by wide-field fluorescence video microscopy. These methods provide quantitative data on local solute dynamics in sub-femtoliter volumes, and thus reveal the intrinsic diffusion behaviors of nanoconfined solutes. We are presently investigating how nanoscale demixing in binary solvent mixtures confined within anodic aluminum oxide (AAO) nanopores governs the diffusion dynamics of model solutes.

Recent Progress.

We recently reported FCS investigations of Rhodamine B (RhB) diffusion in 10 and 20 nm diameter AAO nanopores filled with ethanol-water mixtures (see Figure panel A) of relatively low water volume fraction ($\phi_w = 0 - 33\%$). RhB diffusion was found to occur by two distinct mechanisms comprising fast and slow diffusion and having diffusion coefficients D_f and D_s differing by two orders of magnitude. The faster component was attributed to hindered, bulk-like diffusion in the nanopore cavity and was modestly slowed by hydrodynamic and/or electrostatic drag due to pore surface interactions. The slower component was attributed to RhB diffusion involving frequent adsorption/desorption on the nanopore surface.

We have since continued to explore solute dynamics in ethanol-water mixtures confined within AAO nanopores in much greater depth. Our latest investigations comprise a complete study of RhB diffusion across the full range of possible ethanol-water mixtures ($\phi_w = 0 - 100\%$). The results support our previous assignment of RhB diffusion to a two-component mechanism. The fast diffusion data (D_f) revealed a clear viscosity-dependent trend (Figure panel B), confirming it arises from bulk-like Brownian motion of the dye within the nanopores.

The slow diffusion component (D_s) exhibited an altogether different trend. A much greater dependence on pore size was observed, as shown in plots of D_s relative to the bulk diffusion coefficient (D_s/D_b , Figure panel C). Interestingly, these data reveal clear correlations between D_s/D_b and RhB solubility (Figure panel D). The data show D_s was smallest in pure ethanol and pure water, in which RhB is least soluble, and largest in intermediate mixtures of the two, where RhB is most soluble. It was concluded that slow RhB diffusion was governed primarily by solvation-dependent adsorption of the dye to the pore surface. Indeed, surface

adsorption of RhB was observed in confocal fluorescence time transients and also in wide-field fluorescence videos acquired from AAO membrane cross-sections. MD simulations performed by our collaborators (Servis and Wang) at Argonne National Labs revealed that the dye was solvated primarily by ethanol across much of the range of mixtures employed, while the pore surface was covered by a layer of water (Figure panel E). Taken together, these observations suggest that adsorption of the dye to the pore surface from ethanol-water mixtures requires a significant change to its solvation shell, thus providing an energetic barrier to adsorption. Dye-pore collisions are also believed to be important in this model, with contributions by the slow diffusion mechanism becoming more important and D_s decreasing between the 20 nm and 10 nm nanopores, as the dye-pore collision frequency increases.

Future Plans.

Super-resolved single molecule tracking data acquired by wide-field fluorescence microscopy will be used to verify that slow solute diffusion under nanoconfinement occurs by a desorption-mediated mechanism. The pore size dependence of diffusion by the fast and slow mechanisms will also be explored in greater depth.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. T. Ito, D. A. Higgins “Fluorescence Microscopic Investigations of Molecular Dynamics in Self-Assembled Nanostructures”, *Chem. Rec.* **2021**, 21, 1417–1429 (DOI: 10.1002/tcr.202000173).
2. L. Xue, S. Jin, S. Nagasaka, D. A. Higgins, T. Ito “Investigation of Molecular Diffusion at Block Copolymer Thin Films Using Maximum Entropy Method-Based Fluorescence Correlation Spectroscopy and Single Molecule Tracking”, *J. Fluoresc.* **2022**, 32, 1779–1787 (DOI: 10.1007/s10895-022-02975-6).
3. H. Coceancigh, L. Xue, S. Nagasaka, D. A. Higgins, T. Ito “Solvent-Induced Swelling Behaviors of Microphase-Separated Polystyrene-block-Poly(ethylene oxide) Thin Films Investigated Using In Situ Spectroscopic Ellipsometry and Single-Molecule Fluorescence Microscopy”, *J. Phys. Chem. B*, **2022**, 126, 8338–8349 (DOI: 10.1021/acs.jpcc.2c05025).
4. H. Rashidi, K. J. Howard, T. Ito, D. A. Higgins, “Random Walks and Sticky Surfaces: Single Molecule Measurements of Solute Diffusion in Ethanol/Water-Filled Anodic Alumina Nanopores”, *J. Phys. Chem. C* **2023**, 127, 411-420 (DOI: 10.1021/acs.jpcc.2c07083).
5. O. Shafiee, S. G. Jenkins, T. Ito, D. A. Higgins “Diffusion of Hydrophilic to Hydrophobic Forms of Nile Red in Aqueous

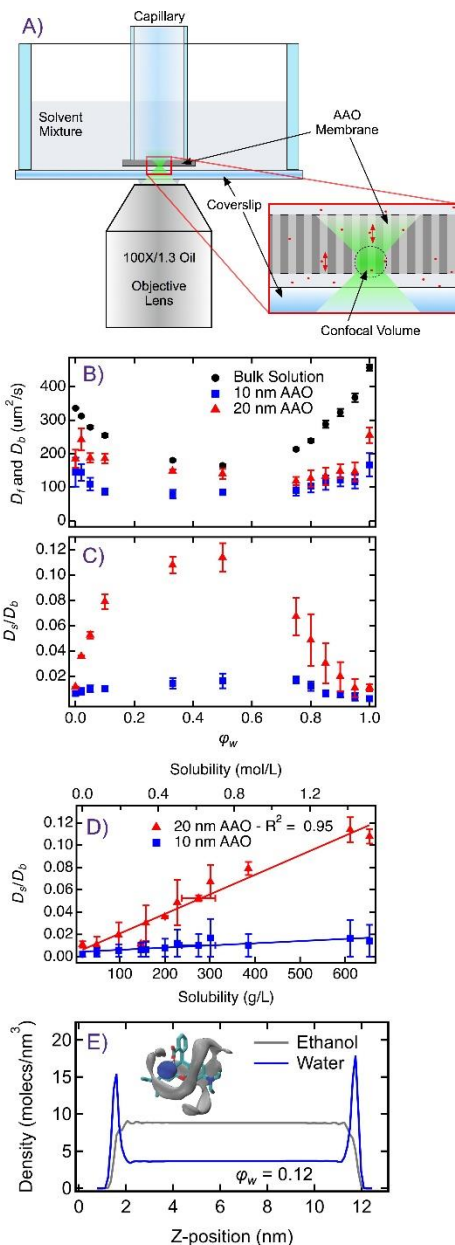


Figure. A) Experimental configuration used for confocal FCS studies of RhB diffusion in ethanol/water-filled AAO nanopores. B) D_f and D_b for RhB diffusion in 10 and 20 nm ethanol-water filled AAO nanopores as a function of mixture composition. C) D_f/D_b as a function of mixture composition for 10 and 20 nm nanopores. D) Correlation between D_f/D_b and solubility of RhB in the mixtures. E) Simulations showing the preferential solvation of RhB (inset) by ethanol and of a 1 nm nanoslit surface by water.

C12EO10 Gels by Variable Area

- Fluorescence Correlation Spectroscopy”, *Phys. Chem. Chem. Phys.* **2023**, *25*, 2853–2861 (DOI: 10.1039/D2CP05578C).
6. T. Ito “Single-Molecule Fluorescence Investigations of Solute Transport Dynamics in Nanostructured Membrane Separation Materials”, *J. Phys. Chem. B* **2023**, *127*, 5733-5741 (DOI: 10.1021/acs.jpcc.3c02807).
 7. H. Rashidi, A. Nathani, X. Wang, M. J. Servis, T. Ito, D. A. Higgins “Adsorption and Solvation Modulate Rhodamine B Diffusion in Ethanol/Water-Filled Anodic Alumina Nanopores”, *J. Phys. Chem. C*, in press (jp-2024-03189a).

Grant cited but not intellectually led by this award:

1. A. Usman, S. L. Weatherbee, M. M. Collinson, K. L. Hohn, D. A. Higgins. Single Molecule Spectroscopy Studies of Acid-Base Chemical Gradients using Nile Red as a Probe of Local Surface Acidity. *Langmuir* **2021**, *37*, 12138-12147 (DOI: 10.1021/acs.langmuir.1c02059).
2. T. Ito, S. Seifert, K. N. Moeller, A. Uysal “In Situ Synchrotron X-Ray Scattering Investigation of Cathodic ZIF-8 Deposition on Graphite Using 3D-Printed Cells”, *Anal. Chem.* **2023**, *95*, 8206-8213 (DOI: 10.1021/acs.analchem.2c05668).
3. T. Ito, S. G. Jenkins, S. Seifert, A. Uysal “Electrochemistry-Induced Direct Deposition of Nanoscale Thin Zeolitic Imidazolate Framework-8 Films on Insulator Substrates”, *Cryst. Growth Des.* **2023**, *23*, 6369-6377 (DOI: 10.1021/acs.cgd.3c00329).
4. H. Rashidi, O. Shafiee, D. A. Higgins “Fluorescence Correlation Spectroscopy Studies of Dye Diffusion on Fresh and Aged Polyethylene Terephthalate”, *Anal. Chem.* **2023**, *95*, 11849-11853 (DOI: 10.1021/acs.analchem.3c02283).

Coordination-Chemistry-Derived Materials Featuring Nanoscale Porosity and Selective Chemical Separation Capabilities

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Key Words: Confinement; Gas Phase; Non-Thermal Separation Mechanisms; Theory/Simulation

DE-FG02-08ER15967: Coordination-Chemistry-Derived Materials Featuring Nanoscale Porosity and Selective Chemical Separation Capabilities

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Research Project Scope.

This project aims to explore, develop, and exploit new concepts for energy-efficient separation of gas, vapor, or liquid mixtures. The project will take advantage of – and further develop – recent advances in the synthesis of new metal-organic frameworks (MOFs), framework-integrated guests, and related high-porosity compounds. A tight integration of material synthesis, detailed characterization – including DOE-synchrotron-enabled structural characterization, adsorption studies, breakthrough measurements, and electronic structure calculations together with computational molecular (and atomic) modeling will be employed by a team that has creatively melded such tools in the past.

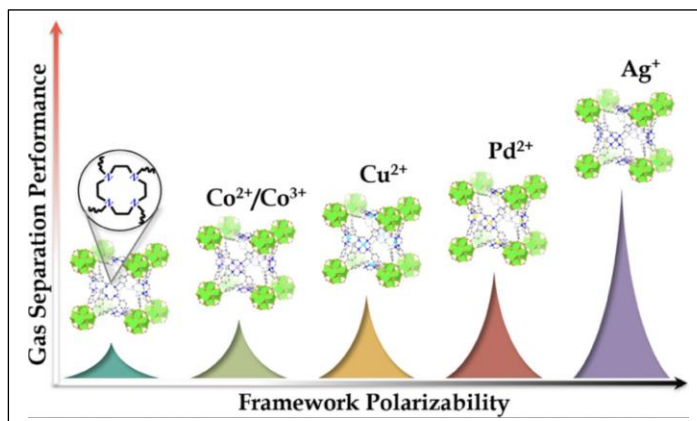
Recent Progress. Among the topics we will highlight in a poster presentation are the following:

- Many important industrial gas separations require separating molecules with subtle (sub-angstrom) differences in size and similar chemical properties, such as hexane isomers, xylene isomers, and olefin/paraffin mixtures. To address this challenge, extremely precise control over a material's pore size is required, as small changes can result in drastic changes in separation capabilities. In effort to establish this sub-angstrom level control, we have designed and synthesized metal-organic frameworks (MOFs) that are built from 3-dimensional linkers (3DLs), i.e. linkers with sterically bulky, symmetrical cores. The bulkiness of the linker can further confine the pore to targeted sizes; further, it mitigates or even eliminates flexibility that results from phase transitions. These phase transitions are common in many MOF structures and can be instigated by changes in temperature and pressure or adsorption of guest molecules. Additionally, because linkers are subject to rotational motion, the symmetrical nature of 3DLs ensures near uniform protrusion, preventing variations in pore size from rotating linkers. Specifically, we synthesized eight new MOF structures and demonstrated their selectivity toward separation hexane isomers and xylene isomers.
- Water separation from air, followed by concentration in liquid form, and then release of the captured water is a compelling problem from the perspective of obtainable potable water in low-humidity environments. Water capture and concentration is also important, however, for catalytic hydrolysis of vapor-phase reactants. Further, it can be important for enhancing the adsorptive separation of selected molecules from air – molecules such as CO₂ (i.e. carbon capture) and ammonia. It can also facilitate transport of molecular guests through porous frameworks. Finally, sorptive vapor capture and release, especially for water with its anomalously high heat capacity, can be exploited for cooling. Repetitive use of frameworks as sorbents brings to light a chemical conundrum: Frameworks featuring micropores or ultra-micropores can be cycled indefinitely, but are characterized by low gravimetric and, especially, volumetric capacity. Frameworks featuring mesopores typically display much higher capacities, but they are susceptible to capillary-force-induced, pore collapse during water removal. Irreversible pore

collapse, in turn, decimates capacity for subsequent cycles. An ideal scenario would be one in which high initial capacity could be obtained, pore collapse could be arrested, and the mesoporous sorbent could be recycled indefinitely.

We developed and experimentally validated a collection of strategies for simultaneously satisfying the seemingly conflicting requirements of high capacity and high stability toward repetitive cycling. Further, we showed that the concept of nanocavitation could be exploited both to explain stability and predictively identify candidate structures or modifications for stable, high-capacity, repetitive capture and release of water.

- We intuitively posited and experimentally demonstrated that systematic tuning of framework polarizability could be used to alter selectivity for sorptive separation of polarizable Xe from less polarizable Kr. These two gases are of particular interest to DOE because they are known products of (i.e. markers for) nuclear fission.



DOE Separation Science Publications (DE-FG02-08ER15967)

August 2021 – August 2024

1. Moghadam, P.Z.; Chung, Y.G.; Snurr, R.Q. “Progress toward the computational discovery of new MOF adsorbents for energy applications,” *Nature Energy* **2024**, *9*, 121-133. DOI: <https://doi.org/10.1038/s41560-023-01417-2>
2. Goncalves, R. B.; Collados, C. C.; Malliakas, C. D.; Wang, Z.; Thommes, M.; Snurr, R. Q.; Hupp, J. T. “Chemically Reversible CO₂ Uptake by Dendrimer-Impregnated Metal–Organic Frameworks,” *Langmuir* **2024**, *40*, 9299-9309 DOI: <https://doi.org/10.1021/acs.langmuir.4c00885>
3. Lancheros, A.; Goswami, S.; Zarate, X.; Schott, E.; Hupp, J. T. “Nitrogen-enriched flexible metal–organic framework for CO₂ adsorption.” *Dalton Trans.* **2024**, Advance Article, DOI: <https://doi.org/10.1039/D4DT01457J>
4. Gong, W.; Chen, X.; Wahiduzzaman, M.; Xie, H.; Kirlikovali, K. O.; Dong, J.; Maurin, G.; Farha, O. K.; Cui, Y. “Chiral Reticular Chemistry: A Tailored Approach Crafting Highly Porous and Hydrolytically Robust Metal–Organic Frameworks for Intelligent Humidity Control.” *J. Am. Chem. Soc.* **2024**, *146*, 2141-2150. DOI: <https://doi.org/10.1021/jacs.3c11733>
5. Alhashem, H.; Sengupta, D.; Bose, D.; Wang, X.; Sha, F.; Islamoglu, T.; Farha, O. K. “Effective Strategy toward Obtaining Reliable Breakthrough Curves of Solid Adsorbents.” *ACS Appl. Mater. Interfaces* **2024**, *16*, 5093-5102. DOI: <https://doi.org/10.1021/acsami.3c15859>
6. Shi, L.; Kirlikovali, K. O.; Chen, Z.; Farha, O. K. “Metal–Organic Frameworks for Water Vapor Adsorption.” *Chem* **2024**, *10*, 484-503. DOI: <https://doi.org/10.1016/j.chempr.2023.09.005>

8. Smoljan, C. S.; Snurr, R. Q.; Farha, O. K. "3-Dimensional Linker-Based Metal–Organic Frameworks for Sub-Angstrom Control and Enhanced Thermal Stability." *JMR* **2024**, *39*, 1047-1056. DOI: <https://dx.doi.org/10.1557/s43578-024-01309-5>
9. Smoljan, C. S.; Sha, F.; Campitelli, P.; Xie, H.; Eddaoudi, M. A.; Mian, M. R.; Nicola, C. D.; Kirlikovali, K. O.; Snurr, R. Q.; Farha, O. K. "Constraining Flexibility in the MIL-88 Topology Through Integration of 3-Dimensional Linkers." *Cryst. Growth Des.* **2024**, *24*, 3941-3948. DOI: <https://doi.org/10.1021/acs.cgd.4c00287>
10. Wang, X.; Xie, H.; Sengupta, D.; Sha, F.; Otake, K.-I.; Chen, Y.; Idrees, K. B.; Kirlikovali, K. O.; Son, F.; Wang, M.; Ren, J.; Notestein, J. M.; Kitagawa, S.; Farha, O. K. "Precise Modulation of CO₂ Sorption in Ti₈Ce₂-Oxo Clusters: Elucidating Lewis Acidity of the Ce Metal Sites and Structural Flexibility." *J. Am. Chem. Soc.* **2024**, *146*, 15130-15142. DOI: <https://doi.org/10.1021/jacs.4c01092>
11. Stone, A. E. B. S.; Wang, X.; Fortunato, A.; Saggiaro, E.; Snurr, R. Q.; Arcudi, F.; Hupp, J. T.; Dorđević, L. "Cobaloxime-based homogeneous and metal-organic framework photocatalytic systems for selective reduction of acetylene to ethylene." *Adv. Mater.* **2024**, submitted. Journal-assigned manuscript number: adma.202408658.
12. Lancheros, A; Goswami, S.; Zarate, X.; Blanco, E.; Schott, E.; Hupp, J. T. "New Pillar-MOF with Nitrogen-Donor Sites for CO₂ Adsorption." *Cryst. Growth Des.* **2024**, *24*, 5898-5905. DOI: <https://doi.org/10.1021/acs.cgd.3c01182>
13. Reischauer, S.; Smoljan, C. S.; Rabeah, J.; Xie, H.; Formalik, F.; Chen, Z.; Vornholt, S. M.; Sha, F.; Chapman, K. W.; Snurr, R. Q.; Notestein, J. M.; Farha, O. K. "A Titanium-Based Metal–Organic Framework For Tandem Metallaphotocatalysis." *ACS Appl. Mater. Interfaces* **2024**, *16*, 33371-33378. DOI: <https://doi.org/10.1021/acsami.4c03651>
14. "A Nanocavitation Approach to Understanding Water Capture, Water Release, and Framework Physical Stability in Hierarchically Porous MOFs," Jian Liu, Jesse L. Prelesnik, Roshan Patel, Boris V. Kramar, Rui Wang, Christos D. Malliakas, Lin X. Chen, J. Ilja Siepmann, and Joseph T. Hupp. *Journal of the American Chemical Society*, 2023, *145* (51), 27975-27983 DOI: [10.1021/jacs.3c07624](https://doi.org/10.1021/jacs.3c07624)
15. Gopalan, A.; Snurr, R.Q. "Molecular simulations of the chain length dependent adsorption of C7-C14 n-alkanes in ZIF-8," *Chemie Ing. Technik* **2023**, *95*, 1811-1823. DOI: <https://doi.org/10.1002/cite.202300033>
16. Gong, W. Xie, Y.; Wang, X.; Kirlikovali, K. O.; Idrees, K. B.; Sha, F.; Xie, H.; Liu, Y.; Chen, B.; Cui, Y.; Farha, O. K. "Programmed Polarizability Engineering in a Cyclen-Based Cubic Zr (IV) Metal–Organic Framework to Boost Xe/Kr Separation." *J. Am. Chem. Soc.* **2023**, *145*, 2679-2689. DOI: <https://doi.org/10.1021/jacs.2c13171>
17. Shetty, S.; Idrees, K. B.; Xie, H.; Alameddine, B.; Farha, O. K.; "Synthesis of zirconium-based metal–organic frameworks with iron (ii) clathrochelate ligands." *CrystEngComm* **2023**, *25*, 1550-1555. DOI: <https://doi.org/10.1039/D2CE01686A>
18. Smoljan, C. S.; Li, Z.; Xie, H.; Setter, C. J.; Idrees, K. B.; Son, F. A.; Formalik, F.; Shafaie, S.; Islamoglu, T.; Macreadie, L. K.; Snurr, R. Q.; Farha, O. K. "Engineering Metal–Organic Frameworks for Selective Separation of Hexane Isomers Using 3-Dimensional Linkers." *J. Am. Chem. Soc.* **2023**, *145*, 6434-6441. DOI: <https://doi.org/10.1021/jacs.2c13715>
19. Song, X.; Huang, Q.; Liu, J.; Xie, H.; Idrees, K. B.; Hou, S.; Yu, L.; Wang, X.; Liu, F.; Qiao, Z.; Wang, H.; Chen, Y.; Li, Z.; Farha, O. K. "Reticular Chemistry in Pore Engineering of a Y-Based Metal–Organic Framework for Xenon/Krypton Separation." *ACS Appl. Mater. Interfaces* **2023**, *15*, 18229-18235. DOI: <https://doi.org/10.1021/acsami.3c01229>
20. Lal, B.; Idrees, K. B.; Xie, H.; Smoljan, C. S.; Shafaie, S.; Islamoglu, T.; Farha, O. K. "Pore Aperture Control Toward Size-Exclusion-Based Hydrocarbon Separations." *Angew. Chem. Int. Ed.* **2023**, *62*, e202219053. DOI: <https://doi.org/10.1002/anie.202219053>

21. Macreadie, L. K.; Idrees, K. B.; Smoljan, C. S.; Farha, O. K. "Expanding Linker Dimensionality in Metal–Organic Frameworks for sub-Ångstrom Pore Control for Separation Applications." *Angew. Chem. Int. Ed.* **2023**, e202304094. DOI: <https://doi.org/10.1002/anie.202304094>
22. Shi, L.; Kirlikovali, K. O.; Chen, Z.; Farha, O. K. "Rational Design of Stable Functional Metal–Organic Frameworks." *Mater. Horiz.* **2023**, *10*, 3257-3268. DOI: <https://doi.org/10.1039/D3MH00541K>
23. Su, S.; Zhou, X.; Gong, X.; Idrees, K. B.; Kirlikovali, K. O.; Islamoglu, T.; Farha, O. K.; Gianneschi, N. C. "Metal–Organic Frameworks with a Bioinspired Porous Polymer Coating for Sieving Separation." *J. Am. Chem. Soc.* **2023**, *145*, 13195-13203. DOI: <https://doi.org/10.1021/jacs.3c02195>
24. Gong, W.; Chen, X.; Fahy, K. M.; Dong, J.; Liu, Y.; Farha, O. K.; Cui, Y.; "Reticular Chemistry in Its Chiral Form: Axially Chiral Zr (IV)-Spiro Metal–Organic Framework as a Case Study." *J. Am. Chem. Soc.* **2023**, *145*, 13869-13878. DOI: <https://doi.org/10.1021/jacs.3c03036>
25. Idrees, K. B.; Kirlikovali, K. O.; Setter, C.; Xie, H.; Brand, H.; Lal, B.; Sha, F.; Smoljan, C. S.; Wang, X.; Islamoglu, T.; Macreadie, L. K.; Farha, O. K. "Robust Carborane-Based Metal–Organic Frameworks for Hexanes Separation." *J. Am. Chem. Soc.* **2023**, *145*, 23433-23441. DOI: <https://doi.org/10.1021/jacs.3c04641>
26. Gong, W.; Xie, Y.; Yamano, A.; Ito, S.; Tang, X.; Reinheimer, E. W.; Malliakas, C. D.; Dong, J.; Cui, Y.; Farha, O. K. "Modulator-Dependent Dynamics Synergistically Enabled Record SO₂ Uptake in Zr(IV) Metal–Organic Frameworks Based on Pyrene-Cored Molecular Quadripod Ligand." *J. Am. Chem. Soc.* **2023**, *145*, 26890-26899. DOI: <https://doi.org/10.1021/jacs.3c09648>
27. Gong, W.; Xie, Y.; Yamano, A.; Ito, S.; Reinheimer, E. W.; Dong, J.; Malliakas, C. D.; Proserpio, D. M.; Cui, Y.; Farha, O. K. "Rational Design and Reticulation of Infinite **qbe** Rod Secondary Building Units into Metal-Organic Frameworks through a Global Desymmetrization Approach for Inverse C₃H₈/C₃H₆ Separation." *Angew. Chem. Int. Ed.*, **2023**, e202318475. DOI: <https://doi.org/10.1002/anie.202318475>
28. "Isomer of NU-1000 with a Blocking c-pore Exhibits High Water–Vapor Uptake Capacity and Greatly Enhanced Cycle Stability," Zhiyong Lu, Jiabin Duan, Hao Tan, Liting Du, Xiang Zhao, Rui Wang, Satoshi Kato, Shilong Yang, and Joseph T. Hupp. *J. Am. Chem. Soc.*, **2023**, *145* (7), 4150-4157. DOI: <https://doi.org/10.1021/jacs.2c12362>
30. "Incorporation of isomerHalide Ions Stabilizes Metal–Organic Frameworks (MOFs) Against Pore Collapse and Renders Large-pore Zr-MOFs Functional for Water Harvesting," Z. Lu, J. Duan, L. Du, Q. Liu, N. M. Schweitzer and J. T. Hupp, *J. Mater. Chem. A*, **2022**, *10*, 6442-6447 DOI: <https://doi.org/10.1039/D1TA10217F>
31. Islamoglu, T.; Idrees, K. B.; Son, F. A.; Lee, S.-J.; Li, P.; Farha, O. K. "Are you using the right probe molecules for assessing the textural properties of metal–organic frameworks?" *J. Mater. Chem. A*. **2022**, *10*, 157-173. DOI: <https://doi.org/10.1039/D1TA08021K>
32. Liu, J.; Goetjen, T.; Wang, Q.; Knapp, J. G.; Wasson, M. C.; Yang, Y.; Syed, Z. H.; Delferro, M.; Notestein, J. M.; Farha, O. K.; Hupp, J. T. "MOF-enabled confinement and related effects for chemical catalyst presentation and utilization." *Chem. Soc. Rev.* **2022**, *51*, 1045-1097. DOI: <https://doi.org/10.1039/D1CS00968K>
33. Gong, W.; Xie, Y.; Pham, T. D.; Shetty, S.; Son, F. A.; Idrees, K. B.; Chen, Z.; Xie, H.; Liu, Y.; Snurr, R. Q.; Chen, B.; Alameddine, B.; Cui, Y.; Farha, O. K. "Creating Optimal Pockets in a Clathrochelate-Based Metal–Organic Framework for Gas Adsorption and Separation: Experimental

- and Computational Studies.” *J. Am. Chem. Soc.* **2022**, *144*, 3737-3745. DOI: <https://doi.org/10.1021/jacs.2c00011>
34. Idrees, K. B.; Li, Z.; Xie, H.; Kirlikovali, K. O.; Kazem-Rostami, M.; Wang, X.; Wang, X.; Tai, T.-Y.; Islamoglu, T.; Stoddart, J. F.; Snurr, R. Q.; Farha, O. K. “Separation of Aromatic Hydrocarbons in Porous Materials.” *J. Am. Chem. Soc.* **2022**, *144*, 12212-12218. DOI: <https://doi.org/10.1021/jacs.2c03114>
35. Gong, W.; Kazem-Rostami, M.; Son, F. A.; Su, S.; Fahy, K. M.; Xie, H.; Islamoglu, T.; Liu, Y.; Stoddart, J. F.; Cui, Y.; Farha, O. K. “Tröger’s Base Chemistry in Solution and in Zr(IV)-Based Metal–Organic Frameworks.” *J. Am. Chem. Soc.* **2022**, *144*, 22574-22581. DOI: <https://doi.org/10.1021/jacs.2c08623>
36. Osterrieth, J. W. M.; et al. “How Reproducible Are Surface Areas Calculated from the BET Equation?” *Adv. Mater.* **2022**, *34*, 2201502. DOI: <https://doi.org/10.1002/adma.202201502>
37. “Double-Walled $Zn_{36}@Zn_{104}$ Multicomponent Senary Metal–Organic Polyhedral Framework and Its Isorecticular Evolution,” Lu, Z.; Du, L.; Guo, R.; Zhang, G.; Duan, J.; Zhang, J.; Han, L.; Bai, J.; Hupp, J. T. *J. Am. Chem. Soc.*, **2021**, *143*, 43, 17942-17946.
DOI: [10.1021/jacs.1c08286](https://doi.org/10.1021/jacs.1c08286)
38. Audu, C. O.; Chen, D.; Kung, C.-W.; Snurr, R. Q.; Nguyen, S. T.; Farha, O. K.; Hupp, J. T. “Transport Diffusion of Linear Alkanes (C5–C16) through Thin Films of ZIF-8 as Assessed by Quartz Crystal Microgravimetry.” *Langmuir* **2021**, *37*, 9405-9414. DOI: <https://doi.org/10.1021/acs.langmuir.1c00672>
39. Chen, Z.; Idrees, K. B.; Shetty, S.; Xie, H.; Wasson, M. C.; Gong, W.; Zhang, X.; Alameddine, B.; Farha, O. K. “Regulation of Catenation in Metal–Organic Frameworks with Tunable Clathrochelate-Based Building Blocks.” *Cryst. Growth Des.* **2021**, *21*, 6665-6670. DOI: <https://doi.org/10.1021/acs.cgd.1c01151>

Extraction of Rare Earth Elements from Waste Streams Using Chemically-Enhanced Electrodialysis (CEED)

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Key Words: Field-Driven Separations; Interfaces; Membranes; Recognition (General)

DE-SC0025217: Extraction of Rare Earth Elements from Waste Streams Using Chemically-Enhanced Electrodialysis (CEED)

PI: Kristin Hutchins; co-PIs: Michael Findlater and Weile Yan

Research Project Scope.

The recovery and separation of the rare earth elements (REEs) in a sustainable manner, both economically and environmentally, represents a significant technological problem. The scope of this collaborative project is to develop a novel approach to existing extraction behaviors. Specifically, our team's approach focuses on developing a class of electrodialysis membranes with ion-gating functionality for selective extraction of early lanthanides via molecular recognition in tandem with a conventional electrodialysis strategy. Our strategy will enable an entirely new technological approach to the separation of valuable REEs. Additionally, incorporation of sequestrants on membranes and their applications in low-temperature, aqueous-based systems render the approach to be more chemical- and energy-efficient than many existing technologies.

Recent Progress.

Our team has demonstrated that surface deposition of ion sequestrants is a versatile approach for improving membrane selectivity. Many separation processes including harvesting critical minerals from nonconventional sources often requires extraction of low-level target ions from matrices of background ions at dominant concentrations. In our first proof-of-concept study, we evaluated the selective extraction of Ba^{2+} and Mg^{2+} from synthetic brine solutions. Using a commercially available cation-exchange membrane as a baseline, we functionalized the membrane with crown ether or calixarene host molecules (Figure 1). Compared to the unmodified membrane, the crown ether- and calixarene-modified membranes showed increased selectivity for Ba^{2+} and Mg^{2+} with respect to the dominant ion (Na^+) by up to fourfold.

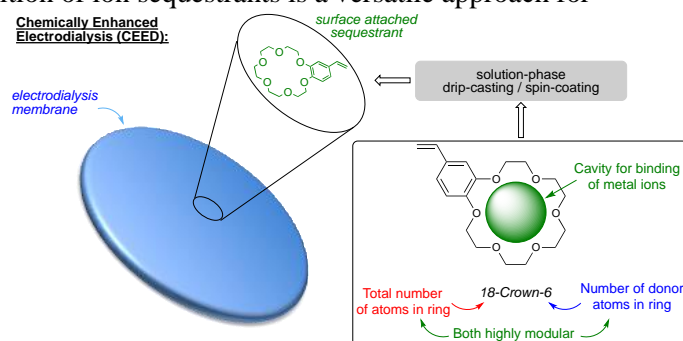


Figure 1. Depiction of CEED with physisorbed modified crown-ether shown as an example.

Once sequestrants are installed on the membrane, there is a subtle balance between strong ion binding and transport in CEED. Sequestrants that bind the strongest in a bulk solution do not necessarily equate to the best overall performance on the membrane surface. Moreover, during electrodialysis, parameters

including current density, REE to background ion ratio, and pH can be systematically varied and will impact ion mobility and ion transport selectivity. Recently, we assessed the binding specificity of sequestrant molecules for REEs (Dy and Nd) and background ion (Na) with extraction studies. Crown ethers and calixarenes of various cavity size were screened in bulk solution, and Dy and Nd were preferentially extracted relative to Na. We observed that the pH of the solution influences ion binding efficiency strongly. A sharp increase in REE sequestration was attained as pH increases above 6, outcompeting background ions such as Na.

Future Plans.

Our next steps include synthesizing ion-specific sequestrants, conducting solution extraction experiments, modifying commercial electro dialysis membranes with the sequestrants, and conducting bench-scale CEED tests.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. K. M. Hutchins, W. Yan, M. Findlater. Chemically Enhanced Electrodialysis (CEED): A Universal Platform for Selective Ion Removal. U.S. Provisional Patent Application No. 63/439,510. International patent application no. PCT/US24/11720 (filed January 17, 2024).
2. L. Ma, J. D. Loya, M. Findlater, and K. M. Hutchins. Improved Syntheses of 4'-Vinylbenzo-3n-Crown-n Ethers ($n = 5-7$). *The Journal of Organic Chemistry*. 2022, 87(21), 14953–14956.
3. N. Barragan, D. Bedi, M. Sivaraman, J. D. Loya, K. Babaguchi, M. Findlater, K. M. Hutchins, and W. Yan. Selective Removal of Barium and Hardness Ions from Brackish Water with Chemically Enhanced Electrodialysis. *ACS ES&T Water*. 2022, 2(2), 288–298.

Leveraging High-throughput Computation and Machine Learning to Discover and Understand Low-Temperature Fast Oxygen Conductors

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Key Words: Data Science; Machine Learning/AI; Theory/Simulation; Transport Phenomena

DE-SC0020419: Leveraging High-throughput Computation and Machine Learning to Discover and Understand Low-Temperature Fast Oxygen Conductors

PI: Ryan Jacobs; co-PI: Dane Morgan

Research Project Scope.

There is high demand for transformative innovations of new materials for improved applications of future energy devices. Dense ceramic oxygen-active materials are key components in many energy-related applications, including solid oxide and protonic fuel cells, electrolyzers, solid-oxide metal-air redox batteries, gas sensors and gas separation membranes for fuel production and gas purification and chemical looping. New highly oxygen-active materials may enhance many energy-related technologies by enabling efficient oxygen-ion transport at lower temperatures, e.g., below

≈ 400 °C. This work combines materials data mining, physics-informed descriptors, high-throughput *ab initio* calculations, and detailed experiments to discover and understand totally new classes of oxide materials promising for reduced temperature applications. Using these approaches, we were successful in discovering and validating outstanding oxygen conduction performance in multiple new families of interstitial and vacancy conducting materials, as described more below.

Recent Progress.

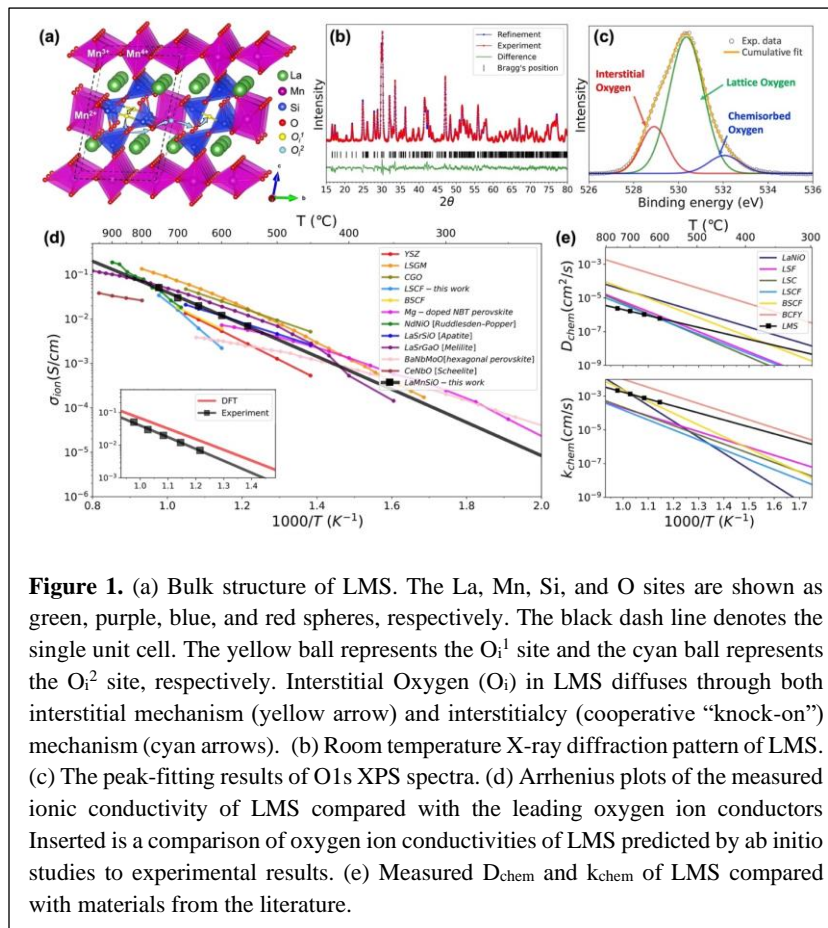
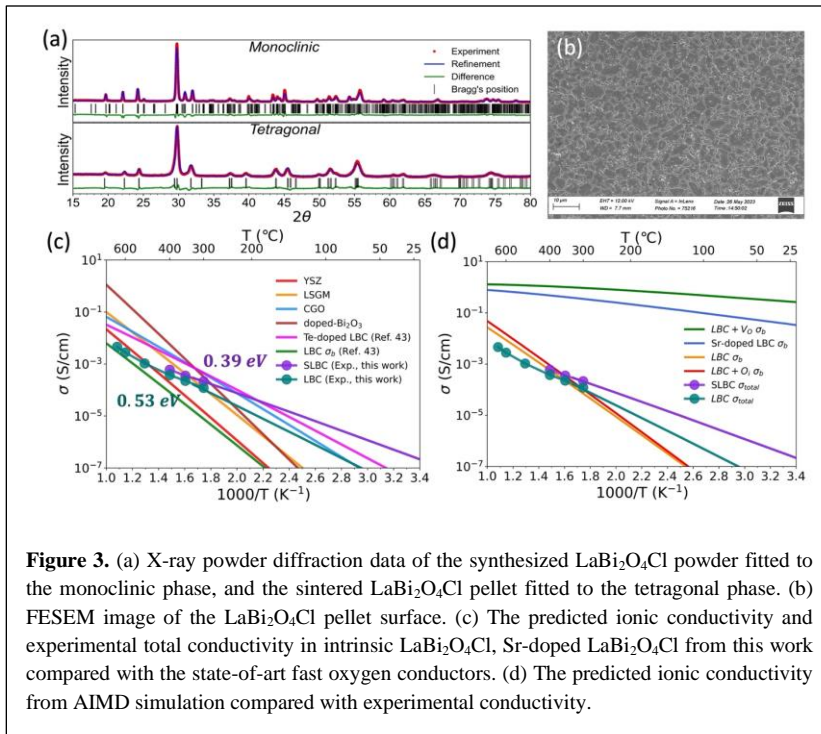
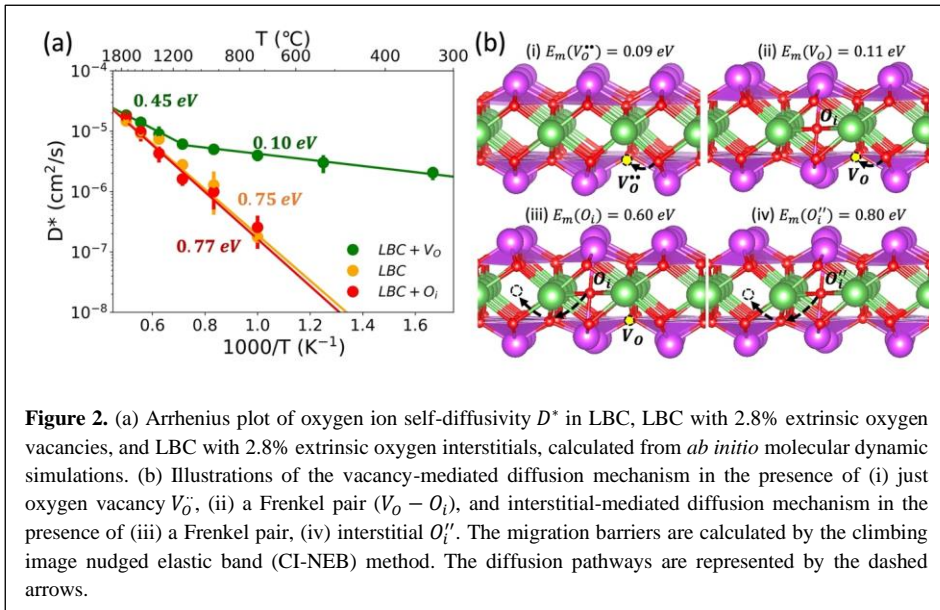


Figure 1. (a) Bulk structure of LMS. The La, Mn, Si, and O sites are shown as green, purple, blue, and red spheres, respectively. The black dash line denotes the single unit cell. The yellow ball represents the O_i¹ site and the cyan ball represents the O_i² site, respectively. Interstitial Oxygen (O_i) in LMS diffuses through both interstitial mechanism (yellow arrow) and interstitialcy (cooperative “knock-on”) mechanism (cyan arrows). (b) Room temperature X-ray diffraction pattern of LMS. (c) The peak-fitting results of O1s XPS spectra. (d) Arrhenius plots of the measured ionic conductivity of LMS compared with the leading oxygen ion conductors. Inserted is a comparison of oxygen ion conductivities of LMS predicted by *ab initio* studies to experimental results. (e) Measured D_{chem} and k_{chem} of LMS compared with materials from the literature.

First, oxygen interstitial-mediated conductors have the potential to realize outstanding performance but have received far less attention than vacancy-mediated conductors. Multiple new families of high-performing interstitial conductors were found which adopt completely different structures from known



we identified the $\text{MBi}_2\text{O}_4\text{X}$ (M =rare-earth, X =halogen) structure as an ultra-fast oxygen vacancy conductor, which adopts a triple-fluorite layered structure. *Ab initio* simulations of the representative material $\text{LaBi}_2\text{O}_4\text{Cl}$ (LBC) reveal migration barriers of 0.1-0.8 eV, depending on the mediating defect (see **Figure 2**). Experimental results demonstrate that LBC and Sr-doped LBC have comparable or higher oxygen conductivity than commonly used solid-state oxygen electrolyte materials at temperatures of < 400 °C, but

oxygen conductors. From these families, we synthesized and studied the oxygen kinetics in $\text{La}_4\text{Mn}_5\text{Si}_4\text{O}_{22+\delta}$ (LMS), a representative member of perrierite/chevkinite family. We found LMS has higher oxygen ionic conductivity than the widely used yttria-stabilized ZrO_2 , and among the highest surface oxygen exchange rates at intermediate

temperature of known materials (see **Figure 1**). From investigating the newly discovered and previously known oxygen interstitial conductors, we proposed that the essential features for forming an effective interstitial oxygen conductor are the availability of electrons and structural flexibility enabling sufficient accessible volume. Overall, this work provides a powerful approach for discovering and understanding new interstitial oxygen conductors.

Second, employing a structure-similarity analysis of $>60\text{k}$ oxygen-containing compounds,

lower than the theoretical predictions (see **Figure 3**). We believe realizing the exceptional predicted high oxygen conductivity of LBC resides in creation of extrinsic oxygen vacancies (e.g., through aliovalent doping) and through microstructural engineering (e.g., through grain size refinement).

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. Meng, J., Sheikh, S., Jacobs, R., Liu, J., Nachlas, W., Li, X., Morgan, D., *Computational Discovery of Fast Interstitial Oxygen Conductors*. Nature Materials (2024). <https://www.nature.com/articles/s41563-024-01919-8>

Grant cited but not intellectually led by this award:

1. Lv, X.-L., Sullivan, P. Li, W., Fu, H.-C., Jacobs, R., Chen, C.-J., Morgan, D., Jin, S., Feng, D. *Modular dimerization of organic radicals for stable and dense flow battery catholyte*. Nature Energy 8, 10 (2023). <https://www.nature.com/articles/s41560-023-01320-w>
2. Giordano, L., Jacobs, R., Akkiraju, K., Vivona, D., Morgan, D., Shao-Horn, Y. “Using O Electronic Structure to Understand and Design Catalytic Activity of Oxides”, Accounts of Chemical Research 55, 3 (2022). <https://pubs.acs.org/doi/full/10.1021/acs.accounts.1c00509>
3. Shourov, E. H., Jacobs, R., Strohbeen, P. J., Morgan, D., Kawasaki, J. “Semi adsorption-controlled growth window for half Heusler FeVSb epitaxial films”, Physical Review Materials 4 (7) (2020). <https://journals.aps.org/prmaterials/abstract/10.1103/PhysRevMaterials.4.073401>
4. Zheng, X., Meng J., Guisinger, N., Guest, J., Su, K., Morgan, D., Arnold, M. “Evolution of PTCDA-derived seeds prior to graphene nanoribbon growth on Ge(001)”, Carbon, 229 (119468) (2024) <https://doi.org/10.1016/j.carbon.2024.119468>.

Transforming Critical Materials Separation using Precision Control

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¹Oak Ridge National Laboratory, ²Vanderbilt University

Key Words: Liquid-Liquid Phase; Recognition (General); Reactive Separations; Solvation

DE-SC00ERKCG21: Transforming Critical Materials Separation using Precision Control

PI: Santa Jansone Popova; co-PI: Alex Ivanov, Ilja Popovs, Albina Borisevich, De-en Jiang

Research Project Scope.

The research objective is to explore how the combination of "strong" interactions at the ligand-metal binding site and "weak" interactions in the outer coordination sphere can be exploited for the targeted separation of adjacent lanthanides. Aim 1 investigates the donor atom-metal ion interactions within the first coordination sphere to uncover ligand design principles and structural descriptors that influence selectivity across the trivalent lanthanide series. Aim 2 focuses on the role of water and its interactions in both the inner and outer coordination spheres of lanthanide complexes. Aim 3 designs stimuli-responsive lanthanide separation systems utilizing electrochemically active ligands.

Recent Progress.

This project delves into the intricate chemistries required for the selective separation of critical materials by manipulating both local and extended chemical environments. The challenge of separating lanthanides into individual elements stems from their similar chemical and physical properties. While existing organic compound libraries can distinguish between heavier and lighter lanthanides, they often fall short in selectively separating adjacent elements within the series.

Our recent work focuses on novel organic ligands with varying degrees of preorganization and their effects on lanthanide separation.¹ The structural rigidity of the bis-lactam-1,10-phenanthroline (BLPhen) ligand enforces size-based selectivity, showing exceptional affinity for lanthanides with larger ionic radii, such as La. Modifying the ligand by removing one preorganization element (BLBPy) results in fast complexation with light lanthanides, with peak selectivity shifting toward middle lanthanides (Sm) over time, enabling time-resolved separation. At low nitric acid concentrations, the neutral tetradentate ligand complexes with Ln³⁺ ions, while at higher concentrations, the extraction mechanism changes, leading to the formation and preferential extraction of anionic heavy lanthanide species, [Ln(NO₃)_{x+3}]^{x-}, which self-assemble with two protonated ligands to form intricate supramolecular architectures. Removing two preorganizing elements in the bis-lactam-1,10-phenanthroline ligand (DAPhen) maintains its size-based selectivity across the lanthanide series but reduces its affinity for lanthanides by 50%. These insights will help guide the design of novel separation systems for targeted lanthanide recognition.

Our team also conducted the first fundamental investigation of promethium (Pm), the rarest lanthanide, uniquely produced by Oak Ridge National Laboratory's isotope program.² Using a combination of synthetic efforts, X-ray absorption spectroscopy, and ab initio MD simulations, we characterized the

complexation of Pm by diglycolamide. This study provided the first experimental opportunity to investigate the effect of lanthanide contraction across the entire Ln series, revealing structural and electronic features beyond the simple change in ionic radii of Ln³⁺ ions.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. S. Pramanik, B. Li, D. M. Driscoll, K. R. Johnson, B. R. Evans, J. T. Damron, A. S. Ivanov, D. Jiang, J. Einkauf, I. Popovs, S. Jansone-Popova. Tetradentate Ligand's Chameleon-like Behavior Offers Recognition of Specific Lanthanides. *JACS*. **2024**, 146, 25669.
2. D. M. Driscoll, F. D. White, S. Pramanik, J. Einkauf, B. Ravel, D. Bykov, S. Roy, R. T. Mayes, L. Delmau, S. Schrell, T. Dyke, A. Miller, M. Silveira, S. van Cleve, R. Copping, S. Davern, S. Jansone-Popova, I. Popovs, A. S. Ivanov. Observation of a promethium complex in solution, *Nature* **2024**, 629, 819.
3. S. Pramanik, S. Kaur, I. Popovs, A. S. Ivanov, S. Jansone-Popova. Emerging Rare Earth Element Separation Technologies. *EurJIC*. **2024**, asap. DOI: 10.1002/ejic.202400064.
4. S. Li, S. Jansone-Popova, D. Jiang. Insights into Coordination and Ligand Trends of Lanthanide Complexes from the Cambridge Structural Database, *Scientific Reports*. **2024**, 14, 11301.
5. T. N. D. Reddy, A. S. Ivanov, D. M. Driscoll, S. Jansone-Popova, D. Jiang. Changes in nitrate binding with lanthanides in BLPhen complexes. *J. Mol. Liq.* **2023**, 387, 122573.
6. K. R. Johnson, D. M. Driscoll, J. T. Damron, A. S. Ivanov, S. Jansone-Popova. Size Selective Ligand Tug of War Strategy to Separate Rare Earth Elements. *JACS Au*. **2023**, 3, 584.
7. T. Liu, A. S. Ivanov, I. Popovs, S. Jansone-Popova, D. Jiang. N-oxide ligands for selective separations of lanthanides: insights from computation. *RSC Advances*. **2023**, 13, 764.
8. C. Do-Thanh, H. Luo, S. Dai. A perspective on task-specific ionic liquids for the separation of rare earth elements. *RSC Sustainability*. **2023**, 1, 1168.
9. C. Do-Thanh, H. Luo, J. A. Gaugler, S. Dai. A task-specific ionic liquid based on hydroxypyridinone for lanthanide separation. *Sep. Purif. Technol.* **2022**, 301, 121939.
10. D. M. Driscoll, H. Liu, B. Reinhart, I. Popovs, V. Bocharova, S. Jansone-Popova, D. Jiang, A. S. Ivanov. Noncoordinating outer-sphere nitrate ion modulates supramolecular clustering of lanthanides in nonpolar media. *J. Phys. Chem. Lett.* **2022**, 13, 12076.
11. T. Liu, K. R. Johnson, S. Jansone-Popova, D. Jiang. Advancing Rare-Earth Separation by Machine Learning. *JACS Au*. **2022**, 6, 1428.
12. T. N. D. Reddy, A. S. Ivanov, D. M. Driscoll, S. Jansone-Popova, D. Jiang. Atomistic Insights into Structure and Dynamics of Neodymium (III) Complexation with a Bis-lactam Phenanthroline Ligand in the Organic Phase. *ACS Omega*. **2022**, 7, 21317.
13. S. Jansone-Popova, I. Popovs, K. Johnson. Method for separation of adjacent lanthanide elements. US Patent App. No. 63/339,996, May 10, **2022**.

Grant cited but not intellectually led by this award:

1. M. Toro-González, N. Akingbesote, A. Webb, B. Sanders, A. S. Ivanov, S. Jansone-Popova, I. Popovs, P. Benny, R. Perry, S. Davern. Development of ²²⁵Ac-doped Biocompatible Nanoparticles for Targeted Alpha Therapy. *J. Nanobiotechnology*. **2024**, 22, 306.
2. S. M. Davern, M. T. Gonzalez, I. Popovs, S. Jansone-Popova. Biocompatible radionuclide-containing compositions and methods of use. 2024, US Patent App. No. 18/385,428, May 16, **2024**.

Driving Selectivity Among Rare Earth Elements through Phase Modifiers

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Key Words: Assembly/Ordering; Kinetics; Liquid-Liquid Phase; Machine Learning/AI; Membranes

DE-SC0022217: Driving Selectivity Among Rare Earth Elements through Phase Modifiers

PI: Mark Jensen; co-PIs: Jenifer Shafer, Aurora Clark, and Stosh Kozimor

Research Project Scope.

To overcome marginal separations performance in current liquid-liquid extractants, we are striving to understand how to harness the properties of the organic solution itself to significantly enhance metal ion separations. Instead of focusing on the metal-ligand bonds of the extracted rare earth complexes, we are pursuing a novel separations principle for rare earth elements wherein altering the properties of the organic solution by introducing phase modifiers improves the separations selectivity by tuning the thermodynamic selectivity for particular rare earth ions through solute-solvent interactions in the outer coordination spheres of the extracted complexes in the bulk organic phase, or by shifting the balance of the metal ion phase transfer kinetics at the aqueous/organic interface.

Recent Progress.

A comprehensive understanding of the effect of phase modifiers on metal ion selectivity in solvent extraction requires measurements across a wide range of solution compositions, such as the identity and total concentration of the acid, phase modifier, diluent and metal ion. To achieve the degree of data collection required we have used the Los Alamos SuperSeparator to collect thousands of distribution ratios in lanthanide-tetraoctyldiglycolamide (TODGA) extraction system. These results are being analyzed by burgeoning machine learning algorithms to isolate key variables that can help us understand the features of phase modifiers that can enhance selectivity for rare earth ions in these extractions. Adding low concentrations of short-chain normal alcohols to TODGA/*n*-dodecane extraction systems increases the intra-lanthanide selectivity for some lanthanides toward the end of the lanthanide series, as we initially hypothesized. We also find that Alcoholic phase modifiers alter the rare earth extraction without directly coordinating the metal or altering the core $M(\text{TODGA})_3(\text{anion})_3$ complexes that are extracted in the absence of the phase modifier. This is not the case when tributylphosphate is used as a phase modifier with a different

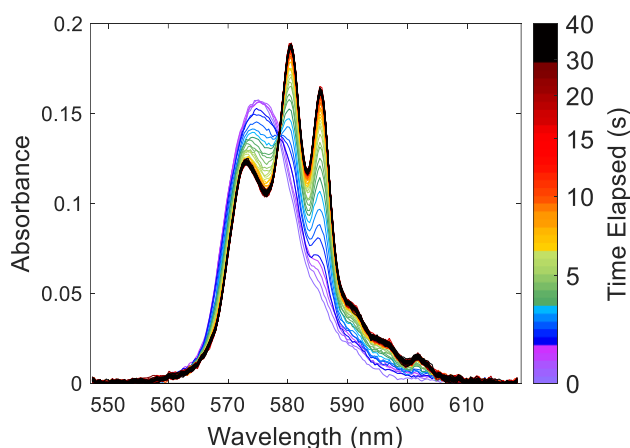


Figure 1. Operando optical spectra of Nd extraction from 2.6M HNO_3 into 0.1 M TODGA/*n*-dodecane show reversible pseudofirst order phase partitioning kinetics in a rapidly stirred cell.

diamide extractant. Despite the expected stronger metal-extractant interactions in this system, the presence of the tributyl phosphate phase modifier alters the lanthanide coordination environment.

The kinetics of neodymium(III) extraction by TODGA have also been investigated to understand how phase modifiers affect the actual partitioning of rare earth ions. Using operando optical spectroscopy in a highly stirred cell, the rapid phase transfer reactions of the rare earth ions are easily followed, even though the reaction can reach equilibrium in 10 seconds or less (Figure 1). In the absence of the phase modifiers, we find that the rate of the phase transfer reaction is controlled by slow absorption and desorption reactions at the interface, the core $M(\text{TODGA})_3(\text{NO}_3)_3$ complex is formed by the time the metal migrates from the interface into the bulk organic phase, and additional extractant or nitric acid molecules bind in the outer sphere after detachment. Contrary to our initial hypothesis that metal interactions with organized interfacial structures are rate limiting species at the interface for the forward reaction, in the absence of phase modifier the primary favorable contribution to the rare earth extraction is the complete dissociation of the metal-TODGA-nitrate-nitric acid assembly, and this is the kinetic feature that should be exploited to generate selectivity. When phase modifier is added to the system, the position of the rate determining step or the overall mechanism changes for even a few volume percent of 1- or 2-octanol. However, increasing the phase modifier the more branched 3-octanol has no significant effect on the phase transfer rate or the mechanism.

Future Plans.

While some of our initial hypotheses have been demonstrated and others have been shown to be incorrect, key areas for our future work include:

- Computational modelling of interactions between the phase modifier and extracted complexes in the bulk phase.
- Gaining a systematic understanding of the effect of alcohol phase modifiers on the equilibria driving the extraction and separations.
- Optical spectroscopy of the interfacial complexes to validate or alter proposed reaction mechanisms and help us understand the effect of phase modifiers on the extraction kinetics.
- Linking observed kinetic behavior to computational models of interfacial metal-extractant interactions.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. Sadhu, B.; Clark, A. E. "Modulating Aggregation in Microemulsions: The Dispersion by Competitive Intermolecular Interaction Model." *The Journal of Physical Chemistry Letters* **13** (2022): 10981-10987.
2. Peroutka, A. A.; Galley, S. S.; Shafer, J. C. "Elucidating the speciation of extracted lanthanides by diglycolamides." *Coordination Chemistry Reviews* **482** (2023): 215071.
3. Peroutka, A. A.; Galley, S. S.; Shafer, J. C. "A multi-faceted approach to probe organic phase composition in TODGA systems with 1-alcohol phase modifiers." *RSC Advances* **13** (2023): 6017-6026.
4. Peroutka, A. A.; Fontan, R.; Jackson, J. A.; Johnson, M.; Gale, S. S.; Servios, M. J.; Shafer, J.C. "Enhancing f-Element Separations with ADAAM-EH: The Impact of Phase Modifiers and a DGA Aqueous Complexant." *Industrial & Engineering Chemistry Research* **63** (2024) 9203-9213.

5. Peroutka, A. A.; Wang, X.; Servis, M. J.; Shafer; J. C. "Influence of Aqueous Phase Acidity on Ln(III) Coordination by *N,N,N',N'*-Tetraoctyldiglycolamide." *Inorganic Chemistry* **63** (2024): 10466-10470.

Ion Separations with Functionalized Laminate Membranes

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Key Words: Confinement, Interfaces, Membranes, Solvation

PNNL 81462: Harnessing Confinement Effects, Stimuli, and Reactive Intermediates in Separations

PI: David J. Heldebrant; co-PI: Grant E. Johnson

Research Project Scope.

Achieving efficient and selective critical material separations from liquid feedstocks such as produced waters, geothermal brines, and leachates is a grand scientific challenge essential to enabling the transition to a clean energy economy and ensuring national security. Spatially confining environments are one promising approach to accomplishing such separations. Our studies employ well-defined graphene oxide (GO) laminates with nanoscale functionalized interlayer transport channels. Knowledge gaps remain in the fundamental understanding of how the size, charge, surface functionality, and hydrophobicity of nanoconfined transport channels influence the selective adsorption/desorption, transport, and sieving of solvated metal cations and the flux of water molecules. Our work aims to understand how differences in the interactions of solvated metal ions and water molecules with confined functionalized interfaces may be exploited to promote the atom- and energy-efficient extraction of critical minerals and pollutants from widely available domestic liquid feedstocks.

Recent Progress.

One challenge to using laminate membranes in separations is understanding how different surface functional groups influence the adsorption of solvated ions. We hypothesized that the reversible binding of aqueous metal ions on GO laminates may be achieved through surface functionalization with carboxylic acid groups. We tested this hypothesis by increasing the surface coverage of carboxylic acid groups on GO using hydrothermal synthesis methods. Ion adsorption and permeation experiments combined with characterization and theoretical modeling revealed the reversible adsorption and desorption of lead cations at low and high pH values, respectively. These findings demonstrate a scalable approach to synthesizing adsorption media that may be regenerated through a simple pH change. Due to the small size of the transport channels in GO membranes, achieving a sufficient flux of water molecules for practical separations remains

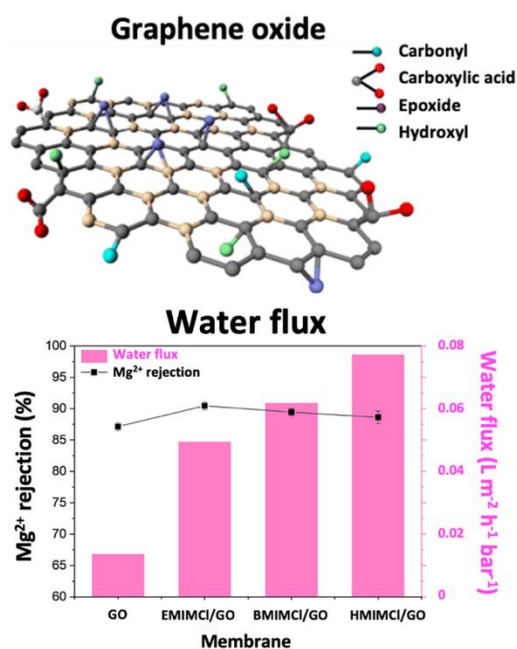


Figure 1. Controlled oxygen functionality of GO membranes. The introduction and removal of different oxygen functional groups from GO surfaces modulate the selective adsorption and transport of metal ions through nanoconfined transport channels and increase the overall flux of water molecules for scalable separations.

challenging. We hypothesized that functionalizing the basal planes of GO with hydrophobic ionic liquid molecules may increase the flux of water through membranes. To test this hypothesis, we covalently anchored imidazolium-based ionic liquids to the surface epoxide groups of GO. Ion permeation experiments revealed a substantially increased water flux without sacrificing selectivity between different metal ions. Until recently, the primary mechanism of ion separation in GO membranes was proposed to be size-selective sieving. We hypothesized that a different mechanism involving the adsorption and desorption of different ions at surface oxygen sites may underlie selective ion permeation rates. To test this hypothesis, we selectively removed hydroxyl groups from the basal planes of GO using ultraviolet radiation. This scalable modification approach enhanced the interactions of metal cations with functional groups located at the edges of GO, resulting in a lower transport rate of smaller monovalent ions than larger divalent cations. Our findings inform the design of nanoconfined media that may be used for selectively recovering critical minerals and pollutants from abundant domestic feedstocks.

Future Plans.

Future work will develop the understanding needed to improve the selectivity of GO membranes by controlling their oxygen functionality through photoreduction at different pH values and modulating their interlayer spacing using boronic acid linker molecules.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. M.-T. Nguyen, J. Zhang, V. Prabhakaran, S. Tan, E.T. Baxter, V. Shutthanandan, G.E. Johnson, R. Rousseau, V.-A. Glezakou. Graphene Oxide as a Pb(II) Separation Medium: Has Part of the Story Been Overlooked? *JACS Au*. 2021, 1, 766-776.
2. E. T. Baxter, J. Zhang, S. Tan, M.-T. Nguyen, D. Zhang, Q. Yuan, W. Cao, X.-B. Wang, V. Prabhakaran, V.-A. Glezakou, G. E. Johnson. Functionalization of Electrodes with Tunable [EMIM]_x[Cl]_{x+1}⁻ Ionic Liquid Clusters for Electrochemical Separations. *Chemistry of Materials*. 2022, 34, 2612-2623.
3. S. Tan, D. Zhang, M.-T. Nguyen, V. Shutthanandan, T. Varga, R. Rousseau, G.E. Johnson, V.-A. Glezakou, V. Prabhakaran. Tuning the Charge and Hydrophobicity of Graphene Oxide Membranes by Functionalization with Ionic Liquids at Epoxide Sites. *ACS Applied Materials and Interfaces*. 2022, 14, 19031-19042.
4. S. Tan, M.-T. Nguyen, D. Zhang, L. Zhong, Z. Cheng, S. China, G.E. Johnson, V. Prabhakaran. Electric-Field-Induced Assembly of an Ionic Liquid–Water Interphase Enables Efficient Heavy Metal Electrosorption. *ACS Applied Materials & Interfaces*. 2023, 15, 44469-44481.
5. S. Tan, D. Zhang, Y. Chen, B.A. Helfrecht, E.T. Baxter, W. Cao, X.-B Wang, M.-T. Nguyen, G.E. Johnson, V. Prabhakaran. Complexation of Heavy Metal Cations with Imidazolium Ionic Liquids Lowers their Reduction Energy: Implications for Electrochemical Separations. *Green Chemistry*. 2024, 26, 1566-1576.
6. Y. Yin, S. Tan, D. Zhang, R.C. Shiery, M.-T. Nguyen, V. Shutthanandan, V. Prabhakaran, G.E. Johnson, Distinct Ion Transport Behavior Between Graphene Oxide and UV-Irradiated Reduced Graphene Oxide Membranes. *Chemical Engineering Journal*. 2024, 493, 152304.
7. J. Edgecomb; D.T. Ngygen, S. Tan, V. Murugesan, G.E. Johnson, V. Prabhakaran. Electrochemical Imaging of Precisely-Defined Redox and Reactive Interfaces. *Angewandte Chemie International Edition* 2024, e202405846.

Grant cited but not intellectually led by this award:

1. M.R. Ligare, K.A. Morrison, M.A. Hewitt, J.U. Reveles, N. Govind, H. Hernandez, B.H. Clowers, J. Laskin, G.E. Johnson. Ion Mobility Spectrometry Characterization of the Intermediate Hydrogen-Containing Gold Cluster $\text{Au}_7(\text{PPh}_3)_7\text{H}_5^{2+}$. *Journal of Physical Chemistry Letters*. 2021, 12, 2502-2508.
2. V. Prabhakaran, J. Romo, A. Bhattarai, K. George, Z.M. Norberg, D. Kalb, E. Apra, P.A. Kottke, A.G. Federov, P.Z. El-Khoury, G.E. Johnson, J. Laskin. Integrated Photoelectrochemical Energy Storage Cells Prepared by Benchtop Ion Soft Landing. *Chemical Communications*. 2022, 58, 9060-9063.
3. V. Prabhakaran, G.E. Johnson, J. Laskin. Ion Soft Landing: A Unique Tool for Understanding Electrochemical Processes. *Current Opinion in Electrochemistry*. 2023, 40, 101310.
4. O.M. Primera-Pedrozo, S. Tan, D. Zhang, B.T. O'Callahan, W. Cao, E.T. Baxter, X.-B. Wang, P.Z. El-Khoury, V. Prabhakaran, V.A. Glezakou, G.E. Johnson. Influence of Surface and Intermolecular Interactions on the Properties of Supported Polyoxometalates. *Nanoscale* 2023, 15, 5786-5797.
5. R. Candeago, H. Wang, M.-T. Nguyen, M. Doucet, V.A. Glezakou, J.F. Browning, X. Su. Unraveling the Role of Solvation and Ion Valency on Redox-Mediated Electrosorption through In Situ Neutron Reflectometry and Ab Initio Molecular Dynamics. *JACS Au*. 2024, 4, 919-929.

Ion Transport in Highly Charged Polymer Membranes: Specific Ion Effects

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Key Words: Membranes; Solvation; Theory/Simulation; Transport Phenomena

DE-SC0022040: Ion Transport in Highly Charged Polymer Membranes with Subnanometer Free Volume Elements

PI: Jovan Kamcev

Research Project Scope.

Charged polymer membranes play a crucial role in various ion separation processes, such as electrodialysis and diffusion dialysis, as well as in energy generation systems like reverse electrodialysis, electrolysis, and fuel cells. Enhancing membrane selectivity and throughput can significantly improve the efficiency of these technologies and support emerging environmental and energy applications, including redox flow batteries, microbial fuel cells, ion-exchange membrane bioreactors, and electrochemical CO₂ reduction. Achieving this requires a deeper understanding of how polymer structure influences transport properties, which would accelerate the design of new membranes with tailored functionalities. The primary objective of the proposed research is to develop a fundamental understanding of ion transport in highly charged polymer membranes that feature subnanometer free volume elements.

Recent Progress.

This presentation will highlight our recent work on understanding specific ion effects (SIEs) on ion diffusion in highly charged polymer membranes. To advance this understanding, we synthesized homogeneous ion-exchange membranes (IEMs) and measured the diffusion coefficients and activation energies of diffusion of 15 different counter-ions in the membranes. These experimental findings were

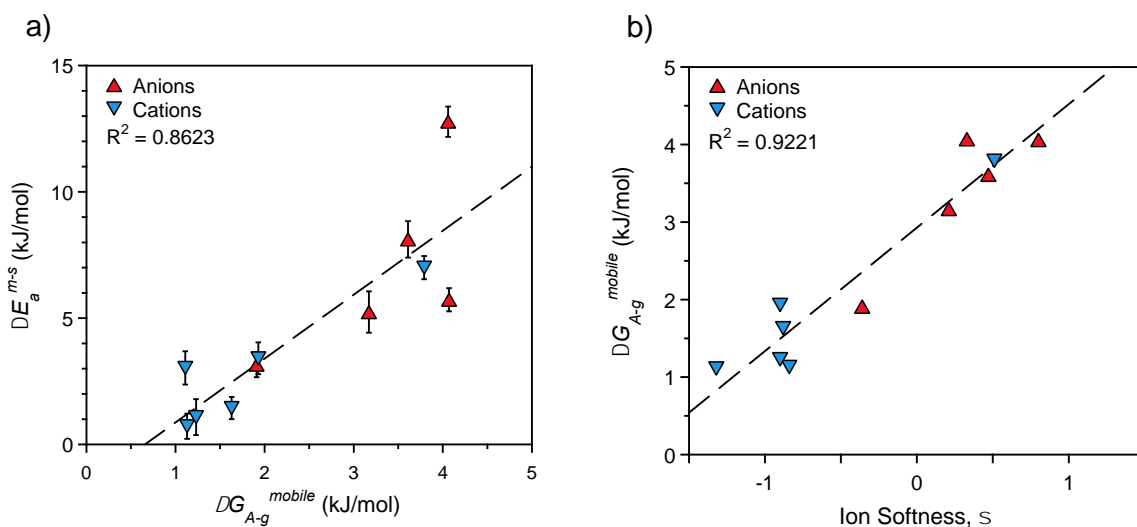


Figure 1. a) Difference in experimental activation energy of diffusion between the membrane and solution, ΔE_a^{m-s} , plotted vs. the strength of interactions between the fixed charges and mobile ions in the MD simulations, ΔG_{A-g}^{mobile} . b) ΔG_{A-g}^{mobile} plotted vs. the tabulated ion softness, σ .

complemented by atomistic molecular dynamics (MD) simulations using a subset of 11 counter-ions. The results reveal highly ion-specific diffusion behaviors, with ion transport properties in the membranes diverging from those in aqueous solutions to varying degrees, depending on the counter-ion identity. Our findings suggest that solvent-mediated interactions between ions and fixed charge groups are the primary drivers of SIEs in these IEMs. The increased energy barrier for diffusion within the IEM, experienced by each ion, strongly correlates with the free energies of interaction between fixed charge groups and mobile counter-ions as determined from the simulations (Figure 1a). These interaction energies also correlate with ion softness (Figure 1b), which is often used to predict ion/fixed charge group interactions based on Pearson's Hard/Soft Acid/Base (HSAB) theory. The HSAB mechanism, characterized by electrostatic interactions driven by ion/water coordination, aligns with the cooperative hydration observed in the simulations.

Other recent progress on this project includes several key developments. We published a comprehensive review article on analytical models for equilibrium ion partitioning and diffusion in charged polymer membranes.⁶ Additionally, we explored the fundamental ion transport properties of adsorptive membranes, which consist of a continuous charged polymer matrix with embedded highly selective adsorbents.⁵ Our findings revealed that interfacial interactions between the polymer and adsorbent particles significantly affect the ion transport properties of these membranes. We also published a detailed guide on accurately measuring the ionic conductivity of charged polymer membranes, addressing a topic that has been widely debated in recent literature.⁴ Furthermore, we conducted an extensive analysis of approximately 1,000 recently reported charged polymer membranes, which showed that existing membranes fall within a narrow range of charge densities, limiting their performance and contributing to the observed trade-off between ion conductivity and selectivity.³ Building on this, we developed an analytical model that predicts the ionic conductivity/selectivity trade-off and the upper bound line in charged polymer membranes.¹ Notably, the model suggests that increasing membrane charge densities could significantly enhance performance and shift the trade-off boundary.

Future Plans.

As part of this project, we have discovered synthetic strategies for membranes with unprecedented charge densities. Future work will focus on developing these synthetic strategies further and investigating the ion transport properties of these unique systems.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. D. Kitto, J. Kamcev, "Predicting the conductivity/selectivity trade-off and upper bound in ion-exchange membranes", *ACS Energy Letters*, **2024**, 9, 1346-1352.
2. J. C. Díaz, J. Park, A. Shapiro, H. Patel, L. Santiago-Pagán, D. Kitto, J. Kamcev, "Understanding monovalent cation diffusion in negatively charged membranes and the role of membrane water content", *Macromolecules*, **2024**, 57 (5), 2468-2481.
3. D. Kitto, J. Kamcev, "The need for ion exchange membranes with high charge densities", *Journal of Membrane Science*, **2023**, 677, 121608.
4. J. C. Díaz, D. Kitto, J. Kamcev, "Accurately measuring the ionic conductivity of membranes via the direct contact method", *Journal of Membrane Science*, **2023**, 669, 121304.
5. C. Carey, J. C. Díaz, D. Kitto, C. Espinoza, E. Ahn, J. Kamcev, "Interfacial interactions between

polymers and selective adsorbents influence ion transport properties of boron scavenging ion-exchange membranes”, *Journal of Membrane Science*, **2023**, 669, 121301.

6. D. Kitto, J. Kamcev, “Manning condensation in ion-exchange membranes: A review on ion partitioning and diffusion models”, *Journal of Polymer Science*, **2022**, 60, 2929-2973.

A Macromolecular Selection Platform for the Isolation of Lanthanide Ions

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Key Words: Assembly/Ordering; Bioinspired Recognition; Dynamics; Machine Learning/AI

DE-SC0021295: A Macromolecular Selection Platform for the Isolation of Lanthanide Ions

PI: Abigail Knight

Research Project Scope. We are developing a macromolecular selection platform focused on lanthanide ion separations as a model system. Lanthanides (Ln: La-Lu), scandium, and yttrium are rare earth (RE) metals crucial to industries like technology, renewable energy, and medicine. Polymers are ideal for separations due to their multifunctional nanoscale environment and scalability. Our research aims to uncover the fundamental polymer properties needed for selective RE ion coordination and create a scalable material design platform for chemical separations. This platform connects polymer sequence (composition, monomer distribution, architecture) to structure (local, analogous to protein secondary structure, and global, analogous to tertiary and quaternary structure) to function through both systematic studies and machine learning workflows.

Recent Progress.

Leveraging protein-mimetic structure for functional materials. Engineering each facet of protein-mimetic hierarchical structure into synthetic copolymers enables a unique opportunity to develop scalable, functional materials that begin to approach the affinity and selectivity of natural proteins. Towards this, we designed a bioinspired di(phenylalanine) (FF) moiety that engenders local, secondary-like structure and global, tertiary-like structure within amphiphilic copolymers (*J. Am. Chem. Soc.*, **2021**, *143*, 13228; **Fig. 1a**). We qualitatively elucidated the role of hydrogen bonding, aromatic interactions, and hydrophobicity on both the local and global structure through synthesizing copolymers containing analogous monomers. Monomers containing a single phenylalanine- and alanine-phenylalanine- were synthesized, revealing β -sheet-like interactions unique to FF. In collaboration with Drs. Laura Stingaciu and Changwoo Do (Oak Ridge National Laboratory), we performed neutron spin echo spectroscopy (*ACS Macro. Lett.*, **2024**, *13*, 889) to quantitatively probe the impact of each interaction on polymer dynamics. Copolymers containing FF as the hydrophobic moiety demonstrated increased internal friction (i.e., local rigidity) as compared to copolymers containing the single phenylalanine monomer and commercial *N*-benzylacrylamide, highlighting the significance of non-covalent interactions to tune polymer structure and dynamics.

In an inaugural effort to identify connections between sequence parameters, hierarchical structure, and function we have identified how the arrangement of FF within the polymer primary sequence impacts local structure and binding affinity/selectivity to target rare earth ions (*J. Am. Chem. Soc.*, **2024**, *146*, 8607; **Fig. 1b**). A series of compositionally identical copolymers were synthesized, and kinetic Monte Carlo simulations were used to visualize and quantify overlap between the unique polymer ensembles using CopolymerSequenceGeneration (available Knight Group GitHub). Single-chain collapse and the distribution of single- and multichain assemblies were both impacted by multiple sequence descriptors,

while conformational freedom of chain segments (secondary-like interactions) was impacted by the patchiness (i.e., density) of FF within hydrophobic domains. Sequence, structure, and target function, were all connected through a model system incorporating a functional acrylic acid monomer (AA) that demonstrated the impact of hierarchical structure on the affinity for rare earth elements. Collectively, these results highlight the potential and boundaries of sequence control via multiblock polymerizations to drive primary sequence ensembles hierarchical structures, and ultimately the functionality of compositionally identical polymeric materials.

To develop materials with both desirable binding and reusability, we embarked on fundamental analyses of kinetic pathways of thermoresponsive polymers (*J. Am. Chem. Soc.*, **2023**, *145*, 6554) to understand how temperature protocols and polymer composition can be orthogonally tuned to selectively precipitate with target ions bound. Nonequilibrium dynamics are intrinsic to many biological and synthetic materials, but due to the variety of confounding variables, they are challenging to understand and subsequently exploit. In collaboration with Allie Obermeyer (Columbia University), an expert in biomolecular condensates, we demonstrated that hysteresis is not solely determined by a polymer's cloud point, and that features of the temperature protocol (ramp rate and minimum/maximum temperatures) impact both the overall intensity of hysteresis and whether the hysteresis is maintained over multiple heat-cool cycles. Recent work has demonstrated that these principles can be applied to the design of copolymers that extract lanthanide ions from solution, with both hydrophobicity and sequence control tuning the binding affinity (*ChemRxiv*, **2024**, DOI: 10.26434/chemrxiv-2024-w6ckv). Further, characterization of solution-phase conformations before and after metal-binding supports a binding-then-assembly mechanism for the metal extraction process.

High-throughput platform development to reveal essential design principles. To engineer materials that can effectively address emerging challenges, connections between macromolecular composition, structure, and the desired properties must be established. With a vast array of macromolecule structures at our disposal, this task is daunting with iterative design. The incorporation of machine learning strategies is rapidly enhancing our ability to derive essential design principles, particularly within expansive design spaces (described in our perspective, *ACS Polym. Au*, **2023**, *3*, 406). However, to effectively harness the potential of these algorithms, it is imperative to develop high-throughput workflows that can generate the requisite datasets.

Our initial efforts in this area were coupled to the investigations of copolymer catalysts ((*J. Am. Chem. Soc.*, **2023**, *145*, 9686 and *J. Am. Chem. Soc.*, **2024**, *146*, 17404). Using multivariate linear regression, we

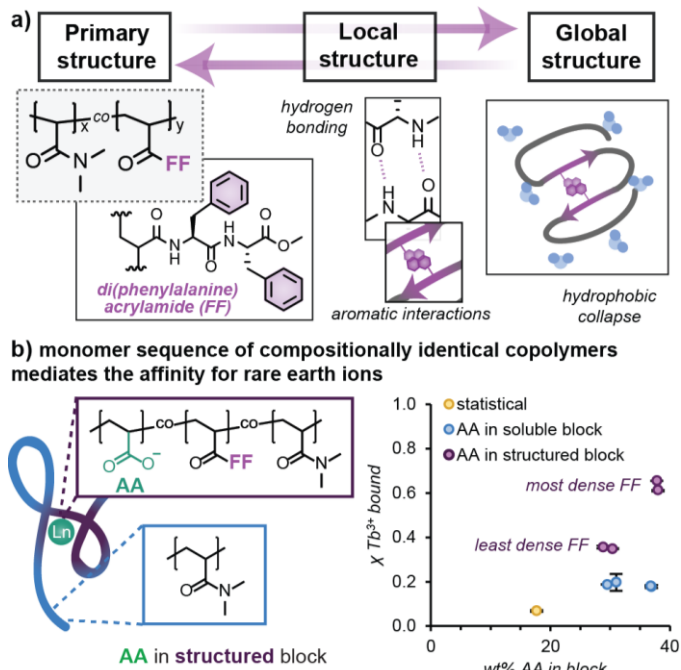


Figure 1. Structural control with di(phenylalanine) (FF). a) Overview of the global and local structural control provided. b) Representative schematic of sequence-controlled copolymer of FF, dimethylacrylamide, and acrylic acid (AA) and plot comparing fraction of Tb(III) bound by sequence-controlled copolymers.

uncovered complex correlations, such as the relationship between polymer composition and reaction temperature in an initial study. We have extended this analysis in recent work, harnessing diverse chemical featurization strategies (e.g., DFT calculations and chemical connectivity metrics) to capture differences within a selected substrate scope. While these efforts yielded promising results, the sequential synthesis of polymers remains a bottleneck in the workflow. Hence, multiple of our ongoing endeavors are dedicated to platforms capable of simultaneously screening thousands to hundreds of thousands of molecules for structural or functional attributes.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. Warren, J. L.; Dykeman-Birmingham, P. A.; **Knight, A. S.*** Controlling Amphiphilic Polymer Folding beyond the Primary Structure with Protein-Mimetic Di(Phenylalanine). *J. Am. Chem. Soc.* 2021. *143* (33), 13228–13234. DOI: [10.1021/jacs.1c05659](https://doi.org/10.1021/jacs.1c05659).
2. Chittari, S. S.; Obermeyer, A. C.; **Knight, A. S.*** Temperature sensitive copolymers as a model system for understanding the physical basis of nonequilibrium assembly. *J. Am. Chem. Soc.* 2023. *145* (11), 6554–6561. DOI: [10.1021/jacs.3c00883](https://doi.org/10.1021/jacs.3c00883)
3. Sanders, M. A.; Chittari, S. S.; Sherman, N.; Foley, J. R.; **Knight, A. S.*** Versatile triphenylphosphine-containing polymeric catalysts and elucidation of structure-function relationships. *J. Am. Chem. Soc.* **2023**. *145* (17), 9686–9692. DOI: [10.1021/jacs.3c01092](https://doi.org/10.1021/jacs.3c01092)
4. (*perspective – partially led by this grant*) Day, E. C.; Chittari, S. S.; Bogen, M. P.; **Knight, A. S.*** Navigating the Expansive Landscapes of Soft Materials: A User Guide for High-throughput Workflows. *ACS Polym. Au.* **2023**. *3* (6) 406–427. DOI: [10.1021/acspolymersau.3c00025](https://doi.org/10.1021/acspolymersau.3c00025).
 - i. Highlighted on the [front cover](#)
5. Dykeman-Birmingham, P.A.; Bogen, M.P., Chittari, S.S., [Grizzard, S.F.](#); **Knight, A.S.***; Tailoring Hierarchical Structure and Rare Earth Affinity of Compositionally Identical Polymers via Sequence Control. **2024**. *J. Am. Chem. Soc.* *146*. 8607–8617. DOI: [10.1021/jacs.4c00440](https://doi.org/10.1021/jacs.4c00440).
 - i. U.S. Provisional Patent Application No. 63/597,154 filed on November 08, 2023.
6. Sanders, M.A.; Chittari, S.S.; [Foley, J.R.](#); [Swofford, W.M.](#); [Elder, B.M.](#); **Knight, A.S.***; Leveraging Triphenylphosphine-Containing Polymers to Explore Design Principles for Protein-Mimetic Catalysts. **2024**. *J. Am. Chem. Soc.* *146*. 17404–17413. DOI: [10.1021/jacs.4c05040](https://doi.org/10.1021/jacs.4c05040).
7. Dykeman-Birmingham, P.A.†; [Stingaciu, L. R.](#) †; [Do, C.](#); **Knight, A. S.*** Dynamic Implications of Non-Covalent Interactions in Amphiphilic Single-Chain Polymer Nanoparticles. **2024**. *ACS Macro Lett.* *13*, 889–895. DOI: [10.1021/acsmacrolett.4c00269](https://doi.org/10.1021/acsmacrolett.4c00269).

Developing Metal-Oxo Cluster Chemistry for Critical Materials Separations

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Key Words: Assembly/Ordering; Inorganic Chelation; Kinetics; Theory/Simulation

DE-SC0023477: Transforming Critical Materials Separations through Metal-Oxo Cluster

Chemistry

PI: Karah Knope; co-PI: May Nyman, Pere Miro

Research Project Scope. create broadly applicable design rules for metal oxocluster-based separations that can be translated to separating any chemically similar metal cations. Towards this end, we are investigating and demonstrating the broad utility of oxocluster-based separations in two critical separation scenarios: 1) separation of any two or more rare earth elements, and 2) separation of precious metals Pd/Pt²⁺ and Au³⁺. In addition to these systems, we are also developing Zr/Hf cluster chemistry as a model system for cluster-based separations more broadly. Towards this end, we have sought to define aqueous conditions that lead to differentiating cluster topologies for different but similar metals, elucidate oxocluster properties that enhance separations, understand the role that counterions play in cluster assembly and separations, and invoke speciation changes to differentiate metals at the interface via ligand exchange or aggregation processes.

Recent Progress.

Towards our overarching goal, we have examined the aqueous and nonaqueous assembly and speciation of lanthanide, precious metal, and zirconium/hafnium clusters.

1. Rare Earth Element Cluster Chemistry. A survey of the Cambridge Structural Database suggests that lanthanide ions may exhibit differentiating cluster chemistry that arises from subtle differences in metal ion hydrolysis and condensation behavior. However, these data are notably biased towards the solid-state and thus our efforts have focused on examining the solution and solid-state speciation of homo- and heterometallic lanthanide complexes and oxoclusters in different ligand systems, including β -diketonates and nitrate. For the β -diketonates, we found that the early lanthanides precipitated as dinuclear, ligand bridged complexes while the later lanthanides yielded no solid-state products under identical synthetic conditions. We further probed these differences using solution-based techniques (i.e. nanospray

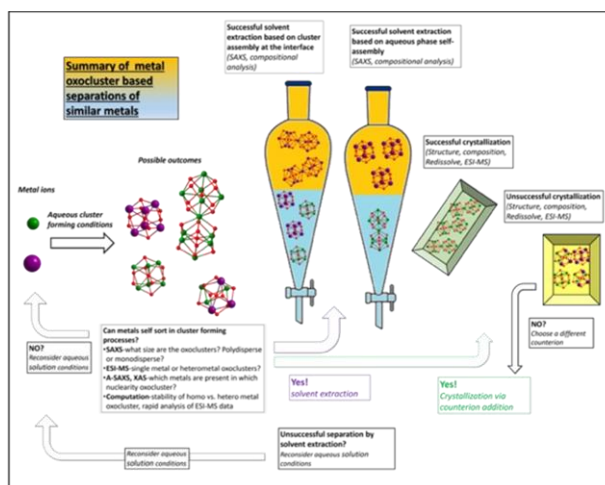


Figure 1. Overview of our approach to developing metal-oxo cluster based separations.

electrospray ionization mass spectrometry) and found that despite apparent differences in the solid-state, the solution speciation of the early and later lanthanides was similar. We attempted to leverage differences in solubility in a crystallization-based separation; however, ESI-MS data suggests that both homometal and heterometal complexes are present in solution and thus limit separations. In aqueous nitrate ligand systems, we focused on the assembly and isolation of homo- and heterometal hexameric clusters. We found that clusters prepared from mixed metal solutions showed a preference for the heavier lanthanide ion; however, these systems suffered from low yield. To address the yield, we prepared the hexamer via bulk electrolysis and examined solution speciation both pre- and post-electrolysis using small angle X-ray scattering. These data showed that the hexamer accounted for roughly 1% of the solution species. Taken together, these data provide important insight into the solution stability of different cluster topologies and considerations for developing lanthanide oxocluster based separations.

2. Hf/Zr Separations. We have examined Hf/Zr oxo cluster chemistry as a model for developing general guidelines for cluster-based separations. Using O-17 solid-state NMR, we confirmed that Hf/Zr form mixed metal compositions of $[\text{OM}_4(\text{OH})_6(\text{SCN})_{12}]^{4+}$, and that the Hf-analogue exhibits lower solubility that can be harnessed for separation. Carbon-13 NMR of $[\text{OM}_4(\text{OH})_6(\text{SCN})_{12}]^{4+}$ collected across a variety of solution conditions was used to determine ligand exchange rates, and thereby differentiate Zr-SCN and Hf-SCN ligation; however, fast ligand exchange rates complicated these studies. We thus turned to Raman spectroscopy and were able to measure bound versus unbound thiocyanate for dissolved $[\text{OZr}_4(\text{OH})_6(\text{SCN})_{12}]^{4+}$ and $[\text{OHf}_4(\text{OH})_6(\text{SCN})_{12}]^{4+}$. These showed that the Hf-analogue consistently exhibits more bound thiocyanate in equilibrium with unbound thiocyanate, in comparison to the Zr-analogue. This could indicate that 1) the poorer solubility of $[\text{OHf}_4(\text{OH})_6(\text{SCN})_{12}]^{4+}$ (as well as favored solvent extraction) is derived from the greater stability of the Hf-SCN bond and/or 2) a difference in the speciation equilibrium of Zr and Hf between $[\text{M}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8-}$ (speciation in the absence of structure-directing ligands) and $[\text{OM}_4(\text{OH})_6(\text{SCN})_{12}]^{4+}$ (speciation in the presence of structure-directing SCN^- ligands) exists which could explain selective precipitation due to the large differences in aqueous solubility between these two competing species. We are currently attempting to show this by computation and identify a descriptor that explains the underlying differentiating properties of Zr/Hf^{IV}, leading to the observed behavior. Although most of the studies on precipitation-based separation of $[\text{OM}_4(\text{OH})_6(\text{SCN})_{12}]^{4+}$ (M=Hf, Zr), as well as the characterization of mixed-metal clusters, was executed with tetramethylammonium counteranions (TMA), we are seeking a more industrially friendly cation. We have found that choline works very well for this purpose.

3. PGE Separations. Towards platinum group element separations, we have developed palladium cluster chemistry. We synthesized and characterized a phenylphosphonate-capped Pd₁₅-type cluster that is rare earth (REE) templated. Furthermore, we isolated a catalogue of nano star-shaped palladium clusters containing Yttrium and REEs (REE = La, Ce, Nd, Sm, Eu, Gd) $[\text{X}^{\text{III}}\text{O}_{10}\text{Pd}_{15}(\text{PhPO}_3)_{10}]^{7-}$, and for Yb crystallized (Yb^{III}O₈Pd₁₂(PhPO₃)₈). The variation in topology of the Yb templated cluster can be attributed to its smaller ionic radius compared to the other REEs. We used P-31 NMR, SAXS and ESI-MS to understand solution speciation behavior and its correlation with crystallization. We examined the counteranions' role in palladium based oxo cluster (known as Polyoxopalladate, POP) assembly, crystallization, and solvent extraction as an initial step. We further described the role of capping agents (R, phenylarsonic acid, PhAs and phenylphosphonic acid PhP) and host-guest chemistry of $[\text{XO}_8\text{Pd}_{12}\text{R}_8]$ (Guest X = Y, Gd, Cu, Zn) in the crystallization and extraction of different POP topologies. In the first step, Li, Na, K, Rb, and Cs counter-ions extracted Pd₁₃ POP (cube-shaped), with K being the most efficient. Meanwhile, phenylarsonate-capped POP resulted in the crystallization of cube-shaped POP

$[\text{XO}_8\text{Pd}_{12}(\text{C}_6\text{H}_5\text{AsO}_4)_8]^{5-}$, which extracts more effectively than the phenylphosphonate-capped crystallized star-shaped POP $[\text{X}^{\text{III}}\text{O}_{10}\text{Pd}_{15}(\text{C}_6\text{H}_5\text{PO}_3)_{10}]^{7-}$.

Fundamental Studies of Carbon Molecular Sieve Membranes for Energy Intensive Separations

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Key Words: Membranes; Non-thermal Separation Mechanisms; Transport Phenomenon; Gas Phase

DE-FG02-04ER1550: Fundamental Studies of Carbon Molecular Sieve Membranes for Energy Intensive Separations

PI: William J. Koros

Research Project Scope.

Reducing energy intensity and CO₂ footprints of important large-scale separations involving natural gas, olefin-paraffin streams, and hydrogen from various other gaseous components can be done using carbon molecular sieve (CMS) membranes. Such membranes have superior transport, mechanical and processability advantages over other molecular sieving materials for these large-scale processes. We focus on fundamental understanding using a hypothesis-driven path to significantly advance the state-of-the-art in CMS membranes, an approach that aligns with BES core values. We use fundamental pressure, composition, and temperature measurements of membrane transport properties to estimate thermodynamic factors (sorption enthalpies) and kinetic factors (activation energies and entropies for diffusion). These specialized studies are complemented by thermal analysis, microscopy, and spectroscopy. Our specialized techniques to study the CMS membranes, combined with classical materials science characterization methods, ensure the insights gained through program supported research will continue to advance the broader materials and core separations communities.

Recent Progress.

In our previous work, we expanded upon the fundamental understanding of structure-property relationships for polyimide derived CMS by establishing an integrated self-consistent framework relating CMS morphology to direct measurements of gas sorption and diffusion. During pyrolysis, entangled polymer chains undergo backbone scission and aromatization, forming short, rigid carbon strands with different degrees of subtle kinks. These strands are driven to organize into well-packed plates analogous to liquid crystal systems, and they further assemble into microporous cellular structures. Due to kinetic limitations, some of the aromatic strands are unable to organize effectively, leaving an additional continuous network of chaotically arranged single strands. Each of these two resulting environments displays unique sorption and diffusion characteristics that contribute to overall CMS performance due to local equilibrium between the domains. The cellular

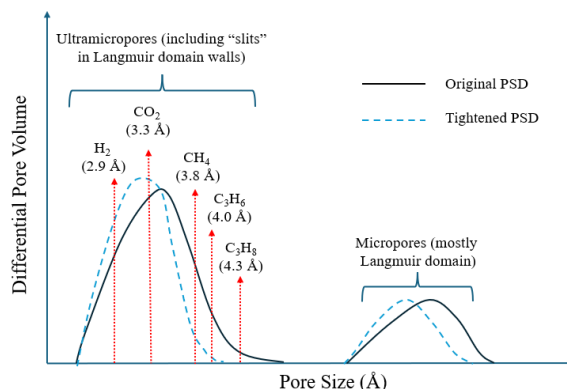


Figure 1. Qualitative Pore Size Distributions (PSD) and impact on different sized gases. The “tightened” PSD can be achieved with straighter aromatic strands and higher pyrolysis temperatures.

structures, referred to as the “Langmuir” domain, enclose a significant quantity of micropore volume, giving rise to a horizontally asymptotic contribution in CMS sorption isotherms for which the domain is named. Narrow ultramicropores within the walls of Langmuir plates can effectively discriminate between gas molecules based on size and shape, resulting in elevated diffusion selectivity. The “continuous” domain of randomly dispersed strands comprises predominantly larger ultramicropores and obeys Henry’s law for gas sorption. Wider spacing between aromatic strands in the Henry’s Law environment allows for rapid gas diffusion, increasing the intrinsic productivity of CMS membranes. Our current research has its foundation in this mathematically coherent and physically meaningful framework and focuses on modifying aromatic strand structure to selectively tune gas transport and sorption properties within the respective environments of CMS membranes.

The effects of structural modifications of aromatic strands can best be visualized through consideration of hypothesized pore size distributions, with special emphasis on ultramicropore dimensions as shown in Figure 1. Subtle differences in the kinetic diameters and shapes of relevant gas pairs can be leveraged to fabricate CMS membranes with outstanding permselectivities. Each of the critical gas separation processes mentioned previously benefits from a unique range of ultramicropore sizes. For example, separating small, pseudo-cylindrical CO₂ molecules (kinetic diameter 3.3 Å) from bulkier methane molecules (kinetic diameter 3.8 Å) is best achieved with a narrow distribution of small ultramicropores. Our recent direct gas sorption measurements for CMS derived from the commercial polyimide Matrimid® show that the combined effects of short, rigid aromatic strands and high final pyrolysis temperatures (up to 900 °C) not only bolster diffusion selectivity but also promote *thermodynamic exclusion* of methane from micropores in Langmuir domains (1). The resulting membranes have unmatched permselectivity paired with high CO₂ permeability. We hypothesize that this highly desirable combination of CO₂/CH₄ selectivity and CO₂ permeability results from the unique nature of aromatic strands formed from Matrimid® polyimide. The dianhydride in Matrimid®, 3,3’-4,4’-benzophenone tetracarboxylic dianhydride (BTDA), contains a weak benzophenone link that is more likely to break due to the mechanical stress that occurs during pyrolysis (compared to other common dianhydride links such as biphenyl and hexafluoroisopropylidene groups). This is envisioned to lead to shorter aromatic strands. The diamine, 5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane (DAPI), consists of two isomeric units, one of which is relatively straight while the other contains an abrupt kink. Together, the structures of these monomers may lead to a mixture of straight and crooked aromatic strands which enrich the Langmuir and continuous domains, respectively. Tighter ultramicropores between straight strands in the Langmuir walls augment selectivity, while impeded packing of crooked strands in the continuous domain grants higher permeability. To gain even more precise control over ultramicropore size distributions and thus gas separation properties, we have undertaken the challenging process of separating the DAPI isomers in order to synthesize BTDA-DAPI-derived CMS with modulated ratios of straight to crooked DAPI units. We have recently succeeded in separating the two isomers and confirmed the result with differential scanning calorimetry and plan to collect NMR spectra as well. Incorporating more of the straight isomer is hypothesized to lead to narrower pore size distributions, which may be advantageous for natural gas and hydrogen separations. Larger gas pairs, such as olefin-paraffin mixtures, will benefit from higher productivity achieved with more crooked DAPI segments. By connecting precursor structure, CMS morphology, and gas transport phenomenon, our work has continued to advance capabilities for developing next-generation CMS membranes.

Future Plans.

The specific example of BTDA-DAPI as a CMS precursor is one of several approaches we plan to pursue. Analogous tuning of the dual-mode structures of polyimide-derived CMS membranes can be accomplished for a wide variety of polymeric precursors, including those containing free-volume-generating trifluoromethyl groups and cross-linkable moieties. In addition to pursuing further understanding of the fundamental relationships between aromatic strand structure and dual-mode morphology, we will continue to make advances in the processability of the materials studied here, especially regarding fabrication of thin-skinned asymmetric CMS hollow-fiber membranes (2,3). By combining fundamental knowledge with improvements in membrane manufacturing processes, we hope to maximize the positive impacts of CMS membranes on energy and carbon efficient gas separations worldwide.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. Vessel TC, Liu Z, Koros WJ. Directly measured pyrolysis temperature dependence of sorption selectivity for carbon dioxide/methane in Matrimid® polyimide-derived carbon molecular sieve membranes. *Materials Chemistry and Physics*. 2024. 314, 128847.
2. Cao Y, Liu Z, Koros WJ. Above-Tg Annealing Benefits in Nanoparticle-Stabilized Carbon Molecular Sieve Membrane Pyrolysis for Improved Gas Separation. *Angewandte Chemie - International Edition*. 2024. 63(8), e202317864.
3. Liu Z, Cao Y, Koros WJ. Polyimide-derived carbon molecule sieve membranes for gas separations. *Nature Chemical Engineering*. 2024. 1(2), 119–123.
4. Cao Y, Liu Z, Qiu W, Koros WJ. Appealing sheath-core spun high-performance composite carbon molecular sieve membranes. *Angew Chem Int Ed*. 2023. 62(27), e202303915.
5. Liu Z, Qiu W, Quan W, Koros WJ. Advanced carbon molecular sieve membranes derived from molecularly engineered cross-linkable copolyimide for gas separations. *Nat Mater*. 2023. 22(1):109–116.
6. Liu Z, Qiu W, Koros WJ. New Insights into Physical Aging-Induced Structure Evolution in Carbon Molecular Sieve Membranes. *Angew Chem Int Ed*. 2022. 61(45), e202210831.
7. Cao Y, Zhang K, Zhang C, Koros WJ. Carbon molecular sieve hollow fiber membranes derived from dip-coated precursor hollow fibers comprising nanoparticles. *Journal of Membrane Science*. 2022. 649, 120279.
8. Arab P, Liu Z, Nasser M, Qiu W, Martinez M, Flick D, et al. Subtle penetrant size effects on separation of carbon molecular sieve membranes derived from 6FDA:BPDA-DAM polyimide. *Carbon*. 2021. 184, 214–222.
9. Qiu W, Leisen JE, Liu Z, Quan W, Koros WJ. Key Features of Polyimide-Derived Carbon Molecular Sieves. *Angew Chem Int Ed*. 2021. 60(41), 22322–22331.
10. Qiu W, Xu L, Liu Z, Liu Y, Arab P, Brayden M, et al. Surprising olefin/paraffin separation performance recovery of highly aged carbon molecular sieve hollow fiber membranes by a super-hyperaging treatment. *Journal of Membrane Science*. 2021. 620, 118701.

Grant cited but not intellectually led by this award:

1. Irani M, León N, Liu Z, Koros WJ. Overlooked glassy polymer attributes illustrated by asymmetric polyimide hollow fibers. *Journal of Membrane Science Letters*. 2022. 2(1), n. pag.

2. León NE, Liu Z, Irani M, Koros WJ. How to Get the Best Gas Separation Membranes from State-of-the-Art Glassy Polymers. *Macromolecules*. 2022. 55(5), 1457–1473.
3. Liu Z, Qiu W, Quan W, Liu Y, Koros WJ. Fine-tuned thermally cross-linkable 6FDA-based polyimide membranes for aggressive natural gas separation. *Journal of Membrane Science*. 2021. 635, 119474.
4. Liu Y, Liu Z, Kraftschik BE, Babu VP, Bhuwania N, Chinn D, et al. Natural gas sweetening using TEGMC polyimide hollow fiber membranes. *Journal of Membrane Science*. 2021. 632, 119361.
5. Liu Y, Chen Z, Qiu W, Liu G, Eddaoudi M, Koros WJ. Penetrant competition and plasticization in membranes: How negatives can be positives in natural gas sweetening. *Journal of Membrane Science*. 2021. 627, 119201.

Bridging the Length Scales in Electrochemical Ionic Separations using Experiments, Molecular Simulations, and Machine Learning

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Key Words: Machine Learning/AI; Membranes; Theory/Simulation; Other (Electrochemical Separations)

DE-SC0022304: Bridging the Length Scales in Ionic Separations via Data-Driven Machine Learning

PI: Revati Kumar; co-PI: Christopher G. Arges and José A. Romagnoli

Research Project Scope.

Electrochemical separations are poised to play an important role in securing critical minerals supply chains, environmental remediation and nutrient recovery, organic acid collection from processed biomass, and other applications involving carbon management, hydrogen, and water purification. Because electrochemical separations are electrified, they can use renewable energy sources to drive separations. Our team has pursued a multi-faceted approach that combines advanced metrology with molecular simulations and machine learning to advance the science of electrochemical separations involving ion-exchange membranes.

Recent Progress.

In one research thrust, we have used molecular simulations and machine learning along with experimental data to understand ion-partitioning behavior of composite and non-composite ion-exchange membrane materials. The selective removal of one ionic species over another in polyelectrolyte-based ion-exchange membranes is related to the product of the partitioning factor, a thermodynamic property, and the ionic mobility ratio, a transport coefficient. The partitioning factor relates to the activity coefficient of the different ionic species in the interfaced solution and membrane. Activity coefficients are governed by the Gibbs excess free energy; however, activity coefficient models are based on complex semi-empirical equations that capture long-range and short-range electrostatic and van der Waals forces and is strongly impacted by the solvent/dielectric behavior of the environment. To overcome to time-consuming nature in developing semi-empirical models and determining the viral coefficients for different ions and ion-exchange membranes chemistries, our group has developed a machine learning based alternative to accurately predicting the ion activity coefficient. Our framework uses a relatively small experimental activity coefficient dataset along with polymer structure information and molecular level attributes describing the solvation of ions and polymers from molecular dynamics

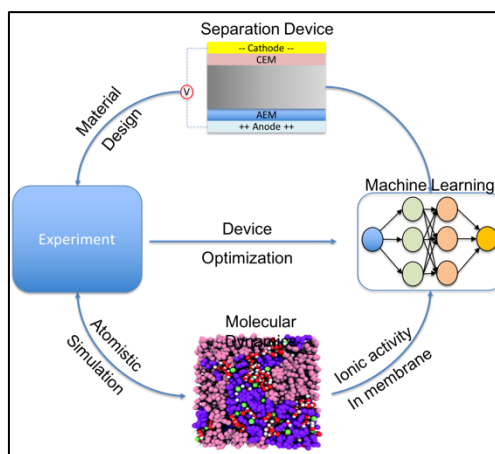


Figure 1. A schematic of our synergistic approach that combines experiment, molecular simulations, and machine learning to electrochemical separations.

data to predict the ion activity coefficient in polymeric ion-exchange membranes. We will present the main considerations in the development of the machine model, the validation and the intrinsic properties of the polymer electrolytes that were found to affect activity coefficients.

The second research thrust aims to advance selective ion separations using composite ion-exchange membranes and new separation mechanism strategies in electrochemical platforms. The experimental effort in this area has been complemented with molecular simulations to understand how metal oxide particle additives in anion exchange membranes promote selective phosphate uptake from model wastewater solutions. Furthermore, the combined strategy of experiments and molecular simulations have revealed the molecular origins behind ‘pH inversion’ in forward bias bipolar membrane capacitive deionization units. This unique in-situ pH adjustment strategy was exploited for selective lithium capture from model geothermal brines while simultaneously producing lithium hydroxide upon lithium release. Lithium hydroxide is the precursor of choice in battery electrode manufacturing.

Finally, we will present a machine learning framework that leverages ion-exchange material properties to the performance attributes of electrochemical separations platforms. Overall, we have devised a comprehensive machine learning scheme that takes molecular simulations information to predict thermodynamic properties of ion-exchange membranes while also relating transport and thermodynamic properties of membranes to electrochemical separations platform attributes.

Future Plans.

The final tasks for this project involve modifying the machine learning framework for selective ion separations at the platform level with in-situ pH adjustment using bipolar membranes. This work also includes a molecular modeling and machine learning effort to relate the chemistry attributes of bipolar membranes to the activation barriers for water dissociation and water association.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. B. Yang, X. Zhang, B. Shrimant, T. Kulkarni, R. Kumar, C.G. Arges, Selective phosphate removal with manganese oxide composite anion exchange membranes in membrane capacitive deionization, *Chemical Engineering Journal*, **2024**, 495, 153468.
2. T. Olayiwola, R. Kumar, and J. Romagnoli, Empowering Capacitive Devices: Harnessing Transfer Learning for Enhanced Data-Driven Optimization, *Industrial and Engineering Chemistry Research*, **2024**, 63, 1197.
3. T. Kulkarni, B. Yang, X. Zhang, R. Kumar, C.G. Arges, ACS Spotlight: Bipolar membranes for electrochemical energy conversion, chemical manufacturing, and separations, *ACS Applied Energy Materials*, **2024**, ASAP, <https://doi.org/10.1021/acsaem.3c03260>
4. C.G. Arges, The Chalkboard: An introduction to electrochemical separations, *Electrochemical Society Interface*, **2024**, 33, 42.
5. X. Zhang, C.G. Arges, R. Kumar, Computational investigations of the water structure at α -Al₂O₃(0001)-water interfaces, *Journal of Physical Chemistry C*, **2023**, 127, 15600.
6. H.K. Gallage, Dona, T. Olayiwola, L.A. Briceno-Mena, C.G. Arges, R. Kumar, and J.A. Romagnoli, Determining ion activity coefficients in ion-exchange membranes with machine learning and molecular dynamics simulations, *Industrial & Engineering Chemistry Research*, **2023**, 62, 9553.

7. T. Kulkarni, A. Muhammad I Al Dhamen, and C.G. Arges, Bipolar membrane capacitive deionization for pH-assisted ionic separations, *ACS ES&T Engineering*, **2023**, 3, 2171.
8. M.V. Ramos-Garcés, D.I. Senadheera, K. Arunagiri, P.P. Angelopoulou, G. Sakellariou, K. Li, B.D. Vogt, R. Kumar, and C.G. Arges, Ion transport on self-assembled block copolymer electrolytes with different side chain chemistries, *Materials Advances*, **2023**, 4, 965.
9. M.L. Jordan, G. Kokoszka, H.K. Gollage Dona, D.I. Senadheera, R. Kumar, Y.J. Lin, and C.G. Arges, Integrated ion-exchange membrane resin wafer assemblies for aromatic organic acid separations using electrodeionization, *ACS Sustainable Chemistry & Engineering*, **2023**, 11, 945.
10. M.L. Jordan, T. Kulkarni, D. Senadheera, R. Kumar, Y.J. Lin, and C.G. Arges, Imidazolium-type anion exchange membranes for improved organic acid transport and permselectivity in electrodialysis, *Journal of the Electrochemical Society*, **2022**, 169, 043511.
11. T. Kulkarni, H. Zhang, A.M. Al Dhamen, F. Shi, and C.G. Arges, Selective recovery of Li from brine solutions and conversion to LiOH in a single electrochemical cell, U.S. Patent Application # 63/600,167, **2023**

Grant cited but not intellectually led by this award:

1. E.J. Park, C.G. Arges^a, H. Xu, and Y.S. Kim, Membrane Strategies for Water Electrolysis, *ACS Energy Letters*, **2022**, 7, 3447–3457.
2. M. Nnadili, A. N. Okafor, T. Olayiwola, D. Akinpelu, R. Kumar, and J. Romagnoli, Surface Specific AI Driven Molecular Design: Integrating Generative Models, Predictive Modeling, and Reinforced Learning for Tailored Surfactant Synthesis, *Industrial and Engineering Chemistry Research*, **2024**, 63, 6313.

Characterization of Non-ionic Deep Eutectic Solvents as Media for Separation

Daniel G. Kuroda, Laura Sepulveda-Montaño, Revati Kumar

¹Louisiana State University

Key Words: Assembly/Ordering; Dynamics; Solvation; Theory/Simulation; Transport Phenomena

DE-SC0025202: Microscopic Insights into the Solvation Properties of Complex Deep Eutectic Solvents: A Deconstructive Approach for Improved Understanding in Separation Sciences

PI: Daniel G. Kuroda; co-PI: Revati Kumar

Research Project Scope.

Deep eutectic solvents have emerged as a new class of designer solvents with interesting physicochemical properties for separations, which arise due to their microscopic structure. Deep eutectic solvents are formed by mixing and melting two solids into a liquid at room temperature. By selecting the components that make up the deep eutectic solvent, it is possible to create one with built-in structures that look like either oil or water, and thus can dissolve both molecules with strong and those with weak water affinity. This work links the microscopic intricacies of the deep eutectic solvent to its separation properties through a combination of theory and experiment.

Recent Progress.

The non-ionic deep eutectic solvent formed by lauric acid (LA) and N-methylacetamide (NMA) has a complex liquid structure with LA nanoscopic heterogeneities, which are directly observed via X-ray scattering (SAXS). The discovery of such heterogeneous domains has led to the possibility of employing the NMA-LA DESs as polarity-based separation media for complex mixtures. However, previous studies have indicated that the ability of the non-polar LA to separate non-polar solutes is, surprisingly, limited. Here, a characterization of the DES non-polar domains using IR spectroscopy and molecular dynamics simulations is presented. The simulation results show good agreement with the experimental characterization of the system. In particular, the MD simulation correctly describes not only

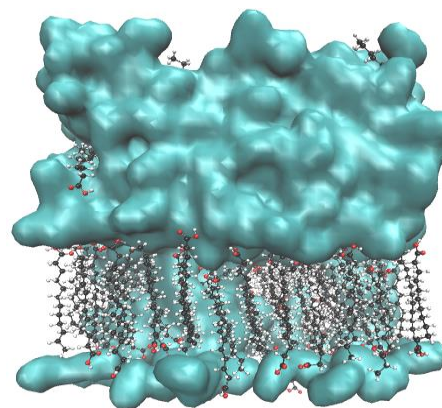


Figure. Structure of the heterogeneous domain derived from the MD simulations.

intermolecular interactions, such as hydrogen bonds, but also the X-ray spectrum, where a pre-peak in real space of 20.2 Å is observed. The MD simulations also demonstrate that the X-ray pre-peak is a consequence of the formation of highly organized LA aggregates, as previously proposed. These LA aggregates are tightly packed where the LA interacts in an interdigitated manner and does not allow the insertion of solutes/probes into them. To investigate the dynamics of the aggregated LA domain, a vibrational probe is used. Our results from 2DIR spectroscopic experiments show that the probe observes the heterogeneity of the system through its long-time dynamics, which correlates with the trend of the pre-peak intensities in the SAXS experiments. These computational and spectroscopic findings answer long-standing questions on the structure of the system and the dynamics experienced by different non-polar probes, whose spectroscopic

results could not be interpreted in terms of a molecular framework of ideal solutions. Finally, this newfound understanding of the microscopic structures of the heterogeneous domains and how to predict their behavior brings the possibility of tailoring these systems to better separations.

Future Plans.

Next steps will focus on understanding how to tailor the molecular heterogeneity in the DES.

Integrated Direct Air Capture and H₂-Free CO₂ Valorization

Hongfei Lin¹, Sheng Dai², Zhenzhen Yang², David Prendergast³, Ji Su³, De-en Jiang⁴, Jian Zhi Hu⁵, Farid El Gabaly Marquez⁶

¹Washington State University, ²Oak Ridge National Laboratory, ³Lawrence Berkeley National Laboratory, ⁴Vanderbilt University, ⁵Pacific Northwest National Laboratory, ⁶Sandia National Laboratory

Key Words: Confinement; Dilute Species; Kinetics; Transport Phenomena

DE-SC0022273: Integrated Direct Air Capture and H₂-Free CO₂ Valorization

PI: Hongfei Lin; co-PI: Sheng Dai, Zhenzhen Yang, David Prendergast, Ji Su, De-en Jiang, Jian Zhi Hu, Farid El Gabaly Marquez

Research Project Scope.

This project aims to overcome key scientific and technical barriers in the direct air capture (DAC) of CO₂ using supported ionic liquid adsorbents (SILAs) and convert captured CO₂ into long-lasting and valuable products, such as polyketones, without external hydrogen. The research focuses on designing supported ionic liquid sorbents with precise thermodynamic control and developing highly dispersed single-site/binuclear-site catalysts (SSCs) for CO₂ conversion using ethane as a hydrogen source. This work contributes to the Separation Science Program by advancing CO₂ capture technologies and carbon valorization processes to address climate change mitigation and circular carbon management.

Recent Progress.

We have demonstrated that composite sorbents with a thin film of superbase-derived ionic liquid (SIL) on porous supports, such as metal-organic frameworks (MOFs), significantly improved dilute CO₂ adsorption capacity and stability. By leveraging the confinement effect of the porous MOF substrate, we enhanced the

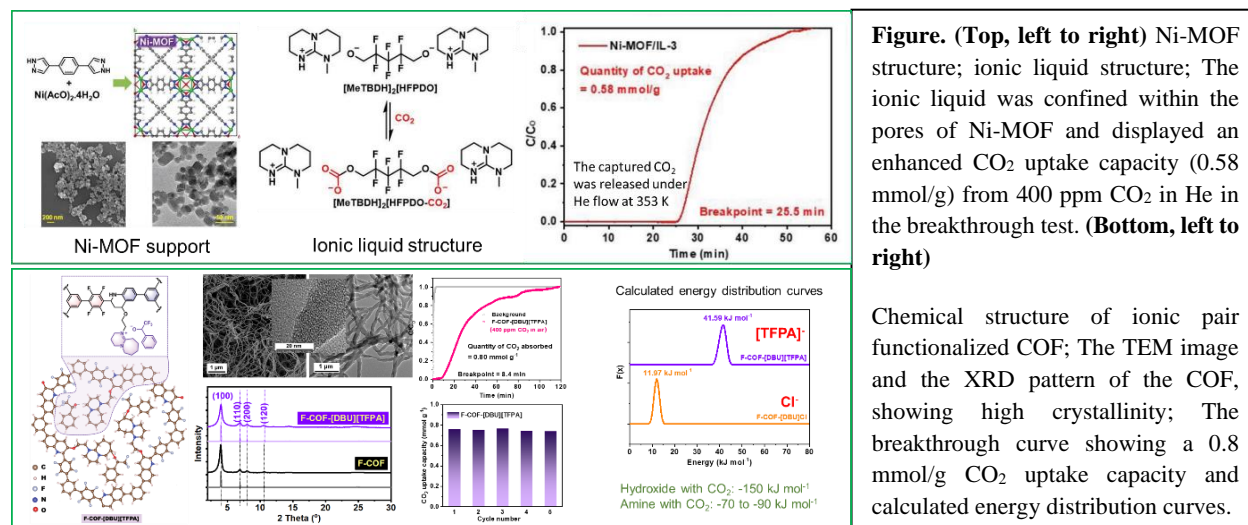


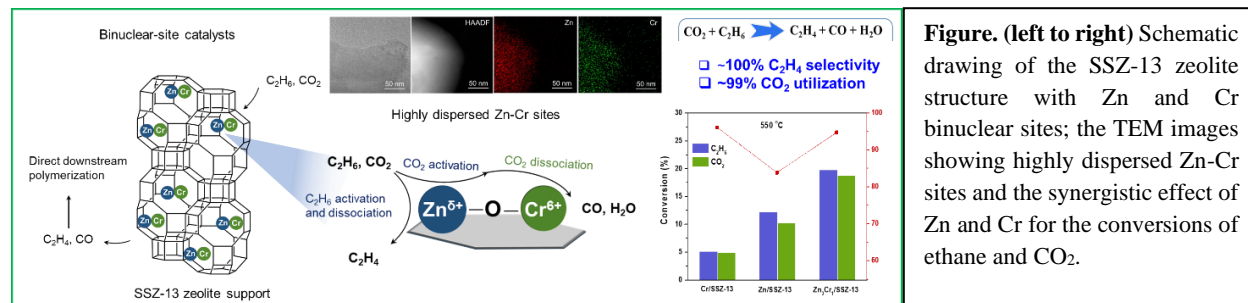
Figure. (Top, left to right) Ni-MOF structure; ionic liquid structure; The ionic liquid was confined within the pores of Ni-MOF and displayed an enhanced CO₂ uptake capacity (0.58 mmol/g) from 400 ppm CO₂ in He in the breakthrough test. **(Bottom, left to right)**

Chemical structure of ionic pair functionalized COF; The TEM image and the XRD pattern of the COF, showing high crystallinity; The breakthrough curve showing a 0.8 mmol/g CO₂ uptake capacity and calculated energy distribution curves.

interaction strength between the active anionic sites and CO₂. Additionally, we successfully constructed the first highly crystalline ionic pair-functionalized covalent organic frameworks (COFs) with strong CO₂

capture from air. The SIL active sites, combined with fluorinated alcoholate anions, enabled efficient capture and low-temperature release.

On the catalytic front, we developed a novel "dry deposition" strategy to fabricate an atomically synergistic binuclear-site catalyst with Zn acidic and Cr redox sites ($\text{Zn}^{\delta+}\text{-O-Cr}^{6+}$ on SSZ-13). This catalyst achieved ~100% ethylene selectivity and near-complete CO_2 utilization during ethane-to-ethylene conversion, representing a significant advance in CO_2 valorization.



Future Plans.

Future work will focus on developing kinetic and thermodynamic models to simulate breakthrough experiments of supported ionic liquids for CO_2 capture and performing classical molecular dynamics simulations of IL sorbents confined in porous supports. Quantum mechanical calculations will be used to study reactions between CO_2 and IL sorbents, simulating the influence of porous supports on CO_2 chemisorption energetics. We will design next-generation DAC CO_2 adsorbents by optimizing anions and leveraging substrate geometry effects to identify the ideal reaction enthalpy, balancing capacity and energy consumption. Additionally, we plan to investigate the effect of moisture and analyze the structural assembly of these next-generation sorbents to create hydrophobic surfaces with abundant CO_2 -binding sites. On the catalytic side, we will design new catalysts for the carbonylation of CO and ethylene into polyketones, focusing on controlling polyketone quality. In parallel, we will explore high-entropy alloy (HEA) catalysts for alkane and CO_2 co-conversion, studying how elemental composition and atomic structure affect catalytic performance and uncovering fundamental reaction mechanisms.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. Zhun Dong, Wenda Hu, Hongjun Liu, Zhenzhen Yang, Debabrata Moitra, De-en Jiang, Sheng Dai, Jian Zhi Hu, Di Wu, and Hongfei Lin. "Solvent-treated zirconium-based nanoporous UiO-66 metal-organic frameworks for enhanced CO_2 capture." *ACS Applied Nano Materials*. 2023, 6 (13), 12159-67.
2. Liqi Qiu, Li Peng, Debabrata Moitra, Hongjun Liu, Yuqing Fu, Zhun Dong, Wenda Hu, Ming Lei, De-en Jiang, Hongfei Lin, Jianzhi Hu, Kathryn A McGarry, Ilja Popovs, Meijia Li, Alexander S Ivanov, Zhenzhen Yang, Sheng Dai. "Harnessing the Hybridization of a Metal-Organic Framework and Superbase-Derived Ionic Liquid for High-Performance Direct Air Capture of CO_2 ." *Small*. 2023, 19 (41), 2302708.
3. Debabrata Moitra, Narges Mokhtari-Nori, Kevin M. Siniard, Liqi Qiu, Juntian Fan, Zhun Dong, Wenda Hu, Hongjun Liu, De-en Jiang, Hongfei Lin, Jianzhi Hu, Meijia Li, Zhenzhen Yang, Sheng Dai. "High-

- Performance CO₂ Capture from Air by Harnessing the Power of CaO- and Superbase-Ionic-Liquid-Engineered Sorbents." *ChemSusChem*. 2023, 16 (20), e202300808.
4. Liqi Qiu, Ming Lei, Caiqi Wang, Jianzhi Hu, Lilin He, Alexander S. Ivanov, De-en Jiang, Hongfei Lin, Ilja Popovs, Yanpei Song, Juntian Fan, Meijia Li, Shannon M. Mahurin, Zhenzhen Yang, Sheng Dai. "Ionic Pairs-Engineered Fluorinated Covalent Organic Frameworks Toward Direct Air Capture of CO₂." *Small*. 2024, 20 (36), 2401798.
 5. Hongjun Liu, Hongfei Lin, Sheng Dai, De-en Jiang. "Minimal Kinetic Model of Direct Air Capture of CO₂ by Supported Amine Sorbents in Dry and Humid Conditions." *Industrial & Engineering Chemistry Research*. 2024, 63, 5871-5879.
 6. Yang, J.; Wang, L.; Wan, J.; El Gabaly, F.; Fernandes Cauduro, A. L.; Mills, B. E.; Chen, J.-L.; Hsu, L.-C.; Lee, D.; Zhao, X.; Zheng, H.; Salmeron, M.; Wang, C.; Dong, Z.; Lin, H.; Somorjai, G. A.; Rosner, F.; Breunig, H.; Prendergast, D.; Jiang, D.-e.; Singh, S.; Su, J. "Atomically synergistic Zn-Cr catalyst for iso-stoichiometric co-conversion of ethane and CO₂ to ethylene and CO." *Nature Communications*. 2024, 15, 911.

Lithium-Ion Transport in Micropores Filled with Liquid Electrolyte

Jerry Y.S. Lin, Christopher Muhich, Lance Lai, Vedant Bhat, Hao Yu

Arizona State University

Key Words: Field-Driven Separations; Membranes; Theory/Simulation; Transport Phenomena

DE-SC0024194 Understanding Lithium-Ion Transport in Micropores Filled with Liquid Electrolyte

PI: Jerry Lin; co-PI: Christopher Muhich

Research Project Scope.

Li-ion transport in liquid filled micropores plays a key role in membrane separation processes for lithium extraction or recovery, and many energy storage devices including lithium-ion and lithium-metal batteries for energy storage. There exists a gap in knowledge about the mechanism of lithium-ion transport through the micropores of porous materials filled with liquid solvent or electrolyte. The goal of our research is to understand if and how Li ions diffuse through the micropores and the role of the pore size, solvent, and counter ion on the Li transport mechanism and rate in zeolite micropores. Both experimental and computational work will be conducted to prove the hypothesis that Li diffuses fastest through zeolite pores via structural transport, and thus that configurations which minimize solvation shell formation in the pores, but are still energetically favorable to have lithium intercalate, will have the fastest diffusion.

Recent Progress.

Experimentally, we have concentrated on the synthesis and characterization of intermediate pore MFI zeolite crystals and membranes. Both randomly oriented and b-oriented MFI zeolite membranes were successfully synthesized on macroporous alumina and stainless-steel supports. Additionally, small pore DDR zeolites were synthesized. These zeolite membranes and crystals will be used to investigate the accessibility of solvents within the zeolite structures. We have also established the setups to study both the solvent accessibility in zeolite pores and Li-ion conductivity in zeolite membranes. Preliminary results indicate that our new setup effectively measures the uptake and rate of solvent transport into zeolite crystals.

Initial computational efforts have focused on understanding the accessibility of solvents and Li salts within zeolite pores. Specifically, we have been examining the interaction of LiCl and water with MFI zeolites. Atomistic energies and forces were calculated from atomic geometries using a combination of density functional theory (DFT), force fields (FF), and machine learning-enhanced force fields (ML-FF). Grand Canonical Monte Carlo (GCMC) simulations were employed to determine solvent concentrations in zeolite pores as a function of solvent chemical potential, which can be correlated with salt concentration dependence in solution. Due to the complexities of applying the GCMC method to charged species while maintaining charge neutrality, the calculations were performed with a constant number of salt molecules, focusing the GCMC simulations on water molecules.

Future Plans.

We will execute the experimental and computational work outlined for the first year of the project. This includes Task 1: Understanding the accessibility of solvent and li salt in zeolitic pores. Additionally, since both Ph.D. students joined the project earlier than expected, we anticipate accelerating progress and aim to complete a portion of Task 2: Determining the diffusion rate and mechanism of Li-ion transport through MFI in water and ethylene carbonate, within the coming year.

Single-Crystalline and Polycrystalline Covalent Organic Framework Membranes: Experimentally and Theoretically Connecting Formation Conditions to Mass Transfer and Selectivity Performance

Katie D. Li-Oakey,¹ William Dichtel,² Adri van Duin³

¹Department of Chemical and Biomedical Engineering University of Wyoming, ²Department of Chemistry Northwestern University, ³ Department of Mechanical Engineering, Chemical Engineering, Engineering Science and Mechanics, Chemistry, Materials Science and Engineering, Pennsylvania State University

Key Words: Assembly/Ordering; Confinement; Membranes; Transport Phenomena.

DE-SC0003177: Single-Crystalline and Polycrystalline Covalent Organic Framework Membranes: Experimentally and Theoretically Connecting Formation Conditions to Mass Transfer and Selectivity Performance

PI: Katie Li-Oakey; co-PIs: William Dichtel, Adri van Duin

Research Project Scope.

Despite intense academic interest in two-dimensional covalent organic frameworks (2D COFs) and their exciting potential to break the permeability-selectivity tradeoff, 2D COFs have not yet been successfully developed for any large-scale separation applications. As shown in Figure 1, ideal predicted separation performance, predicated by atomistic modeling, has not been demonstrated in commercial COF membranes, primarily due to the poor long-range order found in most experimental samples, which prevents the formation of functional, defect-free membranes. Until recently, few high-quality COFs had been reported, with even fewer based upon robust chemical linkages and mild, rapid synthesis conditions, each of which are necessary for their broad adoption in separation fields. To address these challenges and provide more accurate transport mechanism of COF membranes, we propose to use large single crystal COFs, recently synthesized under mild conditions for a short period of time by our team members, as membrane materials for mass transfer mechanism study and their potential for membrane manufacturing in large scale. This project involves two interacting activities that will advance the potential of 2D COFs as separation materials. The project's objectives are: **1)** To identify the key drivers, via atomistic modeling and direct experimental verification, that are responsible for single crystal, as opposed to polycrystalline COF formation during the self-assembly (nucleation ripening) process. Understanding the self-assembly step in synthesized COFs will accelerate new separation materials discovery and their deployment in large scale engineering applications. **2)** To add external forces into our atomistic model to simulate external pressures used in experimental filtration processes, instead of only molecular diffusion. **3)** To use critical mineral (CM) recovery as a case study, together with dyes of different sizes and charges, to quantify the adsorption of the chosen COF platforms, which can be utilized for expedited material discovery and process design for next generation, energy-efficient CM purification.

Recent Progress.

While the project is new, it is built upon past work in the PI and co-PIs' group. In this poster, we highlight the common challenges in COF membrane separation, especially the discrepancies between predicated COF performance and current modeling predications, including polycrystallinity of COFs,

defects in COF membranes and role of adsorption.

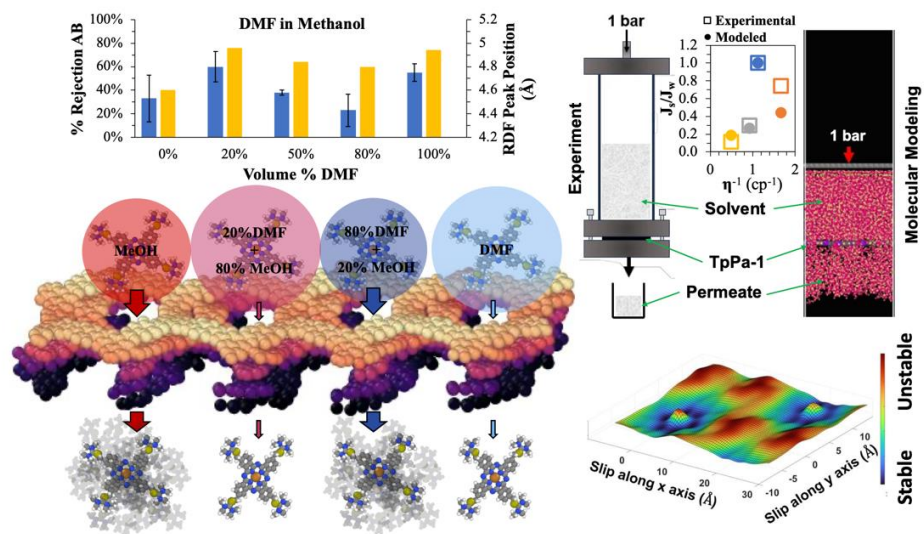


Figure 1. Mapping molecular interactions of covalent organic framework (COF) membrane from commercial TpPa-1 in mixed solvents via atomistic modeling and experimental study.

Probing the Coordination in Confinement for Electrochemical Separation among Rare Earth Elements

Chong Liu¹

¹University of Chicago

Key Words: Confinement; Field-Driven Separations; Interfaces; Solvation

DE-SC0022984: Probing the coordination in confinement for electrochemical separation among rare earth elements

PI: Chong Liu

Research Project Scope.

The goal of this early career project is to probe the fundamental limit of a new mechanism, electrochemical intercalation, for rare earth elements (REEs) separation from one another and to understand REE coordination in confinement restricted by crystalline host materials. We hypothesize that the rigidity of the lattice structure can amplify the energy penalty to unfavorable coordination configurations, promoting collective behaviors among the same elements for separation. To approach this goal, we will build model host systems, develop multimodal correlative characterization to resolve the REE coordination, establish a feedback loop to tune the coordination environments and evaluate the effect of different synthetic strategies on REE selectivity. We expect to pinpoint the material characteristics governing REE selectivity and generalize these characteristics into design rules for predictive RE separation.

Recent Progress.

The structural, coordination, and hydration change during electrochemical intercalation was correlated to understand their effects on the separation among lanthanides.

The electrochemical intercalation of individual lanthanide ions (Ln^{3+}) was measured. The electrochemical intercalation potential is proven to be an effective indicator for the preference of Ln^{3+} in the model hydrated MnO_2 host materials. The intercalation potential increases throughout the lanthanide series, and hydrated MnO_2

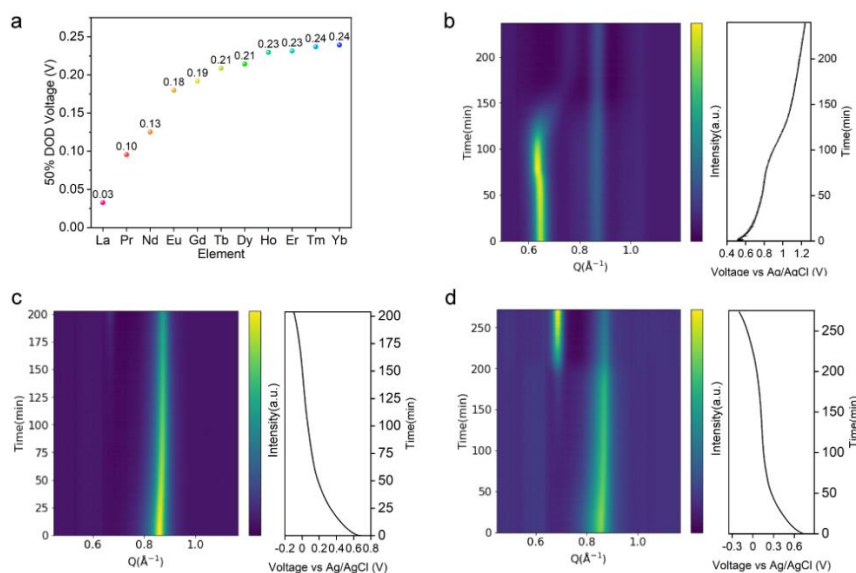


Figure 1. a, Electrochemical potentials at 50% depth of discharge (DOD) for each of the Ln^{3+} . Synchrotron XRD spectra of in situ (b) Mg deintercalation to empty structure showing the disappearance of the (001) peak; (c) Nd^{3+} intercalation from the empty structure; (d) Dy^{3+} intercalation from the empty structure.

favors heavier Ln^{3+} , which shows a higher intercalation potential (Figure 1a). Inductively coupled plasma mass spectrometry (ICP-MS) was used to measure the selectivity between neighboring pairs.

Structural Change – The structural change of the host material during deintercalation of Mg^{2+} and intercalation of La^{3+} , Nd^{3+} , and Dy^{3+} were characterized using in situ synchrotron X-ray diffraction (XRD). The starting $\text{Mg}_{0.16}\text{MnO}_2 \cdot n\text{H}_2\text{O}$ showed a dominating signature interlayer spacing of 9.7 Å with the presence of a weak peak with interlayer spacing of 7.2 Å. During deintercalation, the XRD at 9.7 Å first left shifted, indicating an expansion of interlayer spacing, and started to diminish halfway through deintercalation with a weak signal showing right shifting (Figure 1b). This indicates the crystallinity decrease along the [001] direction without pillar ions. The final empty state still showed a weak peak with 7.2 Å interlayer spacing. Starting from this empty host structure, La^{3+} , Nd^{3+} , and Dy^{3+} showed very different structural responses during intercalation. Dy^{3+} showed a strong crystalline peak approaching the end of the intercalation with the interlayer spacing of ~9.2 Å. In contrast, La^{3+} and Nd^{3+} did not show any recovery of the ordering of the host along [001] direction (Figure 1c, d). During intercalation, all La^{3+} , Nd^{3+} , and Dy^{3+} are inserted in between the MnO_2 layers in their hydrated ion forms. We hypothesize that the structural change difference is due to the difference in the hydration level of inserted ions. Both the water amount and the speciation of the ion (surface charge density) affect the structural ordering and, therefore, determine the position and intensity of the (001) peaks. These structural differences can be utilized for the separation among Ln^{3+} .

Coordination Change – X-ray absorption spectroscopy (XAS) was used to characterize the L3-edge of Dy to resolve its coordination environment during electrochemical intercalation at four intermediate states. The results show that as more Dy^{3+} are inserted in between the MnO_2 layers, the coordination numbers of Dy^{3+} decrease.

Hydration Change – X-ray photoelectron spectroscopy (XPS) was used to characterize the persistent water amount in the structure in vacuum. O1s was probed for samples with different inserted ions (Na^+ , Mg^{2+} , and La^{3+} - Nd^{3+} mixture). The results showed that the total persistent water amount in the material depends on the ion type. After electrochemical intercalation, the empty structure has an overall less persistent water amount than the starting $\text{Mg}_{0.16}\text{MnO}_2$. It indicates the possibility that when Mg^{2+} leaves the host structure, it carries some amount of its hydration water. However, this result cannot rule out the possibility of water entering the structure during Mg^{2+} deintercalation, and if so, such water was loosely bonded to the host framework and will evaporate in vacuum. Moreover, parallel samples with Dy^{3+} intercalation at different filling ratios were characterized. The persistent water amounts show a clear increase from the filling ratio of 50% to 100% of the theoretical capacity, which means a stronger water retention capability.

In parallel, we have developed scanning transmission electron microscopy (STEM) to characterize Ln^{3+} in confinement with spatial resolution approaching atomic level. This is important to reveal ion-to-ion distance, especially during competitions with more than one type of ion. We have also synthesized new types of host materials to investigate 3D confined structures for cation separation. Using the same characterization toolset, we have revealed the relationship between the inserted ion storage site and redox species.

Future Plans.

In our future work, we will design electrochemical methods to achieve active control and quantification of the metastable state and hydration level of the host materials for the separation among lanthanide ions.

Exploring the Potential of “Sorpvection” as a Separation Modality for the Recovery of Dilute High Value Species

Ryan P. Lively

School of Chemical and Biomolecular Engineering, Georgia Institute of Technology

Key Words: Dilute Species; Membranes; Non-Thermal Separation Mechanisms; Transport Phenomena

DE-SC0024573: Exploring the Potential of “Sorpvection” as a Separation Modality for the Recovery of Dilute High Value Species

PI: Ryan Lively

Research Project Scope.

Pressure-driven membrane processes typically enable simple and low energy separation processes; however, it is well known that these types of membrane units struggle to recover diluted compounds from a complex feed mixture in an energy-efficient way.¹ The root cause of this is the need to provide a driving force for the dilute compound to permeate through the membrane. As permeation is driven by chemical potential gradients across a membrane, the dilute compound typically must exist in a state of higher chemical potential in the feed relative to the permeate for permeation to occur. Supplying this driving force is often expensive: either very high feed pressures or deep permeate vacuums are required, or an energy-intensive phase change across the membrane (e.g., pervaporation) is needed. This fact is usually listed as a “showstopper” for the exploration or application of membranes in this area of separations science.

Recent Progress.

We have recently found an unusual transport modality that may address this long-standing showstopper. We have observed that rigid carbon membrane materials preferentially permeate diluted organics from an aqueous stream, resulting in significant concentration factors (3-4x) of the organic in the permeate relative to the feed.³ Surprisingly, detailed thermodynamic calculations on the chemical potential of the organic contaminant revealed that the organic species has a higher chemical potential on the permeate side of the membrane than on the feed side of the membrane (Fig. 1). This unusual observation challenges conventional membrane transport theory that posits that all permeating species move from high chemical potential states to lower chemical potential states. Recently, we have also observed this phenomenon in bio-oil separations using polymeric membranes. In this case,

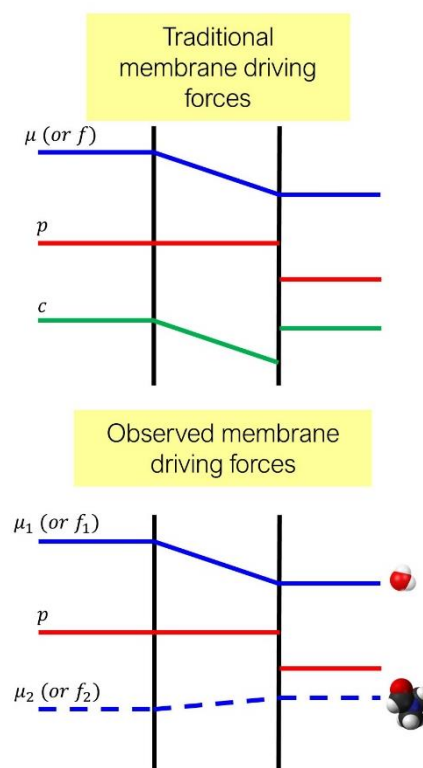


Figure 1: Diagrams depicting driving forces for membrane permeation. (top) Classical depiction of membrane driving forces, highlighting permeation of a molecule from a state of high chemical potential to a state of low chemical potential (blue line). (bottom) Observed driving forces in sorpvection experiments. Here, water (solid blue) permeates from a state of high chemical potential to a state of low chemical potential while DMF (dashed blue) permeates from a state of low chemical potential to a state of high chemical potential.

we permeate through a glassy polytriazole membrane a model bio-oil feed containing water and methanol as the concentrated compounds with guaiacol (a phenol) and glucose as dilute compounds. As with the surprising DMF concentration in the carbon membranes, we observe that the diluted guaiacol is concentrated in the membrane permeate, while the glucose is almost quantitatively rejected, thus achieving an otherwise difficult chemical separation. Detailed thermodynamic calculations indicate that the guaiacol is transporting through the membrane with no chemical potential gradient, again challenging conventional membrane transport theory notions. Our experiments reveal that the guaiacol transport is closely linked to the transport of methanol through the membrane, thus providing an initial clue at the separation mechanism under which the membrane is operating.

With this enticing preliminary data, we hypothesize that dilute compounds can be preferentially concentrated via pressure-driven membrane permeation via favorable binding interactions between the compound and the membrane. The dilute compound is then swept through the membrane by coupling with another permeating compound in a process known as “sorpvection”, originally discovered by Koros and coworkers in 2005. We calculate that some of the driving force for the “sorpvecting agent” (the compound that couples to the dilute constituent) is utilized to transport the dilute compound “uphill” against its chemical potential gradient. Because of this coupling, the uphill chemical potential permeation of the dilute compound does not result in second law violations.

Interrogating Selective Metal-Adsorbate Interactions in Metal–Organic Frameworks

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¹University of California Berkeley, ²Lawrence Berkeley National Laboratory

Key Words: Bioinspired Recognition; Inorganic Chelation; Reactive Separations

DE-SC0019992 (UC Berkeley) and CH19DRI01 (LBNL): Interrogating Selective Metal-Adsorbate Interactions in Metal–Organic Frameworks

PI: Jeffrey R. Long; co-PI: Jeffrey A. Reimer, Jeffrey B. Neaton, Walter S. Drisdell

Research Project Scope.

Separations of commodity chemicals in industry are carried out on a massive scale worldwide, accounting for a substantial proportion of global CO₂ emissions. Metal–organic frameworks (MOFs) are a class of solid adsorbents that have emerged as leading candidates for energy-efficient adsorption-based separations that could supplement, or even replace, energy-intensive processes such as cryogenic distillation. MOFs exhibit highly porous, robust structures, and their chemical tunability sets them apart from other adsorbents, including zeolites and porous carbons. As a result of this tunability, MOFs can be designed to feature gas binding sites specifically tailored for the targeted removal of certain gas molecules from complex mixtures near ambient temperatures, based on a range of selectivity handles. The further development and optimization of such next-generation adsorbents necessitates a rigorous understanding of the local physical and electronic structures that promote gas binding, and how these properties change upon guest uptake. Our research uses advanced *in situ* characterization methods, such as nuclear magnetic resonance, x-ray absorption spectroscopies, and x-ray diffraction, that enable direct, real-time characterization of selective metal–adsorbate binding processes at the atomic level, with relevance to a number of industrial gas separations.

Recent Progress.

A. High-temperature CO₂ capture in a porous material with terminal zinc–hydride sites. Carbon capture is an imperative strategy to mitigate point-source CO₂ emissions, but substantial hurdles still impede the widespread adoption of amine-based technologies. The capture of CO₂ at temperatures closer to those of many industrial flue streams (>200 °C) has attracted considerable interest, although candidate dense metal oxide adsorbents that operate at these temperatures typically exhibit sluggish CO₂ absorption kinetics and poor stability to cycling. We discovered that a highly porous MOF featuring terminal zinc–hydride sites (Figure 1a) reversibly chemisorbs CO₂ at temperatures above 200 °C—conditions that are

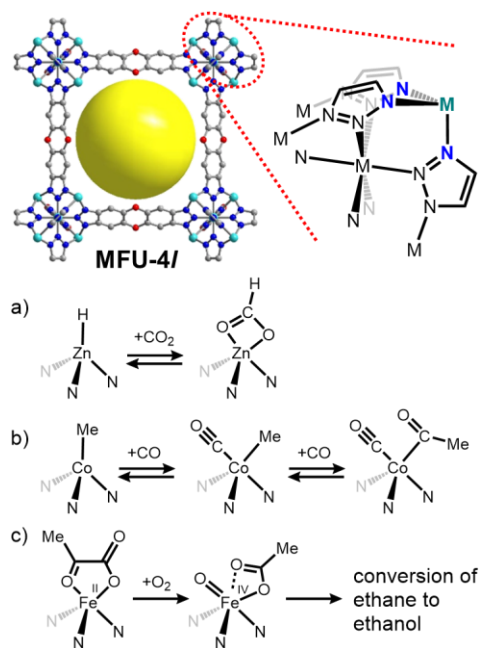


Figure 1. (upper) Structure of MFU-4l and a portion of the inorganic cluster. (lower) Reaction schemes illustrating (a) CO₂ and (b) CO adsorption processes and ethane oxidation (c).

unprecedented for an intrinsically porous material. Gas adsorption, structural, spectroscopic, and computational analyses were used to elucidate the rapid, reversible nature of this transformation at high temperatures. Extended cycling and breakthrough analyses revealed that the material is capable of deep CO₂ capture at low concentrations and high temperatures relevant to post-combustion CO₂ capture.

B. Cooperative binding of multiple gas molecules at a single framework metal site enabled by reversible alkyl migration. Some of the most promising MOFs studied for gas separations feature coordinatively unsaturated metal sites that can selectively bind guest molecules. In essentially all cases, these sites can bind only a single guest molecule. However, there is significant interest in the development of MOFs featuring metal sites that can bind two or more gases, as such materials would exhibit enhanced volumetric and gravimetric capacities relative to those accessible with traditional frameworks. Recently, we discovered that a framework featuring cobalt(II)–methyl (Figure 1b) is capable of reversibly coordinating two equivalents of CO at ambient temperatures and pressures. Spectroscopic characterization and computations revealed that binding of the first equivalent of CO occurs concomitant with a transition from a high- to a low-spin cobalt(II) site, followed by methyl migration and chemisorption of a second CO to yield a mono-acyl, mono-CO adduct. This mechanism is fully reversible at ambient temperature, and the material is highly robust to extended CO adsorption–desorption cycling. Multicomponent breakthrough analysis revealed that the framework has a high affinity for CO at low partial pressures relevant to CO separations from alkene mixtures and syngas and is highly selective for CO over other gases, such as ethylene. In addition to elucidating a new mechanism of gas binding in a MOF, this work highlights new avenues for the design of frameworks capable of binding multiple gas molecules at coordinatively unsaturated metal sites.

C. Reactive high-spin iron(IV)-oxo sites through dioxygen activation in a metal–organic framework (ref. 5). The discovery of new catalysts for the selective oxygenation of light hydrocarbons using O₂ remains a formidable challenge in the global effort to develop green technologies for the valorization of natural gas components. Nature uses nonheme iron-containing enzymes and abundant dioxygen to generate high-spin Fe(IV)=O species for a variety of oxygenation reactions. One well-studied enzyme in this class is taurine- α -ketoglutarate dioxygenase (TauD), which oxygenates one of the C–H bonds of taurine alpha to the sulfonate group. Key to the reactivity of TauD and its family of dioxygenases is a high-spin ($S = 2$) Fe(IV)=O intermediate, which is formed following oxidation of Fe(II) with O₂, coupled with oxidation and decarboxylation of the α -ketoglutarate co-substrate. Although scientists have long sought to mimic this reactivity, the enzyme-like activation of O₂ to form high-spin Fe(IV)=O species remains an unrealized goal in synthetic chemistry. We prepared a framework featuring iron(II) sites coordinated by pyruvate, whose local structure is similar to that in α -ketoglutarate-dependent dioxygenases (Figure 1c). The framework reacts with O₂ at low temperatures to form high-spin Fe(IV)=O species, which are the first of their kind in a synthetic system and were rigorously characterized using *in situ* infrared, *in situ* and variable-field Mössbauer, Fe K β X-ray emission, and nuclear resonance vibrational spectroscopies. In the presence of O₂, the framework is competent for catalytic oxygenation of cyclohexane and the stoichiometric conversion of ethane to ethanol.

D. A ligand insertion mechanism for cooperative NH₃ capture in metal–organic frameworks (ref. 6). Ammonia is a critical chemical in agriculture and industry that is produced on a massive scale via the Haber–Bosch process. The environmental impact of this process, which uses methane as a fuel and feedstock for hydrogen, has motivated research into more sustainable routes to ammonia production.

However, many strategies that use renewable H₂ are not compatible with existing methods for ammonia production. It has been proposed that ammonia could be produced more efficiently by replacing the condensation separation step with alternative technologies such as those involving solid absorbents. Given their high surface areas and structural and chemical versatility, MOFs have also attracted interest for ammonia separations. However, most MOFs bind ammonia irreversibly or degrade on exposure to this corrosive gas. We discovered that a tunable copper-based framework reversibly binds ammonia via a mechanism involving cooperative ammonia insertion into its metal–carboxylate bonds, which results in the formation of a dense, one-dimensional coordination polymer. This unusual adsorption mechanism provides considerable intrinsic thermal management and affords the material with large ammonia capacities under conditions relevant to proposed alternative methods for renewable ammonia production. Further, the threshold pressure for ammonia adsorption can be tuned by almost five orders of magnitude through simple synthetic modifications. This work points to a broader strategy for the development of energy-efficient adsorbents compatible with sustainable ammonia synthesis.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. H. Wang, G. M. Su, B. R. Barnett, W. S. Drisdell, J. R. Long, D. Prendergast, Understanding 2p core-level excitons of late transition metals by analysis of mixed-valence copper in a metal–organic framework, *Phys. Chem. Chem. Phys.* 2024, 26(15) 11980–11987.
2. K. M. Carsch, A. J. Huang, M. N. Dods, S. T. Parker, R. C. Rohde, H. Z. H. Jiang, Y. Yabuuchi, S. L. Karstens, H. Kwon, R. Chakraborty, K. C. Bustillo, K. R. Meihaus, H. Furukawa, A. M. Minor, M. Head-Gordon, J. R. Long, Selective adsorption of oxygen from humid air in a metal–organic framework with trigonal pyramidal copper(I) sites, *J. Am. Chem. Soc.* 2024, 146(5) 3160–3170.
3. Z. Zhu, H. Tsai, S. T. Parker, J.-H. Lee, Y. Yabuuchi, H. Z. H. Jiang, Y. Wang, S. Xiong, A. C. Forse, B. Dinakar, A. Huang, C. Dun, P. J. Milner, A. Smith, P. Guimarães Martins, K. R. Meihaus, J. J. Urban, J. A. Reimer, J. B. Neaton, J. R. Long, High-capacity, cooperative CO₂ capture in a diamine-appended metal–organic framework through a combined chemisorptive and physisorptive mechanism, *J. Am. Chem. Soc.* 2024, 146(9), 6072–6083.
4. Y. Shaidu, W. DeSnoo, A. Smith, E. Taw, J. B. Neaton, Entropic effects on diamine dynamics and CO₂ capture in diamine-appended Mg₂(dopbdc) metal–organic frameworks, *J. Phys. Chem. Lett.* 2024, 15(4), 1130–1134.
5. K. Hou, J. Börgel, H. Z. H. Jiang, D. J. SantaLucia, H. Kwon, H. Zhuang, K. Chakarawet, R. C. Rohde, J. W. Taylor, C. Dun, M. V. Paley, A. B. Turkiewicz, J. G. Park, H. Mao, Z. Zhu, E. E. Alp, J. Zhao, M. Y. Hu, B. Lavina, S. Peredkov, X. Lv, J. Oktawiec, K. R. Meihaus, D. A. Pantazis, M. Vandone, V. Colombo, E. Bill, J. J. Urban, R. D. Britt, F. Grandjean, G. J. Long, S. DeBeer, F. Neese, J. A. Reimer, J. R. Long, Reactive high-spin iron(IV)-oxo sites through dioxygen activation in a metal–organic framework, *Science* 2023, 382(6670), 547–553.
6. B. E. R. Snyder, A. B. Turkiewicz, H. Furukawa, M. V. Paley, E. O. Velasquez, M. N. Dods, J. R. Long, A ligand insertion mechanism for cooperative NH₃ capture in metal–organic frameworks, *Nature* 2023, 613(7943), 287–291.
7. L. M. Funke, R. Chakraborty, K. M. Carsch, M. Head-Gordon, J. R. Long, J. A. Reimer, Assessment of adsorbate π -backbonding in copper(I) metal–organic frameworks via multinuclear NMR spectroscopy and density functional theory calculations, *J. Phys. Chem. C* 2023, 127(15), 7513–7519.
8. Y. Shaidu, A. Smith, E. Taw, J. B. Neaton, Carbon capture phenomena in metal–organic frameworks with neural network potentials, *PRX Energy* 2023, 2(2), 023005.
9. D. E. Jaramillo, A. Jaffe, B. E. R. Snyder, A. Smith, E. Taw, R. C. Rohde, M. N. Dods, W. DeSnoo, K. R. Meihaus, T. D. Harris, J. B. Neaton, J. R. Long, Metal–organic frameworks as O₂-selective

- adsorbents for air separations, *Chem. Sci.* 2022, 13(35), 10216–10237.
10. J.-H. Lee, P. Hyldgaard, J. B. Neaton, An assessment of density functionals for predicting CO₂ adsorption in diamine-functionalized metal–organic frameworks, *J. Chem. Phys.* 2022, 156(15), 154113.
 11. B. Dinakar, A. C. Forse, H. Z. H. Jiang, Z. Zhu, J.-H. Lee, E. J. Kim, S. T. Parker, C. J. Pollak, R. L. Siegelman, P. J. Milner, J. A. Reimer, J. R. Long, Overcoming metastable CO₂ adsorption in a bulky diamine-appended metal–organic framework, *J. Am. Chem. Soc.* 2021, 143(37), 15258–15270.
 12. G. M. Su, H. Wang, B. R. Barnett, J. R. Long, D. Prendergast, W. S. Drisdell, Backbonding contributions to small molecule chemisorption in a metal–organic framework with open copper(I) centers, *Chem. Sci.* 2021, 12(6), 2156–2164.
 13. J. Oktawiec, H. Z. H. Jiang, A. B. Turkiewicz, J. R. Long, Influence of the primary and secondary coordination spheres on nitric oxide adsorption and reactivity in cobalt(II)–triazolate frameworks, *Chem. Sci.* 2021, 12(43), 14590–14598.

Grant cited but not intellectually led by this award:

1. S. N. Fricke, M. Salgado, T. Menezes, K. M. Costa Santos, N. B. Gallagher, A. Song, J. Wang, K. Engler, Y. Wang, H. Mao, J. A. Reimer, Multivariate machine learning models of nanoscale porosity from ultrafast NMR relaxometry, *Angew. Chem. Int. Ed.* 2024, 63(13), e202316664.
2. Z. Zhu, S. T. Parker, A. C. Forse, J.-H. Lee, R. L. Siegelman, P. J. Milner, H. Tsai, M. Ye, S. Xiong, M. V. Paley, A. A. Uliana, J. Oktawiec, B. Dinakar, S. A. Didas, K. R. Meihaus, J. A. Reimer, J. B. Neaton, J. R. Long, Cooperative carbon dioxide capture in diamine-appended magnesium–olsalazine frameworks, *J. Am. Chem. Soc.* 2023, 145(31), 17151–17163.
3. H. Babaei, K. R. Meihaus, J. R. Long, Reversible thermal conductivity switching using flexible metal–organic frameworks, *Chem. Mater.* 2023, 35(16), 6220–6226.
4. L. M. Funke, A. Lund, H. Zhuang, J. A. Reimer, Metal–organic frameworks: Challenges addressed via magnetic resonance spectroscopy, *Appl. Magn. Reason.* 2023, 54(11–12), 1193–1220.
5. Y. Fu, Y. Yao, A. C. Forse, J. Li, K. Mochizuki, J. R. Long, J. A. Reimer, G. De Paëpe, X. Kong, Solvent-derived defects suppress adsorption in MOF-74, *Nat. Commun.* 2023, 14, 2386.
6. Y. Fu, A. C. Forse, Z. Kang, M. J. Cliffe, W. Cao, J. Yin, L. Gao, Z. Pang, T. He, Q. Chen, Q. Wang, J. R. Long, J. A. Reimer, X. Kong, One-dimensional alignment of defects in a flexible metal-organic framework, *Sci. Adv.* 2023, 9(6), eade6975.
7. Y. Yuan, Y. Yang, K. R. Meihaus, S. Zhang, X. Ge, W. Zhang, R. Faller, J. R. Long, G. Zhu, Selective scandium ion capture through coordination templating in a covalent organic framework, *Nat. Chem.* 2023, 15(11), 1599–1606.
8. Z. Li, C. Liu, J. J. Frick, A. K. Davey, M. N. Dods, C. Carraro, D. G. Senesky, R. Maboudian, Synthesis and characterization of UiO-66-NH₂ incorporated graphene aerogel composites and their utilization for absorption of organic liquids, *Carbon* 2023, 201, 561–567.
9. S. T. Parker, A. Smith, A. C. Forse, W.-C. Liao, F. Brown-Altvater, R. L. Siegelman, E. J. Kim, N. A. Zill, W. Zhang, J. B. Neaton, J. A. Reimer, J. R. Long, Evaluation of the stability of diamine-appended Mg₂(dobpdc) frameworks to sulfur dioxide, *J. Am. Chem. Soc.* 2022, 144(43), 19849–19860.
10. R. L. Siegelman, J. A. Thompson, J. A. Mason, T. M. McDonald, J. R. Long, A cooperative adsorbent for the switch-like capture of carbon dioxide from crude natural gas, *Chem. Sci.* 2022, 13(40), 11772–11784.
11. P. Perlepe, I. Oyarzabal, L. Voigt, M. Kubus, D. N. Woodruff, S. E. Reyes-Lillo, M. L. Aubrey, P. Négrier, M. Rouzières, F. Wilhelm, A. Rogalev, J. B. Neaton, J. R. Long, C. Mathonière, B. Vignolle, K. S. Pedersen, R. Clérac, From an antiferromagnetic insulator to a strongly correlated metal in square-lattice MCl₂(pyrazine)₂ coordination solids, *Nat. Commun.* 2022, 13, 5766.
12. V. Shukla, Y. Jiao, J.-H. Lee, E. Schröder, J. B. Neaton, P. Hyldgaard, Accurate nonempirical range-separated hybrid van der Waals density functional for complex molecular problems, solids, and

- surfaces, *Phys. Rev. X* 2022, 12(4), 041003.
13. E. Taw, J. B. Neaton, Accelerated discovery of CH₄ uptake capacity metal–organic frameworks using Bayesian optimization, *Adv. Theory Simul.* 2022, 5(3), 2100515.
 14. W. Lu, E. Zhang, J. Qian, C. Weeraratna, M. N. Jackson, C. Zhu, J. R. Long, M. Ahmed, Probing growth of metal–organic frameworks with X-ray scattering and vibrational spectroscopy, *Phys. Chem. Chem. Phys.* 2022, 24(42), 26102–26110.
 - a. A. Uliana, N. T. Bui, J. Kamcev, M. K. Taylor, J. J. Urban, J. R. Long, Ion-capture electro dialysis using multifunctional adsorptive membranes, *Science* 2021, 372(6539), 296–299.
 - b. K. Davey, X. Gao, Y. Xia, Z. Li, M. N. Dods, S. Delacruz, A. Pan, S. Swamy, D. Gardner, C. Carraro, R. Maboudian, Amine-functionalized metal–organic framework ZIF-8 toward colorimetric CO₂ sensing in indoor air environment, *Sens. Actuators B: Chem.* 2021, 344, 130313.
 15. M. E. Zick, J.-H. Lee, M. I. Gonzalez, E. O. Velasquez, A. A. Uliana, J. Kim, J. R. Long, P. J. Milner, Fluoroarene separations in metal–organic frameworks with two proximal Mg²⁺ coordination sites, *J. Am. Chem. Soc.* 2021, 143(4), 1948–1958.

Investigating and Modulating Phase-Change Kinetics of Flexible Metal–Organic Frameworks Using Multivariate Derivatization

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¹Colorado School of Mines

Key Words: Dynamics; Gas Phase; Kinetics; Thermodynamics

DE-SC0024164: Building a Scientific Foundation for a New Generation of Low Energy Adsorptive Separations: Probing the Role of Responsive Structural Flexibility Using Synthetic Porous Frameworks

PI: Michael McGuirk

Research Project Scope.

Our objective is to understand the key structural and energetic variables of cooperative flexibility in metal–organic frameworks that influence selectivity and kinetics of adsorption, and thus separations from relevant mixtures. These efforts will significantly advance the atomic- to meso-scale understanding of responsive cooperative flexibility in porous adsorbents and construct a scientific foundation that promotes the intuitive design and application of cooperative flexibility in the pursuit of low-energy adsorptive separations for societally critical separations, such as purification of commodity chemicals, removal of pollutants from the environment, and isolation of critical minerals and elements.

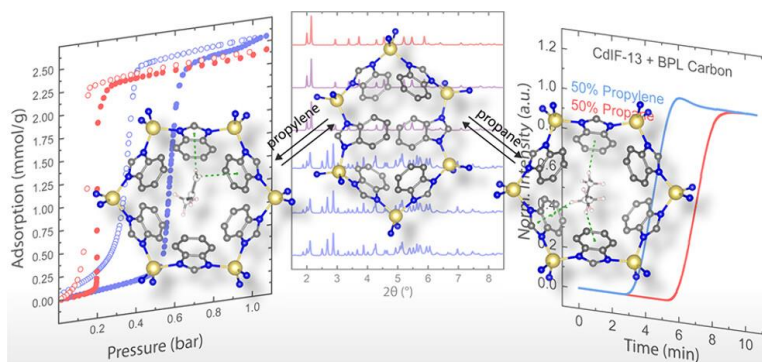


Figure 1: We have previously observed that flexibility in metal–organic frameworks can give rise to unusual and high performing separation properties, namely the inverse selectivity for propane over propylene. Our current work seeks to understand why this is and how to further control flexibility to enhance performance.

Recent Progress.

This project is initially motivated by results our group published in 2023 in which we report a cooperatively flexible metal–organic framework, CdIF-13 (*sod*-Cd(benzimidazole)₂), that exhibits record-setting inverse selectivity for propane over propylene across a large range of mixture compositions.¹ We determined that the adsorption-induced first order phase change in this material results in bespoke binding pockets that enable the observed selectivity. In parallel, we have worked to understand how subtle compositional variations to the framework’s ligands, such as replacing a hydrogen for a fluorine atom, influences the pressure at which an adsorbate, such as propane, induces the phase change responsible for adsorption.² While we have observed that such modifications can dramatically alter the pressure at which adsorption occurs for a single gas, these are single-component measurements done under equilibrium conditions. Accordingly, our ongoing efforts are to probe how these modifications that affect single component adsorption under equilibrium influence the kinetics of adsorption-induced phase changes and

performance for separations. To do so, we are leveraging both transient adsorption measurements with a gas adsorption analyzer and breakthrough measurements using a prototypical home-built instrument. Measurements are being performed with a family of fully characterized derivatives of CdIF-13 containing functionalized organic linkers. Through these efforts we will better understand the relationship between the thermodynamics and kinetics of adsorption-induced phase changes and how they can be modulated to enhance performance in separations.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

1. Klein, R. A.; Bingel, L. W.; Halder, A.; Carter, M.; Trump, B. A.; Bloch, E. D.; Zhou, W.; Walton, K. S.; Brown, C. M.; McGuirk, C. M. Adaptive Pore Opening to Form Tailored Adsorption Sites in a Cooperatively Flexible Framework Enables Record Inverse Propane/Propylene Separation. *Journal of the American Chemical Society* **2023**, *145*, 21955–21965.
2. Halder, A.; McGuirk, C. M. Exploring the Influence of Linker Substitution and Ratios on Cooperative Framework Flexibility through the Mixed-Linker Approach. *Crystal Growth & Design* **2024**, *24*, 3, 1200–1213.

Carbon Dioxide Capture Beyond Amines Using Oxygen-Based Nucleophiles

Phillip Milner¹, S. Alexandra Lim,¹ Mary E. Zick,¹ Sijing Meng¹, Tristan H. Lambert,¹ Alexander C. Forse,² Jung-Hoon Lee³

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Key Words: Confinement; Kinetics; Thermodynamics; Transport Phenomena

DE-SC0021000: New Molecular Mechanisms for Greenhouse Gas Capture in Metal-Organic Frameworks: Carbon Dioxide and Beyond

PI: Phillip Milner

Research Project Scope.

New chemical pathways for separating greenhouse gases such as carbon dioxide, methane, nitrous oxide, and hydrofluorocarbons from emission streams are needed to address the looming climate crisis. We are studying how to engineer new reactivity-based interactions for these gases inside of porous materials, including metal-organic frameworks and carbons. This talk will focus on our efforts to achieve carbon dioxide capture “beyond amines” using reactive hydroxide and tertiary amine *N*-oxide sites embedded within materials. These materials exhibit improved oxidative and thermal stability compared to traditional amines.

Recent Progress.

We have shown that hydroxide sites can be incorporated into metal-organic frameworks (MOFs), specifically cationic frameworks based on cyclodextrin linkers, to facilitate post-combustion and direct air capture of CO₂. In addition, we have shown that electrochemical charging enables incorporation of the same reactive sites into inexpensive porous carbons, which can facilitate direct air capture while exhibiting excellent oxidative stability. Last, we have found that the *N*-oxides of tertiary amines, one of the oxidative degradation products naturally arising during carbon capture cycling, can bind carbon dioxide via bicarbonate formation. These molecules are inexpensive, non-toxic, non-corrosive, and non-volatile, making them potential drop-in replacements for amines. Beyond carbon dioxide capture, we have also shown that hydrofluorocarbons such as fluoroform can be bound within MOFs through hydrogen- and halogen-bonding interactions and studied nitrous oxide sorption in a range of redox-active materials.

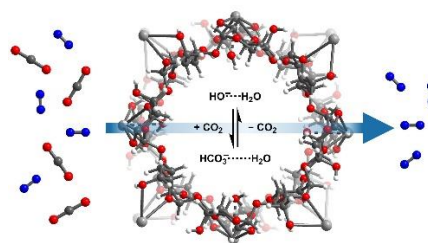


Figure. Carbon capture at hydroxide sites in metal-organic frameworks.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. Huaiguang Li, Mary E. Zick, Teedhat Trisukhon, Matteo Signorile, Xinyu Liu, Helen Eastmond, Shivani Sharma, Tristan Spreng, Jack Taylor, Jamie Gittins, Cavan Farrow, S. Alexandra Lim, Valentina Crocellà, Phillip J. Milner, Alexander C. Forse. “Capturing Carbon Dioxide from Air with

- Charged Sorbents.” *Nature*, **2024**, *630*, 654–659.
2. Bevan S. Whitehead, William W. Brennessel, Shane S. Michtavy, Hope A. Silva, Jaehwan Kim, Phillip J. Milner, Marc D. Porosoff, Brandon R. Barnett. “Selective Adsorption of Fluorinated Super Greenhouse Gases within a Metal–Organic Framework with Dynamic Corrugated Ultramicropores.” *Chem. Sci.* **2024**, *15*, 5964–5972.
 3. Tristan A. Pitt, Haojun Jia, Tyler J. Azbell, Mary E. Zick, Aditya Nandy, Heather J. Kulik, Phillip J. Milner. “Benchmarking Nitrous Oxide Adsorption and Activation in Metal–Organic Frameworks Bearing Coordinatively Unsaturated Metal Centers.” *J. Mater. Chem. C*, **2024**, *12*, 3164–3174.
 4. Mary E. Zick, Donovan Cho,[‡] Jianheng Ling,[‡] Phillip J. Milner*. “Carbon Capture Beyond Amines: CO₂ Sorption at Nucleophilic Oxygen Sites in Materials.” *ChemNanoMat* **2023**, *9*, e202200436.
 5. Elena Y. Chen, Ruth M. Mandel, Phillip J. Milner. “Evaluating Solvothermal and Mechanochemical Routes towards the Metal–Organic Framework Mg₂(*m*-dobdc).” *CrystEngComm*, **2022**, *24*, 7292–7297.
 6. Mary E. Zick, Suzi M. Pugh, Jung-Hoon Lee, Alexander C. Forse, Phillip J. Milner. “Carbon Dioxide Capture at Nucleophilic Hydroxide Sites in Oxidation-Resistant Cyclodextrin-Based Metal–Organic Frameworks.” *Angew. Chem. Int. Ed.* **2022**, *61*, e202206718.

Exploring the Feasibility of Aqua-Mining for Recovery of Critical Metals Using Computational Molecular Modeling

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Key Words: Dilute Species; Field-Driven Separations; Interfaces; Solvation

DE-SC0025289:

PI: Sohail Murad

Research Project Scope.

The main focus of the proposed research is on harvesting “critical metals” from waste-streams using a process we call aqua-mining. Many of these metals are used as components in manufacturing of a range of products and devices which are considered essential to US economy and national security. Our choice of investigating aqua-mining for the purpose of extracting critical metals, while still at the lab-scale stage, offers a new paradigm as an alternative to and/or augmentation of traditional mining of ores, would reduce reliance on international supply chains and the need for importation of some critical metals. It also offers an alternate technology to traditional mining which by itself is an environmentally polluting technology that outlines the project's scientific scope, approach, and relevance to the Separation Science Program.

Recent Progress.

We have begun simulations to use reverse osmosis (RO) with zeolite membranes to determine the upper limit of concentration that can be achieved using RO. The system we have designed for such RO based concentration of the solution is shown in Figure 1 below. Depending on the outcome of this step, we will either separate e.g. Li using selective permeation from the solutions, or follow up with separations using ion exchange or adsorption. We have developed strategies to accelerate these separations when using computational molecular modeling.

Future Plans.

Our future plans include evaluating the upper limit of the concentration of the waste solutions possible using RO only. This will be accomplished by using zeolite membranes with pores that will allow none of the ions present in the solution from permeating the membrane, just water. Once this is accomplished the next challenge would be to identify a membrane that would only allow Li ions to permeate the membrane and no other ions. Depending on these outcomes we will plan on using other strategies including ion exchange, and/or adsorption.

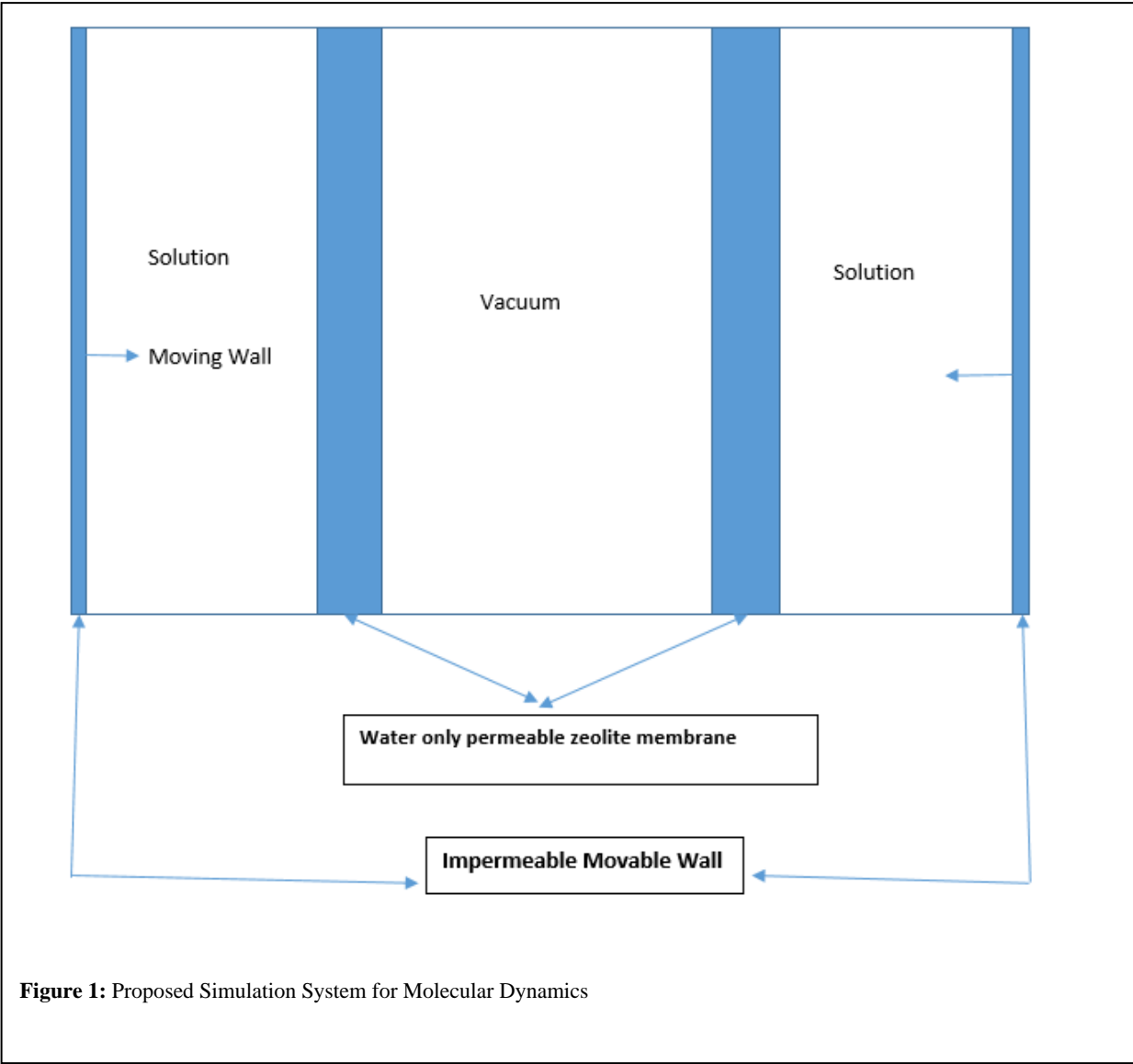


Figure 1: Proposed Simulation System for Molecular Dynamics

Materials and Data-Driven Computer Simulations for Seawater Mining of Valuable Metals

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Key Words: Confinement; Dilute Species; Thermodynamics; Theory/Simulation

DE-SC0024500: Reticular Materials and Data-Driven Computer Simulations for Seawater Mining of Valuable Metals

PI: Francesco Paesani; co-PI: Tod Pascal, Omar M. Yaghi

Research Project Scope.

Our research program explores the potential of metal-organic frameworks (MOFs) as efficient sorbent materials for the extraction and recovery of essential metals. By integrating reticular chemistry with advanced molecular dynamics simulations, we aim to develop novel MOFs optimized for the selective mining of valuable metals from seawater. Our research provides critical insights into the mechanisms that enable MOFs to selectively bind and release these metals from dilute solutions, contributing to the establishment of design principles for creating efficient materials for seawater mining.

Recent Progress.

In the first eight months of our project, we focused our efforts on MOF-808 due to its hydrothermal stability, making it an ideal model system. Specifically, we investigated the thermodynamics of the adsorption process and the local solvation structure of Li^+ , Na^+ , and K^+ ions adsorbed in MOF-808 (Figure). Specifically, through alchemical free-energy calculations and enhanced sampling simulations, we found that the internal environment of MOF-808 provides a favorable setting for the uptake of these ions from dilute aqueous solutions. While the dehydrated ions are stable in the small pores of MOF-808, further hydration of the ions is thermodynamically even more favorable, although it requires overcoming high energy barriers. Systematic analyses of our simulation and experimental results allowed us to determine the physical mechanisms governing the adsorption process. These insights are currently being used to optimize the MOF-808 framework for improved ion selectivity and kinetics.

Future Plans.

Our future objectives include further characterization of MOF-808's uptake performance, particularly in more concentrated ion solutions and the time dependence of metal ion uptake. Additionally, we are exploring multivariate versions of MOF-808, where different functional groups are incorporated into the MOF-808 framework to improve its selectivity for Li^+ ions.

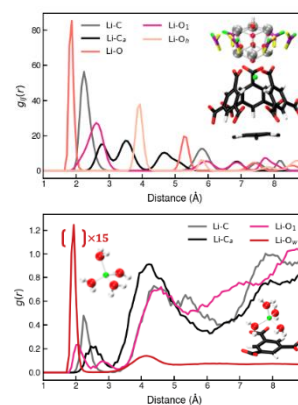


Figure. Hydration structure of Li^+ ions in the small (top) and large (bottom) pores of MOF-808.

Electric Field Driven Ionic Liquid Interphase Formation for Separation of Critical Minerals

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Key Words: Field-Driven Separations; Non-Thermal Separation Mechanisms; Reactive Separations; Solvation

PNNL 81462: Harnessing Confinement Effects, Stimuli, and Reactive Intermediates in Separations

PI: David J. Heldebrant; co-PI: Grant E. Johnson

Research Project Scope.

Nonthermal approaches using electric fields, such as electrophoresis and electro dialysis, are generally more sustainable and energy-efficient routes to achieving high selectivity for critical mineral separation than current chemical methods. Controlling the transport and enrichment of targeted ions at electrified interfaces and promoting their selective adsorption and reduction is a grand scientific challenge in electrochemical separations. The desolvation processes occurring at electrochemical interfaces play a key role in the partitioning of metal ions from the bulk solution and facilitate stable and selective transport as well as non-Faradaic (capacitive) and Faradaic (redox) enrichment of targeted ions. A critical knowledge gap remains in our fundamental understanding of the effect of hydrophobic domains and redox-active species on ion solvation, transport, and selective adsorption at electrified interfaces. Our work aims to obtain a predictive understanding of the factors influencing the separation of targeted heavy metal and lanthanide ions by modulating interfacial solvation dynamics and potential energy profiles using surface functionality, hydrophobic domains, and electric fields.

Recent Progress.

We hypothesized that the hydrophobicity and Faradaic adsorption and reduction properties of electrified interfaces may be modulated through functionalizing with task-specific imidazolium-based ionic liquid cluster ions and multi-electron redox-active polyoxometalate anions. The size, stoichiometry, and charge state of the ionic liquid cluster ions at the electrode interface were precisely tuned using distinguishing ion soft landing deposition capabilities. We obtained kinetic and mechanistic insights into the metal ion desolvation and electro sorption properties of electric-field-assembled interphases using *operando* electrochemical Raman spectroscopy, atomic force microscopy, and electrochemical impedance spectroscopy combined with advanced

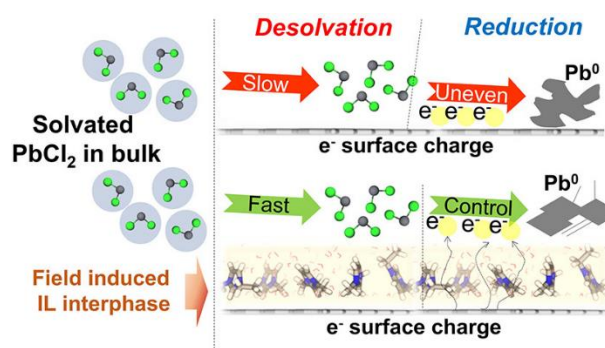


Figure 1. Electric field-induced assembly of 1-ethyl-3-methylimidazolium chloride (EMIMCl) ionic liquid molecules into a negatively charged aqueous electrode-electrolyte interphase (EEI). The oriented EEI accelerates ion desolvation and electron transfer during reduction of heavy metals like Pb^{2+} , enabling efficient pathways for electrochemical removal of metals from contaminated feed streams.

machine-learning-enabled theoretical simulations. We found that the imidazolium-based ionic liquids and heavy metal ions such as Pb^{2+} formed different complexes in solution than in the gas phase. The presence of water resulted in more reducible complexes. By understanding the role of solvents in controlling the molecular interactions and energetics of complexes formed between ionic liquids and heavy metals, the rational design of more efficient and selective separation processes using environmentally friendly ionic liquids will be achieved.

We also investigated how electric fields may be leveraged to control the complexation between ionic liquids and targeted ions. We demonstrated that applying a negative potential to the electrode resulted in the formation of well-oriented ionic-liquid layers at electrified interfaces with the hydrophobic alkyl chains of the imidazolium cations extending into the bulk solution (**Figure 1**). The hydrophobic chains of the ionic liquid efficiently desolvated heavy metal ions, enabling their efficient electrosorption and selective separation by controlling their nucleation behavior. Our research demonstrates that adding small quantities of hydrophobic ionic liquids to aqueous waste streams leads to the formation of ionic-liquid-based aqueous interphases with the potential to promote the electrochemical separation of heavy metals and lanthanides with similar chemical and electrochemical properties. Our findings inform the design of novel non-thermal separation methods that may be used for decontaminating water and recovering critical minerals from abundant domestic liquid feedstocks.

Future Plans.

Future work will focus on understanding how the length of the alkyl chain of ionic liquids and co-solvents affects the selectivity and efficiency of the adsorption of heavy metals and critical metals from different feedstocks.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. E. T. Baxter, J. Zhang, S. Tan, M.-T. Nguyen, D. Zhang, Q. Yuan, W. Cao, X.-B. Wang, V. Prabhakaran, V.-A. Glezakou, G. E. Johnson. Functionalization of Electrodes with Tunable $[\text{EMIM}]_x[\text{Cl}]_{x+1}$ Ionic Liquid Clusters for Electrochemical Separations. *Chemistry of Materials*. 2022, 34 (6), 2612-2623.
2. S. Tan, M.-T. Nguyen, D. Zhang, L. Zhong, Z. Cheng, S. China, G. E. Johnson, V. Prabhakaran. Electric-Field-Induced Assembly of an Ionic Liquid–Water Interphase Enables Efficient Heavy Metal Electrosorption. *ACS Applied Materials & Interfaces*. 2023, 15 (37), 44469-44481.
3. S. Tan, D. Zhang, Y. Chen, B. Helfrecht, E. T. Baxter, W. Cao, X.-B. Wang, M.-T. Nguyen, G. E. Johnson, V. Prabhakaran. Complexation of heavy metal cations with imidazolium ionic liquids lowers their reduction energy: implications for electrochemical separations. *Green Chemistry*. 2024, 26 (3), 1566-1576.
4. J. Edgecomb; D. T. Nguyen, S. Tan, V. Murugesan, G.E. Johnson, V. Prabhakaran. Electrochemical Imaging of Precisely-Defined Redox and Reactive Interfaces. *Angewandte Chemie International Edition* 2024, e202405846.

Geo-Inspired Separation of Rare Earth Elements

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Ames National Laboratory, US DOE, Division of Chemical and Biological Sciences

Key Words: Field-Assisted Chemistry; Rare Earth Elements; Adsorptive Separation Process; Cluster Formation

AL-21-380-078: Geo-inspired Separation of Rare Earth Elements

PI: Tanya Prozorov; co-PIs: Jared L. Anderson, Frédéric A. Perras, Julia Zaikina

Research Project Scope.

The long-term goal of this project is to gain a fundamental understanding of the chemical environment and mechanisms of adsorption, separation, and extraction of rare earth elements (REEs) ion-adsorption clays. This acquired deep knowledge will underpin future developments in REE separations and recovery from domestic secondary sources. We envision that the fundamental knowledge gained as a part of this effort will further enable us to devise pathways to synthesize novel adsorbent platforms and chemically tunable extractants with improved REE retention, separation, and recovery.

Recent Progress.

Due to their complex structure and presence of impurities, natural clays offer limited control over the rational tunability of their interactions with REEs. It is difficult to work with clay minerals in their natural settings, making it necessary to use laboratory-controlled conditions and compositions in REE adsorption experiments. We used MCM-22 type layered zeolites as a well-studied model platform to explore the tunability of the REE capture [1,2]. It was demonstrated that increasing the Al content in the material lead to improved Yb (HREE) capture by ionic interactions, likely due to the enhancement in the anionic Brønsted acid sites (BAS) and Al-bridged siloxanes. The interplay between Brønsted acid sites and Lewis acid sites offers important clues into the mechanism of REE binding to the adsorbent [2,3]. MCM-22 served as a well-controlled synthetic platform to aid the understanding of REE capture in natural ionic adsorption clays.

To understand the solvation mechanism of rare earth cations at the molecular level and test the extraction of REEs using ILs, we explored solvation phenomena and complexation phenomena of bare RE cations in RITL and examined whether the selected IL prefers to bind with the light or the heavy REEs [4,5].

We performed theoretical and experimental analyses on the binding of RE nitrates in a pure silica-alumina zeolitic MCM-22 platform. We considered Brønsted acid sites (BAS), Al-bridged siloxanes, silanol sites, as a possible site that could play a key role in REE binding existing either at internal pore surfaces or external surfaces. We utilized Density Functional Theory (DFT) to comprehensively assess relative binding strengths, to show BAS > siloxane > silanol. We found little difference between binding at internal and external surfaces. We utilized both periodic plane-wave DFT incorporating the entire MCM-22 unit cell and localized-basis DFT

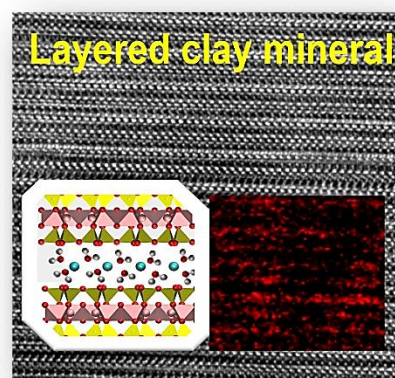


Figure. Spatio-chemical characterization of ion-adsorption clays.

for cluster models of MCM-22. This fundamental understanding of the relative strength of various binding sites will guide the design of novel, selective adsorbents [6,7].

Exerting control over materials' composition and structure to selectively adsorb REEs is important for critical ions separation, and understanding how local electric potentials influence REE adsorption and how they can be modified via chemical substitution is essential to the realization of such a control.

Our recent experimental results show that micas adsorb Nd (LREE) more readily than Yb (HREE). Clays and micas are structurally and chemically similar, however, lanthanide adsorption in muscovite and phlogopite micas appears different from a well-documented trend of regolith-hosted ionic adsorption clays to retain preferentially HREEs. These findings offer an important experimental clue that impurity ions can be used as tuning agents for REE adsorption and separation in layered matrices. Substitutions into the clay and mica can significantly alter the extent of the electrostatic environment to either selectively enhance or suppress interactions with the REE cations as well as with their coordinating ligands e.g., nitrate (NO_3^-) groups. Investigating the REE-specific chemical and spatio-chemical environment of micas and clays will deepen our understanding of the REE adsorption process in these minerals. Our ongoing work considers the connection between the localized charges in natural clays and micas and their REE adsorption trends.

Future Plans.

MCM-22 type layered aluminosilicates provided a well-characterized model suitable for testing specific parameters our early project aimed to identify.

However, MCM-22 type zeolites are different from ion-adsorption clays, both structurally and chemically. As a result, this class of materials offers limited synthetic adaptability. As we learned about the importance of Al-bridged sites in the REE capture by ionic interactions in aluminosilicate frameworks [6,7], we have turned to layered double hydroxide-types for their greater chemical versatility.

The complexation and mobility of supported REE complexes was examined using advanced NMR techniques [6]. In particular, ^{45}Sc chemical shift has proven to be highly sensitive to the coordination environment of the metal, going so far as to reveal the presence of secondary dative interactions with the support. It was shown that ^{45}Sc - ^{27}Al distance measurements can be used to probe the proximity and binding of REEs near negatively charged sites in zeolitic platforms. Solid-state NMR will be used to reveal the coordination environment and location of REE cation in the clay interlayer and inform about how the binding is affected by changes in coordination while in the presence of water.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. Yong Han, An Evaluation for Geometries, Formation Enthalpies, and Dissociation Energies of Diatomic and Triatomic (C, H, N, O), NO_3 , and HNO_3 Molecules from the PAW DFT Method with PBE and optB88-vdW Functionals. *AIP Adv.* 2022, 12, 125009.
2. Y. Han, P. Chatterjee, S. B. Alam, T. Prozorov, I. I. Slowing, J. W. Evans, Interlayer spacing in pillared and grafted MCM-22 type silicas: Density functional theory analysis versus experiment. *Phys. Chem. Chem. Phys.* 2023, 25, 4680-4689.
3. X. Wang and Yong Han. Dependence of Predicted Bulk Properties of Hexagonal Hydroxyapatite on Exchange–Correlation Functional, *Comput. Mater. Sci.* 2023, 224, 112153.
4. S.-A. Hsieh, D. Shamsaei, I. Ocaña-Rios, J. L. Anderson, Batch Scale Production of 3D Printed Extraction Sorbents Using a Low-Cost Modification to a Desktop Printer. *Anal. Chem.* 95, 36, 2023, 13417–13422.

5. T. Ash, T. L. Windus, "DFT-based investigation of solvation of Nd(III)/Yb(III) cations in room-temperature ionic-liquid". *J. Mol. Liq.* 2023, 393, 123650.
6. P. Chatterjee, Y. Han, T. Kobayashi, K. K. Verma, M. Mais, R. K. Behera, T. H. Johnson, T. Prozorov, J. W. Evans, I.I. Slowing, W. Huang, Capturing Rare-Earth Elements by Synthetic Aluminosilicate MCM-22: Mechanistic Understanding of Yb(III) Capture. *ACS App. Mat. & Interf.* 2023, 15, 54192-54201.
7. Y. Han, T. Ash, P. Chatterjee, W. Huang, T. L. Windus, J. W. Evans, "DFT Analysis of the Binding of Rare Earth Nitrates at Internal and External Surfaces of MCM-22", *J. Phys. Chem. C* 2024, 128, 15, 6309–6318.

Advancing Selective, Reactive Separations of Rare Earth Elements through Tailored Coordination Chemistry and Photochemistry

Eric J. Schelter,¹ Kevin P. Ruoff,¹ Randall K. Wilharm,¹ Mitchell H. Zembower,¹ Tyler G. Gong,¹ Morgan K. Noody,¹ Tuna Sagdan,¹ Michael R. Gau,¹ Alexandra M. Bacon,¹ and Dirk Trauner¹

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Key Words: Inorganic Chelation; Kinetics; Non-Thermal Separation Mechanisms; Reactive Separations

DE-SC0017259: Advancing Selective, Reactive Separations of Rare Earth Elements through Tailored Coordination Chemistry and Photochemistry

PI: Eric J. Schelter

Research Project Scope.

Current rare earth (RE) element and other critical metals separations at scale are accomplished by chemical complexation and equilibria between RE and organic extractants in biphasic, aqueous/organic solvent extraction. Solvment extraction delivers stepwise purification of RE from one another. In this project, the team is working to develop alternative modes of reactivity that accomplish efficient separations in fundamentally new ways.

Recent Progress.

Recent results include the discovery of a Ta/Nb photochemical separations system based on different chloride salts. Irradiation of certain mixtures of those cations led to selective reaction and precipitation, providing a new means to separate those critical metals. This was the first reported photochemical separations system for Ta/Nb. We have also recently expanded studies of redox chemistry at the rare earth element cerium to understand how metal-ligand redox cooperativity occurs. These results broadly inform the design of new redox active ligand systems that may be relevant in oxidation-reduction based reactive separations methods for rare earths. Work is also underway to study how the excited state properties of certain rare earth elements can be tied to their reactive separations.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. Yang, Q.; Furigay, M.; Chaudhuri, S.; Gau, Michael; Schatz, George; Schelter, E. J. "Towards Redox- and Photoredox-Based Niobium/Tantalum Separations," *ACS Sustainable Chem. Eng.* **2024**, *12*, 22, 8503–8511.
2. Uruburo, C.; Y. P. Rupasinghe, D. M. R.; Gupta, H.; Knieser, R. M.; Lopez, L. M.; Furigay, M. H.; Higgins, R. F.; Pandey, P.; Baxter, M. R.; Carroll, P. J.; et al. "Metal–Ligand Redox Cooperativity in Cerium Amine-/Amido-Phenolate-Type Complexes," *Inorg. Chem.* **2024**, *63*, 9418–9426.
3. Higgins, R. F.; Ruoff, K. P.; Kumar, A.; Schelter, E. J. "Coordination Chemistry-Driven Approaches to Rare Earth Element Separations," *Acc. Chem. Res.* **2022**, *55*, 18, 2616–2627.
4. Kumar, A.; Geng, H.; Schelter, E. J. "Harnessing Magnetic Fields for Rare-Earth Complex Crystallization Separations in Aqueous Solutions," *RSC Adv.*, **2022**, *12*, 27895–27898
5. Kumar, A.; Pandey, P.; Gau, M. R.; Carroll, P. J.; Schelter, E. J. "Metalating ROY: Understanding the

Denticity and Speciation of Complexes of the ROY Anion," *Inorg. Chem.* **2022**, *61*, 20785–20792.
DOI: 10.1021/acs.inorgchem.2c02629

Grant cited but not intellectually led by this award:

1. "Mediating Photochemical Reaction Rates at Lewis Acidic Lanthanides by Selective Energy Loss to 4f-Electron States," Ruoff, K.; Gish, M.; Song, E.; Douair, I.; Steger, M.; Johnson, J.; Carroll, P.; Gau, M.; Chang, C.; Larsen, R.; Ferguson, A.; Schelter, E. *J. Am. Chem. Soc.* **2023**, *145* (30), 16374–16382.
2. "Observing Similarities and Differences in the Properties of Isostructural Niobium(V)/Tantalum(V) Coordination Compounds with Strong Pi-Donor Ligands," Furigay, M. H.; Chaudhuri, S.; Li, C.; Zhou, J.; Pandey, P.; Higgins, R. F.; Gupta, H.; Carroll, P. J.; Gau, M. R.; Anna, J. M.; et al. *Inorg. Chem.* **2023**, *62*, 19238–19247.
3. Galley, S.; Higgins, R.; Kiernicki, J.; Walensky, J.; Schelter, E.; Zeller, M.; Bart, S. "Synthesis, Characterization, and Reduction of Thorium Pyridine Diimine Complexes," *Inorg. Chem.* **2023**, *62*, 39, 15819–15823. DOI: 10.1021/acs.inorgchem.3c01957
4. Rupasinghe, Y. P.; Ramitha, D. M.; Baxter, M.; Himanshu, G.; Poore, A.; Higgins, R.; Zeller, M.; Tian, S.; Schelter, E. J.; Bart, S. "Actinide-Oxygen Multiple Bonds from Air: Synthesis and Characterization of a Thorium Oxo Supported by Redox-Active Ligands," *J. Am. Chem. Soc.* **2022**, *144*, 38, 17423–17431.
5. Ramitha, D. M.; Rupasinghe, Y. P.; Higgins, R. F.; Baxter, M. R.; Zeller, M.; Schelter, E. J.; Bart, S. C. "Elucidation of pyridine Redox-Active Ligand Complexes: Evidence for a Thorium-Tri(radical) Species," *Inorg. Chem.* **2021**, *60*, 18, 14302–14309.
6. Galley, S. S.; Pattenaude, S. A.; Ray, D.; Gaggioli, C. A.; Whitefoot, M. A.; Qiao, Y.; Higgins, R. F.; Nelson, W. L.; Baumbach, R.; Sperling, J. M.; Zeller, M.; Collins, T. S.; Schelter, E. J.; Gagliardi, L.; Albrecht-Schönzart, T. E.; Bart, S. C. "Using Redox-Active Ligands to Generate Actinide Ligand Radical Species," *Inorg. Chem.* **2021**, *60*, 20, 15242–15252.

Ion-Extractant Coordination at Liquid Interfaces Relevant to Solvent Extraction

Mark L. Schlossman

University of Illinois Chicago

Key Words: Assembly/Ordering; Interfaces; Liquid-Liquid Phase; Transport Phenomena

DE-SC0018200: Ion-Extractant Coordination at Liquid Interfaces Relevant to Solvent Extraction

PI: Mark L. Schlossman

Research Project Scope.

Liquid interfaces play a role in the liquid-liquid extraction and separation of rare earth elements because the interface is the primary location where metal ions encounter amphiphilic extractants. Recent advances are starting to reveal the role of the interface in the formation of ion-extractant complexes, the complexes that form there, and the influence of the interface on kinetics, selectivity, and other interfacial aspects of the extraction process. We utilize synchrotron X-ray scattering from liquid surfaces and interfaces, as well as optical techniques and molecular dynamics simulations (in collaboration with Ilan Benjamin) to address these issues.

Recent Progress.

Our recent work has addressed the effect of metal ion-extractant complexation in the bulk aqueous phase, which competes with their complexation at the liquid interface (1). We used tensiometry and X-ray scattering to characterize the surface of aqueous solutions of lanthanide chlorides and the water-soluble extractant HDEHP, in the absence of a coexisting organic solvent. These studies restricted ion-extractant interactions to the aqueous phase and its liquid-vapor interface, which allowed us to explore the consequences that one or the other is the location of ion-extractant complexation. Unexpectedly, we found that light lanthanides preferentially occupy the liquid-vapor interface. This contradicted our expectation that heavy lanthanides should have a higher interfacial density since they are preferentially extracted by HDEHP in liquid-liquid extraction processes. Comparison experiments with DHDP, which is a water-insoluble extractant with the same phosphoric acid headgroup as HDEHP, revealed the expected higher interfacial density of heavy lanthanides. Similar effects were observed for Ni(II) and Co(II) where the extractant HEHEHP was also considered because of its use in their separation (3). These results revealed the antagonistic role played by ion-extractant complexation within the bulk aqueous phase and clarified the advantages of complexation at the interface.

Extending this work to the liquid-liquid interface revealed unexpected transport phenomena that can lead to a substantial transfer of extractant into the aqueous phase even if its solubility is low (4). We observed the formation of metastable ion-extractant precipitates in the aqueous phase but separated from the liquid-liquid interface by a depletion region without precipitates. Although the precipitate is soluble in the organic phase, the depletion region separates the two and ions can be sequestered in a long-lived metastable state. Since precipitation removes extractants from the aqueous phase, even extractants that are sparingly soluble in water will continue to be withdrawn from the organic phase to feed the aqueous precipitation process. This work in a liquid-liquid bi-phase system supported the counter-intuitive phenomena observed at the free surface of aqueous solutions, for which ions with higher binding affinity

for the extractant were preferentially depleted from the interface (1). Here, precipitation in the aqueous phase preferentially sequesters the more strongly interacting ions. Aqueous ion-extractant precipitation during liquid-liquid extraction provides a reaction path that can influence the extraction kinetics, which plays an important role in designing advanced processes to separate rare earths and other minerals.

In collaboration with Ilan Benjamin (current key personnel and former co-PI on this project) we are exploring the binding reaction of DEHP⁻ to Er(III) (2). This reaction involves the displacement of water molecules from the tightly bound first hydration shell of the metal ion by oxygen atoms from phosphoric acid headgroups. Approach of the headgroup into the region between the first and second hydration shells leads to fast ejection of a water molecule that is accompanied by reordering of the hydration water molecules, including discretization of their angular positions and collective rotation about the metal ion. The water molecule ejected from the first shell is located diametrically opposite from the binding oxygen. Current work has extended these simulations to multiple extractant binding in the bulk water and at the liquid-liquid interface with dodecane (manuscript in preparation).

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. Pan Sun, Erik Binter, Zhu Liang, M. Alex Brown, Artem V. Gelis, Ilan Benjamin, Mrinal K. Bera, Binhua Lin, Wei Bu, and Mark L. Schlossman. Antagonistic Role of Aqueous Complexation in the Solvent Extraction and Separation of Rare Earth Ions. *ACS Central Science*. 2021, 7, 1908-1918.
2. Zhu Liang, Trung Vo, Karl J. Schweighofer, Ilan Benjamin, and Mark L. Schlossman. DEHP⁻ extractant binding to trivalent lanthanide Er³⁺: Fast binding accompanied by concerted angular motions of hydration water. *J. Chem. Phys.* 2023, 158, 134715.
3. Pan Sun, Erik A. Binter, Trung Vo, Ilan Benjamin, Mrinal K. Bera, Binhua Lin, Wei Bu, Mark L. Schlossman. Relevance of Surface Adsorption and Aqueous Complexation for the Separation of Co(II), Ni(II), and Fe(III). *J. Phys. Chem. B*. 2023, 127(15), 3505-3515.
4. Pan Sun, Xiao-Min Lin, Mrinal K. Bera, Binhua Lin, Dongchen Ying, Tieyan Chang, Wei Bu, Mark L. Schlossman. Metastable precipitation and ion-extractant transport in liquid-liquid separations of trivalent elements. *Proceedings of the National Academy of Sciences (USA)*. 2024, 121, e2315584121.

Polymeric Chelators for Rare-Earth Element Extraction and Separation

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¹Virginia Tech

Key Words: Bioinspired Recognition; Solvation; Thermodynamics

DE-SC0023035: Polymeric Chelators for Rare-Earth Element Extraction and Separation

PI: Michael Schulz

Research Project Scope.

In this project, we aim to study and ultimately control the interaction between polymers and metal ions (specifically rare-earth elements (REEs)) to improve extraction and purification processes. Our overarching hypothesis is that in addition to the specific chelating ligand, polymer structure affects metal chelation due to its effects on (1) the conformation and orientation of the chelating groups, (2) the secondary coordination sphere of the solvated metal, and (3) the solvent molecules (water) surrounding the polymer chelating group and the metal. We will elucidate these structure–property relationships of polymeric metal chelators by investigating the fundamental thermodynamics of the underlying polymer–metal interaction, primarily using isothermal titration calorimetry (ITC). This information directly corresponds to key materials parameters underpinning effective extraction and separation, including capacity, selectivity, and robustness to environmental perturbations.

Recent Progress.

We have synthesized linear modular polymers and appended ligands with systematic variations in the linker between the chelating site and the polymer backbone. We hypothesize that this change will both alter the hydrophobicity of the material as well as the conformational flexibility of the chelating ligand—both critical factors in metal binding. ITC experiments on this series of materials revealed complex polymer-metal interactions involving (de)solvation processes and conformational rearrangements. We also conducted a series of ITC experiments in solutions of varying ionic strength to shed light on the effects of salt identity and concentration on polymer-metal interaction thermodynamics.

To study tacticity effects on polymer-metal binding interactions, we synthesized a series of five poly(methacrylic acid)s with systematic variations in tacticity (20–99% m diads) and measured (by ITC) the thermodynamics of lanthanide binding to each material (ΔH , ΔG , ΔS , K_a , and stoichiometry). We found that both $|\Delta H|$ and $|\Delta S|$ decreased with decreasing m diad content, while ΔG remained roughly similar across the tacticity series (demonstrating enthalpy-entropy compensation). Molecular dynamics simulations of the polymer–metal interactions revealed that the observed differences in binding thermodynamics may be largely ascribed to differences in polymer flexibility, though we believe changes in solvation around the polymer backbone are also playing a role. These combined experimental and computational results demonstrate that metal binding can be influenced by altering the polymer stereochemistry, ultimately informing the design of more efficient metal-chelating materials.

Future Plans.

Briefly, we plan to more fully investigate effects of degree of polymerization, linker length effects, and metal-binding polysaccharides. We will expand our synthetic efforts on systematically varied pendant ligands appended to linear and branched polymers and branched topologies, and conduct ITC experiments on those materials. We will also leverage complementary techniques and computational experiments when appropriate.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. Gallagher, C. M. B.; Schulz, M. D., "Effect of Ionic Strength and Anion Identity on Rare-Earth Element Chelation by Poly(Acrylic Acid)", *Macromolecular Chemistry and Physics* **2023**, 224, 2300235. DOI: 10.1002/macp.202300235.
2. Archer, W. R.; Chen T.; Welborn, V. V.; Schulz, M. D., "Polymer tacticity effects in polymer-lanthanide chelation thermodynamics", *Macromolecules* **2023**, 56, 9062. DOI: 10.1021/acs.macromol.3c01163.

Grant cited but not intellectually led by this award:

1. Valerie Vassier Welborn, William R. Archer, Michael D. Schulz, "Characterizing Ion-Polymer Interactions in Aqueous Environment with Electric Fields", *Journal of Chemical Information and Modeling*, Published, DOI: 10.1021/acs.jcim.2c01048.
2. A. Matson, J. B.; Steele, A. Q.; Mase, J. D.; Schulz, M. D. "Polymer characterization by size-exclusion chromatography with multi-angle light scattering (SEC-MALS): a tutorial review" *Polym. Chem.* **2024**, 15, 127–142.

Active Transport in Complex, Heterogeneous, and Dynamic Environments

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Key Words: Confinement; Interfaces; Membranes; Transport Phenomena

DE-SC0001854: Single-molecule Dynamics in Complex and Interface-Rich Separations Environment

PI: Daniel K. Schwartz

Research Project Scope.

This research focuses on understanding the transport of solute molecules and nanoparticles in complex porous and non-porous environments. The project utilizes advanced single molecule/nanoparticle super-resolution imaging to capture high-resolution spatiotemporal trajectories across a wide range of time- and length-scales. Computational simulations are employed to analyze and interpret the experimental findings. We aim to enumerate and understand the microscopic mechanisms underlying transport (driven by thermal motion, pressure gradients, external fields, and self-propulsion) in separations environments that include real-world complexities such as inter-particle interactions, interfacial effects, dynamic motion of porous matrices, external force fields, and structural heterogeneity. The transport models resulting from these new insights are expected to enable advances in permeability of highly selective membranes, anti-fouling strategies, field-assisted separation design and porous materials design.

Recent Progress.

Despite extensive experiments and simulations, models that describe transport processes in complex settings remain a major challenge. Utilizing 3D single-nanoparticle super-resolution imaging, we capture high-resolution dynamics at both macroscale and sub-microscale, allowing us to generate a transport model for realistic complex systems. For example, we have developed and employed a *successive-escape* model to describe the long-time diffusive motion of nanoparticles in porous environments. In analogy with a random walk, by dividing the transport into multiple cavity escape events, a linear correlation is observed between the long-time ensemble-averaged diffusion coefficient (D) and a quantity involving the characteristic cavity size (r) and particle trapping time (t_{trap}): $D \sim r^2/t_{\text{trap}}$, where the proportionality coefficient depends on pore accessibility. This correlation is broadly applicable to heterogeneous

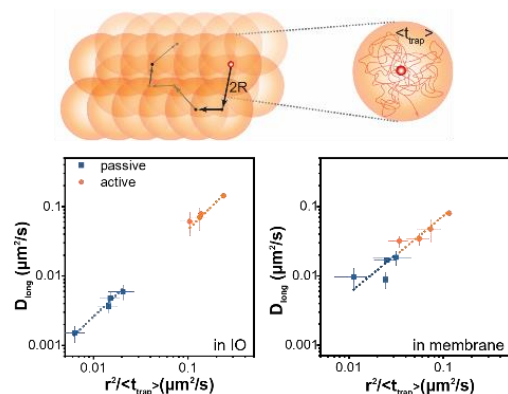


Figure 1. $D_{\text{long}} \sim r^2/t_{\text{trap}}$ for different nanoparticles in environments with varied heterogeneity.

environments (e.g., filtration membranes) and regardless of the mechanism driving particle motion (e.g., Brownian motion and self-propulsion), offering a succinct connection between nanoscopic structures and dynamics to macroscopic effective diffusivity.

In previous work under this award, we found that self-propelled nanoparticles exhibit anomalously fast motion in interconnected porous environments vs. unconfined liquid. This rapid transport was due to a unique surface-searching mechanism for cavity exits and the ability to overcome electrostatic barriers. In the current reporting period, we found that within confined and interconnected porous environments, self-propelled nanoparticles generate effects that greatly enhance the motion of coexisting passive Brownian particles. In a porous medium these hydrodynamic/electrokinetic interactions are greatly amplified and act over long distances (at least 10 body lengths) (Fig. 2A). This unique extended hydrodynamic effect in porous media suggests the potential of dilute nanomotors as mobilizers of passive species in confined pore spaces, even when incorporated at very low concentrations.

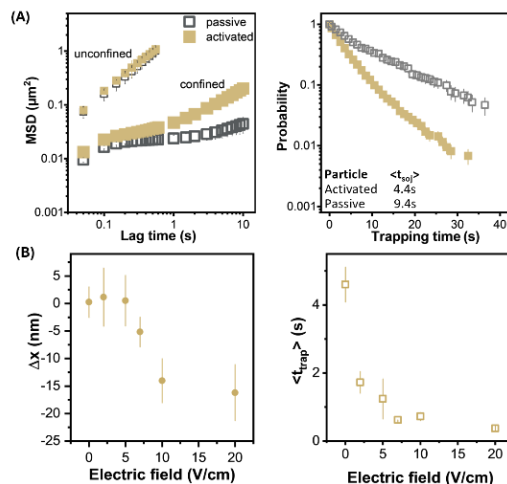


Figure 2. (A) Activated transport by extended hydrodynamic effects; (B) Independence of transport bias and efficiency with electric fields.

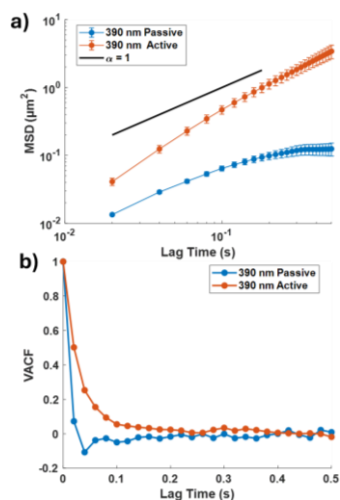


Figure 3. Transport of 390nm Janus particle in a dynamic highly confining environment. (a) Mean squared displacements of active and passive 390 nm tracer particles in a highly confined fluctuating environment. (b) Velocity autocorrelation function of the particles from part (a).

We are leveraging the methods and modeling used to study diffusive and self-propelled motion to study the fundamental mechanisms of electrophoretic motion of charged nanoparticles in porous environments. Specifically, in the context of a successive cavity escape model, the cavity escape time and directional bias both contribute to overall field-driven drift, and by employing single-particle tracking we are studying the effects of these two phenomena independently. Unexpectedly, while the cavity escape time is observed to decrease dramatically under the influence of a low DC field, the directional bias of cavity escape does not become significant until the electric field strength reaches a critical value (Fig. 2B). This observation revealed a surprising decoupling between cavity translocation and directional transport bias driven by an external field. With our theoretical collaborators, we are currently seeking to understand the electrokinetic origins of these phenomena.

We are also studying the effects of porous matrix complexity in the form of dynamic motion. In previous work under this award, we compared the diffusion of nanoparticles within static and fluctuating porous environments that were otherwise structurally identical, and found that thermal matrix fluctuations increased the effective diffusion of probe particles by approximately 50%. This was due to a combination of accelerated short-time diffusion and a concerted “gate-opening” mechanism that allowed probe particles to escape from highly confined scenarios. In the current reporting period, we investigated how thermal fluctuations of a porous matrix affect active nanoswimmer transport. Our findings indicate a

synergistic coupling of active particle motion and matrix fluctuations that is dramatically influenced by the level of confinement. At lower levels of confinement (i.e. greater free volume), self-propelled nanoparticles exhibit only modest transport enhancement over Brownian particles, similar to that observed in unconfined liquid. Surprisingly, at very high degree of confinement, active nanoparticles exhibit transport that is not only anomalously fast, but also superdiffusive and positively correlated (Figs. 3A, 3B). This emergent behavior manifests as persistent, seemingly intelligent motion. Interestingly, the efficiency of transport is not only dramatically greater than that of Brownian nanoparticles within the porous medium but even greater than Brownian particles in unconfined liquid. Moreover, the motion itself is distinctive, with directional bias persisting much longer than the characteristic rotation time in free fluid, and the superdiffusive behavior endures, with an anomalous exponent of 1.45 over all timescales observed. These findings suggest that technologies incorporating active particle transport may offer greater advantages than previously anticipated, as the nuances in particle and medium dynamics significantly enhance the transport process.

In the current grant period, we have also developed methods to study the transport of ions in dense polymer materials that are used in a variety of energy technologies, including energy storage devices, ion exchange membrane fuel cells, redox flow batteries, and solid-state lithium batteries. The ion diffusion coefficient (D_{ion}) is a key parameter in theoretical models of ion-polymer interactions to predict the limiting current and is commonly measured macroscopically using NMR and electrochemical techniques. Remarkably, using single-molecule fluorescence microscopy (TIRFM), our observations revealed severe sub-diffusion of fluorescent anions in Nafion membranes. Analysis of MSDs showed significant decays in time-dependent 2D diffusion coefficients across various time and length scales (Fig. 4). These results indicate that D_{ion} in polymer conductivity models is not a well-defined parameter as previously assumed. Our ongoing research aims to identify the nature of this anomalous ion diffusion and its dependence on solvent effects and membrane chemistry, complementing the gap in the understanding of sub-diffusive motion in proton/ion exchange membranes and polymer electrolytes.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. Daniel F. Kienle and Daniel K. Schwartz, "Single molecule characterization of anomalous transport in a thin, anisotropic film," *Analytica Chimica Acta*, **1154**, 338331 (2021); doi:10.1016/j.aca.2021.338331
2. Raphael Sarfati, Christopher P. Calderon, and Daniel K. Schwartz, "Enhanced Diffusive Transport in Fluctuating Porous Media," *ACS Nano*, **15**, 7392-7398 (2021); doi:10.1021/acsnano.1c00744
3. Haichao Wu, Benjamin Greydanus, and Daniel K. Schwartz, "Mechanisms of Transport

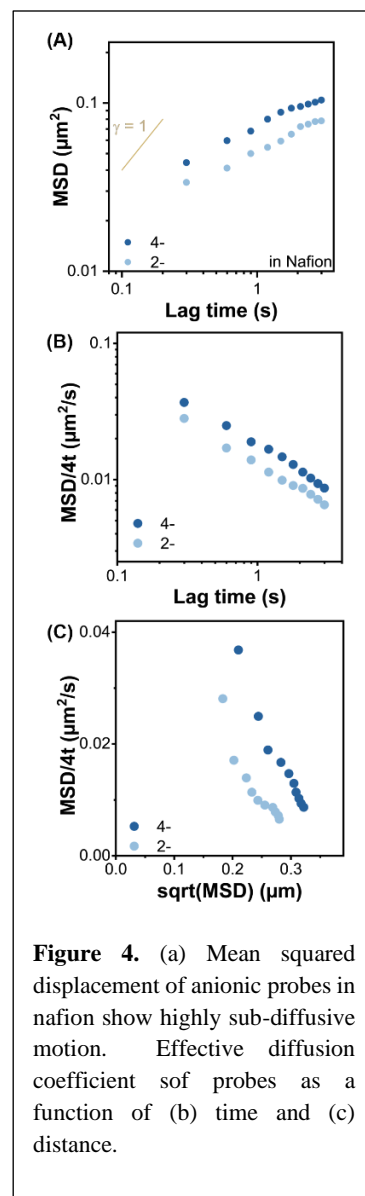


Figure 4. (a) Mean squared displacement of anionic probes in nafion show highly sub-diffusive motion. Effective diffusion coefficient of probes as a function of (b) time and (c) distance.

Enhancement for Self-Propelled Nanoswimmers in a Porous Matrix,” *Proceedings of the National Academy of Sciences*, **118**, e2101801118 (2021); doi:10.1073/pnas.2101807118

4. Gregory T. Morrin and Daniel K. Schwartz, “Diffusion of Short Semi-Flexible DNA in Strong and Moderate Confinement,” *ACS Macro Letters*, **10**, 1191-1195 (2021); 10.1021/acsmacrolett.1c00470
5. Anni Shi, Daniel K. Schwartz, “Bridging Macroscopic Diffusion and Microscopic Cavity Escape of Brownian and Active Particles in Irregular Porous Networks.” *ACS Nano*. 2024, in press
6. Anni Shi, Haichao Wu, Daniel K. Schwartz, “Nanomotor-enhanced transport of passive Brownian particles in porous media.” *Science Advances*. 2023, 9(43), eadj2208.

Grant cited but not intellectually led by this award:

1. Ohad Vilka, Erez Aghion, Carsten Beta, Oliver Nagel, Matthias Weiss, Adal Sabri, Diego Krapff, Raphael Sarfati, Daniel K. Schwartz, Ralf Metzler, Ran Nathan, Michael Assafa, “Unravelling the Origins of Anomalous Diffusion: from Molecules to Migrating Storks,” *Phys. Rev. Research*, **4**, 033055 (2022) doi:10.1103/PhysRevResearch.4.033055

Probing Phase Transitions and Mesoscale Aggregation in Liquid-Liquid Extraction of Rare Earths

Michael Servis, Brian Stephenson, Tasnim Rahman, Brittany Bonnett, Allison Peroutka

Argonne National Laboratory

Key Words: Dynamics; Liquid-Liquid Phase; Thermodynamics; Theory/Simulation

DE-AC02-06CH11357: Probing Phase Transitions and Mesoscale Aggregation in Liquid-Liquid Extraction of Rare Earths

PI: Michael Servis; co-PI: Brian Stephenson, Subramanian Sankaranarayanan

Research Project Scope.

Recovery and recycling of critical materials through chemical separations enables a wide range of important technologies. The predominant method for rare earth separations is liquid-liquid extraction (LLE). In this project, we connect two key phenomena in LLE of metal ions: phase splitting of the organic phase and the impact of organic phase aggregation extraction energetics. Our ongoing work demonstrates how these phase splitting and aggregation are fundamentally connected. Using the theory of critical phenomena, we can quantify and understand the aggregation behavior of these complex, multi-component systems with remarkably generality. By connecting x-ray scattering measurements of critical fluctuations with molecular simulation and thermodynamic modeling, we are creating a comprehensive picture spanning lengthscales of the relationships between molecular structure and composition with aggregation and phase behavior.

Recent Progress.

We have developed a strategy for combining 1) experiment (SAXS and XPCS), 2) thermodynamic modeling and 3) molecular simulation. This provides a cohesive picture, where each provides unique information while also providing overlap between each other technique for validation and comparison (Fig. 1). We performed small angle x-ray scattering (SAXS) and x-ray photon correlation spectroscopy data (XPCS), finding that structure across the entirety of a complex (4-component) phase diagram results from critical fluctuations, providing concrete and robust justification for our governing hypotheses. Temperature-dependent SAXS data allowed us to fit static critical exponents, demonstrating universal scaling of the fluctuations between these systems. We used scaling laws to show linear relationships between solute concentration and spinodal temperature, providing a fundamental link between composition and temperature. XPCS data of the 4-component systems show that the dynamic also show scaling consistent with critical phenomena theory.

Using experimental composition data, we have developed a

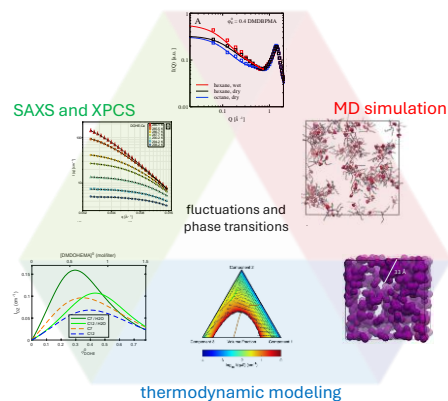


Figure 1. Combined scattering, simulation and thermodynamic modelling approach.

thermodynamic model for phase equilibria in ternary LLE systems. This model can quantitatively capture the water extraction behavior across the entire range of extractant concentrations. We developed a method to calculate fluctuations from just the thermodynamic model, allowing us to predict scattering at all temperatures and compositions. This enabled us to connect macroscopic behavior (compositions, fluctuation intensities, phase boundaries, critical compositions) with molecular-scale descriptions of solution speciation, linking experimental data to molecular simulation. In addition to all-atom models of ternary and quaternary systems, we implemented coarse-grained simulations of binary mixtures where we extract static and dynamic temperature scaling. This involved developing computational capabilities to calculate dynamic scattering that is directly analogous to experimental XPCS measurements. We are using this capability to analyze dynamic scattering from simulation, which provides a real-space picture of where dynamic scattering comes from, including isolating diffusive and phonon contributions at different scattering wavevectors.

Peer Reviewed Publications Acknowledging this Grant in 2023-2024.

Intellectually led by this grant:

1. Rahman, T., Bonnett, B. L., Poe, D., Wimalasiri, P. N., Seifert, S., Lal, J., Stephenson, G. B., Servis, M. J., Decomposition of liquid-liquid extraction organic phase structure into critical and pre-peak contributions. *Journal of Molecular Liquids*, **2024**, 393, 123625.
2. Bonnett, B. L., Rahman, T., Poe, D., Seifert, S., Stephenson, G. B., & Servis, M. J., Insights into Water Extraction and Aggregation Mechanisms of Malonamide-Alkane Mixtures. *Physical Chemistry Chemical Physics*, **2024**, 26, 18089-18101.
3. Bonnett, B. L., Sheyfer, D., Wimalasiri, P. N., Nayak, S., Lal, J., Zhang, Q., Seifert, S., Stephenson, G. B., Servis, M. J. *Physical Chemistry Chemical Physics*. **2023**, 25, 16389-16403.
4. Chandra, A., Loeffler, T., Chan, H., Wang, X., Stephenson, G. B., Servis, M. J., Sankaranarayanan, S. K. *The Journal of Chemical Physics*. **2023**, 159, 024114.

Grant cited but not intellectually led by this award:

1. Poe, D., Seifert, S., & Servis, M. J., Molecular-scale understanding of diluent effects on ligand assembly for metal ion separations. *Physical Chemistry Chemical Physics*, **2024**, 26 (19), 14108–14121.
2. Nayak, S., Servis, M. J., Combs, D., Szeliga, K., & Seifert, S., Speciation and organic phase structure in nitric acid extraction with trioctylamine. *The Journal of Physical Chemistry B*, **2024**, 128 (13), 3236–3248.

Receptor-based Approaches to Separations

Jonathan L. Sessler,¹ Sheng-Yin Huang,¹ Gabriel Juarez¹

¹The University of Texas at Austin

Key Words: Inorganic Chelation; Non-Thermal Separation Mechanisms; Organic Ligand Recognition; Solvation

DE-SC0024393: Receptor-based Approaches to Separations

PI: Jonathan L. Sessler

Research Project Scope.

This project commenced September 1, 2023. It has three primary objectives that consist of i) enhancing the selectivity, affinity, and reversibility of immobilized supramolecular receptors that may compete with, or outperform current separations of critical elements (i.e., Li, Co Ni, Ln), ii) developing receptors that allow the pH of a caustic aqueous medium to be lowered via direct capture of basic anions, such as hydroxide and carbonate, and iii) preparing new ligands that allow for optical-based sensing of the f-elements while facilitating purification. All three of these objectives involve separations, relate to chemical species, and address unsolved problems relevant to the DOE mission. These problems include tank waste remediation, critical materials recycling, and f-element purification.

Recent Progress.

Cobalt extraction

Cobalt recycling from electronic waste has been recognized as a sustainable and ethical solution to the growing demand for this critical material. Therefore, we designed a new system that utilized high-performance ion separation by tuning pore size and geometric control. Our approach combines highly selective supramolecular receptors, nanoporous materials, and high-resolution 3D printing. Supported receptors were prepared using polymerization-induced phase separation (PIPS) from a photocurable resin. This resin was used to install nanopores during the DLP printing process. A cobalt-selective methacrylate functionalized tetradentate bisdicyclohexyl acetamide (BDCA) receptor was directly incorporated into the 3D prints. A polymerizable methacrylate handle was installed on the BDCA receptor, resulting in the modified receptor BDCA-MA. This modified receptor was then used for copolymerization with carbitol acrylate initiated by phenylbis-(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO). The 3D printing nanoporous via PIPS was obtained and then cast in films between glass slides with 75 mm spacers and irradiated, yielding a range of monomer to porogen ratios, and 1-decanol to cyclohexanol ratios. This strategy allowed us to obtain resins with tunable pore size (pore diameter = 100–270 nm) and receptor content. We prepared three resins bearing different microarchitectures (cube, kelvin, and gyroid) and the Co²⁺ binding profiles were carried out in anhydrous ethanol, which exhibited effective CoCl₂ binding. A change in solvent polarity achieved when contacted with water was used to release Co²⁺. The Freundlich isotherms of BDCA in the presence of other cations (Li⁺ and Mn²⁺), revealed that the resins are selective for cobalt. This work was carried out in collaboration with the group of Prof. Page at The University of Texas at Austin. It was published in 2024 in the *J. Am. Chem. Soc.* A patent application was also filed.

Thermal-based cobalt capture

Quite recently we explored the heat-driven catch-and-release of CoCl_2 using an immobilized neutral dicyclohexylacetamide-based receptor (L). We used a hexadentate ligand (L) that allows us to use 95% EtOH and overcome the high hydration energy of Co^{2+} . We took advantage of cobalt's thermochromism coordination transition in ethanol to enable heat-mediated catch and release of cobalt. We employed an immobilized receptor onto chemically inert polystyrene to obtain a solid substrate for an efficient capture and release process. Cobalt binding by L was investigated by UV-vis spectroscopy at various temperatures (22 °C to 65 °C), wherein a dramatic change from octahedral to tetrahedral coordination occurred. Upon adding two equivalents of L, only octahedral cobalt coordination was observed and binding constants increased from 40.8 M^{-1} to 111 M^{-1} . The heat-mediated catch-and-release of CoCl_2 was studied using receptor-functionalized polystyrene PS-L at variant temperatures in 95% ethanol. The absorption isotherms revealed that a rise of cobalt uptake by PS-L was achieved with rising temperature ($K = 33.6 \text{ M}^{-1}$ to 88.5 M^{-1}). The absorption spectrum analysis of the dried PS-L cobalt-containing system corresponded to octahedral and tetrahedral species, supporting the conclusion that CoCl_2 binds to the PS-L ligand as a $[\text{PS-L} \times \text{Co}] \cdot [\text{CoCl}_4]$. Analysis of the inductively-coupled plasma mass spectrometry (ICP-MS) results after exposure of PS-L to the mixture ($\text{NiCl}_2:\text{CoCl}_2:\text{MnCl}_2$, 33.6%:32.2%:34.2%) for 12 h at 72 °C followed by an exposure of the resin to fresh ethanol for 12 h at 22 °C, revealed a recovery of 52% of Co^{2+} . Therefore, our PS-L resin exhibits higher binding affinity for CoCl_2 than NiCl_2 and MnCl_2 , with a process mediated by heat. This work, carried out in collaboration with Dr. Byranstev and coworkers at Oak Ridge National Lab, has just been published on line in the *J. Am. Chem. Soc.* in 2024.

ExJade-Ln coordination

Industrial separation of lanthanides and actinides remains heavily reliant on liquid-liquid extractions (LLEs) and ion exchange resins. The Sessler group has identified an alternative selective precipitation process using derivatives of the metal chelator deferasirox (ExJade). A first report involving the separation of lutetium from other lanthanides was published prior to the start of this grant. Current work, being carried out in collaboration with Dr. Tondreau of the Los Alamos National Laboratory, involves looking at ExJade derivatives as ligands for the actinides. No papers have as yet come from this effort.

Coordination of Th by expanded porphyrins

We explored the axial coordination chemistry of thorium when coordinated to an expanded porphyrin. The organometallic complex $[\text{Th}(\text{dipyriamethyrin})(\text{Cp})\text{F}]$ (**1**) was obtained in 94% yield by reacting NaCp with $[\text{Th}(\text{dipyriamethyrin})\text{Cl}_2]$ (**2**) in a glass scintillation vial. Single crystal X-ray diffraction analysis revealed an octahedral coordination complex wherein the Cp is coordinated in one axial position and a fluoride anion is coordinated in the other axial position. The anion exchange observed in the complex was attributed to the reaction of the cationic intermediate **1**⁺ with the fluoride ions present in the scintillation glass vial. Additionally, we observed that in the solid state, the dipyriamethyrin ligand in **1** retained its characteristic buckled geometry. UV-vis spectroscopic analysis of **1** revealed the formation of a new peak at 428 nm; however, its spectrum is similar to that of complex **2**, which was rationalized as Cp coordination causes no gross changes to the core electronic configuration of the expanded porphyrin. Reaction with benzoate yielded a Th(IV)-dipyriamethyrin complex with two benzoates coordinated in the axial positions. Passing from the strongly basic Cp anion to the weakly basic benzoate resulted in a shortening of the separation between the thorium and the porphyrinoid core. The shortening of these bonds is taken as an indication that

weakening the axial ligand–Th(IV) leads to a strengthening of the in-plane porphyrinoid Th(IV)actinide cation interactions. This work was published in *ChemComm* in 2023.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. D. N. Mangel, J. T. Brewster, Juarez, G. J., V. M. Lynch, J. L. Sessler. Cyclopentadienyl capped thorium(IV) porphyrinoid complex *ChemComm*, 2023, 60, 1020. DOI: 10.1039/D3CC05283
2. K. Mason, S.-Y.; Huang, S. K. Emslie, Q. Zhang, S. M. Humphrey, J. L. Sessler, Z. A. Page 3D Printed Porous Supramolecular Sorbents for Cobalt Recycling, *Journal of the American Chemical Society*, 2024, 146, 4078. DOI: 10.1021/jacs.3c12635.
3. S.-Y.; Huang, D. Ray, Q. Zhang, J. Yang, V. S. Bryantsev, J. L. Sessler Thermally-Driven Catch-and-Release of CoCl₂,” *Journal of the American Chemical Society*, 2024, online. DOI: [10.1021/jacs.4c07530](https://doi.org/10.1021/jacs.4c07530)

Grant cited but not intellectually led by this award:

1. N. J. Heo, J. H. Oh, A. Li, K. Lee, Q. He, J. L. Sessler, S. K. Kim Ion Pair Extractant Selective for LiCl and LiBr, *Chemical Science*, accepted.

Engineering Non-aqueous Solutions for Reactive Carbon Capture

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¹Oklahoma State University, ²University of Illinois, Chicago

Key Words: Direct Air Capture; Field-Driven Separations; Reactive Separations; Solvation; Theory/Simulation

DE- DE-SC0022321: Ionic Liquids for Direct Air Capture of CO₂ using Electric-Field-Mediated Moisture Gradient Process

PI: Jindal Shah; co-PI: Meenesh Singh

Research Project Scope. The overall objective of the proposed research is to address limitations of the current direct air capture technologies by using ionic liquid-organic solvent mixtures to capture CO₂ and driving the transport of product of the reaction across a membrane using electric field. The combined experimental and molecular simulation-based approach involves screening of ionic liquid solutions for ionic conductivity and CO₂ solubility and providing theoretical and atomistic-level detailed understanding of structure-property relationships for selection of mixture for direct air capture of CO₂. The project also focuses on evaluating the gains in the energy efficiency when ionic liquid-organic mixtures are employed for CO₂ capture. The relevance of the project to the Separations Sciences program stems from its emphasis on removal of species in dilute concentrations and decarbonization towards a net-zero economy.

Recent Progress.

The project has enabled development of two high-throughput screening systems that are based on conductivity measurements of solutions: (a) CO₂ solubility in ionic liquids is obtained based on cyclic voltammogram; (b) determination of ionic conductivity of ionic solutions. Measurements from automated system coupled with quantum mechanical calculations have generated fundamental understanding of molecular-level factors such as the role of electrostatic interactions and void fractions in ionic liquids responsible for CO₂ solubility and permeance in ionic liquids.¹ Similarly, we have been able to establish a theoretical framework elucidating the behavior of ion mobility on the ionic conductivity maximum observed in ionic liquid-organic solvent (ethylene glycol) mixtures.² The relative ion dissociation concept provided a clear explanation for ion mobility and thus the overall ionic conductivity across the entire concentration range, from dilute solutions to neat ionic liquids. This behavior can be attributed to the interplay between free ions and viscous forces, which impact ion diffusion and ultimately affect ionic conductivity. We were able to identify that the ionic liquid 1-ethyl-3-methylimidazolium dicyanamide when mixed with ethylene glycol (EG) (60:40 molar ratio) resulted in the maximum ionic conductivity of 3.4 S/m amongst all the ionic liquid simulations examined. When employed in the migration-assisted moisture gradient process (MAMG), the ionic liquid solution offered

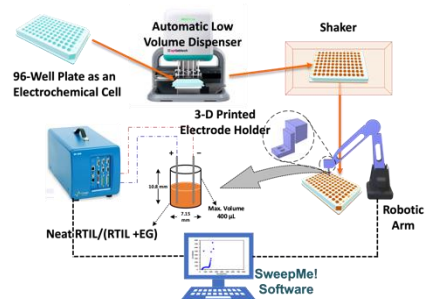


Figure. High-throughput screening of ionic solutions for ionic conductivity

superior conductivity and energy efficiency for CO₂ capture when compared with ionic liquid-free solutions highlighting the promising role ionic liquids are likely to play in the MAMG process.

Molecular dynamics simulations of 1-ethyl-3-methylimidazolium tetrafluoroborate and its mixtures with EG revealed that the fluctuations in the number of ions in the first solvation of cations and anion play a pivotal role in the determination of ionic conductivity with highest fluctuations coinciding with experimentally observed ionic conductivity maximum. This approach opens up another avenue for screening ionic liquid-organic solvent mixtures and narrowing the concentration range over which experiments need to be carried out to identify concentrations at which ionic conductivity maximum is observed which is directly coupled to the energy efficiency of the MAMG process. Quantum mechanical calculations on various KOH-EG molar ratios identified the presence of multiple hydrogen bonding interactions and variation in the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies providing us clues to the reactivity of these solutions towards CO₂.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. R. Chauhan, R. Sartape, R. Mishra, J. K. Shah, M. R. Singh. High-throughput measurements of CO₂ permeance and solubility in ionic liquid reveal a synergistic role of ionic interactions and void fractions. Chemical Engineering Journal, 2024, 496, 153697.
2. A. S. Thorat, R. Chauhan, R. Sartape, M. R. Singh, J. K. Shah. Effect of K⁺ Force Fields on Ionic Conductivity and Charge Dynamics of KOH in Ethylene Glycol. The Journal of Physical Chemistry B. 2024, 128(15), 3707-3719.
3. R. Chauhan, R. Sartape, A. S. Thorat, J. K. Shah, M. R. Singh. Theory-Enabled High-Throughput Screening of Ion Dissociation Explains Conductivity Enhancements in Diluted Ionic Liquid Mixtures. ACS Sustainable Chemistry & Engineering. 2023, 11 (41), 14932-14946.

Grant cited but not intellectually led by this award:

1. M. R. Singh, P. G. Singh, V. V. Gande, R. Chauhan, N. Minocha Simplified Universal Equations for Ionic Conductivity and Transference Number. Journal of the Electrochemical Society. 2024, 171, 073502.
2. R. Chauhan, R. Sartape, N. Minocha, I. Goyal, M. R. Singh. Advancements in Environmentally Sustainable Technologies for Ethylene Production. Energy and Fuels, 2023, 37, 12589-12622.
3. A. Prajapati, R. Sartape, T. Rojas, N. K. Dandu, P. Dhakal, A. S. Thorat, J. Xie, I. Bessa, M. T. Galante, M. H. S. Andrade, R. T. Somich, M. V. Rebouças, G. T. Hutras, N. Diniz, A. T. Ngo, J. K. Shah, M. R. Singh. Reply to the ‘Comment on “Migration-assisted, moisture gradient process for ultrafast, continuous CO₂ capture from dilute sources at ambient conditions”’ by J. Casado, *Energy Environ. Sci.*, 2022, 10.1039/D2EE00555G. Energy and Environmental Science. 2022, 15 (9), 3994-3996.
4. A. Prajapati, R. Sartape, T. Rojas, N. K. Dandu, P. Dhakal, A. S. Thorat, J. Xie, I. Bessa, M. T. Galante, M. H. S. Andrade, R. T. Somich, M. V. Rebouças, G. T. Hutras, N. Diniz, A. T. Ngo, J. K. Shah, M. R. Singh. Migration-assisted, moisture gradient process for ultrafast, continuous CO₂ capture from dilute sources at ambient conditions. Energy and Environmental Science. 2022, 15 (2), 680-692.

Securing the supply chain of lithium by unlocking unconventional lithium resources through sustainable electrochemical leaching

Feifei Shi¹

¹Penn State University

Key Words: Interfaces; Reactive Separations; Thermodynamics; Transport Phenomena

DE-SC0025307: Project Title: Securing the supply chain of lithium by unlocking unconventional lithium resources through sustainable electrochemical leaching

PI: Feifei Shi

Research Project Scope.

Lithium (Li), a key element in batteries for electric cars and other devices, has experienced a major demand surge in the past decade. While the primary source of lithium is from salt lakes, lithium-containing ores and clay sources are widely distributed in the US and offer a potential alternative source for this important element. The challenge of using lithium found in clays and ores is separating the element from the complex sample, a process that is, in part, limited by the low reactivity of the aluminosilicate host structure. Current separation methods for lithium from ores or clay require high energy and/or chemical consumption needs. The objectives of this research are to develop a sustainable, electrochemical-facilitated leaching method to extract lithium from ores and clay.

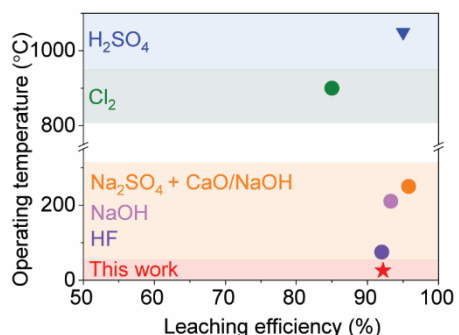


Figure.1 State-of-art of leaching technologies for Li-containing ores

Recent Progress.

We developed an electrochemical based leaching technology to selectively separate Li ions from spodumene ores. Faradaic efficiency of 72.2% and leaching efficiency of 92.2% are achieved at room temperature.

Future Plans.

We plan to further the electrochemical leaching mechanism on other Li-containing ores and improve the efficiency.

Role of Energy in Continuous Dielectrophoretic Separations

Craig Snoeyink¹, Gaurav Anand¹

¹University at Buffalo

Key Words: Field-Driven Separations; Non-Thermal Separation Mechanisms; Thermodynamics; Transport Phenomena

DE-SC0025463: Role of Energy in Continuous Dielectrophoretic Molecular Separations

PI: Craig Snoeyink

Research Project Scope.

Dielectrophoretic molecular separations is orders of magnitude more effective than predicted by current models. This project hypothesizes that models can be made more accurate through a local coupling of the electric and solution composition. Using high electric-field microfluidics that provide optical access to the solution this hypothesis will be tested and models for separations efficiency, throughput, and sensitivity will be developed. Special attention will be paid to how small variations in solvent-solute molecular interactions, like those in the rare-earth series ions, will impact transport rates and selectivity.

Recent Progress.

Preliminary implementations of this model, results of which are shown in the figure, predict concentration changes that are within a factor of 3 of experimental results. This is a large improvement over prior models which underestimate concentration variations due to the electric field by over two orders of magnitude.

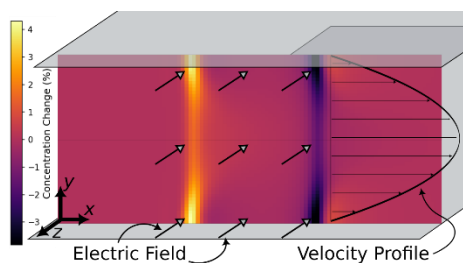


Figure. 2D simulation of dielectrophoretic molecular separations assuming a local coupling of electric field strength and solution composition.

Investigation of Thermodynamic and Kinetic Selectivity Mechanisms In Redox-Mediated Electrochemical Separations

Xiao Su, Riccardo Candeago, Kihyun Cho, S. Cotty, Raylin Chen, Ade Faniyan, Johannes Elbert

Department of Chemical and Biomolecular Engineering, University of Illinois Urbana-Champaign

Key Words: Field-Driven Separations; Interfaces; Reactive Separations; Solvation

DE- SC0021409: Investigation of Thermodynamic and Kinetic Selectivity Mechanisms In Redox-Mediated Electrochemical Separations

PI: Xiao Su

Research Project Scope. The development of new ion-selective technologies is key for critical element recovery and environmental remediation. Separation of valuable transition metal ions from a “needle-in-a-haystack” challenge, where aim to discriminate between elements close in size, valency, and chemical structure, in the presence of excess competing salts. Electrochemically-driven separation processes can offer a sustainable and modular pathway for removing ions, by controlling the adsorption and release based solely on electrochemical control. However, molecular selectivity remains a major challenge. Within this project, we leverage redox-active polymers as heterogeneous electrosorbents, which can be a powerful platform by offering control of specific binding through reversible electron-transfer. We seek to elucidate key selectivity mechanisms in redox-interfaces, including electrostatics, solvation, and charge-transfer effects during ion-adsorbate binding, by integrating operando electrochemical methods (including neutron reflectometry), with thermodynamic binding studies and macroscopic electrosorption measurements. Our proposed research is expected to advance fundamental understanding of the electrochemically-driven molecular separations, and establish design rules tailored molecular selectivity, which can lead to low waste, energy-efficient, and highly modular separation technologies.

Recent Progress.

Through the project, we have explored supramolecular binding mechanisms of redox-polymers, including controlling underlying thermodynamic and kinetic effects, and evaluating their impact on electrochemically-driven molecular selectivity.¹⁻⁸ Through the rational design and synthesis of new redox-polymers and copolymers, we precisely tune the of electric field, solvation, and charge-transfer interactions to achieve multicomponent selectivity towards for rare-earth elements (REEs),² and valuable transition metals such as cobalt, nickel, rhenium and molybdenum.^{1-4, 17} Through synthetic control of the redox unit and structural position, we have modulated selectivity towards transition metal oxyanions (*e.g.*, subtle differences ion selectivity using main-chain polymers vs side-chain polymers), and demonstrated electrochemically-controlled adsorption and release.¹

Fundamentally, we have elucidated of ion–solvent–polymer interactions, in combination with the rational design of tailored copolymers. We created a thermo-electrochemical responsive polymer of N-isopropylacrylamide (NIPAM) and ferrocene redox-units, which can tune ion selectivity between oxyanions based on copolymer ratio, applied potential, and temperature.⁴ Through a collaboration, with Oak Ridge National Laboratory we have unraveled solvation effects, through a combination of in-situ neutron reflectometry and computational simulations.^{3-4, 14} Solvation and ion valency play a critical role in

determining macroscopic selectivity for redox-polymers under potential. Finally, we have translated these concepts of electrochemical separations for both electrosorption and continuous extraction platforms, implementing them for the ion-selective recovery of valuable elements from waste streams.⁷⁻⁸ To date, the project has yielded 8 directly related papers,¹⁻⁸ 3 submitted U.S. patents⁹⁻¹¹, and 6 associated papers.¹²⁻¹⁷

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. R. Chen, J. Feng, J. Jeon, T. Sheehan, C. Ruttiger, M. Gallei, D. Shukla, X. Su. “Structure and Potential-Dependent Selectivity in Redox-Metallopolymers: Electrochemically Mediated Multicomponent Metal Separations.” *Advanced Functional Materials*, **2021**, 31 (15), 2009307.
2. H. Vapnik, J. Elbert, X. Su. “Redox-Copolymers for the Recovery of Rare-Earth Elements by Electrochemically-Regenerated Ion Exchange.” *Journal of Materials Chemistry A*, **2021**, 9, 20068-20077.
3. R. Candeago, H. Wang, M.T. Nguyen, M. Doucet, V.A. Glezakou, J. F. Browning, X. Su, “Unraveling the Role of Solvation and Ion Valency on Redox-Mediated Electrosorption through In Situ Neutron Reflectometry and Ab Initio Molecular Dynamics,” *JACS Au*, **2024**, 4, 3, 919–929.
4. R. Chen, H. Wang, M. Doucet, J. Browning, X. Su, “Thermo-Electro-Responsive Redox-Copolymers for Amplified Solvation, Morphological Control, and Tunable Ion Interactions,” *JACS Au*, **2023**, 3, 12, 3333-3344.
5. K. Cho, R. Chen, J. Elbert, X. Su, “Redox-functionalized Semiconductor Interfaces for Photoelectrochemical Separations,” *Small*, **2023**, 2305275.
6. N. Kim, W. Oh, K. N. Knust, F. Z. Galetto, X. Su, “Molecularly Selective Polymer Interfaces for Electrochemical Separations,” *Langmuir*, **2023**, 39, 47, 16685–16700
7. S. Cotty, N. Kim, X. Su, “Electrochemically Mediated Recovery and Purification of Gold for Sustainable Mining and Electronic Waste Recycling,” *ACS Sustainable Chemistry & Engineering*, **2023**, 11, 9, 3975-3986.
8. S. Cotty, A. Faniyan, J. Elbert, X. Su, “Redox-Mediated Electrochemical Liquid-Liquid Extraction (e-LLE) for Selective Metal Recovery,” *Nature Chemical Engineering*, **2024**, **1**, 281–292 (2024).
9. X. Su, H. Vapnik, J. Elbert, U.S. Patent Application No. 18/568,609. *Electrochemically-Regenerated Ion Exchange Using Redox-Polymers*.
10. X. Su, S. Cotty, Ade Faniyan, No. 18/739,942, *Electrified Liquid-liquid Extraction System for the Selective Extraction of Precious Metal Species*.
11. X. Su, S. Cotty, U.S. Provisional patent application. No.: 18/436,586. *Electrochemical System And Method For Selective Recovery Of Gold From Electronic Waste And Mining Streams*.

Grant cited but not intellectually led by this award:

1. C. H. Chung, S. Cotty, J. Jeon, J. Elbert, X. Su, “Auto-oxidation of Redox-Electrodes for the Selective Recovery of Platinum Group Metals,” *Journal of Materials Chemistry A*, **2024**, 12, 15006 – 15018.
2. M. Doucet, R. Candeago, H. Wang, J. F. Browning, X. Su, “Studying Transient Phenomena in Thin Films with Reinforcement Learning,” *Journal of Physical Chemistry Letters*, **2024**, 15 (16), 4444-4450.
3. Y. Kim, K. Kim, H. Eom, X. Su, J. Lee. “Electrochemically-assisted Removal of Cadmium Ions by Redox Active Cu-based Metal-organic Framework.” *Chemical Engineering Journal*, **2021**, 421, 129765.
4. K. Kim, R. Candeago, G. Rim, D. Raymond, A.H. Park, X. Su. “Electrochemical Approaches for Selective Recovery of Critical Elements in Hydrometallurgical Processes of Complex

- Feedstocks.” *iScience*, **2021**, 24 (5), 102374. *Special Issue on Material Criticality*.
5. K. Kim, D. Raymond, R. Candeago, X. Su. “Selective cobalt and nickel electrodeposition for lithium-ion battery recycling through integrated electrolyte and interface control.” *Nature Communications*, **2021**, 12, 6554.

Data Science-Enabled Ion Transport in Metallopolymer-Based Anion-Exchange Membranes

Chuanbing Tang, Qi Wang, Sophia Garashchuk

University of South Carolina

Key Words: Machine Learning/AI; Membranes; Theory/Simulation; Transport Phenomena

DE- SC0020272: Data-Science Enabled Investigation of the Mechanisms for Multiscale Ion Transport in Functional Electrolytes and for the Radical Generation in Crystalline Assemblies

PI: Qi Wang; co-PI: Chuanbing Tang, Sophia Garashchuk, Linda Shimizu, Jianjun Hu

Research Project Scope.

- (1) synthesized cationic cobaltocenium-containing polymers;
- (2) elucidated structure-property relationships on metal-complex cations and the electronic and steric effects of chemical structures on alkaline stabilities.
- (3) established thermodynamically consistent (TC) hydrodynamical models for charged particle transport.
- (4) utilized DFT calculation to produce database of cobaltocenium electronic structure and other properties.
- (5) innovated chemistry-informed and quadratic neuron network to make predictions from a small dataset.

Recent Progress.

Cations are crucial components in an anion exchange membrane (AEM) of a fuel cell. Rapid development in this area necessitates the exploration of new cations with advanced properties. Cobaltocenium cations demonstrate excellent thermal and alkaline stability, which can be improved by the chemical modification of the cyclopentadienyl rings with substituent groups. We have combined computational and experimental design of metallo-cations that have distinct electronic and redox properties. The relation between the bond dissociation energy (BDE) and chemistry-informed descriptors obtained from the electronic structural calculations is established. The analysis of 12 molecular descriptors for various derivatives reveals a nonlinear dependence of the BDE on the electron donating-withdrawing character of the substituent groups coupled to the energy of the frontier molecular orbitals. A chemistry-informed feed-forward neural network trained using k-fold cross-validation over the modest data set can predict the BDE from the molecular descriptors with the mean absolute error of about 1 kcal/mol. We have also analyzed the hydroxide diffusion in the presence of cobaltocenium cations in an aqueous environment based on the molecular dynamics of model systems confined in one dimension to mimic the AEM channels. We find that the hydroxide diffusion proceeds via both the vehicular and structural diffusion mechanisms with the latter playing a larger (up to 50%) role at low diffusion coefficients. The role of the

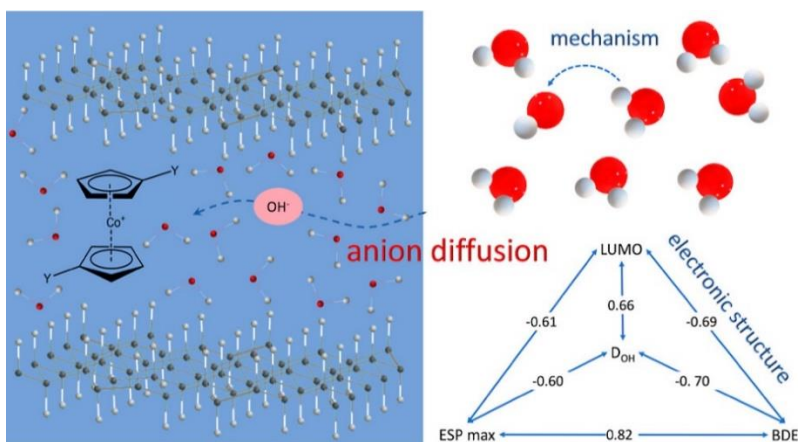


Figure. Hydroxide transport in cobaltocenium-containing Polymers.

hydration level, found to be optimal at 50% of liquid water, is found to be particularly important for the hydroxide transport under confinement.

Peer Reviewed Publications Acknowledging this Grant.

1. Tianyu Zhu, Yanying Lu, Kevin Huang, and Chuanbing Tang. Metallopolymer as a solid electrolyte for rechargeable Zn-metal alkaline batteries. *ACS Mater. Lett.* 2021, 3(6):799–806.
2. Steph-Yves Louis, Edirisuriya M. Dilanga Siriwardane, Rajendra P. Joshi, Sadman Sadeed Omeed, Neeraj Kumar, and Jianjun Hu. Accurate prediction of voltage of battery electrode materials using attention-based graph neural networks. *ACS Appl. Mater. Interfaces*, 2022, 14(23):26587–26594.
3. Christian Loftis, Kunpeng Yuan, Yong Zhao, Ming Hu, and Jianjun Hu. Lattice thermal conductivity prediction using symbolic regression and machine learning. *J. Phys. Chem. A*, 2021, 125(1):435–450.
4. Xiaowen Shen and Qi Wang. Thermodynamically consistent algorithms for models of deblock copolymer solutions interacting with electric and magnetic fields. *J. Sci. Comput.* 2021, 88(2):43.
5. Chunyan Li, Shehani T. Wetthasinghe, Huina Lin, Tianyu Zhu, Chuanbing Tang, Vitaly Rassolov, Qi Wang, and Sophia Garashchuk. Stability analysis of substituted cobaltocenium[bis(cyclopentadienyl)cobalt(iii)] employing chemistry-informed neural networks. *J. Chem. Theory Comput.* 2022, 18(5):3099–3110.
6. Di Wang, Yongyong Cai, and Qi Wang. Central vortex steady states and dynamics of boseinstein condensates interacting with a microwave field. *Phys. D: Nonlinear Phenom.* 2021, 419:132852.
7. Shehani Wetthasinghe, Chunyan Li, Huina Lin, Tianyu Zhu, Chuanbing Tang, Vitaly Rassolov, Qi Wang, and Sophia Garashchuk. Correlation between the stability of substituted cobaltocenium and molecular descriptors. *J. Phys. Chem. A*, 2022, 126(1):80–87.
8. Lin Lu, Qi Wang, Yongzhong Song, and Yushun Wang. Local energy dissipation rate preserving approximations to driven gradient flows with applications to graphene growth. *J. Sci. Comput* 2022, 90(1):6.
9. Muhammad Saddam Hossain, Fiaz Ahmed, Stavros G. Karakalos, Mark D. Smith, Nam-rata Pant, Sophia Garashchuk, Andrew B. Greytak, Pablo Docampo, and Linda S. Shimizu. Structure-property

- investigations in urea tethered iodinated triphenylamines. *Phys. Chem. Chem. Phys.* 2022, 24(31):18729–18737.
16. Yuezheng Gong, Qi Hong, and Qi Wang. Supplementary variable method for thermo-dynamically consistent partial differential equations. *Comput. Methods Appl. Mech. Eng.* 2021, 381:113746.
 17. Nghia Nguyen, Steph-Yves V. Louis, Lai Wei, Kamal Choudhary, Ming Hu, and Jianjun Hu. Predicting lattice vibrational frequencies using deep graph neural networks. *ACS Omega*, 2022, 7(30):26641–26649.
 18. Huina Lin, Luis Ramos, JiHyeon Hwang, Tianyu Zhu, Md Waliullah Hossain, Qi Wang, Sophya Garashchuk, and Chuanbing Tang. Main-Chain Cobaltocenium-Containing Ionomers for Alkaline Anion-Exchange Membranes. *Macromolecules*, 2023, 56(16):6375-6384.
 19. Sachith Wickramasinghe, Alexandria Hoehn, Shehani T. Wetthasinghe, Huina Lin, Qi Wang, Jacek Jakowski, Vitaly Rassolov, Chuanbing Tang, and Sophya Garashchuk. Theoretical examination of the hydroxide transport in cobaltocenium-containing polyelectrolytes. *J. Phys. Chem. B*, 2023, 127(47):10129-10141.
 20. Shehani Wettashinge, S. Garashchuk, and V. Rassolov. Stability trends in di-substituted cobaltocenium based on the analysis of the machine learning models. *J. Phys. Chem. A*, 2023, 127(50):10701–10708.

Long-Range Cooperativity among Rare-Earth Binding Sites in Organic Materials

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¹University of Maryland, College Park

Key Words: Assembly/Ordering; Confinement; Inorganic Chelation; Recognition (General)

DE-SC0024088: Long-Range Cooperativity among Rare-Earth Binding Sites in Organic Materials

PI: Mercedes Taylor

Research Project Scope.

The major goals of this project are a) to design novel adsorbents with rare-earth binding sites and b) to study these adsorbents for the capture of rare-earth elements from aqueous solution. We are targeting a series of 3+ cations (Y^{3+} , Nd^{3+} , Eu^{3+} , Tb^{3+} , and Dy^{3+}) determined by the U.S. Department of Energy (DOE) to be the most critical rare-earth elements in terms of their supply risk and their importance to clean energy. The major areas of DOE relevance for the proposed work include supply chain risk mitigation for critical rare earth elements and the discovery of new synthetic approaches for materials with hierarchical functionality. This work advances the goals of the DOE Separation Science program by pursuing cooperative phenomena that propagate local effects into an amplified chemical outcome.

Recent Progress.

Our work in the early stages of the project has been focused on adsorbent synthesis and characterization. We have successfully synthesized a library of novel organic ligands, which are needed to build the proposed supramolecular cages, helicates, and metal-organic frameworks. These ligands require 2–5 synthetic steps to make, and we have optimized the synthetic routes to obtain pure products in high yields. We have characterized the products through nuclear magnetic resonance (NMR) spectroscopy, along with mass spectrometry when necessary for conclusive structural assignment. To date, we have synthesized 9 novel ligands and 6 known ligands, for subsequent use in the construction of rare-earth adsorbents. We have made significant headway in the synthesis of novel supramolecular complexes, using the ligands described above. We have successfully synthesized 7 tetrahedral cages with M_4L_4 geometry (M = rare earth metal; L = ligand) by reacting our novel ligands with the following rare earth elements: yttrium, holmium, dysprosium, and terbium. These tetrahedral cages were characterized with NMR spectroscopy and high-resolution mass spectrometry. We have also synthesized several linear polymers by linking the reactive tails of the ligands end-to-end, which we characterized through NMR spectroscopy and MALDI-TOF mass spectrometry.

Through numerous rounds of metal-organic framework synthesis, we identified a suitable platform for inter-ligand crosslinking. We synthesized this framework with reactive groups tethered to the linkers, so that the linkers could then react with a crosslinker. We carried out the crosslinking step using various crosslinkers as guests, through which we identified the most effective crosslinking chemistries. We subsequently demetallated the crosslinked framework to leave behind an organic network, which we characterized through solid-state NMR, infrared (IR) spectroscopy, electron microscopy, gas adsorption

measurements, and thermogravimetric analysis (TGA). We discovered that the pre-crosslinking framework is photoactive, capable of absorbing UV light to generate reactive ligand-centered radicals (which we then employed to initiate the crosslinking reaction), while the post-crosslinking framework has negligible absorption at the same wavelength. These exciting results open the door to spatially-resolved crosslinking in this framework.

Permeation Properties of Disordered Metal-Organic Framework Membranes Made by Vapor Phase Deposition and Irradiation Treatments

Michael Tsapatsis¹, J. Anibal Boscoboinik², J. Ilja Siepmann³, D. Howard Fairbrother¹, Liwei Zhuang⁴, Peter Corkery¹, Mueed Ahmad², Andrea Kraetz¹, Prerna³, Dennis T. Lee^{1,2}, Prince Kumar Verma¹, Yurun Miao¹, Kayley E. Waltz¹, Patrick M. Eckhert¹, Swapnil Ambade¹, Eliseo Perez Gomez², Ramanish Singh³, Pragma Parihar³

¹Johns Hopkins University, ²Stony Brook University and Brookhaven National Laboratory, ³University of Minnesota, ⁴East China University of Science and Technology

Key Words: Assembly/Ordering; Interfaces; Membranes; Theory/Simulation

DE-SC0021212: Permeation Properties of Disordered Metal-Organic Framework Membranes Made by Vapor Phase Deposition and Irradiation Treatments

PI: Michael Tsapatsis; co-PIs: J. Anibal Boscoboinik, J. Ilja Siepmann³, D. Howard Fairbrother¹

Research Project Scope.

Our team introduced and is currently further developing a solvent-free synthesis and modification methodology for thin-film MOF membranes, which creates intricate microstructures with highly tunable permeation properties. It consists of a combination of vapor phase and irradiation-induced MOF deposition and modification methods. We systematically investigate processing-structure-separation performance relationships by determining MOF membrane structure, adsorption, and permeation properties during the synthesis and modification processes.

Recent Progress.

We developed a new method for atomic/molecular layer deposition (ALD/MLD) of amorphous zinc-2-methylimidazolate (aZnMIm) films and we have shown that these films can be converted to crystalline ZIF-8 (Advanced Functional Materials 34(12), 2311149 (2024)). We also demonstrated synthesis of selective membranes by our new method (not yet published work, see **Figure 1**).

In our recent publication (ACS Applied Materials & Interfaces 16, 21, 27887–27897 (2024)), we provided a comprehensive understanding of the vibrational spectra of ZIF-8 and its defect-induced variations and resolved conflicting assignments from the literature. This work will enable precise quality control and aid the design of ZIF-8-based materials for separation applications.

We have developed spin-on and liquid phase deposition methods of ZIFs, as well as a vapor phase treatment method to incorporate halogenated ligands in ZIF films deposited on silicon wafers (reported in Nature Materials 22, 1387-1393 (2023)), and are currently extending these studies to porous supports for membrane performance testing before and after e-beam exposure.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

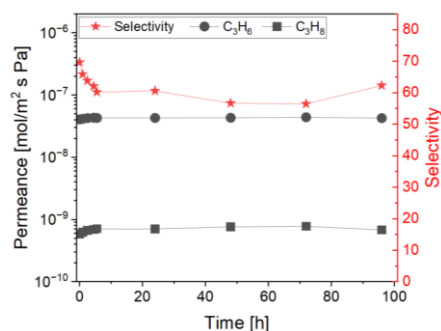


Figure 1. Separation performance of ZIF-8 membrane made by ALD/MLD.

Intellectually led by this grant:

1. Mueed Ahmad, Roshan Patel, Dennis T. Lee, Peter Corkery, Andrea Kraetz, Prerna, Samuel A. Tenney, Dmytro Nykypanchuk, Xiao Tong, J. Ilja Siepmann, Michael Tsapatsis, and J. Anibal Boscoboinik, "ZIF-8 Vibrational Spectra: Peak Assignments and Defect Signals", ACS Applied Materials and Interfaces, 2024, 16(21), 26967-28010 <https://doi.org/10.1021/acsami.4c02396>
2. Peter Corkery, Kayley E. Waltz, Patrick M. Eckhart, Mueed Ahmad, Andrea Kraetz, Yurun Miao, Dennis T. Lee, Mohammed K. Abdel-Rahman, Yucheng Lan, Paul Haghi-Ashtiani, Aaron Stein, J. Anibal Boscoboinik, Michael Tsapatsis, and D. Howard Fairbrother, "Zinc-Imidazolate Films as an All-Dry Resist Technology", Advanced Functional Materials, 2024, 34, 2311149, <https://doi.org/10.1002/adfm.202311149>
3. Qi Liu, Yurun Miao, Luis Francisco Villalobos, Shaoxian Li, Heng-Yu Chi, Cailing Chen, Mohammad Tohidi Vahdat, Shuqing, Song, Deepu J. Babu, Jian Hao, Yu Han, Michael Tsapatsis and Kumar Varoon Agrawal, "Unit-cell-thick zeolitic imidazolate framework films for membrane application", Nature Materials, 2023, 22, 1387-1393, <https://doi.org/10.1038/s41563-023-01669-z>
4. Yuchen Yuan, Huihui Ping, Dennis T. Lee, Peter Corkery, Zhen Zhang, Cui Liu, Shuang-mei Xue, Liwei Zhuang, and Michael Tsapatsis, "CFD Simulation of the Dosing Behavior within the Atomic Layer Deposition Feeding System", Industrial and Engineering Chemistry Research, 2023, 62(23), 9335-9347, <https://doi.org/10.1021/acs.iecr.3c01151>
5. Dornelles de Mello, M., Ahmad M., Lee D.T., Dimitrakellis P., Miao Y., Zheng W., Nykypanchuk D. Vlachos D.G., Tsapatsis M., Boscoboinik J.A., "In situ Tracking of Nonthermal Plasma Etching of ZIF-8 Films", ACS Applied Materials & Interfaces, 2022, 14(16), 19023-19030, <https://doi.org/10.1021/acsami.2c00259>
6. Lee D.T., Corkery P., Park S., Jeong H.-K., Tsapatsis M., "Zeolitic Imidazolate Framework Membranes: Novel Synthesis Methods and Progress Toward Industrial Use", Annual Review of Chemical and Biomolecular Engineering, 2022, 13, 529-555, <https://doi.org/10.1146/annurev-chembioeng-092320-120148>
7. Miao Y., Lee D.T., Dornelles de Mello M., Ahmad M., Abdel-Rahman M.K., Eckhart P.M., Boscoboinik J.A., Fairbrother D.H. and Tsapatsis M., "Solvent-Free Bottom-up Patterning of Zeolitic Imidazolate Frameworks", Nature Communications, 2022, 13, 420, <https://doi.org/10.1038/s41467-022-28050-z>
8. Hao Gu, Dennis T. Lee, Peter Corkery, Yurun Miao, Jung-Sik Kim, Yuchen Yuan, Zhen-liang Xu, Gance Dai, Gregory N. Parsons, Ioannis G. Kevrekidis, Liwei Zhuang, Michael Tsapatsis, "Modeling of deposit formation in mesoporous substrates via atomic layer deposition: Insights from pore-scale simulation", AIChE Journal, 2022, 68, e17889, <https://doi.org/10.1002/aic.17889>
9. Miao Y., Lee D.T., Dornelles de Mello M., Abdel-Rahman M., Corkery P., Boscoboinik J.A., Fairbrother D.H. and Tsapatsis M., "Electron beam induced modification of ZIF-8 membrane permeation properties", Chemical Communications, 2021, 57, 5250-5253, <https://doi.org/10.1039/d1cc00252j>
10. Zhang L., Corkery P., Lee D.T., Lee S., Kooshkbaghi M., Xu Z.L., Dai G., Kevrekidis I.G. and Tsapatsis M., "Numerical simulation of atomic layer deposition for thin deposit formation in a mesoporous substrate", AIChE Journal, 2021, 67, e17305, <https://doi.org/10.1002/aic.17305>
11. Hayashi M., Lee D.T., Dornelles de Mello M., Boscoboinik J.A. and Tsapatsis M., "ZIF-8 Membrane Permselectivity Modification by Manganese(II) Acetylacetonate Vapor Treatment", Angewandte Chemie International Edition, 2021, 60, 9316-9320, <https://doi.org/10.1002/anie.202100173>

Grant cited but not intellectually led by this award:

1. Patel R., Castro J., Tsapatsis M., Siepmann J.I., "Molecular Simulations Probing the Adsorption and Diffusion of Ammonia, Nitrogen, Hydrogen, and Their Mixtures in Bulk MFI Zeolite and MFI

Nanosheets at High Temperature and Pressure", Journal of Chemical & Engineering Data, 2022, 67(7), 1779-1791, <https://doi.org/10.1021/acs.jced.2c00086>

Ion and Water Interactions with Graphene and Graphene Oxide Surfaces

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Key Words: Confinement; Interfaces; Non-Thermal Separation Mechanisms; Solvation

Project Title: Mechanistic Understanding of Heavy Ion Adsorption, Chemistry, and Separations at Graphene Based 2D Materials Interfaces

PI: Ahmet Uysal

Research Project Scope.

The main objective of this FWP is to investigate the interactions between heavy ions and graphene-based materials, such as graphene, graphene oxide, and functionalized graphene at the molecular level, with a focus on developing predictive understanding of heavy element separations. To achieve this objective, we utilize various surface-specific techniques such as synchrotron X-ray scattering and vibrational sum frequency generation spectroscopy. Our primary research interest lies in identifying the key factors that determine the surface interactions of heavy ions with the graphene/water interface.

Recent Progress.

$Y^{(III)}$ adsorption on pristine graphene under electrochemical control has been studied using resonant anomalous X-ray scattering. This marks the first-ever measurement of its kind in the literature, yielding very surprising results. $Y^{(III)}$ ions primarily adsorb in a diffuse layer without losing their hydration shell. The amount of adsorbed yttrium ions significantly exceeds the amount needed to compensate the surface charge of the graphene.

A simple yet effective method for preparing thin graphene oxide (GO) films at the air/water interface has been developed. This new method has enhanced the sensitivity of our measurements to nanoscale perturbations at the graphene oxide interface. A notable achievement resulting from this method is our discovery that heavy water (D_2O) and regular water (H_2O) interact differently with GO thin films. These differences can be exploited for isotopic separations.

The adsorption of $Cs^{(I)}$, $Sr^{(II)}$, and $Y^{(III)}$ on graphene oxide membranes has been studied, focusing on GO film structure and interfacial water behavior, using synchrotron X-ray scattering, surface-specific X-ray fluorescence, and vibrational sum-frequency generation spectroscopy. This is the first comprehensive study of ion adsorption on GO thin films.

We have demonstrated that the selectivity of GO films for rare earth ions is concentration-dependent. $La^{(III)}$ and $Lu^{(III)}$ adsorb similarly at low metal ion concentrations, but almost 8 times more $Lu^{(III)}$ than $La^{(III)}$ adsorbs at higher bulk concentrations. This phenomenon can be partially reproduced with pure carboxylic acid films. By comparing and contrasting pure carboxylic films with GO, we have identified the unique properties of GO in lanthanide adsorption.

Furthermore, we have shown that carboxylic acid groups on GO primarily control GO-monovalent ion

interactions. This is in contrast to GO-trivalent ion interactions, which informs strategies to enhance separations by tuning the functional groups on GO.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. Lee, S. E., Carr, A. J., Kumal, R. R., Uysal, A., Monovalent ion–graphene oxide interactions are controlled by carboxylic acid groups: Sum frequency generation spectroscopy studies, *J. Chem. Phys.*, 2024, 160, 084707, DOI: 10.1063/5.0189203
2. Kumal, R. R., Carr, A. J., Uysal, A., A simple method for floating graphene oxide films facilitates nanoscale investigations of ion and water adsorption, *RSC Adv.*, 2024, 14, 7582-7591, DOI: 10.1039/D3RA07254A
3. Carr, A. J., Lee, S. E., Uysal, A., Ion and water adsorption to graphene and graphene oxide surfaces, *Nanoscale*, 2023, 15, 14319-14337, DOI: 10.1039/d3nr02452k
4. Carr, A. J., Lee, S. E., Uysal, A., Heavy versus Light Lanthanide Selectivity for Graphene Oxide Films is Concentration-Dependent, *J. Phys. Chem. C*, 2023, 127 (29), 14363-14373, DOI: 10.1021/acs.jpcc.3c01350
5. Carr, A. J., Lee, S. E., Kumal, R. R., Bu, W., Uysal, A., Convenient Confinement: Interplay of Solution Conditions and Graphene Oxide Film Structure on Rare Earth Separations. *ACS Appl. Mater. Interfaces.*, 2022, 14 (51), 57133-57143, DOI: 10.1021/acsami.2c16156
6. Carr, A. J., Resonant Anomalous X-Ray Reflectivity for Revealing Ion Distributions Near Electrodes, *Nat. Rev. Phys.*, 2022, 4, 743, DOI: 10.1038/s42254-022-00519-2.
7. Carr, A. J., Kumal, R. R., Bu, W., Uysal, A., Effects of Ion Adsorption on Graphene Oxide Films and Interfacial Water Structure: A Molecular-Scale Description, *Carbon*, 2022, 195, 131-140. DOI: 10.1016/j.carbon.2022.03.077
8. Carr, A.J., Lee, S.S., Uysal, A., Trivalent Ion Overcharging on Electrified Graphene, *J. Phys. Condens. Matter.*, 2022, 34, 144001, DOI: 10.1088/1361-648X/ac4a58

Memristor Effects for the Selective Ion Enrichment and Entrapment at Asymmetric Nanointerfaces

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Key Words: Field-Driven Separations; Interface Confinement; Reactive Separations; Dynamic Transport Phenomena

DE-SC00024457: Project Title: Selective Ion Enrichment and Entrapment Enabled by Asymmetric Nanointerfaces

PI: Gangli Wang; co-PI: Xuefei Li

Research Project Scope.

Our overarching goal is developing kinetics-based and generalizable separation strategies founded on our unique capabilities to enrich and entrap ions in asymmetric nanopores. Our main hypothesis is that the unique electrokinetic ion enrichment and entrapment (ion-EE) effects in asymmetric nanopores will be able to kinetically overcome thermodynamic limitations in a spatiotemporal resolved fashion. Correspondingly, mechanistic insight will enable new capabilities for better separations.

Recent Progress.

Memory effect or hysteresis in ion transport is unique in that the conductance depends on or ‘memorizes’ the previous states. The property constitutes new mechanism with exciting potentials to improve the efficiency of energy conversation and electrochemical processes, to overcome the selectivity-throughput bottleneck in the enrichment of low abundant species for environment- and energy-friendly separation, and to develop advanced iontronic and neuromorphic computing functions.

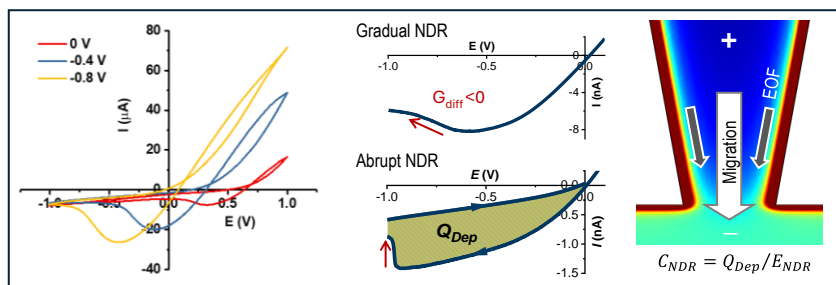


Figure. Characteristic memristor ion transport through asymmetric nanopores and membranes. **Left:** ion current rectification, hysteresis and NDR regulated by transmembrane potential. **Middle:** two types of NDR transitions. **Right:** mechanistic insights from finite element simulation.

In this report, hysteretic effects in the rectified electrokinetic ion transport through nanoscale solid-solution interfaces are discovered in anodized aluminum oxide (AAO) membranes containing highly ordered arrays of cylindrical nanochannels as well as single conical nanopipettes. Characteristic memristor responses of pinched current-potential loops are resolved in voltametric experiments and successfully reproduced through finite element simulation. Further, negative differential resistance (NDR), decrease in conductance with increasing potential, is resolved in these time-dependent instead of steady-state nanoscale electrokinetic ion transport. The emerging ion transport properties arise from the broken symmetry across the AAO membrane imposed by the barrier oxide layers on one end of the nanochannels. The physical origin of those transport properties is attributed to the gradient(s) in space charge density in the barrier

oxide layer. A new strategy is developed accordingly for controlling the preferential ion transport direction and selectivity via counterion intercalation or extraction. Intense rectification and hysteresis prevail at very high ionic concentrations up to 1-2 M, unrestricted to lower ionic strength regime which is a fundamental limitation of surface charge governed effects widely exploited in single nanopore-nanochannel systems. Mechanistic understanding is elucidated through parameter variations such as potential scan rate and ionic strength which also demonstrates convenient controls of the related functions. Discovery of these history-dependent transport properties from the multiplex nanochannel arrays in the easily accessible macroscopic membranes constitutes significant advances in the fundamental insights toward aforementioned applications.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. Yang, R.; Balogun, Y.; Ake, S.; Baram, D.; Brown, W.; Wang, G., Negative Differential Resistance in Conical Nanopore Iontronic Memristors. *J. Am. Chem. Soc.* 2024, 146 (19), 13183-13190.
2. Brown, W.; Kvetny, M.; Yang, R.; Wang, G., Selective Ion Enrichment and Charge Storage through Transport Hysteresis in Conical Nanopipettes. *J. Phys. Chem. C* 2022, 126 (26), 10872-10879.
3. Brown, W.; Kvetny, M.; Yang, R.; Wang, G., Higher Ion Selectivity with Lower Energy Usage Promoted by Electro-osmotic Flow in the Transport through Conical Nanopores. *J. Phys. Chem. C* 2021, 125 (6), 3269-3276.

Leveraging Macrocyclic Chelators for Rare Earth Element Separations

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Key Words: Inorganic Chelation; Thermodynamics

DE-SC0021662: Leveraging Macrocyclic Chelators for Rare Earth Element Separations

PI: Justin Wilson

Research Project Scope.

Achieving clean, energy-efficient, and sustainable rare earth element separations is critically needed in order to ensure the domestic availability of these important elements. The goal of this project is to design macrocyclic chelating agents that can effectively discriminate between rare earth elements of different sizes. In particular, we seek to leverage chelators with novel size-selectivity patterns that are distinct from conventional ligands that have previously been applied for this application.

Recent Progress.

Developing chelating agents with unique selectivity patterns. To optimally use chelating agents for rare earth element separations, they should possess unique size-based selectivity properties. In specific, many common chelators for rare earth elements already exist, but their selectivity patterns exhibit distinct preferences for either large or small ions. In our research, we have identified a class of chelators that have a non-monotonic trend in binding affinity across the rare earth series. One of these chelators py₂-macrodipa was recently disclosed (*Inorg. Chem.* **2022**, *61*, 12847). This chelator is unique in that it has a high overall binding affinity for the rare earth elements and also has a

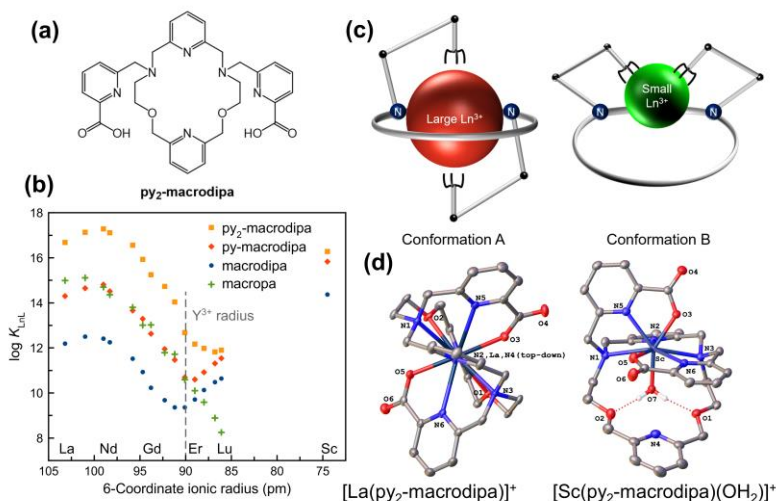


Figure 1. (a) Structure of py₂-macrodipa. (b) Thermodynamic stability constants (log K_{ML}) of py₂-macrodipa in comparison to several other chelators. (c) Cartoon depiction of the conformational changes of complexes of this chelator. (d) Crystal structures of the La³⁺ and Sc³⁺ complexes of this chelator, showing these conformational changes.

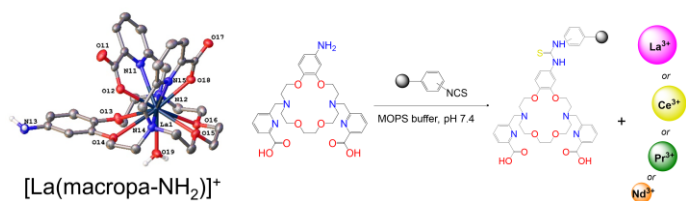


Figure 2. Structure of macropa-NH₂ and its La³⁺ complex, as well as the approach used to attach it to solid resin.

selectivity properties discerned, novel chelators can then be applied for practical rare earth element separations. Toward this goal, we have synthesized an analogue of macropa, called macropa-NH₂ (*Bioconjugate Chem.* **2022**, 33, 1222), that contains a reactive amine group on its backbone that can be used for attachment to solid-resins (Figure 2). The macropa-functionalized resin can extract rare earth elements from solution and afford mild selectivity based on their ionic radii.

Chelators to modulate precipitation of rare earth carbonates. A novel chelator G-macropa was synthesized and applied for achieving rare earth element separations via precipitation (*Angew. Chem., Int. Ed.* **2024**, doi: 10.1002/anie.202410233).

In this approach, G-macropa can be used to separate Nd³⁺ and Dy³⁺ in aqueous solution (Figure 3). This chelator has a higher affinity for Nd³⁺, enabling Dy³⁺ to be selectively precipitated with carbonate ion.



Figure 3. Structure of G-macropa and photographs showing how its presence can lead to selective precipitation of Dy³⁺ from an aqueous solution containing both Nd³⁺ and Dy³⁺.

Future Plans.

Future work on this project will interface our novel dual size selective chelators (like py₂-macrodiapa) with our practical separation approaches involving adsorption to solid resin and precipitation with counterions. These dual size selective chelators should in principle be able to separate mid-sized lanthanides from the early and late lanthanides.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. Y. Gao, G. L. Licup, N. P. Bigham, D. C. Cantu*, J. J. Wilson.* “Chelator-Assisted Precipitation-Based Separation of the Rare Earth Elements Neodymium and Dysprosium from Aqueous Solutions.” *Angew. Chem., Int. Ed.* **2024**, doi: 10.1002/anie.202410233
2. A. Hu, M. E. Simms, V. Kertesz, J. J. Wilson*, N. A. Thiele*. “Chelating Rare-Earth Metals (Ln³⁺) and ²²⁵Ac³⁺ with the Dual-Size-Selective Macrocyclic Ligand Py₂-Macrodiapa.” *Inorg. Chem.* **2022**, 61, 12847–12855.

Grant cited but not intellectually led by this award:

1. K. J. Kadassery, A. P. King, S. Fayn, K. E. Baidoo, S. N. MacMillan, F. E. Escorcia*, J. J. Wilson*. "H₂BZmacropa-NCS: A Bifunctional Chelator for Actinium-225 Targeted Alpha Therapy" *Bioconjugate Chem.* **2022**, *33*, 1222–1231.

Understanding the Structure-Property Relationships and Aging Behavior of Microporous CANAL Polymer Membranes for Gas Separation

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Key Words: Ladder polymers; Microporosity; Transport Phenomena; Aging

DE-SC0023252: Understanding the Structure-Property Relationships and Aging Behavior of Microporous CANAL Polymer Membranes for Gas Separation

PI: Yan Xia; co-PI: Zachary Smith

Research Project Scope.

Highly selective and permeable membranes are critical for reducing the carbon footprint of gas separations. We recently developed a new type of microporous ladder polymers, termed CANAL polymers, that exhibit high performance in gas separations upon aging. We investigated how the structural features of CANAL polymers affect their gas separation performance and aging behavior. Understanding of the factors that control the gas transport properties and aging of microporous polymers will allow us to establish principles for custom-designing microporous polymer membranes for various separation applications.

Recent Progress.

We performed 3 types of ladder polymer structural variation to elucidate the effects of structural features of CANAL polymers on gas transport. (1) We compared isomeric ladder polymer structures, and found that introducing spirocyclic backbone linkages to CANAL polymers reduced the microporosity and gas permeability. (2) We investigated the effect of incorporating a controlled amount of variable single-bond linkage, and found approximately the minimal length of complete rigid ladder backbone segment to maintain the gas transport performance of complete CANAL ladder polymers. Interestingly, both types of backbone structural variations did not change the unusual selective aging behavior of CANAL polymers. (3) We compared copolymers containing more flexible linkages and polymer blends at the same compositions, and found polymer blends can maintain the gas separation performance and aging behavior of CANAL polymers, but the copolymers cannot once the flexible linkage exceeds a certain fraction. Additionally, we discovered that trace amounts of absorbed organic vapor facilitate the aging of CANAL polymers.

Future Plans.

We will finish the structural variation 2 and 3 with quantitatively defined chain rigidity and packing and complete gas permeation evaluation including plasticization using mixed gases. We will investigate the effect of environmental organic vapor on aging in detail to understand the aging mechanism.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. Robinson, A. M. and Xia, Y. Regioisomeric Spirobifluorene CANAL Ladder Polymers and Their Gas Separation Performance *ACS Macro Lett.* **2024**, 13, 118–123.

Autonomous Discovery of Selective Separation of f-Elements for Clean Energy: SeparationML

Ping Yang,¹ Stosh A Kozimor,² Joshua Schrier,³ Michael G Taylor,¹ Enrique Batista,¹ Marc Cawkwell,¹ Nicholas Lubbers,⁴ Danny Perez,¹ Logan Augustine,¹ Yufei Wang,² Sara L Adelman,² Jan Janssen,¹ Daniel J Burrill,¹ Jiyoung Lee,¹ Thomas Summers,¹ Michael Tynes¹

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Key Words: Machine Learning/AI; Inorganic Chelation; Kinetics; Liquid-Liquid Phase; Theory/Simulation.

DE-2024LANLE3M2: Autonomous Discovery of Selective Separation of f-Elements for Clean Energy

PI: Ping Yang; co-PI: Stosh A Kozimor, Joshua Schrier

Research Project Scope.

Critical 4*f* rare earths and minor 5*f* actinides are all +3 *f*-elements with similar chemistries, but often very different applications. Separating these elements from one another in high purity and in high yield is essential to the success of the DOE Clean Energy Initiative, but separation is extremely difficult given their nearly indistinguishable chemical characteristics. Despite extensive community efforts in the last seven decades, the solution to the +3 *f*-element separation problem remains elusive, largely because of the large number of factors that contribute to successful separations, e.g. extractant, solvent, aqueous and organic matrix identity, binding kinetics, hold-back agent, temperature, counter-ions, process conditions, etc. The lack of predictive models for 4*f*/4*f* and 4*f*/5*f* separations has made innovation slow, incremental, and labor intensive, resulting in only fragmentary exploration of the vast chemical space. Our central scientific goal is to accelerate *f*-element separation science design using an integrated data-driven autonomous discovery loop that explores the vast space of separation chemistries with minimal human bias, in a way that provides fundamental molecular-level understanding of the separation process.

Recent Progress.

We developed a software package called Architector^{7,8} that can rapidly generate chemically-sensible 3D molecular structures, enabling high-throughput simulations of *f*-element complexes. Coupled with automated workflows for liquid-liquid extraction screening, this allows us to run tens of thousands of density functional theory simulations at high-performance computing centers such as NERSC, thoroughly investigating chemical effects like metal coordination, ligand denticity, pH, etc. Recent advancements in Architector have further enhanced its capabilities for *f*-element separation science, particularly in secondary solvation sampling, multi-metal construction, and ligand binding site prediction. This allows for an unbiased exploration of distinct configurational and compositional variations for each metal. This capability has recently demonstrated with three diverse extractants—a crown ether, a phenanthroline monocarboxamide, and a malonamide—that sampling the metal-ligand configuration space is critical for correctly predicting solvation structures and explaining experimentally observed selectivity. We established the LANL Super Separator, a robotic system designed for the separation of radioactive actinides. This system automates the development of new separation protocols, optimizes operational

conditions, increases throughput, and minimizes human error.^{10, 12,}

¹³ By integrating machine learning techniques, including Bayesian Optimization and data-driven chemical reaction network training, with high-throughput robotic experiments, we reduced experimental efforts by 74% compared to traditional methods. This significant reduction in time-consuming and costly experiments for radioactive materials not only contributes to sustainability but also enables the exploration of a vast experimental space necessary for finding optimal separation conditions.

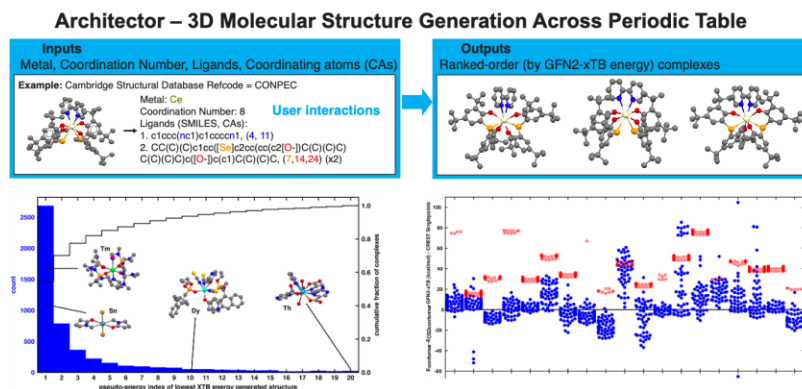


Figure. Cross-periodic table 3D construction of molecular complexes, including highly coordinated lanthanides and actinides.

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. Michael Tynes, Michael G Taylor, Jan Janssen, Daniel J Burrill, Danny Perez, Ping Yang, Nicholas Lubbers, “Linear Graphlet Models for Accurate and Interpretable Cheminformatics”, submitted to Digital Discovery”. *Digital Discovery*. 2024, Advance Article, DOI:10.1039/D4DD00089G
2. MinervaChem Software: <https://github.com/lanl/minervachem>, 2024
3. S. Kim, Y. Jung, J. Schrier, “Large Language Models for Inorganic Synthesis Predictions” *J. Am. Chem. Soc.* 2024, 146, 19654-19659. DOI:10.1021/jacs.4c05840
4. L Augustine, Y Wang, E R Batista, S Adelman, S Kozimor, D Perez, J Schrier, P Yang “Advancing f-element Separation through machine-learning and automated high-throughput experiment”, *ACS Sustainable Chemistry and Engineering*, 2024, in press.
5. SAFE Database: Separation Archive for f-Elements: <https://safe.lanl.gov>
6. D J Burrill, C Liu, M G Taylor, M J Cawkwell, D Perez, E R Batista, N Lubbers, P Yang “MLTB: Enhancing Transferability and Extensibility of Density Functional Tight Binding Theory with Multi-body Interaction Corrections”, *J. Chem. Theory Comput*, 2024, Accepted
7. Taylor, M. G.; Burrill, D. J.; Janssen, J.; Batista, E. R.; Perez, D.; Yang, P., Architector for high-throughput cross-periodic table 3D complex building. *Nature Communications* **2023**, 14 (1), 2786.10.1038/s41467-023-38169-2
8. Architector software: <https://github.com/lanl/Architector>
9. Augustine, L. J.; Kasper, J. M.; Forbes, T. Z.; Mason, S. E.; Batista, E. R.; Yang, P., Influencing Bonding Interactions of the Neptunyl (V, VI) Cations with Electron-Donating and -Withdrawing Groups. *Inorganic Chemistry* **2023**, 62 (15), 6055-6064.10.1021/acs.inorgchem.2c04538
10. Arko, B. T.; Dan, D.; Adelman, S. L.; Kimball, D. B.; Kozimor, S. A.; Martinez, Marki, M.; Mastren, T.; Huber, D. L.; Mocko, V.; Rim, J.; Shafer, J. C.; Stein, B. W.; Wylie, E. M.; “Exploring how exposure to radiolysis and harsh chemical reagents impact americium-241 extraction chromatography.” *Mater Adv.* **2023**, 4, 265-283. DOI: 10.1039/d2ma00859a
11. Su, J.; Gong, Y.; Batista, E. R.; Lucena, A. F.; Marçalo, J.; Van Stipdonk, M. J.; Berden, G.; Martens, J.; Oomens, J.; Gibson, J. K.; Yang, P. Unusual Actinyl Complexes with a Redox-Active N,S-Donor Ligand. *Inorganic Chemistry* **2023**, 62, 11016-11027. DOI:10.1021/acs.inorgchem.3c00990

12. Zhang, X.; Adelman, S. L.; De Silva, C. R.; Su, J.; Kozimor, S. A.; Mocko, V.; Stein, B. W.; Schrechenbach, G.; Batista, E.R.; Yang, P. Advancing Am Extractant Design Through the Interplay Among Planarity, Preorganization and Substitution Effects, *INORG. CHEM.* **2022**, *61*,11556-11570. DOI:10.1021/acs.inorgchem.2c00534
13. Arko, B. T.; Dan, D.; Adelman, S. L.; Huber, D. L.; Kimball, D. B.; Kozimor, S. A.; Lam, N. H.; Mocko, V.; Shafer, J. C.; Stein, B. W.; Thiemann, S. L. “Characterizing Extraction Chromatography For Large-Scale Americium-241 Processing.” *IND. ENG. CHEM. RES.* **2021**, *60*, 14282 – 14296. DOI:10.21/acs.iecr.1c02360

Separation of Lithium Ions from Competing Alkali Metal Cations in Brine Mixtures Using Switchable Solvent Selective Extraction (S³E)

Ngai Yin Yip, Eliza Dach, Juliana Marston, Daniel Galperin, Shinyoung Park

Columbia University

Key Words: Liquid-Liquid Phase; Recognition (General); Thermodynamics

DE-SC0024574: Targeted Selective Separation of Lithium Ions from Alkali Metal Cations in Brine Mixtures Using Switchable Solvents

PI: Ngai Yin Yip

Research Project Scope.

To meet the impending surge in lithium demand, direct lithium extraction (DLE) technologies that are economical and sustainable are urgently needed to enable increased production from conventional sources, access “technologically-locked” lithium assets in unconventional sources, e.g., geothermal brines and produced water, and realize recycling and reuse of existing lithium stock. We propose a novel DLE technology, termed switchable solvent selective extraction (S³E), which utilizes temperature-responsive switchable solvents, for the selective extraction of Li⁺ over much higher concentrations of background cations, in particular Na⁺ and K⁺. The overarching aim of this project is to advance fundamental understanding of the principal phenomena governing competitive ion partitioning in biphasic systems of switchable solvents and lithium brines.

Recent Progress.

We show that switchable solvent selective extraction, S³E, demonstrates > 1 order of magnitude preference for Li⁺ over other alkali metal cations, Na⁺ and K⁺, in hypersaline lithium brines with only a moderate temperature stimulus (<80 °C). Furthermore, the selectivity is preserved even when Li⁺ concentrations are several orders of magnitude lower than Na⁺ and K⁺.

To elucidate the fundamental interactions between water, solvent, and ions/ion-pairs, we employed combined differential wide-angle x-ray scattering and pair distribution analysis, integrated with small angle x-ray scattering characterizations, molecular dynamics structural modeling, and bulk phase liquid-liquid equilibrium measurements, to carry out a careful analysis of the lower critical solution temperature behavior of mixtures of water and switchable amine solvents. We demonstrate that the double differential pair distribution functions from experimental measurements are consistently reproducible and, critically, exhibit strong agreement with the signals from computational molecular dynamics simulations. This outcome is significant (and technically difficult to achieve) as it allows us to interrogate the underlying mechanisms from both experimental and simulation approaches. The study results strongly indicate that the interactions through hydrogen bonding between water and the switchable hydrophilicity amine yield molecular cluster structures that are ordered over ≈ 12 Å. We quantitatively showed that the decrease in hydrogen bonding between amine and water as temperature increases is significantly greater than the change in water-water H-bonds. The presence of molecular cluster structures is further corroborated by small angle x-ray scattering characterizations. The inverse micelles of water in the low-polarity organic

phase are determined to be ≈ 12 Å across, housing 60–90 water molecules each. Interestingly, changes in temperature do not affect the size of these molecular cluster structures but have a reciprocal effect on the number density of the structures. These findings offer, to-date, the most direct evidence for strong directional interactions in lower critical solution temperature systems that lower the entropy of mixing at higher temperatures through molecular-scale ordering.

To shed light on the principal ion properties governing competitive partitioning behavior in biphasic mixtures of thermally switchable solvents and hypersaline brines, we systematically investigated 11 ion properties across four alkali metal cations, namely Li^+ , Na^+ , K^+ , and Rb^+ , and four halide anions of F^- , Cl^- , Br^- , and I^- for a total of nine alkali-halide electrolytes (LiCl , NaF , NaCl , NaBr , NaI , KCl , KBr , KI , and RbCl). Advancing our fundamental understanding of the intrinsic ion properties that govern salt partitioning in the biphasic systems is critical for the informed development of selective ion separation in S^3E .

Peer Reviewed Publications Acknowledging this Grant in 2021-2024.

Intellectually led by this grant:

1. Billinge, I.H., Barbosa, G.D., Tao, S., Terban, M., Turner, C.H., Billinge, S.J.L., Yip, N.Y., “A structural underpinning of the lower critical solution temperature (LCST) behavior behind temperature-switchable liquids”, *Matter*, accepted.

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Yang, Ping	Los Alamos National Laboratory
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Appendix

Appendix A: Meeting Presentation Slides

2024 Separation Science PI Meeting:

Introduction, Overview, and Meeting Charge

BES Chemical Sciences, Geosciences, and Biosciences (CSGB) Division

Amanda Haes, Program Manager

September 10-12, 2024



U.S. DEPARTMENT OF
ENERGY

Office of
Science

energy.gov/science
science.osti.gov/csgb/

Welcome and Code of Conduct

Most of the attendees are on-site for the first time since 2019!

There are a few people who are attending virtually, so **please use the microphone to ask questions.**

Code of Conduct

The Office of Science (SC) expects the scientific community participating in SC-sponsored events to conduct themselves in a manner that is respectful, ethical, professional, inclusive, and non-disruptive. By attending such events, participants agree to conduct themselves according to these expectations. If a participant does not adhere to such expectations, SC reserves the right to take appropriate action.

<https://science.osti.gov/SW-DEI/SC-Statement-of-Commitment/Potential-Consequences>

Thank You

Co-Organizers



Vanda Glezakou
Detailee from ORNL



Carrie Farberow
Detailee from NREL

Co-Chairs – Breakout Organizers/Leaders



Ryan Lively



Santa Jansone-Popova



Michael Tsapatsis

Session Chairs



Francesco Paesani



Abigail Knight



Eric Schelter



Justin Wilson



Jerry Lin

All of You

The Purpose of the Meeting is to Accelerate Research Progress through Collegial Interactions

- Develop a common understanding of present activities
- Maximize potential for collaboration
- Identify the scientific needs of the research community
- Discuss future research directions



PI Talks (23 total including several Early Career PIs)



Poster Presentations and Lightning Round Introductions (44)



Breakout Session 1 – Looking Back to Look Forward – Where are the Fundamental Research Opportunities for Separation Science?



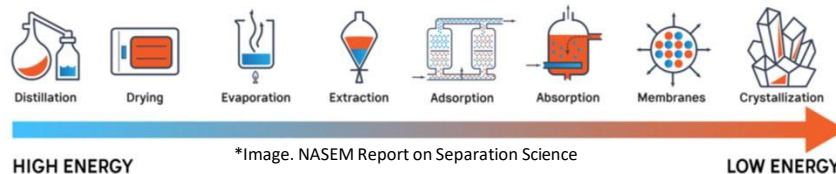
Breakout Session 2 – Separation Science and Data Science – What Should the Venn Diagram Look Like?



Build Community, Catch-up with Acquaintances, and Meet New People

Separation Science Program Overview

The Separation Science Program supports **fundamental, hypothesis-driven molecular-level** experimental and computation research that addresses questions to discover, understand predict, and control de-mixing transitions, with the goal of **enabling chemical separation paradigms** that may become the basis for solutions to current and long-term energy challenges.



*Understanding **molecular interactions & energy exchanges** that determine the efficiency of chemical separations*

*Advancing the discovery & predictive design of **chemical separation paradigms**...for solutions to the world's energy challenges*

*Gaining more precise control of **energy & matter** transformations of complex domestic resources*



*Understanding & controlling **atomic & molecular interactions** between target species & separations media as well as the relevant molecular structures, dynamics, kinetics, & transport properties that govern separations*

Separation Science is an Evolving Field, Well-Posed to Address Many of Today's Energy Challenges

Fundamental Scientific Scope of Program:

- **Discovering, understanding, and predicting paradigms** for removal of **dilute constituents** from a mixture;
- **Elucidating factors** that cause a separation system to approach mass transfer limitations;
- **Advancing non-thermal and other sustainable separation mechanisms** that have the potential to drive efficient and selective energy-relevant separations;
- **Elucidating** how **separation parameters** and **processes** such as high selectivity, capacity, and throughput are impacted by **complex and/or interconnected system properties**;
- **Understanding and controlling temporal changes** in separation systems such as activation, degradation, self-repair, or solvation.

User-Inspired DOE Themes:

- Critical materials and minerals
- Carbon dioxide removal
- Sustainable chemistry separation processes
- Separation and utilization of rare isotopes or heavy elements from nuclear waste

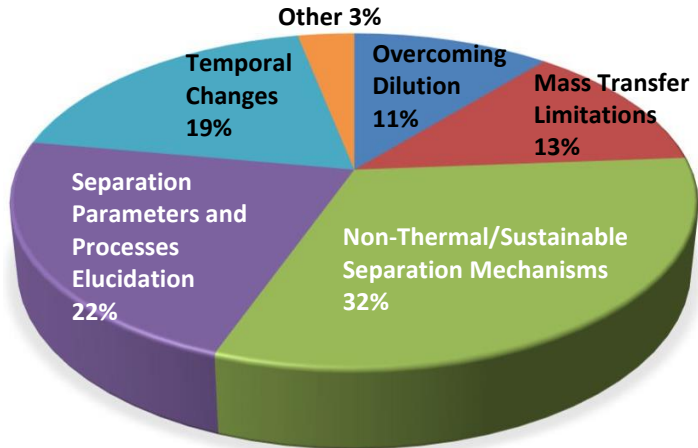
Separation Science Program – Current Portfolio and Scope

Lab Projects

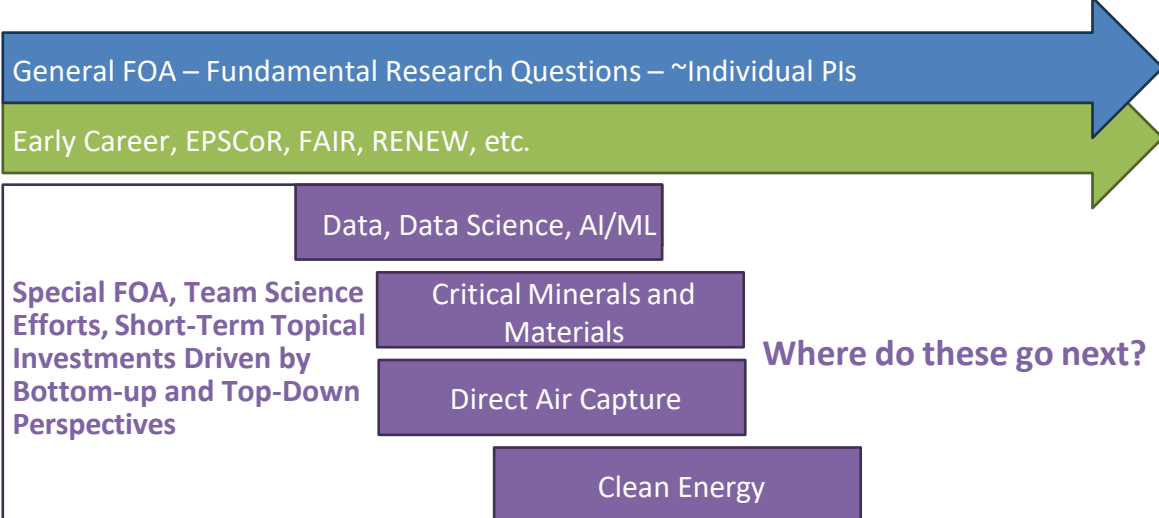
- FWPs at National Labs
- Integrated efforts spanning several emerging topics with emphasis in unique tools

University Projects

- ~65 active PI
- Includes some large special FOA projects



Separation Science Program Evolution and Opportunities



NASEM Report – A Research Agenda for Transforming Separation Science



- Assesses the state of separation science with a focus on advances since the prior report in 1987
- Identifies critical roles separation science plays in society
- Emphasizes that separations are integral to many industrial processes yet often not always considered
- Develops an agenda for foundational research directions (i.e., an agenda) for the field
- Categorizes the agenda into two major themes
 - Designing separation systems that have high selectivity, capacity, and throughput
 - Understanding temporal changes that occur in separations
- Identifies two cross-cutting topics
 - Establishing standards to enhanced reproducibility
 - Adapting data-science methods to accelerate the development of separation systems

BES Roundtable – Foundational Science for Carbon Dioxide Removal (CDR) Technologies

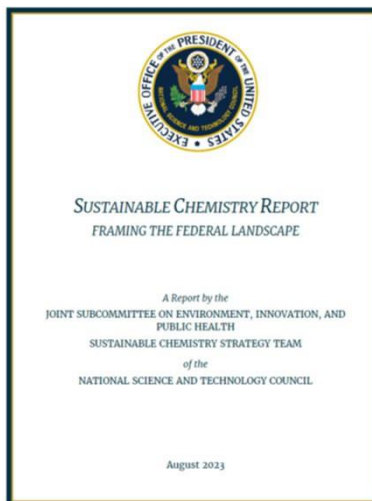
Determine the fundamental knowledge base that underpins the Carbon Negative Shot by identifying critical scientific understanding needs to overcome scientific and technical barriers to development and implementation of effective, efficient, and safe CDR technologies



- Advancements that could reduce atmospheric CO₂ thereby transforming the technological landscape of CDR include:
 - **direct CO₂ capture and concentration** from ambient air and other dilute sources
 - **durable carbon storage** through mineralization and synthetic conversion
 - **CO₂ sequestration** in underground geologic formations
- Innovations rely on a **molecular-level understanding** of CO₂ interactions with interfaces in complex environments and **coupling of methods** including novel operando experimental techniques, predictive theory and modeling, and data science
- Foundational knowledge generated could enable advances in multifunctional materials, mitigation strategies for degradation processes, and overall control of CO₂ interactions with molecules, minerals, and materials

Office of Science and Technology Policy (OSTP) Interagency Working Group and Report on Sustainable Chemistry

- Develop a consensus definition of sustainable chemistry
- Perform a landscape analysis of all current Federal sustainable chemistry activities
- Develop a strategic plan to characterize and assess sustainable chemistry
- Coordinate Federal efforts in the areas of regulation, R&D, and challenges
- Integrate sustainable chemistry into Federal R&D through awarded Federal grants, prizes, and loans
- Increase workforce training and development in sustainable chemistry



First Report Published in August 2023

BES Research Priorities Related to Separation Science

Science in support of **clean energy and sustainable manufacturing**

- Supported by strategic planning and cross-DOE initiatives, including Energy Earthshots
- Strategic planning reports in recent years include hydrogen, carbon dioxide removal, solar fuels, microelectronics, manufacturing, nuclear energy

Science addressing **national priorities**

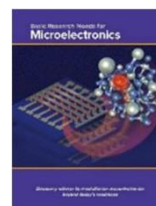
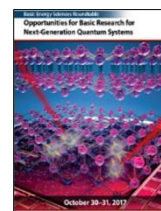
- Quantum Information Science, including National QIS Research Centers
- Microelectronics
- Data, artificial intelligence, and machine learning
- Accelerate transition of science advances to technologies

Forefront science in **core research foundations** (assessed annually)

- Continuation of Solicitation for the Office of Science Financial Assistance Programs
- BESAC charge to provide advice on prioritization strategies

Support to **broaden participation** in research

- Early Career, EPSCoR, RENEW, and FAIR





How can the Separation Science community address fundamental scientific challenges that underpin DOE Energy Earthshots?



Hydrogen Shot™ | Accelerate innovation and increase demand for clean hydrogen by reducing the cost by 80%—to \$1 per 1 kilogram of clean hydrogen—within the decade.



Clean Fuels & Products Shot™ | Decarbonize the fuel and chemical industry through alternative sources of carbon by advancing cost-effective technologies that achieve 85% lower net greenhouse gas emissions by 2035.



Carbon Negative Shot™ | Enable removal of CO₂ from the atmosphere and durable storage at meaningful scales for less than \$100/net metric ton of CO₂- equivalent within a decade.



Industrial Heat Shot™ | Develop cost-competitive industrial heat decarbonization technologies with at least 85% lower greenhouse gas emissions by 2035 to put the American industrial sector on course to reduce its carbon- equivalent emissions by 575 million metric tons by 2050.

Breakout Session A

Closing Session Preview - How Can You Help Me Help You?

- Send me your highlights
 - Properly acknowledge your awards
- Submit your reports in a timely manner
- Submit your new and renewal proposals in a timely manner (whitepapers are encouraged)
- Consider time constraints and practice/policy

- Ask questions
 - Think creatively
- Communicate clearly
 - Articulate how your research directly addresses molecular based and fundamental knowledge gaps in separation science

- Volunteer to review when you can
- Let me know of potential new PIs

Acknowledging BES Support in a Publication

- Acknowledging sole DOE BES program support:
 - Grant: “This research was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Award XXX.”
 - FWP: “This research was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division.”

<https://science.osti.gov/Funding-Opportunities/Acknowledgements>
- When the work was only partially supported by a Separation Science grant, it is important to clearly state which aspect of the research was funded under the grant and which other part of the work was supported by each of the acknowledged sponsors. The preferred method for acknowledgments in this case is “distinction by scope/specific aspects of the research:”
- “This research was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Award XXX (neutron scattering studies), by the National Science Foundation (NSF) under Award # <insert grant award number> (computational studies), and by the National Institutes of Health (NIH) under Award # <insert grant award number> (synthesis of samples).”

Appendix B: Conclusions from the Breakout Sessions

The discussions held by the PIs during the breakout sessions led to independent observations and conclusions that they will publish on their own in the open literature shortly. A reference to that publication will appear here when it is available.