

Materials Research Laboratory

University of California Santa Barbara

Materials Research Outreach Program 2024

Corwin Pavilion, Monday January 29th and Tuesday January 30th 2024

Program and Speaker Bios



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NSF Materials Research Science and Engineering Center [DMR-2308708]

Program: Monday January 29th

Day 1: Monday, January 29, 2024

<i>Session Chair: Omar Saleh</i>		
8:45 am	Opening Remarks	
9:00 am	Rachel Segalman and Scott Shell (UCSB) IRG-1: Electrostatically Mediated Polymer Processing	
9:30 am	Eloise Masquelier (UCSB)	Electroreduction as a Surrogate for Phosphorylation-Controlled Folding and Assembly of Proteins
10:00 am Break		
<i>Session Chair: Chris Bates</i>		
10:30 am	Jason Lipton (HRL)	Toward Wafer Scalability of the SiC Quantum Photonic Platform <i>via</i> Dopant-Selective Photoelectrochemical Etching
11:00 am	Ahra Yi (UCSB)	Low-Temperature Processing in Perovskite Solar Cell Technology
11:30 am	Simon Jones (Fluid Efficiency)	Megasupramolecules: Big Polymers from a Small Startup
12:00 pm Lunch		
<i>Session Chair: Angela Pitenis</i>		
1:30 pm	Morgan Jones (UCSB)	Dislocation Glide Mechanisms in Refractory Multi-Principal Element Alloys at Extreme Temperatures
2:00 pm	Linus Kautzsch (UCSB)	Single Crystal Growth Using High-Pressure Laser Floating Zone Furnaces
2:30 pm Break		
<i>Session Chair: Glenn Fredrickson</i>		
3:00 pm	Frank Bates, Minnesota, <i>Cheetham Lecture</i>	
4:15 pm	Reception and Posters	

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Program: Tuesday January 30th

Day 2: Tuesday, January 30, 2024

Session Chair: Quyen Nguyen

9:00 am

Angela Pitenis and Omar Saleh (UCSB)
IRG-2: Bioinspired Plasticity

9:30 am

Andrea Carlini (UCSB)

Stimuli-Responsive Fluorogenic Hydrogels and Probes Using NITEC Click Chemistry

10:00 am Break

Session Chair: Ram Seshadri

10:30 am

Chunghao Phillip Shih
(COI Ceramics)

Introduction to COI Ceramic's Matrix Composites

11:00 am

Kseniia Karnaukh (UCSB)

Electrostatic Compatibilization of Immiscible Polymers

11:30 am

Daniel Conroy-Beam
(UCSB)

Mating in Mind: Human Mate Choice in Evolutionary and Computational Perspective

12:00 pm Lunch

Session Chair: Nadia Léonard

1:30 pm

Louis Perez (Apeel Sciences)

From Idea to Product: Leveraging Materials to Reduce Food Waste

2:00 pm

Aurland Watkins (UCSB)

Data-driven Identification and *Ab Initio* Characterization of Topological Superconductors

2:30 pm

Rui Zhang (BASF)

Driving Innovation Through Industry-Academia Collaboration

3:00 pm Break

Session Chair: Fred Wudl

3:30 pm

Heather Maynard (UCLA)

Responsive Medicines for Diabetes and Pain

4:00 pm

Bert Meijer (TU Eindhoven)

Supramolecular Polymers and their Role in Liquid-Liquid Phase Separation

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Frank S. Bates is a Regents Professor and a member of the Chemical Engineering and Materials Science department at the University of Minnesota. He received a B.S. in Mathematics from SUNY Albany and M.S. and Sc.D. degrees in Chemical Engineering from MIT. Between 1982 and 1989 Bates was a member of the technical staff at AT&T Bell Laboratories then joined the University of Minnesota where he served as Department Head from 1999 to 2014. Bates conducts research on a range of topics related to polymers, including the thermodynamics, dynamics, structure, and properties of block polymers, polymer blends and solutions. He is a member of the US National Academy of Engineering and the National Academy of Sciences, and the American Academy of Arts and Sciences.



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Andrea S. Carlini is an Assistant Professor of Biomaterials in the Department of Chemistry & Biochemistry at the University of California Santa Barbara. She received her Ph.D. in Chemistry & Biochemistry at the University of California San Diego under the guidance of Prof. Nathan C. Gianneschi. Her doctoral thesis work on “Dynamic Biosynthetic Polymers for Myocardial Tissue Engineering” was supported as an NSF-GRFP. She conducted her postdoctoral work with Prof. John A. Rogers on wearable thermal flow sensors, conductive elastomers, and microfluidic devices. Broadly, her research focuses on the design of structurally dynamic polymers and flexible devices.

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Morgan Jones is a PhD candidate at UC Santa Barbara in the Materials Department. After receiving her Bachelor's degree in Mechanical Engineering and Master's degree in materials science and engineering from the University of Florida, she worked for three years in a mechanics of materials R&D group at Sandia National Labs specializing in the deformation mechanisms of advanced alloys. Now, she uses mesoscale modelling techniques to study the deformation mechanisms of refractory multi-principal element alloys.

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Simon Jones is the CEO of Fluid Efficiency, a Caltech-originated polymer chemistry startup. He has previously worked at NASA's Jet Propulsion Laboratory as well as a number of startups after completing his D. Phil at the University of Oxford, UK

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Kseniia Karnaukh is a fourth-year Ph.D. candidate in the Chemistry Department at UC Santa Barbara, advised by Javier Read de Alaniz. Her current research focuses on the electrostatic compatibilization of immiscible polymers and the development of new light-responsive functional materials. Prior to joining UCSB, Kseniia received her M.S. in Chemical Physics at the Moscow Institute of Physics and Technology, where she worked with Prof. A. Polezhaev to design binuclear and trinuclear transition metal complexes with imidazole-based ligands. Before that, she obtained her B.S. in Chemical Technology of Polymeric Materials at D. Mendeleev University of Chemical Technology of Russia, where she conducted research on novel polyhedral oligomeric silsesquioxanes.

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Linus Kautzsch is a fifth-year PhD student co-advised by Stephen Wilson and Ram Seshadri. He is part of the UC Santa Barbara Quantum Foundry and studies single crystal growth using high-pressure laser floating zone furnaces. His work focusses on magnetic and superconducting nitride compounds and he utilizes neutron scattering facilities to probe the structure and magnetic ground state of these materials.

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Jason Lipton is a Research Staff Scientist in the Materials and Microsystems Laboratory at HRL Laboratories. He received his B.S. in Chemistry from UC Santa Barbara and a PhD in Chemical Engineering from New York University, where he studied photo-accelerated fast charging in Li-ion battery materials. His research at HRL focuses on photoelectrochemical etching of semiconductors for the purpose of scalable manufacturing of quantum photonic integrated circuits and next generation power electronics. Jason also has active programs to improve safety and state-of-health monitoring in EV Li-ion batteries.

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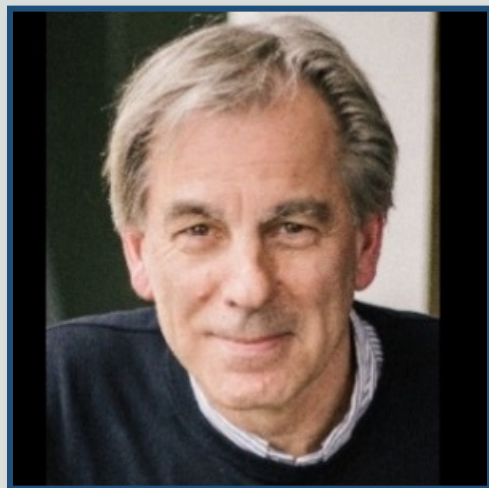


Heather D. Maynard is the Dr. Myung Ki Hong Professor in Polymer Science at UCLA. Maynard has made major contributions in of protein-polymer conjugates, which are important therapeutics for a variety of diseases. She develops new synthetic methods to make the materials, invents new polymers to improve properties such as stability, and demonstrates preclinical efficacy of her conjugates with an eye towards translation for human health. Maynard's research and teaching have been recognized by numerous awards including induction into the American Academy of Arts and Sciences and the American Chemical Society Arthur Cope Scholar Award. At UCLA Maynard serves as Co-Director of the National Science Foundation funded BioPACIFIC MIP and as Associate Director of the California NanoSystems Institute. Maynard is also an Associate Editor of the Journal of the American Chemical Society. Maynard received her PhD from the California Institute of Technology and was an American Cancer Society Postdoctoral fellow at the Swiss Federal Institute of Technology (ETH).

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Eloise Masquelier is a fourth-year PhD candidate in the Materials Department at UCSB, advised by Michael Gordon (ChemE), Daniel Morse (MCDB), and Lior Sepunaru (Chem). She develops new methods that enables triggering and controlling protein assembly, which allow to study pathological mechanisms of protein misfolding related to diseases. Before coming to UCSB, she received her Bachelor and Master degrees in Materials Science from EPFL (Lausanne, Switzerland), and worked at the Lawrence Berkeley National Laboratory (LBNL) on perovskite solar cells.

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E. W. "Bert" Meijer is Distinguished University Professor in the Molecular Sciences, Professor of Organic Chemistry at the Eindhoven University of Technology, and co-director of the Institute for Complex Molecular Systems. After receiving his PhD degree at the University of Groningen with Hans Wynberg, he worked for 10 years in industry (Philips and DSM) before moving to Eindhoven in 1991. He is a member of many editorial advisory boards, including Advanced Materials and is associate editor of the Journal of the American Chemical Society. He has received several awards, including the Spinoza Award (2001), the ACS Award for Polymer Chemistry (2006), the Cope Scholar Award of the ACS (2012), and the Hermann Staudinger Award (2022). In 2020 he was knighted by the king to be Commander in the Order of the Netherlands Lion. He is an honorable member of several academies and societies, including the US National Academy of Sciences and the Royal Netherlands Academy of Science, where he was appointed to Academy Professor in 2014.

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Lou Pérez is a Co-Founder and currently Senior Vice President of Technology at Apeel Sciences, a start-up based in Santa Barbara, CA that focuses on developing technologies and products that create a more resilient fresh food system. At Apeel Sciences, Pérez has helped develop novel plant-based material coatings that prevent transpiration and oxidation, the two major abiotic stressors that lead to food waste; quantitative produce quality measurement tools; utilized AI and ML to produce lifespan prediction models to help optimize fresh produce supply chains; and plant-based antifungals to address biological stressors. At Apeel Sciences, Pérez currently heads the R&D, Engineering, Software, and Data Science efforts and oversees the development and execution of Apeel's Technology Roadmap and IP Portfolio. He is a listed inventor on 15 patents for technology developed at Apeel Sciences. Dr. Pérez earned a BS in Materials Science and Engineering from the University of Florida and worked at the University of Massachusetts, Amherst, in the Polymer Science and Engineering department, and the DuPont Experimental Station before starting his PhD in Materials Engineering at the University of California, Santa Barbara. He published 15 peer reviewed articles and was awarded several fellowships during his graduate studies, the NSF GRFP, NSF IGERT, and GEM. Louis' PhD work focused on the molecular design, synthesis and structure-property relationships of innovative, functional materials for applications in organic thin film electronics.

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Dr. Chunghao Phillip Shih is currently serving as a Chief Engineer at COI Ceramics. He earned his PhD in Materials Science and Engineering from University of Florida in 2010. After completing this PhD, Dr. Shih has worked at various institutions and companies, including Oak Ridge National Laboratory, General Atomics, Kyocera and Qualcomm. The majority of his work is focused on improving and developing fabrication processes and understanding process/property relationships of ceramics matrix composites (CMCs) including Ox/Ox, C/SiC and SiC/SiC systems. With experiences and connections spanning from academic to industry, Dr Shih is considered a world expert in CMC manufacturing, research, and application.

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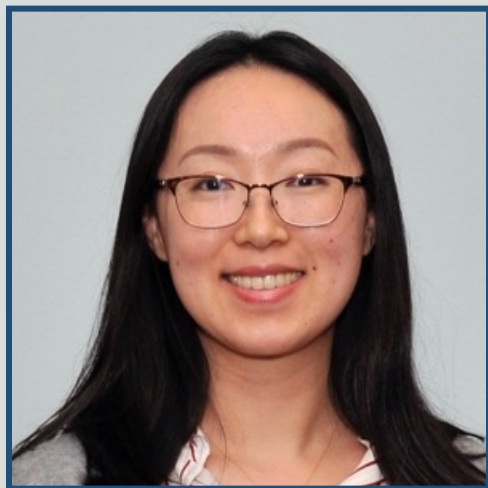


Aurland Watkins is a fourth-year Ph.D. candidate and Quantum Foundry Fellow in the Materials Department at UC Santa Barbara advised by Professor Ram Seshadri. She received her bachelor's degree in Chemistry from Wellesley College where she worked with Professor Christopher Arumainayagam on differentiating between energetic processes that result in prebiotic molecule formation in extraterrestrial environments. Her graduate research centers on identifying and characterizing topological superconductors, a class of materials with promising application for fault-tolerant quantum computing. She uses first-principles computational techniques to study the electronic behavior and topological properties of these systems.

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Ahra Yi earned her Ph.D. in the School of Chemical Engineering from Pusan National University (PNU), South Korea, in February 2022. Currently working as a postdoctoral researcher at the University of California, Santa Barbara, she specializes in chemical engineering and material science. Her expertise encompasses polymer physics, semiconductor physics, and synchrotron-based analysis for advancing next-generation electronics.

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Rui Zhang is an innovation manager at BASF Corporation. She received her PhD from the University of Southern California in Chemistry in 2012. After graduation, she joined BASF Corporation as a research scientist, focusing on the synthesis, formulation, and patterning of ultra-thin metal nanowires. In 2017, she transitioned to a business role and lead a product development team to provide customer-oriented formulations to the North American semiconductor industry. Since 2020, she has been working in her current role, coordinating industry-academia collaborations with Californian universities. Her current portfolio includes topics in battery materials and recycling, electronics materials, catalysis, and advanced analytics.

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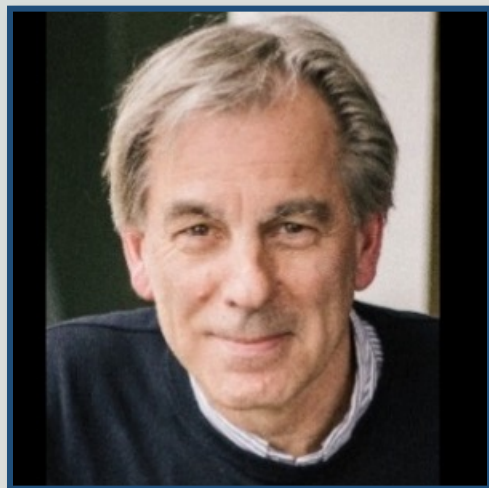


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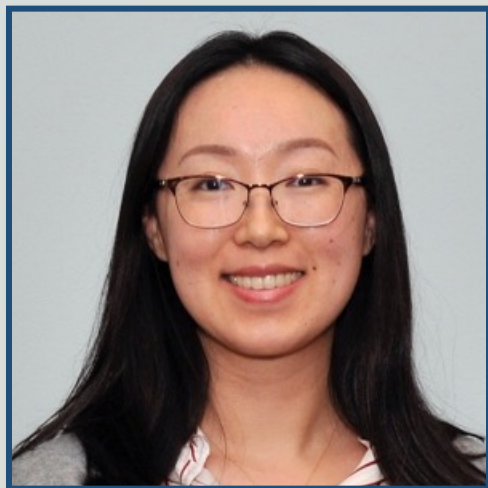


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Rui Zhang is an innovation manager at BASF Corporation. She received her PhD from the University of Southern California in Chemistry in 2012. After graduation, she joined BASF Corporation as a research scientist, focusing on the synthesis, formulation, and patterning of ultra-thin metal nanowires. In 2017, she transitioned to a business role and lead a product development team to provide customer-oriented formulations to the North American semiconductor industry. Since 2020, she has been working in her current role, coordinating industry-academia collaborations with Californian universities. Her current portfolio includes topics in battery materials and recycling, electronics materials, catalysis, and advanced analytics.

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Incorporating Iodine as a Sensitivity-Boosting Agent in Polypeptoid Photoresists for Extreme Ultraviolet Lithography.

C. P. Adams^a, C. Yuan^b, O. Kostko^c, C. K. Ober^b, and R. A. Segalman^a

^aUniversity of California, Santa Barbara

^bCornell University

^cLawrence Berkeley National Laboratory

Polymers have long played a crucial role in patterning silicon to create microelectronic devices. However, as state-of-the-art “extreme ultraviolet” (EUV, 13.5 nanometer wavelength) photolithography tools now allow for the patterning of sub-10 nm features, polymeric photoresists are hindered by significant challenges with stochastics and sensitivity. To address these issues, we have developed polypeptoid-based photoresists as a platform to investigate the effects of polymer sequence and dispersity on patternability. In traditional polymeric systems, dispersities in molecular weight, composition, and sequence are unavoidable due to synthetic limitations. These are compounded by both material heterogeneities in photoresist formulations and poor EUV photon absorption which contribute to patterning defects that can cause chip failures. Sequence specificity of the peptoid system eliminates these variations between polymer chains, enabling precise study of the effects of sequence and dispersity on patternability. Additionally, incorporating halogens into peptoids allows us to probe the impacts of strongly EUV-absorbing elements on photoresist sensitivity at industrially relevant conditions.

Incorporation of Long-Lived Interactions into Metal-Ligand Coordinating Polymer Electrolytes to Improve Bulk Mechanical Properties

J. T. Bamford^a, S. D. Jones^{a,b}, N. S. Schauer^a, B. J. Pedretti^{c,d}, L. W. Gordon^a, N. A. Lynd^c, R. J. Clement^a, and R. A. Segalman^a

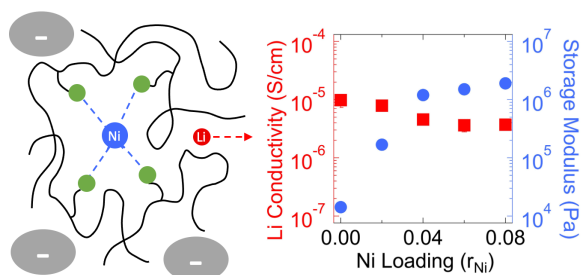
^aUniversity of California, Santa Barbara, Santa Barbara, CA

^bCalifornia Polytechnic State University, San Luis Obispo, CA

^cUniversity of Texas at Austin, Austin, TX

^dMassachusetts Institute of Technology, Cambridge, MA

Nonflammable and electrochemically stable solid polymer electrolytes (SPEs) may enable the next generation of safe and energy-dense Li⁺ batteries. However, designing SPEs that simultaneously exhibit robust mechanical properties and high Li⁺ conductivity is fundamentally challenging due to their liquid-like ion transport mechanism. Recently, bulk mechanics and *total* conductivity have been partially decoupled in dynamic network SPEs, including “mixed salt” electrolytes that use metal-ligand interactions to form transient crosslinks. However, the impact of network formation on Li⁺ transport is not well understood. Herein, a polymer electrolyte with one type of ligand functionality is simultaneously blended with two metal-cation salts, one of which forms long lasting dynamic crosslinks with the ligand to improve bulk mechanics and the other comprises electrochemically-relevant Li⁺. The polymer backbone is based on polyethylene oxide (PEO), the ligand comprises an imidazole (Im) side chain, and the salts are nickel bis(trifluoromethanesulfonyl)imide and lithium bis(trifluoromethanesulfonyl)imide. Oscillatory shear rheology reveals a mechanically-reinforcing rubbery plateau in systems with Ni²⁺-Im bonding that is not present in systems with only Li⁺-Im bonding. Consequently, adding Ni²⁺ improves the shear storage modulus from 0.014 to 1.907 MPa. Meanwhile, adding Ni²⁺ only marginally reduces Li⁺ conductivity from 9.8 to 3.7 *10⁻⁶ S/cm at 90 °C. Transient Ni-Im crosslinks primarily affects bulk mechanics and the diffusion of polymer chains at larger length scales, whereas the local dynamics that govern conductivity are relatively unaffected. As a result, blending metal-coordinating polymer electrolytes with multiple metal cations offers a straightforward route to independently tuning mechanical properties and Li⁺ transport.



Ni²⁺-imidazole bonding forms transient crosslinks that improve mechanical properties without inhibiting Li⁺ transport.

Immiscible Polymer Blend Compatibilization through Pendant Ionic Interactions in Semi-Crystalline Polymer Systems

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Polymer recycling is an important avenue to reduce commodity plastic waste, but various challenges result in less than 10% of plastics actually being recycled in the U.S.¹ One issue that limits mechanical recycling is the immiscibility between dissimilar polymers that results in macrophase separation and poor material properties, necessitating sorting of different polymeric materials.

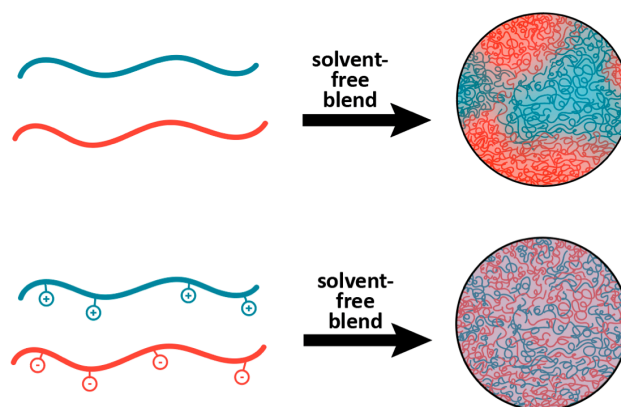
Prior theoretical work has suggested that small numbers of ionic interactions can be used for immiscible polymer blend compatibilization.² Recent work has demonstrated that low levels of incorporation of ionic bonds formed via an acid-base proton transfer mechanism results in the formation of optically clear blends in an otherwise incompatible poly(dimethylsiloxane) and poly(*n*-butyl acrylate) mixture. Unlike this model elastomeric system, hydrocarbon polymers that dominate industry (polyethylene and polypropylene) are semi-crystalline,

introducing additional processing considerations. To this end, the model system is extended to study amorphous (polystyrene) and semi-crystalline (polyethylene) high- T_g polymers containing low levels of ionic bond incorporation. Blends of ionically compatibilized high- and low- T_g polymers result in flexible films. These films are characterized with differential scanning calorimetry, dynamic mechanical analysis, and small angle X-ray scattering, highlighting the underlying rich physics of immiscible polymer blends with sparse incorporation of charged groups.

This work is supported by the National Science Foundation through the Materials Research Science and Engineering Center (MRSEC) at UC Santa Barbara: NSF DMR-2308708 (IRG-1).

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Incompatible polymers are modified with sparse pendant ionic groups to enable thermodynamic compatibilization and improve blend properties.

Experimental Modeling of Li-Ion Battery Recycling

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The adoption of renewable sources of energy and the electrification of cars have been proposed to reduce CO₂ emissions, but both rely on Li-ion batteries (LIBs). At present, only about 58% of the 300,000 tonnes of LIBs reaching end-of-life every year are recycled.¹ LIB recycling remains a challenge because of the wide variety of elements and compounds found within each battery. This leads to a feedstock that, while concentrated with many valuable elements, is chemically challenging to separate.

While many different LIB recycling methods have been proposed, commercial recyclers generally follow a process of shredding, heat treating, and leaching to recover valuable materials.² The intermediate products of this process are known as ‘black mass’ due to their complex composition. The production of this black mass during the heat treatment step is not completely understood due to the wide variety of possible chemical reactions between the numerous LIB components. The reactivity of the mixtures is also highly dependent on the processing conditions such as temperature, component ratio, and atmosphere.³

Although there have been prior investigations into the pyrolysis of LIB materials, past studies have neglected to examine the extended wealth of battery components that can react during heat treatment. Polymer separators and binders can act as reducing agents and metallic current collectors form complex oxides. Advances in LIB technology have led to novel materials entering the market and ultimately the recycling stream where their impact will have to be evaluated. To date, nobody has systematically surveyed the reactions and products possible. This work will be essential to responding to future changes in LIB feedstocks.

This research has in part been supported by BASF SE under the CARA program.



‘Black mass’ is the complex mix of compounds resulting from the pyrolysis of LIBs.

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Trivially Parallelizable Hybrid Model for Full Sequence Simulation of Free Radical Polymerization

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Efficiently modeling uncontrolled free radical polymerization (FRP) using kinetic Monte Carlo (KMC) simulations has long been a challenge of kinetic modeling due to inherent simultaneous fast and slow reactions (propagation and termination respectively). Despite many advances in algorithmic and hardware acceleration,^{1,2} the speed of KMC simulations often limits its reliable applications towards optimization and machine learning. Here, we present a novel algorithm for the simulation of FRP that enables significant acceleration. Because polymer lifetimes during FRP are very short, reaction probabilities during polymer growth can be assumed constant. These reaction probabilities can be calculated using a deterministic model and stochastically sampled to emulate the full detail of KMC simulations at a fraction of the computation. Unlike traditional KMC, this algorithm can also be efficiently parallelized on GPUs to greatly accelerate the simulations of FRP. We successfully reduce the cost of simulation by two orders of magnitude, from minutes to less than 10 seconds. This speed up will enable applications of machine learning for complex reaction engineering optimization.

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A Universal Platform for The Introduction of Sensitive Molecules in Liquid Crystal Elastomers

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Liquid crystal elastomers (LCEs) are a class of materials capable of exhibiting strong mechanical responses to external stimuli.¹ Added to this, when these systems are enhanced by covalently attaching photoswitches, due to the nature of these molecules, multiple responses (spectroscopical, structural, thermal, hydrophobic/hydrophilic, ionic, pH etc.) are seen. Given this elementary concept, photoswitches have been introduced in LCEs in many reports to show simultaneous response to light, temperature, humidity, etc.² however, every time a new photoswitch is introduced, it is done on a specific polymer matrix through a specific polymerization technique that yields a very unique material incapable of comparing or standardizing to the rest of materials previously done in the literature.³ It exists a lot of potential in fusing these photoswitches and LCEs field, however, due to the chemically sensitive nature of photoswitches and the chemically harsh conditions used to polymerize these liquid crystal elastomers, to this day, no platform capable of bringing these two fields together has been developed.

In this work, a universal platform capable of introducing sensitive photoswitches in LCEs is developed. Azobenzenes, Spiropyrans, Donor-acceptor Stenhouse adducts, and highly absorbing organic dyes are covalently introduced in liquid crystal elastomers enabling novel responses of these family of materials. Simultaneously, we believe that this work has the potential to develop fundamental studies on the force produced by the mechanochemical isomerization of these photoswitches that will allow, for the first time, to quantify the mechanical work output done by each single molecule of the photoswitch.

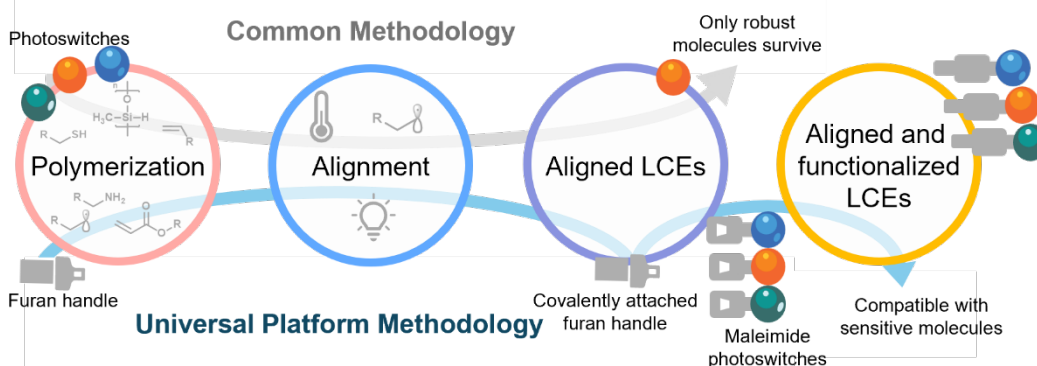


Figure 1. Schematics of the methodology followed to functionalize LCEs with sensitive molecules while retaining the molecular properties of both the polymer and the switches.

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Multiphase DNA Nanostar Liquids and their Morphologies

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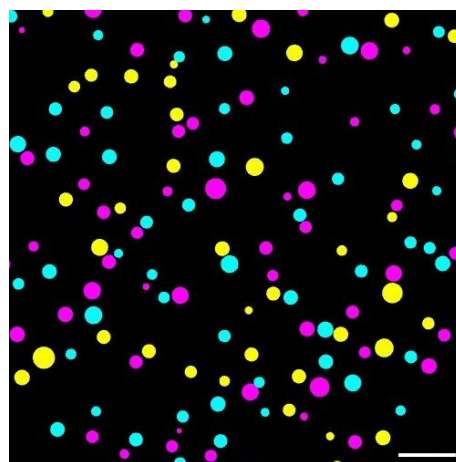
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Multiphase liquid droplets in the cell allow for spatial compartmentalization of biomolecules which support different chemical processes in each region. Inspired by the diversity of coexisting membrane-less organelles, we seek to better understand the thermodynamic limits to the number of phases which can simultaneously exist outside the confines of a cell, and the complex morphological structures they can create. Using a model DNA liquid system, we construct multiple immiscible liquids by exploiting the sequence-specific nature of DNA hybridization. We also discuss how tuning interactions between phases can allow different mesoscale droplet structures to be realized.

This work was partially supported by the MRSEC Program of the National Science Foundation under Award No. DMR 2308708, and by the W.M. Keck Foundation.



Three distinct, immiscible liquid phases of DNA, colored yellow, blue, and pink, formed via liquid-liquid phase separation. Scale bar: 50µm

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Constructing Functional Ionic Polymeric Materials with Alkyl Sulfonates

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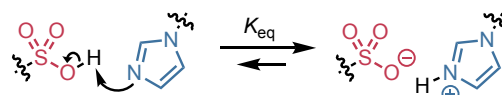
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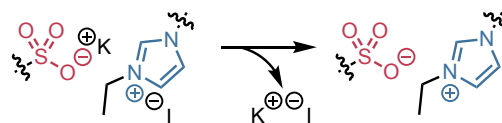
A comprehensive understanding of the relationship between the ionic bond formation mechanism and resulting properties of the compatibilized polymer blend is critical for utilizing electrostatic interactions in the recycling of mixed plastic waste. Ionic bonds between polymer chains are typically formed by the reversible proton transfer process between acid- and base-containing polymers, or counterion release *via* a coacervation process upon solution mixing of polyanions and polycations. Utilizing an immiscible polymer blend of poly(*n*-butyl acrylate) (PnBA) and poly(dimethylsiloxane) (PDMS) as a model system, we demonstrate the quaternization of tertiary amines with alkyl sulfonates as a novel synthetic pathway towards counterion free polymer blends compatibilized by unscreened, strong ionic bonds. The neutral ethyl sulfonate acrylate monomer is derived from its anionic sulfonate analogue, and subsequent reversible addition-fragmentation chain-transfer (RAFT) polymerization yields the homopolymer containing reactive, but neutral ethyl sulfonate units along the backbone. Reaction of these groups with tertiary amine small molecules leads to quaternization and the formation of polyanions. Sparse (*i.e.*, 1 mol%) incorporation of pendant ionic bonds along the polymer backbones provides blend compatibilization, whereby ethyl sulfonate groups incorporated along PnBA (≈ 70 kDa) *via* RAFT copolymerization quaternizes quinuclidine groups tethered along PDMS (≈ 30 kDa), resulting in a microphase separated network. The single ionic bond per polymer chain prevents blend macroscopic phase separation as shown by the formation of a lamellae-forming supramolecular PDMS-PnBA block copolymer through the end group quaternization of quinuclidine with ethyl sulfonate, the latter installed *via* RAFT single unit monomer insertion chemistry.

This work is supported by the National Science Foundation through the Materials Research Science and Engineering Center (MRSEC) at UC Santa Barbara: NSF DMR 2308708 (IRG-1).

Acid-Base Proton Transfer

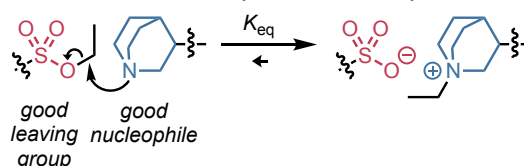


Counterion Release *via* Coacervation



This Work:

Quaternization of Tertiary Amines with Alkyl Sulfonates



The quaternization of tertiary amines with alkyl sulfonates approach is hypothesized to yield counterion free polymer blends compatibilized by strong ionic bonds.

Acidic Conditions Enhance the Fusion of Extracellular Vesicles with Synthetic Liposomes: Towards the Development of Hybrid Drug Delivery Vectors

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Exosomes are cell-secreted vesicles less than ≈ 150 nm in diameter which contain gene-encoding and gene-silencing RNA and cytosolic proteins and have roles in intercellular communication. Exosomes have been shown to bind to specific cells and deliver intact genetic material to the cytosol of target cells, indicating they are capable of targeting and endosomal escape and thus ideal candidates for use in hydrophobic cancer drug delivery. The use of exosomes as drug delivery vehicles requires efficient loading of intact exosomes with hydrophobic drug. An emergent method for doing this involves the fusion of exosomes with synthetic vesicles containing hydrophobic drug, which has been achieved using depletion attraction and freeze-thaw cycling in the past. Here we demonstrate the viability of a novel method to induce fusion of exosomes and synthetic vesicles using low pH with relatively low impact on exosome integrity compared to established methods.

Towards Magnetic Cluster Expansion Monte Carlo Simulations of Battery Electrodes

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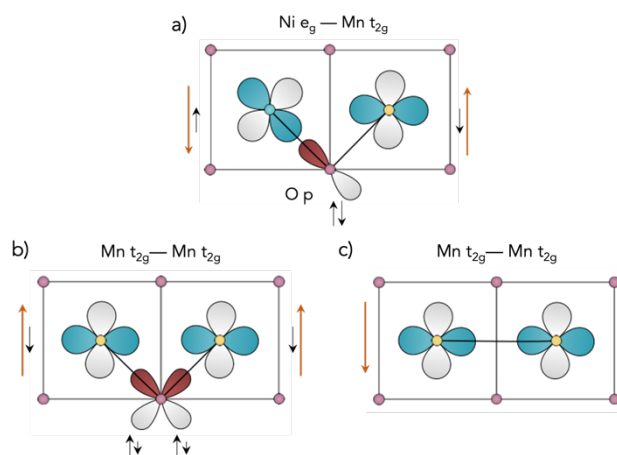
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Constructing and employing computational models to analyze magnetic interactions in Li-ion battery materials offers insights into the underlying dynamics that govern favored spin orientations. These configurations can have great implications in understanding the driving forces behind their redox processes, degradation, and failure mechanisms. In addition, these comprehensive simulations can equip us with a robust toolset to analyze experimental data such as magnetometry and Electron Paramagnetic Resonance (EPR).

In this work, we utilized first principles alongside statistical mechanical methods such as cluster expansions and Monte Carlo, implemented via the CASM software package, to model magnetic interactions in the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) spinel battery material. Density functional theory (DFT) calculations of several Ni-Mn orderings, including the ordered ground state (space group $P4_332$), reveal a preference for an antiferromagnetic arrangement of the Ni and Mn sublattices due to strong superexchange interactions between Mn^{4+} and Ni^{2+} ions. Magnetic cluster expansions of these structures further verify these results, with strong antiferromagnetic Ni-Mn J coupling constants and ferromagnetic Mn-Mn and Ni-Ni exchange interactions among adjacent transition metals (interactions illustrated in figure above).

Further simulations of the LNMO magnetic system as a function of temperature were carried out through Metropolis Monte Carlo, using the Ising magnetic model. While effectively replicating the experimental magnetic states at both high and low temperatures, this model fell short in accurately predicting the experimental transition temperature between ordered and disordered magnetic states. To address this discrepancy, we transitioned to the more representative Heisenberg magnetic model, better aligned with actual spin behavior. To efficiently sample intricate Heisenberg statistics, we adopted the Hamiltonian Monte Carlo algorithm. This approach utilizes Hamiltonian dynamics to evolve the system, effectively mitigating random walk behavior within Monte Carlo iterations. By proposing distant states with a high probability of acceptance, this method significantly enhances sampling efficiency.



a) Strong AFM superexchange magnetic coupling between Ni^{2+} and Mn^{4+} . For Mn^{4+} - Mn^{4+} interactions, there are two competing mechanisms: b) superexchange resulting in a FM ordering and c) direct exchange, which favors an AFM ordering.

Design of 1D-0D Heterostructures Based Photocatalyst Using WO₃ Nanowire-Gold Nanoparticles

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There is a need for a photocatalyst to degrade organic pollutants in drinking water. Tungsten oxide has been shown to degrade organic dye and destroy bacteria via the photocatalytic effect. To reduce the recombination of electron hole pairs and enhance the overall reactive oxygen species generation, we have designed a heterostructure of plasmonic gold nanoparticles and WO₃ nanowire. The photocatalyst was able to degrade methylene blue more efficiently under laser irradiation in our observation than with tungsten oxide alone. Further study must be done to improve the sunlight irradiation process.

A Hybrid Monomer to Bridge the Gap Between Silicones and Traditional Organic Polymers

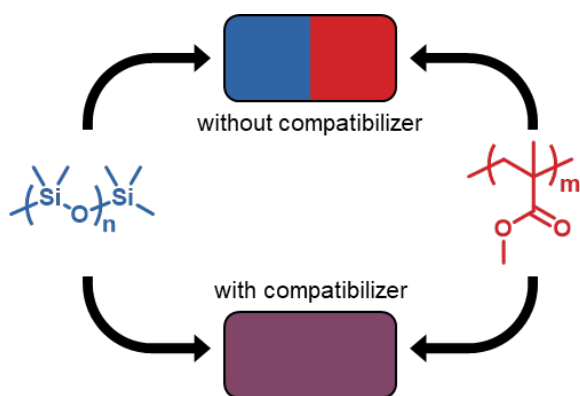
P. T. Getty^a, A. Abdilla^{b,e}, M. Czuczola^b, C. A. D'Ambra^a, E. A. Murphy^b, S. Biswas^f, J. M. Mecca^e, S. Swier^e, T. D. Bekemeier^f, A. Fielitz^f, C. M. Bates^{a,b,c,d}, and C. J. Hawker^{a,b,d}

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Ubiquitous in daily life, silicones possess desirable material properties that arise from the unique character of their Si–O bonds. However, the nature of these bonds also renders silicones incompatible with most traditional organic polymers, necessitating improvements in current compatibilization strategies. Here, we examine the fundamental interactions of a novel silicone-containing methacrylate monomer with polydimethylsiloxane and poly(methyl methacrylate). Well-defined block, random, and block-random copolymer libraries of these three building blocks were synthesized and characterized. Specifically, to elucidate the effect of varying hybrid monomer content on the material properties of these copolymers, differential scanning calorimetry, small-angle X-ray scattering, and rheology were employed.



Without a compatibilizer, silicones (left, blue) will macrophase separate from traditional organic polymers (right, red). A compatibilizer will prevent this macrophase separation, allowing the development of novel materials.

Fluid Lipid Micelle Nanoparticles as Vectors of the Hydrophobic Cancer Drug Paclitaxel: Synthesis and Characterization

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Since their initial discovery in 1964, the use of lipid nanoparticles (LNPs) in drug delivery has been the subject of intense research that has resulted in numerous FDA-approved therapies.¹ Comprised of an aqueous core surrounded by a hydrophobic bilayer, LNPs are attractive drug delivery vehicles owing to their ability to encapsulate a wide variety of molecules, ease of functionalization, and biocompatibility. A long-standing obstacle facing LNP-based drug delivery is their short half-life in blood—on the order of minutes for bare LNPs.² The hydrophilic polymer polyethylene glycol (PEG) dramatically prolongs LNP blood circulation time when affixed to the particle surface and has come to be an essential component of LNP formulations.³

In contrast to the extensive attention received by LNPs within drug delivery, **micellar nanoparticles have yet to be thoroughly investigated**. Lacking an aqueous core and consisting solely of a lipid monolayer, **micelle sizes (diameter ca. 5-20 nm) are an order of magnitude smaller than LNPs (diameter ca. 50-200 nm)**.⁴ With small particle size being a crucial parameter for improving nanoparticle tumor penetration and blood circulation time, micelle nanoparticles hold significant promise for the delivery of cancer therapeutics. For these reasons, there is significant benefit to further exploring micelles as drug delivery vectors.

This project aims to synthesize and characterize a set of novel high-curvature (lipid head group size > tail size) branched PEG-lipids, which are expected to promote formation of **ultra-small, stealth fluid micelles**. Starting with basic building blocks, complete synthesis of multiple branched PEG-lipids has been completed. Characterization of the molecules has been performed using thin layer chromatography, ¹H NMR, and ESI-MS. Additionally, kinetic drug loading experiments have been conducted on micelles formed with these molecules. Future experiments will explore the potential of these molecules to form fluid micelles for the delivery of PTX both in vitro and in vivo, to develop a new class of precision cancer therapeutics utilizing fluid micelles.

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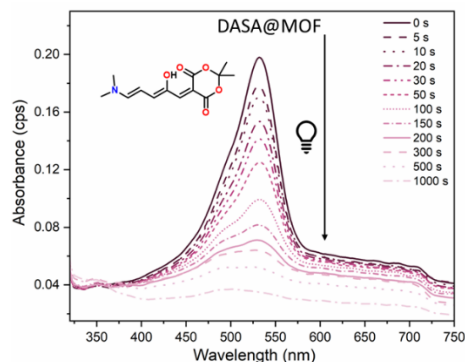
Solid-State Switching of Donor-Acceptor Stenhouse Adducts Using Isomeric Metal-Organic Frameworks

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Light, as a stimulus, can initiate various molecular transformations and can be harnessed by smart materials that respond dynamically to exposure of light. One notable category of photoswitchable molecules well suited for designing these smart materials is donor acceptor Stenhouse adducts (DASA). DASA molecules are light sensitive molecules capable of exhibiting unique properties in their switchable linear (colored) and cyclic (colorless) forms when triggered with light. However, in most cases, the photoswitching of the molecules is observed in the solution-state. In addition, DASA can decompose to their starting materials in the presence of polar protic solvents, further limiting their use. To address the challenges, this work seeks to leverage a class of porous materials, called metal-organic frameworks (MOFs). We hypothesize the MOF will protect DASA from outside environment such as polar protic media and will provide a pore environment that can enable solid-state switching. One of the challenges in working with such intricately complicated systems like MOFs and DASAs is that there could be a lot of cooperative factors working together to generate a specific response, which make their understanding difficult. This motivates us to systematically unravel the different dictating factors and achieve DASA@MOF materials exhibiting efficient switching and reversibility. Specifically, we aim to understand what's a more confounding factor for DASAs to switch in the MOF environment: the pore size of the MOF, inherent hydrophobicity of pore, DASA architecture. For this, we chose a hydrophobic MOF with 1D pore channels, MIL-140, to fabricate three DASAs@140A and studied their photo/thermal switching capabilities. A representative example is shown in the figure.



Solid-state reflectance spectra of DASA@140A under the effect of light.

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Feeling the Stress: Color-Changing Polymer Networks with Functional Motifs

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Stimuli-responsive motifs can change their molecular structure and/or properties in response to a range of external stimuli, including temperature, pH, visible light, or mechanical force. Such motifs have enabled the design of smart materials that respond to their environment, leading to innovative advancements of flexible sensors, soft robotics, and drug delivery systems.¹ However, the commercial success of widespread stimuli-responsive materials remains modest with temperature-responsive mugs and photochromic sunglasses being two of only few examples. The challenges faced in widespread commercial adoption of stimuli-responsive materials can be attributed to the complexity, inefficiency, and incompatibility of the chemistry involved in their synthesis and integration.² To address this, we developed a new class of halo-, photo-, and mechanochromic motifs based on Stenhouse salt adducts that are cheap and scalable to synthesize. These functional motifs can undergo a reversible structural change between their colorless (closed cyclopentenone) and brightly colored (open triene) state.³

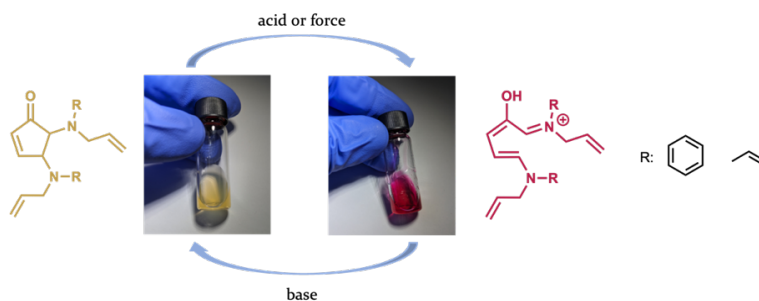


Figure 2: Visual and structural schematic of our halochromic motif

Furthermore, we modify these motifs with reactive vinyl handles that allow for integration into polydimethylsiloxane (PDMS) networks to highlight the value of this new class of functional motifs for the development of novel stimuli-responsive materials.

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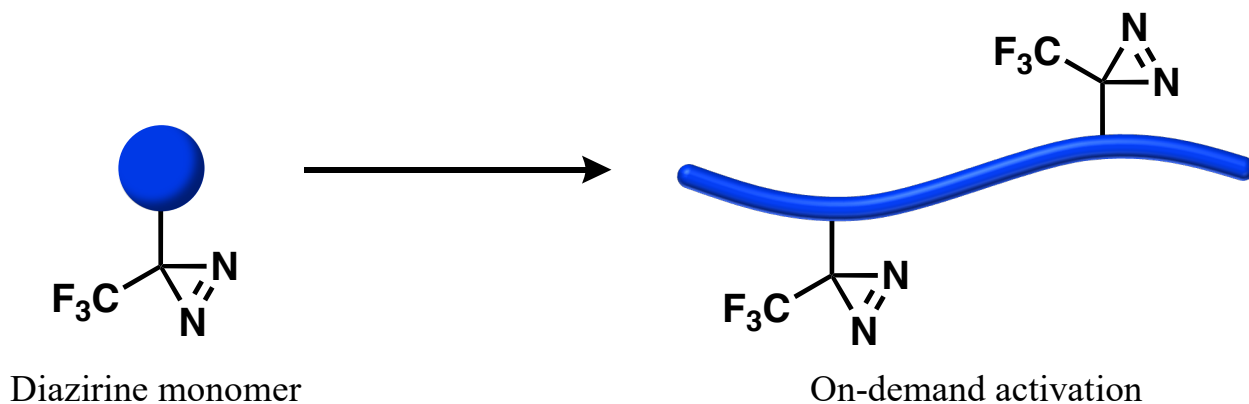
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Synthesis and Reactivity of Diazirine-Containing Copolymers

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Diazirines are a class of versatile functional groups that can serve as precursors for carbenes, enabling downstream reactions such as σ -bond insertion for C–H functionalization of polymer backbones. The efficient generation of carbene intermediates can be achieved through either thermal or photochemical activation of diazirines with recent studies highlighting bis-diazirines as efficient cross-linkers for various commodity polymers. However, the preparation and application of polymeric diazirine compounds remain elusive. Herein, we report the synthesis and polymerization of diazirine-containing monomers resulting in polymers featuring diazirine sidechains. These polymeric diazirine materials can undergo on-demand activation, facilitating diverse post-polymerization modification of commodity polymers and the preparation of a wide range of functional materials.



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Phase Behavior Studies of Mixtures of Intrinsically Disordered Protein Tau and Anionic Liposomes

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Intrinsically disordered protein tau, an overall positive polyampholyte, is a microtubule (MT)-associated protein localized to axons in vertebrate neurons. Tau regulates MT dynamic instability and aberrant tau-MT interactions is implicated in Alzheimer's and other neurodegenerative diseases. While there is incomplete understanding of the mechanisms driving neurodegenerative pathology, some evidence exists that aside from tubulin and MTs (tau's natural substrates) tau can interact with other anionic macromolecules including lipids. However, the extent and conditions of these interactions are not understood. Our goal is to understand the structural implications of the electrostatic associations of isoforms of human tau with anionic liposomes. We studied the phase behavior of mixtures of full 4RL-tau and anionic liposomes, both as a function of salt concentration and lipid/tau charge ratio, using differential interference contrast and fluorescence microscopy. We will describe our findings, which include spontaneous formation of anionic liposome-tau complexes and liquid-phase tau coacervates.

Ionic Conductivity of Zwitterionic System with Various Li Salts Concentration

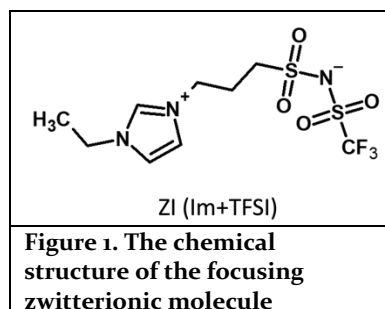
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Zwitterions are the organic salts which contains cation and anion that are covalently tethered; therefore, they have large dipole moments and zero net-charge. Owing to these characteristics, zwitterions have been applied as electrolyte materials of Li-ion batteries aiming high ionic conductivity and high transference numbers as large dipole moments dissociate Li salts into ions, which hinders salts aggregation, and zero net-charge suppresses transport of zwitterions, which enhances transportation of the target lithium ions.^{1, 2} It is generally favorable to increase Li salts concentration since the total ionic conductivity proportionally increases with Li salts concentration, but the electrolytes with different salts concentrations show distinct structures and ionic transport mechanism becomes more complicated.



Here in this poster session, we focus on the zwitterion (Figure 1) which contains imidazole and TFSI moieties. This chemical structure has bulky cationic and anionic moieties which delocalize positive and negative charge and reduce the interaction with LiTFSI, leading to the higher Li ion conductivity. Utilizing this zwitterion, we discuss the relationship between the salts concentration and ionic conductivity and transference number while elucidating the effect of the structures of zwitterion/LiTFSI mixtures.

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Photoresin for Light-Mediated Additive Manufacturing by Diels-Alder Chemistry

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3D printing has broadened the scope of bioprinting and tissue engineering to develop complex structures similar to natural cells and tissues.¹ However, conventional 3D printing techniques that use radical photopolymerization reactions can be problematic for biological systems.² This is because the radicals produced during the initiation and propagation of polymers can harm cell viability or modify proteins in an undesirable way. Therefore, alternative 3D printing methods that are highly selective and compatible with biological systems, and not based on radical chemistry, are highly desirable. Recently, we developed photo-gated cyclopentadiene (Cp) derivatives that allow for efficient bioconjugation and control of polymer click reactions without the need for radicals.³ We used this method to create novel photo-resins for 3D printing that can undergo rapid gelation through the Diels-Alder click reaction. Initial studies indicate that these systems quickly form hydrogel networks when exposed to light, thereby allowing for radical-free step-growth polymerization. The rheological properties of the resulting hydrogel networks were evaluated under UV irradiation, demonstrating their suitability for 3D printing applications. To demonstrate its printability, we tested the resin to form several 2D-patterned hydrogels with high fidelity, showcasing the potential of photo-gated click chemistry for biocompatible 3D printing.

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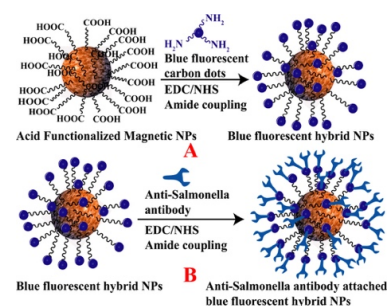
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Design of Bioconjugated Magneto-Fluorescent Carbon Dots for the Separation, Identification, and Eradication of Superbugs

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Superbugs leading to sepsis are responsible for more than 40% of mortality rate associated with antimicrobial resistance. Rapid identification of these superbugs at early stages will greatly enhance health care and save lives (Neu 1992, Spellberg 2004). Here we will discuss the design of bioconjugated multifunctional carbon-based nanodots (carbon dots) which can be used for the separation, identification, and eradication of superbugs. In our design, fluorescent carbon dots were synthesized by a solvothermal method (Jiang 2015). The synthesized carbon dots were combined with carboxylic acid-functionalized magnetic nanoparticles made via coprecipitation method from ferric chloride and 1,6-hexanedioic acid (Pramanik 2016). Specific antibodies were attached to the magneto-fluorescent carbon dots using EDC/NHS amide coupling for the isolation and identification of methicillin-resistant *Staphylococcus aureus* (MRSA) and *Salmonella* DT104 superbugs (Pramanik 2016). The magneto-fluorescent carbon dots were also attached with pardaxin antimicrobial peptide for the separation and eradication of both superbugs from infected blood samples. The experiment shows that multifunctional carbon dot nano systems can be used for the identification and eradication of multi-drug resistant bacteria in clinical settings.



Design of antibody-attached magneto-fluorescent carbon dots for the separation of superbugs.

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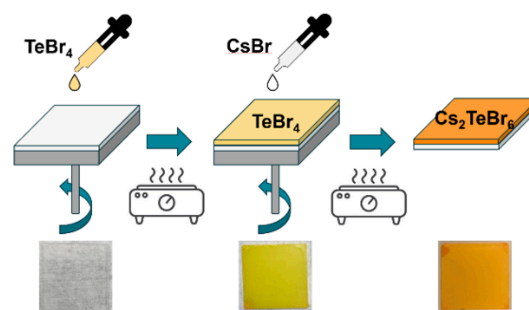
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High Purity Vacancy-Ordered Double Perovskite Films Formed Via a Two-Step Deposition Process

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In this work, we report a new procedure for spin coating vacancy-ordered double perovskite Cs_2TeX_6 ($X = \text{Cl}, \text{Br}, \text{I}$) films with high purity. Research interest in metal-halide perovskite semiconductors has recently skyrocketed due to their outstanding photophysical properties and solution-based processing methods, but growing films from solution frequently elicits the formation of defects that reduce their stability and performance.¹ A two-step deposition method has been shown to suppress defect formation and is especially helpful for all-inorganic perovskites where precursors commonly have conflicting solubilities.² The sequential spin coating of TeX_4 and CsX produces uniform films with homogeneous crystallite size and high purity confirmed with scanning electron microscopy and X-ray diffraction, respectively. In-situ photoluminescence data of film crystallization illuminates the dynamics of this process as well as the absence of quantum confinement effects when compared to 3-dimensional CsPbBr_3 . A two-step deposition procedure is additionally well-suited for synthesizing mixed halide alloys of perovskite materials; UV-Vis diffuse reflectance spectroscopy reveals band gap tunability by simply varying the concentration of dispensed cesium salt solution. This study will inform future development of vacancy-ordered double perovskites as a viable alternative to higher dimensional lead-based perovskites such as methylammonium lead iodide.



Graphical depiction of 2-step spin-coating method for Cs_2TeBr_6 . Photos of a blank quartz substrate, TeBr_4 film, and final Cs_2TeBr_6 film are shown below the graphic.

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Fluorinated Graphene Oxide Based Nanoarchitecture for Efficient Removal of PFAS, Pharmaceutical Toxins, and Pathogens

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Ensuring access to clean and safe drinking water remains a critical global challenge, impacting a substantial portion of the world's population as stated by the United Nations. Our research aims to address this issue through the creation of a 3D porous nanoplatfrom employing two-dimensional fluorinated graphene oxide (FGO) and polyethyleneimine (PEI) to efficiently remove polyfluoroalkyl substances (PFAS), pharmaceutical contaminants, and waterborne pathogens from polluted water sources. The nanoplatfrom demonstrates impressive capabilities. It efficiently adsorbs perfluoro nonanoic acid (PFNA) and achieves a high removal rate for various short- and long-chain PFAS. Comparative studies highlight the effectiveness of the FGO-PEI nanoplatfrom in PFAS removal. Additionally, it exhibits exceptional removal efficiency for moxifloxacin antibiotics. The nanoplatfrom's smaller nanopores allow the complete elimination of *Salmonella* and *Escherichia coli* bacteria from water. Our data indicates that the FGO-PEI nanoplatfrom successfully removes PFAS, pharmaceutical contaminants, and pathogens from water samples collected from various sources, including rivers, lakes, and tap water.

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Temperature Dependent Latent Transformation of 3D-Printed Polymer Composite Foams with Tailored Mechanical Properties

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Utilizing diverse additive manufacturing (AM) techniques, high-performance polymer composites with superior properties have been fabricated, opening a wide array of engineered applications. However, defects and processing-related latent impacts could restrict their full potential. We previously developed polymer composite foams using digital light processing (DLP) method, involving photopolymerization, thermal curing, and heat treatment.[1] In-depth mechanical analysis on porosity-controlled 3D printed composite foams demonstrated high stiffness to weight ratio, energy dissipation capabilities, and remark fatigue tolerance under compression.[2] Here, we employed differential scanning calorimetry (DSC), dynamic mechanical analyzer (DMA) and Fourier transform infrared spectroscopy (FTIR) to unravel the complex evolution of material properties, morphologies, and mechanical behaviors. Our results revealed a notable exothermic reaction at elevated temperatures, attributed to residual unreacted monomers inducing thermally induced network curing and enhancing material stiffness. Further, we demonstrated that thermal polymerization could be kinetically controllable by varying annealing conditions to tailor mechanical properties. The morphological transition from a two-phase structure to a fully cured single-phase network was elucidated, providing insights into processing-structure-property relationships. This work advances the understanding of additive manufacturing, offering the way for the precise engineering of composite foams with tailored functionalities.

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Manipulation of Multiphase Fluid Using Photo-Responsive Surfactants

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The precise manipulation of droplets and bubbles holds immense potential for various applications, such as boiling, condensation, microfluidics, and electrocatalysis. These systems provide an attractive platform for handling small liquid volumes using a contactless approach and minimal energy input. On Earth, gravity predominantly influences most fluid systems, maintaining the stability of fluid interfaces. Moreover, buoyancy serves as a natural driving force for fluidic systems, enabling efficient control of fluid motion. However, in microgravity environments, conventional methods of fluid manipulation become increasingly challenging. In processes like boiling and water splitting, the absence of buoyancy may cause bubbles to stagnate, leading to dry patches that can decrease system performance and even trigger failure. Furthermore, when heat dissipation is required in a system, the loss of natural convection in space can result in heat accumulation, causing abrupt increases in temperature and reduced efficiency.

Compared to previous methods, light stimuli possess high spatial resolution, easy control, and contactless characteristics. Light can be fine-tuned in terms of wavelength, intensity, beam size, and frequency, providing real-time control through simple modifications of light conditions or positions. This flexibility allows for the generation of light gradients within a system. Previous research has demonstrated light stimuli to locally heat fluids, creating Marangoni flow. However, in most applications, temperature is a controlled variable, with reactions and processes requiring specific temperatures or isothermal conditions. Thermal instability may arise in some physical systems due to temperature-dependent properties. Thus, the use of photo-responsive surfactants to tune fluids is more appealing because it provides opportunities to control fluids without an additional heating effect.

In our study, light-induced photoisomerization prompts surfactants to switch between two isomers under different light conditions, initiating Marangoni flow due to the chemical gradient instead of temperature differences. The experiment evaluates the effect of surface tension by using representative fluids with distinct surface properties, including aqueous solution, Krytox, toluene and methanol. Depending on the combination, light may either increase or decrease surface tension. We propose that this innovative method is well-suited for multi-phase systems, such as bubble departure, droplet sliding, and bubble migration. To validate the method, we initially conducted ground-based experiments. When a bubble was injected into a bulk fluid containing surfactants and illuminated from the top, it detached from the substrate within 60 s. Moreover, a single droplet could be either drawn towards or repelled by a light source on a lubricant-infused surface or the lubricant itself.

In microgravity, Marangoni effects can become the dominant source of fluid motion. Using a CubeLab implemented by Space Tango, our microgravity experiments enabled precise bubble motion control and quantitative analysis of fluid motion, induced by the photo-Marangoni effect. Our research showed that light irradiation could instantaneously awaken stagnant air bubbles. By alternating LEDs on and off, we obtained continuous bubble motion, guiding the bubble moving

to the rhythm of light. This back-and-forth performance endured for over 30 minutes, attesting to the long-term stability of the surfactants and the reliability of the system.

The proposed method enables the investigation of chemical and physical properties in multiphase system using photochemistry, providing valuable insights into fluid dynamics. Furthermore, this method allows real-time, contactless control of droplets and bubbles with minimal energy input, creating a gateway to potential applications across various microgravity fields. This study presents a simple and promising new approach for dynamically manipulating fluids in microfluidic, thermal, and water harvesting devices in space exploration.

Acknowledgment:

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Self-Healing and Reprocessing of Saturated Hydroxyl-Terminated Polybutadiene-Based Networks Enabled by Dynamic Covalent Chemistry

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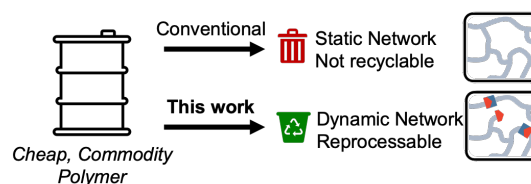
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Hydroxyl-terminated polybutadiene (HTPB) is found in many applications due to its ease of manufacturing, useful mechanical properties over a wide temperature range, and reactive hydroxyl chain ends.^{1,2} Typically, HTPB is crosslinked with isocyanates to form polyurethane thermosets. Limitations of this approach include the use of toxic

isocyanates and the oxidative instability of backbone alkenes. To avoid degradation pathways enabled by undesired alkene reactivity, a fully saturated version of HTPB (“sHTPB”) is often preferred. This clear aliphatic liquid polyol provides improved light- and weather-stability and can be used to make polyurethane coatings with tunable mechanical properties such as flexibility, adhesion, elongation, and strength.³ In this work, saturated HTPB is used to form reprocessable covalent adaptable networks that are capable of stress relaxation and reprocessing, without relying on isocyanates or unstable alkenes. This approach introduces dynamic chemistry to the HTPB-network via chain-extension and subsequent crosslinking with 4-methyl caprolactone (4mCL) and a novel bislactone crosslinker. Using benzenesulfonic acid (BSA) as a transesterification catalyst, stress relaxation times were measured at temperatures of 70 °C to 100 °C. Despite crosslinking, these networks behave elastically, as evidenced by strain-at-break values of 93% for pristine samples, and dynamically, as shown by a strain-at-break of 72% after reprocessing the damaged samples. Shape reprogramming is also demonstrated by straining the crosslinked networks and heating to elevated temperatures where bond exchange occurs. These findings illustrate the advantageous properties that can be achieved by using cheap commodity building blocks to achieve dynamic properties.



Saturated Hydroxyl-Terminated Polybutadiene

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Hydration Dynamics and Structure of Charge-Screened Polymeric Zwitterions

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Polymeric zwitterions exhibit exceptional fouling resistance through formation of a strongly hydrated surface of immobilized water molecules. While extensively tested for application-specific performance, the characteristics of this hydration layer and the role of molecular design on broad fouling resistance remain unclear. In this work, Overhauser dynamic nuclear polarization (ODNP) relaxometry and sum frequency generation (SFG) vibrational spectroscopy analyze the hydration dynamics and structure of polymeric zwitterions over salt conditions of a range of common antifouling applications. These zwitterions are found to possess rapid water diffusion within their first 2-3 hydration shells, which accelerate toward bulk behavior in highly saline, charge-screened environments. Faster dynamics correlate with a measurable reduction in bound surface water through weakened electrostatic interactions. Furthermore, charge delocalization is identified as a useful parameter for tuning the hydration structure and dynamics around polymeric zwitterions. SFG spectroscopy reveals that delocalized zwitterions form more hydrated surfaces. This finding correlates with ODNP measurements, which show slower water dynamics for delocalized zwitterions, potentially as a result of increased hydrophobic interactions.

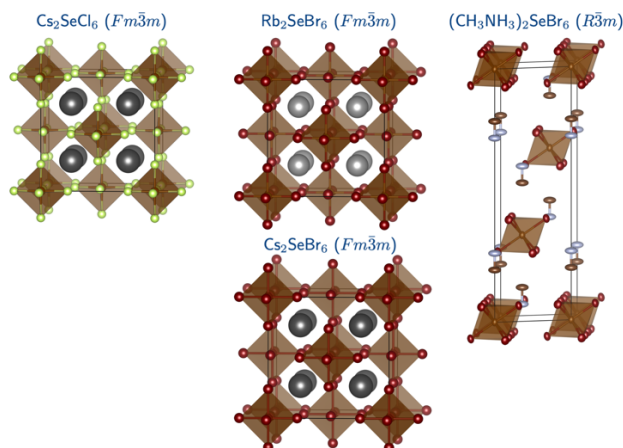
This research was primarily supported by the Office of Naval Research awards N00014-16-1-2960, N00014-20-1-2152, N00014-20-1-2234, and N00014-23-1-2127. Polymer synthesis and purification leveraged shared experimental facilities supported by the BioPACIFIC Materials Innovation Platform of the National Science Foundation under Award No. DMR-1933487. Magnetic resonance experiments leveraged shared experimental facilities supported by the NSF MRSEC program under Award No. DMR 1720256. SDM acknowledges support from the National Science Foundation Graduate Research Fellowship (DGE 2139319).

Prototype Inorganic and Hybrid Halide Perovskite Derived $A_2\text{SeX}_6$ Compounds

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Halide perovskites are promising for applications in optoelectronic and photovoltaic (PV) devices.¹ Besides conventional halide perovskites with the formula $AM^{\text{II}}X_3$, vacancy-ordered double perovskites with the formula $A_2M^{\text{IV}}X_6$ have been receiving increasing attention. These compounds resemble the double perovskites $A_2M^{\text{I}}M^{\text{III}}X_6$, with alternating M -site vacant. The ability to engineer these materials for desired applications hinges on cultivating a comprehensive understanding of how their electronic structures impact relevant properties. A notable area of interest encompasses perovskite compounds that contain lone pairs which often do not impact their average structure but display signs of their presence locally.² Vacancy-ordered halide double perovskites of $4s^2 \text{Se}^{4+}$ with the formula $A_2\text{SeX}_6$ ($A = \text{CH}_3\text{NH}_3^+$, K^+ , Rb^+ , Cs^+ ; $X = \text{Cl}^-$, Br^-) exhibit crystal structures seemingly unaffected by the presence of Se lone pairs. Several of these compounds, especially with hybrid cations have not previously been reported. The compounds were prepared using solution-based and hydrothermal methods. The poster will present structural and optical characterization, and band structures calculated using the Vienna Ab initio Simulation Package (VASP) software suite.



Representative structures of $A_2\text{SeX}_6$ ($T = 298 \text{ K}$) vacancy-ordered double perovskites. For the hybrid compound, H atoms are excluded, and 50% thermal ellipsoids are depicted.

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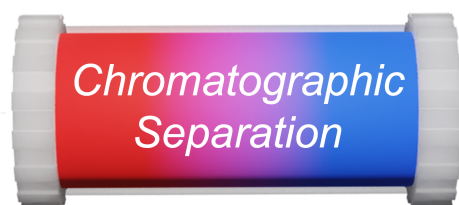
Accelerated Discovery of Block Copolymers Via Automated Chromatography

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Block copolymers are widely used in many applications due to their spontaneous self-assembly into a variety of nanoscale morphologies. However, a grand challenge in navigating this diverse and ever-growing array of possible structures is the accelerated discovery, design, and implementation of new materials. Here, we report a versatile and efficient strategy to accelerate materials discovery by rapidly building expansive and high-quality block copolymer libraries through a combination of controlled polymerization and chromatographic separation. Fractionation of a small number of as-synthesized samples gives rise to large polymer libraries spanning a wide range of compositions. Small angle X-ray scattering reveals fractionation significantly enhances long-range order compared to as-synthesized materials and enables the preparation of detailed phase diagrams. This user-friendly, scalable, and automated approach to discovery significantly increases the availability of well-defined block copolymers with tailored molecular weights, molar-mass dispersities, compositions, and segregation strengths, accelerating the study of structure–property relationships in advanced soft materials.



- ✓ Efficient & scalable
- ✓ Wide material scope
- ✓ Accelerated discovery

Automated chromatographic fractionation of an as-synthesized parent diblock copolymer leads to a well-defined library of samples enabling the accelerated development of comprehensive phase diagrams.

Emerging 2D Materials-Based Nanoarchitecture for Water Purification

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Even today, getting safe drinking water is one of the big challenges for society. As per World Health Organization (WHO), several millions of people are lacking drinking water that is free from viruses, toxic chemicals, and bacteria. Here, we discuss the new development of a water filtration systems using a two-dimensional (2D) nanomaterials. Due to atomically thin surface and good mechanical strength, 2D graphene, graphene oxide, as well as transition metal dichalcogenides are considered to be advanced membrane materials. This chapter highlights the recent reports on how emerging material-based membranes have been used to tackle water desalination. Notably, we discuss the synthetic method development for the design of novel membranes which have the capability for the separation of toxic chemicals and pathogens. Finally, we have discussed the future challenges and prospects of current development.

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Tuning Dithiolane Reactivity Towards Designer Degradable Polymers

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1,2-dithiolanes are desirable moieties in degradable polymers because of their ability to be selectively reduced and then re-oxidized in a closed loop while at the same time being compatible with free-radical polymerization. In particular, lipoic acid, a cheap natural product containing a 1,2-dithiolane ring, has been demonstrated to copolymerize in both controlled and uncontrolled radical polymerization with n-butyl acrylate. These copolymers have been shown to be degradable with the use of reducing agents, and then re-polymerized through oxidation. However, lipoic acid cannot be copolymerized with many other comonomers such as styrene, severely limiting the space for varying mechanical properties for lipoic acid-containing degradable polymers. In this work, the effect of different structural features on 1,2-dithiolanes on their reactivity, and their compatibility with a more diverse selection of copolymers, are explored. Simple and accessible syntheses of disulfide ring-containing monomers and kinetic studies of polymerizations are presented in order to probe the effect of size and substitution on monomer reactivity.

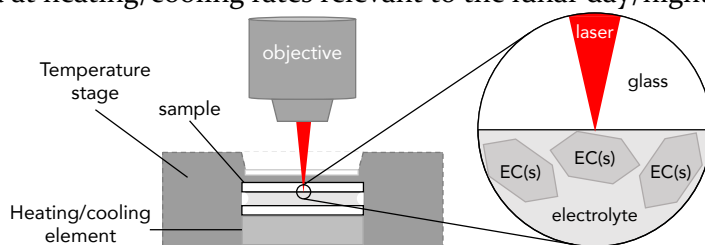
Probing Commercial Li-Ion Battery Electrolyte Dynamics through Cryogenic Freeze-Thaw

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Commercial Li-ion batteries have the potential to significantly reduce the costs of auxiliary power systems for future lunar missions, however, their ability to survive exposure to cryogenic temperatures during lunar night has not been rigorously evaluated. While previous missions have employed thermal management systems to prevent battery performance reductions and safety issues which arise at low temperatures, there is interest in whether batteries employed in applications which would only operate during the moderate temperatures of lunar day could avoid use of costly and bulky thermal management systems.¹ Among the components which comprise a battery, we have characterized the composition and phase transformations of a commercial electrolyte using a micro-Raman spectrometer interfaced with a temperature stage that can be operated across all lunar temperatures and at heating/cooling rates relevant to the lunar day/night transition. While the electrolyte was expected to behave like a binary mixture, solidification was only observed at temperatures significantly below the solidus line ($-30\text{ }^{\circ}\text{C}$ vs. $-18\text{ }^{\circ}\text{C}$) with some regions found to remain a liquid at temperatures as low as $-70\text{ }^{\circ}\text{C}$.² Furthermore, as the electrolyte was warmed back to room temperature, some regions were found to remain solid well above the liquidus line ($15\text{ }^{\circ}\text{C}$ vs. $3\text{ }^{\circ}\text{C}$). In spite of the anomalous behaviors exhibited by the electrolyte, the processes ultimately appear to be reversible which suggests that the electrolyte can survive the freeze-thaw process associated with the transition between lunar day and night.



Schematic of experimental setup for probing temperature-dependent electrolyte dynamics

This work was supported by an Early Career Faculty grant from NASA's Space Technology Research Grants Program (grant number 80NSSC23K0072). The authors acknowledge the use of the Quantum Structures Facility within the California NanoSystems Institute, supported by the University of California, Santa Barbara and the University of California, Office of the President.

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Photoresponsive Size of Disordered Protein Complexes Via Electrostatic Co-Assembly with Oppositely Charged Azobenzene Switch

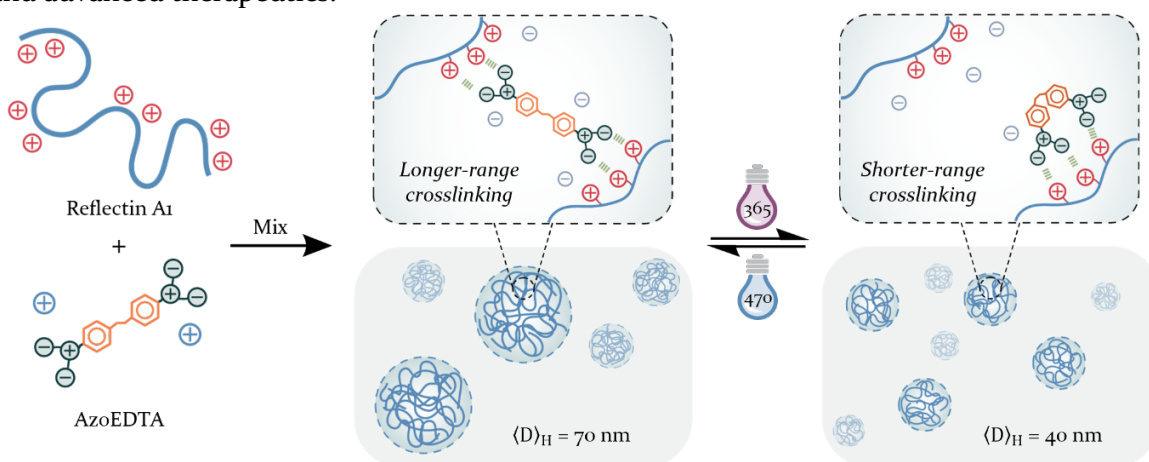
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Disordered proteins often undergo a stimuli-responsive, disorder-to-order transition which facilitates dynamic processes that modulate a cell's material properties such as strength, chemical composition, and reflectance. It remains challenging to gain rapid and spatiotemporal control over this disorder-to-order transition, which limits these proteins' incorporation into novel materials. The reflectin A₁ protein is a cationic, intrinsically disordered protein whose assembly is responsible for adaptive color camouflage in cephalopods, and it would be advantageous to control this behavior within a synthetic material.¹ Herein, we present light-responsive electrostatic co-assembly with a multivalent azobenzene photoswitch as a non-invasive and tunable strategy to control reflectin's assembly. We study the co-assembly behavior of a novel azobenzene photoswitch with reflectin and show that *E*–*Z* photoisomerization of azobenzene cycles the diameter of the photoswitch-protein assemblies between 70 nm and 40 nm. The protein assemblies formed with the (*E*) and (*Z*) isomers show differences in interaction stoichiometry and secondary structure, which indicate that photoisomerization modulates photoswitch-protein interactions to change assembly size. We hypothesize these photoswitchable interactions are regulated by the change in planarity, polarity, and conformation of azobenzene upon photoisomerization. Our promising results offer a novel strategy to control the assembly and function of disordered proteins like reflectin and the implications of this work have applications in functional materials, biocatalysis, and advanced therapeutics.



Schematic of photocontrolled electrostatic interactions between disordered reflectin protein and multivalent azobenzene photoswitch with anionic end groups.

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Utilizing a Single Component, Cyclopentadiene, to Synthesize and Recycle Diels–Alder Commodity Polymers

T. M. Tran and J. Read de Alaniz

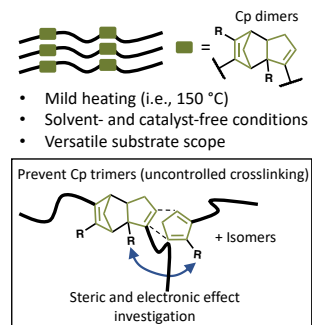
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The first detailed study of Diels–Alder linear polymers was reported in 1961, followed by a stream of investigations. However, such materials generally suffer from insolubility, low-molecular-weight, non-reversibility, and thus remain underexplored for potential construction of recyclable thermoplastics. Cyclopentadiene (Cp), structurally elucidated in the 1890s, has been known as one of the most reactive and desirable dienes for Diels–Alder material synthesis. Regardless of the compelling chemistry, its propensity to dimerize and oligomerize, making monomer synthesis and controlled polymerization notoriously challenging. In fact, only two prominent reports have appeared in the literature since the first attempt to homopolymerize Cp by Staudinger in 1926. In our previous paper, a strategy was demonstrated to synthesize and isolate a pure tetrafunctional Cp monomer under mild conditions, a single component that allows access to a better-defined degradable elastomer. In this work, we will focus on the reactivity investigation of different Cp derivatives, revealing the first controlled synthesis and characterization of soluble linear Cp homopolymers. The potential applications in closed-loop recycling were also studied. The Cp-incorporated commodity materials can be thermally depolymerized (up to 70%) and repolymerized to the parent analogs in solvent- and catalyst-free conditions. Furthermore, full recovery persisted over three cycles, confirming the efficient chemical recyclability. Overall, this work provides a versatile platform to access and study new cyclopentadiene-based polymers with promising applications in advanced closed-loop recycling.

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Steric and electronic effect investigation of different cyclopentadiene derivatives leads to controlled synthesis and characterization of soluble linear homopolymers

Introduction of Donor-Acceptor Stenhouse Adducts (DASAs) into Liquid Crystal Elastomers for White Light Motion of Soft Robots

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This study enhances light-responsive liquid crystal elastomers (LCEs) for diverse applications by introducing Donor-Acceptor Stenhouse Adducts photoswitches. Unlike azobenzene, these photoswitches transition from highly colored to colorless forms, improving interaction with thick LCEs (>100 μm). The approach enables efficient 3D fabrication of light-responsive actuators, featuring user-friendly actuation at lower light intensities, even underwater and with white light. In our investigation, we initially employed Fickelmann's Method for the synthesis of DASA LCE films. Aniline donor was introduced alongside the conventional LCE recipe (crosslinker, mesogen, and PHMS). The characterizations on DASA LCE were performed (including 2D-WAXS, DSC, UV-Vis, etc.) and the kinetics associated with the switching nature of DASA were studied. By incorporating a second-generation DASA (with aniline as the donor and barbituric acid as the acceptor), an LCE film measuring 0.55 cm in thickness can undergo contraction to about 80% of its original dimensions. This transformation is accompanied by a shift from a highly colored state to a colorless one, induced by exposure to visible light. From the results, we concluded that due to the photochemical nature of DASA, the mechanical and optical responses of DASA LCEs can be stimulated by visible light. Furthermore, DASA LCEs are anticipated to serve as a significant advancement in the development of future photo-responsive materials.

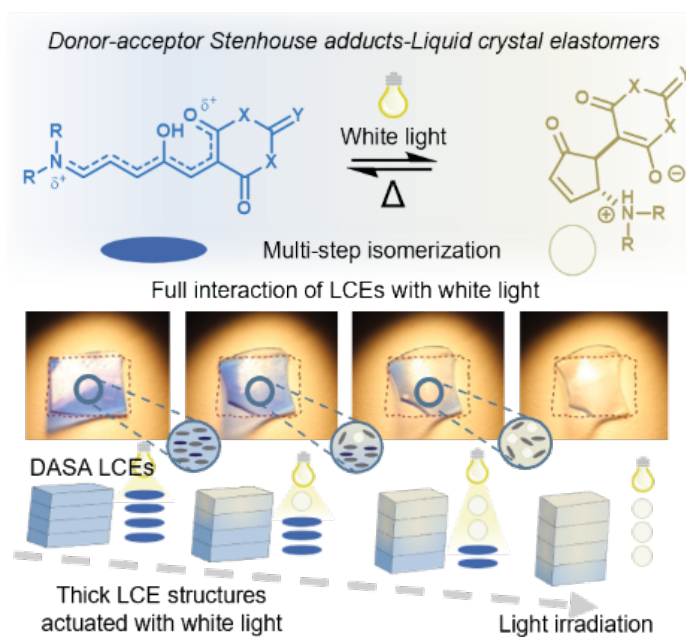


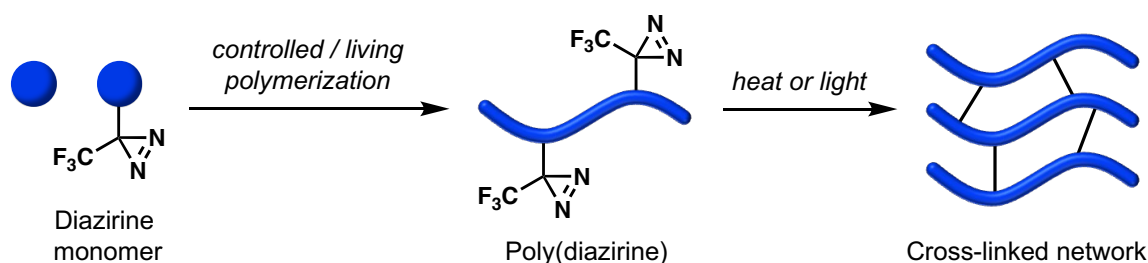
Figure 3. Schematics of the uses of negative photochromism in liquid crystal elastomers enabled by DASA

Polymeric Diazirines as Efficient Cross-Linking Agents

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The formation of polymer networks through cross-linking of linear polymers is an important process for enhancing the mechanical properties and stability of the resulting materials. Among the various strategies for introduction of cross-links, carbene insertion into the abundant C-H bonds in polymer backbones is potentially an attractive and universal cross-linking strategy. Recently, diazirine, as a stable carbene precursor, has garnered significant attention for functionalization of different polymer backbones due to its mild activation under either thermal or photochemical conditions, rapid C-H insertion capabilities, and commercial accessibility. While diazirine small molecules have been designed for cross-linking and functionalizing commodity polymers, the synthesis and utilization of polymeric diazirines remains unexplored. In this study, we demonstrate the synthesis and polymerization of diazirine-based monomers under different controlled radical conditions. Gelation of the resulting polymers is achieved upon activation of the diazirine moieties through either thermal or photochemical means.



Synthesis of Highly Branched Polymers Via High Throughput Screening

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Highly branched polymers represent an appealing polymer architecture due to their unique properties. However, in many instances, the monomer conversion needs to be carefully controlled to prevent network formation or gelation at high polymer concentrations. Given the multiple factors involved in the polymerization, high throughput screening (HTS) techniques emerge as invaluable tools for rapidly optimizing conditions and ensuring successful production of highly branched polymers without the formation of insoluble networks. The Chemspeed robotic polymer synthesis platform within BioPACIFIC MIP enabled HTS for optimizing reaction conditions in the synthesis of highly branched, multi-functional polymers (Figure 1). This study focuses on an acrylate as the primary monomer, with a bifunctional vinyl monomer as the main branching agent in the synthesis of highly branched polyacrylates. Gelation threshold, molecular weight and polydispersity were systematically investigated with a range of variables via parallel reactions conducted on the Chemspeed synthesis platform. This work confirms the effectiveness of HTS for optimizing the synthesis of highly branched polymers using the Strathclyde method. The Chemspeed automated synthesis platform facilitates efficient exploration of various polymerization parameters, including concentrations, feed ratios, branching agents, chain-transfer agents (CTAs), and reaction times. The findings show consistent trends in gelation thresholds and molecular weight variations, with reliable reproducibility.

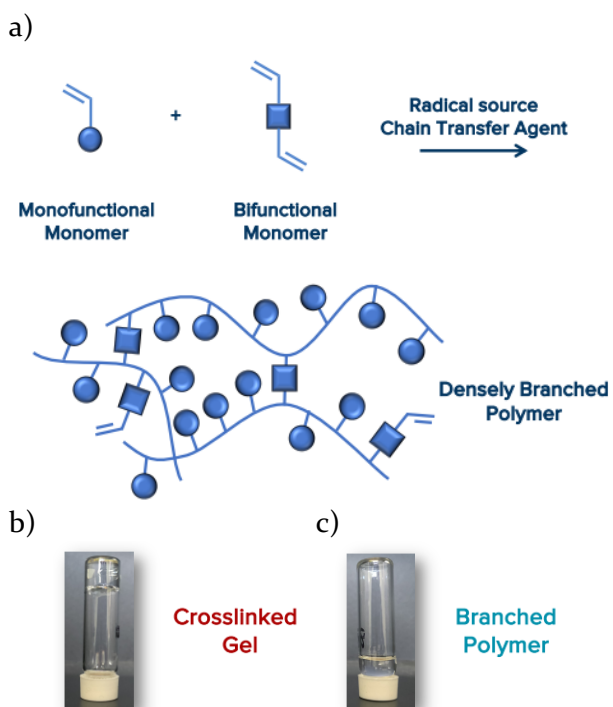


Figure 1. a) Scheme of hyperbranched polymer synthesis and b) photographs of gels produced under unoptimized conditions and c) hyperbranched polymers produced under optimized conditions.

Influence of Cationic and Anionic Charge Densities on Zwitterionic Hydrogel Membranes

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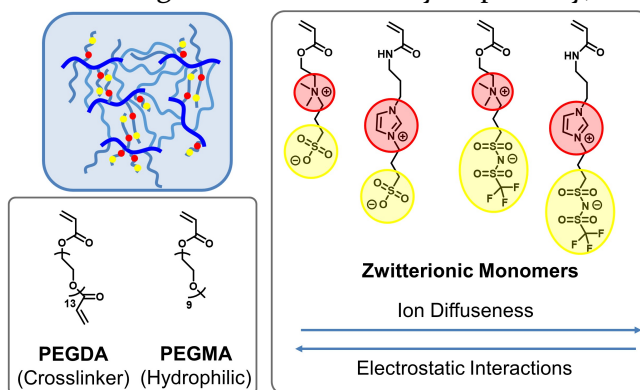
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Polymeric zwitterions, due to their exceptional fouling resistance and hydrophilicity, are extensively used for biomedical applications and coatings, but the effect of zwitterionic functionalities on water filtration membranes has been underexplored. This study incorporates a library of zwitterionic monomers of varying diffuseness (molecular volume over which the cation/anion charge is delocalized) into polyethylene glycol (PEG)-based non-porous hydrogels. ~0.5 mm thick films prepared via UV polymerization were optically clear and exhibited high gel fractions (>95%) up to 40 wt% zwitterion incorporation. 3-point bend testing and dynamic mechanical analysis (DMA) measured the modulus of the dried films and a two orders of magnitude difference in storage modulus is seen between the imidazolium-trifluorosulfonylimide (TFSI) networks (5 MPa) and the ammonium-sulfonate (SO₃) networks (0.5 GPa), indicating stronger electrostatic-dipole interactions between the zwitterions with smaller ion diffuseness. NaCl and LiCl permeability measurements were conducted using concentration driven flux cells. At equivalent covalent crosslink densities, ammonium sulfonate membranes exhibited similar ϕ_{water} and ~25-50% higher salt permeabilities compared to unfunctionalized PEGDA networks while membranes containing more diffuse charges showed lower ϕ_{water} and lower salt permeabilities. Differences in permeability can be attributed to both tortuosity differences in the hydrogel due to water uptake and electrostatic ion hopping between zwitterion sites which becomes outstanding at more localized charges.



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