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University of California Santa Barbara

Materials Research Outreach Program 2026
Day 1

Corwin Pavilion, Wednesday January 26th 2026

Speaker Bios, and Poster Abstracts

UC Santa Barbara MRL | Materials Research Laboratory

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

Professor **Grace Han** obtained a PhD in Chemistry at MIT with Prof. Timothy Swager, focusing on organic semiconductor synthesis. After completing her PhD, she joined the Department of Materials Science and Engineering at MIT as a postdoctoral associate with Prof. Jeffrey Grossman. In 2018, Grace started her independent career in the Department of Chemistry at Brandeis University, where she was promoted to Associate Professor with tenure in 2024. Since July 2025, Grace has joined UC Santa Barbara as an Associate Professor, building an interdisciplinary research program in Materials Chemistry and Energy Sciences. Her group's research focuses on developing molecular photoswitches and photochemistry for solar energy storage and optically-controlled recycling of polymers, catalysts, and critical minerals. Grace has been awarded honors during her independent career, including NSF CAREER Award, AFOSR Young Investigator Award, Alfred P. Sloan Fellowship, Camille Dreyfus Teacher-Scholar Award, ChemComm Emerging Investigator Lectureship, AAAS Marion Milligan Mason Award, Cram-Lehn-Pedersen Prize in Supramolecular Chemistry, and Moore Inventor Fellowship.

Katie Shaffer is a fourth-year Ph.D. Candidate in the Materials Department at the University of California, Santa Barbara. She received a B.S. in Materials Science and Engineering from North Carolina State University in 2022 where she worked in several labs honing her materials characterization skills. Currently, she works in the Interfacial Engineering Laboratory with Dr. Angela Pitenis and studies the structure-property relationships of hydrogels surfaces with neutron reflectivity.

Jerrick Edmund is a fifth-year Ph.D. candidate in the Department of Chemical Engineering at the University of California, Santa Barbara, advised by Professors Craig Hawker and Rachel Segalman. His research explores the use of electrostatic interactions to compatibilize immiscible polymer blends. He earned his Bachelor of Chemical Engineering from the University of Minnesota in 2021, where he conducted research on polymer self-assembly with Professors Frank Bates and Tim Lodge.

Professor **Frank Bates** is a Regent's Professor (2007–present), a Distinguished McKnight University Professor (1996–present) in the department of chemical engineering and materials science at the University of Minnesota, where he has been a faculty member since 1989. Prior to his appointment at the University of Minnesota, Bates was a member of the technical staff at AT&T Bell Laboratories from 1982–1989. He is known for his wide-ranging research in polymer science, especially, his contributions to the fundamental understanding of the phase behavior of polymer blends and to the physics of microphase separated block copolymers. He was elected to the National Academy of Engineering in 2002, the American Academy of Arts and Sciences in 2010, and National Academy of Sciences in 2017.

Starting Winter 2026, Professor Bates holds the position of Distinguished Visiting Professor, UC Santa Barbara

Professor **Simon Billinge** has more than 25 years of experience developing and applying techniques to study local structure in materials using x-ray, neutron and electron diffraction including the development of novel data analysis methods including graph theoretic, artificial intelligence and machine learning approaches. He earned his Ph.D in Materials Science and Engineering from University of Pennsylvania in 1992. After 13 years as a faculty member at Michigan State University, and 18 years at Columbia University he took up his current position as Professor of Materials Science and Director of the California Nanosystems Institute (CNSI) at UC Santa Barbara. He also held a joint position of Physicist at Brookhaven National Laboratory between 2008 and 2022. Prof. Billinge has published more than 350 papers in scholarly journals. He is a fellow of the American Physical Society and the Neutron Scattering Society of America, a former Fulbright and Sloan fellow and has earned a number of awards including, in 2025, the Gregori Aminoff prize of the Royal Swedish Academy of sciences, and the Innovation in Materials Characterization Award of the Materials Research Society. He was honored in 2011 for contributions to the nation as an immigrant by the Carnegie Corporation of New York. He is Section Editor of *Acta Crystallographica Section A: Advances and Foundations*. He regularly chairs and participates in reviews of major facilities and federally funded programs.

Devon Callan is a sixth-year Ph.D. candidate in the Chemical Engineering department at UC Santa Barbara. He received his B.S. in Chemical Engineering in 2020 from the University of Texas at Austin, where he worked under the guidance of C. Grant Willson on the directed self-assembly of block copolymers. Currently, he is advised by Chris Bates and is developing accelerated methods to model reversible copolymerization and predict polymer properties. He is also passionate about developing accessible open-source scientific software.

Komal is a PhD candidate in Chemistry at UC Santa Barbara, working in the Read de Alaniz Group. Their research focuses on designing macrocyclic cyclopentadiene–maleimide (Cp–Mal) systems to understand and control material behavior across hard and soft matter. By studying topology-driven thermomechanical properties in thermosets and applying the same Cp–Mal chemistry to create responsive hydrogels, Komal demonstrates how a single dynamic reaction can tune mechanics over a wide range of stiffness.

Professor **Charlotte K. Williams** FRS is the Professor Charlotte Williams is the Statutory Chair in Inorganic Chemistry at the University of Oxford. Her research interests address sustainable chemistry and the circular economy for polymers. Recent discoveries include methods to transform carbon dioxide and/or bioderived monomers into engineering plastics, elastomers and adhesives. She is also working to understand structure-performance relationships in polymerization and depolymerization catalysis. and discovery of efficient and selective plastic recycling processes. Charlotte's research has been recognized by recent prizes including the Leverhulme Medal of the Royal Society (2022), The Royal Society of Chemistry Tilden Medal (2021), by election as a Fellow of the Royal Society (2021) and by an OBE from Queen Elizabeth II for Services to Chemistry (2020). Charlotte is the director of the EPSRC Sustainable Chemicals and Materials Manufacturing Hub (SCHEMA) and the UK Catalysis Hub (Cat Hub) – both are large-scale, multidisciplinary research programmes involving multiple academic, commercial and international partners. Charlotte is the founder and a director of econic technologies, which sells catalysts for carbon dioxide transformation into polymers to customers worldwide. Earlier in her career, she was professor of catalysis and polymer chemistry at Imperial College London (2003-2016), a postdoctoral researcher at University of Cambridge, working with Profs. Andrew Holmes FRS and Prof. Sir Richard Friend FRS, and a postdoctoral researcher at the University of Minnesota, working with Profs. Marc Hillmyer and Bill Tolman. She was awarded her PhD in ethene polymerization catalysis, supervised by Prof. Sir Vernon Gibson FRS and Prof. Nick Long. She received her BSc in Chemistry with Spanish from Imperial College London.

Inflammation, Mechanics, & Lubricity Modulated Through Mucin Gel Networks

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Mucins are highly glycosylated biopolymers produced by epithelial cells that act as a barrier preventing bacterial and viral invasion[1] while also providing lubricity at tribologically challenging interfaces due to their high water content. One such interface exists within the ocular system between the eyelid and the cornea, where mucins dissipate frictional shear stress by cyclically disassociating within the tear film. In diseased conditions such as dry eye, which affects 300 million people globally[2], tear film depletion causes increased mechanical stress on the underlying epithelium. To model this disease condition, we modulated the density of surface tethered transmembrane mucins on human corneal epithelial cells using the enzyme StcE, then subjected these cells to *in situ* microrheological measurements, indentation experiments, and friction tests using a custom built micro-tribometer. Following friction experiments, cells were lysed and RNA was collected to measure transcriptional changes in apoptotic and inflammatory markers. Reducing mucin density led to a 30-fold decrease in apparent viscosity near the cell surface (mucin deficient: 6.4 ± 0.7 cps vs mucin rich: 183.6 ± 8.4 cps), though this remained elevated compared to free solvent away from the surface (mucin deficient: 1.74 ± 0.06 cps vs mucin rich: 1.78 ± 0.05 cps). Single cell indentation experiments revealed that mucin cleaved cells were significantly stiffer (3.0 ± 0.7 kPa vs 1.4 ± 0.2 kPa). Surprisingly, while friction measurements using hydrogel probes[3] showed minimal differences in frictional shear stress between control and mucin deficient cells (58.0 ± 5.0 Pa vs 54.9 ± 8.3 Pa), the cellular inflammatory response differed greatly. Mucin cleaved cells downregulated IL-1β while maintaining IL-6 levels comparable to controls, whereas in the presence of mucin, IL-1β and IL-6 levels were elevated when compared to the non-sliding controls. These results suggest a decoupling between transmembrane mucin mechanics and inflammatory signaling in the epithelium. Clinically, this indicates that therapeutic strategies for dry eye disease may need to address lubrication and inflammation as independent targets.

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Mechanical Characterization of Graded Hydrogels

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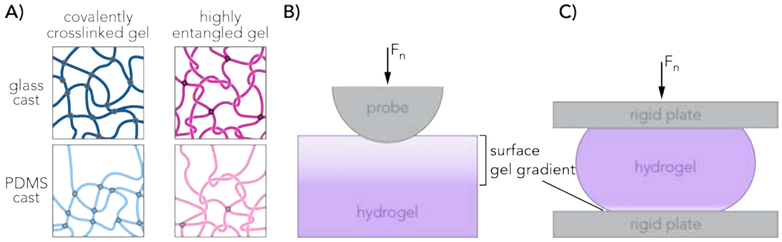

A) Hydrogel samples are covalently-crosslinked or highly entangled and cast against glass or PDMS. B-C) Schematics of nanoindentation and rigid plate compression experiments of the four gel samples.

Stress modulation of biological tissue is crucial in understanding how extended durations of static loading (e.g. standing) lead to articular cartilage thinning and damaged joint functionality.[1] Hydrogels are swellable polymer networks with high solvent content and are excellent synthetic models to understand stress modulation in compositionally graded biological materials, including articular cartilage. This work explores how varying gradient thickness and crosslinker mobility impact the surface and bulk elastic modulus of polyacrylamide (PAAm) hydrogels. Exposure to oxygen inhibits the free-radical polymerization of polyacrylamide (PAAm) hydrogels,[2] forming a depth-wise gradient of low polymer density within the gel referred to as a surface gel layer. By casting hydrogel samples against oxygen-impermeable glass and oxygen-permeable polydimethylsiloxane (PDMS) surfaces, we can control the thickness and polymer density of surface gel layers. We further modify the polymer architecture of the bulk by tuning the concentration of the covalent crosslinker, *N,N'*-methylenebisacrylamide (MBAm). Gels with high MBAm concentrations (54:1 monomer to crosslinker) contain rigid covalent crosslinking nodes that greatly restrict polymer chain rearrangement relative to gels with low MBAm concentrations (2000:1 monomer to crosslinker) dominated by physical entanglements. Four sample types of covalently crosslinked and highly entangled gels cast against glass and PDMS represent varied crosslinker mobility and surface gel layer thickness. We estimate surface gel layer thickness of our samples using fluorescent confocal microscopy. We then probe surface elastic modulus with nanoindentation of the surface gel layers and bulk elastic modulus with compression of the hydrogel samples between two rigid plates. Results demonstrate that gels cast against oxygen-permeable PDMS surfaces have thicker surface gel layers that are softer than their counterparts cast against oxygen-impermeable glass surfaces. Gels dominated by covalent crosslinks were stiffer than those dominated by more mobile physical crosslinks both at the surface and across the bulk. Elastic moduli found from bulk compression were independent of surface gel layer properties.

References:

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Crosslinked and doped polyaniline films for low voltage switching of wettability

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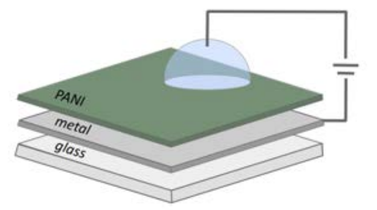
Polyaniline (PANI) characteristics have been well reported with numerous studies characterizing its conductive and electrochemical properties. However, the characteristics of switchable wettability with different polyaniline oxidation states have not been shown as a viable solution to applications like electrowetting. Current research faces various challenges including in hydrophobicity and low voltage actuation. This work shows the capability of low voltage switching with a polyaniline film for moving droplets in electrowetting applications. We report a doped and crosslinked polyaniline film that can be reversibly switched in wettability depending on the oxidation state of polyaniline and with voltage. By doping polyaniline with a long chain fluoropolymer, the polyaniline film becomes significantly more hydrophobic. In addition, polyaniline is physically and electrochemically crosslinked with dibromopropane to improve film quality and lower film stress. This work demonstrates the polyaniline changes in oxidation states upon application of low voltages and at small timescales, which are necessary for electrowetting applications. The low voltage wettability switching not only overcomes the typical electrowetting limitations that require over 250V for switching, but also expands electrowetting capabilities for biological studies in both static and transient environments.



Schematic of electrical contact for wettability switching

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Nanostar-mediated nucleation and condensate-driven spatial organization of tiled DNA nanotubes

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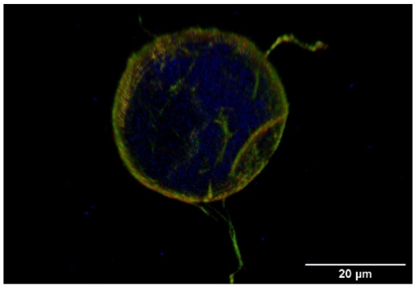
Modularity and programmability make DNA-based molecular architecture a powerful platform for the development of advanced functional materials. DNA nanotubes, self-assembling supramolecular polymers of rectangular assemblies of DNA strands called tiles, and DNA nanostar condensates, dense liquid phases of rationally designed macromolecules, can be programmed to interact with one another through complementary base-pairing. However, DNA condensates and nanotubes have not yet been studied in the literature as a coupled system with base-pair programmed mutual affinity between the nanostar and tile components. Here, we explore the effect of DNA nanostar condensate on tiled nanotube assembly and spatial organization within cell-like water-in-oil emulsion droplets. We find that nanostar-tile affinity accelerates the timescale of nanotube self-assembly, promotes nanotube bundling, and organizes nanotubes in and around condensate. By elucidating the mechanism by which astral structures arise, in which nanotubes nucleate in the bulk phase before diffusing and anchoring to the condensate surface, we provide a framework for using programmed affinity and phase separation to control the nucleation kinetics and spatial organization of supramolecular polymers in biomimetic systems.



Confocal image of condensate (blue), sticky (red), and smooth (green) tiles. Imaged at UCSB NRI Leica Confocal Microscope.

Electrostatic Complexation of Conjugated Polyelectrolytes: Processing and Functionality

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Conjugated polyelectrolytes (CPEs) are water-soluble semiconducting polymers offering unique opportunities for controlling processability and electronic properties through ionic interactions, particularly in polymer blends. Blends of conjugated polymers and insulating polymers have proven useful for applications such as transistors, memory devices, and light-emitting electrochemical devices. Herein, we discuss how electrostatic complexation between oppositely charged polyelectrolytes enables the formation of complex coacervates - dense polymer phases with enhanced processability. Unlike dilute solutions commonly used in thin-film electronics, complex coacervates achieve polymer concentrations exceeding 0.1 M, facilitating applications requiring thick semiconducting layers, including battery binders, thermoelectrics, and 3D printing. Additionally, this approach enables independent characterization of both polymer components and systematic control of composition and molecular weight. We discuss how blended electronically insulating polyelectrolyte structure - including charge fraction, molecular weight, polydispersity, and backbone composition - profoundly influences electronic properties of resulting solid blends. By connecting observations from traditional in-situ polymerization blends (e.g., PEDOT:PSS) with controlled post-synthetic complexation, we present possible design principles for engineering processable semiconductor blends with optimized charge transport and functionality.

Diverse, Distinct, and Densely Packed DNA Droplets

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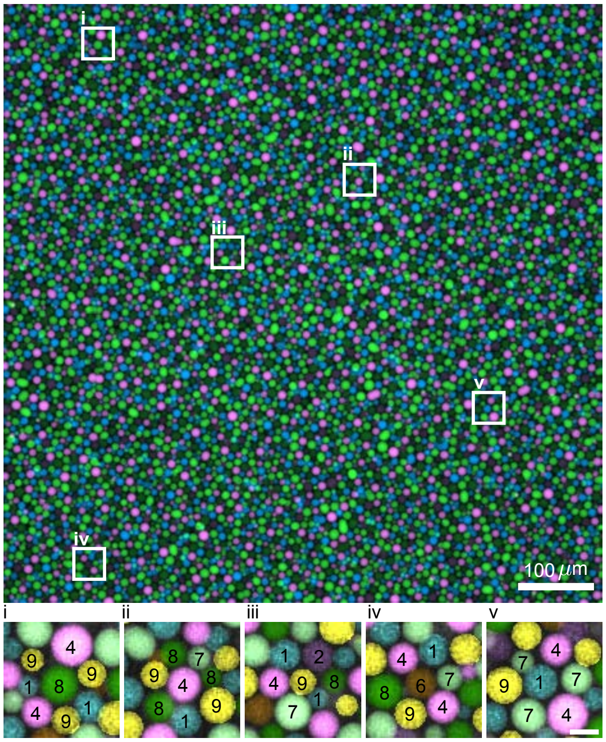
The cell consists of many liquid compartments phase-separated from the cytosol, but also apparently immiscible with each other. To explore such multi-condensate systems, we have created an artificial mixture of many immiscible biomolecular liquids. Each liquid phase consists of similar DNA particles, but the distinct liquids remain immiscible due to DNA sequence-specificity. In such a system, two droplets can coalesce if they belong to the same species, but will otherwise interact as hard-sphere colloids. Our synthetic multi-phase system has the ability to form a densely packed 2-D layer of droplets which is transiently stabilized by local caging. At this stage, the system is jammed and exhibits dynamic heterogeneity. Nonetheless, rare coalescence events do still occur, enabling the system to slowly unpack itself (over the course of days) and fluidize.



Seven distinct, densely packed immiscible liquid phases of DNA. Insets demonstrate caging by unlike phases; droplets in the insets were false-colored and labeled according to DNA species (scale bar: 10 µm).

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.

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Bio-inspired polypeptoid materials: strategies for enabling functional architectures in next generation microelectronics.

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Polypeptoids represent a class of bio-inspired materials that retain the sequence definition of polypeptides while offering greater chemical stability, ease of synthesis, and a broader range of accessible side-chain moieties. These features make polypeptoids an ideal scaffold for programmable architecture and site-specific functionalities desirable in next-generation microelectronics. Here, as part of a large-scale effort, we outline synthetic and characterization strategies being employed to unlock the capabilities of polypeptoids in single-molecule device applications.

i) Synthetic routes for more complex architectures:

While the solid-phase synthesis technique used to create polypeptoids is powerful, stepwise addition is slow, and chain aggregation limits molecular size. By incorporating SuFEx and CuACC click handles into polypeptoid chains, it is possible to create polypeptoids hundreds of monomers in length.

Branching to create dendritic peptoids would allow for incorporating more functionalities into a smaller footprint, accessing new structural conformations, and assisting in creating tunable, responsive materials. Various routes for achieving branched polypeptoids are being explored, such as branching from a dibrominated backbone, using click handles, and incorporating diamines during synthesis.

ii) High throughput characterization of structure and functionality:

Secondary and tertiary structure are known to impact protein behavior, changing things such as accessibility to reaction sites on the chain. Designing polypeptoids with site-specific functionalities requires understanding how structure changes with sequence and composition. High-throughput methods are necessary to rapidly screen through a library of materials. By incorporating hetero-FRET donors and acceptors into peptoid molecules, the end-to-end chain distance can be rapidly measured. This allows for easy monitoring of how different sequences change conformation. Additionally, HPLC can be used to monitor reaction conversion rate, allowing for determining changes in catalytic efficiency based on chain sequence.

Overcoming reactivity barriers in methacrylate–lipoate copolymerization through dual thermal–photochemical polymerization

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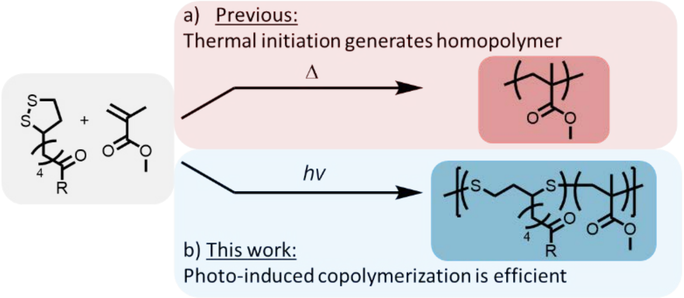

1,2-Dithiolanes have previously been shown to be incompatible with methacrylates under thermal conditions. In this work we report the copolymerization of ethyl lipoate and methyl methacrylate using light to photoexcite the ring.

The synthesis of degradable methacrylic copolymers remains challenging due to the high radical stability of propagating methacrylate, which prevents copolymerization with degradable monomers, such as 1,2-dithiolanes and thionolactones.[1,2] Here, we report a dual-stimuli strategy that combines thermal initiation with photochemical excitation to overcome this reactivity mismatch with 1,2-dithiolanes. Concurrent mild heating (30 °C) and irradiating (405 nm, 50 mW/cm^2) enabled efficient copolymerization of methyl methacrylate and ethyl lipoate, monomers previously considered incompatible, yielding products with unimodal SEC traces (M_n up to 37 kg mol^{-1}) and moderate dispersities ($Đ \approx 2.0$). ^{1}H NMR spectroscopic analyses confirmed covalent insertion of ethyl lipoate repeat units into the *poly*(methyl methacrylate) backbone, imparting backbone degradability under disulfide-reducing conditions (32 kg mol^{-1} → 2 kg mol^{-1}). Notably, light intensity selectively influenced the polymerization rate of ethyl lipoate, whereas temperature primarily affected methyl methacrylate propagation. This orthogonal control enables access to degradable methacrylic materials with tunable functionality.

This work provides an avenue to obtain degradable *poly*(methyl methacrylate), a valuable and challenging synthetic target, as well as highlighting the value of a multi-stimuli approach to synthesize precise copolymers.

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Tuning EUV sensitivity of chemically amplified polypeptoid photoresists through iodine incorporation

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Polymeric chemically amplified resists (CARs) have long been central to high-resolution patterning in microelectronics manufacturing. However, conventional synthetic polymers exhibit inherent dispersity in molecular weight, composition, and monomer sequence. Additionally, CARs are formulated as multicomponent mixtures, resulting in local heterogeneities that contribute to line roughness and defects as printed features shrink below 10 nanometers. To address these limitations, we have used polypeptoids, a polymer platform that allows for complete sequence control and narrow dispersity, to develop photoresists that allow precise control over monomer placement while accommodating the diverse functionalities required for CARs. Our prior work demonstrated that polypeptoids with identical chemical compositions, but different monomer sequences, show distinct differences in both pattern resolution and sensitivity, revealing tunable patterning behavior. In this work, we incorporate strongly absorbing elements such as iodine into polypeptoid photoresists to further modulate sensitivity to extreme ultraviolet (EUV, 13.5 nm) radiation and introduce an additional handle for tailoring resist performance.

Resin formulation design for interfacially controlled multimaterial 3D prints with mechanical contrast

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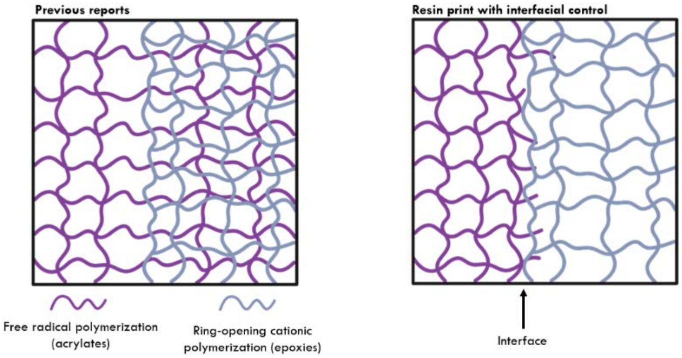
3D printing is a form of advanced manufacturing that is used in various fields including biomedical devices, manufacturing applications and robotics. The ability to incorporate multiple different material properties within one print, known as multimaterial 3D printing, has made significant advancements within recent years, with recent reports capable of printing materials with different colors, mechanical properties, and swelling properties[1-3]. These have been achieved using single-vat digital light processing 3D printing, in which the resin can perform two different orthogonal chemistries that initiate in response to two different wavelengths of light. Unfortunately, chemistries that are commonly used, such as free radical photopolymerization and ring-opening cationic photopolymerization, are not purely orthogonal due to the degradation processes of these initiating systems, which has limited the degree of contrast between the different materials and the degree of control between the differing materials. This presentation highlights early findings of a multimaterial single-vat resin system with interfacial control, where extreme mechanical contrast between the two regions can be defined and the interface between the separate materials can be controlled. Future work aims to understand the kinetics of these photoinitating systems and better characterize this interface to help enhance and diversify the properties of 3D printed systems.



Comparison of network structure of multimaterial 3D prints without (left) and with (right) interfacial control

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Predicting Sequence-Dependent Solubility in Polypeptoids: A Multiscale Approach

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Polymer synthesis has become increasingly sophisticated, enabling the creation of precise sequence-controlled polymers with tailored properties. However, the vast number of potential sequences demands robust and efficient modeling to predict how sequence impacts macromolecular interactions. Polypeptoids (a biomimetic of polypeptides) serve as an ideal platform for establishing design rules as they are routinely synthesized at gram scale with hundreds of different side chain functionalities. However, polypeptoid simulations encounter major sampling challenges due to their long-time scales associated with conformational transitions, limiting studies on longer and multiple peptoid chain systems. To address this challenge, we present a multiscale modeling framework that enables high-throughput screening of sequence-dependent solubility. We use atomistic molecular dynamics simulations to parameterize coarse-grained, sequence-specific field-theoretic models. Our results reveal that sequence plays a critical role in solubility, beyond what is predicted by conventional models that consider only overall composition. These findings expand our understanding of sequence-dependent behavior in polymers across longer length scales and offer new strategies for using sequence to design materials with tailored solubility and performance.

Ion Dynamics in Low Tg Polyelectrolyte Complexes

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Polyelectrolyte complexes (PECs) exhibit high dielectric constants and can solvate large number of ions, offering a versatile platform for designing ion conductors. However, most studies on ion dynamics in PECs are restricted to high Tg materials with strong ionic interactions and understandings of how ionic environment and backbone dynamics impact the ion conductivity is lacking. To address these gaps, cationic and anionic poly(ionic liquids) (PILs) with a siloxane backbone were synthesized through click chemistry. When mixed in non-aqueous solution, the oppositely charged PILs undergo spontaneous liquid–liquid phase separation to form coacervates. The concentration of ion carriers is tuned by adjusting the lithium salts prior to mixing. After drying, the PECs are characterized by differential scanning calorimetry (DSC) and electron impedance spectroscopy (EIS) over a range of temperatures to elucidate how ionic environment impact polymer dynamics and ion mobilities.

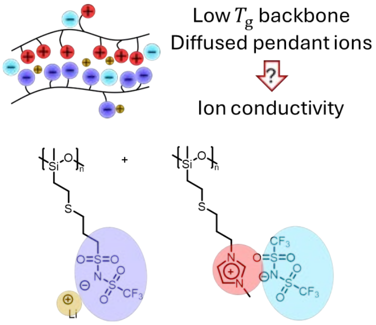

Figure. Accelerating ion dynamic in Polyelectrolyte complex (PEC) for battery applications

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Counterion-dependent morphology and charge transport in the self-doped conjugated polyelectrolyte CPE-K

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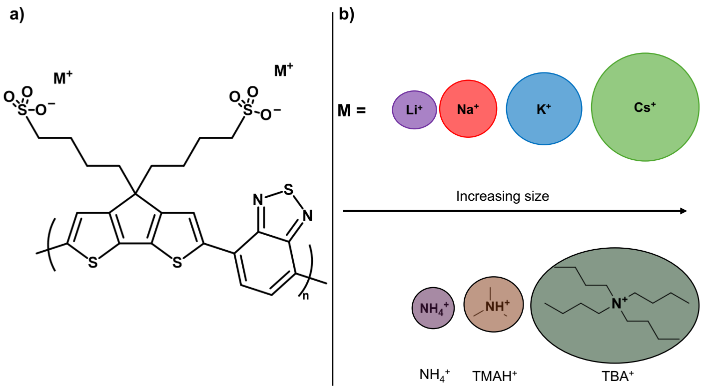
Self-doped conjugated polyelectrolytes (CPE) are unique materials in that they combine aqueous processability with intrinsic electronic doping.[1] This type of CPE has been investigated and valued for their intrinsic doping properties and water solubility since the late 1980's.[2] Here we isolate the role of the counterion in self-doped CPE to investigate how exchanging the counterion affects the self-doping capability, optoelectrical properties and film morphology of the self-doped CPE. Utilizing multiple derivatives from a single batch of CPE polymer starting with the K^+ counterion (CPE-K), the K^+ was exchanged for different alkali metal counterions (Li^+, Na^+, Cs^+), and organic ammonium counterions (NH_4^+, $TMAH^+$, and TBA^+) via dialysis. Self-doping capacity was compared across all derivatives by using UV-Vis-NIR absorption comparing the ratio between the bipolaron peak ($\lambda_{bipolaron}$) and the intra-charge transfer peak (λ_{max}). For the alkali metal series, Li^+ showed a ratio ($\lambda_{bipolaron}/\ \lambda_{max}$) of 0.89 ± 0.13, Na^+ and K^+ both show similar ratios (0.73 ± 0.13 for Na^+, and 0.74 ± 0.02 for K^+), while Cs^+ showed a slightly lower ratio of 0.61 ± 0.03. Organic ammonium based showed a different trend when having an additional proton to acidify the solution medium (NH_4^+ ratio = 0.86 ± 0.02 and $TMAH^+$ = 0.80 ± 0.02). The drastic difference came from the largest, bulkiest counterion (TBA^+) having a peak ratio of 0.24 ± 0.04 showing the lowest degree of self-doping. It was observed that the charge transport depends on the identity of the counterion: the in-plane conductivity of CPE decreases by 10^6 from Li^+ to TBA^+. GIWAXS analysis shows a reduction in Hermans factor from ~.25 for smaller counter ions (Li^+, Na^+, K^+) to 0.10 for TBA^+, consistent with disrupted percolation pathways for the larger counterions. We attribute these trends to increased disorder and larger interpolymer chain distances for larger ammonium counterions that perturb intermolecular spacing and film packing. OECT-extracted mobility shows that as size and disorder increased, a slight decrease in the mobility was observed. These results establish the counterion identity as a key design parameter for tuning morphology, self-doping capacity and charge transport in self-doped CPE.



Chemical structure of CPE-K (right). Counterions exchanged (left).

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Electro-assisted Pressure Sensitive Adhesives based on Ion-containing Bottlebrush Elastomers

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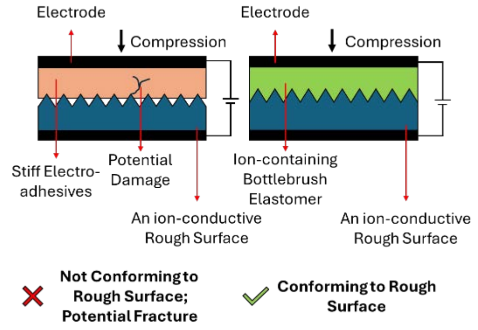
This study presents a materials-design framework for low-voltage operation electroadhesives based on ion-containing bottlebrush polymers. Such adhesives offer the advantages of electroadhesives, including reversibility, addressability, and tunability, while also providing the surface conformability typical of pressure sensitive adhesives (PSAs).[1] Using ring-opening metathesis polymerization two complementary bottlebrush polymers bearing pendant anions or cations were synthesized and cross-linked to form soft and tough elastomers. When two oppositely charged networks are brought into contact, a smooth, continuous interface forms, which is locally charged neutral due to the presence of mobile counterions.[2] When a low voltage (≤ 2 V) is applied, the mobile ions migrate toward the electrodes and an interfacial heterojunction forms, thus generating significant electrostatic attraction and enhancing adhesion. Such low-voltage operation and PSA-like bottlebrush polymers enable adhesives with superior electro-mechanical performance, and thus have strong potential for use in soft robots, haptic devices, and biomedical applications.



A comparison between common electroadhesives (left) and ion-containing bottlebrush elastomers (right). Here we demonstrate that the ion-containing bottlebrush elastomers have dual functions, i.e. they can be applied to various surfaces as PSAs and are switchable due to their responsivity to the electric field .

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Sb^{5+}-Controlled Color and Optical Property Evolution in $Cs_2AgSbCl_6$

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Lead-free halide double perovskites are promising for stable, low-toxicity optoelectronics, yet their optical properties can be highly sensitive to subtle chemical changes. Here we show that the color and band-gap evolution of $Cs_2AgSbCl_6$ is controlled by trace Sb^{5+} species rather than changes in the average crystal structure. Using solution and hydrothermal syntheses while varying reducing conditions (H_3PO_2), we obtained $Cs_2AgSbCl_6$ with distinct colors. Upon annealing at 473 K under N_2 for 72 h, black samples irreversibly convert to yellow while retaining the cubic Fm-3m framework. Synchrotron XRD indicates a consistent unit-cell contraction after heating, accompanied by longer Sb–Cl and shorter Ag–Cl bonds. XPS directly links the black coloration to Sb^{5+}, which is removed by annealing. We propose a decomposition-assisted pathway ($Cs_2Ag_{1-x}SbCl_6 \rightarrow CsCl + SbCl_5$; $SbCl_5 \rightarrow SbCl_3 + Cl_2$) and conclude that Sb^{5+} affects the band gap primarily through the unit-cell size change it induces rather than a direct electronic contribution.

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The Role Charge-based Interactions on Hydration Dynamics and Material Functionality

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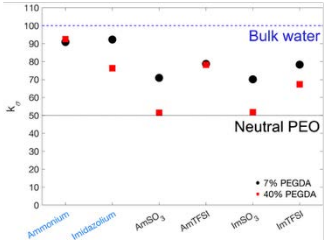
Interactions between charge-containing polymers and local solvent molecules enable essential applications such as protective coatings and selective ion-separation membranes. Polymer-solvent interactions dictate the local surface environment near the material surface, which in turn regulates the ability of surrounding ions and foulants to interact with the surface. Therefore, rational design of the material solvation environment is crucial. However, the properties and dynamics of local hydration water vary greatly from the behavior of bulk water. Overhauser Dynamic Nuclear Polarization (ODNP) relaxometry studies allow direct measurements of the local hydration dynamics within 15 Å of nitroxide spin labels distributed across polymer surfaces. This technique allows local hydration dynamics to be directly correlated to macroscopic properties such as bubble contact angle and material fouling to formulate a molecular understanding of water and ion transport and surface hydrophilicity.



Hydration dynamics in the vicinity of zwitterionic groups are enhanced to almost bulk-like magnitudes and depend on crosslinking density and anion charge delocalization

Zwitterion-functionalized polymer networks were studied due to their reported antifouling properties. ODNP experiments reveal the importance of material architecture, with network geometries revealing distinctly different local hydration trends compared to small molecules. Measurements of the relaxivity parameter k_σ, which directly correlates with hydration dynamics swiftness, show that zwitterionic groups promote enhanced hydration dynamics compared to neutral polymers and that network crosslinking density and anion charge delocalization control the degree of hydration dynamics enhancement. Notably, the measured hydration dynamics are slower in zwitterionic networks compared to cationic membranes, suggesting that a "Goldilocks regime" may exist for hydration dynamics that impart antifouling. These results emphasize the importance of charged-group surface presentation on resulting material properties and highlight the crucial nature of analyzing materials in contexts that mirror real-world applications.

Additionally, the ODNP technique was used to characterize the dynamics around linear poly(acrylic acid) (PAA) chains, known for their "superabsorbent" properties. In PAA solutions, measurements of the relaxivity parameter k_σ, suggest that water dynamics fluctuate between bulk-water-like to highly constrained depending on polymer concentration and the ionic environment. This lends direct insights into the conformation of PAA chains in solution. Deprotonated carboxylic acid groups promote extended chain conformations, with fast local water dynamics close to the polymer surface. Conversely, protonated carboxylic acid groups form intrachain hydrogen bonds, resulting in a collapsed polymer conformations and constrained water dynamics. This study highlights the importance of charged groups in moderating the local surface environment.

This work was supported as part of the Center for Materials for Water and Energy Systems (M-WET), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award #DE-SC0019272 as well as support from the Office of Naval Research award N00014-23-1-2140.

Ionic Crosslinking and its Influence on the Properties of Self-Doped Conjugated Polyelectrolytes

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Self-doped conjugated polyelectrolytes (CPEs) offer a unique combination of π-conjugated backbones and ionic side chains, enabling solution-processability, mixed ionic-electronic conductivity, and applications in aqueous environments. However, their high water solubility hinders long-term stability, necessitating effective cross-linking strategies. Here, we systematically investigate ionic cross-linking of the benchmark p-type self-doped poly[2,6-(4,4-bis-potassium butanylsulfonate-4H-cyclopenta-[2,1-b;3,4-b′]-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)], CPE-K, using a post-deposition approach with divalent cations (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}). Thin films immersed in aqueous salt solutions exhibit complete ion exchange, as confirmed by XPS. AFM and liquid-mode AFM reveal that swelling suppression and morphological stability depend strongly on the cation identity and concentration, with Ba^{2+} forming the most rigid cross-linking network. GIWAXS shows that ionic cross-linking expands lamellar spacing while preserving π–π stacking. Electronic conductivity measurements demonstrate that Ba^{2+}-treated films maintain high conductivity in the swollen state due to improved network integrity. Impedance spectroscopy further shows decreasing ionic conductivity with increasing cross-linking density. These findings establish structure–property relationships for ionic cross-linking in CPEs and provide design insights into processing protocols to form robust CPE films casted from water.

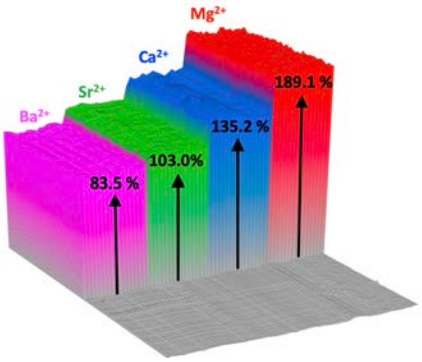

Figure 1. Swelling percentage of different ionic cross-linked CPE-K films in aqueous system.

Extracting molecular-level insights into wormlike micelle systems in complex flows using a fluidic four-roll mill

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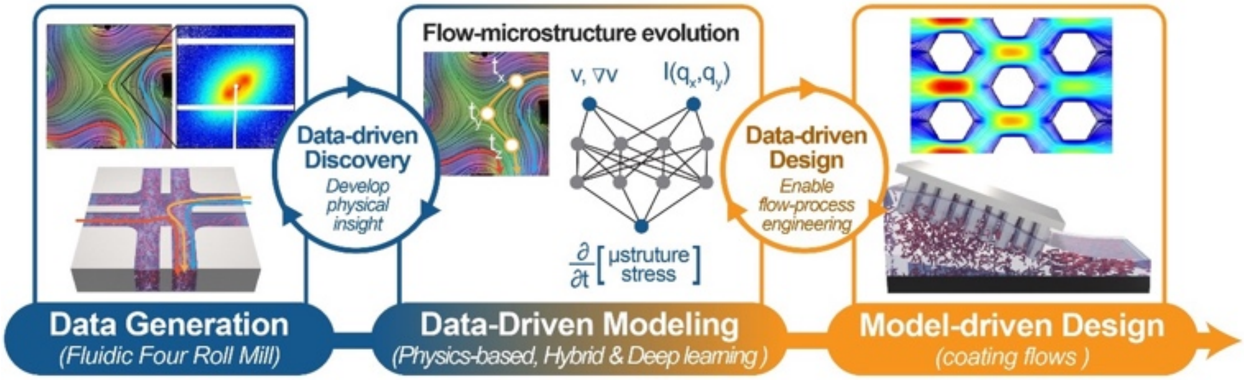
Engineering flow processes to control the microstructure and properties of semiflexible polymers and molecular assemblies is critical for a wide range of industrial applications. A major challenge to this aim lies in understanding the intricate relationship between flow history, microstructure, and rheology in the complex deformation histories typical of processing applications. To address this, we have developed a fluidic four-roll mill (FFoRM) coupled with scanning small-angle X-ray scattering (sSAXS) to generate large flow-microstructure datasets to model microstructural evolution in complex processing flows.[1,2] Here, we demonstrate the capabilities of this technique by analyzing a wormlike micelle (WLM) solution using a recently-developed connected-rod scattering model.[3] This model has been validated for WLMs in simple, steady shear flows, but not yet in flows featuring strong extensional or rotational components relevant in industrial processes. The analysis will yield the evolution of key structural and dynamic parameters that describe micellar orientation, stretch, and inter-micellar interactions along Lagrangian trajectories. These insights provide a direct means to test and refine rheological theories and quantify the history-dependent responses of the molecules. By quantitatively characterizing history-dependent material behavior in complex flows, we aim to accelerate the development of predictive constitutive models for complex fluids and enable inverse model-driven design of flow protocols for soft materials processing.



(Left) Flow-microstructure data are gathered in the FFoRM. (Center) Streamlines are used to assemble a library of Lagrangian trajectories with which to train data-driven models. (Right) The resulting models are used to design optimal and novel processing flows.

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Degradable Bottlebrush Polymers for Dual-Wavelength 3D Printing

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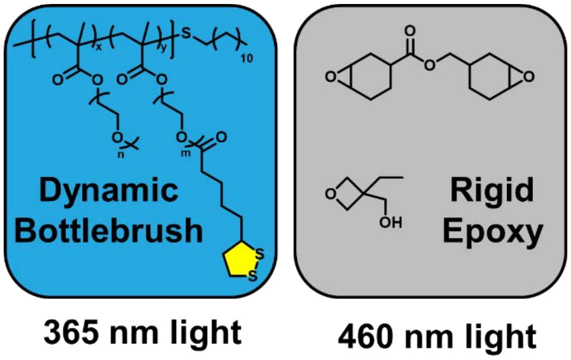
Polymers cross-linked via dynamic (reversible) bonds are prominent materials to achieve time-dependent mechanical properties and recyclability. Additive manufacturing (3D printing) of soft materials is an emerging field that can make use of easily degradable polymers as dissolvable supports to access freestanding structures. In this work, we developed polyethylene glycol-based bottlebrush polymers with cyclic disulfides on pendant chain-ends which can subsequently form crosslinks under 365 nm light in ambient conditions. For this purpose, 1,2-dithiolane-containing α-lipoic acid was esterified onto polyethylene glycol methacrylate and copolymerized with polyethylene glycol macromonomers via free radical polymerization at various ratios. These polymers can form crosslinked bottlebrush elastomers under UV light with or without an exogenous photoinitiator in a time scale of seconds, enabling the use for additive manufacturing techniques such as digital light processing. The elastic moduli and strain at break of the resulting materials could be varied via crosslink concentration or with the addition of a copolymerizing acrylate. Dual cure networks and multimaterials with up to tenfold in stiffness contrast in the supersoft-soft regime (1–70 MPa) were made using orthogonal cationic chemistry utilizing blue (460 nm) light and epoxide network formation. Furthermore, disulfide crosslinks enabled selective degradation of the bottlebrush network using mild reducing conditions. This work highlights the use of polymeric dithiolanes as a robust method to print supersoft dynamic materials.



Dual-wavelength resin used to print radical and cationic networks in one pot.

Direct Microwave Pyrolysis of Cellulose to Hard Carbon Anodes for Na-Ion Batteries

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Adopting intermittent renewable energy demands the development of Na-ion batteries as an earth abundant alternative to Li-ion batteries for grid scale storage. Hard carbons are the leading anode material in Na-ion batteries due to their considerable ability to store Na, and the ease with which they can be produced from inexpensive precursors such as cellulose through pyrolysis in inert atmospheres. We report a rapid one-step conversion of cellulose to hard carbons in under 15 min in a modified domestic microwave oven. This is in contrast to more conventional furnace-based pyrolysis which can take several hours. From optical pyrometry, we find that under different microwave power conditions, the hard carbons can be tunably formed at temperatures between 900◦C to 1250◦C under the conditions employed. Hard carbons were characterized using complementary structural, spectroscopic, and porosity measurements, revealing that increasing microwave power produces materials with similar local structure but enhanced crystallinity and evidence of an increased proportion of closed pores. The formation of closed pores appears to directly contribute to significant gains in Na storage capacity throughout the plateau region during electrochemical cycling. These results demonstrate a convenient and scalable strategy for rapidly producing hard carbons with tunable porosity.

$M_{n+1}AX_n$ phase nitrides as topological superconductor candidates

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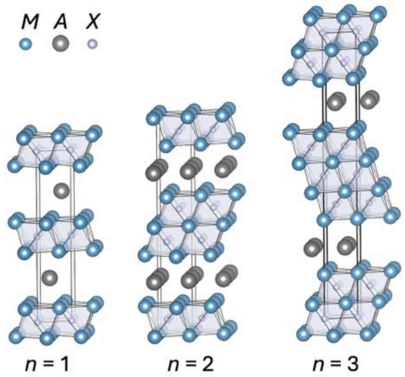
The rise of quantum information technology demands new superconductors to realize large-scale quantum computing and address energy demands. One promising class of materials is the MAX phases, compounds with the formula $M_{n+1}AX_n$ that have a layered hexagonal crystal structure.[1] There are several known and predicted superconductors within the nitride MAX phases.[2,3] Additionally, electronic structures of the nitride MAX phases suggest the possibility of topological surface states in these compounds.[4] We use density functional theory and topological invariant calculations to investigate electronic structure and topology within a specific class of nitride MAX compounds, $\mathrm{Ti}_{n+1}A\mathrm{N}_n$, with A = Al, Ga, In. Simultaneously, we synthesize $\mathrm{Ti}_{n+1}A\mathrm{N}_n$ to experimentally search for and better understand superconductivity in the nitride MAX phases.



Crystal structure of $M_{n+1}AX_n$ phases with n = 1, 2, 3

We acknowledge support from the InTriQATe NRT program under NSF award #2152201.

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The Influence of Hydration on Ion Transport in Single Ion-Conducting Polymer Electrolytes

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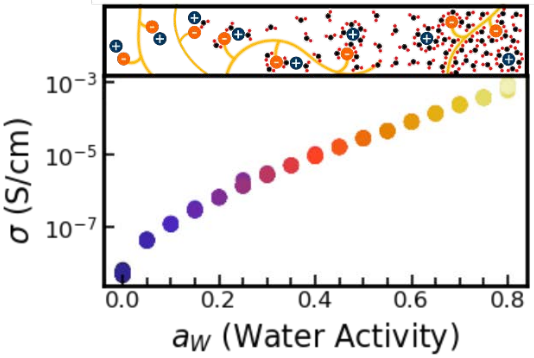

Ion transport in hydrated polymer electrolytes is governed by the coupled effects of polymer segmental dynamics, ion–polymer interactions, and water solvation. Although these mechanisms are well established in the limiting cases of fully dry and fully hydrated electrolytes, transport behavior at intermediate hydration levels remains poorly understood. A key challenge in characterizing this regime is isolating cation transport behavior, which is essential for energy and separation technologies but is obscured in conventional salt-doped systems by the concurrent motion of cations and anions. Single ion-conducting polymer electrolytes (SICPEs), in which charged groups are covalently tethered to the polymer backbone leaving only a single mobile counterion, overcome this limitation by immobilizing the anionic species. Consequently, SICPEs provide a model platform to probe the fundamental influence of water content and anion identity on cation transport. Here, SICPEs are prepared by post-polymerization functionalization of poly(ethylene oxide-co-allyl glycidyl ether) copolymers with a series of charged pendant groups. Electrochemical impedance spectroscopy and Raman spectroscopy under controlled hydration are used to quantify lithium-ion transport and probe changes in ion coordination. Ionic conductivity increases nonlinearly with hydration and depends on pendant anion identity. At low hydration, conductivity scales with the glass transition temperature, indicating ion transport coupled to polymer segmental motion. With increasing hydration, conductivities converge across chemistries, consistent with water-mediated decoupling of ion motion from polymer dynamics. Raman spectroscopy corroborates this transition through hydration-dependent changes in sulfonate symmetric stretching modes, reflecting reduced lithium–sulfonate ion pairing as water content increases.

This work was supported as part of the Center for Materials for Water and Energy Systems (MWET), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Award #DE-SC0019272.

Bending of gradient polyacrylamide hydrogels from differential swelling

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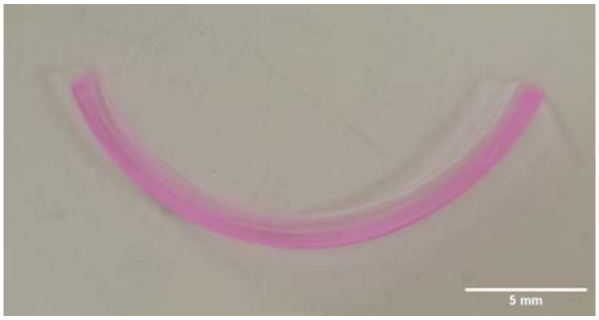

Polyacrylamide hydrogel synthesized against heterogeneous substrates demonstrates curvature after swelling in water (unpublished data).

Hydrogels have gained traction in recent years for their use as soft actuators due to their stretchability, unique swelling and shrinking properties, and tunable mechanical properties (Shojaeifard et al. 2022). Taking inspiration from biological systems, hydrogels with structural gradients are useful in achieving shape changes through differential swelling. In contrast with bilayer systems, gradient hydrogels avoid the issue of stress at the interface between two layers. While curvature has been previously demonstrated in these types of hydrogels (Gong et al. 2001), less attention has been given to correlating experimental results with theoretical models of their bending behavior. In this work, polyacrylamide hydrogels with surface gradients in crosslink density are synthesized, characterized, and modeled using finite element analysis. Gels of three different weight percentages of polymer and crosslinker were studied to investigate the relationships between the curvature of the gel strips, the difference in elastic modulus between the surface gradient layer and the bulk hydrogel, and the thickness of the surface layer. These results indicate that more extreme differences in elastic modulus correlate with higher curvature up to a point, after which the stiffness of the bulk layer appears to resist bending. Additionally, thicker surface gradient layers contribute to higher curvature. Finite element models were able to help decouple these two effects, which are difficult to control independently in experimental setups. Understanding these structure-property relationships is essential for being able to control shape changes in these materials. In the future, applying these methods to systems such as temperature or pH responsive hydrogels will enable the development of more complex and precisely controlled soft actuators.

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Strong, Yet Split Hydrogen Bonding with Ice Rules in Delafossite (H/D)RhO_2

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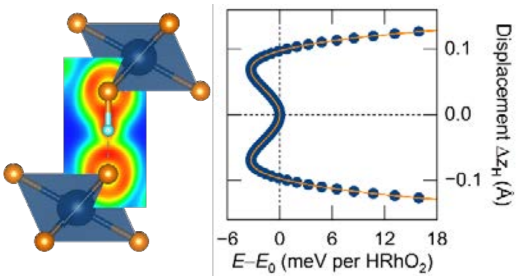
Despite remaining enigmatic, strong hydrogen bonding provides an advanced design handle for tailoring the properties of functional materials.[1] Here, 3R–(H/D)RhO_2 delafossites (prepared by ion exchange of Na^+ from $NaRhO_2$) contain H/D in linear coordination with O, linking $Rh^{III}O_2$ layers. Bragg and real-space X-ray and neutron scattering analysis, vibrational and solid-state NMR spectroscopy, and density functional theory–based electronic structure calculations have been employed to understand the nature of the hydrogen bonding. Despite short distances between H/D and the two O to which they are bonded, a clear double-minimum corresponding to a shorter and longer (H/D)–O distance is established.[2] The triangular lattices formed by H/D appear to display ice-like disorder corroborated by low-temperature heat capacity measurements.[3]



Strong, yet split! DFT calculations reveal a double-well potential for H displacements along the O–H–O bond in $HRhO_2$, favoring off-centered positions. Electron localization, ssNMR, Bragg and diffuse scattering support enhanced bonding in the off-centered state, illustrating strong yet split hydrogen bonds on a triangular lattice with no long-range ordering, analogous to frustrated Ising spins.

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Additive manufacturing of high-performance tungsten-integrated photopolymer composites for chemical resistance and radiation shielding

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The advancement of space, nuclear, and advanced chemical-processing technologies requires materials capable of withstanding combined chemical exposure and ionizing radiation while maintaining structural integrity. Current materials often provide resistance to either chemical or radiation environments or lack compatibility with advanced additive manufacturing techniques needed to fabricate complex, high-resolution geometries. To address this gap, we developed a photopolymer composite for VAT photopolymerization using a hydrophobic aromatic acrylate and multifunctional cross-linkers, loaded with tungsten-based fillers (Ammonium metatungstate hydrate (AMT) and tungsten (III) oxide (WO_3)). The printed parts were subjected to accelerated aging in aggressive chemicals (acids, bases, and solvents) for up to 30 days. The composites exhibited excellent mechanical and thermal properties while maintaining structural integrity throughout extended chemical exposure. The formulation containing 35 wt.% AMT (R35) demonstrated superior chemical resistance, with < 3% ultimate stress loss, < 16% modulus loss after 7 days, and minimal mass change (< 3%) after 30 days across all environments, outperforming those with combined AMT-WO_3 fillers. Remarkably, after 30 days in acetone, the most degrading solvent, the R35 composite retained over 92% of its ultimate stress and 78% of its modulus. Using silane-treated AMT filler further reduced mass change (< 1 %), significantly enhancing long-term durability. This work establishes a manufacturable platform for chemically durable, tungsten-loaded composites, forming a critical foundation for the development of materials requiring simultaneous chemical and radiation resistance.

Diazirine-functionalized norbornenes enable tunable ring-opening metathesis polymerization-derived polymer networks

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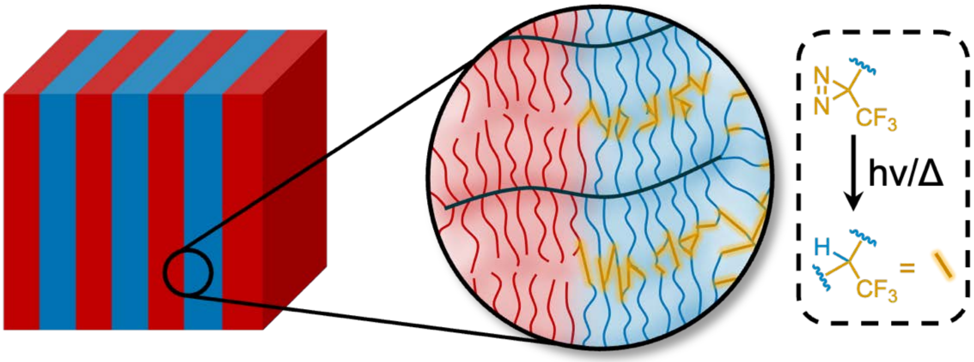
Diazirines are versatile groups used to cross-link and functionalize diverse commodity materials. Upon photochemically or thermally induced activation of the diazirine moieties, carbene intermediates are generated, followed by facile C–H insertion into polymer chains. However, the state-of-the-art synthetic methods for diazirine-containing polymers are limited to controlled radical polymerization strategies. To broaden the scope of accessible materials, we demonstrate the synthesis of novel diazirine-containing bottlebrush polymers via ring-opening metathesis polymerization (ROMP). This work establishes the compatibility of diazirines with ROMP conditions, enabling direct incorporation of cross-linkable functionalities into advanced polymer architectures through tailored norbornene-based monomers bearing diazirine units. By integrating cross-linkable moieties directly into the polymer through synthetic design, we mitigate incompatibility challenges associated with small-molecule cross-linkers and increase the cross-linking efficiency. This work provides a powerful route for synthesizing bottlebrush elastomers and advanced cross-linked materials, expanding the utility of ROMP for accessing novel functional materials.



Morphological stabilization is achieved through photochemical or thermal diazirine crosslinking between bottlebrush side chains.

Diffusive and enzymatic modulation of the dynamic size distribution of DNA droplets

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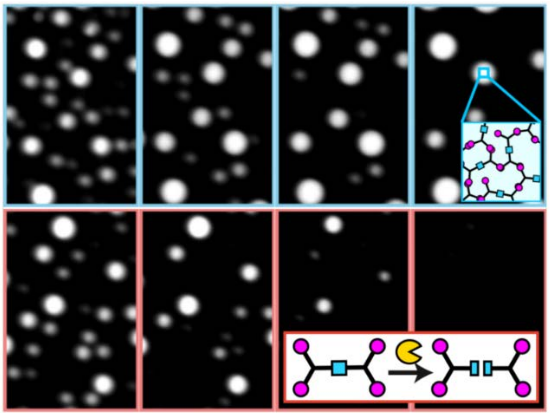
Material transport via thermal diffusion is a key mechanism for controlling the size of biomolecular phase-separated droplets, as highlighted by many recent studies inspired by the role of such processes within cells. However, experimental investigations that directly quantify the role of diffusive transport in the evolution of droplet-size distributions remain limited.

Here, we exploit sequence-specific adhesion to immobilize DNA-nanoparticle droplets on a substrate. This strategy, combined with wide-field confocal imaging, allows us to track the evolution of the radii of thousands of droplets with high precision while eliminating inter-droplet Brownian coalescence.

Using this approach, we observe Ostwald ripening at the single-droplet level where material is transported from smaller to larger droplets via thermal diffusion driven by Laplace pressure differences; this is the first such observation in a biomolecular system. The measured dynamics quantitatively reproduce key features of mean-field (Lifshitz–Slyozov–Wagner) theory. In addition, we use the system to study droplet shrinkage as induced by enzymatic degradation of the DNA nanoparticles. We uncover an unusual dynamic regime in which time and radius decouple, causing the average radius to remain constant despite a decrease in total droplet volume.

Our quantitative characterization of inter-droplet diffusive transport, and the novel behavior that emerged during droplet degradation, offer fundamental insights into phase transition dynamics relevant to diverse biomolecular processes.



The image series in the top and bottom rows respectively illustrate the thermal coarsening process (Ostwald ripening) of DNA droplets in the absence of enzymatic reactions, and the degradation process of the droplets in the presence of enzymatic reactions.

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1. M. Tateno and O. A. Saleh, Diffusive and enzymatic modulation of the dynamic size distribution of DNA droplets, *Phys. Rev. Lett.,* In press.

Local Hydration Properties of Zwitterionic Functional Groups from Molecular Dynamics Simulations

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Polymer membrane–based water purification is a highly efficient method for producing clean water and has been widely implemented in water filtration facilities. However, these systems face persistent challenges associated with membrane fouling. Membrane fouling, which arises from the accumulation of organic or inorganic foulants such as microbes, sediments, and oils on or within the membrane pores, degrades performance, shortens lifespan, and increases operational costs.

Zwitterionic materials (ZIs), known for forming strong hydration shells through electrostatic interactions, have shown great promise in mitigating membrane fouling. Nonetheless, most studies have focused on a limited set of zwitterionic chemistries, leaving the broader effects of ZI molecular structure largely unexplored. While local water hydration properties are key to antifouling performance, experimental characterization of these properties remains challenging. Among the few available techniques, Overhauser Dynamic Nuclear Polarization (ODNP) spectroscopy provides valuable insights into local hydration dynamics. Recent experimental work has applied ODNP to investigate water dynamics around zwitterionic functional groups in synthesized oligo-peptoids. These studies reveal that water dynamics can be sensitive to both the extent of cationic charge delocalization in ZIs and the surrounding salt concentration.

In this study, we complement the experimental work by providing an understanding of how zwitterion (ZI) chemistry influences hydration properties using all-atom molecular dynamics (MD) simulations of (1) small-molecule ZIs and (2) ZI-tethered oligo-peptoids in the aqueous solution. We aim to interpret experimentally measured water dynamics via molecular-level descriptors for dynamical behavior, including translational diffusion coefficients, dipolar rotational rates, and escape rates within each hydration layer. Furthermore, we correlate water dynamics with equilibrium enthalpic and entropic driving forces, including water structuring around the ZI functional group and solvation free energy. Our study spans the parameter space of varying salt concentration, chemistry, and environment of the ZI functional group to establish broadly accessible design principles in membrane surface modification for antifouling applications.

Nanoparticle transport in gradient hydrogels subjected to mechanical stress

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Gradient hydrogels have recently been introduced as a model system to mimic the superficial zone in articular cartilage.[1] Due to cartilage avascularity, nanoparticle transport into, through (e.g., nutrients and signaling molecules), and out of (e.g., waste) this hydrogel network is critical in maintaining joint health. Irregularities in nanoparticle transport are typically associated with joint disorders (e.g., osteoarthritis), and understanding its behavior under physiologically relevant mechanical loading is imperative in designing strategies for therapeutics. In this study, we investigated the effect of frictional shear stress on nanoparticle transport through and out of gradient hydrogels as shear-induced hydrodynamic advection can considerably exceed diffusive transport.[2] Gradient hydrogels were made using polyacrylamide (7.5 wt% AAm) polymerized against a smooth polyether ether ketone (PEEK) surface. Particle transport was quantified through fluorescence recovery after photobleaching (FRAP), using fluorescent beads with a diameter of 26nm. Each hydrogel was divided in sections subjected to shear stress (experimental sections) and not subjected to shear stress (control sections). A central region in each section was photobleached at the start of every experiment and fluorescence recovery was monitored for 24 hours. Sliding experiments were conducted using a custom microtribometer attached to the condenser turret of a confocal microscope. Frictional shear stress was applied using a non-functionalized glass probe sliding reciprocally at a speed of 1 mm/s against the gradient hydrogel at a normal force of 250 μN. Under frictional shear stress, the total recovered fluorescence was 1.8x greater than the control and, based on recovery kinetics, the hydrogel's calculated effective mesh size increased by 15%. This suggests greater nanoparticle transport through the hydrogel when it is subjected to shear stress. A 3x reduction in total fluorescence was observed between the experimental and control group, indicating that frictional shear stress increases the efflux of nanoparticles from the hydrogel. These findings indicate that frictional shear stress facilitates nanoparticle transport through and out of the superficial zone in articular cartilage, revealing a tribological mechanism for nutrient, signaling molecule, and waste transport in moving joints.

The authors acknowledge funding support from the NSF CAREER award (CMMI-CAREER-2048043), California Institute for Regenerative Medicine, USA (EDUC4-1282) and by the National Institutes of Health, USA (1T32GM141846).

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Quintuple Layer Dependent Antisuperbug Properties from 2D Bi_2Se_3 Topological Quantum Material

Olorunsola Praise Kolawole, Shivangee Rai, Avijit Pramanik, Kaelin Gates, Trinity Stark, Zoe Edorodion, Sanchita Kundu, Paresh C Ray
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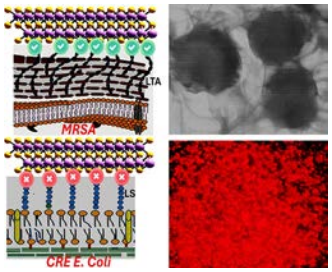
Staphylococcus aureus (MRSA) biofilms significantly hinder the effectiveness of conventional antimicrobial agents, which pose a major challenge in treating biofilm infections in clinics. In the current paper, we unveiled targeted superbug biofilm eradication using Bi_2Se_3 nanoplate based quantum material, where antisuperbug properties are strongly influenced by its unique layered structure composed of quintuple layers (QLs). We show that control over targeted eradication of MRSA superbugs can be achieved by harnessing QL dependent anti-MRSA properties for the Bi_2Se_3 nanoplate. Reported data demonstrated that the quantum material has the capability for 100% selective eradication of MRSA by selectively targeting the lipoteichoic acid (LTA) of Gram-positive bacteria. However, due to the lack of binding with lipopolysaccharide of Gram-negative superbugs, the quantum material lacks effective eradication of carbapenem-resistant *E. coli* and *Salmonella DT104* superbugs. Experimental data show that the 3QL thick Bi_2Se_3 nanoplate has the capability for wrapping MRSA bacteria very strongly via binding with LTA, which can physically enclose the MRSA and allow superbugs to effectively isolate them from their environment, ultimately inhibiting bacterial proliferation. In addition, the minimum inhibitory concentration (MIC) value changes by an order of magnitude (~10 to ~100 µg mL^{-1}) as the thickness of the nanoplate varies from 3 to 15 QLs. Moreover, the nanoplate has the capability for the selective inhibition of MRSA biofilm growth, where the minimum biofilm eradication concentration (MBEC) varies by more than an order of magnitude with the variation of QLs. These findings demonstrate the potential of quantum materials to address the growing threat of MRSA infections.



Bi_2Se_3 quantum material for selective killing of MRSA

Dr. Ray thanks NSF-PREM grant # DMR-1826886, DMR-2423854, and NSF Expand QISE track 1 grant # 2426522 for their generous funding.

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Photoclick chemistry for the determination of available reactive sites on an elastomer surface

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Performing NITEC on a functionalized surface “turns-on” fluorescence of surface-grafted moieties, allowing characterization via fluorescence microscopy.

The surface-functionalization of biocompatible, flexible materials is critical for biomedical applications such as drug delivery patches, sensors, and soft devices. However, characterizing these functionalized surfaces using existing methods is challenging, especially when grafting small organic molecules onto flexible surfaces. State-of-the-art characterization methods struggle with these systems due to low signal-to-noise ratios. This severely limits the options for characterization methods to expensive and inaccessible methods such as X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray spectroscopy (EDX). In this work, we present a new, inexpensive and facile method using NITEC photochemistry and fluorescence microscopy to visualize the degree of norbornene functionalization on a PDMS surface. Performing NITEC photochemistry on a norbornene-functionalized surface yields a fluorophore that is conjugated to the surface. Thus by measuring fluorescence intensity, it can measure differences in the amount of surface-grafted norbornenes across samples. This method is fast and reproducible, yielding a determination of the degree of functionalization. We envision this method can be used to quantify the loading of various functional groups onto flexible surfaces.

Controlling matrix-bound nanovesicle release from mechanically tunable alginate hydrogels

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Matrix-bound nanovesicles (MBVs) are cell-secreted lipid bilayer-bound nanoparticles residing within tissues throughout the body that encapsulate cellular signaling molecules such as RNAs, proteins, and lipids. Functionally, MBVs possess unique immunomodulatory properties and show promise as therapeutics, including in the treatment of rheumatoid arthritis, mitigation of osteolysis, and repair of skeletal tissue. Unfortunately, current MBV administration methods rely on bolus injections that offer poor control of MBV bioavailability and persistence at the target site, thus limiting their long-term therapeutic effects. We hypothesized that alginate hydrogels offer an alternative and more ideal MBV delivery system due to their ability to entrap MBVs in a matrix that can be engineered to control MBV release and retention on therapeutically relevant timeframes. In this study, we encapsulated MBVs in alginate hydrogels of varying stiffness and stress-relaxation rates to determine the impact of material mechanical properties on MBV release and retention over a period of 14 days. Stiff, fast-relaxing alginate hydrogels promoted increased MBV release compared to their softer counterparts in the first four days of release experiments. In contrast, slow-relaxing hydrogels demonstrated little MBV release throughout the 14-day period regardless of material stiffness modulation. When compared at the same stiffness, slow-relaxing hydrogels exhibited significantly increased MBV retention compared to fast-relaxing hydrogels. In summary, we show that not only can MBVs be effectively incorporated into alginate hydrogels, but their release and retention can also be fine-tuned by modulating material stiffness and stress relaxation rate. Our results indicate a promising potential for combining MBVs and alginate hydrogels to more precisely control MBV delivery in the body and overcome limitations associated with current MBV administration methods.

Investigating How Molecular Structure Drives Self-Assembly and Charge Transport in Conjugated Polyelectrolytes

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Owing to their combination of chemical tunability, mixed conduction, and aqueous processability, conjugated polyelectrolytes (CPEs) have been explored in a wide range of applications, including bioelectronic interfaces, organic electrochemical transistors, light-emitting diodes, photovoltaic devices, and sensors. Optimizing CPE charge transport for these diverse applications requires careful control over polymer synthesis and processing to achieve the desired performance characteristics. However, systematic studies linking molecular structure to solution self-assembly, solid-state film morphology, and charge transport are lacking. This work investigates how variations in molecular structure influence solution self-assembly and how these nanostructures impact film morphology and charge transport. Within a structure–function–property framework, we focus on the role of ionic charge density (number of charged groups per repeat unit) in directing self-assembly behavior. Using cryogenic transmission electron microscopy (cryo-TEM) to directly visualize solution-phase aggregates, we examine how differences in backbone conformation and ionic functionality govern nanoscale self-assembly, which can be preserved in the solid state and influence film morphology, ultimately providing a foundation for tuning CPE structure–property relationships.

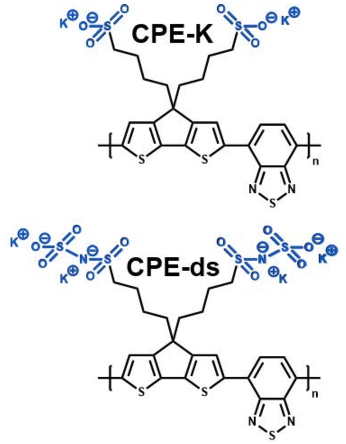

Figure 1. Chemical structures of CPEs of varying ionic charge density.

This work is supported by the National Science Foundation Division of Chemistry (2404409).

Diazirine-containing Polymer Cross-linker Enhances Device Lifetime of PM6:Y6 Organic Photovoltaics

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Advancing organic photovoltaics (OPVs) toward commercialization requires the combined attainment of high-power conversion efficiency (PCE) and extended operational lifetimes. Here, we introduce an efficient diazirine-containing polymer cross-linker (PDzA–P*n*BA) that maintains PCE by stabilizing the active layer morphology. Incorporation of only 0.5 wt % of this cross-linker in PM6:Y6 active layer prolongs device lifetimes: under 85 °C in a nitrogen-filled glovebox, devices retain 92% of their initial PCE after 2000 hours, compared with 67% for pristine devices and 82% for devices containing P*n*BA, a non-cross-linking additive. These findings highlight the pivotal role of cross-linking in sustaining device performance, supported by comprehensive characterization using solid-state nuclear magnetic resonance (ssNMR), electron paramagnetic resonance (EPR), detailed device physics analysis, and reactive force field molecular dynamics (ReaxFF) simulations. Moreover, we show that the choice of activation method for the cross-linking reaction (thermal vs light-induced) is crucial, and that UV activation is particularly effective for PDzA–P*n*BA cross-linker, surpassing the performance of the previously studied azide-based 6Bx cross-linker.

Non-Halogenated Solvent Processed Shortwave Infrared Organic Photodetectors Using Sub-1 eV Bandgap Acceptor with Cyano Substitution

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Shortwave infrared (SWIR) organic photodetectors (OPDs) are attractive for low-cost, flexible sensing applications but are often limited by low responsivity and high noise under reverse bias. Here, we report high-performance SWIR OPDs enabled by a newly designed ultranarrow-bandgap non-fullerene acceptor, 6CN. Featuring a fused-cyclopentadithiophene core and cyano-substituted π-bridges, 6CN exhibits an optical bandgap of ≈0.98 eV, extending absorption to ~1250 nm. When blended with the polymer donor PTB7-Th, the resulting bulk-heterojunction shows strong charge transfer, broad spectral coverage, and robust charge transport. Importantly, optimized devices are fabricated using the non-halogenated solvent o-xylene without solvent additives, yielding superior photoresponse compared to conventional chlorinated processing. The resulting OPDs achieve responsivities up to ≈0.2 A W^{-1} at 1200 nm and specific detectivities exceeding 3 × 10^{11} Jones across the 300–1200 nm range. These results demonstrate a promising pathway toward environmentally friendly, high-sensitivity SWIR OPDs suitable for scalable and flexible photodetection technologies.

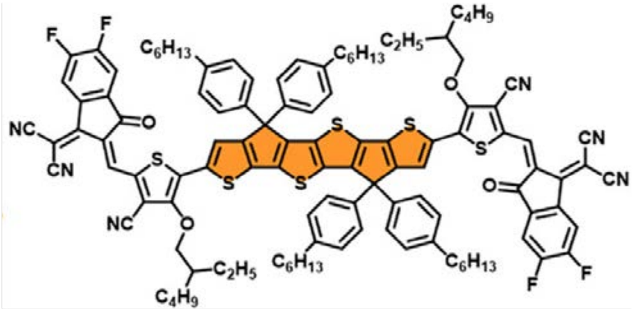

Figure 1. Chemical structure of 6CN.

This work was supported by the Mitsubishi Chemical Center for Advanced Materials (MC-CAM). Synchrotron measurements were conducted at beamline 7-ID-1 (SST-1) of the National Synchrotron Light Source II, a U.S. DOE Office of Science User Facility at Brookhaven National Laboratory (DE-SC0012704). Additional support was provided by the Goodnight Innovation Distinguished Professor endowment, the Ratchadaphiseksomphot Endowment Fund (Chulalongkorn University), the National Research Foundation of Korea (RS-2024-00444458), and the U.S. National Science Foundation (DMR-2308708, 2404409).

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Investigating the unique photoreactivity of 1,2-dithiane with vinyl monomers

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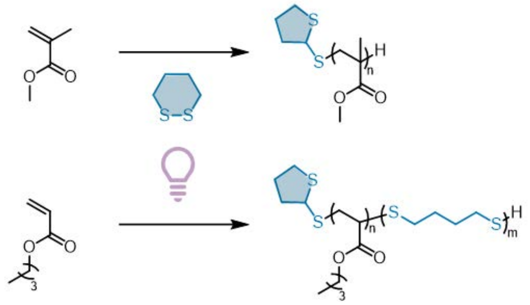
α-Lipoic acid and its derivatives are known to thermally copolymerize with certain vinyl monomers, such as acrylates, via uncontrolled free radical polymerization.[1] Recently, it has been shown that by using light, a range of thermally incompatible vinyl monomers can form random copolymers with these 5-membered heterocyclic disulfides.[2] Given this observed difference in reactivity, we set out to explore how the larger 6-membered ring, 1,2-dithiane, interacts with vinyl monomers under photochemical conditions. Irradiating 1,2-dithiane with high-energy ultraviolet light causes a well-documented rapid intramolecular rearrangement to thiophane-2-thiol.[3] In a reaction mixture of 1,2-dithiane with the monomer methyl methacrylate (MMA), this thiol proceeds to help initiate homopolymerization of MMA while also serving as a chain transfer agent throughout the reaction. Thus, chains of poly(MMA) with exactly one thiophane-2-thiol-derived chain end are obtained. This structure was confirmed by analyzing the products of similar reactions conducted using the 1,2-dithiane analog, oxidized dithiothreitol, functionalized with easily characterized handles. In contrast to methacrylates, the photopolymerization of acrylates, such as *n*-butyl acrylate (*n*BA), in the presence of 1,2-dithiane produces copolymers, although the thiophane-2-thiol chain transfer agent still participates in the reaction. The tendency of 1,2-dithiane to convert into a thiol significantly impacts its copolymerization reactivity with vinyl monomers under photochemical conditions.



Photopolymerizing methacrylates and acrylates in the presence of 1,2-dithiane.

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Combined Electrochemical and Spectroscopic Insights into Redox Pathways and Structural Distortion in Prussian Blue Analogs

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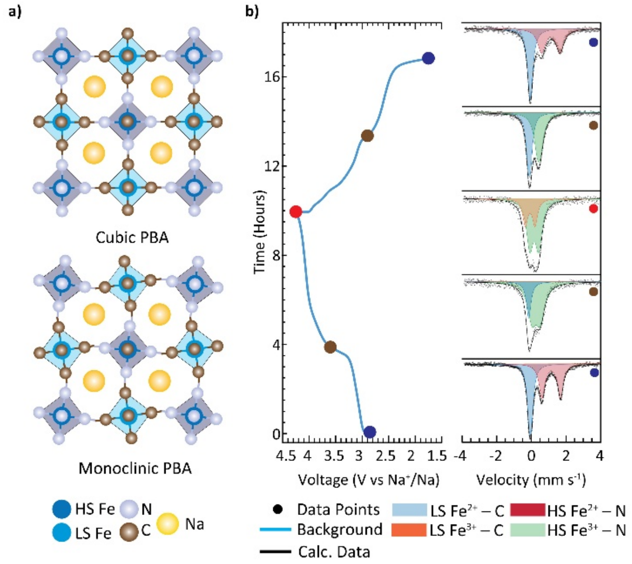
Prussian Blue Analogs (PBAs) offer a unique platform for sustainable Na-ion batteries. Their long-term performance is governed by subtle relationships between vacancy content, Fe oxidation state distribution, and distortion-driven redox chemistry, and understanding these is important for their deployment. We have investigated $Na_{2-x}Fe[Fe(CN)_6]$ compositions spanning reduced, vacancy-poor to highly oxidized, vacancy-rich regimes to uncover the fundamental origins of degradation. At high sodium content, PBA undergoes rapid capacity fade because the high-spin (HS)-Fe^{2+} and high-spin-Fe^{3+} redox couple is intrinsically distortion-prone. We employ Mössbauer spectroscopy and XANES reveal that oxidation of HS-Fe^{2+} generates significant local strain, which accumulates in a vacancy-deficient structure and progressively deactivates Fe^{2+} sites, directly reflected in the loss of redox activity. In sharp contrast, PBAs synthesized under ambient conditions contain higher baseline Fe^{3+} and greater vacancy fractions. These electrochemically inactive Fe^{3+} centers act as rigid framework anchors that distribute strain and suppress distortion-induced collapse, resulting in exceptional capacity retention despite lower theoretical capacity. Our results reveal a clear design principle: vacancy-rich, partially oxidized PBAs offer enhanced durability, providing a foundation for engineering long-life Na-ion cathodes through controlled defect and oxidation-state chemistry.



(a) Schematic illustration of PBA. (b) Ex-situ Mössbauer spectroscopy pointing to changes in Fe sites.

Dispersity Stabilization of Complex Sphere Phases in Diblock Copolymer Melts

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Bidisperse and homopolymer blending techniques have emerged as effective routes to stabilize a variety of complex sphere phases in block copolymers, but suffer from phase coexistence, limited windows of stability, and large molecular weight dependencies that preclude the targeting of specific phases.[1-3] Here, we demonstrate how tailoring molecular weight dispersity alleviates these limitations and enables precise morphological control in conformationally-asymmetric diblock copolymers. By synergistically combining atom-transfer radical polymerization with automated chromatographic fractionation, we generate high-resolution polymer libraries of a model poly(acrylate)-based system with tunable dispersity in each block and minimal synthetic variations. This approach stabilizes all known sphere phases and provides broad regions of stability with limited macrophase separation, outperforming traditional blending approaches. These insights highlight the power of dispersity in the rational design of block copolymers with targeted morphologies for next-generation materials.

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Radical-Free Digital Light Processing of Hydrogels via Photo-Caged Cyclopentadiene Diels–Alder Click Chemistry

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Light-controlled chemistries have revolutionized 3D printing and microfabrication by providing spatial and temporal precision in material patterning, particularly for soft materials in biomedical contexts.[1] Synthetic hydrogels that mimic the extracellular matrix underpin technologies in 3D cell culture, therapeutic delivery, and soft robotics. Digital light processing (DLP) has become a leading platform for high-resolution hydrogel printing, yet most systems depend on radical-mediated photopolymerization. While efficient, these radical reactions can damage sensitive biomolecules and restrict subsequent chemical modification.[2] Here, we report a radical-free DLP strategy based on aqueous photoresins that exploits a Diels–Alder click reaction between photo-caged cyclopentadiene (Cp) and maleimide.[3] Upon 365 nm irradiation, Cp is rapidly uncaged to undergo efficient cycloaddition with maleimide partners, yielding covalent hydrogel networks with high fidelity. The two-component resin design allows tunable mechanical properties and sub-millimeter feature resolution. Importantly, residual reactive groups remain available after printing, enabling post-fabrication spatial patterning of small molecules without any radical chemistry. This chemically orthogonal and biocompatible approach introduces a new class of photoresins for 3D printing, overcoming the intrinsic limitations of radical-based systems. Additionally, this chemistry can be combined with conventional radical reactions, as applied to dual-wavelength vat photopolymerization (DWVP) using two different wavelengths of light. It provides a versatile foundation for fabricating adaptive soft materials, architected biomaterials, and 4D-printed constructs that demand precise control over network chemistry and functionalization.

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Water-Developable Ionic Liquid Polymer Enables Sub-20 µm Patterning and Humidity-Sensing Capability

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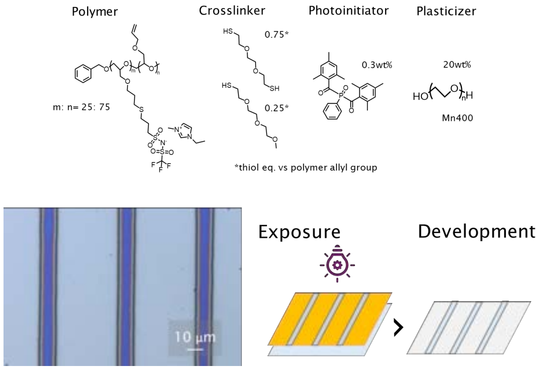

Water-Developable Ionic Liquid Polymer

Polymeric ionic liquids (i.e., PILs) have diverse sensing capabilities, including humidity, temperature, pH and strain monitoring in part due to their ionic conductivity properties. While multi-modal sensor arrays fabricated by lithographic techniques have recently attracted attention [1)], photo-patternable PILs[2)] with feature sizes below 20 µm, those utilizing 365 nm UV exposure and water development are particularly attractive due to their compatibility with large-scale production and low damage processes. Herein, a photo-patternable PIL was developed via thiol-ene crosslinking. A system of poly(allyl glycidyl ether) bearing 25 mol% of [((3-mercaptopropyl)sulfonyl) ((trifluoromethyl)sulfonyl)imide] 1-ethyl-3-methylimidazolium side groups (PAGE-TFSI-EMIm+) was photocured with 2,2'-(ethylenedioxy)diethanethiol (EDDT) and 2-[2-(2-methoxyethoxy)ethoxy]-ethanethiol (MEET) in the presence of a photo initiator and a plasticizer. Optical photothermal infrared spectroscopy (O-PTIR) demonstrated spatially resolved crosslinking, evidenced by significant contrast in the allyl C=C bond peak at 1645 cm^{-1} between exposed and unexposed areas. For an EDDT/MEET ratio of 75:25, ~ 17 µm resolution patterning was achieved with ~280 nm-thick films while maintaining high ionic conductivity (3.9×10^{-6} S / cm) at room temperature. An impedance type humidity sensor was fabricated by integrating interdigitated electrodes with a 3 mm diameter patterned PAGE-TFSI-$EMIm^+$. The sensor demonstrated excellent sensitivity (1.0 kΩ / %RH) with low hysteresis (2.1 %) across a humidity range of 0 - 85 %RH, along with robust repeatability over 40 cycles with 0 - 80 %RH. Equivalent circuit fitting of electrochemical impedance spectroscopy (EIS) data revealed a strong correlation between the bulk resistance and impedance, suggesting that the sensing mechanism is primarily governed by variations in ionic mobility within the bulk material. This approach underscores the potential of photopatterned PILs for advanced sensor architectures and next-generation multi-modal arrays.

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Enhancing Thermal Stability of Organic Photodetectors with Polymer Acceptors

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Organic photodetectors (OPDs) have emerged as promising candidates for next-generation optoelectronic applications due to their mechanical flexibility, lightweight nature, and tunable optical properties. However, their widespread adoption is hindered by stability challenges, particularly under thermal stress encountered in industrial processing. This study addresses the critical issue of thermal stability by investigating the performance of OPDs employing three polymer acceptors: PF5-Y5, PYTS-C2, and PY2TS-C2, which are based on the Y6 structure, paired with the PBDB-T donor. Devices fabricated with polymer acceptors demonstrate significantly improved resistance to thermal annealing at 150 °C for 1 hour, maintaining good operational performance ($D^*_{\mathrm{wh}} = 9.5\times10^{11}$ Jones at 770 nm at -2 V). Detailed analysis reveals that PF5-Y5-based OPDs display only a modest reduction in external quantum efficiency (EQE) due to decreased electron mobility after annealing, and devices based on PY2TS-C2 and Y6 suffer from increased dark current, primarily attributed to morphological changes and electrode diffusion. These results highlight the advantages of polymer acceptors in enhancing thermal robustness and provide design strategies for developing high-performance, thermally stable OPDs suitable for integration with advanced electronic systems.

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Characterization of Peptoid Hairpin Structures Using Magnetic Tweezers

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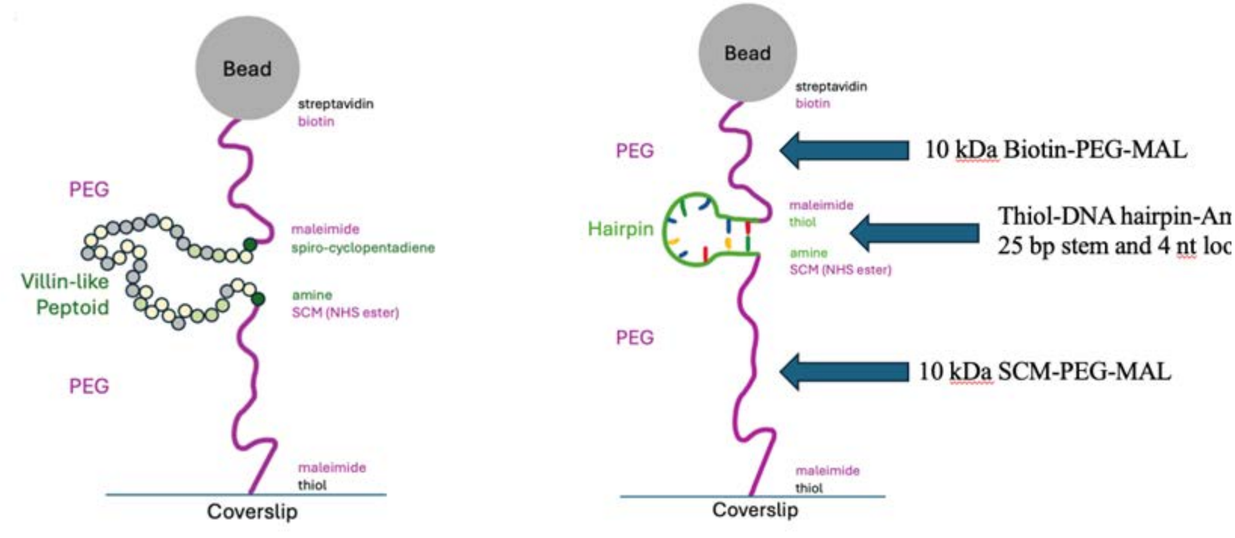
Peptoids are sequence-defined, protein-inspired polymers that lack the backbone hydrogen bonding found in proteins. This project aims to test whether cooperative folding and unfolding behavior can be engineered purely through sequence design in a synthetic polymer. Single-molecule magnetic tweezers will be used to investigate how peptoid sequence and length influence folding and unfolding under applied force, with a focus on designed peptoid hairpins. The project further seeks to translate these molecular-scale mechanical responses into bulk materials by incorporating peptoids as stress-responsive crosslinkers in hydrogels, enabling tougher and more tunable soft materials. As a preliminary step toward peptoid measurements, a simplified conjugation system based on a DNA hairpin with PEG handles is being used to validate end-group chemistry and experimental workflows. The PEG reagents were validated by GPC and NMR, and gel electrophoresis was used to assess conjugation yield. HPLC was employed to further analyze and purify the conjugated products. In the next step, magnetic tweezers will be used to probe the mechanical properties of PEG–DNA hairpin–PEG constructs.



Final goal: peptoid hairpin with PEG handles

Preliminary experiment: DNA hairpin with PEG handles

Final goal (Peptoid hairpin with PEG handles, left) of this project and our preliminary experiment (DNA hairpin with PEG handles, right).

Electrostatic Complexation of Conjugated and Bottlebrush Polyelectrolytes Forms Printable Conductive Inks

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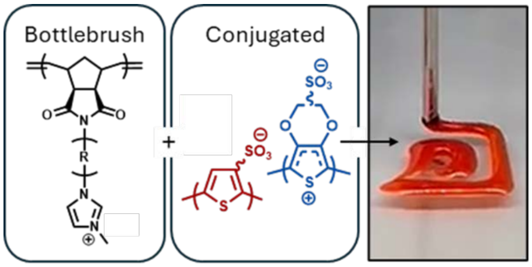
Long-standing challenges in the field of organic electronics include processability, scalability, and trade-offs between mechanical and electrical performance. Historically, blends of conjugated and insulating polymers have shown interesting properties – from transparency to high electrical conductivities (1-100 S cm^{-1}); however, traditionally, many blends have suffered from processability challenges, limited film thicknesses, and poor mechanical performance.[1–3] So, new ways to obtain orthogonal properties of blended components are important to investigate and some advances have been made leveraging the electrostatic compatibilization of conjugated and insulating polyelectrolytes.[4–7] Electrostatic complexation of polyelectrolytes is a versatile method for forming blends of polymers that would phase separate without the presence of ionic moieties.

In this work, we explore the design rules for the electrostatic compatibilization of conjugated and bottlebrush polyelectrolytes, resulting in functional and polymer-dense materials that are processable by direct-ink writing. Conjugated polyelectrolytes provide electronic properties, while bottlebrush polyelectrolytes provide mechanical softness, compliance, and stickiness. We investigate the usage of these blends as soft conductors, allowing for extrusion-based printing into thick films (mm – cm scale). Our work focuses on expanding the design rules of conjugated polyelectrolyte: bottlebrush polyelectrolyte (CPE:BPE) complexes to include differences in CPE chemistries, charge fractions, electrical doping mechanisms, and processing formulations. We investigate the impact of CPE variation on electrostatic compatibilization and final blend properties, such as printability, rheological behavior, and electromechanical properties. We show that printable inks can be readily formulated for direct-ink writing of thick structures of organic semiconductors that show sufficient electrical conductivity, stretchability, and adhesive properties for applications such as bioelectronic sensors and conductive adhesives.



Polyelectrolyte complexes enable printing.

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