

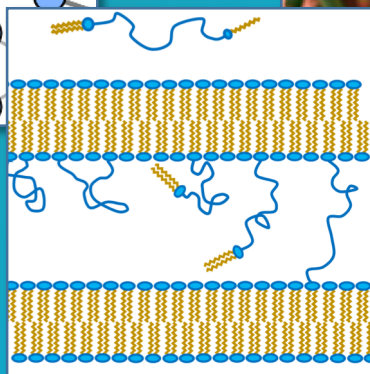
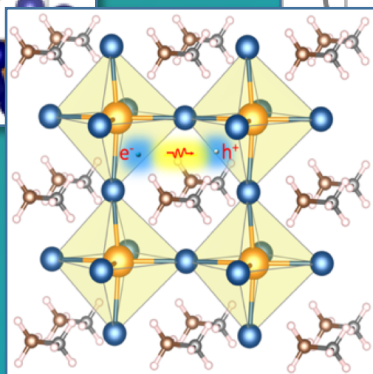
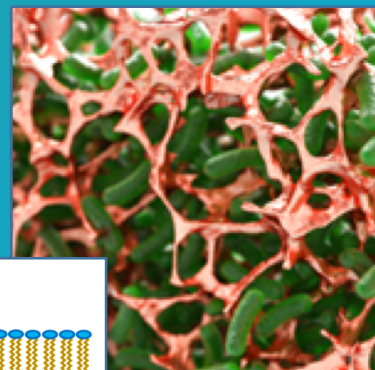
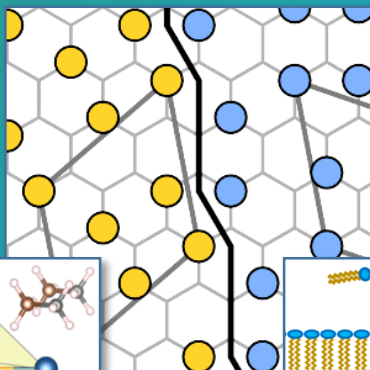
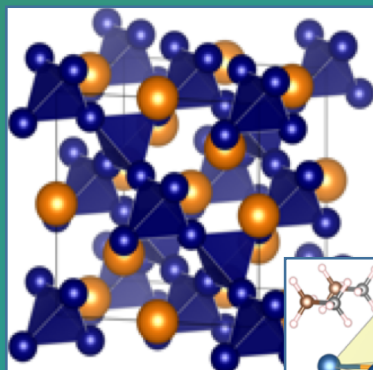
UC SANTA BARBARA
MRL

Materials
Research
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NSF Materials Research Science and Engineering Center [DMR 1720256]



Materials Research Outreach Program, 2018
Wednesday January 30th and Thursday January 31st 2019
Corwin Pavilion, UC Santa Barbara
Schedule and Poster Abstracts



Materials Research Outreach Program

January 30th and 31st, 2019 at the Corwin Pavilion

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Support for this symposium is generously provided by the Materials Research Science and Engineering Center Program of the National Science Foundation and the University of California, Santa Barbara.

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Session 1, Wednesday Morning, January 30, 2019, Corwin Pavilion, UC Santa Barbara
Session Chair: Ram Seshadri

8:15 am	<i>Breakfast</i>	
8:50 am	<i>Welcome remarks from Dean Rod Alferness (College of Engineering, UC Santa Barbara)</i>	
9:00 am	Ram Seshadri UC Santa Barbara	The State of the MRL
9:30 am	Natalie Larson Lawrence Berkeley Laboratory	X-Ray Computed Tomography of Microstructure Evolution During Processing of Ceramic Matrix Composites
10:00 am	<i>Refreshment Break</i>	
10:30 am	Phil Christopher UC Santa Barbara	Catalysts are Dynamic Materials
11:00 am	Brent Melot University of Southern California	Holistic Design of Model Materials for Heterogeneous Catalysis
11:30 am	Lior Sepunaru UC Santa Barbara	<i>In Situ</i> Detection and Characterization of Nanomaterials at the Single Entity Level
12:00 pm	<i>Lunch</i>	

Session 2, Wednesday Afternoon, January 30, 2019, Corwin Pavilion, UC Santa Barbara
Session Chair: Anton Van der Ven

1:30 pm	Joshua Bocarsly UC Santa Barbara	Magnetocaloric Materials for Next-Generation Refrigeration and Waste Heat Recovery
2:00 pm	Raphaële Clément UC Santa Barbara	Cation-Disordered Lithium Transition Metal Oxyfluoride Cathodes
2:30 pm	Julija Vinckevičiūtė UC Santa Barbara	Electronic Structure Implications for Atom Migration in Layered Cathode Materials
3:00 pm	<i>Refreshment Break</i>	
CHEETHAM LECTURE [CHAIR BY CRAIG HAWKER]		
3:30 pm	Clare Grey FRS University of Cambridge	Developing and Applying New Tools to Understand How Materials for Li and "Beyond-Li" Battery Technologies Function
4:30 pm	<i>Posters and Reception</i>	

Session 3, Thursday Morning, January 31, 2019, Corwin Pavilion, UC Santa Barbara

Session Chair: Chris Van de Walle

8:30 am	<i>Breakfast</i>	
9:00 am	Tom Devereaux Stanford/SLAC	Theoretical Understanding of Photon Spectroscopies in Correlated Materials
9:30 am	Dave Righer Raytheon	III-V Superlattice Materials for Infrared Sensors
10:00 am	<i>Refreshment Break</i>	
10:30 am	Nadya Mason University of Illinois	Electronic Transport in Strain-Engineered Graphene
11:00 am	Joshua Lequieu UC Santa Barbara	Architecture and Asymmetry in Block Polymer Self-Assembly
11:30 am	Meredith Wiseman DSM	Processable Multiple Network Composite Design Using Insights from Sequential Interpenetrating Networks
12:00 pm	<i>Lunch</i>	

Session 4, Thursday Afternoon, January 31, 2019, Corwin Pavilion, UC Santa Barbara

Session Chair: Chris Bates

1:30 pm	Benny Freeman UT Austin	Surface Modification of Porous Polymer Membranes to Reduce Fouling by Oil/Water Emulsions
2:00 pm	Nancy Eisenmenger Nike	Rheology and Kinetics of Thermoplastic Urethanes During Processing
2:30 pm	Matthew Kade Tricida	Slowing the Progression of Chronic Kidney Disease Through the Treatment of Metabolic Acidosis
3:00 pm	<i>Refreshment Break</i>	
3:30 am	Paresh Ray Jackson State University	Molecular Designs of Multi-Photon Absorbing Materials for Bioimaging Applications
4:00 pm	Caitlin Sample UC Santa Barbara	Metal-Free Synthesis of Functional Silicones
4:30 pm	<i>Posters and Reception</i>	

About the MROP

Initiated in 1999 under the leadership of the late Professor Edward Kramer to annually showcase MRL research to our Industrial and Venture partners, the Materials Research Outreach Program has evolved into so much more. In addition to providing a wonderful opportunity to interface with our corporate colleagues — including, and perhaps especially, local start-ups — the MROP has emerged as the principal occasion to hear about and share UCSB research in the broad Materials arena.

The MROP has traditionally encouraged many new faculty members from a cross-section of UCSB departments to showcase their research vision, leading to the nucleation of numerous collaborations. Key academic scientists, particularly from neighboring campuses, are also invited. Finally, the MROP has become an integral part of the undergraduate and graduate education, and post-doctoral experience of literally hundreds of students and fellows from Science and Engineering Departments on this campus.

No matter which category best fits you, please feel welcome to attend the 2019 MROP, and thank you for your continued support. We hope you enjoy the MROP as much as we enjoy organizing it.

Josh Bocarsly joined the Ph.D. program in the Materials Department at UC Santa Barbara in Fall 2015 following his bachelor's degree from the Chemistry Department at Princeton University, with a certificate in Materials Science and Engineering. At Princeton, he began his education in solid state chemistry while working in the lab of Professor Bob Cava, completing a thesis on manipulating the electronic structure of tungsten bronzes. At UC Santa Barbara, Josh researches the chemistry and physics of magnetic materials under the co-advisement of Professors Ram Seshadri and Stephen Wilson. Specifically, he is interested in understanding the interplay between atomic and magnetic structure in materials with applications in next-generation technologies such as magnetic refrigeration and spintronics. To study this, he uses a combination of experimental and computational techniques, including synchrotron and neutron scattering, magnetic measurements, and density functional theory calculations.



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Phillip Christopher received his B.S. from University of California, Santa Barbara in 2006 and his M.S and Ph.D. from University of Michigan in 2011, all in Chemical Engineering. From 2011-2017 he was an Assistant Professor at University of California, Riverside. In 2017 he moved with his group to the University of California, Santa Barbara where he is an Associate Professor and the Mellichamp Chair in Sustainable Manufacturing. His research interests are in sustainability, heterogeneous catalysis, *in-situ* characterization of the dynamic behavior of catalysts, and photocatalysis by metal nanostructures.

Raphaële Clément received her B.A. and M.Sc in Natural Sciences and her Ph.D. in Chemistry from the University of Cambridge. She did her Master of Science research project and Ph.D. in the group of Prof. Clare Grey, using experimental and theoretical solid-state NMR methods to investigate electrode materials for Li- and Na-ion rechargeable battery applications. She then moved to UC Berkeley to pursue a postdoc in the group of Professor Gerbrand Ceder, where she continued to apply NMR methods to the study of battery components (Li-, Na-, K-ion cathodes and solid electrolytes) while learning about ab initio methods to predict the thermodynamic stability and synthesizability of electrode materials. She recently joined the Materials Department at UCSB as an Assistant Professor (as of July 2018). Her current research interests span the investigation of electrode and solid electrolyte materials for batteries and fuel cells, as well as the development of magnetic resonance techniques (NMR and EPR) for ex situ and operando measurements on electrochemical devices.



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Professor Tom Devereaux received his Ph.D. in Physics from the University of Oregon in 1991, M.S. from University of Oregon in 1988, and B.S from New York University in 1986. He is currently the Director of the Stanford Institute for Materials and Energy Sciences (SIMES), a professor in the Photon Science Faculty at SLAC National Accelerator Laboratory and Stanford University and a Senior Fellow of the Precourt Institute for Energy. SIMES is a joint institute between Stanford main campus and SLAC, a national laboratory, focusing on scientific foundations related to the energy challenge facing our society.

His research effort focuses on using the tools of computational physics to understand quantum materials. The goal of his research is to understand equilibrium and ultrafast non-equilibrium electron dynamics via a combination of analytical theory and numerical simulations to provide insight into materials of relevance to energy science. The specific focus of the group is the development of numerical methods and theories of photon-based spectroscopies of strongly correlated materials.

Nancy Eisenmenger is currently a Materials Researcher in the Polymers R&D group at Nike Air Manufacturing Innovation near Portland, Oregon. She studied Chemistry at Harvey Mudd College, earning a BS with high distinction and departmental honors. Nancy completed a PhD in Materials Science at the University of California, Santa Barbara with an NSF Fellowship and a Chancellor's Fellowship. She was advised by Professor Chabynyc and co-advised by Prof. Fredrickson (ChemE) and Prof. Ganesan (UT Austin). Her dissertation included both experimental and computational work exploring the intricate device physics of organic and hybrid solar cells. After graduate school, Nancy accepted a position as a Research Scientist with DSM. After three years with the DSM Materials Science Center, Nancy joined Nike Air Manufacturing Innovation. As in her graduate work, Nancy uses a combination of experimental and computational techniques to elucidate materials systems; however, her current work involves different polymers and applications. Currently, she researches structure-property-processing relationships in materials used for Nike footwear, especially focusing on Nike Air shoe soles.



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Benny Freeman is the Richard B. Curran Centennial Chair in Engineering at The University of Texas at Austin. His research is in polymer science and engineering and, more specifically, in mass transport of small molecules in solid polymers. He currently directs 25 Ph.D. students and 1 postdoctoral fellow performing fundamental research in gas and liquid separations using polymer membranes and barrier packaging. His research group focuses on structure/property correlation development for desalination and gas separation membrane materials, new materials for hydrogen separation, natural gas purification, carbon capture, reactive barrier packaging materials, and new materials for improving fouling resistance and permeation performance in liquid separation membranes. He leads the Center for Materials for Water and Energy Systems (M-WET), a Dept. of Energy Energy Frontier Research Center.

Clare P. Grey, FRS is the Geoffrey Moorhouse-Gibson Professor of Chemistry at Cambridge University and a Fellow of Pembroke College Cambridge. She holds a Royal Society Professorship. She received a BA and D. Phil. (1991) in Chemistry from the University of Oxford. After post-doctoral fellowships in the Netherlands and at DuPont CR&D in Wilmington, DE, joined the faculty at Stony Brook University (SBU) as an Assistant (1994), Associate (1997) and then Full Professor (2001-2015). She moved to Cambridge in 2009, maintaining an adjunct position at SBU. She is currently the director of the EPSRC Centre for Advanced Materials for Integrated Energy Systems (CAM-IES). Her recent honors and awards include the 2011 Royal Society Kavli Lecture and Medal for work relating to the Environment/Energy. She is a foreign member of the American Academy of Arts and Sciences (2017) and a Fellow of the Electrochemical Society (2017). Her current research interests include the use of solid-state NMR and diffraction-based methods to determine structure-function relationships in materials for energy storage (batteries and supercapacitors), conversion (fuel cells) and carbon capture.



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Matthew Kade is a Principal Scientist at Tricida in the Chemistry, Manufacturing, and Control group. Matt attended the University of Massachusetts, Amherst and received his B.S. in Chemistry and Economics in 2005. After graduating, Matt joined Prof. Craig Hawker's group at the University of California, Santa Barbara to study supramolecular bonding in polymers. He completed postdoctoral work with Prof Matthew Tirrell at the University of California, Berkeley and the University of Chicago, where he made a polymer that was sent to the International Space Station. Matt went on to join the team at Tricida in 2014 and has since been a co-inventor of the polymer drug TRC101, co-authoring multiple patents on the subject, and currently helping in its manufacture.

Natalie Larson earned her Ph.D. in Materials in December 2018 from UCSB, where she was a recipient of a NSF Graduate Research Fellowship, a Chancellor's Fellowship, a Holbrook Foundation Fellowship, and an Advanced Light Source (ALS) Doctoral Fellowship. From 2016-2018, she was a Doctoral Fellow in residence at the ALS at Lawrence Berkeley National Laboratory. She earned her B.S. in Materials Science and Engineering from the University of Washington in 2013. Her research interests include development of advanced structural materials for more efficient energy use and production. Her current research uses in-situ X-ray computed tomography to study microstructure evolution during processing of ceramic matrix composites for more efficient aerospace engines.



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Joshua Lequieu received his B.S. in Chemical Engineering from Cornell University, and his Ph.D. in Molecular Engineering from the University of Chicago under the guidance of Juan J. de Pablo. He is currently a Postdoctoral Researcher with Glenn H. Fredrickson at University of California, Santa Barbara working on block polymer self-assembly.

Nadya Mason is a professor of Physics at the University of Illinois at Urbana-Champaign. She earned her PhD in Physics from Stanford University and engaged in postdoctoral research as a Junior Fellow at Harvard University. A condensed matter experimentalist, Dr. Mason focuses on electron behavior in low-dimensional materials such as nanowires, graphene, and nano-structured superconductors. In addition to maintaining a rigorous research program and teaching, Dr. Mason works to increase diversity in the physical sciences. Dr. Mason was named a 2008 Emerging Scholar by *Diverse Issues in Higher Education* magazine, was a recipient of the 2009 Denise Denton Emerging Leader Award, the 2012 Maria Goeppert Mayer Award of the American Physical Society (APS), and was named an APS Fellow in 2018. She is a former General Councillor of the APS and Chair of the APS Committee on Minorities, and currently serves as Director of the Illinois Materials Research Science and Engineering Center (I-MRSEC).



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Brent C. Melot received his Ph.D. from the Materials Department at the University of California, Santa Barbara in 2010. His research at UCSB focused on understanding the relationship between complex superexchange pathways and the resulting magnetic properties of oxide spinels. After completing his doctoral work, he joined the Laboratoire de Réactivité et Chimie des Solides in Amiens as a postdoctoral research associate under Jean-Marie Tarascon developing new materials for Li-ion batteries. He began his independent career in 2012 at the University of Southern California where he is Associate Professor, and with his group, develops materials design principles for improving the performance of a wide range of functional materials including: heterogeneous catalysts, photovoltaics, and intercalation electrodes.

Paresh C Ray is Professor of Chemistry at Jackson State University. He obtained his PhD degree in Chemistry from Indian Institute of Science in 1997. Following postdoctoral fellowships at the University of Chicago, Ohio State University and Columbia University, he worked as a research scientist in Blacklight Power Inc, NJ, USA. In 2003, he joined as Assistant Professor in the Department of Chemistry, Jackson State University and was promoted to Full Professor in 2012. His research addresses new chemical strategies for the design of emerging material, creating new nanobased sensors for different chemical and biological toxins, designing multifunctional nanomaterial for multimodal imaging, and enhancing our understanding of biomolecular interaction with nanosurfaces. Professor Ray has directed the NSF-PREM grant at JSU for the past 12 years. He has also served as program director for NSF-REU grants for past 9 years.



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David R. Rhiger is a senior scientist at Raytheon Vision Systems in Goleta, California. He has approximately 40 years' experience in the technology of infrared sensors. His work has focused on the physics of semiconductor devices and the materials for detecting infrared light in a wide variety of applications. Recently he has been developing III-V strained-layer superlattice materials and devices for MWIR, LWIR, and dual-band detection. He has produced innovative methods for analyzing the device characteristics and contributed to our understanding of how the devices function. His earlier work has focused on CdZnTe substrate improvement, LWIR HgCdTe detector design, and diagnosis of p-n junction performance in less-common semiconductors. He has also addressed problems of surface characteristics and surface passivation in these materials, and designed gamma-ray detectors.

David holds a Ph.D. in Physics from the University of Washington (Seattle) and a B.S. in Physics from Stanford University. In 2017 he was awarded the Raytheon company-wide individual Excellence in Engineering and Technology Award. He is a Fellow of the Military Sensing Symposium.

Caitlin S. Sample earned her S.B. in Materials Science and Engineering and Applied Mathematics from MIT in 2014, working in the Rubner-Cohen group on hydrogen-bonded polymeric thin films and in the Gibson group investigating the mechanical properties of cricket wings. She is currently a doctoral candidate in the Materials Department at UCSB. Her work in the Hawker and Bates group focuses on developing efficient and robust chemistries for the synthesis of functional polymeric networks.



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Lior Sepunaru completed (2017) his post-doctoral studies as a Marie Curie research fellow at the University of Oxford working on bio-nanoelectrochemistry under the tutelage of Prof. Richard G. Compton. Prior to this, he completed his Ph.D. at the Weizmann Institute of Science in 2014 working on solid state bioelectronics under the supervision of Professors David Cahen and Mordechai Sheves. Lior's research is focused on electrochemistry coupled to high resolution imaging of catalyst at the nanoscale, including the study of enzyme catalysis and development of new generation of biosensors.

Julija Vinckevičiūtė is a graduate student in the Van der Ven group at University of California, Santa Barbara. She completed her Bachelors in Materials Science and Engineering and Environmental Engineering at Northwestern University. At UCSB, she uses first-principles methods to study layered cathode materials and how changes in composition can affect battery performance. She uses tools like density functional theory and Monte Carlo methods as implemented in a Clusters Approach to Statistical Mechanics (CASM). When not in lab, Julija spends her time volunteering, whether by promoting science in local schools, helping on water projects in Kenya as part of Engineers Without Borders, or lending a hand at the Santa Barbara bunny shelter.



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Meredith Wiseman studied chemical engineering at Caltech and Stanford and received her PhD in 2012 working with Professor Curt Frank. In 2012 she moved to the Netherlands to join DSM, a purpose-led global science-based company active in nutrition, health, and sustainable living. There she has been working as a scientist and project leader supporting its Biomedical product portfolio including ingredients for silicone hydrogel contact lenses, lubricious coatings, and thermoplastic polyurethanes, as well as in application development for Dyneema® UHMWPE fiber in textiles and flexible composites. Her research interests include synthesis-structure-property relations of polymers and polymer networks, tribology and lubrication, and fracture mechanics of soft materials.

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1. A generalized probabilistic framework for endogenous cellular lineage reconstruction

C. Wangsanuwat

Department of Chemical Engineering, University of California, Santa Barbara, CA

During mammalian tissue development, proliferation and differentiation of cells are tightly regulated and dysregulation has been associated with a variety of diseases. Insights into cell proliferation and differentiation can be gained using lineage reconstruction, a method to establish the evolutionary relationship between individual cells at a particular stage of tissue development. While powerful techniques have been developed to infer cellular relationships, these methods only have clonal resolution and involve genetic modifications, rendering the methods unsuitable to study human tissues directly. To move past current limitations, it is critical to resolve the lineage relationships between cells in an organism endogenously at a single cell-division resolution and combine this knowledge with their transcriptomes to distinguish between different cell types. We developed a probabilistic model that uses 5-hydroxymethylcytosine (5hmC), an epigenetic mark found in the genome of mammalian cells, to reconstruct cellular lineages. The model takes advantage of the fact that 5hmC is not maintained through cell division [1] and the existence of sister chromatid exchange (SCE) events, a phenomenon that naturally occurs during cell division, to infer lineage relationships between cells in a developing embryo. The model predicts the full lineage of simulated 8-cell stage embryos with greater than 95% accuracy, which is much higher than that of a comparable method with the same resolution [2]. While the predictive power reduces at the 16-cell stage, the model still provides accurate relationships between 12 to 14 out of 16 cells in most simulations. Moreover, the model becomes better and is able to predict the correct tree lineage when SCE rates are sufficiently high. Finally, the model was successfully applied to infer the full lineages of real 8-cell stage mouse embryos. This model can be directly applied to other non-maintained epigenetic marks, such as 5-formylcytosine and 5-carboxylcytosine, and can endogenously determine the phylogeny of cells in various biological systems.

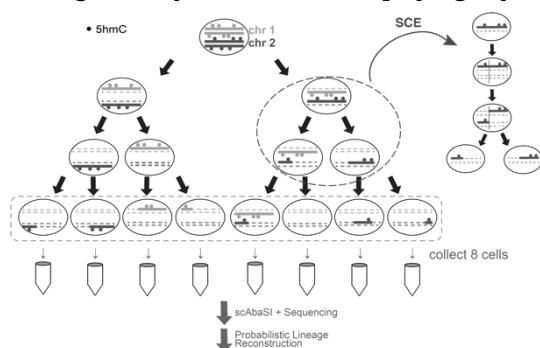


Figure 1: Experimental procedure prediction

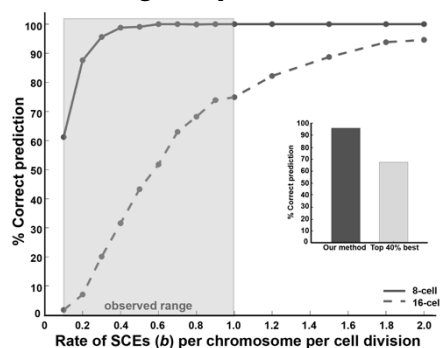


Figure 2: Accuracy of the model's prediction

References:

1. Mooijman, D.; Dey, S. S.; Boisset, J.-C.; Crosetto, N.; Oudenaarden, A. V. *Nature Biotechnology* **2016**, *34* (8), 852–856.
2. Frieda, K. L.; Linton, J. M.; Hormoz, S.; Choi, J.; Chow, K.-H. K.; Singer, Z. S.; Budde, M. W.; Elowitz, M. B.; Cai, L. *Nature* **2017**, *541* (7635), 107–111.

2. A rapid ζ potential analysis tool to unfold chemical surface reactions in real time

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^bDepartment of Mechanical Engineering

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Here we display a novel technique for real-time monitoring of chemical surface reactions using electroosmotic flow (EOF) in a nanochannel. This versatile tool allows precise, non-destructive analysis of surface charge in a minimal design.

At the interface between any charged surface and electrolyte solution, ions will accumulate, forming an electric double layer. A glass (silica) surface is lined with negatively charged silanol groups (SiO^-) in water. This negative surface will attract positive ions from the bulk, forming immobile (Stern) and mobile (diffuse) layers. In the presence of an electric field, the positively charged diffuse layer will migrate toward the cathode (-) and consequently drag the electroneutral bulk fluid, a phenomenon known as EOF. By measuring EOF in an applied field,¹ we can calculate the ζ potential (the residual potential at the Stern-diffuse layer interface), which is dominated by the net charge on surfaces. Thus, a method for continuous measurement of EOF shall be a promising analytical tool to show real-time charge changes on surfaces. In this aim, we propose to simply alternate the flow between two reservoirs of unequal electrolyte concentration and record consecutive channel traversals as the time required to move between two stable current readings.

To validate this scheme, we modified $1\ \mu\text{m}$ silica capillary tubing with a positively charged surface coating, 3-aminopropyltriethoxysilane (APTES), and monitored EOF in real-time to extract reaction kinetics. The ζ potential was expected to change dramatically as the SiO^-/SiOH surface is covered by the $\text{NH}_2/\text{NH}_3^+$ -capped monolayer (Figure 1). Our ζ potential monitoring program was set to alternate flow between borate buffered saline (pH 10) reservoirs every 5 min. After the first ζ potential was measured, we added 10mM APTES and observed the ζ potential increase from approx. $-45\ \text{mV}$ to $+20\ \text{mV}$ in 24 hours. The steep, linear change observed in the first hour ($>75\%$ of total) and the slow change thereafter is useful kinetic data to characterize the reaction: the actual APTES-silica reaction is rapid, but the densification of the monolayer is a long-term process. Our ability to monitor ζ potential continuously and reproducibly for the APTES monolayer formation shows the promising capability of this robust technique for quantifying chemical kinetics in a highly affordable and versatile design.

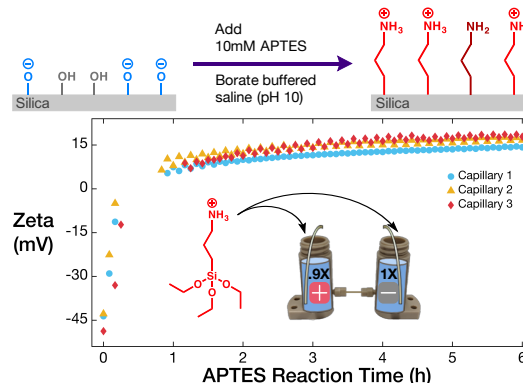


Figure 1. Continuous zeta potential monitoring of the APTES monolayer formation in three $1\ \mu\text{m}$ glass (silica) capillaries

References:

1. K. Chou, C. McCallum, D. Gillespie, and S. Pennathur, An experimental approach to systematically probe charge inversion in nanofluidic channels, *Nano Lett.* **18** (2018) 1191–1195. DOI: 10.1021/acs.nanolett.7b04736

3. Arrested mobility effects on the spinodal decomposition of ternary polymer solutions

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Many polymer membranes are made by immersion precipitation: a polymer solution film is immersed in a nonsolvent bath, inducing phase separation of the film into a polymer-rich phase that becomes the membrane matrix and a polymer-poor phase that becomes the membrane pores. Microstructure formation of these membranes is still not fully understood, given the interdependent nature of several physical processes: the mass transfer of solvent and nonsolvent through the film-bath interface, the ensuing phase separation of the film, the coarsening of domains, and finally the vitrification of the polymer-rich phase that arrests the membrane microstructure. In this work, we use phase-field models of the ternary polymer-nonsolvent-solvent system to solve the coupled convection-diffusion and momentum equations that describe the immersion precipitation process. We model the glass transition using contrasts in the viscosity and mobility of the polymer-rich and polymer-poor phases. We report how the glassy dynamics change the microstructures formed by bulk spinodal decomposition. We also study how the mass transfer kinetics between the bath and film are changed by the formation of a glassy interface.

4. Branched side chains govern counterion position and doping mechanism in conjugated polythiophenes

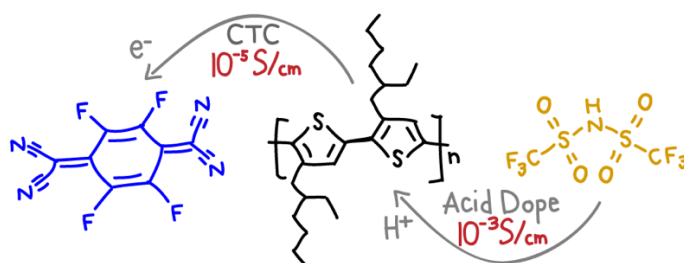
E. M. Thomas,^a E. C. Davidson,^b R. Katsumata,^b R. A. Segalman,^{a,b} and M. L. Chabinye^a

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Predicting the interactions between a semiconducting polymer and dopant is not straightforward due to the intrinsic structural and energetic disorder in polymeric systems. Although the driving force for efficient charge transfer depends on a favorable offset between the electron donor and acceptor, we demonstrate that the efficacy of doping also relies on structural constraints of incorporating a dopant molecule into the semiconducting polymer film. Here, we report the evolution in spectroscopic and electrical properties of a model conjugated polymer upon exposure to two dopant types: one that directly oxidizes the polymeric backbone and one that protonates the polymer backbone.

Through vapor phase infiltration, the common charge transfer dopant, F₄-TCNQ, forms a charge transfer complex (CTC) with the polymer poly(3-(2'-ethyl)hexylthiophene) (P3EHT), a conjugated polymer with the same backbone as the well-characterized polymer P3HT, resulting in a maximum electrical conductivity of $3 \times 10^{-5} \text{ S cm}^{-1}$. We postulate that the branched side chains of P3EHT force F₄-TCNQ to reside between the π -faces of the crystallites, resulting in partial charge transfer between the donor and the acceptor. Conversely, protonation of the polymeric backbone using the strong acid, HTFSI, increases the electrical conductivity of P3EHT to a maximum of $4 \times 10^{-3} \text{ S cm}^{-1}$, two orders of magnitude higher than when a charge transfer dopant is used. The ability for the backbone of P3EHT to be protonated by an acid dopant, but not oxidized directly by F₄-TCNQ, suggests that steric hindrance plays a significant role in the degree of charge transfer between dopant and polymer, even when the driving force for charge transfer is sufficient.



Branched side chains on the polymeric semiconductor P3EHT allow for two doping mechanisms to be observed, depending on the size of the counterion that is formed. As a result, the maximum electrical conductivity from the dopants used in the study differs by two orders of magnitude.

5. Bridging the gap between the bulk and nanoscale in 2D layered hybrid perovskites

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Hybrid organic-inorganic perovskites (HOIPs) are promising semiconductors with remarkable photocurrent conversion efficiencies, nearly matching crystalline Si, even when prepared through scalable solution-processing techniques¹. However, lead halide HOIPs are beset by instability to light, heat, and humidity. Recently, quasi-2D layered derivatives of metal halide HOIPs, such as the Ruddlesden-Popper (RP) phases, have shown improved stability and continuous tunability in optical and electronic properties. 2D RP perovskite phases are prepared by adding insulating ‘spacer’ cations, such as butylammonium, to the perovskite precursor to create stacks of lead halide sheets, only several lead

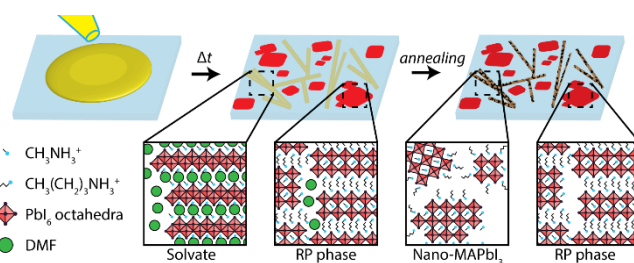
halide octahedra thick, arranged in a layered crystalline bulk structure. To great practical advantage, the ratio between lead halide octahedra and insulating spacer layers can be tuned to alter the bandgap and other properties through dielectric and quantum confinement². However, this additional compositional degree of freedom presents challenges in controlling structural homogeneity.

RP phases can be carefully grown as bulk single crystals, with precisely defined layering geometry and narrow optical features. However, when RP phases are grown as thin films for device applications, sub-populations of different layering orders form alongside poorly understood defect phases³. Typically, film deposition occurs too quickly to resolve different reaction intermediates and products that form during crystallization. Therefore, drop-cast precursor solutions were studied *in situ* by observing the evolution of X-ray diffraction, photoluminescence, and optical micrographs with time. We find that RP phases crystallize alongside intermediate solvated phases, leading to heterogeneous final products. *In situ* measurements of these parallel reaction products allow us to resolve a common discrepancy observed between the optical properties of thin-films and single crystals of RP phases, which is directly caused by the formation of solvated intermediate phases. Leveraging this understanding, we direct growth kinetics to prepare thin films with optical properties that converge with ideal single crystals of RP phases by rapid precipitation of the alkylammonium lead halide precursors with an antisolvent rinse.

The research is supported by the Defense Threat Reduction Agency under Award HDTRA1-15-1-0023. This work also used the shared facilities of the UCSB MRSEC (National Science Foundation DMR 1720256), a member of the Materials Research Facilities Network(www.mrfn.org).

References:

1. Snaith, H. J. *Nat. Mater.* **2018**, *17*, 372–76.
2. Stoumpos *et al.* *Chem. Mater.* **2016**, *28*, 2852–67.
3. Venkatesan *et al.* *Chem. Mater.* **2018**, *30*, 8615–8623.



A schematic showing parallel growth of lead halide solvate intermediates and 2D-layered perovskites during deposition.

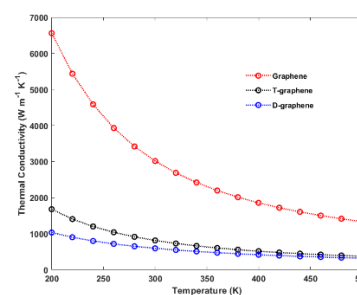
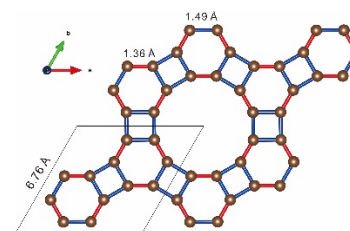
6. Coherent phonon transport in a two-dimensional graphene superstructure

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Coherent wave effects of thermal phonons hold promise of transformative opportunities in thermal transport control but remain largely unexplored due to the small wavelength of thermal phonons, typically below a few nanometers. This small length scale indicates that, instead of artificial phononic crystals, a more promising direction is to examine the coherent phonon effects in natural materials with hierarchical superstructures matching the thermal phonon wavelength. In this work, we characterize the thermal properties of D-graphene, a previously unstudied two-dimensional carbon allotrope based upon the traditional graphene structure but containing a secondary, in-plane periodicity. We use density functional theory (DFT) to calculate harmonic and anharmonic interatomic force constants (IFCs), which are then used to calculate the phonon dispersion, scattering rates, group velocities, and lattice thermal conductivity via an iterative solution to the linearized Boltzmann Transport Equation (BTE). We find that despite a very similar atomic structure, D-graphene possesses significantly different thermal properties than that of pristine graphene. At room temperature the calculated thermal conductivity of D-graphene is $600 \text{ W m}^{-1} \text{ K}^{-1}$ compared to $3000 \text{ W m}^{-1} \text{ K}^{-1}$ for graphene. The out of plane acoustic (ZA) mode contribution decreases from 84% in graphene to 47% in D-graphene. We attribute these distinct properties to the presence of three naturally occurring, low frequency optical phonon modes that possess characteristics of phonon coherence and arise from a folding of the acoustic modes and the associated frequency gap opening, a phenomenon also found in superlattices where an out of plane periodicity is introduced. The optical modes make a significant contribution to the thermal conductivity due to enhanced dispersion, comprising over 18% of the thermal conductivity, while the three coherent branches contribute 9% of the total conductivity. The construction of the D-graphene unit cell presents a new method with which the thermal conductivity of 2D materials can be reduced without making drastic changes to its fundamental composition and demonstrates the potential of using coherent phonon effects to significantly modify thermal transport.

This work is supported by a Department of Energy Early Career Research Program under award number DE-SC0019244.



Top: Graphene allotrope structure and unit cell
Bottom: Thermal conductivity of graphene and two graphene allotropes

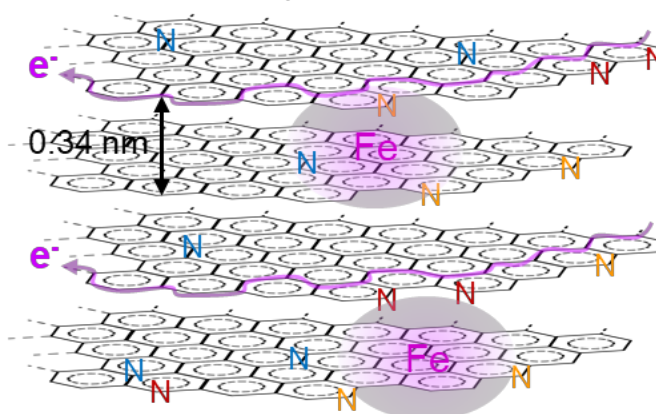
7. Compositions, structures, and properties of mesoporous-Fe,N-containing carbon materials for oxygen reduction electrocatalysts

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Mesoporous-Fe,N-doped carbon materials exhibit high and accessible surface areas, high conductivities, and high electrocatalytic activities for oxygen reduction, making them attractive as inexpensive alternatives to precious-metal fuel cell catalysts. The synthesis conditions, precursor compositions, and choice of templating material (e.g., salt-mixture or mesoporous-SBA-15 silica) influence the types, quantities, and distributions of Fe and N heteroatom environments, which strongly affect macroscopic oxygen reduction activities. However, it has been challenging to measure and correlate local Fe or N heteroatom environments and their distributions in graphitic carbon materials with macroscopic electrocatalytic properties. This has been due, in part, to their paramagnetic and/or conductive characters, complicated distributions of disordered and ordered regions, and heterogeneous material compositions. Nevertheless, using advanced nuclear magnetic resonance (NMR) techniques, detailed new insights can be obtained on the local atomic environments and distributions of N and Fe heteroatoms in high N content (~28 wt%) carbon materials.

Different synthesis conditions are shown to lead to distinct surface compositions that influence the electrocatalytic properties of the materials. Materials synthesized with ^{13}C , ^{15}N -enriched precursors yield increased NMR signal sensitivity that enables powerful 2D $^{13}\text{C}\{^{15}\text{N}\}$ NMR correlation analyses, which are combined with insights from nitrogen sorption, X-ray photoelectron spectroscopy, Raman spectroscopy, ^{57}Fe Mossbauer spectroscopy, X-ray



Schematic diagram of Fe and N heteroatom sites in mesoporous Fe,N-carbon material

diffraction, and electrocatalytic reaction analyses. The 2D $^{13}\text{C}\{^{15}\text{N}\}$ NMR spectra resolve and correlate signals from ^{15}N heteroatom sites and directly bonded ^{13}C atoms within the mesoporous carbon materials. Furthermore, relaxation-resolved ^{15}N NMR spectra and ^{15}N spin-lattice (T_1) relaxation time measurements resolve ^{15}N signals from ^{15}N species proximate to paramagnetic Fe heteroatoms and provide approximate ^{15}N -Fe distances. The NMR results and analyses establish the types, atomic environments, and distributions of ^{15}N heteroatoms in the mesoporous Fe,N-carbon materials, which, until now, have been infeasible to distinguish by scattering or other spectroscopic techniques. These analyses identify specific ^{15}N and ^{57}Fe heteroatom environments that correlate with increased ORR activity, providing new insights for the design of improved electrocatalysts for applications in energy storage and conversion.

8. Condensation of divalent metal ions by MAP-Tau remodels Tau-microtubule bundle architecture

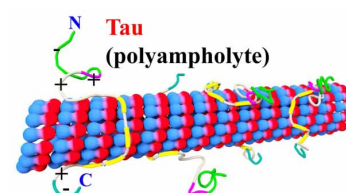
B. Fletcher,^a C. Song,^a P. Kohl,^a P. J. Chung,^{b,a} H. Miller,^a Y. Li,^a M. C. Choi,^c L. Wilson,^a S. C. Feinstein,^a and C. R. Safinya^a

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The neuronal microtubule-associated protein Tau binds to and stabilizes individual microtubules (MTs) and mediates MT-MT interactions. In order to understand the mechanisms governing the formation and stability of Tau-MT complexes, we have developed synchrotron small-angle x-ray scattering (SAXS) techniques to characterize nanoscale structural properties of these dissipative active macromolecular complexes in biological buffer containing GTP. While fascicles or linear arrays of ordered MTs have been observed in the axons of mature neurons, synchrotron SAXS shows that MTs polymerized in the presence of Tau *in vitro* primarily self-assemble into hexagonally ordered bundles (P. J. Chung, C. Song, et al. 2016 and 2018). Combining SAXS with transmission electron microscopy, we show that addition of metal ions (e.g. Mg²⁺) above threshold concentrations within a biologically relevant regime drastically reduces the wall-to-wall distance between bundled MTs followed by a remodeling transition with increasing time. Our data support a model where Tau's projection domain is in an extended brush-like state at low metal ion concentrations and, above a threshold concentration, collapses due to cation condensation, which leads to the overall structural remodeling of the Tau-MT complex.



Cartoon showing Tau bound to a microtubule.

References:

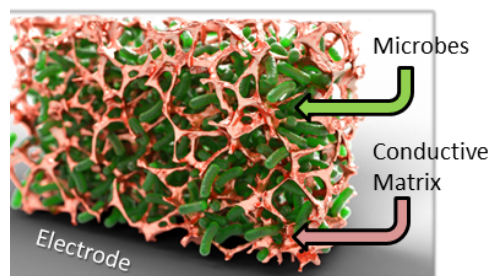
1. Chung, P. J.; Song, C.; Deek, J.; Miller, H. P.; Li, Y.; Choi, M. C.; Wilson, L.; Feinstein, S. C.; Safinya, C. R.: Comparison Between 102k and 20k Poly(ethylene oxide) Depletants in Osmotic Pressure Measurements of Interfilament Forces in Cytoskeletal Systems. *ACS Macro Lett.* **7** (2018) 228-232. DOI: 10.1021/acsmacrolett.7b00937
2. Chung, P. J.; Song, C.; Deek, J.; Miller, H. P.; Li, Y.; Choi, M. C.; Wilson, L.; Feinstein, S. C.; Safinya, C. R.: Tau Mediates Microtubule Bundle Architectures Mimicking Fascicles of Microtubules Found in the Axon Initial Segment. *Nature Commun.* **7** (2016) 12278. DOI: 10.1038/ncomms12278

9. Conductive living composites using conjugated polyelectrolytes

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Anaerobic bacteria routinely interface with abiotic substrates. However, inefficient interfacial contacts pose a primary bottleneck for electron transfer. We foresee that three-dimensional abiotic/biotic composites that combine a soft conductive matrix with exoelectrogenic bacteria will increase our ability to extract current from, or to electronically stimulate, microbial communities by at least three orders of magnitude (see the figure). Understanding and facilitating electron/ion transport in living systems is a fundamental issue with broad potential applications in bioelectronics from microbial fuel cells to biomedical devices. Water compatible conductive polymers for generating these composites are the result of work at UCSB on biosensors and on thermoelectric soft materials that can be solution processed into different form factors [1,2]. These materials are conjugated polyelectrolytes (CPEs) and consist of a pi-delocalized backbone and ionic pendant functionalities. Not only are CPEs suitable for electrical transport, they can also spontaneously form soft solids that permit the nutrient transport required for microbial growth. In this report, we describe our efforts thus far towards reaching the goal of a conductive living composite for bioelectrochemical systems. First, anaerobic respiration probed in the presence of CPEs revealed how molecular structural variation impacts biocurrent generation using *Shewanella oneidensis* MR-1 [3]. Further, this study was extended to *Geobacter sulfurreducens* to untangle contributions from electrostatic binding and CPE-modulated redox transfer on enhanced biocurrent. Finally, the biocompatibility of CPE gels is investigated.



A conductive matrix couples metabolic energetics with electronic contacts.

Funding was provided by the Institute for Collaborative Biotechnologies (ICB) under grant W911F-09-D-0001 from the U.S. Army Research Office. S. R. M is grateful for funding from the National Science Foundation Graduate Research Fellowships Program (NSF GRFP).

References:

1. D. Wang, X. Gong, P. S. Heeger, F. Rininsland, G. C. Bazan, and A. J. Heeger, Biosensors from conjugated polyelectrolyte complexes, *Proc. Natl. Acad. Sci.* **99** (2002) 49–53. DOI: 10.1073/pnas.012581399
2. C.-K. Mai, B. Russ, S. L. Fronk, N. Hu, M. B. Chan-Park, J. J. Urban, R. A. Segalman, M. L. Chabinyk, and G. C. Bazan, Varying the ionic functionalities of conjugated polyelectrolytes leads to both p- and n-type carbon nanotube composites for flexible thermoelectrics, *Energy Environ. Sci.* **8** (2015) 1–11. DOI: 10.1039/C5EE00938C
3. N. D. Kirchhofer, S. R. McCuskey, C. Mai, and G. C. Bazan, Anaerobic Respiration on Self-Doped Conjugated Polyelectrolytes: Impact of Chemical Structure, *Angew. Chemie Int. Ed.* **56** (2017) 6519–6522. DOI: 10.1002/anie.201701964

10. Controlling the doping mechanism in thin film transistors through design of polymeric ionic liquid-gate dielectrics**D. Rawlings,^a E. Thomas,^b R. A. Segalman,^{a,b} and M. L. Chabinyc^b**^aDepartment of Chemical Engineering, University of California, Santa Barbara CA 93106^bMaterials Department, University of California, Santa Barbara CA 93106

Two disparate modes of operation can occur when gating an organic thin film transistor (OTFT) with an electrolyte. An interfacial field effect operation mode occurs when the active layer is impermeable to ions, whereas a bulk electrochemical doping mode occurs when the active layer is ion permeable. Here, we present a method to directly control the mode of operation in an OTFT with a constant active layer by gating with polymeric ionic liquids (PILs) of opposite polarity. Ion infiltration into the active layer is driven by electrostatic attraction between ions and electronic charge carriers of opposite charge. As a result, tethering either the anion or the cation to a polymer backbone in the dielectric provides a method to control ion infiltration. This enables a direct comparison of device characteristics between field effect and electrochemical doping modes. Two PILs of opposite polarity have been synthesized and employed as the dielectric material in p-type OTFTs. Selectively tethering either the anion or the cation is shown to dictate whether ions infiltrate the active layer. Interfacial EDL doping decreases the accumulation layer thickness and increases the carrier concentration as a function of injected charge. The local carrier concentration in the accumulation layer is found to be the main factor effecting the threshold voltage and the conductivity of the devices, despite the difference in doping mechanisms.

11. Correlating treatment conditions and atomic-scale environments of Pt supported on NaY zeolite

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Zeolite-supported transition metal (e.g., Pt, Mo, Fe, Ni, Pd, etc.) catalysts are widely used as heterogeneous catalysts for important industrial and environmental applications, including hydrocarbon cracking, reforming, and selective reduction of nitrogen oxides. The reaction properties of these catalysts depend strongly on the compositions and nanoscale architectures of the zeolite support, as well as the types and locations of metal species within the zeolite pores, which are influenced by the catalyst synthesis and treatment conditions.¹ Understanding the atomic-scale structures of metal-zeolite systems prepared under different conditions is crucial to the development of strategies to control metal dispersal, thereby improving catalyst performance.

In this study, we probe the influences of oxidative processes on the distributions and identities of Pt on NaY and the atomic structures of the support framework (Fig 1). Detailed understanding of Pt environments in Pt-NaY is limited, in part, because of the broadly distributed local metal environments. To overcome these challenges, we used powerful multinuclear solid-state NMR

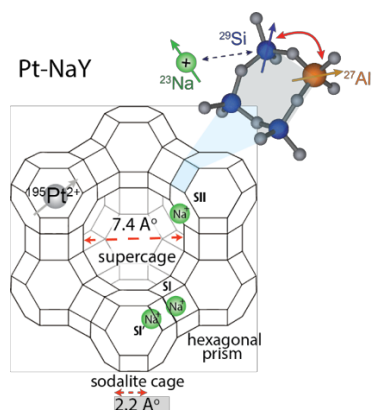


Figure 1. Schematic structure of Pt supported on NaY-zeolite

techniques. Such solid-state ¹⁹⁵Pt NMR spectra have been exceptionally challenging to acquire due to the extremely broad ¹⁹⁵Pt linewidths (~MHz) that are infeasible to measure by using conventional NMR methods. Similar experimental approaches and techniques are expected to be broadly applicable to understanding the structure-function relationships of various heterogeneous materials for diverse applications, thus enabling further development of the materials with improved macroscopic properties.

References:

1. de Graaf, J.; van Dillen, A. J.; de Jong, K. P.; Koningsberger, D. C. J. *Catal.* **2001**, *203*, 307.
2. Pandya, K. I.; Heald, S. M.; Hriljac, J. A.; Petrakis, L.; Fraissard, J. J. *Phy. Chem.* **1996**, *100*, 5070.
3. Gallezot, P. *Catal. Rev. Sci. Eng.* **1979**, *20*, 121.

12. Defect engineering of hydrogen electrolyte materials

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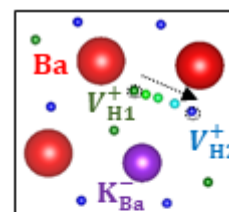
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We have conducted two recent studies on materials with applications as electrolytes in solid-state hydrogen fuel cells. In both, we used *ab initio* calculations based on density functional theory (DFT) with a hybrid functional to study the properties of intrinsic defects, impurities, and dopants. In our study of the alkaline-earth hydrides, we found that hydrogen transport proceeds with a low energy barrier through a vacancy-mediated process. Thus, high conductivity requires high vacancy concentrations, which can be achieved through acceptor doping with alkali metals on the alkaline-earth site. We proposed hydrogen-poor growth conditions and size-tailored alkali-metal doping to achieve high ionic conductivity on par with some of the best proton-conducting oxides [Rowberg 2018]. We have also studied the defect properties of some such oxides, specifically, the alkaline-earth zirconates. Among these, BaZrO₃ is known to be one of the best solid-state proton conductors. We show that alkali-metal doping again holds promise for increasing proton concentration and improving ionic conductivity. Carbon impurities and cation antisite defects can both compete with the incorporation of point defects necessary for proton incorporation; thus, processing conditions must be carefully chosen to avoid their formation. In addition, we compare acceptor dopants on the basis of proton binding energy. Alkali metals are superior to traditional dopants such as Y and Sc in this regard, further highlighting their suitability for maximizing ionic transport [Rowberg 2019].

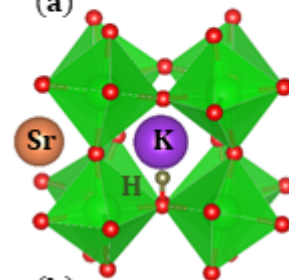
The research reported in these papers has been supported by the National Science Foundation (Graduate Research Fellowship Program, Grant No. 1650114) and by the US DOE Office of Science (Grant No. DE-FG02-07ER46434). Computational resources were provided by NERSC and by the Center for Scientific Computing (CSC) at UCSB.

References:

1. A. J. E. Rowberg, L. Weston, and C. G. Van de Walle, Ion-Transport Engineering of Alkaline-Earth Hydrides for Hydride Electrolyte Applications, *Chem. Mater.* **30** (2018) 5878–5885. DOI: 10.1021/acs.chemmater.8b01593
2. A. J. E. Rowberg, L. Weston, and C. G. Van de Walle, Optimizing proton conductivity in zirconates through defect engineering, Submitted to *ACS Appl. Ener. Mater.* (2019).



(a)



(b)

(a) K-doped BaH₂;
(b) K-doped SrZrO₃.

13. Design strategies for the facile synthesis of miktoarm star polymers

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Miktoarm star polymers are potentially useful in applications ranging from thermoplastic elastomers to drug delivery. In contrast to star homopolymers and radial copolymers, the mikto architecture demands asymmetry in arm connectivity and molar mass distribution, which creates a significant synthetic challenge. Here, we introduce a new design strategy that simplifies the synthesis of miktoarm star polymers using norbornene-functionalized “macromonomers” and grafting-through copolymerization. Self-assembly in the bulk was studied as a function of molecular composition, arm stoichiometry, and backbone degree of polymerization (N). Insights generated from scattering experiments suggest our materials behave as dispersed mikto-star at low N with a transition to brush-like conformations as N increases. The impact of dispersity on the self-assembly behavior at low N was investigated experimentally and simulated using self-consistent field theory.

This research is based upon work supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Award Number DE-SC0019001 and the Mellichamp Academic Initiative in Sustainability. The research reported here made use of shared facilities of the UCSB MRSEC (NSF DMR 1720256), a member of the Materials Research Facilities Network (www.mrfn.org).

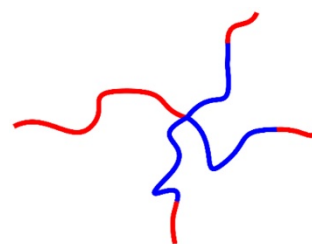


Illustration of a miktoarm star polymer.

References:

1. Kakkar, A. *Miktoarm Star Polymers*, RCS, **2017**. DOI: 10.1039/9781788010429
2. Pesek, S. L.; Li, X.; Hammouda, B.; Hong, K.; Verduzco, R. *Macromolecules* **2013**, 46, 6998–7005. DOI: 10.1021/ma401246b
3. Dalsin, S. J.; Hillmyer, M. A.; and Bates, F.S. *ACS Macro Lett.* **2014**, 3, 423–427. DOI: 10.1021/mz500082h

14. Disordered transport in highly doped materials: vapor doping of a model small molecule system

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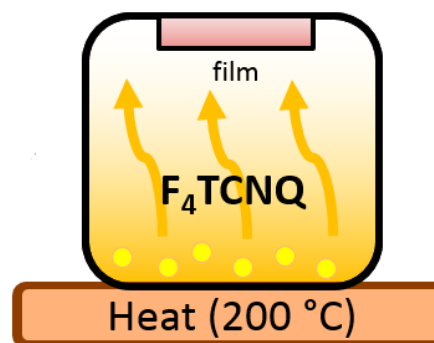
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Amorphous small molecule semiconductor films are widely used in organic light emitting displays and have promising applications in solar cells and thermoelectric devices. Smooth, consistent films can be easily fabricated using vapor deposition or spin casting. Adding dopants increases the conductivity of organic semiconductors, but high concentrations of dopants can disrupt the film structure, alter the shape of the density of states in the material, and increase the effects of Coulomb interactions on charge transport. Understanding how these factors affect disordered charge transport is an important component of a broader picture of charge transport in organic semiconductors.

We chose to use the small molecule spiro-OMeTAD, commonly used as a hole transport layer in OLEDs and solar cells, and dopant F₄TCNQ as the model system. Doping spiro-OMeTAD films with F₄TCNQ vapor allowed us to control the carrier concentration and to reach higher doping ratios, up to 1:2 dopant:host molecules, than possible through mixing the two in solution for casting. Structural characterization confirmed that films remain amorphous even at the highest doping levels with no apparent phase separation. We quantitatively determined the carrier concentration using UV-Vis spectroscopy to interpret the evolution of the electrical conductivity. UV-Vis spectra show the presence of high concentrations of F₄TCNQ⁻ and spiro-OMeTAD⁺ ions in the films. In this range of carrier concentrations (10¹⁹ – 10²⁰ 1/cm³), the electrical conductivity was linear with carrier concentration, while Seebeck coefficient stayed relatively constant. The cause of this unexpected trend in Seebeck coefficient with carrier concentration was investigated in relation to the shape of the density of states and spiro-OMeTAD's electronic structure, which has degenerate HOMO and HOMO-1. Temperature-dependent conductivity measurements were used to further analyze the transport mechanism. We also determined the effect of high dopant concentration and ionic effects on in-plane thermal conductivity measured by a transient grating technique.

This work was supported by the National Science Foundation (NSF) under award nos. DMR 1410438 and DMR 1436263. Portions of this work were carried out at the MRL Shared Experimental Facilities, supported by the NSF MRSEC program under award no. DMR 1720256, and the Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, supported by the U.S. DOE, Office of Science. A.P. was funded by the FLAM program under NSF award no. DMR 1460656.



The vapor doping process uses a small chamber in the glovebox to quickly add dopants to a solid film. When the chamber is heated, F₄TCNQ dopants diffuse into the film. More charges can be introduced in the spiro-OMeTAD film than mixing the dopant in solution.

15. Dopamine-mediated coatings for selective deposition

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The mussel-inspired adhesive moiety, dopamine (Fig.1), is known to be a universal adhesive on a wide range of inorganic and organic surfaces.¹ The mechanism of such a strong adhesion is still controversial; however, catechol and amine are known to be dominating contributors to induce strong interaction with substrates and self-polymerization.¹ Our recent work on dopamine-functionalized polymer (Fig.1) demonstrated that the dopamine end group stabilized the ultrathin (5-10 nm) polymer films and formed conformal coatings on planar and non-planar surfaces.²

In particular, catechol in dopamine is pH-responsive, which can be utilized for selective deposition applications. At low pH (< 6), catechol forms interfacial binding to the metal oxide surfaces, which exhibits stronger adhesion than that with other surfaces.³ At high pH (> 6), formation of quinone plays different roles on metal oxides and other surfaces.⁴ For the metal oxide, the formation of quinone detaches the polymer from the surface, while the

highly reactive quinone reacts with organic surfaces forming a covalent bond. Therefore, controlling pH around catechol can induce selective deposition of catechol-functionalized polymers.

The desired selectivity between metal oxides and other surfaces was achieved via pH control with a photo acid generator (PAG) and a photo base generator (PBG) as shown in Fig.2.

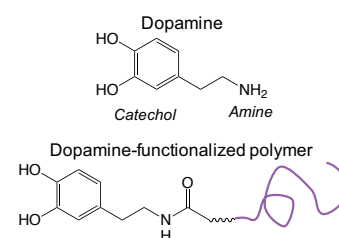


Fig.1: Dopamine and dopamine-functionalized polymer

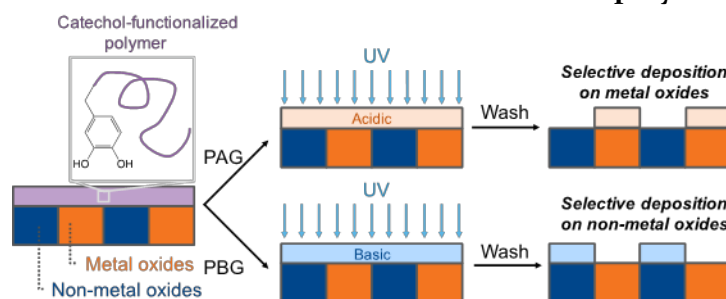


Fig.2: Schematic of selective deposition of polymers mediated by catechol

References:

1. H. Lee, H. S.M. Dellatore, W.M. Miller, P.B. Messersmith, Mussel-Inspired Surface Chemistry for Multifunctional Coatings, *Science* **318**, (2007), 426-430. DOI: 10.1126/science.1147241
2. R. Katsumata, R. Limary, Y. Zhang, B. Popere, A. Heitsch, M. Li, P. Trefonas, R.A. Segalman, Mussel-Inspired Strategy for Stabilizing Ultrathin Polymer Films and Its Application to Spin-On Doping of Semiconductors, *Chem. Mater.* **30**, (2018), 5285-5292. DOI: 10.1021/acs.chemmater.8bo2027
3. J.L. Dalsin, L. Lin, S. Tosatti, J. Vörös, M. Textor, P.B. Messersmith, Protein Resistance of Titanium Oxide Surfaces Modified by Biologically Inspired mPEG-DOPA, *Langmuir* **21**, (2005) 640-646. DOI: 10.1021/la048626g
4. P. Kord Forooshani, B.P. Lee, Recent approaches in designing bioadhesive materials inspired by mussel adhesive protein, *J. Polym. Sci., Part A: Polym. Chem.* **55** (2017) 9-33. DOI: 10.1002/pola.28368

16. Double-end anchored polymers for hierarchical assembly of lipid-based materials

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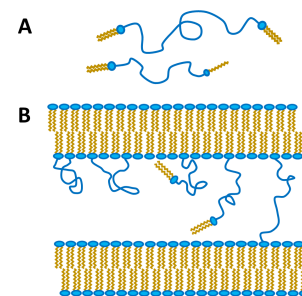
Hierarchical assembly can be used to create complex, functional materials via the interplay of different interactions. In this work, we use PEG (polyethylene glycol) molecules with double-end hydrophobic anchors (DEAs) to achieve hydrophobic-mediated assembly of lipid-coated building blocks. By varying the PEG length, anchor hydrophobicity, and molar fraction of DEA-PEG molecules within a membrane, we can alter the repulsive (steric) and attractive interactions and, thus, the assembly properties of lipid-based systems. This is affected through a change in the equilibrium balance of looping (both anchors in one membrane) and bridging (anchors spanning two membranes) conformations. Using differential interference contrast microscopy, dynamic light scattering, and small angle x-ray scattering, we have demonstrated an ability to tune DEA-PEG-mediated behavior both in pure lipid/water systems [1] and in cationic liposomes condensed using nucleic acids.

Cationic liposomes (CLs) are a common synthetic carrier of nucleic acids for gene delivery and silencing. Optimization of DNA delivery and expression requires understanding of the interactions between cellular membranes and CL–nucleic acid nanoparticles (NPs), affecting NP binding, uptake, endocytic trafficking, and endosomal escape. PEGylation is necessary to sterically stabilize the NPs but also has the effect of inhibiting cell-nanoparticle interactions. Adding DEA-PEG molecules to our NPs allows for the formation of polymer bridges between the NP and endosomal membranes. This increases the rate of collisions between the membranes and promotes fusion and endosomal escape. Confocal imaging of a human prostate cancer cell line (PC3) and colocalization of NPs with recycling (Rab11-GFP) and late endosome/lysosomal (LysoTracker) pathways indicate that NPs modified with DEA-PEG molecules have altered interactions with cellular membranes, similar to the effects of very high membrane charge density [2]. This demonstrates the possibility of using DEA-PEG molecules to tune NP-cell membrane interactions in order to promote endosomal escape and exogenous gene expression.

This work was supported by the U.S. Department of Energy (DE-FG02-06ER46314), the National Institute of Health (GM-59288), and the National Science Foundation (DMR-1401784).

References:

1. C. Liu, K.K. Ewert, E. Wonder, P. Kohl, Y. Li, W. Qiao, C.R. Safinya, Reversible control of Spacing in charged lamellar membrane hydrogels by hydrophobically mediated tethering with symmetric and asymmetric double-end-anchored poly(ethylene glycol)s. *ACS Appl. Mat. Interf.* **10** (2018), 44152–44162. DOI: 10.1021/acsami.8b16456
2. R. M. Majzoub, E. A. Wonder, K. K. Ewert, V. R. Kotamraju, T. Teesalu, C. R. Safinya, Rab11 and LysoTracker Markers Reveal Correlation between Endosomal Pathways and Transfection Efficiency of Surface-Functionalized Cationic Liposome–DNA Nanoparticles, *J. Phys. Chem. B* **120** (2016), 6439–6453. DOI: 10.1021/acs.jpccb.6b04412016



(A) Double-end anchor polymer molecules with PEG linkers and fatty acid anchors (B) in either the looping (left) or bridging (right) conformation.

17. Effects of helical chain shape on lamellae-forming block copolymer self-assembly**B. Yu,^a S. Danielsen,^a A. Patterson,^b E. Davidson,^a and R. Segalman^{a,b}**^aDepartment of Chemical Engineering, University of California, Santa Barbara, 93106^bMaterials Department, University of California, Santa Barbara, 93106

Understanding the effects of non-ideal polymer chain shapes on block copolymer self-assembly is important for designing functional materials such as biopolymers or conjugated polymers with controlled self-assembly behavior. While helical chain shapes in block copolymers have been shown to produce unique morphologies, the details of how chain helicity influences the thermodynamics of self-assembly are still unclear. Here, we utilize model coil-coil and coil-helix block copolymers based on polypeptoids, for which the chain shape can be tuned from helix to coil via monomer chirality with otherwise constant chemistry. This model block copolymer system is used to probe the effects of chain helicity on the thermodynamics of block copolymer self-assembly. Small-angle X-ray scattering of the bulk materials shows that the block copolymers form well-ordered lamellar structures. While having identical domain spacings, the coil-helix block copolymer displays a lower order-disorder transition temperature (T_{ODT}) than its coil-coil analogue. There is minimal difference in the enthalpic contributions to mixing, supported by similar effective Flory-Huggins interaction parameters, χ_{eff} , determined in the disordered state. The most significant contribution to lowering the T_{ODT} of the coil-helix block copolymer appears to be the helical chain experiencing larger chain stretching penalties in the lamellar morphology, which leads to a larger entropic gain upon disordering. This yields insight into the importance of different entropic contributions that arise from polymer chains with non-ideal shapes in block copolymer self-assembly.

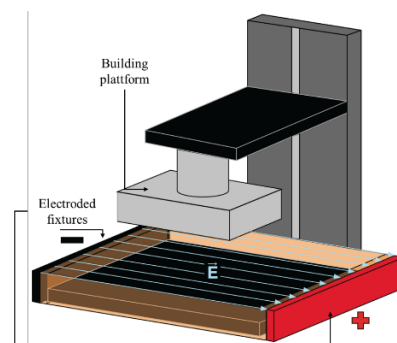
18. Electrical and mechanical tuning of 3D printed photopolymer-CNT nanocomposites through in-situ dispersion

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Carbon nanotubes (CNT) have attracted a significant amount of attention in the scientific community as nanocomposite reinforcement due to their exceptional thermal, electrical, and mechanical properties, and therefore potential application. In this work, the synthesis and fabrication of polymer-carbon composites through stereolithography additive manufacturing technique with electric field-assisted in situ dispersion of multi-walled CNTs (MWCNT) was demonstrated. By introducing MWCNTs, an increase in elastic modulus of 77% was observed. The inclusion of an electric field for in situ dispersion further improved the average elongation at break of the samples with MWCNTs by 32%. Applying an electric field also displayed an increase in ultimate tensile strength of the MWCNT reinforced nanocomposites by 42% and an increase of over 20% in ultimate tensile strength of in situ dispersed MWCNT nanocomposites over the pure polymer material. Lastly, it was demonstrated that the magnitude and direction of the electrical conductivity of CNT nanocomposites can be engineered through the application of in situ electric fields during 3D printing. An increase of 50% in the electrical conductivity was observed when MWCNTs were introduced. A further improvement in electrical conductivity of 26% was achieved through electric field induced dispersion. The presented results help demonstrate the feasibility of tuning the electrical and mechanical properties of CNT reinforced polymer nanocomposites using in situ electrical field assisted 3D printing.



Fabrication set up showing the electric field applied through custom fixtures.

References:

1. A. I. Oliva-Avilés, F. Avilés, V. Sosa, A. I. Oliva and F. Gamboa, Dynamics of carbon nanotube alignment by electric fields, *Nanotechnology* **23** (2012).
2. J. H. Sandoval and R. B. Wicker, Functionalizing stereolithography resins: effects of dispersed multi-walled carbon nanotubes on physical properties, *Rapid Proto. Jour* **12** (2006) 292-303.
3. J. N. Coleman, U. Khan, W. J. Blau and Y. K. Gun'ko, Small but strong: a review of the mechanical properties of carbon nanotube-polymer composites, *Carbon* **44** (2006) 1624-1652.
4. R. B. Ladani, S. Wu, A. J. Kinloch, K. Ghorbani, J. Zhang, A. P. Mouritz and C. H. Wang, Improving the toughness and electrical conductivity of epoxy nanocomposites by using aligned carbon nanofibres, *Comp. Sci. and Tech.* **117** (2015) 146-158.
5. S. Wu, R. B. Ladani, J. Zhang, E. Bafekrpour, K. Ghorbani, A. P. Mouritz, A. J. Kinloch and C. H. Wang, Aligning multilayer graphene flakes with an external electric field to improve multifunctional properties of epoxy nanocomposites, *Carbon* **94** (2015) 607-618.

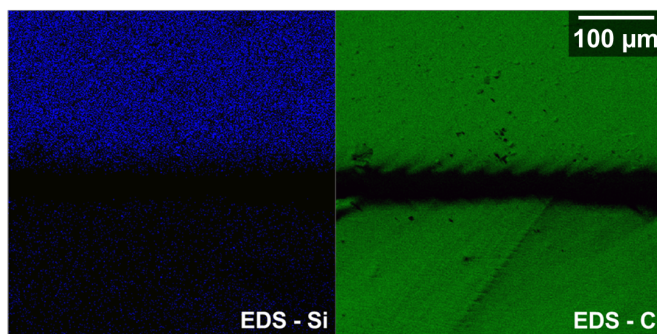
19. Engineering robust 3D printed interfaces with wavelength-selective chemistry

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Additive manufacturing (or 3D printing) has enabled researchers to create materials with precisely engineered macroscopic structure. However, a majority of printing technologies are only capable of printing with a single material at a time, hindering efforts in reproducing interesting motifs found in natural materials.¹ While systems capable of producing ‘multi-material’ parts have been developed, they typically are drastically more complex, and costly compared to traditional 3D printing techniques. To address these shortcomings, a new approach to multi-material printing, Solution Mask Liquid Lithography (SMaLL), has been developed. The key to SMaLL is coupling different wavelengths of visible light, namely green (530 nm) and blue (470 nm) light, to induce orthogonal curing chemistries in a single step.² To demonstrate the robust materials properties this approach can produce, a series of mechanical and compositional measurements are compared across leading multi-material printing techniques, highlighting the outstanding interfacial properties of parts produced by SMaLL.



• Control of local chemistry • Robust interfaces

A multi-material part printed using wavelength-selective chemistry shows stark differences in local composition by energy dispersive x-ray spectroscopy (EDS).

This work was supported by the Institute for Collaborative Bio-technologies through grant W911NF-09-0001 from the U.S. Army Research Office. The content of the information does not necessarily reflect the position or the policy of the Government, and no official endorsement should be inferred.

References:

1. A. R. Studart, Additive manufacturing of biologically-inspired materials, *Chem. Soc. Rev.* **45** (2016) 359–376. DOI: 10.1039/c5cs00836k
2. N. D. Dolinski, Z. A. Page, E. B. Callaway, F. Eisenreich, R. V. Garcia, R. Chavez, D. P. Bothman, S. Hechet, F. W. Zok, C. J. Hawker, Solution mask liquid lithography (SMaLL) for one-step, multimaterial printing, *Adv. Mater.* **30** (2018) 1800364. DOI: 10.1002/adma.201800364

20. First-principles studies of recombination mechanisms in hybrid perovskites

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Hybrid perovskites are strong candidates for photovoltaics with solar conversion efficiencies greater than 22%. While this success is highly impressive, the fundamental reasons for the high efficiency are still being actively debated. Understanding the underlying mechanisms is essential for uncovering new design principles for efficient solar cell materials as well as for designing optimal device structures.

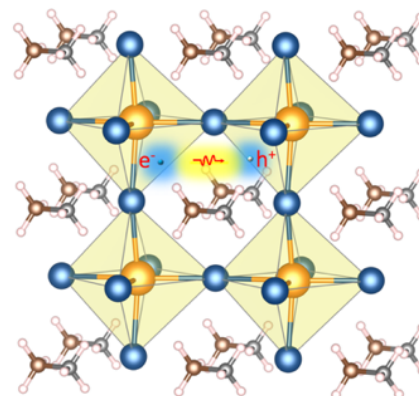
A number of research groups attributed the high efficiency of the hybrid perovskites to their slightly indirect band gap originating from strong spin-orbit coupling effects. It was argued that the indirect nature of the band gap strongly suppresses radiative recombination between electrons and holes, and thus minimizes undesired carrier recombination. By performing explicit first-principles calculations we show that the radiative recombination coefficient in hybrid perovskites is as high as in traditional direct-gap semiconductors [1,2]. While the band gap is indeed slightly indirect, the impact of this feature on radiative recombination is minor.

Strong radiative recombination also enables the possibility of making efficient light emitters with hybrid perovskites. However, the operation of light emitters requires much higher carrier densities, which triggers Auger recombination. Our first-principles calculations reveal unexpectedly strong Auger recombination in hybrid perovskites [3]. We find that the high Auger coefficient originates from a resonance in the band structure and lattice distortions. Our insights demonstrate that Auger losses can be suppressed if lattice distortions are reduced, and we discuss approaches for accomplishing this in real materials.

This work was supported by DOE-BES.

References:

1. X. Zhang, J.-X. Shen, and C. G. Van de Walle, Three-dimensional spin texture in hybrid perovskites and its impact on optical transitions, *J. Phys. Chem. Lett.* **9** (2018) 2903-2908. DOI: 10.1021/acs.jpcclett.8b01004
2. X. Zhang, J.-X. Shen, W. Wang, and C. G. Van de Walle, First-principles analysis of radiative recombination in lead-halide perovskites, *ACS Energy Lett.* **3** (2018) 2329-2334. DOI: 10.1021/acsenerylett.8b01297
3. J.-X. Shen, X. Zhang, S. Das, E. Kioupakis, C. G. Van de Walle, Unexpectedly strong Auger recombination in halide perovskites, *Adv. Energy Mater.* **8** (2018) 1801027. DOI: 10.1002/aenm.201801027



Schematic illustration of carrier recombination in hybrid perovskites.

21. Heteronucleation and epitaxy of rocksalt and orthorhombic IV-selenides on zincblende III-V substrates

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IV-VI materials, specifically the PbSnSe system, are good candidates for classical optoelectronics operating in the far infrared, as well as thermoelectric, topological, and spintronic devices; however, heteronucleation of these strongly ionic materials on zincblende III-V substrates is irregular – often resulting in misoriented grains. We observe that on (001) GaSb surfaces, PbSe nucleates in multiple orientations—(001), (110), and (221)—regardless of surface reconstruction. On arsenide surfaces however, we can suppress the formation of misoriented grains by altering the surface reconstruction with a high-temperature dose of PbSe. This results in a cube-on-cube (001)/(001) epitaxial relationship. Other research has observed weak bonding between IV-VI layers and their substrates as a guiding factor of growth[1,2]. The surface conversion we developed appears to strengthen the interaction between the epitaxial nuclei and the substrate, but the dramatic difference in crystal structure and bonding still prevents layer-by-layer growth. We have also explored nucleation and growth of SnSe on III-V substrates with and without PbSe buffer layers. SnSe is a natively orthorhombic material, but a metastable cubic phase has been demonstrated[3]. Like PbSe, its nucleation appears to heavily depend on the strength of its interaction with the substrate. Nucleated directly on GaAs, orthorhombic SnSe is interrupted by numerous defective tilted grains; however, when grown on a more amenable PbSe buffer layer, SnSe adopts a regular (001) orientation, with separate grains rotated at 90 degrees to each other about the growth axis. These results shed light on the mechanisms of IV-VI growth towards the goal of thin, tunable epitaxial layers.

References:

1. P. Müller, A. Fach, J. John, A.N. Tiwari, H. Zogg, G. Kostorz, Structure of epitaxial PbSe grown on Si(111) and Si(100) without a fluoride buffer layer, *J. Appl. Phys.* **79** (1996) 1911–1916. DOI: 10.1063/1.361076.
2. J. Stoemenos, N.N. Zheleva, M.H. Koparanova, Structural study of PbTe films grown on BaF₂ by hot wall epitaxy, *J. Cryst. Growth.* **97** (1989) 443–452. DOI: 10.1016/0022-0248(89)90225-X.
3. Z. Wang, J. Wang, Y. Zang, Q. Zhang, J.A. Shi, T. Jiang, Y. Gong, C.L. Song, S.H. Ji, L.L. Wang, L. Gu, K. He, W. Duan, X. Ma, X. Chen, Q.K. Xue, Molecular Beam Epitaxy-Grown SnSe in the Rock-Salt Structure: An Artificial Topological Crystalline Insulator Material, *Adv. Mater.* **27** (2015) 4150–4154. DOI: 10.1002/adma.201501676.

22. Ion transport in polymer electrolytes

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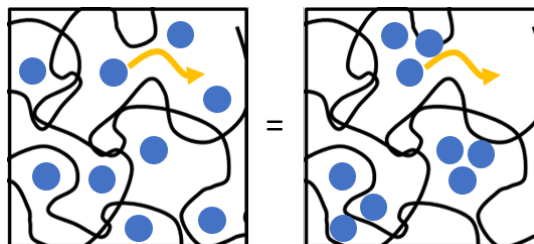
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The development of high ion conductivity polymer electrolytes for energy storage is complicated by the intricate relationship between polymer structure, salt dissociation and local dynamics in affecting macroscopic conductivity. Polymeric ionic liquids capable of conducting multivalent ions are based on metal-ligand coordination interactions. This work explores the roles of polymer backbone chemistry, metal-ligand coordination, and ion concentration on ionic conductivity. In these systems, multivalent ion transport is facilitated via ligands pendant to the polymer backbone. While previous results suggest the matrix dielectric constant affects ion dissociation and aggregate structure (Hall 2011 and Wheatle 2017), this has been studied only in systems where ions interact directly with the polymer backbone. We show that for polymers with pendant imidazole ligands, the local dielectric properties of the polymer backbone, based on either poly(ethylene oxide) (PEO) or poly(butadiene) (PBD), affect ion aggregation but not ionic conductivity at higher ion concentrations. While no aggregation is observed at low salt concentration for the PEO-based polymer, Li^+ , Zn^{2+} and Cu^{2+} show aggregation in the PBD polymer. However, ionic conductivity is invariant between the two backbones after accounting for polymer glass transition temperature. This highlights that brush polymers may be a platform with synthetic flexibility for the design of high conductivity polymer electrolytes.



Ionic conductivity is invariant with the existence of ion aggregation in brush polymers with different backbones.

This work was supported by the MRSEC Program of the National Science Foundation under Award No. DMR 1720256 (IRG-2).

References:

1. L. M. Hall, M. J. Stevens, and A. L. Frischknecht, Effect of polymer architecture and ionic aggregation on the scattering peak in model ionomers, *Phys. Rev. Lett.* **106** (2011) 127801. DOI: 10.1103/PhysRevLett.106.127801
2. B. K. Wheatle, J. R. Keith, S. Mogurampelly, N. A. Lynd, and V. Ganesan, Influence of dielectric constant on ionic transport in polyether-based electrolytes, *ACS Macro Lett.* **6** (2017) 1362–1367. DOI: 10.1021/acsmacrolett.7b00810

23. Guided discovery of magnetocalorics for refrigeration and waste-heat recovery

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Magnetic refrigeration and magnetic waste-heat recovery are accomplished with materials displaying the magnetocaloric effect, associated with a reversible temperature change upon application of a magnetic field. In recent decades, this technology has been proposed as an environmentally friendly alternative to traditional vapor-compression technology, obviating chlorofluorocarbon refrigerants, and potentially capable of greater efficiency.^{1,2} A figure of merit for magnetocalorics is the magnetic entropy change, ΔS_M . It has been recently proposed by some of us that compounds with potentially large ΔS_M can be screened through the use of a computational proxy called the magnetic deformation (Σ_M) [Figure 1(a)] which measures the deformation between structures with and without spin polarization.³ This proxy has identified several binary and ternary compounds as potential magnetocalorics. Here, we prepare and characterize several of these compounds and report their magnetocaloric performance [Figure 1(b)]. This research was supported by the National Science Foundation through DMR-1710638 and the Materials Research Science and Engineering Center, DMR No. 1720256 (IRG-1).

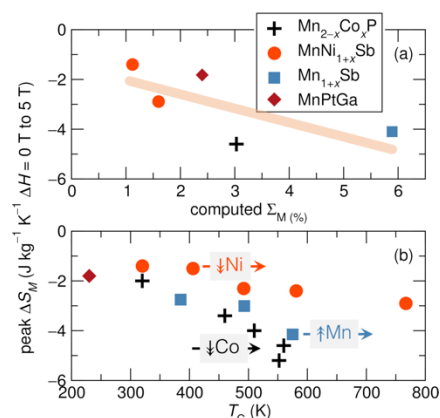


Figure 1 (a) The end-member compounds studied here indeed suggest that peak $|\Delta S_M|$ correlates with Σ_M . (b) The new magnetocalorics reported here, showing the wide range of tunability of the Curie temperature.

References

1. V. K. Pecharsky and K. A. Gschneidner, Jr., Giant magnetocaloric effect in $\text{Gd}_5(\text{Si}_2\text{Ge}_2)$, *Phys. Rev. Lett.* **78** (1997) 4494. DOI: 10.1103/PhysRevLett.78.4494.
2. V. Franco, J. S. Blázquez, B. Ingale, and A. Conde, The magnetocaloric effect and magnetic refrigeration near room temperature: Materials and models, *Annu. Rev. Mater. Res.* **42** (2012) 305. DOI: 10.1146/annurev-matsci-062910-100356.
3. J. D. Bocarsly, E. E. Levin, C. A. C. Garcia, K. Schwennicke, S. D. Wilson, and R. Seshadri, A simple computational proxy for screening magnetocaloric compounds, *Chem. Mater.* **29** (2017) 1613. DOI: 10.1021/acs.chemmater.6b04729.

24. PEGylation and charge determine the morphology and efficacy of lipid nanomaterials for paclitaxel delivery in cancer therapeutics

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Liposomes have advantages as drug delivery nanomaterials including low toxicity, compatibility with a variety of therapeutics, ease of modular processing, and a diverse set of lipid building blocks to tune their physical and chemical properties. Polyethylene glycol (PEG) is a polymer widely used to create “stealth” nanoparticles (NPs). This steric coating increases the circulation time of NPs *in vivo*, delaying immune clearance; additionally, short peptide sequences and other moieties can be installed on the distal end of PEG to target specific tissues. When PEG-lipids are inserted into charge-neutral vesicles at very high PEG-lipid mole fraction (> 0.25), they are known to induce a structural transition to micelles. Here we examine shape changes induced by the incorporation of PEG-lipid, from low to high mole fraction, to a series of liposomes ranging from neutral to high cationic charge. Significantly, we report on how these morphological changes correlate to drug delivery efficacy of paclitaxel (PTXL)—a hydrophobic cancer drug that acts as a mitotic inhibitor, inducing apoptosis and halting the proliferation of tumor cells. Due to its hydrophobic nature, PTXL must be well solubilized for administration. In lipid bilayers and micelles, PTXL loads into the hydrophobic core (Steffes 2017). Here we show how liposome composition correlates to shape changes and to interactions of the particles with cells, ultimately dictating PTXL delivery. Next-generation nanomaterial delivery systems will build upon the “stealth” properties of PEGylated NPs and incorporate components such as receptor-specific peptide sequences for tumor targeting and penetration.

References:

1. V. Steffes, M. Murali, Y. Park, B. Fletcher, K. Ewert, C. Safinya, Distinct solubility and cototoxicity regimes of paclitaxel-loaded cationic liposomes at low and high drug content revealed by kinetic phase behavior and cancer cell viability studies, *Biomaterials*. **145** (2017) 242-255. DOI: 10.1016/j.biomaterials.2017.08.026

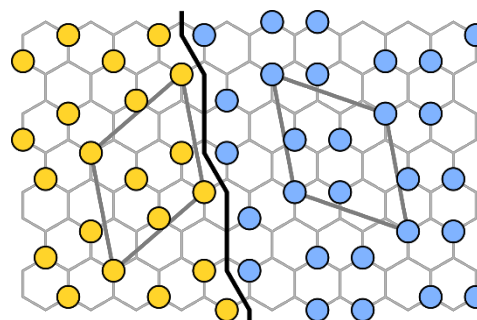
25. Phase stability and ordering in layered Na- and K-ion battery cathode materials

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Layered intercalation compounds have received great attention as electrodes for the emerging Na- and K-ion battery technologies.[1] However, structural phase transitions upon cycling can cause rapid mechanical degradation in these materials. Also, the large Na⁺/K⁺ ions are often stabilized in prismatic coordination, allowing for complex ordering phenomena that greatly influence the voltage profile and ion transport. We have performed first-principles studies of the layered Na_xCoO₂ and K_xCoO₂ cathode materials, which exhibit several stable host structures related by gliding of CoO₂ slabs. Phase stability among these structures and low-energy Na/K orderings within each structure are presented and compared to experiments. We have identified several “Devil’s staircases” of infinite hierarchical orderings that Na_xCoO₂ displays over its composition range, consisting of ordered regions separated by antiphase boundaries.[2] K_xCoO₂ stabilizes similar orderings for intermediate K concentration as well as a new family of distorted structures with mixed octahedral and prismatic coordination in the same layer at higher concentrations. We consider the possibility of such phases appearing in other layered transition-metal oxides.



Composition changes are mediated by antiphase boundaries between well-ordered domains of Na/K.

J.L.K. acknowledges support from the U.S. Department of Energy through the Computational Science Graduate Fellowship (DOE CSGF) under Grant No. DE-FG02-97ER25308. This work was supported as part of the Center for Synthetic Control Across Length-scales for Advancing Rechargeables (SCALAR), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award No. DE-SC0019381. We acknowledge support from the Center for Scientific Computing from the CNSI, MRL: an NSF MRSEC (DMR-1720256). Computing resources were also provided by the National Energy Research Scientific Computing Center (NERSC), a U.S. Department of Energy Office of Science User Facility operated under Contract No. DE-AC02-05CH11231.

References:

1. K. Kubota, M. Dahbi, T. Hosaka, S. Kumakura, and S. Komaba, Towards K-Ion and Na-Ion Batteries as “Beyond Li-Ion”, *Chem. Rev.* **18** (2018) 459-479. DOI: 10.1002/tcr.201700057
2. J. L. Kaufman and A. Van der Ven, Na_xCoO₂ phase stability and hierarchical orderings in the O₃/P₃ structure family, *Phys. Rev. Mater.* **3** (2019) 015402. DOI: 10.1103/PhysRevMaterials.3.015402

26. Point defects in hexagonal boron nitride for quantum information science

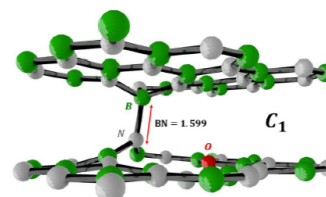
M. E. Turiansky,^a L. Weston,^b D. Wickramaratne,^b J.-X. Shen,^a M. Mackoite,^c A. Alkauskas,^c A. Jayich,^a and C. G. Van de Walle^b

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Hexagonal boron nitride (h-BN) is a van der Waals material with excellent chemical stability [1] and a wide band gap [2], making it a desirable host for quantum information applications. Observation of single-photon emission in h-BN has spurred a flurry of research characterizing the emission [3]. Despite extensive characterization efforts, the microscopic origin of these emitters has proven elusive. Using first-principles density functional theory with a hybrid functional, we have studied the behavior of native defects and common impurities in h-BN. Native defects have relatively high formation energies. While native interstitials may have a low formation energy, their migration barriers are also low, rendering them highly mobile and unlikely to be found as isolated defects. On the other hand, unintentional impurities, such as carbon, oxygen, and hydrogen, have low formation energies and dominate the defect chemistry of h-BN. Our results are an important first step in identifying the microscopic origin of the observed single-photon emission. This work was supported by the NSF MRSEC program (DMR-1720256) and by DOE-BES. Computational resources were provided by XSEDE.



Structure of V_B-O_N complex in the -2 charge state that exhibits large out-of-plane distortions.

References:

1. N. Kostoglou, K. Polychronopoulou, and C. Rebholz, Thermal and chemical stability of hexagonal boron nitride (h-BN) nanoplatelets, *Vacuum* **112**, 42 (2015). DOI: 10.1016/j.vacuum.2014.11.009
2. G. Cassabois, P. Valvin, and B. Gil, Hexagonal boron nitride is an indirect bandgap semiconductor, *Nat. Photonics* **10**, 262 (2016). DOI: 10.1038/nphoton.2015.277
3. T. T. Tran, C. Elbadawi, D. Totonjian, C. J. Lobo, G. Grosso, H. Moon, D. R. Englund, M. J. Ford, I. Aharonovich, and M. Toth, Robust multicolor single photon emission from point defects in hexagonal boron nitride, *ACS Nano* **10**, 7331 (2016). DOI: 10.1021/acsnano.6b03602

27. Polymeric ionic liquid with photoswitchable ionic conductivity by modulating cation-anion interaction

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In this paper polymeric ionic liquids (PILs) with light controllable ionic conductivity was developed. Photochromic diarylethenes (DAEs) bearing imidazolium bridging units were integrated onto polymer structure as ionic units, and the electron density of the central imidazolium ring in DAE can be reversibly modulated using two different wavelengths of light (**Figure 1a**). Such photoinduced changes in electronic properties were used to modulate the binding between anions and imidazolium containing DAE cations, and thus the ionic conductivity of PIL (**Figure 1b**). Despite PILs providing opportunities for new families of functional smart materials, only a few examples of smart PIL materials have been fabricated to date. These PIL materials largely take advantage of their anion-dependent physico-chemical properties, such as solubility, hydrophilicity or volume to induce large scale changes in materials properties, such as switchable surfaces,¹ formation of block copolymer micelles,² and reversible porous polymers.³ The major drawback to the current generation of PIL systems is the need of an additional ion change step and the introduction of another ionic species. To circumvent this issue, light responsive ionic moieties integrated into the structures of PILs offer a means to remotely and orthogonally regulate their properties and thus modulate the behavior of functional systems. This work was supported by the MRSEC Program of the National Science Foundation under Award DMR 1720256.

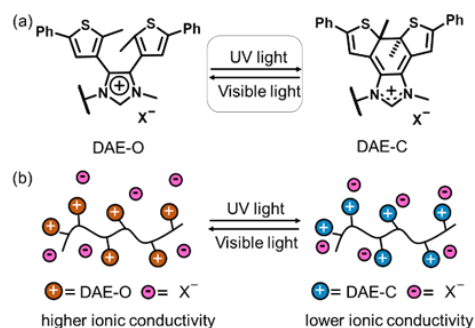


Figure 1 (a) Photochromism of imidazolium bearing DAE; (b) Photoresponsive PIL with DAE ionic units.

References:

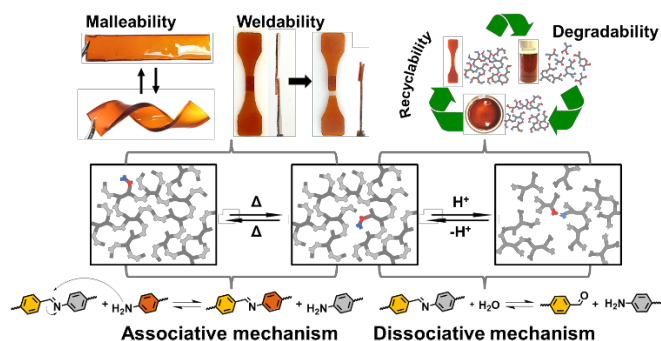
1. O. Azzaroni, A. A. Brown, W. T. S. Huck, Tunable wettability by clicking into polyelectrolyte brushes. *Adv. Mater.* **9** (2007) 151–154. DOI: 10.1002/adma.200601257
2. K. Vijayakrishna, S. K. Jewrajka, A. Ruiz, R. Marcilla, J. A. Pomposo, D. Mecerreyes, D. Taton, Y. Gnanou, Synthesis by RAFT and ionic responsiveness of double hydrophilic block copolymers based on ionic liquid monomer units. *Macromolecules* **41** (2008) 6299–6308. DOI: 10.1021/ma800677h
3. F. Yan, J. Texter, Solvent-reversible poration in ionic liquid copolymers. *Angew. Chem. Int. Edn.* **46** (2007) 2440–2443. DOI: 10.1002/anie.200604127

28. Recyclable, malleable and shape memory thermosetting materials bearing aromatic imine bonds

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Epoxy thermosetting plastics are among the most versatile and widely used materials because of their mechanical strength, chemical and thermal resistance, and excellent insulation. [1] However, because of irreversible covalent cross-links, epoxy thermosets cannot be remolded or reprocessed after their initial formation. [2] A method for preparing reprocessable epoxy thermoset is presented. The process is comprised of synthesis of a bisphenol monomer bridged by an aromatic imine bond, glycidylation of the bisphenol, and cross-linking with a hardener to form thermoset. The resulting epoxy thermoset possesses comparable properties to conventional high-performance thermosets made from bisphenol A. However, when treated by a stimulus like acid, temperature and/or water, the described thermoset exhibits reprocessibility and shape memory property. Degradation and recycling involve hydrolysis and reformation of imine bonds; reshaping and repairing of the thermoset is realized through imine exchange reactions. All the described processes require no metal catalyst, press heating or additional monomer, which significantly widens thermoset reprocessing.



Reprocessable thermosetting materials that are realized through associative and dissociative mechanisms of aromatic imine bonds.

This research was supported by the Center for Direct Conversion of Biomass to Biofuels (C3Bio), an Energy Frontiers Research Center (EFRC) funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award No. DE-SC000097, the University of California, Santa Barbara, and the Mellichamp Academic Initiative in Sustainability. We acknowledge the use of the MRL Shared Experimental Facilities, supported by the MRSEC Program of the National Science Foundation under award NSF DMR 1121053; a member of the NSF-funded Materials Research Facilities Network.

References:

1. T. Vidil, F. Tournilhac, S. Musso, A. Robisson, and L. Leibler, Control of reactions and network structures of epoxy thermosets. *Prog. Polym. Sci.* **62** (2016) 126–179. DOI: 10.1016/j.progpolymsci.2016.06.003
2. D. Montarnal, M. Capelot, F. Tournilhac, and L. Leibler, Silica-like malleable materials from permanent organic networks. *Science* **334**, (2011) 965–968. DOI: 10.1126/science.1212648

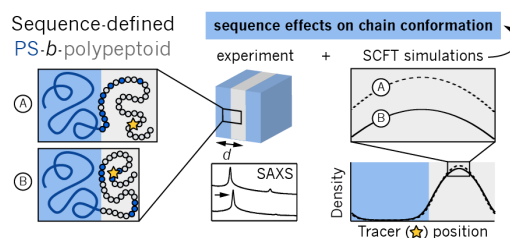
29. Role of monomer sequence in the self-assembly of precise block copolymers

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Polymers composed of multiple types of polymer backbones can self-assemble into long-ranged periodic morphologies with distinct microdomains, enabling the ability to pattern functionality. This controlled heterogeneity can be used to design materials with unique mechanical properties, coexisting transport phenomena, or tunable optical responses. Polymers with precise sequence control offer the possibility of fine-tuning these structures at the molecular level. We have synthesized polystyrene-*block*-polypeptoid diblock copolymers, where the polypeptoid chain is programmed to have different sequences of comonomers, which act as compatibilizers to the polystyrene block. Using small-angle X-ray scattering, we see that these materials self-assemble into lamellae with domain spacings and order-disorder transition temperatures varying with sequence, despite identical composition. The variation in the thermal transition suggests that sequence control at the monomer level alters the enthalpic penalty of mixing (segregation strength), and by comparing domain spacings to simulations using self-consistent field theory, we find that comonomer sequence alters the chain conformation, distorting to localize the compatibilizing comonomers at the block-block interface. These results point to comonomer sequence as a tool to fine-tune self-assembly, and continuing work is further exploring these effects in designing custom compatibilizers for industrially-relevant homopolymer blends.



Precisely-placed comonomers cause distorted chain conformations in self-assembled block copolymers, resulting in variation in the periodic lamellar spacing, as supported by simulations with self-consistent field theory (SCFT), and thermal phase stability.

30. Selective spin-on deposition of polymers on heterogeneous surfaces

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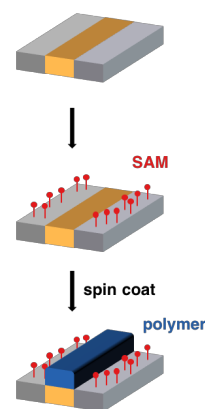
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Surface patterning is a key enabler for the semiconductor industry. The selective manipulation of materials remains a critical component in device fabrication. This work describes a strategy to selectively coat heterogeneous surfaces with polymer thin films via spin dewetting, a technique that refers to the dewetting of a polymer solution on a substrate during spin coating. This approach prevents polymer deposition on certain areas by utilizing hydrophobic self-assembled monolayers (SAMs). A key conclusion is that SAMs with defects are sufficient to induce spin dewetting.

Specifically, selective deposition on metal/dielectric patterns was achieved (poly(acrylic acid) (PAA) on Cu/SiO₂, and polystyrene (PS) on TiN/SiO₂). Firstly, SiO₂ is selectively made hydrophobic by octyltrichlorosilane (OTS, Cl₃Si-C₈H₁₇). Secondly, during the spin coating step, polymers dewet from OTS-functionalized SiO₂ and only deposit on the other surface (Cu or TiN). Importantly, the OTS SAM on SiO₂ need not be perfect to induce spin dewetting. The dewetting kinetics is determined by the spin coating conditions and interactions between polymers and surfaces.

This work was supported in part by Semiconductor Research Corporation (SRC).



Schematic of selective spin dewetting

References:

1. Bhandaru, N.; Das, A.; Salunke, N.; Mukherjee, R. *Nano Lett.* **2014**, *14*, 7009-7016. DOI: 10.1021/nl5033205.

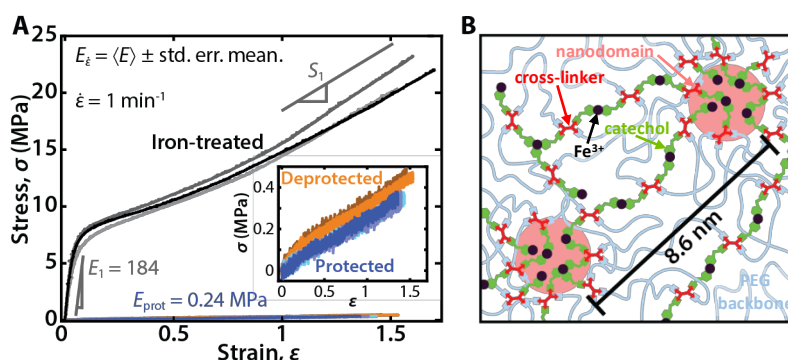
31. Studying the toughening mechanisms of mussel-inspired iron-catechol complexes in dry epoxy networks

T. R. Cristiani,^{a,b} E. Filippidi,^{a,c} C. D. Eisenbach,^{a,d} J. H. Waite,^{a,e} J. N. Israelachvili,^{a,b,f} B. K. Ahn,^g and M. T. Valentine^{a,c}

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It is challenging to synthesize covalent polymer networks which are both stiff and extensible. One strategy to overcome this challenge is to incorporate both permanent covalent bonds and reversible bonds of various chemistries into the same network. Marine mussels have evolved to apply this strategy via reversible iron-catechol coordination complexes in their byssal threads which yield highly extensible and strong materials. In this work, the same iron-catechol complexes found in the mussel system are incorporated into a polyethylene glycol epoxy network. The resulting hybrid network is orders-of-magnitude stiffer than its iron-free equivalent (as measured by a uniaxial tensiometer) and can reversibly dissipate energy upon cyclic loading. Small-angle x-ray scattering

suggests that the iron-catechol complexes form ionomeric nanodomains within the network which may further restrict chain mobility and therefore enhance the effect of the additional reversible cross-links. The ratio of constituent monomers was varied to dilute the network's catechol content and it was found that the observed nanodomains only form above a critical catechol concentration. The effect of humidity was also explored and was shown to reversibly reduce the network's ultimate tensile strength and stiffness. This work demonstrates that iron-catechol complexes can be used to enhance the mechanical properties of polymer networks, however, the mechanism depends heavily on environmental conditions and the network's nanostructure.



A) Stress vs. strain relationship of catechol-containing epoxy networks before (orange, blue, inset) and after (black) iron treatment. The elastic moduli, E , of the iron-treated and protected networks is noted. B) Proposed iron-treated network structure visualizing the spacing of iron-catechol nanodomains. (adapted from Ref. 1)

References:

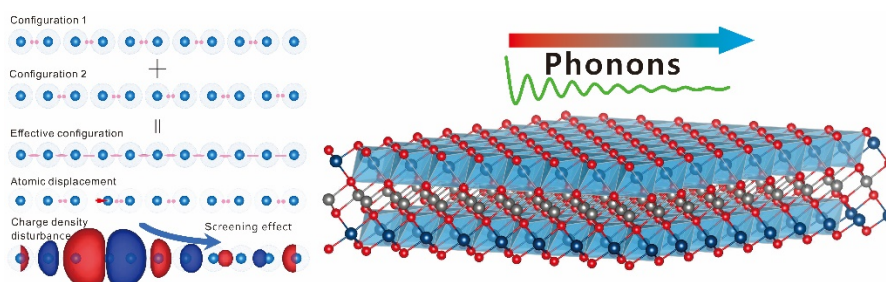
1. Filippidi, E., Cristiani, T.R., Eisenbach, C.D., Waite, J.H., Israelachvili, J.N., Ahn, B.K., Valentine, M.T., Toughening elastomers using mussel-inspired iron-catechol complexes, *Science*. **358**, (2017) 502–505. DOI: 10.1126/science.aa00350

32. Surface-enhanced resonant bonding leads to ultralow thermal conductivity in a two-dimensional material

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Crystalline materials with ultralow thermal conductivity are highly desirable for thermoelectric applications. Many known crystalline materials with low thermal conductivity, including PbTe and Bi₂Te₃, possess a special kind of chemical bond called "resonant bond"¹. Resonant bonds consist of superposition of degenerate bonding configurations that leads to structural instability, anomalous long-range interatomic interaction and soft optical phonons. These factors contribute to large lattice anharmonicity and strong phonon-phonon scattering, which result in low thermal conductivity. In this work, we use first-principles simulation to investigate the effect of resonant bonding in two dimensions (2D), where resonant bonds are in proximity to the surface. We find that the long-range interatomic interaction due to resonant bonding becomes more prominent in 2D due to reduced screening of the atomic-displacement-induced charge density distortion². To demonstrate this effect, we analyze the phonon properties of quasi-2D Bi₂PbTe₄ with an ultralow thermal conductivity of 0.74 W/mK at 300K. By comparing the interatomic force constants of quasi-2D Bi₂PbTe₄ and its bulk counterpart, and the properties of resonant bonds near the surface and in the bulk, we conclude that resonant bonds are significantly enhanced in reduced dimensions and are more effective in reducing the lattice thermal conductivity. Our results will provide new clues to searching for thermal insulators in low-dimensional materials.



The surface-enhanced resonant bonds lead to an ultralow thermal conductivity of quasi-2D Bi₂PbTe₄.

This work is supported by a Department of Energy Early Career Research Program under award number DE-SC0019244.

References:

1. S. Lee, K. Esfarjani, T. Luo, J. Zhou, Z. Tian, and G. Chen, Resonant bonding leads to low lattice thermal conductivity, *Nature Communications* **5** (2014) 3525. DOI: 10.1038/ncomms4525
2. S. Yue, T. Xu, and B. Liao, Ultralow thermal conductivity in a two-dimensional material due to surface-enhanced resonant bonding, *Materials Today Physics* **7** (2018) 89-95. DOI: 10.1016/j.mtphys.2018.11.005

33. The effect of site-specific acetylation-based tau mutations on tau-microtubule associations

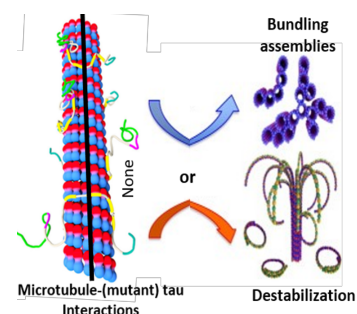
C. Tchounwou,^a B. Fletcher,^a C. Song,^a P. Kohl,^a P. Chung,^{a,b} H.P. Miller,^a Y. Li,^a M. C. Choi,^c L. Wilson,^a S. C. Feinstein,^a and C.R. Safinya^a

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Tau is an intrinsically disordered protein (IDP) crucial to neurons of the central nervous system (CNS) despite the lack of a stable tertiary structure. In neuronal axons one of the most well appreciated and studied functions of tau is the ability to stabilize the cytoskeletal protein, microtubules (MTs), by suppressing dynamic instability[1]. It has been observed in the literature that alterations to the integrity of tau's structure can perturb tau-MT associations causing neurodegenerative tauopathies such as Alzheimer's and frontotemporal dementia with Parkinsonism-17 (FTDP-17). While the most prevalent hypothesis alludes that misregulation of phosphorylation events can promote tau dysfunction, there is emerging evidence that other post-translational modifications such as acetylation can also perturb tau-MT associations and promote toxic tau-tau interactions [2]. Thus, we hypothesize that post-translational modifications such as acetylation to specific residues in close proximity to the MT-binding region of tau may influence how tau mediates tau-MT and tau-tau associations. Furthermore, we demonstrate that purification of site-specific mutagenic tau is now readily achievable with expression of mutant recombinant tau containing a poly-His-tag[3]. Here we probe tau-MT associations using transmission electron microscopy (TEM) and small angle x-ray scattering (SAXS).



MT bundling architecture in the presence of site-specific mutagenic tau.

This research is supported by grants from the Department of Energy (DOE), the National Institutes of Health (NIH), and the National Science Foundation (NSF).

References

1. E. M. Mandelkow, J. Biernat, G. Drewes, N. Gustke, B. Trinczek, and E. Mandelkow, Tau domains, phosphorylation, and interactions with microtubules, *Neurobiol Aging*. **16** (1995) 355-62. DOI: 10.1016/0197-4580(95)00025-A
2. S. W. Min, X. Chen, T.E. Tracy, Y. Li, Y. Zhou, C. Want, K. Shirakawa, S.S. Minami, E. Defensor, S. A. Mok, P.D. Sohn, B. Schilling, X. Cong, L. Ellerby, B.W. Gibson, J. Johnson, N. Krogan, M. Shamloo, J. Gestwicki, E. Masliah, E. Verdin, and L. Gan, Critical role of acetylation in tau-mediated neurodegeneration and cognitive deficits, *Nat Med*. **21**(2015) 1154-62. DOI: 10.1038/nm.3951
3. R. L. Best, P. J. Chung, J. S. J. Benbow, A. Savage, N. E. LaPointe, C. R. Safinya, and S. C. Feinstein, Expression and isolation of recombinant tau, *Meth. Cell Biol*. **141** (2017) 3-26. DOI: 10.1016/bs.mcb.2017.06.001

34. The role of hydrogen bonding in peptoid-based marine antifouling coatings

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The benefits of incorporating amphiphilic properties into antifouling and fouling-release coatings are well-established. The use of sequence-defined peptides and peptoids in these coatings allows precise control over the spacing and chemistry of the amphiphilic groups, but amphiphilic peptoids have generally outperformed analogous peptides for reasons attributed to differences in backbone structure (Patterson 2017). The present work demonstrates that the superior properties of peptoids relative to peptides are primarily attributable to a lack of hydrogen bond donors rather than to their secondary structure. A new amphiphilic peptoid was designed containing functional groups similar to those typically found on a hydrogen-bonding peptide backbone. This peptoid and a non-hydrogen-bonding peptoid analogue were incorporated as side chains in PDMS-based polymer scaffolds. Bioassays with the soft algal fouling organisms *Ulva linza* and *Navicula incerta* indicate that hydrogen bonding largely determines the differences seen between similar peptide and peptoid species, while sum frequency generation vibrational spectroscopy suggests that the presence of hydrogen bond donors enhances interfacial water structuring. This reduced initial *U. linza* adhesion, but attached algae were more strongly bound by hydrogen bonding interactions. Consequently, amphiphilic peptoid materials lacking hydrogen bond donors are better suited to resist marine fouling, with enhanced release of *U. linza* and similar performance against *N. incerta* relative to hydrogen-bonding analogues.

References:

1. A.L. Patterson, B. Wenning, G. Rizis, D.R. Calabrese, J.A. Finlay, S.C. Franco, R.N. Zuckermann, A.S. Clare, E.J. Kramer, C.K. Ober, Role of backbone chemistry and monomer sequence in amphiphilic oligopeptide- and oligopeptoid-functionalized PDMS- and PEO-based block copolymers for marine antifouling and fouling release coatings, *Macromolecules* **50**(7) (2017) 2656-2667. DOI: 10.1021/acs.macromol.6b02505

35. Topological palladium and platinum compound semimetals

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Dirac semimetals are 3D analogs of graphene with unusual electronic transport properties due to symmetry-protected band crossings at the Fermi energy with linear, light-like dispersion. Topological surface states and the enhanced bulk transport due to linear dispersion are hypothesized to enhance catalytic activity.[1] The cubic oxides (Ca,Sr,Na)(Pd,Pt)₃O₄ [Figure 1(a)] are of interest due to their unusual hole-doping-driven metal-insulator transitions and chemical relationship with historically and commercially important catalysts such as the Adams catalyst and PdO. We present first-principles calculations examining potential topologically interesting states in the electronic structure of the cubic Pd and Pt oxides, including the presence of a cubic Dirac-like degeneracy [Figure 1(b)]. Preliminary experimental results on these and related systems under investigation will also be discussed.

This work was supported by the New Partnerships Challenge Grant program of the California Nanosystems Institute (CNSI). ST acknowledges NSF-GRFP support under Grant No. DGE-1650114. Shared experimental and computational facilities of the Materials Research Laboratory (NSF DMR-1720256) are gratefully acknowledged, as is NSF CNS-1725797 to the CNSI (computation).

References

1. J. C. R. Rajamathi, U. Gupta, N. Kumar, H. Yang, Y. Sun, V. Süß, C. Shekhar, M. Schmidt, H. Blumtritt, P. Werner, B. Yan, S. Parkin, C. Felser, and C. N. R. Rao, Weyl semimetals as hydrogen evolution catalysts, *Adv. Mater.* **29** (2017) 1606202. DOI: 10.1002/adma.201606202

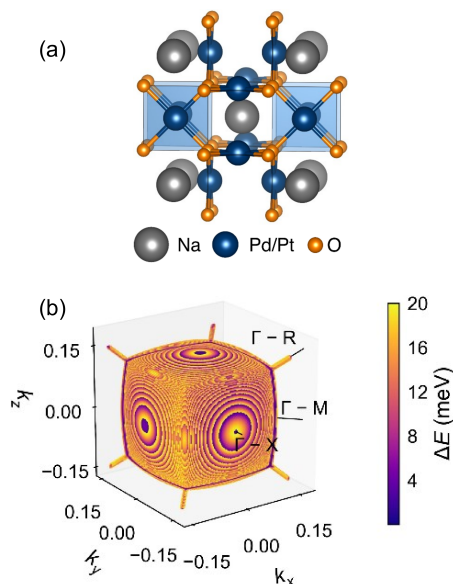


Figure 1. (a) crystal structure of Na(Pd/Pt)₃O₄. (b) rather than isolated Dirac cones, the cubic metals Na(Pd/Pt)₃O₄ form an unusual quasi-cubic Dirac degeneracy region at the center of the Brillouin zone.

36. Tuning the excitonic absorption and emission in hybrid halide Ruddlesden-Popper perovskites for optimal photodetection

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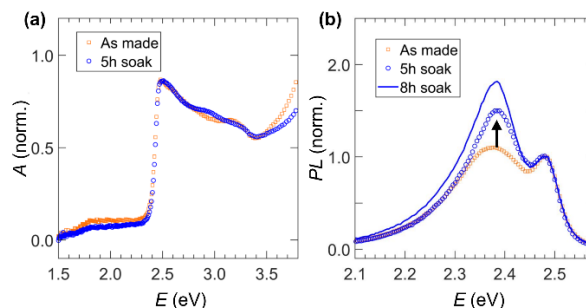
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In this work, the effects of processing on the optical and structural properties of Ruddlesden-Popper (RP) hybrid halide perovskites were assessed, so as to RP efficacy as photodetector materials. Single crystals and spin-cast films of $(C_yH_{2y+1}NH_3)_2PbI_4$ were prepared, with $y = 4, 8,$ and 12 . In all cases, optical absorbance arising from the primary free exciton feature decreased in crystals prepared using a non-aqueous antisolvent-assisted synthesis (Lédée 2017), relative to that in crystals prepared from the traditional aqueous synthesis (Stoumpos 2016). Soaking the crystals in antisolvent post-synthesis caused the appearance of a second photoluminescence emission peak, red-shifted from the primary exciton peak. This red-shifted feature has been correlated with increased photodetector efficacy, (Leng 2018), and our antisolvent method provides a practical way to induce it. Ongoing structural studies aim to clarify the nature of this red-shifted emission (bound, free or self-trapped exciton) as well as the structural features (e.g. vacancies, phase transitions) causing its appearance. Future work will focus on replicating the solvent-induced red-shifted luminescence in RP perovskites of higher n value ($(C_yH_{2y+1}NH_3)_2(CH_3NH_3)_{n-1}Pb_nI_{3n+1}$), to achieve optimal photodetection. These findings yield insight into the correlations between structural defect and optoelectronic properties in Ruddlesden-Popper halide perovskites and offer practical routes to RP photodetector efficacy.

The research reported in the work has in part been supported by the Department of Energy under Grant Award No. DE-SC-0012541 and by the Office of Naval Research through the National Defense Science and Engineering Graduate fellowship program.

References:

1. F. Lédée, G. Trippé-Allard, H. Diab, P. Audebert, D. Garrot, J. S. Lauret, & E. Deleporte, Fast growth of monocrystalline thin films of 2D layered hybrid perovskite, *CrystEngComm*, **19** (2017) 2598-2602. DOI: 10.1039/c7ce00240h
2. C. C. Stoumpos, D. H. Cao, D. J. Clark, J. Young, J. M. Rondinelli, J. I. Jang, J. T. Hupp & M. G. Kanatzidis, Ruddlesden-Popper hybrid lead iodide perovskite 2D homologous semiconductors. *Chem. Mater.* **28** (2016) 2852-2867. DOI: 10.1021/acs.chemmater.6b00847
3. K. Leng, I. Abdelwahab, I. Verzhbitskiy, M. Telychko, L. Chu, W. Fu, X. Chi, N. Guo, Z. Chen, Z. Chen, C. Zhang, Q.-H. Xu, J. Lu, M. Chhowalla, G. Eda & K. P. Loh, Molecularly thin two-dimensional hybrid perovskites with tunable optoelectronic properties due to reversible surface relaxation. *Nat. Mater.* **17** (2018) 908-914. DOI: 10.1038/s41563-018-0164-8



Optical absorbance (a) and photoluminescence emission (b) of $y = 12$ single crystals before and after soaking in antisolvent.

37. Understanding metallicity and magnetism in AB_4Q_8 defect spinel systems

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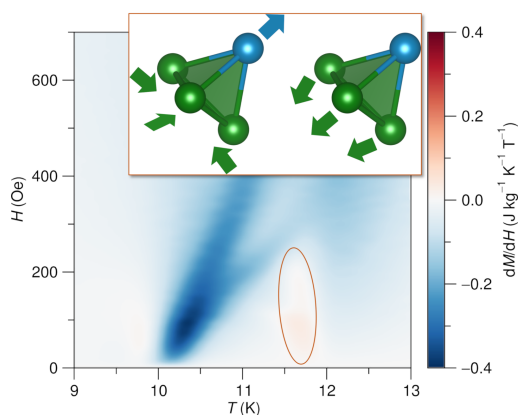
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The lacunar spinel family of AB_4Q_8 compounds, where A is Al, Ga, or Ge, B is an early transition metal like V, Mo, or Ta, and Q is a chalcogen like S or Se, have been studied since the 1970s. They crystallize at room temperature in a $F\bar{4}3m$ defect spinel structure and display a fascinating array of magnetic and electronic properties. Some materials in this family undergo metal-insulator transitions and others host exotic magnetic spin textures such as skyrmions, that are swirls of spins with potential for computing applications.^{1,2} These properties can be related to clustering of the B -site atom, crystalline anisotropy, and the electronic correlations present. We are investigating several of these materials ($B = V, Nb, Mo, Ta$; $Q = S, Se$) using a combination of experimental techniques including high-resolution X-ray diffraction and magnetic measurements, and density functional theory calculations of structural, electronic, and magnetic ground states. We present on some of these, examining the interplay between electronic structure, crystal structure, and magnetic/electronic properties in these systems and develop insights into chemical tuning to optimize functionality.

This research was supported by the National Science Foundation under DMREF Award 1729489. Use of the Shared Experimental Facilities of the Materials Research Science and Engineering Center at UCSB (MRSEC NSF DMR 1720256) is gratefully acknowledged. The UCSB MRSEC is a member of the NSF-supported Materials Research Facilities Network (www.mrnf.org).

References:

1. S. Bordács, A. Butykai, B. G. Szigeti, J. S. White, R. Cubitt, A. O. Leonov, S. Widmann, D. Ehlers, H.-A. Krug von Nidda, V. Tsurkan, A. Loidl, and I. Kézsmárki, Equilibrium skyrmion lattice ground state in a polar easy-plane magnet, *Sci. Rep.*, **7** (2017) 7584. DOI: 10.1038/s41598-017-07996-x
2. V. Ta Phuoc, C. Vaju, B. Corraze, R. Soprocase, A. Perucchi, C. Marini, P. Postorino, M. Chligui, S. Lupi, E. Janod, and L. Cario, Optical conductivity measurements of $GaTa_4Se_8$ under high pressure: evidence of a bandwidth-controlled insulator-to-metal Mott transition, *Phys. Rev. Lett.* **110** (2013) 037401. DOI: 10.1103/PhysRevLett.110.037401



Magnetoentropic mapping of GaV_4S_8 shows a skyrmion pocket (indicated) around 12 K as well as cycloidal to field-polarized transitions. The inset displays distortion modes of V_4 tetrahedra that give rise to the polar ground state structure that hosts skyrmions.

38. Versatile and visible light-mediate polymer brush synthesis via surface-initiated PET-RAFT under ambient conditions

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Surface-initiated polymerizations represent an attractive method for reliable and selective chemical functionalization from a variety of surfaces. In particular, controlled radical polymer strategies, including atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer polymerization (RAFT), and nitroxide-mediated polymerization (NMP), have enabled significant advances in this field.¹ While the aforementioned methods allow a wide variety of brush structures and compositions to be prepared, they require rigorous deoxygenation procedures, have limited substrate scope, and typically rely on organic solvents. In this work, we report the development of a simple, metal-free surface initiated photoinduced electron transfer-reversible addition-fragmentation chain transfer polymerization (SI PET-RAFT) in aqueous solution without the need for rigorous deoxygenation procedures. Key to this discovery was the use of the enzyme glucose oxidase to facilitate in situ removal of oxygen in the polymerization reaction medium.² *N,N*-dimethylacrylamide and Eosin Y were chosen as a model monomer and photoredox catalyst to study SI PET-RAFT in an aqueous condition. In accordance with controlled polymerization growth kinetics, a linear increase in brush height with irradiation time for a range of light intensities is observed. In the absence of glucose oxidase, the brush growth is significantly hindered; confirming the importance of enzymatic deoxygenation for successful polymerization. Additionally, the effects of catalyst loading, wavelength (470 nm vs 530 nm), light intensity, and water purity (DI water vs MilliQ water) on brush growth efficiency were investigated. Lastly, we demonstrate that this process enables the fabrication of well-defined, patterned polymer brush architectures using top-down irradiation with visible light and photomasks (Figure).

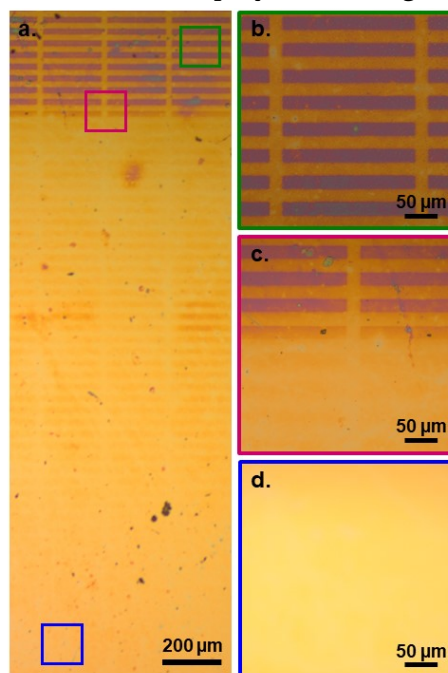


Figure. a-d) Optical micrographs of 20 μm X 200 μm patterns synthesized on a 96 nm thick polymer brush layer. The patterned brush growth is localized on the top half by covering the bottom half of the photomask with black tape (light penetration is blocked). a) Zoomed out view of micron-scale features along with corresponding magnified view of square regions: b) green (patterns), c) red (boundary), and d) blue (no pattern).

References:

1. J. O. Zoppe, N. C. Ataman, P. Mocny, J. Wang, J. Moraes, and H.-A. Klok, Surface-initiated controlled radical polymerization: state-of-the-art, opportunities, and challenges in surface and interface engineering with polymer brushes, *Chem. Rev.* **117** (2017) 1105-1318. DOI: 10.1021/acs.chemrev.6b00314.
2. R. Chapman, A. J. Gormley, K.-L. Herpoldt, and M. M. Stevens, Highly controlled open vessel RAFT polymerizations by enzyme degassing, *Macromolecules* **47** (2014) 8541-8547. DOI: 10.1021/ma5021209.

39. When topology gets active!

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Topology is now a mainstay of condensed matter physics, underlying much of our understanding of equilibrium matter in terms of defects in ordered media and protected edge states in topological insulators. When driven far from equilibrium in an active system, such topological phenomena can take on new and surprising roles. Active materials are composed of interacting units that are self-driven and exhibit large scale collective, and emergent behavior as commonly seen in living systems such as a flock of birds or a bacterial suspension. By focusing on active liquid crystals in two dimensions, with both polar and nematic orientational order, I will show how broken time-reversal symmetry due to the active drive allows polar flocks on a curved surface to support topologically protected sound modes. In an active nematic, activity instead causes topological disclinations to become spontaneously motile, which can defect unbinding and organize novel phases of defect order and chaos. These phenomena extend topological ideas in conventional condensed matter to active and living materials allowing new ways to control and harness their nonequilibrium properties. This work was supported by the NSF grants DMR-1609208, PHY-1748958 (KITP) and a J C Bose Fellowship of the Science & Engineering Research Board (India).

References:

1. S. Shankar, M. J. Bowick, M. C. Marchetti, Topological sound and flocking on curved surfaces, *Phys. Rev. X* **7**, 031039 (2017).
2. S. Shankar, S. Ramaswamy, M. C. Marchetti, M. J. Bowick, Defect unbinding in active nematics, *Phys. Rev. Lett.* **121**, 108002 (2018).

40. *Ab initio* computation for solid-state ^{31}P NMR of inorganic phosphates: Revisiting X-ray structures

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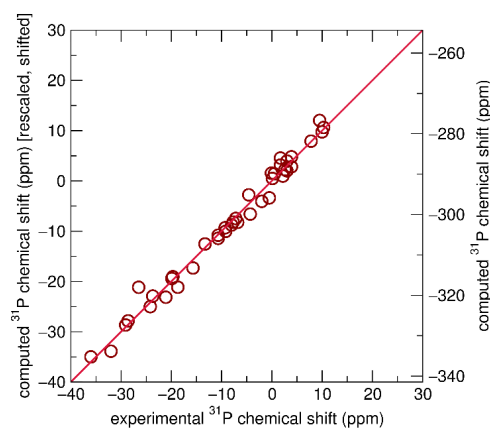
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Solid-state NMR can serve as a precision probe of local atomic environments. However, significant difficulty exists in the interpretation of spectra obtained via solid-state NMR due to broad linewidths caused by an array of interactions, including dipole-dipole, quadrupolar, and chemical shielding anisotropy. Additionally, due to the dependence of the chemical shift on the crystal structure of solid materials, making solid-state NMR peak assignments becomes non-trivial. This work utilizes the gauge-including projector augmented wave (GIPAW) method¹ as implemented within the VASP DFT code to compute ^{31}P NMR chemical shift tensors for 22 phosphate compounds. The computed chemical shift tensor parameters are compared to experimentally obtained parameters previously reported by Cheetham *et al.*² Correlations between calculated chemical shifts and experimental results indicate DFT can be utilized to obtain accurate peak assignments. There is also evidence that the combination of DFT and NMR can provide further refinement of crystal structures beyond the precision of XRD through geometry relaxation.

We acknowledge the Center for Scientific Computing at UC Santa Barbara (supported by NSF CNS-1725797) and the Materials Research Laboratory: an NSF MRSEC (DMR-1720256) for the computing infrastructure, and the Ras al Khaimah Centre for Advanced Materials for financial support.

References:

1. C. J. Pickard, and F. Mauri, All-electron magnetic response with pseudopotentials: NMR chemical shifts, *Phys. Rev. B* **63** (2001) 245101. DOI: 10.1103/PhysRevB.63.245101
2. A. K. Cheetham, N. J. Clayden, C. M. Dobson, R. J. B. Jakeman, Correlations between ^{31}P chemical shifts and structural parameters in crystalline inorganic phosphates, *Chem. Commun.* **3** (1986) 195-197. DOI: 10.1039/c39860000195



Computed isotropic chemical shifts compared to experimental values using relaxed crystal structures.

41. Interfacial strain fields in biphasic Heusler compounds

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Heusler intermetallics have proven to be exceedingly fruitful with respect to functional properties.[1] Ternary systems containing a full Heusler (fH)/half-Heusler (hH) two-phase-field exhibit a biphasic microstructure, enabling the study of the influence of microstructural parameters such as precipitate shape, size and phase fraction on the physical properties.[2,3] The present contribution investigates the strain field due to semicoherent interfaces between fH NbCo₂Sn and hH NbCoSn, which exhibits a 3.3 % lattice mismatch.[4] **Figure 1(a)** shows the biphasic microstructure of NbCo_{1.1}Sn after

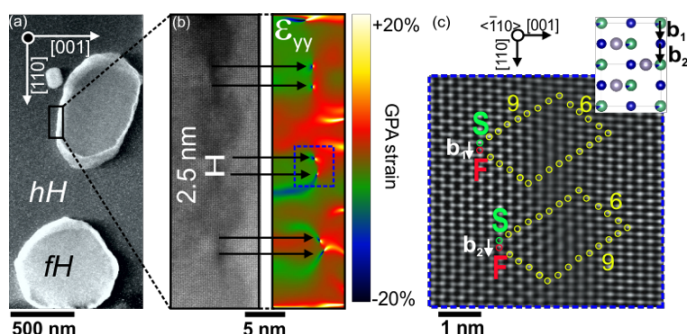


Figure 1 (a) Semicoherent fH precipitates embedded in hH matrix. (b) HRSTEM image and geometric phase analysis of the interface, revealing regularly spaced dislocations. (c) A Burgers circuit analysis of two coupled interface dislocations.

levitation melting and annealing, with fH precipitates embedded in the hH matrix. The selected interfacial region is magnified and analyzed by geometric phase analysis (GPA) in **Figure 1(b)**, displaying two hotspots at the dark regions (marked with arrows). This examination indicates two closely spaced interface dislocations every 6 nm. The burgers circuit analysis in **Figure 1(c)** reveals that the interface dislocations have a burgers vector of $\mathbf{b} = a/4[110]$, consistent with what is expected for the Heusler crystal structure. This research was supported by the National Science Foundation through Materials Research Science and Engineering Center, DMR No. 1720256 (IRG-1).

References

1. T. Graf, C. Felser and S.S. Parkin. Simple rules for the understanding of Heusler compounds, *Prog. Solid State Ch.* **39** (2011) 1-50. DOI: 10.1016/j.progsolidstchem.2011.02.001
2. E. E. Levin, F. Long, J. E. Douglas, M. L. Buffon, L. K. Lamontagne, T. M. Pollock, and R. Seshadri, Enhancing thermoelectric properties through control of nickel interstitials and phase separation in Heusler/half-Heusler TiNi_{1+x}Sn composites, *Materials* **11** (2018) 903. DOI: 10.3390/ma11060903
3. N. Verma, J. E. Douglas, S. Krämer, T. M. Pollock, R. Seshadri, and C. G. Levi, Microstructure evolution of biphasic TiNi_{1+x}Sn thermoelectric materials, *Metall. Mater. Trans. A* **47** (2016) 4116-4127. DOI: 10.1007/s11661-016-3549-9
4. M. L. Buffon, G. Laurita, N. Verma, L. K. Lamontagne, L. Ghadbeigi, D. L. Lloyd, T. D. Sparks, T. M. Pollock, and R. Seshadri, Enhancement of thermoelectric properties in the Nb-Co-Sn half-Heusler/Heusler system through spontaneous inclusion of a coherent second phase, *J. Appl. Phys.* **120** (2016) 075104. DOI: 10.1063/1.4952994