University of Minnesota MRSEC

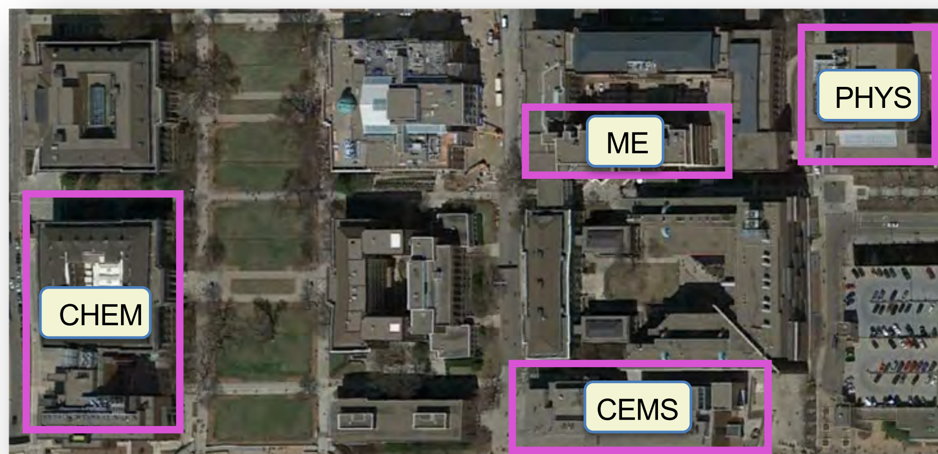
A comprehensive center that integrates interdisciplinary materials research with innovative outreach to inspire excellence in all aspects of science and engineering

The UMN MRSEC is Uniquely Situated

Only R1 school in the state

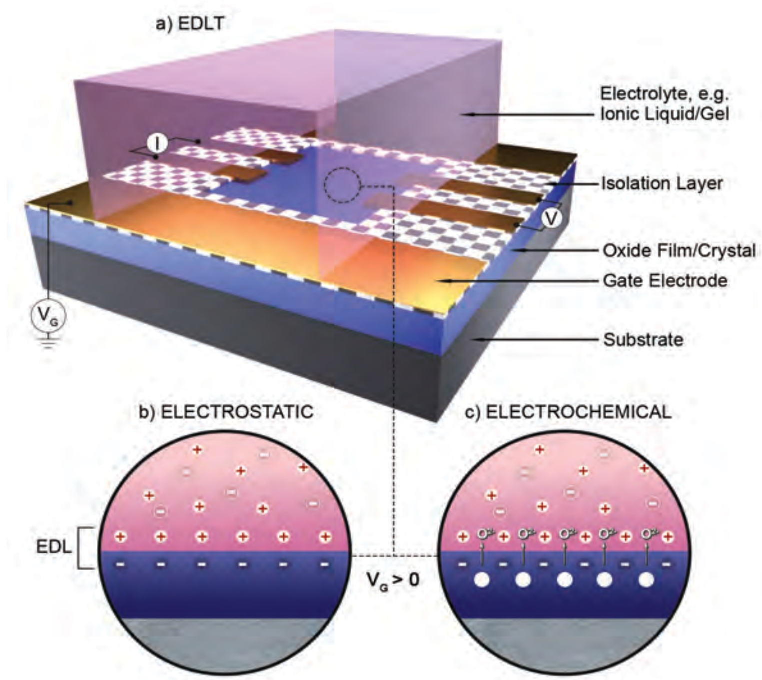
- 1 of 3 states with only one R1 or R2 school
- Urban setting
- 65% of population lives in greater Twin Cities

- College of Science & Engineering (CSE)
- Only R1 school with all physical science and engineering as one unit
- 12 departments, 460 faculty, 8,000 students

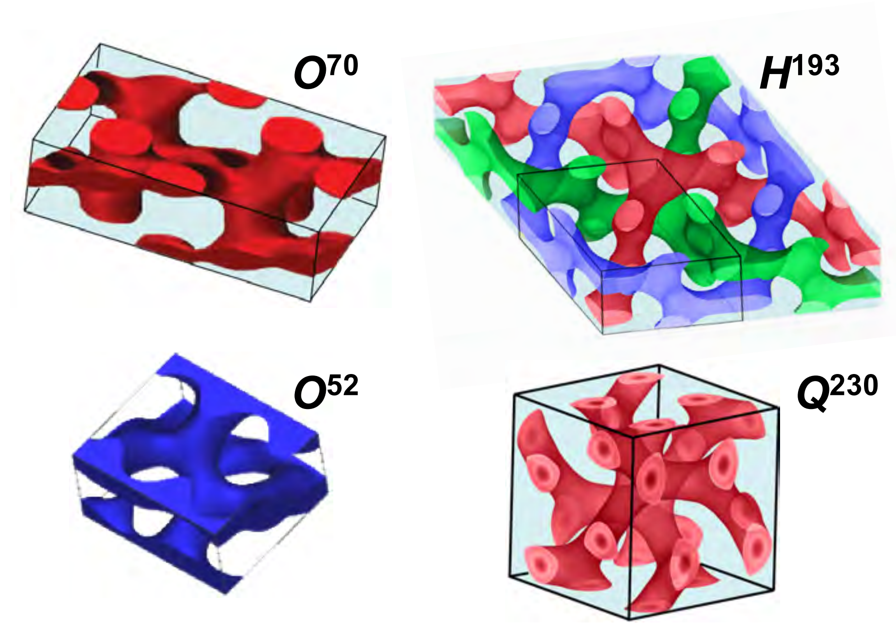


Two Field-Leading IRGs

IRG-1: Ionic Control of Materials

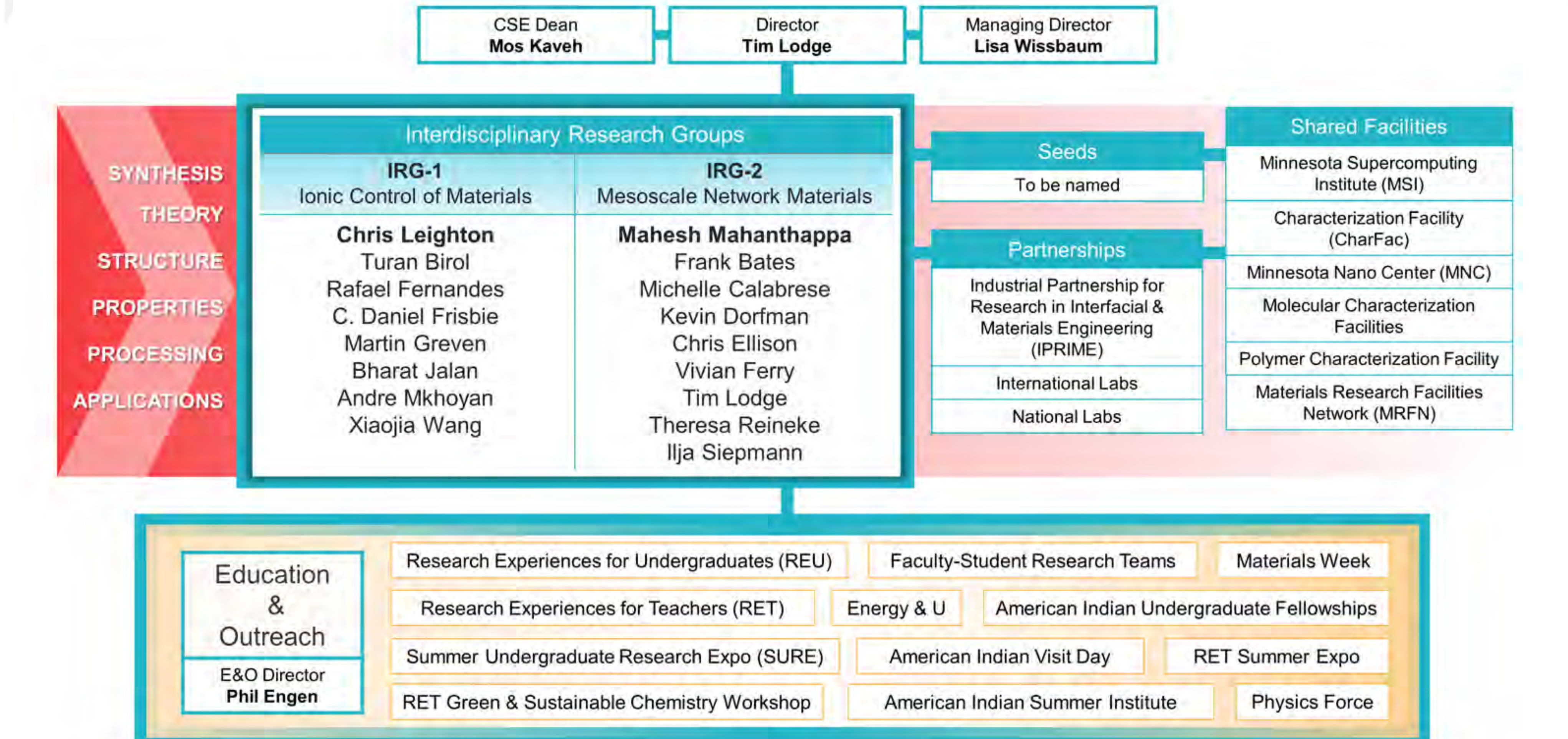


IRG-2: Mesoscopic Network Materials



Selected from 7 proposed IRGs in an internal competition (2019)

UMN MRSEC at a Glance



IRG-1: Ionic Control of Materials

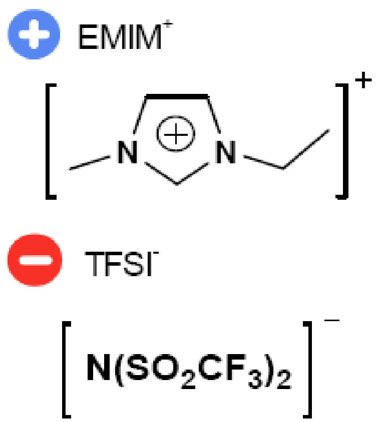
Chris Leighton, IRG Leader

IRG-1 Vision: Ionic Control of Materials

Transform the understanding of mechanisms, capabilities, and applications of **electrolyte-based electrostatic and electrochemical gating**, realizing electrical control over an extraordinary range of electronic phases and function

Ionic Liquids (ILs)

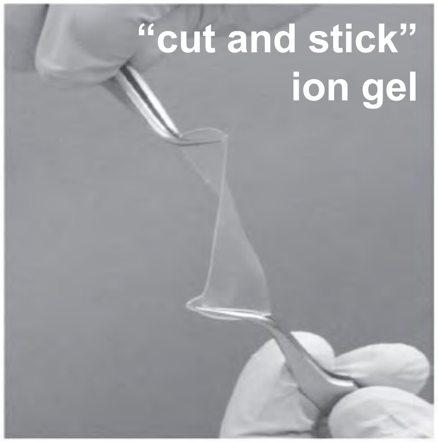
- Molten salts
- Organic ions
- No solvent
- Wide stability
- High mobility



Watanabe *et al.*, *Chem. Rev.*, (2017)

Ion Gels

- ILs in polymer matrices
- ~10% polymer
- Retain ionic mobility, capacitance
- Stiff, rubbery



Lodge, Frisbie, *Nat. Mater.*, (2008)
Lodge, *Science*, (2008)

Electrostatic *vs.* Electrochemical Mechanisms

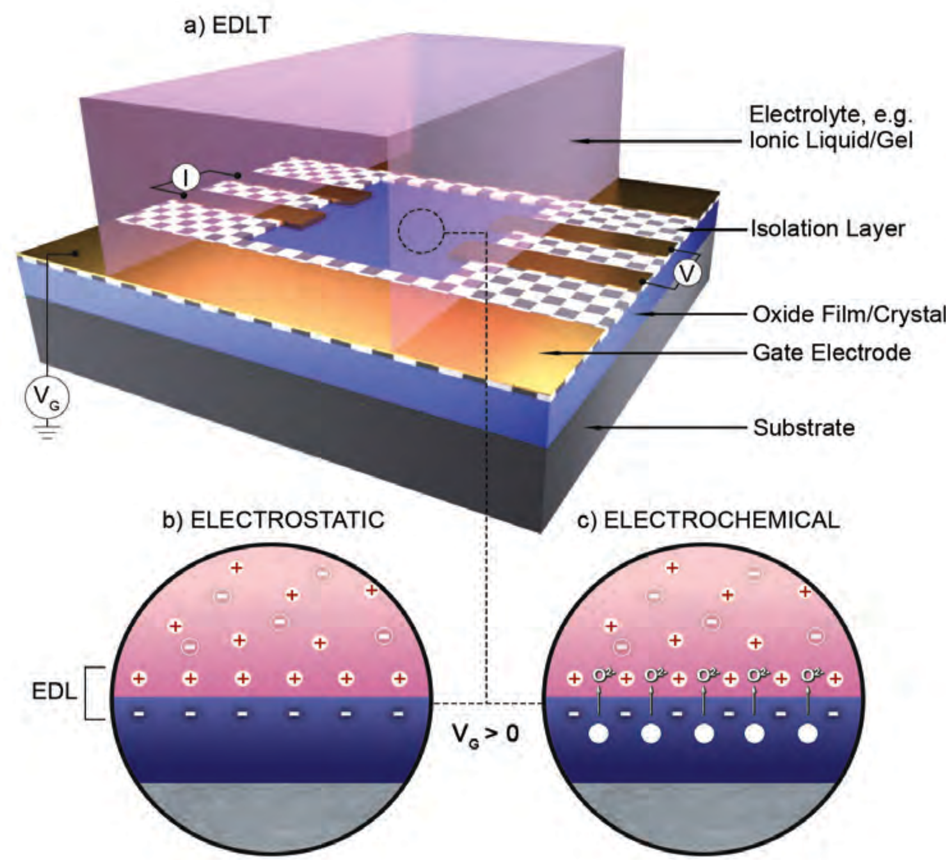
Initial bias: electrostatics

Now unambiguous: electrostatics *and* electrochemistry
(V_O, H^+ formation/annihilation, *etc.*)

From transport, *operando* probes (*e.g.*, IRG-1)

Electrochemical appeal:
- Wide modulation
- Not screening limited (metals!)
- O^{2-}, H^+, Li^+, Na^+,…
- ILs, solid electrolytes, ion conductors,…
- Promising speed, reversibility (5 MHz!*)

New fields/applications
- Magnetoionics (*low power V_g-switchable magnets*)
- Neuromorphic computing (analog tunability)
- Stochastic computing (tunable stability)
- Organic/flexible electronics (low V_g, high ON/OFF)



Leighton, *Nat. Mater.* (2019)

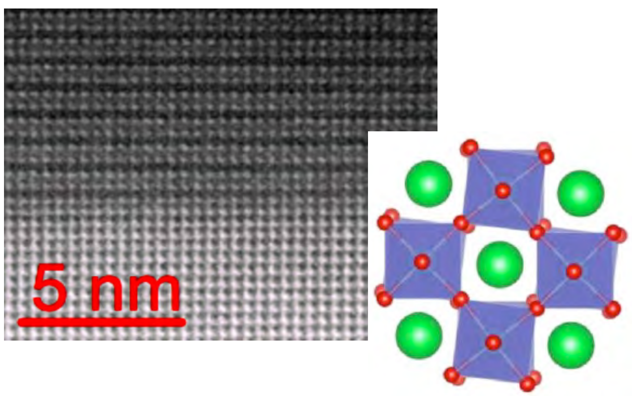
* Koester, Lodge, Frisbie, *Adv. Func. Mater.* (2019); in prep. (2021)

IRG-1 Goals

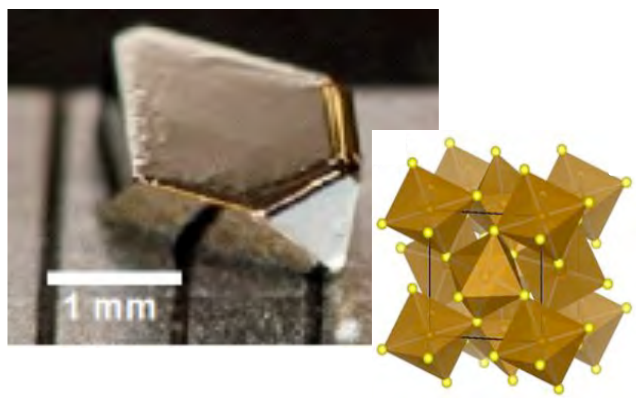
Understand **mechanisms**, **capabilities**, **applications** of **electrostatic *and* electrochemical gating**
Electrical control over **wide range of electronic phases and function**

When and why electrostatics vs. electrochemistry?
Understand interfacial structure, chemistry, ion-carrier interactions? 3D vs. 2D doping? Disorder?
Limits on speed, reversibility, property modulation (devices)? Universality?

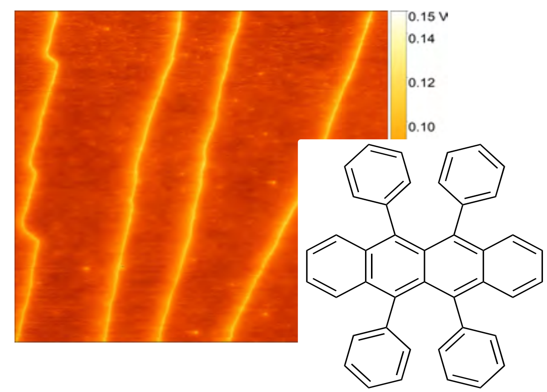
Metal Oxides



Metal Chalcogenides



Molecular Conductors



(Insulator-metal-superconductor), ferro-/antiferro-magnetism (FM/AF), charge order (CO), charge density waves (CDW), Mott insulators, topological states, optical function, crystal structure

Unique Approaches and Facilities

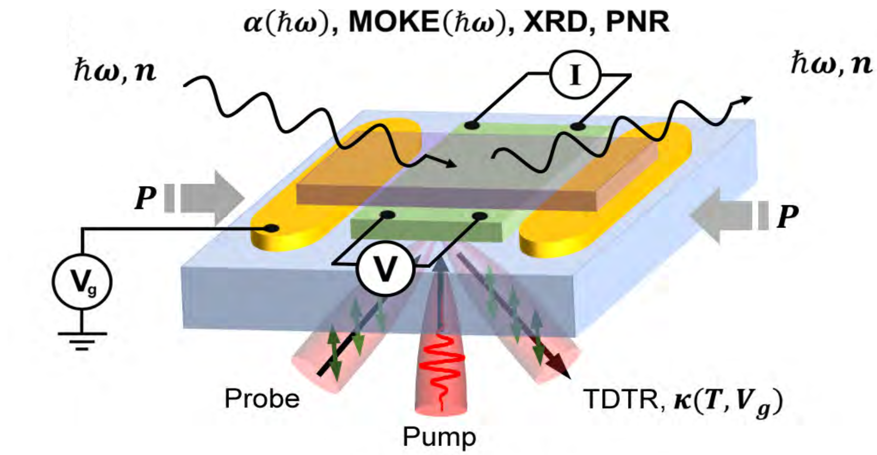
State-of-the-art synthesis Detailed structural characterization Unique measurements
Novel *operando* probes Tightly-coupled theory

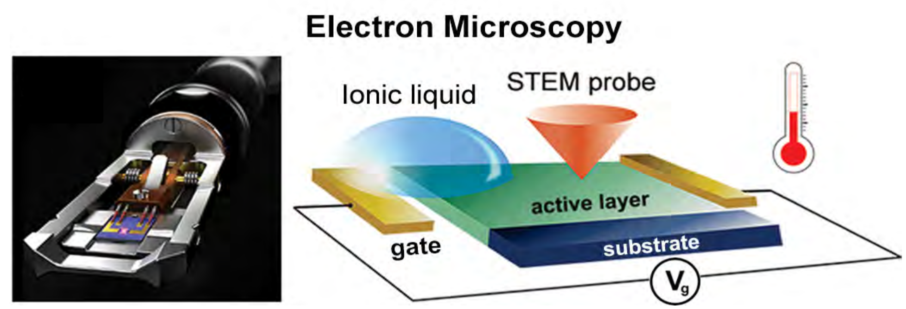
Synthesis:
MBE, high *P* sputtering, crystal growth,
device fab (incl. organics),…

Structural characterization:
STEM/EELS/EDS, X-ray/neutrons,…

Unique measurements/*Operando* probes:
- *Operando* synchrotron XRD, XAS, XMCD, PNR
- *Operando* lab XRD, optical MCD, MOKE
- *Operando* TDTR, χ_{NL}, uniaxial *P*, TEM, optics

Theory:
- DFT+DMFT (correlations)
- DFT/tight-binding/analytical framework
  (*direct* comparison to gating)





Participants and Collaborators

Primary Participants

Chris Leighton (CEMS)	Synthesis, transport, magnetism, scattering, electrolyte gating
Turan Birol (CEMS)	Electronic structure: DFT and DMFT
Rafael Fernandes (PHYS)	Microscopic/phenomenological modeling
Dan Frisbie (CEMS)	Organic conductors, ionic liquids/gels, electrochemistry
Martin Greven (PHYS)	Crystal growth, scattering, superconductivity, uniaxial *P*, χ_{NL}
Bharat Jalan (CEMS)	Oxide semiconductors, MBE
Andre Mkhoyan (CEMS)	TEM, EDS, EELS (*operando*)
Xiaojia Wang (ME)	Thermal transport, TDTR (*operando*)

Secondary Participants

Vivian Ferry (CEMS)	Optics/photonics (*operando*)
Mahesh Mahanthappa (CEMS)	Semiconducting polymer synthesis

Key Collaborators

UMN	B. Shklovskii, K. Wang
US Academic	J.P. Maria, X. Ruan, J. Walter
National Lab	J. Borchers, S. Chambers, S. Crooker, M. Fitzsimmons, C. Petrovic, H. Zhou
International	Y. Li, J.-S. Jeong, J. Ruhman, D. Pelc

Not originally involved in former IRG

Summary: IRG-1, Ionic Control of Materials

Understand mechanisms, capabilities, applications of electrolyte-based electrostatic and electrochemical gating. Realize electrical control over extraordinary range of phases and function.

- ✓ Embrace **electrostatic *and* electrochemical control**; build on leading efforts in previous IRG
- ✓ Understand **mechanisms, capabilities, development of applications** (magnetoionics, neuromorphics, *etc.*)
- ✓ **Broad understanding from multiple systems**: oxides, chalcogenides, organics (many new materials)
  Control: insulator-metal-superconductor, Mott insulators, FM/AF, CDW, CO, optics, structure…
- ✓ State-of-the-art synthesis/characterization, **new/unique *operando* probes, tightly-coupled theory**
- ✓ Fundamentally interdisciplinary, collaborative (multi-investigator), center-scale approach

IRG-2: Mesoscale Network Materials

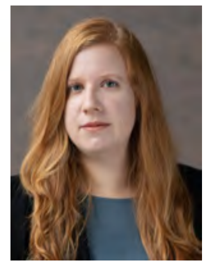
Mahesh Mahanthappa, IRG Leader


M. A. Calabrese
Asst. Prof. CEMS


F. S. Bates
Prof. CEMS


K. D. Dorfman
Prof. CEMS


C. J. Ellison
Prof. CEMS


V. E. Ferry
Assoc. Prof. CEMS


M. K. Mahanthappa
Prof. CEMS

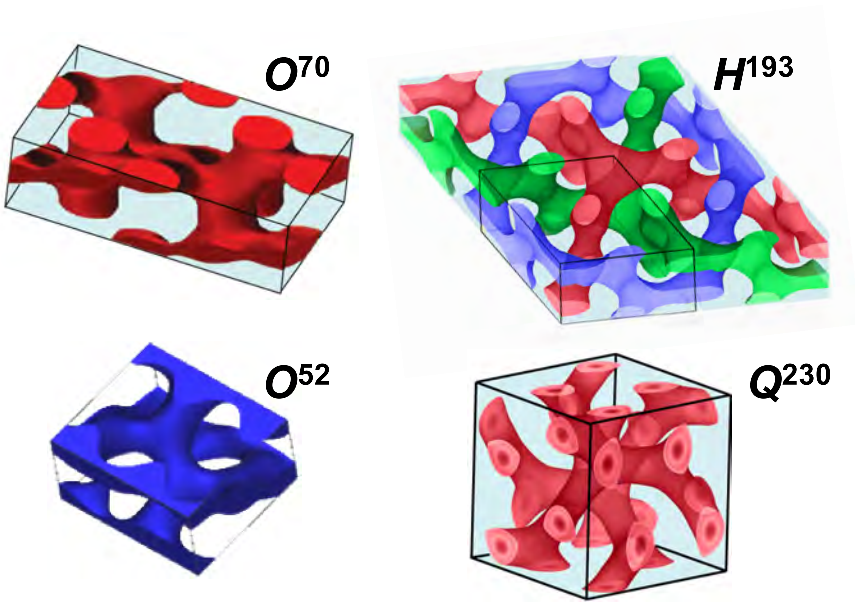

T. P. Lodge
Prof. Chemistry


T. M. Reineke
Prof. Chemistry


J. Ilja Siepmann
Prof. Chemistry

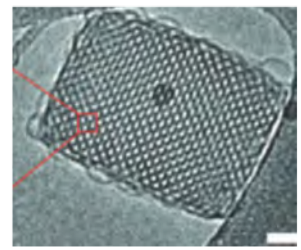
IRG-2 Vision: Mesoscale Network Materials

Develop scale-invariant molecular design principles for ***shape-filling amphiphiles*** (SFAs) that self-assemble into functional mesoscale ***Nets*** with 5–500 nm diameter pores

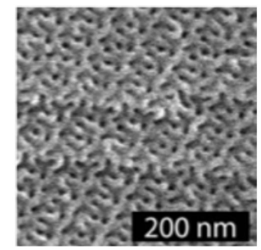


Polycontinuous ***Nets****:* percolating domains
Orthogonal domain properties/functionalities
Narrow phase windows

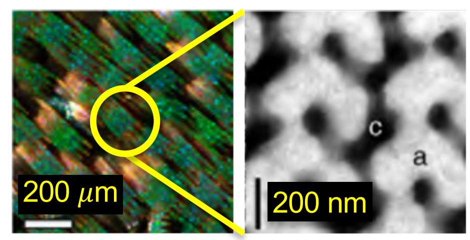
SFA ***Nets*** will drive applications in:



0.7–5 nm pores
Drug delivery



10–50 nm pores
Membranes

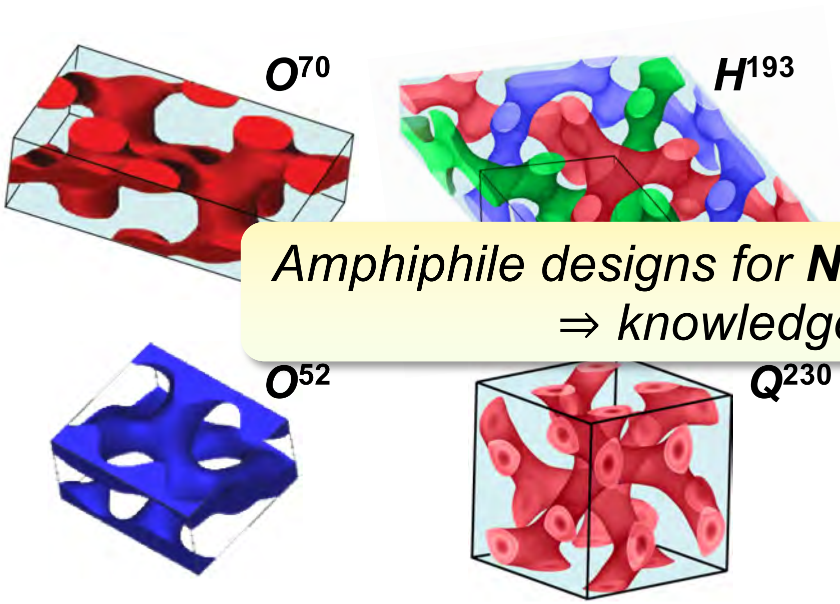


≥ 200 nm pores
Photonics

Thalmann, *Soft Matter*, **2017**
Hillmyer, *Soft Matter*, **2006**
Prum, *PNAS*, **2010**

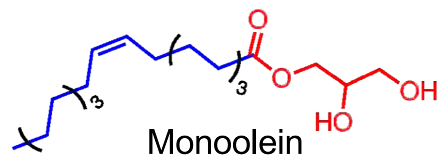
IRG-2 Vision: Mesoscale Network Materials

Develop scale-invariant molecular design principles for ***shape-filling amphiphiles*** (SFAs) that self-assemble into functional mesoscale ***Nets*** with 5–500 nm diameter pores

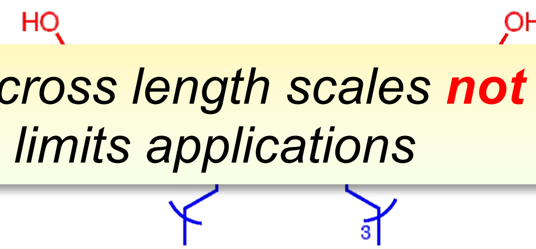


*Amphiphile designs for **Nets** across length scales **not known***
⇒ knowledge gap limits applications

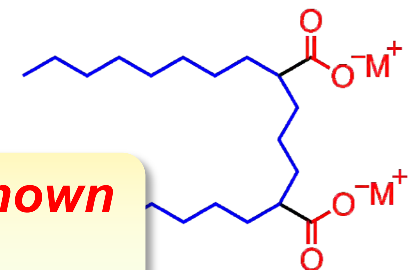
Polycontinuous ***Nets***
Orthogonal domain properties/functionalities
Narrow phase windows



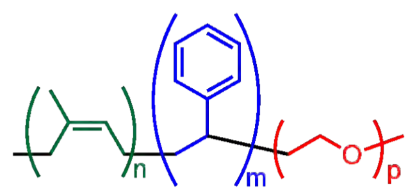
Monoolein



T-shaped amphiphiles



Ionic Gemini Surfactants



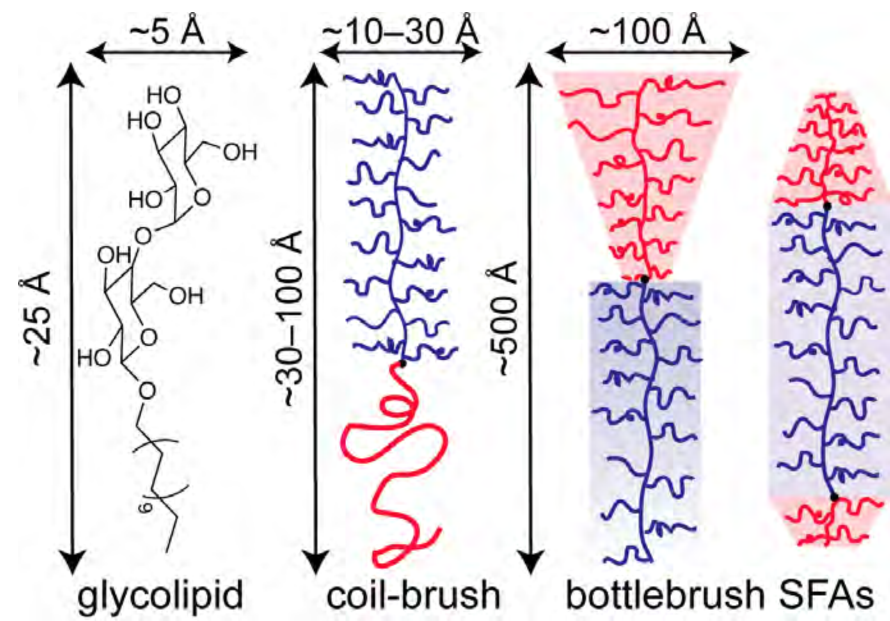
Linear AB and ABC Polymers

Bates, *Macromolecules*, **2004**; Mahanthappa, *J. Phys. Chem. Lett.*, **2015**
Tschierske, *Chem. Commun.*, **2018**; Kulkarni, *Phys. Chem. Chem. Phys.*, **2011**

IRG-2 Goals

Discover and exploit scale-invariant shape-filling amphiphile (SFA) motifs to robustly assemble functional ***Nets*** and to understand how processing impacts their properties

1. Identify anisotropic shape-filling motifs of diblock oligomers that drive ***Net*** self-assembly
2. Scale up to SFAs design to access ***Nets*** with 5–500 nm pores
3. Explore shear and surface field-dependent morphology selection in bulk and in thin films
4. Stabilize ***Nets*** for high performance applications as membranes, photonic, and meta-materials



≤ 5 nm pores

5–50 nm pores

50–500 nm pores

Uniquely Comprehensive Approach

Precision Synthesis Across Length Scales

- Block oligomers
- Bottlebrush block polymers

Assembly Characterization

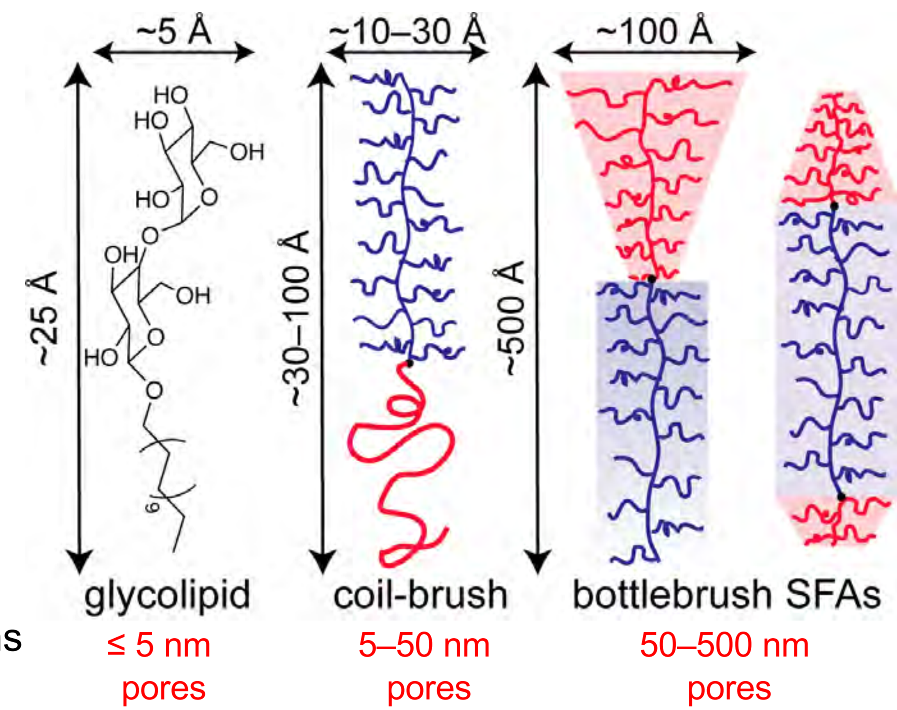
- X-ray/neutron scattering, rheology, microscopy

Processing and Properties

- *in situ* SAXS/SANS
- Thin film and directed self-assembly
- Poroelastic mechanics, optical properties

Tightly-Coupled Theory and Simulations

- Atomistic MD/MC with transferable force fields
- SCFT, field-theoretic MC, and particle-based simulations
- Optical simulations and defect impact modeling



Participants and Collaborators

Primary Participants

Mahesh Mahanthappa (CEMS)	oligomer/polymer synthesis, assembly thermodynamics, scattering
Frank Bates (CEMS)	polymer synthesis, thermodynamics, mechanics
Michelle Calabrese (CEMS)	*in situ* scattering, rheology, polymer dynamics
Kevin Dorfman (CEMS)	mesoscale simulations and theory
Chris Ellison (CEMS)	polymer dynamics, processing, thin film self-assembly
Vivian Ferry (CEMS)	optical characterization, EM simulations/modeling, nanofabrication
Tim Lodge (CHEM)	polymer structure, dynamics
Theresa Reineke (CHEM)	oligomer/polymer synthesis, assembly characterization
Ilja Siepmann (CHEM)	molecular simulations and model development

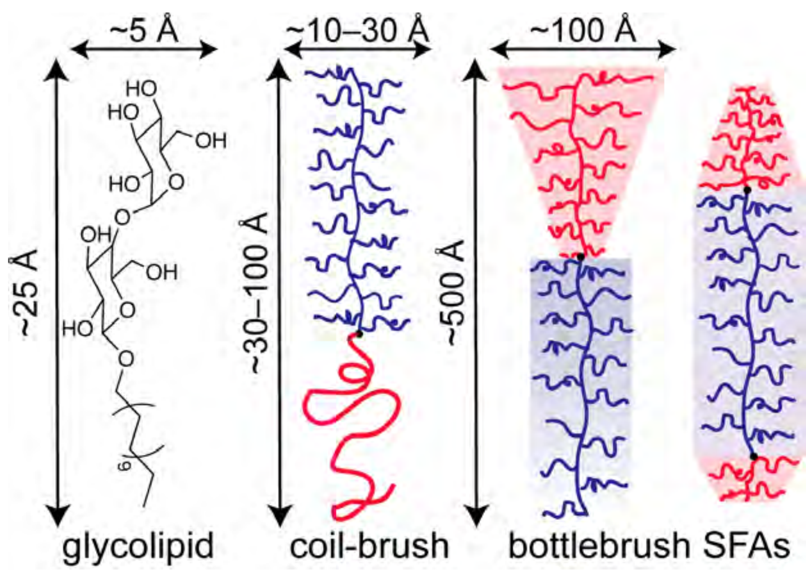
International Collaborators

John Seddon (Imperial College)	glycolipids and lyotropic LCs, scattering, lipid biophysics
Stephan Förster (Jülich)	block polymer assembly, rheoSAXS/rheoSANS, polymer processing

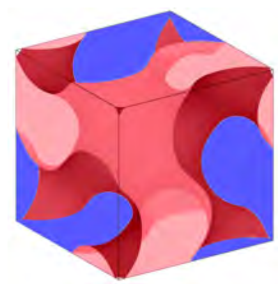
Red: New to the MRSEC

Impact and Outcomes

Robust, scale-invariant design criteria for shape-filling amphiphiles (*SFAs*) that enable broadly scalable known and new ***Net*** phases over wide composition and *T* windows at 5–500 nm length scales inaccessible by other fabrication methods



SFA self-assembly across length scales



"bottom up" network design

Shape-filling
[SC]
Dynamics
Stabilization

Membranes
Photonics
Metamaterials

University of Minnesota MRSEC

iSuperSeed 2018: Bridging the 2D and 3D Worlds with Transition Metal Dichalcogenides

iSuperSeed Team

Turan Birol
Asst. Prof., CEMS
theory (first principles)

Fiona Burnell
Assoc. Prof., PHYS
theory (topology)

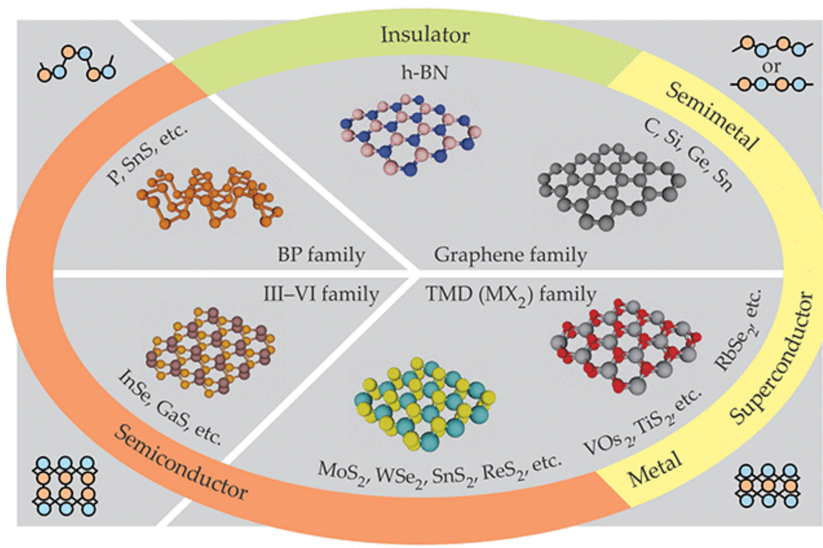
Rafael Fernandes
Assoc. Prof., PHYS
theory (superconductivity)

Vlad Pribiag
Asst. Prof., PHYS
experiment (transport, nanofabrication)

Ke Wang
Asst. Prof., PHYS
experiment (exfoliation, encapsulation)

Vision and Objectives

Explore the unique properties of transition metal dichalcogenides (TMDs) that are between the bulk and monolayer limits by combining properties typically observed in the 3D limit, such as superconductivity and charge-density waves, with features that are typical of the 2D limit, such as strong spin-orbit coupling (SOC) and topological properties.



Ajayan, et al., *Physics Today* (2016)

Primary Accomplishments

- Experimental observation, supported by theoretical modeling, of an unexpected anisotropy in the superconducting properties of few-layer $NbSe_2$, which showed closely competing conventional and unconventional superconducting instabilities.
- Theoretical prediction, based on a microscopic model, of a new nodal topological crystalline superconducting phase that can be realized in monolayer $NbSe_2$.
- Established theoretically the optimal conditions for the possible realization of exotic superconducting states called pair-density waves in various TMDs.
- Modeling of the topological properties of the unusual superconducting state realized in monolayer WTe_2.
- Development of a model that captures the nature of the pairing state of monolayer $NbSe_2$ in the presence of out-of-plane magnetic fields (in cooperation with external collaborators; ongoing project funded by a regular Seed).

Summary of E&O Activities

Goal: Ensure all students have a meaningful, enjoyable exposure to STEM and develop confidence to build on that experience to pursue a STEM career

Grades	Programs	Outcomes
K – 6	Physics Force, Energy and U	~85,000 students Over 50% attendance of: URM, Girls, Low-income
7 – 12	Materials Week: DiscoverSTEM, Eureka!, AI Visit Day, AI Summer Institute, RET, RET Student Expo, RET Workshop	30 teachers 350+ students
Undergraduate	REU, AI Fellows, Faculty-Student Team, SURE	20 REU: 50% URM, 50% Women