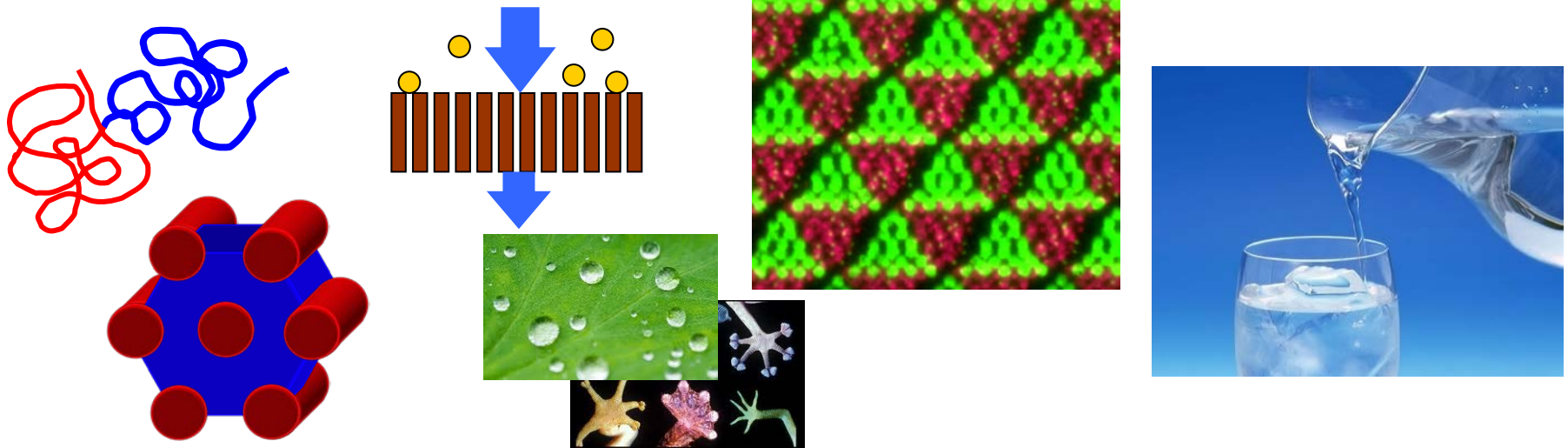


Manufacturing Functional Membranes from Nanostructured Polymers



William A. Phillip

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Department of Chemical and Biomolecular Engineering

University of Notre Dame

Purdue University

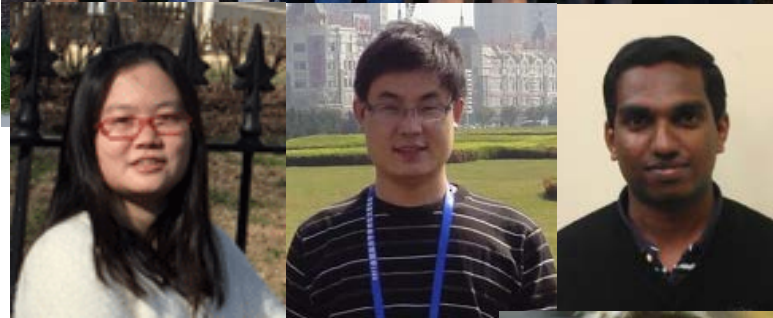
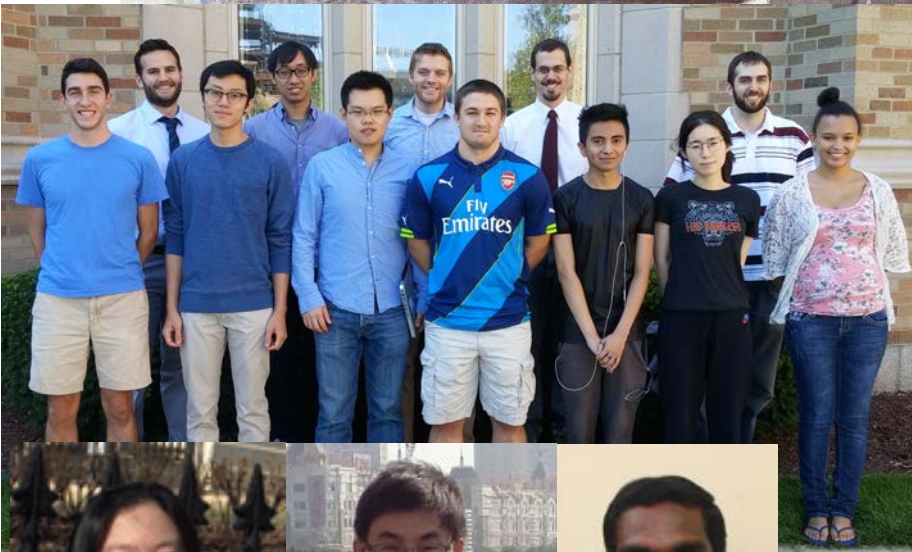
School of Chemical Engineering

Duncan and Suzanne Mellichamp Lecture

Tuesday, October 22, 2019

Acknowledgements

The W.A.T.E.R. Lab



Researcher in the Varma Lab
University of Notre Dame 2002-2006



Acknowledgements



CENTER FOR SUSTAINABLE ENERGY
AT NOTRE DAME



Center for Nano Science and Technology



As well as:

- Center for Environmental Science and Technology (CEST)
- Notre Dame Integrated Imaging Facility (NDIIF)

Why WATER? Because Water is a Global Issue

As water prices soar, lawmakers fear profiteering



JET STREAM
AG AVIATION

By Jerd Smith, Fresh Water News

Posted Oct 20, 2019 at 6:40 PM

Georgia Lawmakers Revisit Tennessee Border Dispute In Bid For Water

MOLLY SAMUEL • MAR 2, 2018

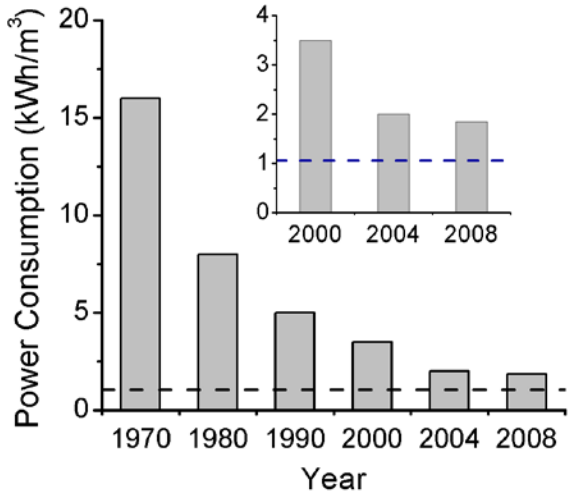
Tennessee, Mississippi await ruling in water rights dispute

June 4, 2019

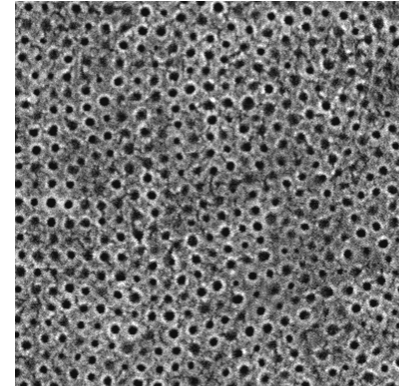
Four Lessons From the Front Lines of California's Water Wars

From mandatory drought restrictions to billions of dollars' worth of drought-proofing projects, San Diego and the entire West has for years had a complicated relationship with its water – and it's not going to get any easier or any cheaper any time soon.

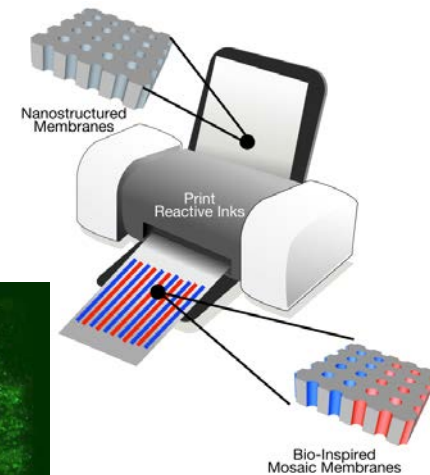
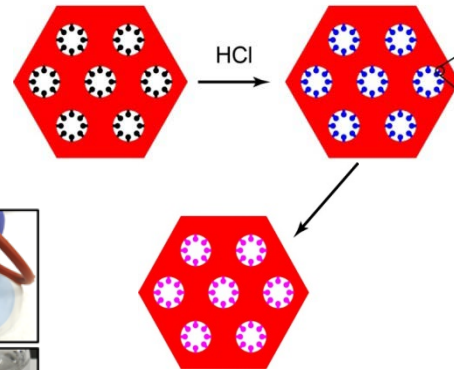
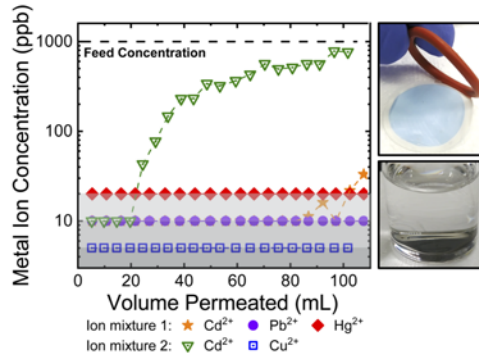
The "Big" Conclusions



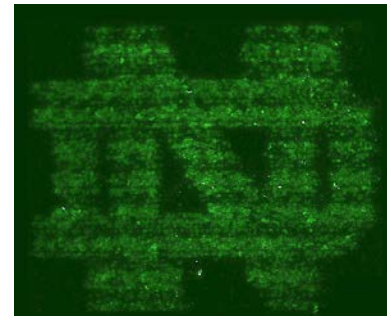
- Size-selective membranes have achieved real commercial successes in liquid-phase separations.
- New material platforms are pushing size-selective membranes to their physical limits.



- Post-assembly modifications result in membranes that lend themselves to new applications.



- Advanced manufacturing techniques can simplify the chemical modification and spatial patterning of nanostructured membranes.



Seawater RO Desalination Produces Drinking Water

Tampa Bay Plant produces 25 MGD of freshwater.



Seawater RO Desalination Produces Drinking Water

In excess of 5×10^{15} gallons of fresh water are produced annually using SWRO

Seawater Intake

- Subsurface intake
- Open ocean intake

Pre-treatment

- Conventional (coagulation and filtration)
- Membrane-based

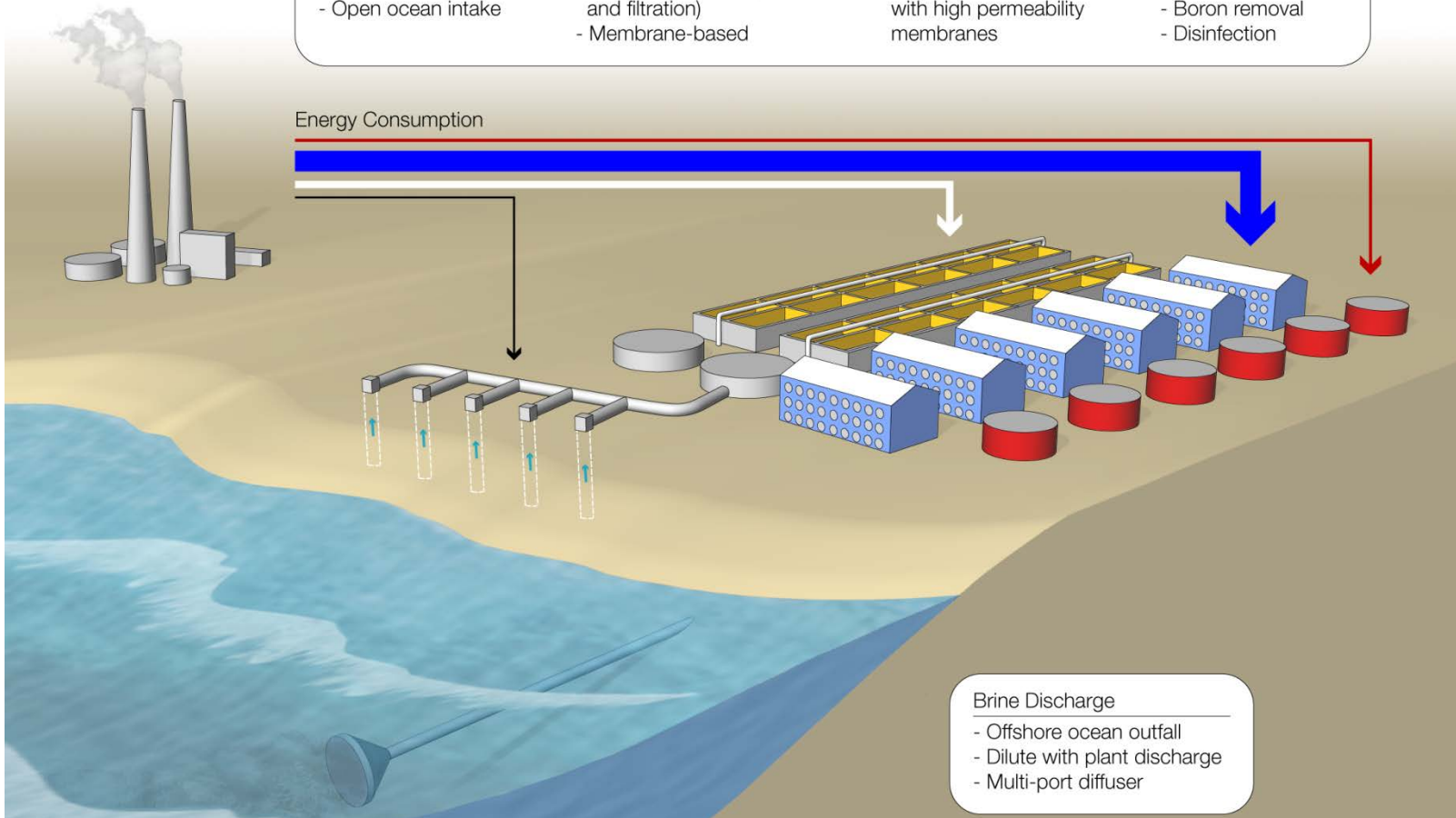
Reverse Osmosis

- Spiral wound modules with high permeability membranes

Post-treatment

- Re-mineralization
- Boron removal
- Disinfection

Energy Consumption

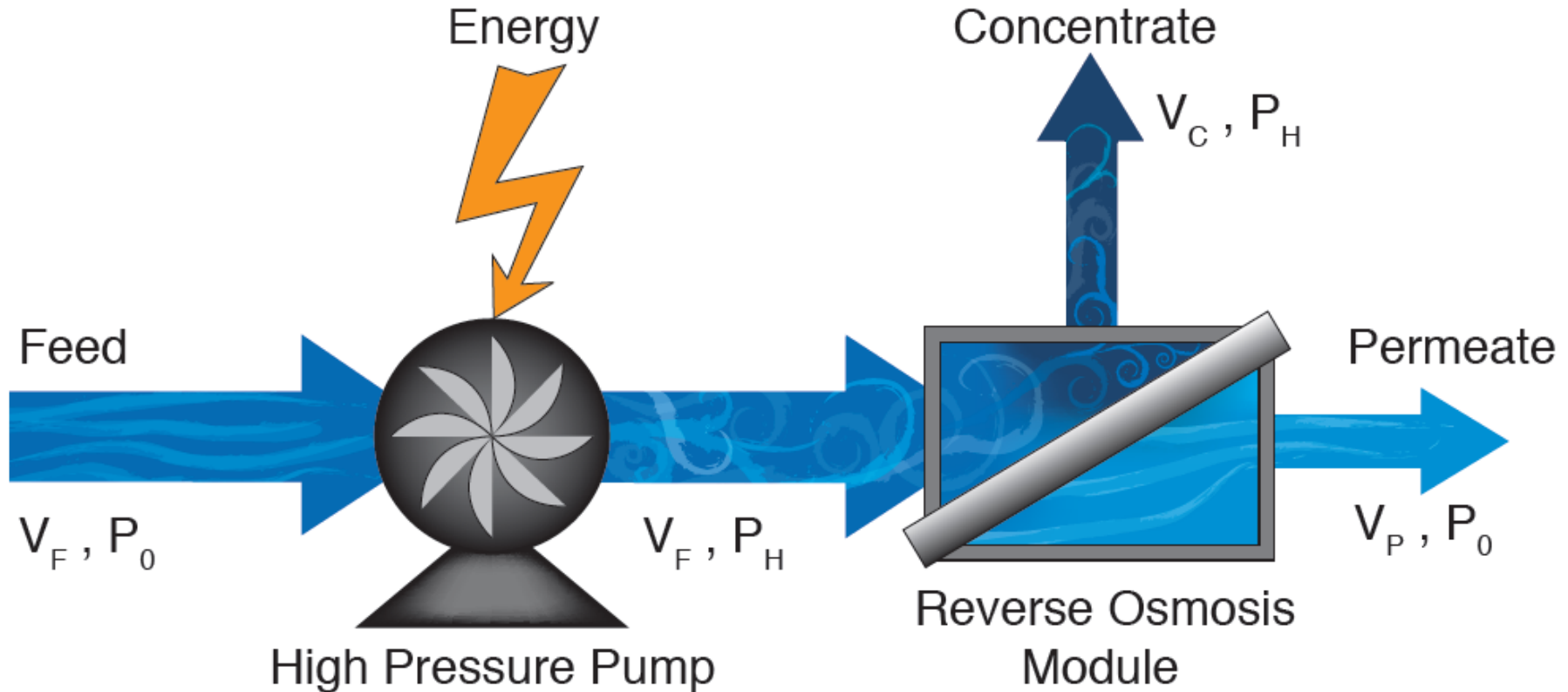


Brine Discharge

- Offshore ocean outfall
- Dilute with plant discharge
- Multi-port diffuser

Seawater RO Desalination Produces Drinking Water

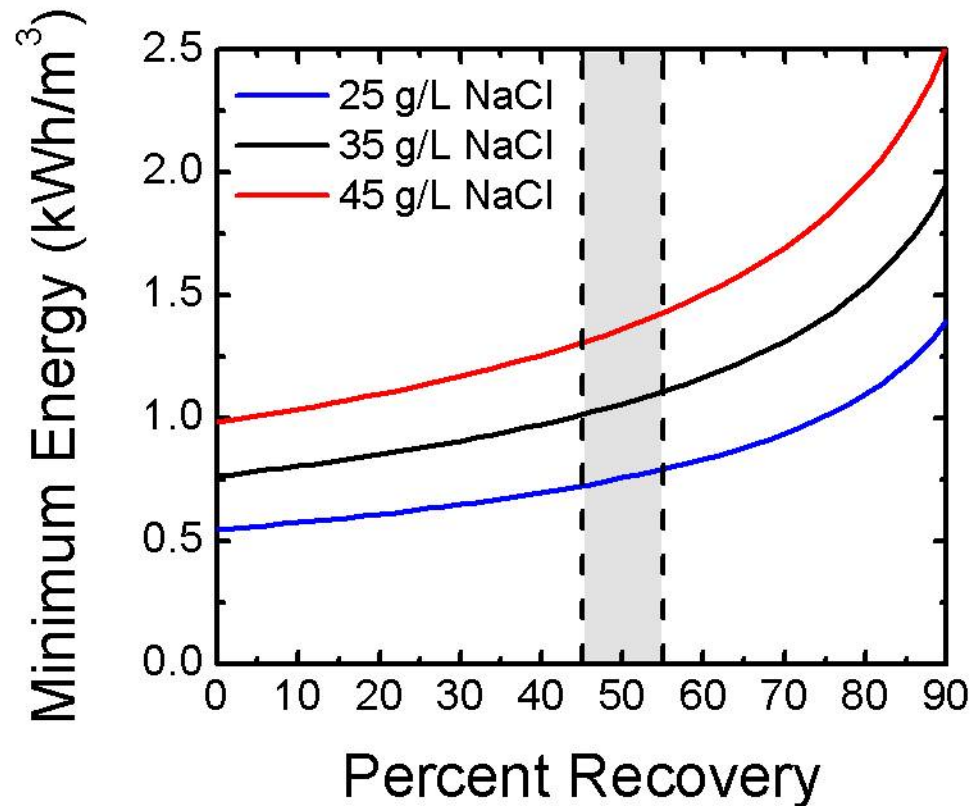
A hydraulic pressure, P_H , is applied to “reverse” osmosis.



Applied Pressure Determines Power Consumption

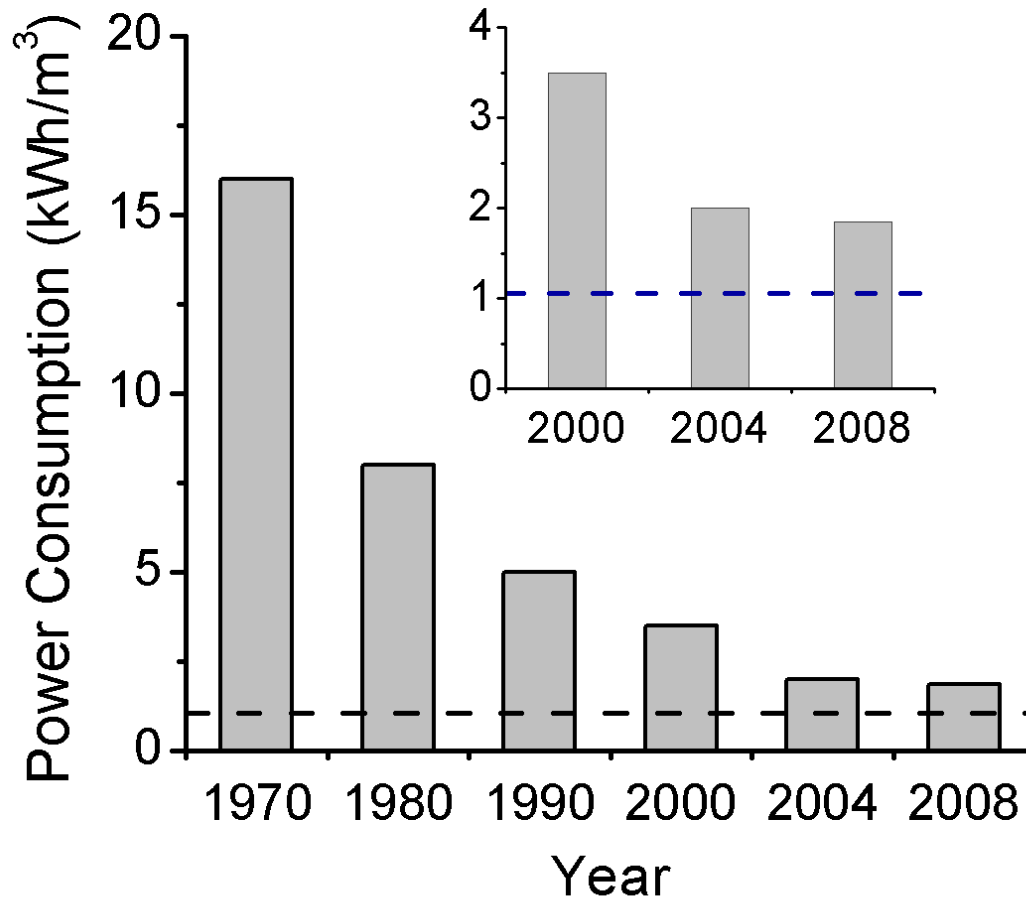
Osmotic pressure of the concentrate determines minimum applied pressure

$$\text{Percent Recovery} = \frac{\text{Volume of Permeate}}{\text{Volume of Feed}}$$



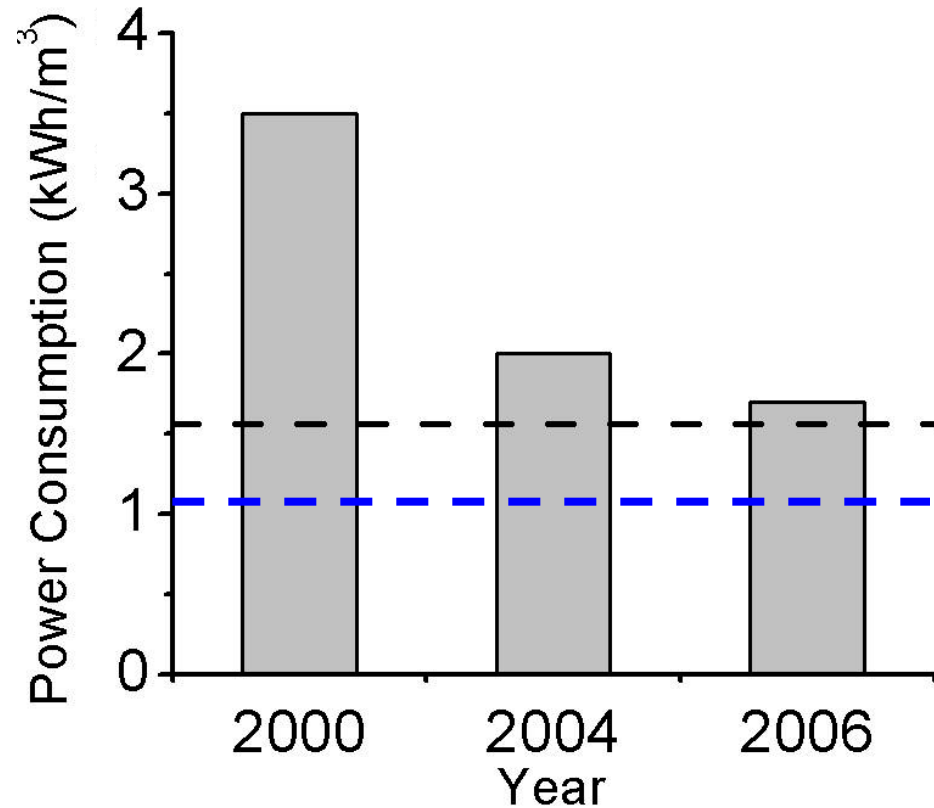
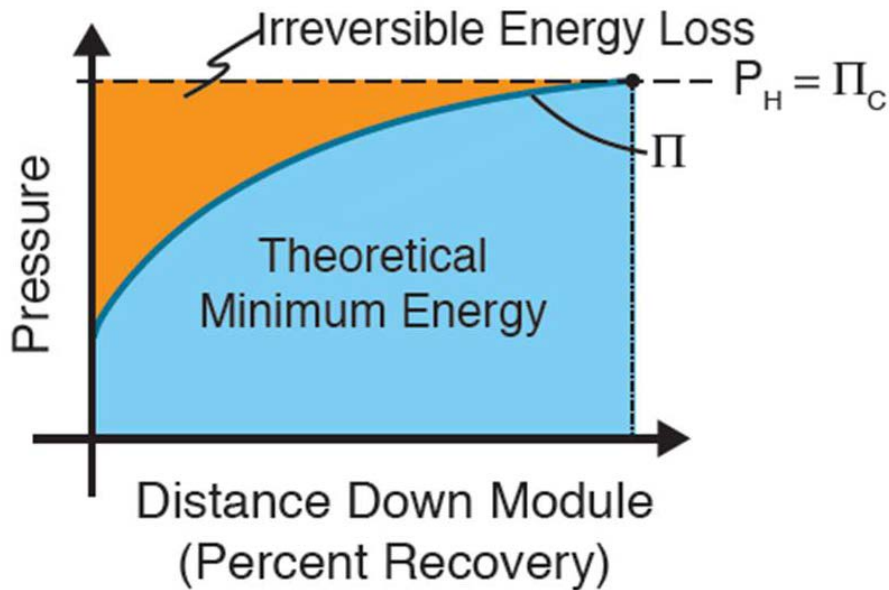
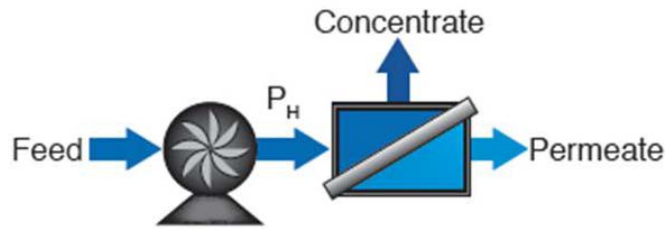
Seawater RO Power Consumption is Reaching Limit

Data for desalination step only.



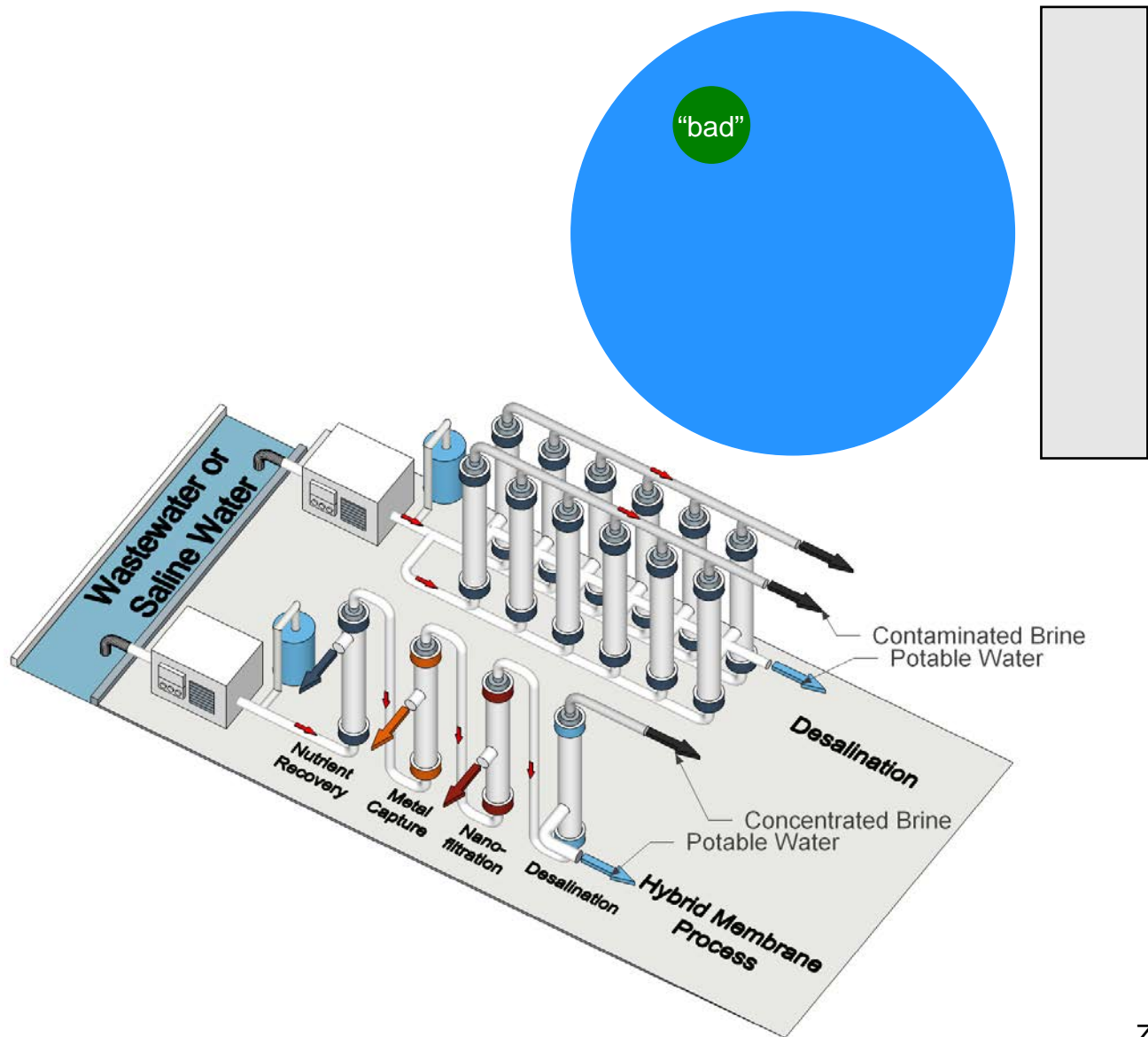
Seawater RO Power Consumption is Reaching Limit

Highly permeable membranes will not greatly reduce energy demand.

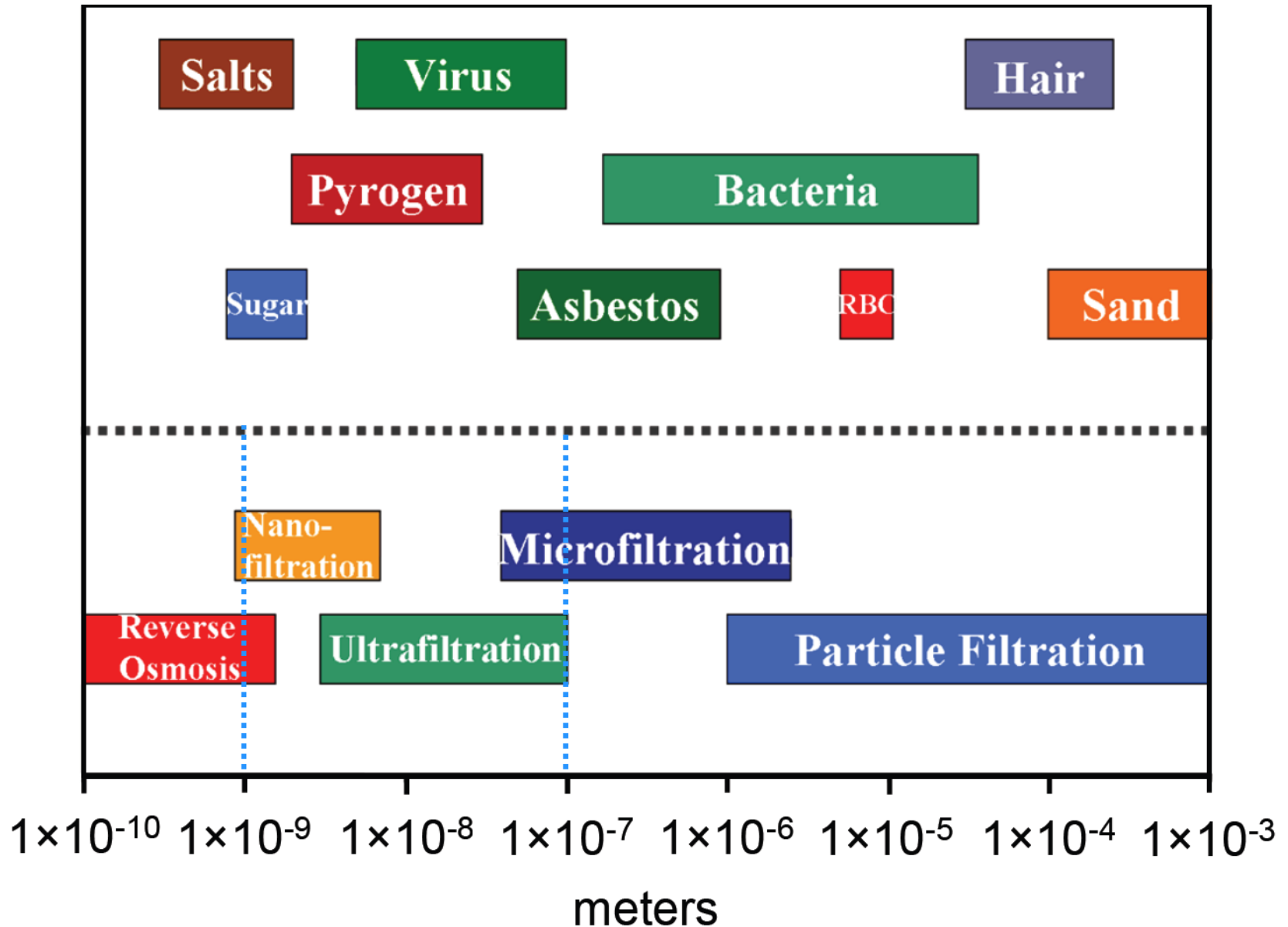


Current Standard for Membrane Separations

Permeate water, retain contaminants; produce potable water

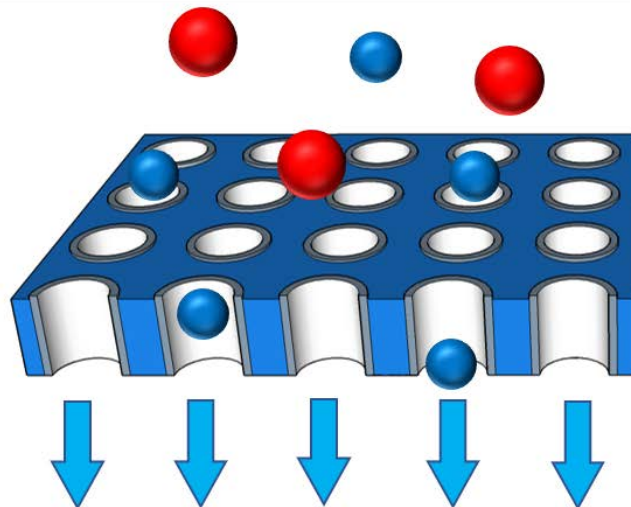
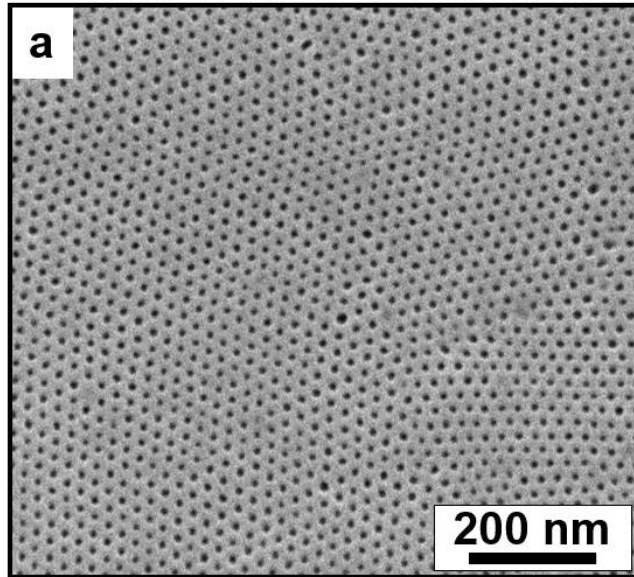


Membrane Separations Are Versatile

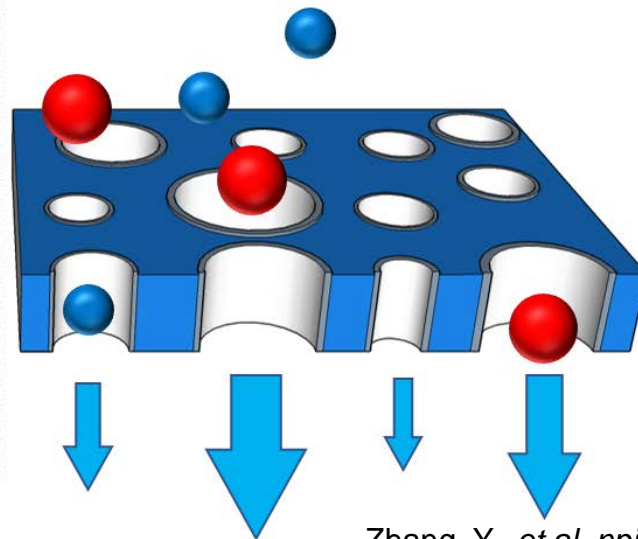
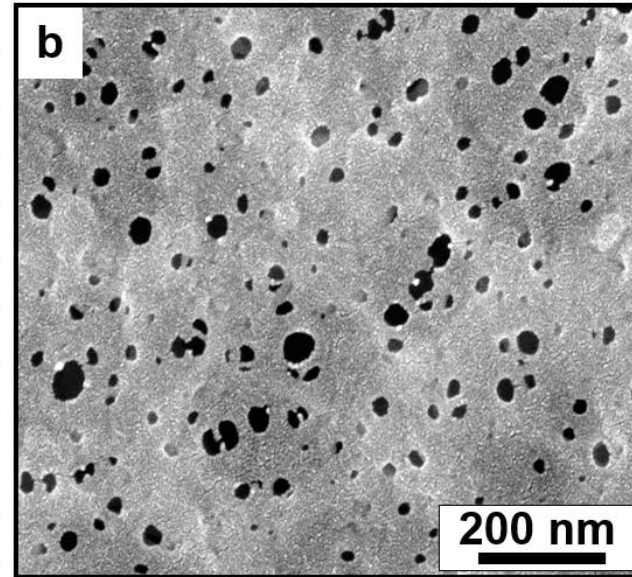


Size-Selective Filtration Membranes

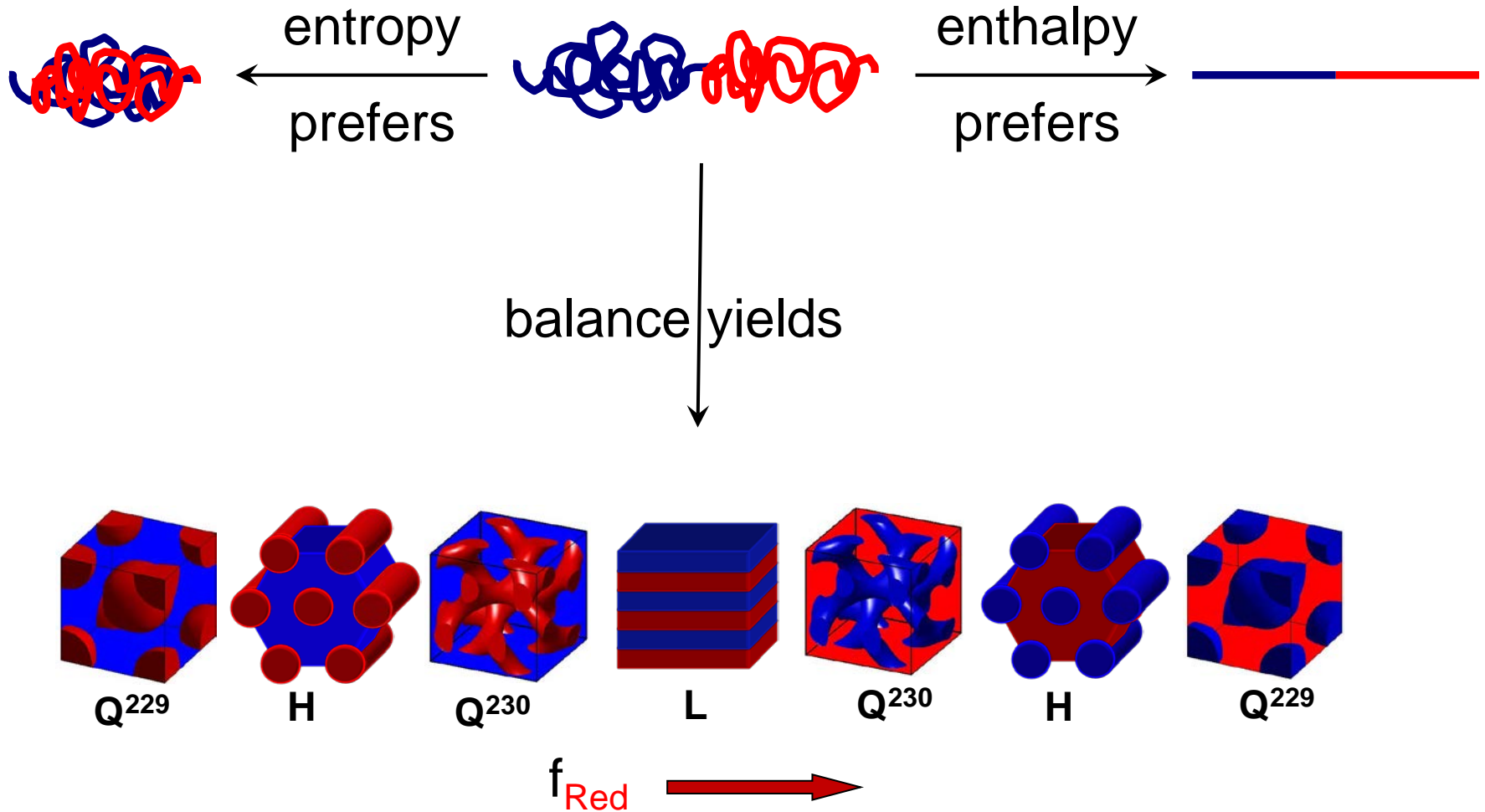
Block Polymer



Phase Inversion



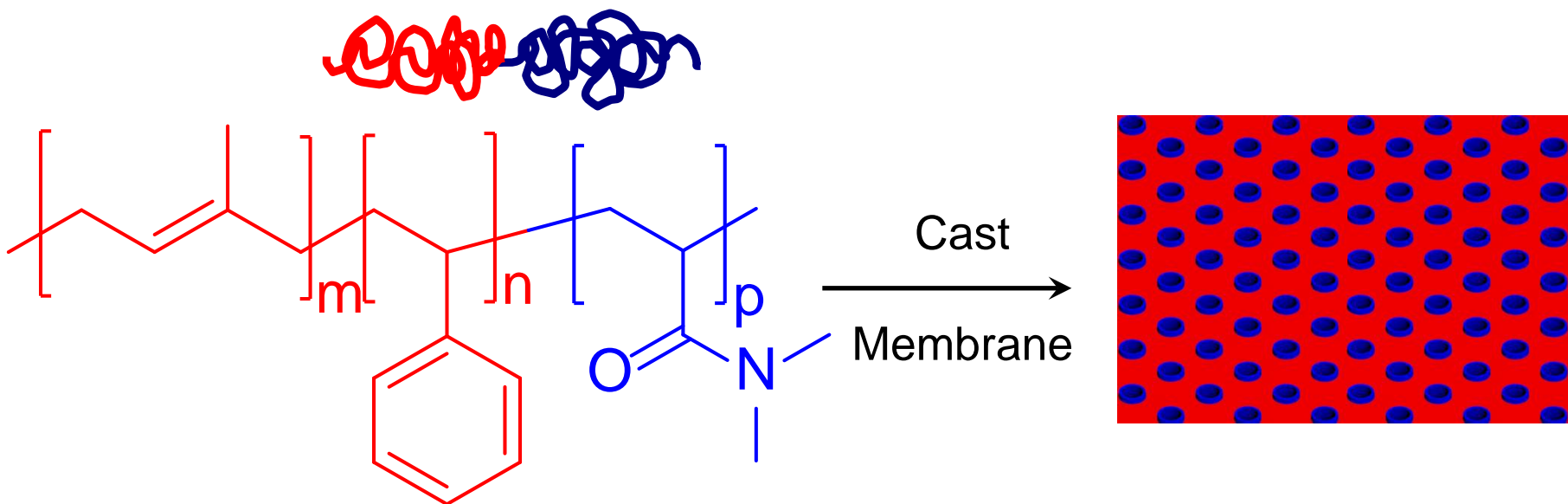
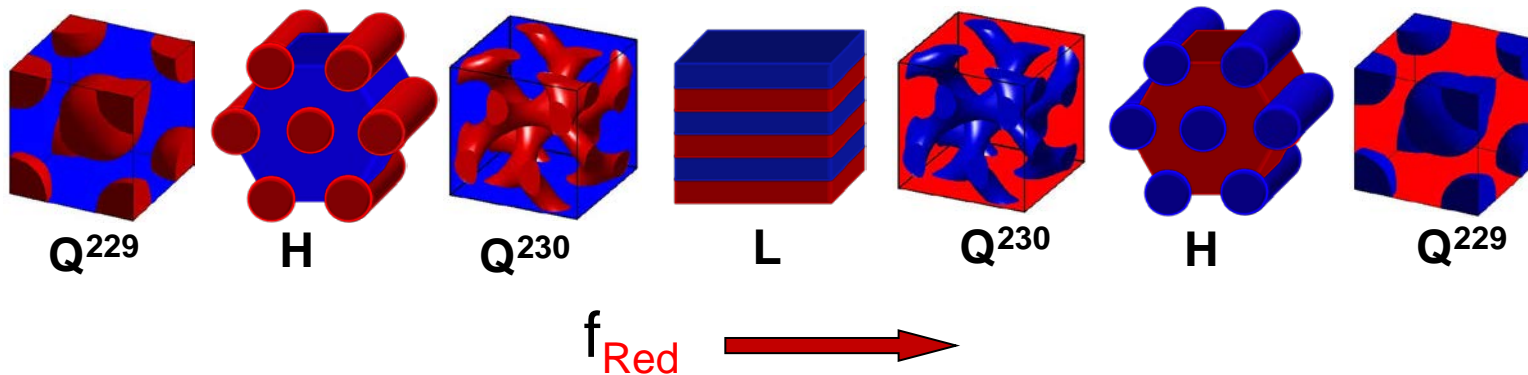
A Versatile Platform: Self-Assembled Block Polymers



Bates, F. S.; Fredrickson, G. H., *Phys. Today* **1999**, *52* (2), 32-38.

Cochran, E. W. *et al. Macromolecules* **2006**, *39*, 2449.

Synthetic Control Used to Target Morphology



Bates, F. S.; Fredrickson, G. H., *Phys. Today* **1999**, *52* (2), 32-38.

Cochran, E. W. *et al. Macromolecules* **2006**, *39*, 2449.

Mulvenna, R. M. *et al. Journal of Membrane Science*, **2014**, *470*, 246-256.

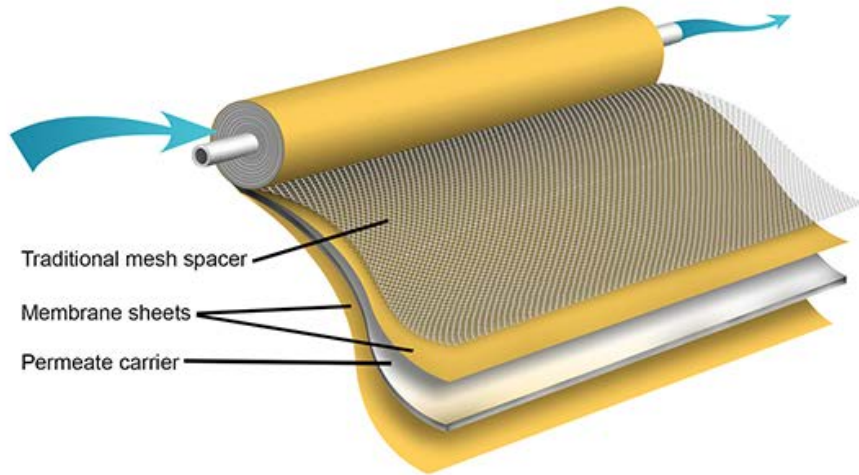
Current Standard for Membrane Separation Processes

Minneapolis Ultrafiltration Plant produces 70 MGD of freshwater using 1.7×10^6 ft² operating at 30-40 psi.



Modules Seek to Increase Membrane Area per Volume

Spiral wound configuration: 300 ft²/ft³



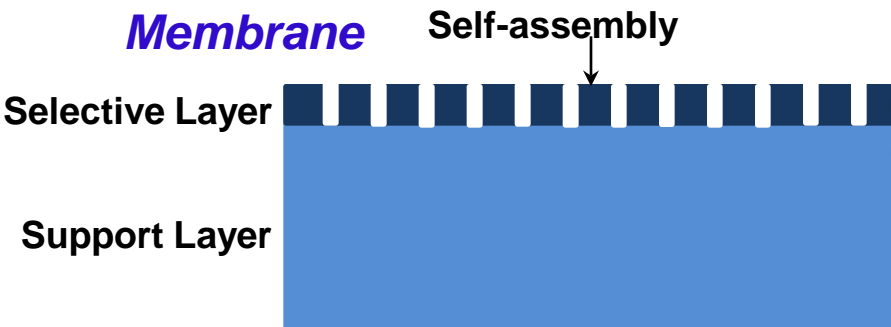
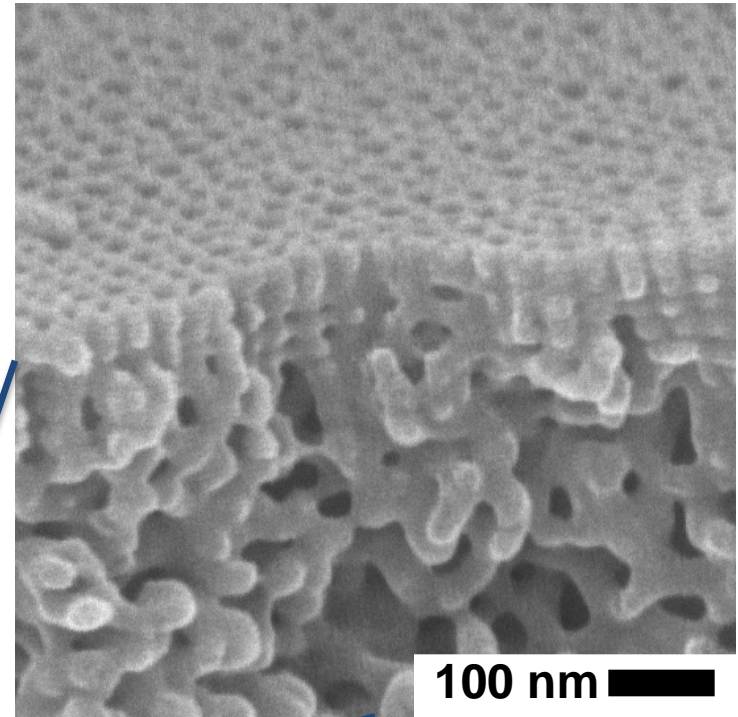
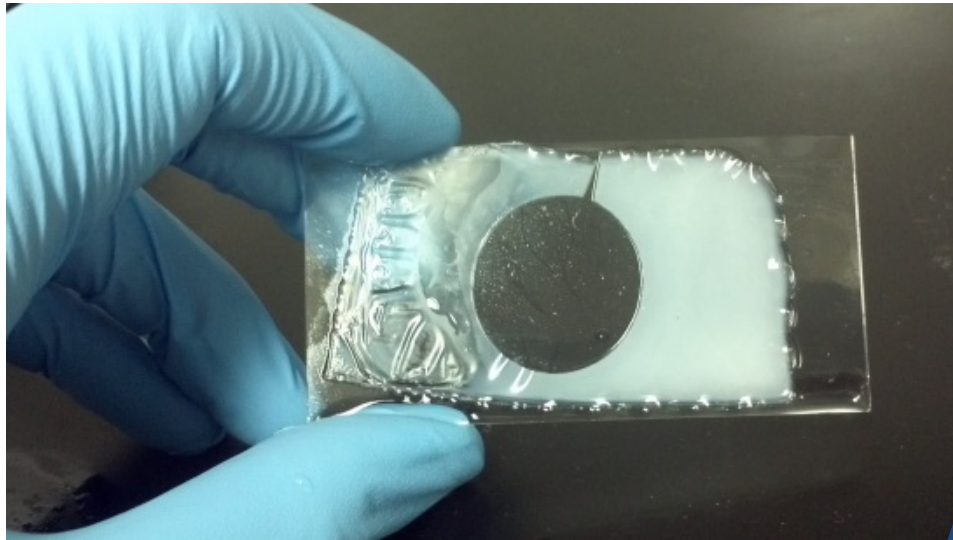
Membranes are Cast Using a NIPS Process

NIPS - Non-solvent Induced Phase Separation



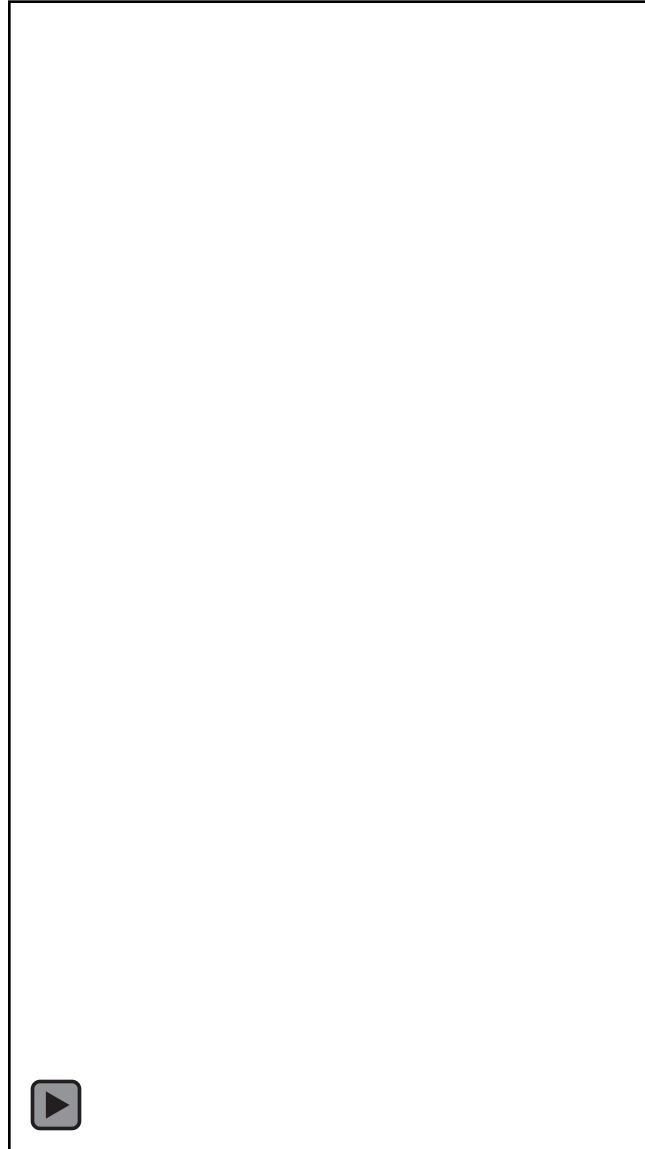
Membranes are Cast Using a SNIPS Process

SNIPS - Self-assembly and Non-solvent Induced Phase Separation



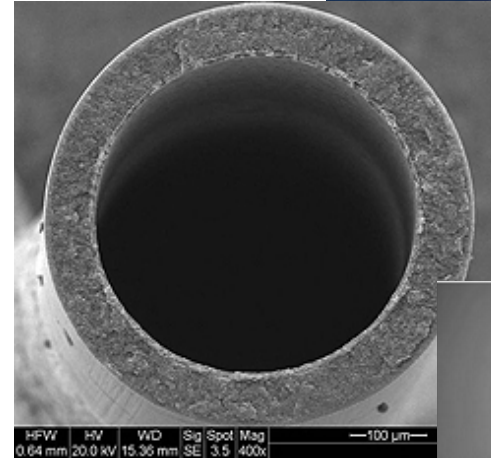
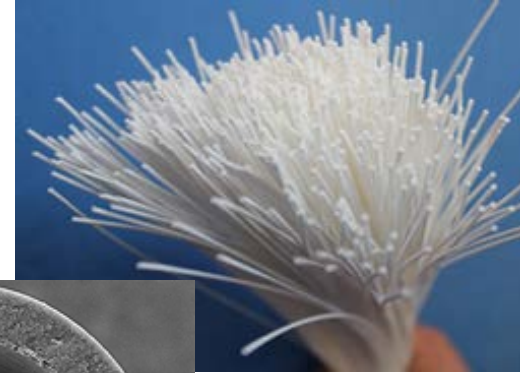
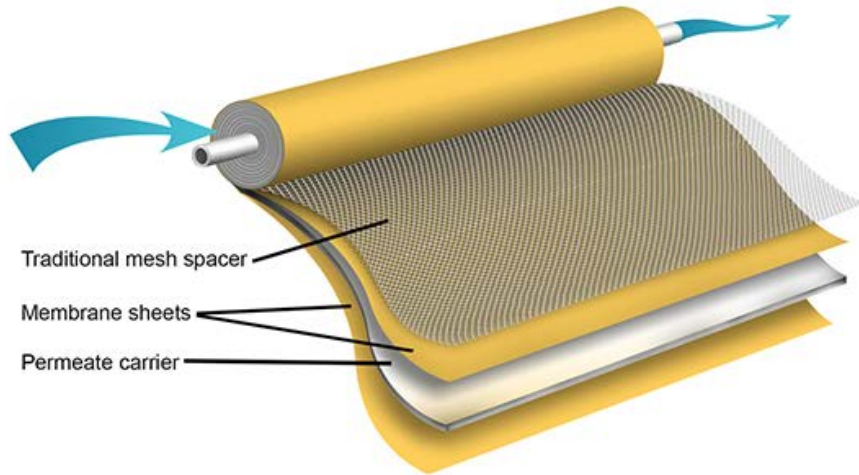
Membranes are Cast Using a SNIPS Process

SNIPS - Self-assembly and Non-solvent Induced Phase Separation

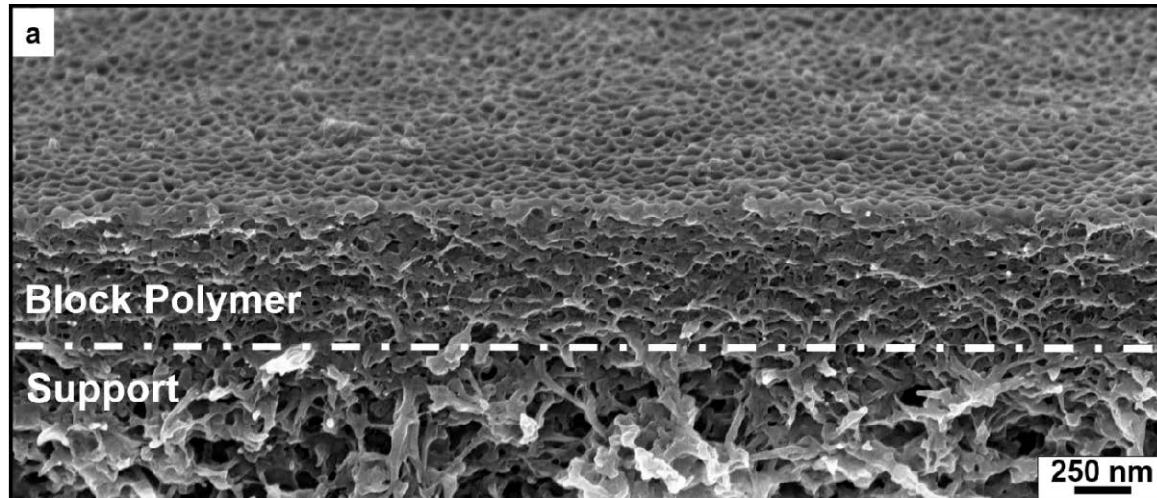
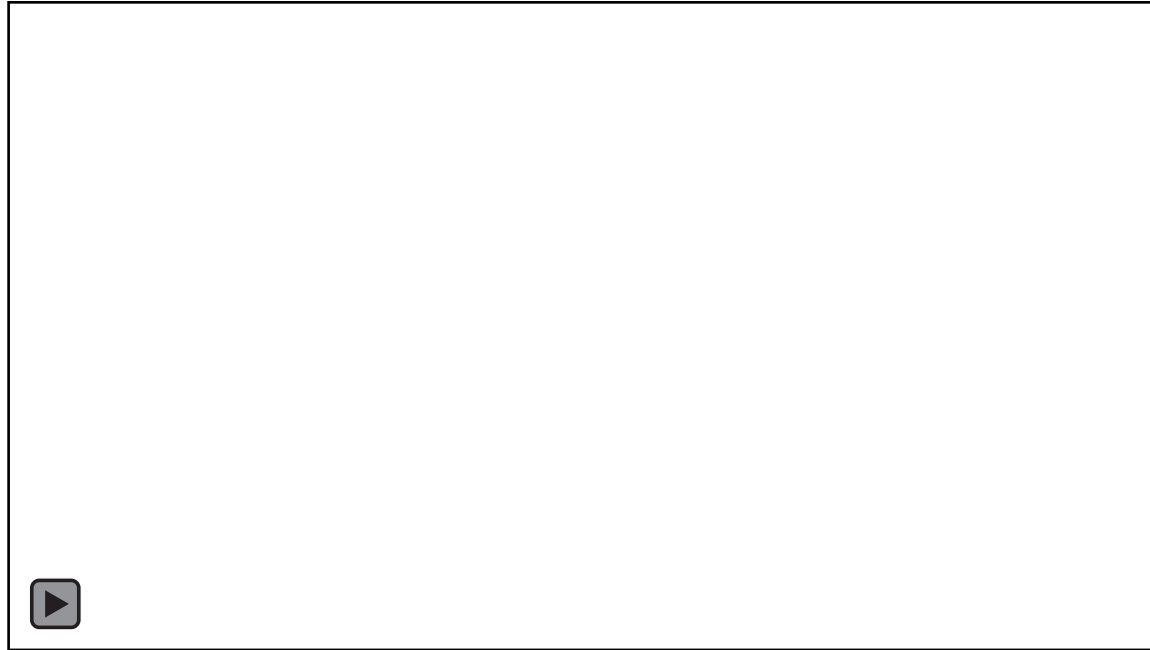


Modules Seek to Increase Membrane Area per Volume

Spiral wound configuration: 300 ft²/ft³ Hollow fiber configuration: 4000 ft²/ft³



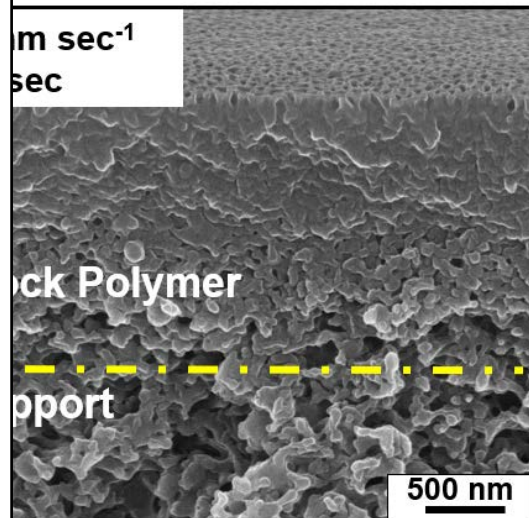
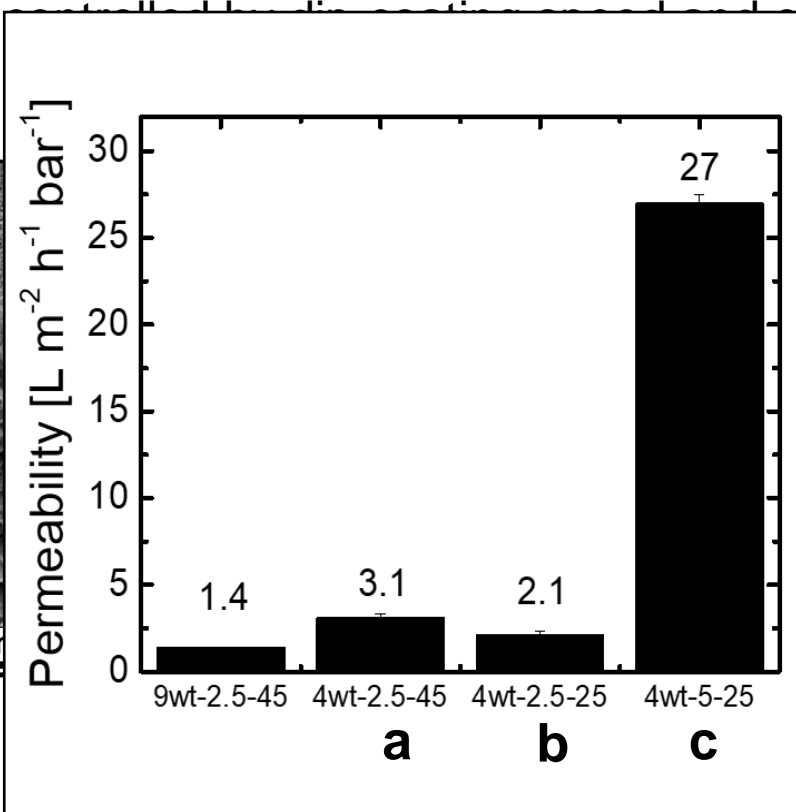
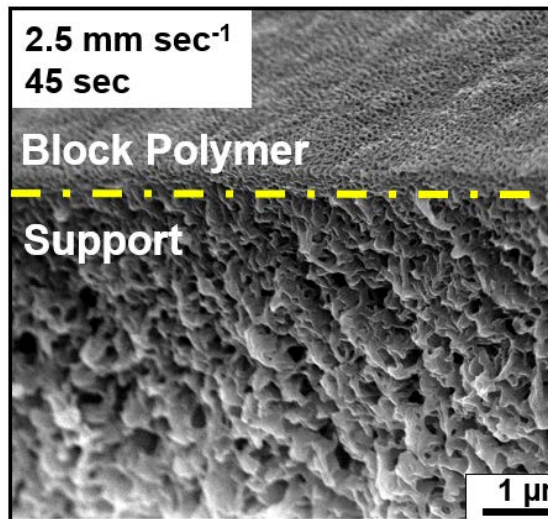
Combining the SNIPS Process with Dip-Coating



Process Control Can be Used to Tune Permeability, L_p

Membrane Architecture is

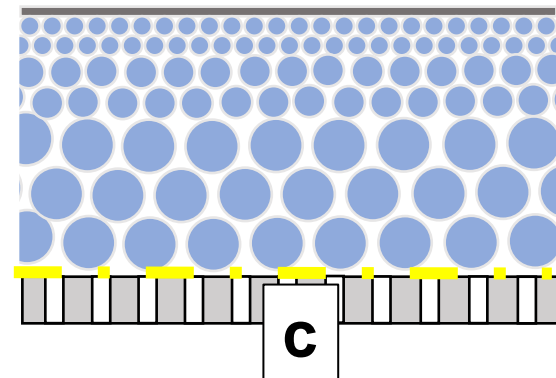
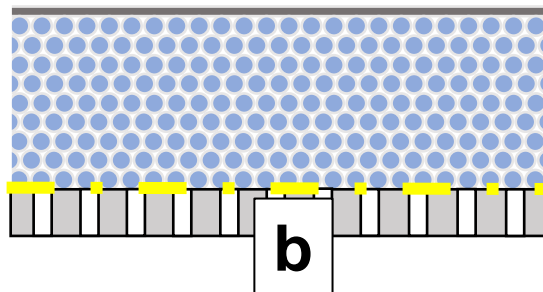
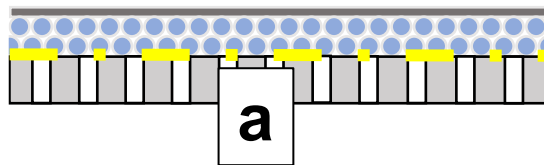
vaporation time.



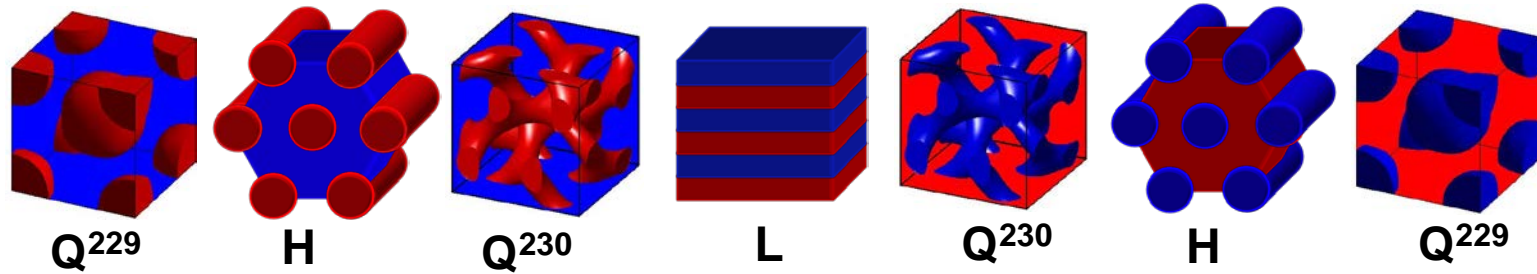
- ❖ Asymmetric
- ❖ ~1.5 μm -thick

- ❖ Symmetric
- ❖ ~200 nm-thick

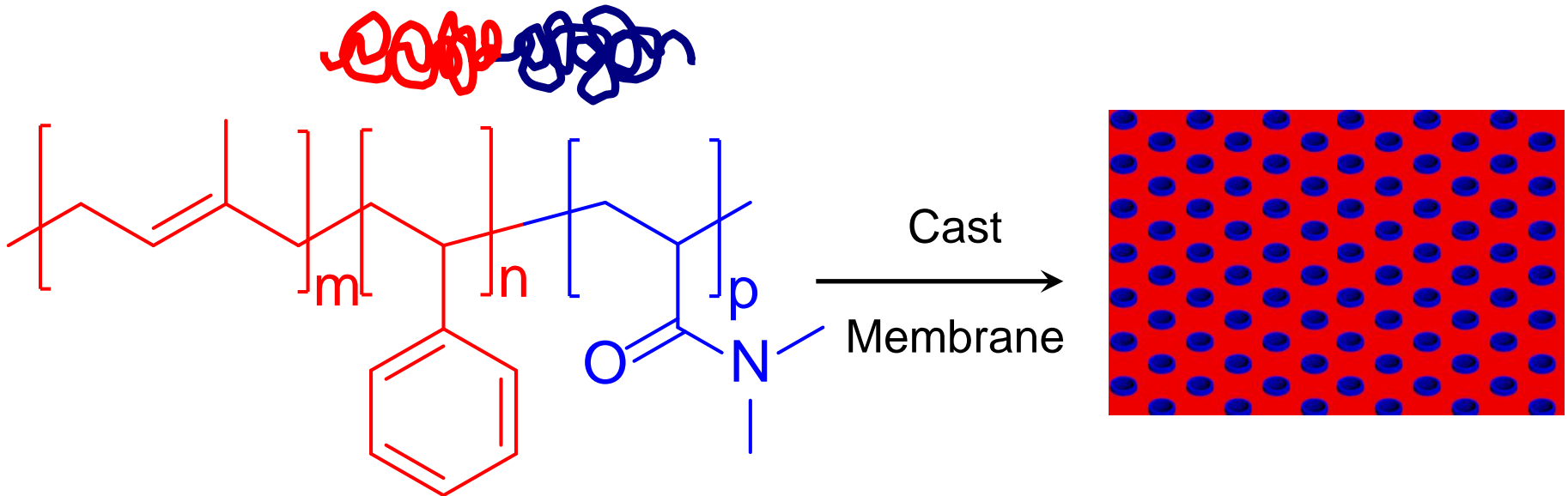
- ❖ Symmetric
- ❖ ~1 μm -thick



Synthetic Control Can be Used to Tune Pore Size



f_{Red} \longrightarrow



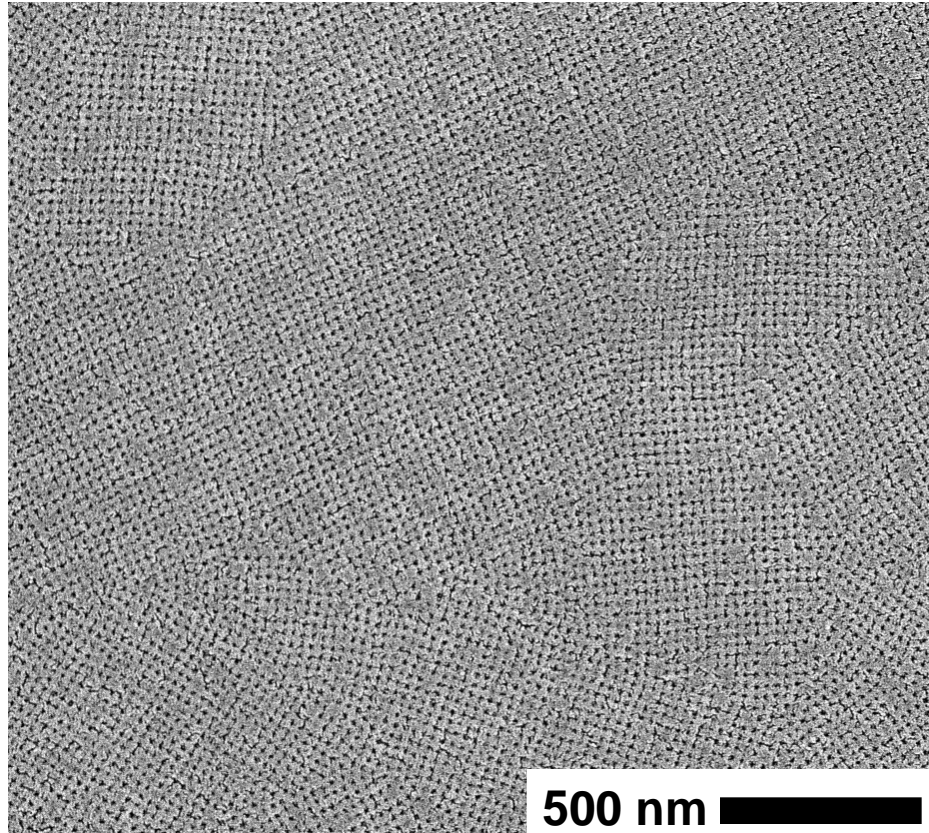
Bates, F. S.; Fredrickson, G. H., *Phys. Today* **1999**, *52* (2), 32-38.

Cochran, E. W. *et al. Macromolecules* **2006**, *39*, 2449.

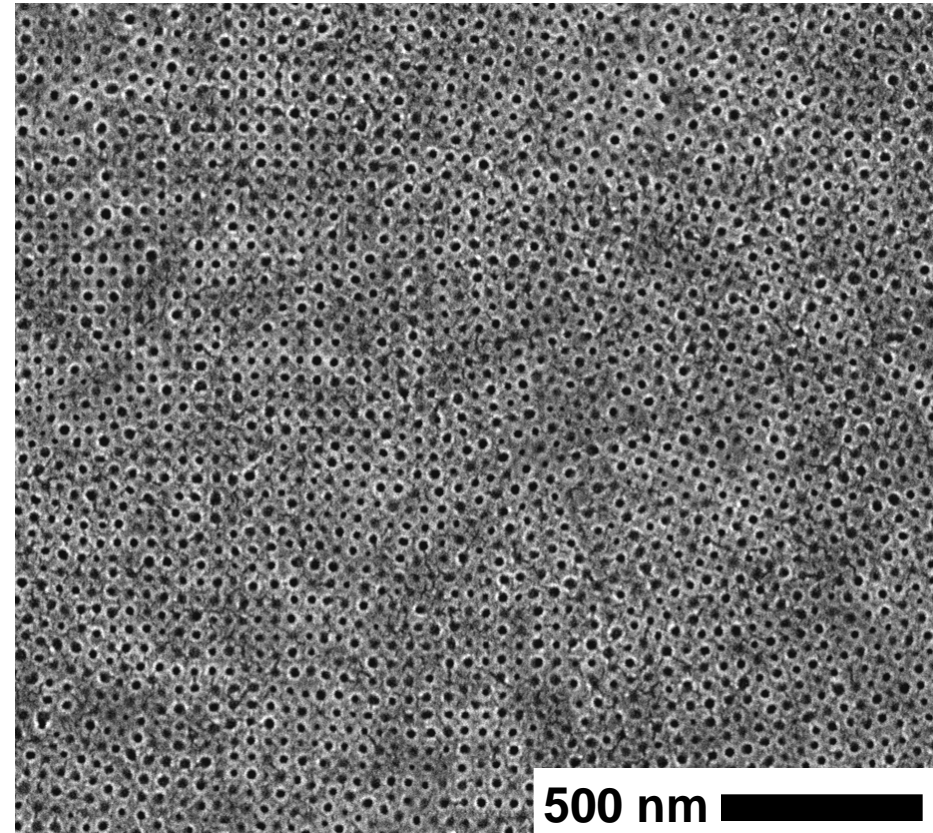
Mulvenna, R. M. *et al. Journal of Membrane Science*, **2014**, *470*, 246-256.

Synthetic Control Can be Used to Tune Pore Size

Overall MW: 43 kDa

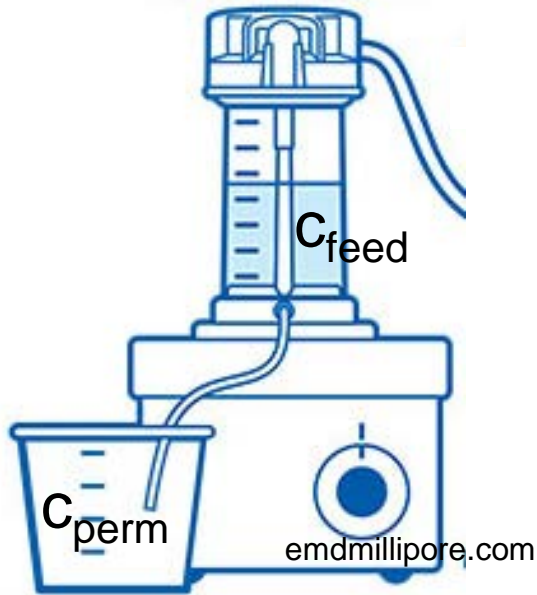


Overall MW: 77 kDa

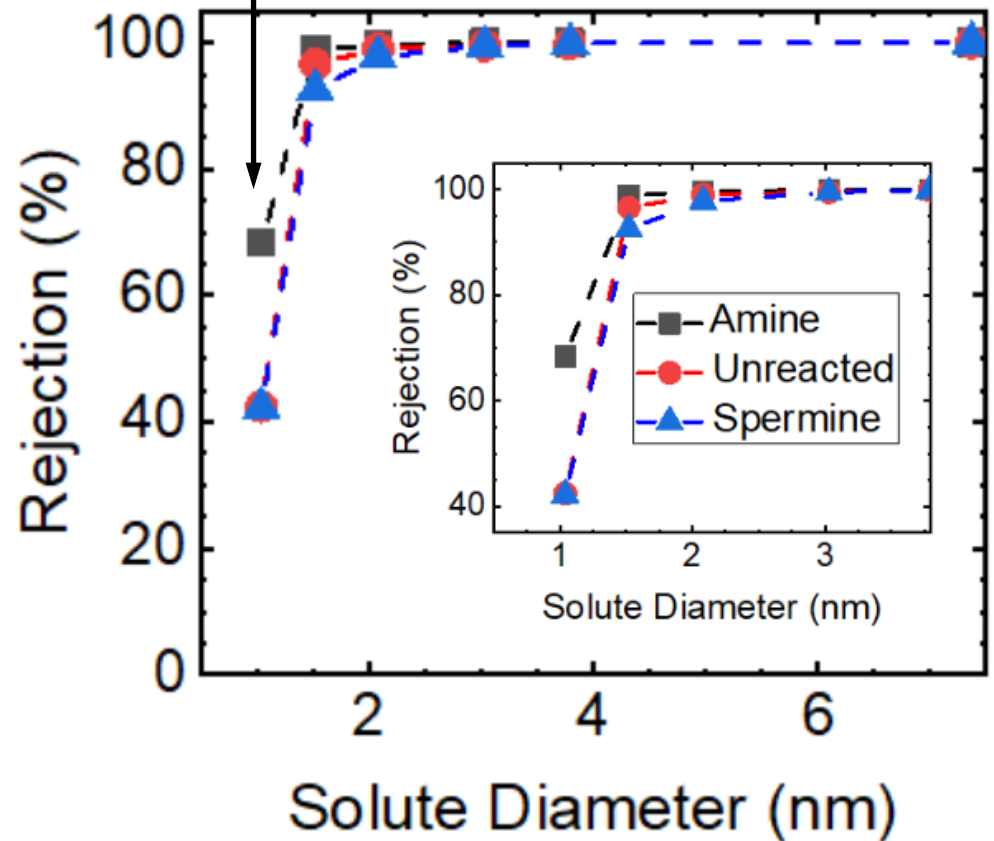


Synthetic Control Can be Used to Tune Pore Size

$$\text{Rejection}(\%) = \left(1 - \frac{C_{perm}}{C_{feed}}\right) \times 100$$



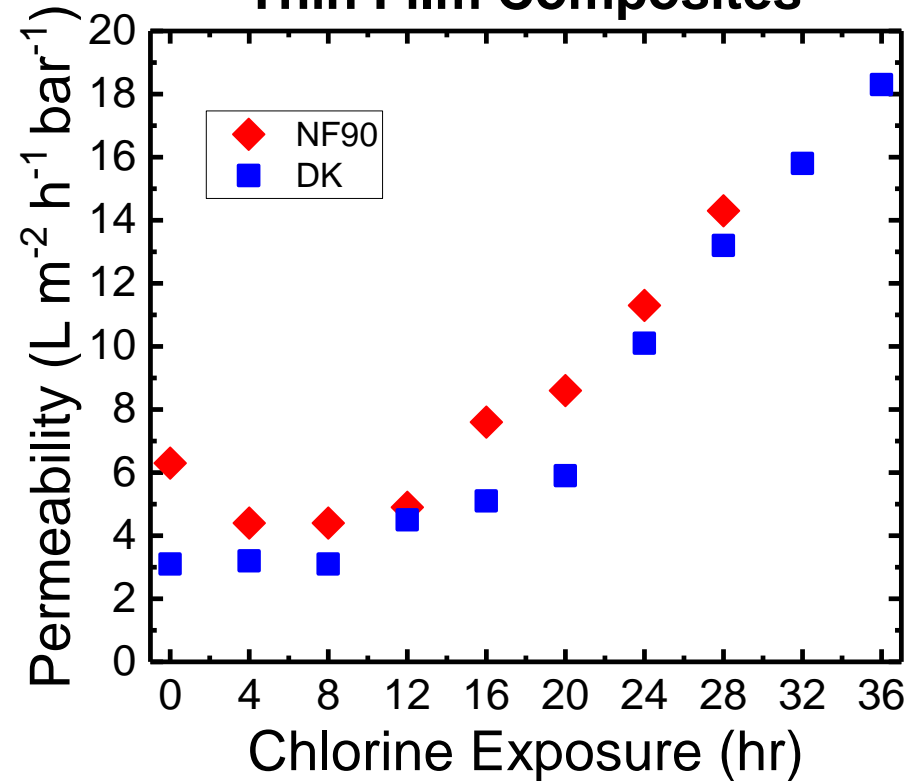
Sucrose: 342 g mol⁻¹



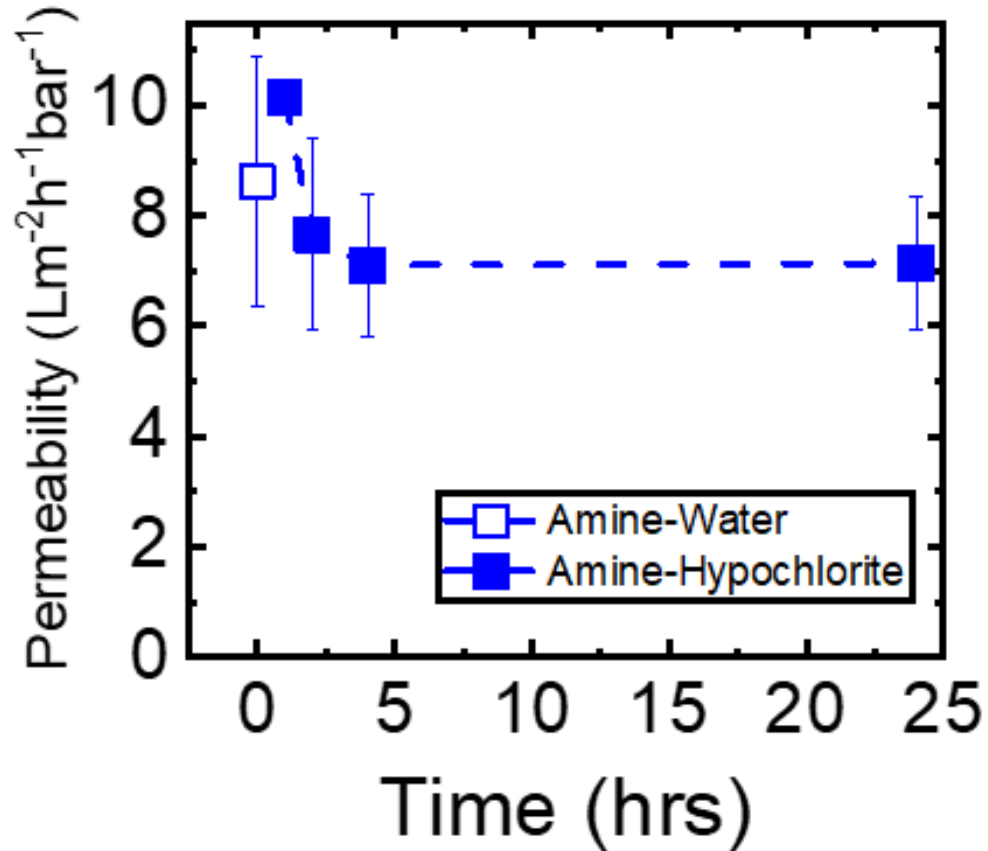
Proper Molecular Design Enhances Chlorine Resistance

Hypochlorite can be dosed into the feed to reduce biofouling

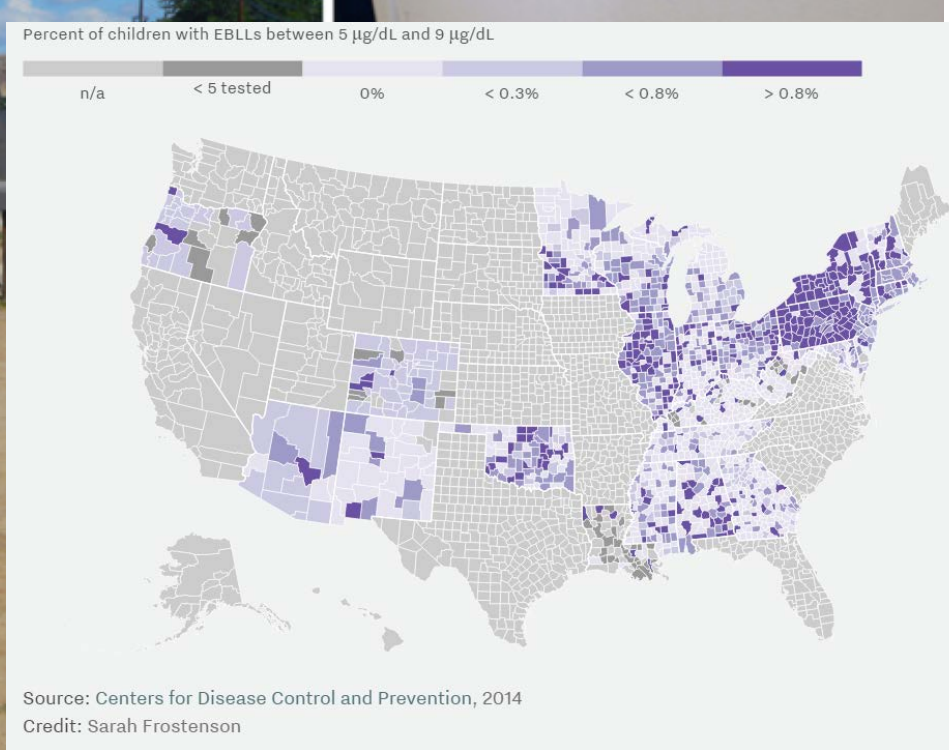
**State-of-the-Art
Thin Film Composites**



**Self-Assembled Copolymer
Membranes**



New Opportunities for Membrane Separations

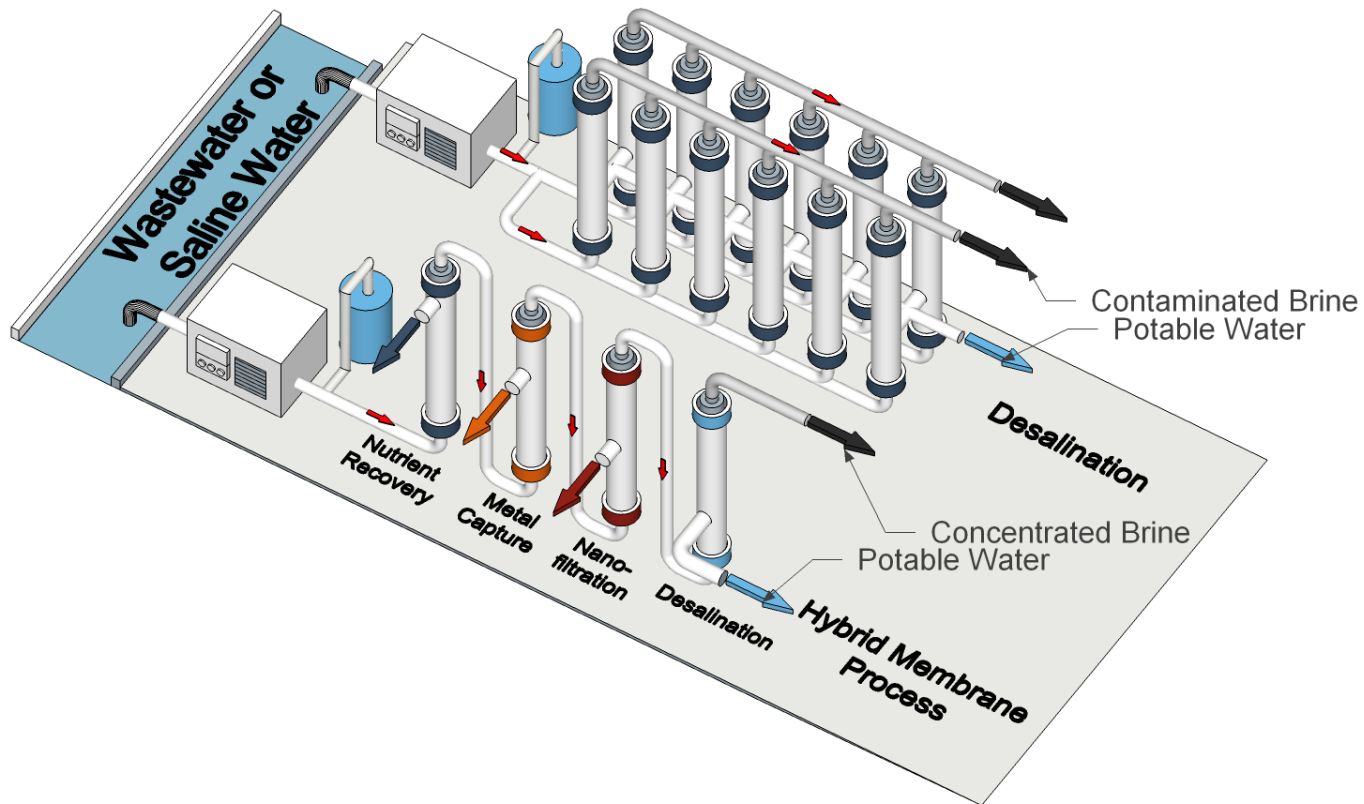


<http://ehatlas.ische.ca/lead/human-impact/health-concerns>

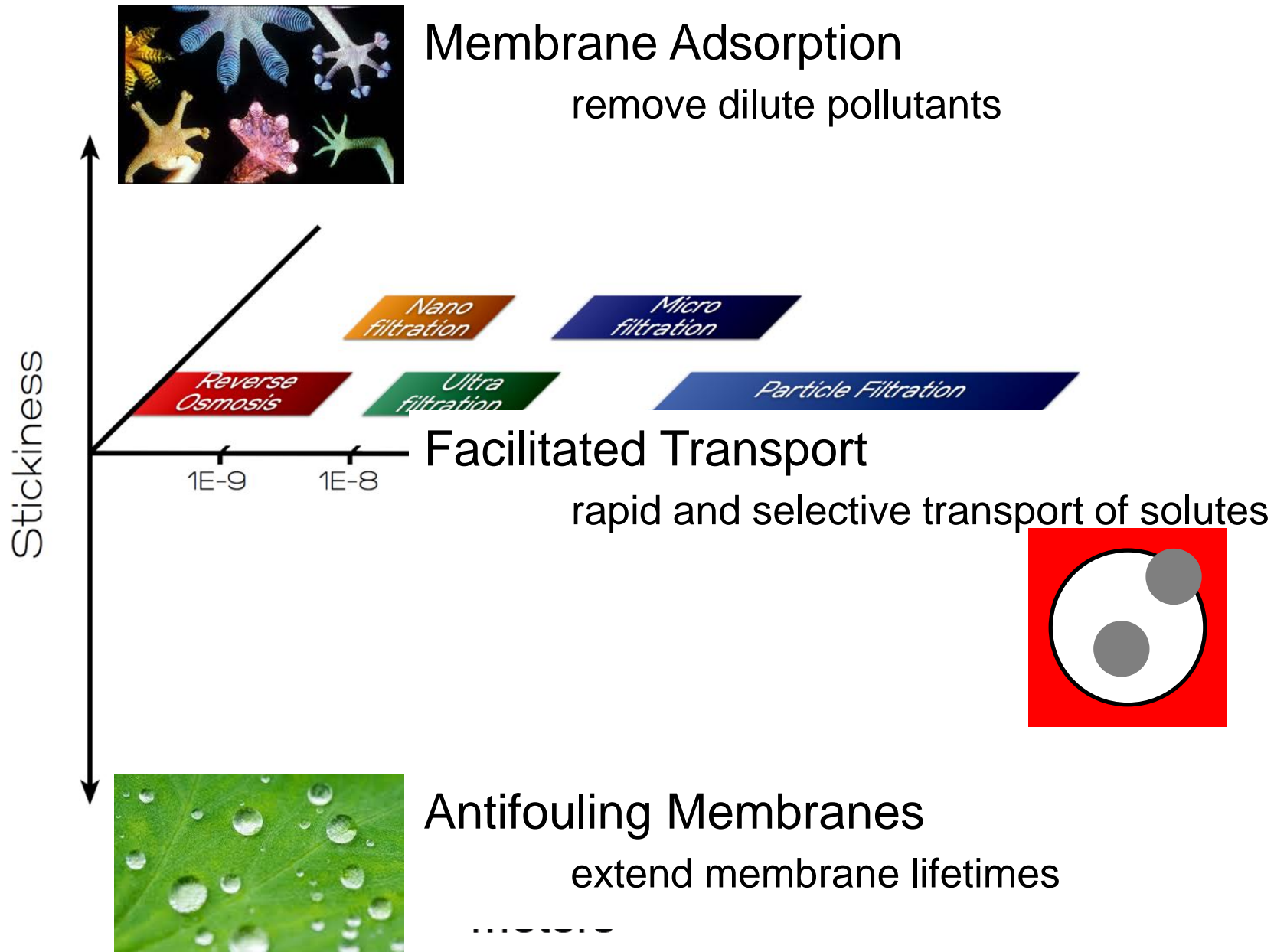
Frostensen, S., "America's lead poisoning problem isn't just in Flint. It's everywhere."
<http://www.vox.com/2016/1/21/10811004/lead-poisoning-cities-us>

New Opportunities for Membrane Separations

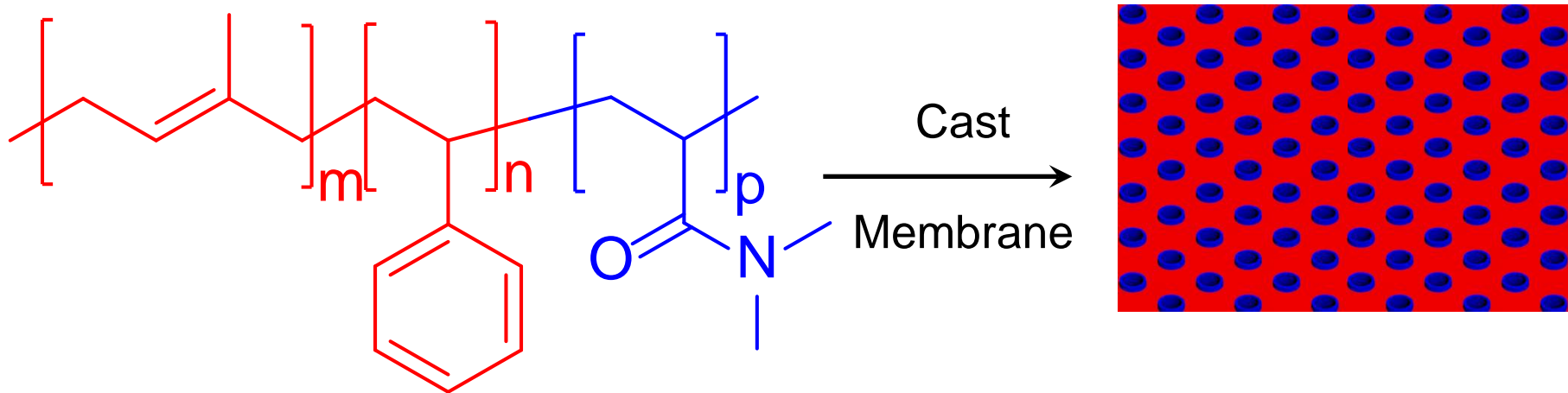
Hybrid processes are needed for municipal and industrial wastewater reuse, resource recovery, and other emerging processes



Functional Membrane Separations Are Versatile

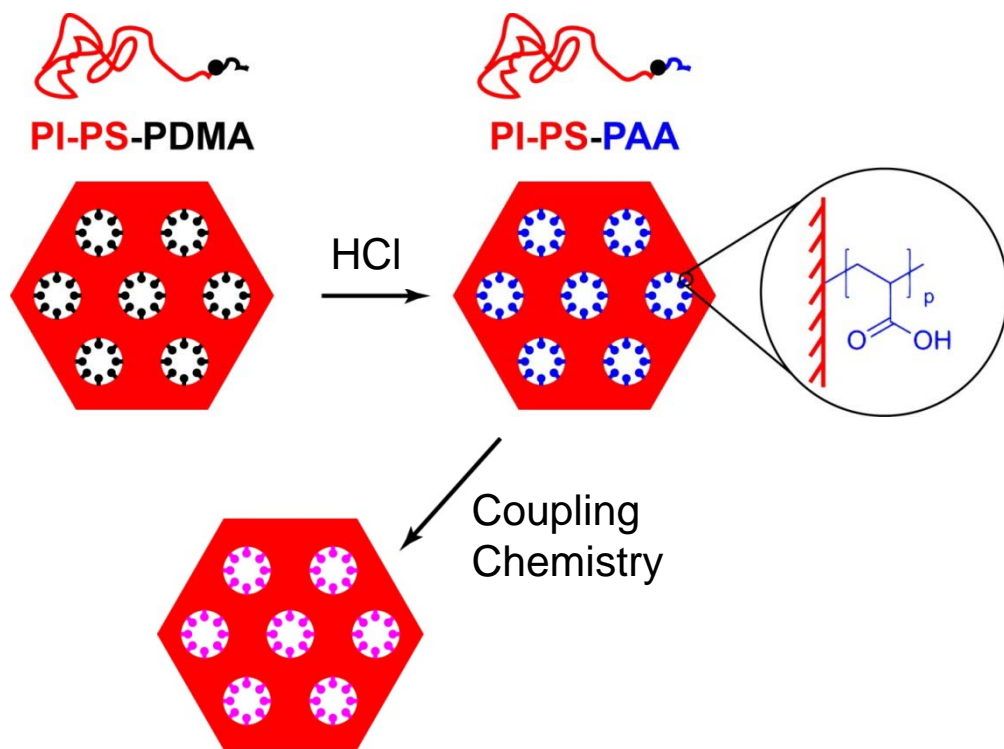


Control of End Block Enables Functionalization

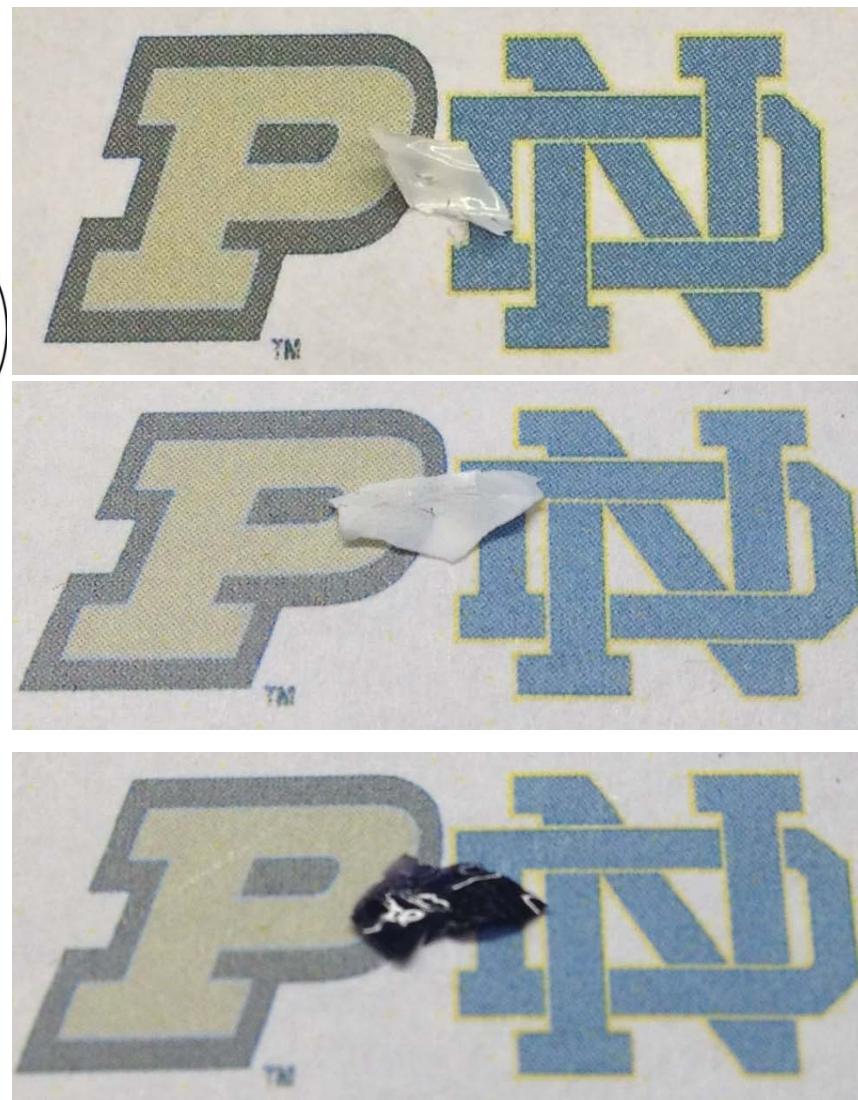
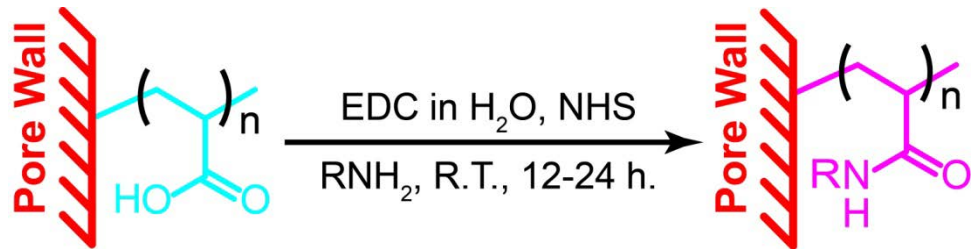


<u>Block</u>	<u>Function</u>
Polyisoprene	Increases Toughness
Polystyrene	Forms matrix
Poly(Dimethylacrylamide)	Readily functionalized for specific applications

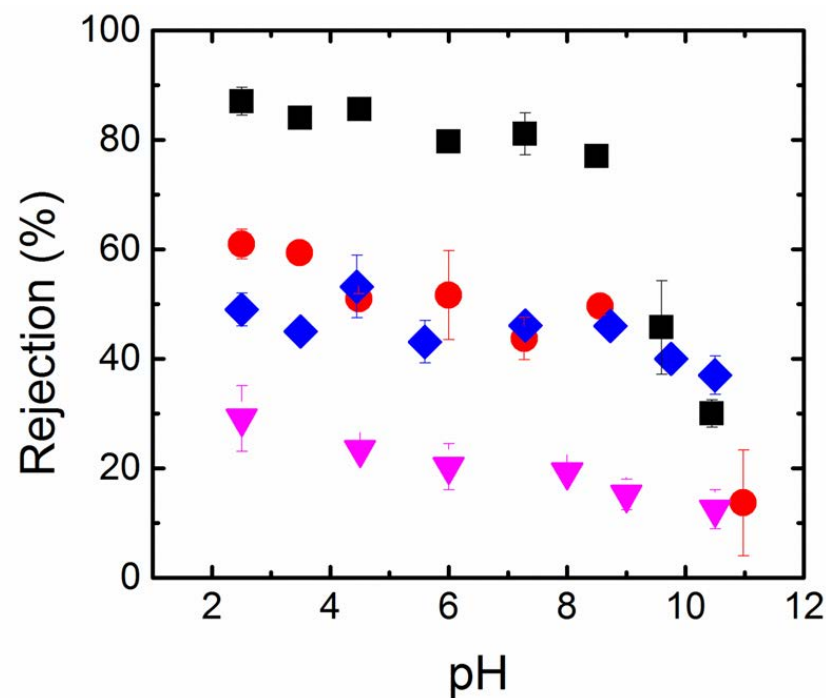
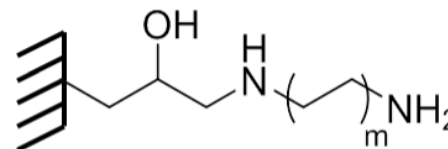
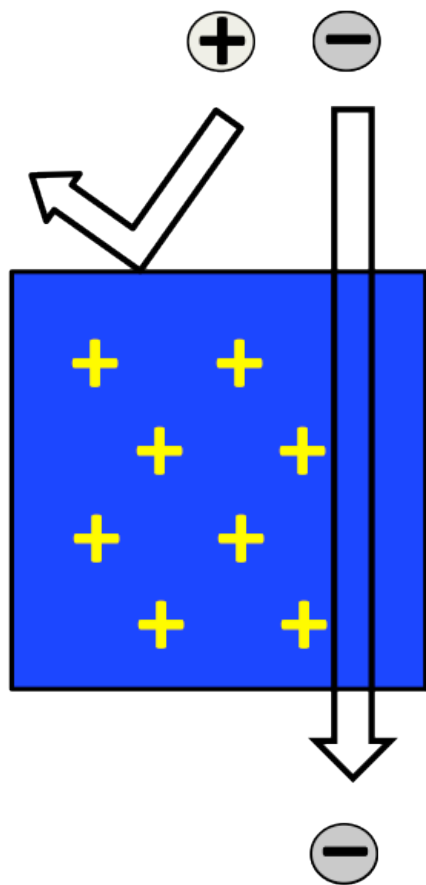
Control of End Block Enables Functionalization



Pore walls can be reacted to a variety of functional groups (pink dots).

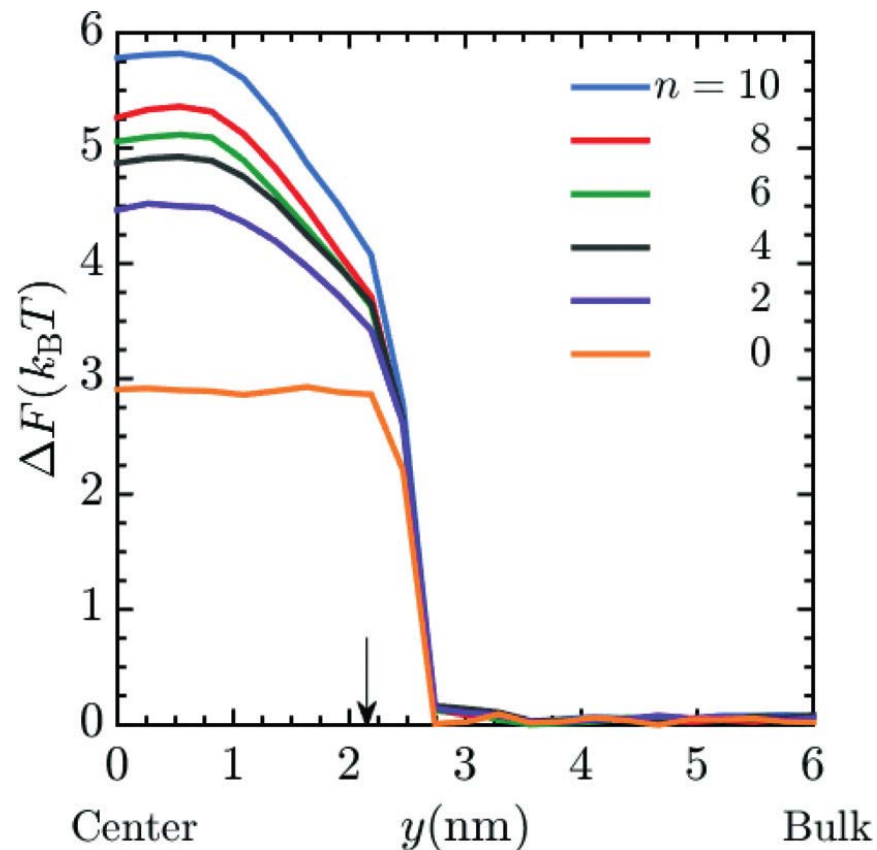
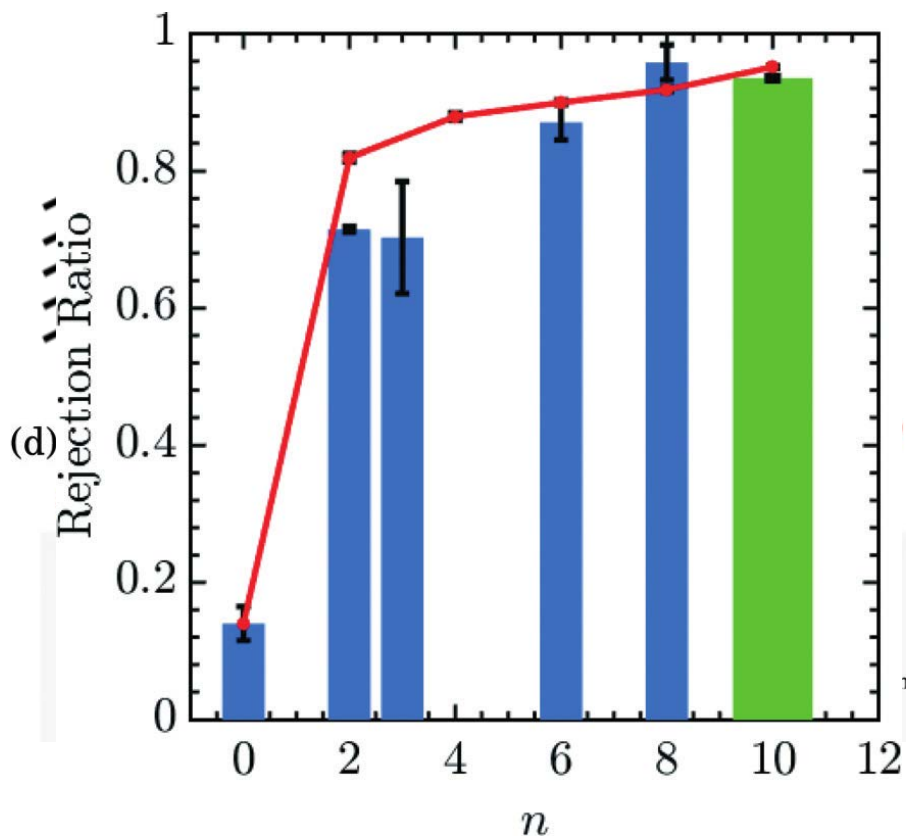


1. Charge-Functionalized Membranes Reject Dissolved Ions



■ MgCl₂ ● NaCl ◆ MgSO₄ ▼ Na₂SO₄

1. Molecular Simulations Capture Essential Phenomena

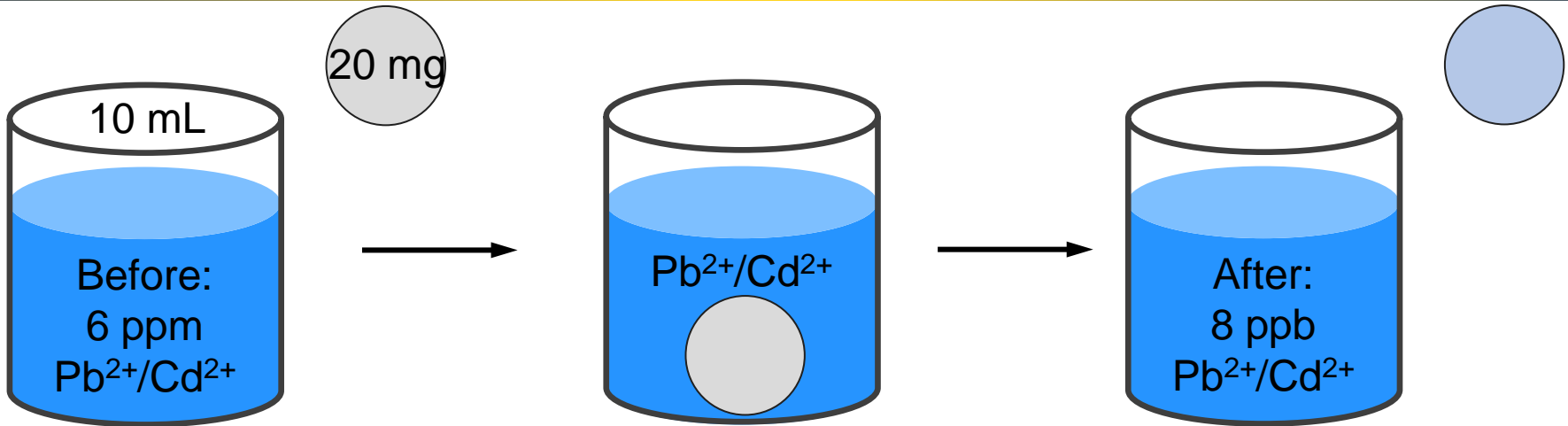


$$R = 1 - \alpha e^{-\beta \Delta F}$$

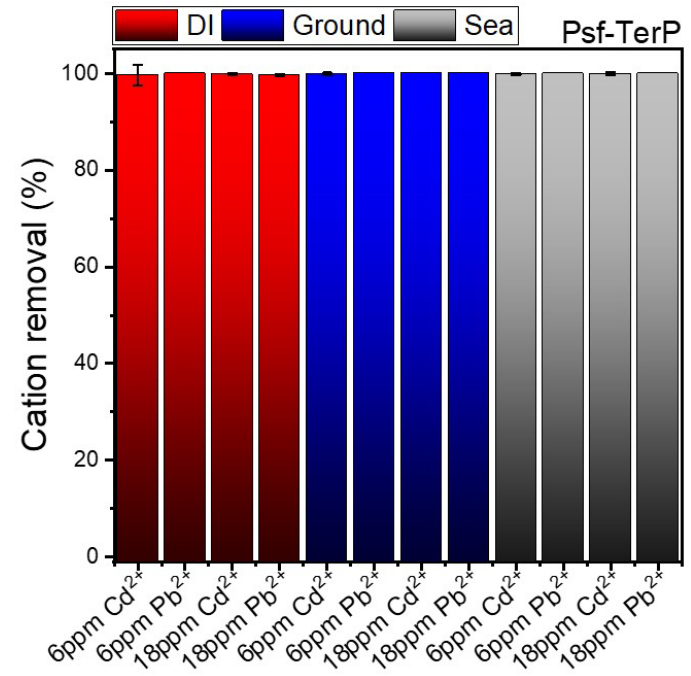
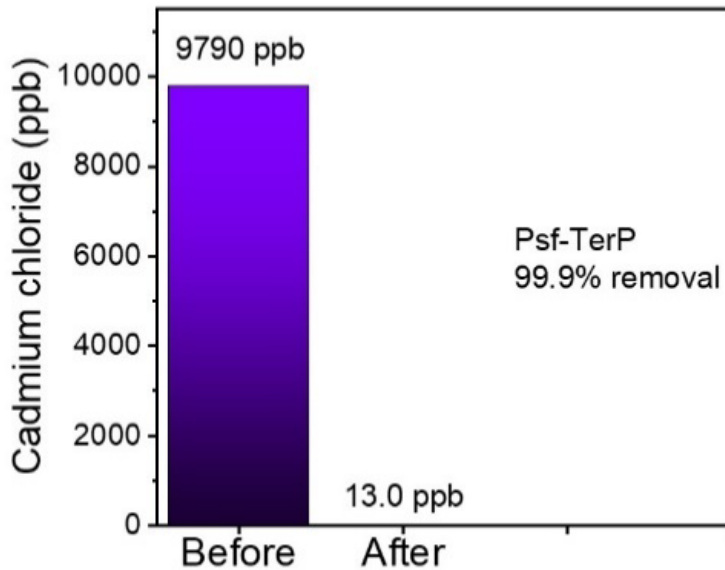
2. Membrane Sorbents Capture and Release Solutes Quickly



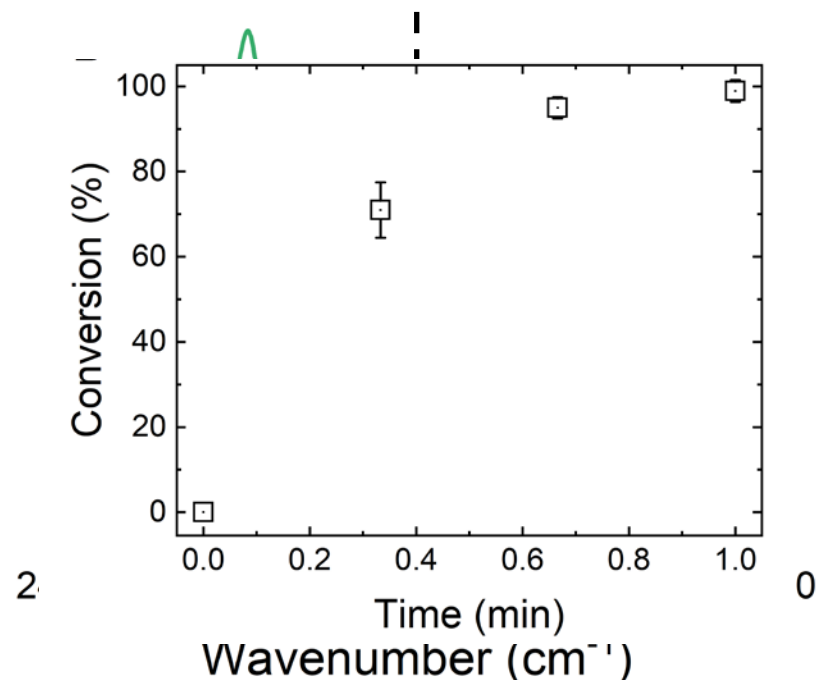
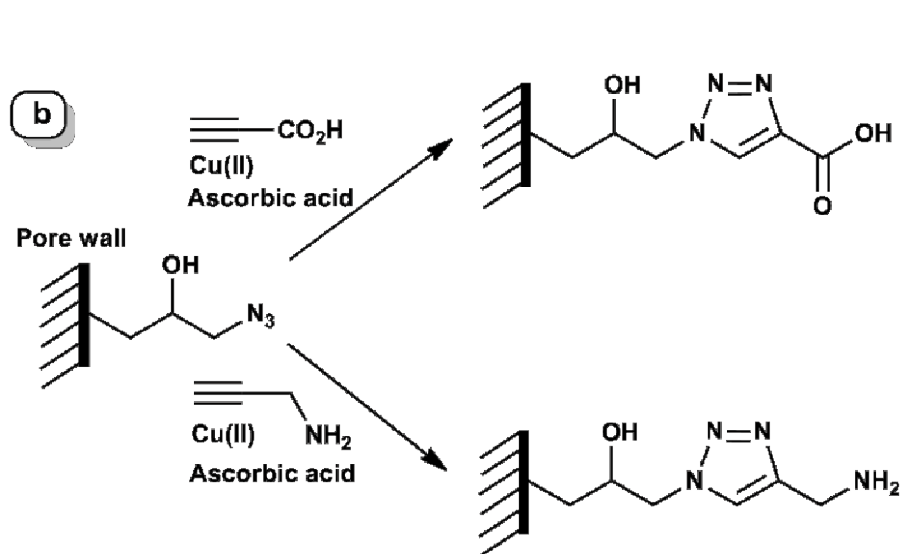
2. Resilient Removal of Heavy Metal Ion Contamination



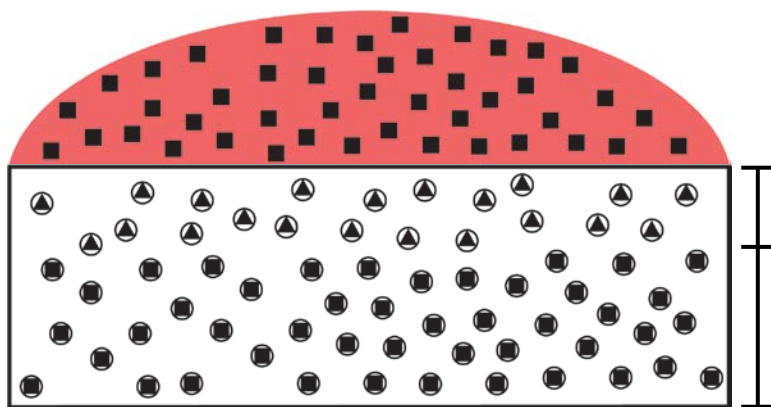
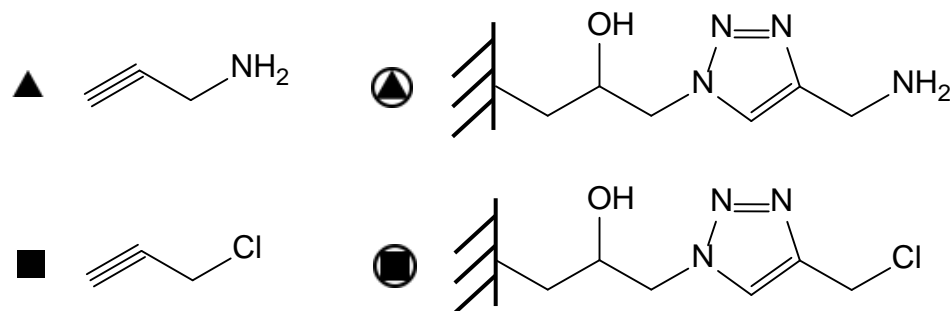
Groundwater: 0.40 mM Mg^{2+} , 1.3 mM Ca^{2+} , 17 mM Na^{+} , 0.25 mM K^{+}
 Seawater: 54.5 mM Mg^{2+} , 10.5 mM Ca^{2+} , 480 mM Na^{+} , 10.2 mM K^{+}



4. Controlling the Deposition of Alkyne-Terminated Reactants

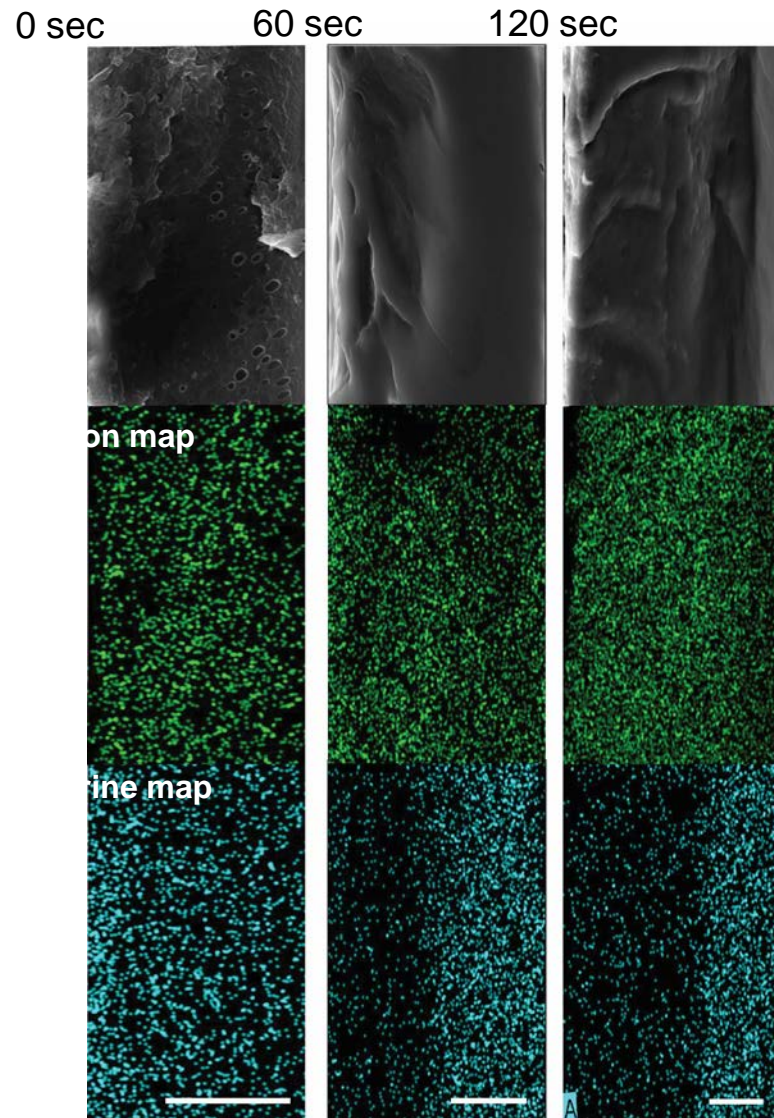


4. Toward Multifunctional Membranes



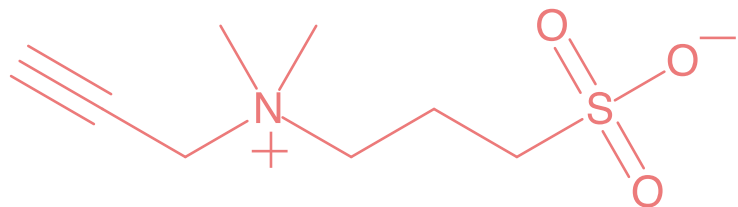
cross-sectional micrographs

* Scale bar is 10 μm

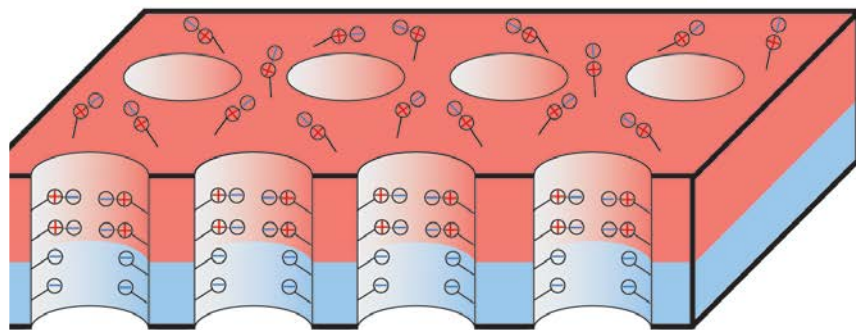
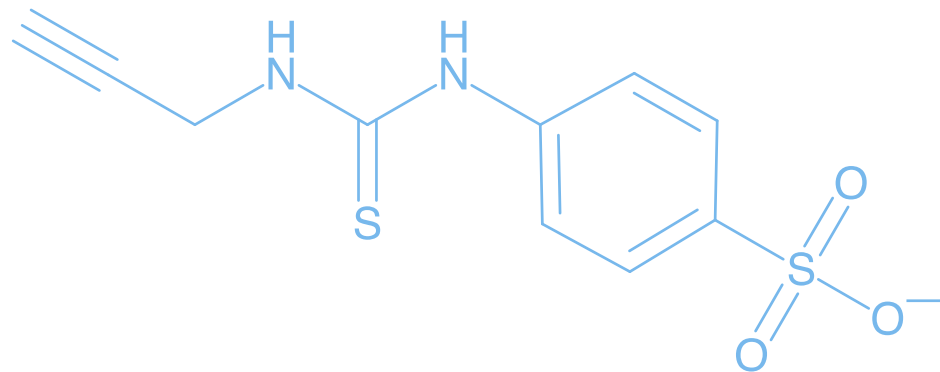


4. Antifouling, Valence-selective Dual-functional Membranes

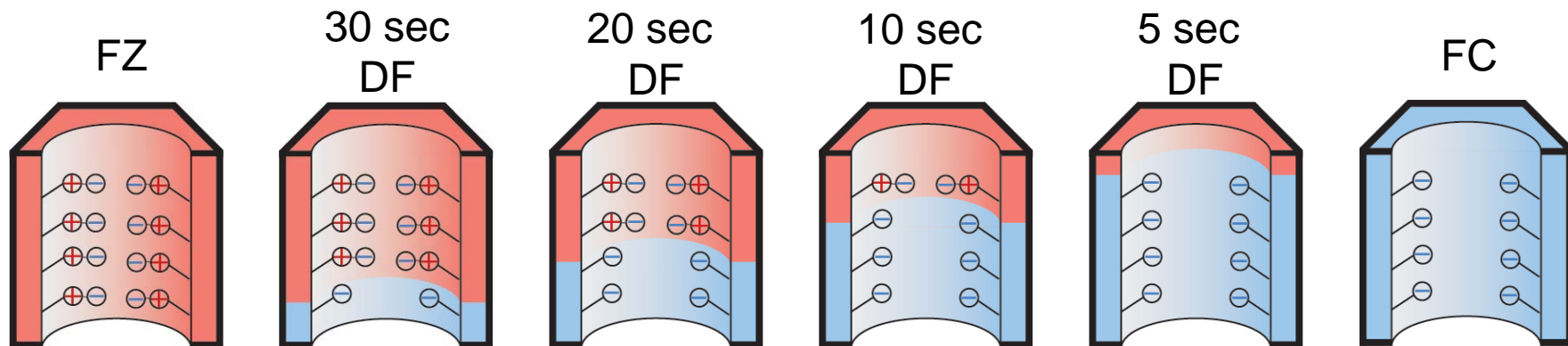
Antifouling, Zwitterionic



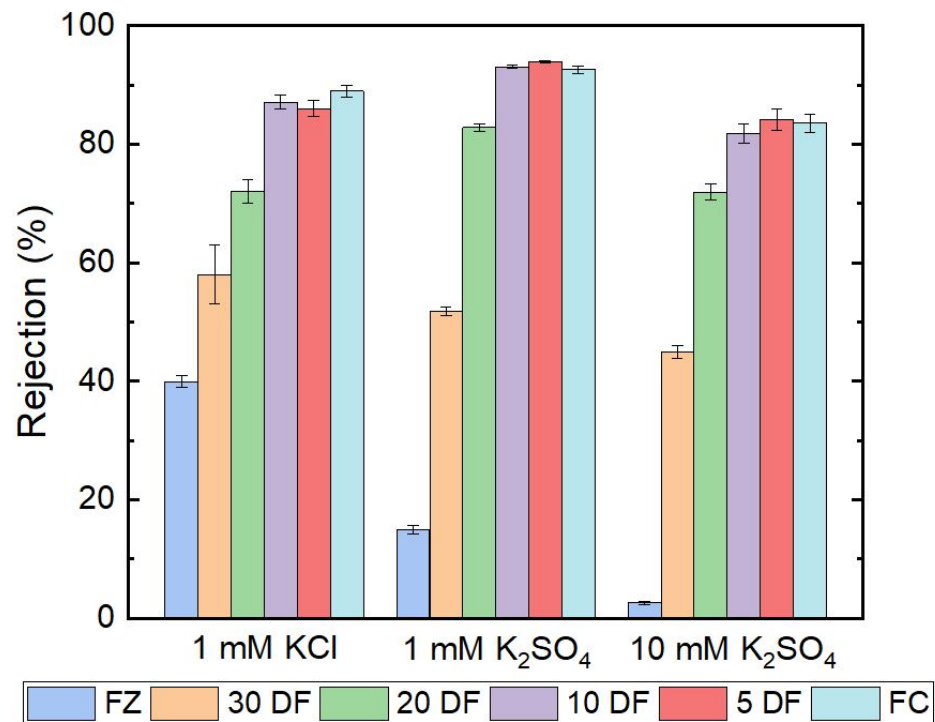
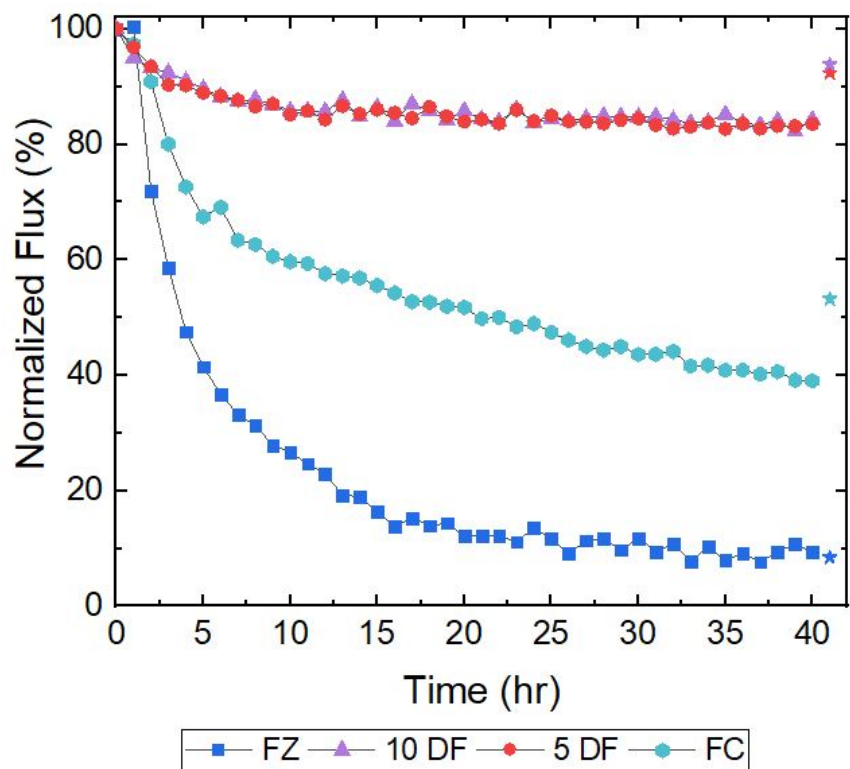
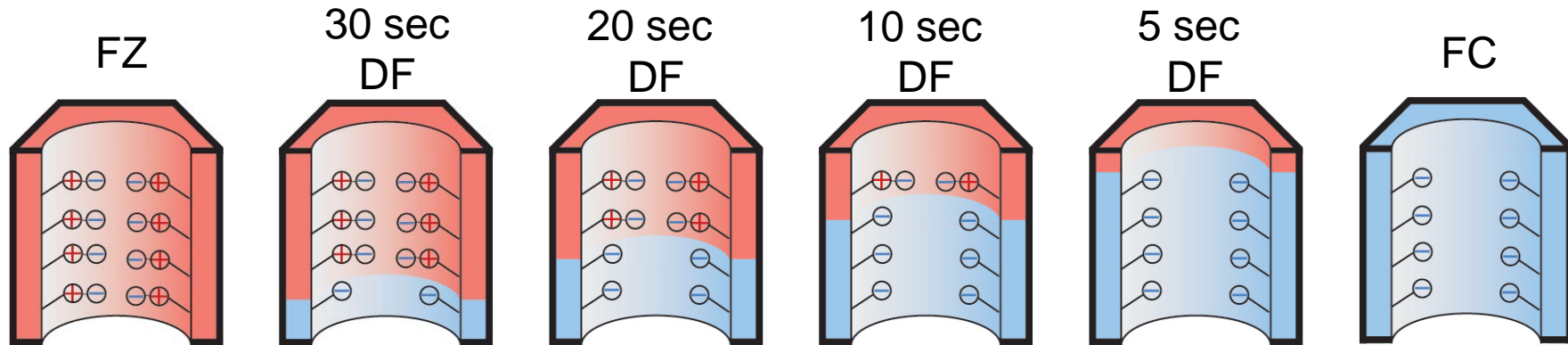
Valence-selective, Sulfonate



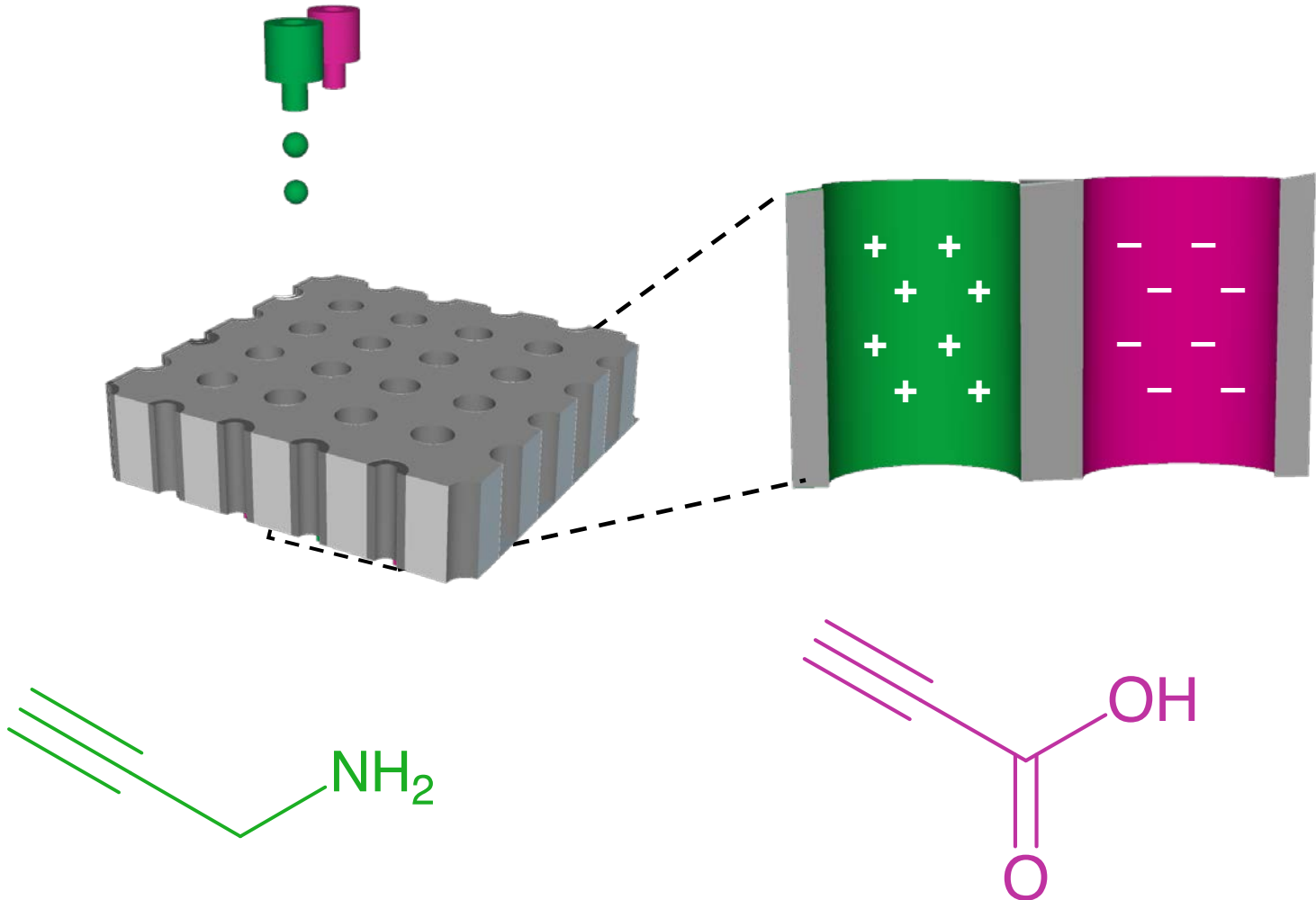
FZ: Full Zwitterion
DF: Dual-Functional
FC: Full Charge



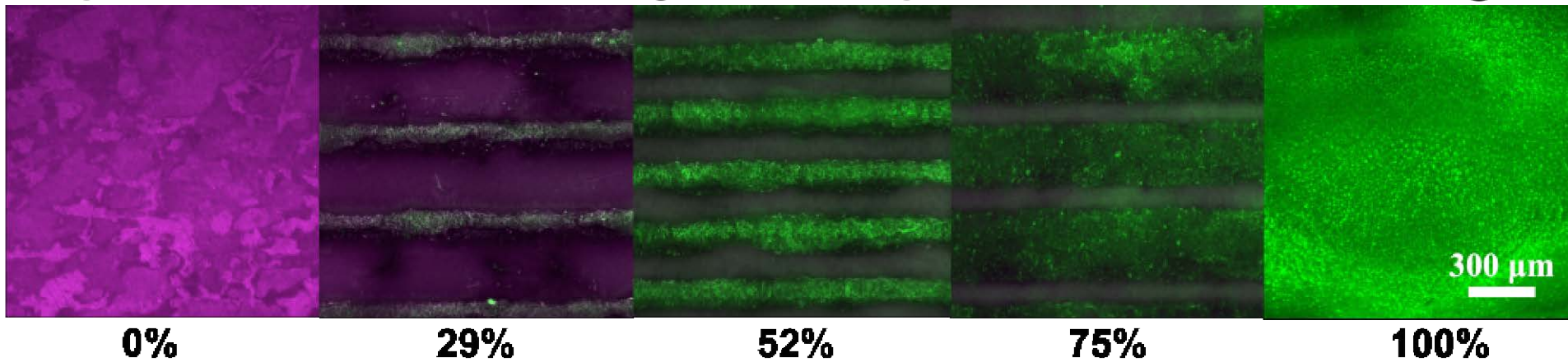
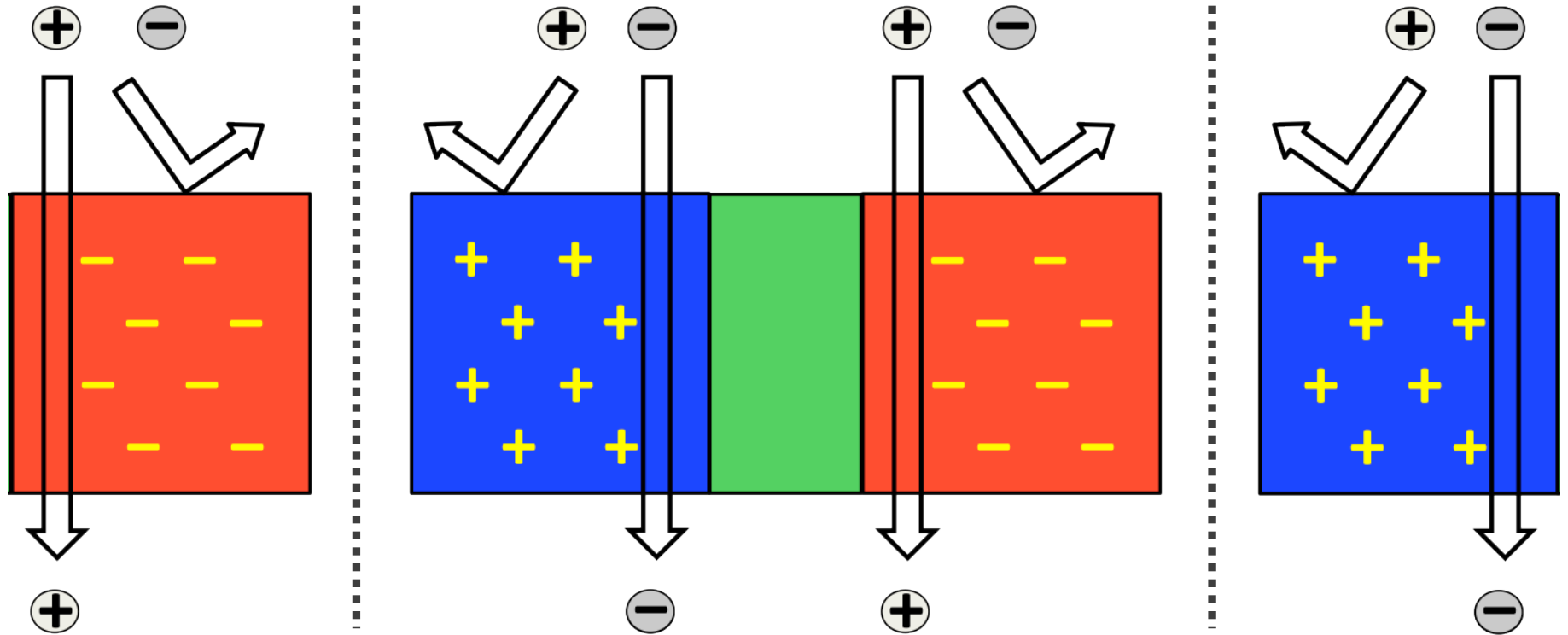
4. Dual-functional Membranes Exhibit Reduced Fouling, High Rejection



5. Inkjet Printing of Charge-Patterned Mosaic Membranes

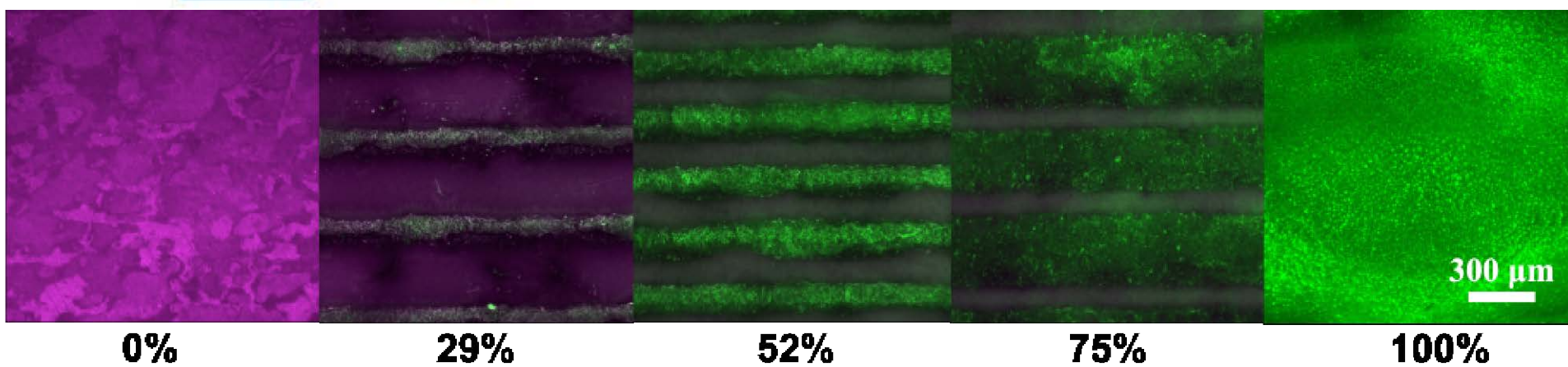
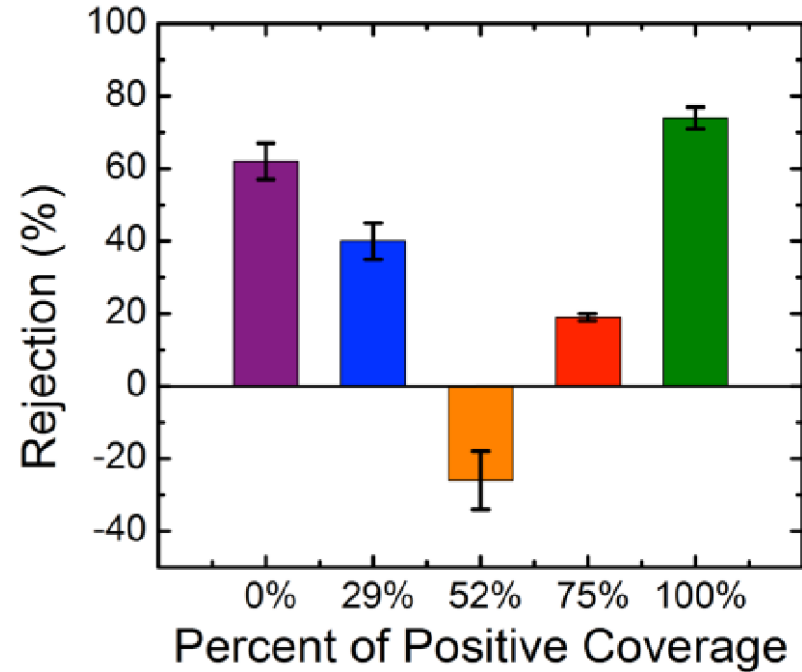
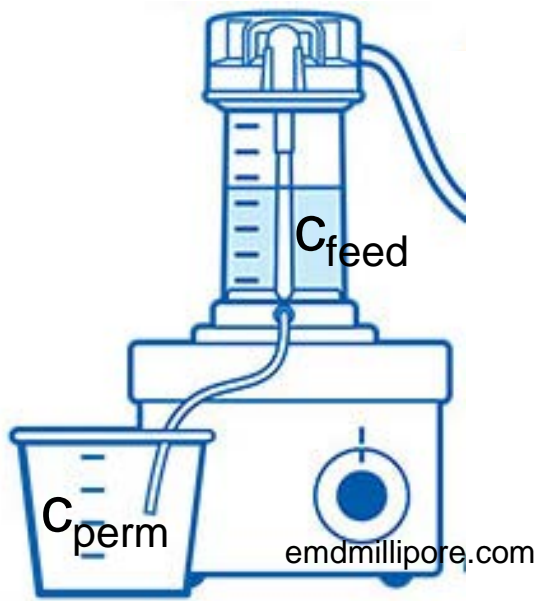


5. Inkjet Printing of Charge-Patterned Mosaic Membranes

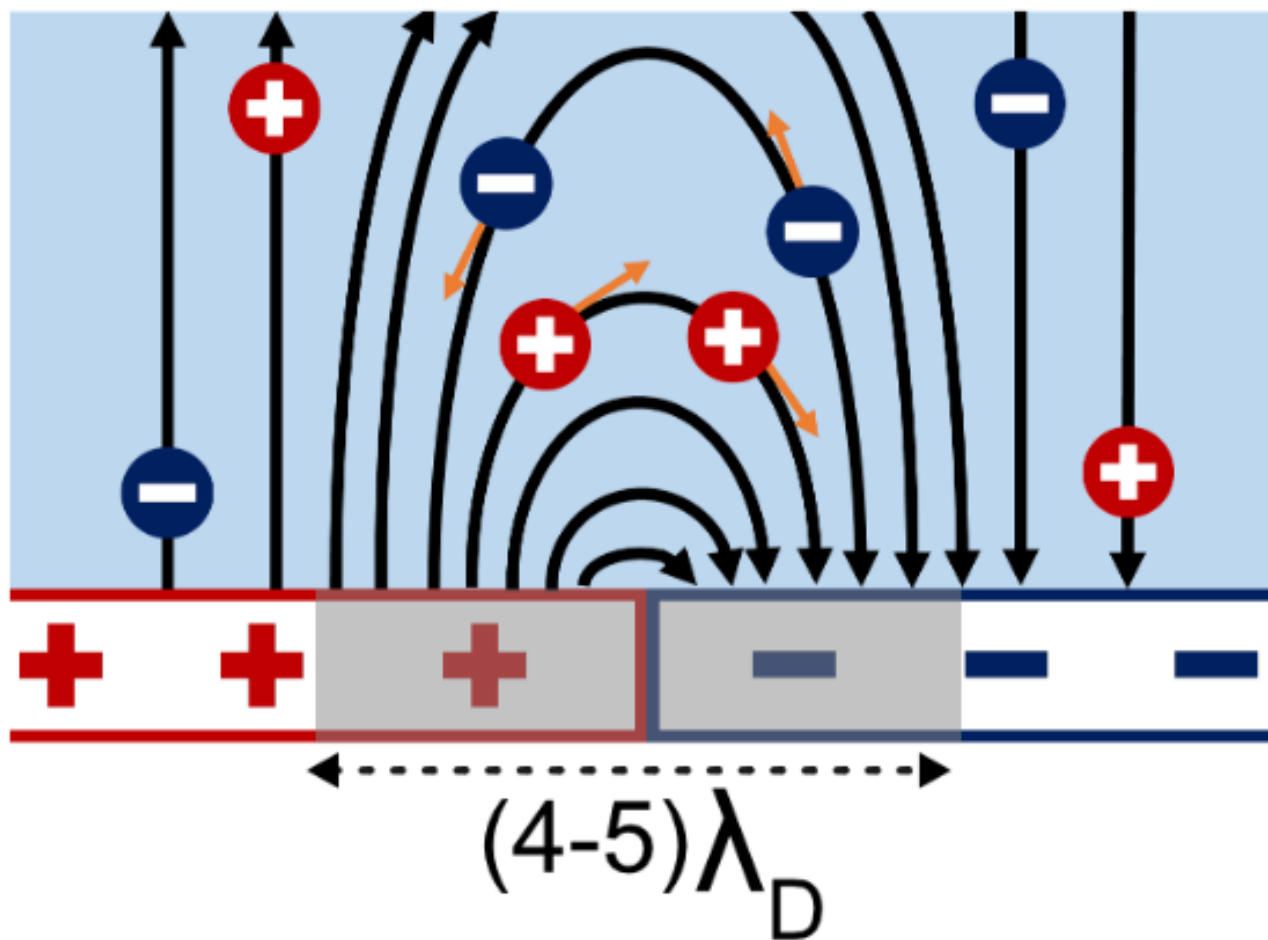


5. Inkjet Printing of Charge-Patterned Mosaic Membranes

$$\text{Rejection}(\%) = \left(1 - \frac{C_{perm}}{C_{feed}}\right) \times 100$$

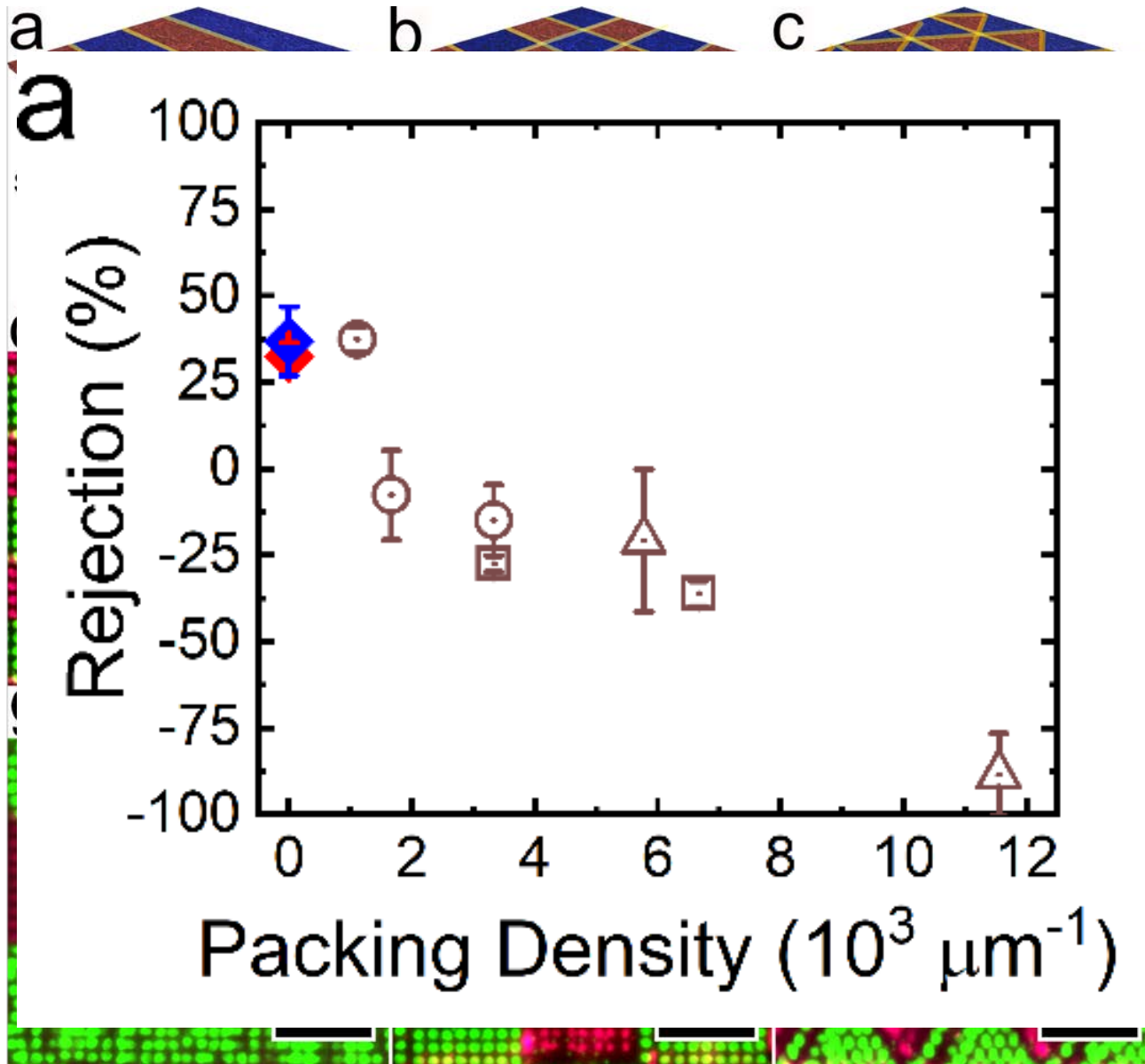


5. Local Variations in Potential Direct Ions Toward Membrane Surface

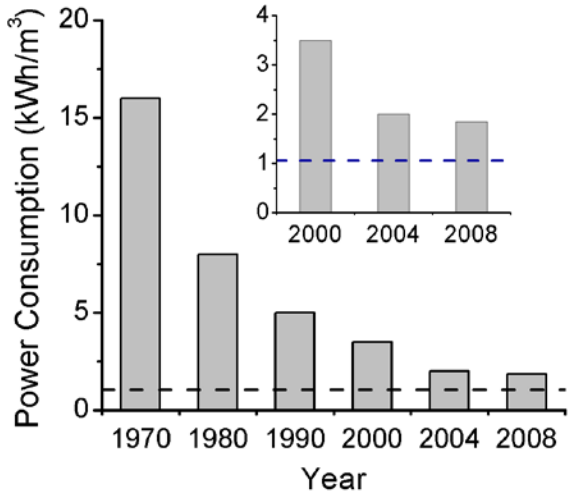


5. Interfacial Junctions Control Electrolyte Transport

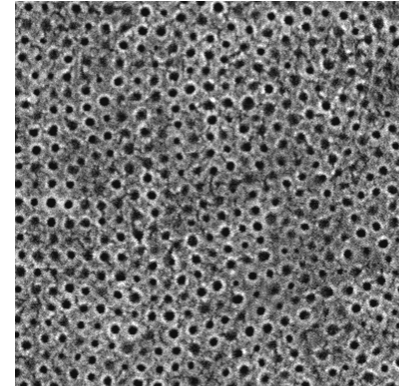
Additive manufacturing is helping to reveal new scientific phenomena



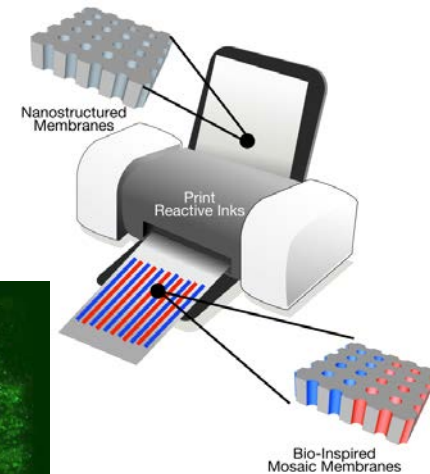
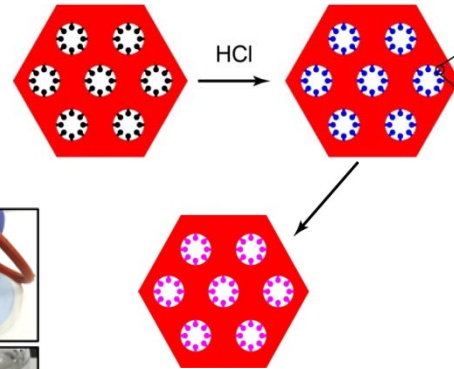
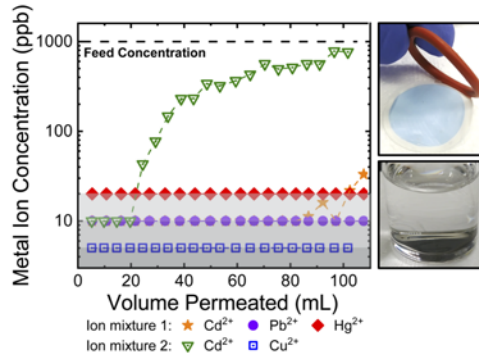
The "Big" Conclusions



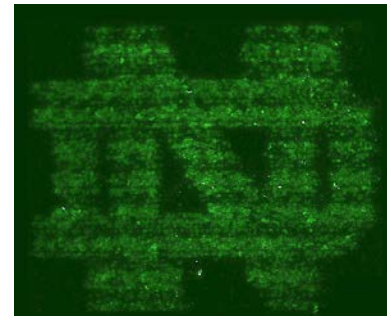
- Size-selective membranes have achieved real commercial successes in liquid-phase separations.
- New material platforms are pushing size-selective membranes to their physical limits.



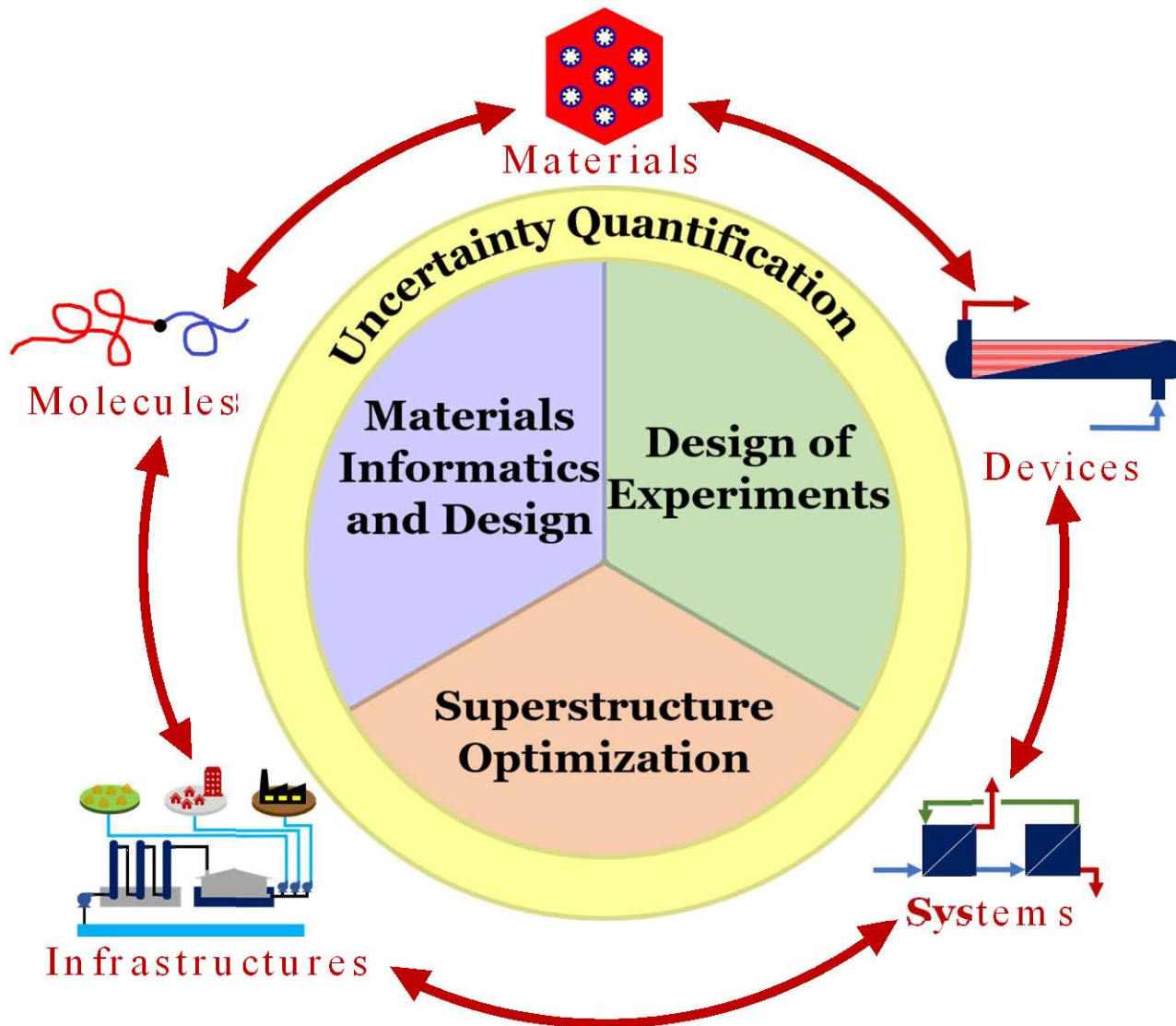
- Post-assembly modifications result in membranes that lend themselves to new applications.



- Advanced manufacturing techniques can simplify the chemical modification and spatial patterning of nanostructured membranes.



Molecular-to-Systems Engineering



Thank You Questions?

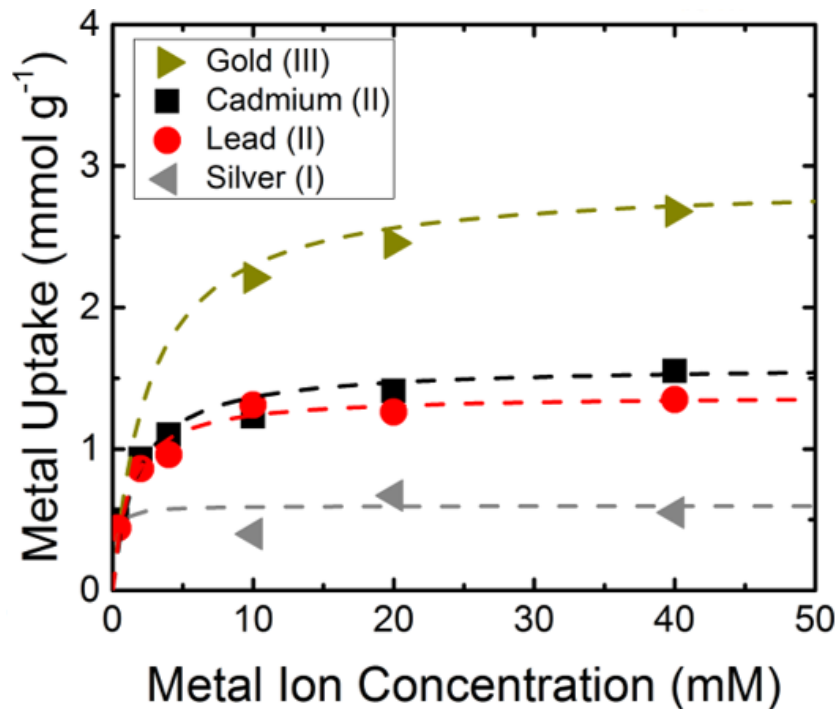
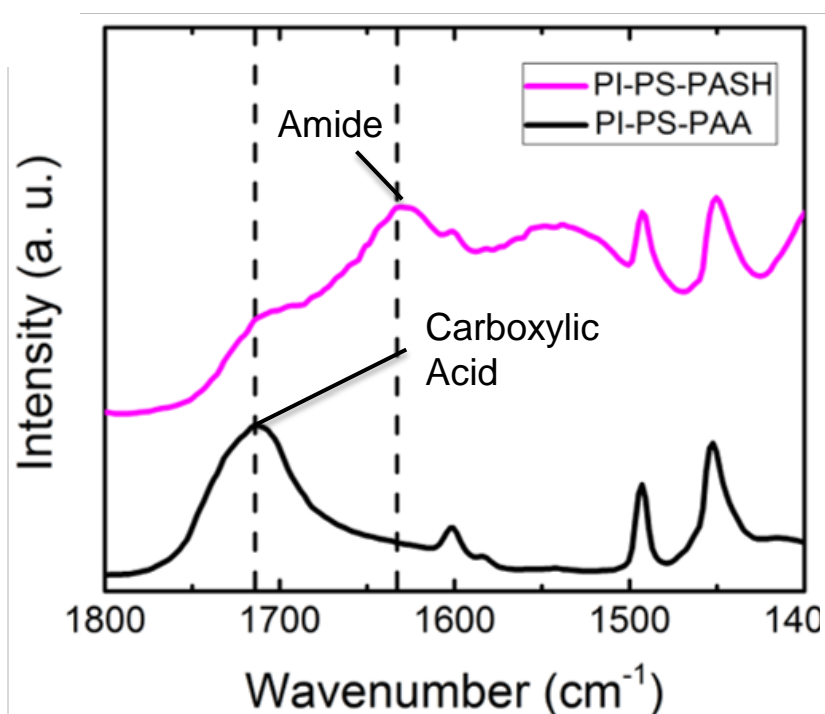
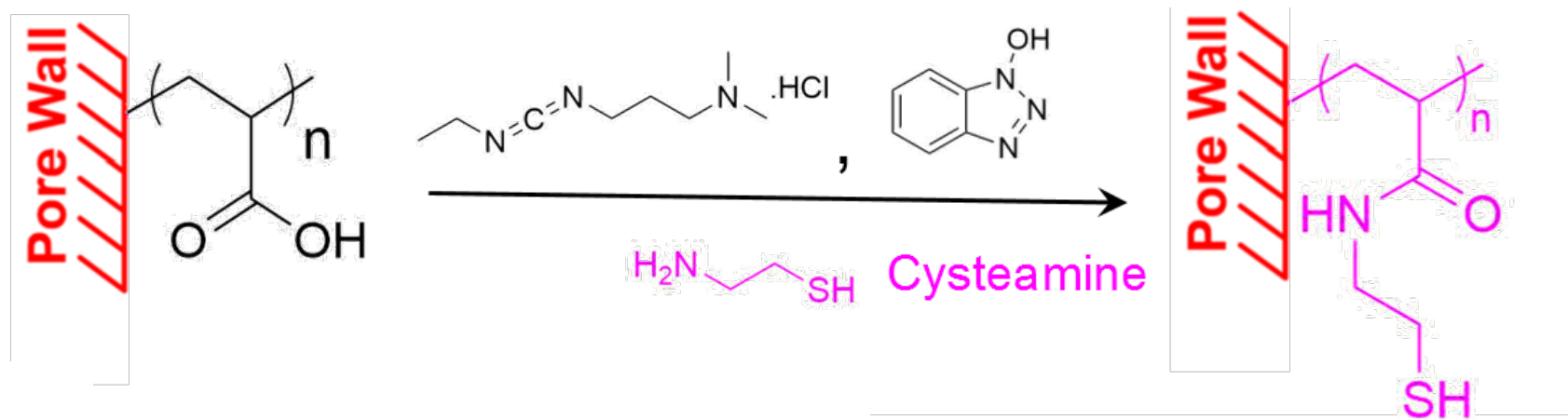
WATER Lab

William A. Phillip

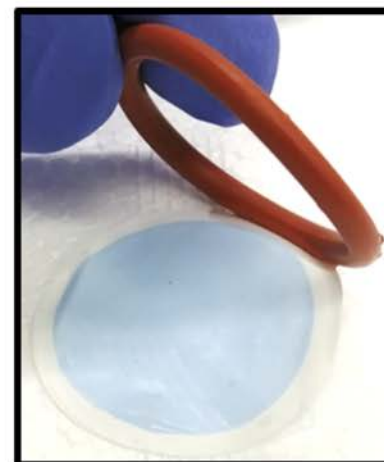
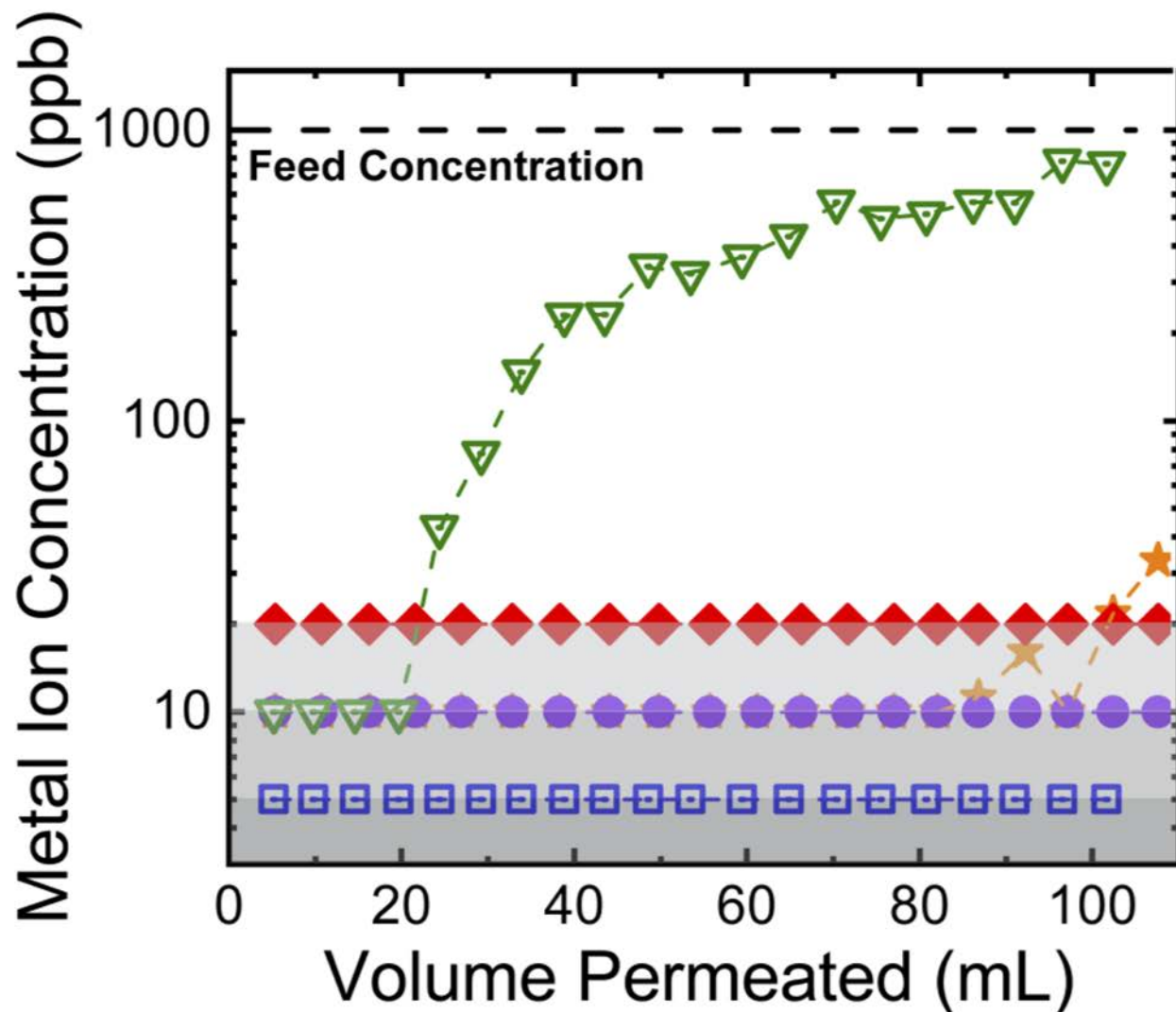
wphillip@nd.edu, 205F McCourtney Hall, O: (574) 631-2708

*Department of Chemical and Biomolecular Engineering
University of Notre Dame*

PASH-Functionalized Membrane Binds Heavy Metal Ions



Membranes Capture and Release Solutes Quickly



Ion mixture 1: ★ Cd^{2+} ● Pb^{2+} ◆ Hg^{2+}
Ion mixture 2: ▼ Cd^{2+} □ Cu^{2+}

New Functionality Through Molecular Design

