NATIONAL ENERGY TECHNOLOGY LABORATORY

Pre-combustion Solvents and Membranes

David Luebke

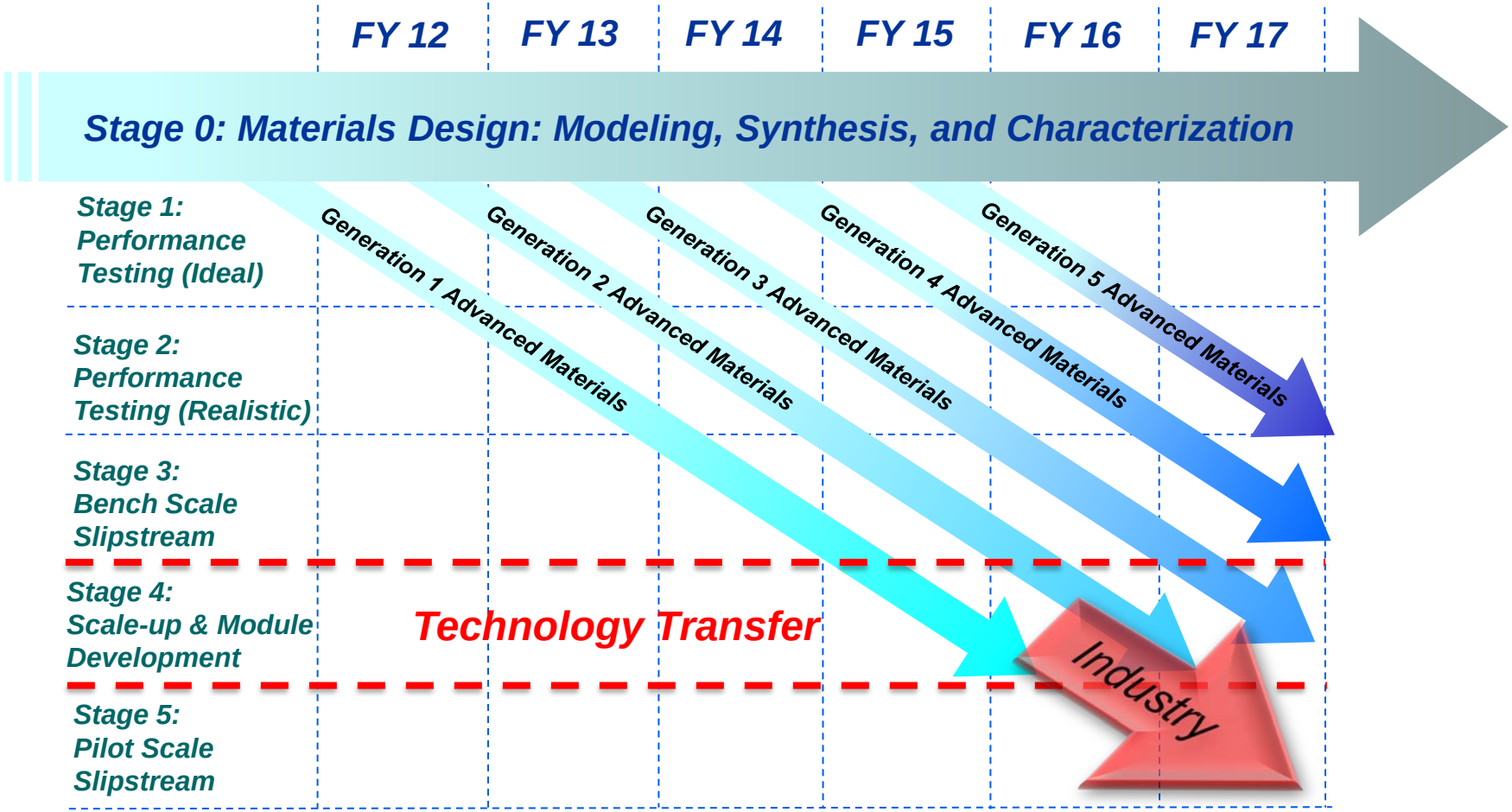
National Energy Technology Laboratory

U.S. DEPARTMENT OF ENERGY

Integrated Technology Development

Integrated Technology Development

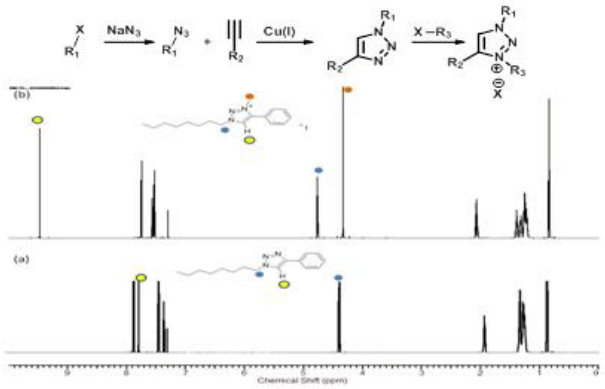
Technology Pathway



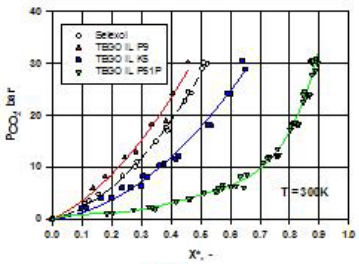
Integrated Technology Development

Multi-disciplinary Approach

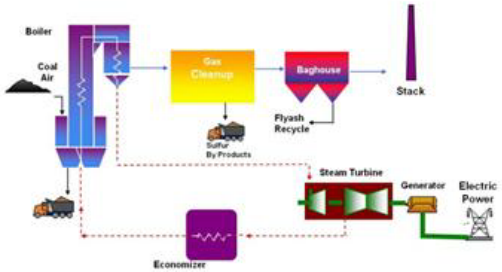
Characterization



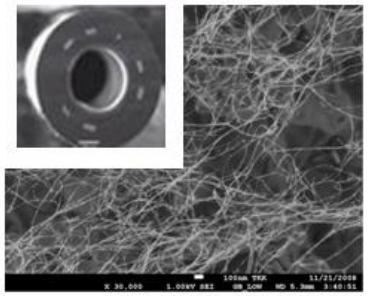
Performance Testing



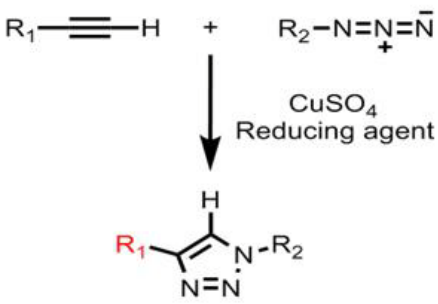
Systems Analysis



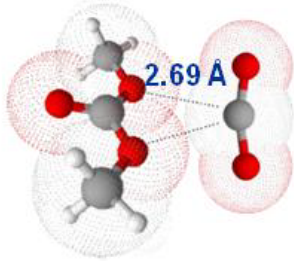
Fabrication



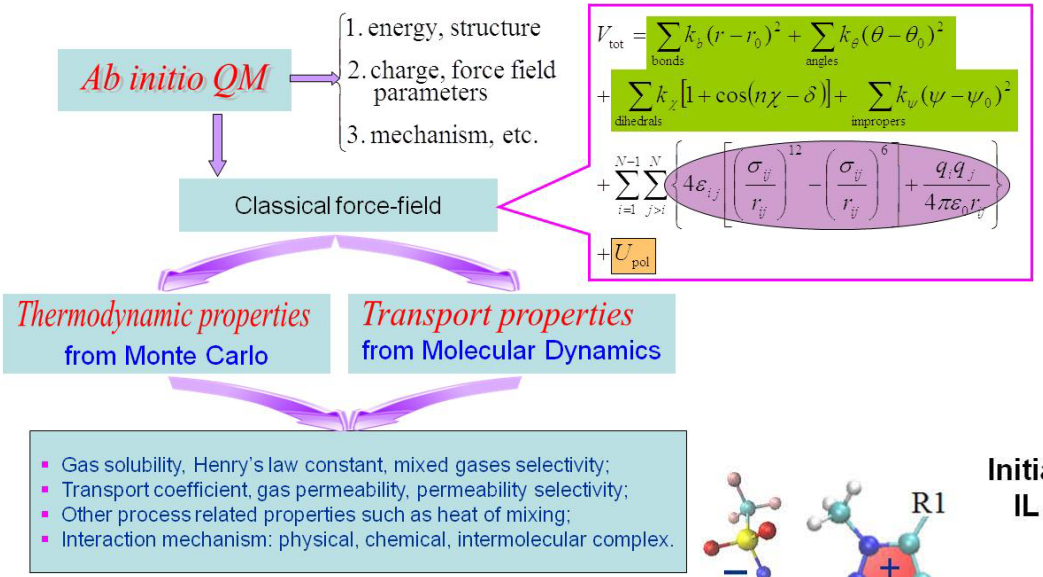
Synthesis



Modeling

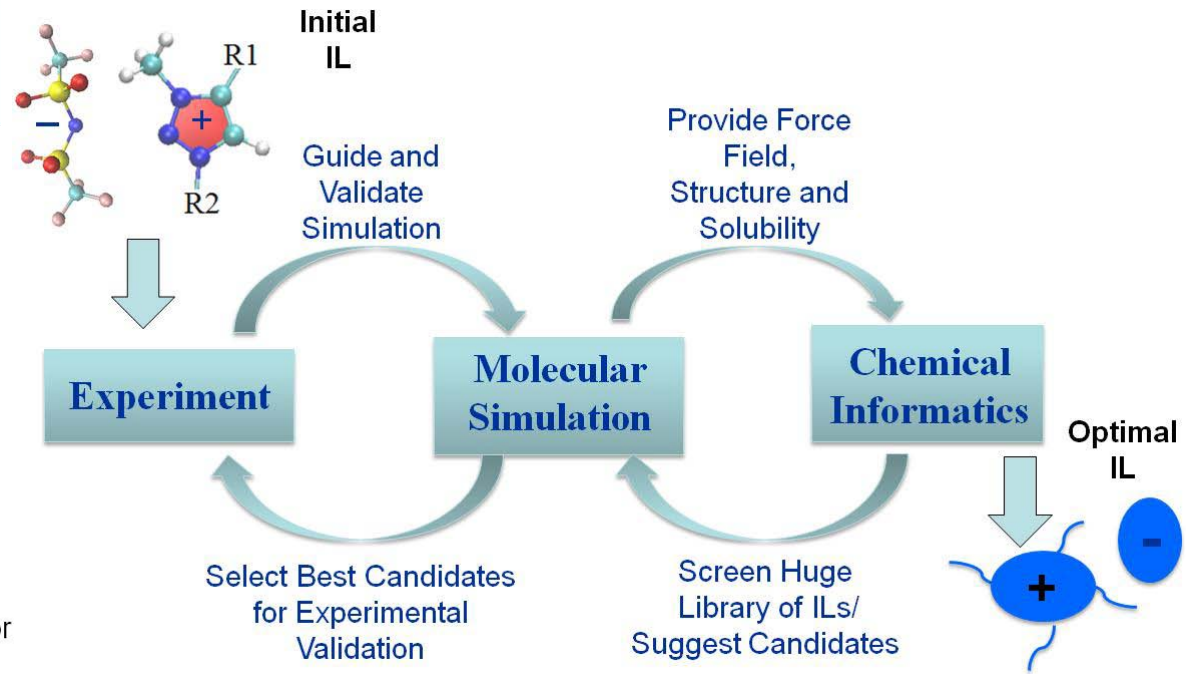


Computational Modeling



Ab initio, molecular dynamics, and Monte Carlo simulations give understanding of effects which are difficult to probe experimentally.

Chemical informatic techniques search huge libraries of potential structures to locate candidates with idea performance characteristics.



Energy Frontiers Research Center for Gas Separations Relevant to Clean Energy Technologies

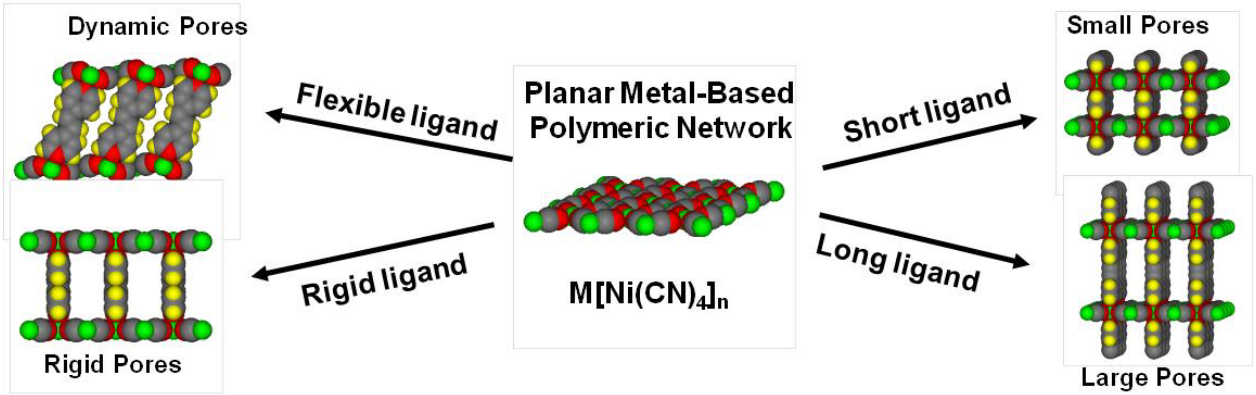
Shi et al., J. Phys. Chem. B, 116 (2012) 283. Shi et al., J. Phys. Chem. B, 114 (2010) 6531.

Synthesis

Ionic Liquids

Cu(I) click chemistry allows rapid synthesis of ILs with any desirable functionality

Metal-Organic Frameworks

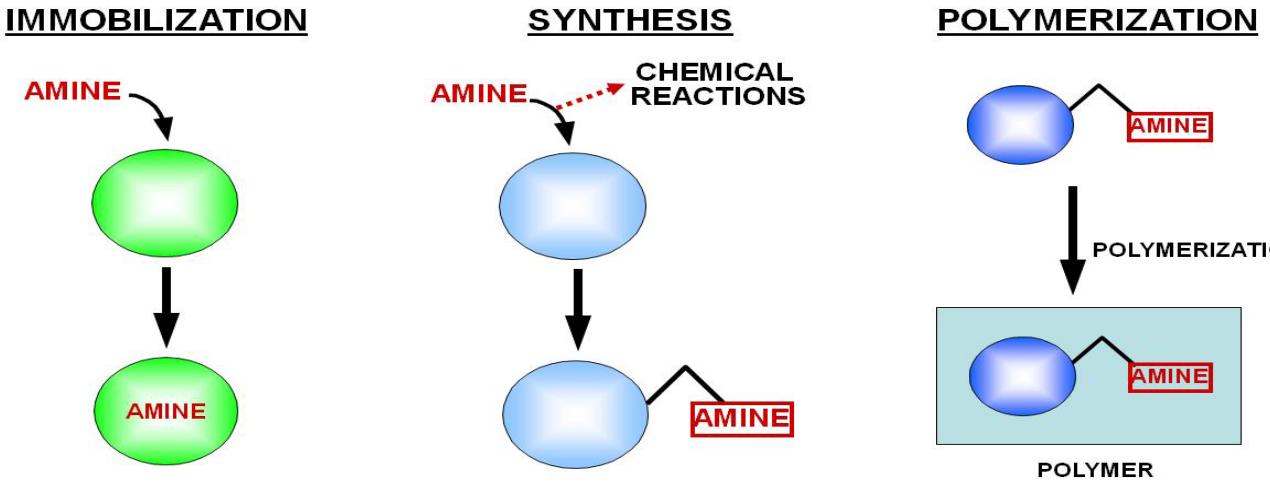


Alteration of ligands leads to MOFs with widely varying structures and properties.

Nulwala et al., Green Chemistry, 13 (2011) 3345. Tang, J. Polym. Science A, 49 (2011) 2024.

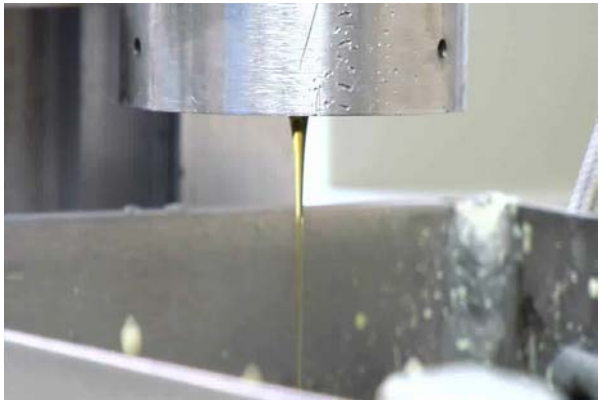
Fabrication

Advanced Supported Amines



Multiple fabrication techniques are under development for creating the most efficient CO_2 sorbents.

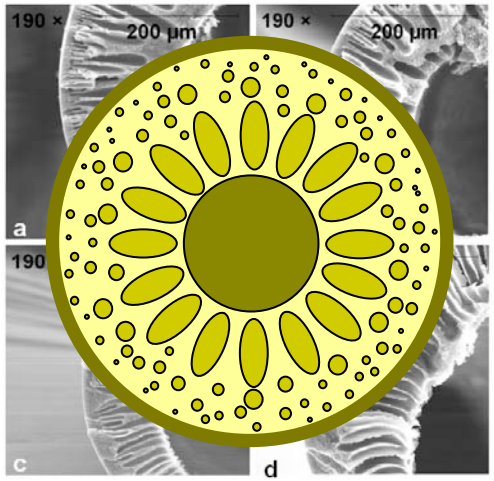
Hollow Fiber Membranes



Fiber spinning converts experimental membranes into practical ones.

Lab-scale Membrane Film

Practical Membrane

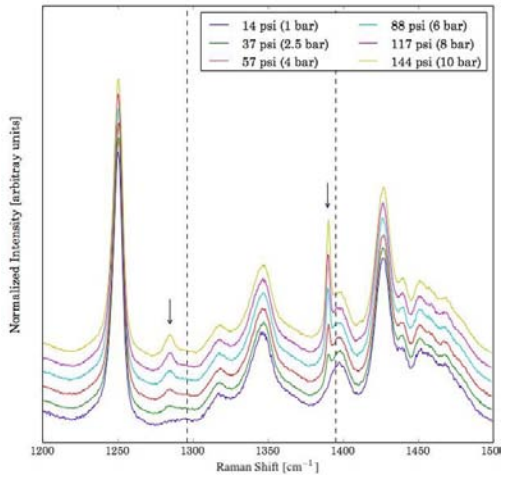


Compact Membrane Systems, Inc.

Myers et al., J. Membr. Science, 322 (2008) 28. Ilconich et al., J. Membr. Science, 298 (2007) 41.

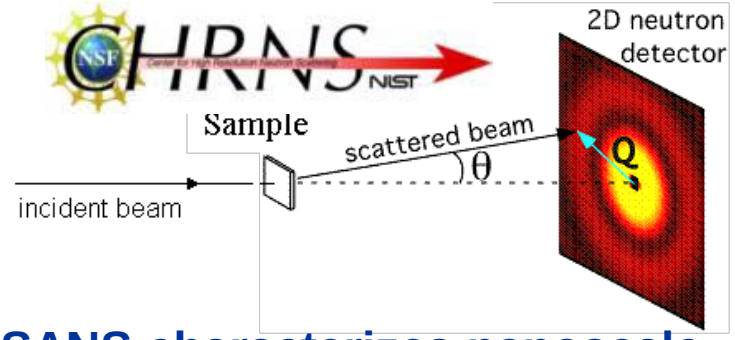
Characterization

Raman



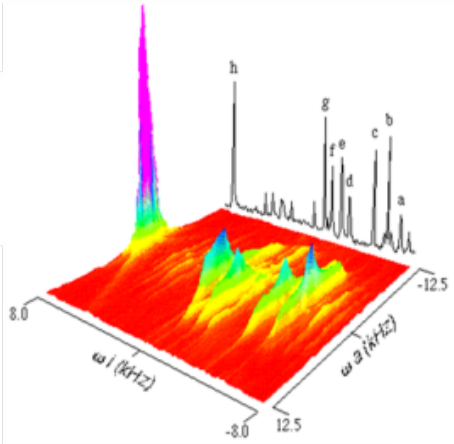
Newly developed Raman techniques probe behavior under extreme conditions of temperature and pressure.

Small Angle Neutron Scattering

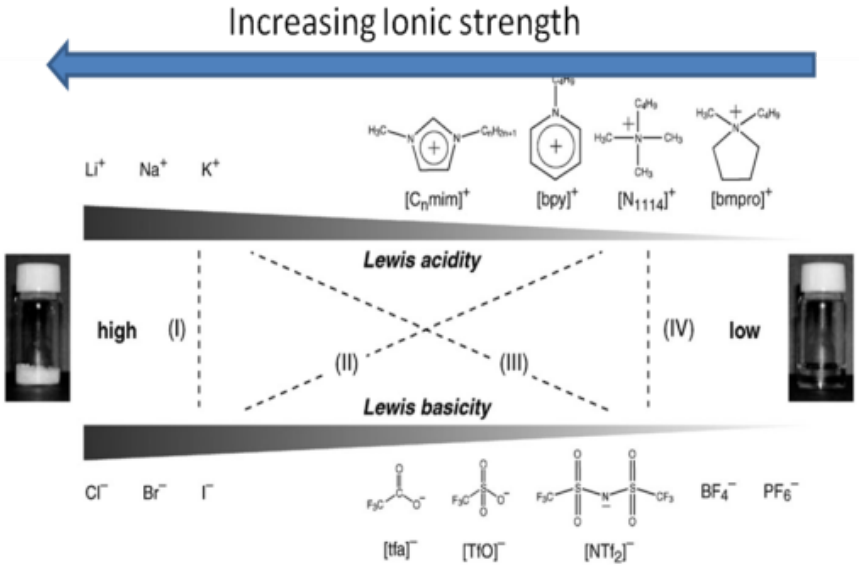


SANS characterizes nanoscale (>1 nm) structure in MOFs.

NMR

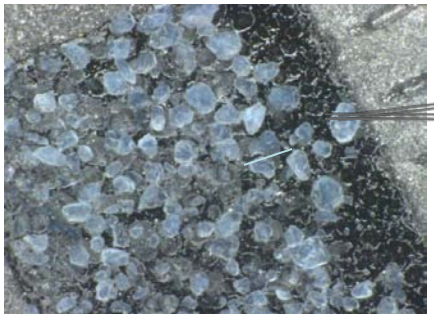


^{1}H NMR 2D Spectra



Advanced NMR techniques give information about structure, electronics reactivity and transport.

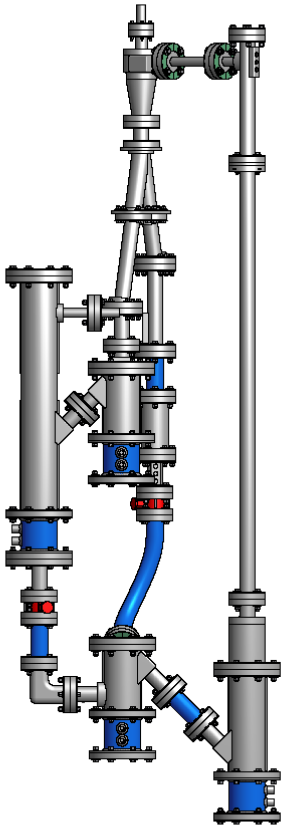
Performance Testing

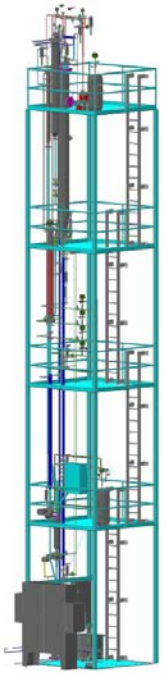


$$H—(HN—CH_2\ CH_2—)_n—NH_2$$

Characterization at laboratory scale demonstrates material behavior.

Bench-scale process testing with simulated flue gas in NETL's C2U system examines reactivity/mass transport effects.

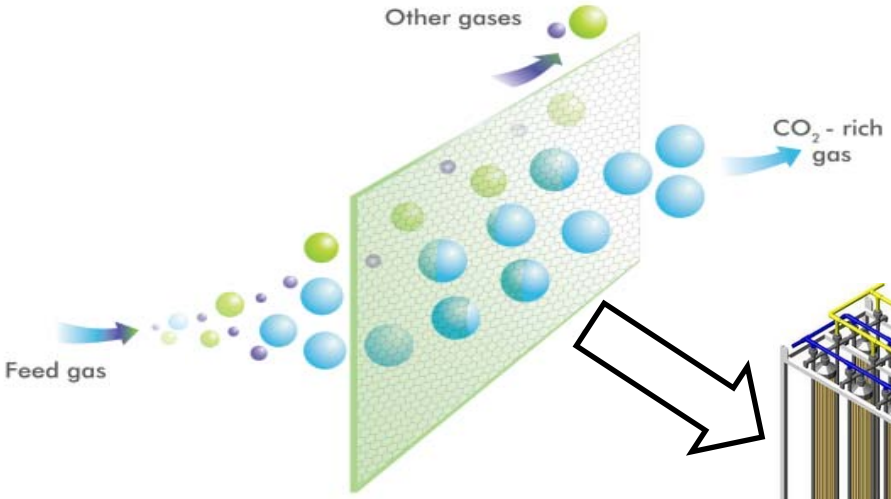




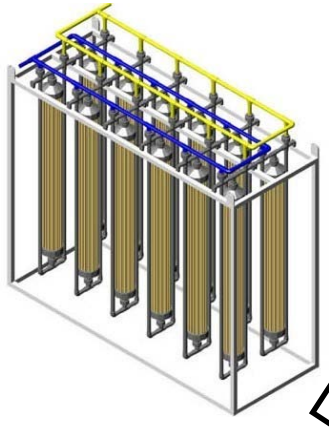
Pilot scale testing at the NCCC begins to address process issues.

Barillas et al., J. Membr. Science, 372 (2011) 29.

Systems Analysis and Integration

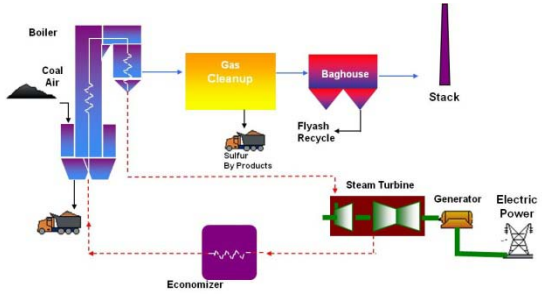


Semi-empirical transport models predict behavior of membrane layers.



Computational fluid dynamics predicts the performance of membrane modules.

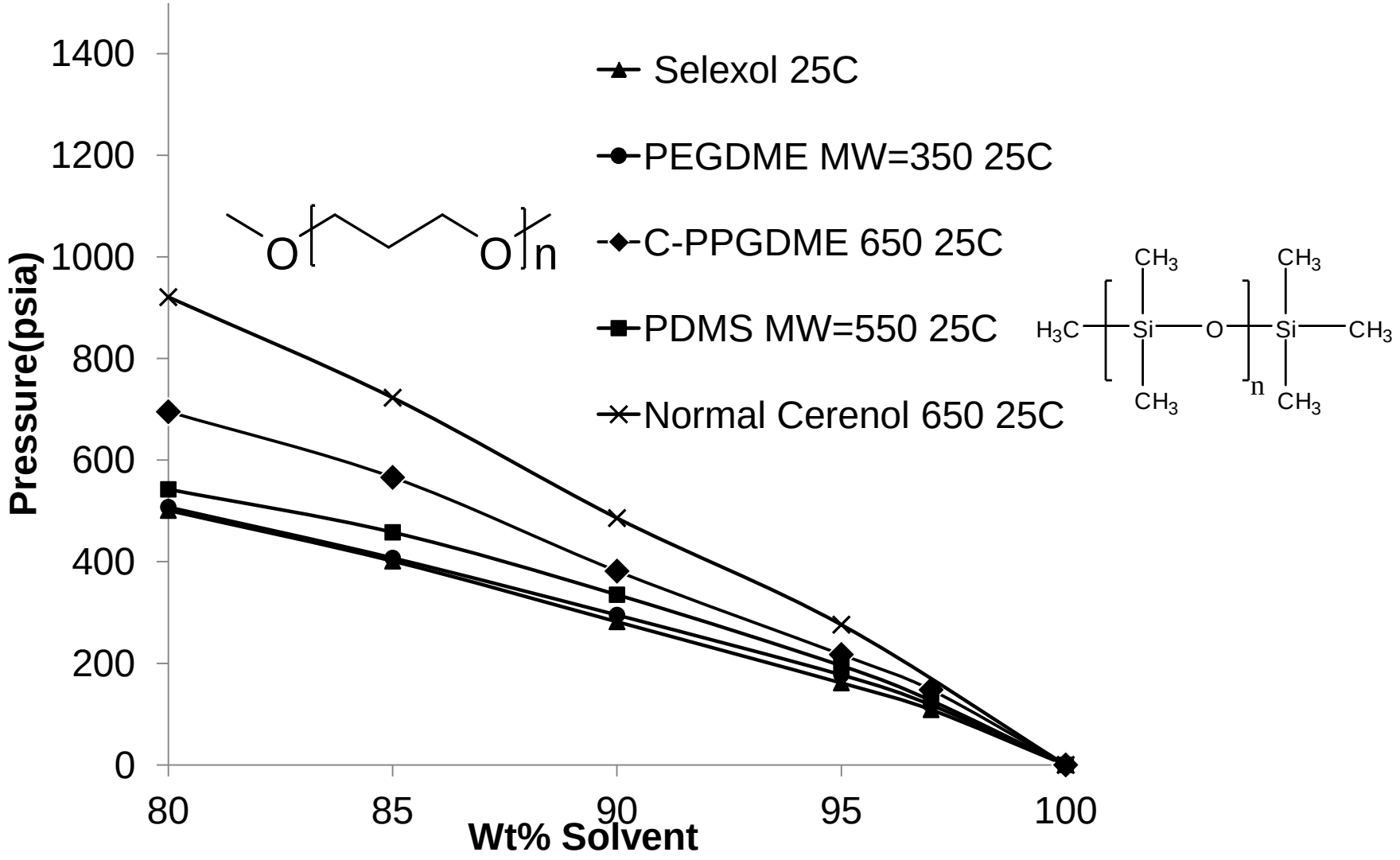
Process simulation used to optimize overall performance and guide future materials development.



Pre-combustion Solvents

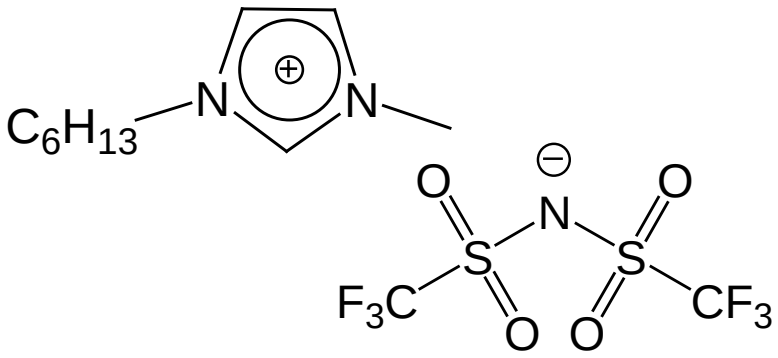
Oligomeric Solvents

PDMS and PPGDME



What is an ionic liquid?

Estimated 10^{18} possible ionic liquids



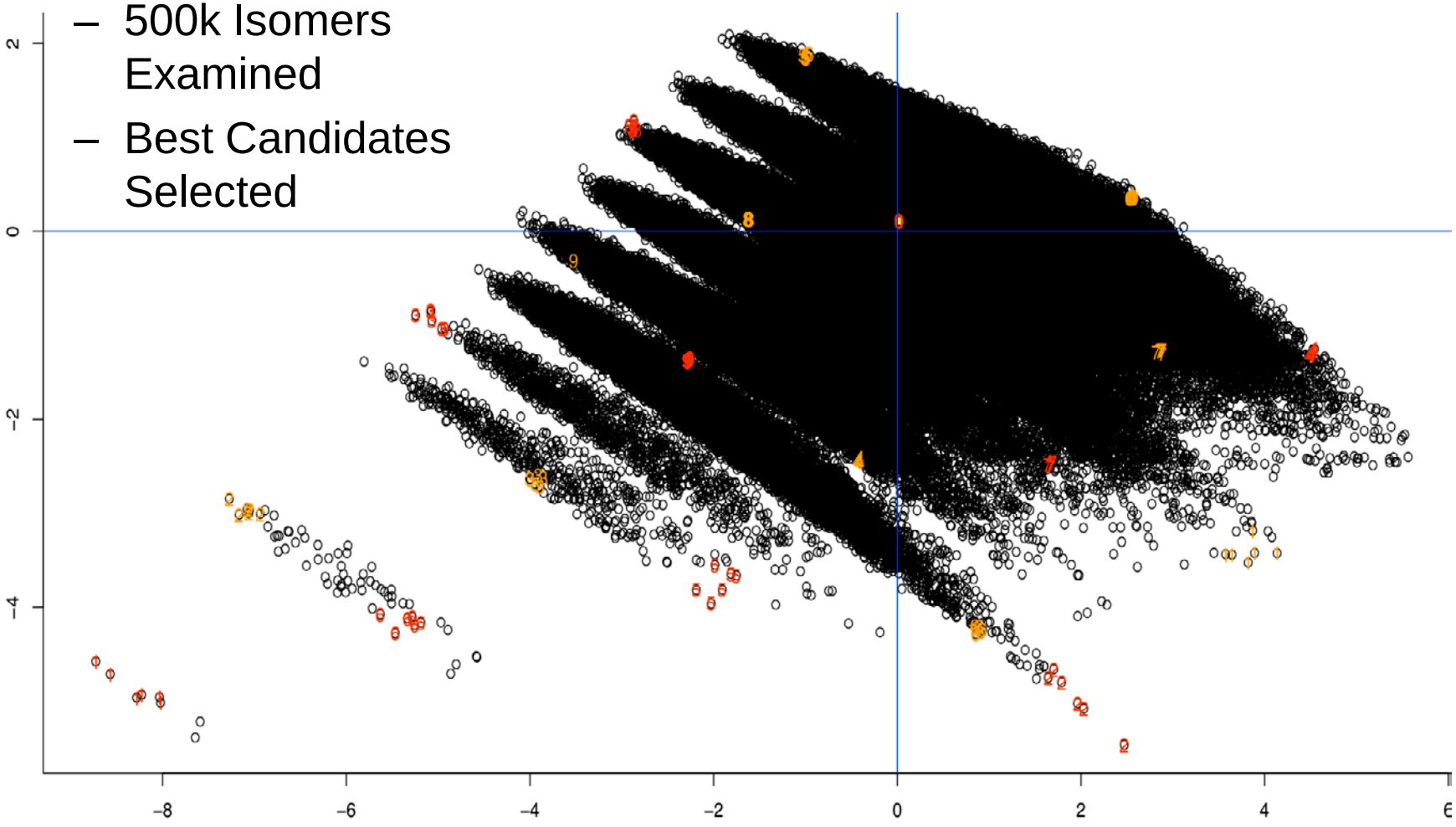
~1000 ionic liquids commercially available

- Highly Tailorable Liquid Salts
  - Negligible Vapor Pressure
  - Good Thermal Stability
  - High CO_2 solubility relative to CH_4, N_2, and H_2

J. Chem Inf. Model. **2007** *47, 1111-1122.*

Chemical Informatics Implemented for ILs

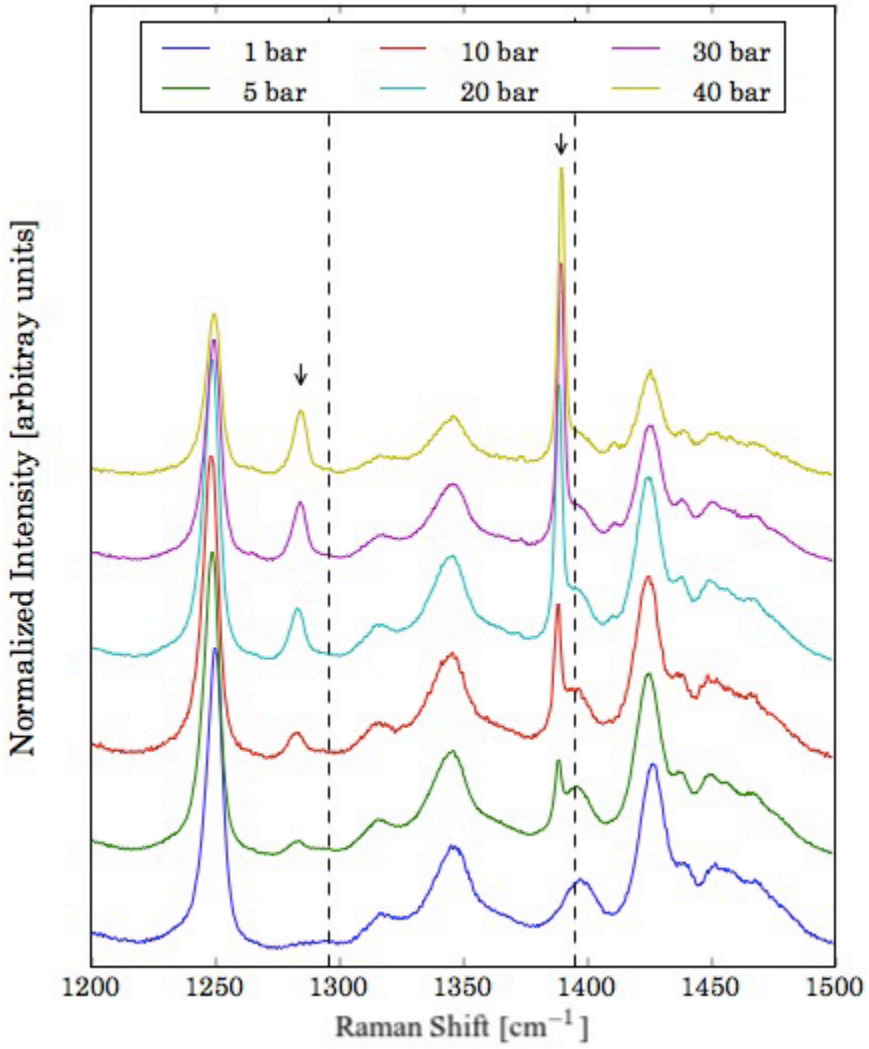
- 500k Isomers Examined
- Best Candidates Selected



Collaboration with Berkeley EFRC

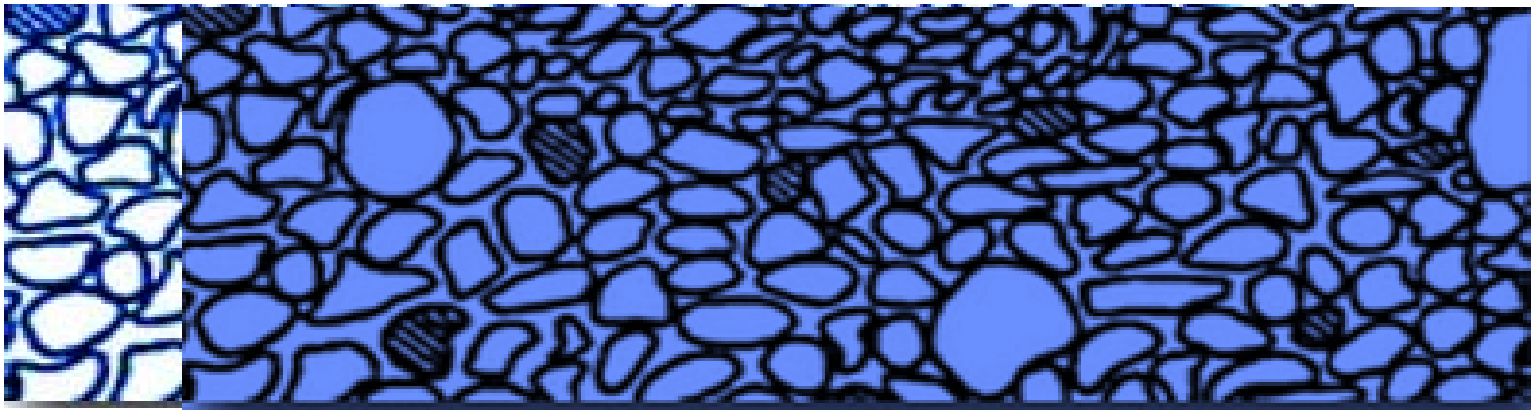
High T/High P Raman Spectroscopy Techniques Developed

- **Provides molecular information about CO_2 under precombustion capture conditions**
  - Capture mechanism
  - Identify chemical reactions and products
- **Target solvents**
  - Oligomeric Solvents
  - Ionic liquids
- **Solvents are available in**
  - Small volumes (less than 1 mL are available in some cases)
- **Conditions Available**
  - High pressures (1-50 bar)
  - High temperatures (25-300 °C)



Pre-combustion Membranes

Supported Ionic Liquid Membranes



IL

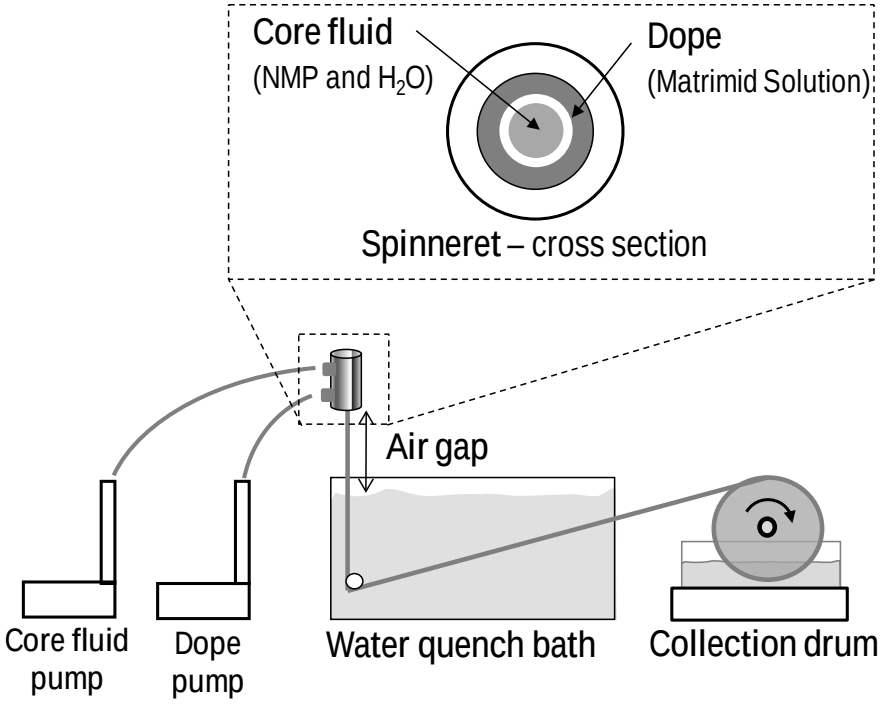
Advantages

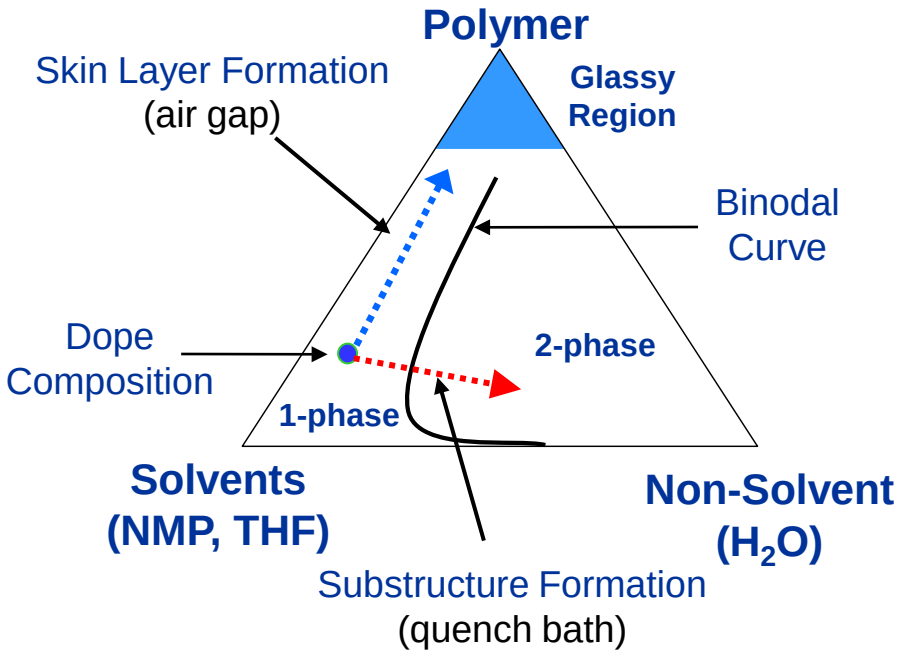
- Can be customized for a variety of separations
- Can include facilitated transport
- Gas transport in liquids is an order of magnitude faster

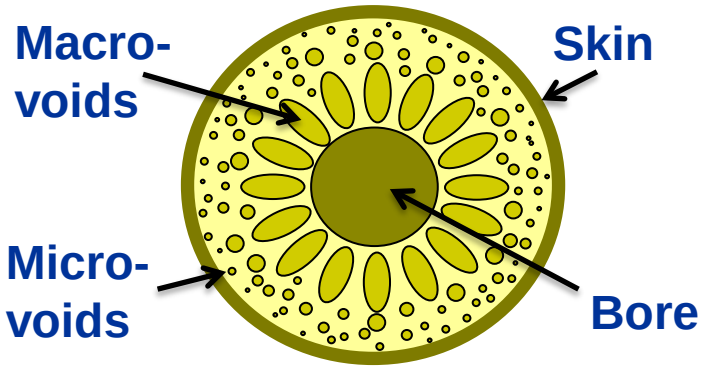
Challenges

- Cannot survive large transmembrane pressure differences
- Fabrication of thin liquid layer requires new techniques
- Huge number of possible materials

Hollow Fiber Structure and Fabrication



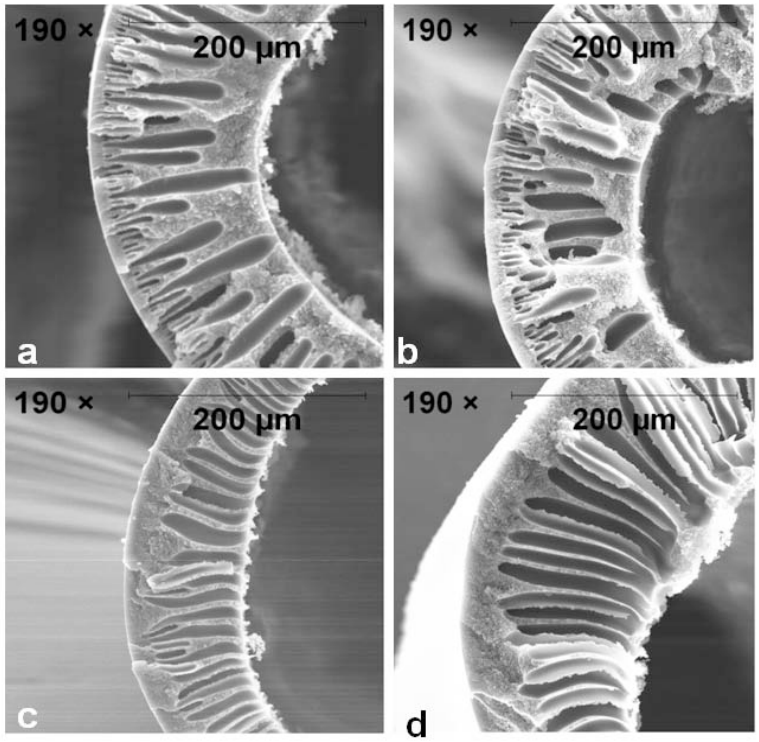




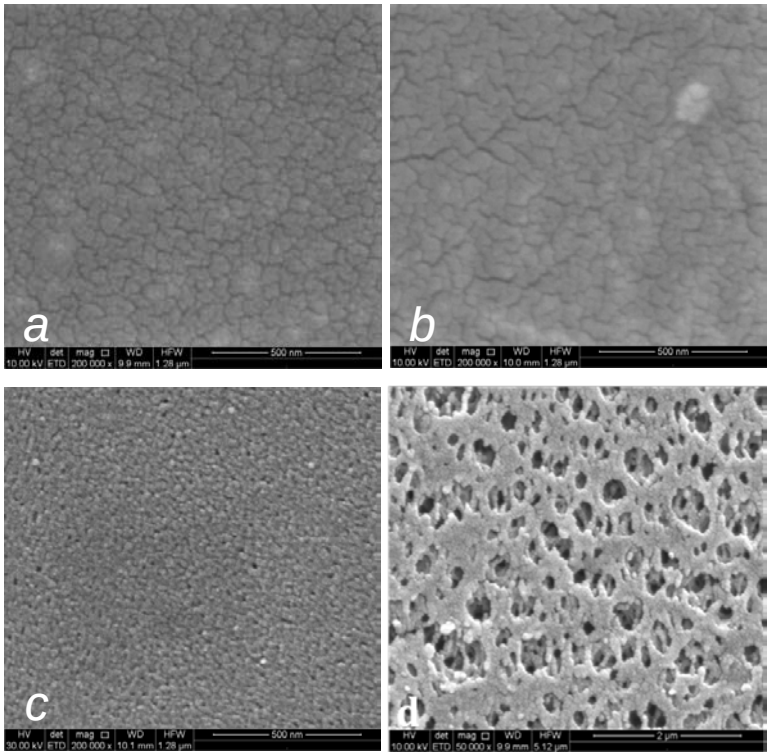
Optimization of Hollow Fibers

Membrane (Matrimid)	Matr. wt.%	NMP wt.%	THF wt.%	$LiNO_3$ wt.%
a	25	65	10	0
b	25	75	0	0
c	21	75	0	4
d	18	78	0	4

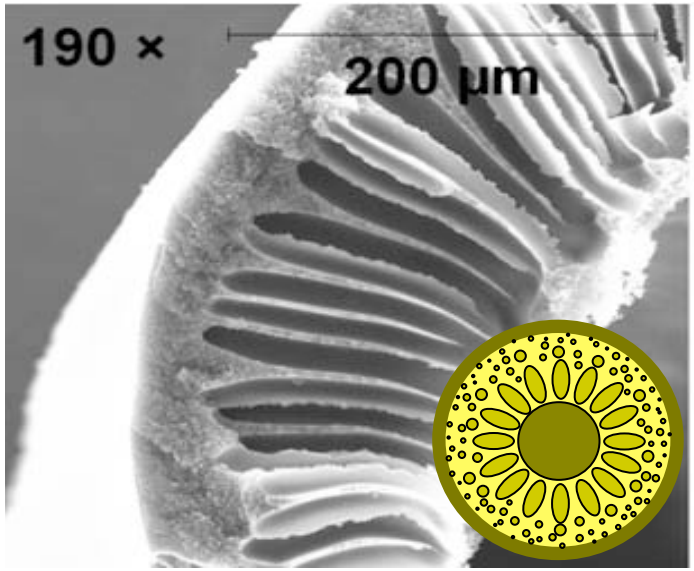
Fiber Cross Section



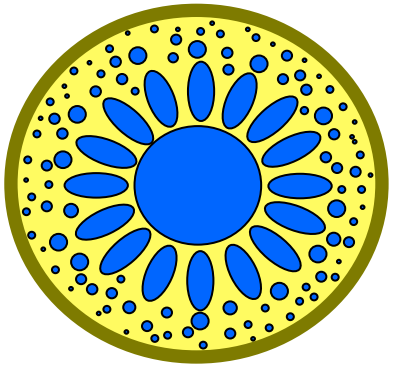
Fiber Surface



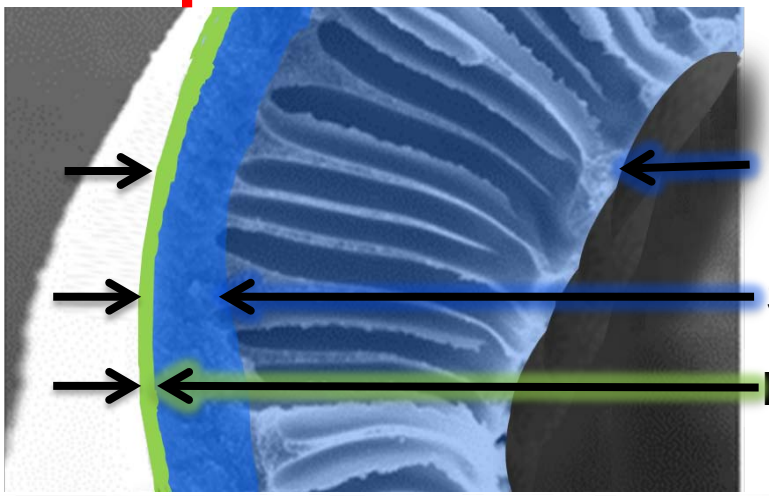
Importance of IL Loading Method



+ IL =



Is it possible to fill only a portion of the pores?



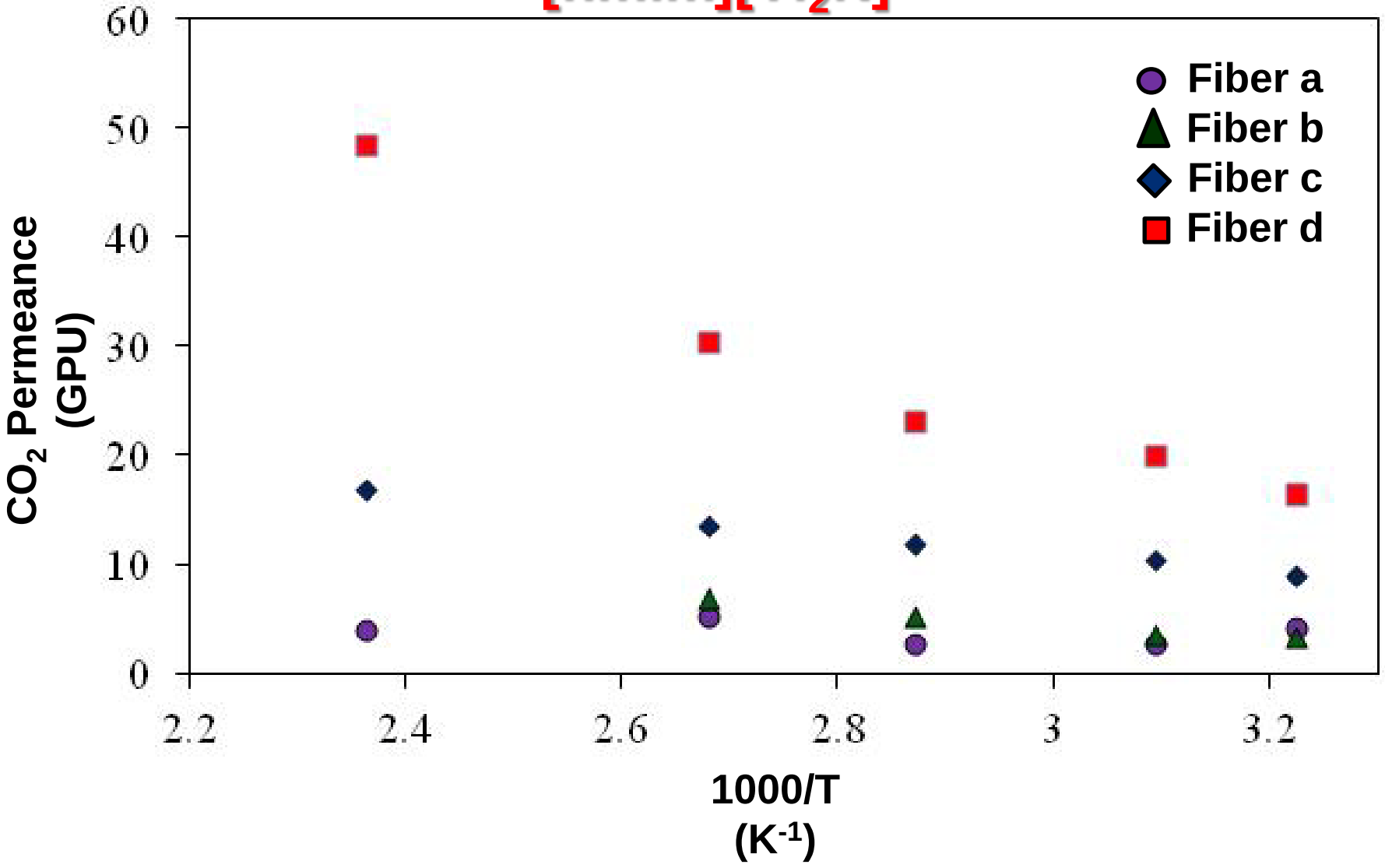
Much Too Thick (~200 micron)

Still Too Thick (~20 micron)

Practical Membrane Thickness (~1 micron)

CO_2 Permeance

[hmim][Tf_2N]



Summary

- Integrated technology development accelerates innovation through multi-disciplinary collaboration.
- Chemical informatics screens huge libraries of materials quickly.
- New synthesis and characterization methods improve technology development efficiency.
- It is possible to impregnate only a portion of a porous material with ionic liquids.
- Hollow fiber ionic liquid membranes can be created with commercially relevant permeances.

Disclaimer:

"This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name,trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof."