Transformational Technologies: Approach and Successes

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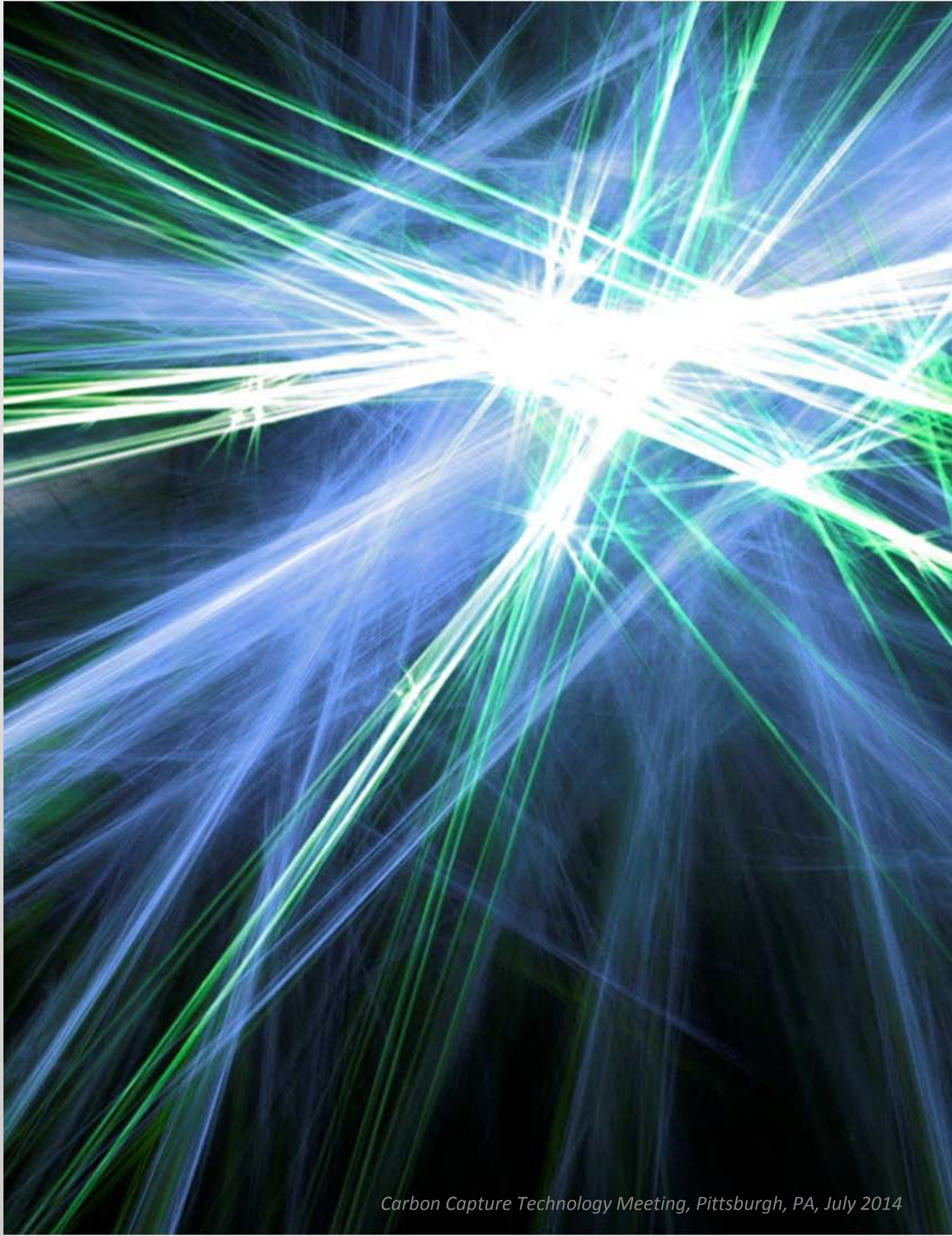
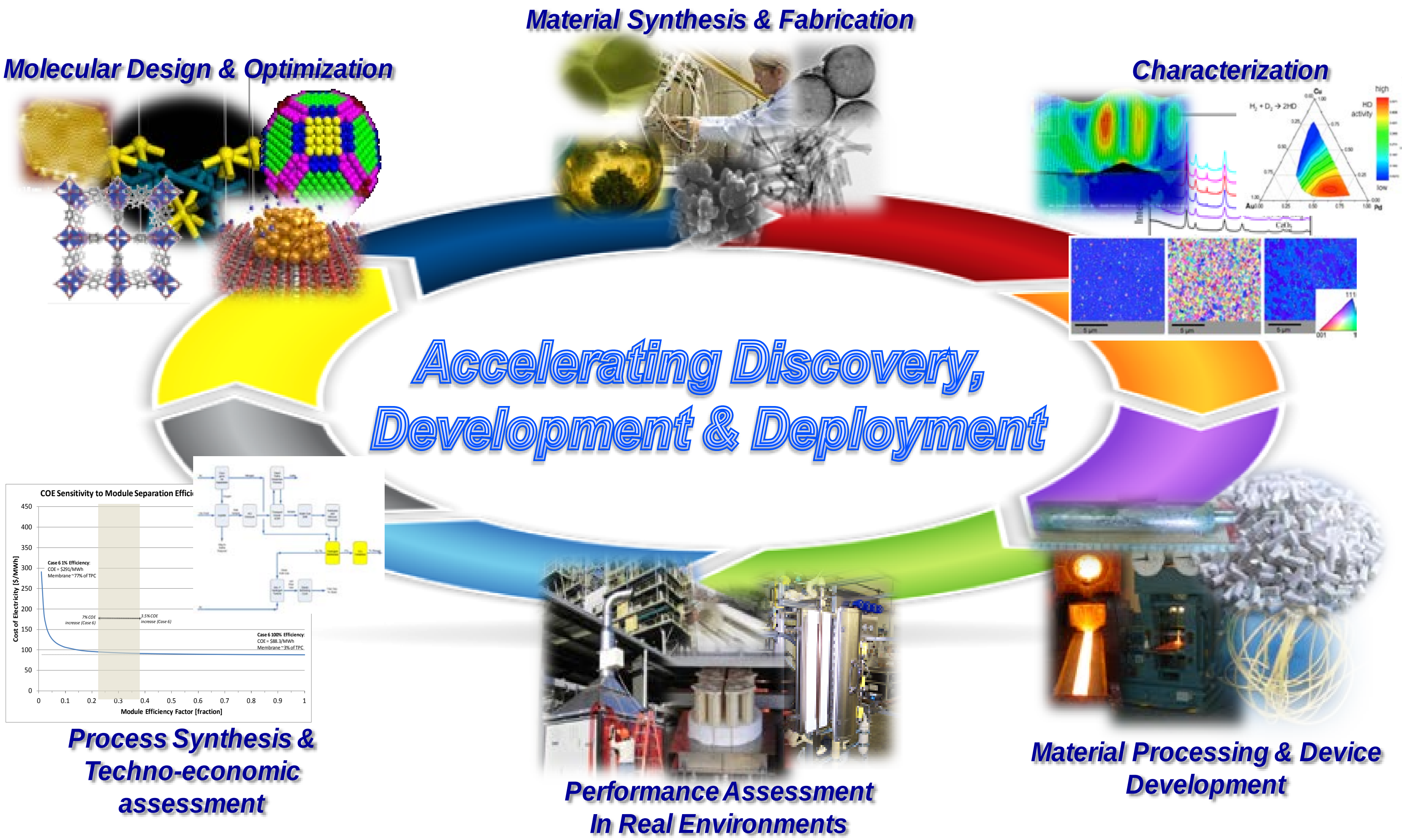
U.S. DEPARTMENT OF ENERGY | National Energy Technology Laboratory

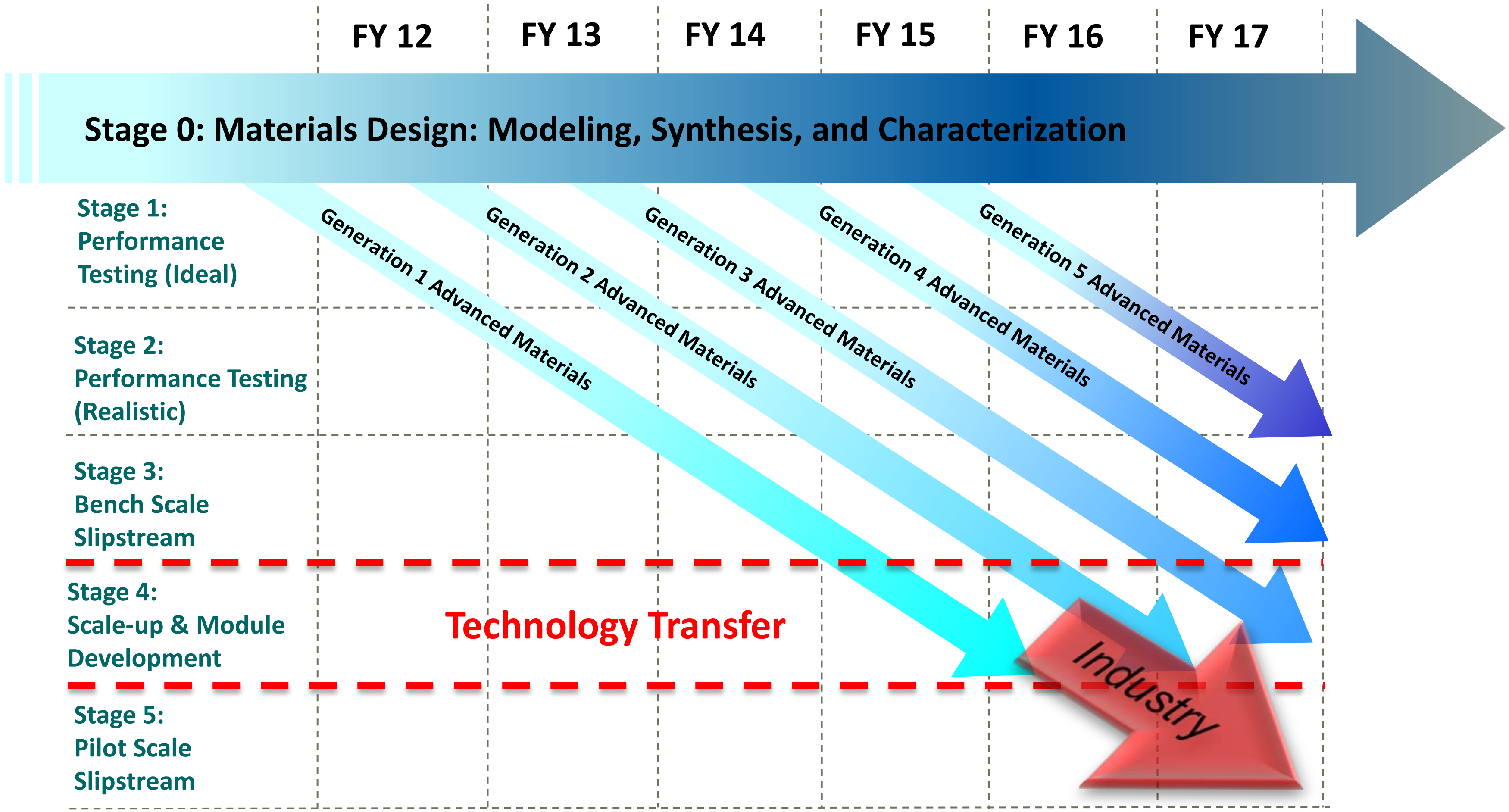


Integrated Technology Development



Integrated Technology Development

Technology Pathway



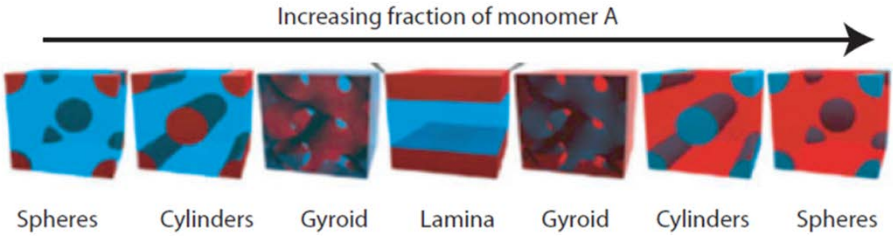
What Is the NETL-ORD Role in Transformation Technology Development?

And what is it not?

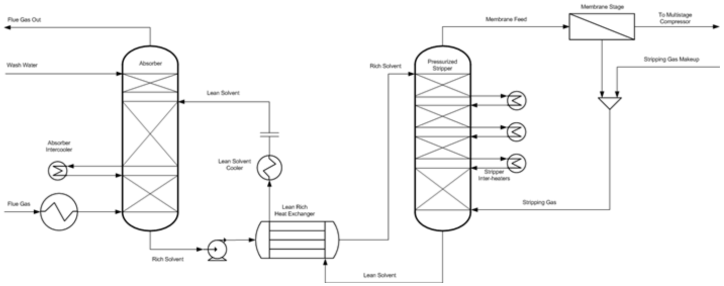
- **It's not:**
  - Basic science
  - Creation/discovery of new classes of materials
  - Pilot-scale testing
  - Commercialization
- **It is:**
  - Examination of novel classes of materials for capture
  - Exploration of innovative process configurations
  - Development of advanced screening approaches

Three Types of Projects

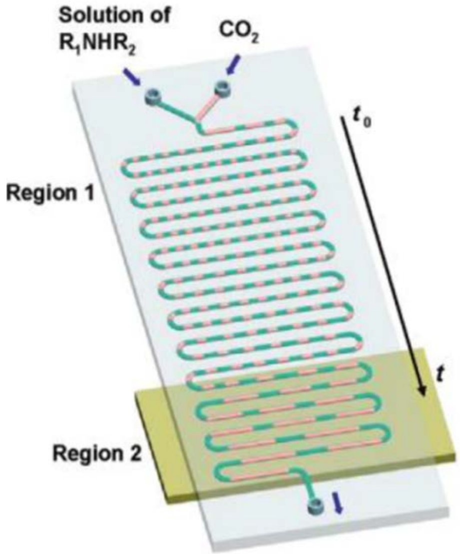
- **Material type with unique properties:**



- **Novel process configuration:**



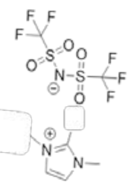
- **Testing method or device allowing accelerated R&D:**



Materials

Eutectic Solvents

- ILs forming crystalline solids tend to have a sharp melting point and low viscosity in the liquid phase.
- These materials also tend to melt well above room temperature.



Identify Simpler compounds (Minimize interactions)

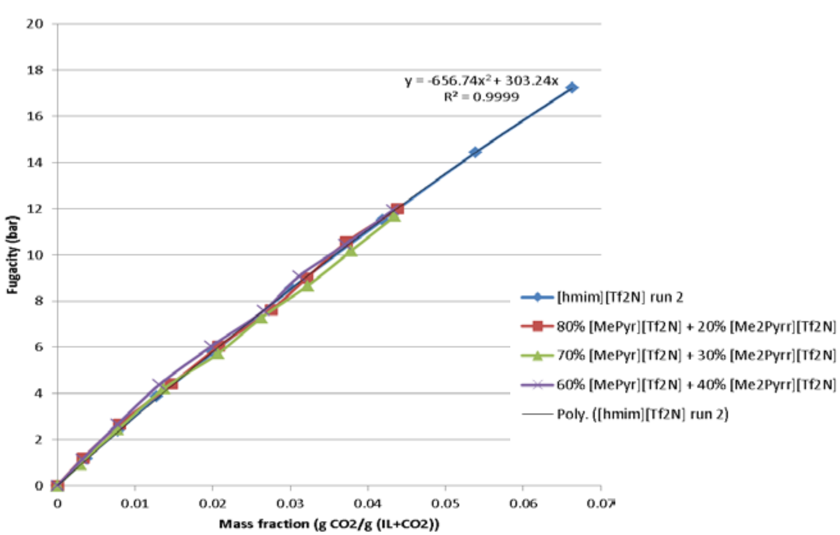
Eutectic

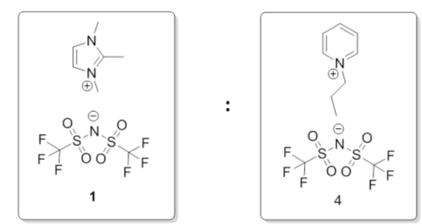
Suppression of T_m

Low viscosity

1. Weakened ionic interaction
2. Packing/Defect

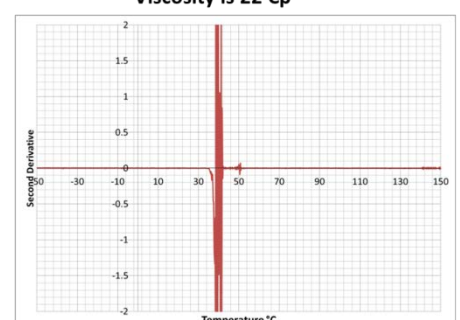
- Forming eutectic mixtures could lead to low viscosity liquids.
- It proved challenging to locate mixtures showing both reduced viscosity and a depressed melting point.





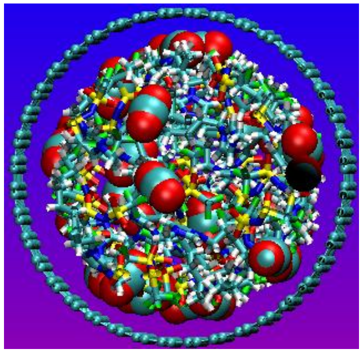
106°C 46.5°C

Viscosity is 22 Cp

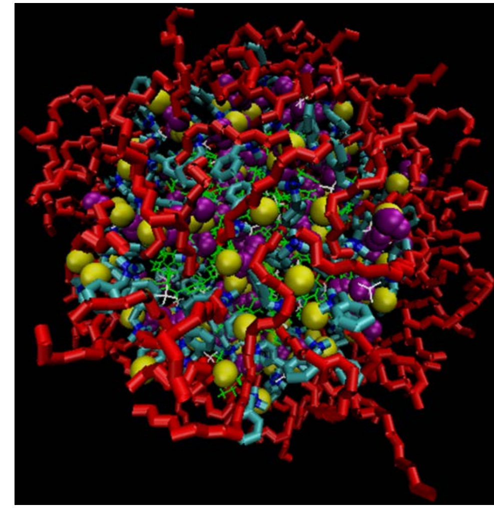


Structured Liquids

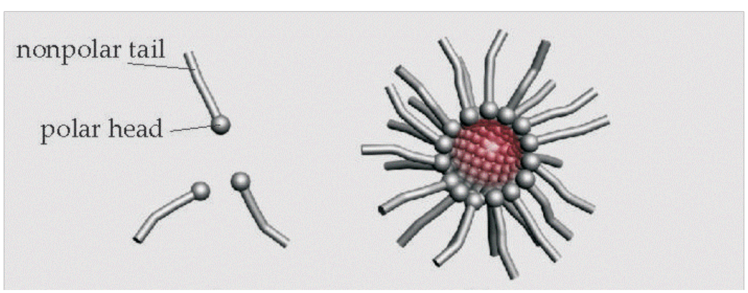
IL Confinement

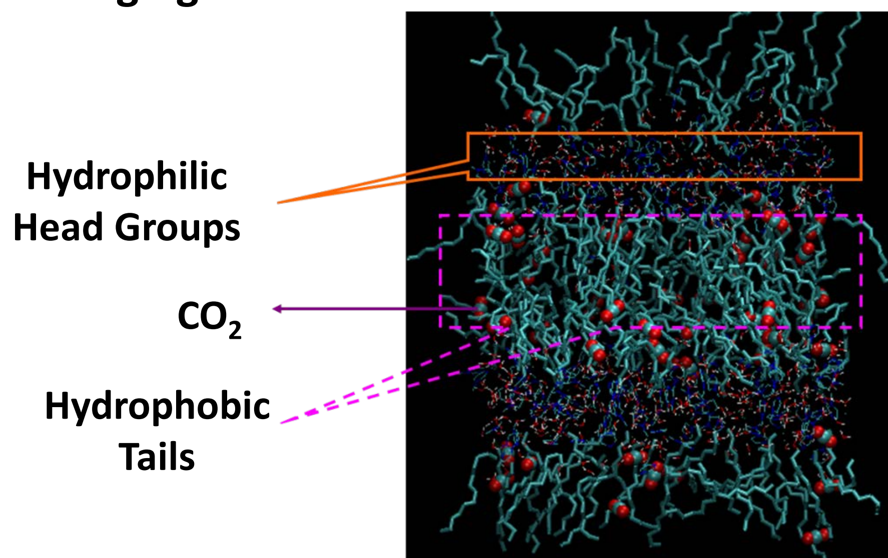


- ILs for semi-ordered structures when confined in pores under 50 nm.
- Structures show unique properties not attainable in bulk ILs.
- Formation of IL micelles results in similar property changes.
- Computational results appeared promising, but fabrication of the materials proved challenging.

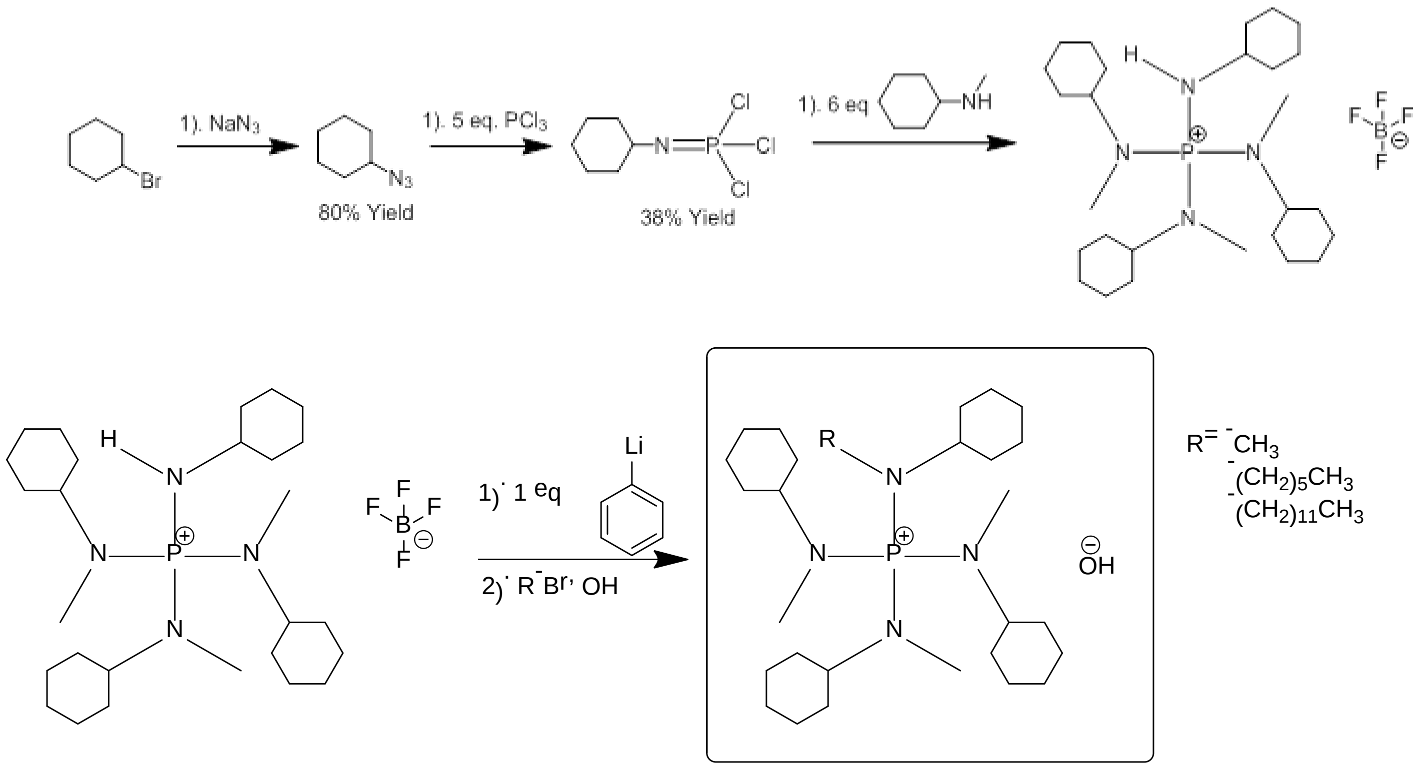


Unconfined Structured ILs





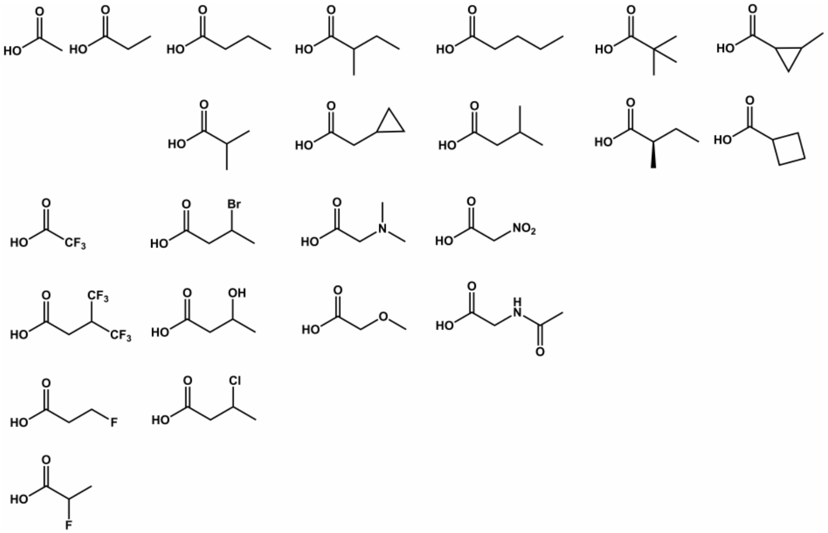
Hybrid Organic-Inorganic Hydroxide Solvents

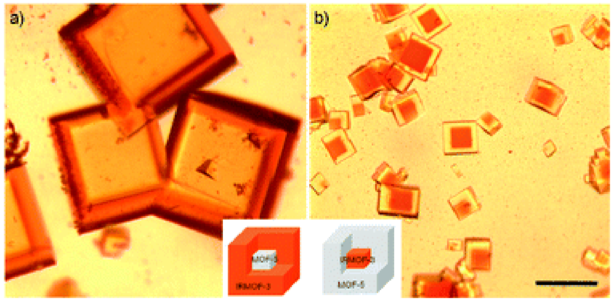


- **Phosphorous-Nitrogen core lends excellent stability and good interaction with CO_2.**
- **Molecular foliage used to control molar volume and add additional CO_2 affinity.**
- **Initial results do not appear favorable.**

Poster

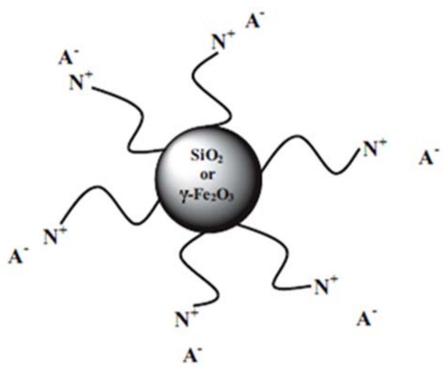
Core-shell MOFs

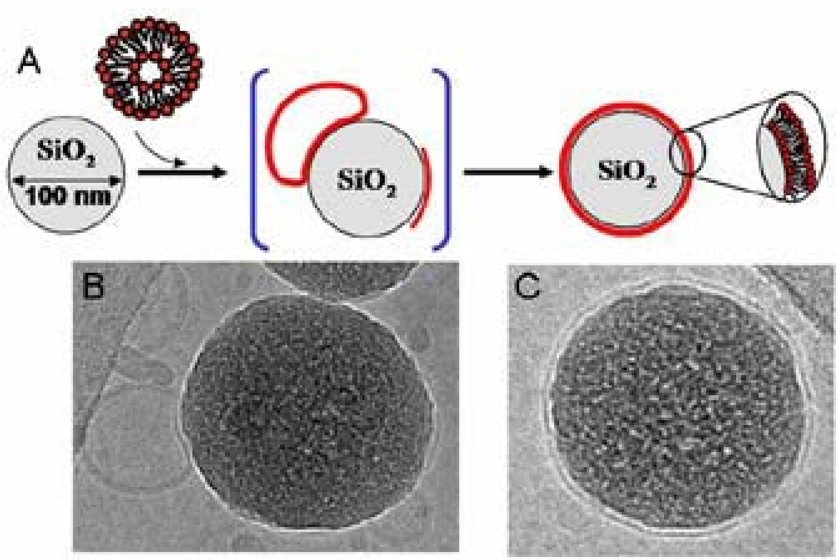




- Many MOFs with desirable properties for CO_2 capture are water sensitive.
- It is possible to grow MOFs with similar crystal lattices in intimate contact with one another.
- MOF particles may be created with a core of CO_2-philic, water sensitive MOF and a hydrophobic protective shell.
- Producing a practical capture material from the MOFs was not possible.

Hybrid Nanoparticle Solvents

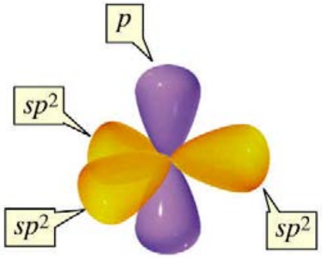




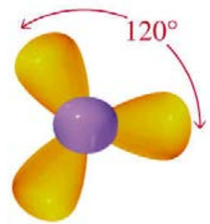
- Nanoparticles with appropriate ligands attached may behave as liquids.
- Depending upon the ligand and core, CO_2 capacity could be considerable.
- Cu-based nanoparticles of 10 nm size with targeted ligands were developed.
- Viscosity of the resulting liquids was too great, and they proved impractical.

Poster

Porous Borazine-coated Silica

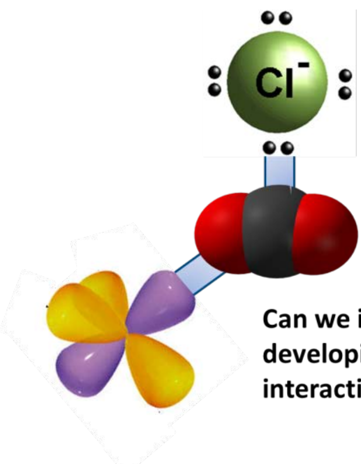


side view

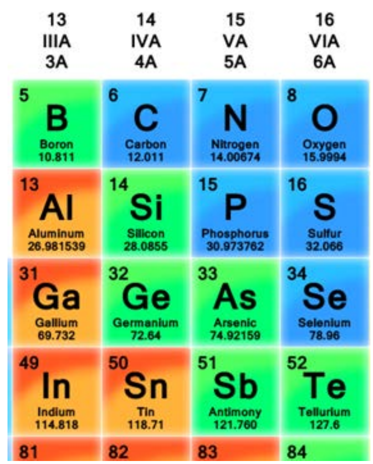


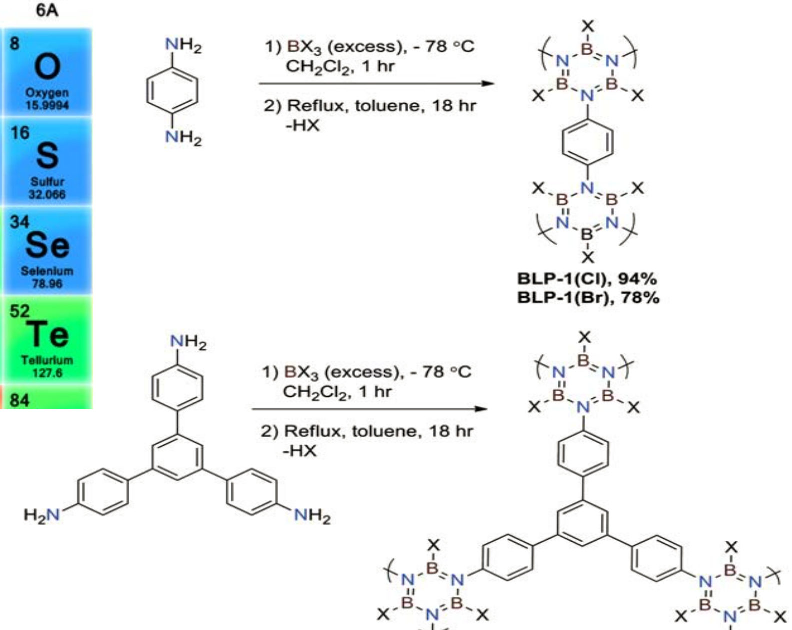
top view

- Boron containing materials have high CO_2 uptake and good stability.
- Capture materials may be made by supporting them on high surface area materials.
- Material fabrication underway.



Can we improve CO_2 interaction by developing a Bidentate type interaction?





Flexible Inorganic Polymer Membranes

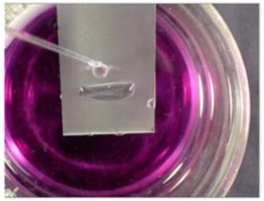
Polyphosphazenes:

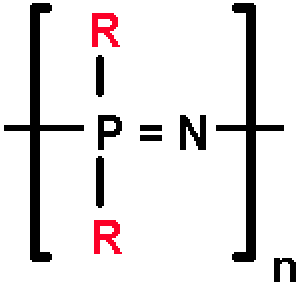
High performance elastomers (aerospace)

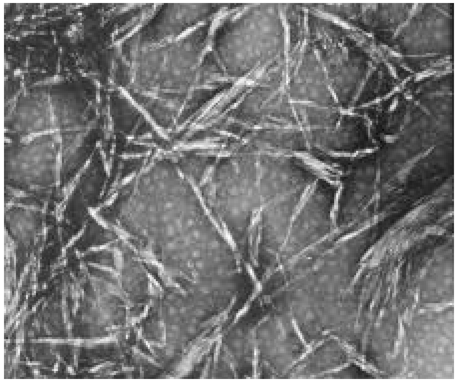
Hydrophobic fibers

Contact angle of water droplets, over 100°

Surface modification by plasma or chemical etching

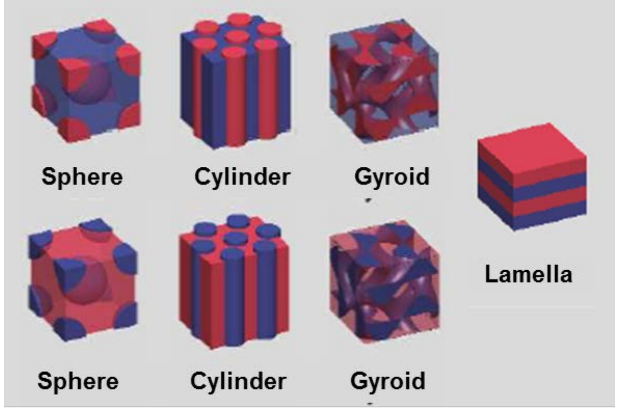


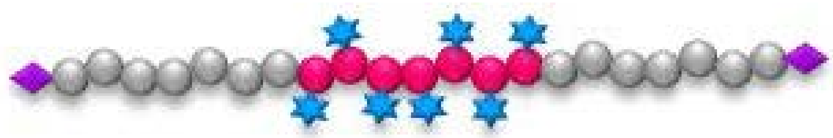


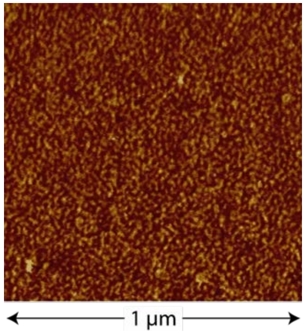


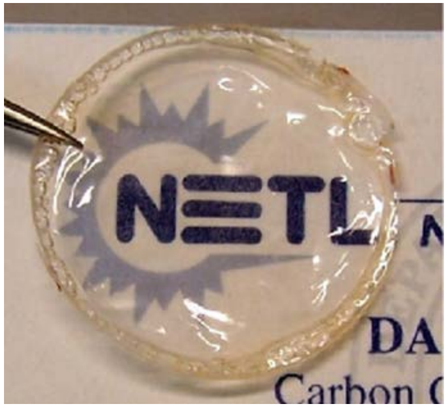
- **Phosphorous-nitrogen backbone shows good CO_2 affinity.**
- **Several new polymers synthesized with properties targeted for CO_2 separations.**
- **Film formation in progress.**

Structured Polymers (PILs)







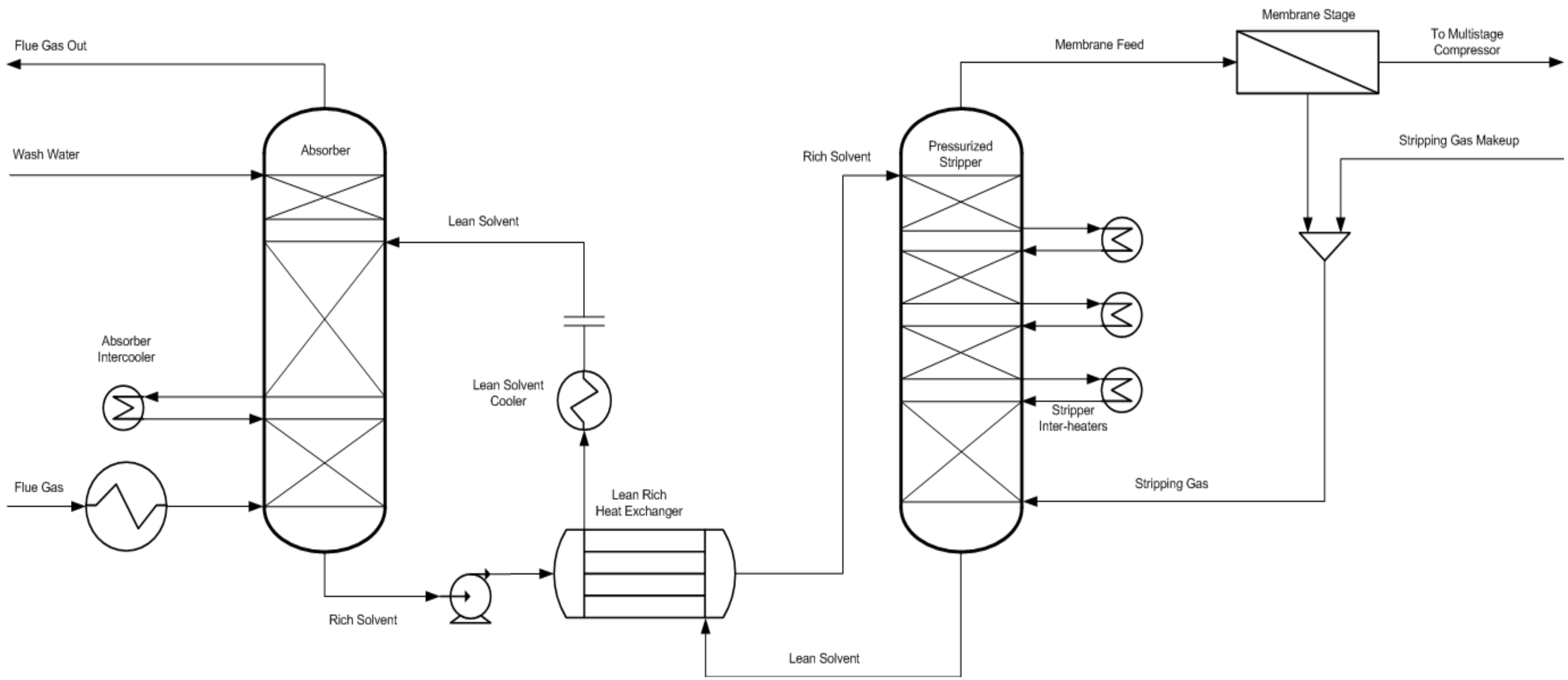


- Plasticization is a problem in CO_2-selective membranes.
- Block copolymers can phase segregate at the nanoscale to produce separate domains.
- The property can be used in a membrane with separate transport and structural phases.
- Membrane films have been created using poly(IL)s as the transport phase.

Poster

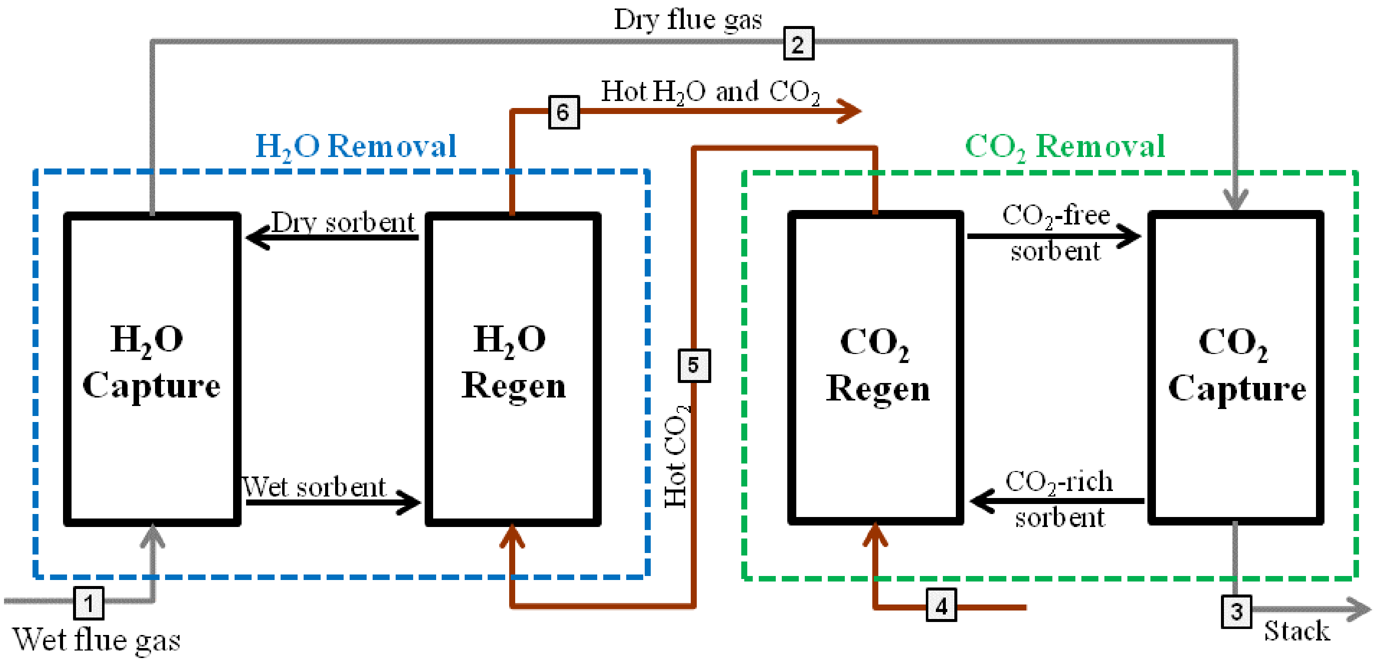
Processes

Solvent-Membrane Hybrid System



- An amine solvent cycle may be used with a sweep gas to compress the CO_2 in the flue gas to higher pressure and concentration.
- A membrane can then be used to produce pure CO_2 ready for sequestration.
- Systems analyses were performed examining the economics of the process and it was found to be competitive with existing processes without materials development.
- Membrane development was undertaken to improve the process.

Integrated Water Removal

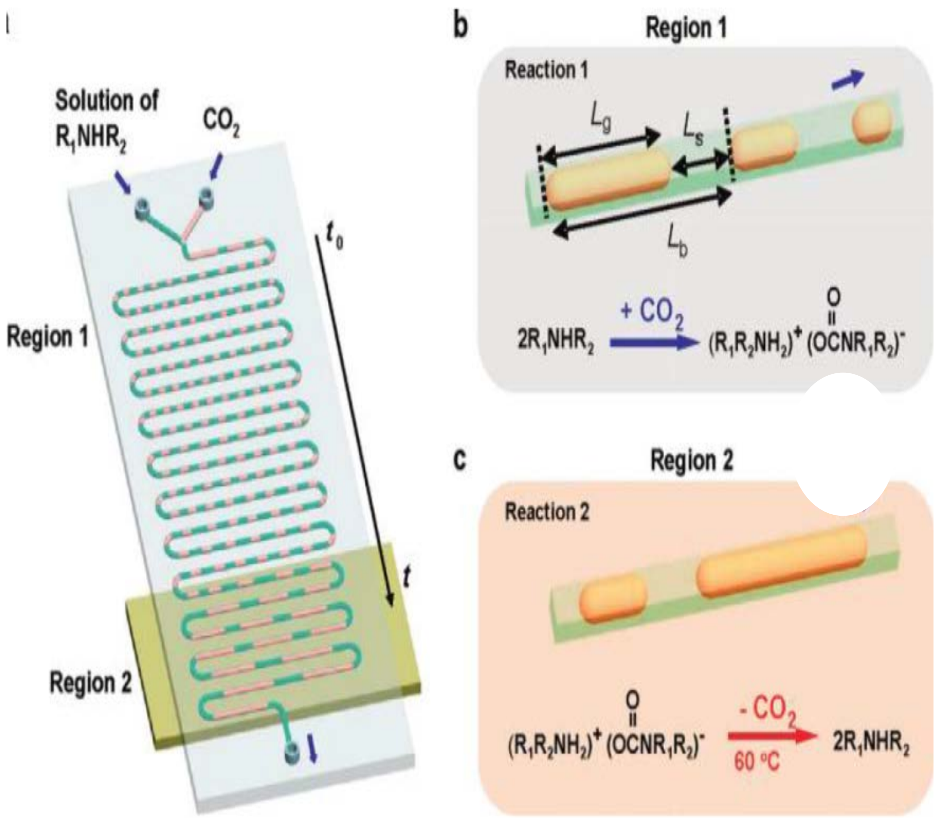


- Many potentially useful CO_2 capture techniques are infeasible because to the presence of water in flue gas.
- Using a low energy physical adsorption and making use of residual heat, the water may be removed concurrent to capture.
- Systems analyses were performed examining the economics of the process and it was found to be potentially competitive based on the capture technology used.

Poster

Methods

Microfluidic Apparatus for Solvent Characterization

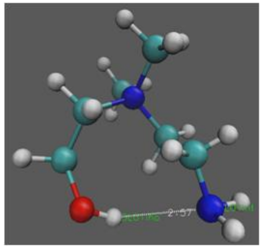


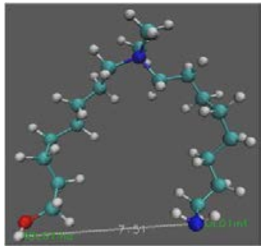
- **Screening of solvents can require large volumes of material and substantial time commitment.**
- **A microfluidic device was developed which examines bubble shrinkage over time in contact with a liquid solvent to determine gas solubility and mass transfer rate.**

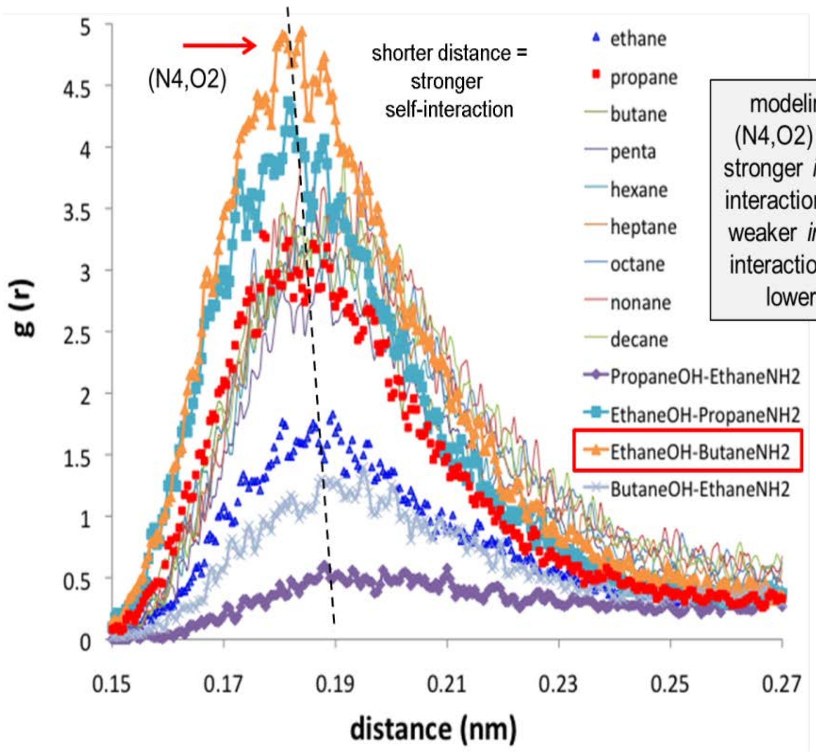
Conclusions

- **NETL-ORD uses an integrated technology development approach which examines a large number of technologies to determine their promise for CO_2 capture.**
- **A variety of materials, processes, and testing methods have been evaluated for their ability to achieve long term CO_2 capture targets.**
- **Some of the technologies show promise and further evaluation will be conducted.**

Choline-based ILs





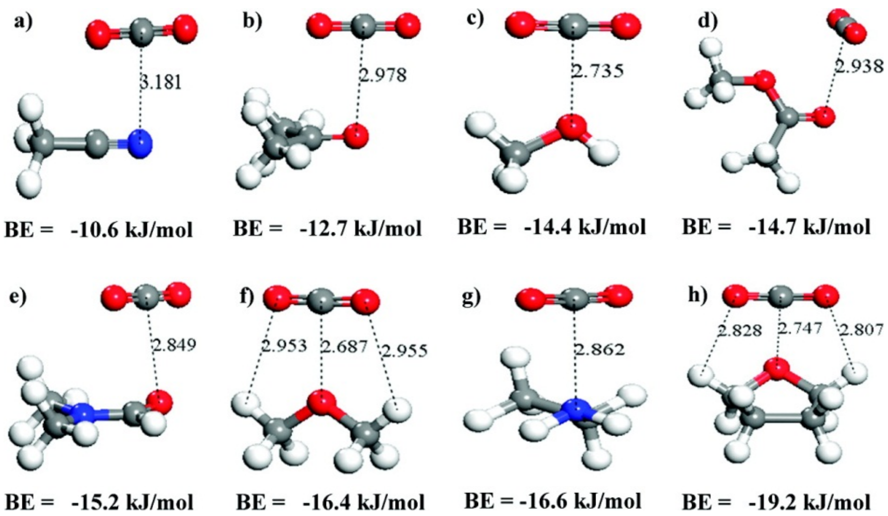


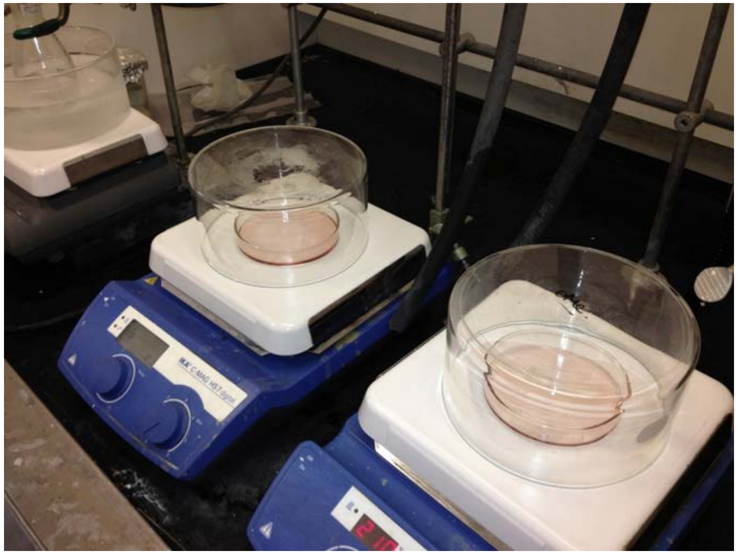
modeling predicts (N4,O2) should have stronger *intra*molecular interactions, leading to weaker *inter*molecular interactions and thus lower viscosity

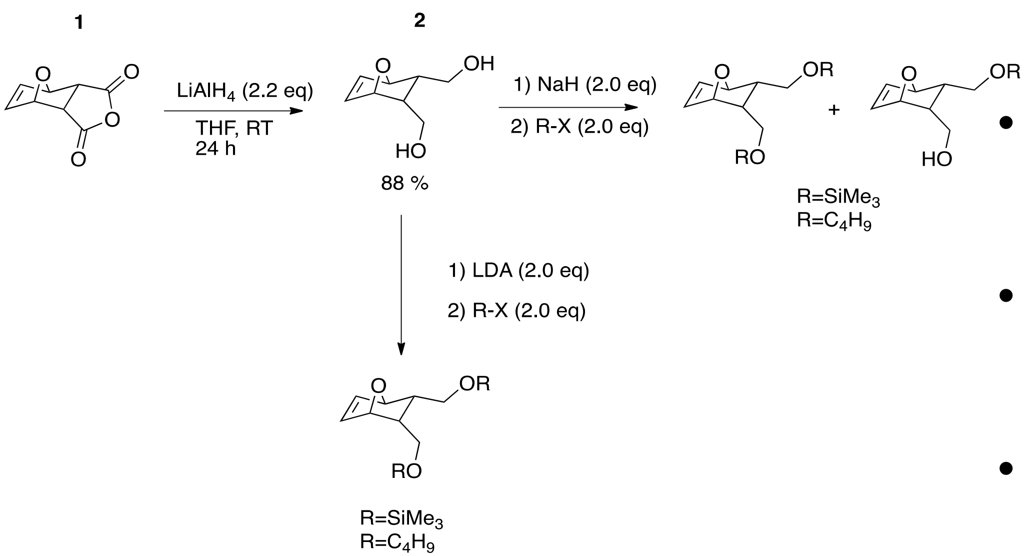
RFIL	viscosity cP	T_g °C	Setaram CO_2 uptake, mol CO_2 / mol IL
$[NH_2(CH_2)_2NMe_2(CH_2)_2OH]Tf_2N$ **(N2, O2)**	4530	-39.4	0.017
$[NH_2(CH_2)_2NMe_2(CH_2)_3OH]Tf_2N$ **(N2, O3)**	1146	-44.6	not determined
$[NH_2(CH_2)_3NMe_2(CH_2)_2OH]Tf_2N$ **(N3, O2)**	1303	-49.6	not determined
$[NH_2(CH_2)_3NMe_2(CH_2)_3OH]Tf_2N$ **(N3, O3)**	1424	-39.2	0.018
$[NH_2(CH_2)_3NMe_2(CH_2)_5CH_3]Tf_2N$ **(N3, hex)**	1084	-46.8	0.018
$[NH_2(CH_2)_4NMe_2(CH_2)_2OH]Tf_2N$ **(N4, O2)**	**280**	**-66.6**	**0.028**

- **Strong interactions with CO_2 are desirable for ILs as solvents and membranes.**
- **Inter-molecular hydrogen bonding leads to increased viscosity and reduced mass transport.**
- **Intra-molecular hydrogen bonding, which may be encouraged with spacer groups allows for reduced viscosity.**

Cyclic Ether-based Polymer Membranes





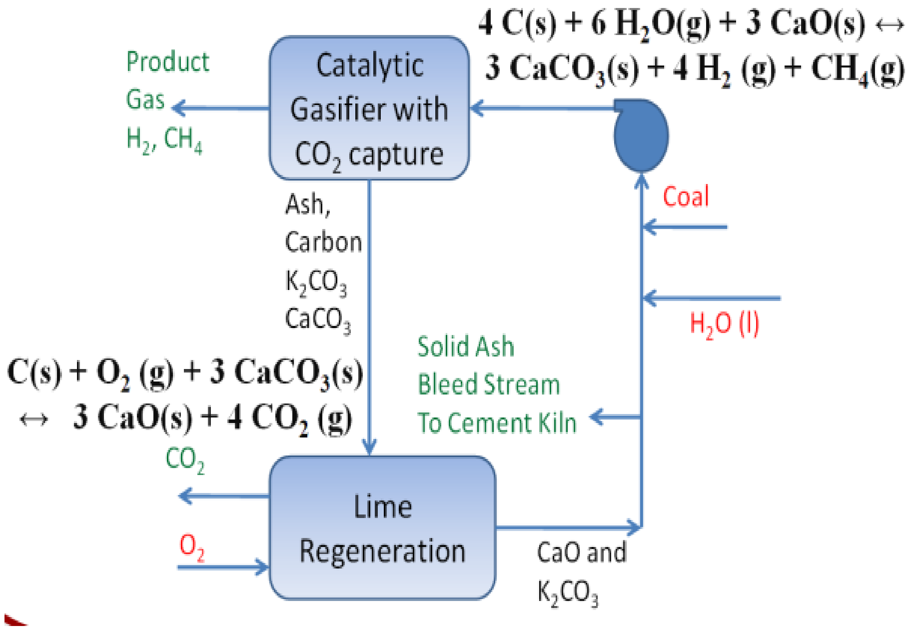


- **Cyclic ether-based polymers have tailorable free volume and molecular affinity for CO_2.**
- **Methodologies invented to synthesize monomers with desirable groups and polymerized these monomers.**
- **Film fabrication techniques developed for new materials.**

Babarao, Ravichandar, Sheng Dai, and De-en Jiang. "Functionalizing porous aromatic frameworks with polar organic groups for high-capacity and selective CO_2 separation: a molecular simulation study." Langmuir The Acs Journal Of Surfaces And Colloids (2011) p. 3451-3460.

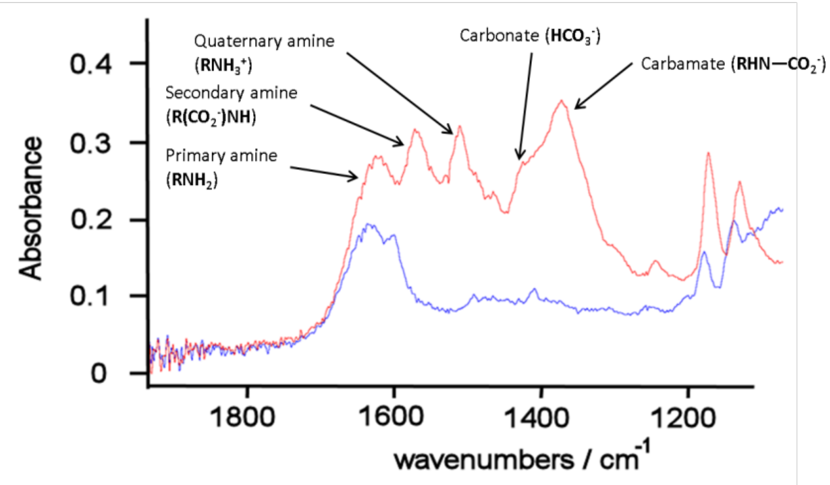
Coal Gasification with In-Situ CO_2 Capture

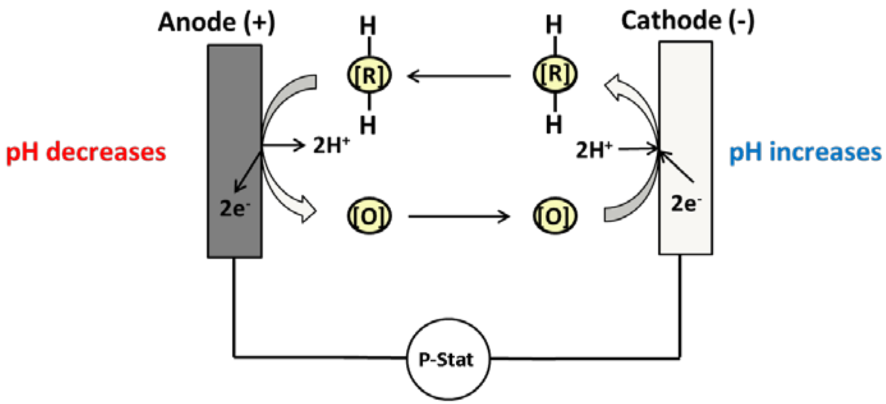
Process Flow Diagram: Gasifier & Lime Regeneration



- Process uses alkali hydroxides and alkali earth metal oxides inside the gasifier as combined gasification catalysts and capture agents.
- The exothermic heat of reaction of the CO_2 capture reaction is utilized to offset the endothermic steam-coal gasification reactions.
- Lab scale coal gasification experiments and systems analyses are underway to examine the feasibility of the process.

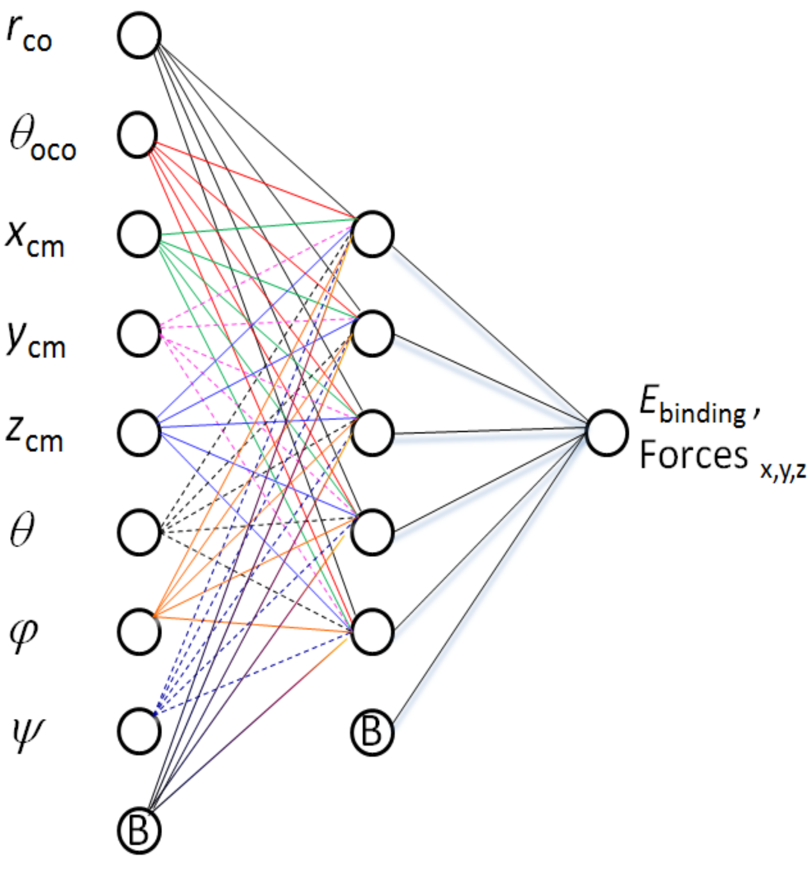
Redox-driven Regeneration of Amines





- Electrically driven pH swing may be used to drive CO2 capture and solvent regeneration in a cycle based on quinone.
- A capture device has been constructed and results show CO_2 concentration swing.
- Device may be employed in a membrane configuration.

Neural Network Modeling



- **NN is a processing system composed of a large number of highly interconnected processing elements.**
- **They work in unison to transform input data into output.**
- **Each neuron is defined by an activation function, which takes a weighted output of multiple input neurons as an argument.**
- **This input is used to train the force fields.**
- **An *ab initio* database for the specific case of CO_2-$[CH_3COO]^-$ anions is being generated.**