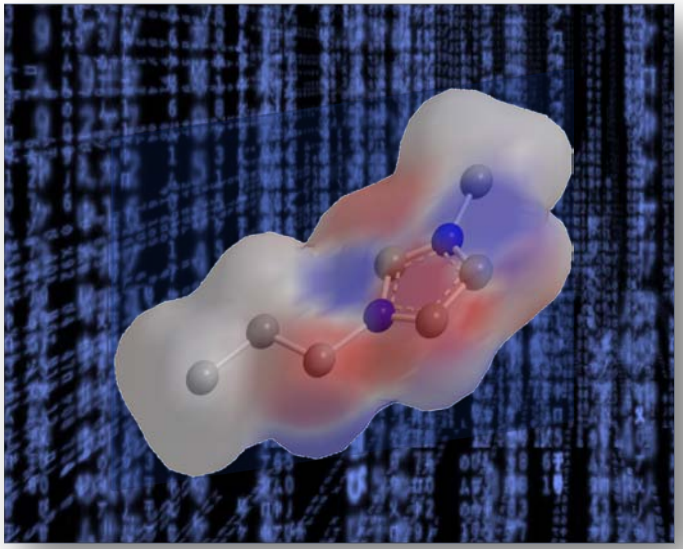
NATIONAL ENERGY TECHNOLOGY LABORATORY

Integrated Computational and Experimental Approaches to Ionic Liquid Development for Pre-combustion Solvents and Membranes



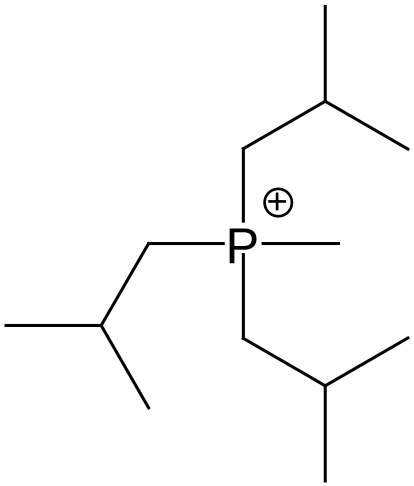
2010 NETL CO_2 Capture Technology Meeting

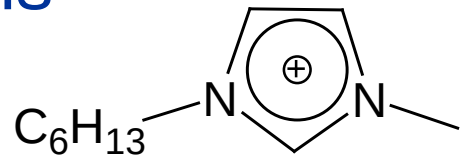
David Luebke, NETL

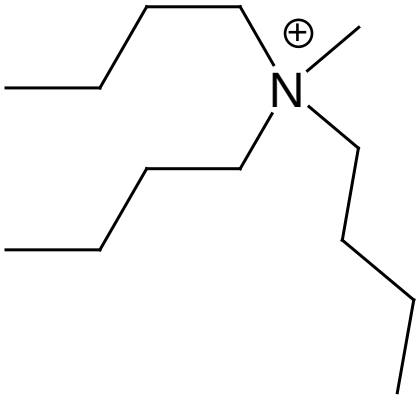
U.S. DEPARTMENT OF ENERGY

What is an ionic liquid?

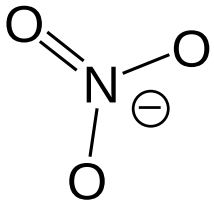
Cations

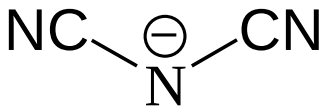


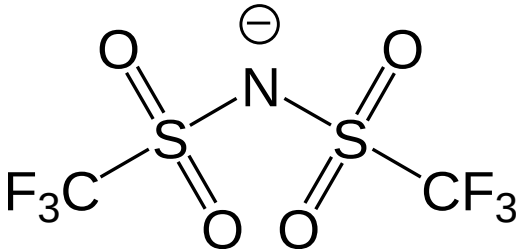




Anions

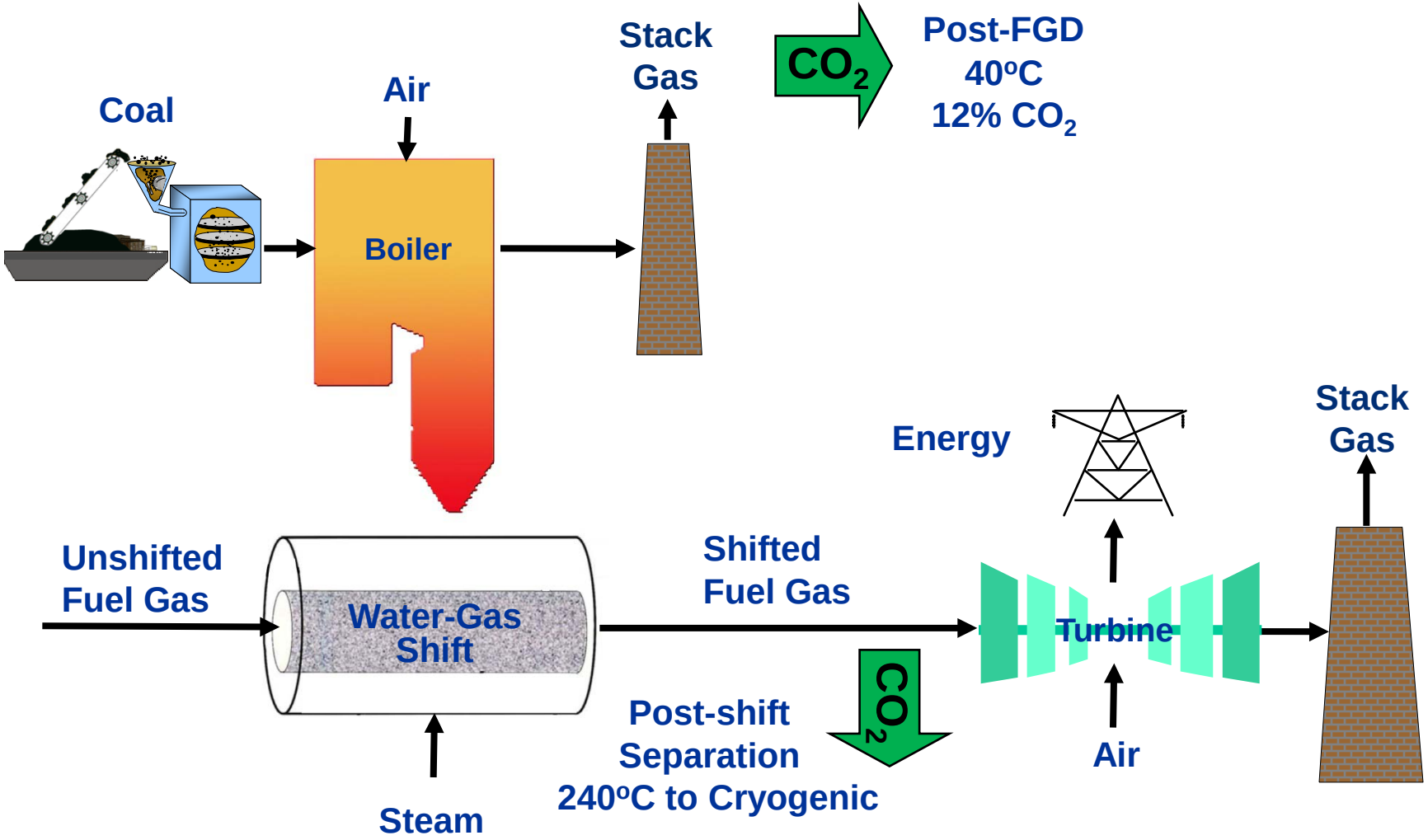






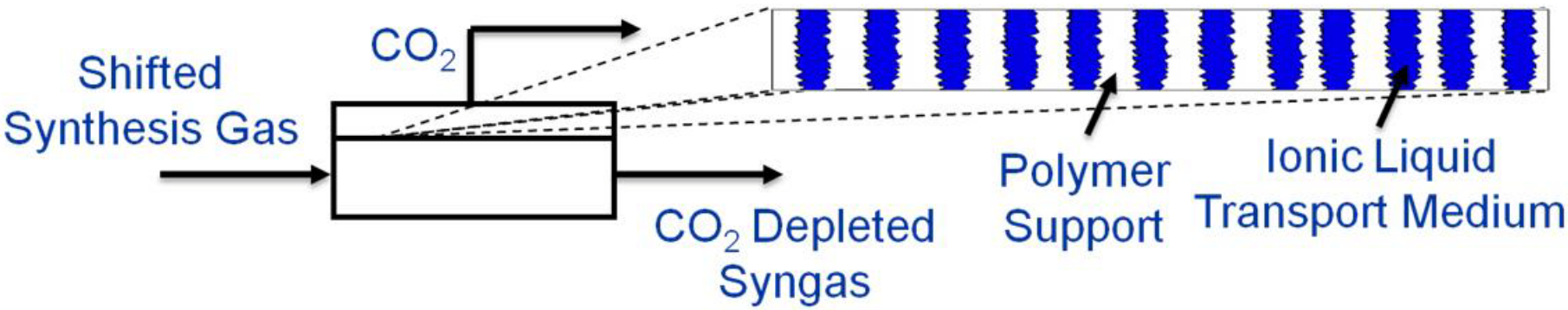
- Negligible vapor pressure
- Thermally stable above 200 ^{o}C
- High CO_2 solubility relative to CH_4, N_2, and H_2

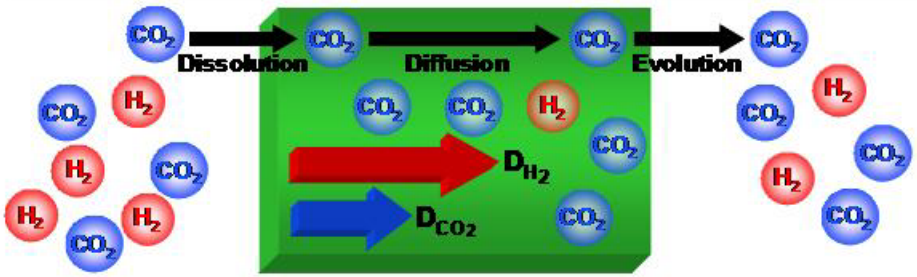
PC and IGCC CO_2 Capture



NETL Report. DOE/NETL-2007/1281

Ionic Liquids in CO_2 Separation

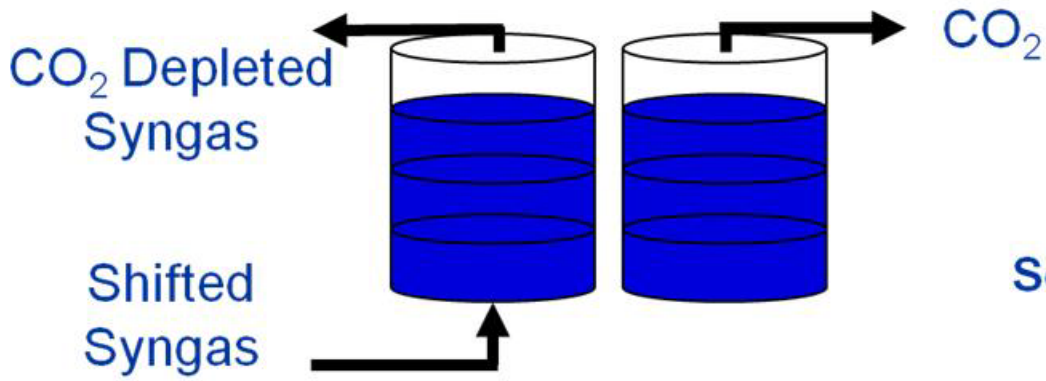




Solution Diffusion

Permeability = Solubility X Diffusivity

$$\text{Selectivity} = \frac{CO_2 \text{ Permeability}}{H_2 \text{ Permeability}}$$

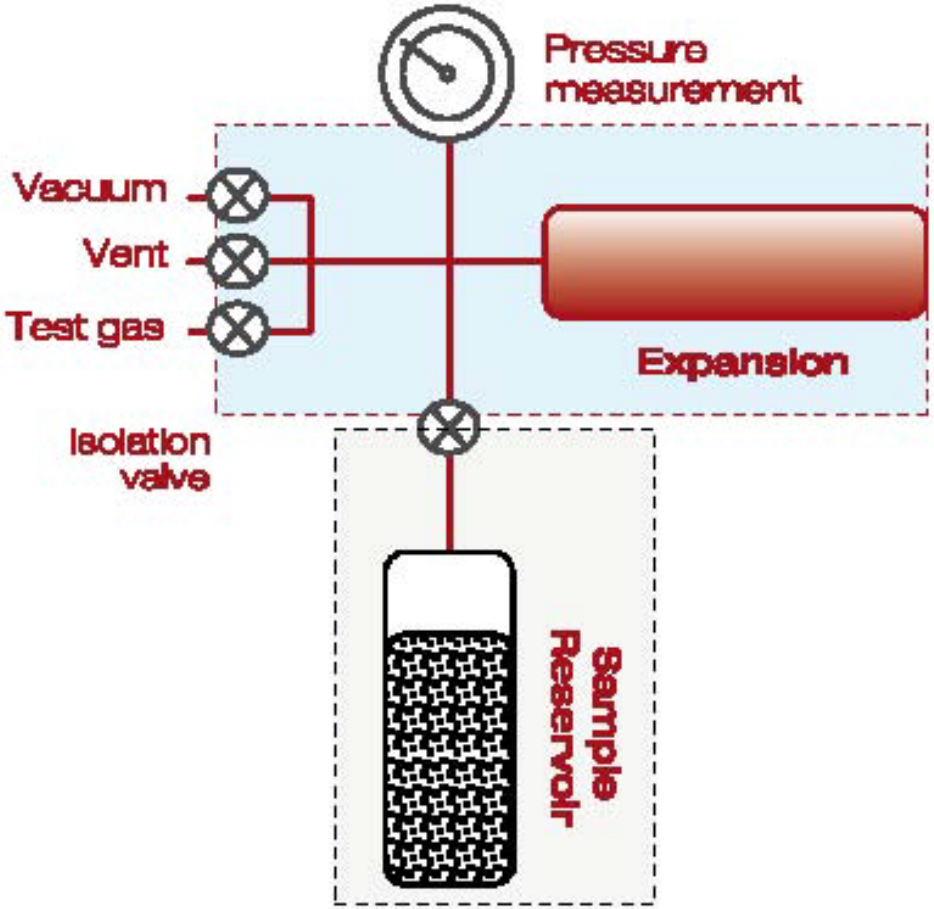


Capacity

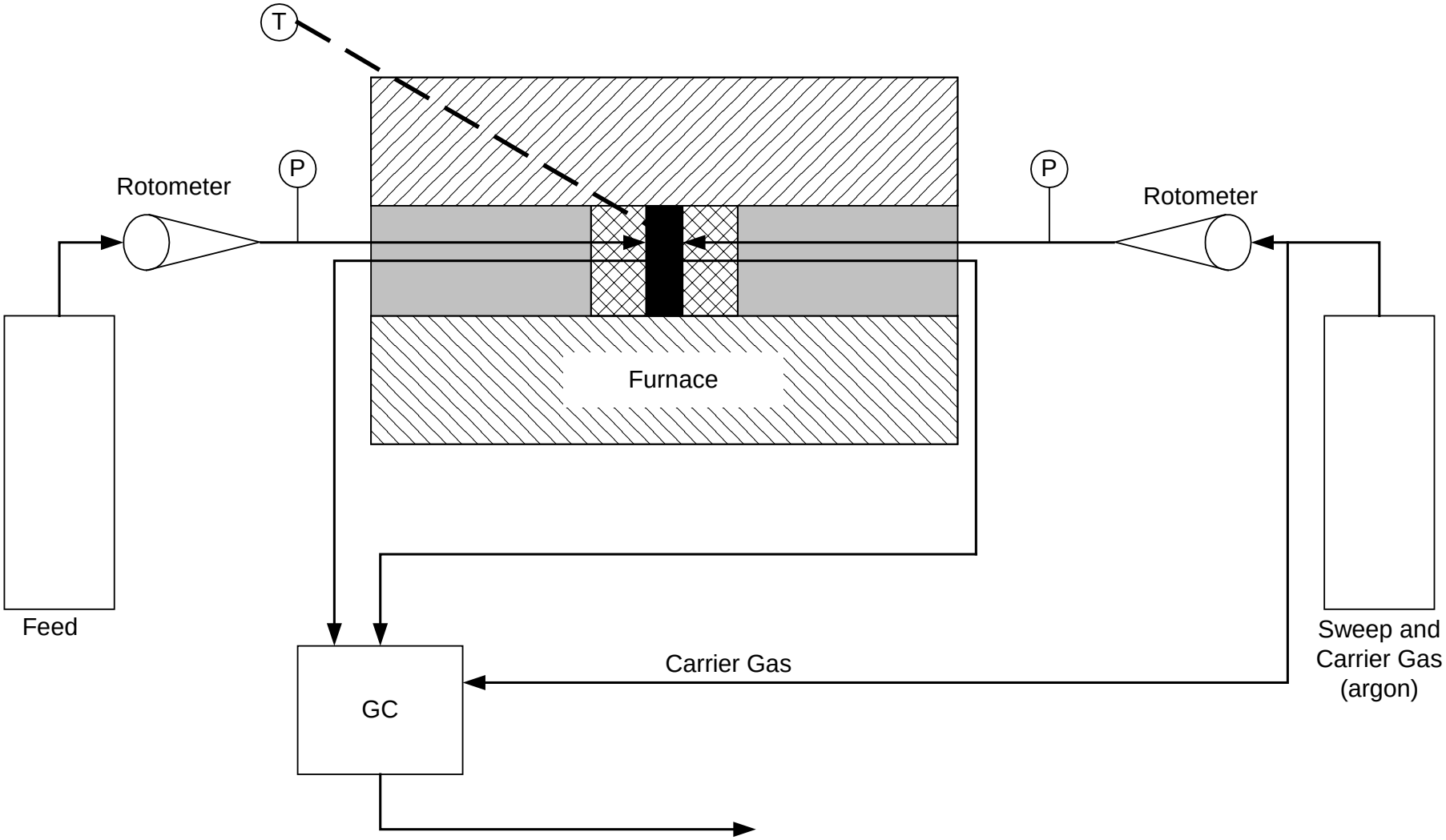
$$\text{Selectivity} = \frac{CO_2 \text{ Solubility}}{H_2 \text{ Solubility}}$$

Solubility Measurements

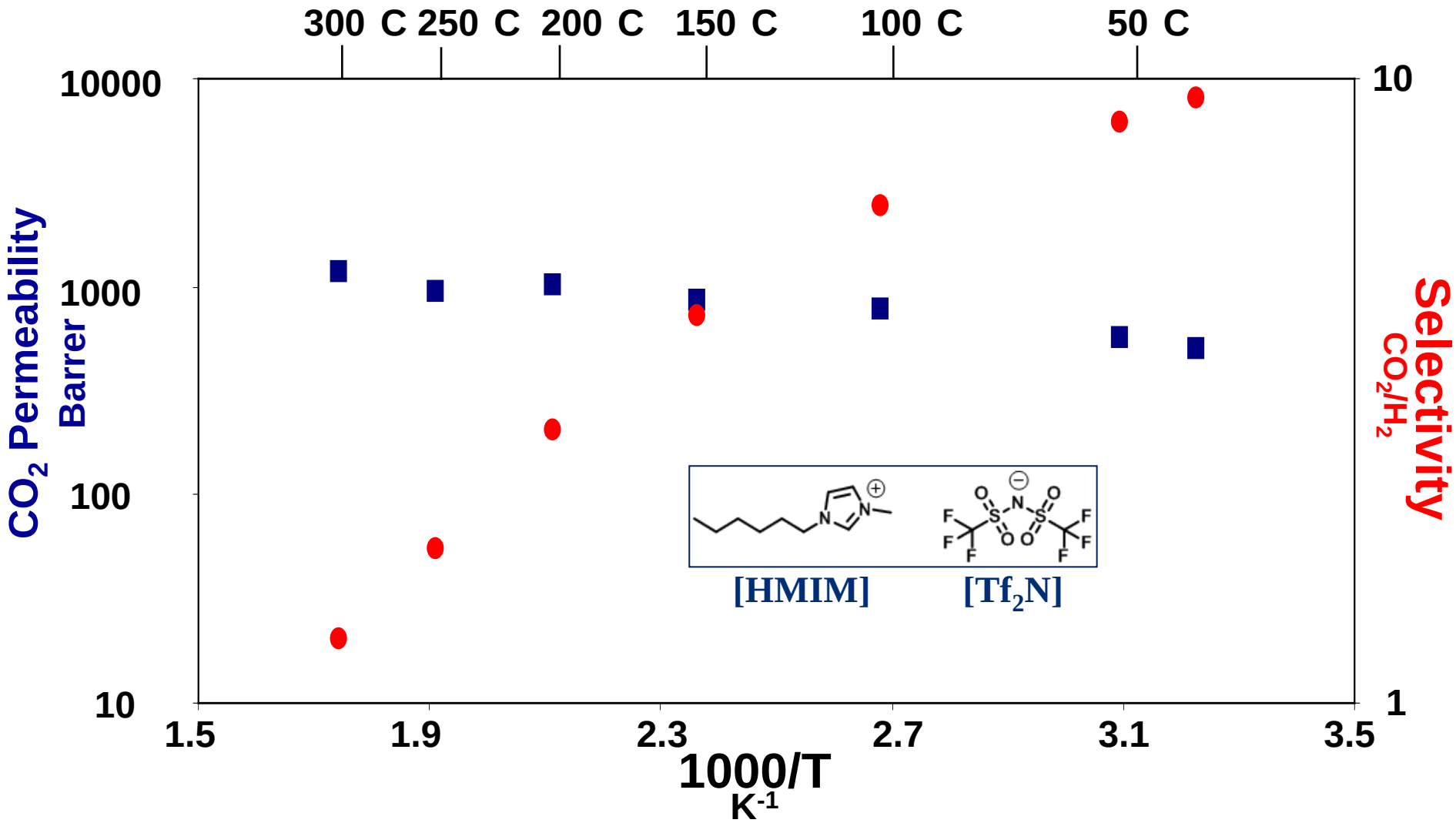
- **Sievert's method**
  - Absorption calculated from pressure change of a known volume
- **Temperature Range:**
  - **Ambient to 400ºC**
- **Pressure Range:**
  - **Vacuum to 200 bar**



Membrane Measurements



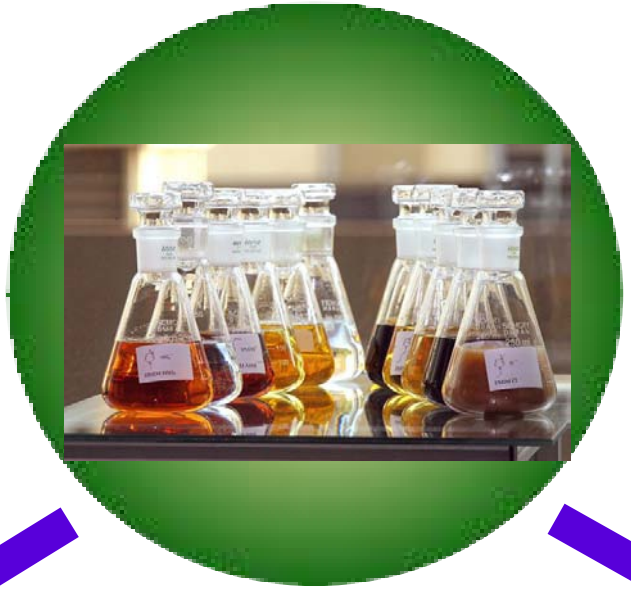
SILM Performance



Ionic Liquid Developmental Challenges

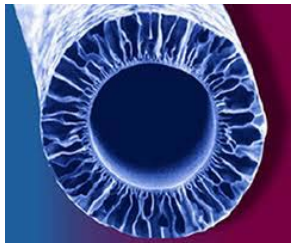
IONIC LIQUIDS

- Thermal and Chemical Stability
- High Hydrophobicity
- High CO_2 Solubility
- High CO_2/H_2 Selectivity



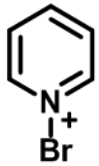
MEMBRANE POLYMERS

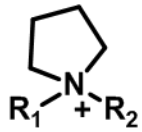
- Thermal, Mechanical and Chemical Stability
- High T_g
- Compatibility with IL
- Configurations which Effectively Contains IL

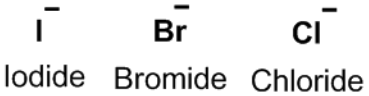


Ionic Liquid Variety

Estimated 10^{14} possible ionic liquids


Pyridinium

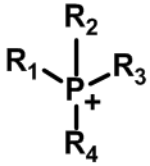

Pyrrolidinium

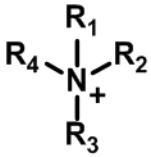


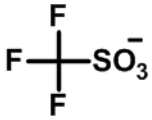
Iodide Bromide Chloride

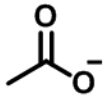
Tetrafluoroborate

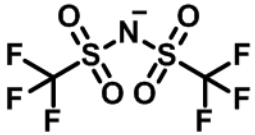
Hexafluorophosphate

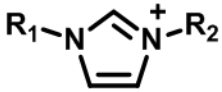

Phosphonium

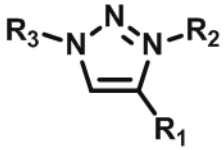

Ammonium

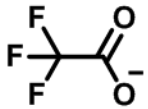

Trifluoromethylsulfonate


Acetate


TF_2N


Imidazolium


Triazolium

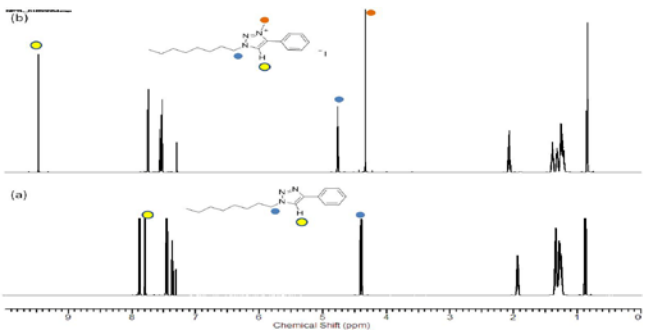

Triflouroacetate

~1000 ionic liquids commercially available

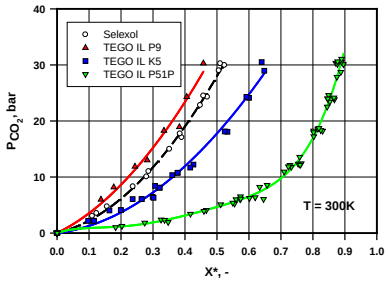
J. Chem Inf. Model. **2007** *47, 1111-1122.*

Integrated Materials Development

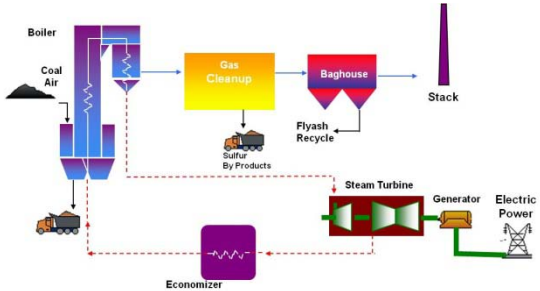
Characterization

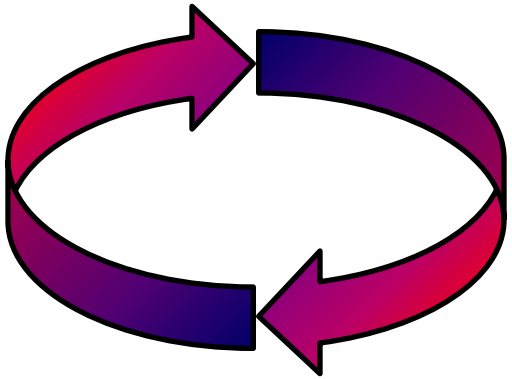


Performance Testing

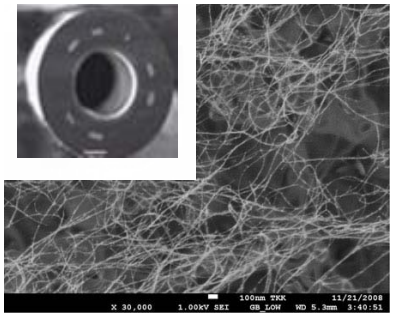


Systems Analysis

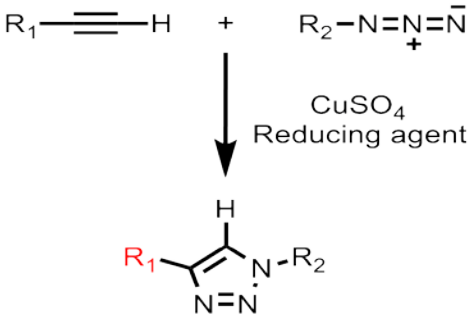




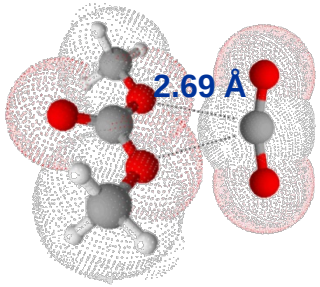
Fabrication



Synthesis



Modeling



Computational Guidance

Ab initio QM →

1. energy, structure
2. charge, force field parameter
3. mechanism, etc.

↓

Classical force-field

$$V_{tot} = \sum_{bonds} k_b (r - r_0)^2 + \sum_{angles} k_\theta (\theta - \theta_0)^2 + \sum_{dihedrals} k_\chi [1 + \cos(n\chi - \delta)] + \sum_{impropers} k_\psi (\psi - \psi_0)^2 + \sum_{i=1}^{N-1} \sum_{j>i}^{N} \left\{ 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \right\} + U_{pol}$$

Thermodynamic properties
from Monte Carlo

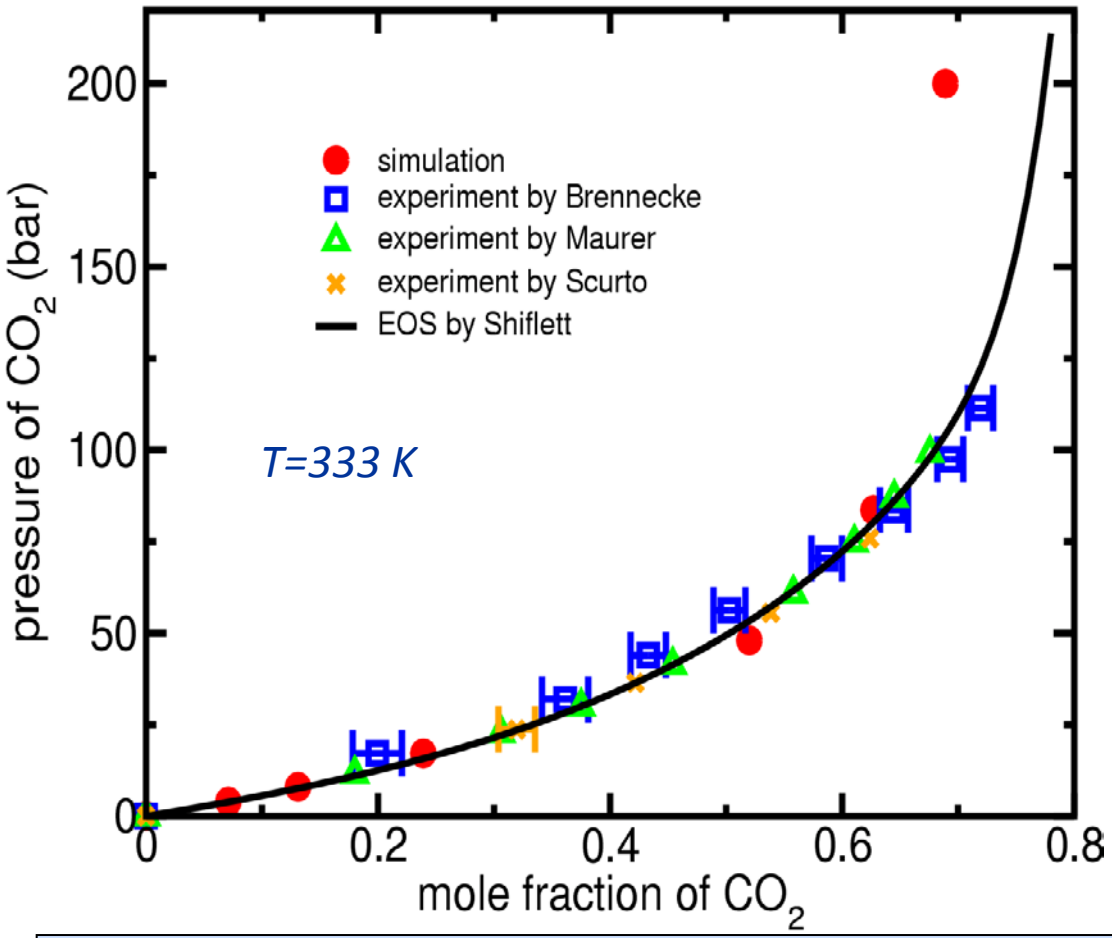
Transport properties
from Molecular Dynamics

- ***Henry's law constant, mixed gas selectivity, transport coefficient;***
- ***Permeability, permeability selectivity;***
- ***Other process related properties such as heat of mixing;***
- ***Interaction mechanism: physical, chemical, intermolecular complex.***

→

- ***Search for better ILs***
- ***Modify IL functionality***
- ***Discover new IL***

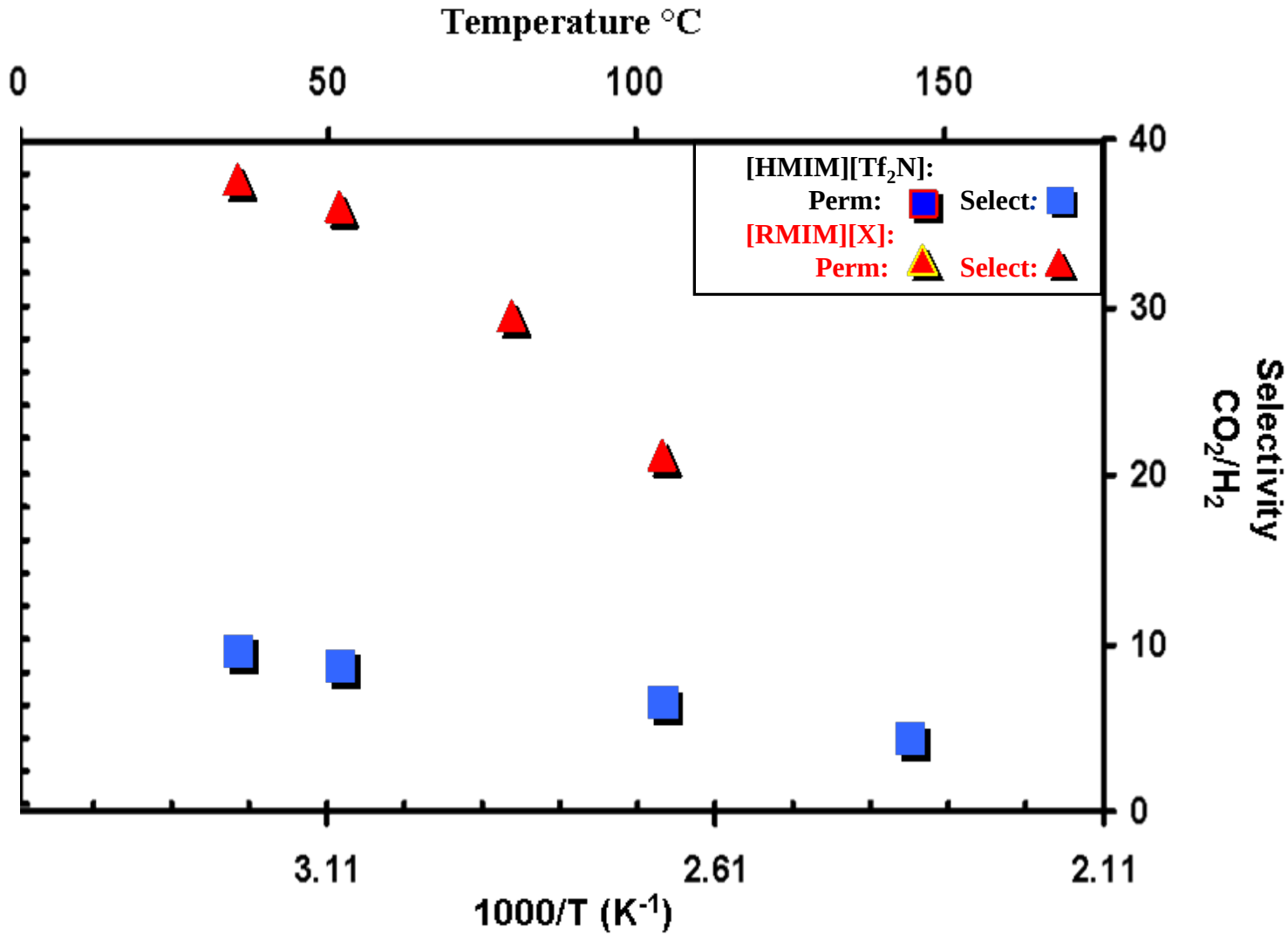
Isotherm of CO_2 / [hmim][Tf_2N]



Experiments:
H = 52.3 bar (Brennecke, et al., J. Phys. Chem. B, (2004))
H = 2.8 bar (Maurer et al., J. Chem. Eng. Data. (2006))
EOS: H = 49.3 bar (Shiflett, et. al., J. Phys. Chem. B, (2007))
Simulation: H = 49.4 bar (Shi, Maginn, et al., J. Phys. Chem. B, (2007))

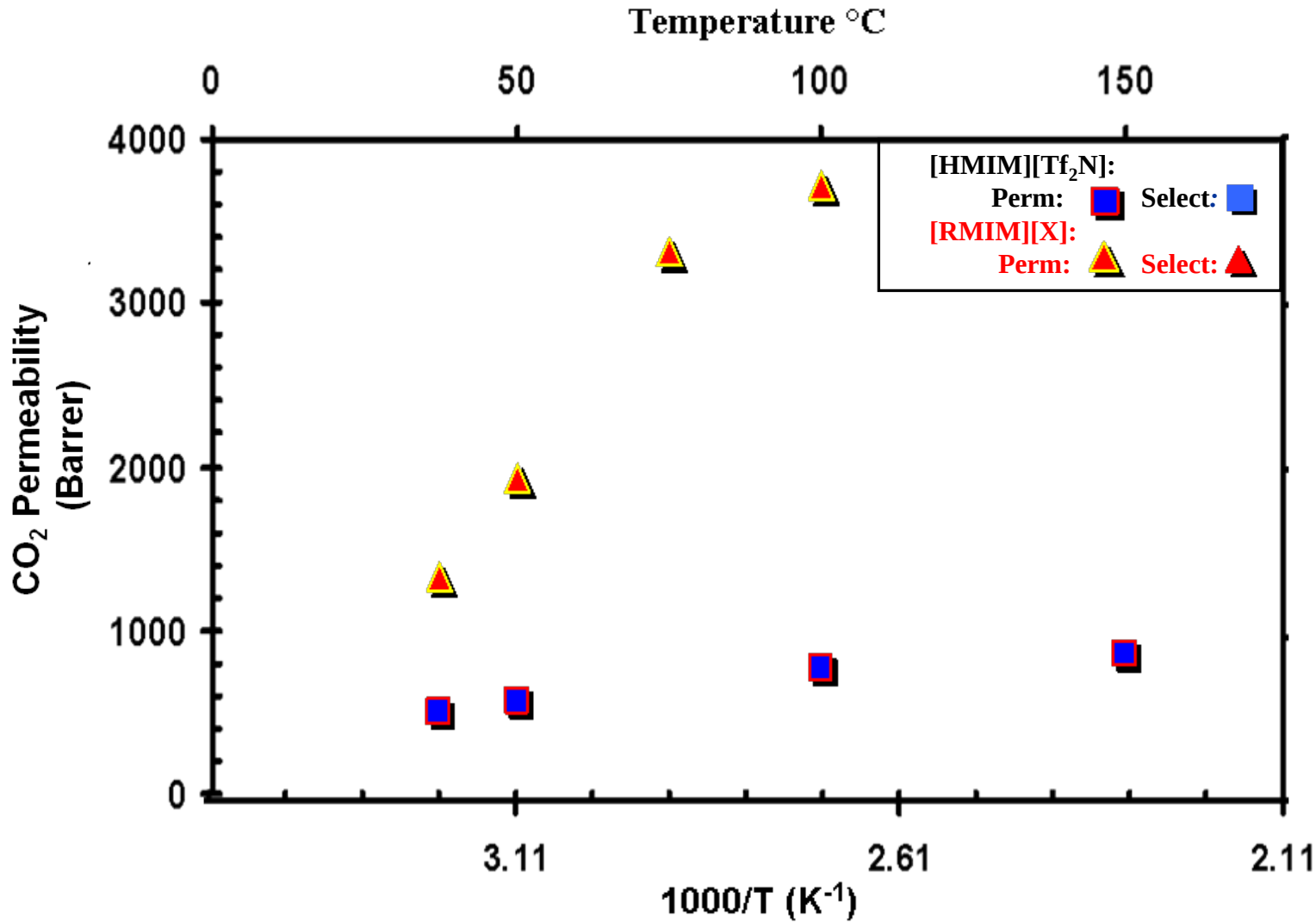
Improvement through Computational Guidance

[HMIM][Tf_2N] & [RMIM][X]



Improvement through Computational Guidance

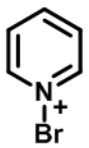
[HMIM][Tf_2N] & [RMIM][X]



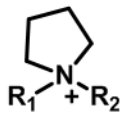
What about solvents?

Synthesis Approach Needed

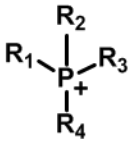
Synthesis approach required which allows rapid creation of computationally desirable ionic liquids



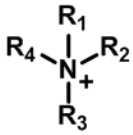
Pyridinium



Pyrrolidinium



Phosphonium



Ammonium

Synthesis Needs:
- **Robust**
- **Functional group tolerant**
- **Modular**
- **Polymerizable (when needed)**

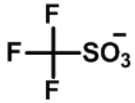
Iodide

Bromide

Chloride

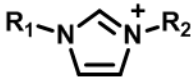
Tetrafluoroborate

Hexafluorophosphate

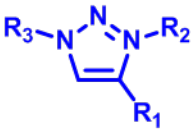


Trifluoromethylsulfonate

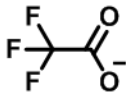
Acetate



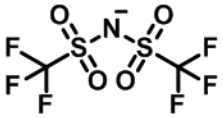
Imidazolium



Triazolium



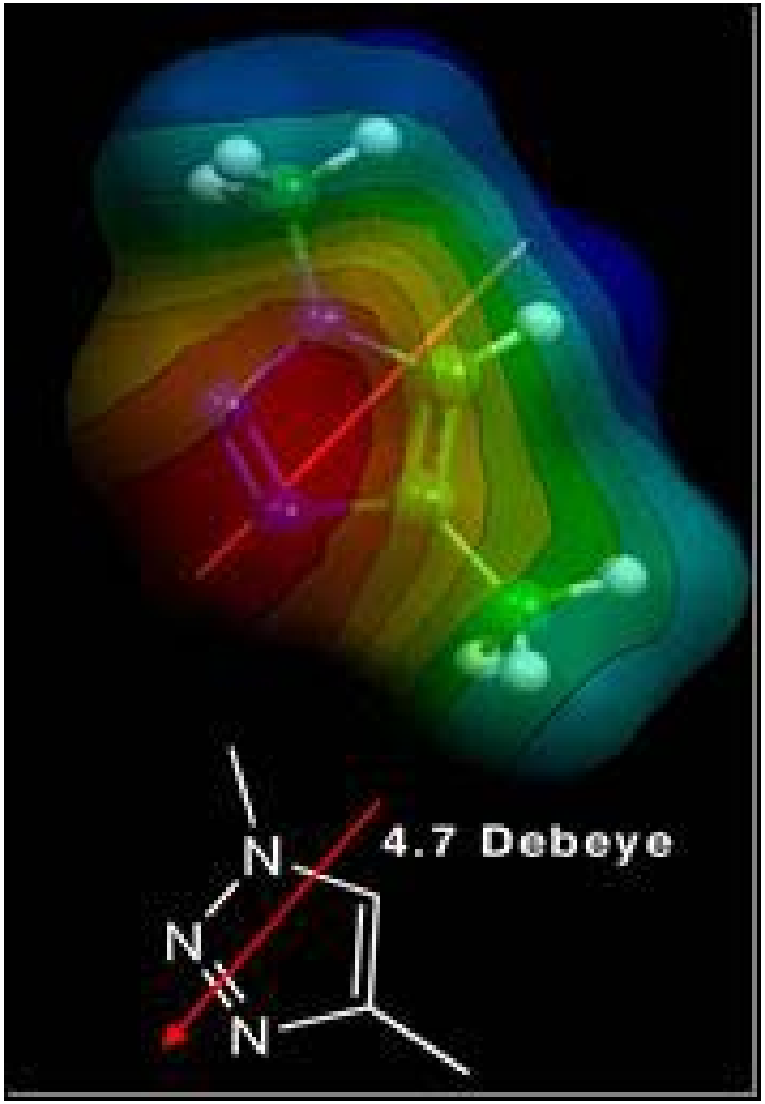
Triflouroacetate



TF_2N

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

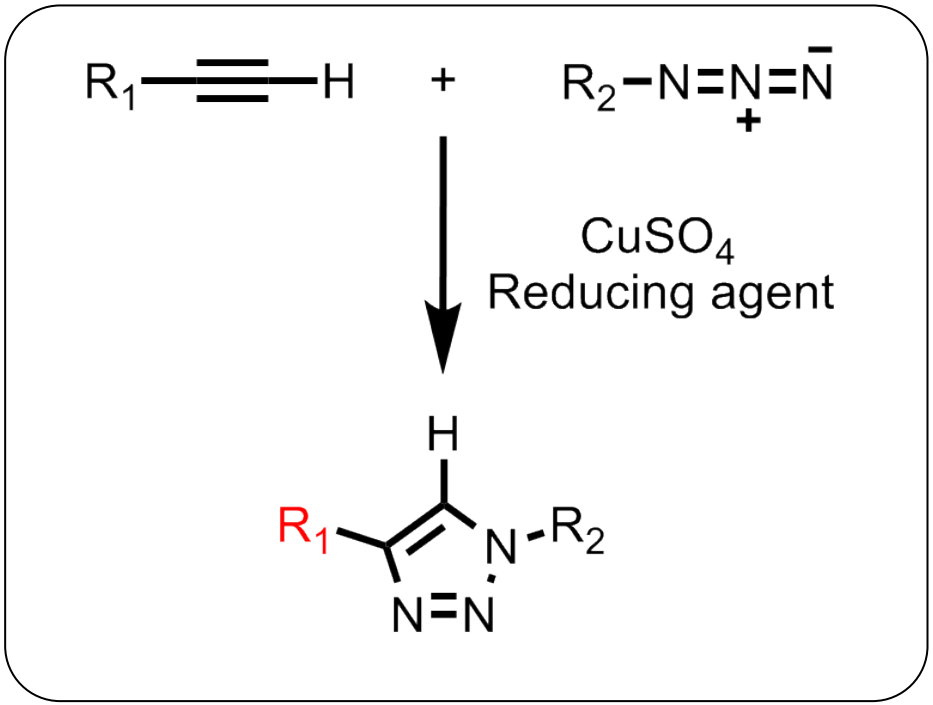
Properties of Triazoles



- Aromatic
- Hydrogen bonding
- Large dipole moment
- Thermally and chemically stable
- Highly modular
- Metal coordination

Cu(I) Catalyzed Synthesis of 1,4 Triazoles

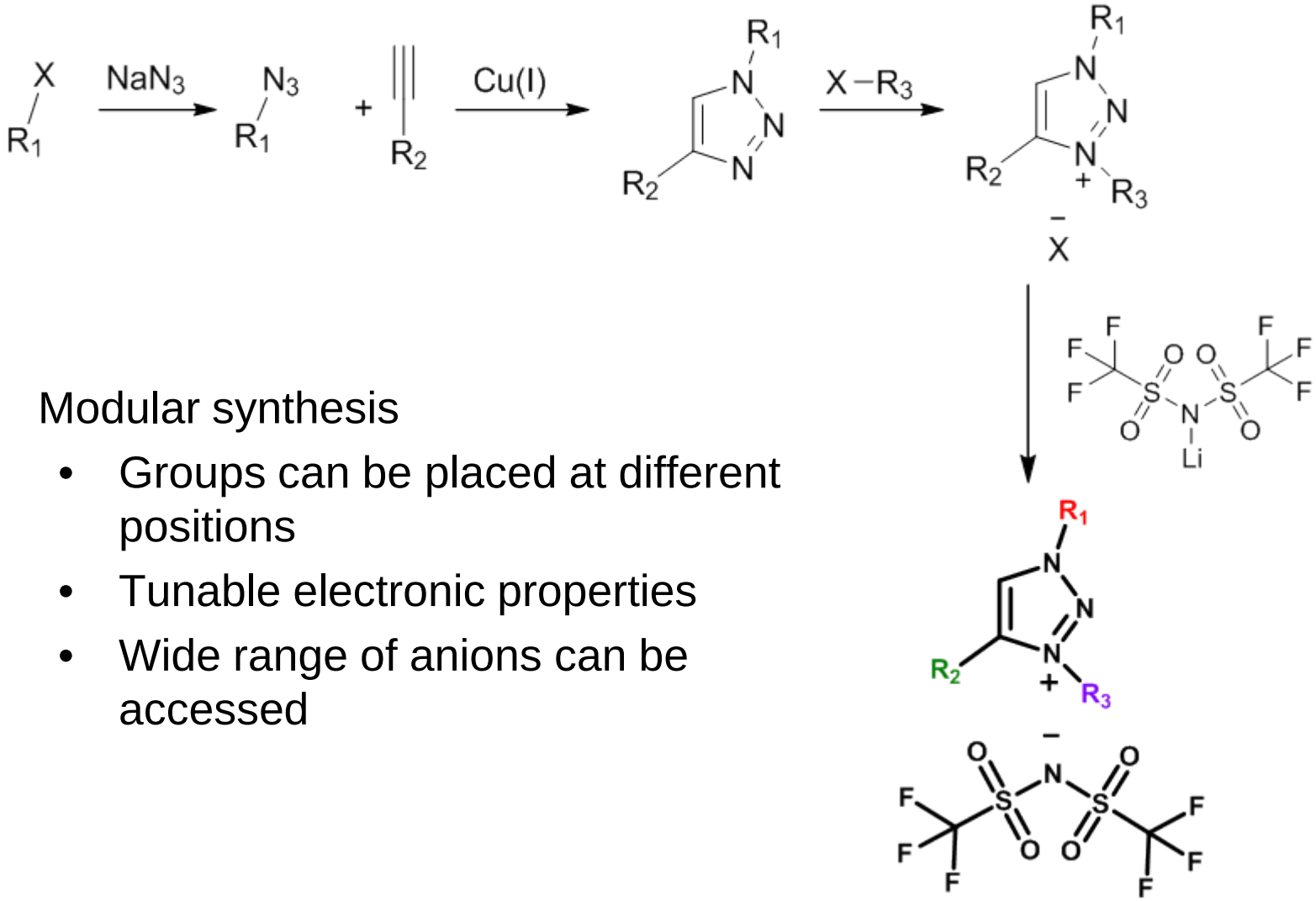
Cu(I) catalyzed click reaction



- **Almost 100% regioselective**
- **Quantitative**
- **Benign reaction conditions**
- **No or little by-products**
- **Functional group tolerant**

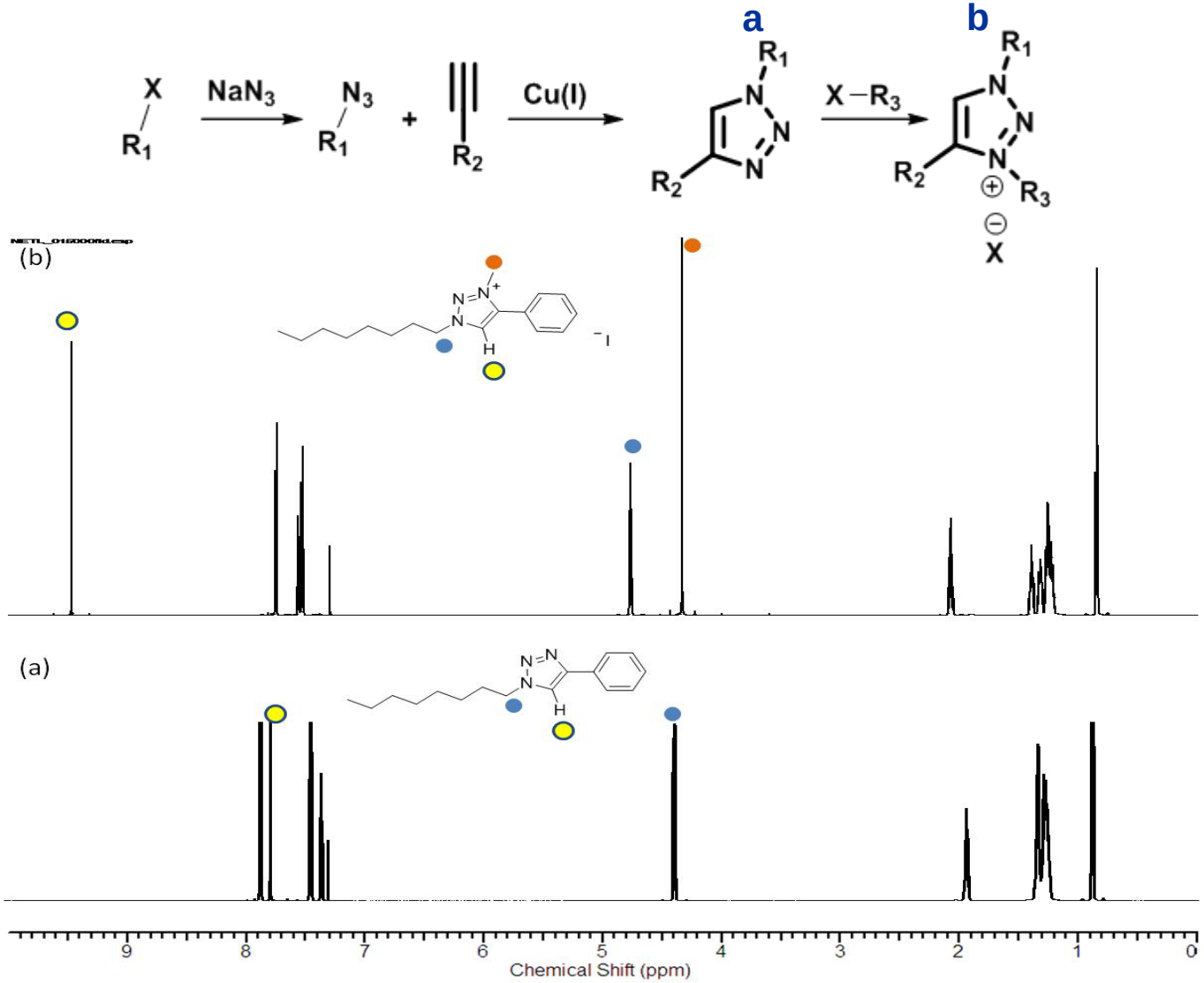
Angew. Chem. Int. Ed. ***2001,*** *40, (11), 2004.*

Synthesis of Triazolium IL

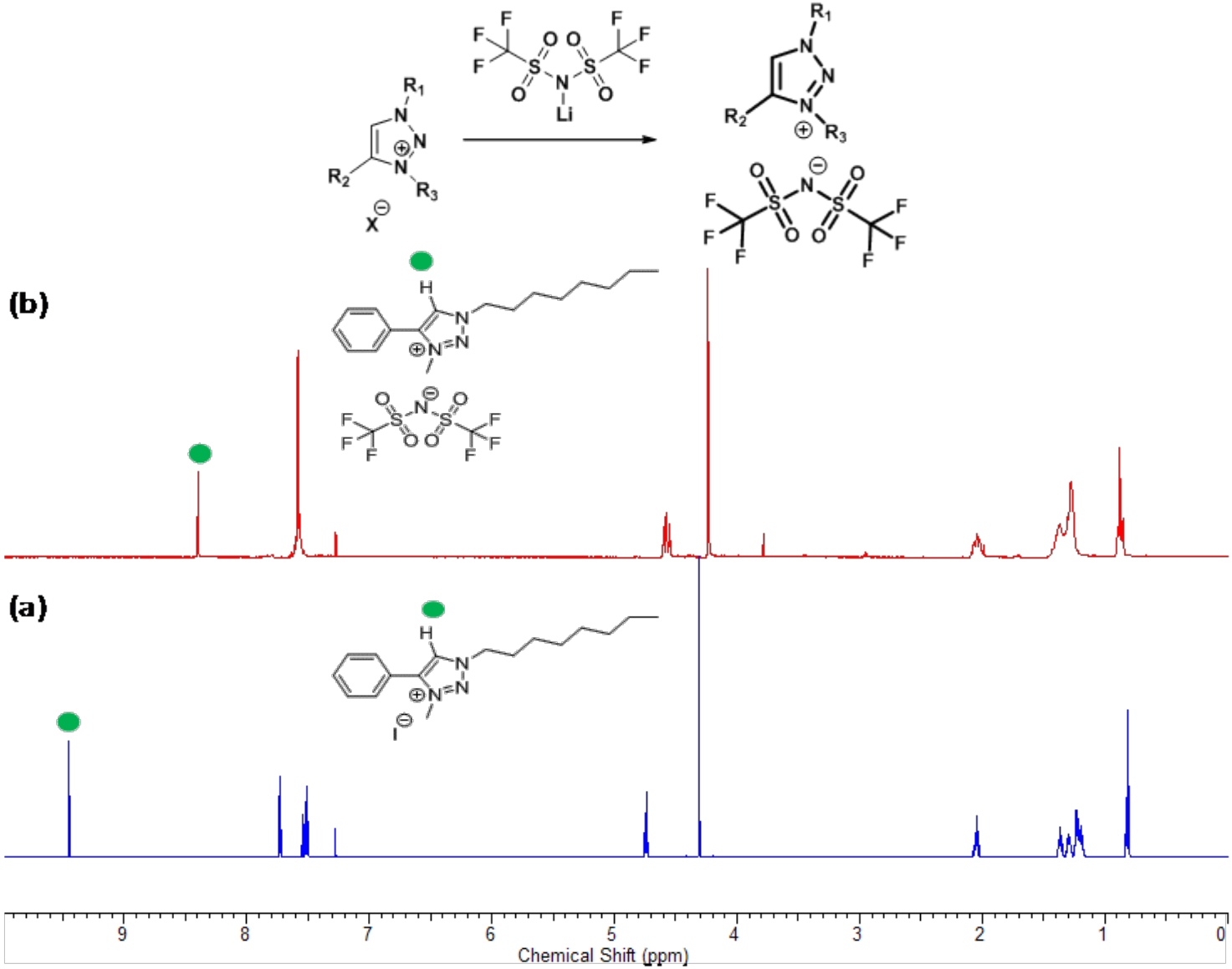


- Modular synthesis
  - Groups can be placed at different positions
  - Tunable electronic properties
  - Wide range of anions can be accessed

NMR Characterization (Click and Quaternization)



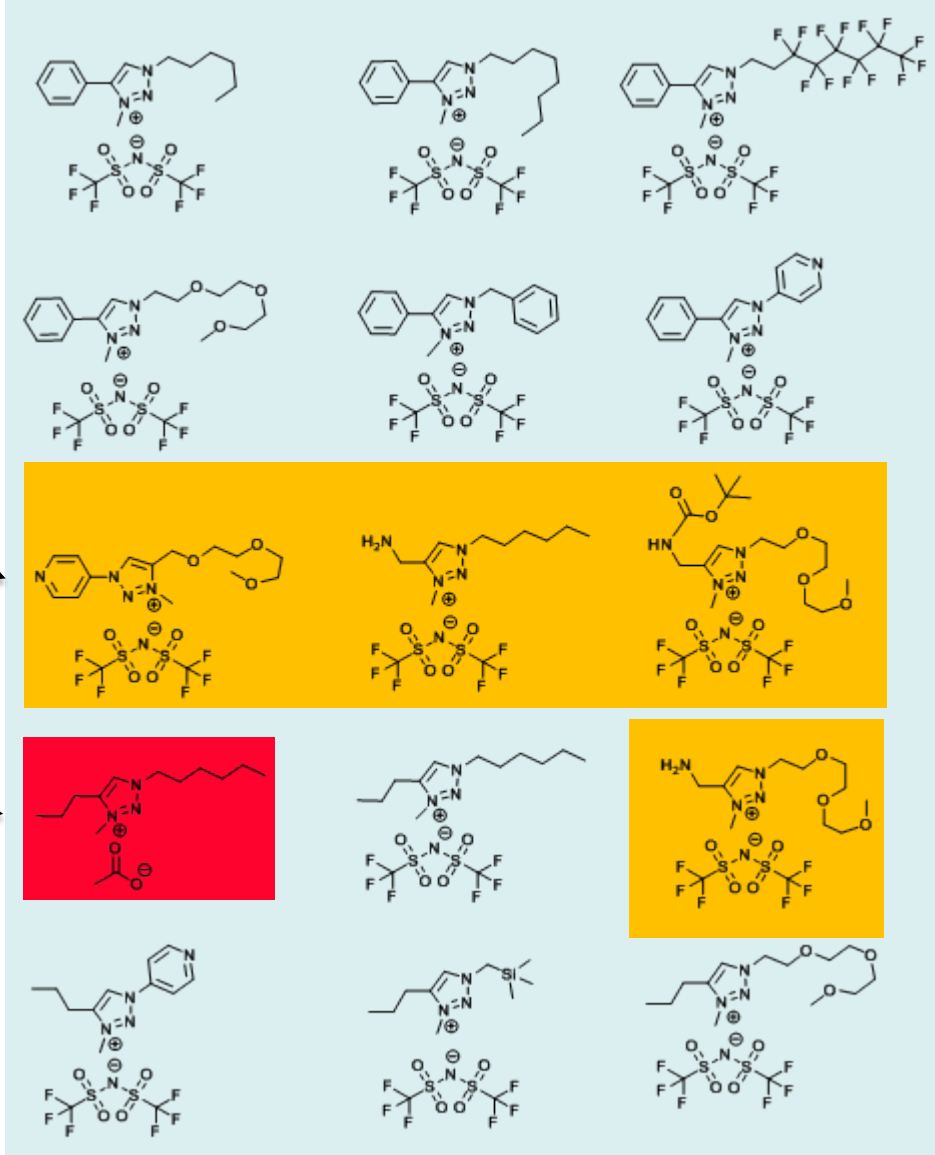
NMR Characterization (Ion Exchange)



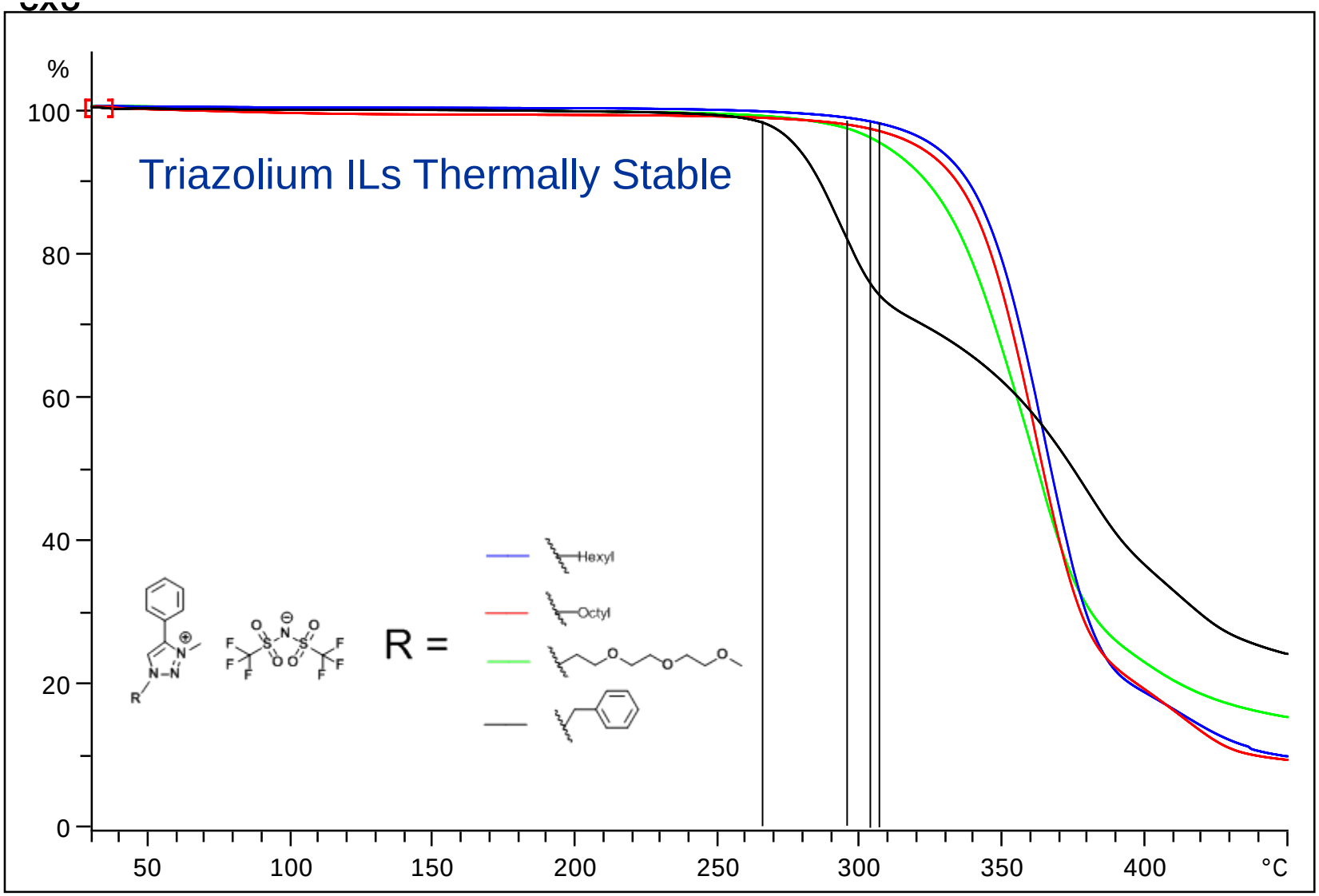
Synthesized Triazolium ILs

Chemically Interacting Cations

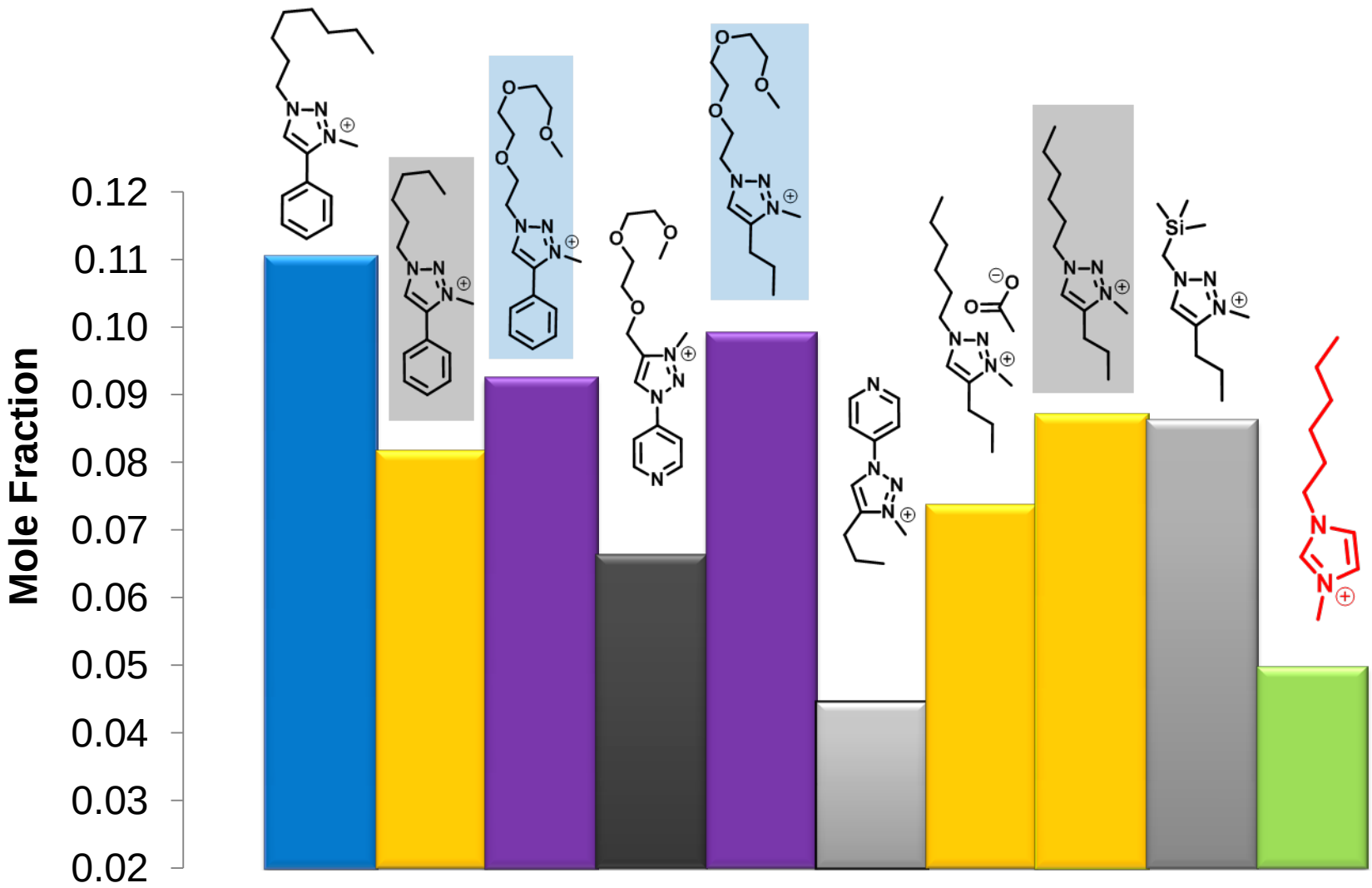
Acetate Anion



Thermal Properties of Triazolium ILs

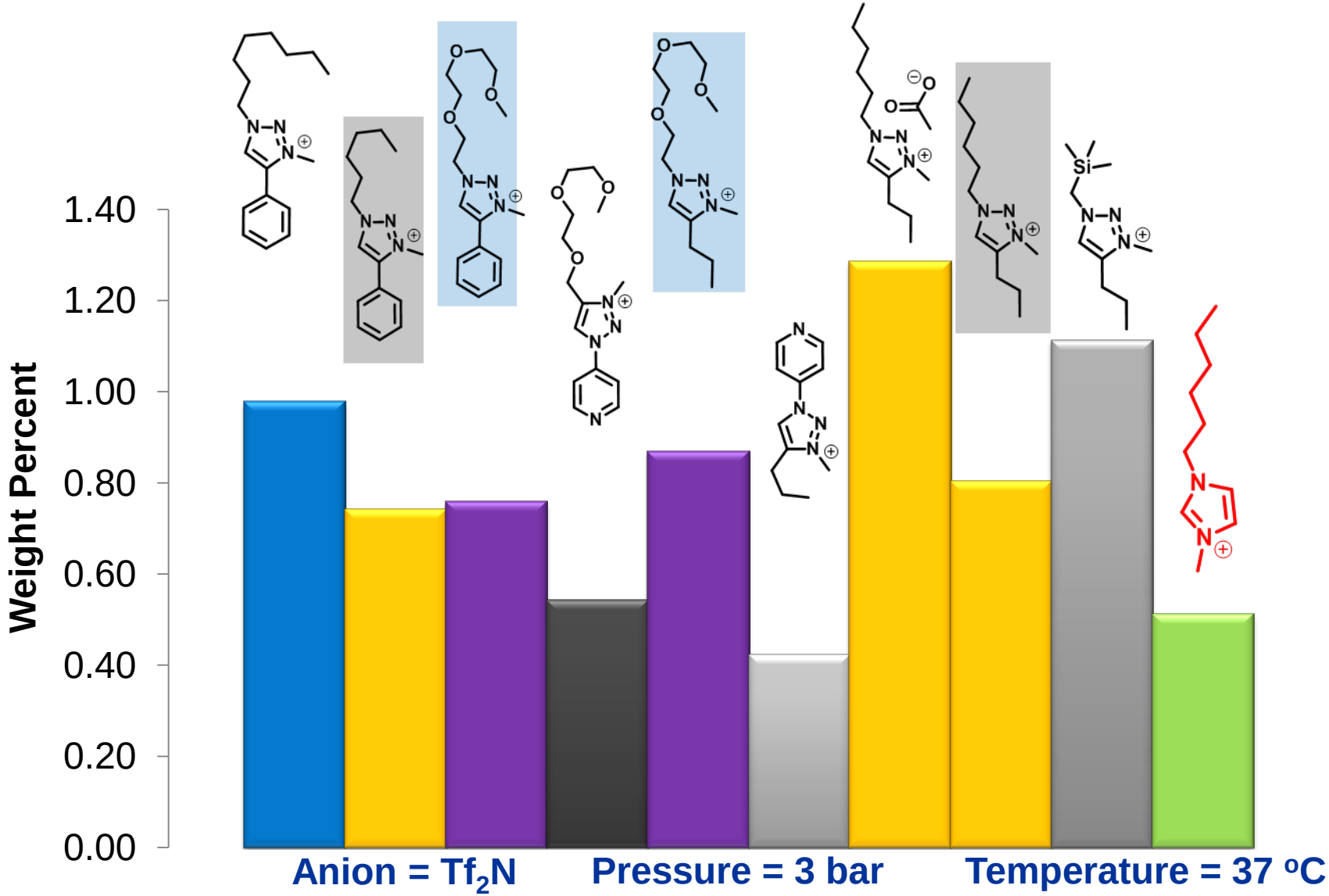


CO_2 Solubility (Molar Basis)

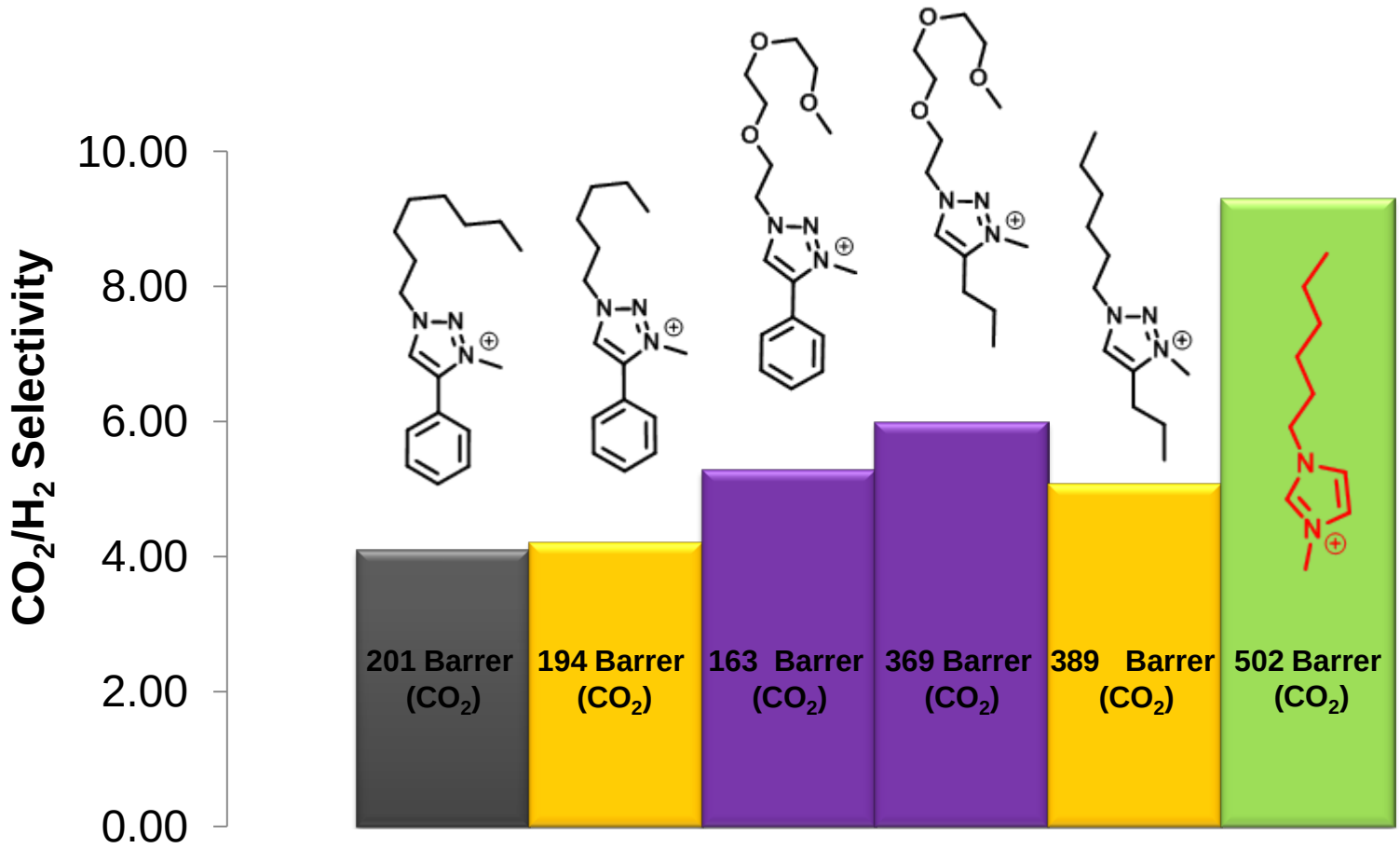


Anion = Tf_2N **Pressure = 3 bar** **Temperature = 37 °C**

CO_2 Solubility (Weight Basis)



Membrane Performance



Anion = Tf_2N

Temperature = 37 ^oC

Summary

- **Different ILs needed for membranes and solvents**
- **Computational guidance very effective in accelerating development of new materials**
- **Triazolium ILs may be easily tailored to desired properties**

Ionic Liquids Team

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Project Objectives

- **Performance Period: FY10**
- **FY10 Funding: $710,000**
- **Participants**
  - NETL Office of Research and Development (ORD)
  - NETL Regional University Alliance (RUA)
  - Berkeley Energy Frontiers Research Center (EFRC)
- **Objective:**
  - Develop ionic liquid solvents and membranes capable of capturing 90% of the CO_2 from a gasification plant at less than a 10% increase in the cost of energy services produced by that plant