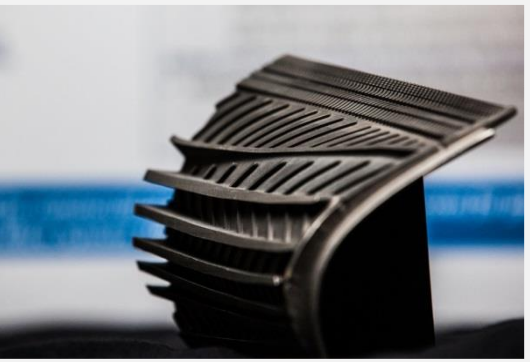
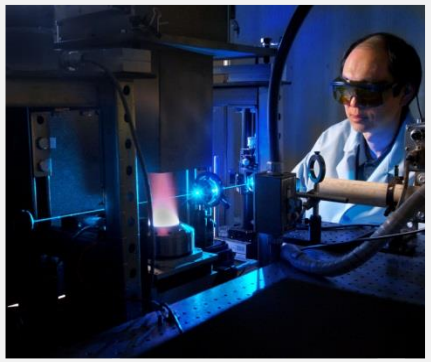
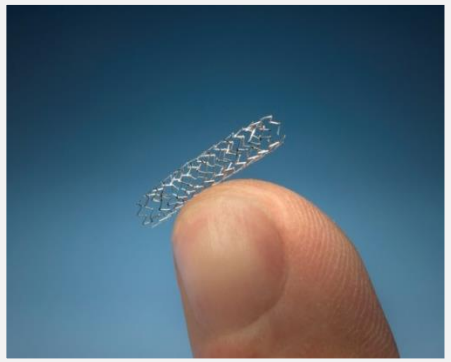
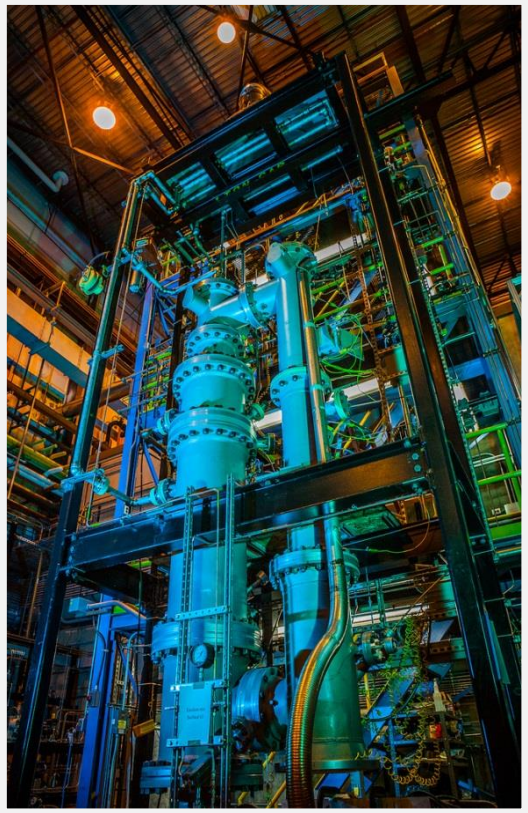
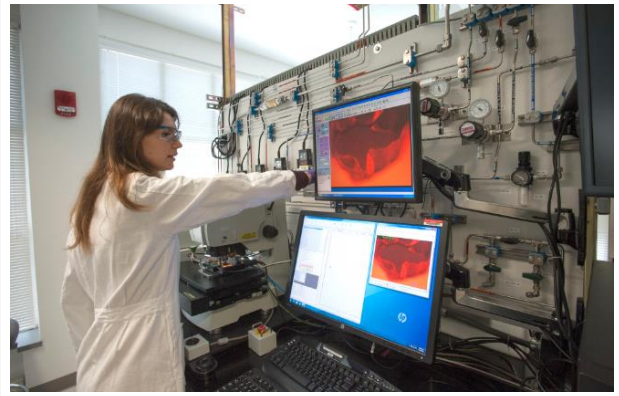
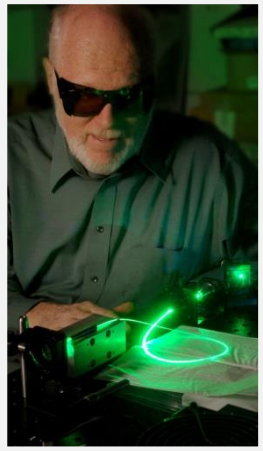
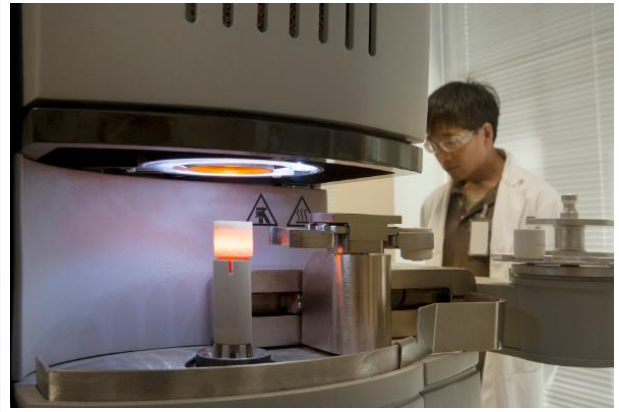
Driving Innovation ♦ Delivering Results





High Throughput Computational Screening of Mixed Matrix Membranes

Samir Budhathoki, Wei Shi, Christopher E. Wilmer and Jan Steckel

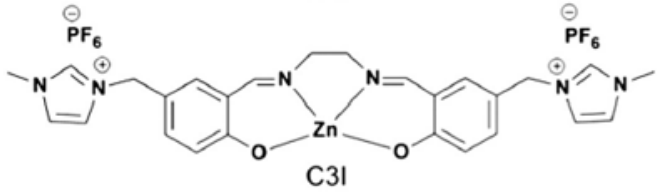
Carbon Capture Technology Meeting, August 8, 2016

Outline

- **Brief Mention of Other Computational Work in CO_2 Capture at NETL**
  - Catalysts: Collaboration With CAER/University of Kentucky
  - Computational Modeling of CO_2 in Physical Solvents: Bulk, Interface, Reverse Micelle
  - Computational Designing and Screening of Solid CO_2 Capture Materials
- **High-Throughput Computational Screening of Mixed Matrix Membranes**
  - Goals and Project Design
  - Hypothetical MOF Generator
  - Simulations
  - Maxwell Equation
  - Predictions of H-H-MMMs

Modeling the Catalytic Process and Foaming (with University of Kentucky)

A series of metal-organic catalysts have been developed by UKy, which increase the CO_2 absorption rate by ~30% in aq. MEA

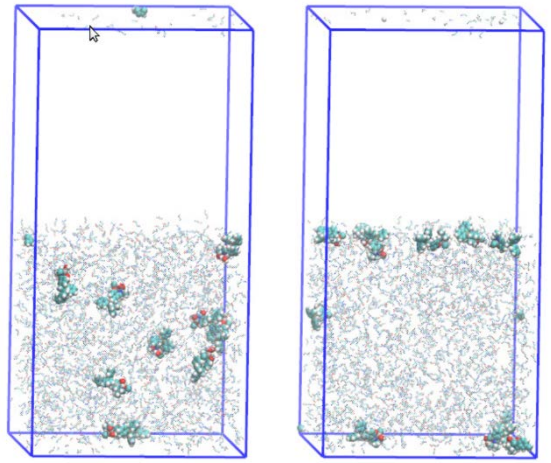


A sample catalyst

The 0.7 MWe slipstream testing facility

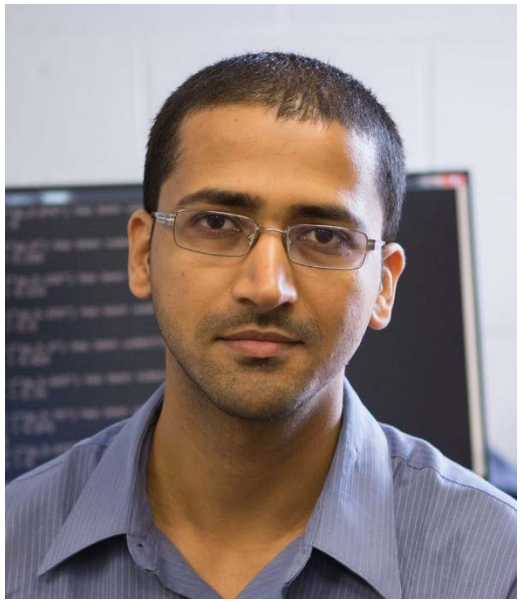
Molecular dynamics simulation of the interface region

15800 water
+
2000 MEA
+
10 catalysts



Initial Equilibrated

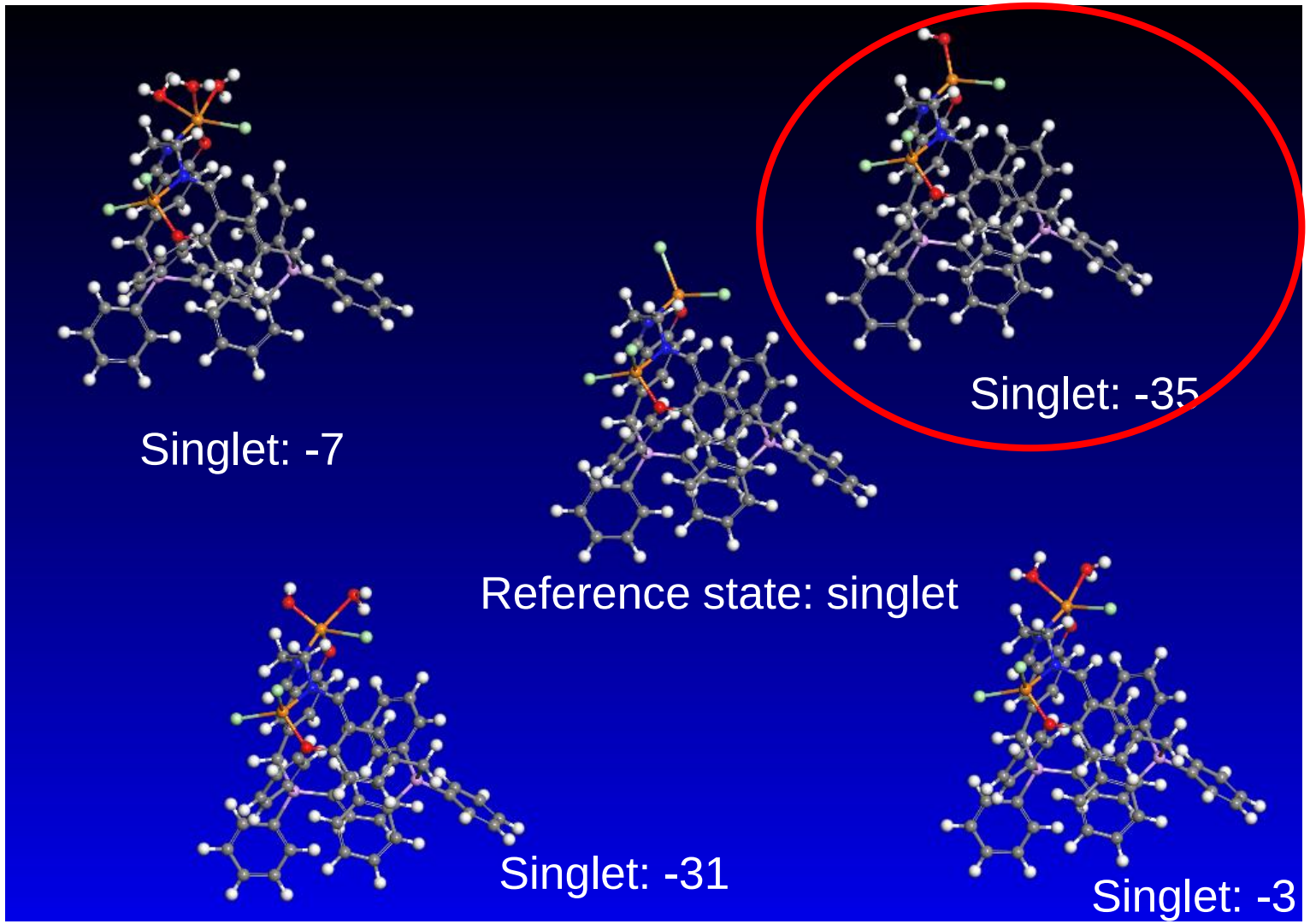
Catalysts concentrate at the surface. This is important in understanding foaming



Surya Prakash Tiwari

Interface properties are difficult to determine from experiment. Our goal is to use simulations to predict the extent of foaming based on solution properties: interface surface tension, density, viscosity, elasticity

Molecular Modeling of UKy Catalysts: First Principles Calculations

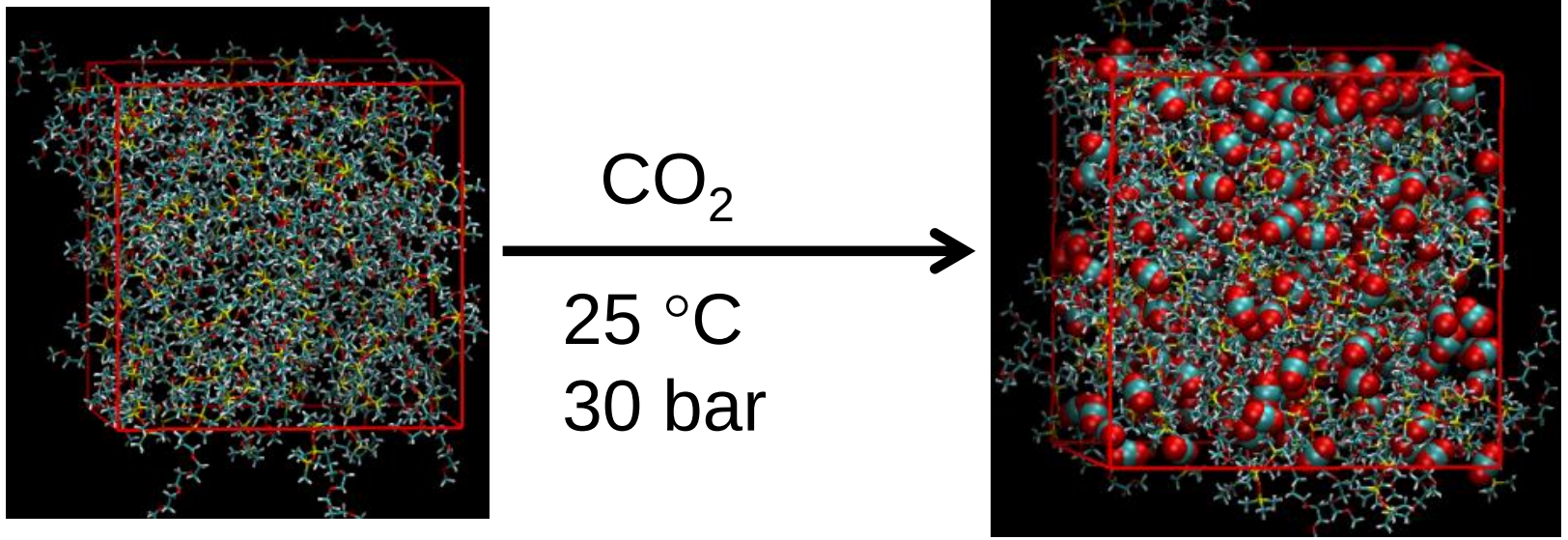


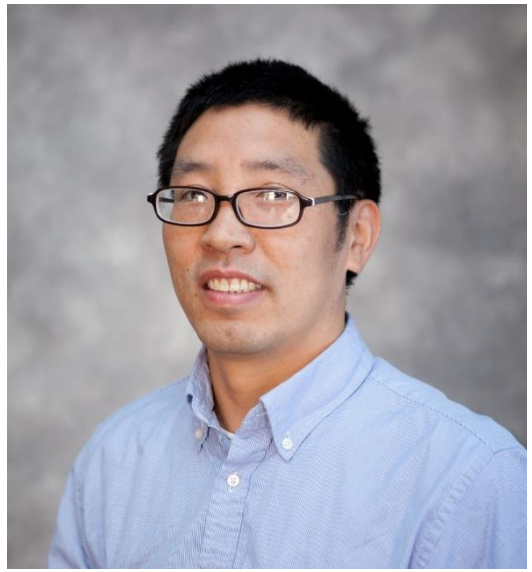
- DFT calculations on a series of catalysts (collaboration with Uky)
- What is the stable structure in amine solution?
- Estimates of reaction enthalpy with respect to the reference state in kcal/mol

Effects of CO_2 Physical Absorption on Solvent Properties

Upon CO_2 loading:

- solvent volume increases by 24%,
- solvent viscosity decreases by 500%
- diffusivity increases by 500%,
- solvent surface tension decreases by 20%



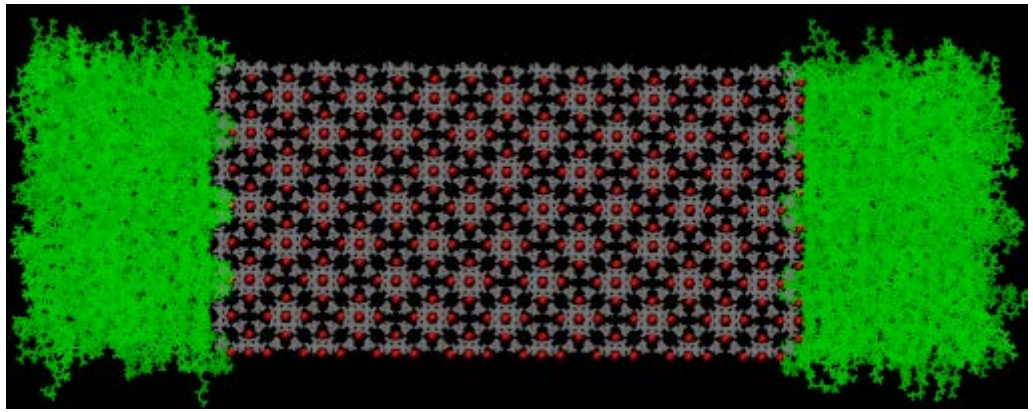


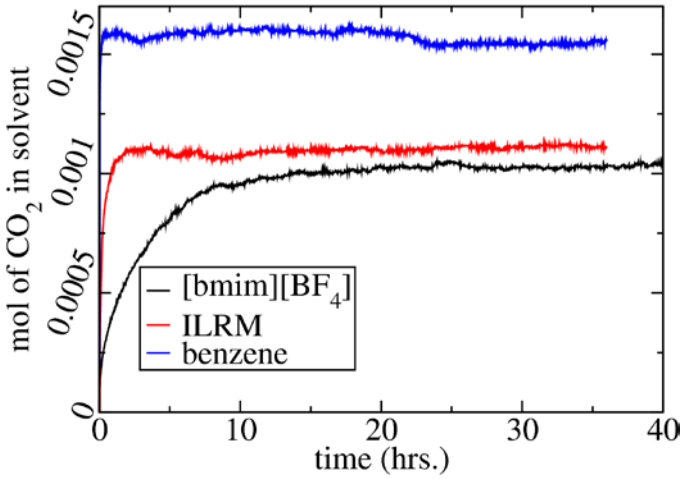
Wei Shi

Wei Shi, et al. J. Phys. Chem. C, 2016, submitted

Modelling CO_2 at Interfaces and Reverse Micelles

- **CO_2 absorption in suspension and the interface between solvent & nano-porous material [1]**
  - Interface region exhibits CO_2 loading , diffusivity and permeability significantly different from the bulk solvent
- **Significantly (10 times) improved CO_2 mass transport in ionic liquid reverse micelle: a multiscale modeling study [2]**
- **Surfactant-like catalyst behavior in aqueous amine solution for CO_2 absorption [3]**





[1] Wei Shi, et al. 2016, in prep.; [2] Wei Shi, et al. 2016, to be submitted; [3] Wei Shi, et al. 2016, in prep.

CO_2 absorption in suspension and the interface between solvent & nano-porous material [1]
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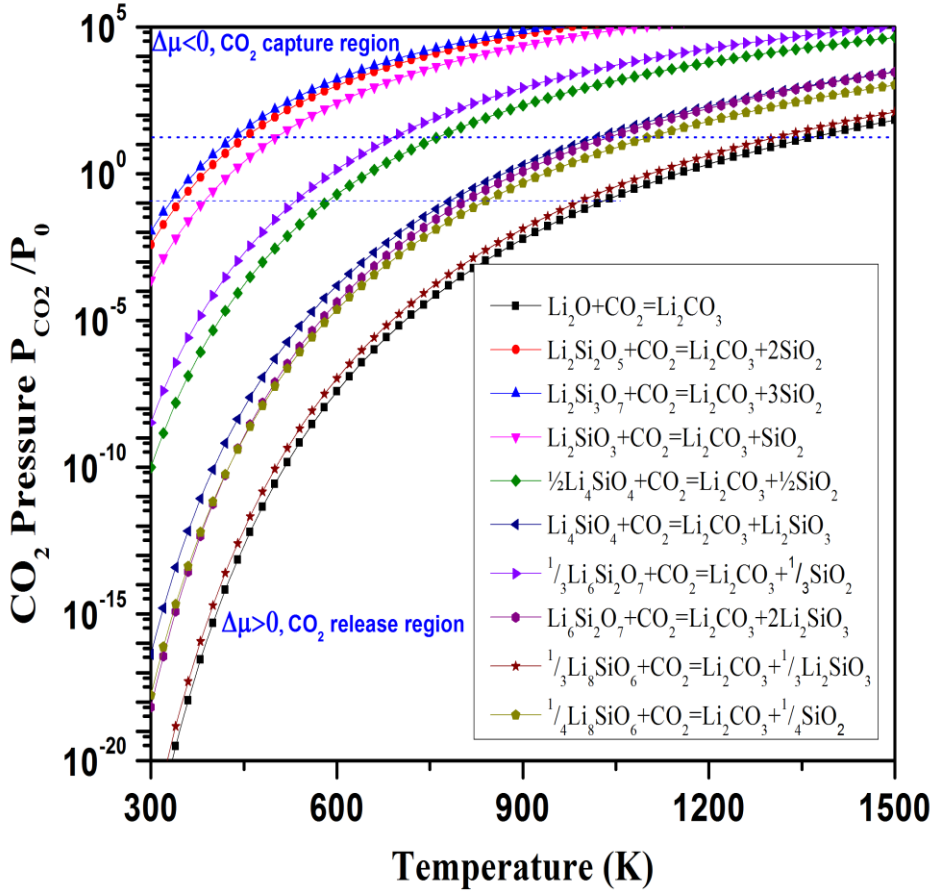
Computational Design and Screening of Solid Materials for CO_2 Capture



Solid materials are potential candidates for CO_2 sorbents. By combining database mining with *ab initio* thermodynamic calculations, we implemented a novel theoretical methodology to screen solid sorbents from known materials databank and to synthesize new materials with improved CO_2 capture capabilities for further experimental validation.

The strength of our method is to screen complex sorbent materials for which thermodynamic properties are not available.

Hundreds of solid materials have been investigated.

Now, we are working on screening of multi-components, substituted, doped, and mixed materials to search for good CO_2 sorbents.

Yuhua Duan

High Throughput Computational Screening of Mixed Matrix Membranes

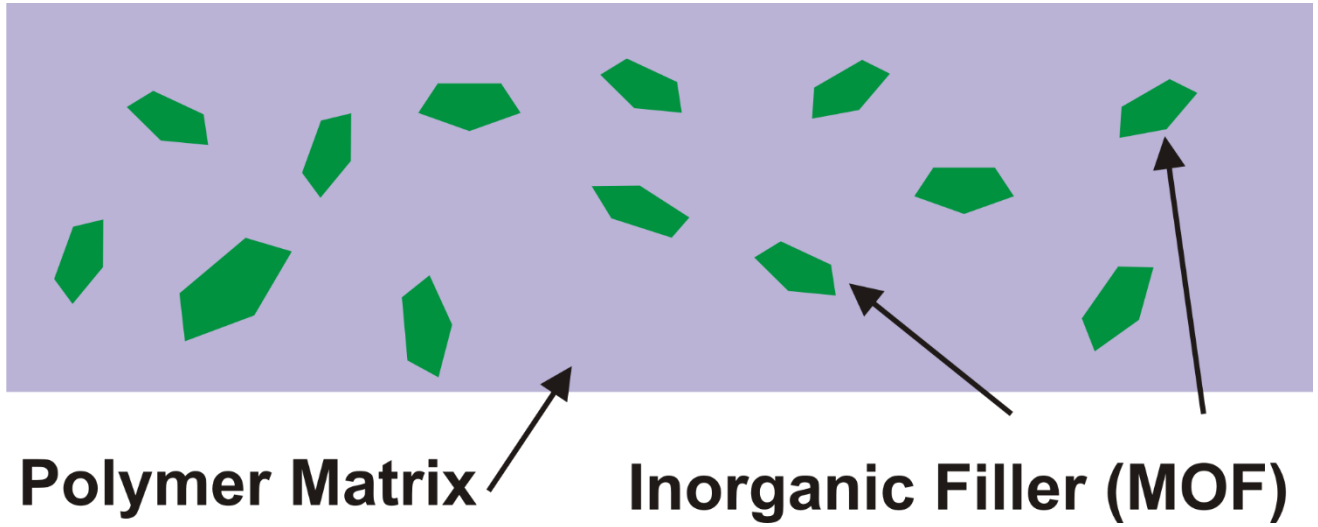
In this project, we have used atomistic simulations in order to predict the properties of a database of hypothetical metal organic frameworks. These properties have been combined with the experimentally measured properties for polymers in order to make predictions, using the Maxwell Equation, about hypothetical mixed matrix membranes. The overall goal is to discover novel mixed matrix membranes that could be useful for CO_2 capture processes.

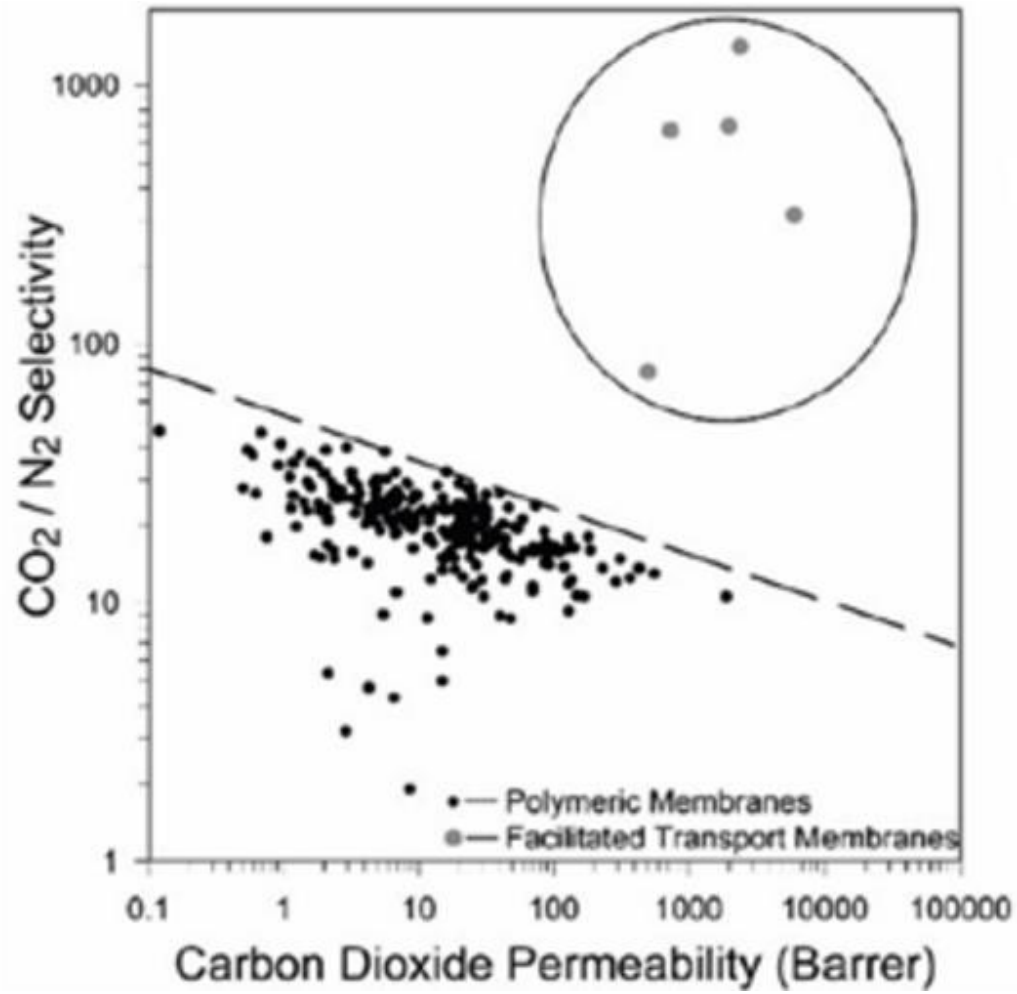
NETL's *Joule Supercomputer* https://hpc.netl.doe.gov/

Mixed Matrix Membranes

Why do we want to predict properties of MMMs?

- MOFs: good selectivity – but expensive, difficult to implement.
- Polymeric membranes – better price, implementation, trade-off.
- In mixed matrix membranes, a small amount of an inorganic filler is introduced into the polymer in order to improve selectivity without sacrificing permeability.





Screening Strategy

We are at this stage currently

~137,000 hypothetical MOFs:

Geometrical analysis
Brief atomistic simulations
MOF atoms held at fixed positions

Top 5%:

Higher accuracy atomistic simulations

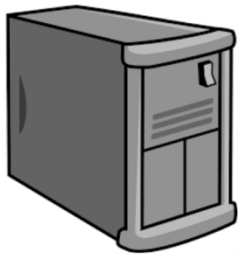
“The 1%”:

Flexible Force Field generation
Density Functional Theory
Molecular modeling of polymer
Model for the interface region

Sketch of the Project

DB of ~137,000
Hypothetical MOFs

+



Simulations

+

MEEP
PIM 1
PIM 7
PTMSP
....

Expt. Props of
~10 Polymers

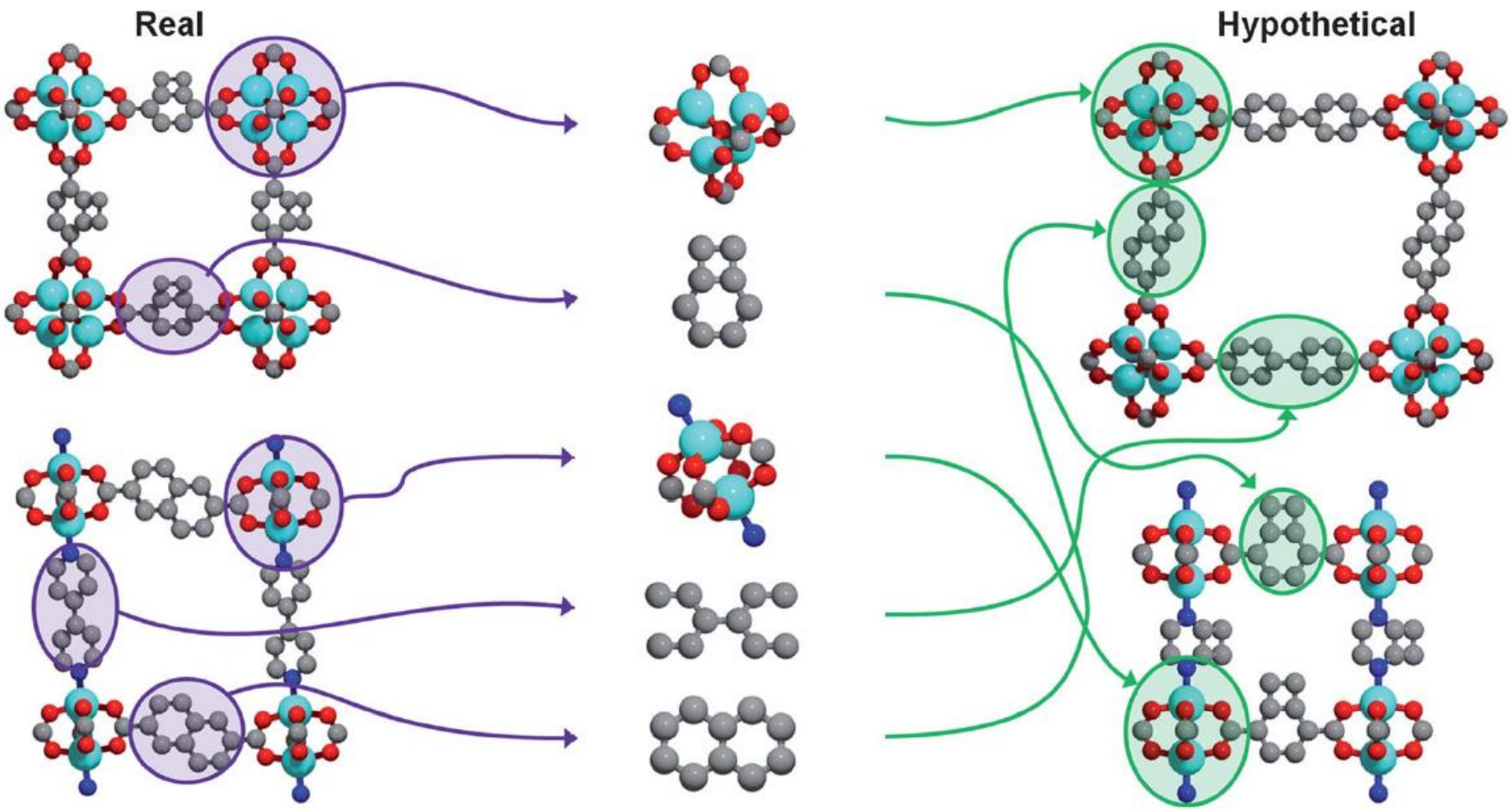
Maxwell Eq.

DB of ~1,370,000
Hypothetical-Hypothetical-MMMs

Creation of the Hypothetical MOF Database

DB of ~137,000
Hypothetical MOFs

Creation of the Hypothetical MOF Database



Existing MOFs deconstructed into a library of building blocks (metal centers and organic ligands). The building blocks are re-assembled to create hypothetical MOFs

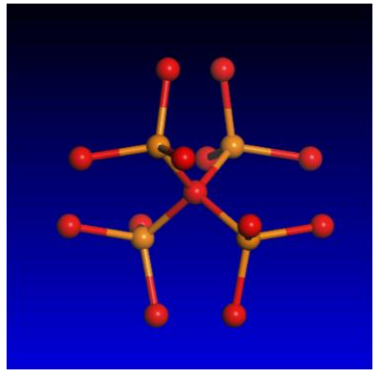
Christopher E. Wilmer

C. E. Wilmer, M. Leaf, C. Y. Lee, O. K. Farha, B. G. Hauser, J. T. Hupp and R. Q. Snurr, Nat. Chem., 2012, 4, 83–89.

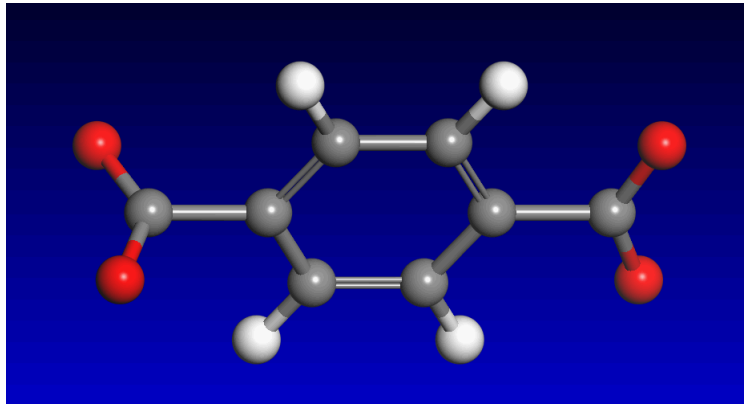
Hypothetical MOF Generation

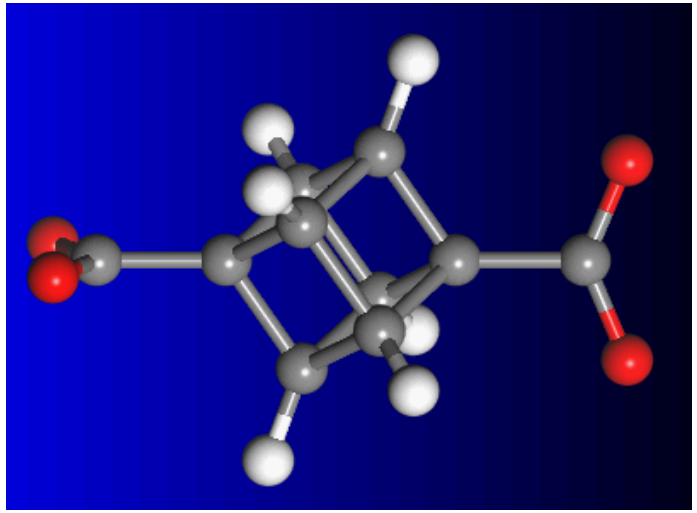
The hypothetical MOF generation program starts by selecting building blocks of three types from its library:

1: Metal Center

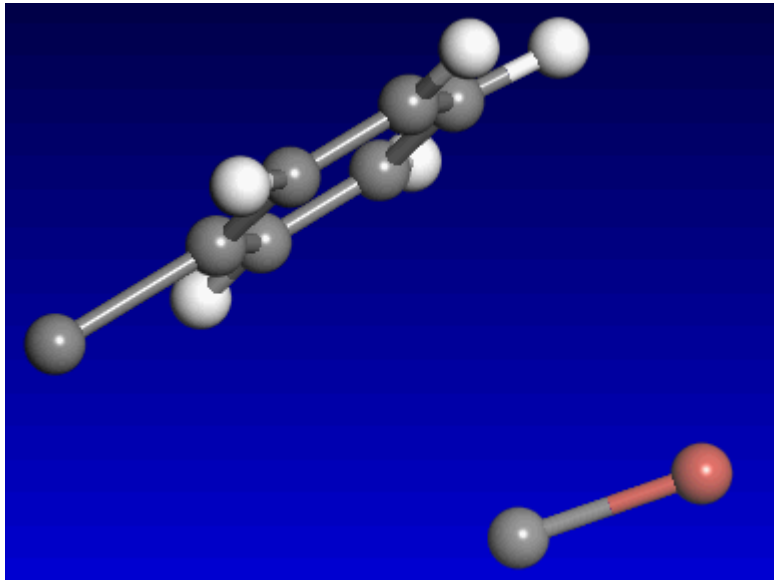


2: Organic Linkers



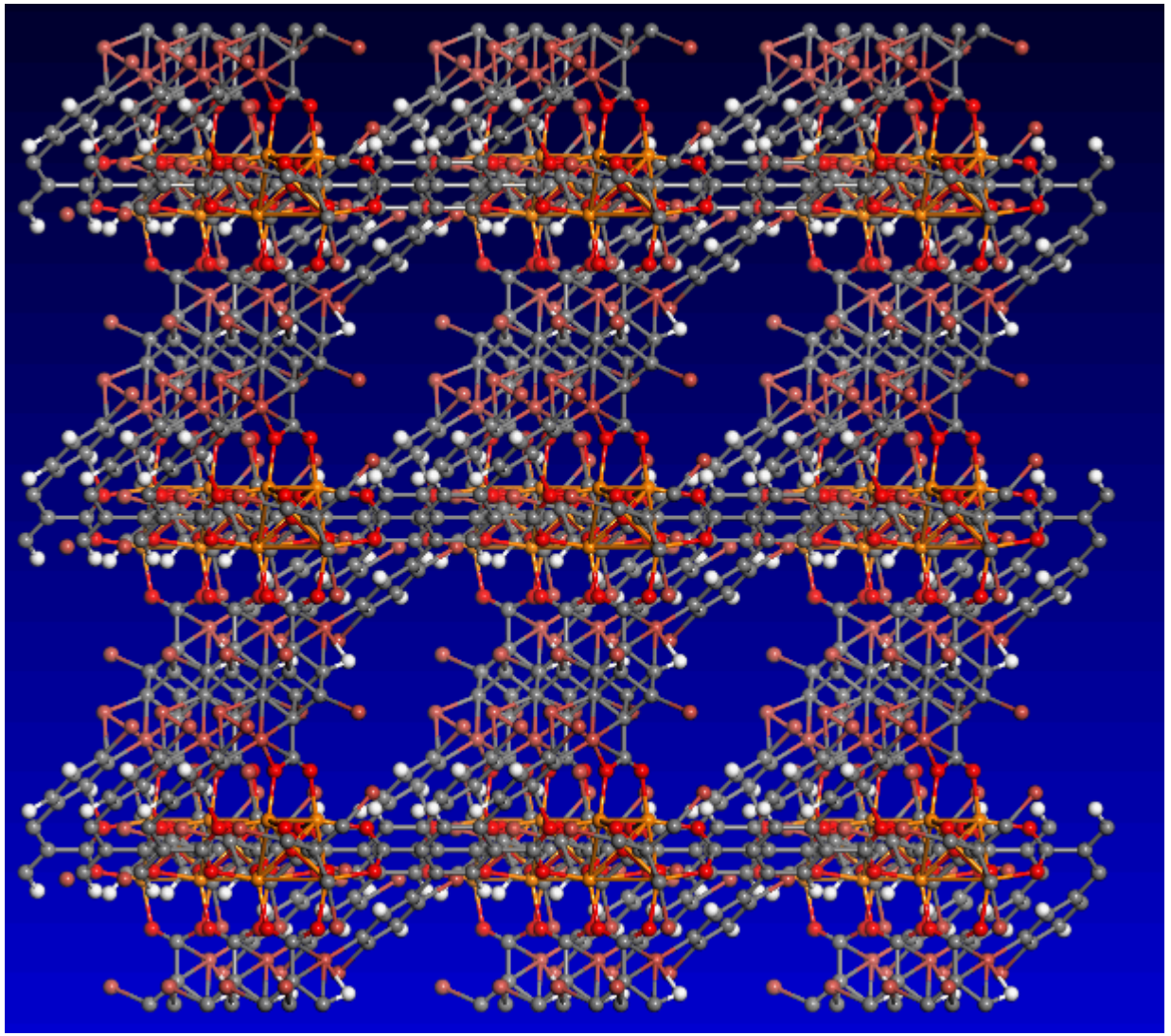


3: Functional Groups

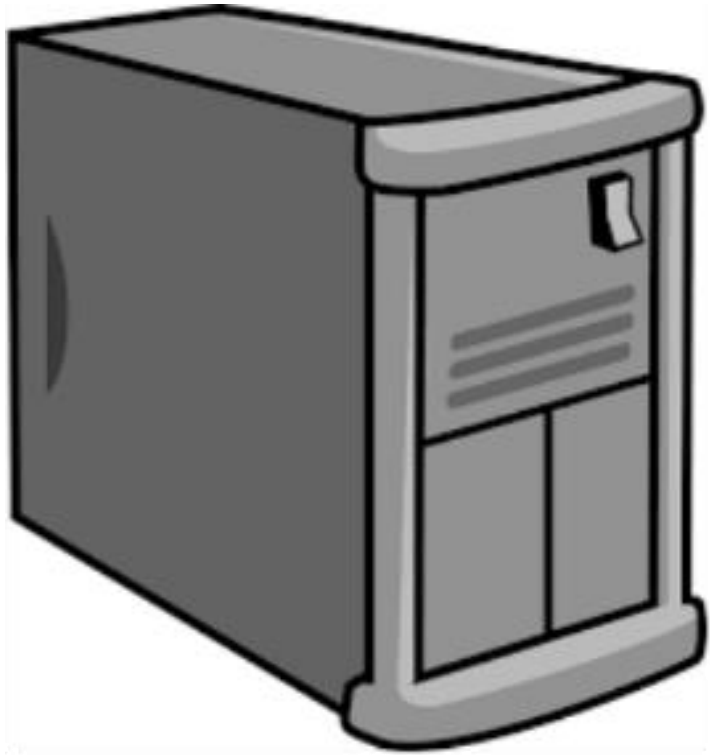


The building blocks are combined using simple geometrical rules in order to create the periodic, 3D structure of a hypothetical MOF →

Building Blocks Combined to Create “Jeff”, a Hypothetical MOF



Simulations of Properties of Hypothetical MOFs



Simulations

Simulations of Properties of Hypothetical MOFs

- **Geometrical Characterization (Zeo++) →**
  - Largest cavity diameter (LCD)
  - Pore limiting diameter (PLD)
  - Surface area
- **MC Calculations → Gas Adsorption**
  - MOF atomic positions held fixed
  - Atomic charges calculated via EqEq Method
  - UFF force field for MOF atoms
  - TraPPE force field for gases
- **MD Simulations → Diffusivity**
  - Force field parameters as in MC Calculations
  - Velocity autocorrelation function used to calculate diffusivity

Samir Budhathoki

Maxwell Equation: Predicting Properties of MMMs

MEEP
PIM 1
PIM 7
PTMSP
....

Expt. Props of
~10 Polymers

Maxwell Eq.

DB of ~1,370,000
Hypothetical-Hypothetical-MMMs

Maxwell Equation: Predicting Properties of MMMs

- Incorporation of a filler material into a membrane will change the behavior of gas permeation through the composite membrane.
- The behavior of gas permeation through the composite may be predicted by application of the Maxwell equation.
- (The theory was developed for predicting the dielectric behavior of composite materials.)

Maxwell Equation

$$P_{eff} = P_c \left[\frac{P_d + 2P_c - 2\varphi_d (P_c - P_d)}{P_d + 2P_c + \varphi_d (P_c - P_d)} \right]$$

P_{eff}– the effective permeability of the MMM

P_c– the permeability of the continuous phase

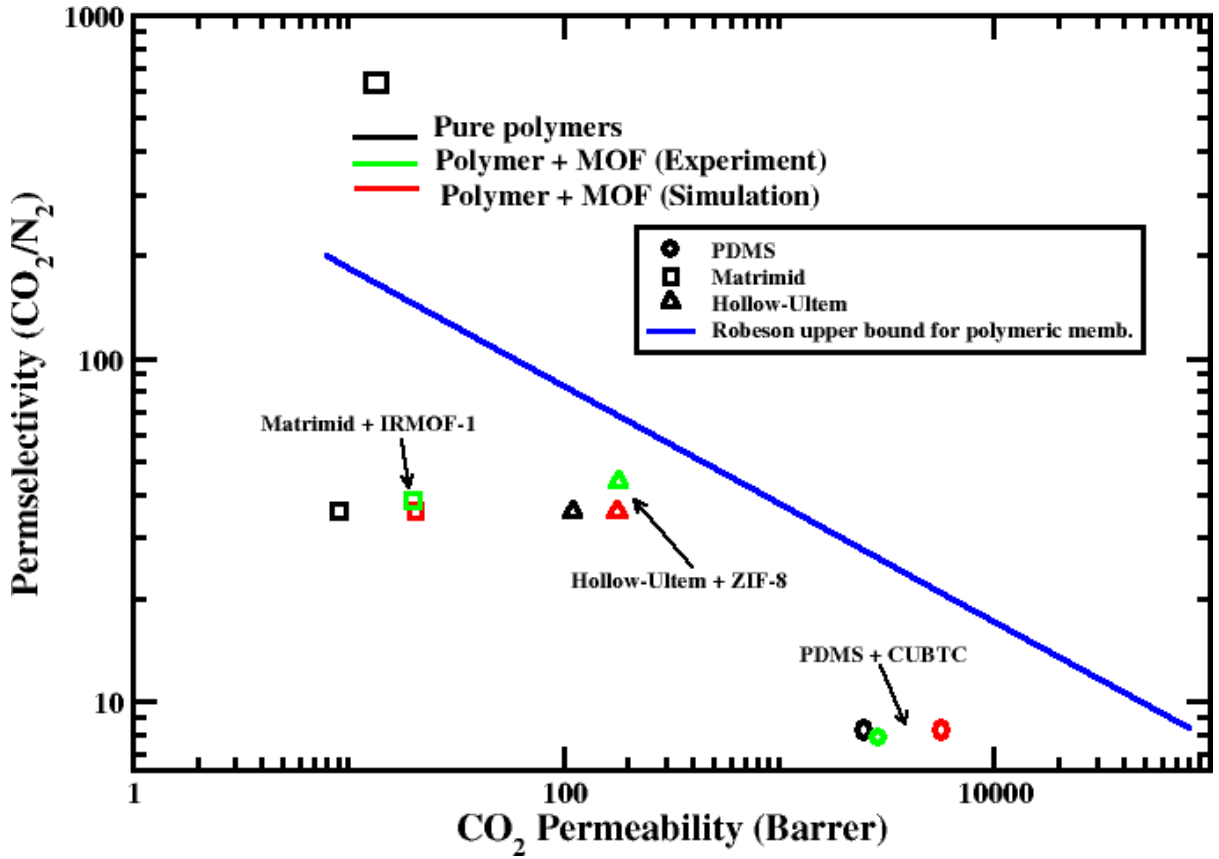
P_d– the permeability of the dispersed phase

φ_d– the volume fraction of the dispersed phase

$$\alpha_{ideal\ i/j} = \frac{(P_{eff})_i}{(P_{eff})_j}$$

R.H.B. Bouma, A. Checchetti, G. Chidichimo, E. Drioli, J. Membrane Science, **128**, 141, 1996.
Seda Keskin and David S. Sholl, En. & Env. Sci., **3**, 343, 2010.

MMM Comparison: Predicted vs. Expt.

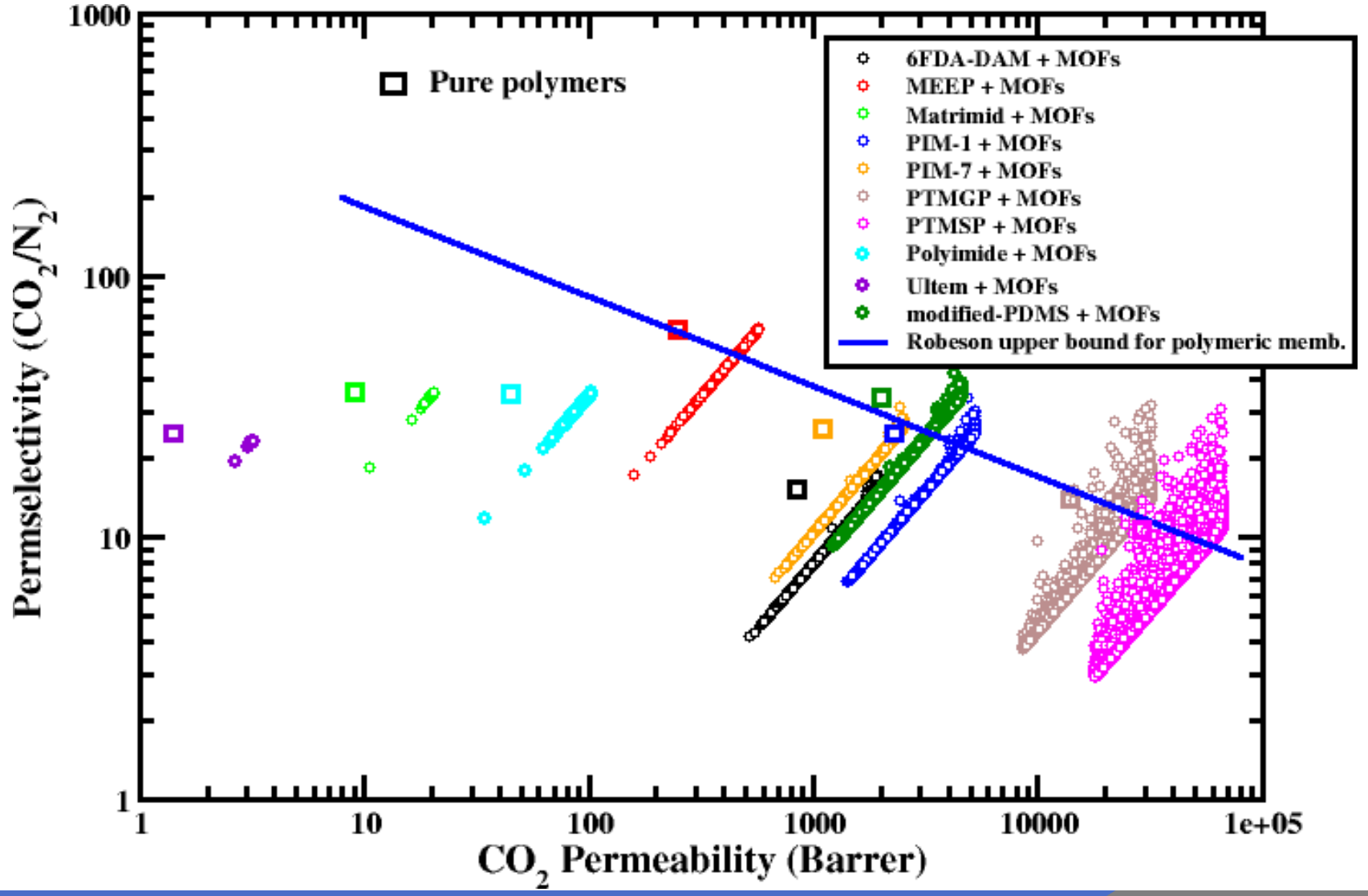


Dai, Y.; Johnson, J. R.; Karvan, O.; Sholl, D. S.; Koros, W. J., *J. Mem. Sci.* 401-402, **2012**, 76-82 (Ultem-hollow-fiber + ZIF-8)

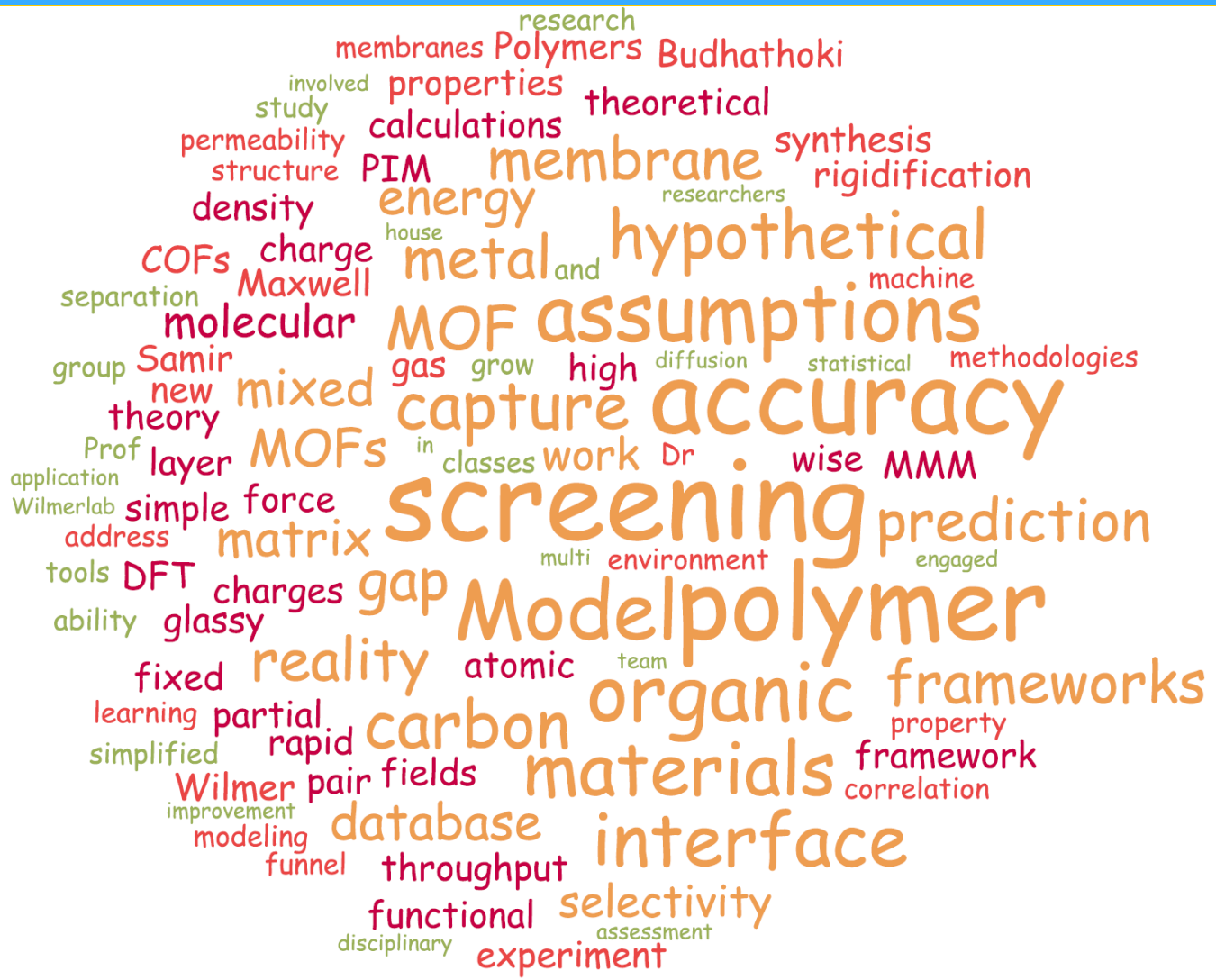
Car, A.; Stropnik, C.; Peinemann, V. K. *Desal.* 200, **2006**, 424-426 (PDMS + CUBTC)

Perez, E. V.; Balkus Jr, K. J.; Ferraris, J. P.; Musselman, I. G. *J. Mem. Sci.* 328, **2009**, 165-173 (Matrimid + IRMOF-1).

Molecular Organic Frameworks



Questions?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