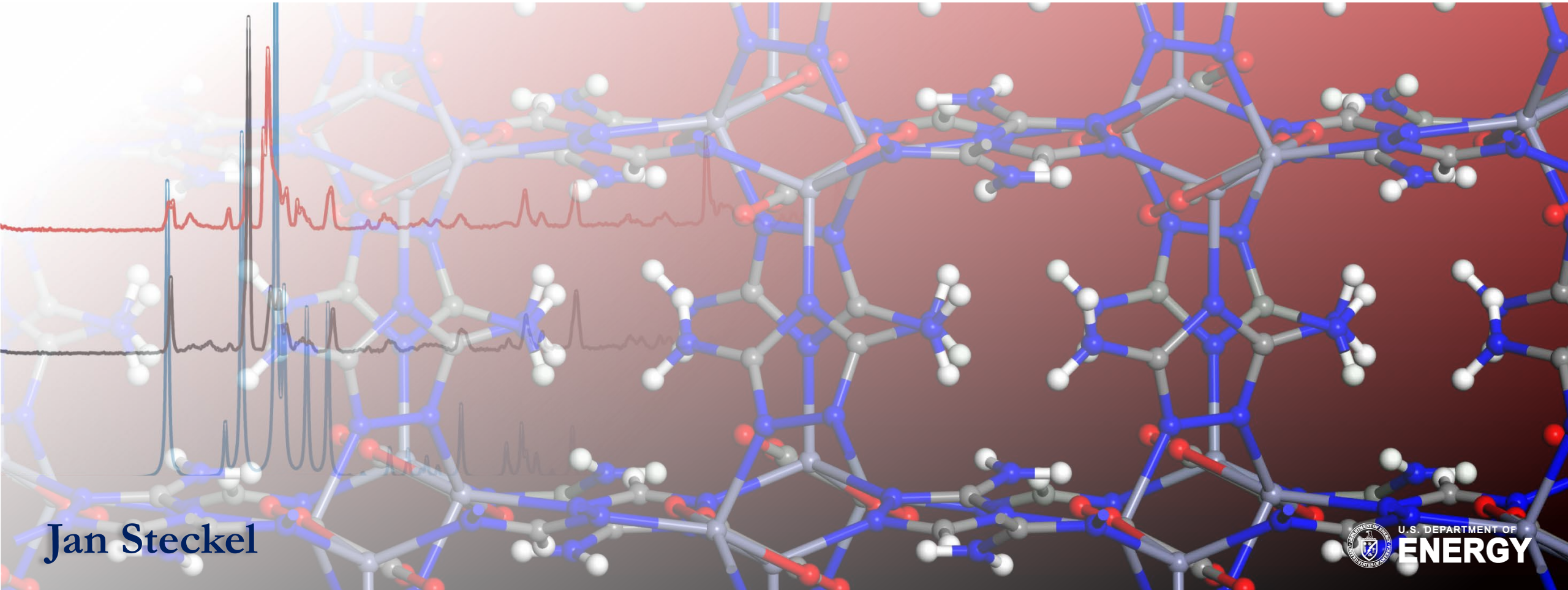
Discovery of New Materials for Carbon Capture by Computational Screening

Carbon Capture Review Meeting

27 August 2019



Jan Steckel

NATIONAL ENERGY TECHNOLOGY LABORATORY

U.S. DEPARTMENT OF ENERGY

Outline

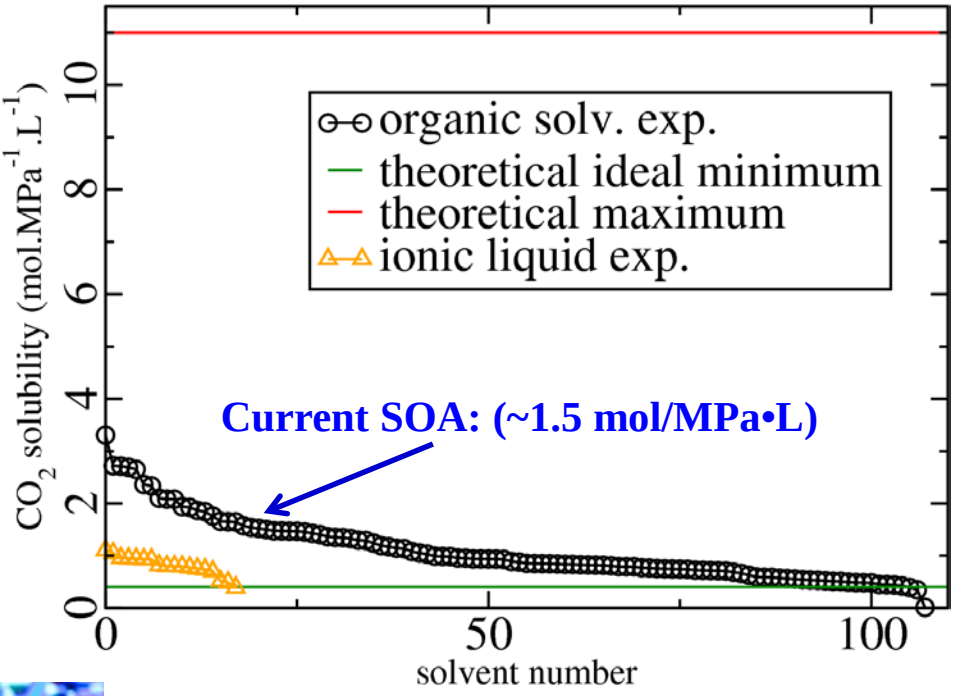
1. Computational Solvent Screening (Task 5)
2. Computational Polymer Screening (Task 12)
3. Simulations to Optimize Polymer Blends (Task 12)
4. Simulations of MOF-Polymer Interactions (Task 12)

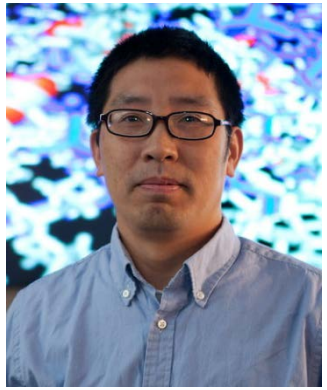
Overall Motivation: We seek to use computational methods to

- provide insight at the atomistic level,
- optimize the properties of existing materials, and
- identify or design new materials for carbon capture.

Computational Solvent Screening

- Previously: screening on NIST DB: 23,000 compounds
- Identified ~25 promising pre-combustion solvents including CASSH-1
- Motivation: Identify commercially available solvents that will outperform the best pre-combustion solvents currently available.
- Computational screening is efficient and effective.
- PUBCHEM DB: 98,000,000 compounds.





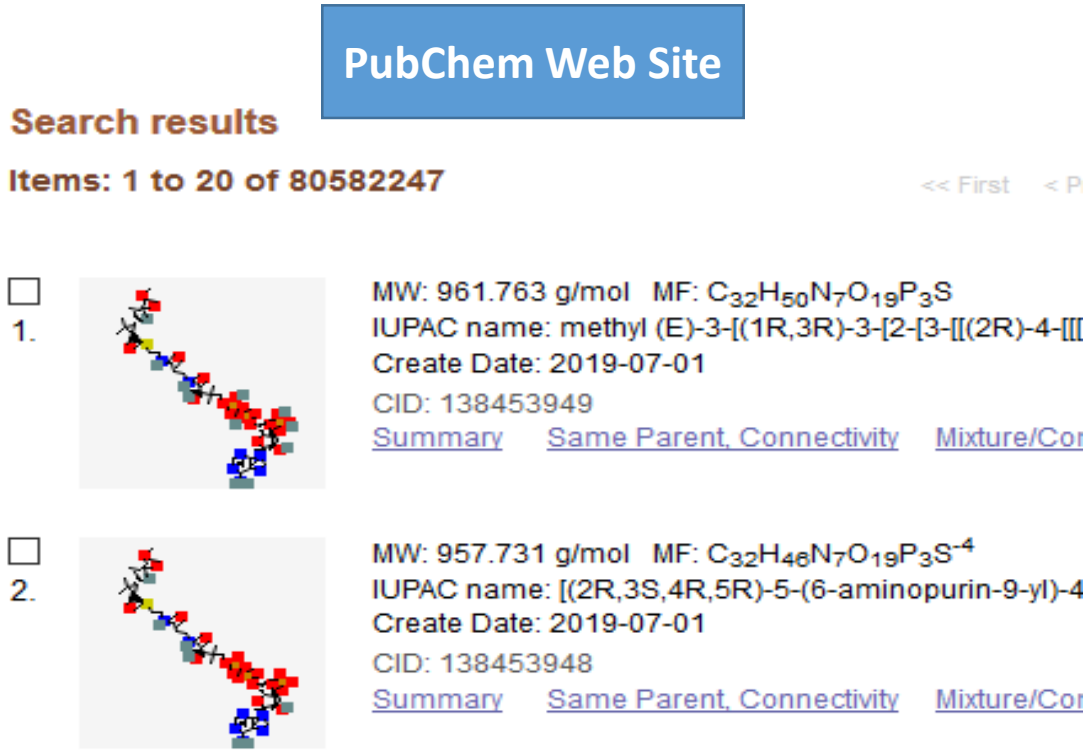
Wei Shi

Poster - Wednesday 5:00 PM

"Computational Efforts to Push the Limits of Current Physical Solvents for Pre-combustion Carbon Capture Applications"

Computational Solvent Screening

PubChem Web Site

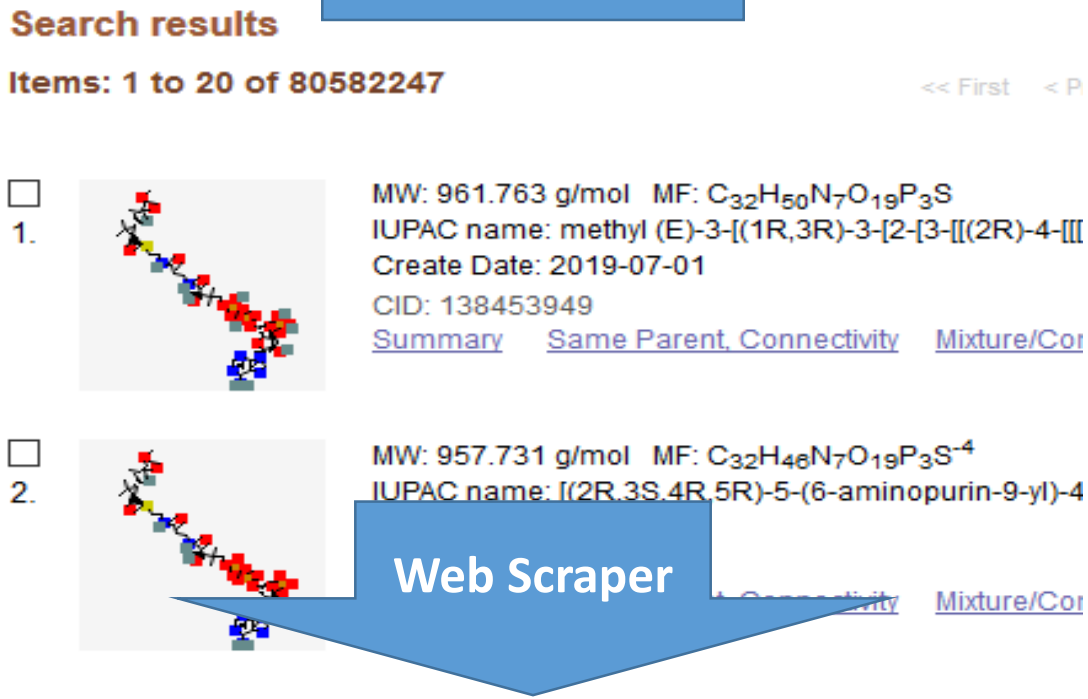


In-House Web Scraper:

- Interacts with website, automatically follows appropriate links
- Gleans specific data from PUBCHEM
- Chemical formula, MP, BP, Molecular weight, vapor pressure, viscosity
- Outputs result in database format to generate large solvent database for in-house use
- Written by Abbie Tran (Mickey Leland Energy Fellow, 2019)
- Target specific classes of compounds (functional groups) to search first

Computational Solvent Screening

PubChem Web Site



Web Scraper

Solvents Database

CID	MP	Density	BP
138453949	-135.4	1.41	64.1
409284845	-10.9	0.71	140.9
856239478	-143.0	0.9734	105.9

In-House Web Scraper:

- Interacts with website, automatically follows appropriate links
- Gleans specific data from PUBCHEM
- Chemical formula, MP, BP, Molecular weight, vapor pressure, viscosity
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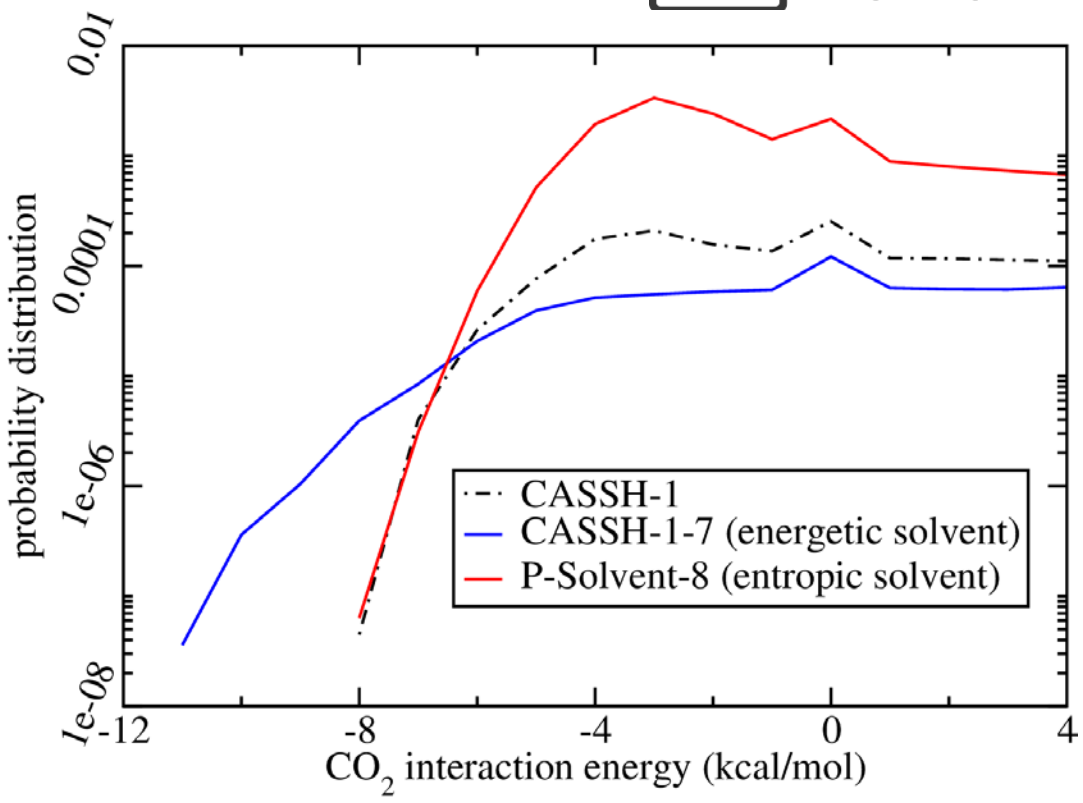
Solvent Design: Two Novel Solvents

- **CASSH-1: (previously identified via screening)**
  - good interaction with CO_2,
  - moderate number of sites for CO_2 interaction
  - successful pre-combustion solvent
- **CASSH-1-7: (energetic solvent, designed)**
  - relatively strong interaction with CO_2,
  - fewer sites for CO_2 interaction
  - novel "deep clean" solvent
- **P-Solvent-8: (entropic solvent, designed)**
  - good interaction with CO_2,
  - more sites for favorable interaction with CO_2
  - novel pre-combustion solvent

Calculated Results	CO_2 Loading (mol/MPa•L)	CO_2/H_2 (Ideal) Selectivity
CASSH-1	1.5	60
CASSH-1-7	10	400
P-Solvent-8	4	55



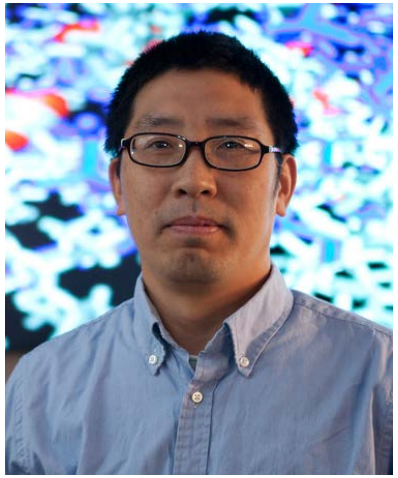
$$\Delta G = \Delta H - T\Delta S$$

x-axis y-axis

Computational Polymer Screening

Motivation: Find (or design) polymers with: high permeability, high gas selectivity and good mechanical properties

- **Databases:**
  - Membrane Society of Australia (MSA) ~1500 entries downloaded, data must be manually checked
  - Chemical Retrieval on the Web (CROW) ~240 entries collected via web scraper
- **Properties from DB:**
  - Molecular Weight
  - Density
  - Glass transition temperature
  - Solubility parameters
- **Properties from Simulations Using In-House Code:**
  - Gas solubility
  - Gas diffusivity
  - Gas permeability
  - Glass transition temperature
- **In-House Database In progress**

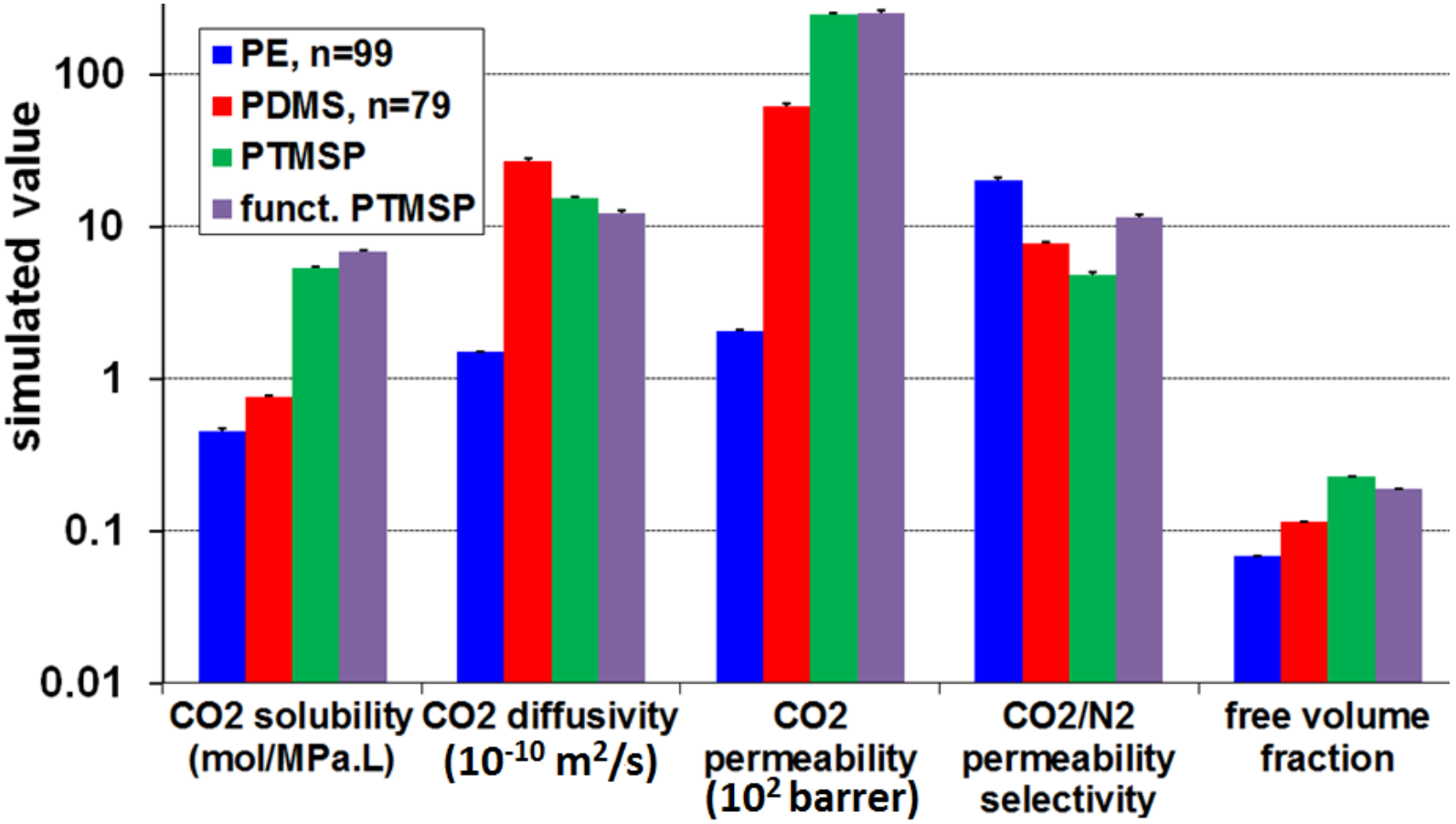


Wei Shi

Poster - Wednesday 5:00 PM
"Systematic Atomistic Simulations of CO_2 and N_2 Permeability in Polymers to Develop Better CO_2 Post-Combustion Membrane"

Polymer Screening: Novel Polymer

- Polyethylene (PE)
- Polydimethyl Siloxane (PDMS)
- Polytrimethyl Silyl-1-Propyne (PTMSP)
- Functionalized PTMSP – Designed



Calculations to Optimize Polymer Blends

- NETL has developed a poly-phosphazene blend that shows good permeability, selectivity and material properties.
- Experiments and simulations used together to optimize the blend
- We are varying the functionality and concentration of phenoxy and ether groups in the side chains to optimize properties:
  - Minimize phase separation
  - Optimize the mechanical properties (durable, elastic, non-sticky)
  - Maximize permeability, selectivity

- Blend A: PIM-1 + MEEP0 (100% phenoxy side chains)
- Blend B: PIM-1 + MEEP80 (80% ether side chains)
- Blend C: PIM-1 + MEEP100 (100% ether side chains)

Simulation Details

Temperature – 313 K

Pressure – 0.05 to 1bar

Polymer Generation – Materials Studio[1]

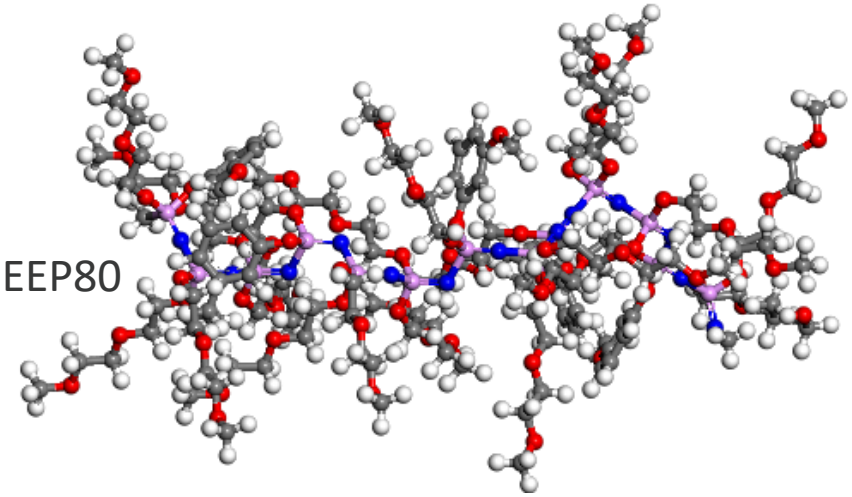
Absorption properties – Monte Carlo (CASSANDRA[3])

Structural and Diffusion properties – Molecular Dynamics (LAMMPS[2])

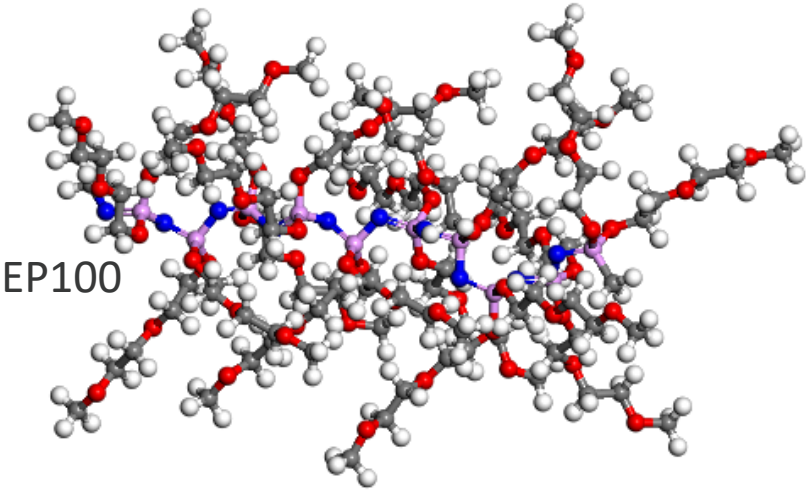
Forcefield – CVFF[4] (Consistent Valence Force Field)

Samir Budhathoki

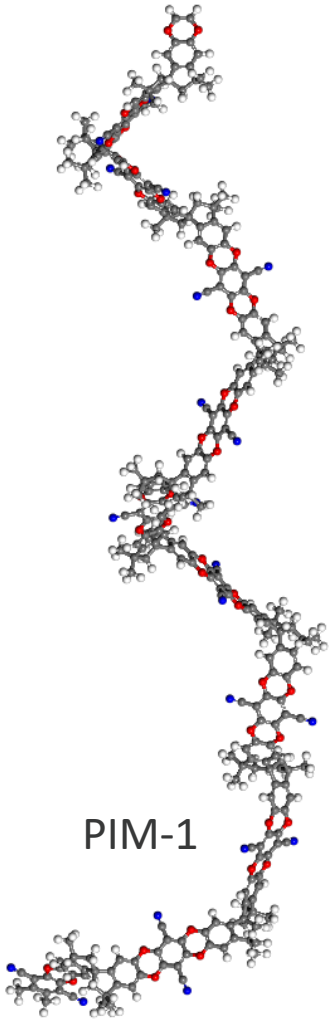
Ali Sekizkardes



MEEP80



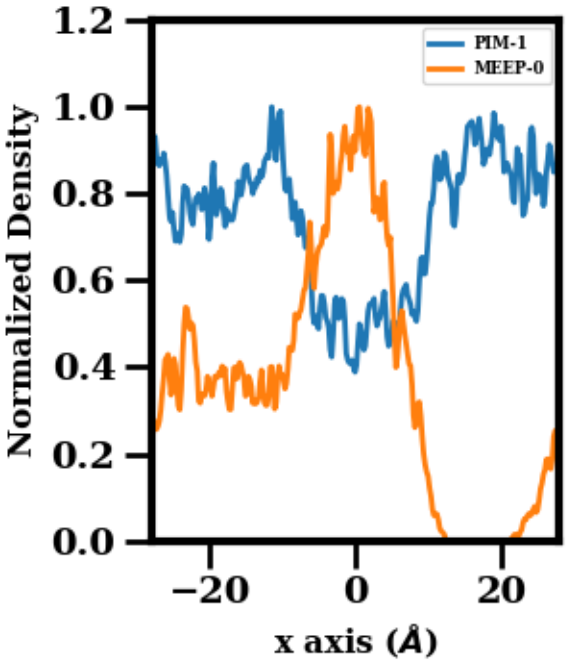
MEEP100

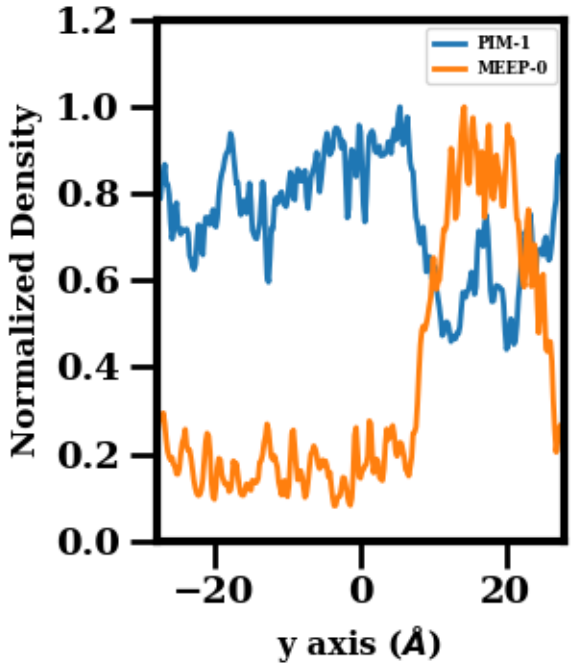


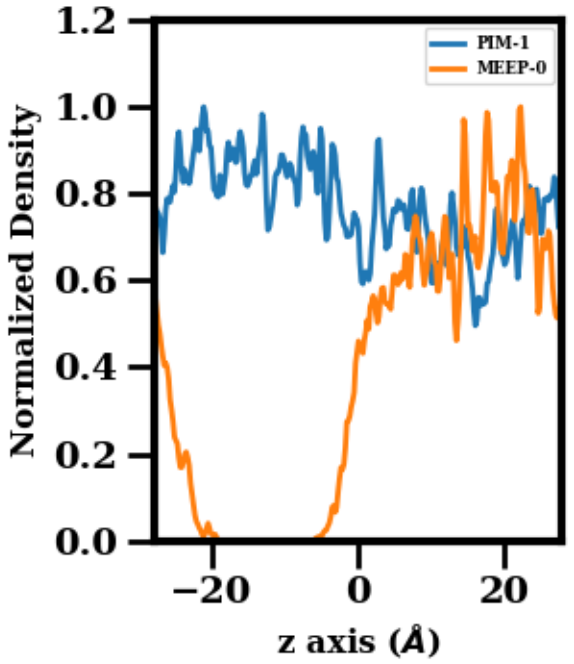
PIM-1

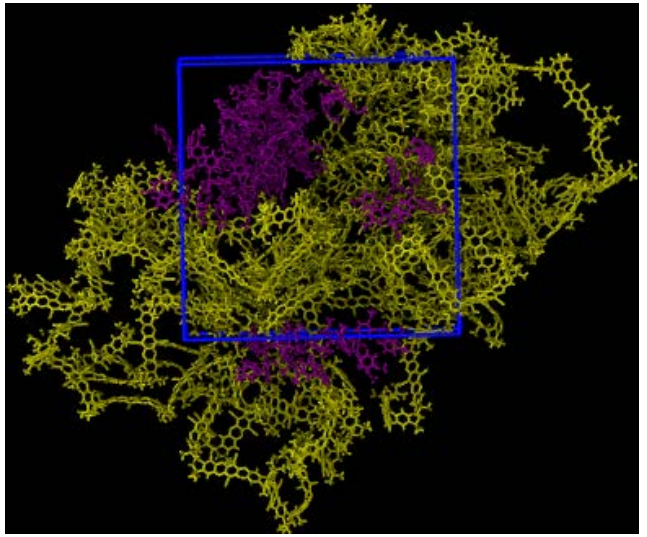
1. Dassault Systèmes BIOVIA, Materials Studio, v8.0.100.21, San Diego: Dassault Systèmes, 2014
2. Plimpton, S. J. Comput. Phys. 1995, 117, 1. LAMMPS, http://lammps.sandia.gov/
3. Maginn. et. al., J. Comput. Chem. 2017, 38, 1727–1739
4. Hagler et. al., Proteins 1998, 4, 31-47

Local Density Blend A (PIM-1/MEEP-0)



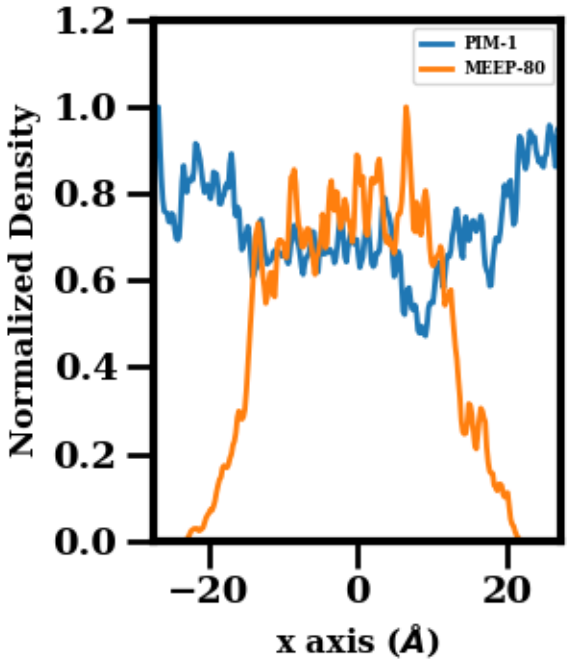


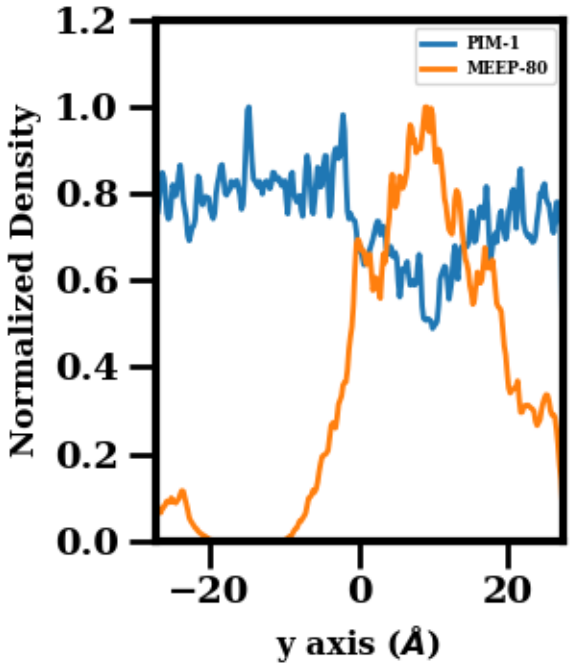


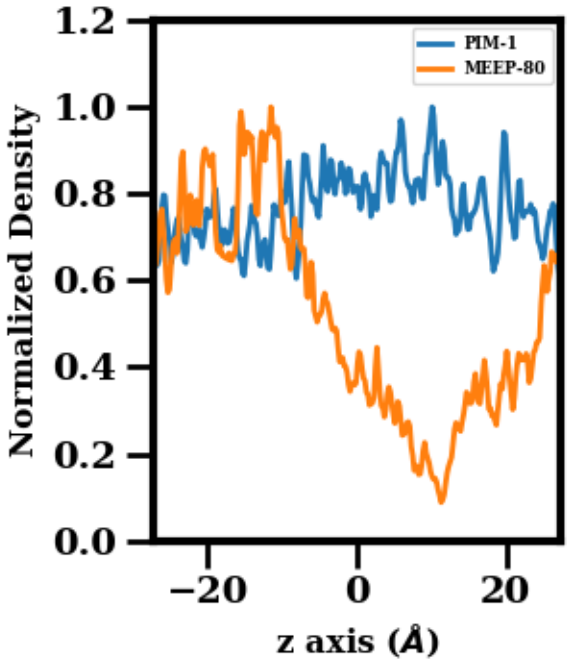


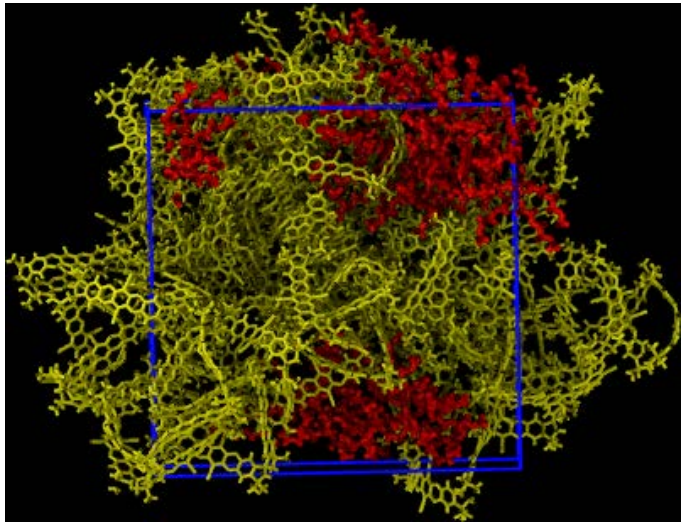
- Notable phase separation
- Very little intercalation
- Gas permeation properties not obtained: film not well blended enough

Local Density Blend B (PIM-1/MEEP-80)

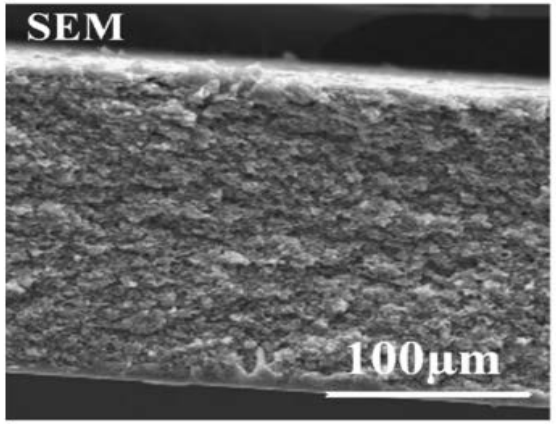




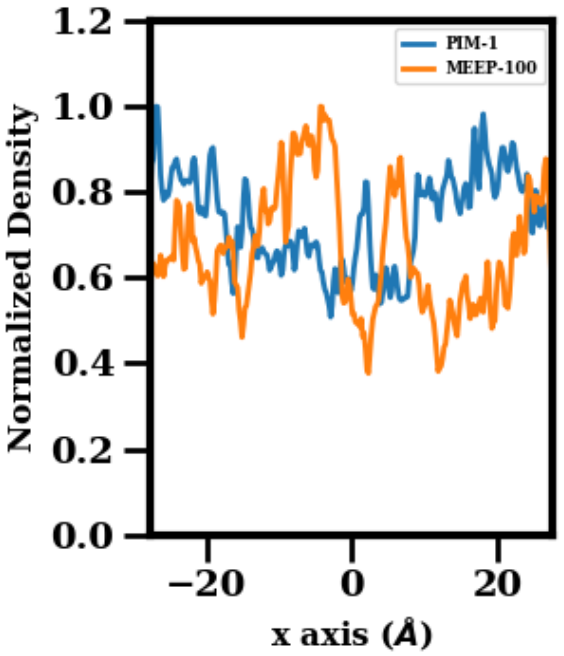


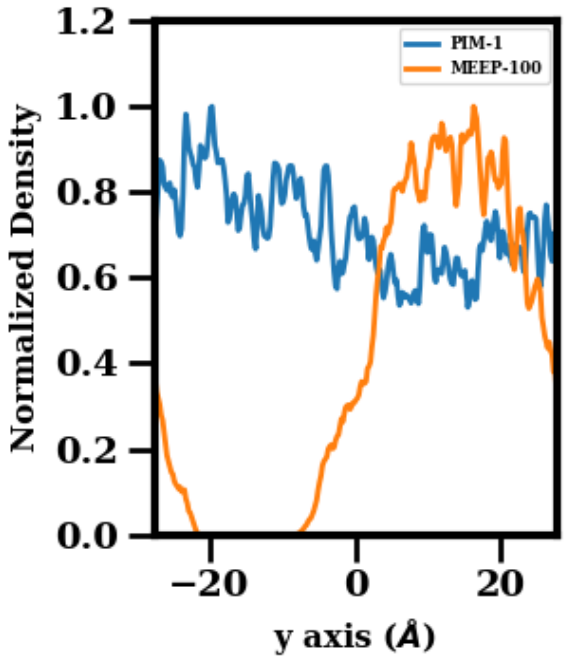


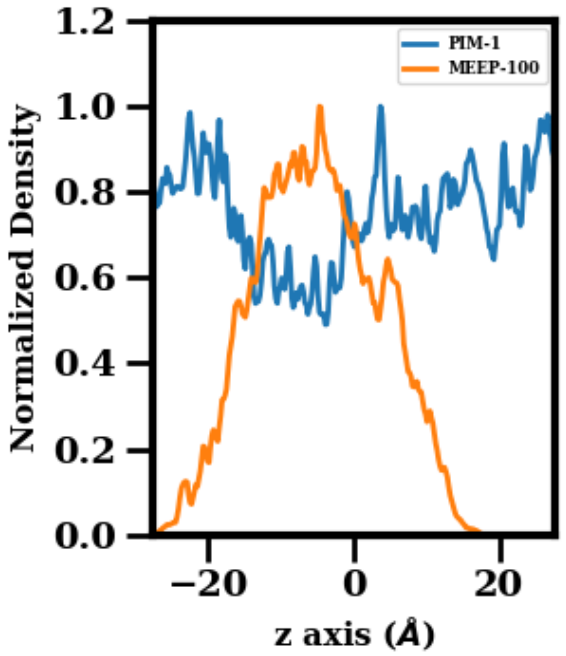
- Blends to form a good membrane

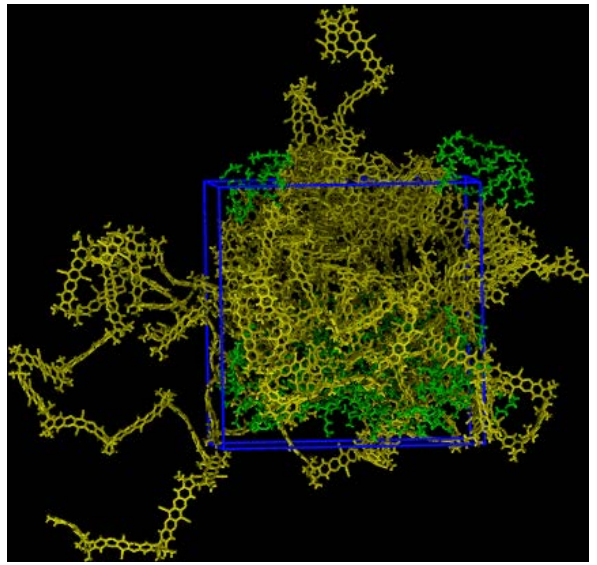


Local Density Blend C (PIM-1/MEEP-100)





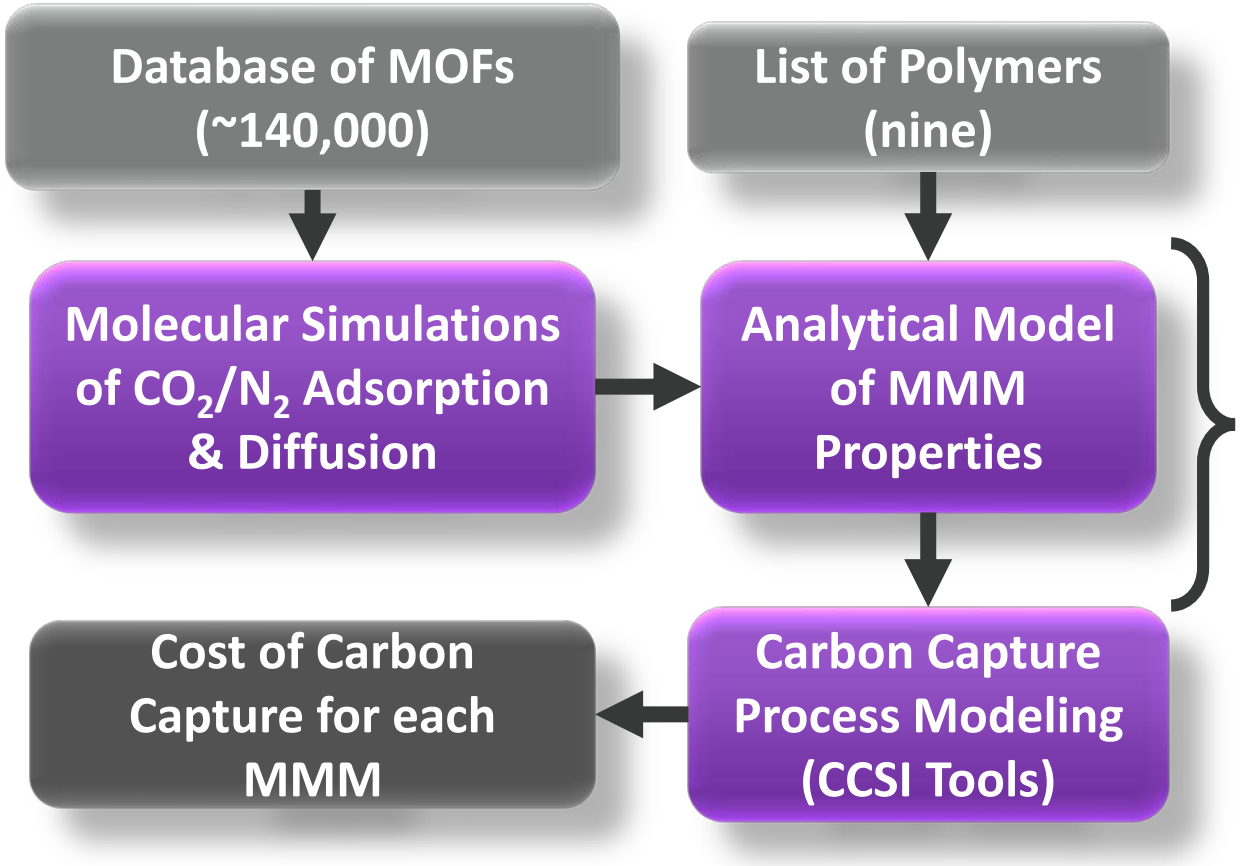




- Optimized blending
- Permeability better
- Insight: smaller ether groups intercalate
- Predictive tool, can be used to test other variations in the polymers

Experimental Results: Mixed gas at 25C		
	CO_2 Permeability (Barrer)	CO_2/N_2 Ideal Selectivity
PIM-1	8000	17
PIM-1/ MEEP0	film is not testable: phase separation	
PIM-1/ MEEP80	3200	24
PIM-1/ MEEP100	5300	24

Computational Screening for Mixed Matrix Membranes



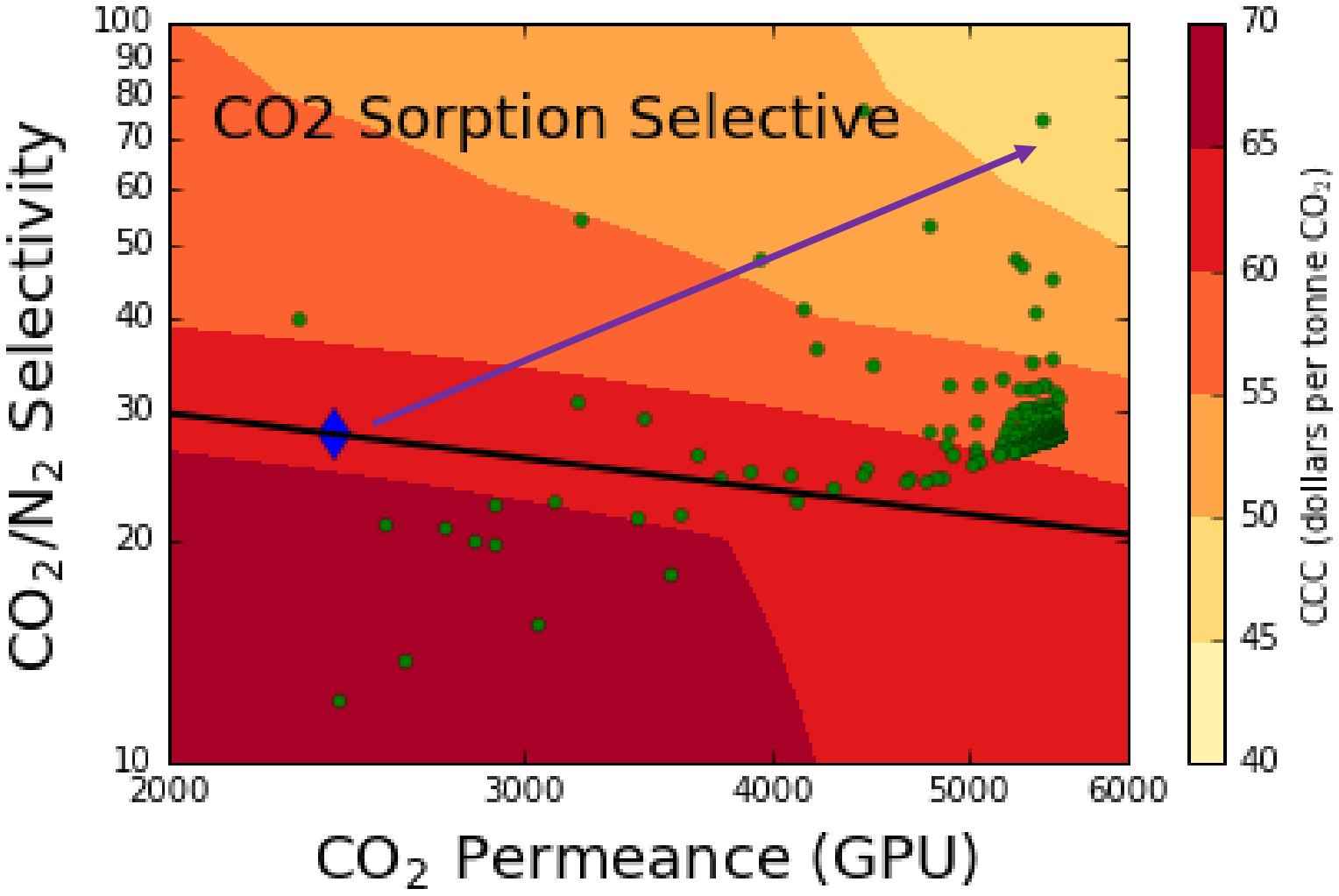
Computational Study Goals:

- Use large screening to determine which MOFs to pair with which polymer.
- Provide insight into the relationship between MOF and MMM properties.
- Connect atomistic calculations with process simulations.

Over 1 million membranes

Christopher E. Wilmer
University of Pittsburgh

MMMs based on PIM-1/MEEP Blend

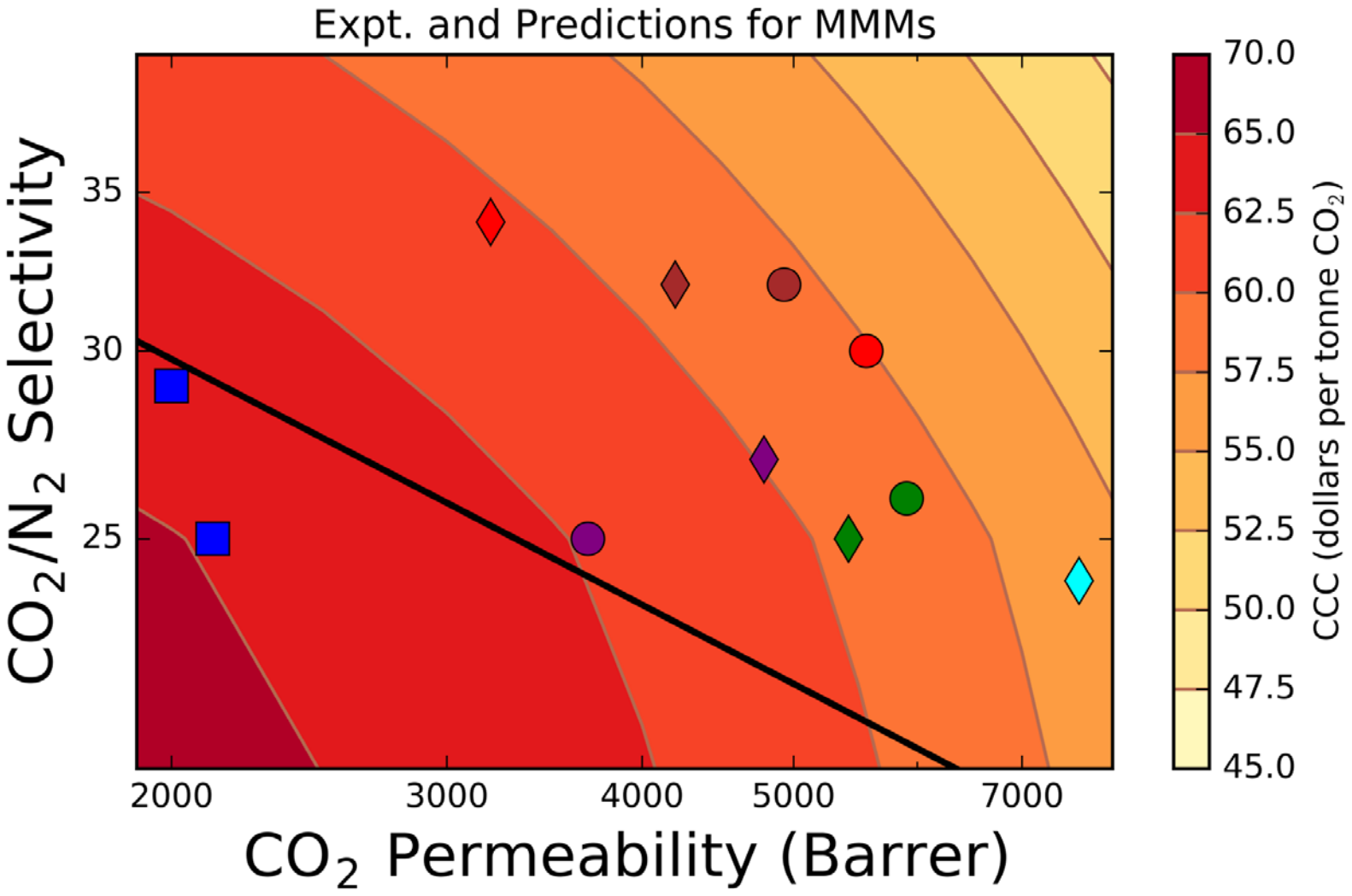


- Best MMM in this set:
  - Predicted CCC Reduction from $62.9 to $42.7 per tonne CO_2
  - This MOF has CO_2/H_2O Sorption Selectivity of 6.7
- The MOFs in this data set are all CO_2/H_2O sorption selective
- Tool for selecting MOFs to pair with polymers

Budhathoki, Ajayi, Steckel, Wilmer, Energy and Environmental Sciences, 2019

Henry's Constants for H_2O in CoRE MOFs courtesy of:Li, S.; Chung, Y. G.; Snurr, R. Q. *Langmuir* **2016**

Experimentally Tested MMMs



Blue squares:
Expt Polymer Blends

Diamonds:
Expt MMMs

Circles:
Comp MMMs

Ali Sekizkardes

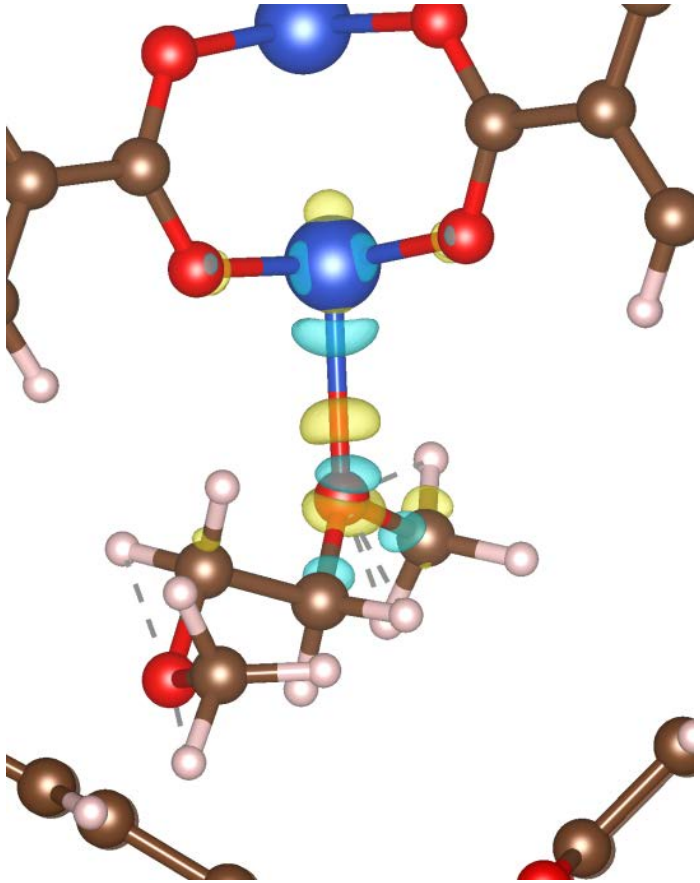
Sameh Elsaidi

Sekizkardes J. Mat. Chem. A 2018, Elsaidi (in preparation)

MOF-Polymer Interactions

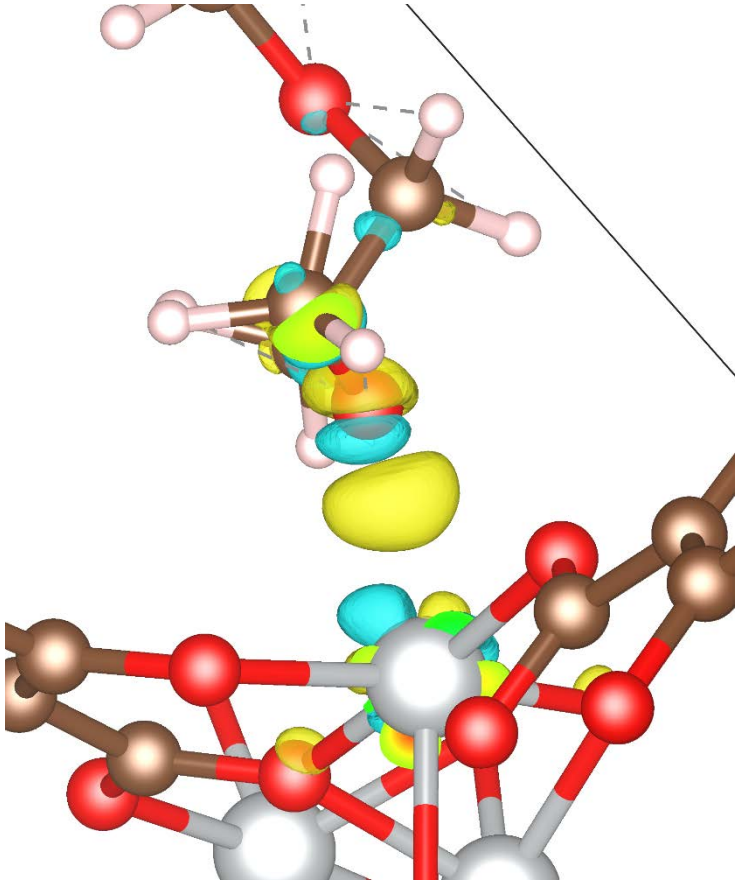
- Density Functional Theory (DFT)
- Calculate **MOF-polymer interactions**
- Charge Density Difference:
  - Yellow: charge increase
  - Blue: charge decrease
- Molecule: functional group (ethoxy) in poly-phosphazene side chains
- Modeling allows us to **choose MOFs** that interact strongly with polymer, **prevent MOF aggregation**

MOF1-MEE: -16 kcal/mol



Stronger:

MOF2-MEE: -45 kcal/mol



Conclusions

- Computational Solvent Screening → Creating New Larger Database, Two Novel Solvents Designed
- Computational Polymer Screening → Database in Progress, A Novel Polymer Designed
- Simulations to Optimize Polymer Blends → Simulations and Experiment to Optimize Blends; Predictive Tool
- Simulations of MOF-Polymer Interactions → Computational Tools for pairing MOFs with Polymers for Optimal MMMs

Acknowledgments

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