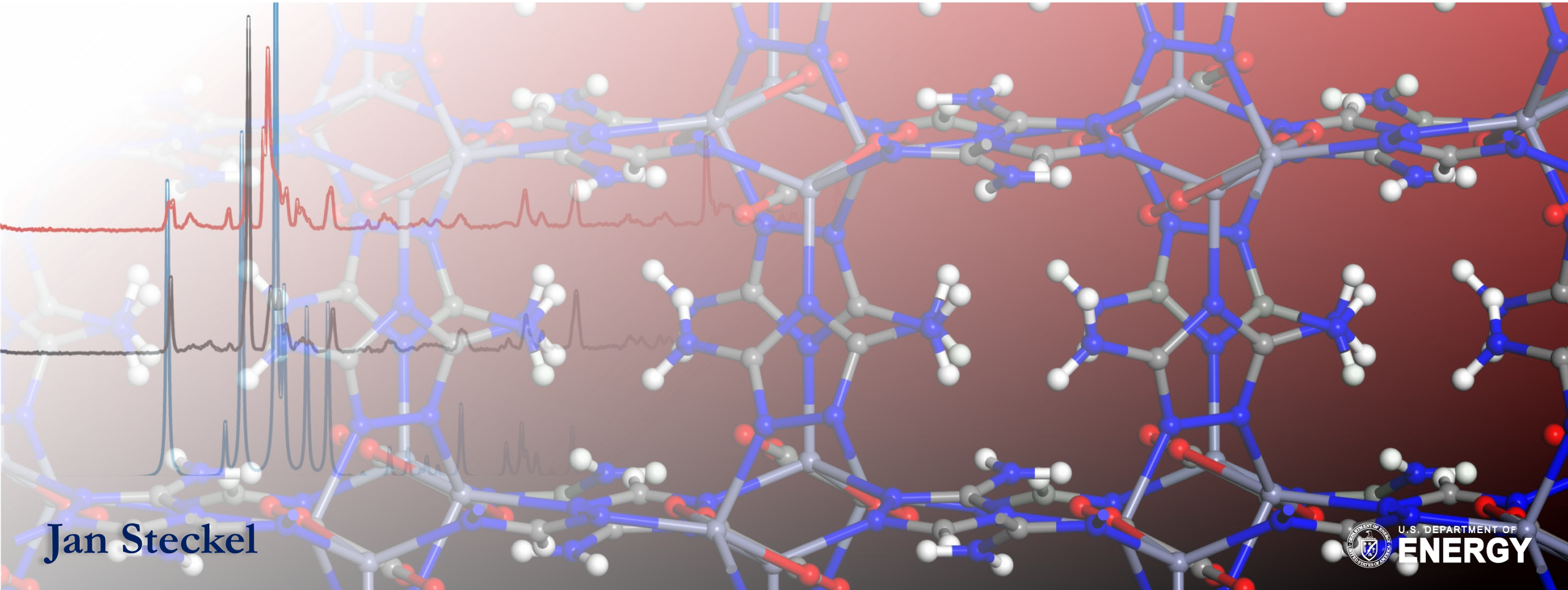
New Materials Discovery in CC Solvents and Membranes Using Computational Methods

Carbon Sequestration Leadership Forum

April 26, 2019, Champaign Urbana



Jan Steckel

NATIONAL ENERGY TECHNOLOGY LABORATORY

U.S. DEPARTMENT OF ENERGY

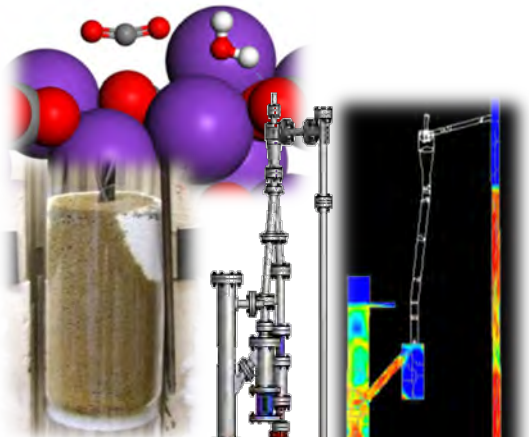
National Energy Technology Laboratory

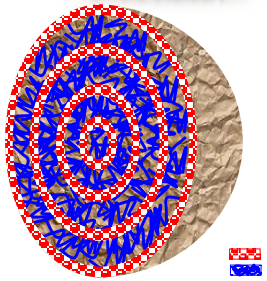
NETL focused on fossil energy – programs related to carbon capture

- National Risk Assessment Partnership (NRAP)
- Carbon Capture Simulation Innitiative (CCSI)
- Institute for the Design of Advanced Energy Systems (IDEAS)
- CO_2 Utilization
- Carbon Storage
- Carbon Capture

Carbon Capture: Materials Discovery & Separation Technologies

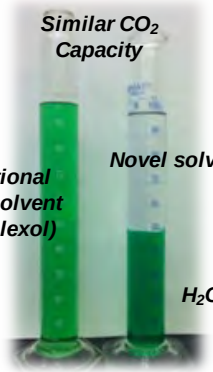
Sorbents



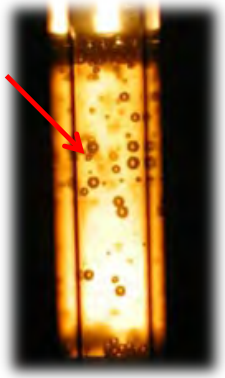


AAIL nano-layers

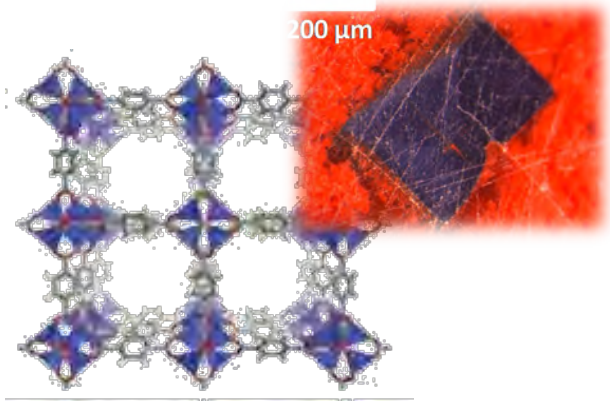
Solvents



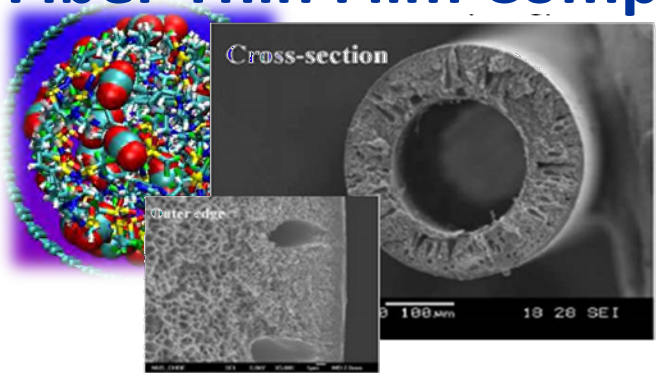
Changes in process conditions results in CO_2-release



Membranes, Mixed Matrix Membranes



Hollow Fiber Thin Film Composites



Development of efficient separation strategies tailored for energy production

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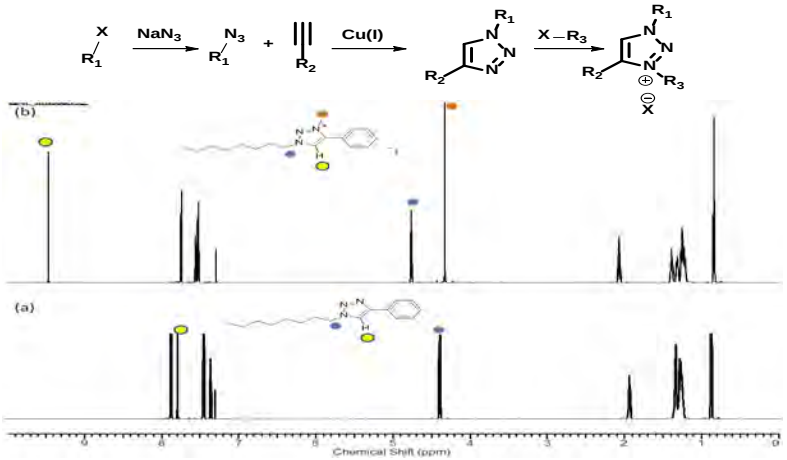
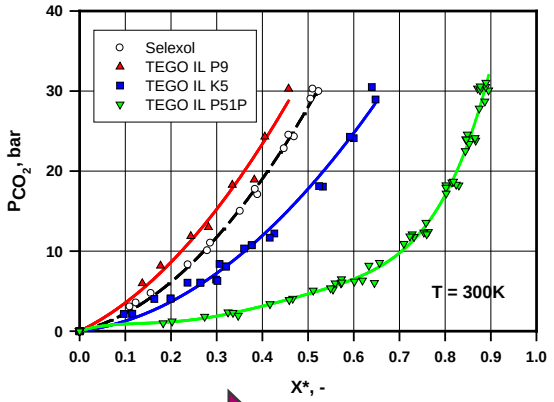
Carbon Capture Group: Integrated Materials Development

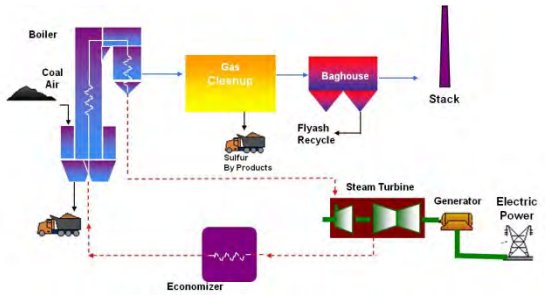
Characterization



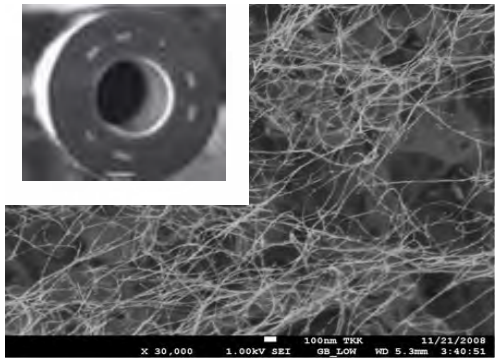
Performance Testing



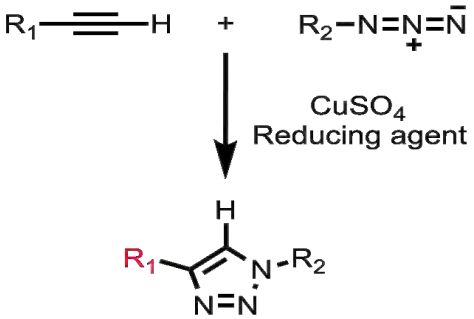
Systems Analysis



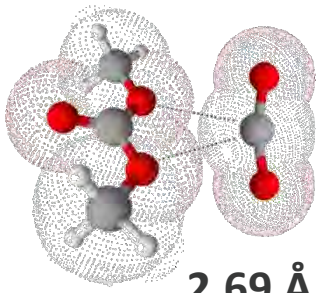
Fabrication



Synthesis

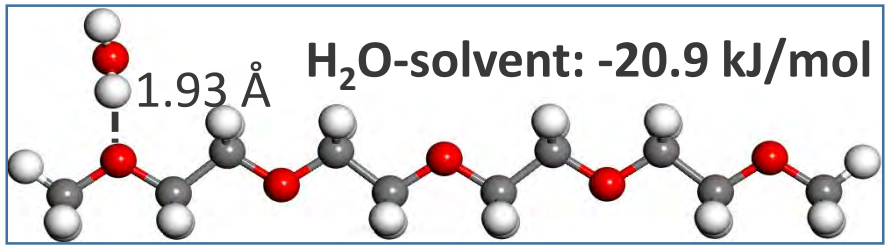


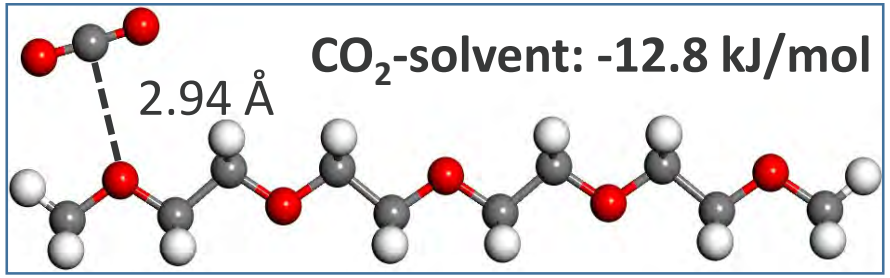
Modeling

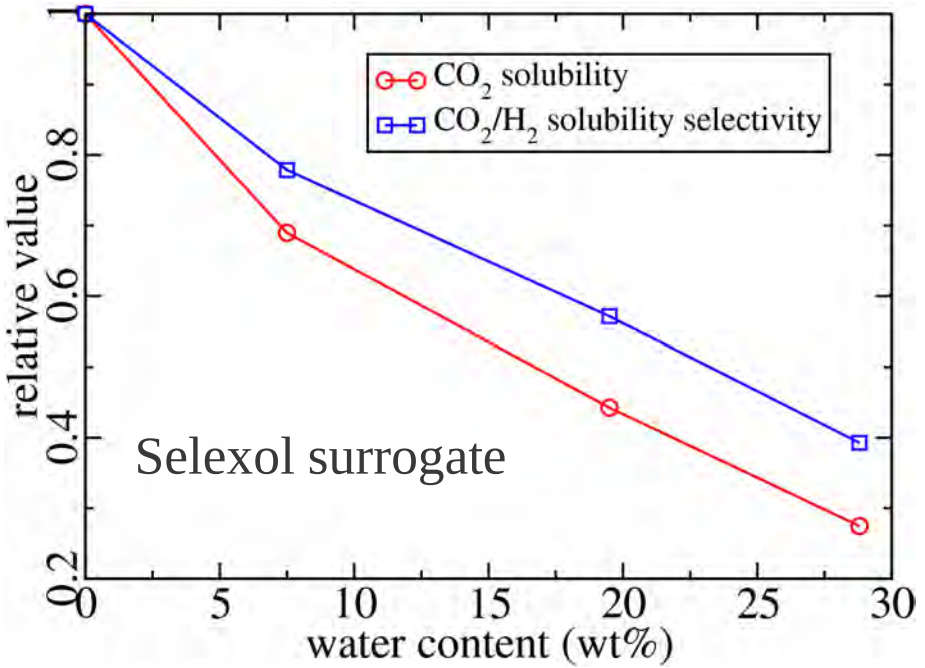


2.69 Å

Hydrophobic Pre-Combustion Solvent Screening







Wei Shi

Presence of water significantly & unfavorably decreases both CO_2 loading and CO_2/H_2 selectivity for Selexol surrogate.

Goal of computational study is to screen for a novel solvent that is:

- Hydrophobic
- Has large CO_2 solubility and large CO_2/H_2 solubility selectivity
- Has low viscosity
- Has low vapor pressure
- Has low foaming tendency

Computational Strategy

NIST database for pure compounds (~23,000)
- Melting (T_m), boiling (T_b) temperatures, viscosity (μ), saturation vapor pressure (P^{sat}), surface tension (σ), density (molar volume)

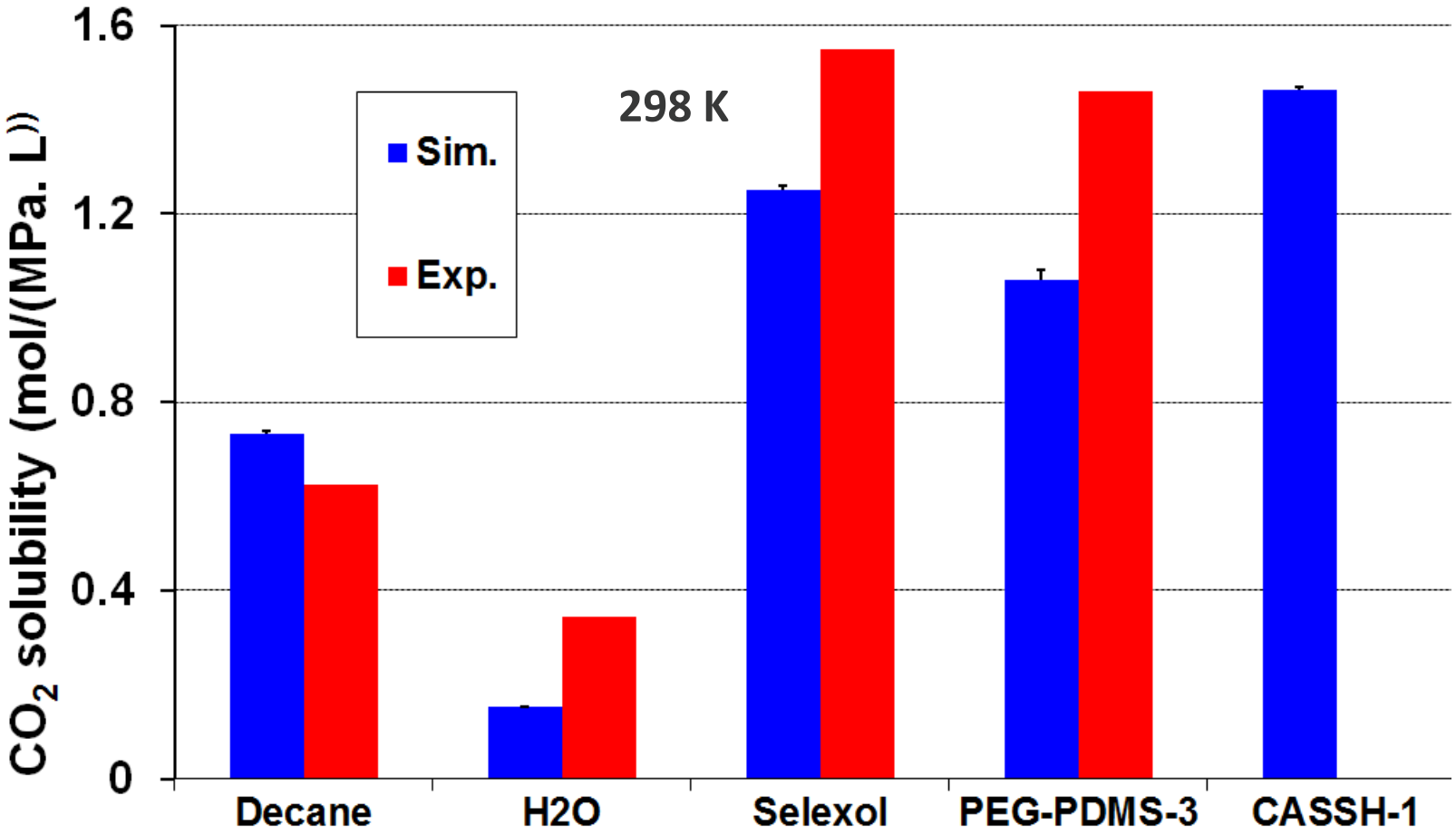
In-house computational database: quantum mechanics for gas – chemical function group interactions
- CO_2, CH_4, H_2, H_2O, H_2S, COS, SO_2, O_2, N_2, etc.

In-house machine learning and Monte Carlo Simulation
- Chief criteria: CO_2 solubility, CO_2/H_2 solubility selectivity, heat of absorption, H_2O solubility

In-house simulation: Molecular Dynamics
- Surface tension, heat capacity, viscosity, CO_2 diffusivity, density, vapor pressure, therm. conduct.

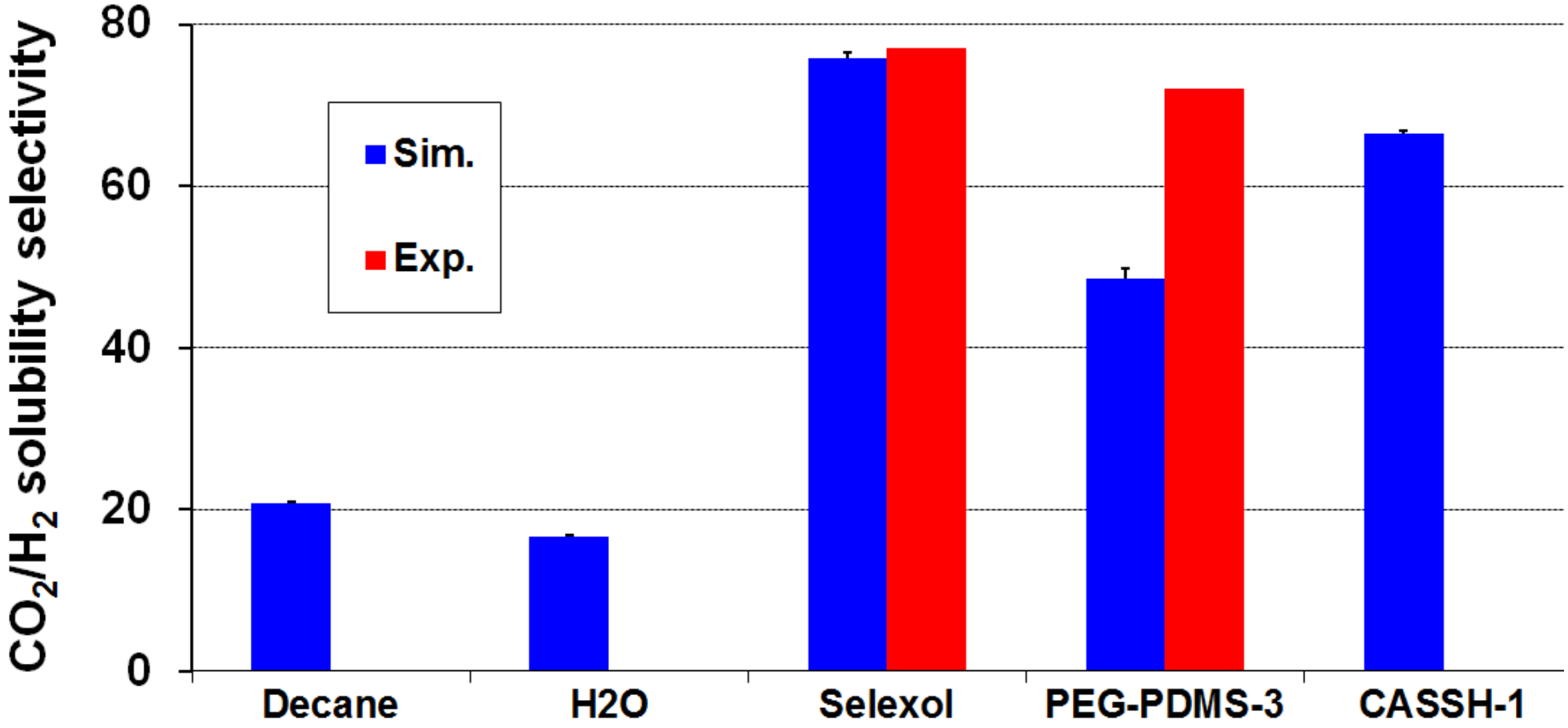
Experimental testing & TEA analysis

Simulated CO_2 Solubility



CASSH-1: identified from the computational screening.

Simulated CO_2/H_2 Solubility Selectivity



- CASSH-1 exhibits high CO_2/H_2 selectivity

Better Solvent Performance Without Refrigeration

NETL solvents tested at University of North Dakota's Energy and Environmental Research Center (EERC)

- 3 solvents:
  - Selexol (polyethylene glycol mixture)
  - PEG-PDMS-3 (NETL-expt.)
  - CASSH-1 (NETL-computational study)
- Gasifier with actual syngas
- Three different temperatures for each solvent.

Nick Siefert

- CASSH-1 and PEG-PDMS-3 performed similar or better *at 40°C* than Selexol did *at 10°C* in both CO_2 uptake and CO_2/H_2 selectivity
- CASSH-1 and PEG-PDMS-3 had much lower soluble moisture levels than Selexol.

EERC | UND UNIVERSITY OF NORTH DAKOTA

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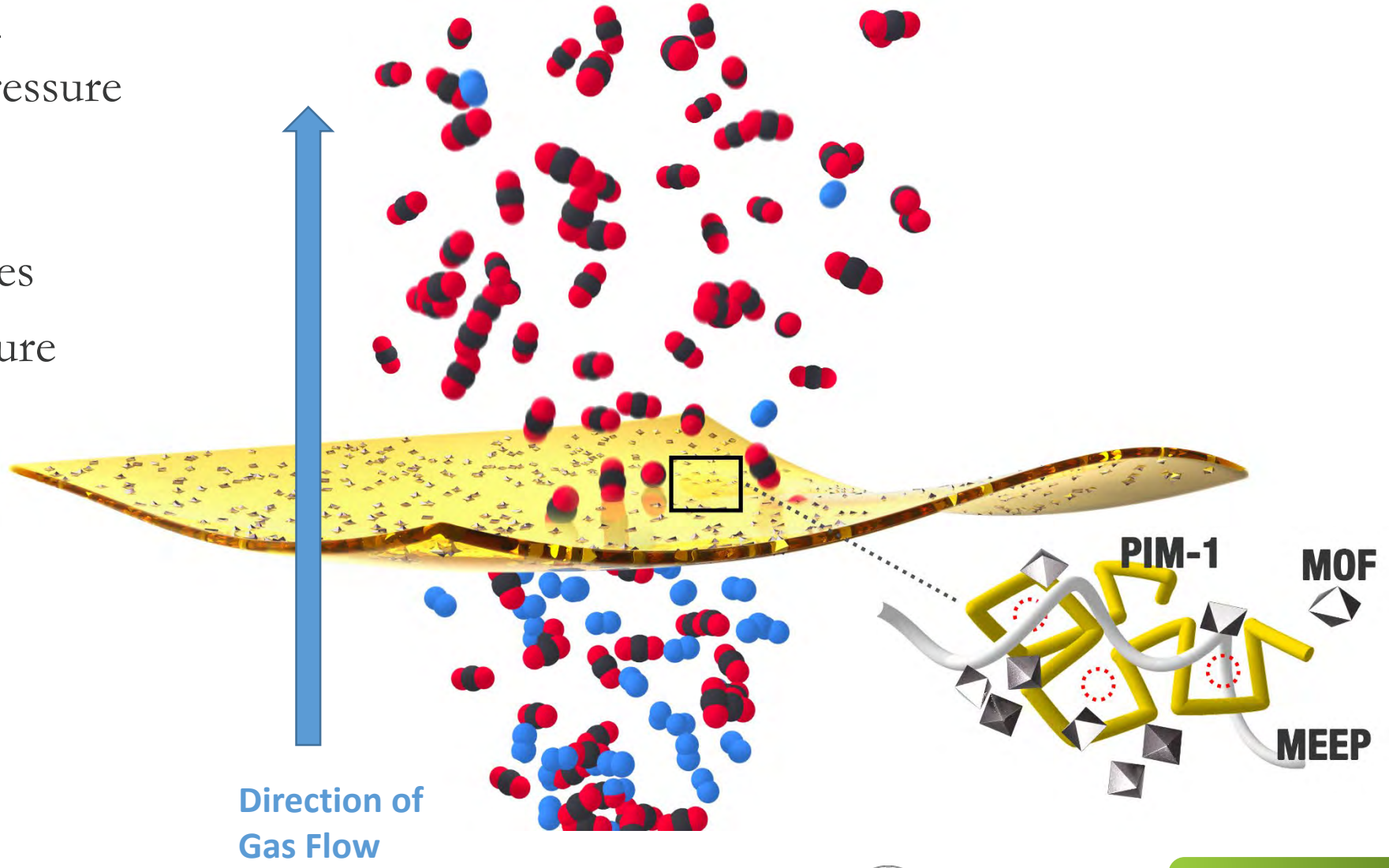
CO_2 Capture: Gas Separation Using Membranes

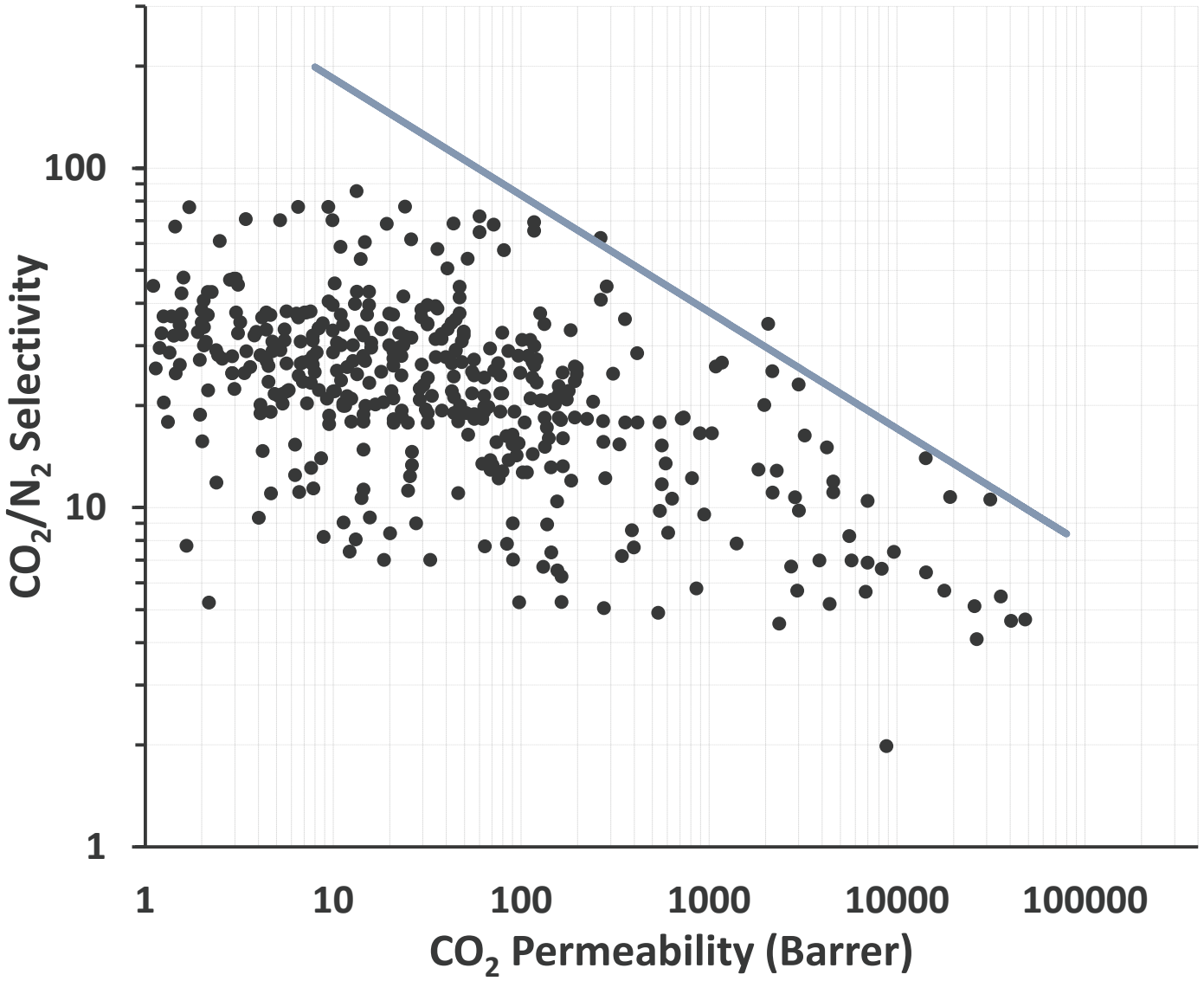
Adsorption/Desorption – requires temperature or pressure swings

Membrane technology - inherent process advantages

- no temperature or pressure swing necessary
- simplicity
- reliability
- compactness
- modularity



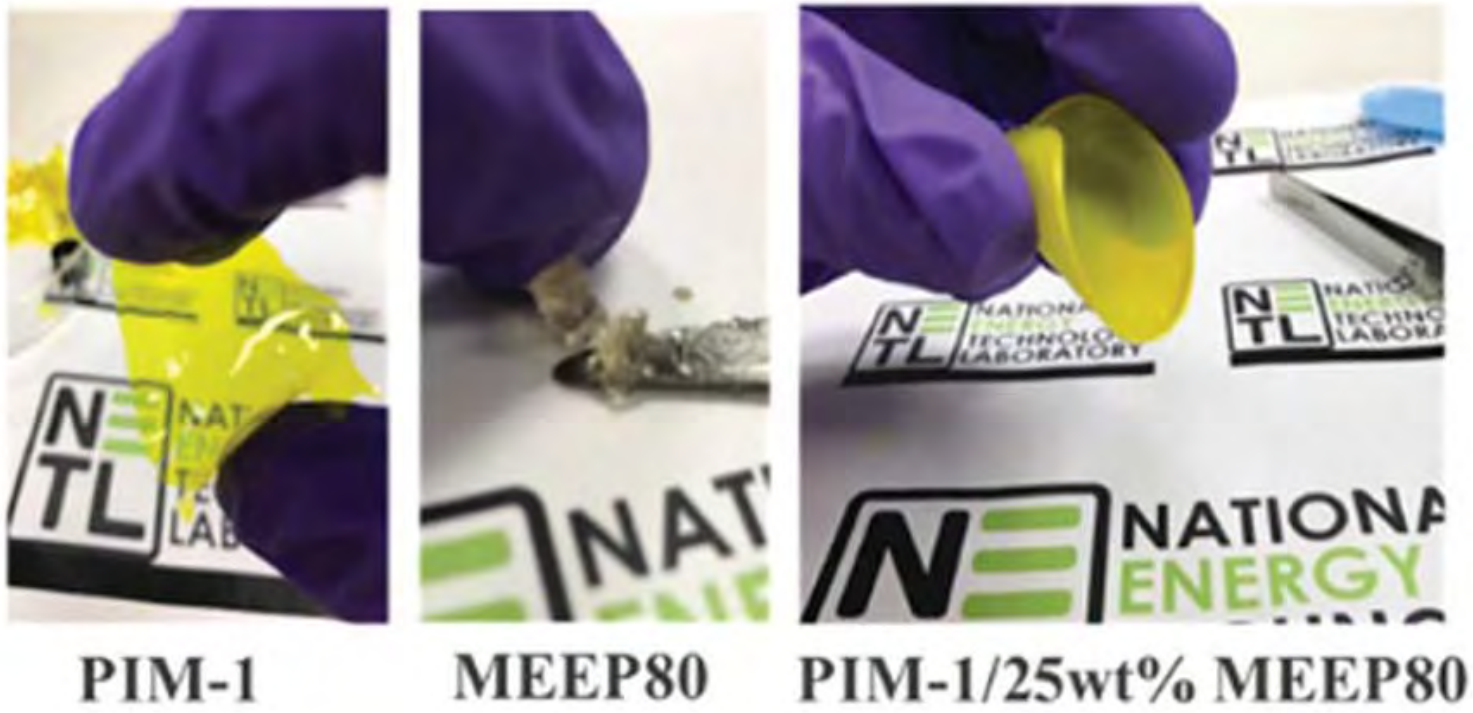
Polymer Membranes: Robeson Bound

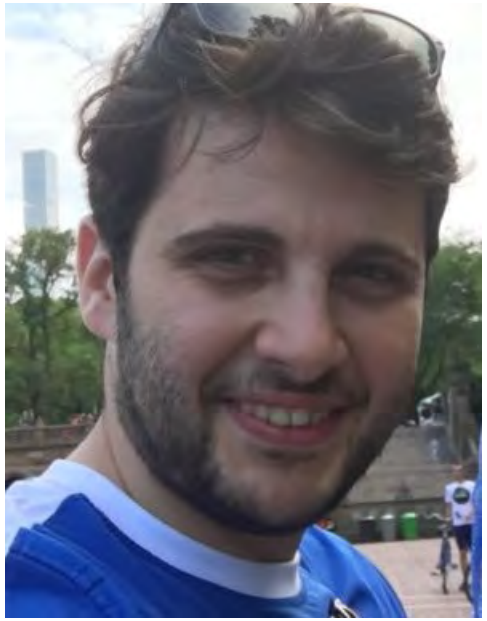


- Trade-off between selectivity and permeability for membrane separation of gases
- Observed for many gas pairs:
  - CO_2/N_2
  - O_2/N_2
  - H_2/N_2
  - H_2/CH_4
  - He/H_2
  - CO_2/CH_4
  - Etc…
- Lloyd M. Robeson, J. Membrane Science, 1991 and 2008

PIM-MEEP Blends: NETL Polymer 3

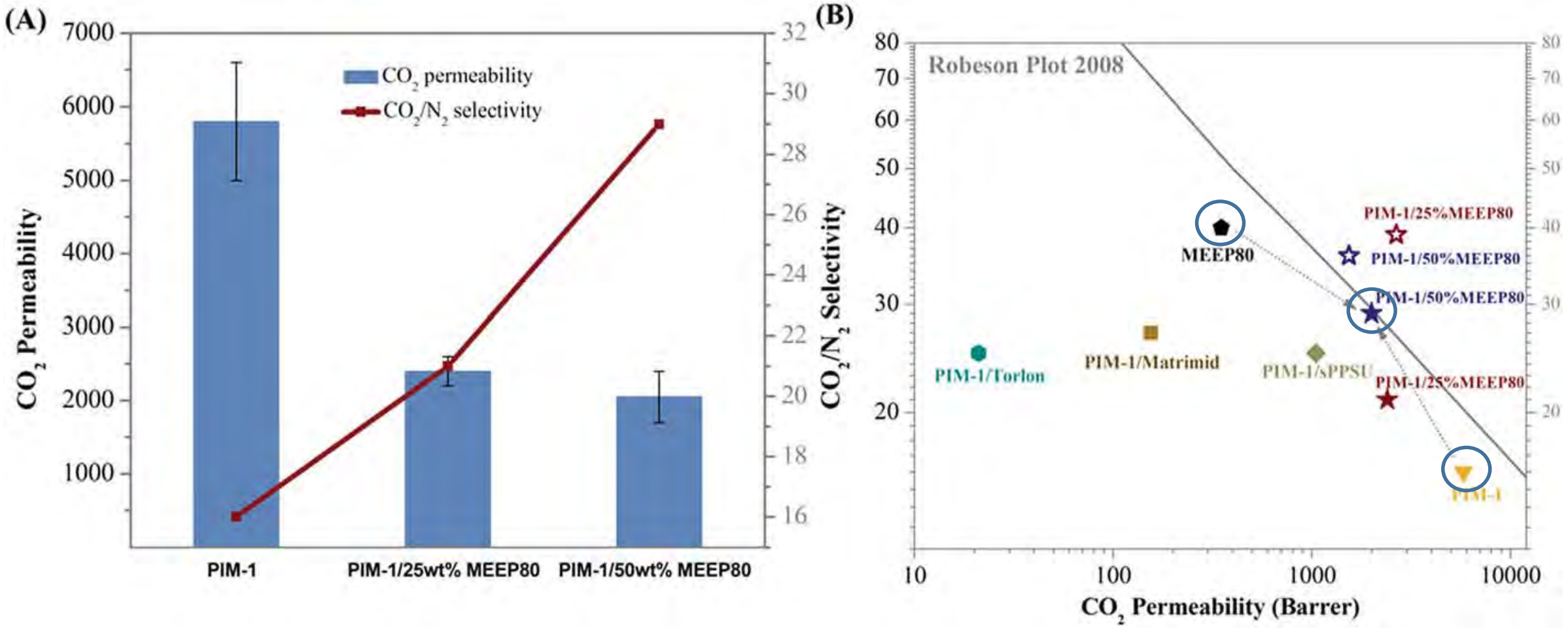
- Polymer blend: PIM-1 + MEEP-80 polyphosphazine
- Overcomes brittleness and low selectivity of PIM-1
- Overcomes the stickiness and low permeance of MEEP-80
- Excellent flexibility and toughness





Sekizkardes J. Mat. Chem. A 2018

PIM-MEEP Blends: NETL Polymer 3



Sekizkardes J. Mat. Chem. A 2018

Can We Improve Upon NETL Polymer 3?

Mixed matrix membranes (MMMs) combine polymer and metal organic framework (MOF) into a composite material :

- Polymer 60-95% of the membrane →good mechanical properties, low cost.
- MOF can boost the performance of the composite material.

Challenges for making MMMs in the lab:

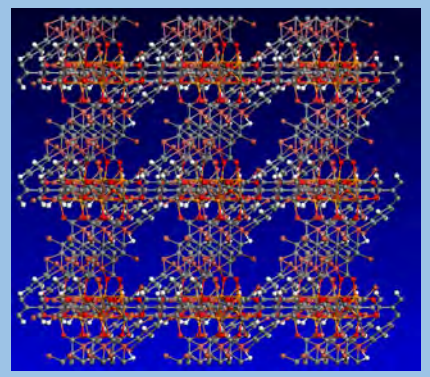
- Pairing the "best" polymer and the "best" MOF → not necessarily "best" MMM.
- Permeability of MOF particles not easily measured.
- MOF space: ~60 building blocks → ~5 million possible MOF structures!

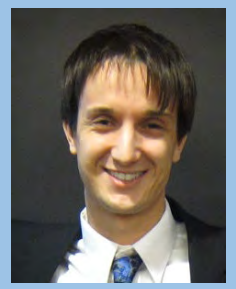
Computational Study Goals:

- 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.

Project Design

Hypothetical MOF Database



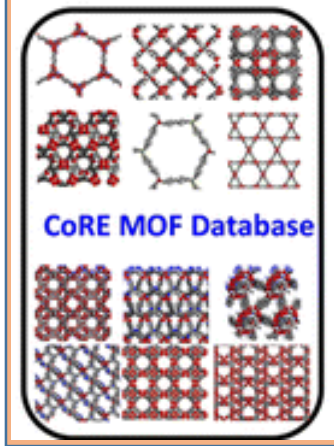


Christopher E. Wilmer
University of Pittsburgh

~130,000 MOFs

Wilmer, et al. Large-Scale Screening of Hypothetical Metal–organic Frameworks. *Nature Chemistry* **2012**, *4* (2), 83.

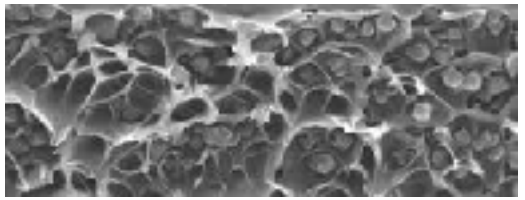
Real MOFs: CoRE MOF Database



~3000 MOFs

Y. G. Chung, et al .Computation-Ready, Experimental Metal–Organic Frameworks: A Tool To Enable High-Throughput Screening of Nanoporous Crystals. *Chem. Mater.* **2014**, *26* (21), 6185–6192.

Maxwell Model



Predicted Properties for over a million possible MMMs

CCSI^2
Carbon Capture Simulation for Industry Impact

Expt. Properties of Nine Neat Polymers

Estimate of Cost of Carbon Capture for each possible MMM

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Calculation of MOF Properties

Geometrical Characterization (Zeo++)

- Largest cavity diameter (LCD)
- Pore limiting diameter (PLD)
- Surface area

Widom insertion→ Gas Adsorption (S)

- MOF atomic positions held fixed
- Atomic charges calculated via EqEq Method
- UFF force field for MOF atoms
- TraPPE force field for gases
- RASPA

MD Simulations → Diffusivity (D)

- PACKMOL, LAMMPS
- Velocity autocorrelation function used to calculate diffusivity

Permeability = S•D (solution diffusion mechanism)

Samir Budhathoki

Maxwell Model to Predict MMM Properties

- The theory was developed for predicting the dielectric behavior of composite materials.[1]
- It has been successfully applied to MMMs.[2]
- Assumptions:
  - spherical, well-dispersed particles
  - volume fraction ≤ 0.3
  - ideal interface

Maxwell Model

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

P_{eff} – effective permeability of the MMM

P_c – permeability of continuous phase (polymer)

P_d – permeability of dispersed phase (MOF)

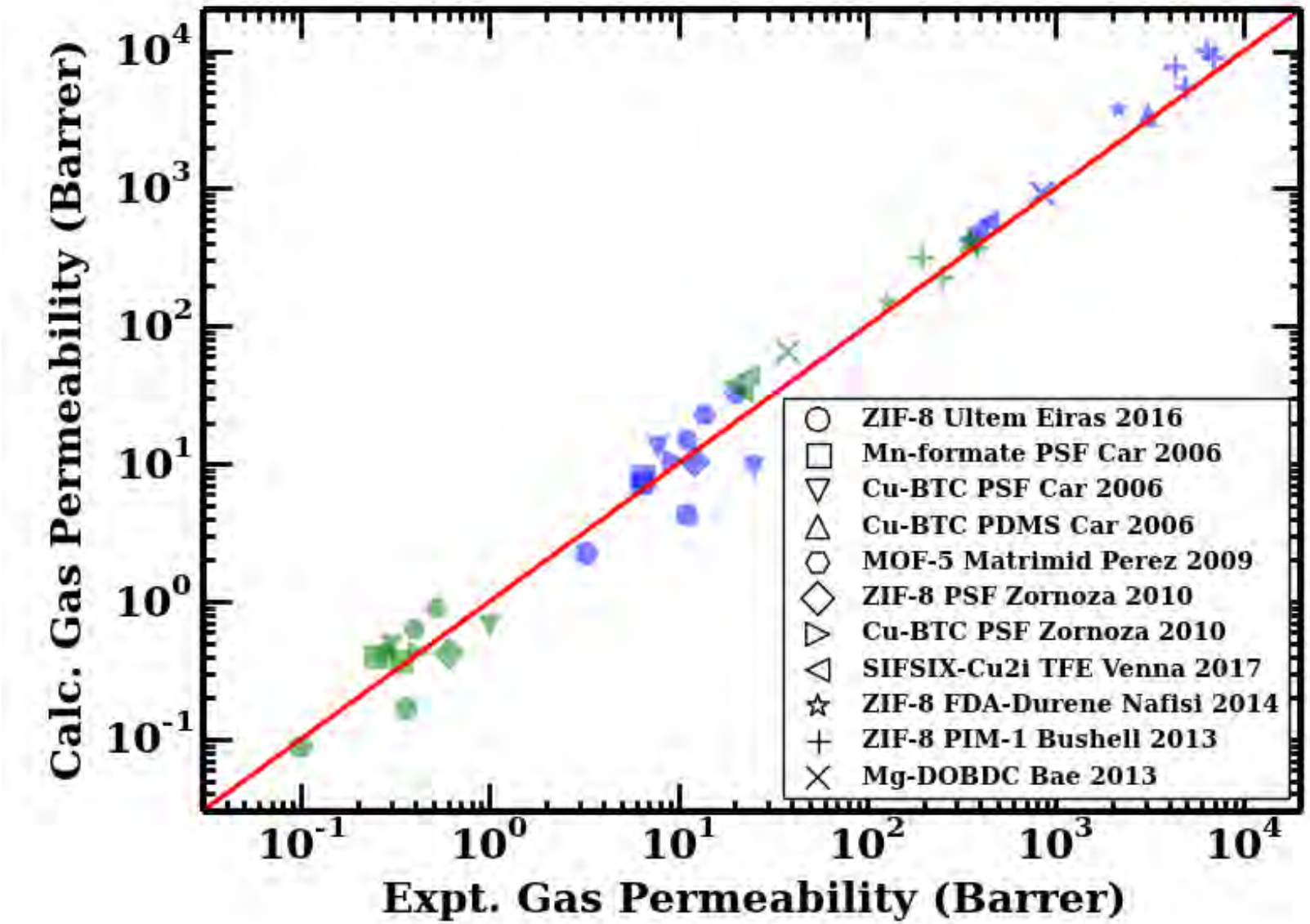
φ_d – volume fraction of the dispersed phase

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

[1]R.H.B. Bouma et al., J. Membrane Science, 128, 141, 1996.

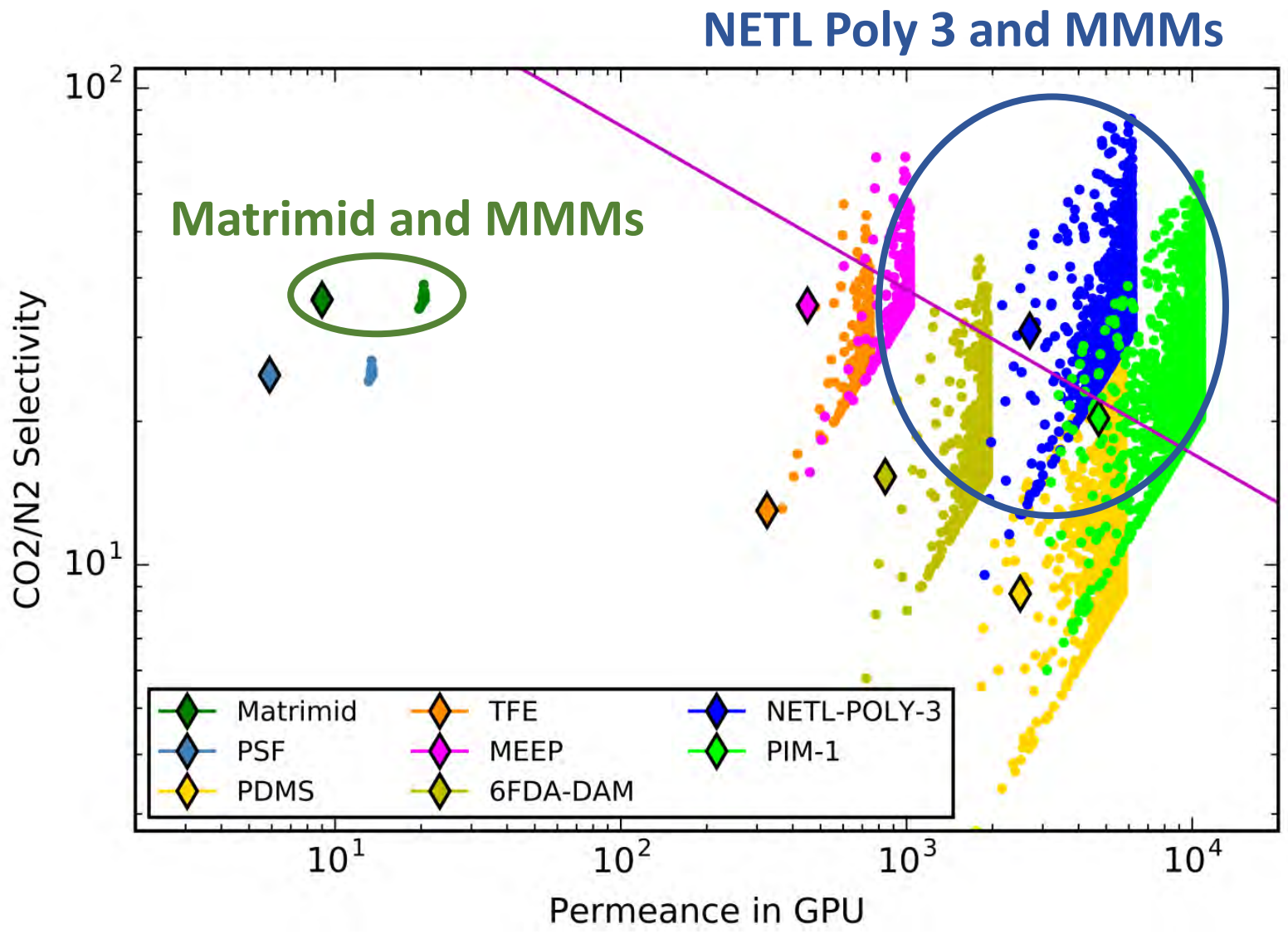
[2]Seda Keskin and David S. Sholl, En. & Env. Sci., 3, 343, 2010.

Validation: Predicted and Expt. MMM Properties



- CO_2 Permeability (blue symbols)
- N_2 Permeability (green symbols)

Properties of MMMs



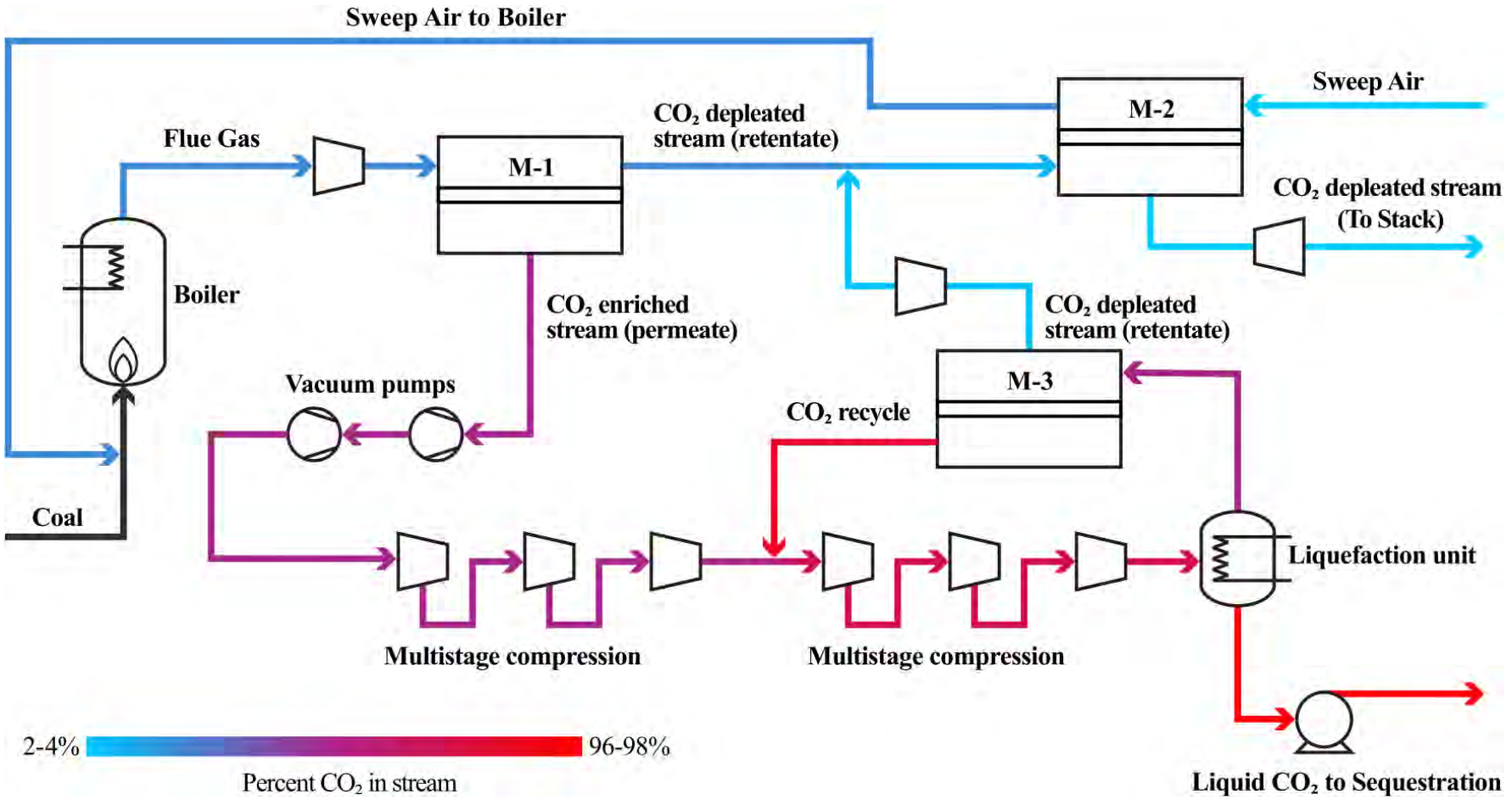
- Major conclusion → can significantly improve membrane properties
- For polymers with low CO_2 permeance, inclusion of any MOF leads to an improvement.
- For polymers with high CO_2 permeance, the effect of the MOF is variable.

Carbon Capture Cost Estimated on 3-Stage Configuration

Assign **Cost of Carbon Capture** (CCC) based on permeance, selectivity

$$CCC = f\left(P_{CO_2}, \alpha_{CO_2/N_2}\right)$$

Kayode Ajayi



CCSI² Carbon Capture Simulation for Industry Impact

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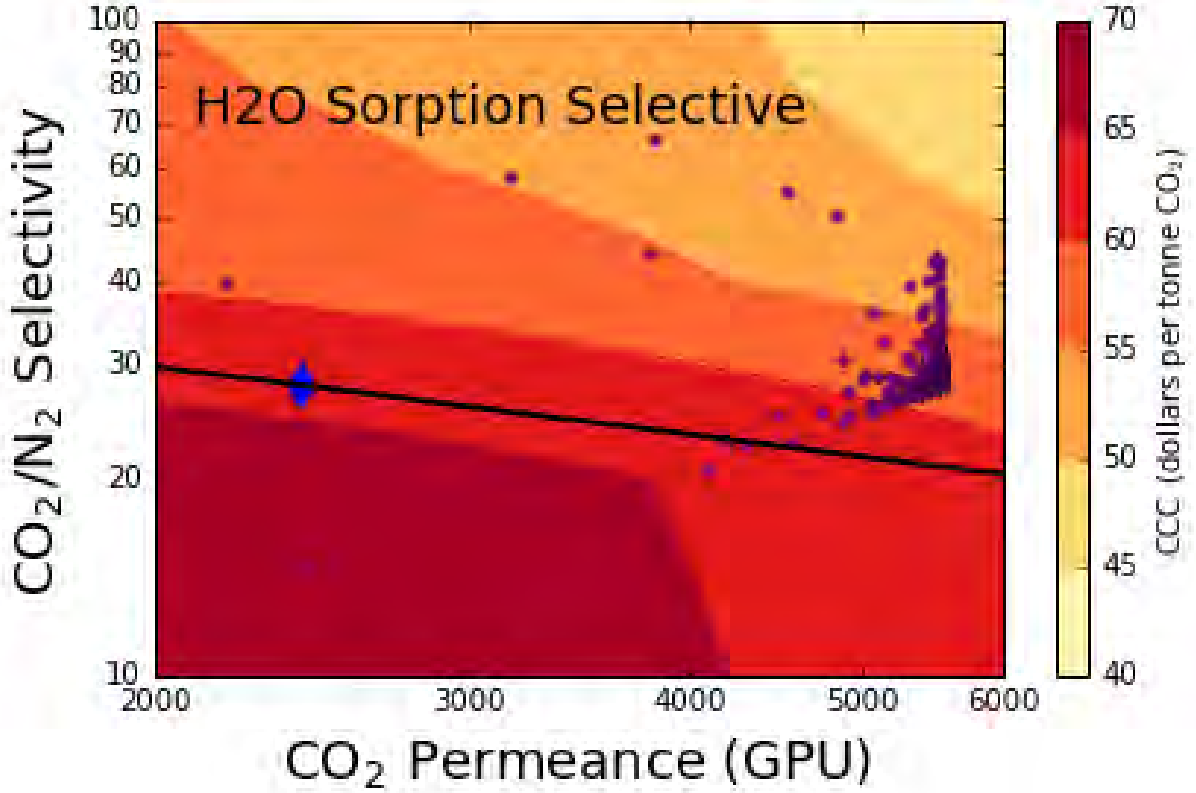
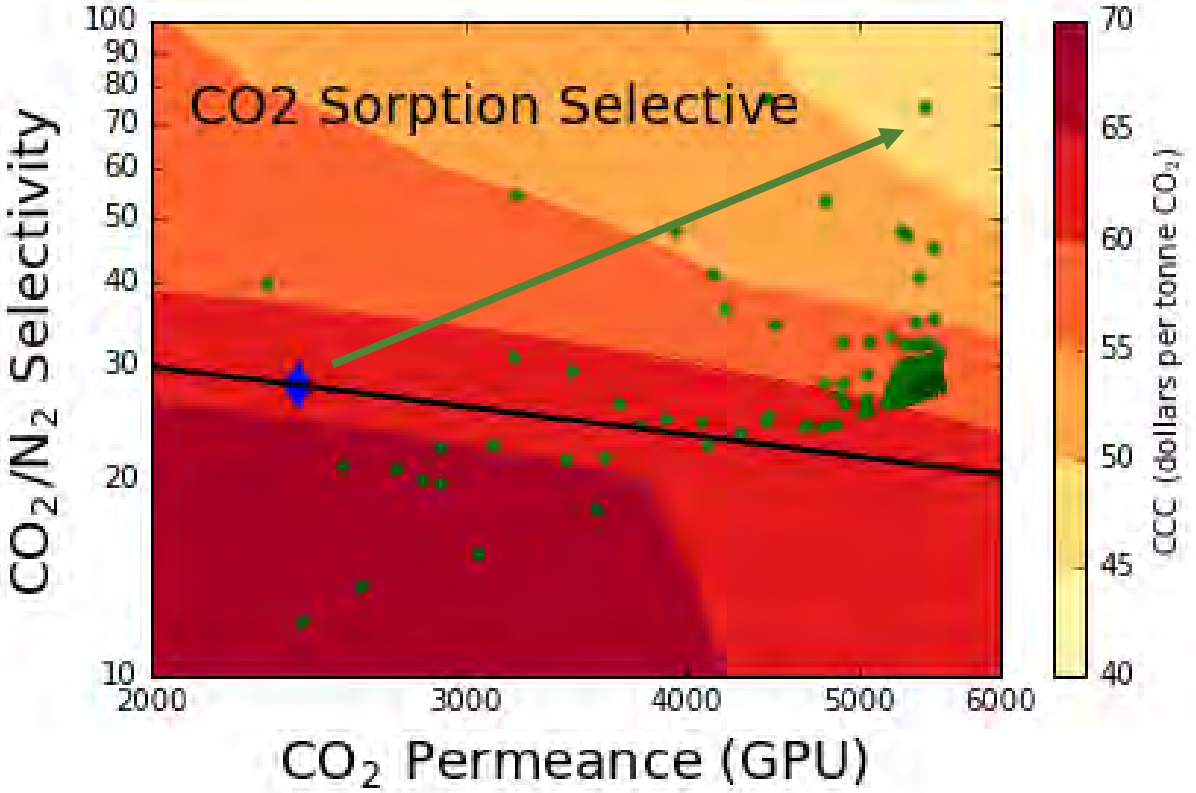
CCC for MMMs - NETL Polymer 3 with CoRE MOFs



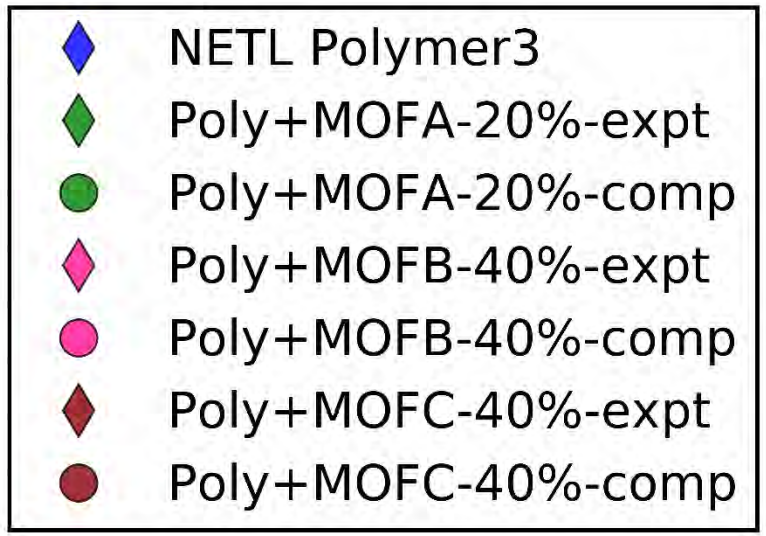


Henry's Constants for H_2O in CoRE MOFs courtesy of:
Li, S.; Chung, Y. G.; Snurr, R. Q. *Langmuir* **2016**, *32* (40), 10368–10376.

(Hypothetical) CCC Reduction from $62.9 to $42.7 per tonne CO_2
CO_2/H_2O Sorption Selectivity of 6.7

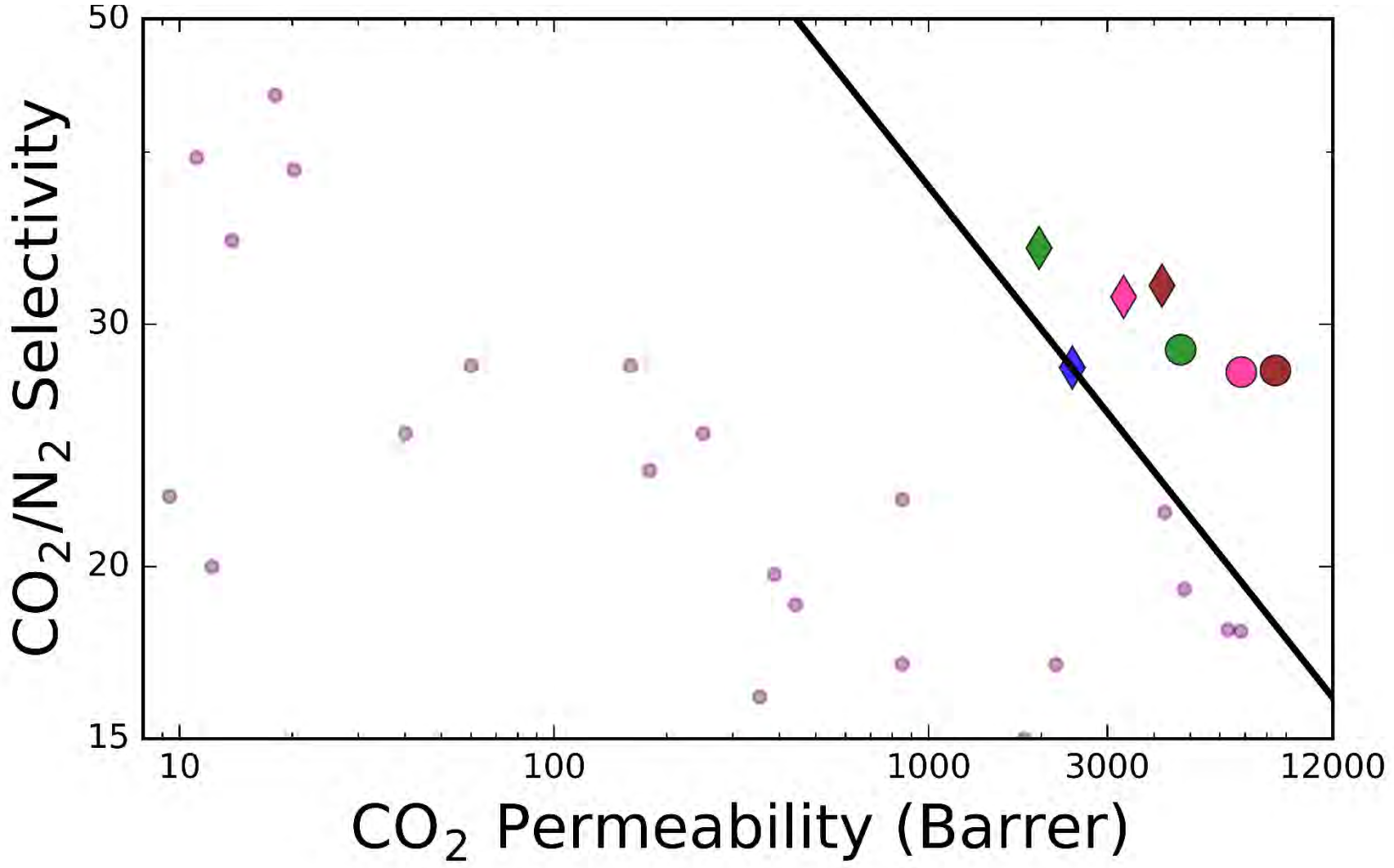
Budhathoki, Ajayi, Steckel, Wilmer, Energy and Environmental Sciences, 2019

Properties of MMMs Based on NETL Polymer 3



Sameh Elsaidi
MOF Synthesis

Surendar Venna
MMM Synthesis



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Sameh Elsaidi

Ali Sekizkardes

Christopher E. Wilmer

David Hopkinson

Anastasia Piacentini (Cover Art)

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