Design of Novel Mixed Matrix Membrane Materials Using High Throughput Computational Methods

Extending Predictions to Include Cost

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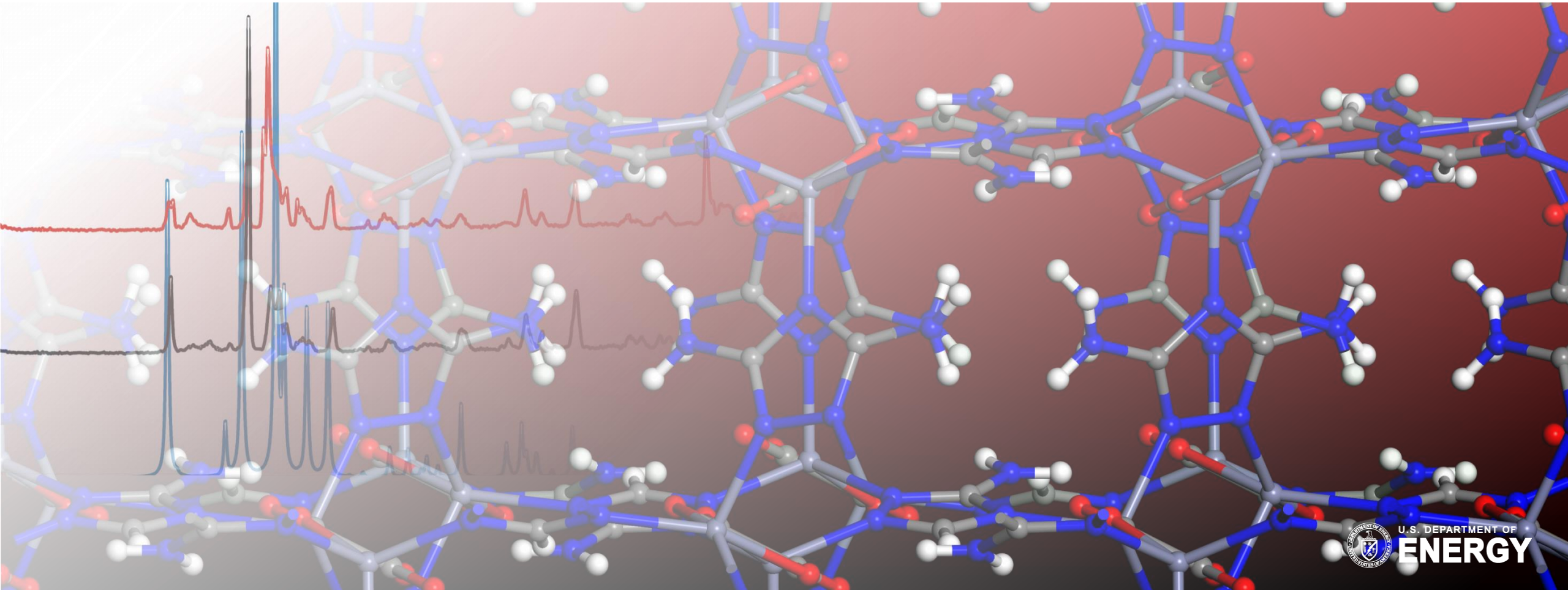
NATIONAL ENERGY TECHNOLOGY LABORATORY



U.S. DEPARTMENT OF ENERGY

Designing Mixed Matrix Membranes

MMMs have great potential to lower the cost of CO_2 separations

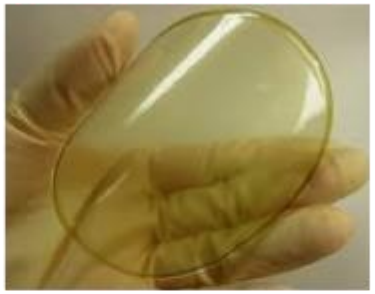
- Challenges in Lab:
  - Pairing the "best" polymer and the "best" MOF → not necessarily "best" MMM.
  - Permeability of MOF particles not easily measured.
  - MOF space: ~60 building blocks can be put together into ~5 million possible MOF structures!
- How can Computations Help?
  - Screen large number of MOFs and MMMs.
  - Understand the relationship between MOF properties and MMM properties.
  - Connect atomistic calculations with process simulations.
  - Create a prediction of CCC for each MOF/polymer pair.
  - ***Use computational methods to aid the design of better MMMs***.

Project Design

MOF Properties
(Predicted by Calculations)

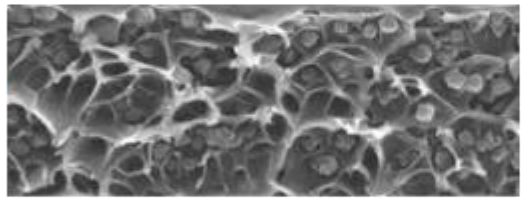
DB of ~137,000
Hypo-MOFs
DB of ~2,500 MOFs
CORE-MOFs

Pure Membrane Properties
for ~10 polymers
measured experimentally

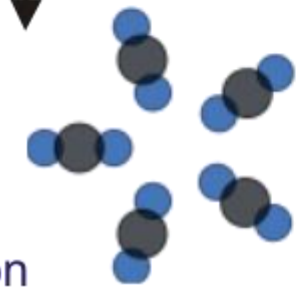


Maxwell Eq.

Predicted Properties
for well over a million
possible MMMs



Estimate of Cost
of Carbon Capture
based on an
assumed configuration

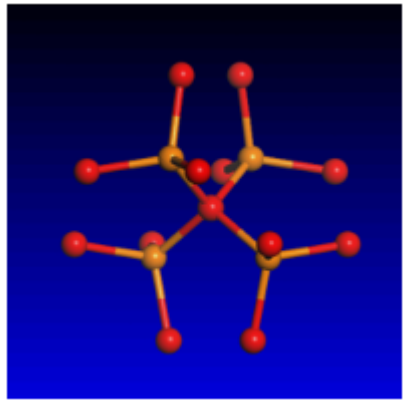


CCSI^2
Carbon Capture Simulation for Industry Impact

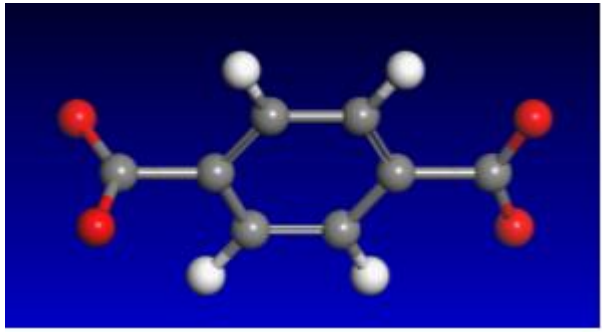
Hypothetical Structures: 137,000 MOFs

Existing MOFs deconstructed into a library of building blocks

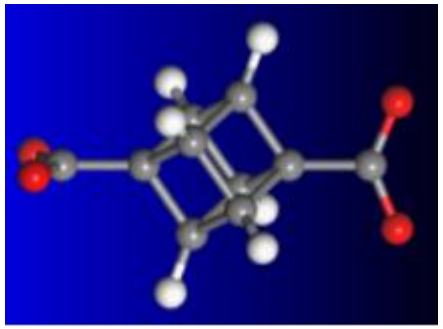
1: Metal Center



2: Organic Linkers

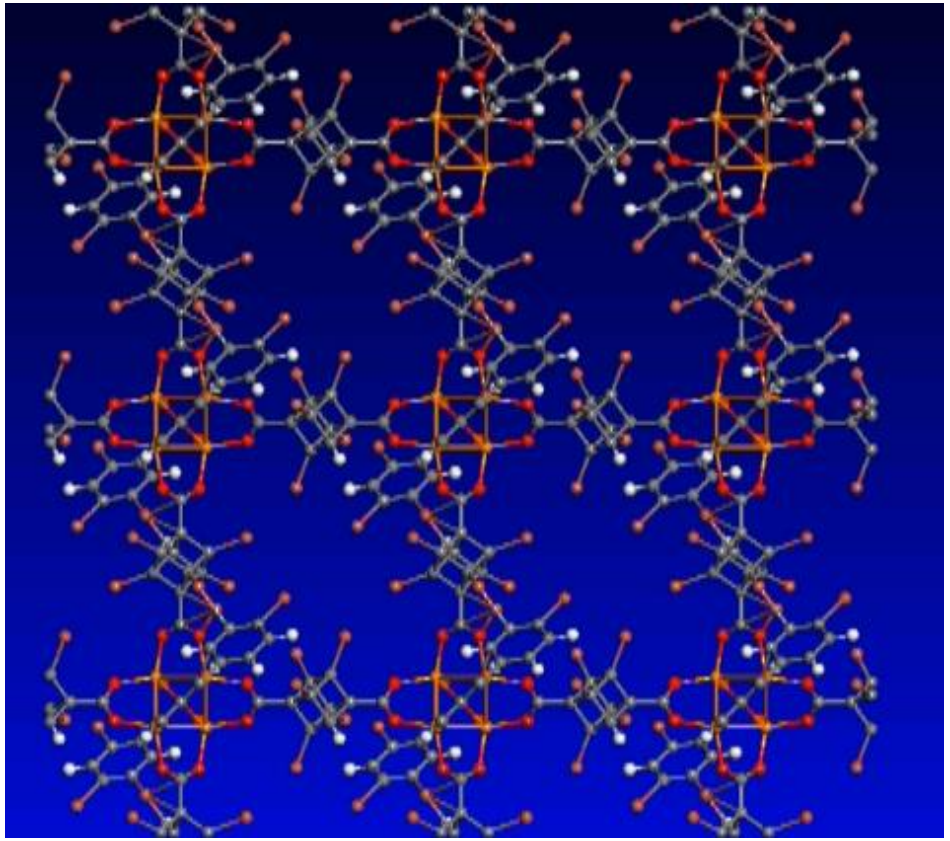


3: Functional Groups
(e.g. –Br, -Cl, phenyl, etc.



Christopher E. Wilmer
University of Pittsburgh

Building blocks re-combined using simple geometrical rules to create periodic, 3D structures



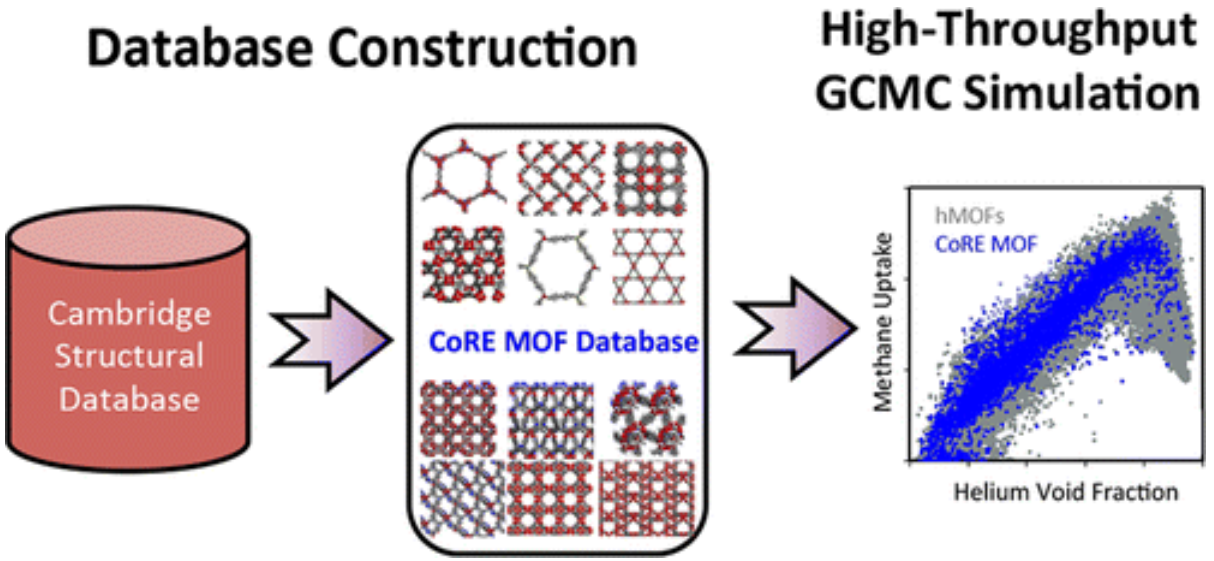
C. E. Wilmer et al., **Nature Chemistry**, 2012, 4, 83–89.

CoRE Database of MOF Structures (Real)

Automated screening of the Cambridge Structural Database to find structures resembling MOFs

- Automated methods to clean experimentally obtained structure files
  - Remove solvent molecules
  - Remove disorder
- ~6,000 structures

We have completed calculations on ~2,500 CoRE MOFs



Y. G. Chung et al., Chemistry of Materials, 2014, *26* (21), 6185–6192.

Calculation of MOF Properties

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

Samir Budhathoki

Poster: Tuesday 5 PM

S. Budhathoki, A. Ajayi, C. E. Wilmer, and J. Steckel, in preparation.

Using the Maxwell Eq. to Predict MMM Properties

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

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– permeability of continuous phase (polymer)

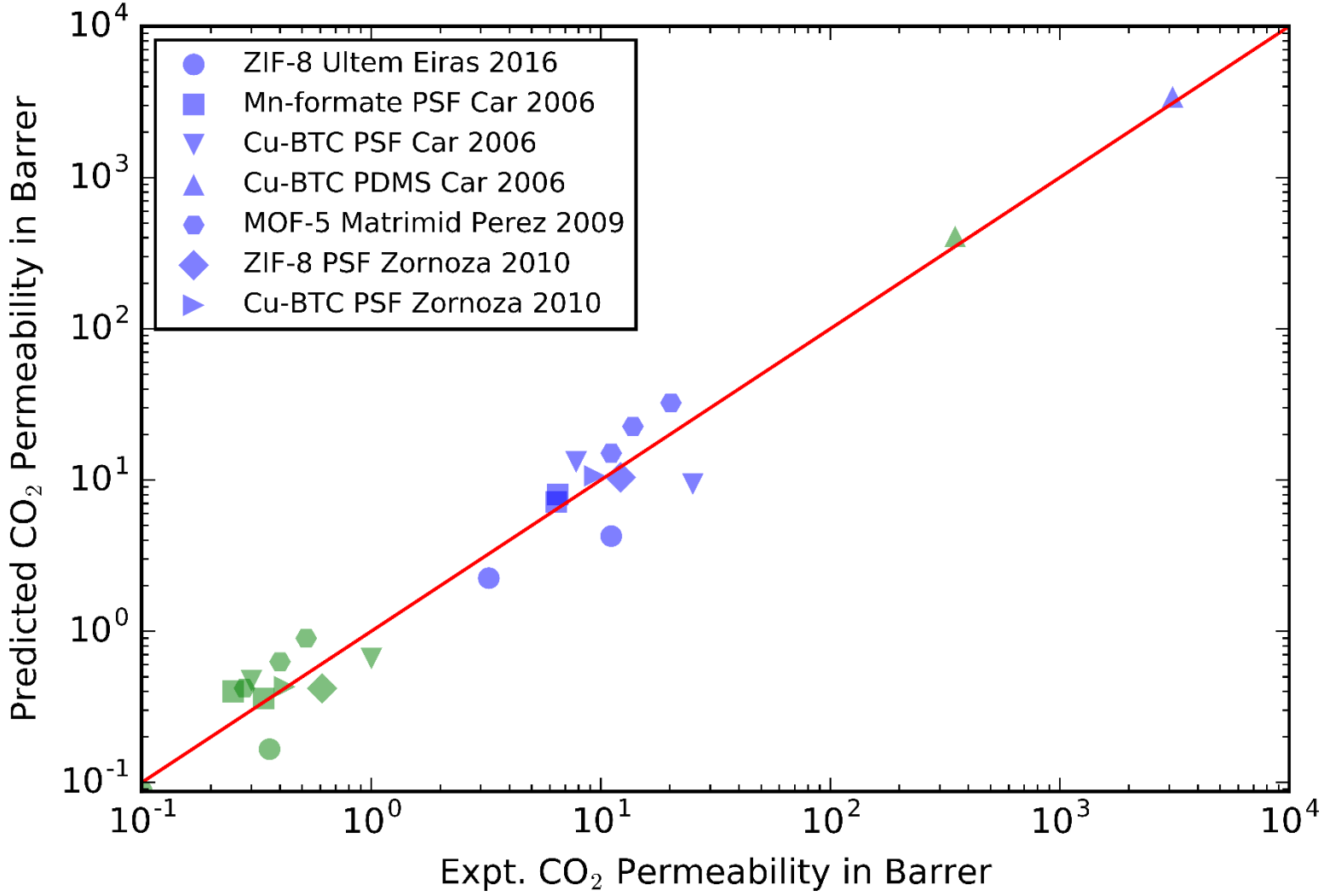
P_d– permeability of dispersed phase (MOF)

φ_d– the volume fraction of the dispersed phase

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

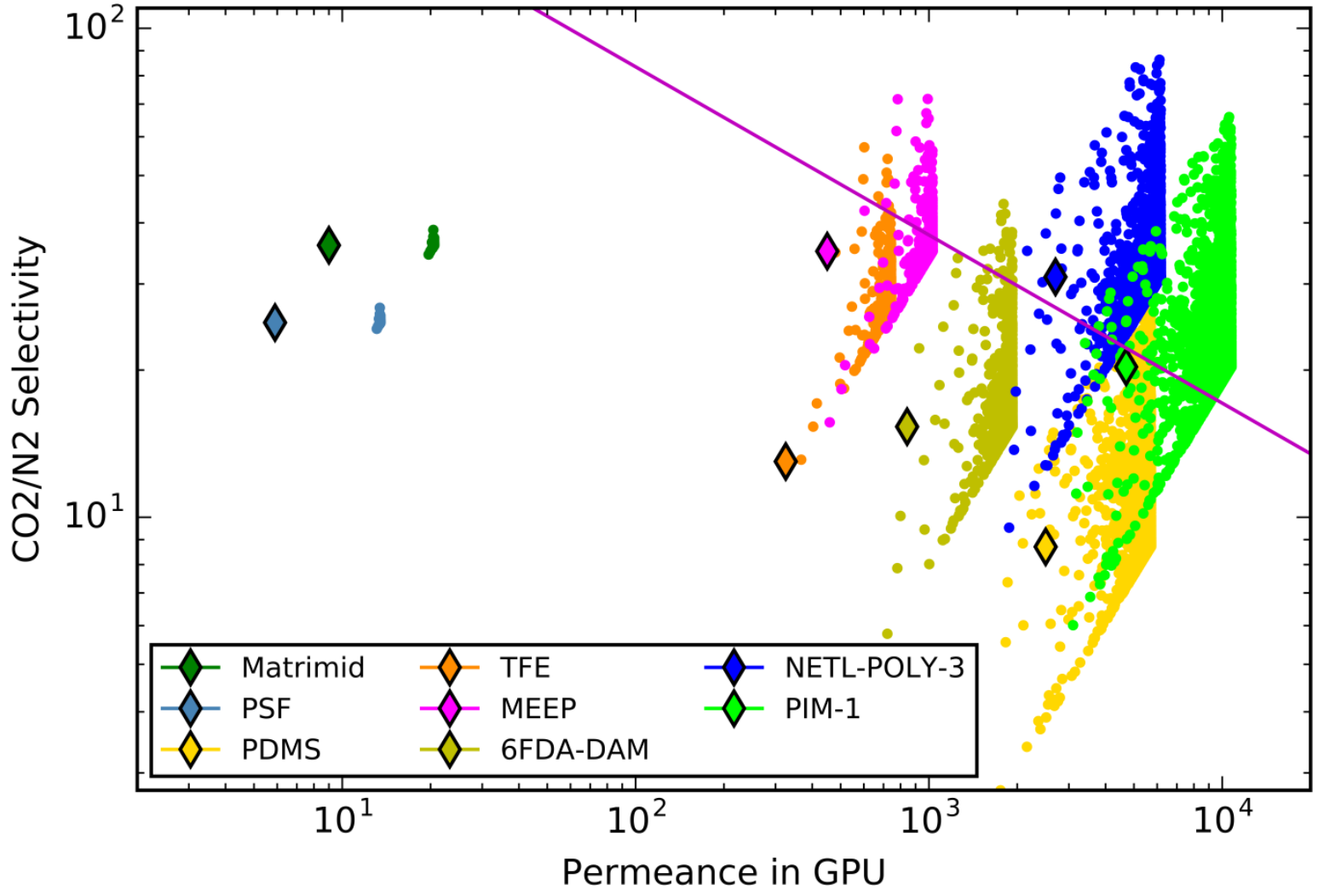
[1]R.H.B. Bouma et al., J. Membrane Science, 128, 141, 1996.
[2]Seda Keskin and David S. Sholl, En. & Env. Sci., 3, 343, 2010.

Validation: Predicted and Expt. MMM Properties



- Comparison between predictions and experimental measurements for MMMs
- CO_2 Permeability (blue symbols) and N_2 Permeability (green symbols)

Properties of MMMs



In this figure, MMMs based on the hypothetical MOF database and range of polymers are shown.

- 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.

Projected Estimate of Carbon Capture Cost

Methodology:

CO_2 capture rate of 90% target

650 MW super critical power plant

Ideal CO_2 selective membrane

Equations developed in Aspen Custom Modeler® (ACM) v8.4.

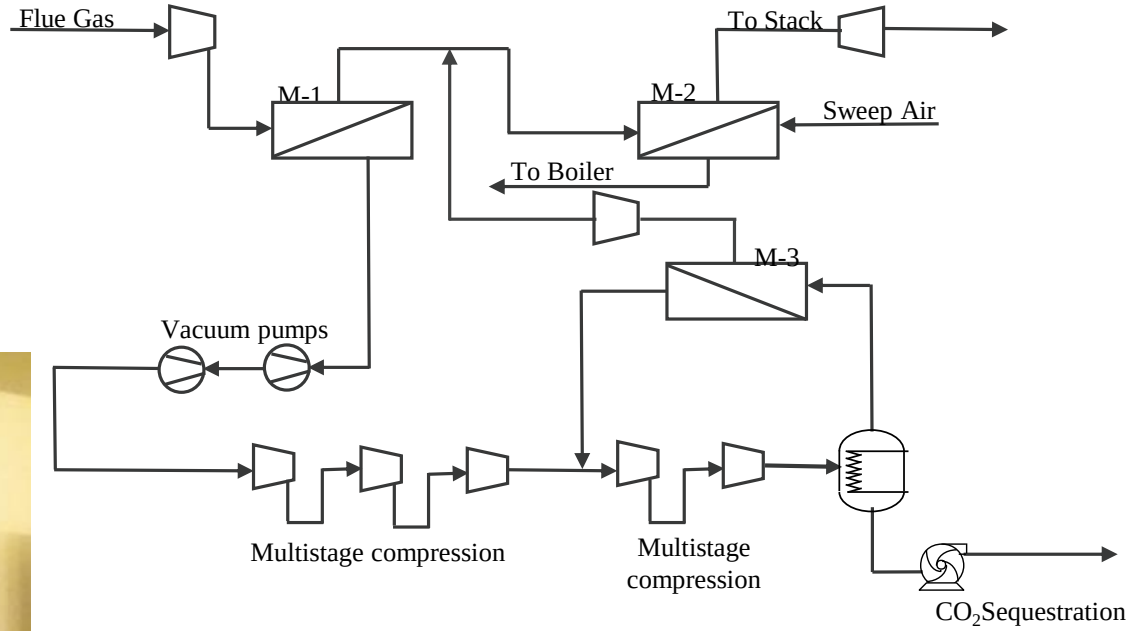
Optimization framework set up in Framework for Optimization, Quantification of Uncertainty and Sensitivity (FOQUS)

Reference cost of electricity$\left(COE_{ref}\right)$ assumed to be \$70/MWh for power plant without carbon capture.

Assumed \$50/m^2 cost for membrane module

Assumed a selective layer of 1 µm.

Kayode Ajayi



Optimized variant of three-stage membrane configuration initially developed by Merkel et al. (2010)

$$\text{Cost of } CO_2 \text{ Captured}\left(\$/ton_{CO_2}\right) = \frac{COE_{CC} - COE_{ref}}{CO_{2_{captured}}}$$

Merkel, T. C., Lin, H., Wei, X., Baker, R. (2010). *Journal of Membrane Science*, 359, 126-139.

Projected Estimate of Carbon Capture Cost

- Allows us to assign a Cost of Carbon Capture (CCC) based on permeance, selectivity of a MMM.
- High-throughput project, survey millions of materials.
- Purpose is to understand link between material properties, process optimization.

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

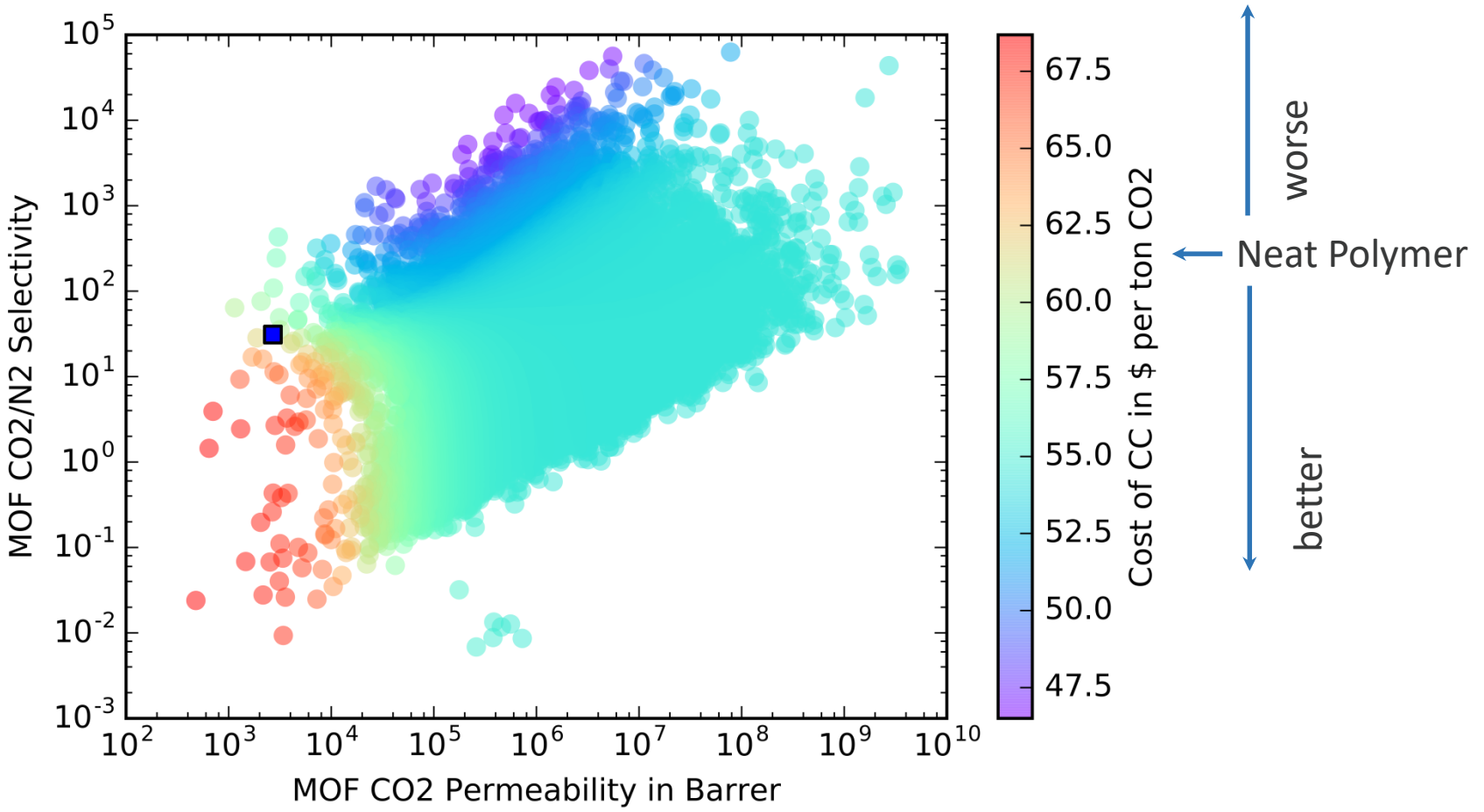
Pairing MOFs with NETL Polymer 3

Each dot represents a MOF in the hypothetical MOF database.

- The ***placement*** of the dot is governed by the MOF properties.
- The ***color*** of the dot is governed by the CCC.

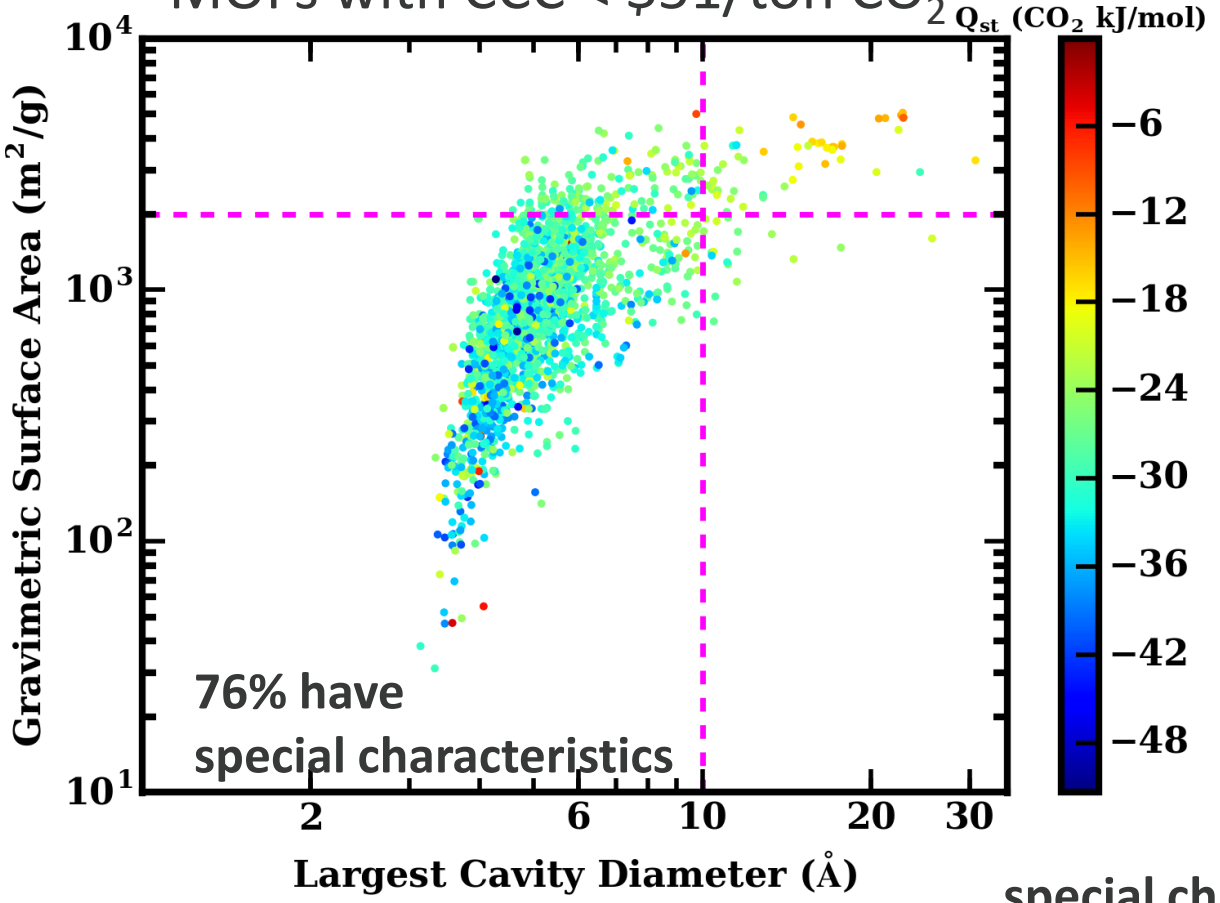
What can we learn?

- Some MOFs improve the membrane
- ***A lot of MOFs make the membrane worse!***
- For this polymer, we should pick MOFs with permeability and selectivity ~3 orders of magnitude larger than that of the polymer.

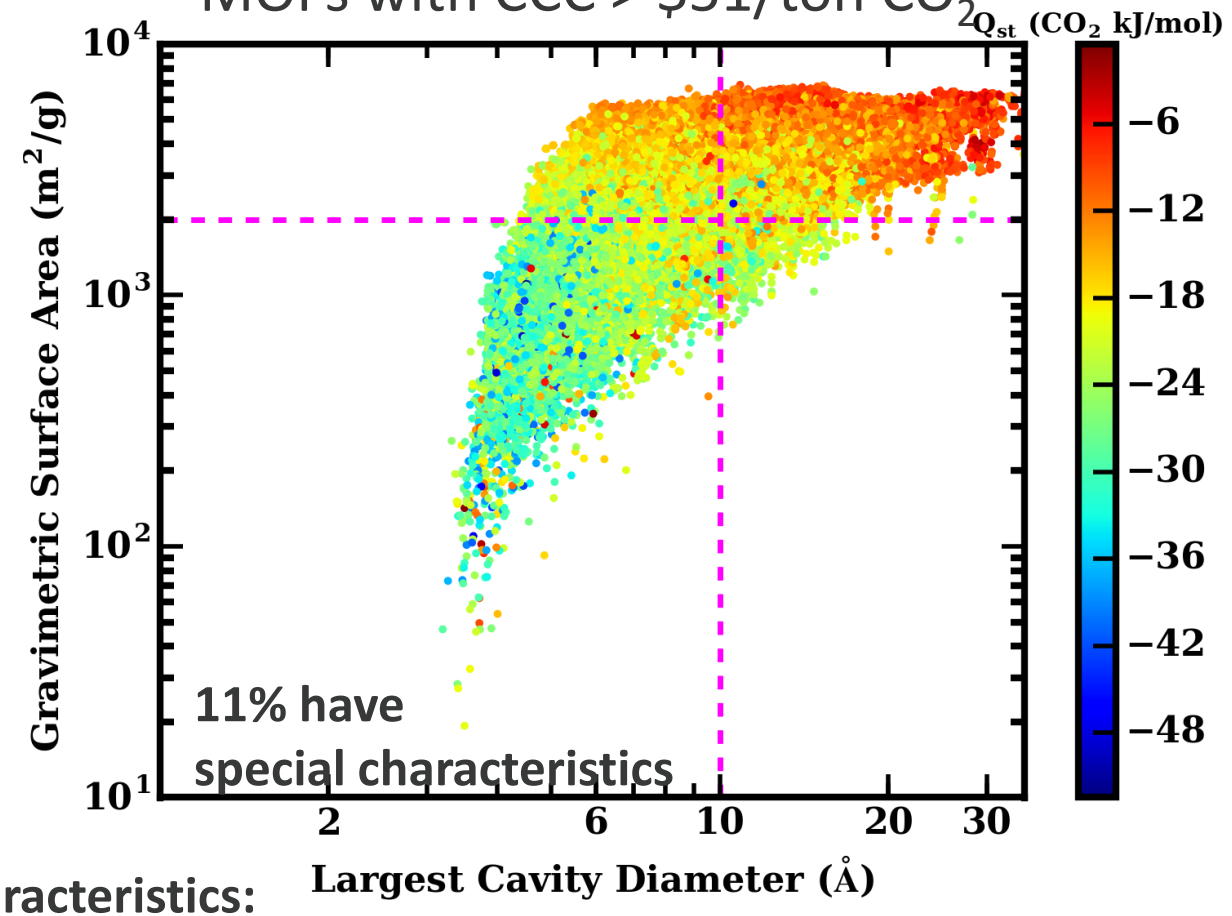


Characteristics of MOFs in Best/Worst MMMs

MOFs with CCC < \$51/ton CO_2



MOFs with CCC > \$51/ton CO_2



special characteristics:

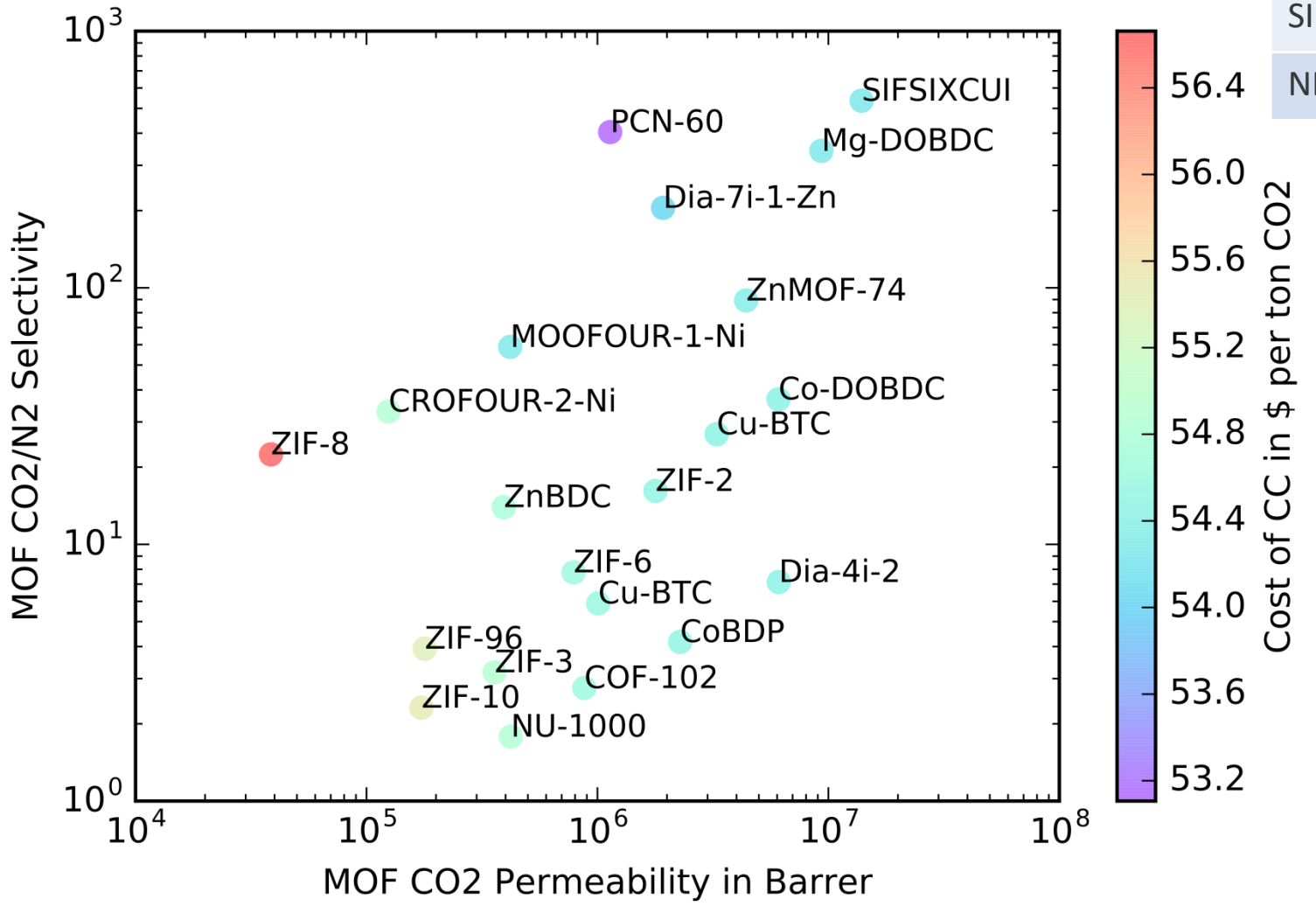
LCD < 10 Å

Grav. Surf. Area < 2000 m^2/g

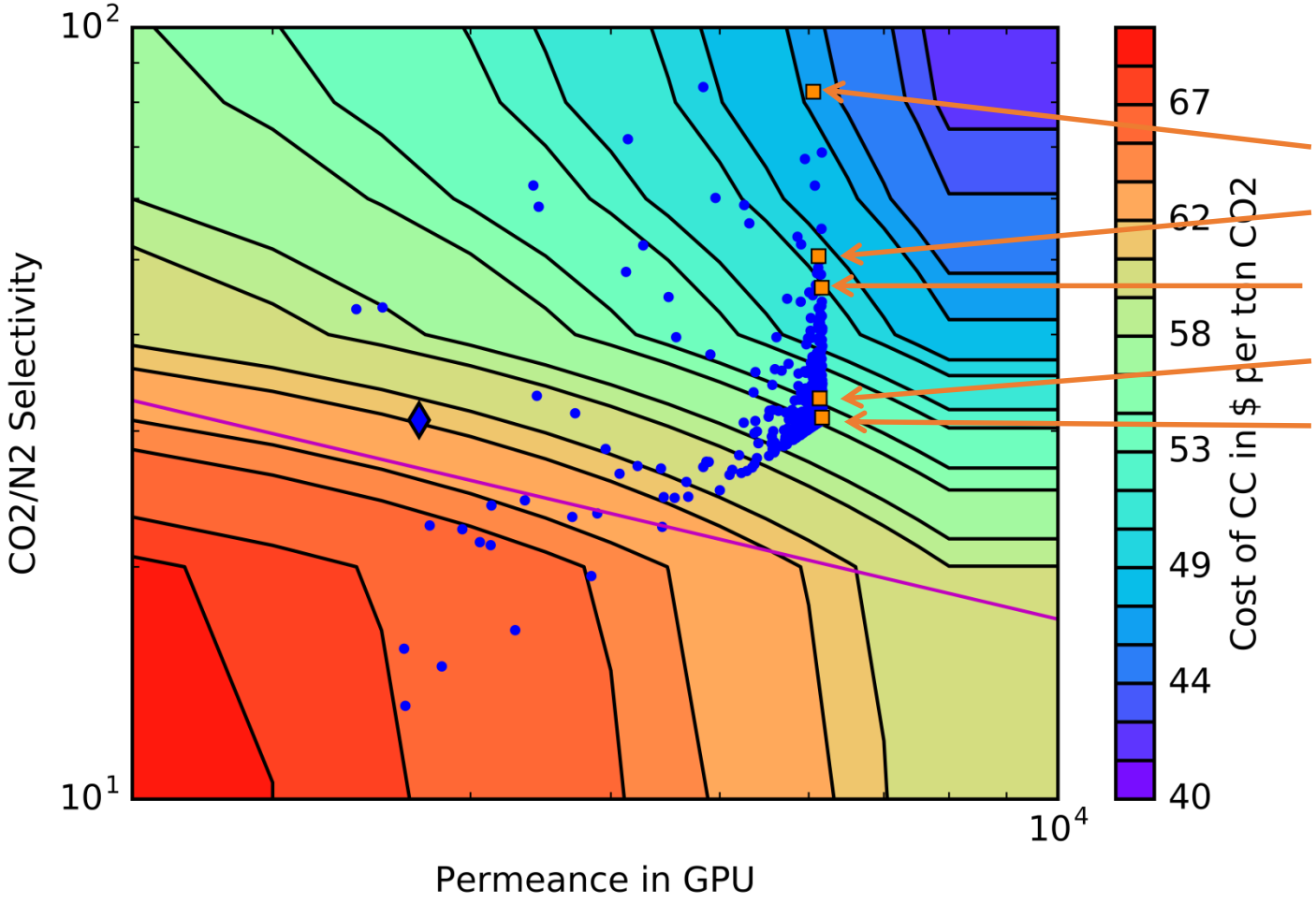
CO_2 heat of ads. -40 to -30 kJ/mol

Results for Some Highly-Studied MOFs

Membrane	CCC ($ per ton CO_2)
PCN-60/NETL Polymer 3	$53
SIFSIX-Cu2i/NETL Polymer 3	$54
NETL Polymer 3 (neat)	$61



NETL Polymer 3 with CoRE MOFs



Membrane	CCC ($/ton CO_2)
Hypo-a/NETL Poly 3	$46
CoRE-a/NETL Poly 3	$47
CoRE-b/NETL Poly 3	$49
CoRE-c/NETL Poly 3	$50
PCN-60/NETL Poly 3	$53
SIFSIX-Cu2i/NETL Poly 3	$54
NETL Poly 3 (neat)	$61

- There are CoRE MOFs that have great potential to improve the MMMs.
- Many CoRE MOFs have not been studied since first reported.

Synthesis of MMMs Based on Predictions

- Focusing on NETL Polymer 3.
- Identified ~40 MOFs from the CoRE database that are predicted to pair well with NETL Polymer 3.
- Three MOFs selected for first round, two synthesized now.

MOF Synthesis:
Anne Marti

MOF Synthesis:
Sameh Elsaidi

Surendar Venna
MMM Fabrication

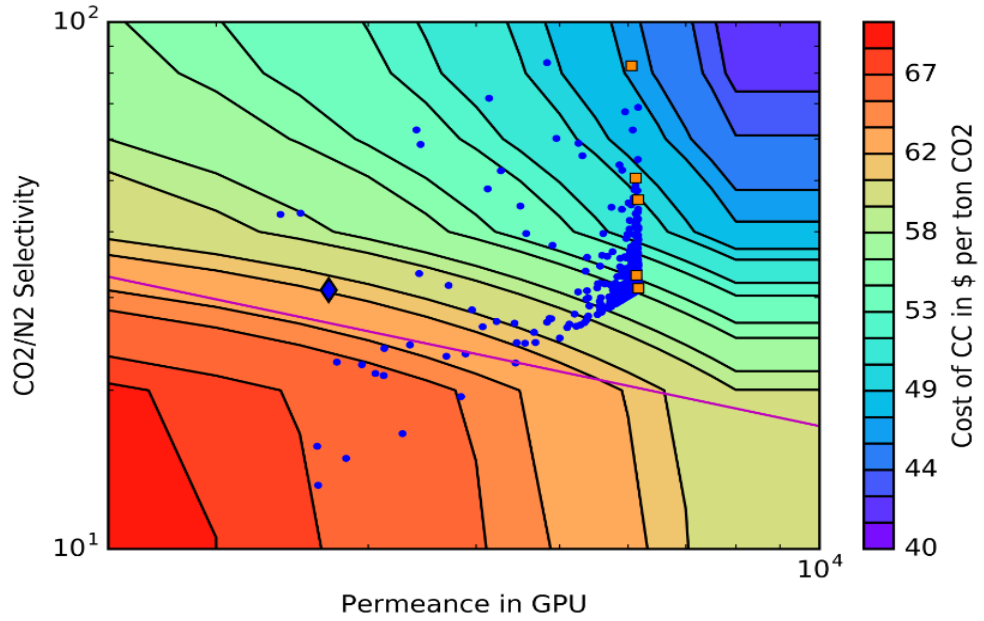
Summary

Connected atomistic simulations to CCC for well over a million MMMs.

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

MMM out NETL Polymer 3:

Predict CCC \$61 → \$46 per ton CO_2



Relationship between polymer and MOF properties can be exploited to design better MMMs.