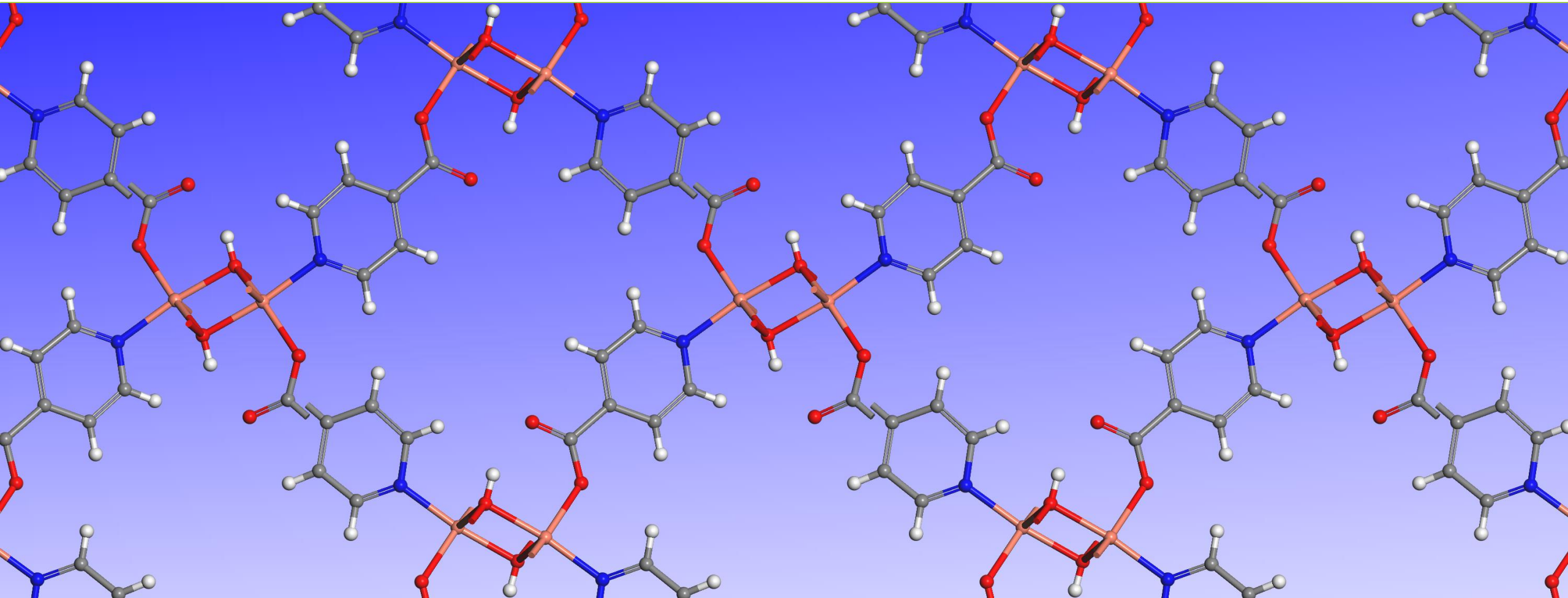
Machine Learned Force Field Modeling of Metal Organic Frameworks for CO_2 Direct Air Capture

John Findley, Samir Budhathoki, Jan Steckel

NATIONAL ENERGY TECHNOLOGY LABORATORY

ACS Meeting, August 2024



Acknowledgements

Co-authors:

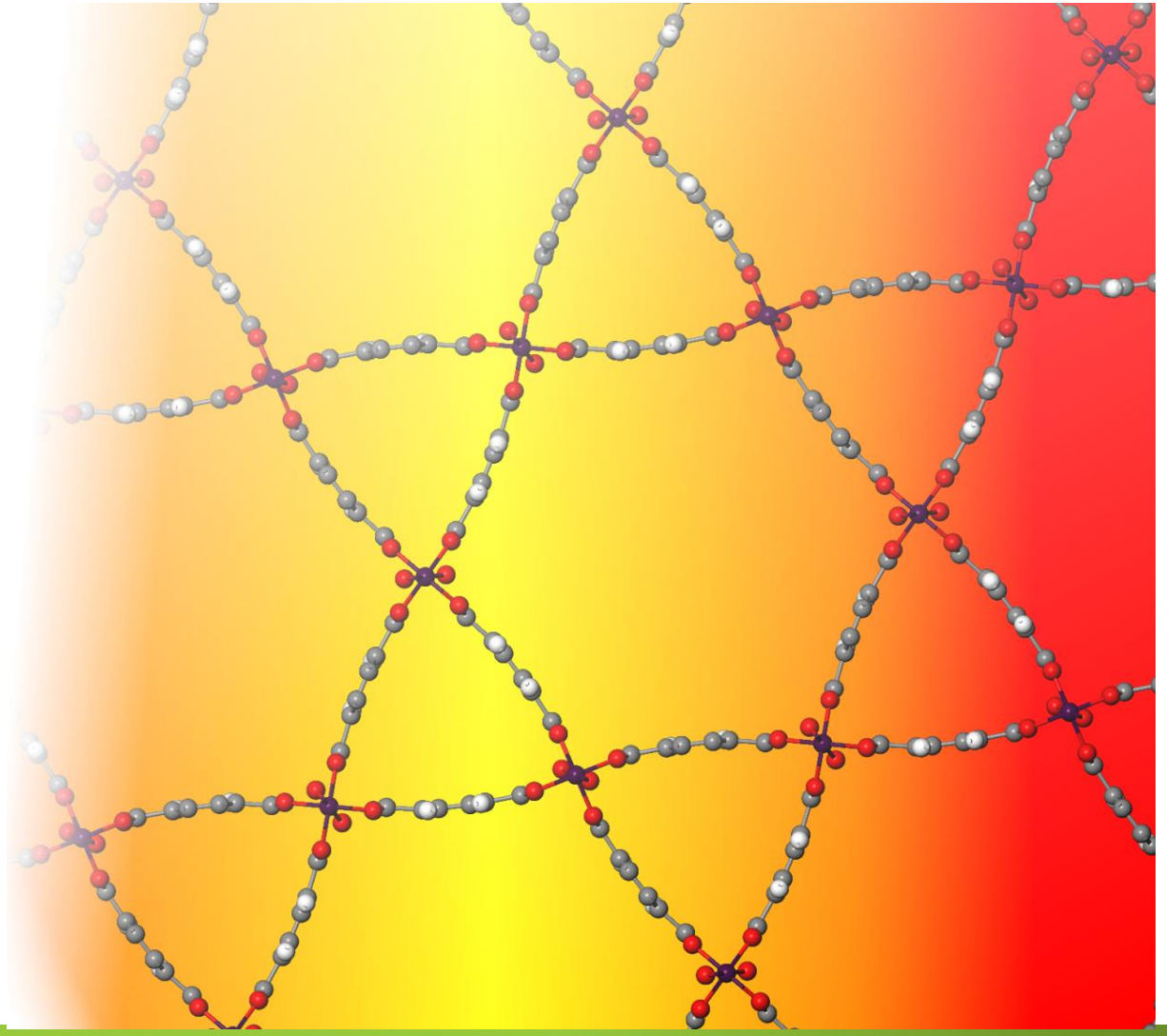
- Jack Findley – NETL
- Samir Budhathoki – formerly at NETL, currently Braskem

Summer Students:

- Tiernan Baucom, Ugrad, currently at University of Michigan
- Clare Martin, Ugrad, currently at University of Michigan
- Laine Roper, Ugrad, currently at Harvard

Collaborators:

- Christopher E. Wilmer, U of Pittsburgh
- Dan Sorescu - NETL



Outline and Disclaimer

Outline: Metal Organic Framework Modeling using three methods:

1. Classical (Rigid) Force Field: Universal Force Field (UFF)
2. Classical Flexible Force Field: QuickFF
3. Machine Learned Force Field: FitSNAP

Disclaimer:

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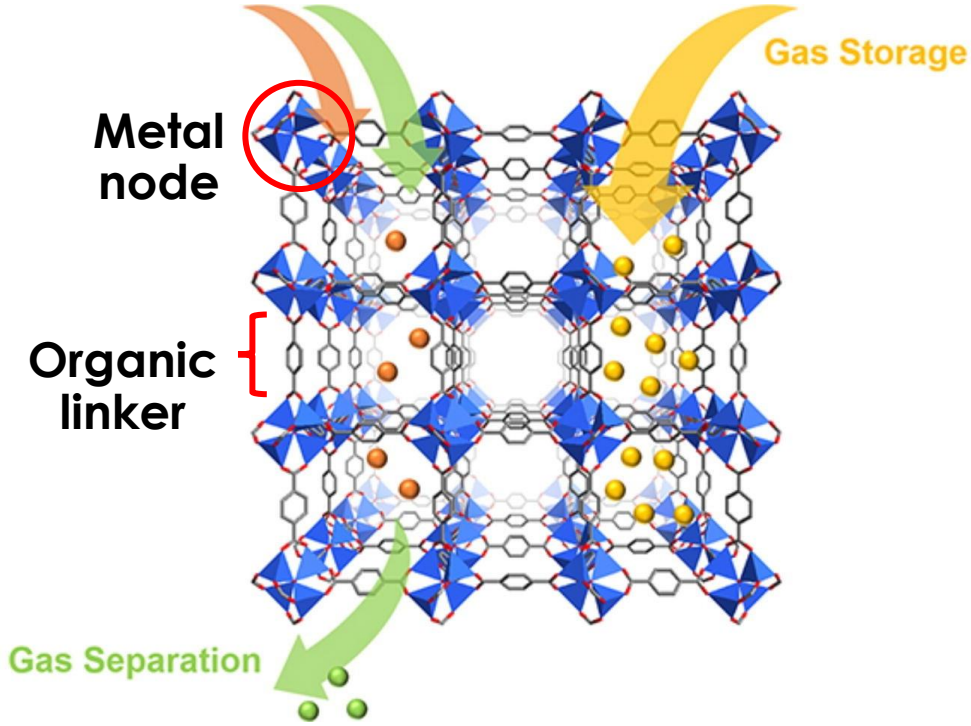
Liu et al. Science (2021)

Metal Organic Frameworks (MOFs)

- Crystalline, porous materials
- Good for gas storage/separation applications
- Large, diverse class of molecules
  - >100,000 synthesized
  - >500,000 predicted



Li et al. *Materials Today* **2018**, *21* (2), 108–121.

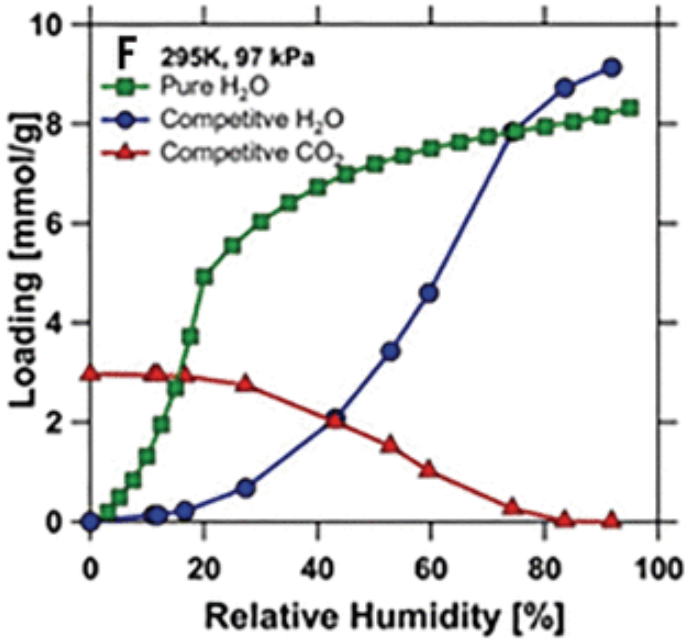
Physisorbent MOFs for CO_2 Capture

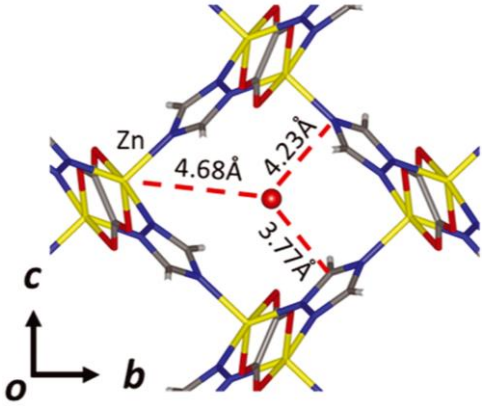
Characteristics of a good capture sorbent

- Strong CO_2 adsorption
- Regenerable
- Not hindered by humidity

Example: CALF-20

- Successfully used for point source
- Little effect of humidity up to 30% RH
- Strong **dispersion** interactions (CO_2 > H_2O)





Lin et al., *Science* (2021)

Computational Screening for Mixed Matrix Membranes (MMMs)

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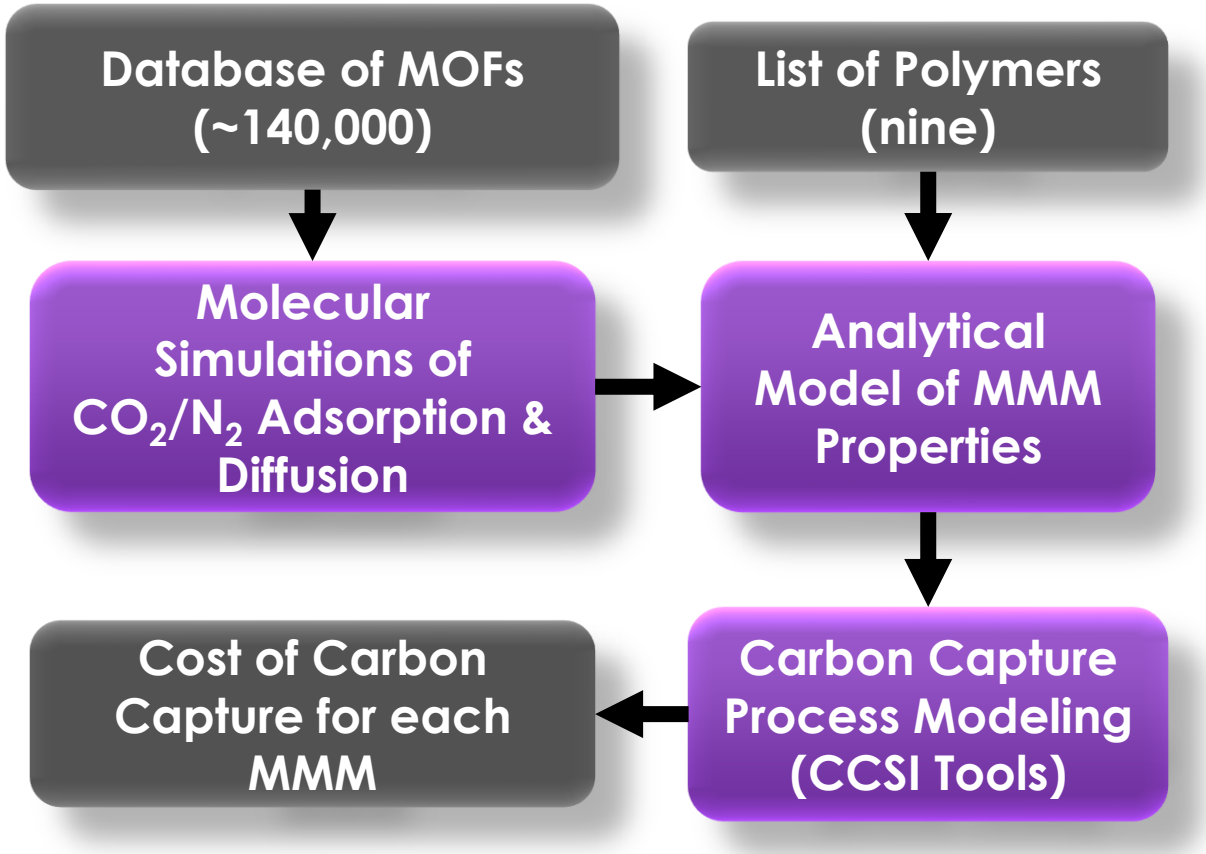
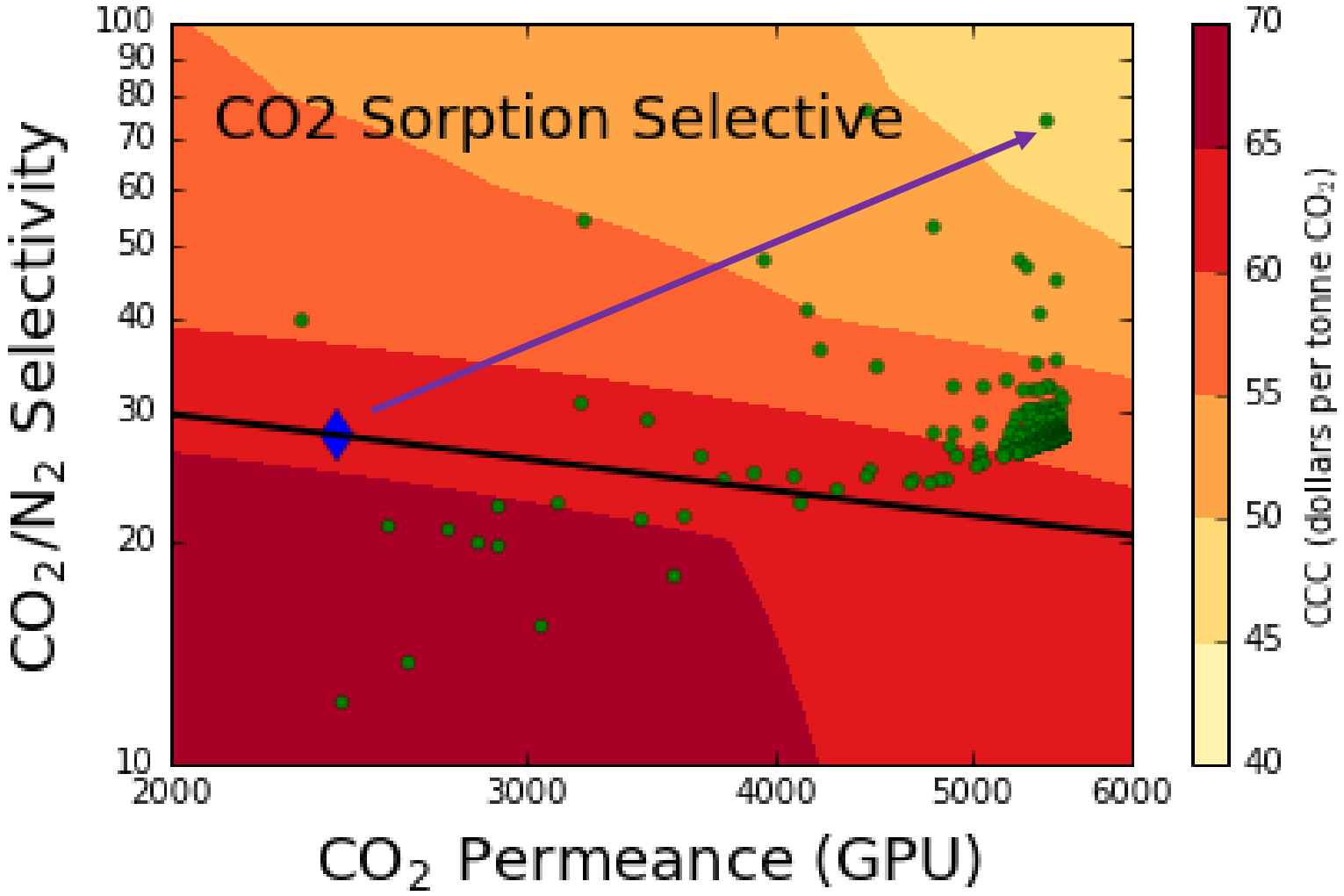
MMMs can be made from Combining MOFs and Polymer Materials



Predicted Cost of Capture Process for >1 million membranes

Samir Budhathoki, Kayode Ajayi, Christopher E. Wilmer

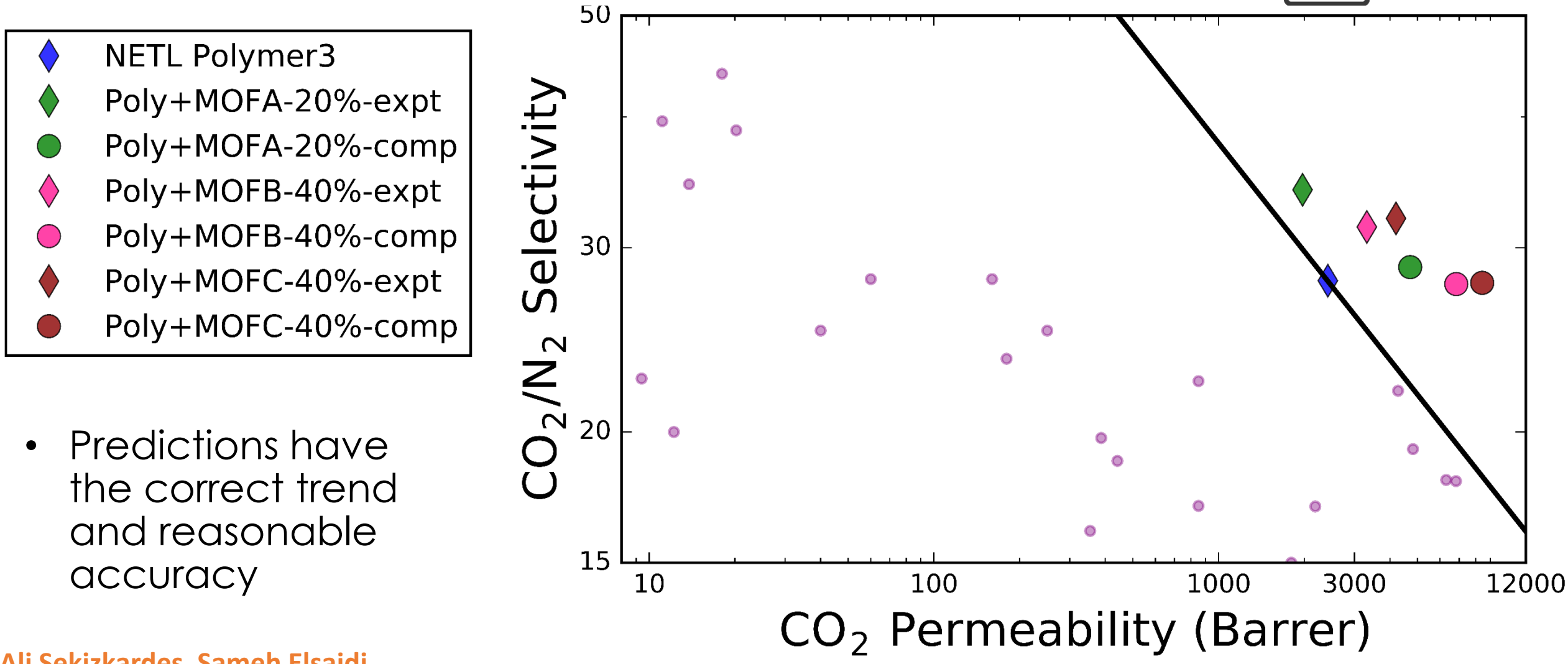
Predictions from High Throughput Computational Screening



- MMMs using NETL Polymer 3 (blend polymer)
- Best MMM in this set:
  - Predicted CCC Reduction from \$62.9 to \$42.7 per tonne CO_2
- 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**

Comparison with Experiment

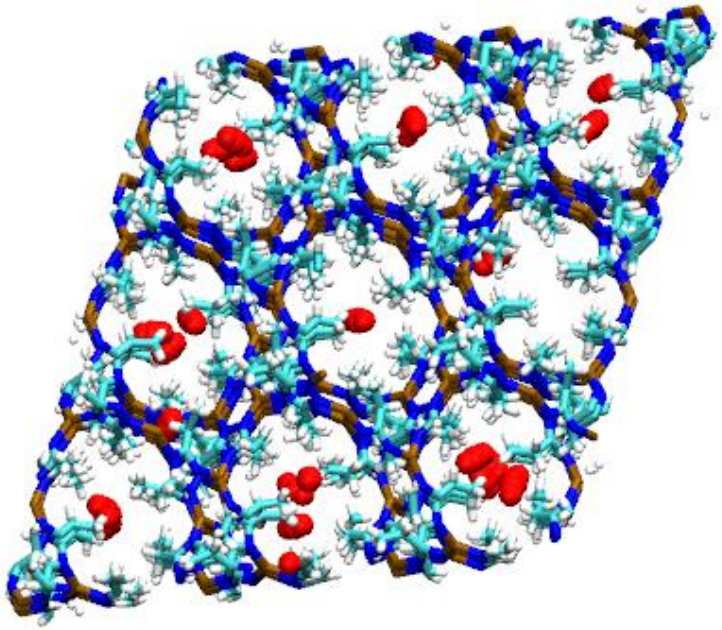


- Predictions have the correct trend and reasonable accuracy

Ali Sekizkardes, Sameh Elsaidi

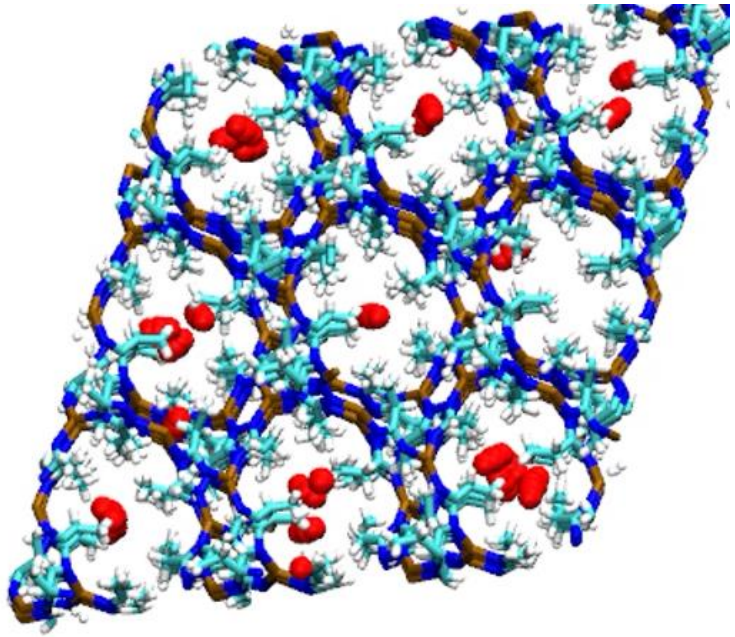
MOF Computational Screening for CO_2 Capture

Past large scale screening studies have modeled MOFs atoms as rigid



Rigid Force Field

- Electrostatic + dispersion
- Low computational cost
- Good for rigid MOFs but most MOFs are flexible
- Easy to obtain

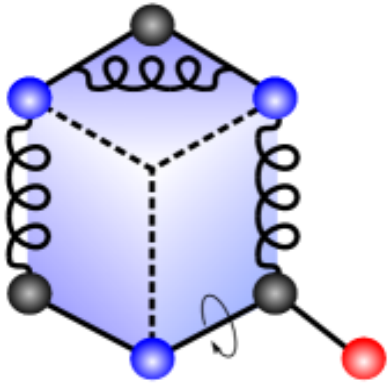


Flexible Force Field

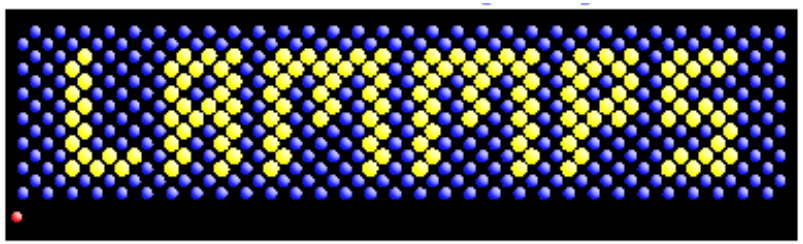
- Electrostatic + dispersion + bond + angle + torsion
- High computational cost
- Accounts for MOF flexibility
- Hard to obtain for a large set of materials

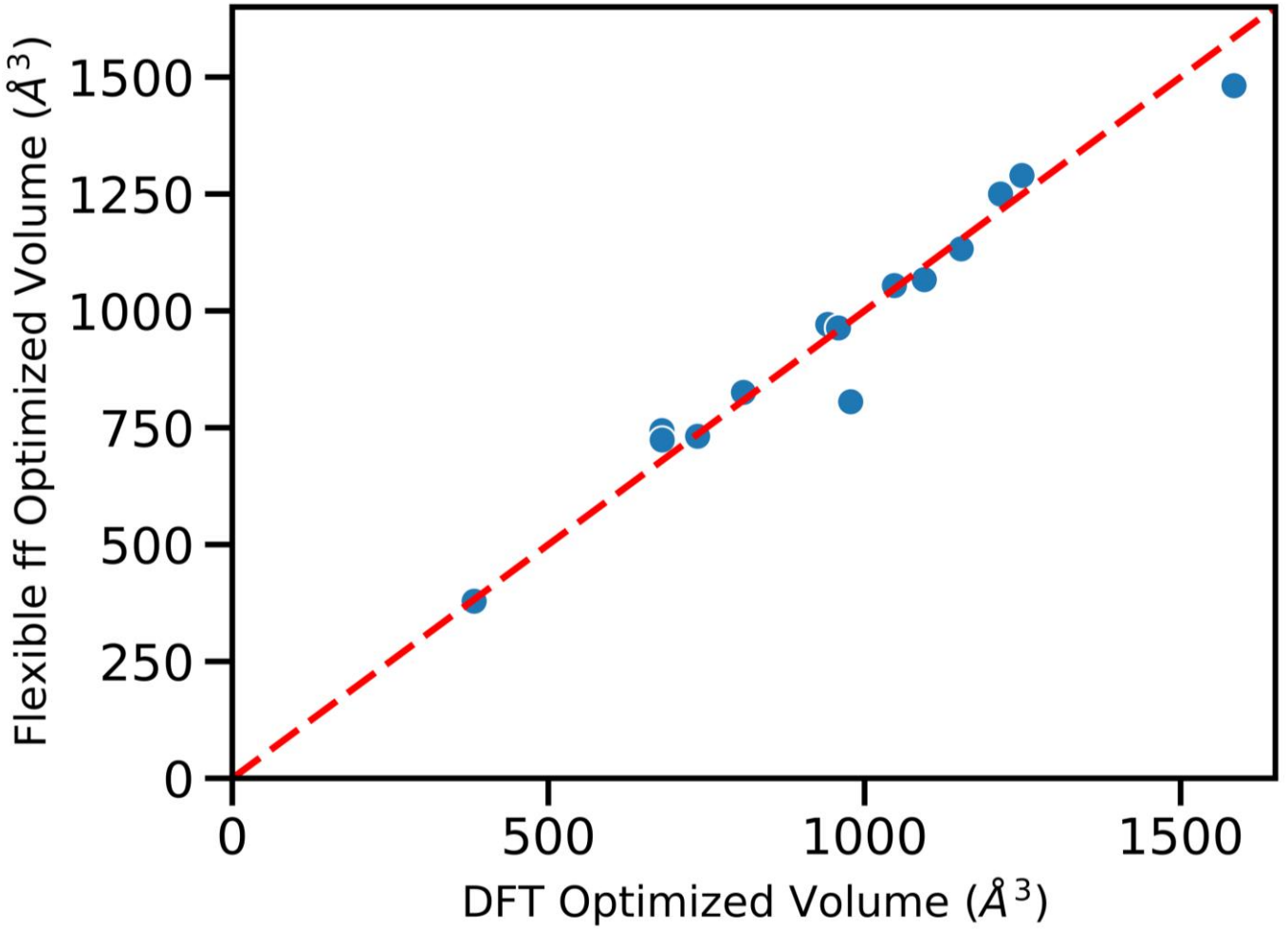
Flexible Force Fields for MOFs

Quick FF used with DFT Vibrational Frequency Calculations to fit flexible FFs



QuickFF

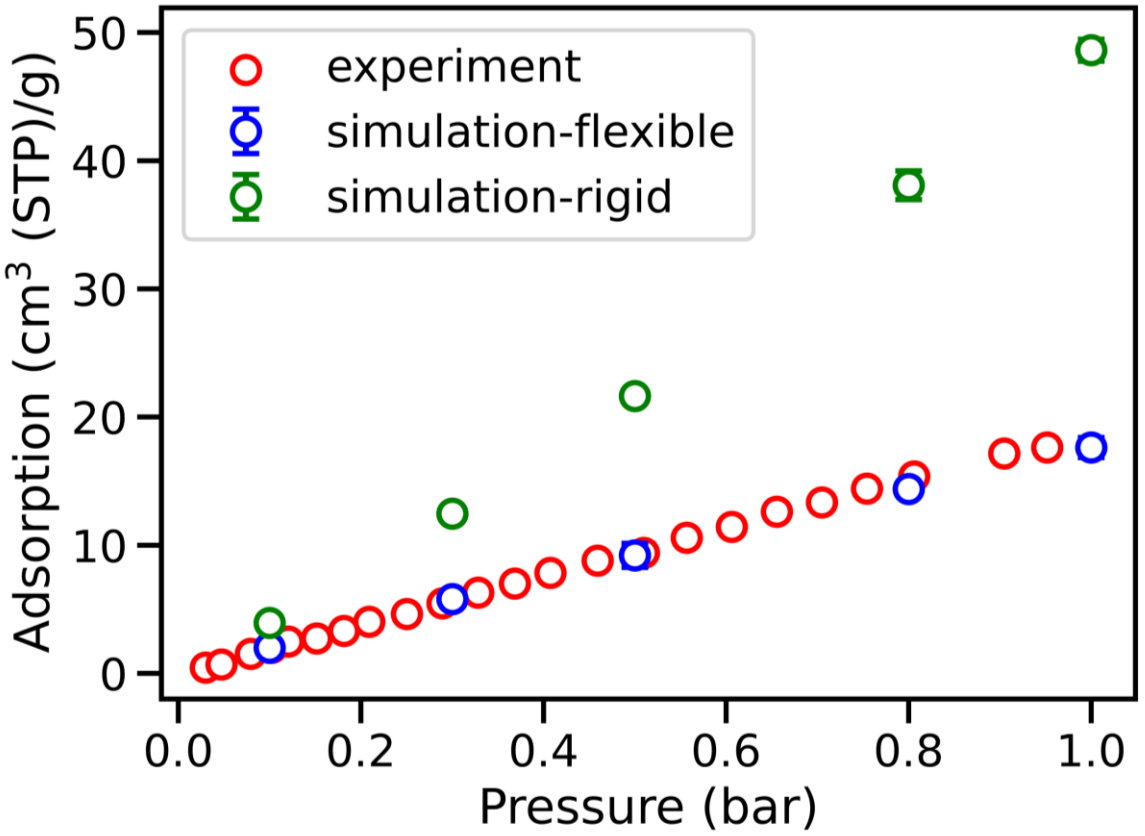


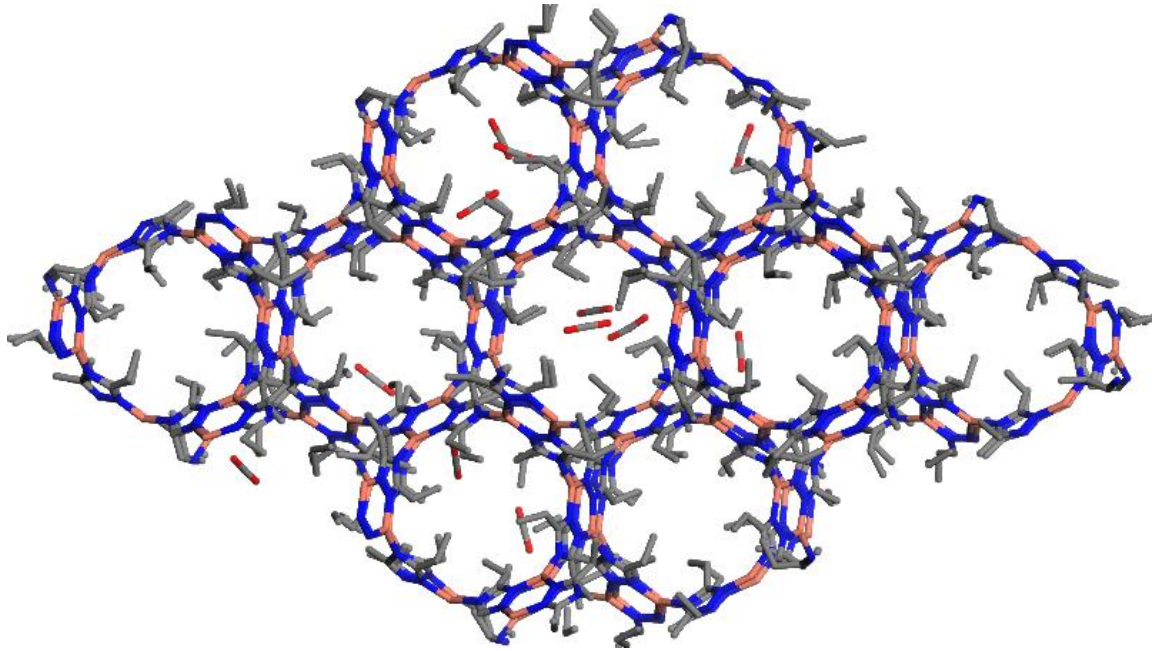


Vanduyfhuys, L. et al. *JCC* **2015**, 36 (13), 1015–1027.
Vanduyfhuys, L. et al. *JCC* **2018**, 39 (16), 999–1011.

Calculated Isotherm: Flexible vs Rigid FF

CO_2 adsorption in MAF-2 (BOGXIF) at 298 K

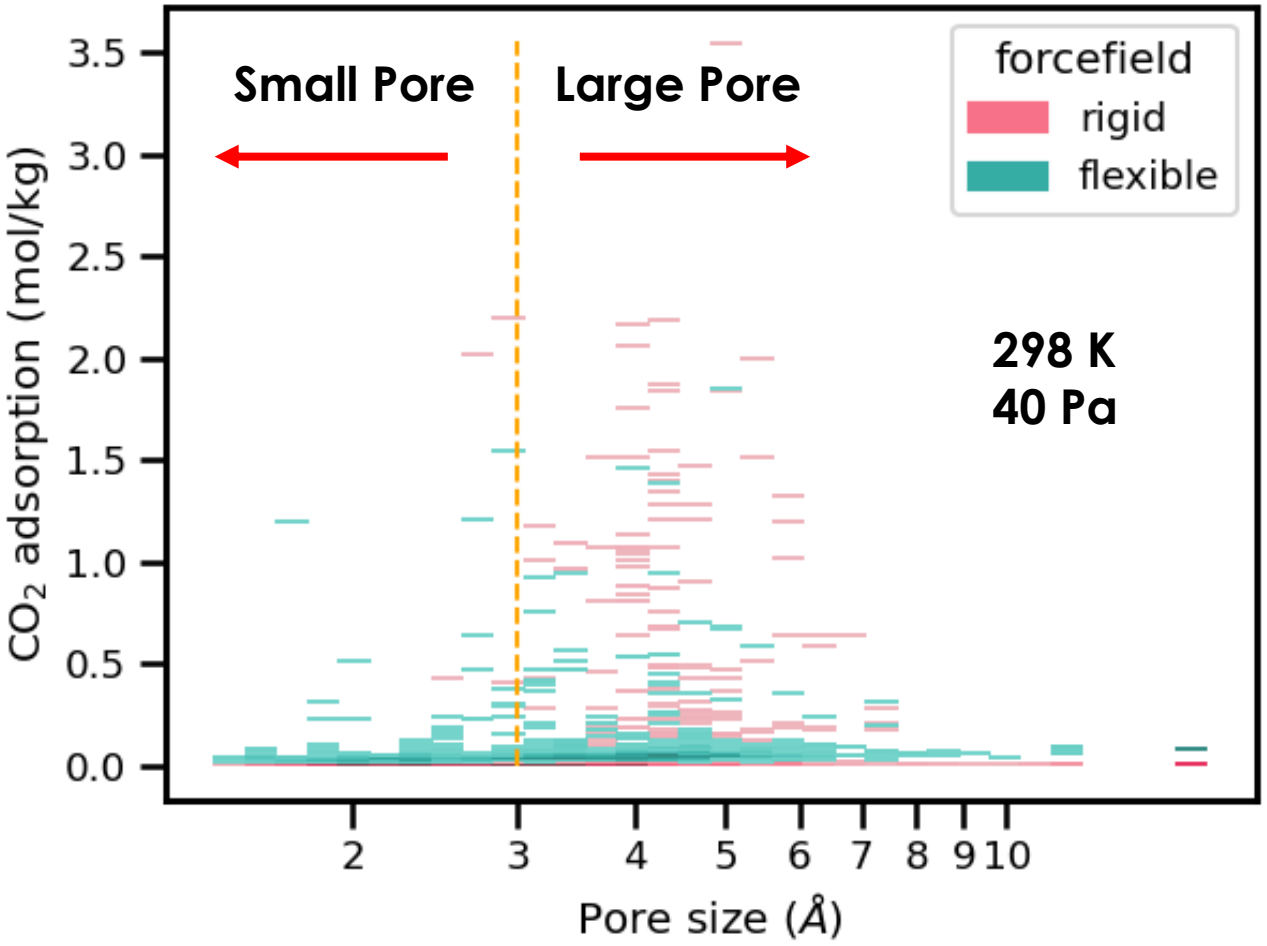




Baucom, T.; Budhathoki, S.; Steckel, J. A. J. Phys. Chem. C **2023**
Zhang, J. P.; Chen, X-M.; *J. Am. Chem. Soc*. **2009**, 131, 15, 5516-5521

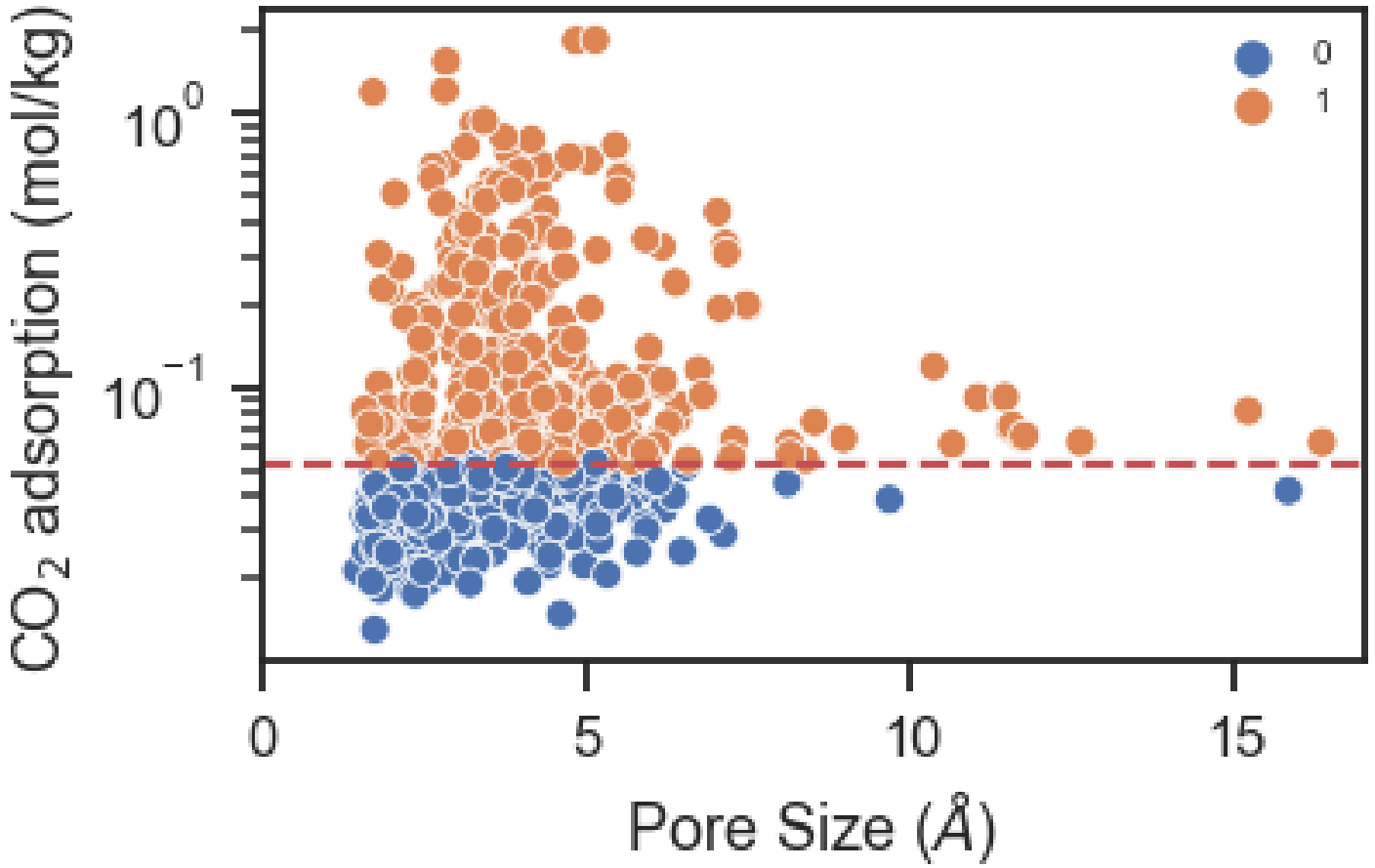
CO_2 Adsorption at Direct Air Capture Conditions

Comparison Between Rigid and Flexible Force Field Results



- Flexible forcefields yield CO_2 adsorption in MOFs with small pore sizes
- Rigid forcefields yield no CO_2 adsorption for MOFs with pore size less than 3 Å in most of the cases
- For some MOFs with pore size greater than 3 Å, rigid forcefields overestimate the CO_2 adsorption

Machine Learning model for MOF classification



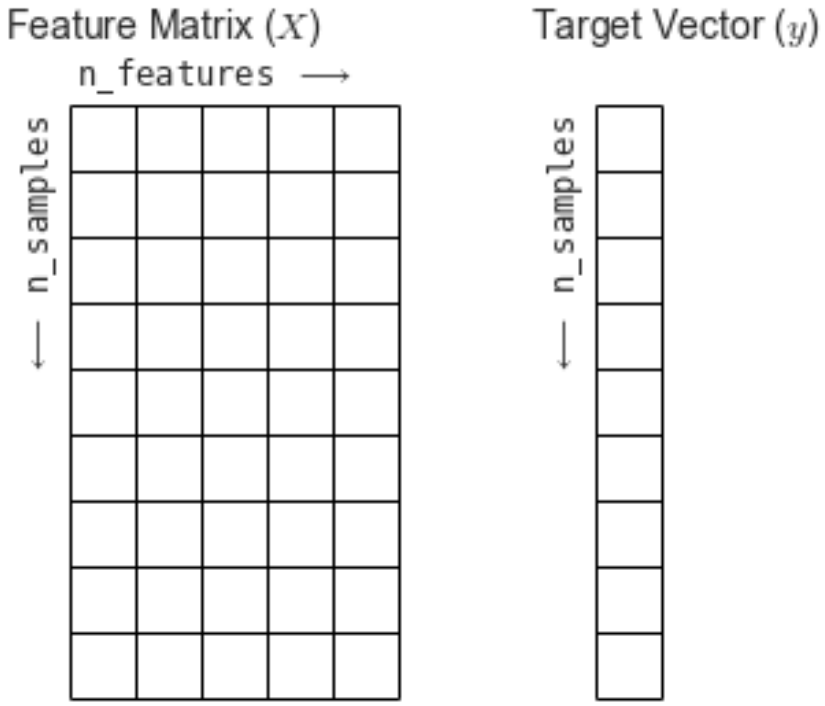
1 – CO_2 ads >= 0.052 mol/kg
0 – CO_2 ads < 0.052 mol/kg

Martin, C.; Budhathoki, S.; Steckel, J. A. Machine Learning Models of CO_2 Sorption and Diffusion in MOFs for Direct Air Capture. *In Preparation* **2023**.

MOF Featurization

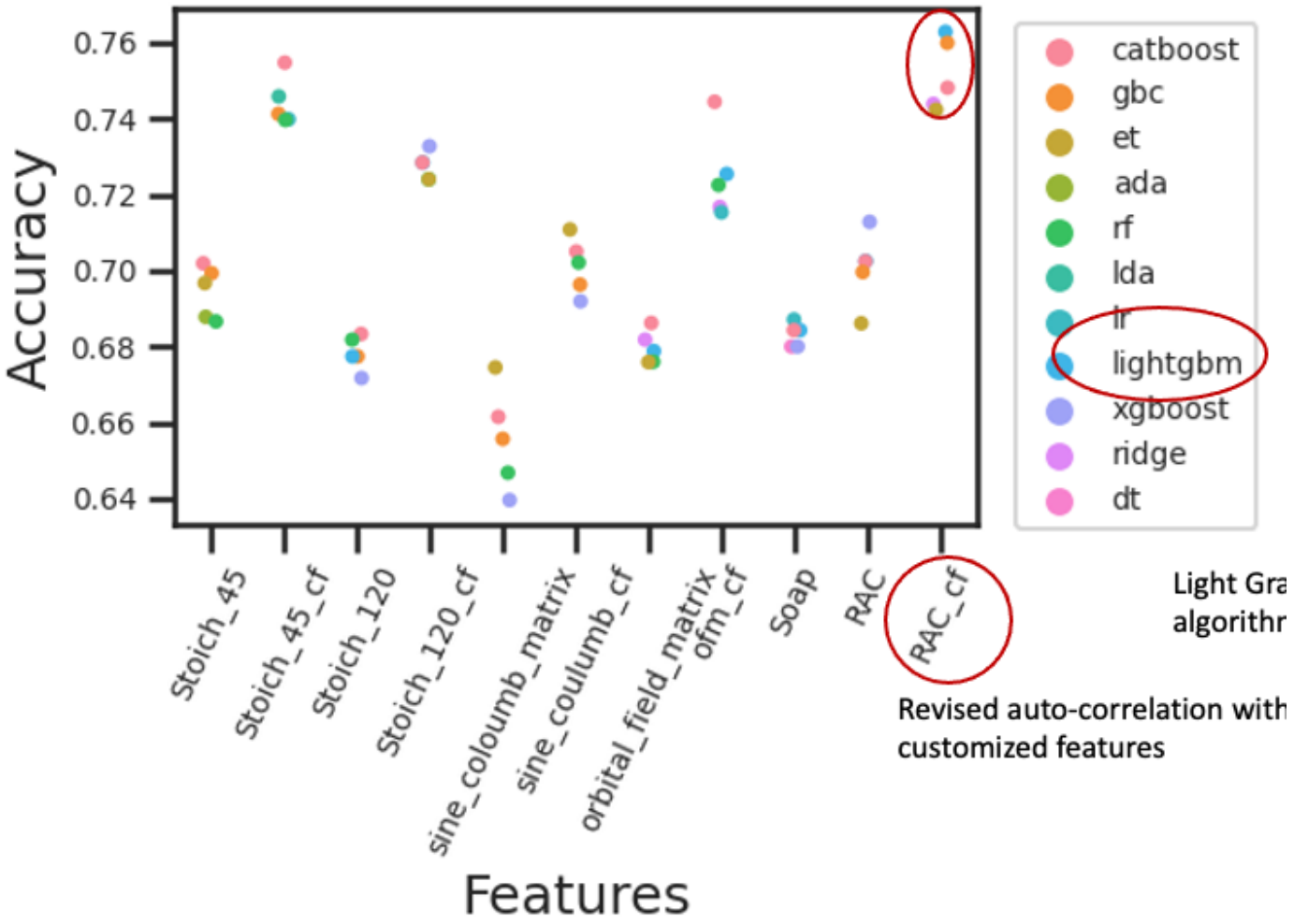
Feature: n-dimensional numerical vector that represents each MOF

1. **Stoichiometric-45**
   - 45 statistical attributes of elemental properties
2. **Stoichiometric-120**
   - 103 attributes describing elemental fractions
   - 7 statistical attributes of elemental properties
3. **Sine Coulomb Matrix**
   - pairwise electrostatic interactions between nuclei
4. **Orbital Field Matrix**
   - distribution of valence electrons
   - interaction of valence subshells between atoms
5. **Smooth Overlap of Atomic Positions (SOAP)**
   - similarity between a pair of local atomic environments
6. **Revised Autocorrelation (RAC) values + Custom features**
   - molecular revised autocorrelation (RAC) values, surface area, volume, density, pore-limiting diameter (PLD), charge difference, epsilon



Matter **2021**, *4* (5), 1578–1597.

Results: ML Classifiers validation results



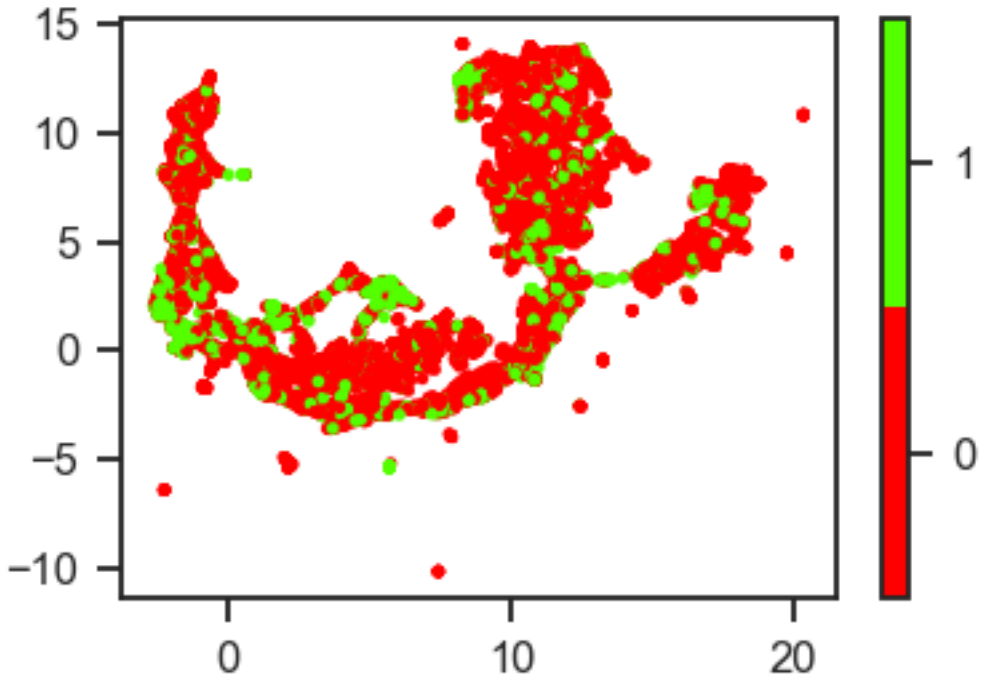
Train size : 80 %
Test size: 20%
Results are averaged from 10 cv folds

- 11 different classification ML models
- All the features were customized (denoted by '_cf' in plot) with geometric features such as surface area, pore size, electrostatics and dispersion term.
- Light Gradient Boosting algorithm performed the best

$$\text{Accuracy} = \frac{True\ Positive + True\ Negative}{True\ Positive + False\ Positive + True\ Negative + False\ Negative} = 76\%$$

Martin, C.; Budhathoki, S.; Steckel, J. A. Machine Learning Models of CO_2 Sorption and Diffusion in MOFs for Direct Air Capture. *In Preparation* **2024**.

Results: Predictions on rest of QMOF Database

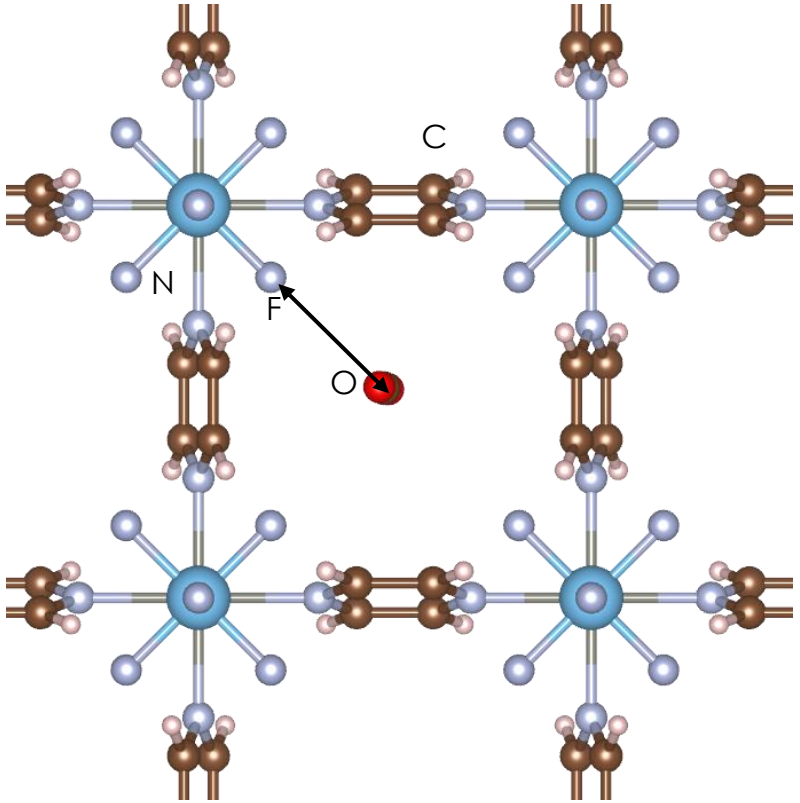


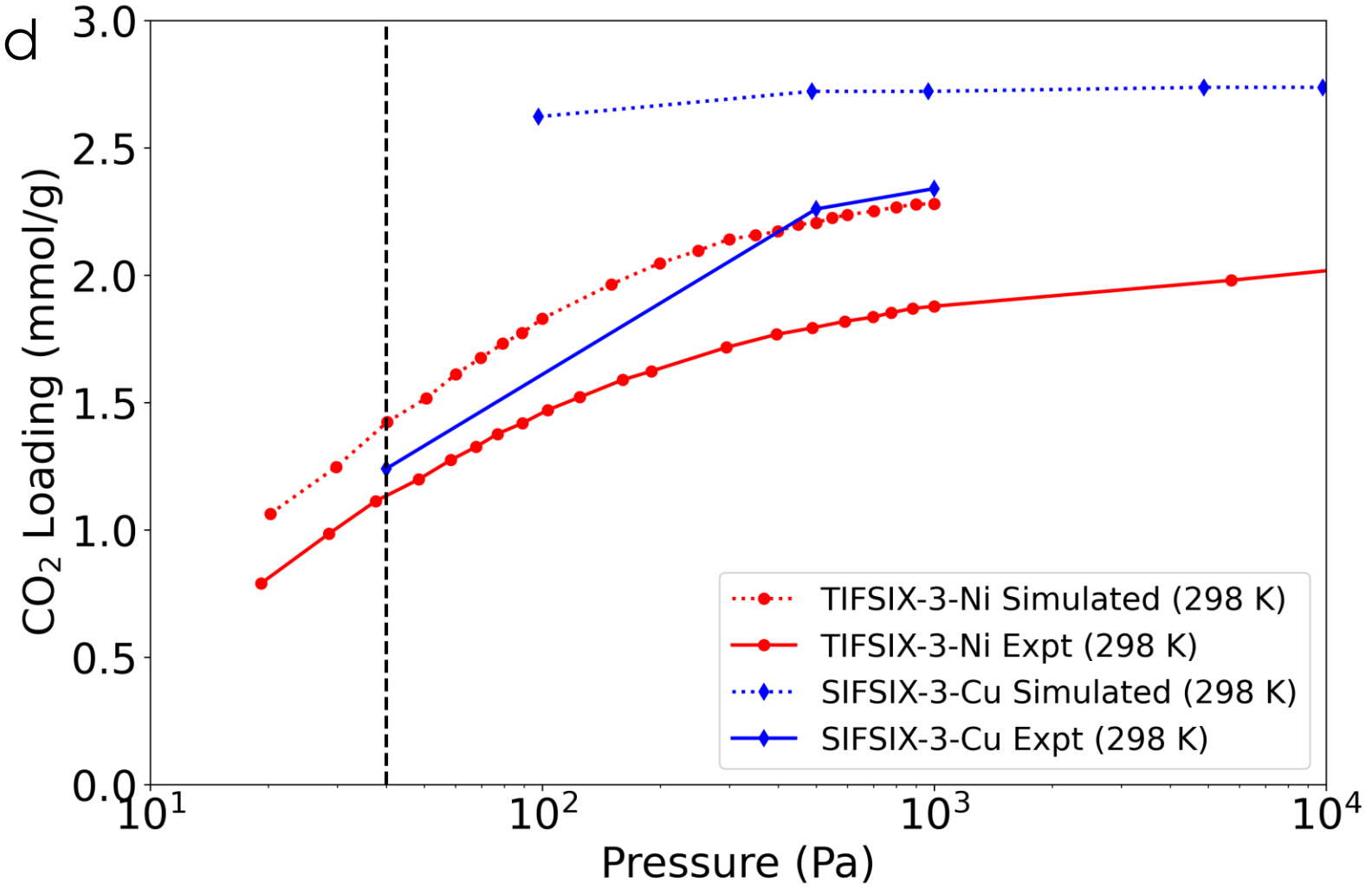
Total MOFs	High adsorbing MOFs (1) (CO_2 adsorption > = 0.05 mol/kg)	Low adsorbing MOFs (0) (CO_2< 0.05 mol/kg)
10,645	2447 (~23 %)	8198 (~77%)

Performance of Classical Force Fields: TIFSIX, SIFSIX

Performance at Low Pressure

CO_2 adsorption overpredicted using rigid force fields



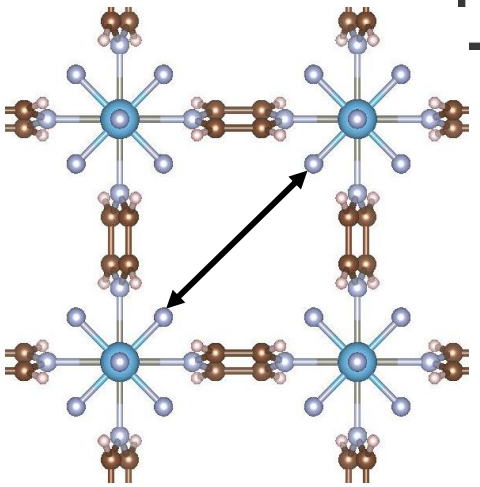


[3]Ullah et al., *Angewandte Chemie* (2022) [4]Low et al. *Energy& Fuels* (2024)
[5]Shekhah et al., *Nature Communications* (2014) [6]Mulcair, *Dissertation* (2017) [7]Forrest et al., *Crystal Growth and Design* (2019)

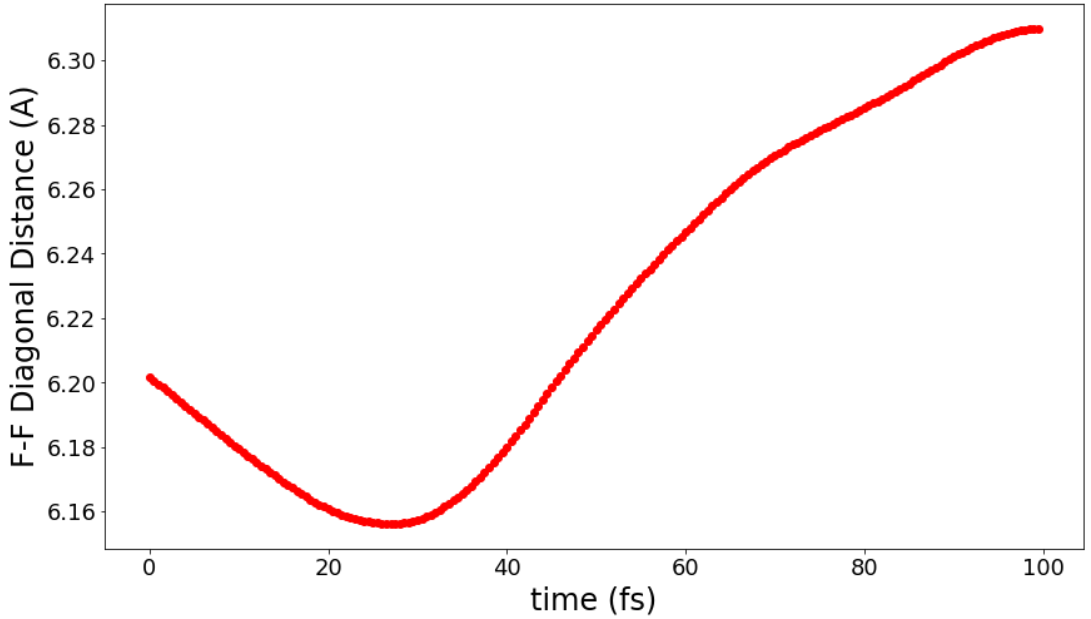
Importance of Flexibility and Accuracy

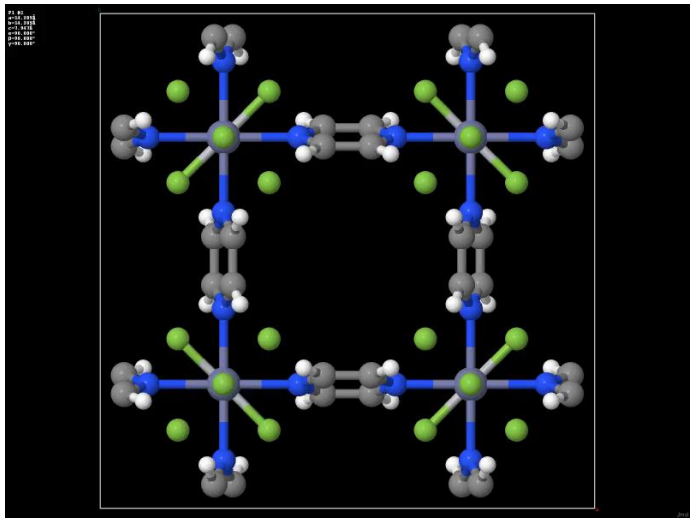
Flexible SiF_6 and TiF_6 can Cause Changes in Window Size

- Poor performance of rigid force fields
  - Overprediction at low P_{CO2}
- DFT molecular dynamics:
  - Significant motion of fluorine atoms
  - Fluorine location affects adsorption strength



F-F diagonal

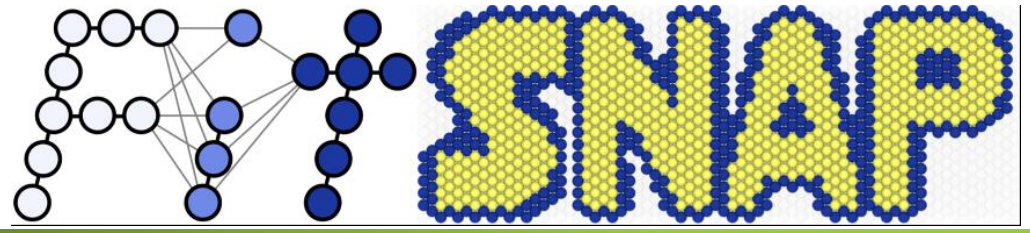




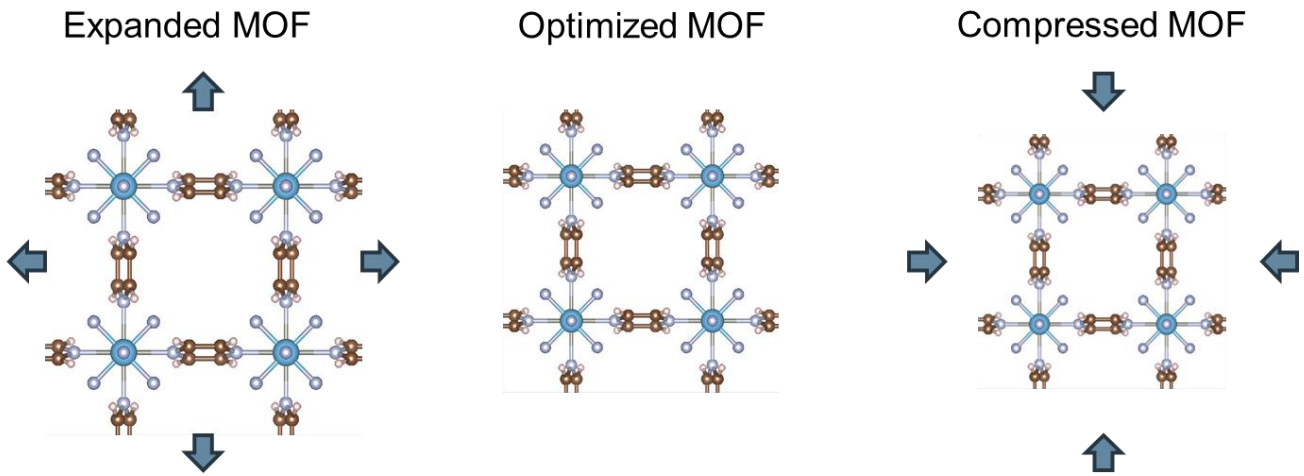
MLFF Training: Spectral Neighbor Analysis Potential

MLFFs Trained on Accurate DFT Data

- **MLFF Method: SNAP**
  - regression model maps local atomic environments to atomic energies and forces
- **Training Configurations**
  - Favorable (low energy) and unfavorable (high energy)
  - MOF with and without CO_2
- **Our Approach**
  - Hybrid SNAP/classical potential
  - MLFF handles short range
  - Classical handles long range



Sample Volume Changes



Sample CO_2 Adsorption

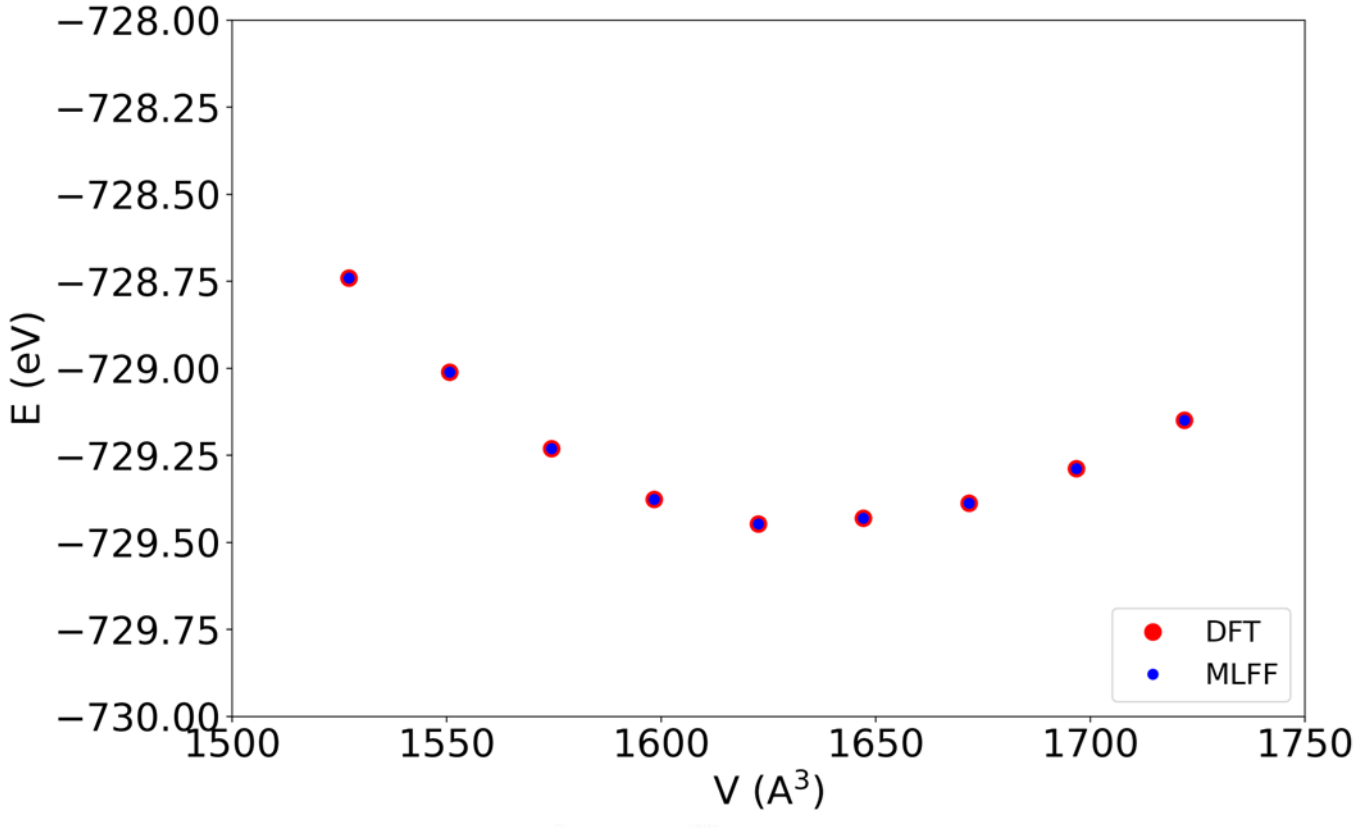
Rohskopf, A. et al. *JOSS* **2023**, *8* (84), 5118.
Thompson, A. P. et al. *JCP* **2015**, *285*, 316–330.

Performance of MLFF Model (Empty)

MLFF Describes MOF Structure and Flexibility (TIFSIX_3_Zn)

- Prediction of energy vs. volume curve is almost perfect (bottom)
  - Related to bulk modulus
- Compared energies/forces in QM-based dynamics calculations, performance is good
  - 7000 training configurations
  - 1800 testing configurations

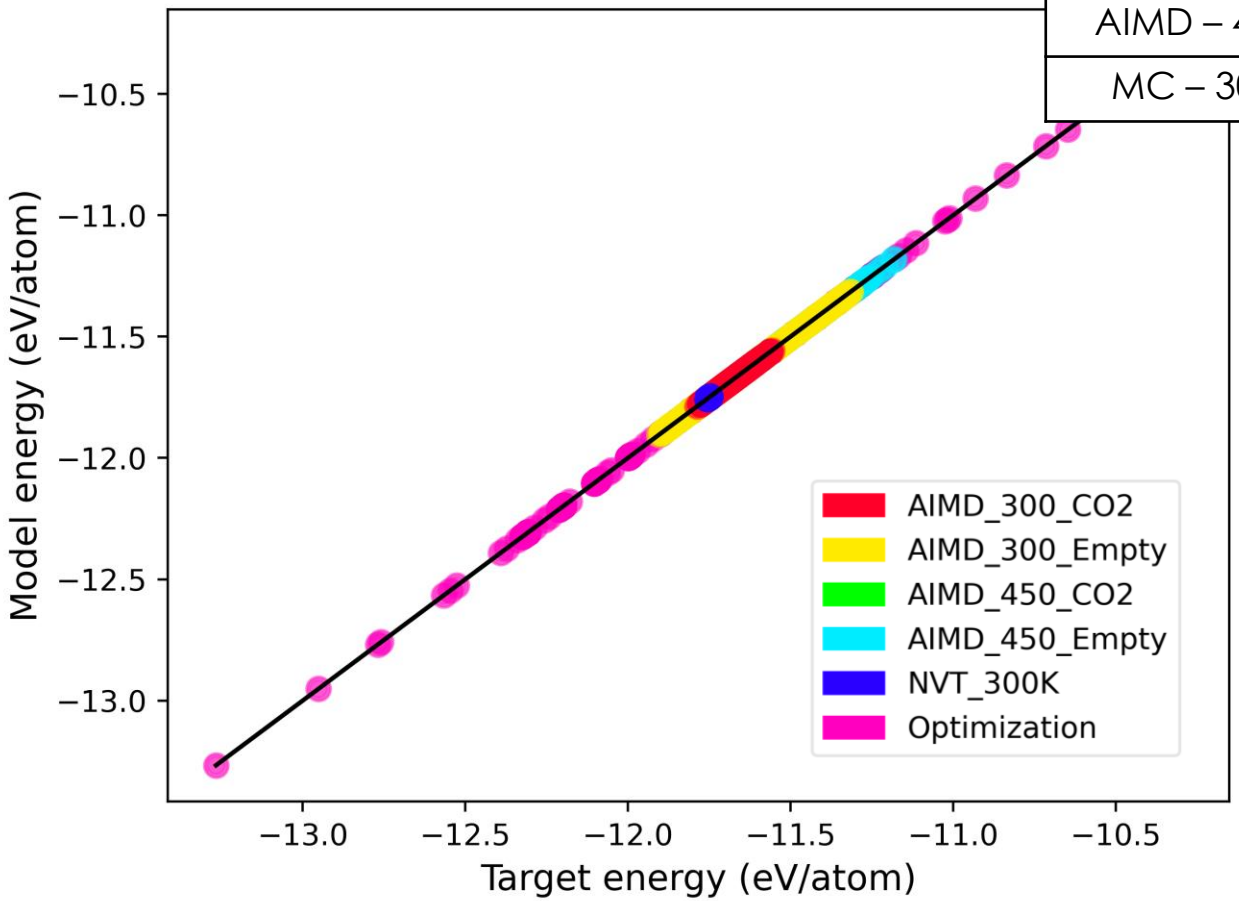
Data Empty MOF (Testing set)	R^2 Energies	R^2 Forces
Structure Optimization	0.998	0.990
AIMD – 300 K	0.991	0.981
AIMD – 450 K	0.990	0.975

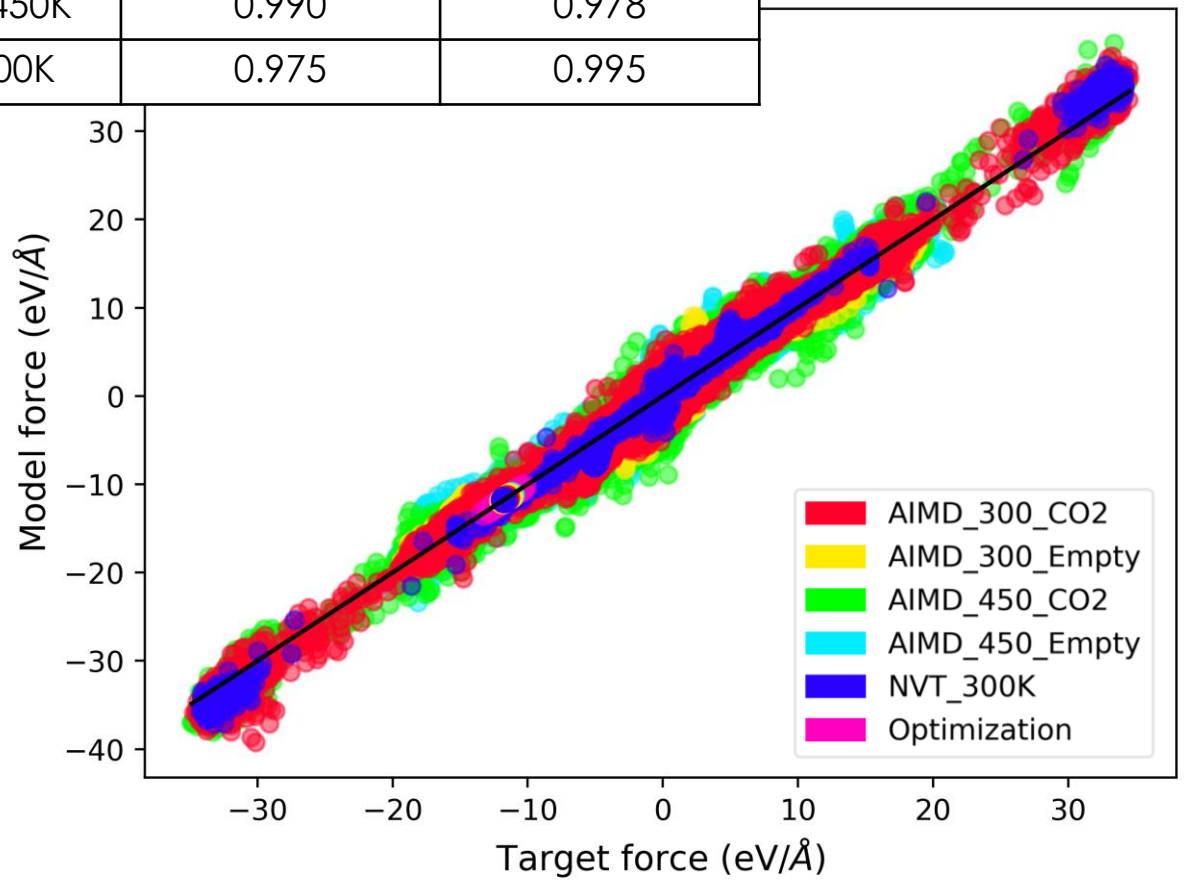


Performance of MLFF: MOF + CO_2

Parity Plots for Energies and Forces

Data MOF + CO_2 (Testing set)	R^2 Energies	R^2 Forces
AIMD – 300K	0.990	0.983
AIMD – 450K	0.990	0.978
MC – 300K	0.975	0.995





Performance of MLFF Force Field: TIFSIX-3-Zn

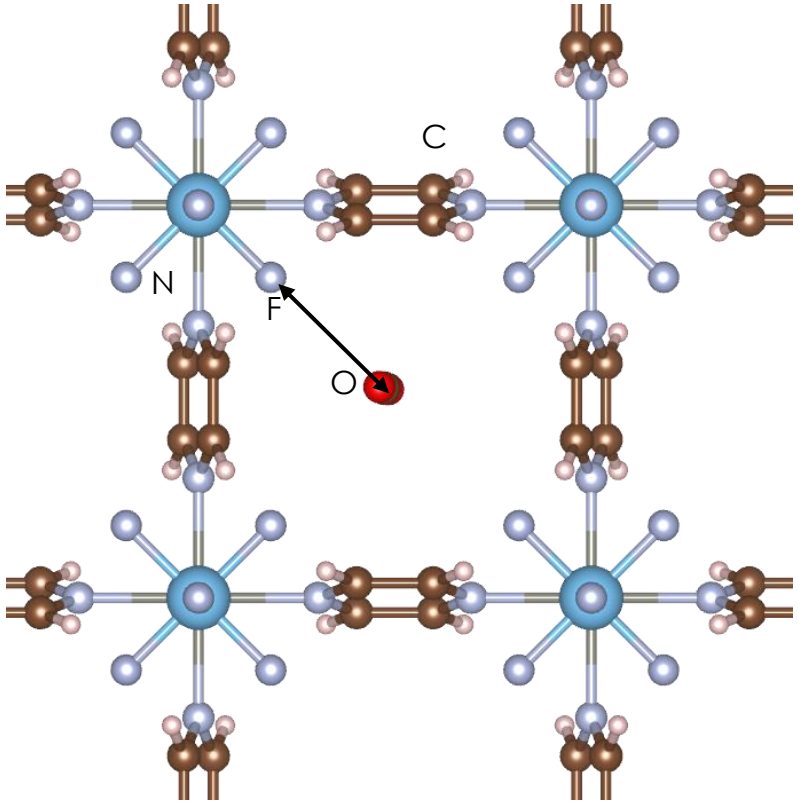
Performance at Low Pressure

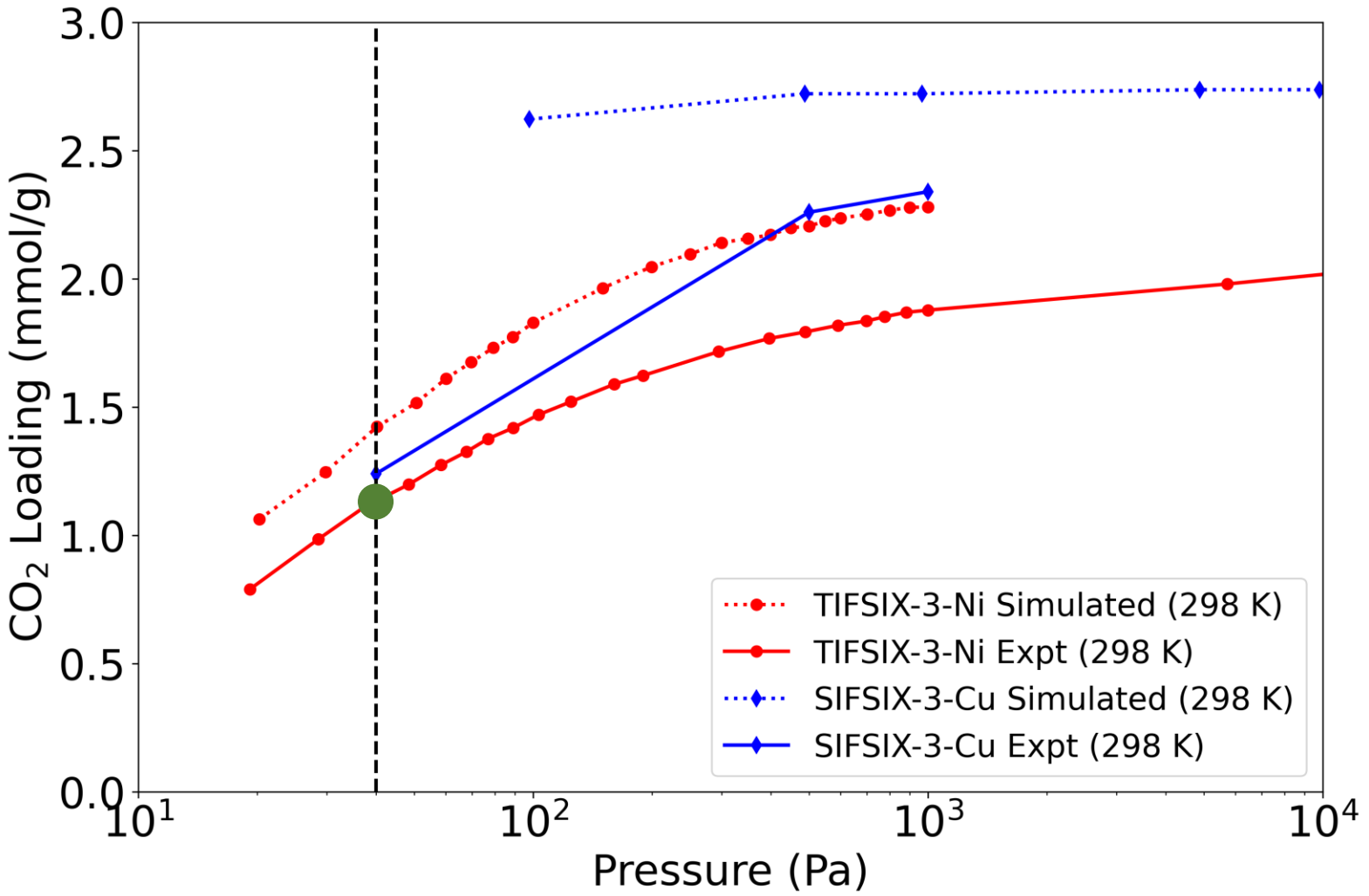
One point on isotherm so far

MLFF Simulation:

TIFSIX-3-Zn adsorbs1.08 mmol/g*

- 400 ppm, 298 K





[3]Ullah et al., *Angewandte Chemie* (2022) [4]Low et al. *Energy& Fuels* (2024)
[5]Shekhah et al., *Nature Communications* (2014) [6]Mulcair, *Dissertation* (2017) [7]Forrest et al., *Crystal Growth and Design* (2019)

Conclusions

- Inclusion of MOFs in polymer membranes can lower the cost of membrane-based CO_2 capture by up to 1/3
- Rigid FF can lead to large overprediction of CO_2 isotherm at low pressure
- MLFF flexible potential accurately describes energies and forces in a MOF loaded with CO_2
- Training on the error of the classical force field improves the MLFF model fit
- TIFSIX-3-Zn $\Delta E_{ads,\ CO2}$, MLFF = -52.9 kJ/mol, DFT -52.1 kJ/mol
- MLFF Prediction: TIFSIX-3-Zn adsorbs 1.08 mmol/g* at 400 ppm, 298 K