

HyMARC Seedling: Theory-Guided Design and Discovery of Materials for Reversible Hydrogen Storage

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DOE Project Award # (DE-EE0008816)

Project ID # ST209

June 7–11, 2021

DOE Hydrogen Program 2021 Annual Merit Review and Peer Evaluation Meeting

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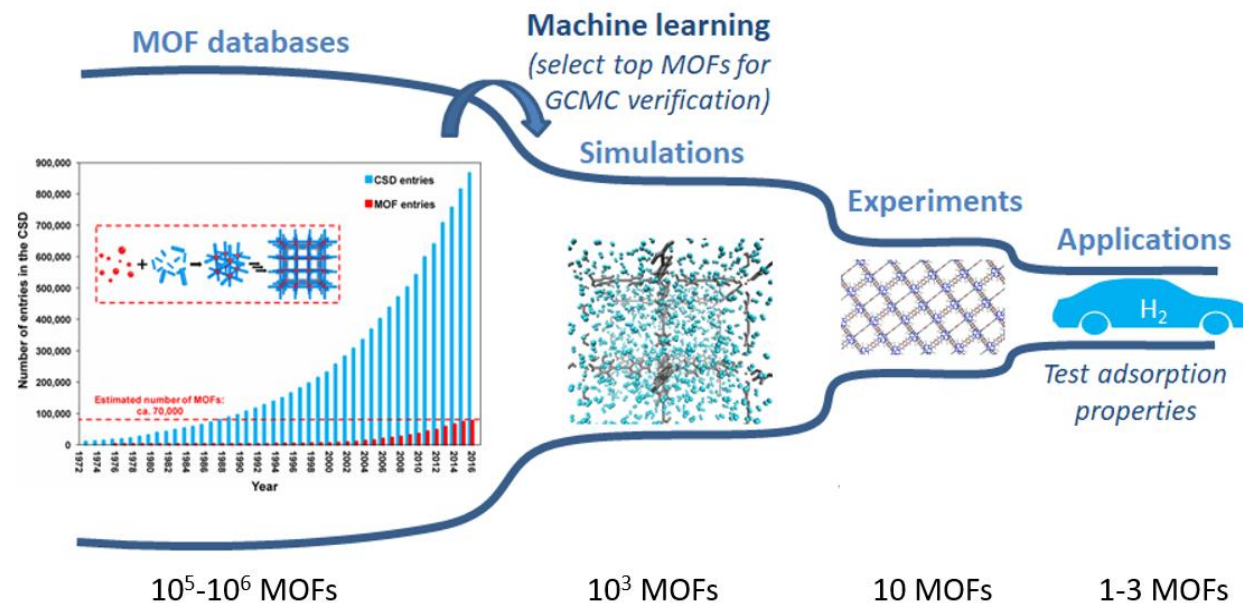
Project Overview

Project Partners

PI: **Omar K Farha**, Northwestern University

Co-PI: **Randall Q. Snurr**, Northwestern University

Co-PI: **Taner Yildirim**, NIST



Timeline and Budget

- Project Start Date: Jan, 2020
- Project End Date: Jan, 2023 (subject to annual evaluation by DOE)
- Total Project Budget: \$1,125,000
 - Total Recipient Share: \$225,000
 - Total Federal Share: \$900,000

Project Goal

- We seek to exploit high performance MOF sorbents by combining synthesis with machine learning to find stable and scalable materials for hydrogen storage while maintaining a reasonable cost of production.

Approach – Summary

Project Motivation

We seek to exploit high performance MOF sorbents for hydrogen storage while maintaining a reasonable cost of production.

• Barriers

- System Weight and Volume
- System Cost
- Efficiency
- Durability/Operability
- Materials of Construction

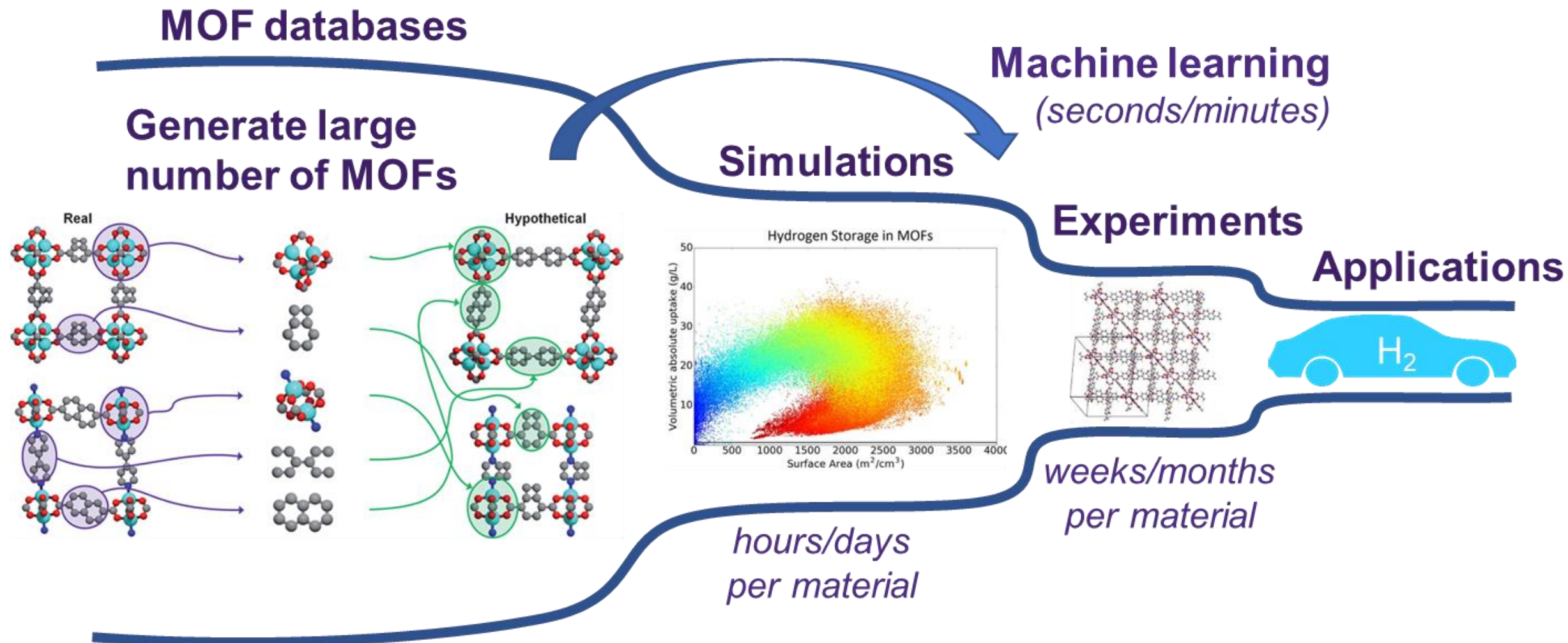
Phase 1: Go/No Go Demonstrate a material with H₂ working capacity exceeding 8 wt% and 52 g/L under pressure and temperature swing operation (5-100 bar and 77-160 K); OR 2.8 wt% and 18 g/L under higher temperature swing operation (5-100 bar and 233-296 K).

Partnerships

National Institute of Standards and Technology (NIST), Dr. Taner Yildirim

National Renewable Energy Laboratory (NREL),
Dr. Philip Parilla

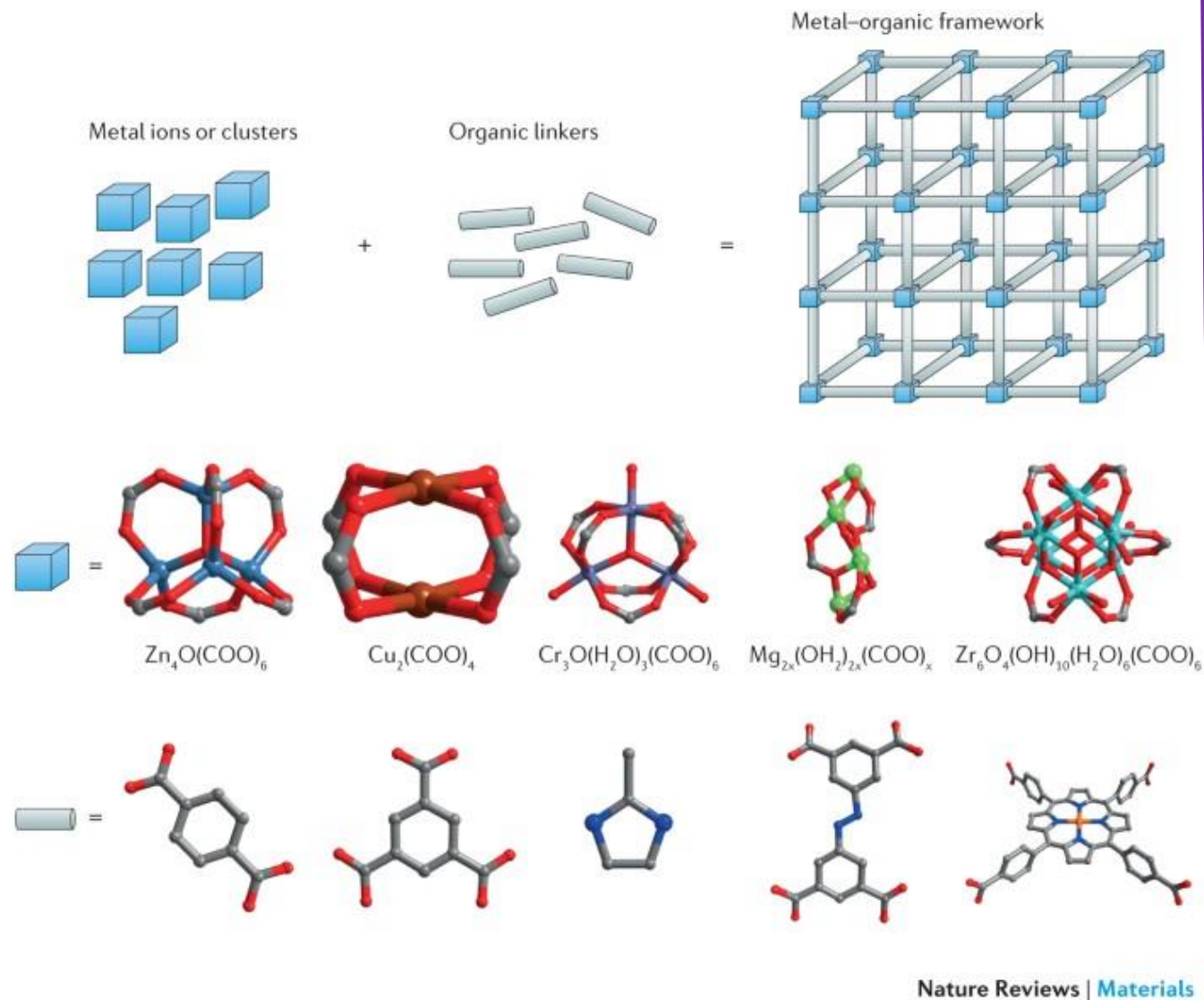
Approach – Innovation



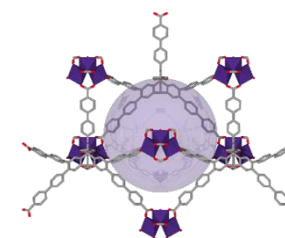
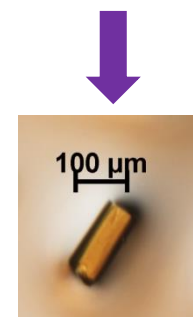
Relevance and Impact

- (1) Perform high-throughput computational discovery:** A key advantage of MOFs is structural predictability that can be leveraged to rapidly search in silico for optimal materials by expanding current databases of predicted MOFs to include various topologies (i.e. 85 topologies) as well as new building blocks from commercially available sources.
- (2) Screen** database of 100,000 MOFs for hydrogen uptake using machine learning algorithm and GCMC for **fast screening** and **identify materials** with total capacity (up to 100 bar) that can reach the storage capacity of hydrogen tank at 700 bar
- (3) Synthesize and characterize the top candidate** MOFs generated in silico for hydrogen storage while keeping in mind stability (thermal, chemical and mechanical stability), scalability and cost.
- (4) Study MOFs under pressure and temperature swing** operation (5-100 bar and 77-160 K).
- (4) Study MOFs in which open metal sites** can be created upon removal of solvent molecules, for storage of molecular hydrogen at and **near room temperature**.

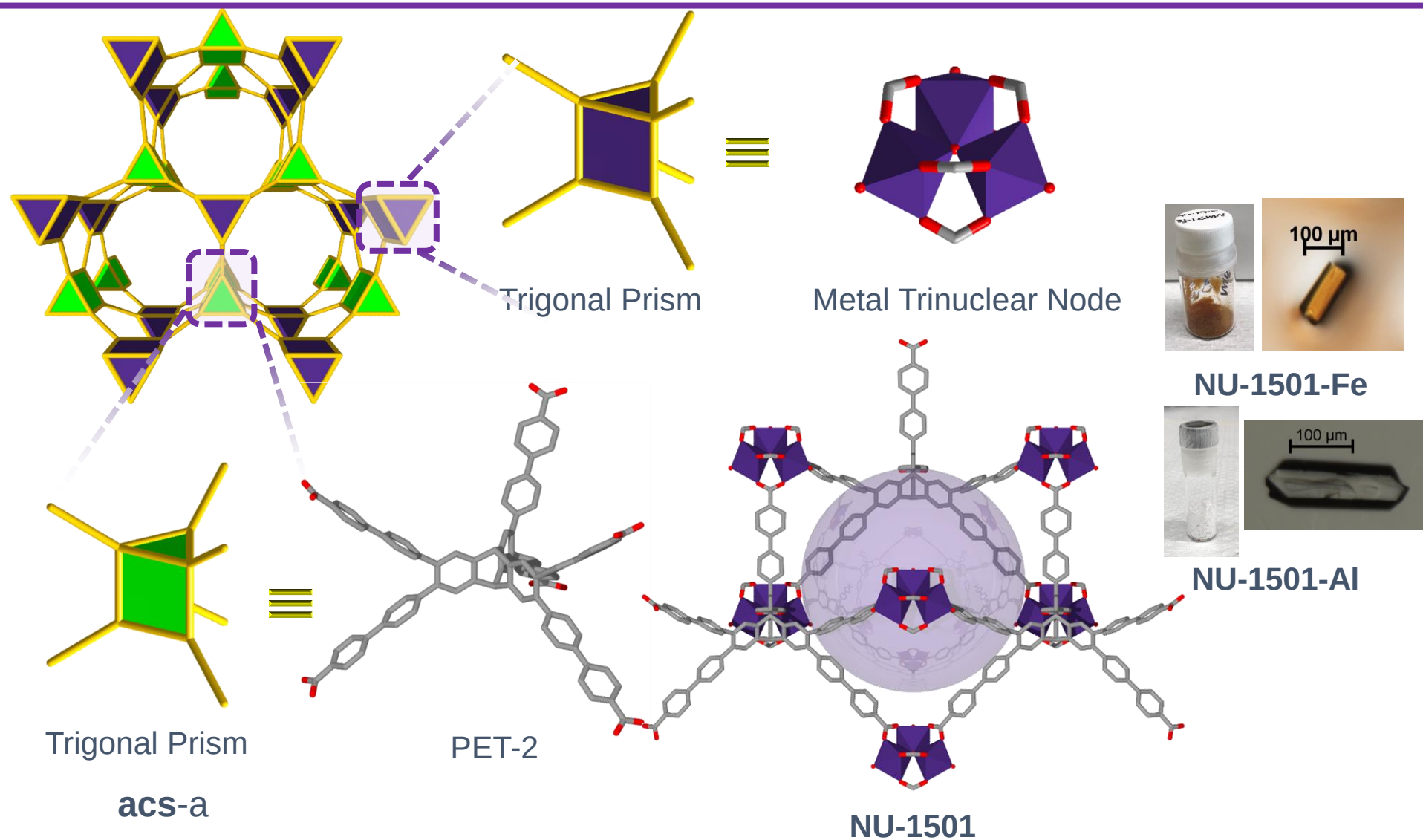
Background: Metal-Organic Frameworks



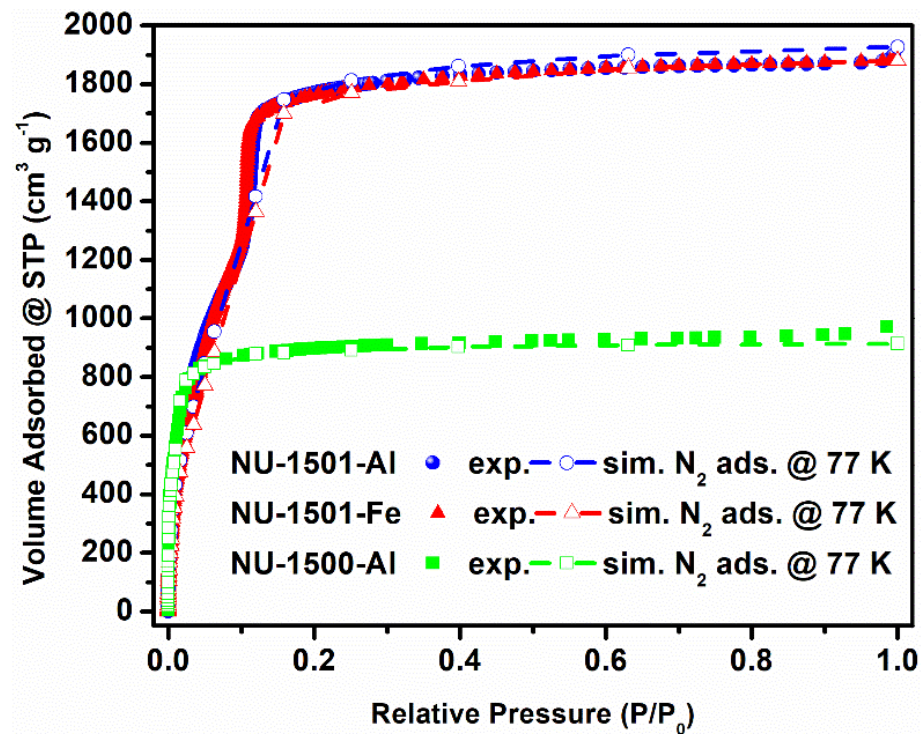
- High surface area
- Highly tunable
- Crystalline



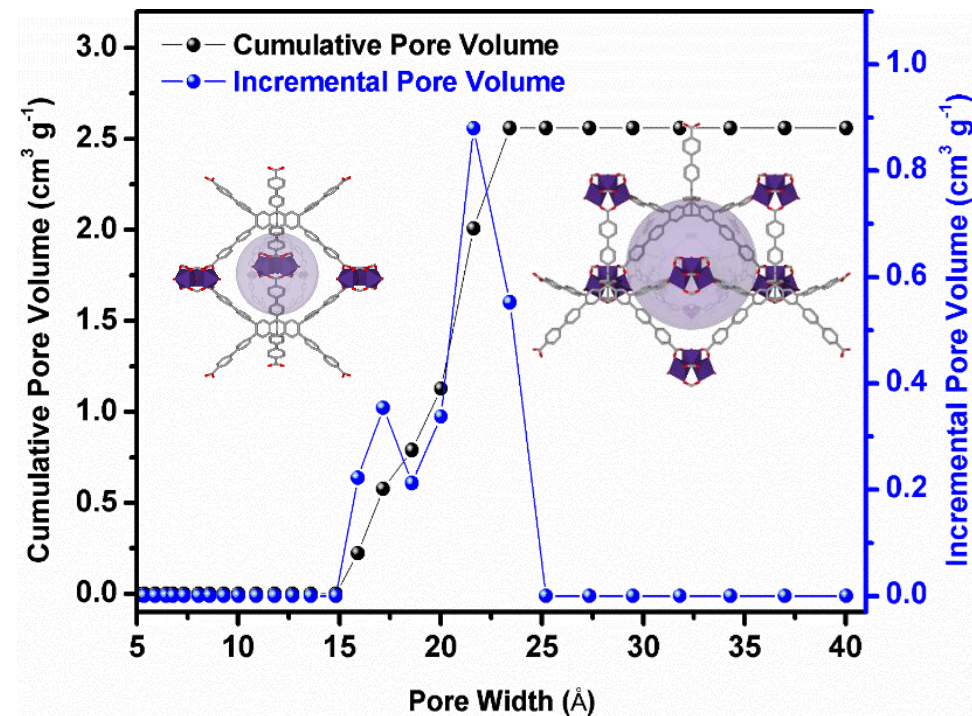
Accomplishments: Design and Synthesis of NU-1501



Accomplishments: Porosity of NU-1501

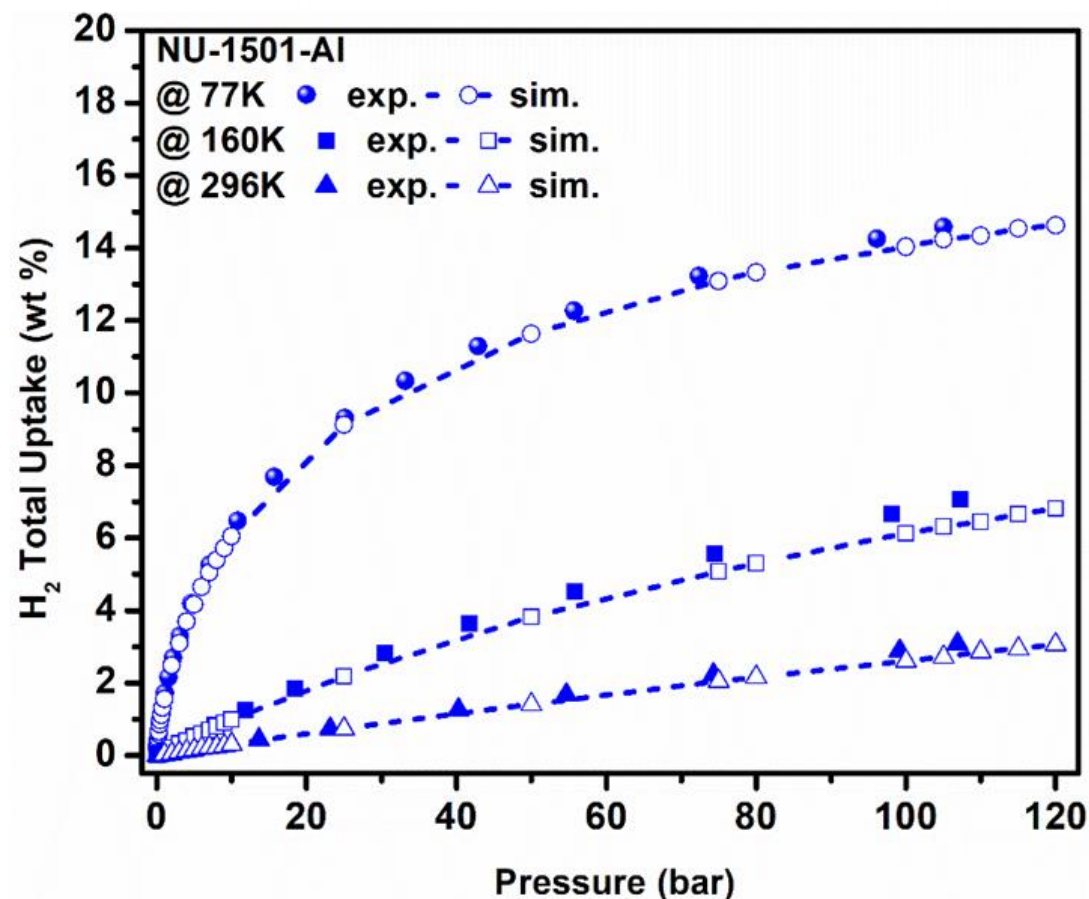


Pore volume: **$2.90 \text{ cm}^3 \text{g}^{-1}$**

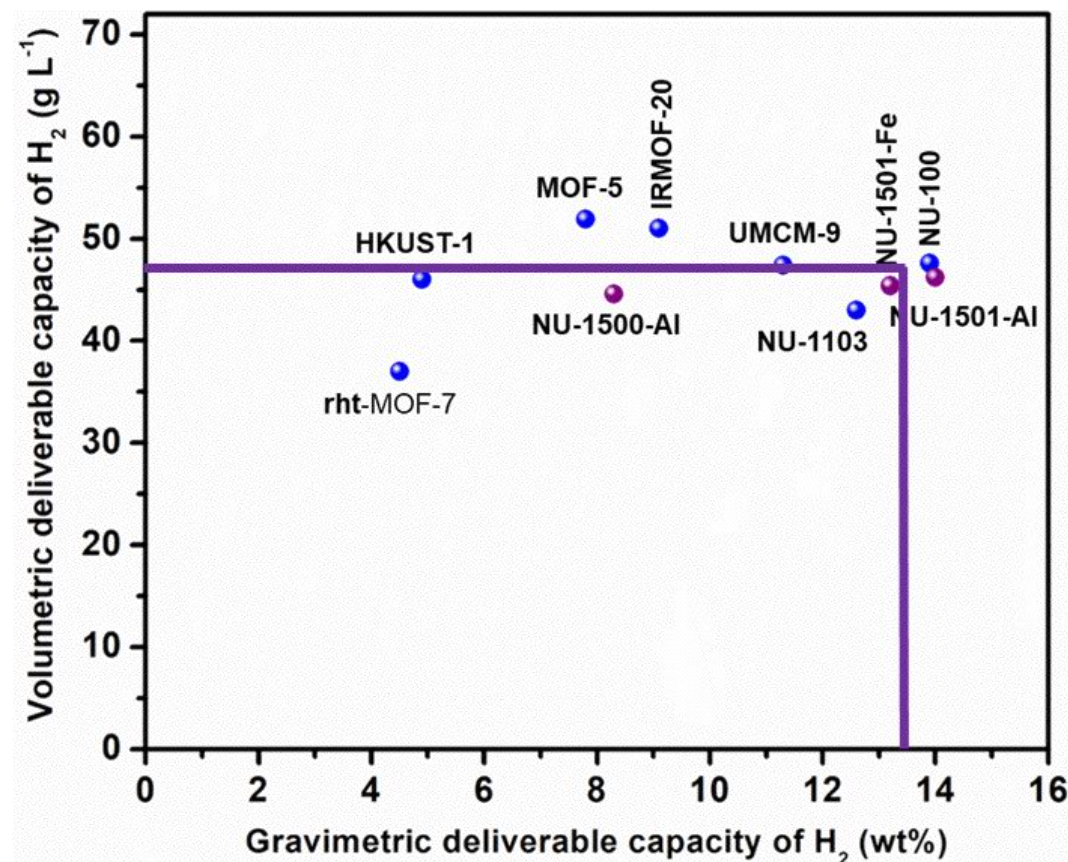


Pore size: about **2.2 nm**

Accomplishments: Hydrogen isotherms collected at NIST



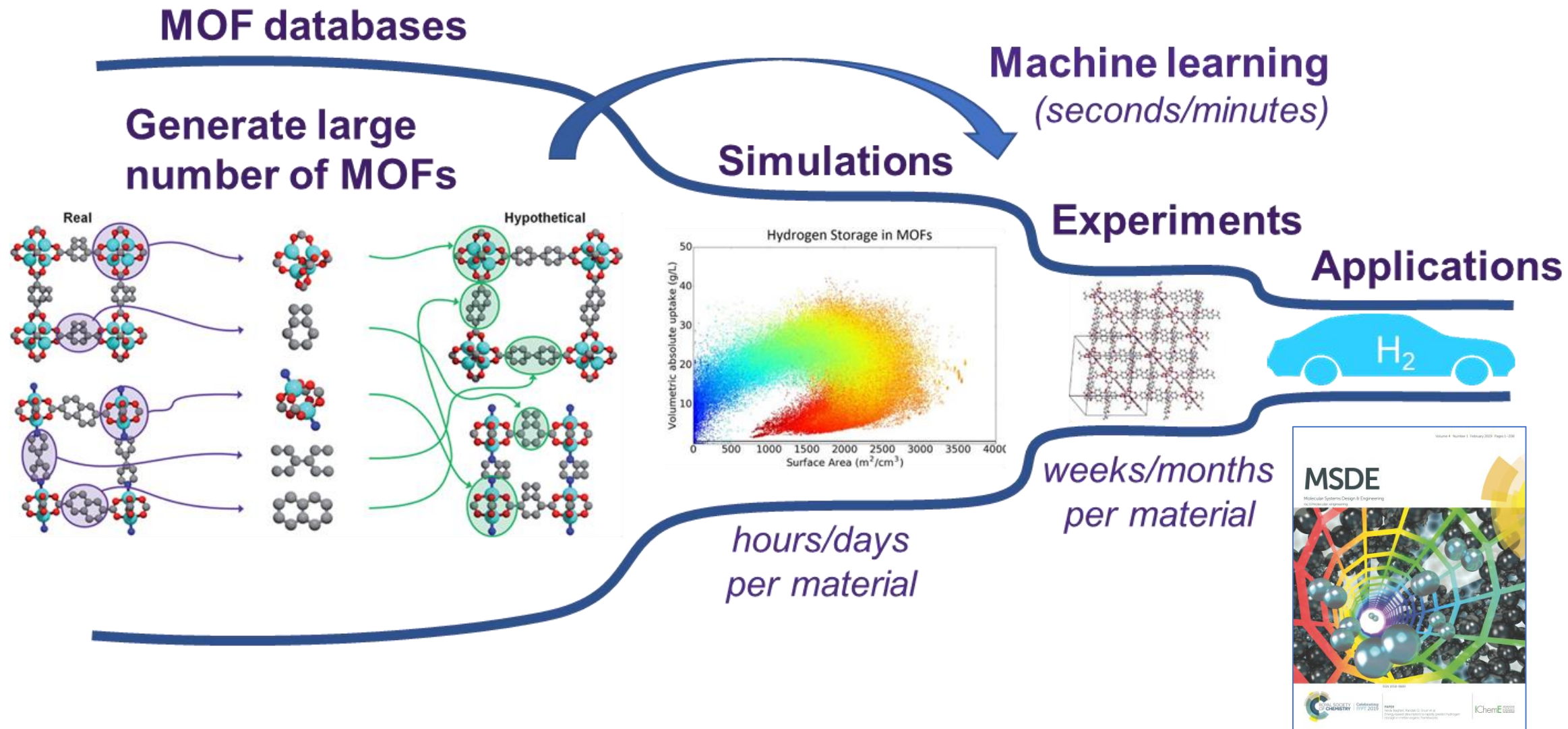
H₂ 100 bar/77 K → 5 bar/160 K



Among the best MOFs for hydrogen storage under combined temperature and pressure swing conditions (77 K/100 bar → 160 K/5 bar) (measured at NIST by Dr. Taner Yildirim)

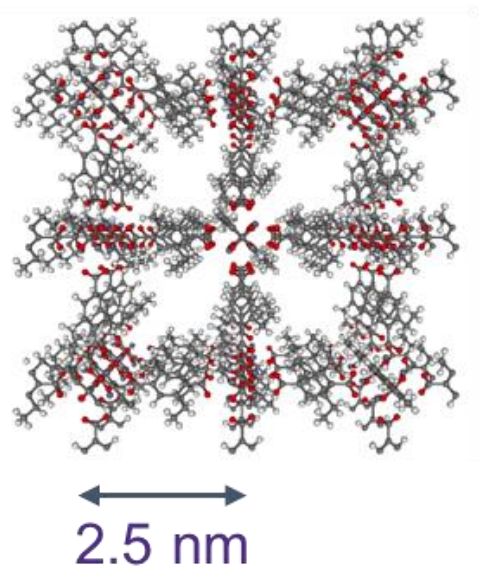
Chen, Z.; Li, P.; Anderson, R.; Wang, X.; Zhang, X.; Robison, L.; Redfern, L. R.; Moribe, S.; Islamoglu, T.; Gómez-Gualdrón, D. A.; Yildirim, T.; Stoddart, J. F.; Farha, O. K. **Science** 2020, 368, 297-303

Accomplishments: High-throughput Computational Screening

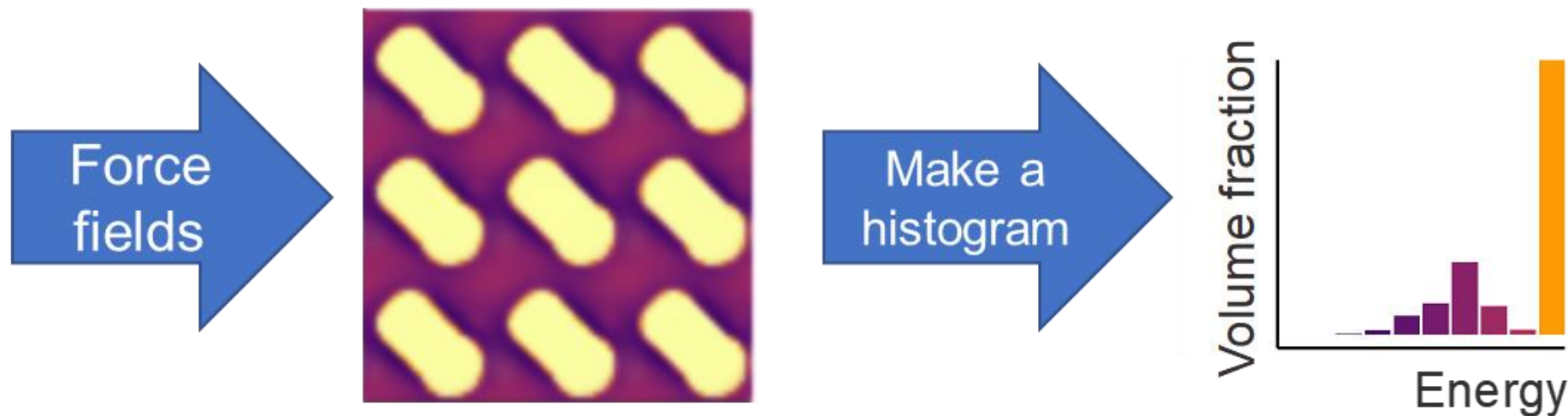


Accomplishments: Energy histogram as a descriptor

MOF structure



H₂-MOF energy grid

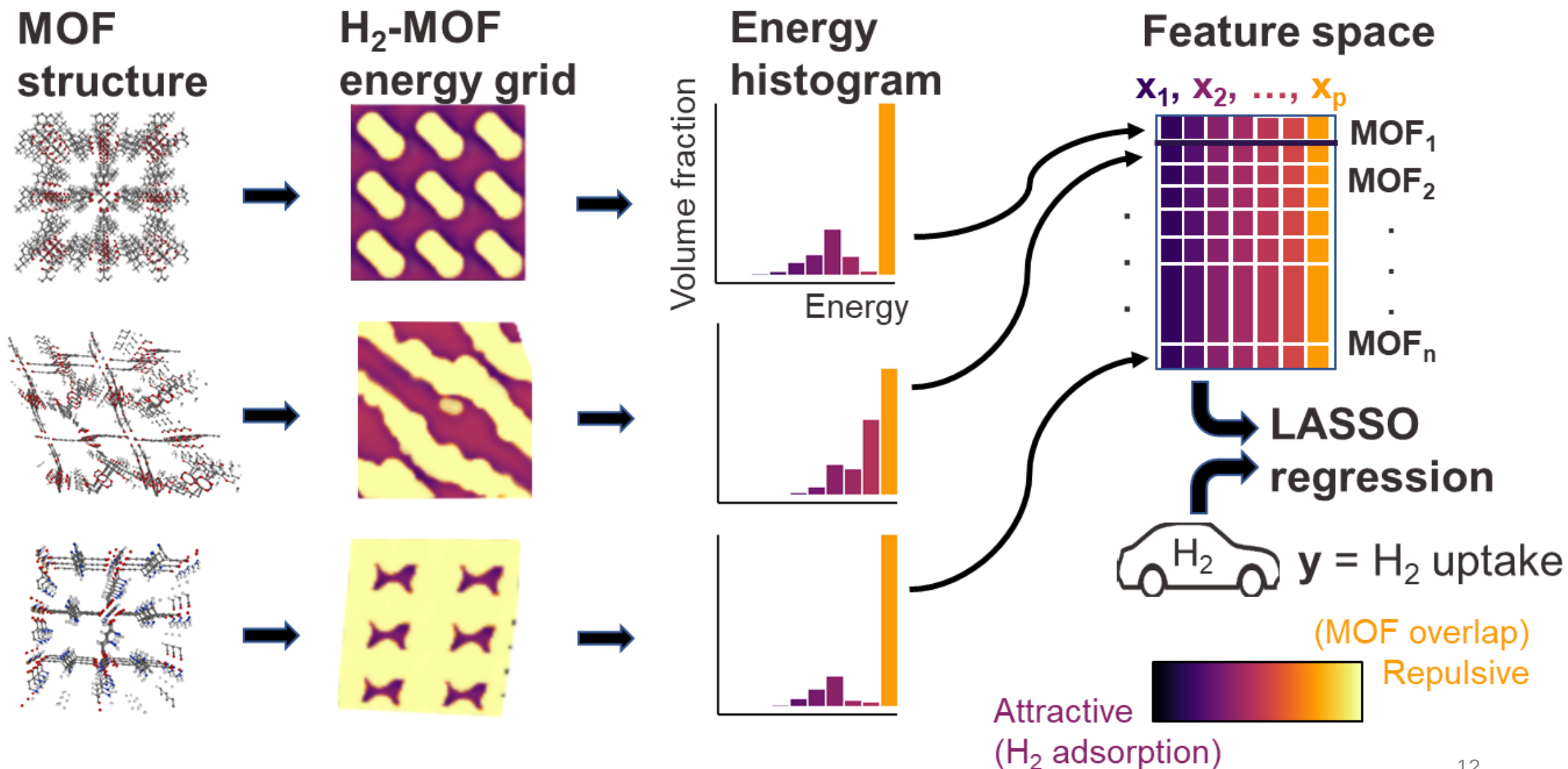


Attractive
(H₂ adsorption)



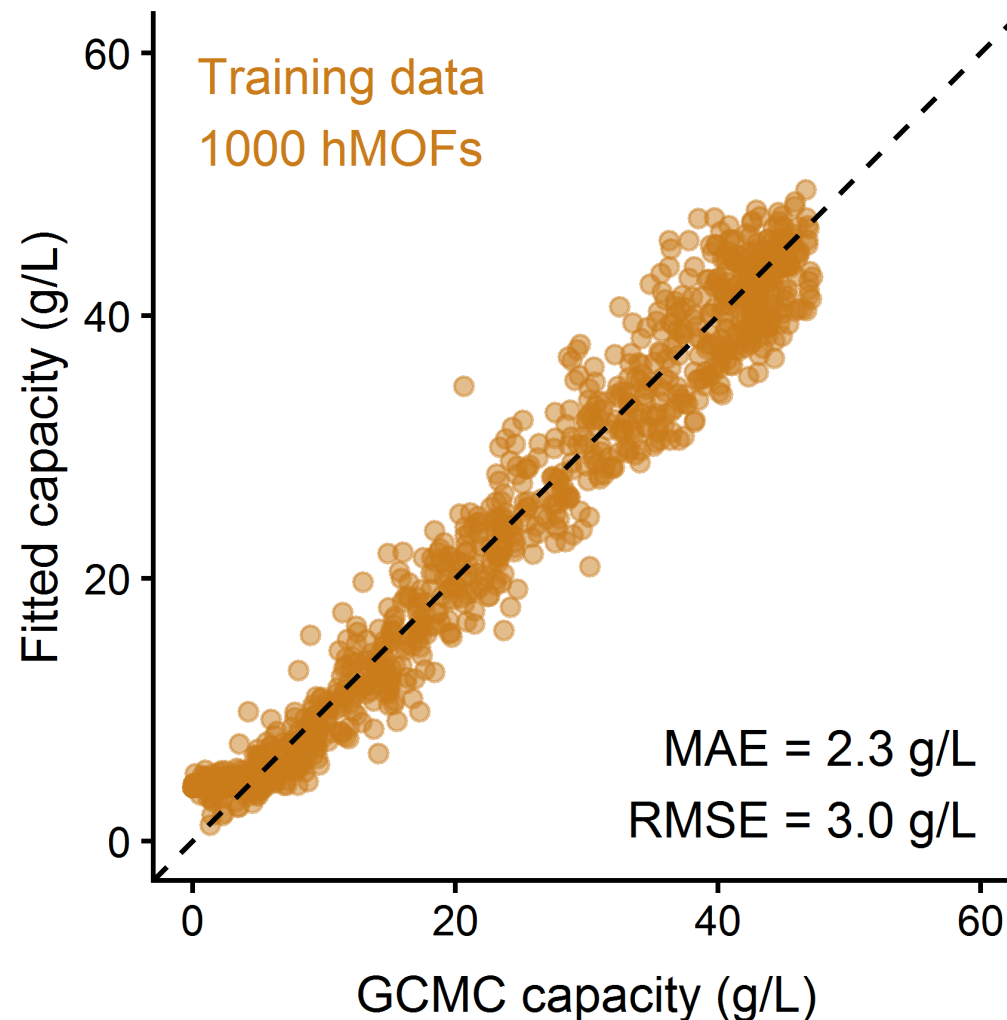
Repulsive
(MOF overlap)

Accomplishments: Energy histogram as a descriptor



Training = 1000 MOFs

Deliverable Capacity
calculated between 100
bar and 2 bar at 77 K.

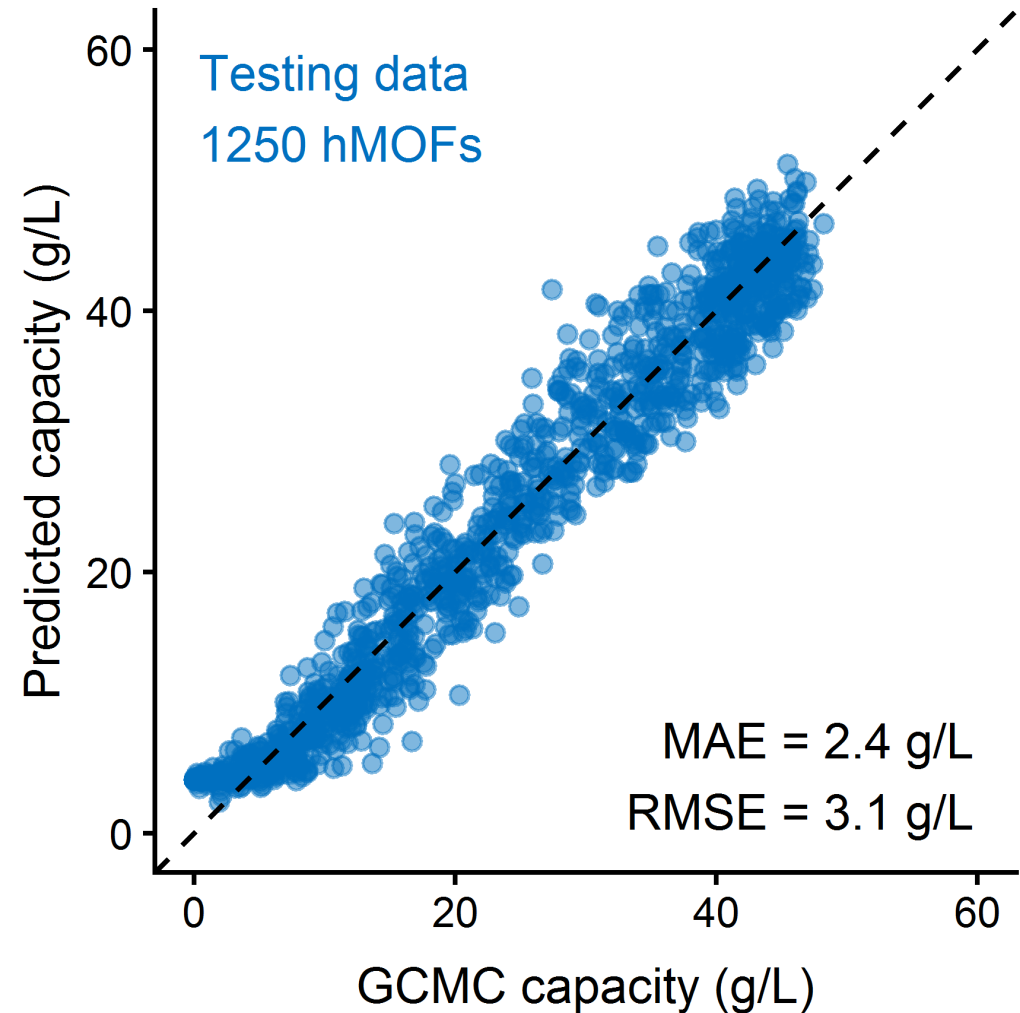


Accomplishments: The model works quite well for hydrogen

Training = 1000 MOFs

Testing = 1250 MOFs
(separate from training set)

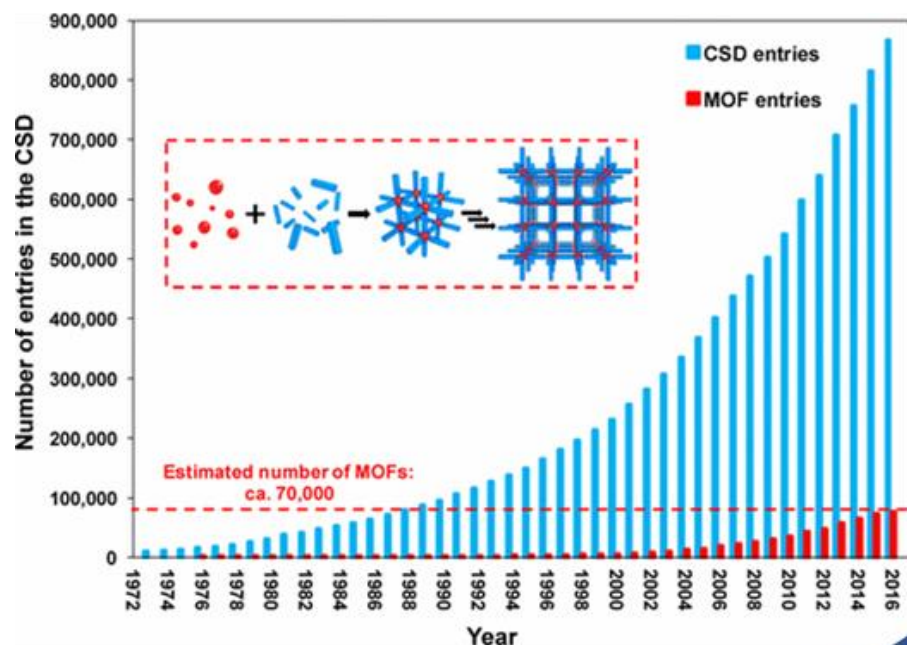
Deliverable Capacity
calculated between 100
bar and 2 bar at 77 K.



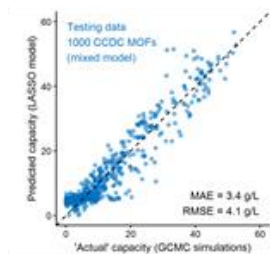
Accomplishments: Screening experimental MOF structures

MOF databases

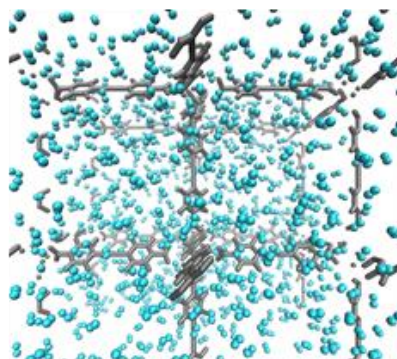
CSD MOF subset
> 50,000 candidates



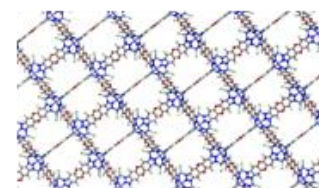
Machine learning (select top MOFs for GCMC verification) Simulations



1,000 simulations

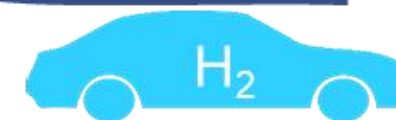


Experiments



Select a
top MOF

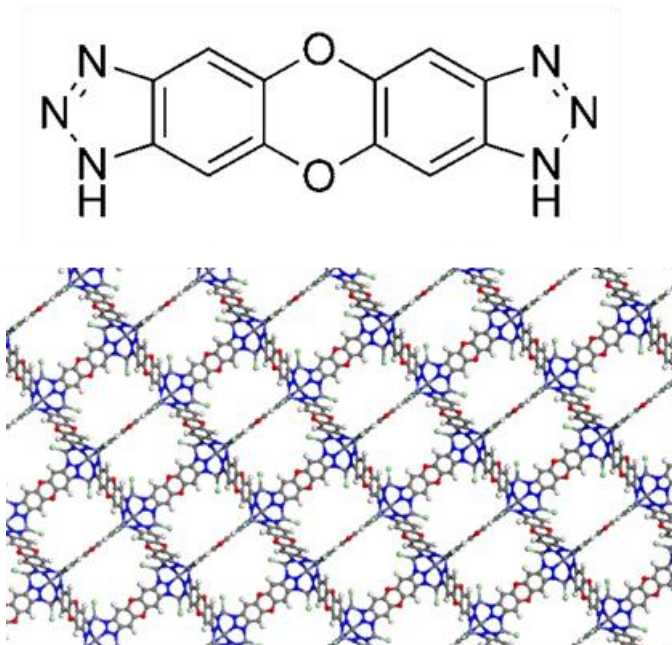
Applications



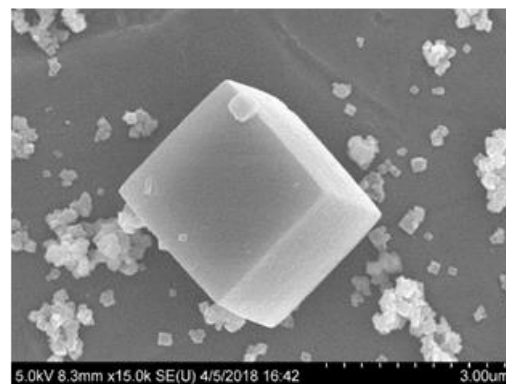
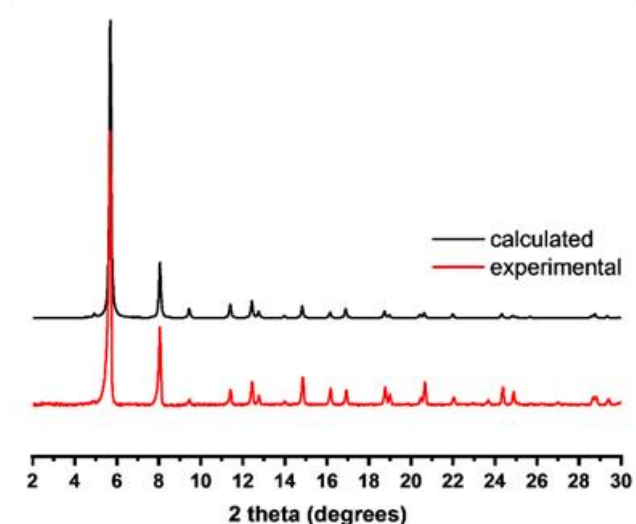
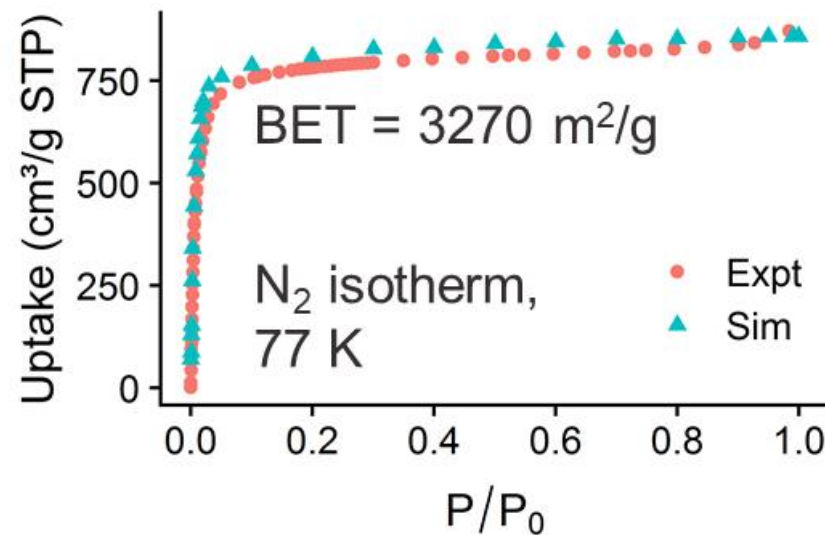
Test adsorption
properties

Accomplishments: Experimental validation of a top candidate

MFU-4L



Denysenko, Grzywa, Tonigold, Streppel, Krkljus, Hirscher, Mugnaioli, Kolb, Hanss, Volkmer. *Chem. Eur. J.*, **2011**, 17, 1837



Timur
Islamoglu



Subhadip
Goswami

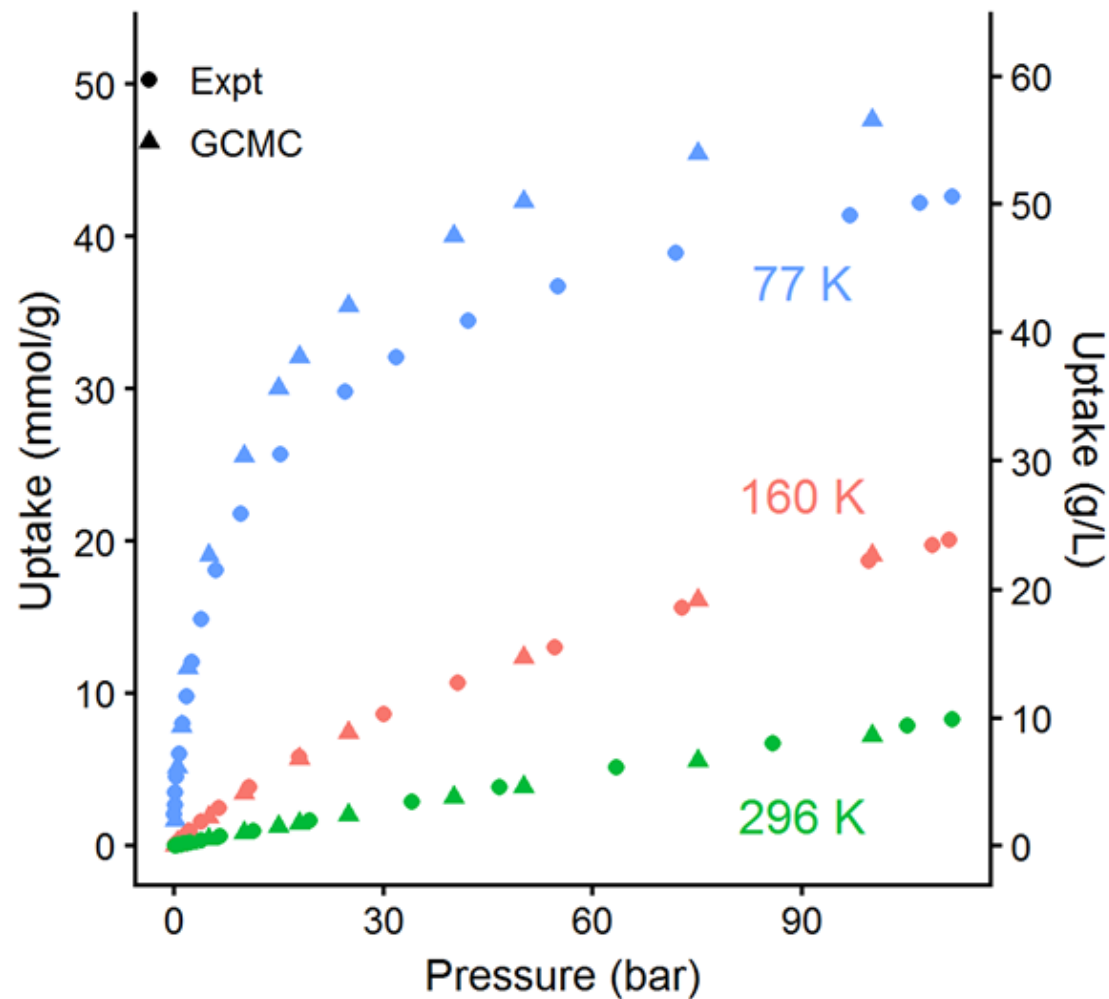


Omar
Farha



Taner
Yildirim

Accomplishments: Hydrogen uptake in MFU-4l



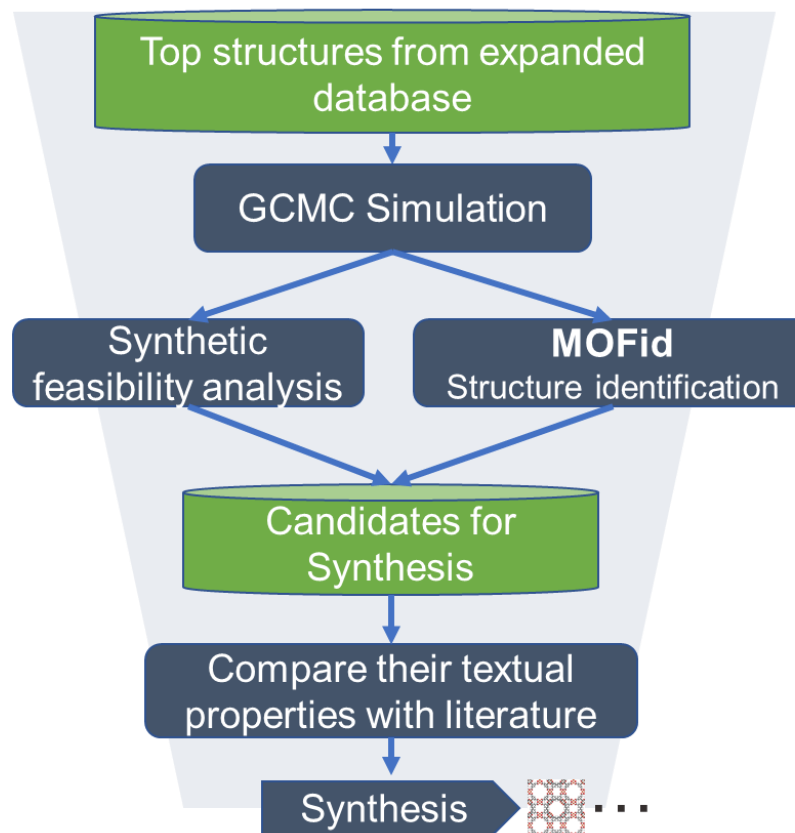
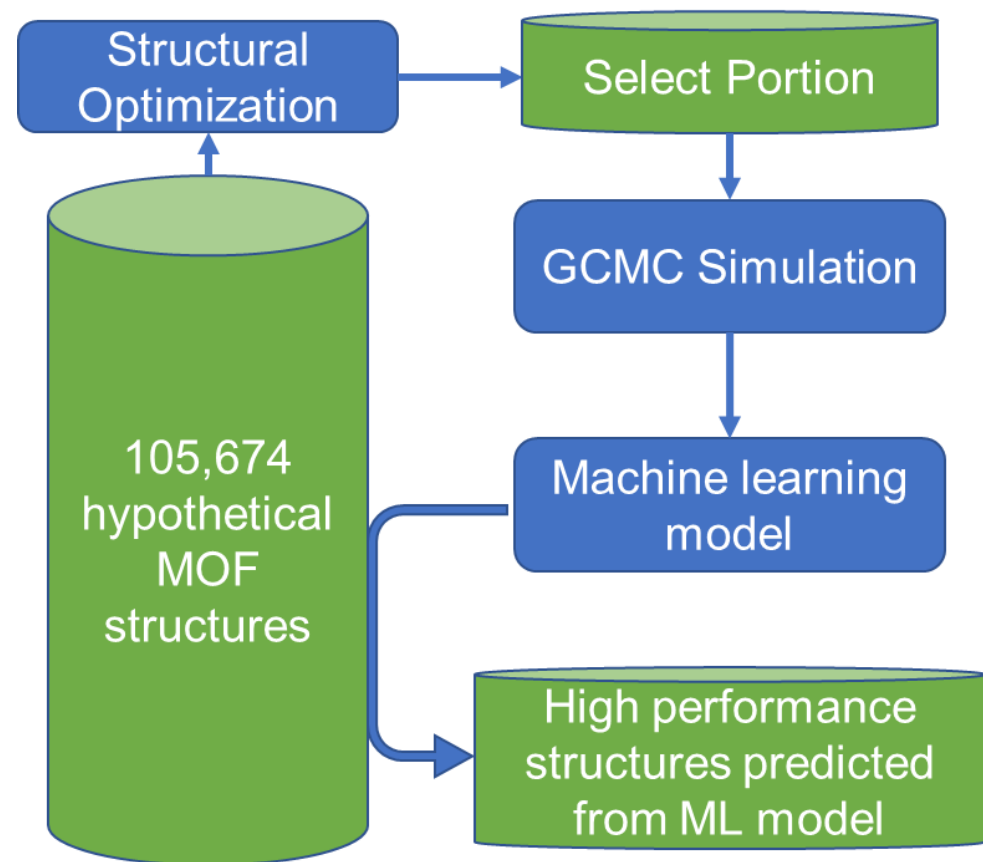
Bucior, Bobbitt, Islamoglu, Goswami, Gopalan, Yildirim, Farha, Bagheri, Snurr. *Mol. Syst. Des. Eng.* **2019**, 4, 162

100 bar/77K → 5 bar/160K

MOF	Capacity ΔH_2 (g/L)
HKUST-1	46
NU-125	49
Cu-MOF-74	39
NU-1000	48
NU-1101	47
UiO-67	41
MFU-4l	47

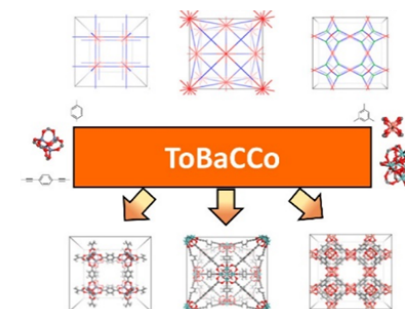
García-Holley, Schweitzer, Islamoglu, Liu, Lin, Rodriguez, Weston, Hupp, Gómez-Gualdrón, Yildirim, Farha. *ACS Energy Lett.* **2018**, 3, 748

Accomplishments: Expanded MOF screening



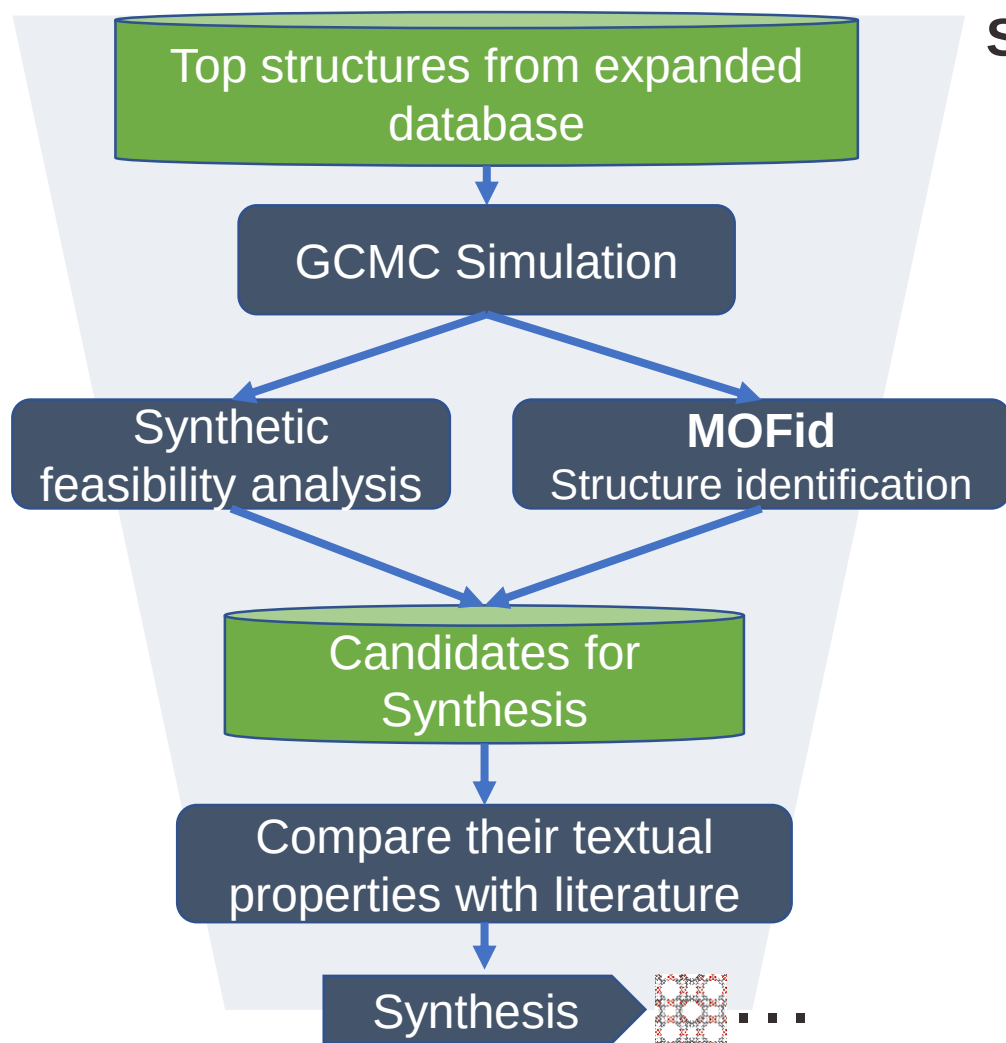
Expanded Database

- Database of 105,674 hypothetical (or proposed) structures



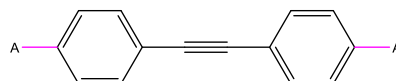
- Assembled with topologies and building units seen in literature

Accomplishments: Expanded MOF screening

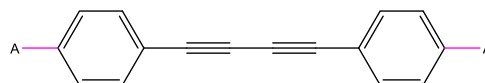


Synthetic Feasibility

- Organic linkers are constructed from nodular and connecting building blocks
- Classify building blocks according to ease of synthesis
 - Easy

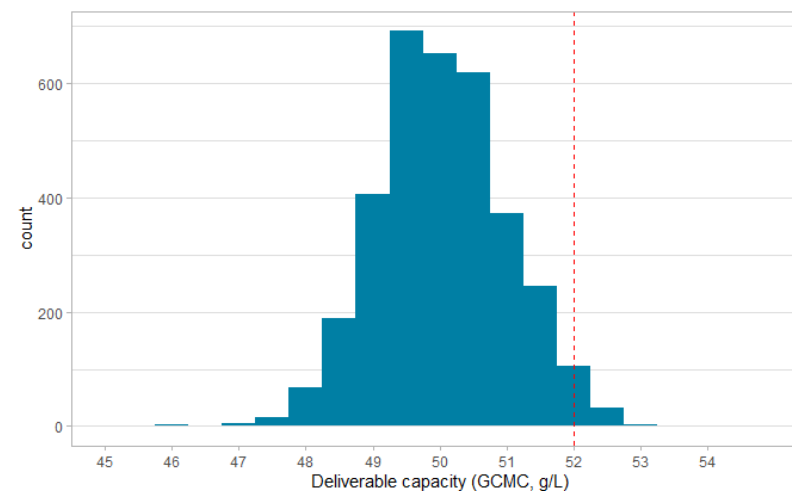


- Challenging

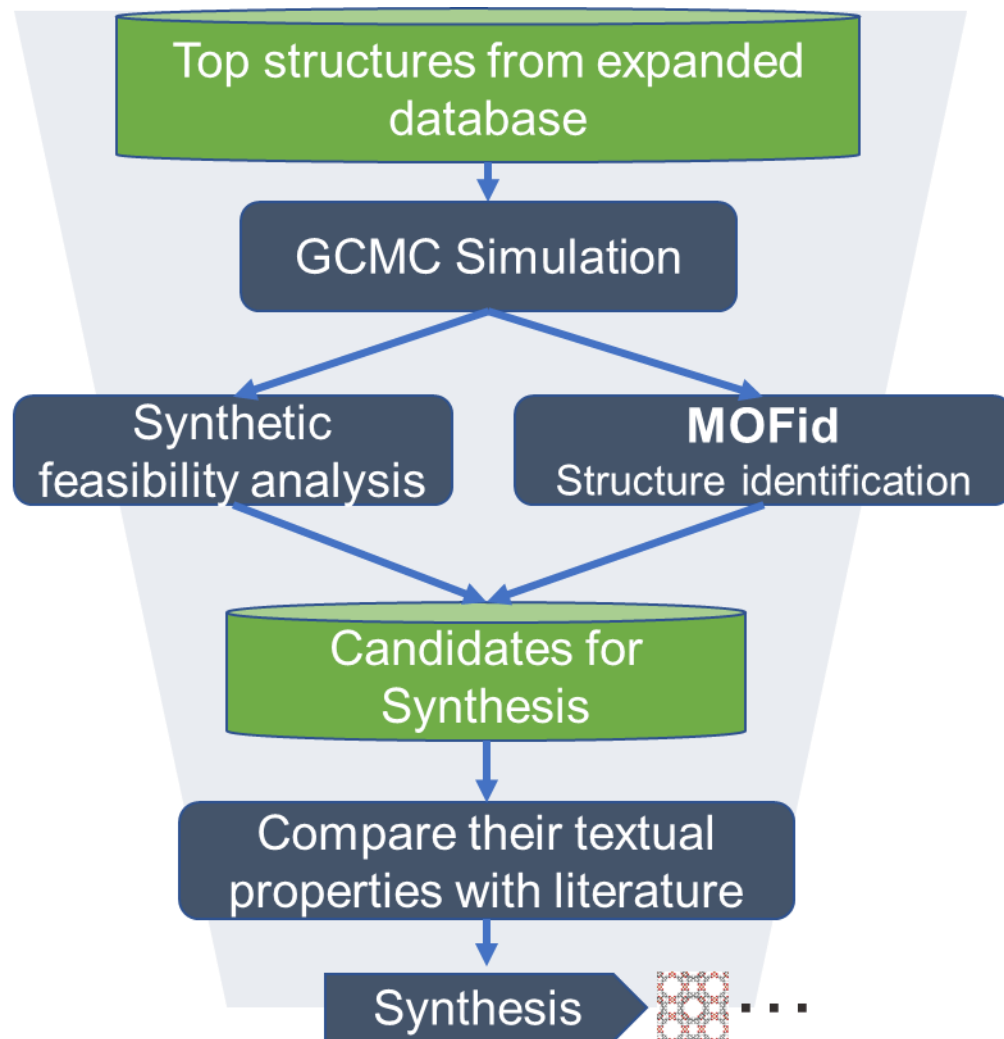


GCMC Simulation

- We ran GCMC simulations for the top structures identified by the machine learning model.
- Goal: Deliverable capacity > 52 g/L

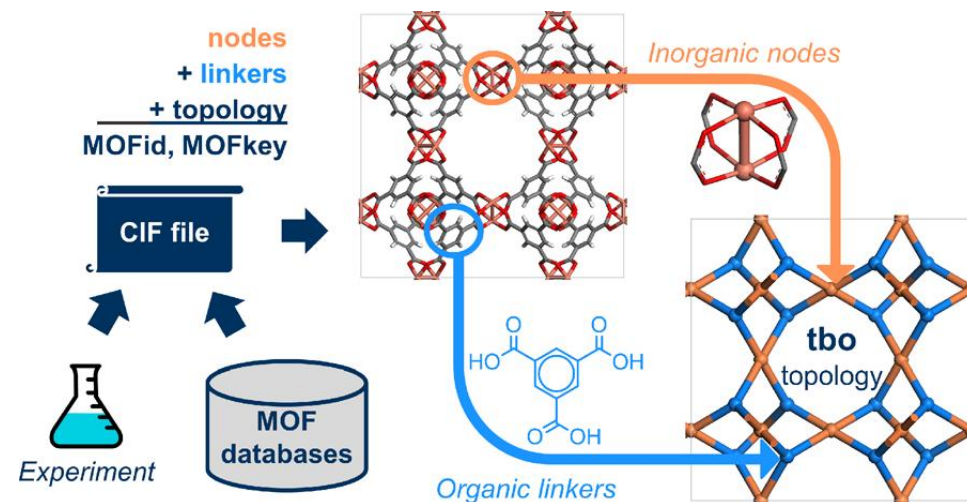


Accomplishments: Expanded MOF screening



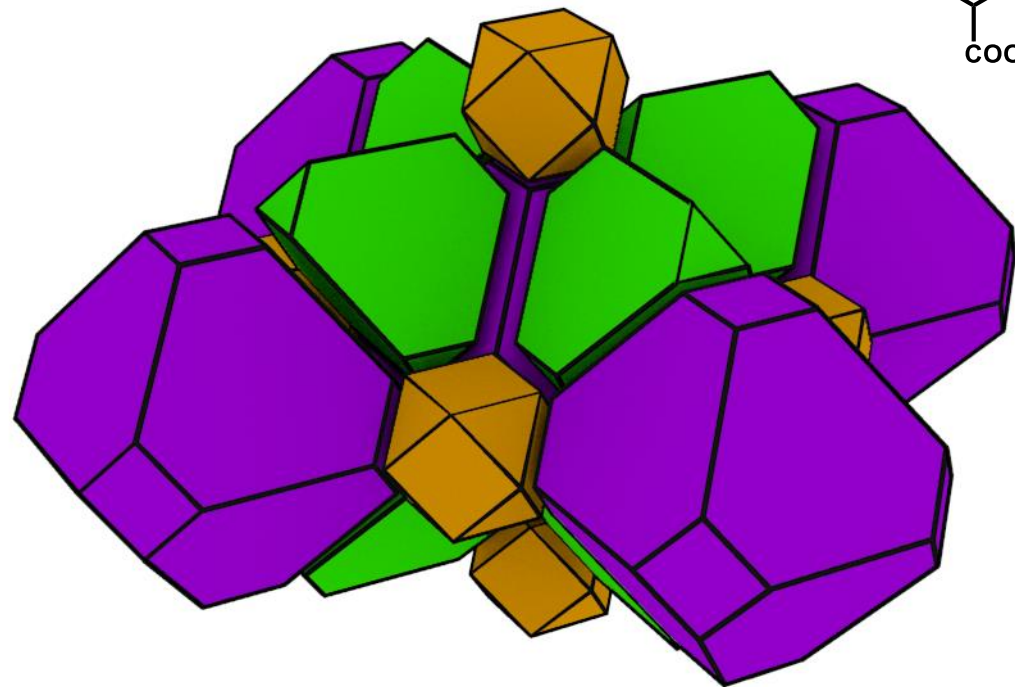
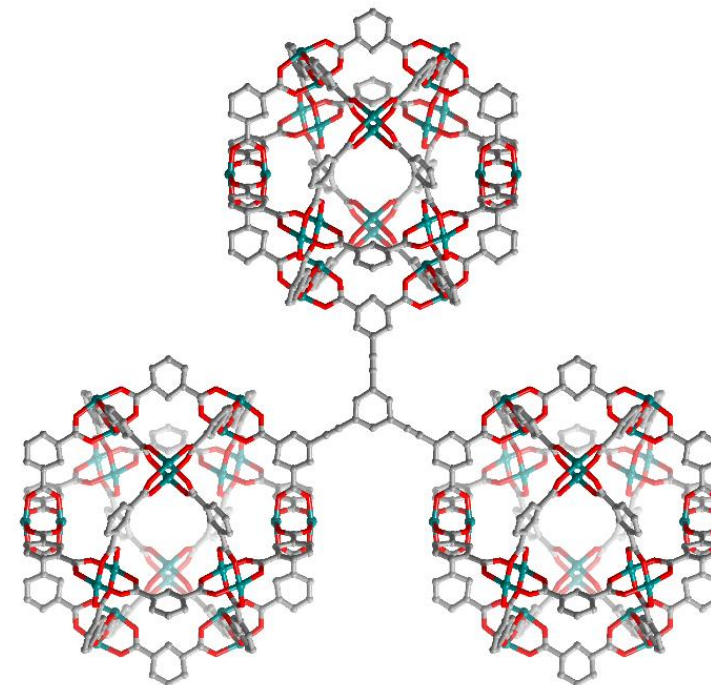
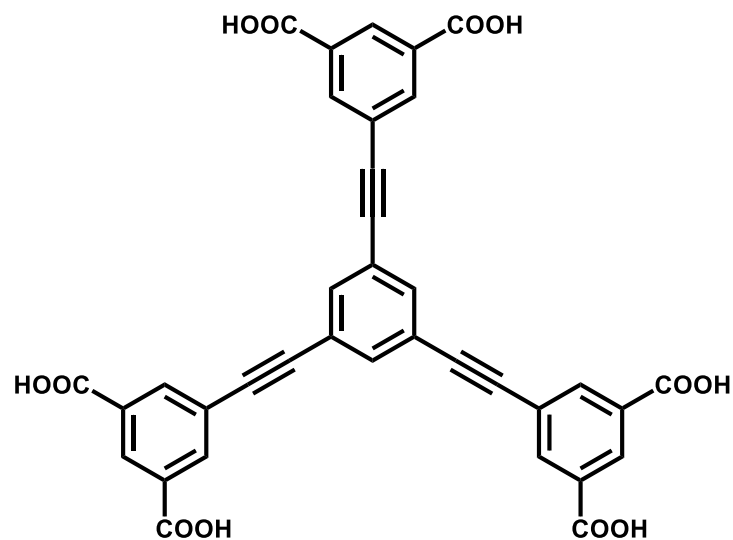
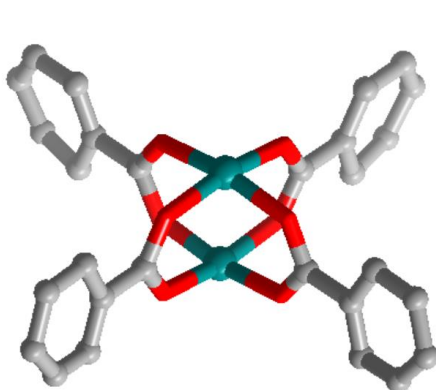
MOFid

- An identification scheme for MOFs



- “Disassemble” the MOF structure into its building blocks
- Have top hypothetical MOFs been synthesized previously?

Accomplishments: Identification of a promising candidate, PCN-61

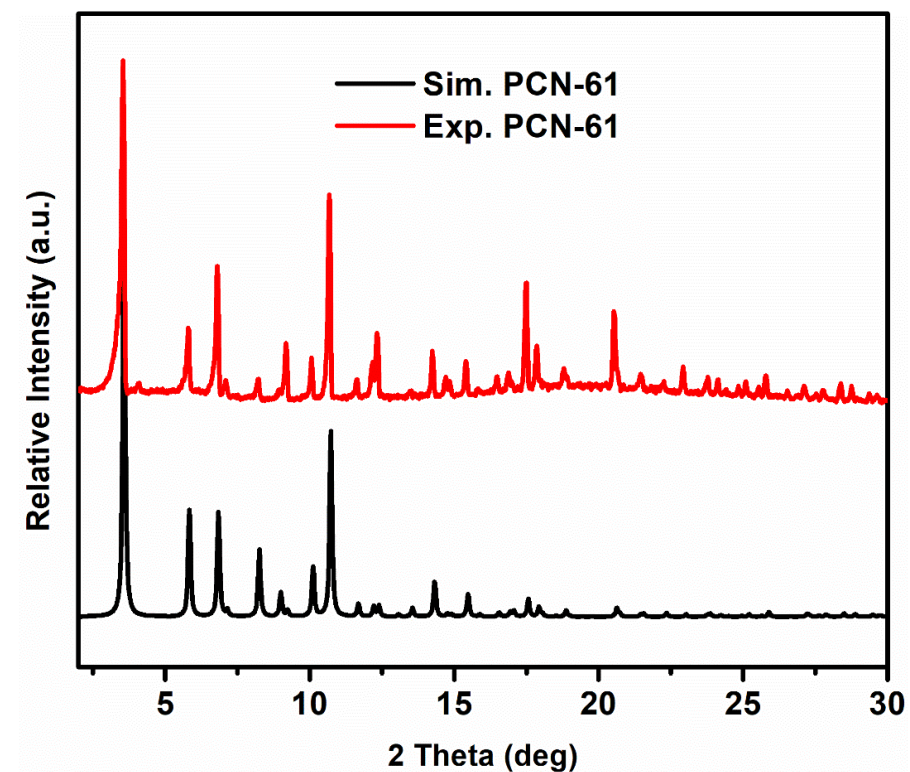
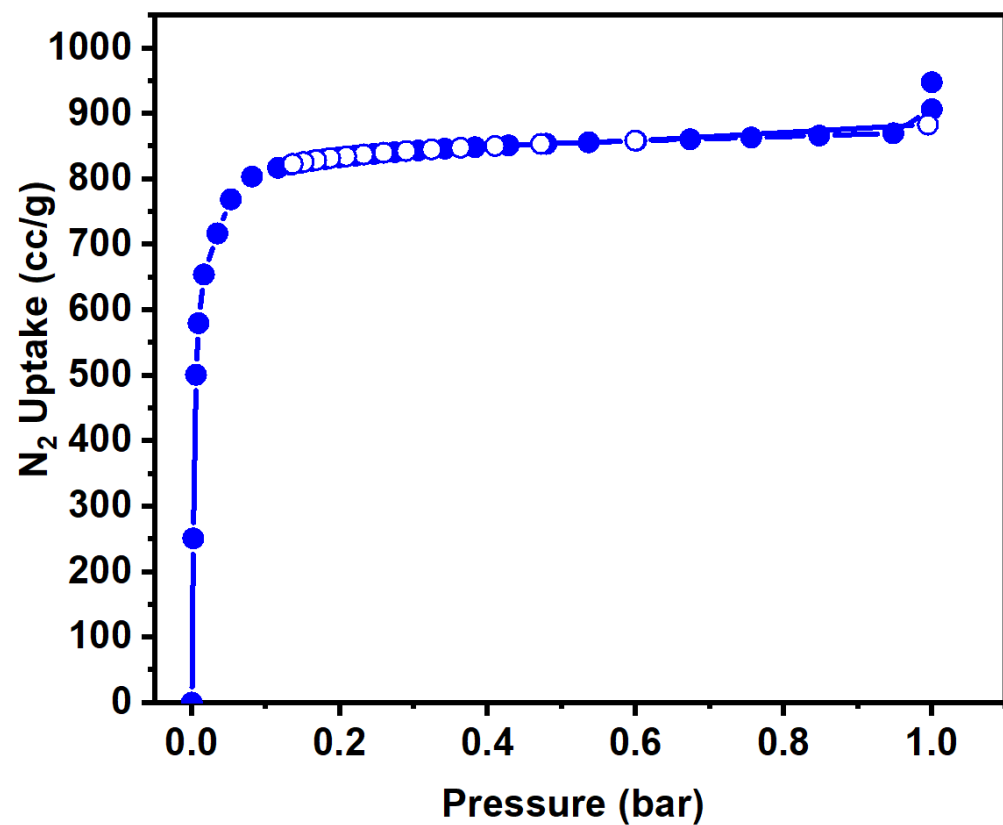


3-Cage Description

Yuan, D., Zhao, D., Sun, D. and Zhou, H.-C. *Angew Chem Int Ed* **2010**, 49, 5357.

- From MOFid, one MOF in the database was identified as PCN-61
- This MOF was selected for experimental testing
 - High theoretical deliverable capacity
 - Predicted: 51.4 g/L and 8.4 wt%

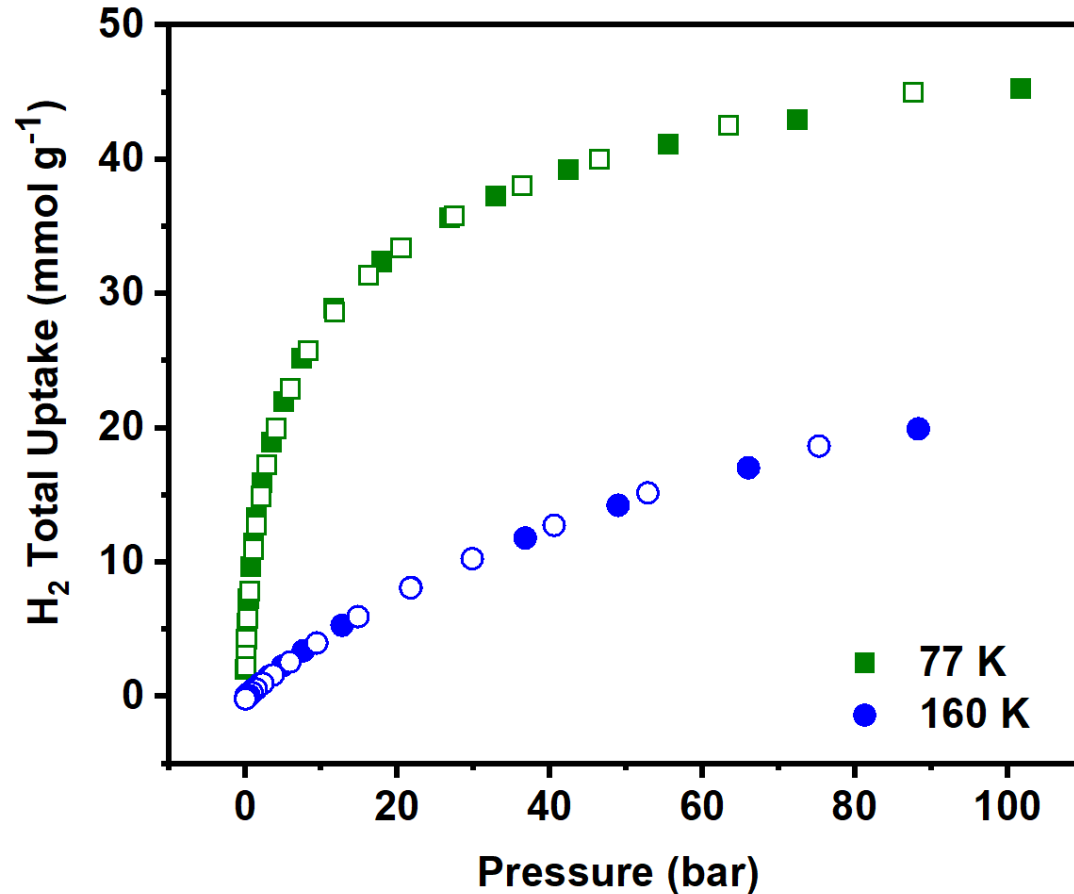
Accomplishments: Characterization of PCN-61



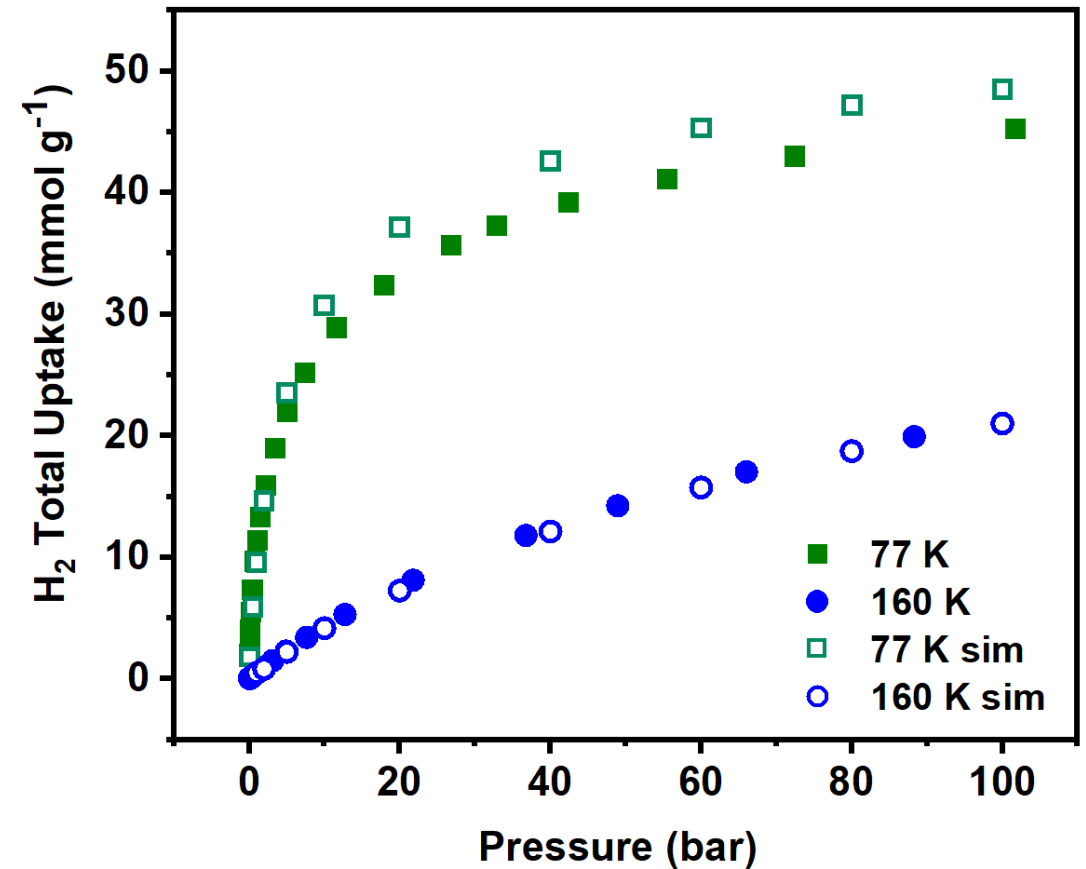
Theoretical pore volume: $1.36 \text{ cm}^3 \text{ g}^{-1}$
Pore volume measured at NIST: $1.35 \text{ cm}^3 \text{ g}^{-1}$.

Accomplishments: Hydrogen Isotherms of PCN-61 from NIST

Experimental ads/des isotherms



Experimental vs simulated ads isotherms



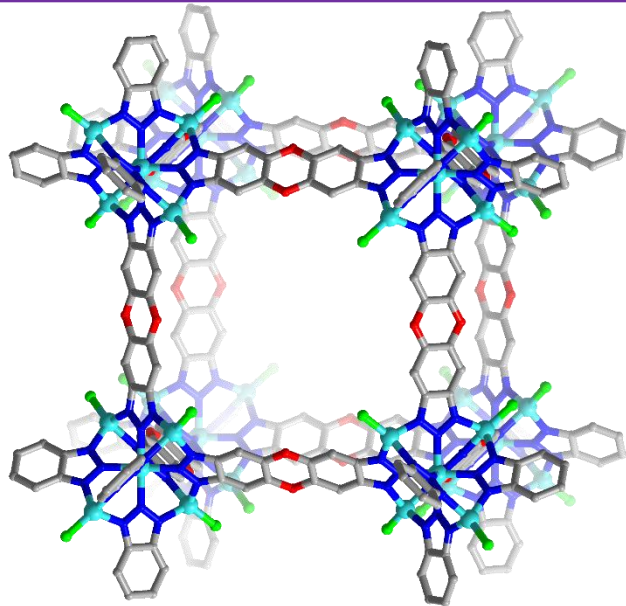
Working capacity

experimental: 7.9 wt% = 48.3 g/L*

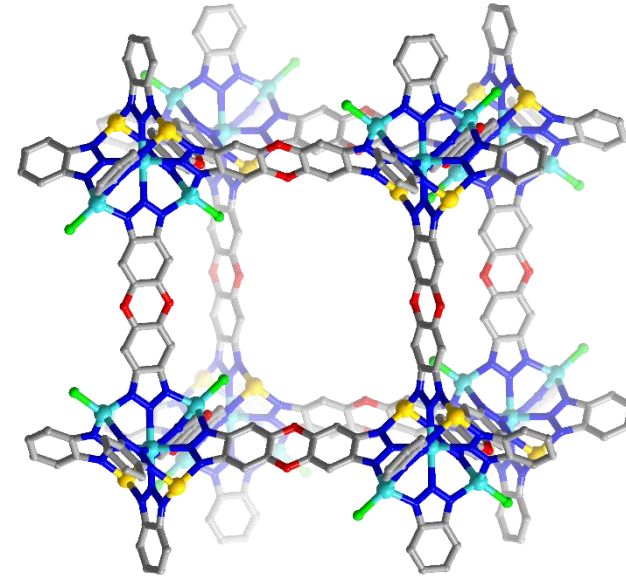
simulated: 8.4 wt% = 51.4 g/L*

*with crystallographic density

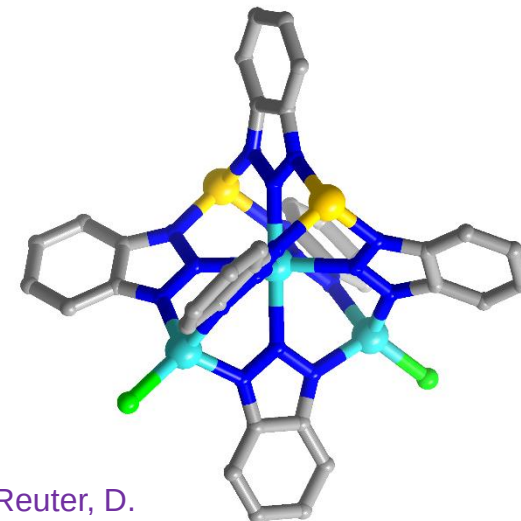
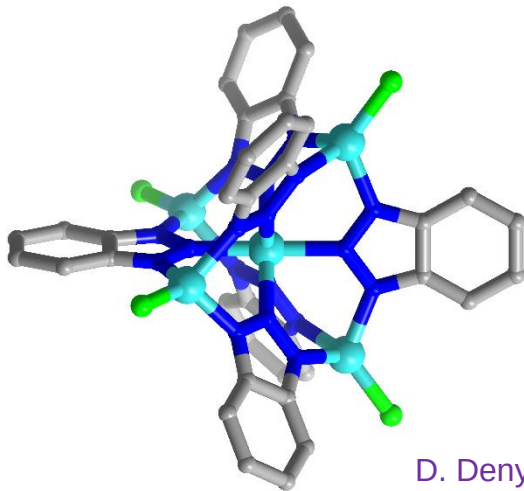
Accomplishments: Fine tuning of a previously identified MOF candidate MFU-4l



MFU-4l

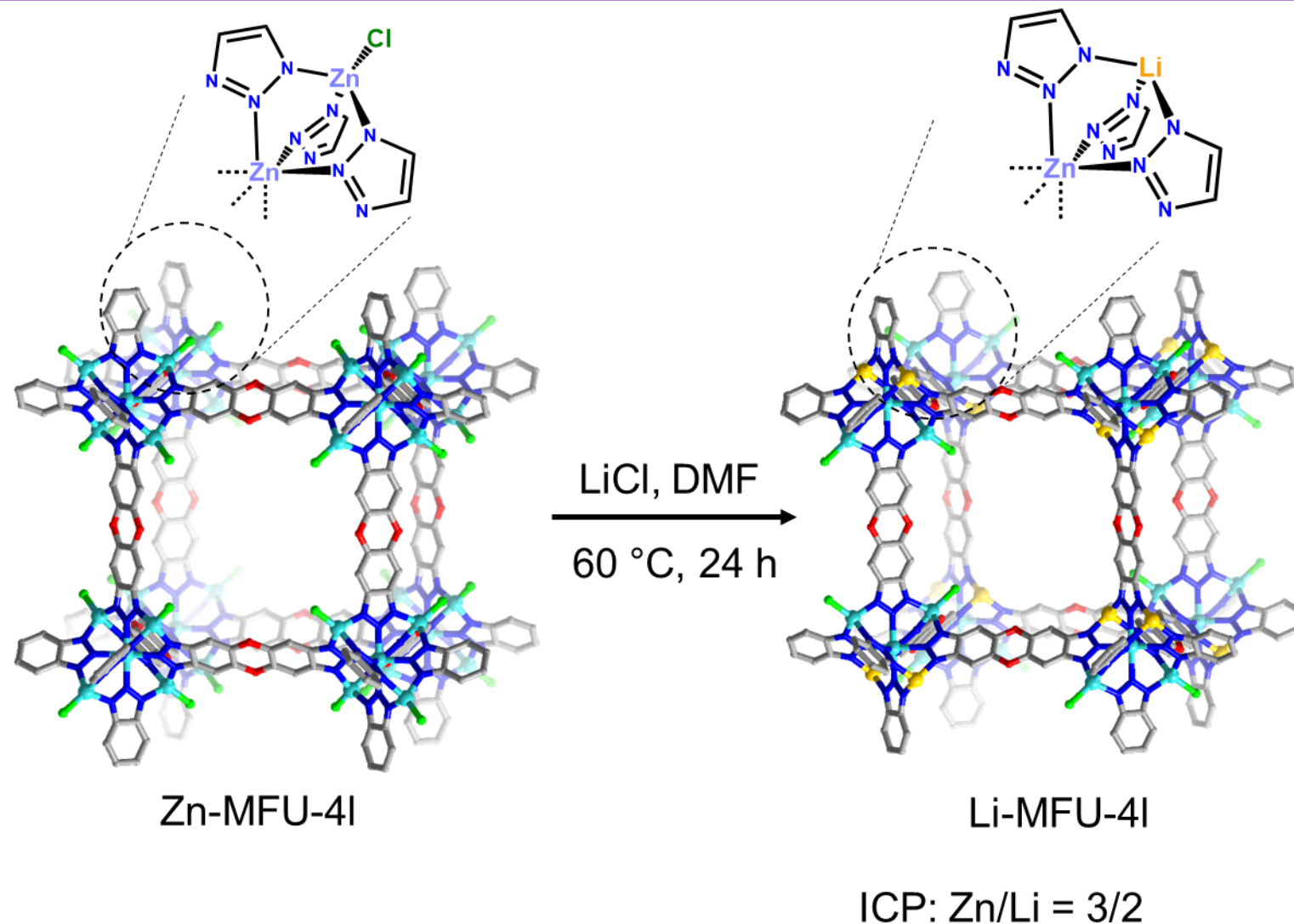


Li-MFU-4l



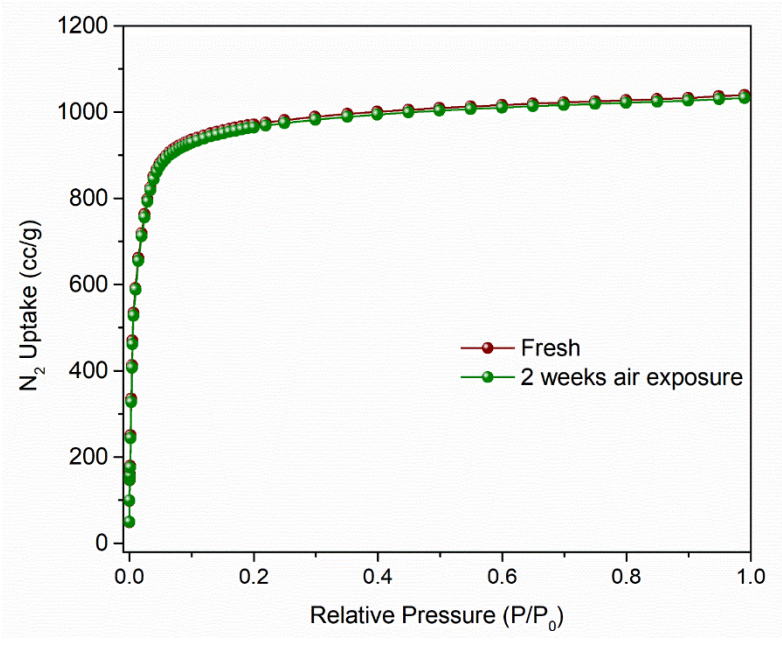
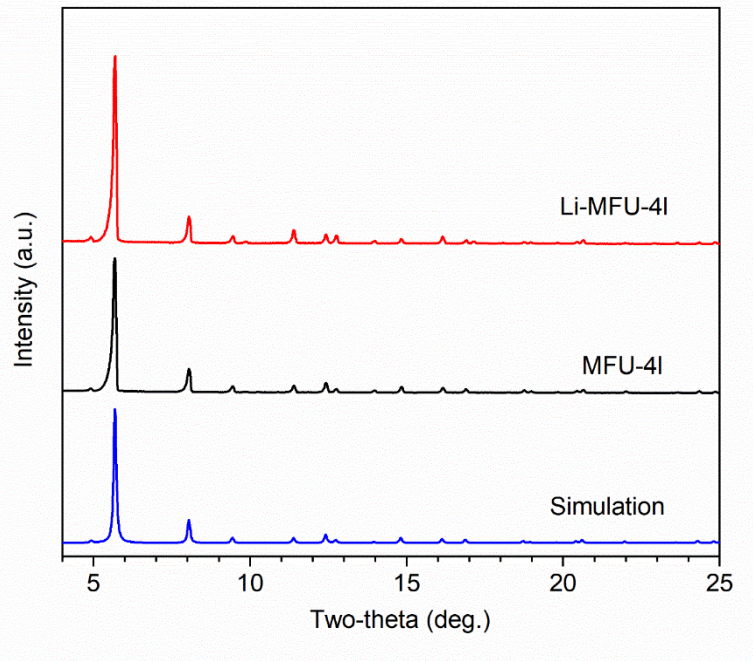
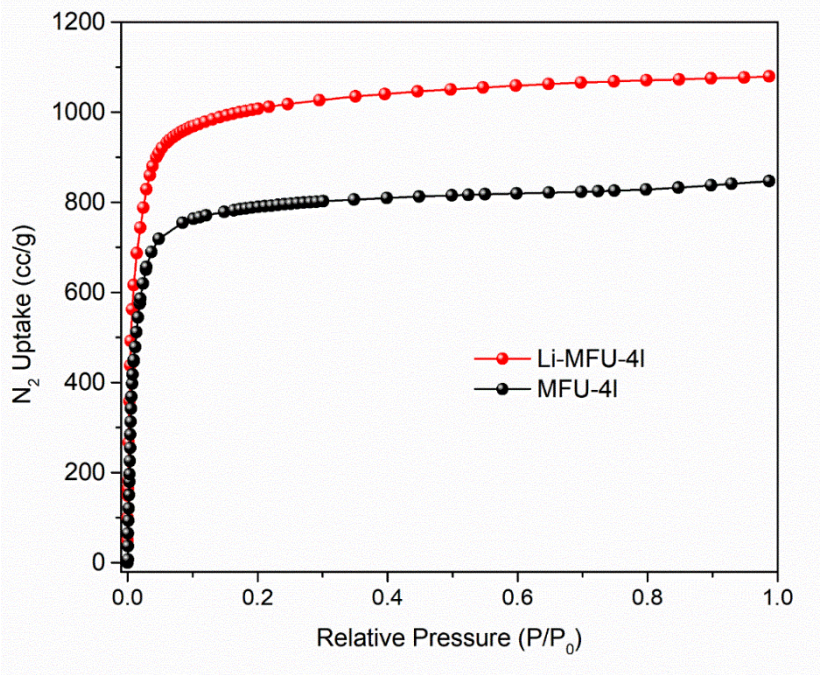
D. Denysenko, J. Jelic, O. V. Magdysyuk, K. Reuter, D. Volkmer, *Microporous Mesoporous Mater.* **2015**, 216, 146.

Accomplishments: Fine tuning of a previously identified MOF candidate MFU-4l



Accomplishments: Fine tuning of a previously identified MOF candidate

MFU-4l

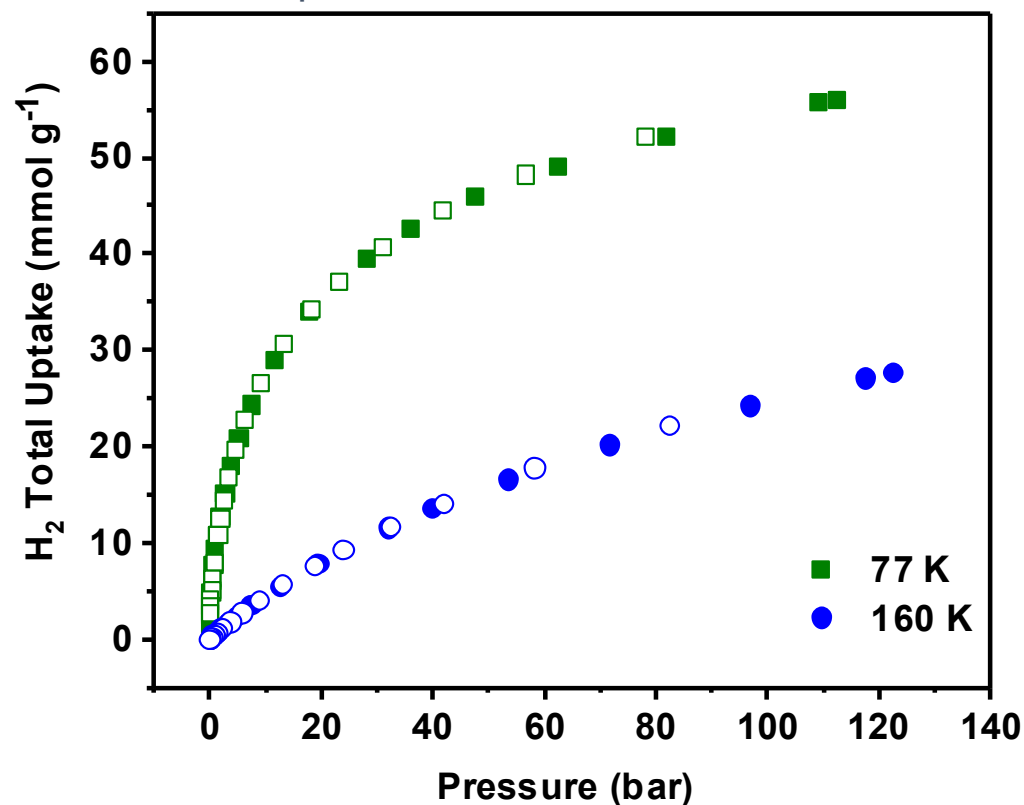


	Zn-MFU-4l	Li-MFU-4l
BET Area	3450 m ² /g	4030 m ² /g
Pore Volume	1.13 cm ³ /g	1.67 cm ³ /g

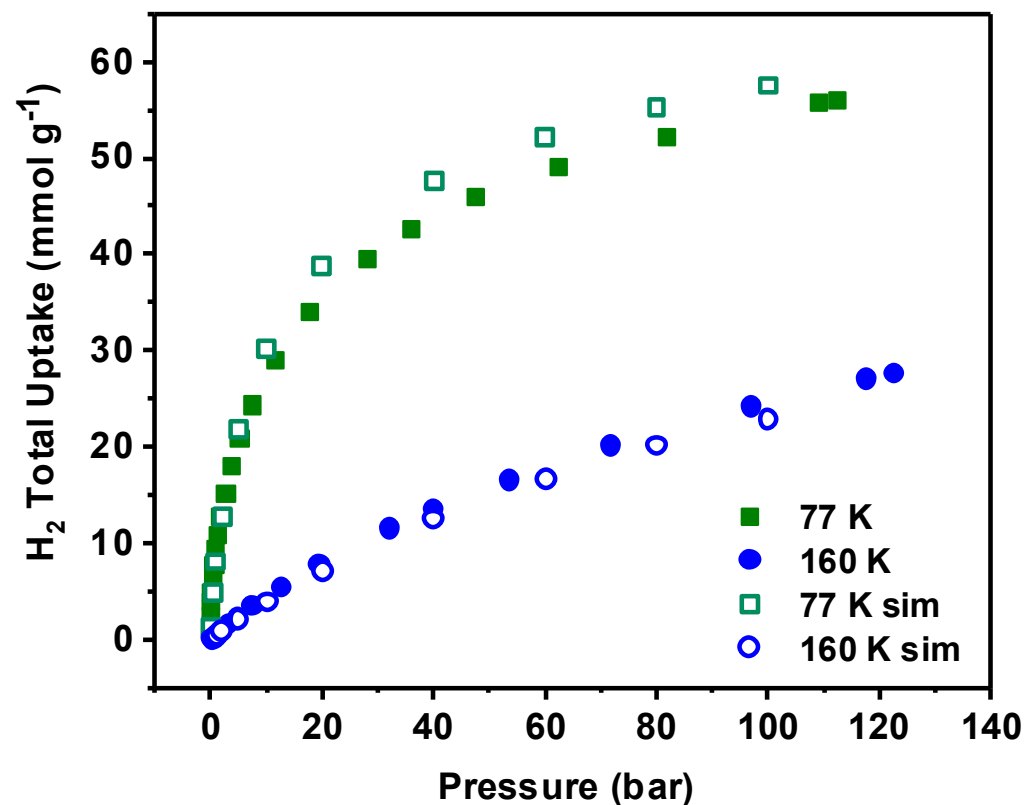
*Sample was reactivated under the activation condition of the fresh sample after air exposure test.

Accomplishments: Hydrogen isotherms of Li-MFU-4l from NIST

Experimental ads/des isotherms



Experimental vs simulated ads isotherms



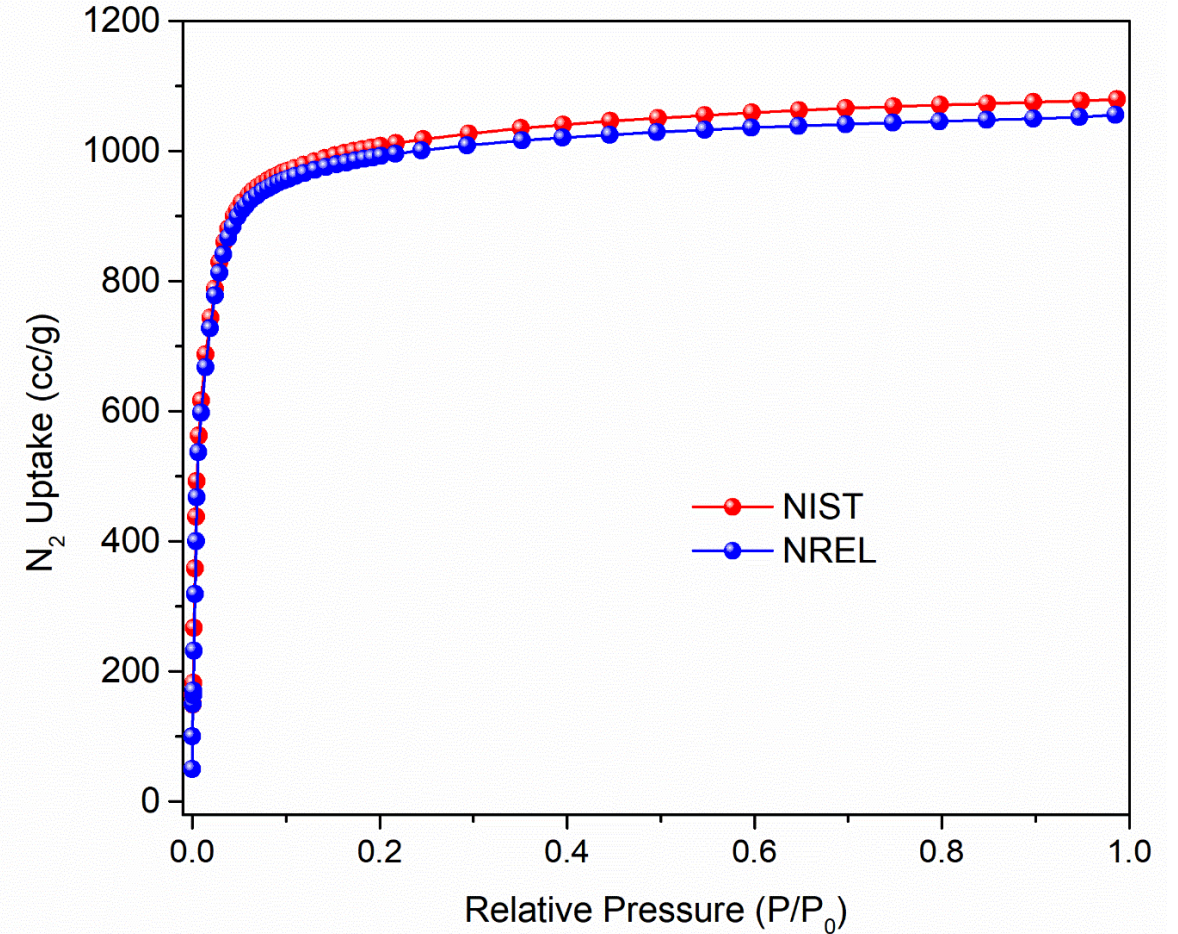
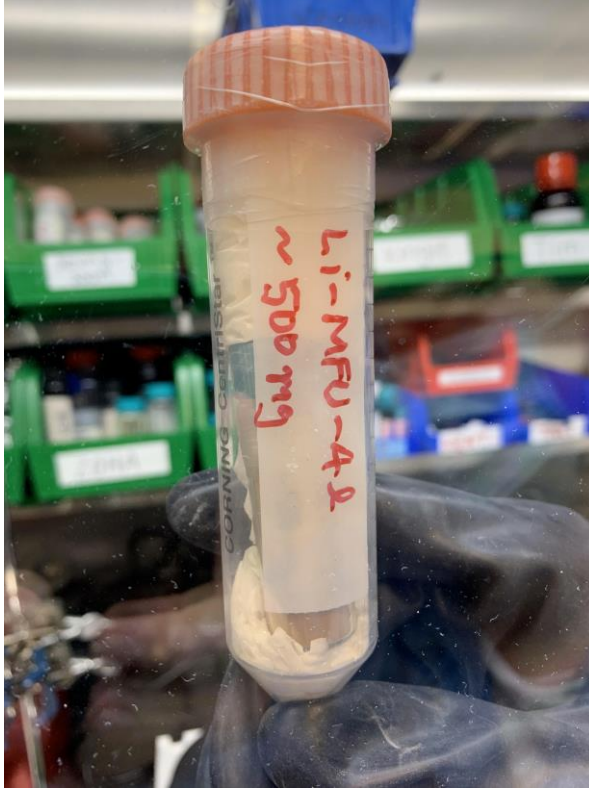
Working capacity

experimental: 9.54 wt% = 50.5 g/L*

simulated: 10.0 wt% = 53.06 g/L*

*density is obtained from the structure refined using experimental PXRD pattern

Accomplishments: Li-MFU-4l sample was delivered to NREL



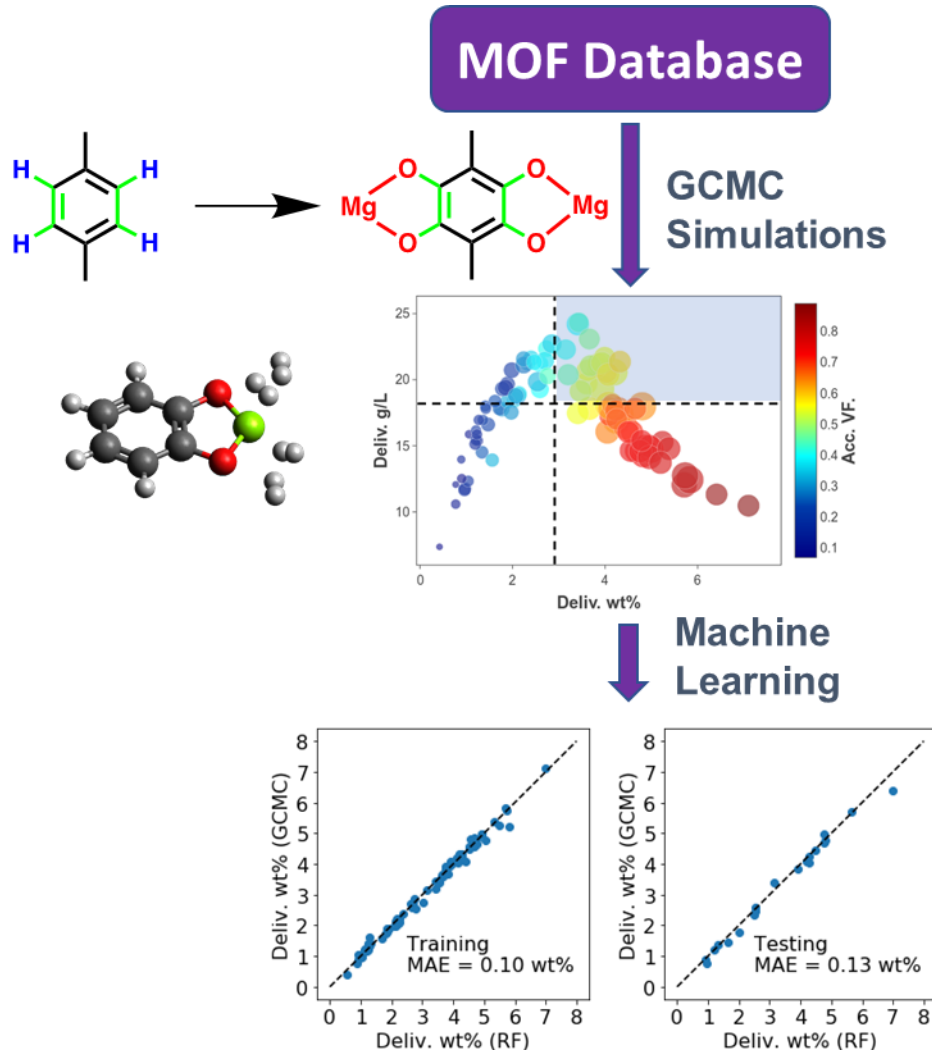
	NIST	NREL
BET Area	4030 m ² /g	4005 m ² /g
Pore Volume	1.67 cm ³ /g	1.63 cm ³ /g

Accomplishments: Responses to Previous Year Reviewers' Comments

The U.S. Department of Energy Hydrogen and Fuel Cells Program 2020 Annual Merit Review and Peer Evaluation (AMR) meeting was cancelled due to concerns about the COVID-19 pandemic. Therefore, **this project was not reviewed last year.**

Proposed Future Work: Metal catecholates for near ambient H₂ storage

Go/No Go for Year 2: Assuming Phase 1 metrics are met, demonstrate a material with a **10% improvement in usable gravimetric and volumetric capacities** compared to that synthesized in Phase 1 at the same conditions; **or** demonstrate a material with **hydrogen binding affinity of equal or larger than 15 kJ/mol determined from experimental isotherms**.



- We explored the possibility of using metal catecholate functionalized MOFs for room temperature (296 K) pressure swing (100bar → 5bar) H₂ storage.
- From a MOF database, we identified a set of MOFs with large numbers of sites that can potentially be functionalized with metal catecholate groups.
- GCMC simulations were performed for the (computationally) functionalized MOFs, in which we found 20 MOFs that meet both gravimetric (2.8 wt%) and volumetric (18 g/L) targets.
- A supervised machine learning model was also developed, which can accurately predict the deliverable H₂ capacity for a MOF using its structural properties.
- Experimental work to test the simulation results is in progress.
(Chen and Snurr, *to be submitted*)
- Any proposed future work is subject to change based on funding levels₃₀

1. National Institute of Standards and Technology (NIST)

Testing isotherms of sorbents from NU

- Novel sorbent synthesis by post-metalation of some sorbents provided from NU
- MFU-4l family and PCN-61 has been tested at NIST

1. National Renewable Energy Laboratory (NREL)

- Final validation of sorbent performances for the samples from NU
- Li-MFU-4l has been sent to NREL for validation

Project Summary

- Machine learning model has been applied to facilitate the process of computational screening on 105,764 MOF structures. The ML-predicted capacity was used as a guide for selecting candidates to run more computationally expensive atomistic GCMC simulations. Among 3,460 MOFs which were selected and simulated by GCMC, 72 structures were predicted to have >52 g/L deliverable capacity.
- We modified the MOF Zn-MFU-4l, a top candidate from a previous screening, by substituting Zn(II)-Cl groups with Li to increase the pore volume. GCMC simulations showed that the deliverable capacity is higher than 52 g/L.
- Li-MFU-4l sample was tested at NIST and showed hydrogen uptake of 9.54 wt% = 50.5 g/L under the PSA/TSA conditions mention in our proposal. Air stability of this sample was demonstrated by exposing the same to air for two weeks. ~500 mg of activated sample was shipped to NREL for validation.
- PCN-61, a MOF identified from high-throughput computational screening with promising uptake capacities, was synthesized and activated with a pore volume promised from crystal structure and hydrogen isotherms were measured at NIST

Technical Backup Slide: Progress Toward Milestones

Milestone Q1.1	Synthesis, characterization and N ₂ isotherm collection for NU-1500 and its isorecticular analogues. Collection of high-pressure hydrogen isotherms of different temperatures for PSA/TSA application to maximize working capacity.	Completed
Milestone Q1.2	Screen databases of real and hypothetical MOFs to find structures with highest density of potential catecholate/bipyridine sites. Down-select from these candidates to 10 most promising materials based on synthetic feasibility. Use atomistic simulations to study hydrogen adsorption in 10 promising materials identified in screening modified with Mg catecholate/bipyridine sites.	Completed
Milestone Q1.3	Expand database of predicted MOFs to include 100,000 MOFs with various topologies as well as new building blocks from commercially available sources. Screen this database for hydrogen uptake at cryogenic temperatures and pressures of interest using machine learning algorithm and GCMC to find top 10 candidates in terms of both volumetric and gravimetric deliverable capacities.	Completed
Go/No Go for Year 1	Demonstrate a material with H ₂ working capacity exceeding 8 wt% and 52 g/L under lower temperature swing operation (5-100 bar and 77-160 K); OR 2.8 wt% and 18 g/L under higher temperature swing operation (5-100 bar and 233-296 K). Here all goals are at material level, not system level and wt% = (mass of H ₂) / (mass of MOF + mass of H ₂) × 100%.	97% completed based on the data obtained from NIST. The sample was delivered to NREL for validation.

Technical Backup Slide: Technology Transfer Activities

- Nothing to report