Project ID: ST144

HyMARC Seedling: Optimized Hydrogen Adsorbents via Machine Learning and Crystal Engineering

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DOE Annual Merit Review, June 15, 2018, Washington, DC

Overview

Timeline and Budget

Project Start Date: Sept 1st, 2017
Project End Date: August 31st, 2018

Total Project Budget: $1,047,000

Federal Share:

UM: $807,000
Ford: $192,000
Total: $999,000

$250,000 (Y1)
$398,000 (Y2)
$351,000 (Y3)

Cost Share: $48,000 (Ford)

Total Funds Spent:* ~$100,000

*Estimated as of 4/30/18

Barriers

Barriers addressed

- Volumetric Density
- Gravimetric Density

Partners

Interactions/collaborations:

Ford Motor Company, Hydrogen Storage Engineering Center of Excellence (HSECoE)

Project lead:

Don Siegel, University of Michigan

Background (1)

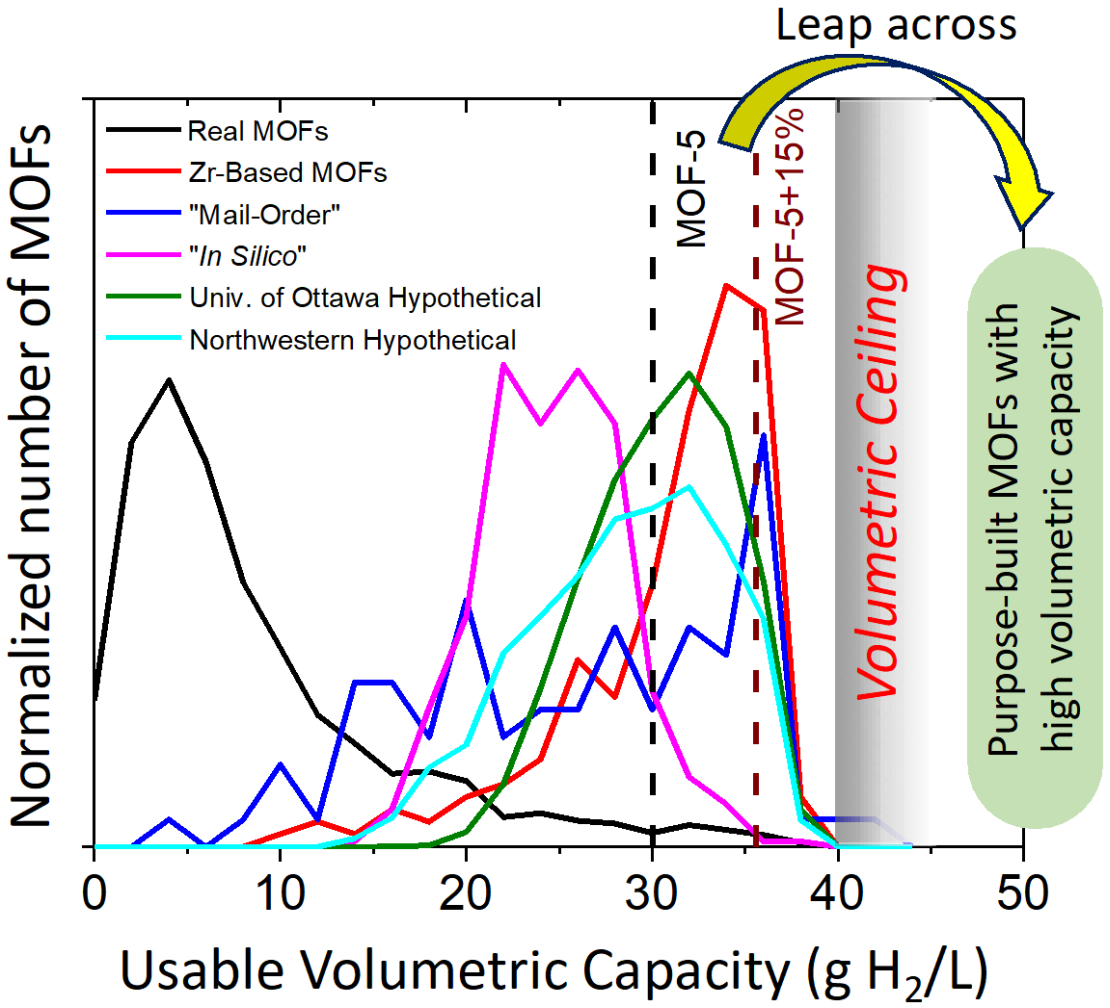
- A high-capacity, low-cost method for storing hydrogen remains one of the primary barriers to the widespread commercialization of fuel cell vehicles
- Storage via adsorption in MOFs is promising due to their fast kinetics, reversibility, and tunable properties
- A viable adsorbent must exhibit a high intrinsic (i.e., materials level) H_2 capacity, and pack in a dense fashion at the system level
  - Our prior screening (project ST122) revealed that no known MOF exhibits a usable volumetric capacity exceeding 40 g H_2/L (assuming an isothermal pressure swing between 100 and 5 bar at 77 K)
  - Analysis by the HSECoE has shown that inefficient materials packing can result in capacity reductions of more than 60% compared to the single-crystal level. These inefficiencies can negate improvements in volumetric performance achieved at the materials level
  - The present project addresses both of these challenges

Project goal: Overcome volumetric limitations associated with physisorptive hydrogen storage at both the materials and systems level in metal-organic frameworks (MOFs)

Relevance (1)

Screening of ~500,000 MOFs reveals that essentially no compounds exceed 40 g/L usable capacity

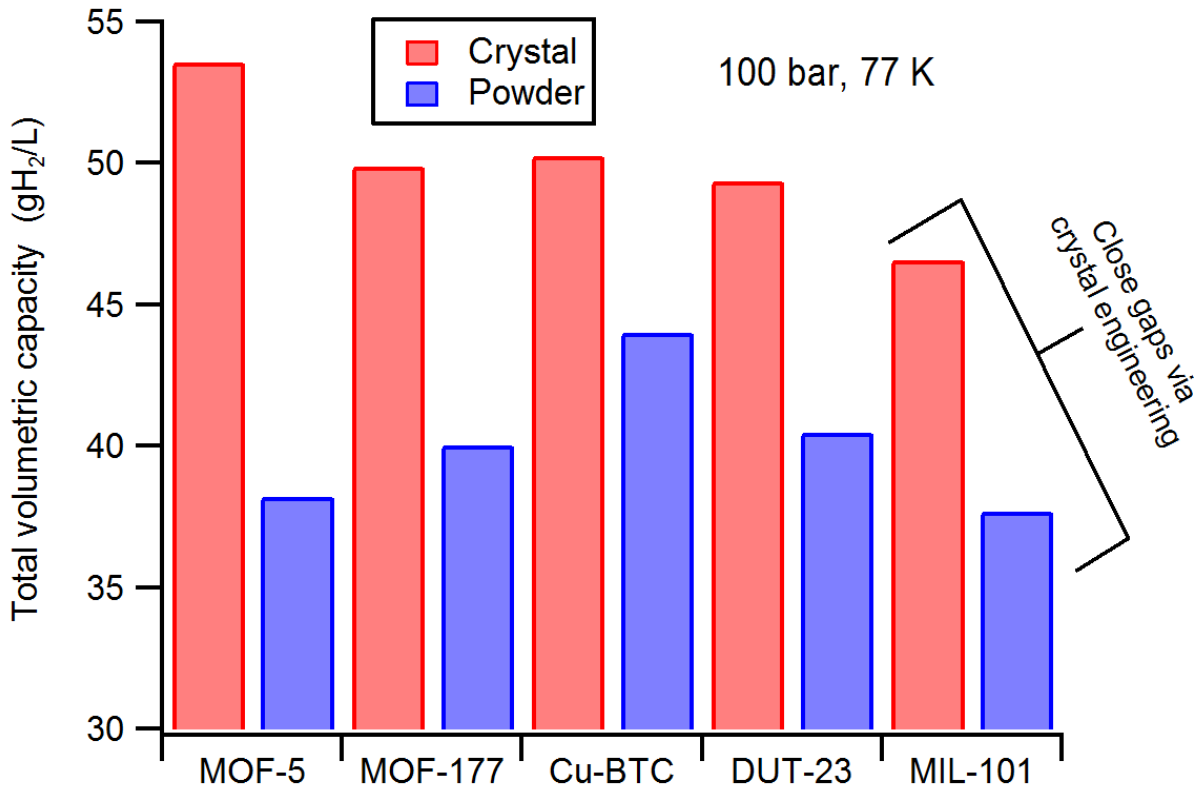
→ New MOFs needed to break through volumetric ceiling



Relevance (2)

Packing inefficiencies result in significant volumetric penalties in adsorptive hydrogen storage systems

→ Increase packing density via crystal engineering



Data courtesy of Justin Purewal, Ford Motor Company

Relevance (3)

Objective 1: Apply machine learning techniques to identify, design, and demonstrate high-capacity MOFs

- Demonstrate usable volumetric capacities exceeding 50 H_2 g/L (single-crystal/pressure swing)
- No compromise to gravimetric capacity, kinetic performance, or reversibility
- If successful, these compounds will set a new high-water mark for H_2 density in adsorbents at cryogenic conditions

Objective 2: Control MOF crystal morphology and crystallite size distribution to increase packing density

- Increase packing density of target high capacity MOF by at least 30% (compared to its powder tap density)
- Do so with less than 15% decrease in gravimetric performance

Year 1 Milestones

Milestone Summary Table							
Recipient Name:		University of Michigan					
Project Title:		Optimized Hydrogen Adsorbents via Machine Learning and Crystal Engineering					
Task Number	**Task or Subtask Title**	**Milestone Type**	**Milestone Number**	**Milestone Description**	**Milestone Verification Process**	**Quarter (from Start)**	**Status**
1.0							
1.1	MOF performance from scratch	Milestone	M1.1.1	Demonstrate ability to predict usable capacity of an arbitrary MOF to within 85% of GCMC capacity using only crystal structure as input	Comparison of machine learning prediction with GCMC calculation	1	**Complete**
1.2	Structure-performance correlations	Milestone	M1.2.1	Correlate MOF geometric properties with capacity	Random forest, latent variable, or support vector machine analysis of MOF properties	2	**Complete**
1.3	MOF reverse engineering	Go/No-Go	D1	Identify ranges for 4 MOF crystallographic properties (surface area, density, pore volume, & porosity) consistent with usable volumetric capacity of at least 40 g/L and usable gravimetric capacity of at least 7 wt. % (assuming an isothermal pressure swing between 100 and 5 bar at 77 K) based on single crystal density. Demonstrate that the identified ranges are within the realm of possibility for the development of new MOFs, and thus provide a pathway for meeting the DOE storage targets.	Random forest or SVM analysis of MOF properties and direct GCMC simulation	4	**On Track**
2.0							
2.1	Morphological engineering	Milestone	M2.1.1	Identify at least 2 additives capable of controlling morphology from cubes to octahedra	Optical microscopy or SEM measurements	3	**In progress – on schedule**

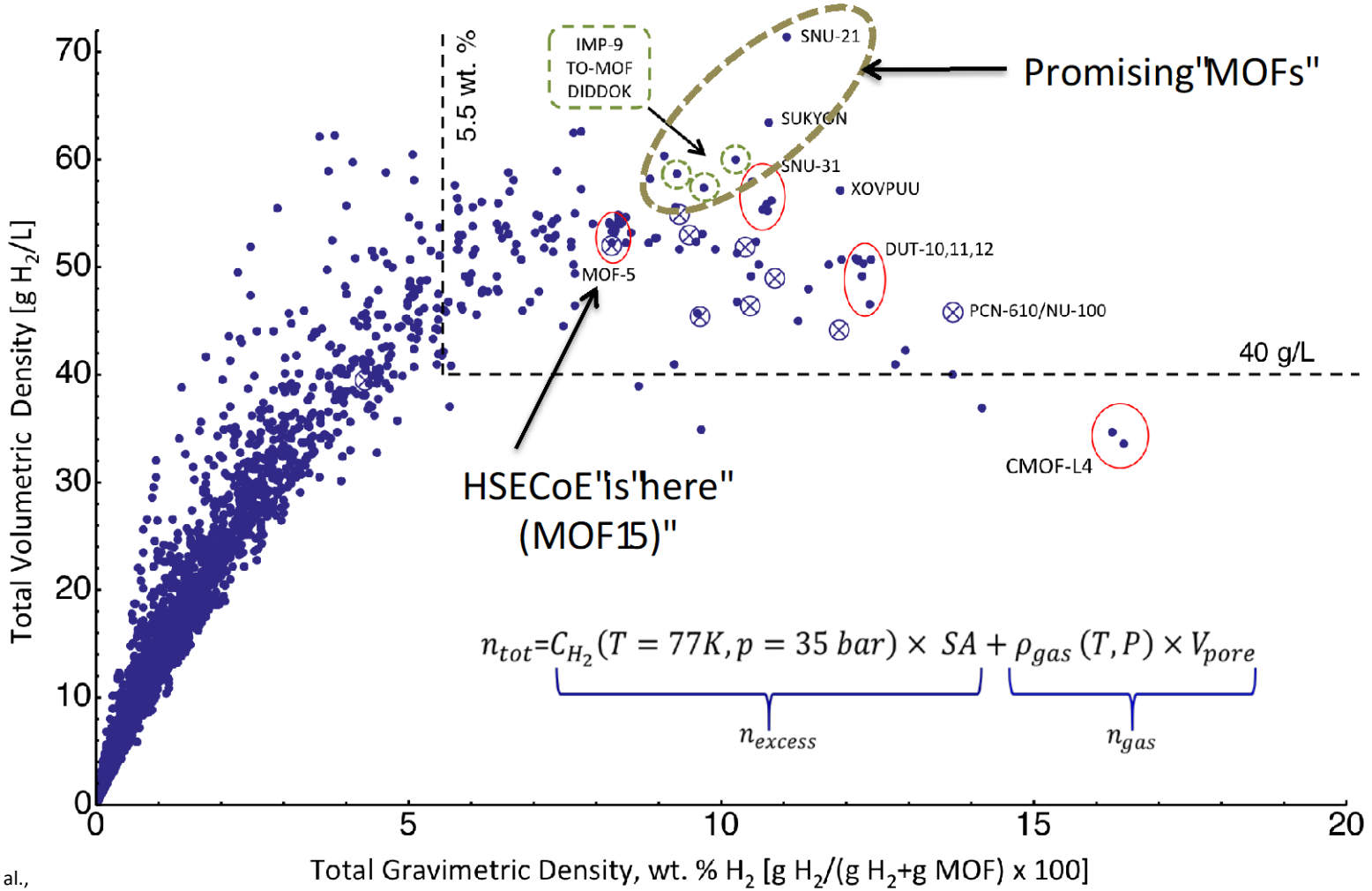
Approach

Notes:

- Unless otherwise stated, all measurements and calculations are performed at T = 77 K.

High-throughput Screening

Prior work: developed a database of MOFs by mining the CSD. Chahine rule and crystal structure were used to predict H_2 capacity in thousands of compounds



J. Goldsmith, et al., Chem. Mater., **25**, 3373 (2013).

MOF Database

Compiled a MOF database of ~500,000 compounds

43,000+ MOFs assessed for temperature+pressure swing storage

~100,000 MOFs assessed for pressure swing storage

Source	Available in database	Zero surface area	H_2 capacity evaluated empirically	H_2 capacity evaluated with GCMC
UM+CoRE+CSD17 (RM)	15,235	2,950	12,285	12,799
Mail-Order MOFs (MO)	112	4	108	112
In Silico MOFs (IS)	2,816	154	2,662	466
In Silico Surface MOFs (ISS)	8, 885	283	8,602	1,058
MOF-74 Analogs (M74)	61	0	61	61
ToBaCCo (TB)	13,512	214	13,298	290
Zr-MOFs (ZR)	204	0	204	204
NW Hypothetical MOFs (NW)	137,000	30,160	106,840	12,374
UO Hypothetical MOFs (UO)	324,500	32,993	291,507	16,372
In-house synthesized via hypothetical design	18	0	18	5
Total	**493,458**	**66,758**	**435,585**	**43,741**

RM: (a) **UM:** J.Goldsmith, A. G. Wong-Foy, M. J. Cafarella, and D. J. Siegel, *Chem. Mater.,* 25 , 3373–3382 (2013); (b) **CoRE:** Y. G. Chung, *et al.*, *Chem. Mater.*, 26, 6185–6192 (2014); (c) **CSD17**: P. Z. Moghadam et al., *Chem. Mater.,* 29, 2618–2625 (2017).

MO: R. L. Martin, L.-C. Lin, K. Jariwala, B. Smit, M. Haranczyk, *J. Phys. Chem. C* 117, 12159-12167 (2013);

IS: Y. Bao, R. L. Martin, M. Haranczyk, M. W. Deem, *J. Phys. Chem. C* 119, 186-195 (2015).

ISS: Y. Bao, R. L. Martin, C. M. Simon, M. Haranczyk, B. Smit, M. W. Deem, *Phys. Chem. Chem. Phys.,* 17, 11962-11973 (2015).

M74: M. Witman, S. Ling, S. Anderson, L. Tong, K.C. Stylianou, B. Slater, B. Smit, M. Haranczyk, *Chem. Sci.*, 7, 6263-6272 (2016).

TB: Y. J. Colón, D. A. Gómez-Gualdrón, and R. Q. Snurr, *Cryst. Growth Des.,* 17, 5801–5810 (2017).

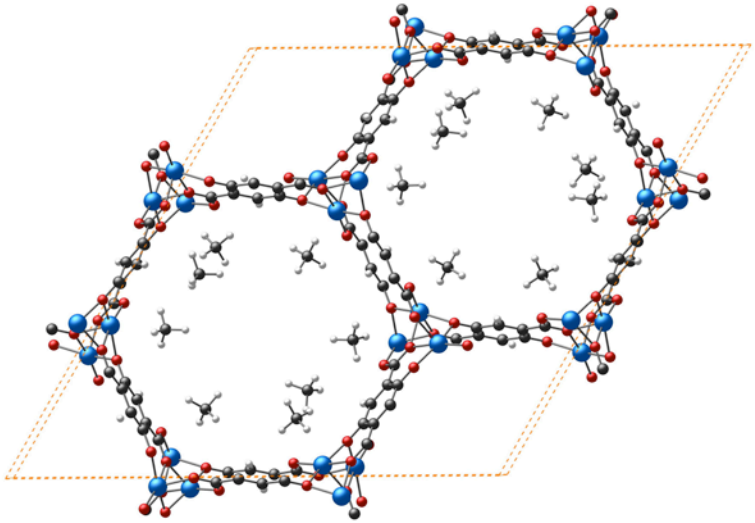
ZR: D. A. Gómez-Gualdrón, O.V. Gutov, V. Krungleviciute, B. Borah, J. E. Mondloch, J. T. Hupp, T. Yildirim, O.K. Farha, R.Q. Snurr, *Chem. Mater.* 26, 5632-5639 (2014).

NW: C. E. Wilmer, M. Leaf, C. Y. Lee, O. K. Farha, B. G. Hauser, J. T. Hupp, R. Q. Snurr, *Nat. Chem.* 4, 83–89 (2012).

UO: M. Z. Aghaji, M. Fernandez, P. G. Boyd, T. D. Daff, and T. K. Woo, *Eur. J. Inorg. Chem.,* 2016, 4505–4511 (2016).

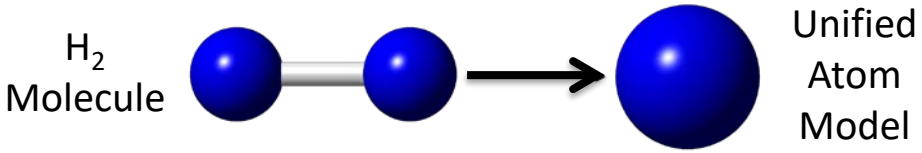
Grand Canonical Monte Carlo

- GCMC = atomistic method that calculates the total amount of H_2 (adsorbed + gas phase) contained within the pore space of a MOF at given T, P
- Does not rely on empirical correlations such as the Chahine-rule



Example GCMC simulation of CH_4 adsorption in Ni-DOBDC at 298 K and 35 bar

- Calculations employ the MGS* and the **Pseudo-FH**** unified atom models for H_2-MOF interactions
- MOF atoms are fixed



$$U_{ij}(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$

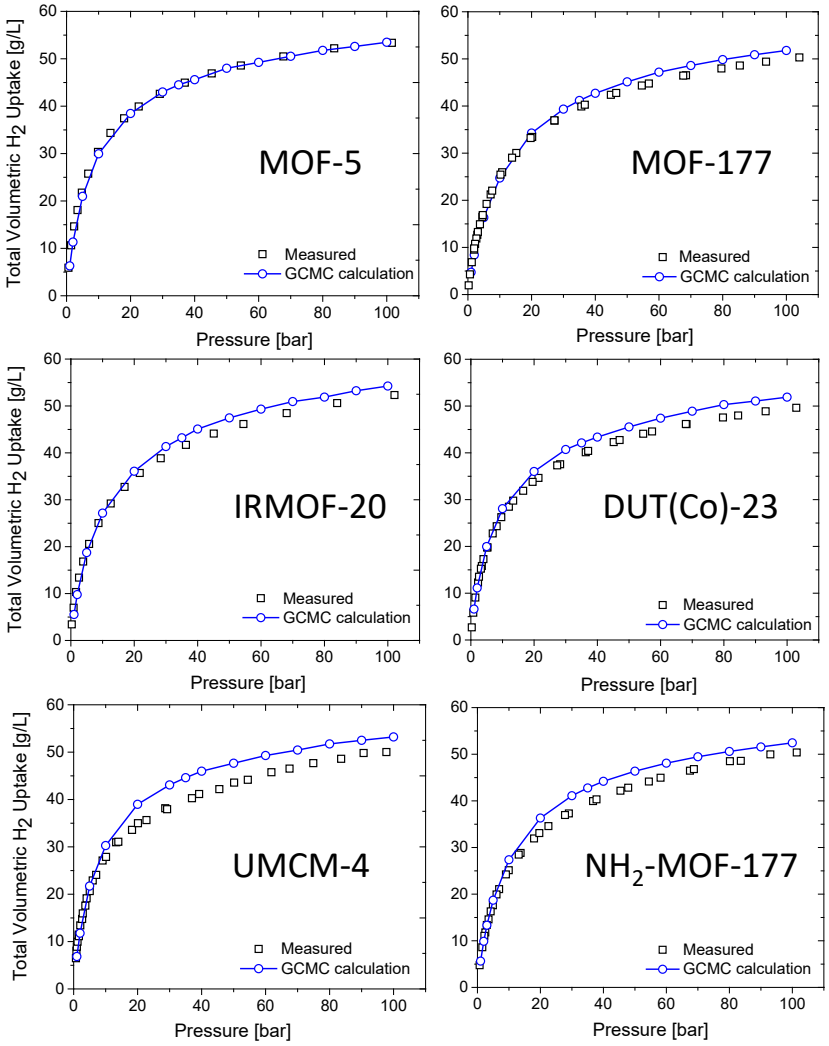
Force Field	Sigma (Å)	Epsilon/k_B (K)
MGS	2.958	36.7
Pseudo-FH	3.064	30.1

*Michels, de Graaff and Seldam, *Physica*, **1960**, 26, 393; Ryan, Broadbelt, and Snurr, *Chem. Comm.* 2008, 4134
Fischer, Hoffmann, Fröba, *ChemPhysChem*, **2009,10, 2647.

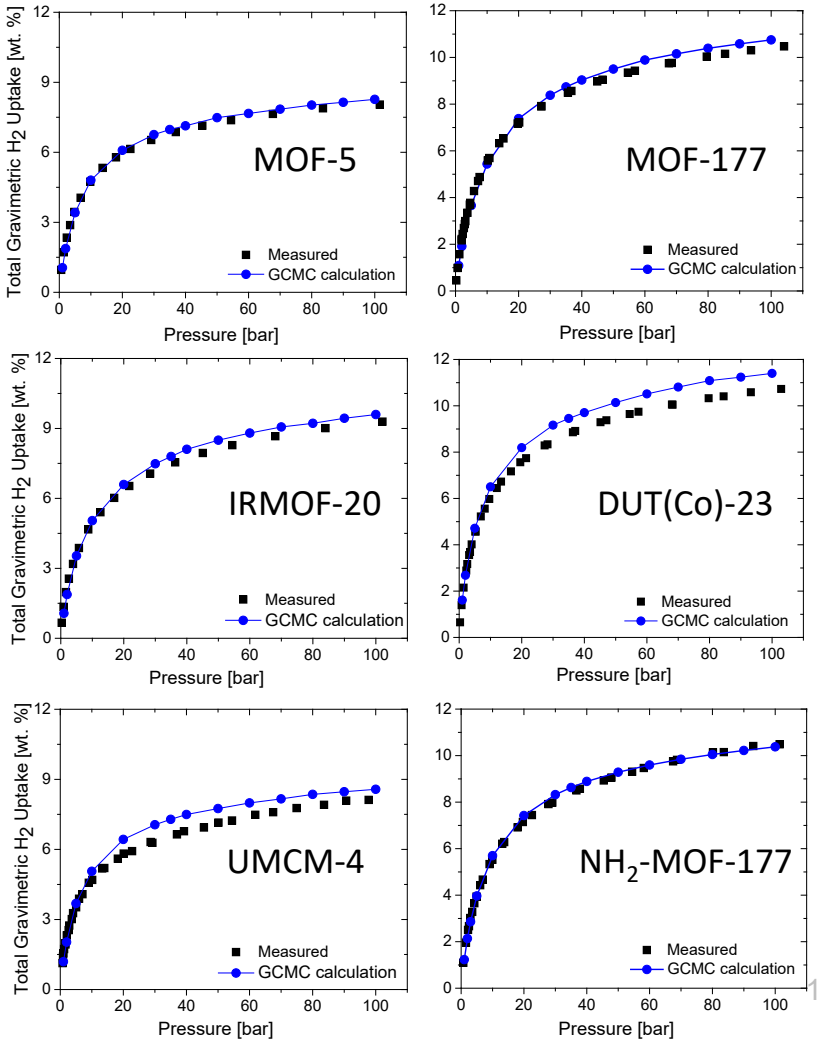
Examples of Simulated Isotherms

GCMC isotherms calculated with the pseudo-Feynman-Hibbs interatomic potential are in very good agreement with our measured isotherms

Total Volumetric H_2 Uptake



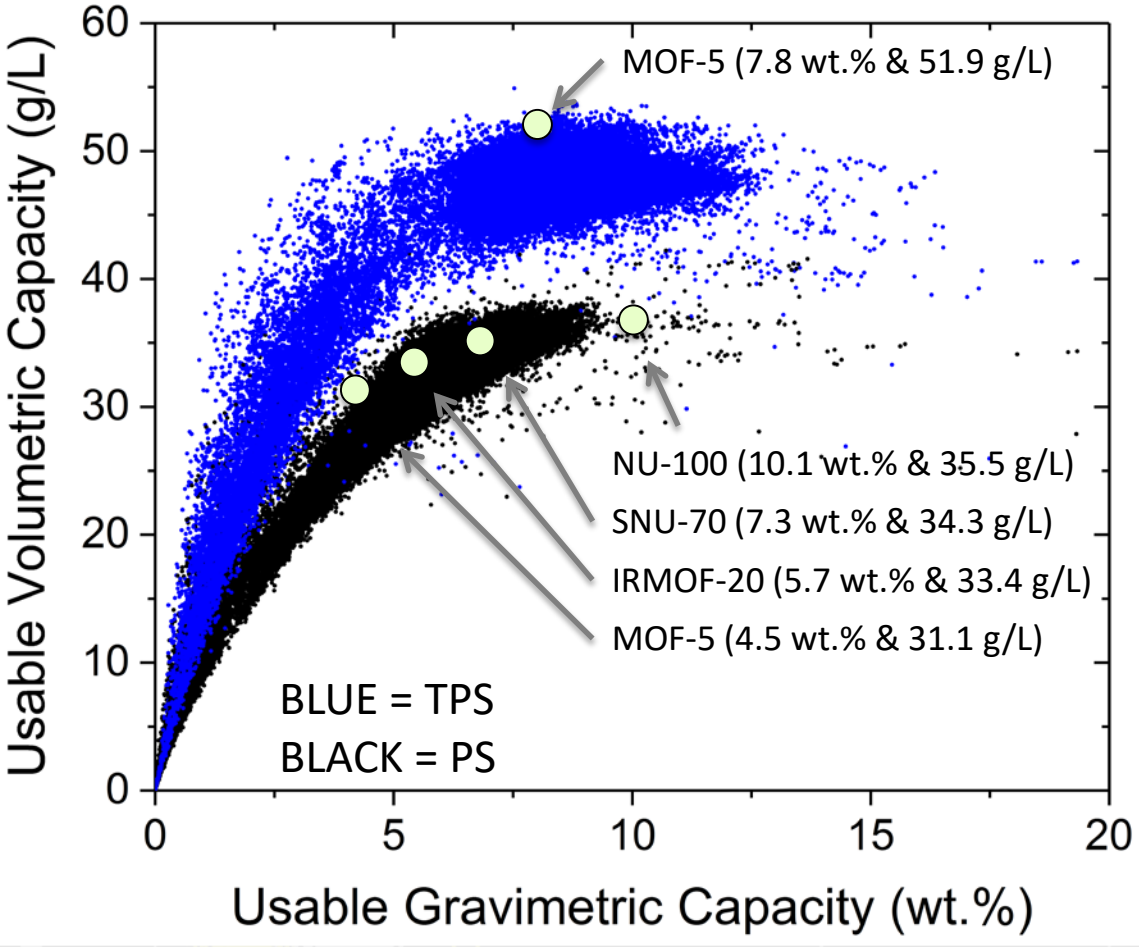
Total Gravimetric H_2 Uptake



High-Throughput Screening

Predicted usable H_2 capacities for PS and TPS conditions

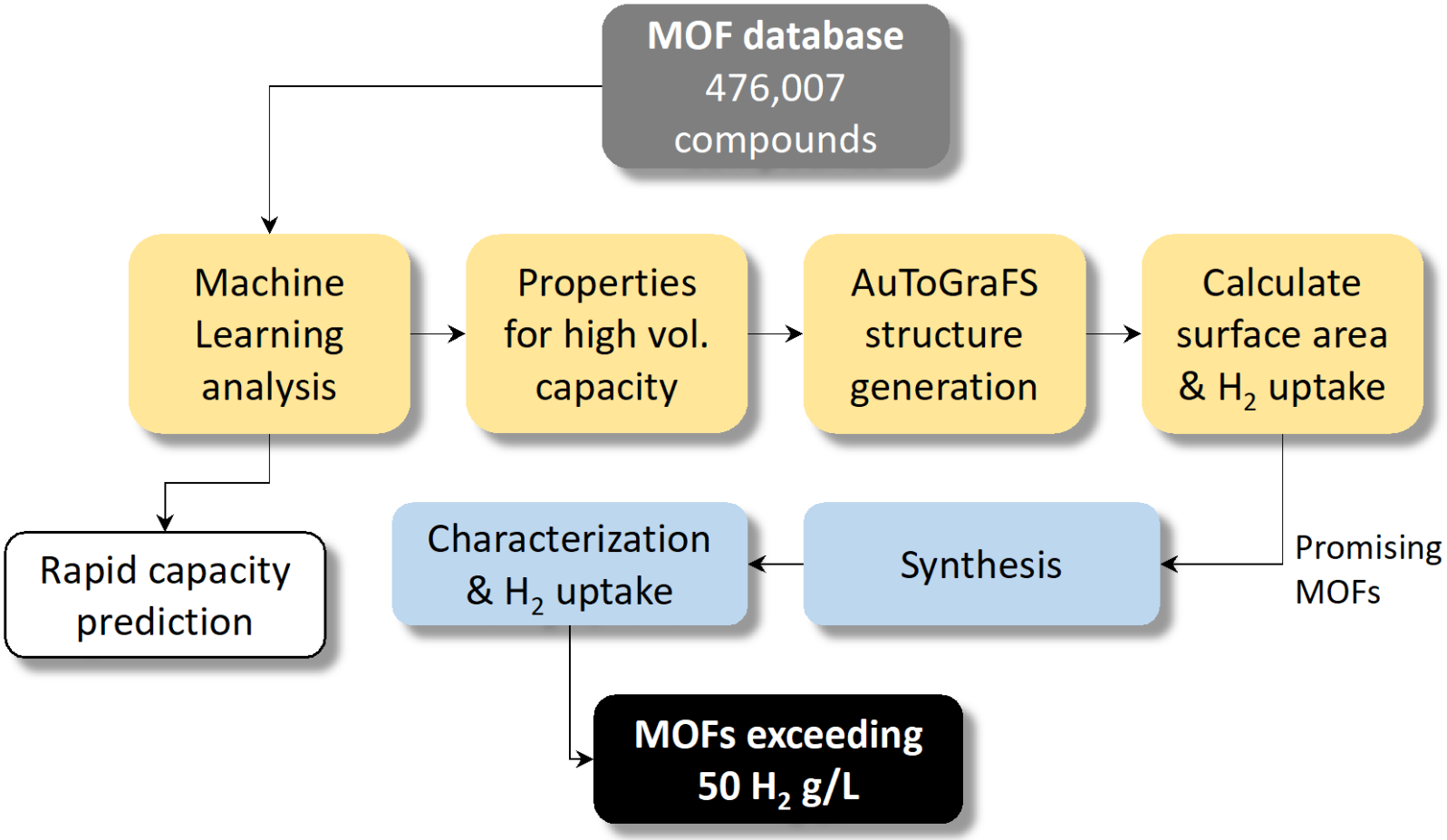
- Pressure swing: P_{max}= 100 bar to P_{min}= 5 bar at 77 K
- Temp+pressure swing: T_{min}= 77 K, P_{max}= 100 bar to T_{max}= 160 K, P_{min}= 5 bar



Only 180 MOFs surpass MOF-5 under TPS conditions.

Concept

Machine learning will be used to guide the development of MOFs with high volumetric H_2 capacities



Crystal Engineering

- Packing of congruent convex objects indicates that particle morphology and the size distribution are key factors in determining packing efficiency
- We shall vary these properties systematically, leveraging advances in colloid science for the controlled growth of MOFs with various shapes and sizes

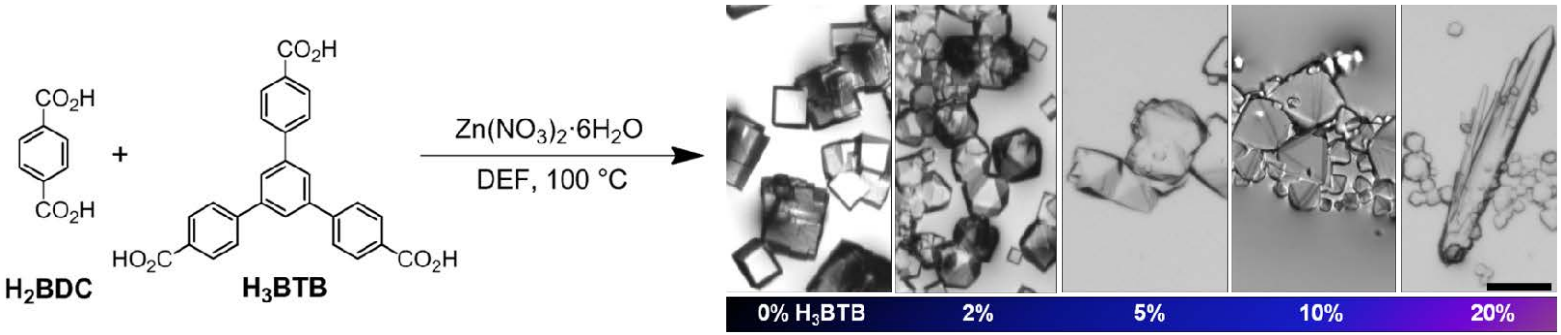
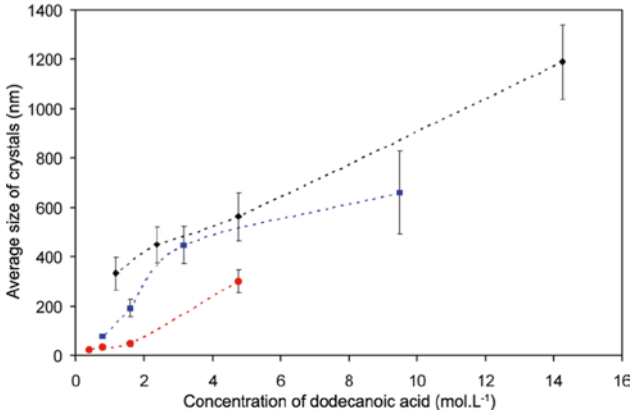


Fig. 1: Synthesis of octahedral-shaped MOF-5 crystals by addition of H_3BTB in the reaction mixture of H_2BDC and $Zn(NO_3)_2 \cdot 6H_2O$. Photographs show the dependence of crystal morphology on the percentage of H_3BTB (scale bar: 100 μm). Another phase (needle shaped UMCM-1) appears at 10 mol% H_3BTB. From Matzger et al., JACS (2011) **133,** 20138

Fig. 2: Average size of HKUST-1 crystals as a function of dodecanoic acid concentration taken at longer and longer times. Colors represent different concentration of dodecanoic acid. From Diring, et al., Chem. Mater., (2010) **22**, 4531



Accomplishments and Progress

Input Features & Output Properties

7 Crystallographic Features

H_2 Adsorption at 10 Conditions

Geometrical Features from Zeo++	H_2 Capacity from GCMC
1. **Pore Volume** (PV, cm^3/g)	1. **TG** and **TV** at at 5 bar & 77K.
2. **Void Fraction** (VF)	2. **TG** and **TV** at 35 bar & 77K
3. **Gravimetric Surface Area** (GSA, m^2/g)	3. **TG** and **TV** at 100 bar & 77K
4. **Volumetric Surface Area** (VSA, m^2/cm^3)	4. **UG** and **UV** for Pressure Swing between 5 and 35 bar at 77 K.
5. **Largest Cavity Diameter** (LCD, Å)	5. **UG** and **UV** for Pressure Swing between 5 and 100 bar at 77 K.
6. **Pore Limiting Diameter** (PLD, Å)	
7. **Density** (D, g/cm^3)	

TG & TV = Total gravimetric and volumetric capacity.
UG & UV = Usable gravimetric and volumetric capacity

*Zeo++: T.F. Willems, C.H. Rycroft, M. Kazi, J.C. Meza, and M. Haranczyk, *Algorithms and tools for high-throughput geometry- based analysis of crystalline porous materials*, Microporous and Mesoporous Materials, 149 ,134-141 (2012).

ML Methods Tested

12 supervised learning methods from 5 different categories were used

Decision Trees (DT)

L. Breiman, J. Friedman, R. Olshen, and C. Stone. Classification and Regression Trees. Wadsworth, Belmont, CA, 1984.

Ensemble Methods

Random Forest (RF)

L. Breiman, "Random Forests", Machine Learning, 45(1), 5-32, 2001.

Bagging with DT; Bagging with RF (Bagging)

L. Breiman, "Bagging predictors", Machine Learning, 24(2), 123-140, 1996.

Boosted DT; Ada Boost with RF (Ada Boost)

H. Drucker. "Improving Regressors using Boosting Techniques", 1997

Gradient Boosting

J. Friedman, Greedy Function Approximation: A Gradient Boosting Machine, The Annals of Statistics, Vol. 29, No. 5, 2001.

Extremely Randomized Trees

P. Geurts, D. Ernst., and L. Wehenkel, "Extremely randomized trees", Machine Learning, 63(1), 3-42, 2006.

K-Nearest Neighbors (K-NN)

N. S. Altman, "An introduction to kernel and nearest-neighbor nonparametric regression". The American Statistician. 46(3), 175–185, 1992.

Support Vector Machine (SVM)

A. J. Smola, B. Schölkopf, "A Tutorial on Support Vector Regression", Statistics and Computing archive, 14(3), 199-222, 2004.

Linear Regression; Ridge Regression (Generalized Linear Model)

T. Hastie, R. Tibshirani and J. Friedman. Elements of Statistical Learning Ed. 2, Springer, 2009.

Machine Learning Software & Code: Scikit-learn, R, & in-house code

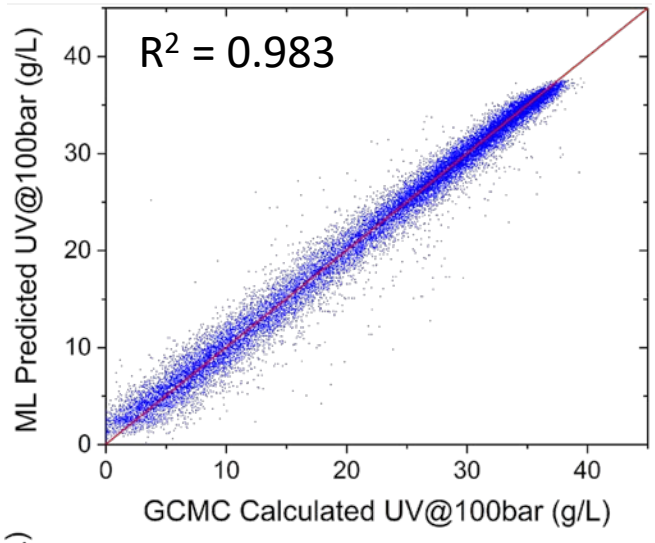
Hyperparameter Optimization Method: Grid search cross validation method

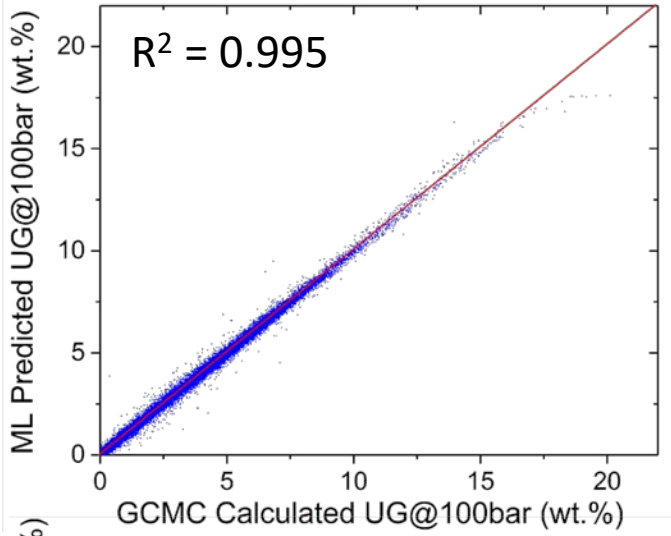
Training Set: 74, 221; Test Set: 24,741; Unseen Data Set: 394,496

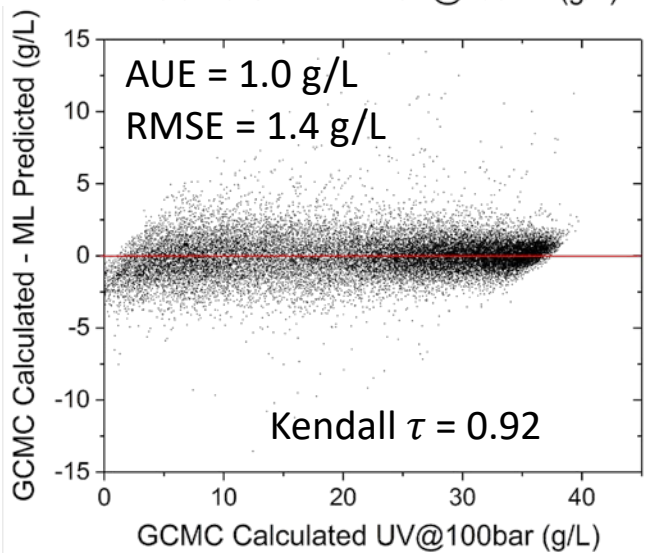
- Scikit-learn: Pedregosa *et al.*, Scikit-learn: Machine Learning in Python, Journal of Machine Learning Research, 12, 2825-2830, 2011.
- R Core Team (2013). R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. URL http://www.R-project.org/.

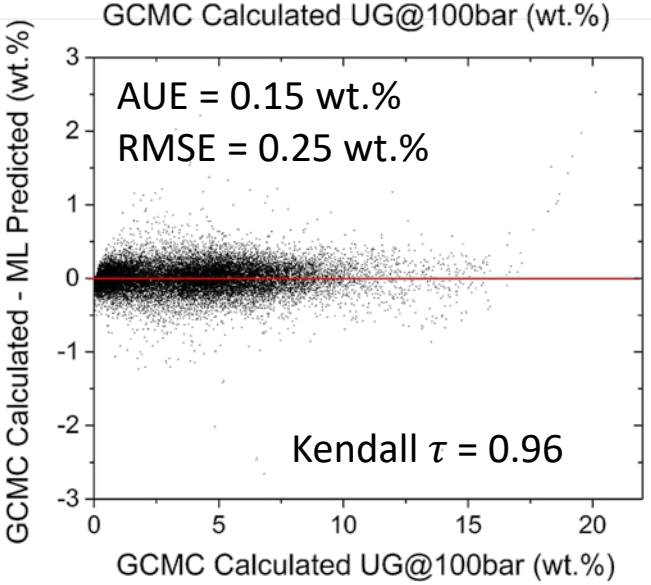
ML Predictions of Capacities

Comparison between Extremely Randomized Trees ML prediction and GCMC







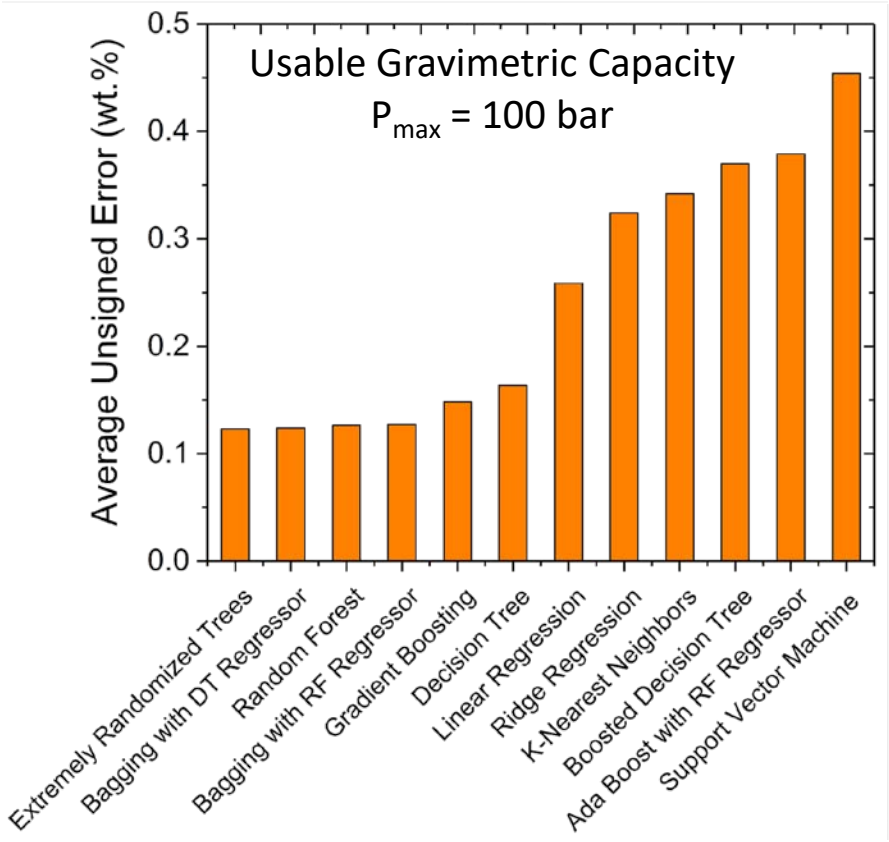


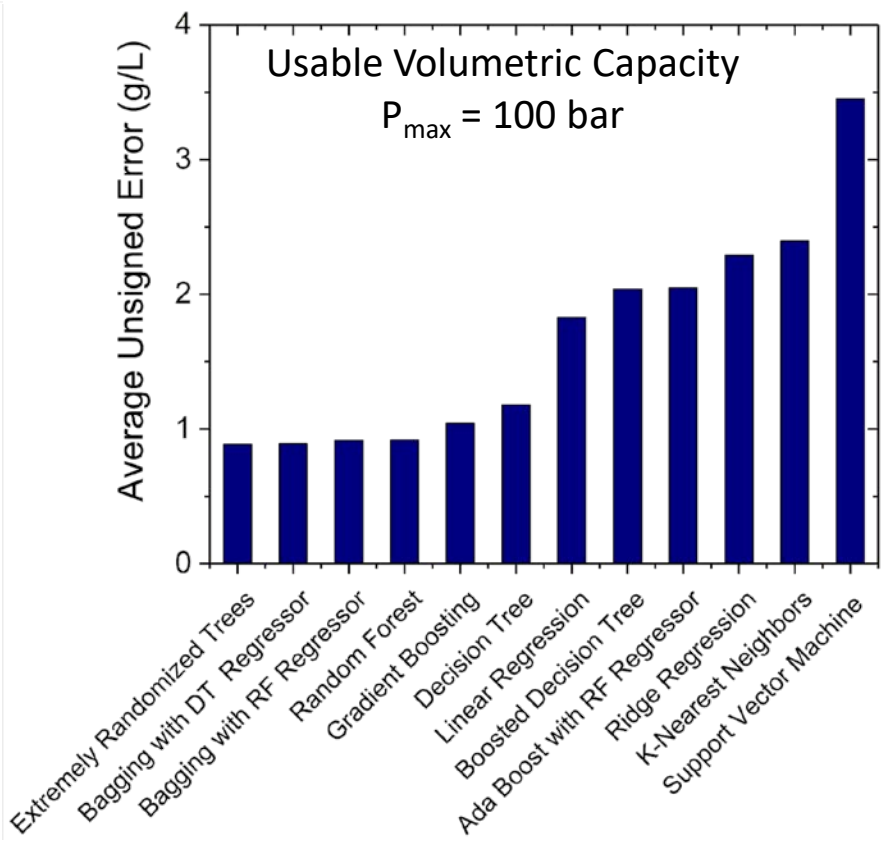
Benchmarking ML Methods

The Extremely Randomized Trees method is the best performing ML algorithm

Comparison of ML Methods

The Extremely Randomized Trees method is the best performing ML algorithm

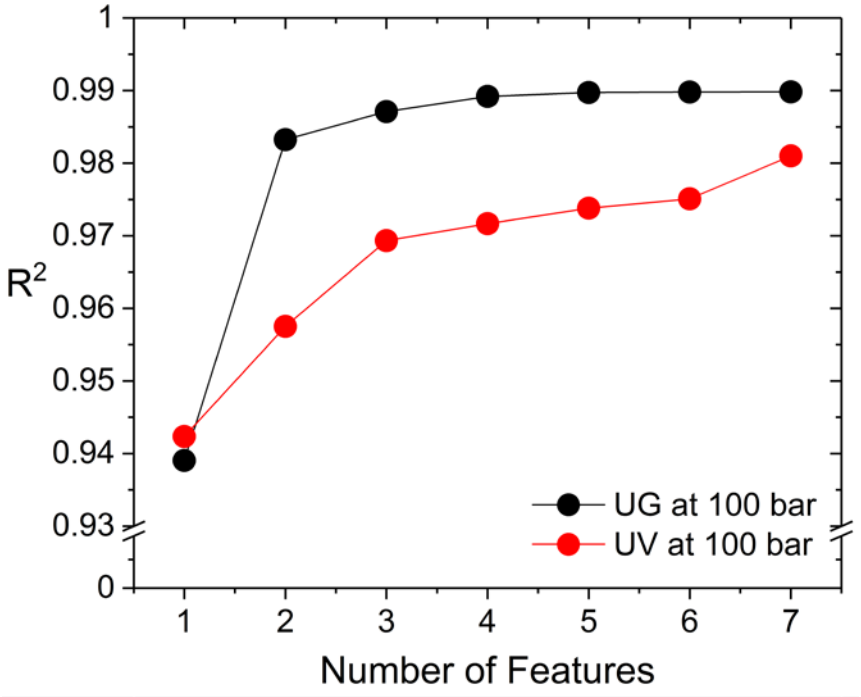




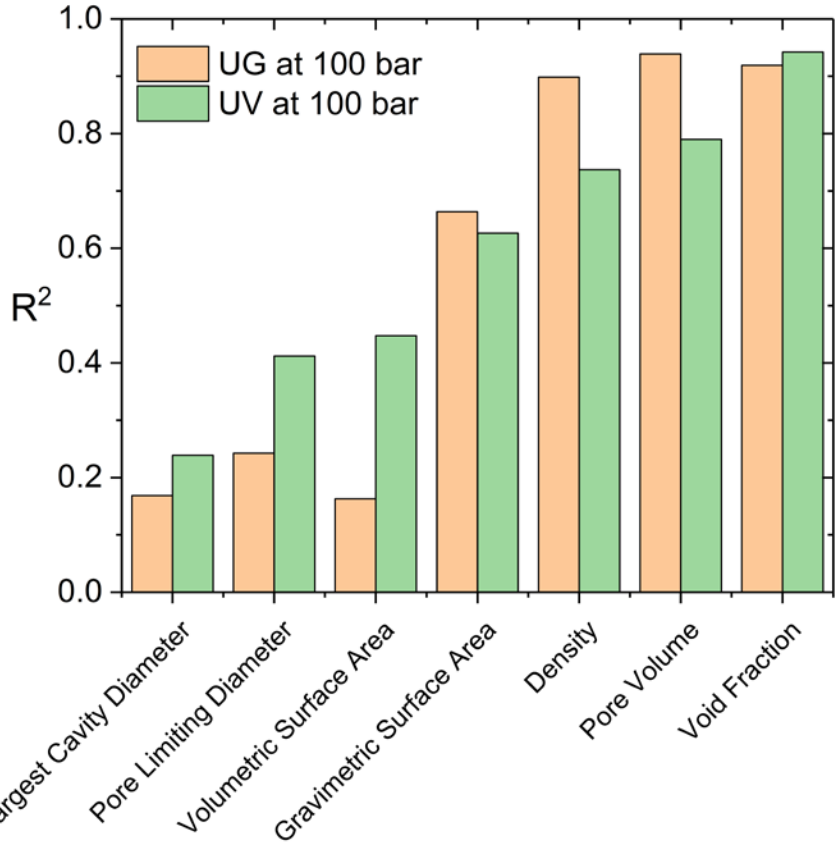
Structure-Property Correlations

- Void fraction shows the strongest correlation with UV
- Only 4 features needed to predict UV with over 96% accuracy

Effect of Number of Features



Single Feature Performance

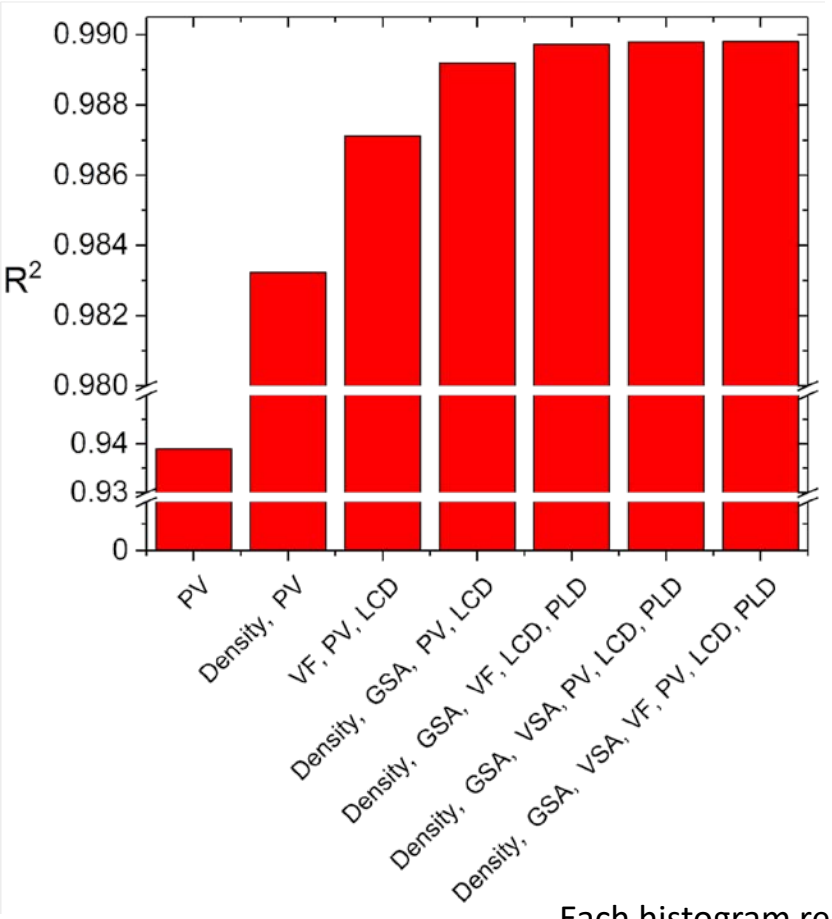


Each point on the plot represents the highest R^2 value among all possible(2^n -1) combinations of (n = 1,2,3,4,5,6,7) features

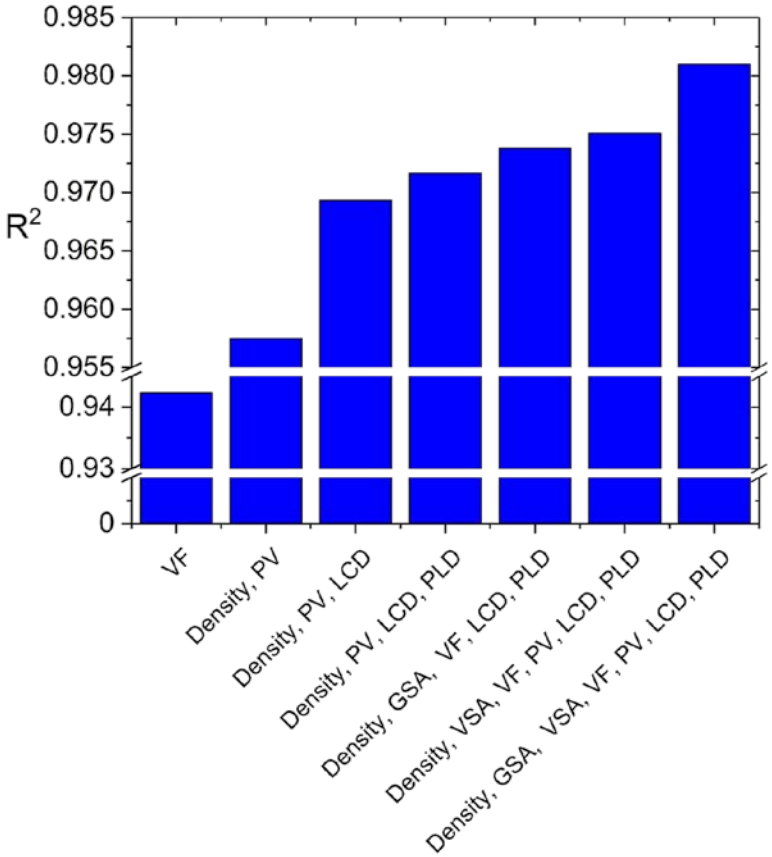
Structure-Property Correlations

ML models were developed for all possible (2^7-1 = 127) combinations of features to identify the optimal feature set

Usable Gravimetric



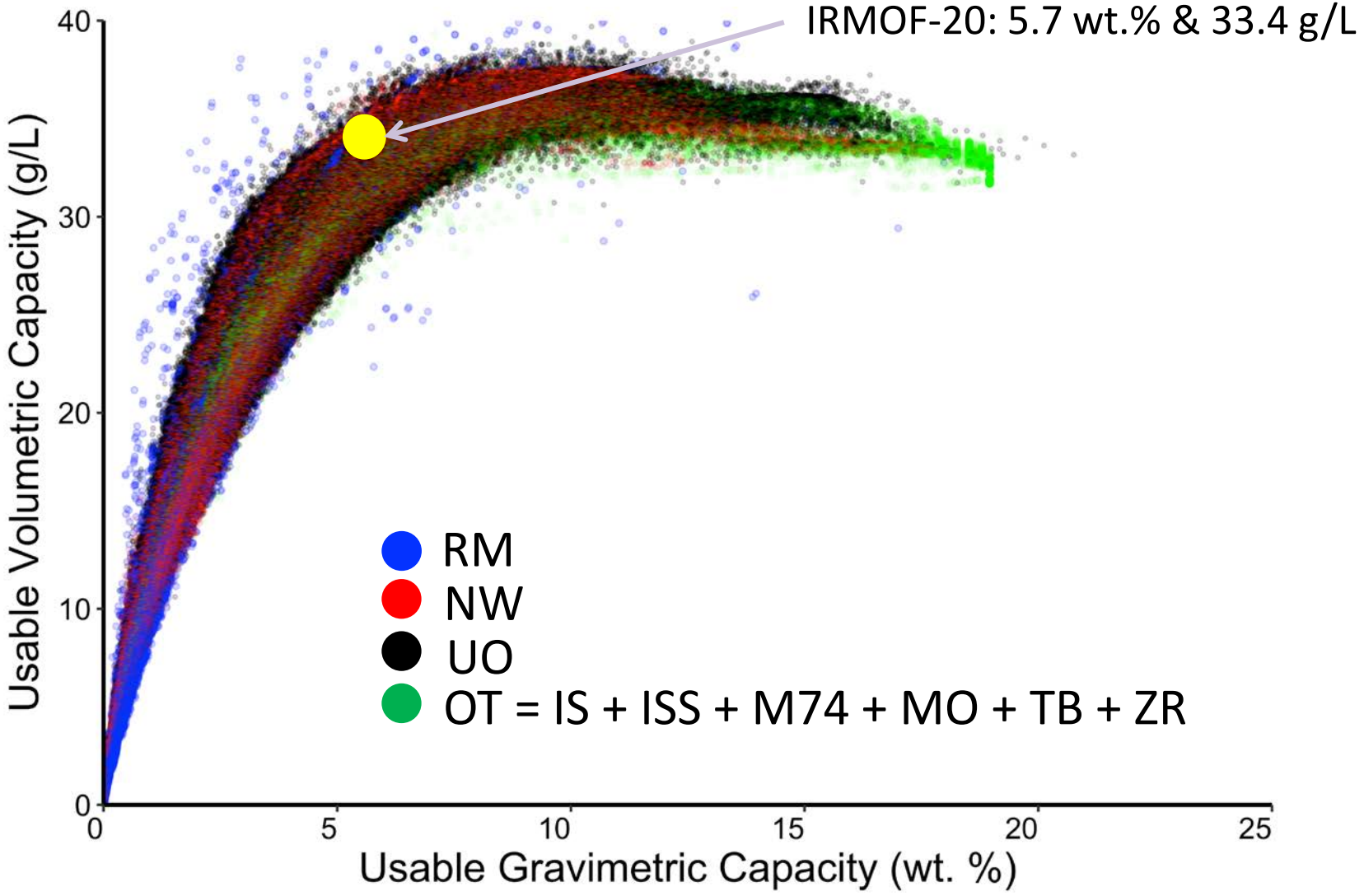
Usable Volumetric



Each histogram represents the highest R^2 value among all possible combinations of a given number of features.

H_2 Storage in 500,000 MOFs

ML reveals 69,363 MOFs that can potentially out-perform IRMOF-20, the top performing MOF on a volumetric basis

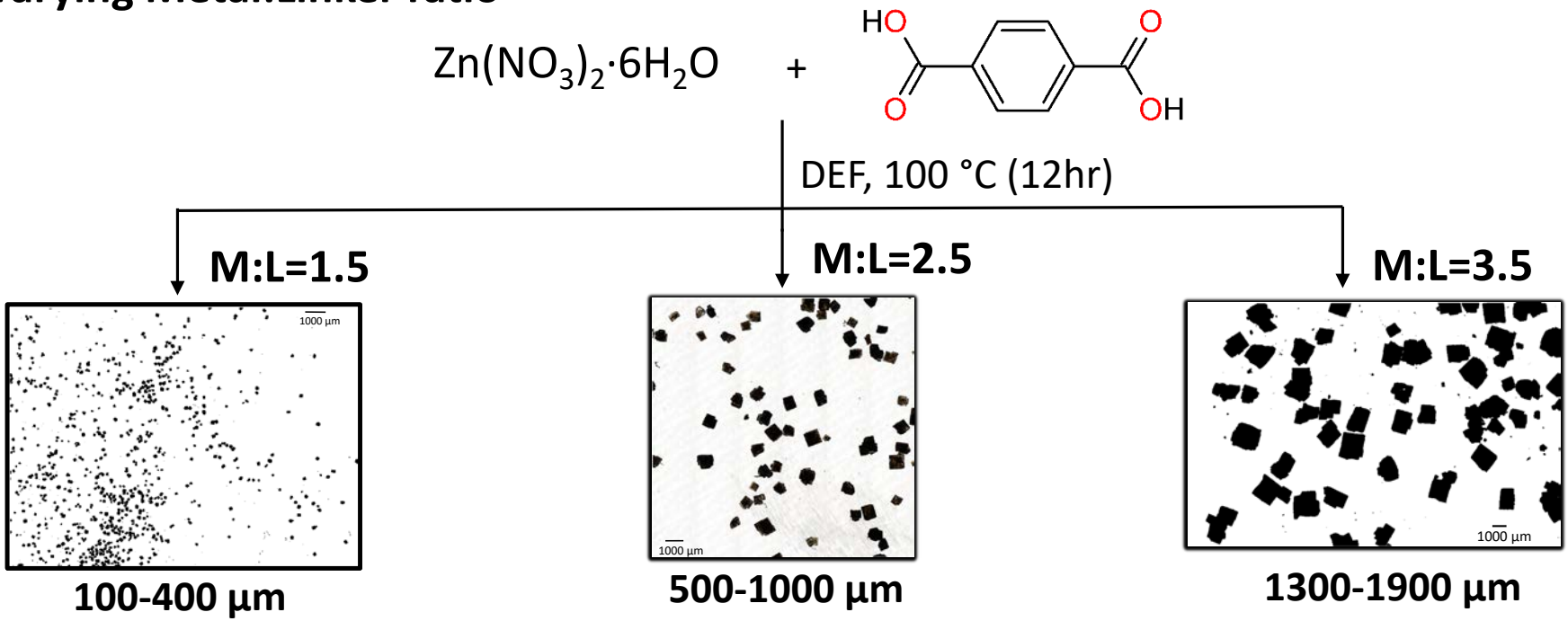


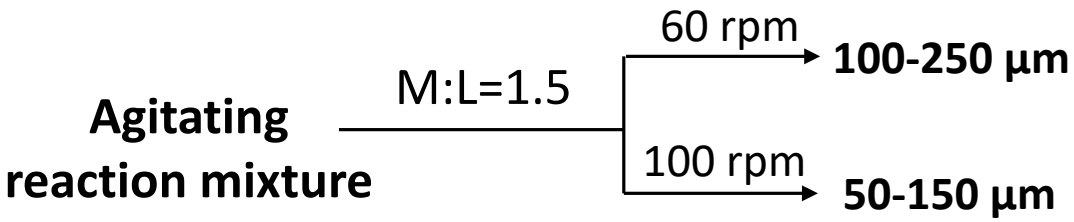
Crystal Size Control (1)

Successfully developed synthesis protocols that produce MOF-5 with different average sizes

Synthesis Protocols

Varying Metal:Linker ratio

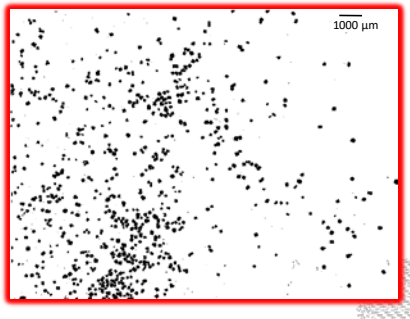




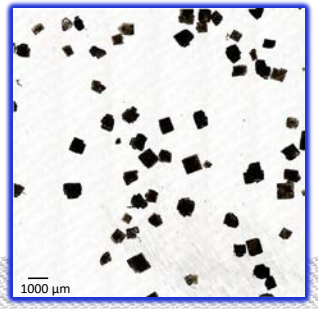
Crystal Size Control (2)

Crystal size histograms indicate the successful control over crystal size

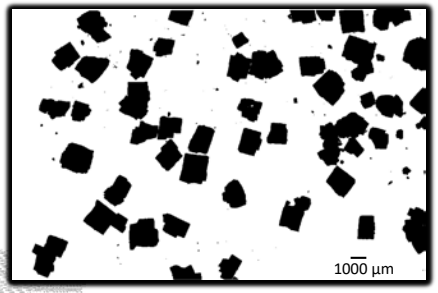
Varying the size distribution of cubic MOF-5 crystallites



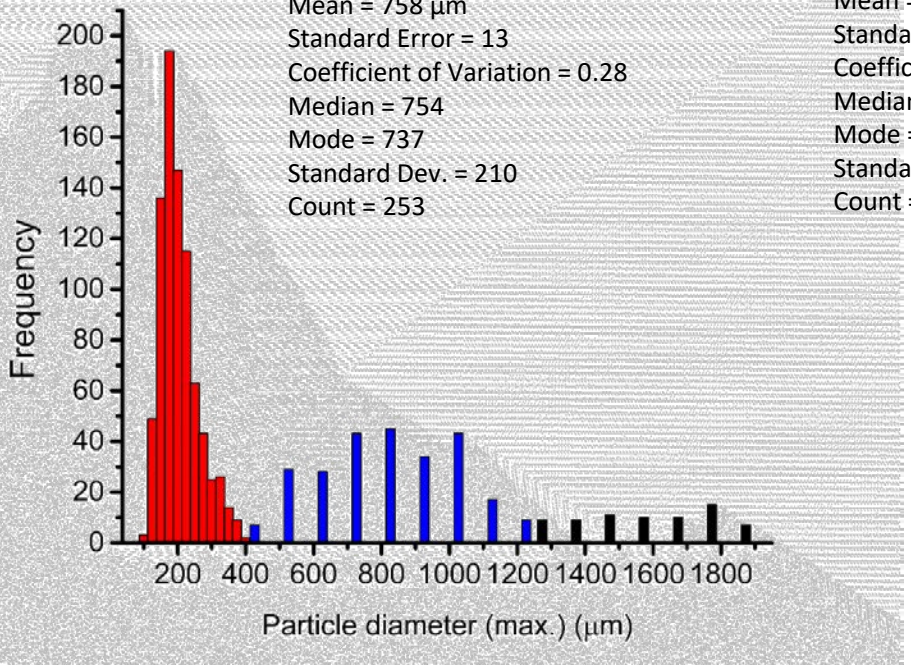
Mean = 192 µm
Standard Error = 1.9
Coefficient of Variation = 0.29
Median = 179
Mode = 174
Standard Dev. = 56
Count = 828



Mean = 758 µm
Standard Error = 13
Coefficient of Variation = 0.28
Median = 754
Mode = 737
Standard Dev. = 210
Count = 253



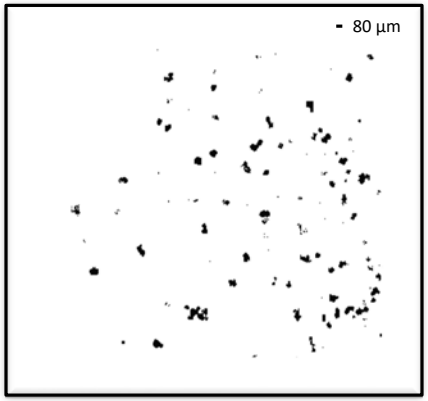
Mean = 1633 µm
Standard Error = 39
Coefficient of Variation = 0.24
Median = 1590
Mode = 1675
Standard Dev. = 389
Count = 97

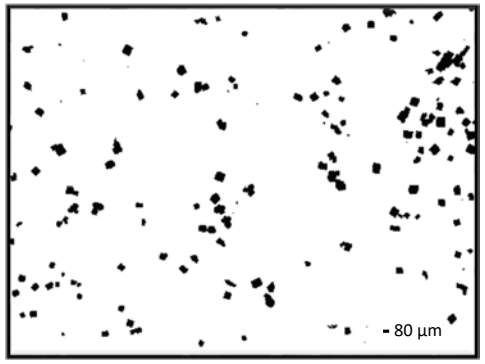


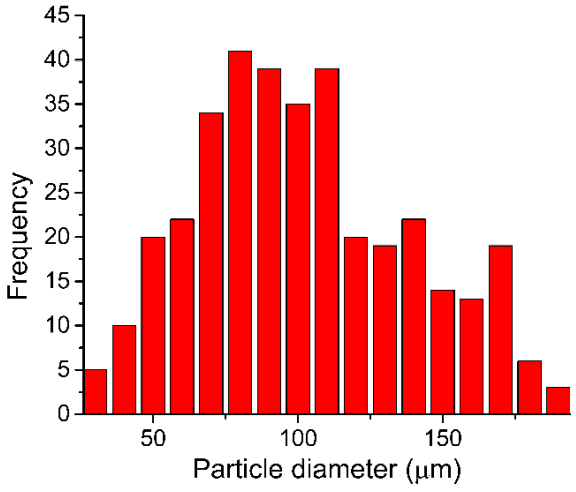
Crystal Size Control (3)

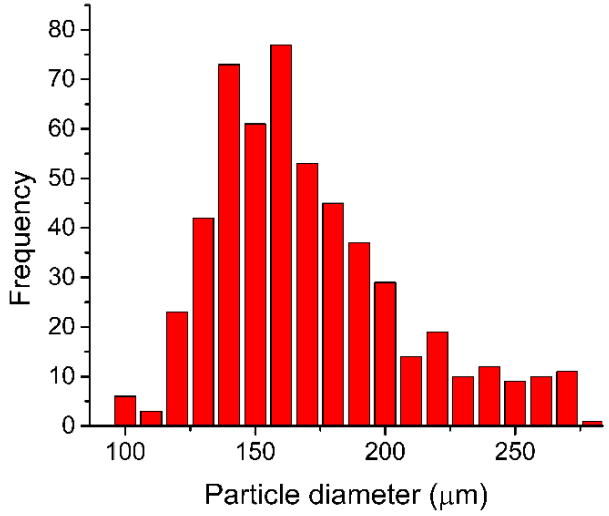
Crystal size histograms indicate the successful control over crystal size

Varying the size distribution of cubic MOF-5 crystallites



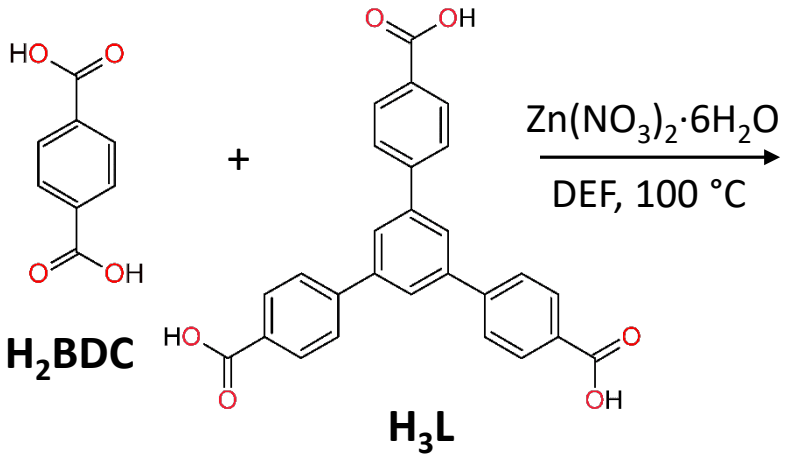


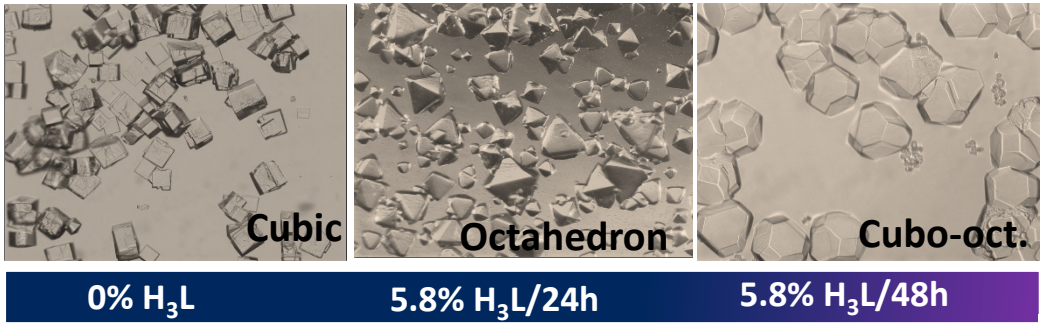




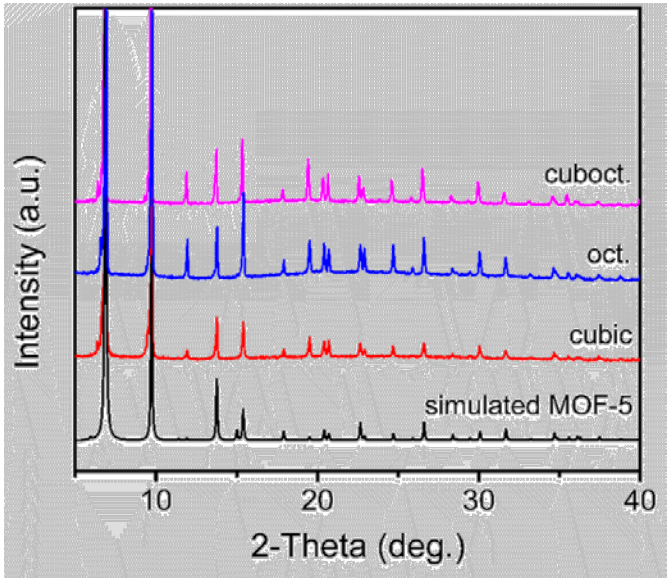
Morphology Control (1)

Identified additive capable of controlling morphology of MOF-5 crystals



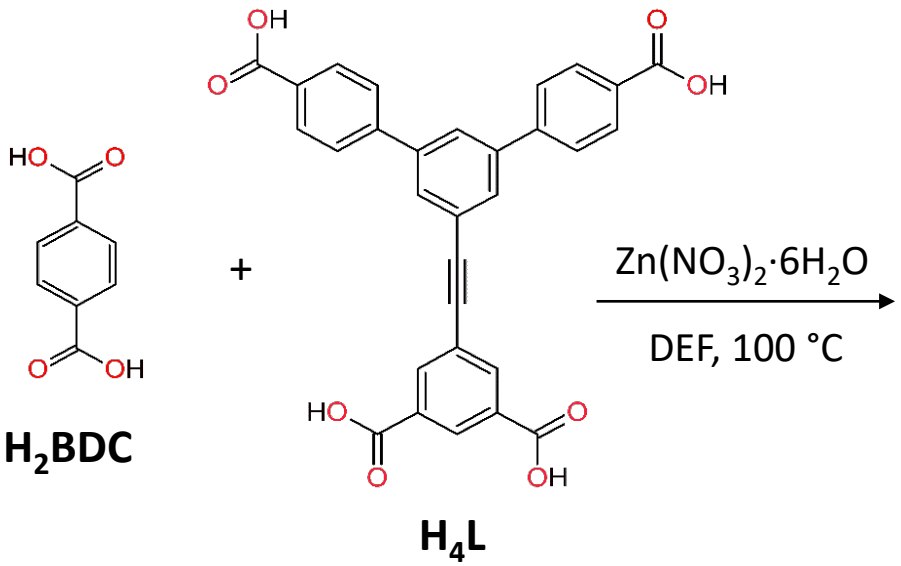


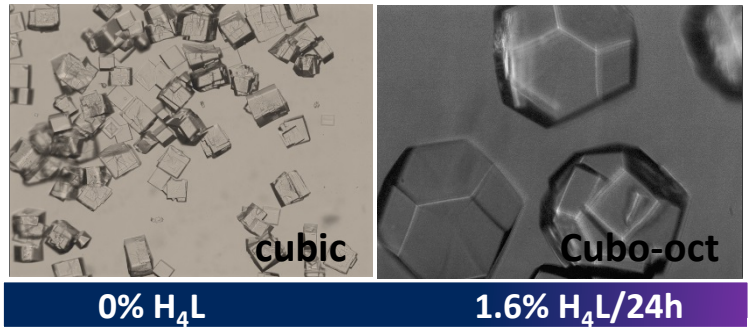
Phase purity

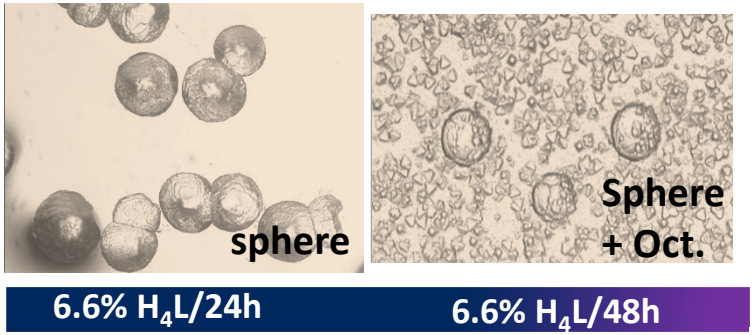


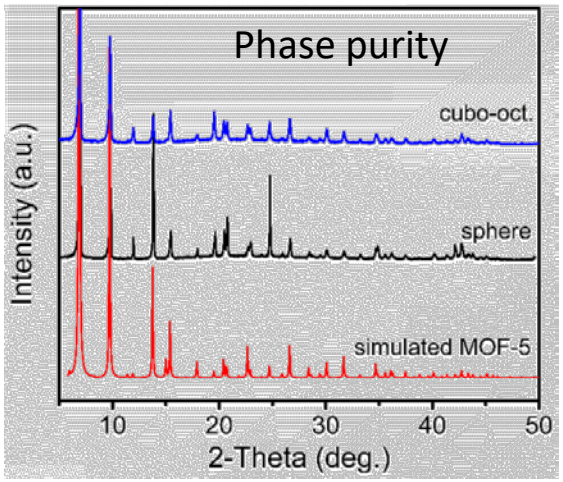
Morphology Control (2)

Identified additive capable of controlling morphology of MOF-5 crystals









H_4L=5'-((3,5-dicarboxyphenyl)ethynyl)-[1,1':3',1''-terphenyl]-4,4''-dicarboxylic acid)

Collaborations

University of Michigan, Mechanical Engineering

- Atomistic simulation and project management

University of Michigan, Dept. of Chemistry

- Synthesis and characterization of targeted MOFs

Ford Motor Company (sub-contractor)

- PCT measurements
- Materials augmentation, characterization, scale-up, and system modeling

HSECoE/SRNL (unfunded collaborator)

- Assistance with system models (David Tamburello)

Challenges and Barriers

- Many more compounds identified by computation than can be synthesized
  - Assessment by a human is needed before synthesis can proceed
  - This is a bottleneck
- Structure collapse or incomplete solvent removal during activation
  - “Can it be made?”
  - Failure to achieve expected surface area and porosity
  - Properties that control “synthesizability” are not well-understood
- Incorrect, incomplete, or disordered crystal structure data
  - Garbage in, garbage out
  - False positives in screening

Potential Future Work

- **Pass 1st go/no-go milestone:** Identify ranges for 4 MOF crystallographic properties consistent with usable volumetric capacity of at least 40 g/L and usable gravimetric capacity of at least 7 wt. %
- **Particle Size Control:** Determine if particle size influences packing efficiency by more than 10% for particles whose size varies by more than 10x
- **Hybrid Approaches to Space Filling:** Identify binary mixtures for a given morphology that yields the highest packing efficiency

Any proposed future work is subject to change based on funding levels

Summary

- **Goal**: Overcome volumetric limitations associated with physisorptive hydrogen storage at both the materials and systems level in metal-organic frameworks (MOFs)
- **Approach**:
  - Control MOF crystal morphology and crystallite size distribution to increase packing density
  - Apply machine learning techniques to identify, design, and demonstrate high-capacity MOFs
- **Accomplishments:**
  - Benchmarked 12 ML algorithms for their ability to predict H_2 storage. The Extra Trees algorithm was found to be highly accurate; used to screen 500,000 MOFs. ML predictions are accurate because the input features are "good"
  - Discovered ~70,000 MOFs capable of outperforming IRMOF-20, the top performing MOF reported to date
  - Successfully developed synthesis protocols that produce MOF-5 with different average sizes. Identified additive capable of controlling morphology of MOF-5 crystals

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The Team

Technical Backup Slides