

ST144

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

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2020 DOE Hydrogen and Fuel Cells Program Annual Merit Review

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Overview



Timeline and Budget

Project Start Date: Sept. 1st, 2017
Project End Date: Dec. 31st, 2020

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:* ~\$750,000

Barriers

Barriers addressed

- Volumetric Density
- Gravimetric Density

Partners

Interactions/collaborations:

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

Project lead:

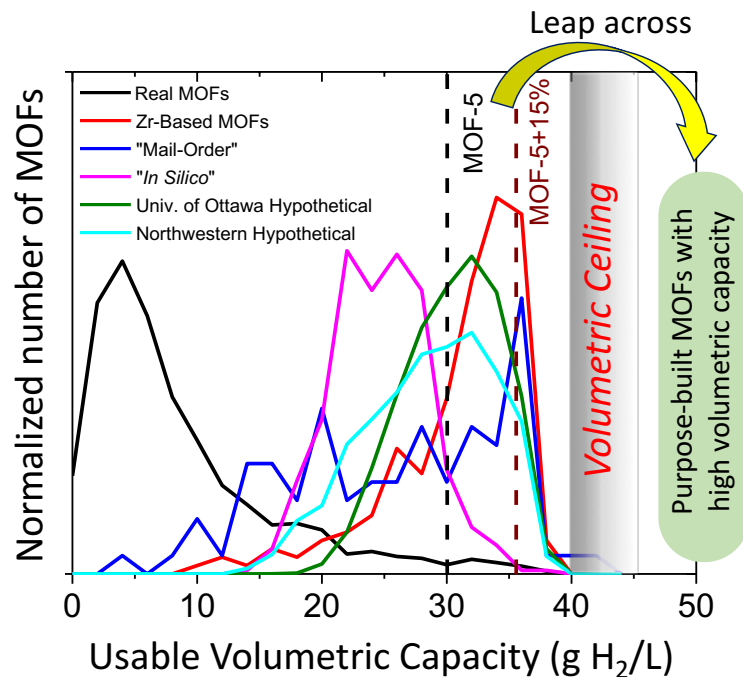
Don Siegel, University of Michigan

*Estimated as of 4/1/20

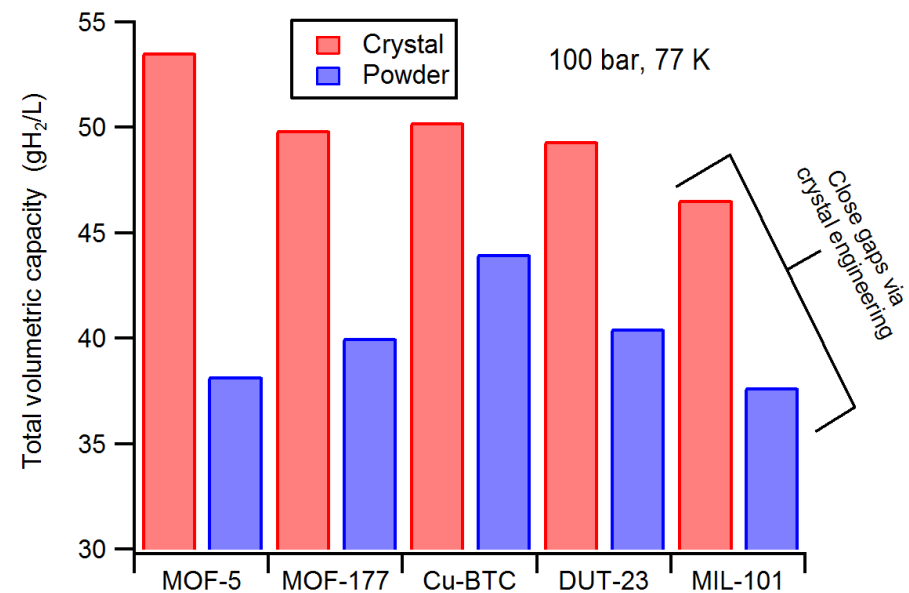
- A high-capacity, low-cost method for storing hydrogen remains one of the primary barriers to the widespread commercialization of fuel cell vehicles
- Storage via adsorption in MOFs is promising due to their fast kinetics, reversibility, and tunable properties
- A viable adsorbent must exhibit a high intrinsic (i.e., materials level) H₂ capacity, and pack in a dense fashion at the system level
 - Our prior screening revealed that no known MOF exhibits a usable volumetric capacity exceeding 40 g H₂/L (assuming a 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
 - **This project addresses both challenges**

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

Screening of ~500,000 MOFs reveals that essentially no compounds exceed 40 g/L usable capacity
 → New MOFs needed to break through volumetric ceiling



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

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

- Demonstrate usable volumetric capacities exceeding 50 H₂ 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 H₂ 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



Milestones

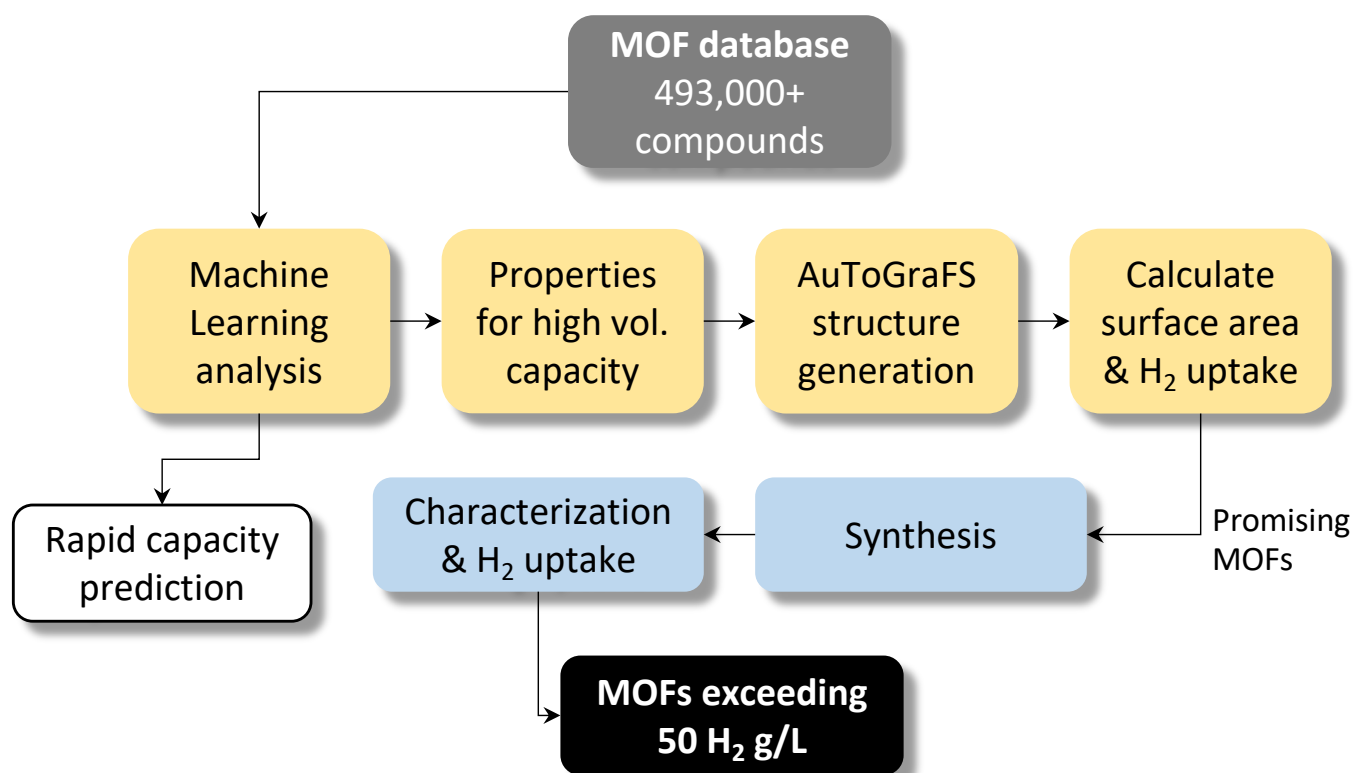


Passed 2nd Go/No-Go.

All other milestones are on-track or have been completed.

Milestone Summary Table							
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	Date (Months from Start)	Quarter (from Start)
1.5	Validate ML predictions	Milestone	M1.5.1	Use GCMC to validate ML predictions of highest capacity MOFs on a pressure swing and temperature+pressure swing basis. Attempt to synthesize 1-2 of the most promising MOF candidates. Assess surface areas; if within 85% of theoretical value perform PCT capacity measurements	GCMC calculations, BET surface area measurements, and PCT measurements	21	7
2.1	Morphological engineering	Go/No-Go	D2	Demonstrate an improvement in either A) a MOF with a single crystal volumetric capacity greater than 39 g/L usable capacity measured at 77 K, and 5-100 bar pressure (i.e., a 10% increase over the current state-of-the-art NU-100) through Machine Learning-directed material development, OR B) a 15% increase in tap density through crystal engineering methods for a specific MOF compared to its non-optimized powder, with a minimal loss in surface area.	Density measurements, surface area measurements, PCT measurements	24	8
1.6	Purpose-built MOFs	Milestone	M1.6.1	Develop ML models that predict MOF capacity based only on building blocks (linker, cluster, etc) and topology. Create a catalog of MOFs that have chemical building blocks (cluster, linker) and topologies that are consistent with the properties identified in Task 1.3 (MOF reverse engineering).	Geometric property analysis (surface area, pore volume, etc)	27	9
2.3	Hybrid approaches to space filling	Milestone	M2.3.1	Synthesize at least 3 MOFs predicted to have high volumetric capacity. Characterize surface area; if surface area is within 15% of theory, measure H ₂ uptake. Characterize packing efficiency of binary mixtures of MOF particles with sizes between 2500 to 200 microns for a given particle morphology.	Void fraction measurements	30	10

Machine learning is being used to guide the development of MOFs with high volumetric H₂ capacities





MOF Database



Our effort leverages a large database of MOFs

~100,000 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	2,854
Zr-MOFs (ZR)	204	0	204	204
NW Hypothetical MOFs (NW)	137,000	30,160	106,840	20,156
UO Hypothetical MOFs (UO)	324,500	32,993	291,507	61,247
In-house synthesized via hypothetical design	18	0	18	5
Total	493,458	66,758	426,700	98,962

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).

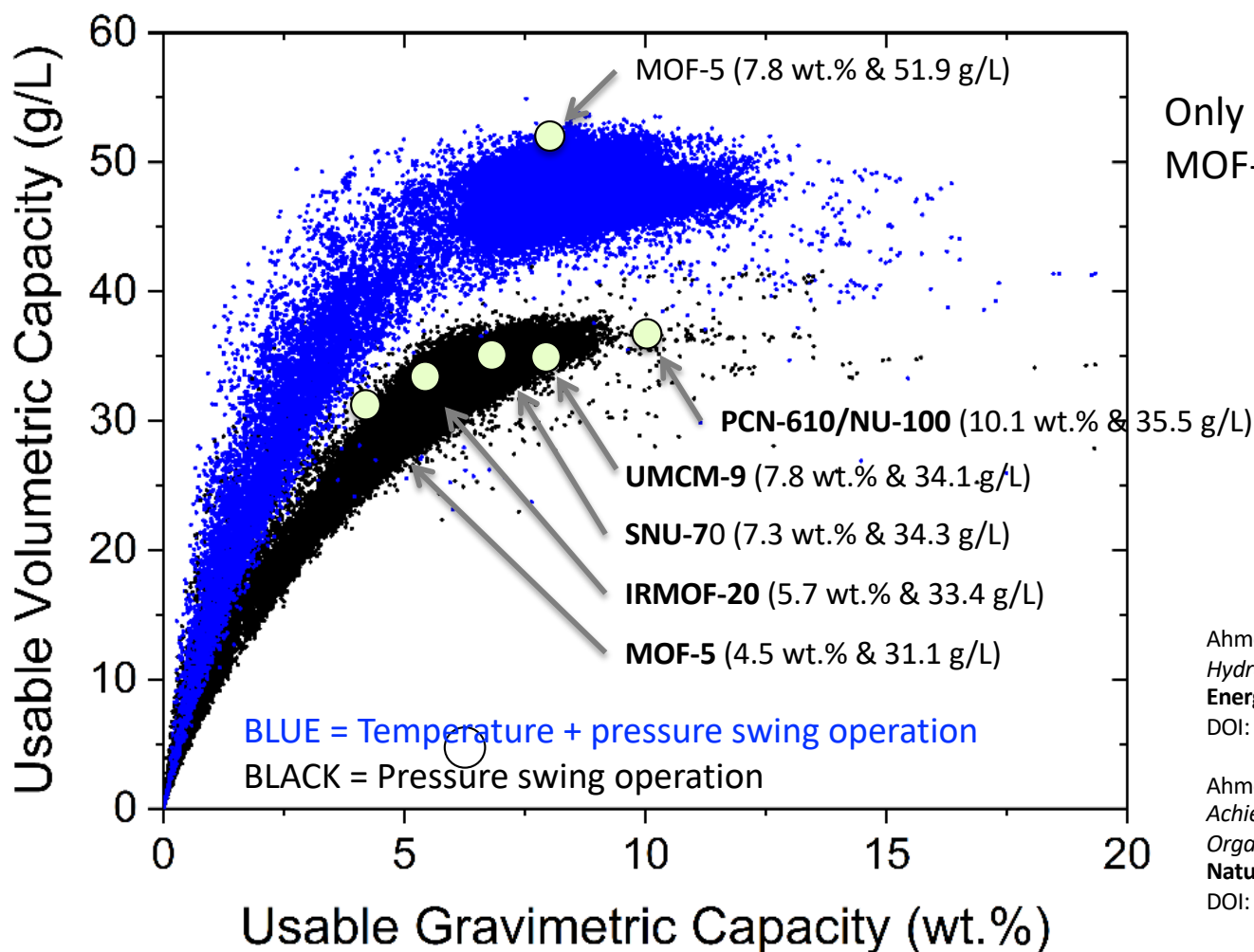
NW: C. E. Wilmer, M. Leaf, C. Y. Lee, O. K. Farha, B. G. Hauser, J. T. Hupp, R. Q. Snurr, *Nat. Chem.* 4, 83–89 (2012).

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

H₂ capacities for pressure swing (PS) and temperature + PS (TPS) conditions are predicted using Grand Canonical Monte Carlo

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

Ahmed et al., *Balancing Gravimetric and Volumetric Hydrogen Density in MOFs*, **Energy & Environmental Science**, 10, 2459 (2017)
DOI: 10.1039/C7EE02477K

Ahmed et al., *Exceptional Hydrogen Storage Achieved by Screening Nearly Half a Million Metal-Organic Frameworks*, **Nature Communications**, 10, 1568 (2019)
DOI: 10.1038/s41467-019-09365-w

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

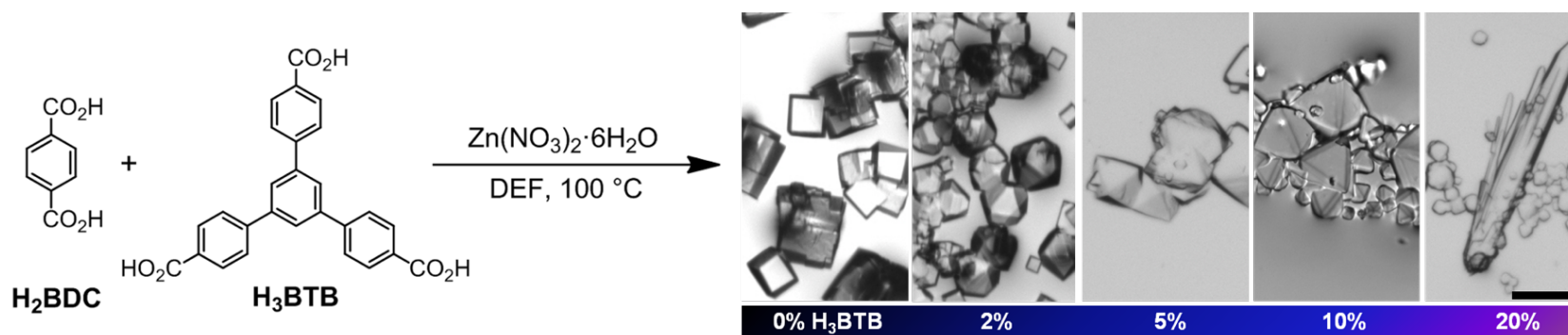
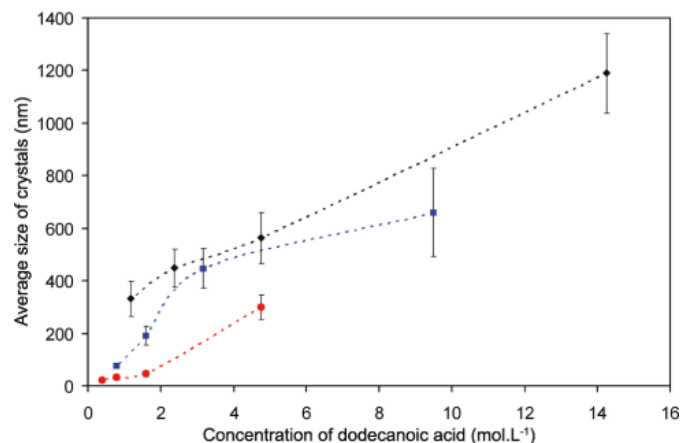


Fig. 1: Synthesis of octahedral-shaped MOF-5 crystals by addition of H₃BTB in the reaction mixture of H₂BDC and Zn(NO₃)₂·6H₂O. Photographs show the dependence of crystal morphology on the percentage of H₃BTB (scale bar: 100 μm). Another phase (needle shaped UMCM-1) appears at 10 mol% H₃BTB. From Matzger 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





ML Using Chemical Building Blocks of MOFs (1)

Developed machine learning (ML) models that predict usable gravimetric and volumetric capacities using only chemical building blocks of MOFs as input

Input:
MOF building blocks

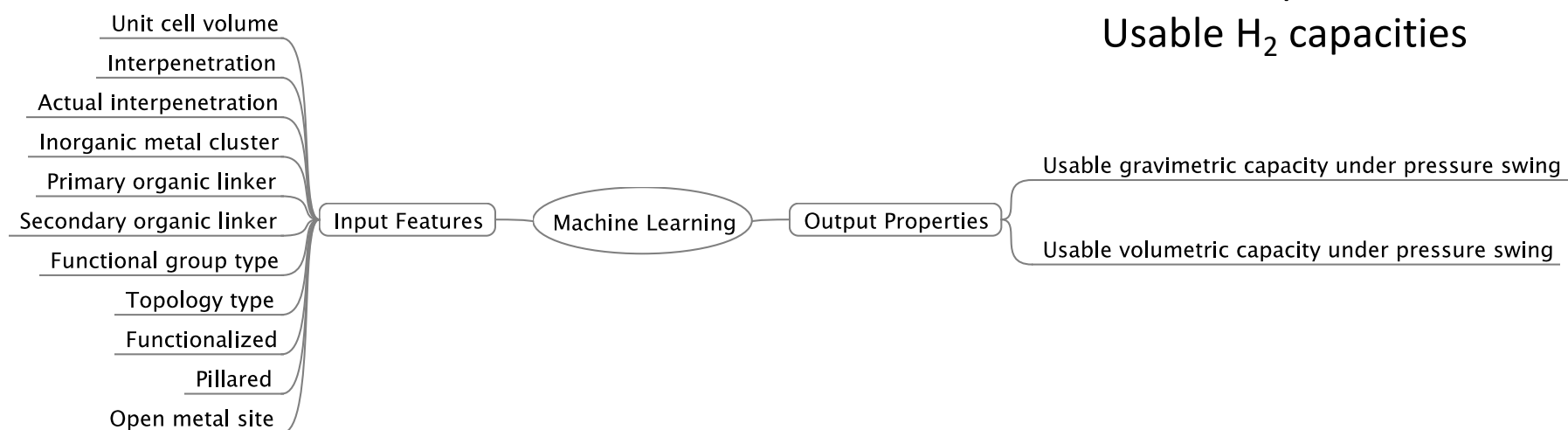


Figure: Flow diagram showing chemical building blocks (input to ML) and usable H₂ storage capacities of MOFs (output from ML).



ML Using Chemical Building Blocks of MOFs (2)

Demonstrated the ability to predict usable gravimetric and volumetric capacities of an arbitrary MOF under pressure swing to within ~95 % of GCMC values using only building blocks as input.

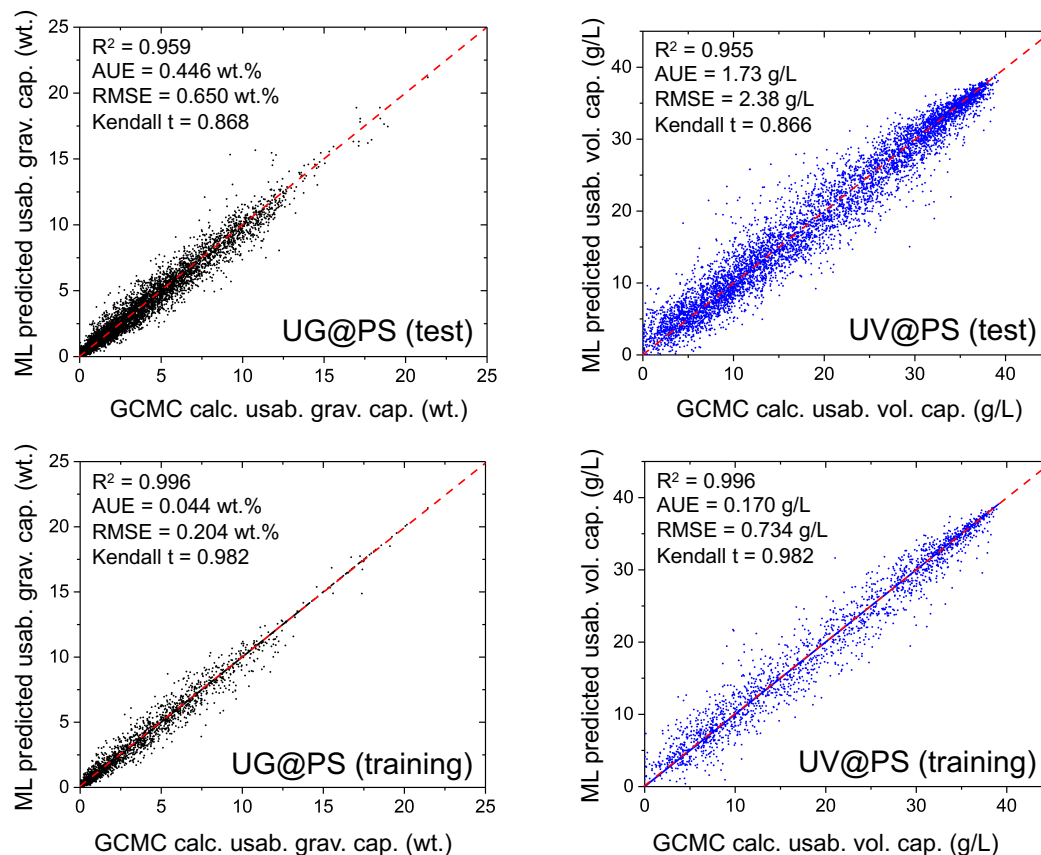


Figure: Correlation between ML predictions and GCMC calculations for usable gravimetric (black dots) and volumetric capacities (blue dots) for 6,176 MOFs. ML models were developed based on a training set of 18,528 MOFs. Top and bottom panels illustrate, respectively, the performance of models in predicting the training set and an unseen test set. Red dashed lines indicate perfect correlation. R^2 , AUE, and RMSE refer, respectively, to the coefficient of determination, the average unsigned error, and the root mean square error.



ML Using Chemical Building Blocks of MOFs (3)

Assessed the importance of 11 MOF features independently on the ability to predict volumetric H₂ uptake.

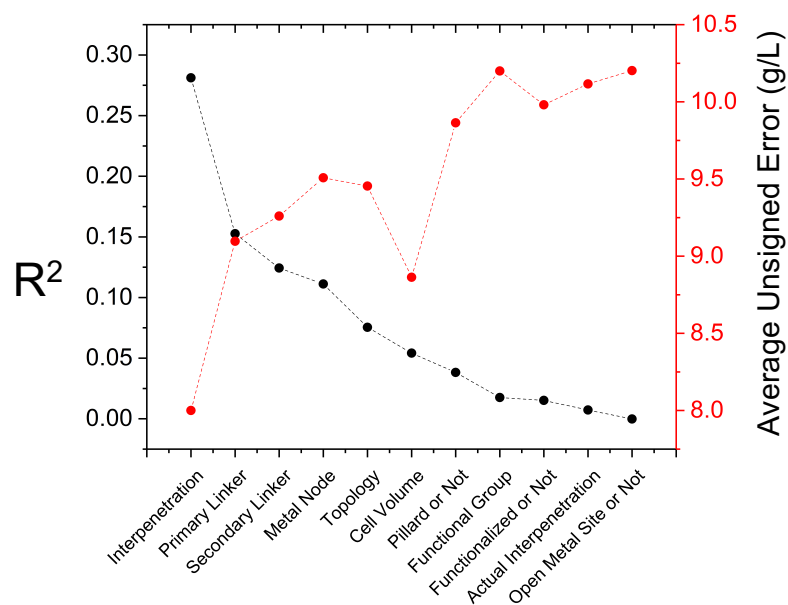


Figure: Importance of 11 individual features in predicting usable volumetric H₂ storage capacities of MOFs under pressure swing conditions. Feature importance was determined by R² values (left axis - black) and AUE (right axis - red). The Extremely Randomized Trees (ERT) model, trained on a dataset of 18,528 MOFs, was used to assess feature importance on a test of 6,176 MOFs.

A combination of four MOF building block features can predict usable volumetric capacities of an arbitrary MOF under pressure swing conditions to within ~90 % of GCMC values.

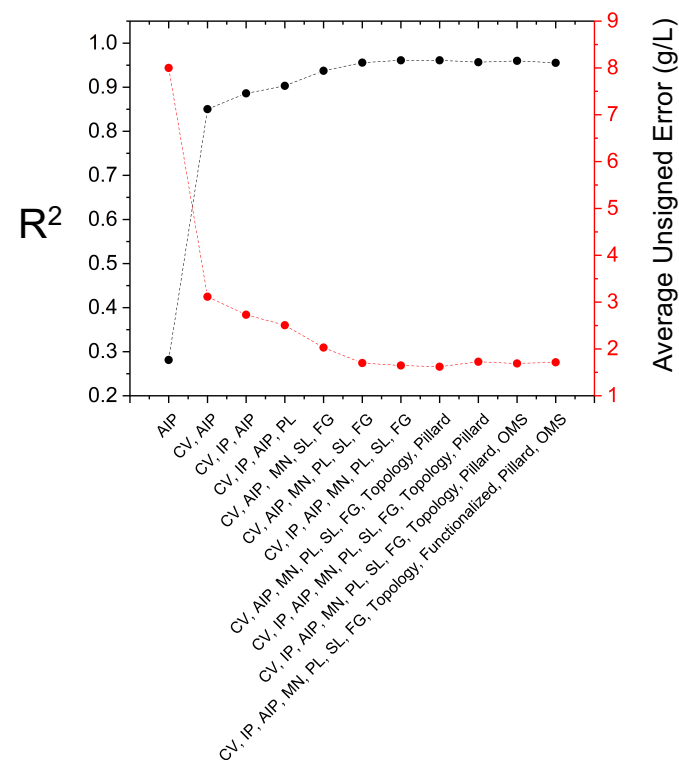


Figure Predicting of usable volumetric H₂ storage capacities in MOFs under PS as a function of input features. The importance of a given combination of features was determined using R² (left y-axis in blue color) and the average unsigned error, AUE (right y-axis in red). The data shown represent the best possible combinations (largest R² and smallest AUE) out of of 2047 possibilities (= 2¹¹-1). (Here, 11 is the number of features.) Extremely Randomized Trees models were trained on a dataset of 18,528 MOFs. Model performance was assessed on a test of 6,176 MOFs.



Catalog of MOFs (1)

A catalog of MOFs has been created that contains chemical building blocks (cluster, linker) and topologies that are consistent with the properties identified from MOF reverse engineering

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.

Crystallographic Property	Range of property yielding high capacity
Density (g/cm ³)	0.49 ± 0.01
Gravimetric Surface Area (m ² /g)	5222 ± 402
Pore Volume (cm ³ /g)	1.74 ± 0.03
Void Fraction	0.86 ± 0.02



Catalog of MOFs (2)

Example catalog of 20 MOFs that have chemical building blocks (inorganic metal cluster and organic linker) and topologies that are consistent with the range of single crystal densities identified from MOF reverse engineering.

Name	Inorganic Metal Cluster	Organic Linker	Topology	Density (g/cm ³)
hypotheticalMOF_5029352_1_0_0_28_20_3	0	28	1	0.49
hypotheticalMOF_1523_0_0_0_17_17_14	0	17	1	0.49
hypotheticalMOF_4563_0_0_0_4_24_4	0	4	1	0.49
hypotheticalMOF_31610_1_0_2_10_25_5	2	10	1	0.49
hypotheticalMOF_5028977_2_1_0_28_18_5	0	28	1	0.49
hypotheticalMOF_5004945_1_0_0_18_13_9	0	18	1	0.49
hypotheticalMOF_5006528_1_0_0_15_2_11	0	15	1	0.49
hypotheticalMOF_12797_0_0_0_14_26_13	0	14	1	0.49
hypotheticalMOF_5017937_1_0_0_19_13_10	0	19	1	0.49
hypotheticalMOF_5000302_1_0_0_12_17_13	0	12	1	0.49
hypotheticalMOF_31272_0_0_2_10_26_1	2	10	1	0.49
hypotheticalMOF_5001686_3_0_0_12_11_2	0	12	1	0.49
hypotheticalMOF_5018465_0_0_0_19_22_12	0	19	1	0.49
hypotheticalMOF_413_1_0_0_26_9_4	0	26	1	0.49
hypotheticalMOF_5013490_3_0_0_20_20_2	0	20	1	0.49
hypotheticalMOF_11903_0_0_0_5_25_10	0	5	1	0.49
hypotheticalMOF_26148_0_0_1_16_24_5	1	16	1	0.49
hypotheticalMOF_5017437_0_0_0_19_1_1	0	19	1	0.49
hypotheticalMOF_5017975_1_0_0_19_13_6	0	19	1	0.49
hypotheticalMOF_35501_0_0_2_14_26_12	2	14	1	0.49

Additional MOFs that have surface areas, void fractions, and pore volumes within the targeted range are given in the backup slides.



Hypothetical MOF Design (1)

- Top 20 hypothetical MOFs (from existing databases) based on volumetric H₂ capacity as identified by ML and GCMC.
- These MOFs were examined for their ability to be synthesized.
 - Two candidates (or their analogues) were identified for experimental study.

MOF Name	Source	Usable Volumetric Capacity			Comments
		GCMC	ML	GCMC-ML	
mof_7642	ToBaCCo	40.5	37.4	3.0	Promising structure for synthesis or analogue production.
mof_7690	ToBaCCo	40.3	37.3	3.0	Promising structure for synthesis or analogue production.
mof_7594	ToBaCCo	39.9	37.0	2.9	Inherent chemical instability of organic linker.
mof_7210	ToBaCCo	39.8	37.1	2.8	Very complicated ligand for potential performance boost.
mof_7738	ToBaCCo	39.7	37.0	2.7	Analog of mof_7690 but much harder to make.
hypotheticalMOF_5045702_i_1_j_24_k_20_m_2	NW	39.7	37.2	2.5	Very weak pillaring ligand. Likely to be unstable.
str_m3_o19_o19_f0_nbo.sym.1.out	UO	39.7	37.1	2.6	Promising structure for synthesis or analog production.
hypotheticalMOF_5037315_i_1_j_20_k_12_m_1	NW	39.7	37.0	2.6	Very weak pillaring ligand. Likely to be unstable.
hypotheticalMOF_5037467_i_1_j_20_k_12_m_8	NW	39.7	37.0	2.7	Very weak pillaring ligand. Likely to be unstable.
str_m3_o5_o20_f0_nbo.sym.1.out	UO	39.7	37.2	2.5	Promising structure for synthesis or analog production.
hypotheticalMOF_5037563_i_1_j_20_k_12_m_13	NW	39.7	37.2	2.5	Very weak pillaring ligand. Likely to be unstable.
hypotheticalMOF_5038404_i_1_j_20_k_20_m_15	NW	39.7	37.2	2.5	Very weak pillaring ligand. Likely to be unstable.
hypotheticalMOF_5037379_i_1_j_20_k_12_m_4	NW	39.6	37.0	2.6	Very weak pillaring ligand. Likely to be unstable.
hypotheticalMOF_5037407_i_1_j_20_k_12_m_5	NW	39.6	37.0	2.6	Very weak pillaring ligand. Likely to be unstable.
hypotheticalMOF_5037479_i_1_j_20_k_12_m_9	NW	39.6	37.0	2.6	Very weak pillaring ligand. Likely to be unstable.
hypotheticalMOF_5055561_i_1_j_28_k_20_m_11	NW	39.6	37.2	2.4	Very weak pillaring ligand. Likely to be unstable.
hypotheticalMOF_5037439_i_1_j_20_k_12_m_7	NW	39.6	37.0	2.6	Very weak pillaring ligand. Likely to be unstable.
hypotheticalMOF_5037499_i_1_j_20_k_12_m_10	NW	39.6	37.0	2.6	Very weak pillaring ligand. Likely to be unstable.
hypotheticalMOF_5037531_i_1_j_20_k_12_m_11	NW	39.6	37.0	2.6	Very weak pillaring ligand. Likely to be unstable.
hypotheticalMOF_5037523_i_1_j_20_k_12_m_11	NW	39.6	37.1	2.5	Very weak pillaring ligand. Likely to be unstable.



Hypothetical MOF Design (2)

Designed 65 hypothetical MOFs

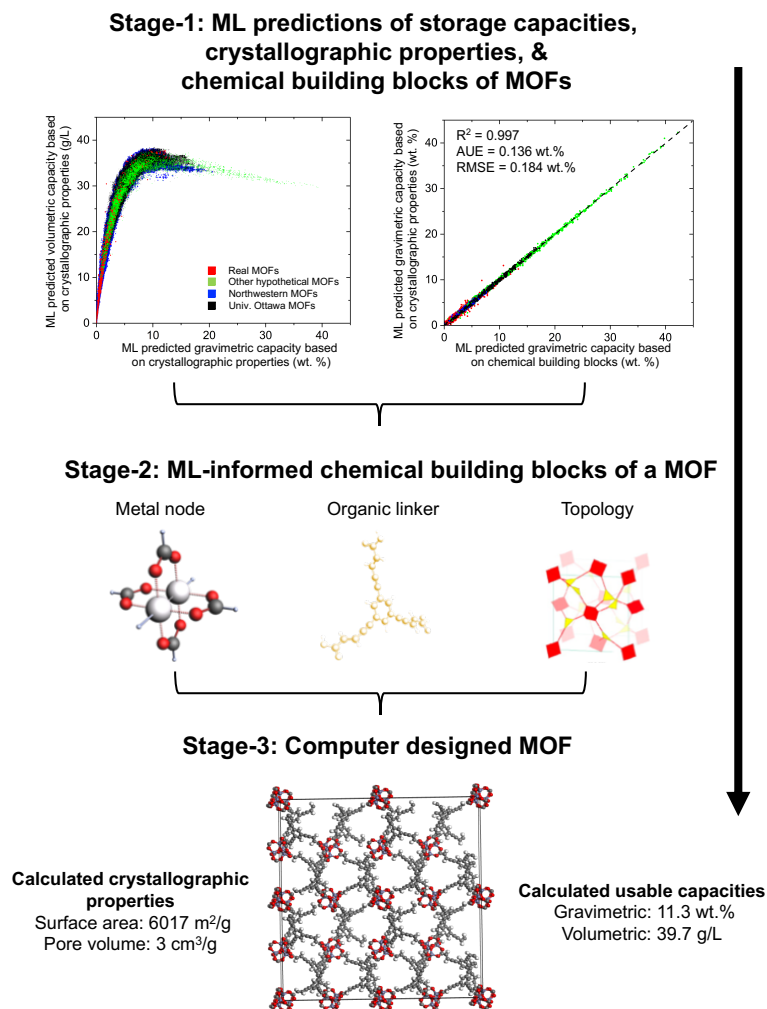
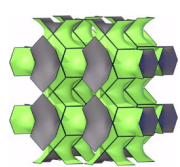


Figure: Example of inverse design of a MOF using chemical building blocks

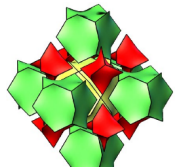


Hypothetical MOF Design Space

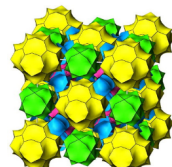
9 topologies



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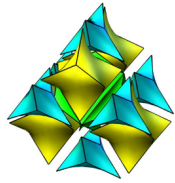
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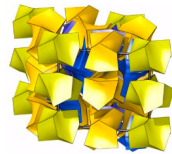
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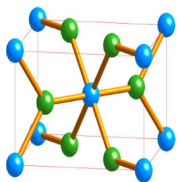
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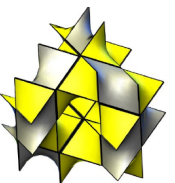
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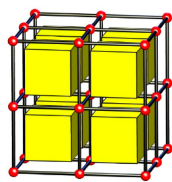
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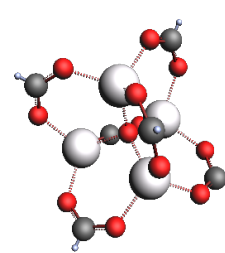
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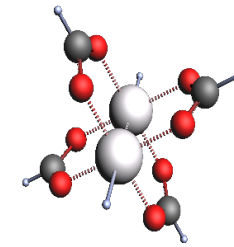
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Image source: <http://rcsr.anu.edu.au/nets>

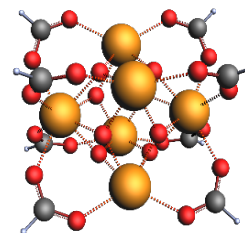
5 metal clusters (SBUs)



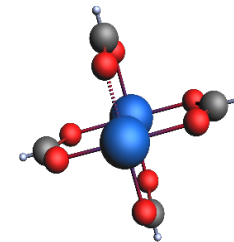
Zn Octahedron



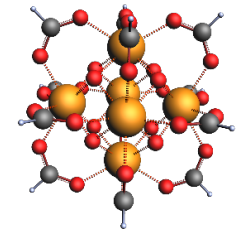
Zn Octahedral Paddlewheel



Zr-cubic

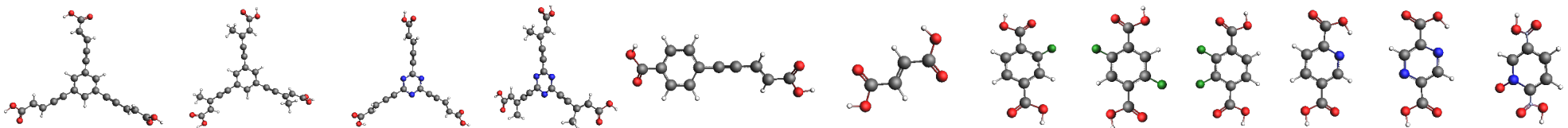


Cu-Paddlewheel



Zr-icosahedral

12 linkers





Screening New MOFs with GCMC

25 hypothetical MOFs were identified that have the potential to surpass the performance of NU-100/PCN-610

Name	Density (g/cm ³)	Void fraction	Pore volume (cm ³ /g)	Volumetric surface area (m ² /cm ³)	Gravimetric surface area (m ² /g)	Largest cavity diameter (Å)	Pore limiting diameter (Å)	Usab. grav. PS (wt. %)	Usab. volum. PS (g/L)	Usab. grav. TPS (wt. %)	Usab. volum. TPS (g/L)
NU-100/PCN-610								10.1	35.5	13.9	47.6
Zn-PDW_Linkers-1_rtl	0.25	0.89	3.61	1772	7195	15.2	13.9	13.1	39.6	15.6	45.9
Zn-PDW_Linkers-3_rtl	0.26	0.89	3.44	1776	6853	15.0	13.7	12.5	39.4	15.0	46.1
Linker-1_CuPW-6_qom	0.25	0.89	3.60	1848	7499	14.3	12.9	13.0	39.4	15.5	45.6
Linker-1_CuPW-4_pto	0.22	0.91	4.10	1532	6914	22.1	11.3	14.3	39.2	16.4	44.1
Linker-3_CuPW-4_pto	0.23	0.91	3.96	1536	6698	22.3	11.2	13.9	39.2	16.0	44.1
Linker-1_CuPW-6_rtl	0.31	0.86	2.83	1928	6308	13.5	12.4	10.6	39.1	13.6	48.4
Zn-Oct_Linkers-1_rtl	0.27	0.90	3.31	1638	6043	16.3	14.9	11.9	39.0	14.3	45.8
Zn-PDW_Linkers-1_qom	0.21	0.91	4.42	1748	8519	15.4	14.2	15.1	38.9	17.4	43.8
Zn-PDW_Linkers-3_qom	0.21	0.91	4.27	1752	8246	14.9	13.0	14.7	38.9	16.9	43.7
Zn-Oct_Linkers-3_rtl	0.28	0.90	3.20	1650	5866	16.3	14.9	11.5	38.8	13.8	45.6
Zn-Oct_Linkers-3_qom	0.23	0.91	3.96	1601	6944	16.3	15.3	13.7	38.5	15.6	43.1
Zn-PDW_Linkers-2_qom	0.22	0.90	4.18	1844	8576	15.4	13.3	14.3	38.2	16.7	43.7
Zn-PDW_Linkers-4_qom	0.27	0.88	3.28	1902	7117	14.3	11.8	11.8	38.1	14.3	44.9
Zn-Oct_Linkers-1_qom	0.22	0.91	4.08	1596	7150	16.6	15.2	13.9	38.1	16.0	42.9
Zn-Oct_Linkers-2_qom	0.23	0.90	3.94	1702	7429	16.9	13.2	13.5	38.0	15.7	43.2
Zn-PDW_Linkers-2_rtl	0.28	0.87	3.09	1876	6702	13.9	12.3	11.2	37.9	14.1	46.3
Linker-2_CuPW-4_pto	0.23	0.90	3.96	1582	6955	20.8	11.7	13.6	37.9	15.9	43.3
Zn-PDW_Linkers-5_pcu	0.24	0.89	3.72	1677	7008	17.4	12.6	12.9	37.9	15.4	44.0
Zn-Oct_Linkers-2_rtl	0.30	0.88	2.95	1740	5843	15.0	13.3	10.7	37.9	13.2	45.9
Zn-Oct_Linkers-4_qom	0.28	0.89	3.17	1753	6253	16.6	13.0	11.3	37.8	13.5	44.2
Zn-PDW_Linkers-4_rtl	0.29	0.87	3.05	1789	6253	15.4	14.1	11.0	37.7	13.6	45.4
Zn-Oct_Linkers-5_pcu	0.25	0.90	3.56	1498	5898	19.6	13.7	12.1	37.2	14.5	43.5
Linker-3_CuPW-4_tbo	0.19	0.93	4.95	1179	6307	30.5	18.1	15.5	36.5	17.8	40.8
Linker-1_CuPW-4_tbo	0.18	0.92	5.17	1168	6537	31.0	18.4	16.0	36.2	18.3	40.6
Linker-2_CuPW-4_tbo	0.19	0.91	4.70	1235	6351	30.7	16.5	14.7	35.9	17.2	41.0



Synthesis and Activation of MOFs

Synthesize at least 3 additional MOFs predicted to have high volumetric capacity. Characterize surface area; if surface area is within 15% of theory, measure H₂ uptake.

Top performing MOFs according to our ML+GCMC calculations at temperature+pressure swing conditions

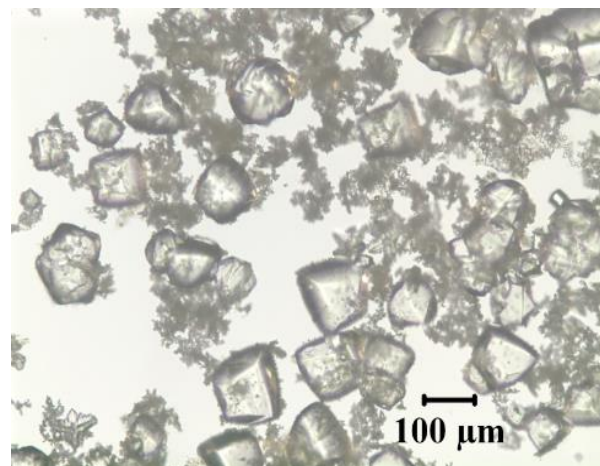
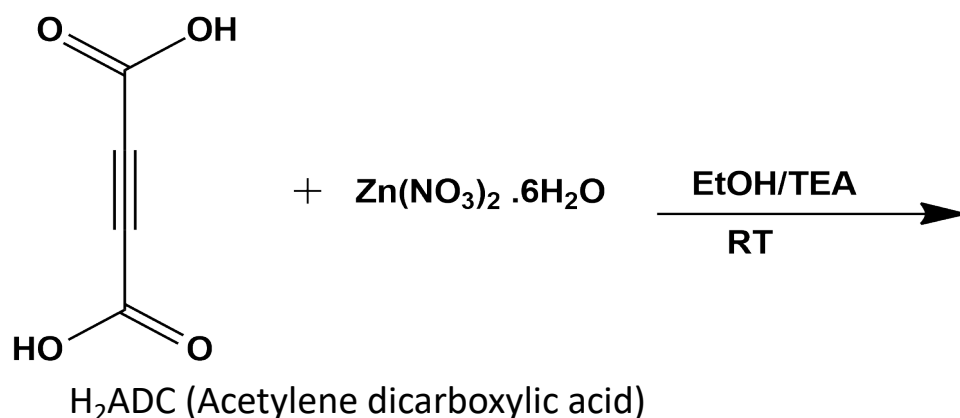
Name	Identity	Density	GSA	VSA	VF	PV	LCD	PLD	TPS UG 100 bar	TPS UV 100 bar
MOF-5_cooH_2_16_4_basic_opt	Mail-order	0.70	3072	2154	0.68	0.68	7.8	12.2	8.0	61.1
MOF-5_cooH_2_2738_1_basic_opt	Mail-order	0.47	4548	2149	0.78	1.34	7.8	15.8	10.8	57.7
BOQQAB (MOF-650)	CSD refcode	0.49	3908	1919	0.85	1.73	18.3	9.9	10.2	56.5
MOF-5_cooH_2_972_1_basic_opt	Mail-order	0.67	3038	2037	0.74	0.95	6.7	11.9	7.5	54.9
hypotheticalMOF_5056615_i_1_j_29_k_2 _m_2_cat_1	Northwestern	0.56	4388	2474	0.79	1.41	7.9	9.6	8.6	53.8
ODIXEG (PCN-516)	CSD refcode	0.55	4090	2259	0.84	1.42	10.4	7.5	8.8	53.7
hypotheticalMOF_5057692_i_1_j_29_k_1 9_m_2	Northwestern	0.55	4546	2489	0.80	1.47	7.2	9.4	8.8	53.6
ENITAX	CSD refcode	0.57	4021	2304	0.83	1.36	10.1	7.2	8.5	53.5
FINJAO	CSD refcode	0.47	6977	3258	0.80	1.70	7.4	6.4	10.2	53.5
TEQPEM	CSD refcode	0.57	3456	1980	0.86	1.45	17.2	9.2	8.5	53.5

Attempts were made to synthesize the MOFs highlighted above in red



Synthesis and Activation of MOFs (1)

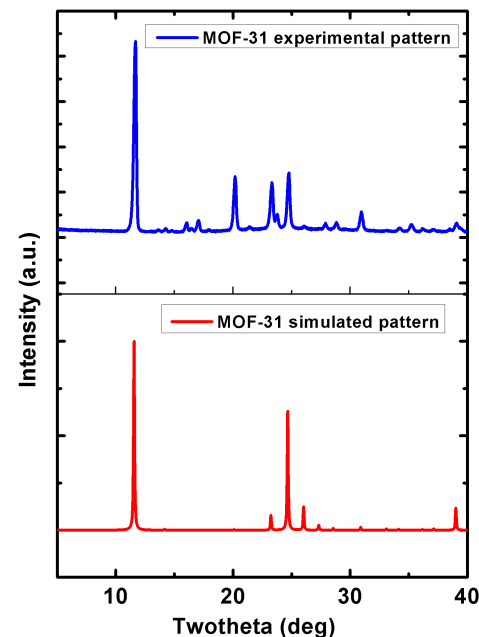
MOF name: MOF-5_cooH_2_16_4_basic_opt (a.k.a. MOF-31)



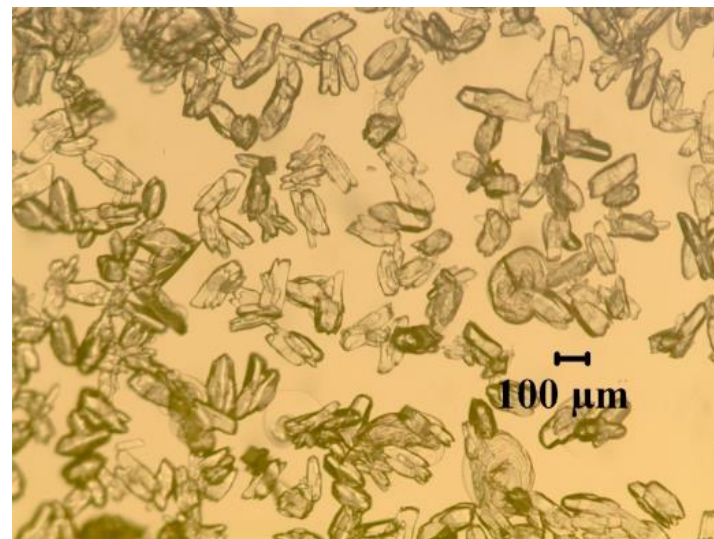
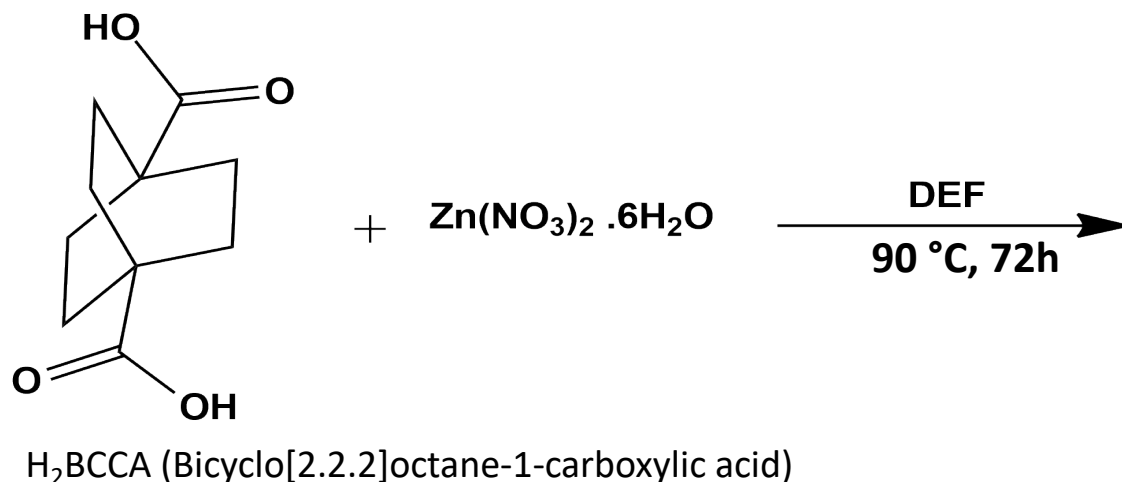
Synthetic process for MOF-31

OM Yaghi et al. J. Am. Chem. Soc., **123**, 8239 (2001)

- The obtained material (in combination with a minor phase) was washed with ethanol two times and underwent solvent exchange with CH₂Cl₂. Activated by dynamic vacuum (10⁻² Torr) at room temperature for 24 h.
- The obtained material exhibits a very low BET surface area of 11 m²/g. The calculated value is 3072 m²/g.
- **Flowing supercritical CO₂ activation:** The ethanol soaked sample was exchanged with supercritical CO₂ at 100 bar resulting in a material with a very low BET surface area of 13 m²/g.



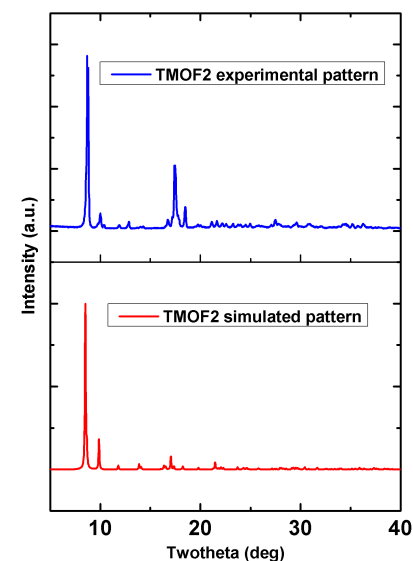
MOF name: MOF-5_cooH_2_972_1_basic_opt (a.k.a. TMOF2)



Synthetic process for TMOF2

PJ Llabres-Campaner, et al., Dalton Trans., **46**, 7397(2017)

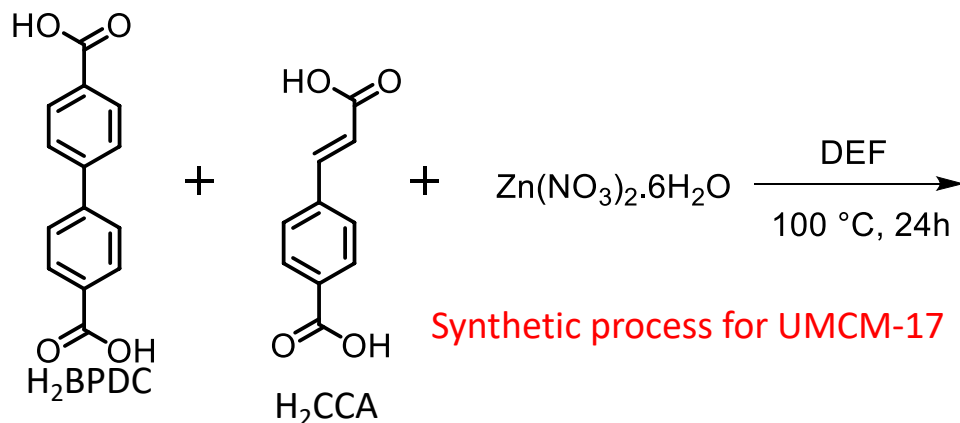
- The obtained MOF underwent solvent exchange with DMF followed by CH₂Cl₂. The material was activated by dynamic vacuum (10⁻² Torr) at room temperature for 24 h.
- The obtained material exhibits a very low BET surface area value of 8 m²/g. The calculated value is 3038 m²/g.
- Flowing supercritical CO₂ activation:** The DMF soaked sample was exchanged with supercritical CO₂ at 100 bar resulting in a material with a BET surface area of 621 m²/g.





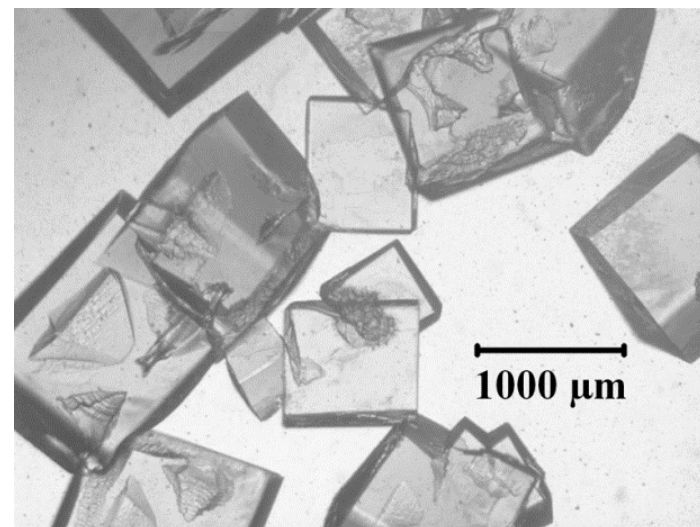
Synthesis and Activation of MOFs (3)

MOF name: UMCM-17

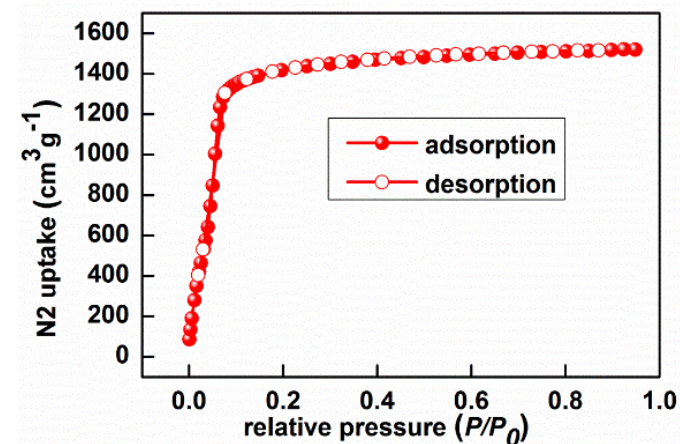


H₂BPDC- Biphenyl-4,4'-dicarboxylic acid

H₂CCA- 4-carboxycinnamic acid

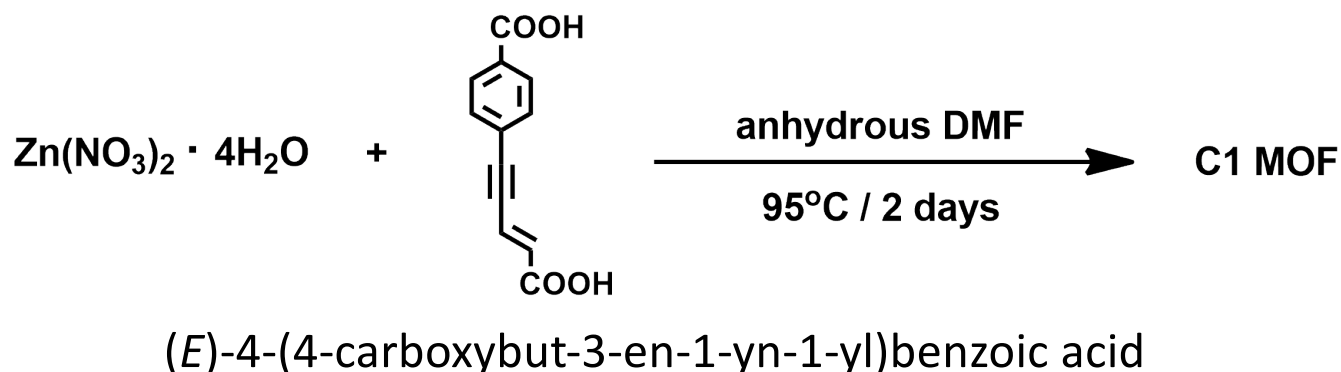


- Targeted to allow greater pore volume while maintaining the linker of SNU-70. Strategy thwarts interpenetration.
- Material washed with DMF and exchanged with CH₂Cl₂. The crystals were soaked in 20 mL of CH₂Cl₂ 3 times over 1h.
- The crystals were then immersed in n-hexane over 1 h replacing the solvent every 20 min.
- Once the solvent exchange is complete, the material was isolated by decanting the n-hexane and the crystals were evacuated under dynamic vacuum (10⁻² Torr) for 12h at room temperature.



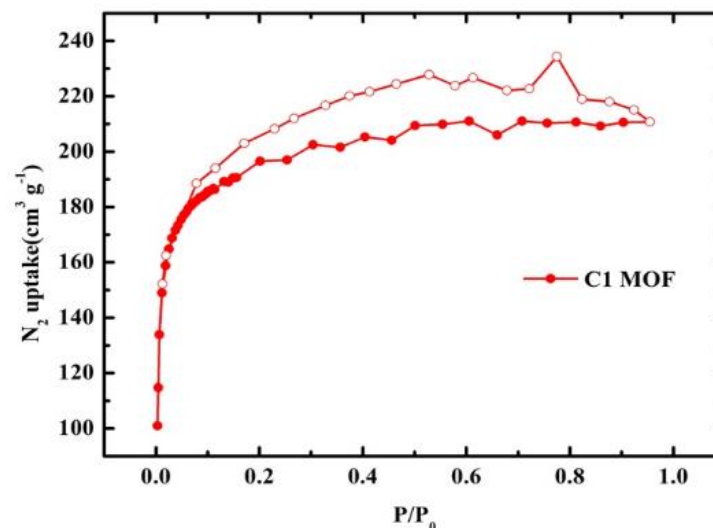
BET surface area: 5609 m²/g

MOF name: Zn-Oct_Linker-5_pcu (a.k.a. C1 MOF)



Synthetic process for C1 MOF

- Initially the material was washed with DMF and was first exchanged with CH_2Cl_2 . The crystals were soaked in 20 mL of CH_2Cl_2 seven times over 24 h.
- The crystals were then immersed in n-hexane over 1 h replacing the solvent every 20 min.
- Once the solvent exchange is complete, the material was isolated by decanting the n-hexane and the crystals were evacuated under dynamic vacuum (10^{-2} Torr) for 12h at room temperature.



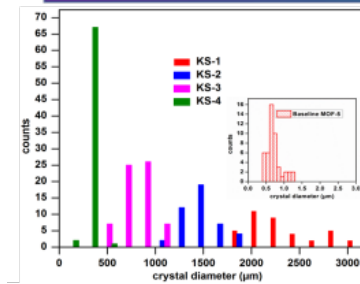
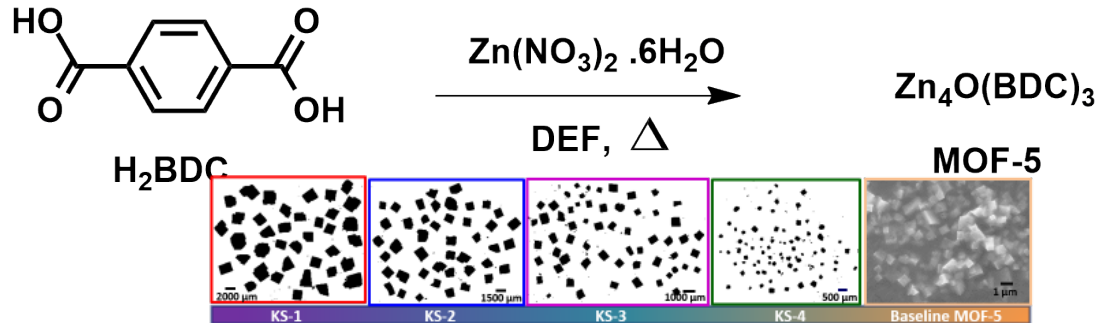
BET surface area = 752 m²/g
 Calculated value = 5898 m²/g



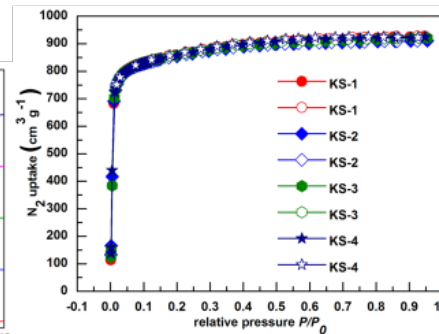
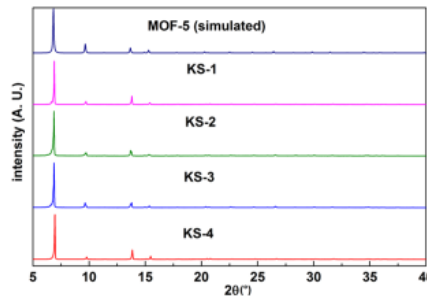
Crystal Size Control

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

Synthesis Protocols: Varying Metal : Linker ratio



sample name	mean (μm)	median (μm)	S.D. (μm)	S.E (μm)
KS-1	2349	2259	334	54
KS-2	1500	1460	189	29
KS-3	808	840	163	20
KS-4	279	269	55	7
Baseline MOF-5	0.72	0.68	0.22	0.03

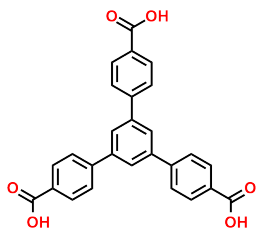
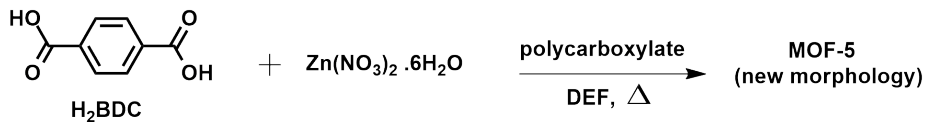


Crystal size histograms for the different batches (KS-1 to KS-4) indicate the successful control over crystal size without compromising surface area

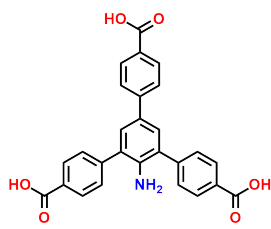


Morphology Control

Identified additive (polycarboxylate) capable of controlling morphology of MOF-5 crystals

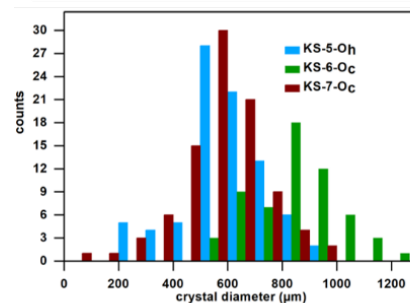
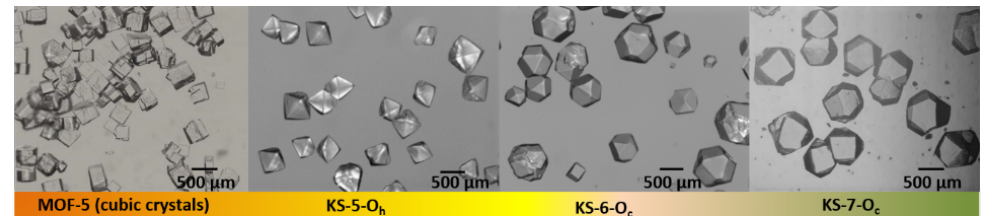


H₃BTB

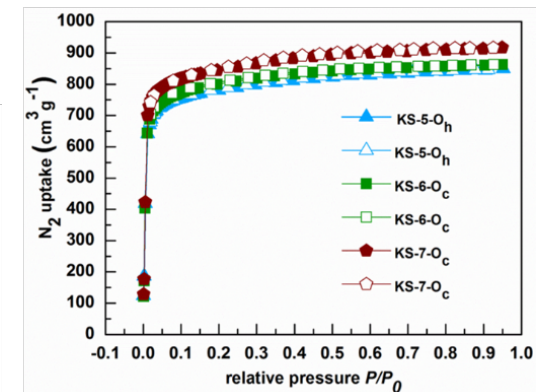
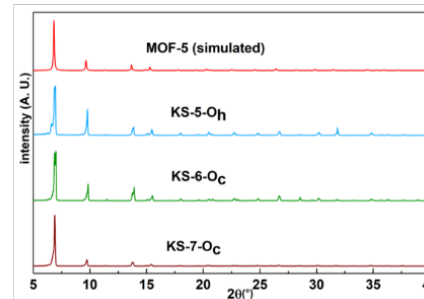


H₃BTB-NH₂

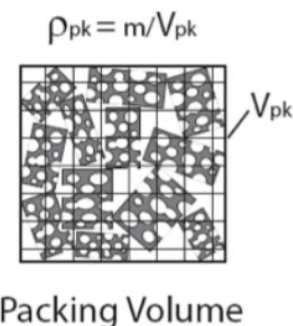
Optical images and BET surface area indicate that morphology control was successful without compromising surface area (at most ~100 m²/g reduction compared to cubic MOF-5)



Sample Name	Mean (μm)	Median (μm)	S.D. (μm)	S.E. (μm)
KS-5-O _h	600	604	151	16
KS-6-O _c	856	873	154	20
KS-7-O _c	575	570	140	14



- The MOF powder baseline was BASF MOF-5 used by the HSECoE
- As recognized by NREL, powder packing density is a critical factor influencing the accuracy of volumetric density measurements
- Packing density can be influenced by:
 1. Technique (manual vs. automated)
 2. Number of taps
 3. Crystal size and morphology



- The MOF-5 baseline powder packing density from HSECoE ranged from 0.13 g/cc for un-tapped powder¹ (10s) to 0.21 g/cc² using thousands of manual taps.

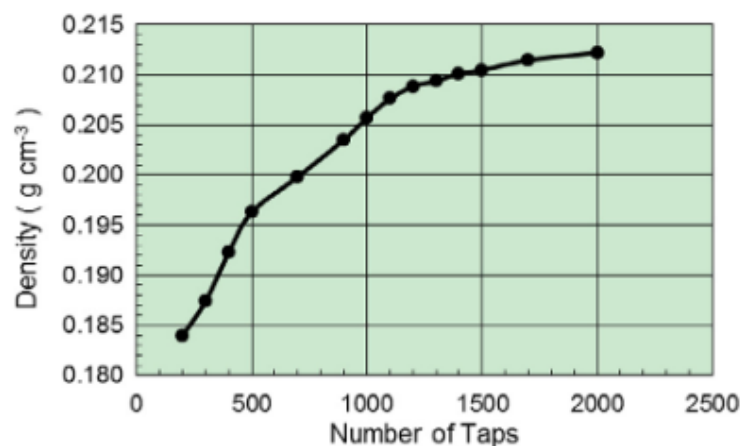


Fig. 4. Tap density of MOF-5 as a function of the number of taps.

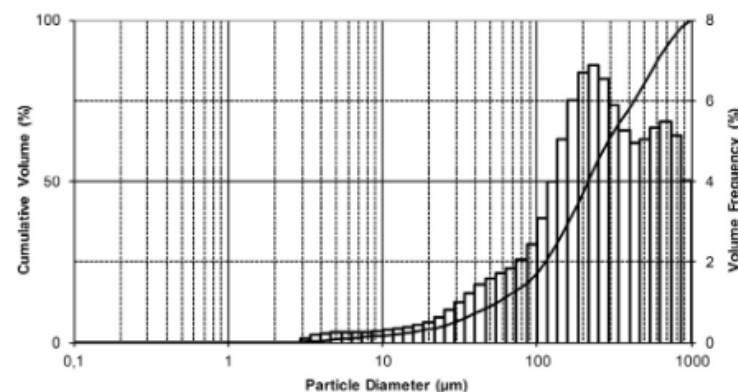
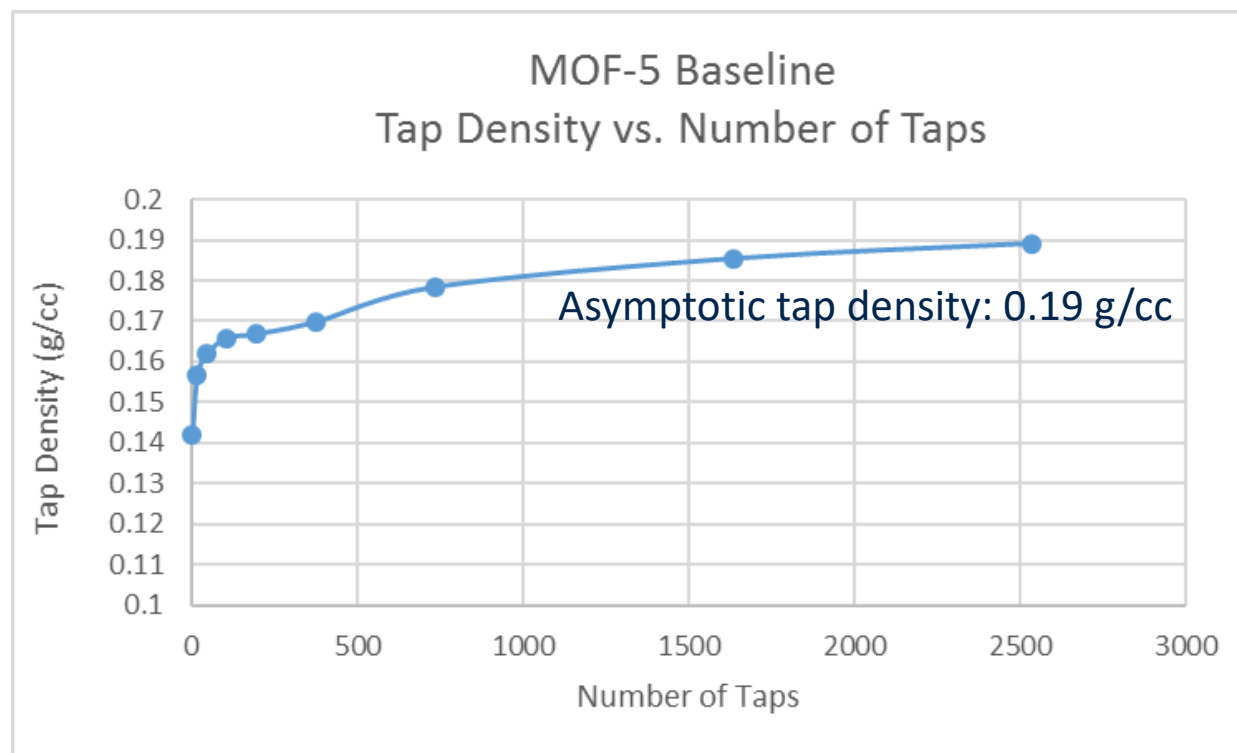
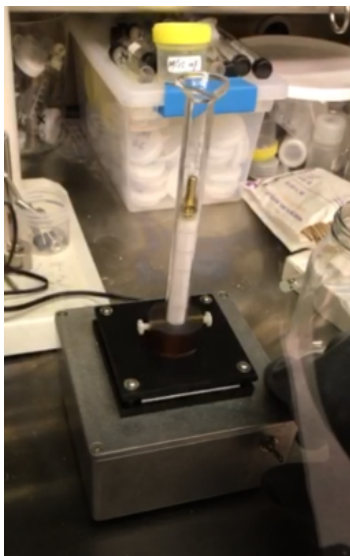


Fig. 3. Particle size distribution and cumulative volume percentage for a representative MOF-5 powder. The distribution has a mean diameter of 215 μm; 99% of the particles have a diameter less than 857 μm.

- MOF-5 packing density measurements were performed using a UM-developed jolting volumeter (shown below in glovebox) with 35 g rod on the powder for containment and consistent tap density. Volumeter frequency = 3 taps/sec
- MOF-5 baseline powder was measured using same technique for 2nd Go/No-Go
- ~10 ml of MOF-5 sample was tapped ~2,500 times until an asymptote in density was observed



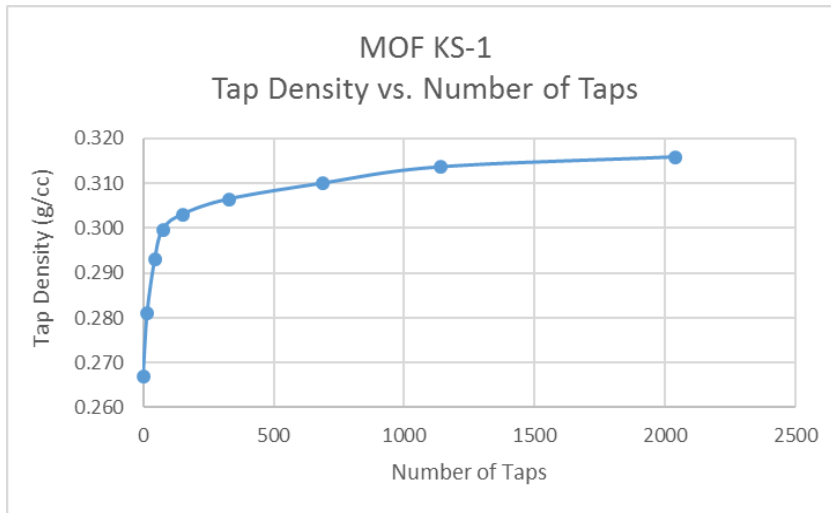


Packing Density Measurements

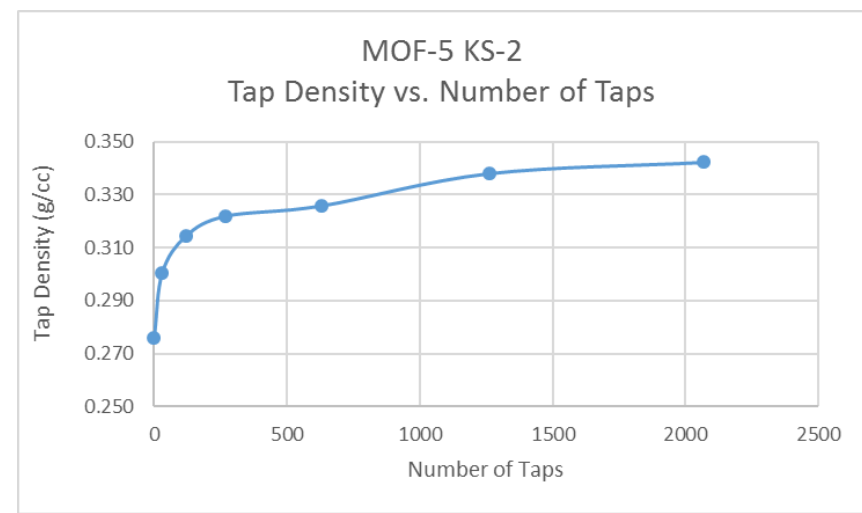


Packing density measurements were performed on UM MOF-5 samples having **controlled particle size**

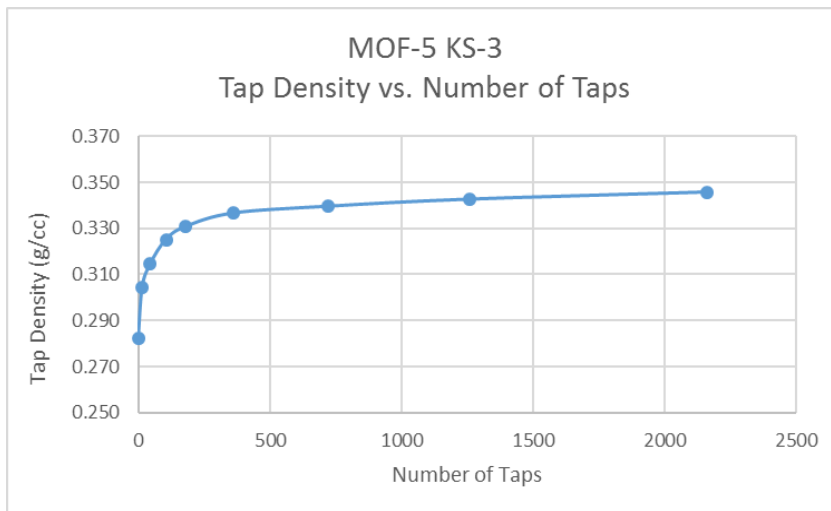
MOF-5 KS-1 Tap Density: 0.36 g/cc



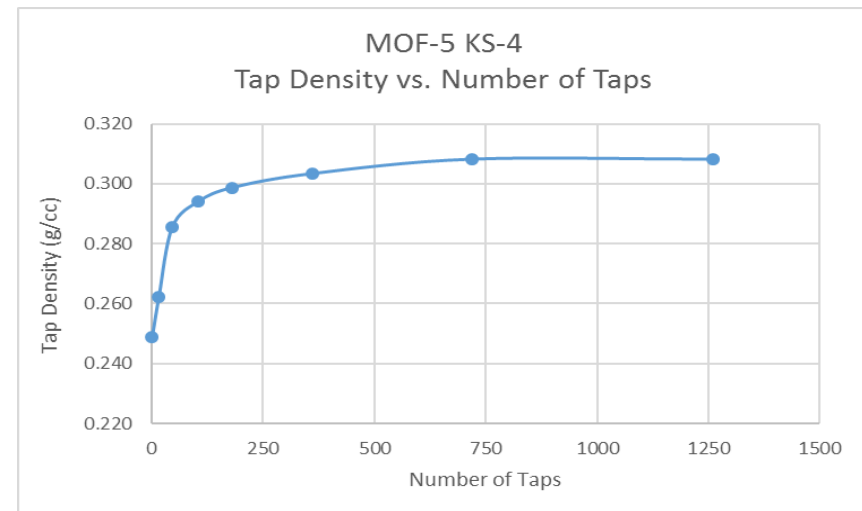
MOF-5 KS-2 Tap Density: 0.32 g/cc



MOF-5 KS-3 Tap Density: 0.35 g/cc



MOF-5 KS-4 Tap Density: 0.31 g/cc





Accomplishments: Packing Density



The packing density of UM MOF-5 samples having **controlled particle size** are up to **87% greater** than that for the baseline powder (BASF MOF-5)

		55	163	189	
Standard deviation particle size (micron)		55	163	189	
Volumeter tap density (g/cc)	0.189	0.308	0.346	0.342	0.355
Improvement over baseline	n/a	63%	83%	81%	87%
Surface area as synthesized (UM)	n/a	3550	3539	3457	3497
Surface area after tap density (Ford)	2937	3435	3435	3428	3447
Degradation	--	None	None	None	None

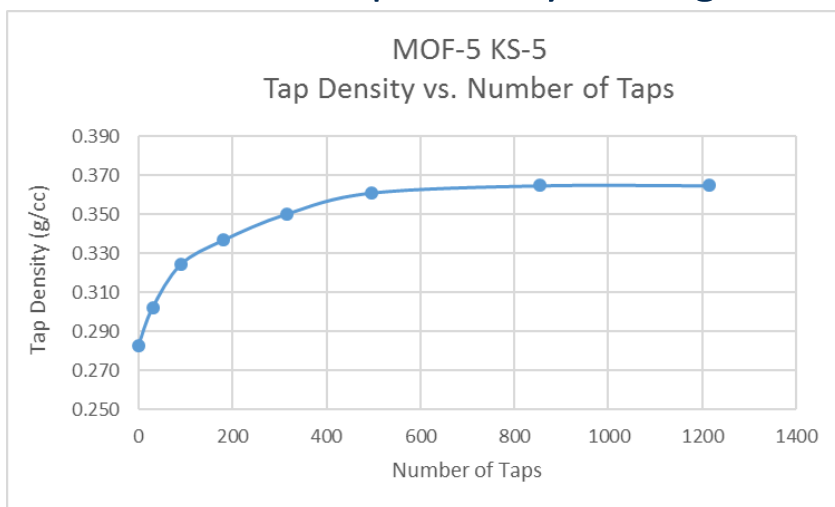


Packing Density Measurements

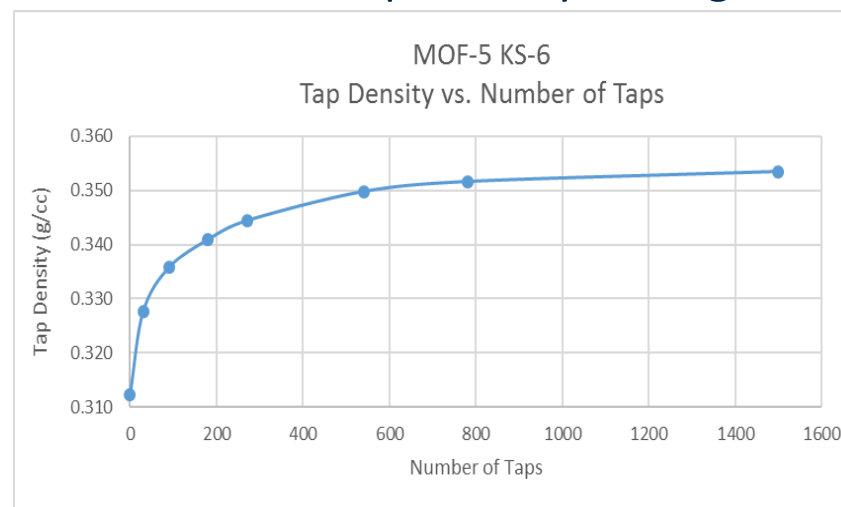


Packing density measurements were conducted on UM MOF-5 samples having **controlled morphology**

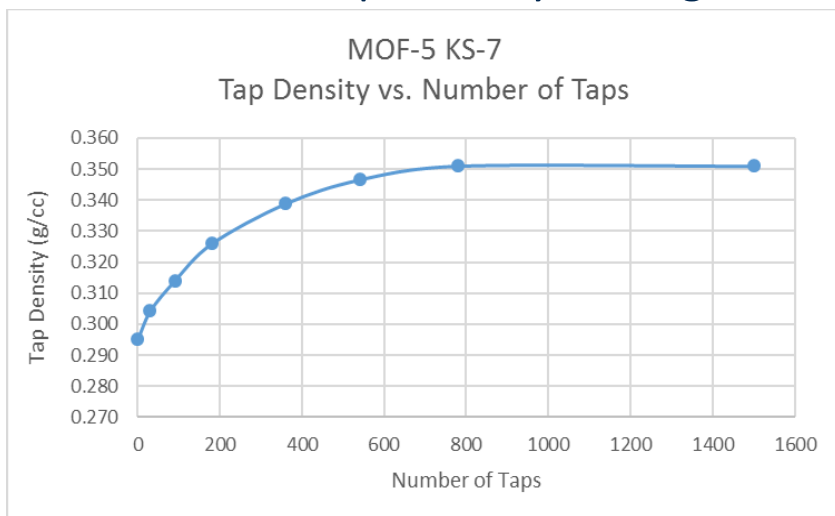
MOF-5 KS-5 Tap Density: 0.37 g/cc



MOF-5 KS-6 Tap Density: 0.35 g/cc



MOF-5 KS-7 Tap Density: 0.35 g/cc





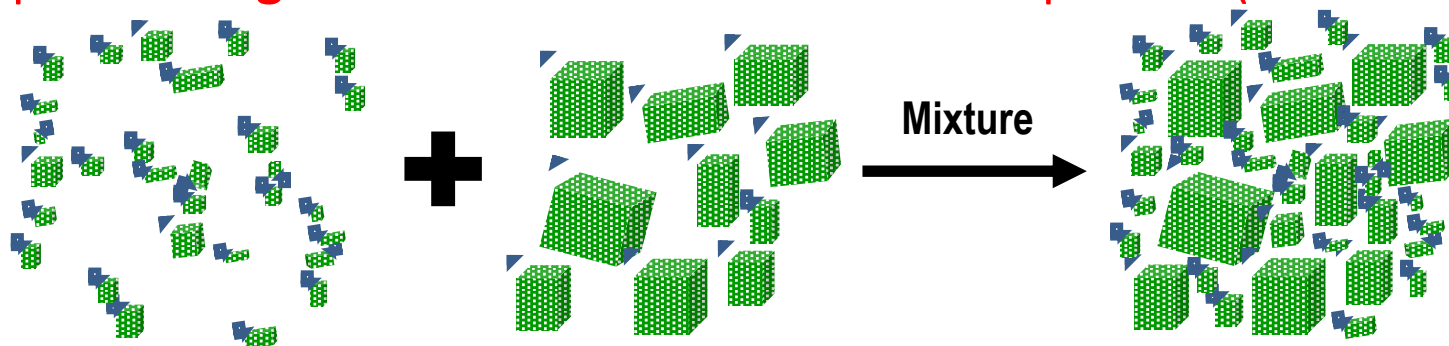
Accomplishments: Packing Density



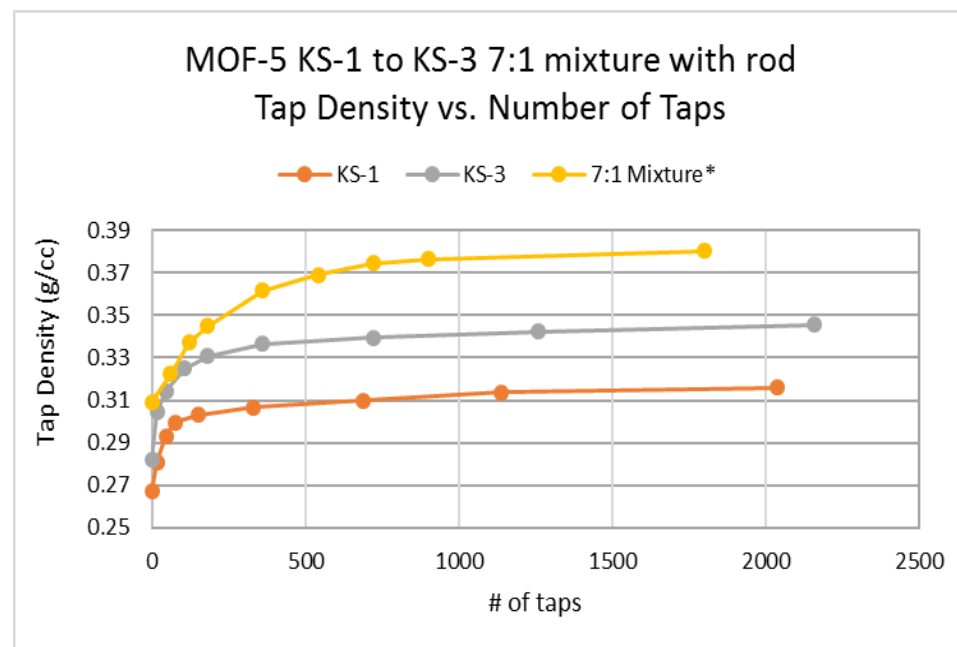
The packing density of UM MOF-5 samples having **controlled morphology** are up to **93% greater** than that for the baseline powder (BASF MOF-5)

		604	570	570
Standard deviation particle size (micron)	<1	151	154	140
Volumeter tap density (g/cc)	0.189	0.365	0.353	0.351
Improvement over baseline	n/a	93%	87%	85%
Surface area as synthesized (UM)	n/a	3434	3367	3352
Surface area after tap density (Ford)	2937	3245	3220	3353
Degradation	--	Minor	Minor	None

The packing density of UM MOF-5 samples with a **mixture of controlled particle sizes** are up to **100% greater** than that for the baseline powder (BASF MOF-5)

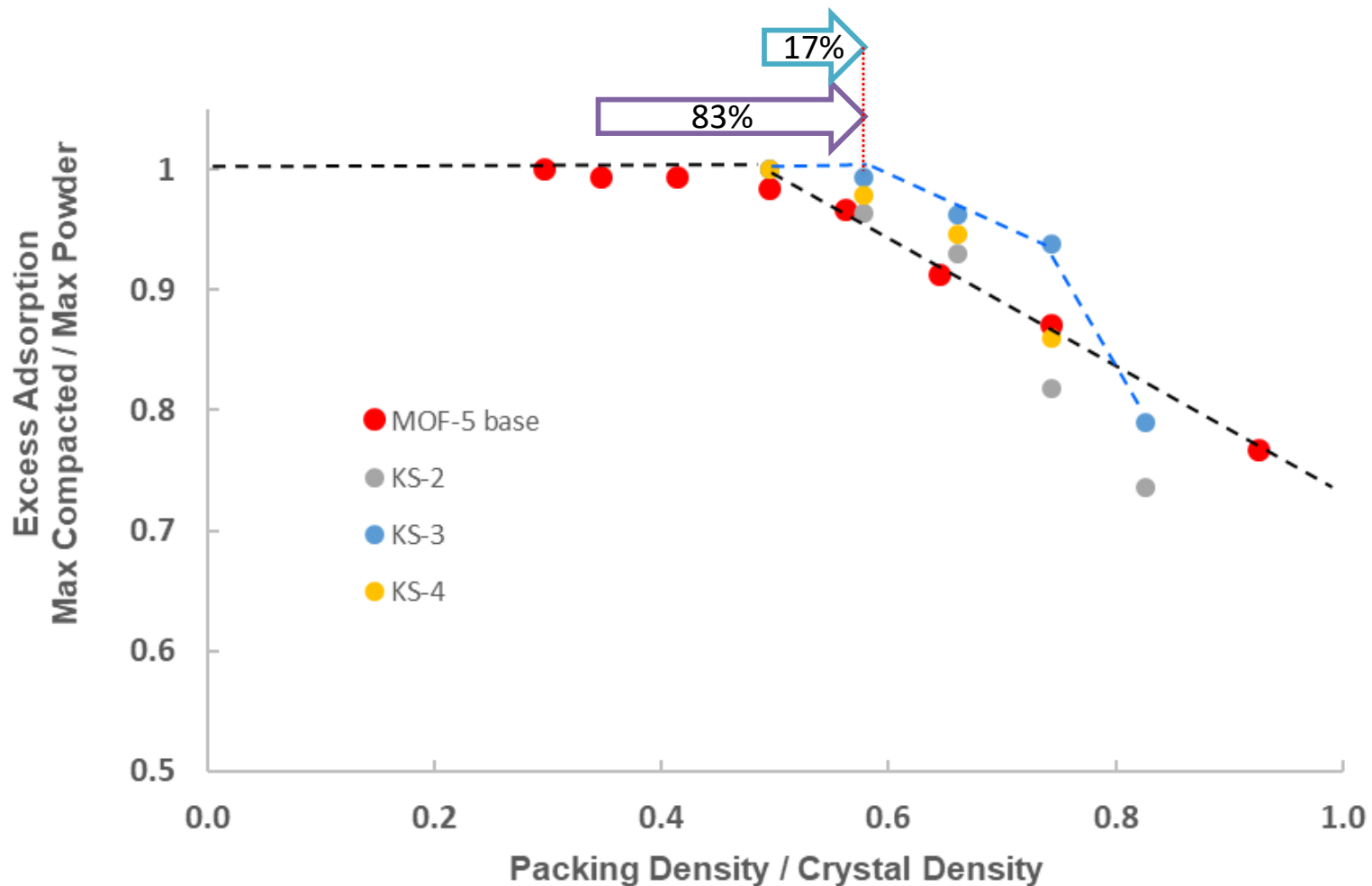


		808 + 2349
Standard deviation particle size (micron)	<1	163 + 334
Volumeter tap density (g/cc)	0.189	0.380
Improvement over baseline	n/a	100%
Degradation	--	None

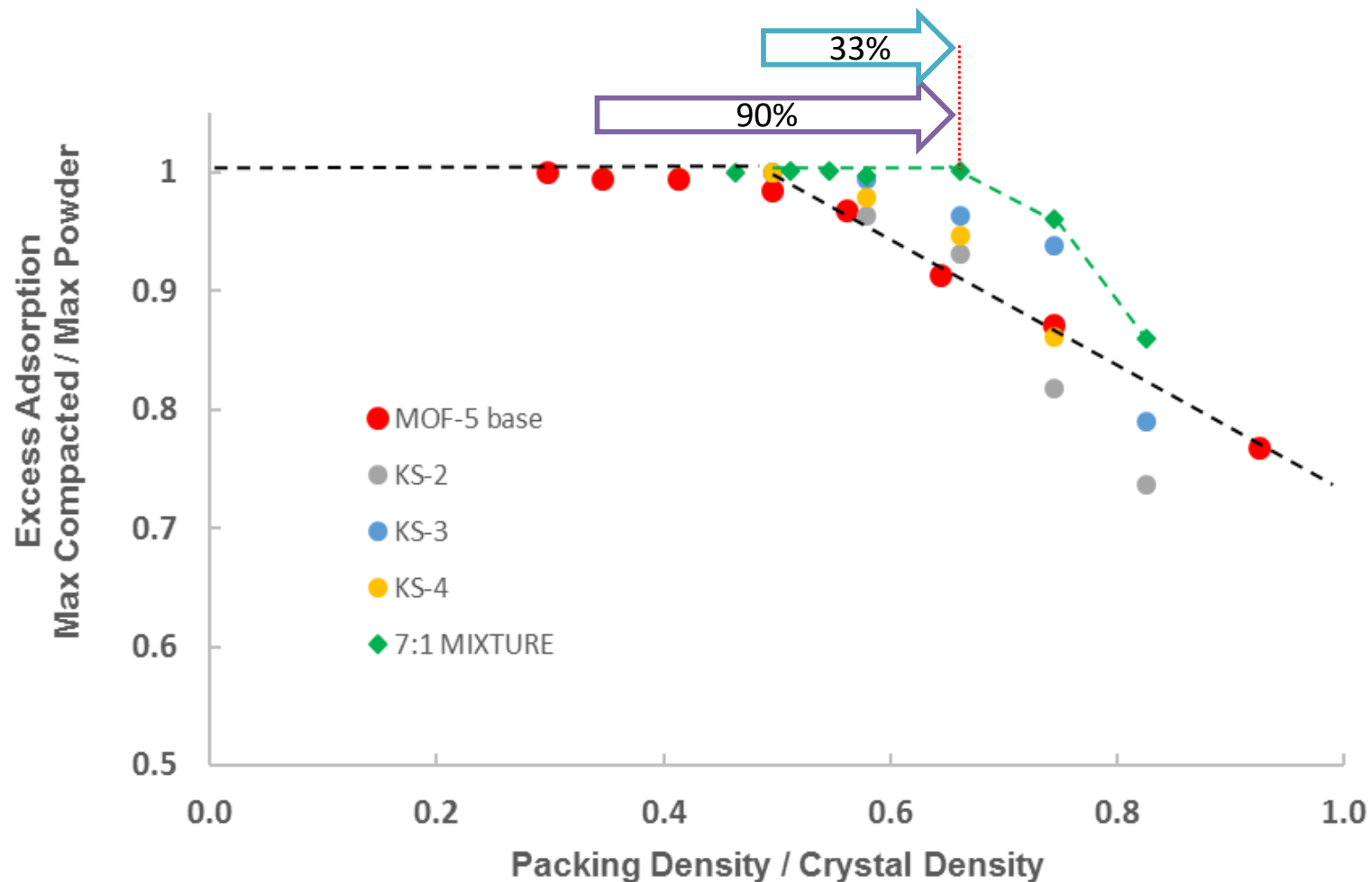


*second tap mixture

- Tapped, **size-controlled** MOF-5 exhibits a **83% improvement** in packing density from the tap density of baseline MOF-5
- Compacted, **size-controlled** MOF-5 exhibits a **17% improvement** over the compacted density of baseline MOF-5, with negligible performance loss



- Tapped, **7:1 mixture** size-controlled MOF-5 exhibits a **90% improvement** in packing density from the tap density of baseline MOF-5
- Compacted, **7:1 mixture** size-controlled MOF-5 exhibits a **33% improvement** over the compacted density of baseline MOF-5, with negligible performance loss

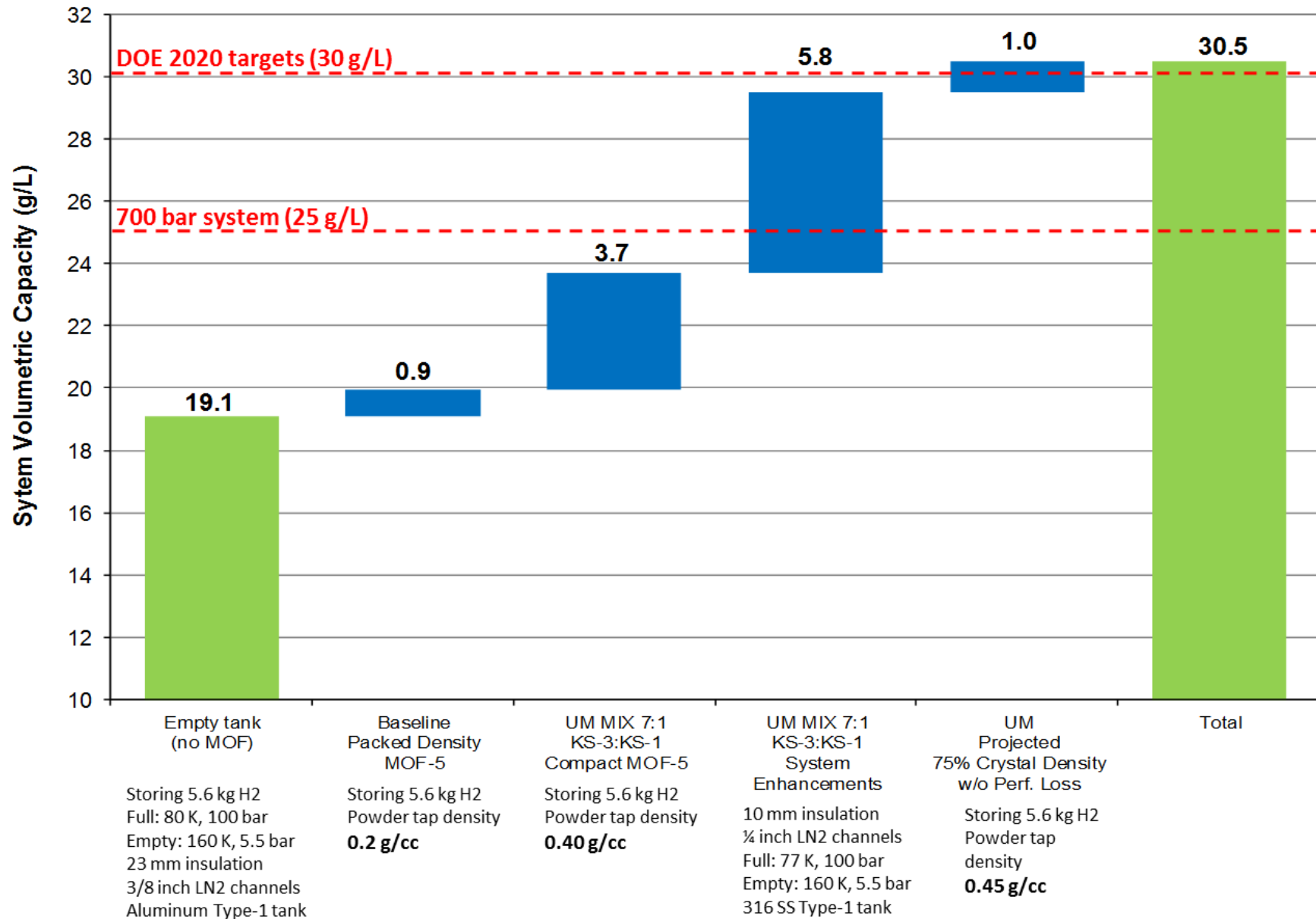




System Model Projections



HSECoE system model projection of pathway needed to achieve DOE 2020 targets





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)

- 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

- Conduct compaction study and isotherm measurements on samples with controlled morphologies
- Evaluate further improvements in tap density using mixtures of controlled particle size samples
- Evaluate further improvements in tap density using controlled morphology samples at different particle sizes
- Conduct compaction study and isotherm measurements on samples containing mixtures of particle size and controlled morphologies
- Continue to design hypothetical MOFs with high volumetric capacities
- Attempt to synthesize and characterize most promising MOF candidates

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 size distribution to increase packing density
- Apply machine learning to identify, design, and demonstrate high-capacity MOFs

- **Accomplishments:**

- Crystal engineering: successfully synthesized MOFs with tailored size and morphology with minimal loss in surface area
- Demonstrated 90% improvement in the tap density of MOF-5 through crystal engineering methods – passed 2nd go/no-go decision point
- Demonstrated ability to predict usable capacity of an arbitrary MOF to within ~95 % of GCMC values using only building blocks as input
- Developed procedure for the ‘inverse design’ of hypothetical MOFs based on building blocks that correlate with high H₂ capacities