Project ID: ST122

Hydrogen Adsorbents with High Volumetric Density:

New Materials and System Projections

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Overview

Timeline and Budget

Project Start Date: August 1st, 2015
Project End Date: July 31st, 2018

Total Project Budget: $1,040,000

Federal Share:

UM: $800,000
Ford: $192,000
Total: $992,000

Cost Share: $48,000 (Ford)

Total Funds Spent:* ~$500,000

*Estimated as of 3/31/17

Barriers

Barriers addressed

- Volumetric Density
- Gravimetric Density

Partners

Interactions/collaborations:

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

Project lead:

D. Siegel, University of Michigan

Background

- 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 is a promising approach due to its fast kinetics, facile reversibility, and high gravimetric densities
- An unfortunate characteristic of adsorptive storage is that high gravimetric densities typically come at the expense of volumetric density (total basis)
- HSECoE developed a 100 bar MOF-5-based storage system that approached competitiveness with 700 bar compressed. Our work in the HSECoE identified additional MOFs that may out-perform MOF-5, potentially resulting in a low-pressure system that could surpass 700 bar

Project goal: Demonstrate best-in-class MOFs that achieve high volumetric and gravimetric H_2 densities *simultaneously*, while maintaining reversibility and fast kinetics

Relevance

Objective 1: Demonstrate MOFs with high volumetric and gravimetric hydrogen densities, exceeding those of MOF-5

- Prior studies typically focus on maximizing gravimetric density alone
- Synthetic efforts guided by high-throughput screening
- If successful, these compounds will **set a new high-water mark** for H_2 density in adsorbents at cryogenic conditions

✓ **Computationally screened H_2 capacity of ~470,000 MOFs**

✓ **Identified 2,000+ compounds that exceed the performance of MOF-5 benchmark by 15%**

Objective 2: System-level projections

- Project performance of most promising compounds to the system level by parameterizing models developed by the HSECoE
- Clarify how materials properties impact system performance

✓ **Completed first demonstration of HSECoE model to IRMOF-20 and DUT-23(Co)-based systems**

Approach

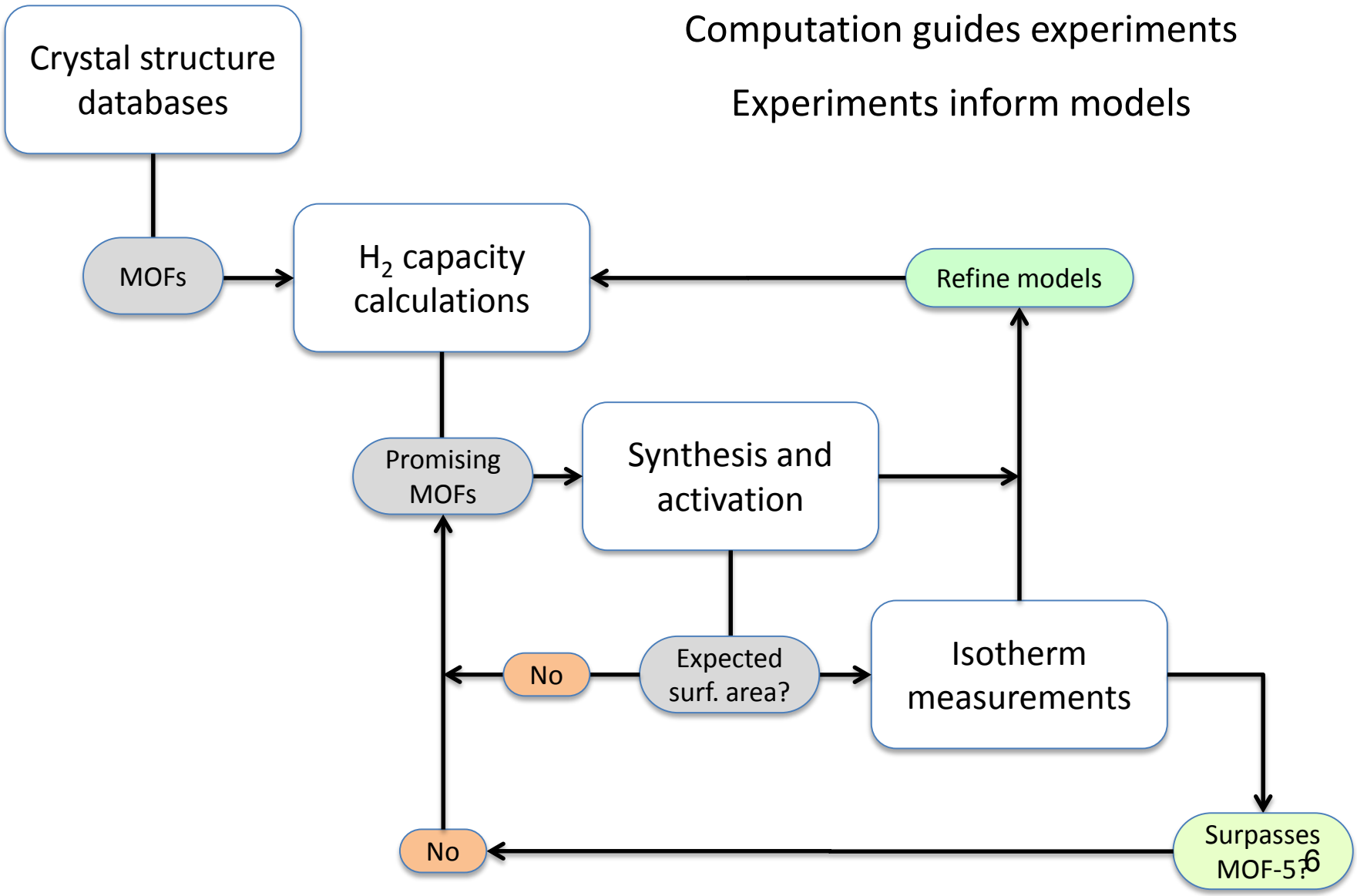
Notes:

- All volumetric hydrogen densities reported assume single-crystal MOF densities.
- Unless otherwise stated, all measurements and calculations are performed at T = 77 K.

Concept

Computation guides experiments

Experiments inform models



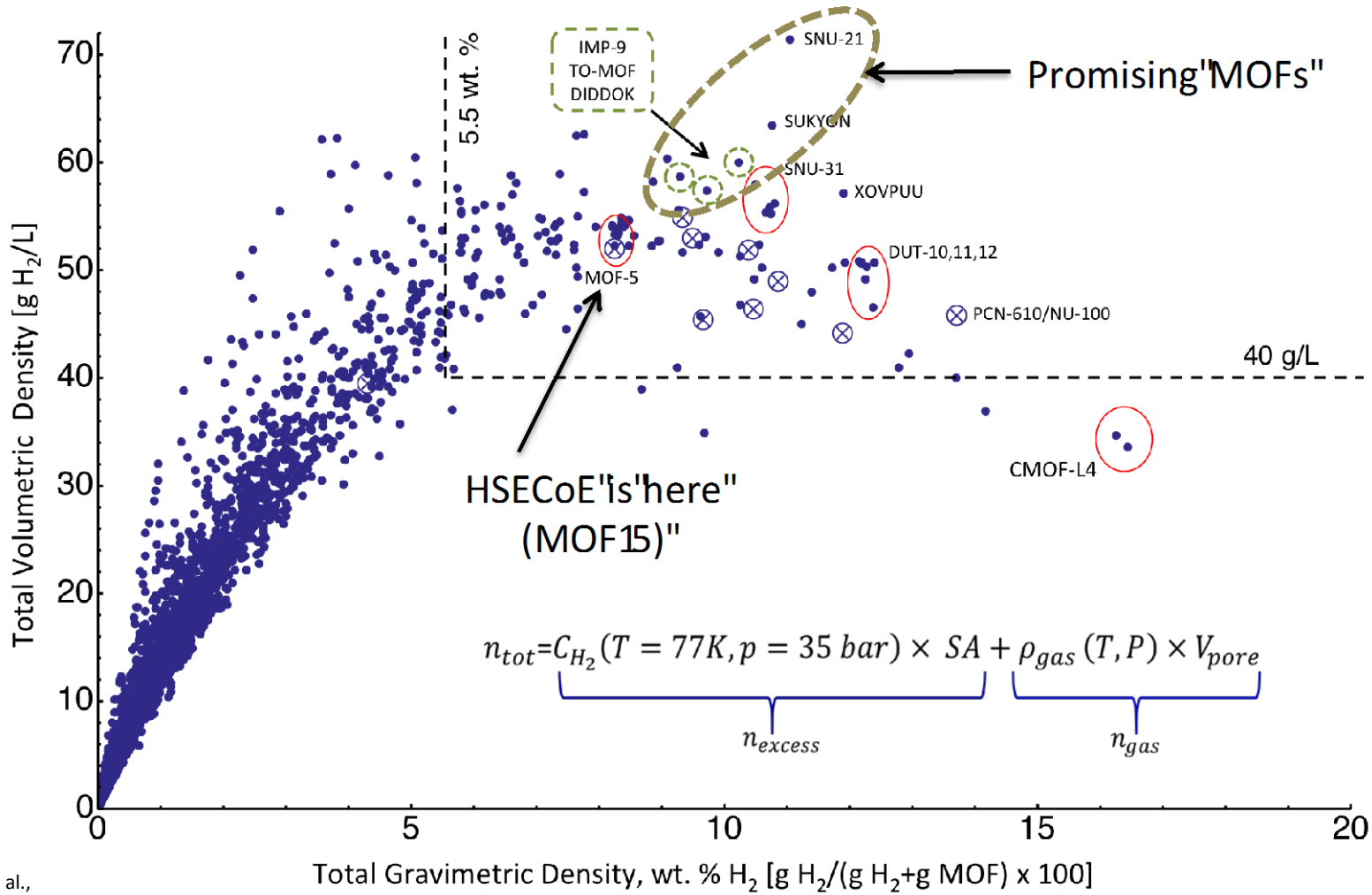
Year 2 Milestones

Our approach links atomic scale computation, experimental synthesis & characterization, and system level modeling

Year	Milestone or Go/No-Go	Due	Description	Status
2	Milestone	10/31/16	Measure degree of residual solvent/salt present in compound from Go/No-go 1; demonstrate less than 5% retention	**Complete**. Good agreement between measured and calculated surface areas of IRMOF-20 indicate nearly complete solvent removal.
2	Milestone	1/31/17	Identify at least 1 MOF from GCMC and refined high-throughput screening from expanded MOF database that has the potential to exceed the performance of MOF-5 baseline system.	**Complete**. 2,000+ compounds identified.
2	Milestone	4/30/17	Synthesize 2 additional promising MOFs identified by the revised screening analysis. The goal is for at least 1 MOF to reach 75% of the projected surface area.	**Complete.** At least 2 MOFs within 90% of calculated SA; a 3rd MOF is within 80%.
1	**Go/No-Go**	7/31/16	Demonstrate at least 1 MOF with >90% projected SA, >3,000 m^2/g, and H_2 capacity matching MOF-5 baseline	**IRMOF-20 demonstrated**
2	**Go/No-Go**	7/31/17	Demonstrate at least 1 MOF with hydrogen capacities exceeding baseline MOF-5 by 15%	**In progress**

High-throughput Screening

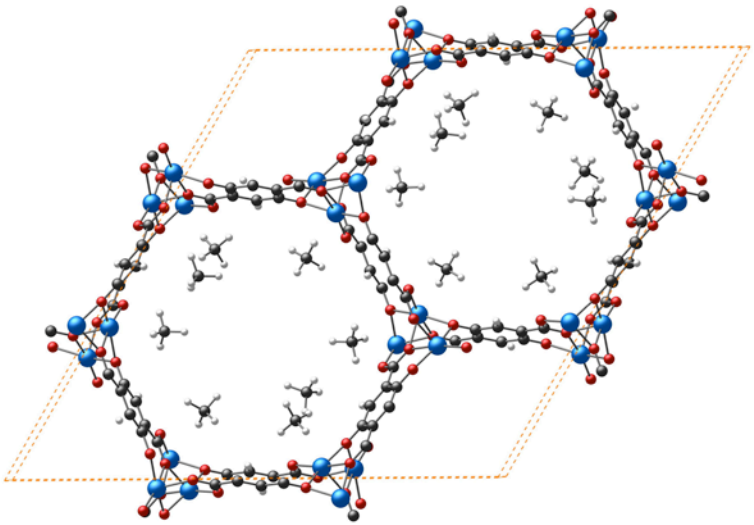
Prior work: developed a database of MOFs by mining the CSD. Chahine rule and crystal structure were used to predict H_2 capacity in thousands of compounds



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

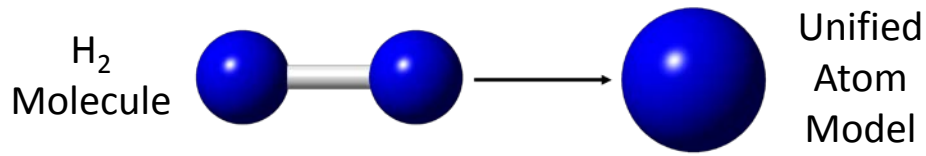
Grand Canonical Monte Carlo

- 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



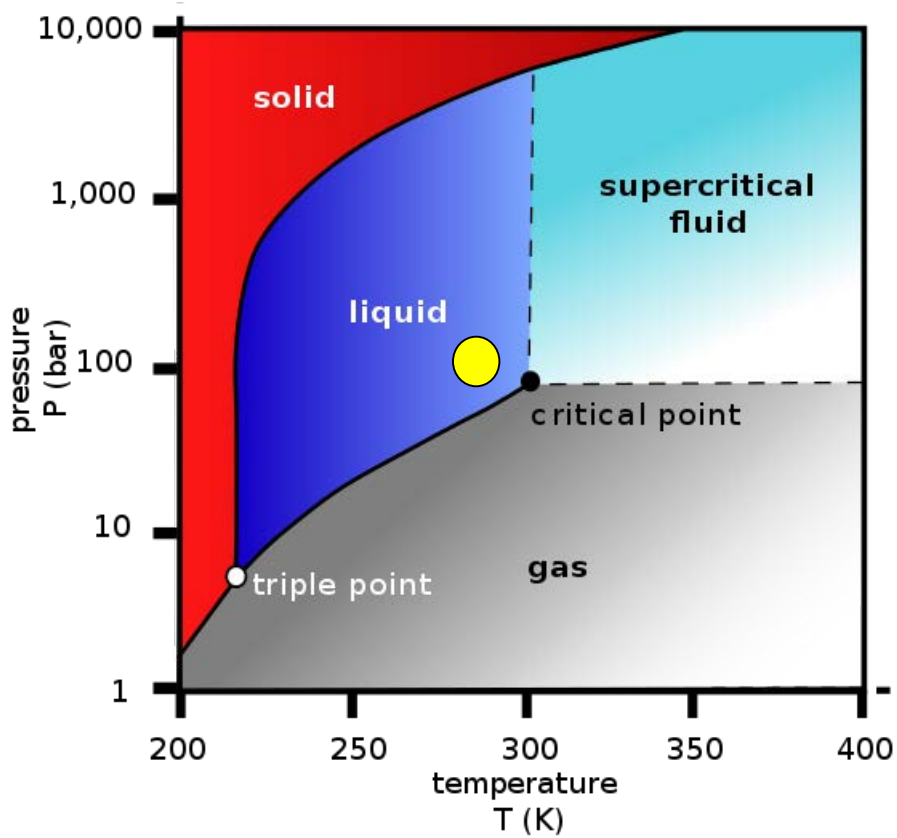
$$U_{ij}(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$

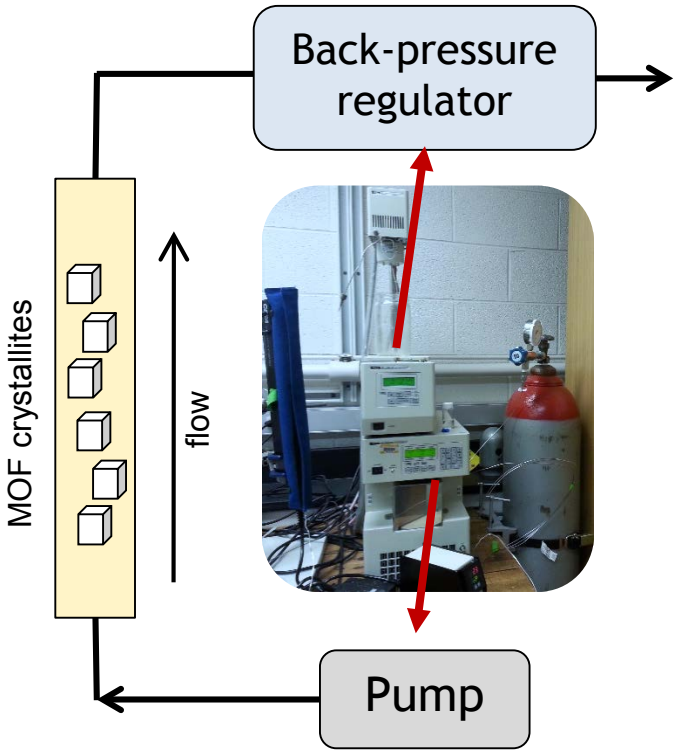
Force Field	Sigma (Å)	Epsilon/k_B (K)
MGS	2.958	36.7
Pseudo-FH	3.064	30.1

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

Flowing Supercritical CO_2 Activation

Flowing supercritical CO_2 activation is milder than vacuum activation
→ minimizes pore collapse and maximizes surface area





Batch activation: Nelson, A. P.; Farha, O. K.; Mulfort, K; Hupp, J. T. *J. Am. Chem. Soc.* **2009**, *131*, 458.
Flow activation: Liu, B.; Wong-Foy, A. G.; Matzger, A. J. *Chem. Commun.* **2013**, *49*, 1419.

Vacuum *vs.* Flow Activation

MOFs activated with flowing sc-CO_2 generally exhibit superior properties

Material	Surface area (flow Sc-CO_2 activation)	Surface area (vacuum/batch Sc-CO_2 activation)
UMCM-9	5357 m^2/g	1330 m^2/g (vac)
FJI	4813 m^2/g	4043 m^2/g (batch)
MOF-74 (Zn/DOBDC)	1108 m^2/g	750-950 m^2/g (vac)
UMCM-10	4001 m^2/g	Structure collapses under vacuum activation
UMCM-12	4849 m^2/g	Structure collapses under vacuum activation
IRMOF-8 (non-interpenetrated)	4461 m^2/g	Structure collapses under vacuum activation
A series of functionalized IRMOF-8 (non-interpenetrated)	~4000 m^2/g	-
HKUST-1	1710-1770 m^2/g (heating required)	682-1944 m^2/g (vac)

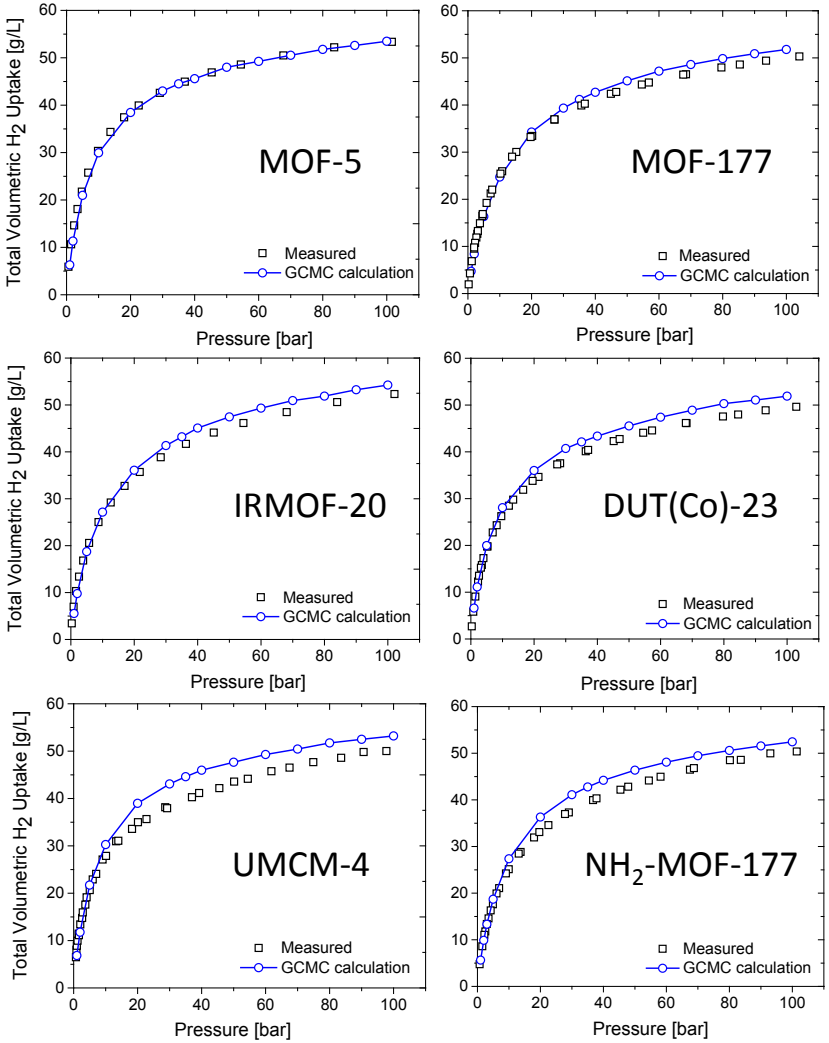
Liu, B.; Wong-Foy, A. G.; Matzger, A. J. *Chem. Commun.* **2013,** *49,* 1419.
Dutta, A.; Wong-Foy, A. G.; Matzger, A. J. *Chem. Sci.* **2014,** *5,* 3729.
Feldblyum, J. I.; Wong-Foy, A. G.; Matzger, A. J. *Chem. Commun.* **2012,** *48,* 9838.
Tran, L. D.; Feldblyum, J. I.; Wong-Foy, A. G.; Matzger, A. J. *Langmuir* **2015,** *31,* 2211.

Accomplishments and Progress

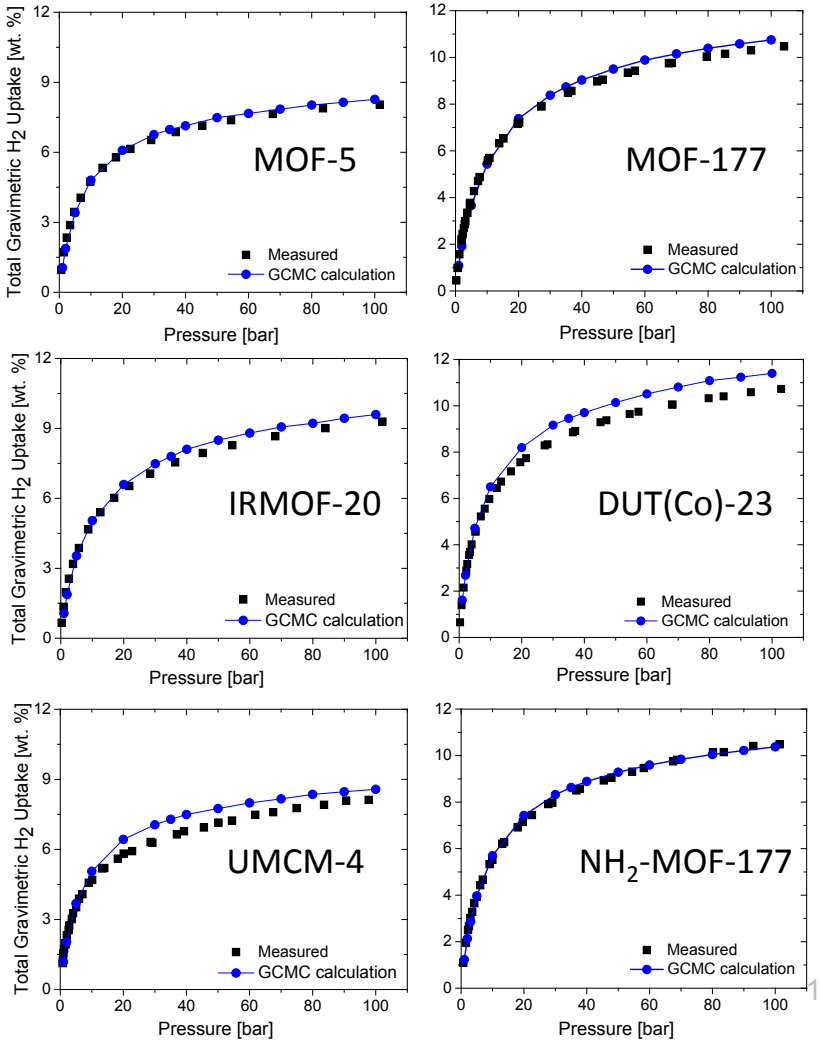
Examples of Simulated Isotherms

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

Total Volumetric H_2 Uptake

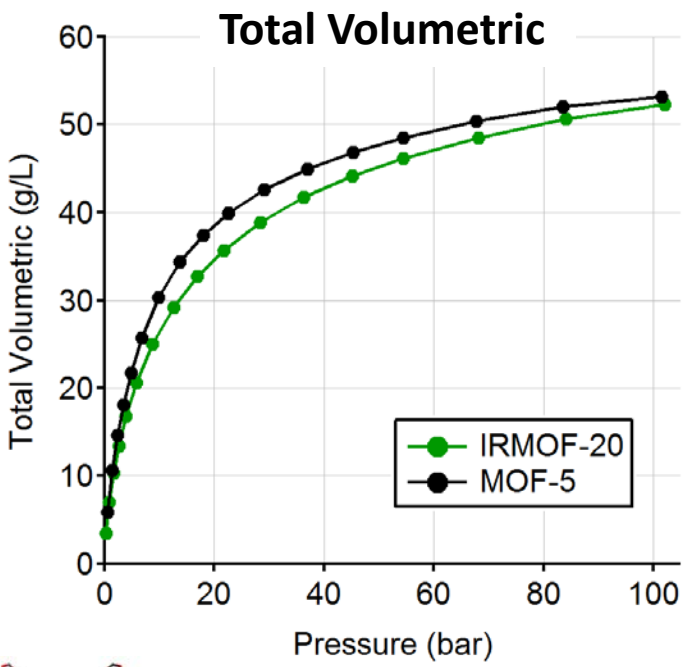


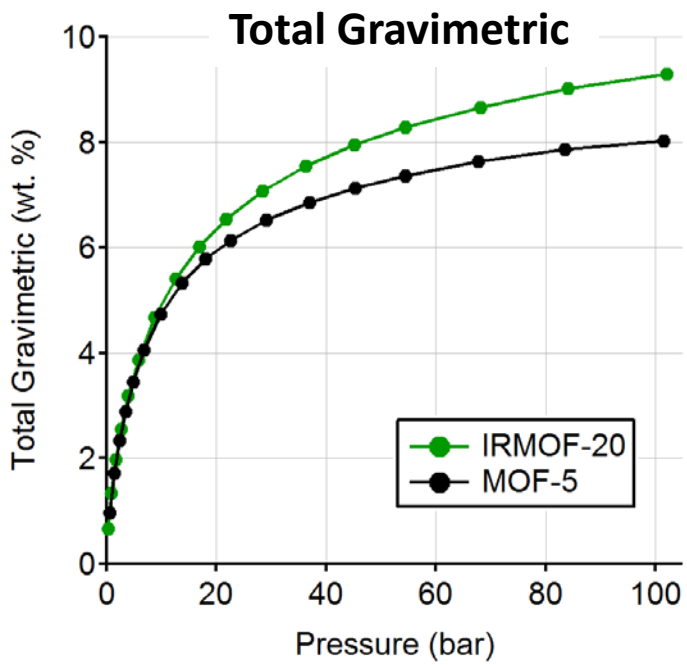
Total Gravimetric H_2 Uptake

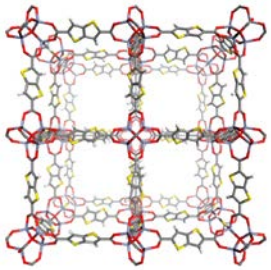


IRMOF-20 Capacity

Met 1st Go/No-Go Milestone: Usable capacity of IRMOF-20 surpasses that of MOF-5







*Pressure swing to P_{min} = 5 bar

	Usable Volumetric* ($g\ H_2/L$)		Usable Gravimetric* (wt. %)	
P (bar)	MOF-5	IRMOF-20	MOF-5	IRMOF-20
35	22.2	22.2	3.3	3.9
50	25.6	26.1	3.8	4.5
100	31.1	33.1	4.5	5.7

BET S.A. = 4073 m^2/g (94% of calc'd)
Calculated = 4324 m^2/g
Literature = 3409 m^2/g

Status: Top 20 Real MOFs

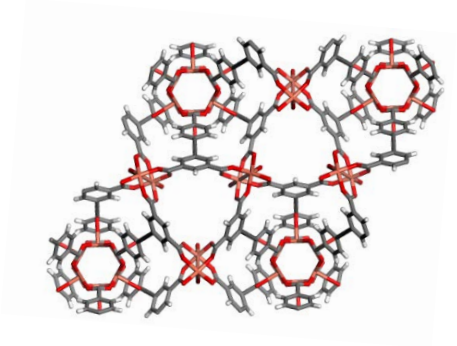
We are synthesizing and testing several MOFs projected to surpass MOF-5 by 15%

CSD REF. CODE	Common Name	Metal Type	Density [g/cm³]	Pore Diameter [Å]	VSA [m²/cm³]	GSA [m²/g]	Void Fraction	Pore Volume [cm³/g]	UG [wt. %]	UV [g/L]	Comment	Status
ECOLEP	–	Co	0.41	11.64	1836	4510	0.89	2.09	8.2	39.0	Stability issue after dehydration	Not attempted
XUKYEI	–	Cu	0.29	13.17	1817	6327	0.88	3.02	10.7	37.4	Rotatable bond; interpenetrated; low accessible surface area	Not attempted
VEBHUG	IRMOF-20	Zn	0.45	17.27	1936	4302	0.87	1.89	7.2	37.4	A version of IRMOF-20	Completed
BAZFUF	MOF-143	Cu	0.34	20.24	1860	5470	0.91	2.54	9.1	37.1	High experimental SA; activated material collapses	Completed
HABQUY	PCN-610	Cu	0.29	25.72	1664	5750	0.91	3.04	10.5	37.1	Lengthy linker synthesis	In progress
GAGZEV	NU-100	Cu	0.28	28.67	1613	5777	0.92	3.17	10.8	37.0	Same as HABQUY	In progress
ZELROZ		Zn	0.36	16.91	1790	4947	0.88	2.4	8.7	36.8	Lengthy linker synthesis	In progress
XAFFIV	DUT-10(Co)	Co	0.36	14.23	1910	5329	0.89	2.36	8.5	36.6	SA too far below calc.	Completed
VAGMAT	SNU-30	Zn	0.36	14.92	1898	5203	0.89	2.33	8.5	36.5	Isostructural to XAFFIV; could not be made	Completed
XAFFAN	DUT-10(Zn)	Zn	0.37	14.91	1892	5181	0.89	2.33	8.3	36.5	Same as VAGMAT	Completed
XAFFOB	DUT-10(Cu)	Cu	0.37	14.84	1907	5195	0.89	2.32	8.3	36.4	Isostructural to XAFFIV; SA too far below calc.	Completed
XAFFER	DUT-11	Zn	0.36	14.22	1861	5171	0.89	2.37	8.5	36.3	Same as VAGMAT	Completed
VAGMEX	SNU-30SC	Zn	0.35	15.28	1815	5152	0.9	2.43	8.7	36.3	Same as VAGMAT	Completed
NIBHOW	PCN-6’	Cu	0.28	27.51	1427	5103	0.92	3.19	10.6	36.2	Interpenetration is an issue; lit. SA is lower than that of interpenetrated MOF	Not attempted
ADATIK	**rht**-MOF	Cu	0.38	24.55	1724	4566	0.89	2.3	8.1	36.0	Flexible	Not attempted
ADATAC	**rht**-MOF	Zn	0.34	26.34	1735	5145	0.9	2.57	8.9	35.9	Flexible	Not attempted
VETMIS	–	Cu	0.31	17.24	1782	5713	0.9	2.77	9.5	35.7	Flexible, complex ligand; measured BET surface area < 1000 m²/g	Not attempted
XAHPON	CMOF-1a	Cu	0.28	17.3	1498	5268	0.92	3.1	10.4	35.5	Flexible	Not attempted
FEBXIV	CMOF-2	Cu	0.29	17.29	1517	5166	0.91	3	10.1	35.5	Flexible	Not attempted
LEJCIO	–	Zn	0.33	18.52	1722	5275	0.91	2.66	8.9	35.4	Flexible	Not attempted
MOF-5		**Zn**	**0.60**			**3512**		**1.14**	**4.5**	**31.1**		

MOFs Synthesized (1)

Several promising MOFs could not be synthesized with high surface area

OGEBAF (ZJU-32)



Cai, J. et al., *Chem. Commun.* **2014**, *50*, 1552.

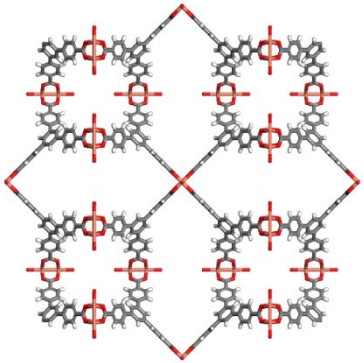
Surface Area

Measured BET = 3714 m^2/g
Calculated = 5163 m^2/g
Literature = 3831 m^2/g

Usable capacities:
P-swing between 5 and 100 bar at 77 K

GCMC calculated grav. = 6.9 wt.%
GCMC calculated vol. = 33.3 g/L

BAZFUF (MOF-143)



Furukawa, H. et al., *Inorg. Chem.* **2011,** *50*, 9147.

Surface Area

Measured BET = 4829 m^2/g
(Unstable after activation; collapses over time)
Calculated = 5470 m^2/g
Literature = not reported

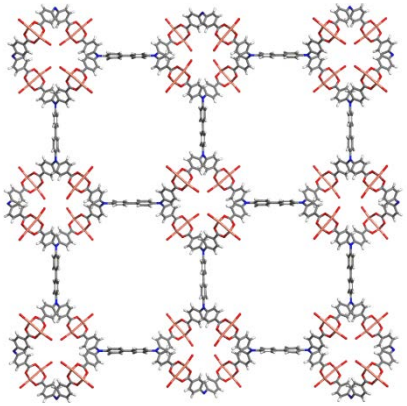
Usable capacities:
P-swing between 5 and 100 bar at 77K

GCMC calculated grav. = 9.1 wt.%
GCMC calculated vol. = 37.1 g/L

MOFs Synthesized (2)

Several promising MOFs could not be synthesized with high surface area

XAFFUH [DUT-12]



Grünker, R. et al., *Eur. J. Inorg. Chem.* **2010,** 3835.

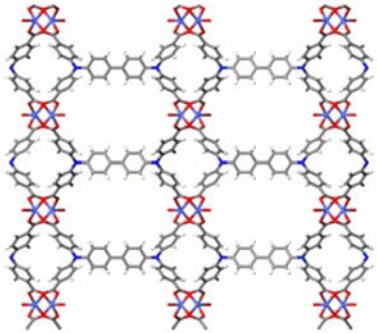
Surface Area

Measured BET	= 958 m^2/g
Calculated	= 5152 m^2/g
Literature	= 824 m^2/g

Usable capacities:
P-swing between 5 and 100 bar at 77K

GCMC calculated grav.	= 8.8 wt.%
GCMC calculated vol.	= 34.8 g/L

XAFFIV [DUT-10(Co)]



Grünker, R. et al., *Eur. J. Inorg. Chem.* **2010,** 3835.

Surface Area

Measured BET	= 456 m^2/g
Calculated	= 5329 m^2/g
Literature	= not reported

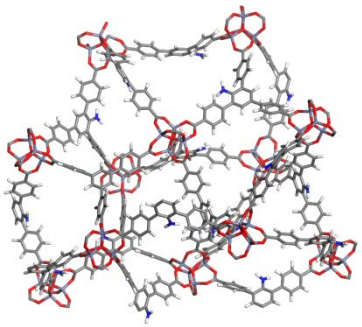
Usable capacities:
P-swing between 5 and 100 bar at 77K

GCMC calculated grav.	= 8.5 wt.%
GCMC calculated vol.	= 36.6 g/L

MOFs Synthesized (3)

Examples of high surface area MOFs with unsatisfactory volumetric capacity

MOF-177-NH2



Dutta, A. et al., *Angew. Chem. Int. Ed.* **2015**, *54*, 3983.

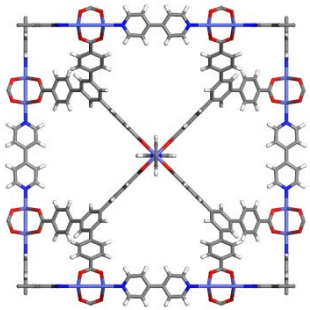
Surface Area

Measured BET	= 4280 m^2/g (fresh)
Calculated	= 4514 m^2/g
Literature	= 4631 m^2/g

Usable capacities:

Measured grav.	= 6.4 wt.%
GCMC calculated grav.	= 6.4 wt.%
Measured vol.	= 32.6 g/L
GCMC calculated vol.	= 33.7 g/L

ICAQIO [DUT-23(Co)]



Klein, N. et al., Chem. *Eur. J. Chem.* **2011**, *17*, 13007.

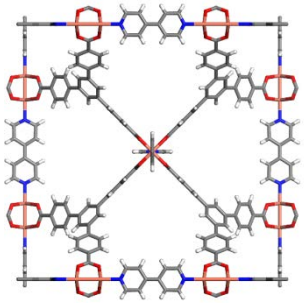
Surface Area

Measured BET	= 4044 m^2/g (fresh)
Calculated	= 4714 m^2/g
Literature	= 4850 m^2/g

Usable capacities:

Measured grav.	= 6.2 wt.%
GCMC calculated grav.	= 6.7 wt.%
Measured vol.	= 30.2 g/L
GCMC calculated vol.	= 31.9 g/L

ICAQOU [DUT-23(Cu)]



Klein, N. et al., Chem. *Eur. J.. Chem.* **2011**, *17*, 13007.

Surface Area

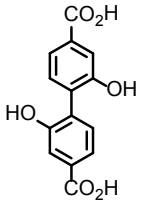
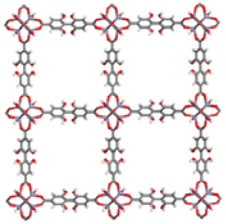
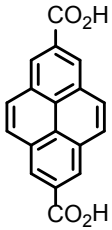
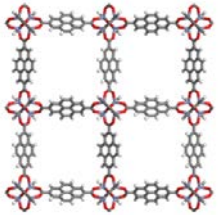
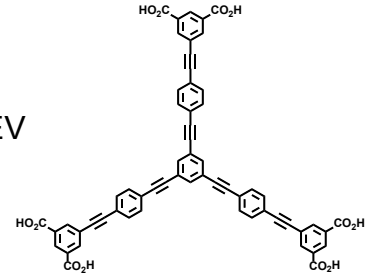
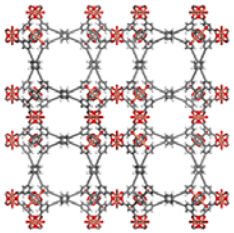
Measured BET	= 4601 m^2/g (fresh)
Calculated	= 4664 m^2/g
Literature	= 4730 m^2/g

Usable capacities:

Measured grav.	= 6.7 wt.%
GCMC calculated grav.	= 6.6 wt.%
Measured vol.	= 32.4 g/L
GCMC calculated vol.	= 31.7 g/L

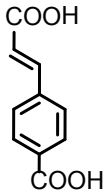
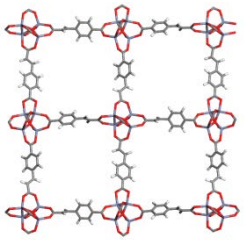
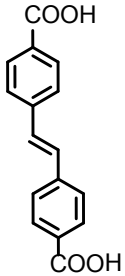
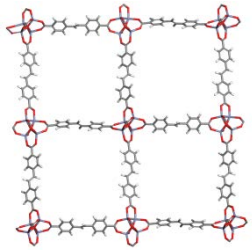
Work in Progress (1)

Examples of real MOFs that are currently being assessed experimentally

CSD REF. CODE	Organic Linker	Structure	BET Surface Area m^2/g		Calculated Usable Capacities (P-swing 5-100 bar)		Reference
			Calculated	Literature	Grav. [wt.%]	Vol. [g/L]	
ZELROZ			4947	2631	8.7	36.8	Rankine, D. et al., *Chem. Commun.* **2012**, *48*, 10328.
EDUVOO			4857	Not reported	8.0	35.0	Eddaoudi, M. et al., *Science* **2002**, *295*, 469.
GAGZEV			5777	6143	10.8	37.0	Yuan, D. et al., *Angew. Chem. Int. Ed.* **2010**, *49*, 5357. Farha, O. K. *Nat. Chem.* **2010**, *2*, 944.

Work in Progress (2)

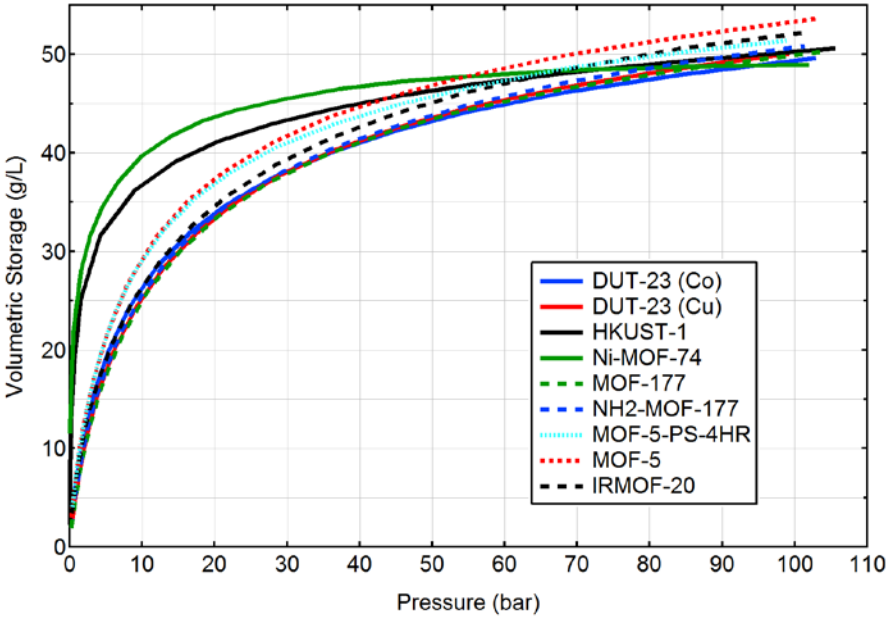
Examples of hypothetical MOFs that are currently being assessed experimentally

Mail-Order MOF #	Organic Linker	Structure	Calc. Surface Area m^2/g	Calculated Usable Capacities (P-swing 5 to 100 bar)	
MOF-5_cooh_2_567			5938	13.1 wt. %	36.7 g/L
MOF-5_cooh_2_646			5781	12.5 wt. %	36.7 g/L

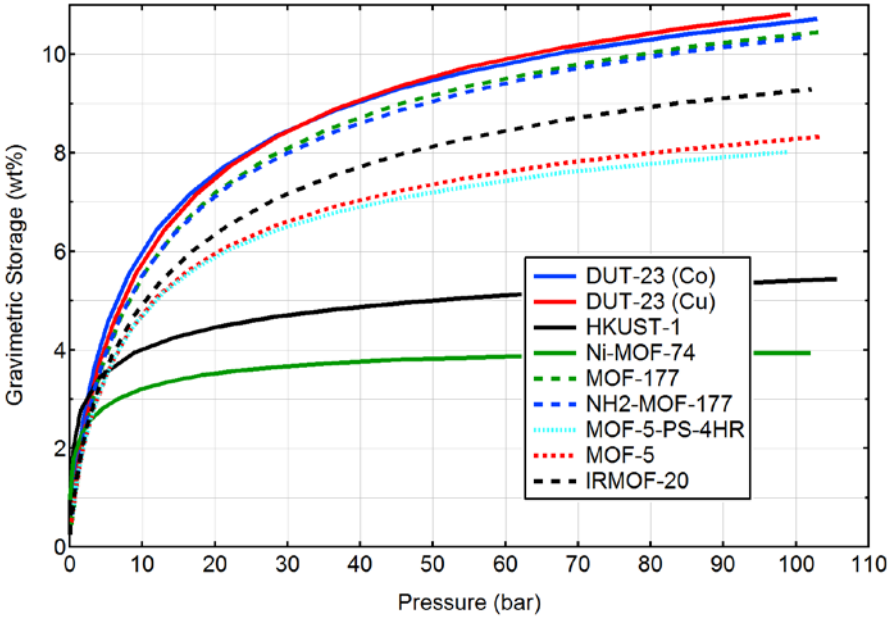
Isotherm Measurements

H_2 isotherms of several promising MOFs at T = 77 K

Total Volumetric Uptake



Total Gravimetric Uptake



- Several MOFs out-perform MOF-5 on a gravimetric basis
- The volumetric performance of MOF-5 is difficult to surpass

Summary of Uptake Measurements

Based on PCT measurements at T = 77 K

MOF	Crystal Density	Volumetric (77 K,100 bar)	Gravimetric (77 K, 100 bar)	Usable Volumetric (5-100 bar)	Usable Gravimetric (5- 100 bar)
	g/cc	*g/L*	*wt%*	*g/L*	*wt%*
NH2-MOF-177	0.44	50.7	10.3	32.6	6.4
MOF-177	0.43	49.9	10.4	32.6	6.5
DUT-23 (Co)	0.413	49.4	10.7	30.2	6.2
DUT-23 (Cu)	0.413	50.1	10.8	32.4	6.7
HKUST-1	0.879	50.3	5.4	17.9	1.9
Ni-MOF-74	1.195	48.9	3.9	13.8	1.1
MOF-5-PS-4HR	0.59	51.5	8.0	30.4	4.6
IRMOF-20	0.51	52.1	9.3	33.1	5.7
MOF-5	0.60	53.3	8.3	31.1	4.5

Expanded Screening

We have expanded our computational screening from ~2,000 MOFs to nearly 500,000

Database	Number of MOFs				Calculated Usable Capacity	
	Available in database	Zero surface area	H_2 capacity evaluated empirically	H_2 capacity evaluated w/ GCMC	Al least equals MOF-5	Exceeds MOF-5 by 15%
Real MOFs (RM) [1,2]	**5,109**	**1,978**	**3,131**	**3,131**	**90**	**20**
Mail-Order MOFs (MO) [3]	112	4	108	112	32	15
In Silico MOFs (IS) [4]	2,816	154	2,662	466	21	1
NW Hypothetical MOFs (NW) [5]	137,000	30,160	106,840	12,374	4,437	768
Zr-MOFs (ZR) [6]	204	0	204	204	126	35
UO Hypothetical MOFs (UO) [7]	324,500	32,993	291,507	16,372	7,768	1,209
Total	**469,741**	65,289	404,452	32,659	**12,474**	**2,048**

1. Goldsmith, J., A.G. Wong-Foy, M.J. Cafarella, and D.J. Siegel, Chem. Mater., 2013. **25**: p. 3373-3382.
2. Chung, Y.G., J. Camp, M. Haranczyk, B.J. Sikora, et al., Chem. Mater., 2014. **26**: 6185-6192.
3. Martin, R.L., L.-C. Lin, K. Jariwala, B. Smit, and M. Haranczyk, J. Phys. Chem C, 2013. **117**: p. 12159-12167.
4. Bao, Y., R.L. Martin, C.M. Simon, M. Haranczyk, B. Smit, et al., J. Phys. Chem. C, 2015. **119**: 186-195.
5. Wilmer, C.E., M. Leaf, C.Y. Lee, O.K. Farha, B.G. Hauser, et al., Nat. Chem., 2012. **4**: 83-89.
6. Gomez-Gualdron, D.A., O.V. Gutov, V. Krungleviciute, et al., Chem. Mater., 2014. **26**: p. 5632-5639.
7. Aghaji, M.Z., M. Fernandez, P.G. Boyd, T.D. Daff, and T.K. Woo, Eur. J. In. Chem., 2016. **2016**: 4505-4511.

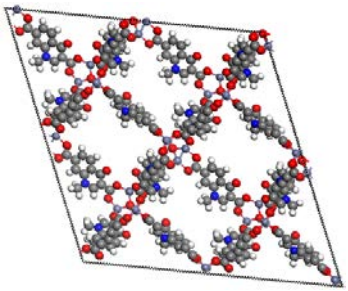
Top 20 Compounds

Computation has identified ~2,000 MOFs that are projected to meet the MOF-5+15% target (Go/No-Go #2)

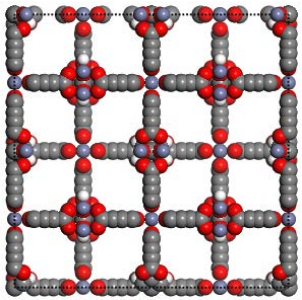
MOF #	$\rho_{crystal}$ [g/cm^3]	$SA_{Accessible}$ [m^2/g]	Void Frac.	$PV_{Accessible}$ [cm^3/g]	Tot. Grav. 100 bar [wt. %]	Tot. Vol. 100 bar [g/L]	Usable Grav. 100 → 5 bar [wt. %]	Usable Vol. 100 → 5 bar [g/L]	Source DB
1	0.47	4548	0.78	1.34	11.2	59.6	7.1	39.3	MO
2	0.41	4510	0.89	2.09	10.9	50.0	8.2	39.0	RM
3	0.42	5147	0.86	2.04	10.6	50.2	7.9	38.2	UO
4	0.42	5119	0.86	2.05	10.6	49.4	7.9	38.2	UO
5	0.48	4686	0.84	1.75	9.6	50.9	7.0	38.2	IS
6	0.40	5428	0.85	2.16	11.2	49.7	8.3	38.2	UO
7	0.40	5285	0.86	2.12	10.9	49.4	8.2	38.1	NW
8	0.36	5957	0.86	2.36	11.9	49.1	8.9	38.1	UO
9	0.43	5031	0.86	1.98	10.3	50.0	7.7	38.1	UO
10	0.41	5164	0.85	2.06	10.9	50.7	8.0	38.1	UO
11	0.35	6165	0.86	2.47	12.3	49.0	9.3	38.1	NW
12	0.41	5255	0.86	2.09	10.6	48.8	8.1	38.0	UO
13	0.43	5081	0.85	1.99	10.3	49.4	7.8	38.0	UO
14	0.37	5817	0.86	2.34	11.8	49.4	8.8	38.0	UO
15	0.43	5030	0.85	1.99	10.3	49.3	7.8	38.0	UO
16	0.42	5147	0.86	2.03	10.4	49.3	7.8	38.0	UO
17	0.41	5319	0.86	2.09	10.7	49.0	8.1	38.0	UO
18	0.43	5049	0.86	1.98	10.4	50.3	7.6	38.0	UO
19	0.36	6037	0.86	2.40	12.1	49.1	9.1	38.0	UO
20	0.42	5127	0.86	2.03	10.4	49.0	7.8	37.9	UO
IRMOF-20							**5.7**	**33.1**	
MOF-5 + 15%							**5.2**	**35.8**	

Examples of High Capacity MOFs

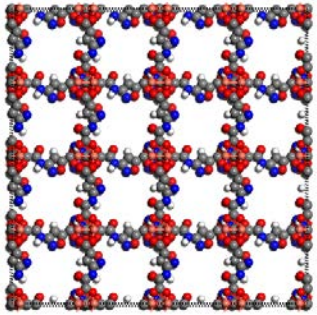
Examples drawn from screening of hypothetical MOF databases



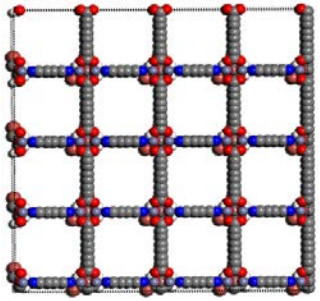
MO: MOF-5_cooh_2_2738_1_basic_opt
UG: 7.1 wt.%; UV: 39.3 g/L
GSA: 4548 m^2/g; D: 0.47 g/cm^3
PV: 1.34 cm^3/g; VF: 0.78



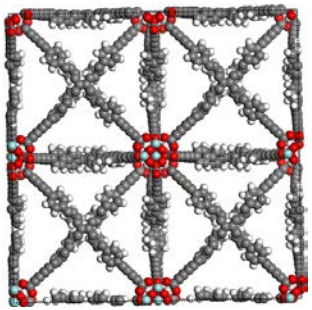
UO: str_m3_o5_o25_f0_nbo.sym.193.out
UG: 7.9 wt.%; UV: 38.2 g/L
GSA: 5147 m^2/g; D: 0.42 g/cm^3
PV: 2.0 cm^3/g; VF: 0.86



IS: Syn014648
UG: 7.0 wt.%; UV: 38.2 g/L
GSA: 4686 m^2/g; D: 0.48 g/cm^3
PV: 1.8 cm^3/g; VF: 0.84



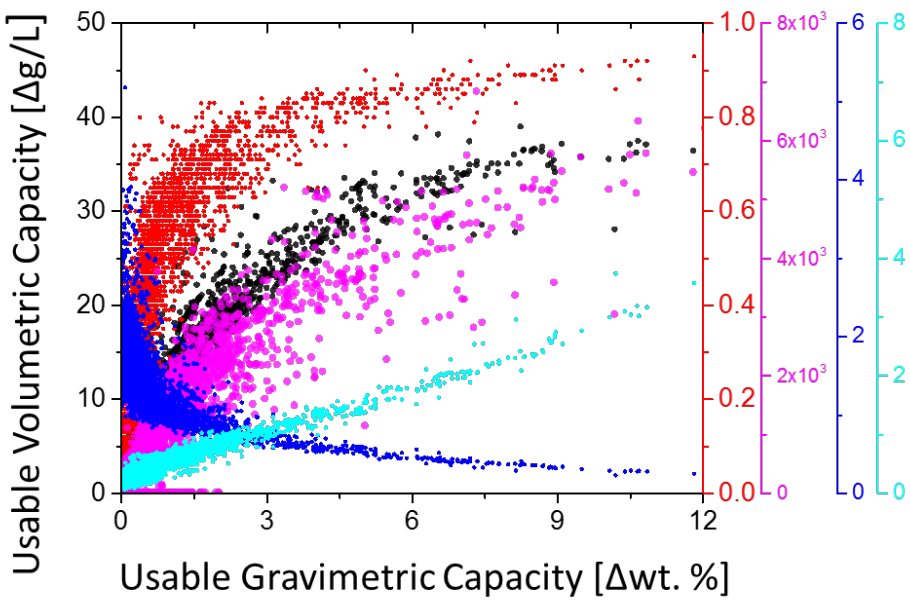
NW: 5048108_i_1_j_25_k_20_m_3
UG: 8.2 wt.%; UV: 38.1 g/L
GSA: 5285 m^2/g; D: 0.40 g/cm^3
PV: 2.1 cm^3/g; VF: 0.86

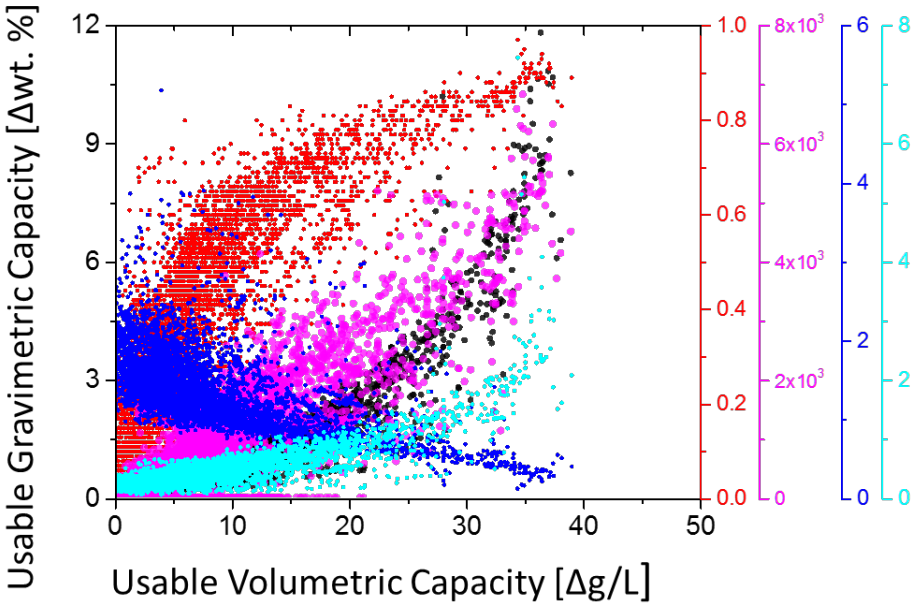


ZR: NU-TPE-4PTT-ftw
UG: 11.5 wt.%; UV: 37.5 g/L
GSA: 6323 m^2/g; D: 0.27 g/cm^3
PV: 3.3 cm^3/g; VF: 0.88

Property-Performance Trends

Our database presents an opportunity to explore correlations between usable capacity and basic materials properties





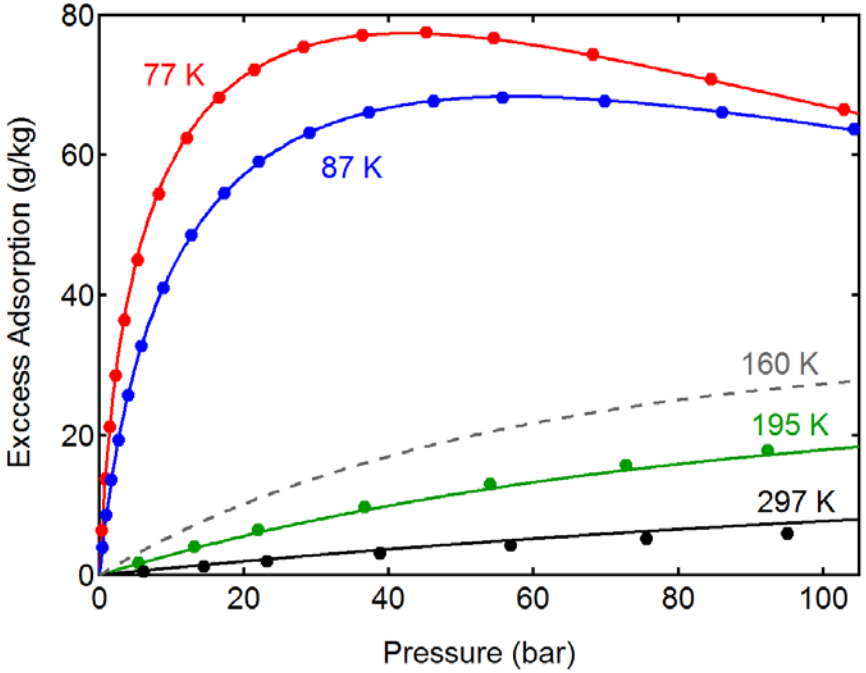
Single Crystal Density [g/cm^3] Porosity

Surface Area [m^2/g] Pore Volume [cm^3/g]

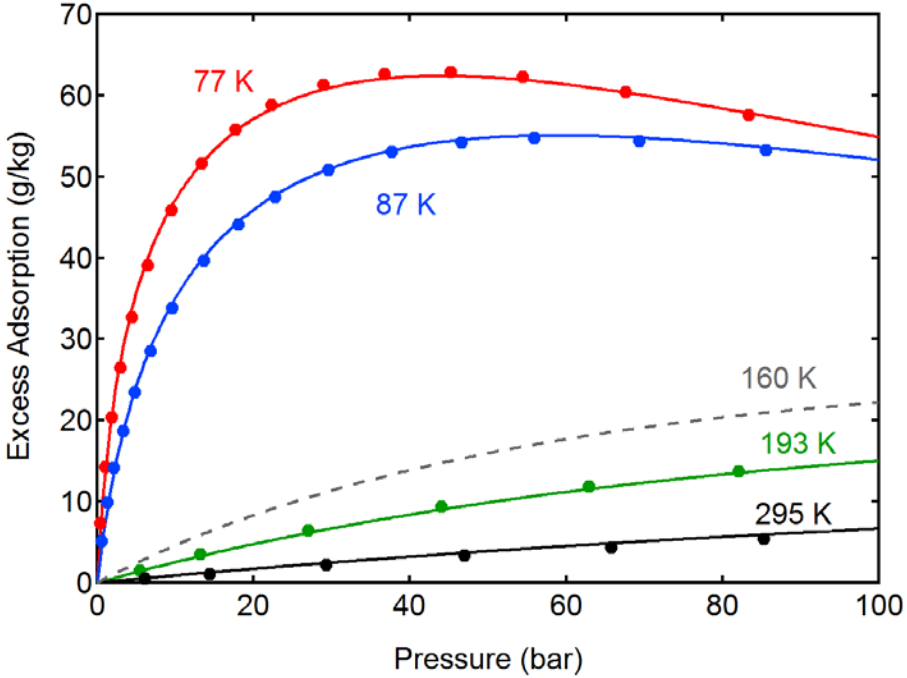
Variable-Temperature Isotherms

H_2 uptake in two of the most promising MOFs were measured at several temperatures to allow for system-level projections

Gravimetric excess uptake: DUT-23 (Co)



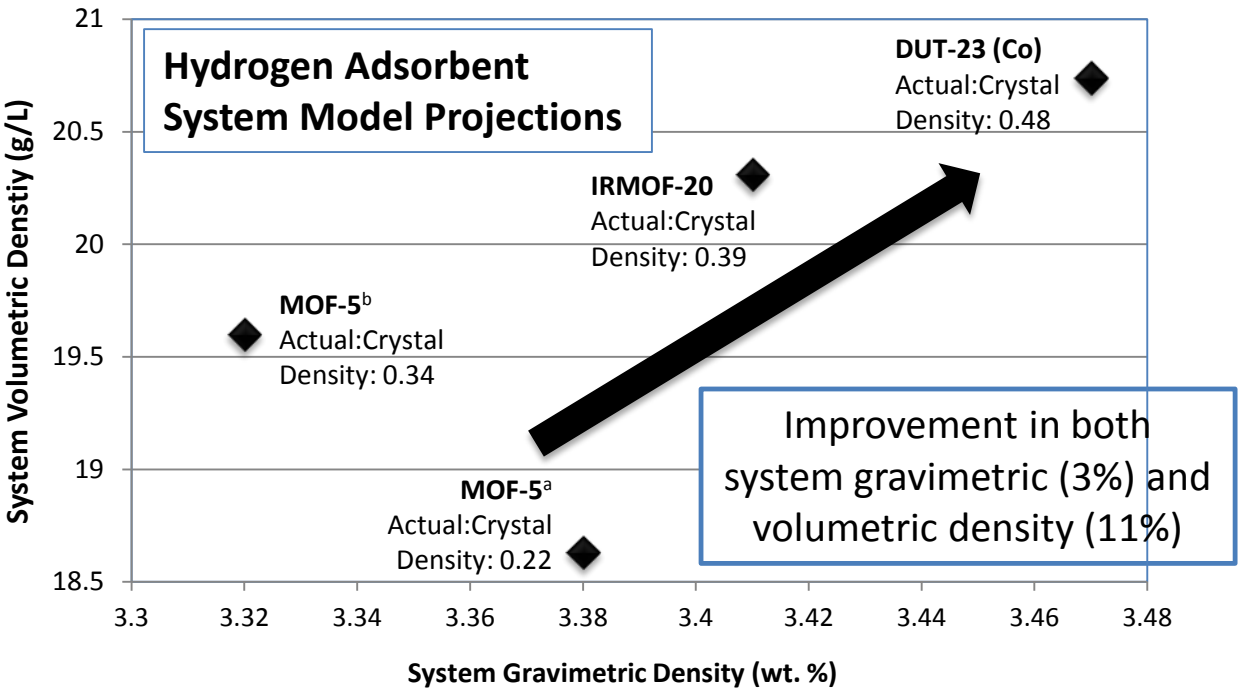
Gravimetric excess uptake: IRMOF-20



- Measurements at 4 temperatures, from cryogenic to ambient conditions
- Data fit to Unilan and D-A isotherm models
- Performance at T = 160 K interpolated based on model projections

System Modeling

The HSECoE System Model was used to project the performance of IRMOF-20 and DUT-23(Co)-based systems



System Assumptions

Initial/Full Pressure:	100 bar
Initial/Full Temp:	80 K
Final/Empty Pressure:	5.5 bar
Final/Empty Temp:	160 K
Useable Hydrogen:	5.6 kg
Heat Exchanger:	HexCell
MOF Density:	Powder (see table)
Pressure Vessel:	Type 1 Al
Insulation Thickness:	23 mm
Outer Shell Thickness:	2 mm

Parameter	MOF-5 [a]	MOF-5 [b]	IRMOF-20	DUT-23(Co)	Units	Comments
alpha	2895.13	2239	2512.09	2675.29	J/mol_{H2}	D.A. Parameter -- Enthalpic contribution to the characeristic free energy of adsorption
beta	15.29	19.5	14.61	15.53	$J/mol_{H2}/K$	D.A. Parameter -- Entropic contribution to the characeristic free energy of adsorption
m	2	2	2	2		D.A. Parameter -- Exponential constant for adsolute adsorption
n_{max}	96.43	125.40	99.22	112.70	mol_{H2}/kg_{Ads}	D.A. Parameter -- Maximum H2 loading of the entire adsorption volume
P_0	1.39E+09	1.69E+09	7.64E+08	1.03E+09	Pa	D.A. Parameter -- Pseodo-saturation pressure (pressure of the gas phase)
rho_{Ads}	130	200	200	200	kg_{Ads}/m^3	D.A. Parameter -- Bulk Density of the MOF-5
V_a	0.00170	0.00201	0.00173	0.00171	m^3/kg_{Ads}	D.A. Parameter -- Adsorbed volume per mass of adsorbent
V_v	0.00725	0.00450	0.00459	0.00429	m^3/kg_{Ads}	D.A. Parameter -- Void volume per mass of adsorbent

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

- Expand screening to additional real MOFs recently reported in Cambridge Structure Database
- Densification of selected MOFs
- Focus on 2nd go/no-go milestone
  - Identify MOFs with 15% improvement in H_2 capacity over MOF-5

Summary

- **Goal**: demonstrate MOFs that achieve high volumetric *and* gravimetric H_2 densities simultaneously (at cryogenic conditions)
  - Establish new high-water mark for H_2 storage in adsorbents
- **Approach**: (*Atoms to systems*) High-throughput screening in combination with experimental synthesis, activation, characterization, and system-level projections
- **Accomplishments:**
  - Demonstrated IRMOF-20: surpasses usable capacity of MOF-5 (1st Go/No-Go)
  - Nearly 500,000 MOFs assessed computationally; more than 2,000 compounds identified that can surpass MOF-5+15%
  - Several promising MOFs synthesized and evaluated with respect to their H_2 uptake; thus far, none exhibit usable volumetric capacities exceeding IRMOF-20
  - Estimated system level performance of IRMOF-20 and DUT-23(Co) using HSECoE system models parameterized from isotherm measurements

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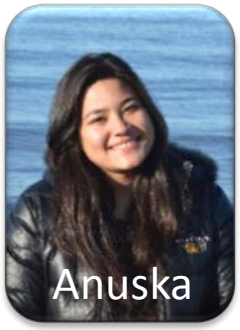
The Team



Technical Backup Slides

Capacity Definitions

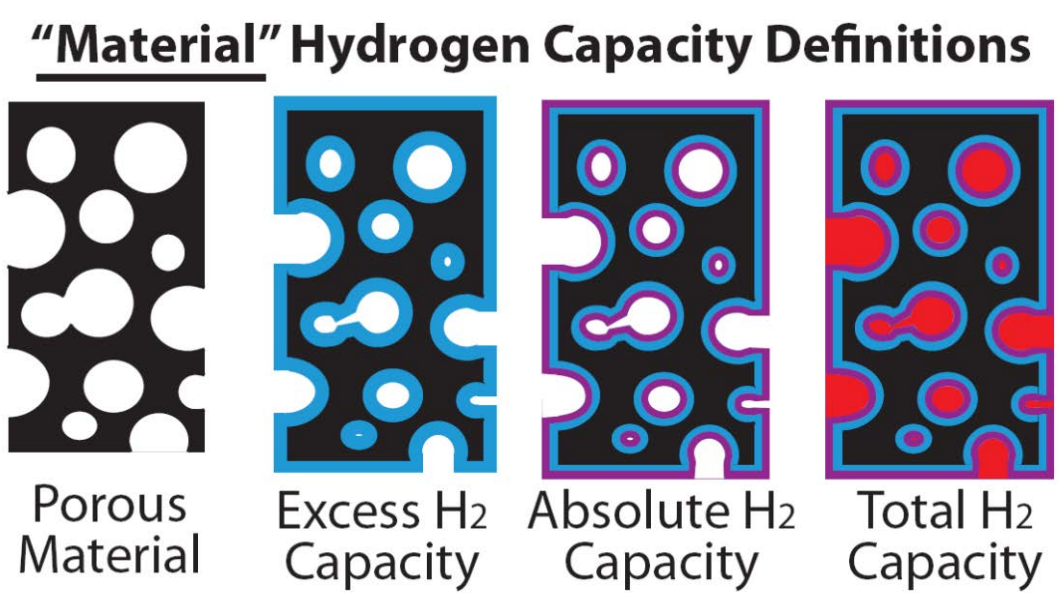
$$C_{tot} = C_{exc} + \frac{100 \times d_g V_{pore}}{1 + d_g V_{pore}}$$

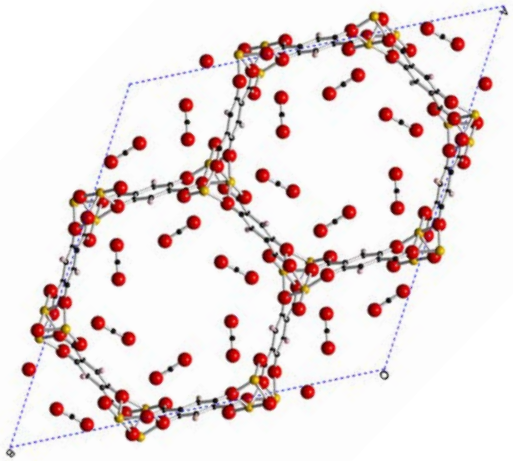
$$V_{pore} = \frac{d_{sk} - d_{bulk}}{d_{sk} d_{bulk}}$$

Recommended Best Practices for the Characterization of Storage Properties of Hydrogen Storage Materials, V3.34, p.223

C_{tot} = total adsorption capacity in wt.%
C_{exc} = excess adsorption in wt.%
V_{pore} = specific pore volume

d_g = density of H_2 gas at T,P
d_{sk} = skeletal density
d_{bulk} = bulk density



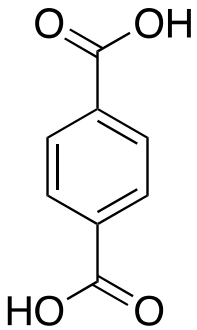


Synthesis of MOF-5

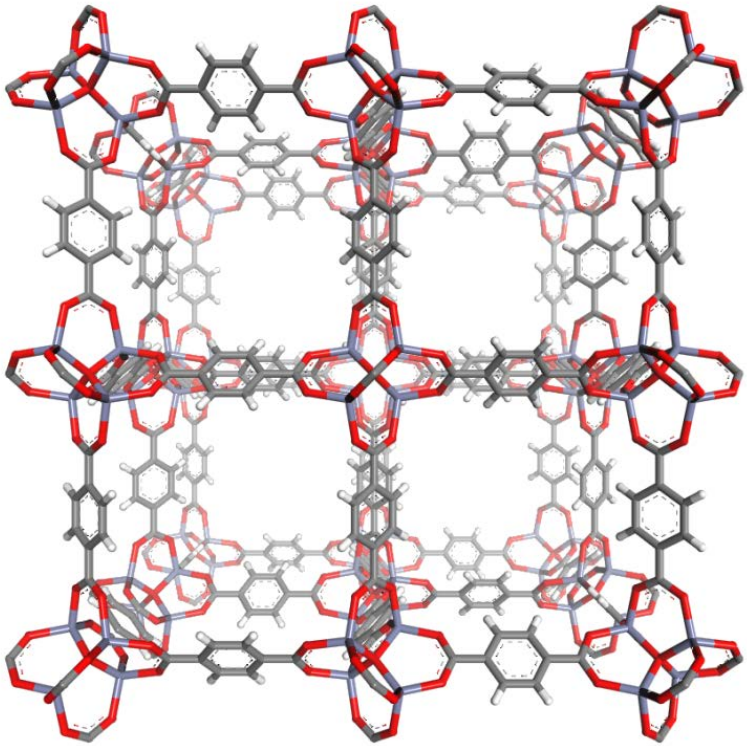
Performed air-free synthesis[1] of the benchmark compound MOF-5

$$H_2BDC + Zn(NO_3)_2 \cdot 6H_2O \xrightarrow[80\ ^oC]{\text{N,N-diethylformamide}} Zn_4O(BDC)_3$$

H_2BDC =



Benzenedicarboxylic acid



Activated by:

1) Multiple solvent exchanges
2) RT vacuum drying

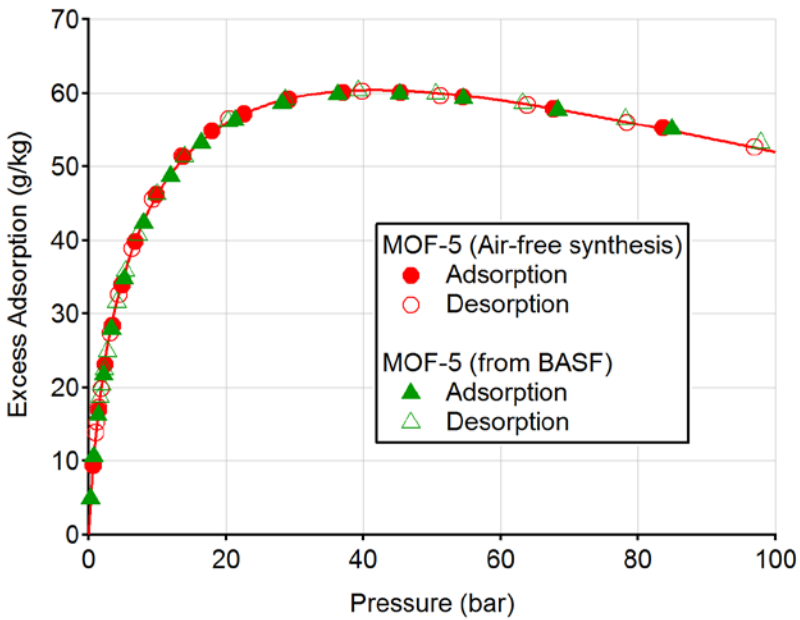
BET S.A. =	3512 m^2/g
Calculated =	3563 m^2/g
Literature =	3800 m^2/g [1]

[1]Kaye, Dailly, Yaghi, and Long, 2007. JACS, 129,14176: 8.4 wt.%, 54 g/L at 35 bar/77K

MOF-5 Hydrogen Uptake

- Measured performance of in-house MOF-5
  - H_2 uptake & BET surface area essentially identical to BASF-supplied MOF-5 (HSECoE)
- Usable capacity (pressure swing to 5 bar) adopted as benchmark

T = 77 K



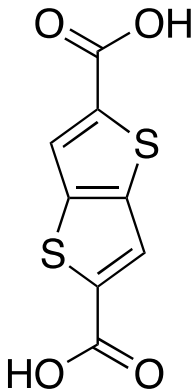
	Total		Usable (P-swing)	
p (bar)	Volumetric (g/L)	Gravimetric (wt.%)	Volumetric (g/L)	Gravimetric (wt.%)
5	22.2	3.5		
35	44.4	6.8	**22.2**	**3.3**
50	47.8	7.3	**25.6**	**3.8**
100	53.3	8.0	**31.1**	**4.5**

A Success Story: IRMOF-20

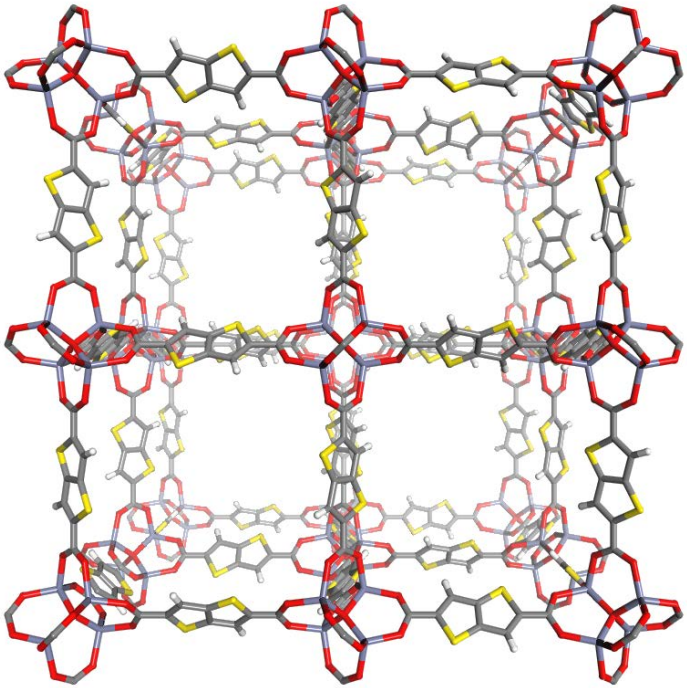
Synthesis of IRMOF-20 was attempted after computation identified it as a promising compound

$$H_2TTDC + Zn(NO_3)_2 \bullet 4H_2O \xrightarrow[100\ ^oC]{N,N\text{-diethylformamide}} Zn_4O(TTDC)_3$$

H_2TTDC =



Thieno[3,2-*b*]thiophene-2,5-dicarboxylic acid



Rowsell, J. L. C.; Yaghi, O.M. *J. Am. Chem. Soc.* **2006**, *128*, 1304.

Activated by:

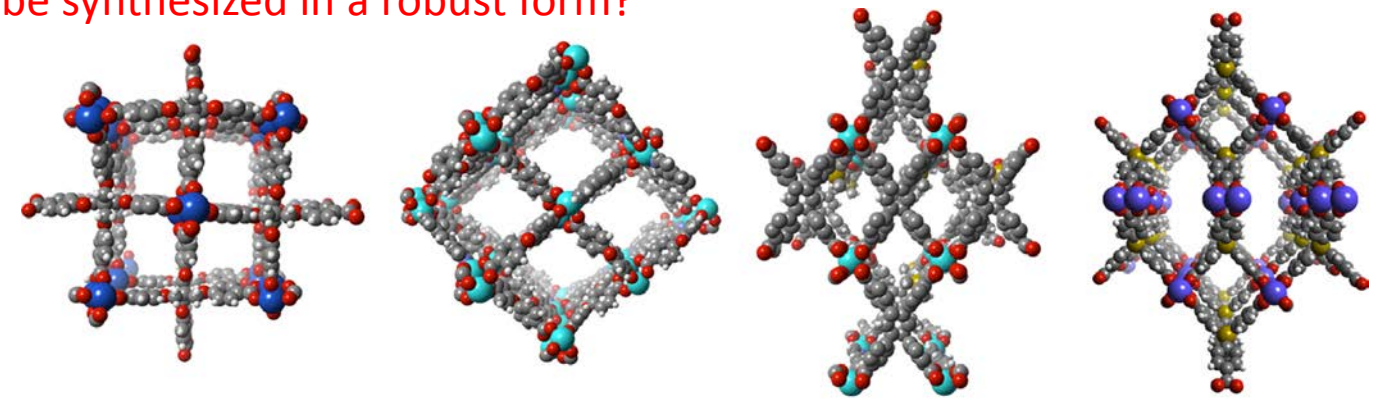
1) Multiple solvent exchanges
2) RT vacuum drying

BET S.A. =	4073 m^2/g (94% of calc'd)
Calculated =	4324 m^2/g
Literature =	3409 m^2/g

MOFs Identified by Prior Screening

Several MOF "Targets of Opportunity" were identified

- Combine high gravimetric and volumetric densities
- Overlooked: no/limited experimental evaluation
- Can these be synthesized in a robust form?

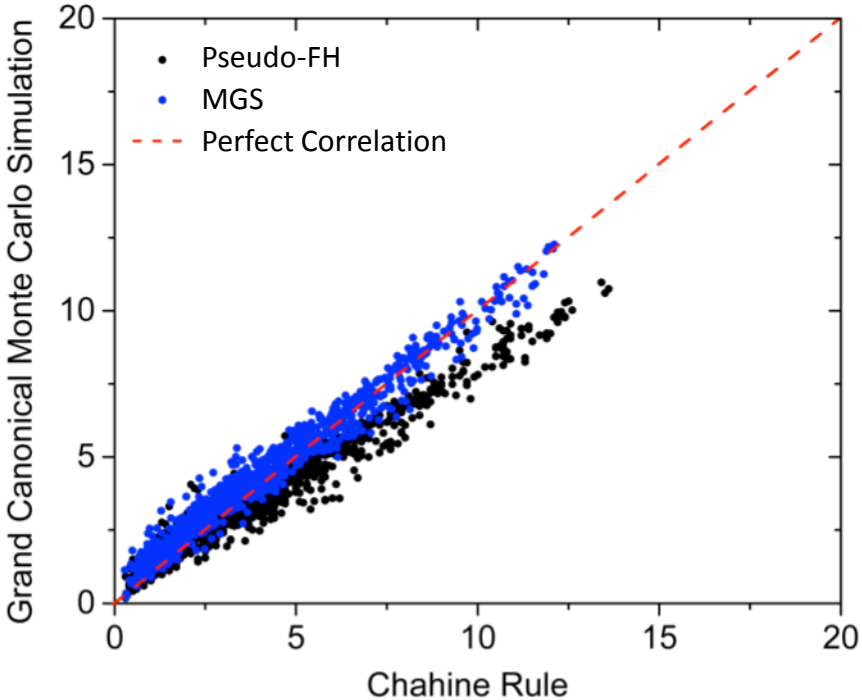


	EPOTAF (SNU-21)	DIDDOK	LURGEL (TO-MOF)	ENITAX (IMP-9)
Total Grav. (wt. %)	11	10.2	9.7	9.3
Total Volumetric (g/L)	71	60	57	59
Crystal Density (g/cm^3)	0.58	0.53	0.53	0.57
Calc'd/Meas. SA (m^2/g)	5208/700-900	4651	4386/680	4162
Notes	Best combination of grav. & vol. density. H_2 uptake measured previously: 5 wt %	No measurements	CO_2 uptake measured.	No measurements

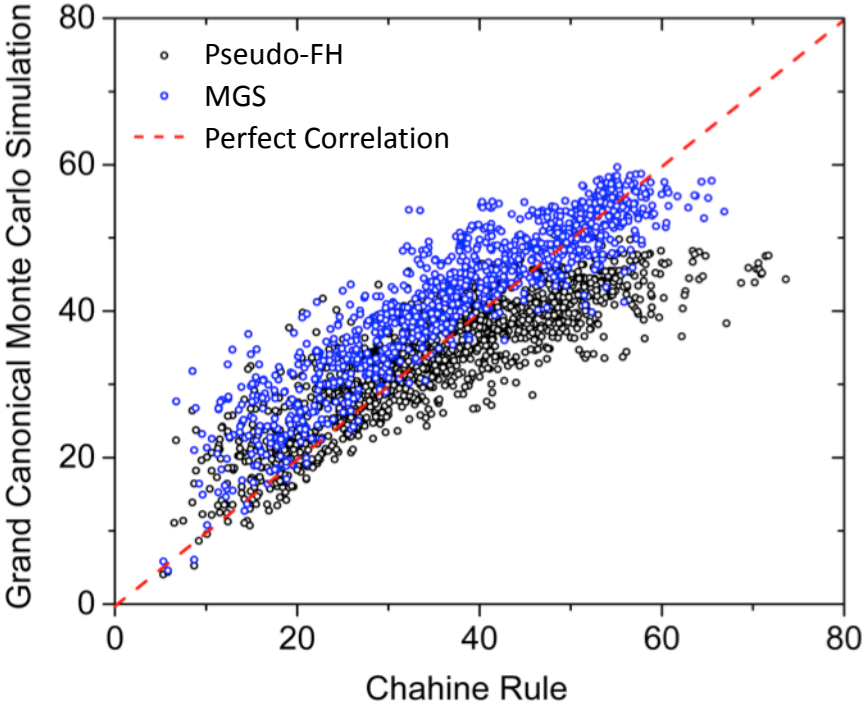
Accuracy of Simulated Isotherms

"Quick and dirty" Chahine-rule predictions of H_2 uptake in MOFs correlate strongly with GCMC calculations

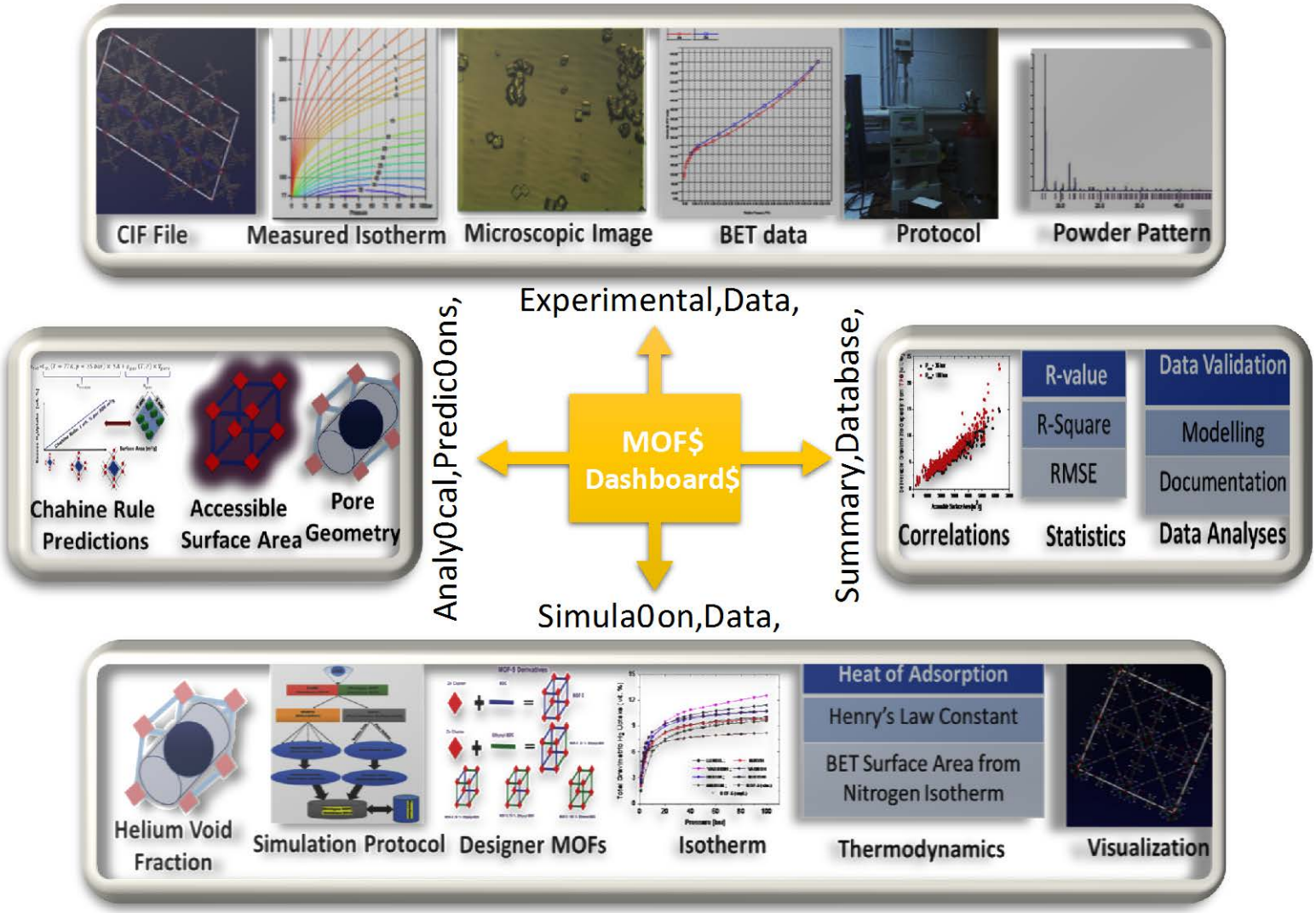
Total gravimetric H_2 (wt.%)



Total volumetric H_2 (g H_2/L MOF)



Although GCMC is more expensive, it provides access to full isotherm and allows estimation of usable capacities

MOF Dashboard

We have developed a database to track promising compounds and share data