Project ID: ST122

Hydrogen Adsorbents with High Volumetric Density:

New Materials and System Projections

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DOE Annual Merit Review, June 8, 2016, Washington, DC

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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:* $150,000

*Estimated as of 3/31/16

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
- 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 (Year 1 emphasis)
- If successful, these compounds will **set a new high-water mark** for H_2 density in adsorbents at cryogenic conditions

✓ **Screened 2,000+ MOFs using GCMC & empirical methods**
✓ **Identified IRMOF-20: exceeds the performance of MOF-5 benchmark**

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

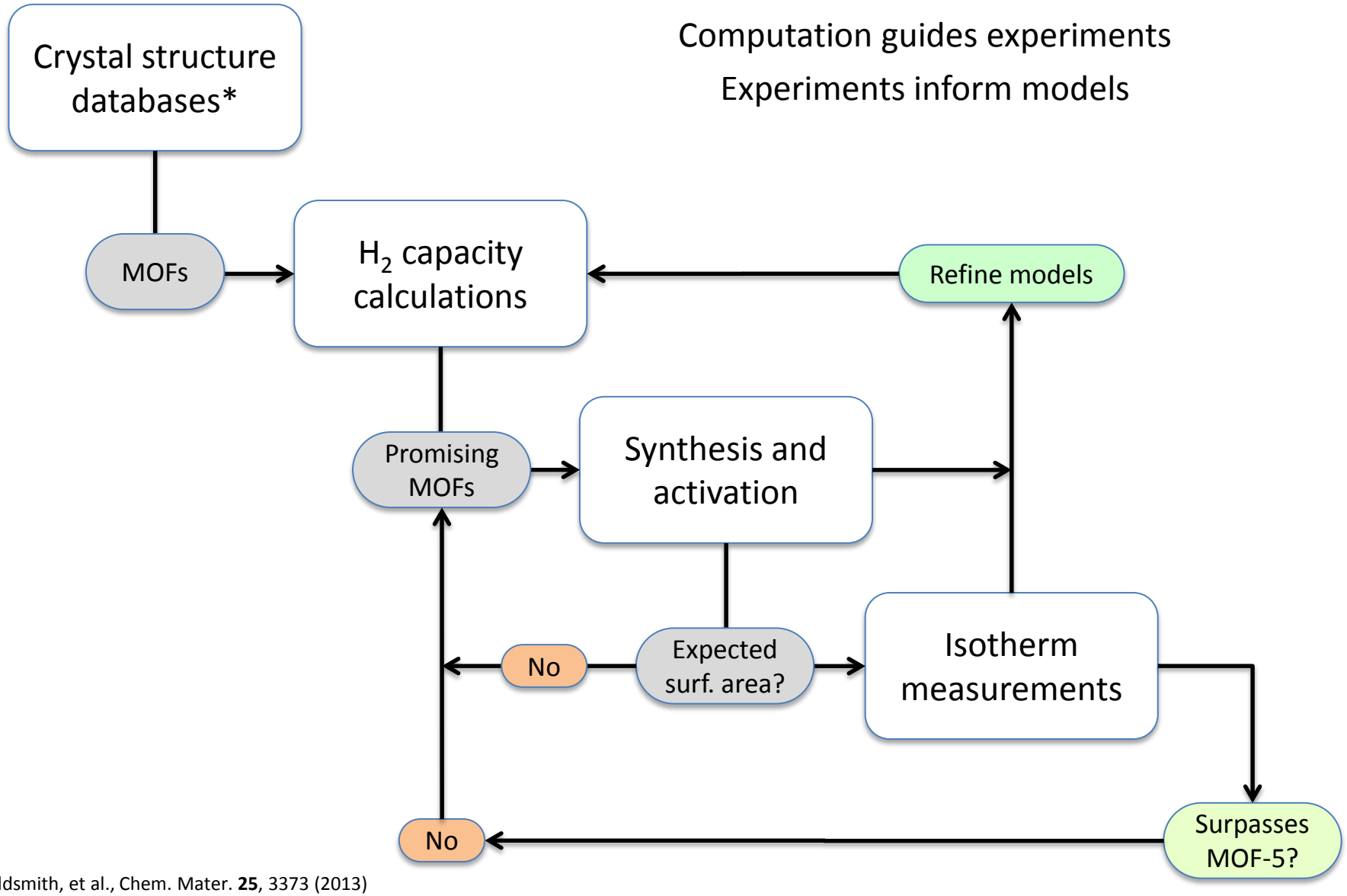
Approach

Note: All volumetric hydrogen densities reported herein assume single-crystal MOF densities

Concept

Computation guides experiments

Experiments inform models



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

*Chung et al., *Chem. Mater.* **26**, 6185 (2014)

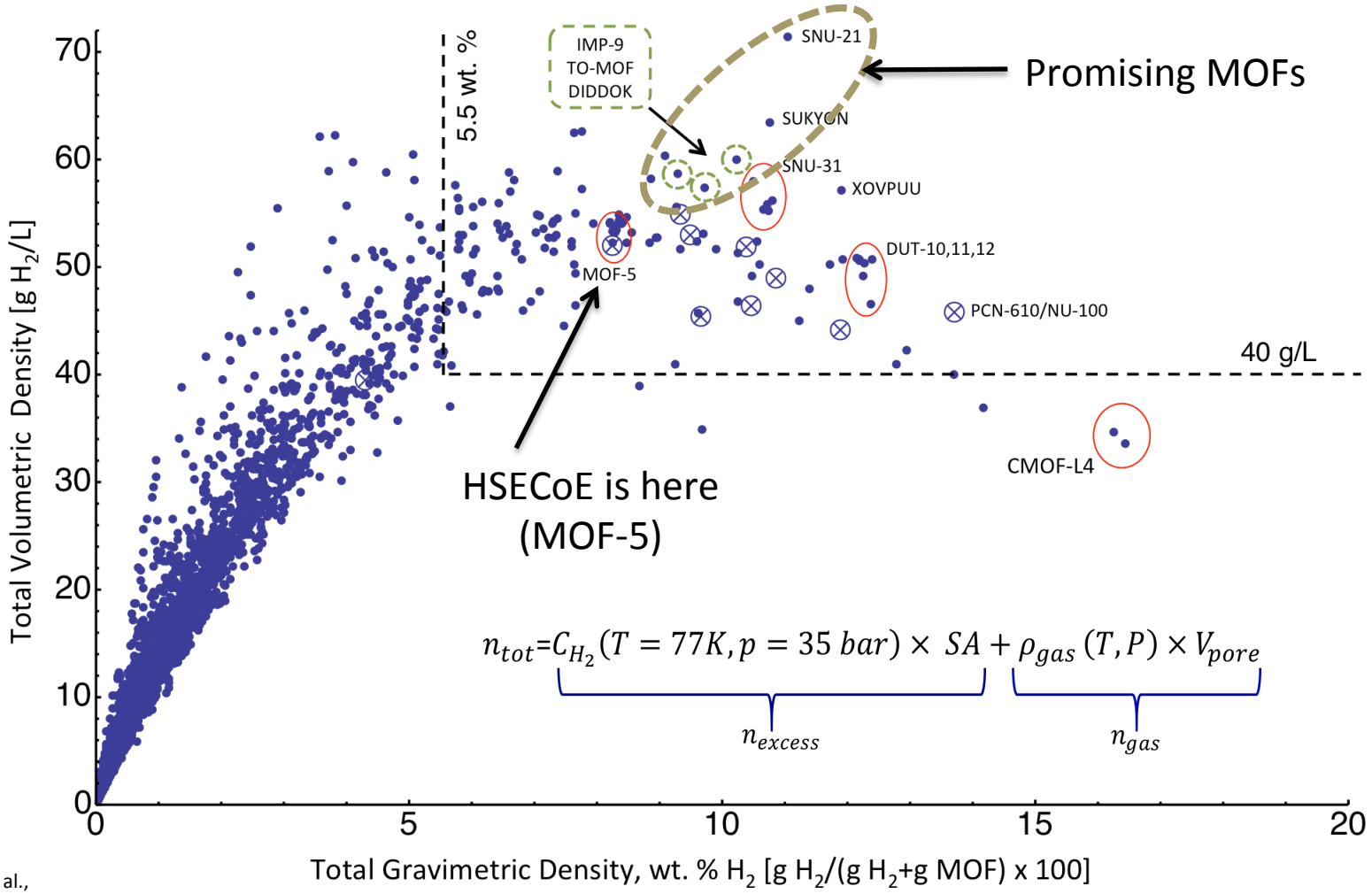
Milestones

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

Year	Milestone or Go/No-Go	Due	Description	Status
1	Update and validate computational methods	10/31/15	• Update screening method to account for impact of adsorbed hydrogen on total volumetric hydrogen density • Validate against experimental capacities for MOF-5 baseline	**Complete**. Added GCMC to screening protocol
1	MOF synthesis	1/31/16	Synthesize at least 3 MOFs with potential to surpass the hydrogen storage capacity of MOF-5 by 15%	**Complete**. 7 MOFs synthesized
1	Extend computational predictions	4/30/16	Extend screening to examine 50,000 new compounds from the Cambridge Structure Database	**Partially complete**
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%	

High-throughput Screening

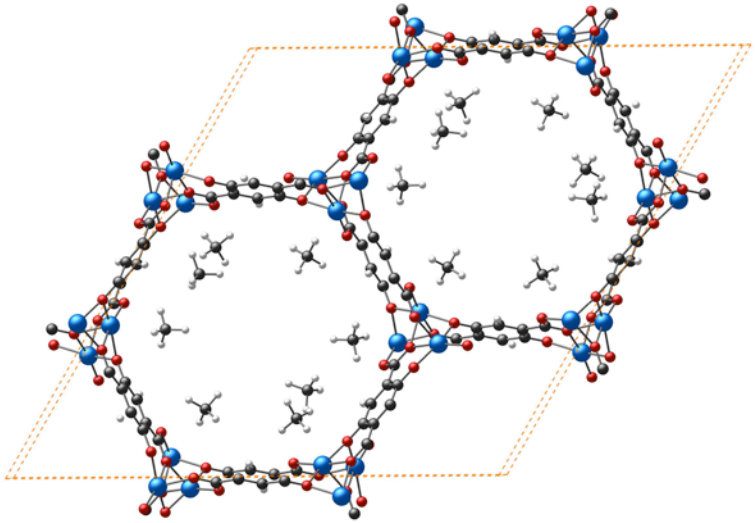
Prior work: developed a database of MOFs by mining the CSD. Chahine rule and crystal structure were used to predict H_2 capacity in thousands of compounds



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

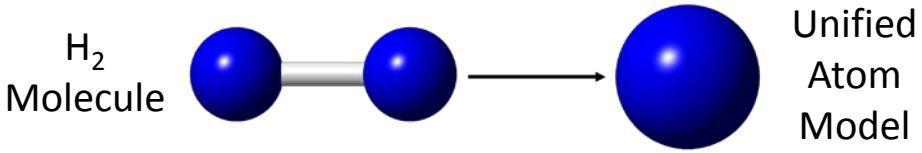
Grand Canonical Monte Carlo

- 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



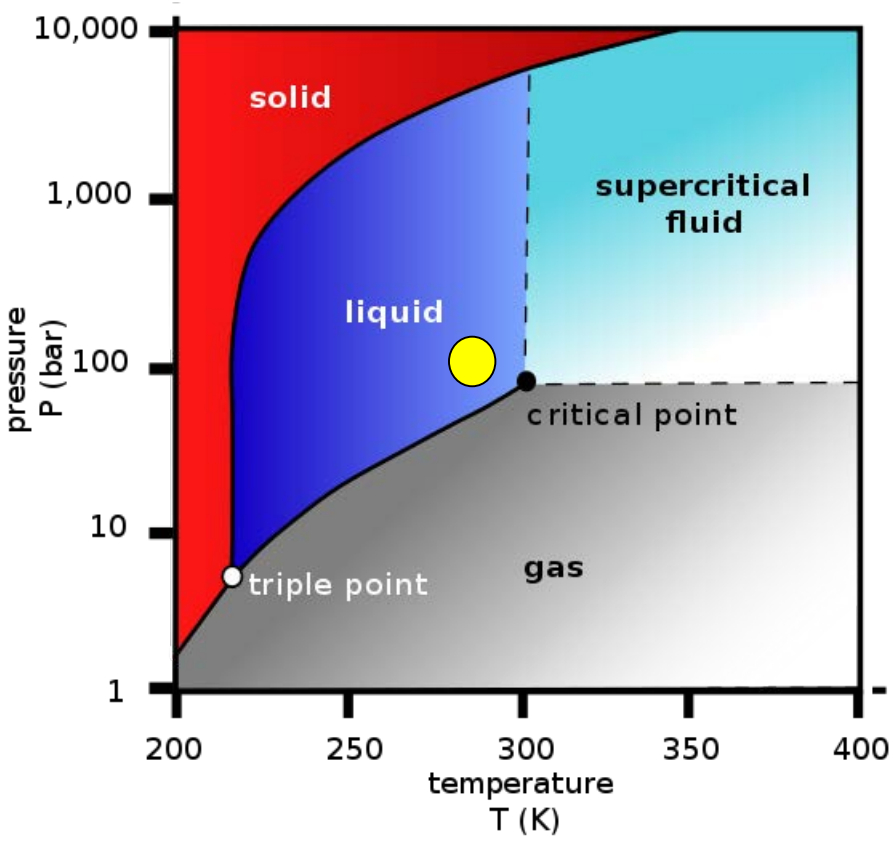
$$U_{ij}(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$

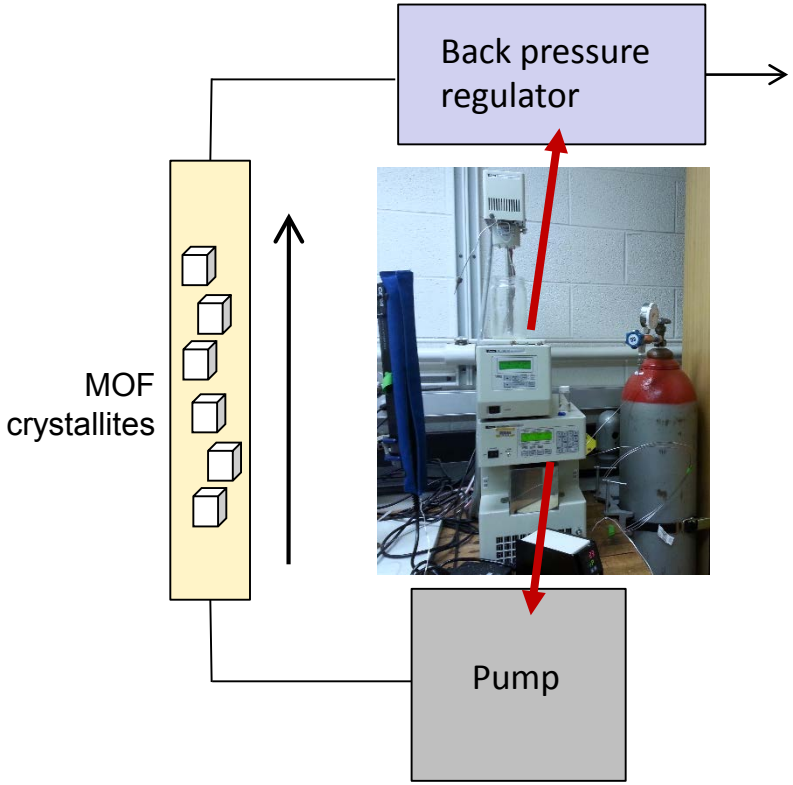
Force Field	Sigma (Å)	Epsilon/k_B (K)
MGS	2.958	36.7
Pseudo-FH	3.064	30.1

*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)

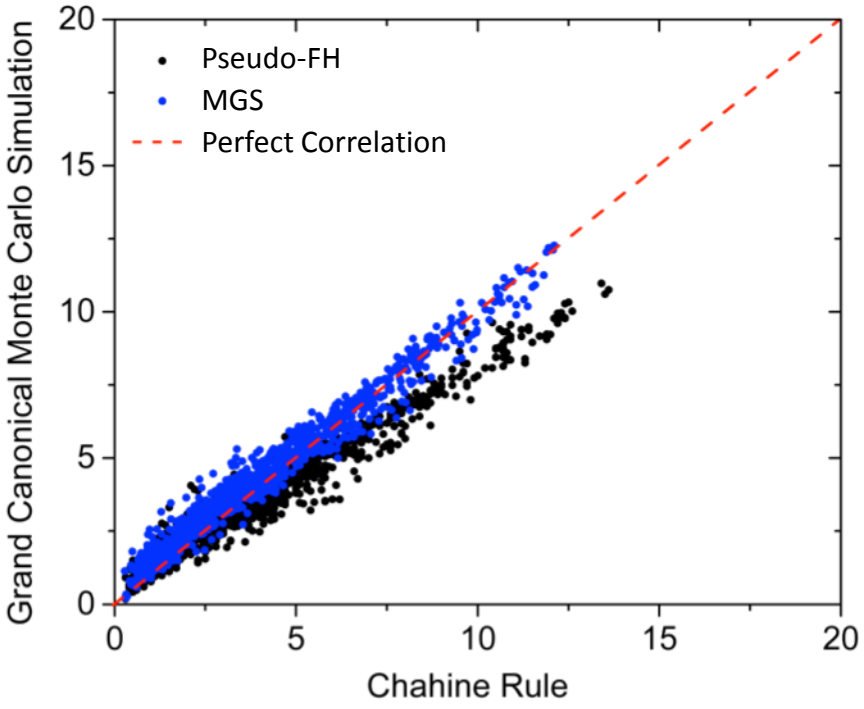
Liu, B.; Wong-Foy, A. G.; Matzger, A. J. *Chem. Commun.* **2013,** *49,* 1419.
Dutta, A.; Wong-Foy, A. G.; Matzger, A. J. *Chem. Sci.* **2014,** *5,* 3729.
Feldblyum, J. I.; Wong-Foy, A. G.; Matzger, A. J. *Chem. Commun.* **2012,** *48,* 9838.
Tran, L. D.; Feldblyum, J. I.; Wong-Foy, A. G.; Matzger,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

Accomplishments

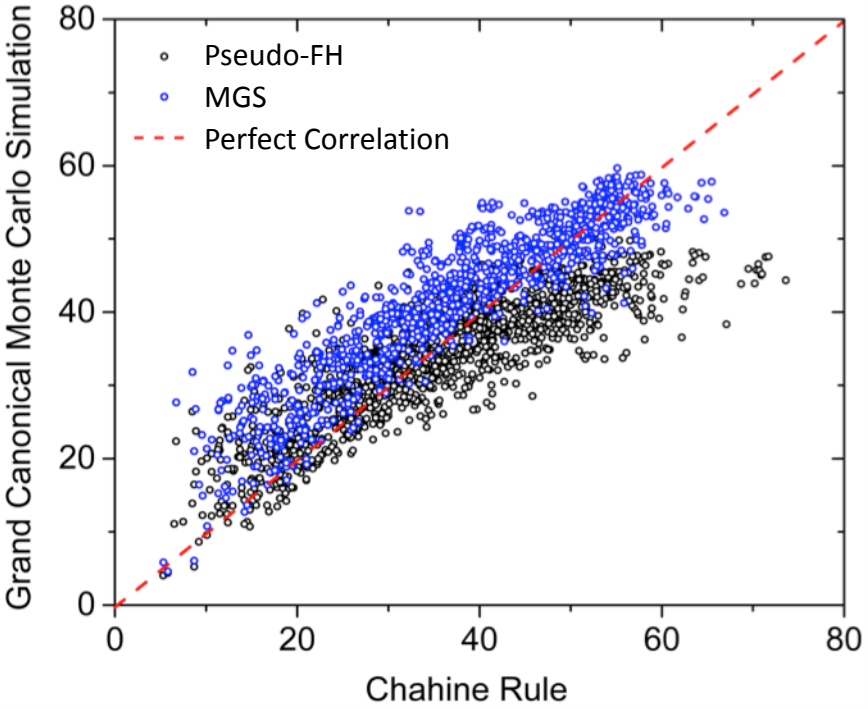
GCMC *vs.* Chahine Rule

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

Total gravimetric H_2 (wt.%)



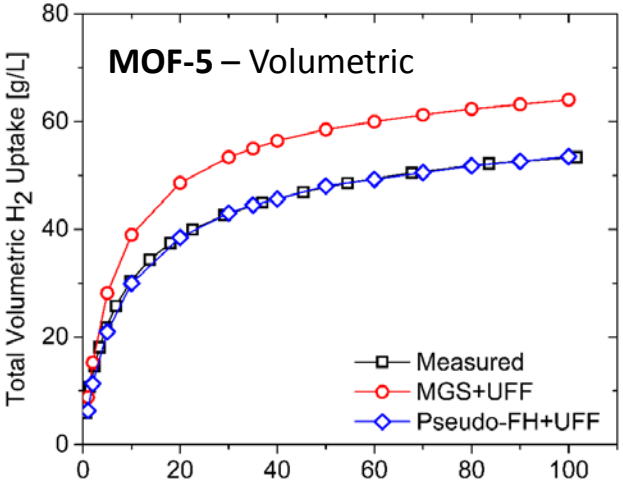
Total volumetric H_2 (g H_2/L MOF)

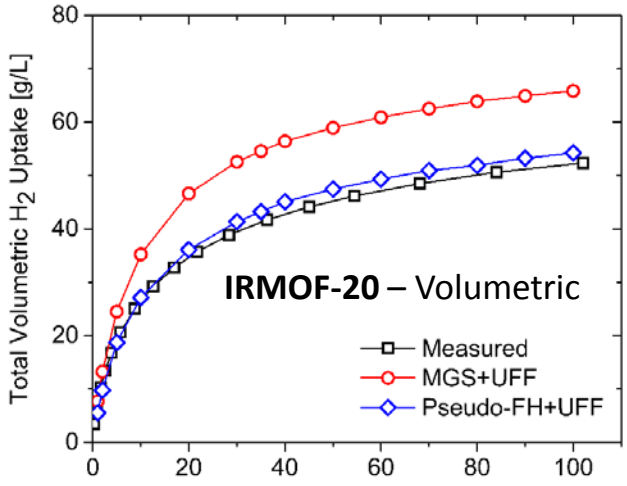


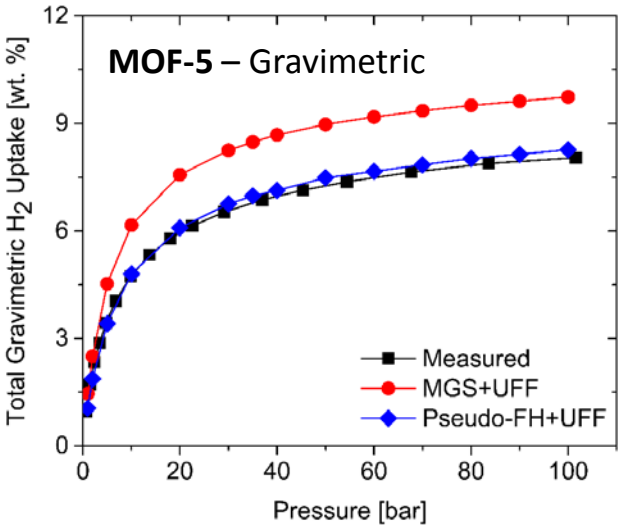
Although GCMC is more expensive, it provides access to full isotherm and allows estimation of usable capacities

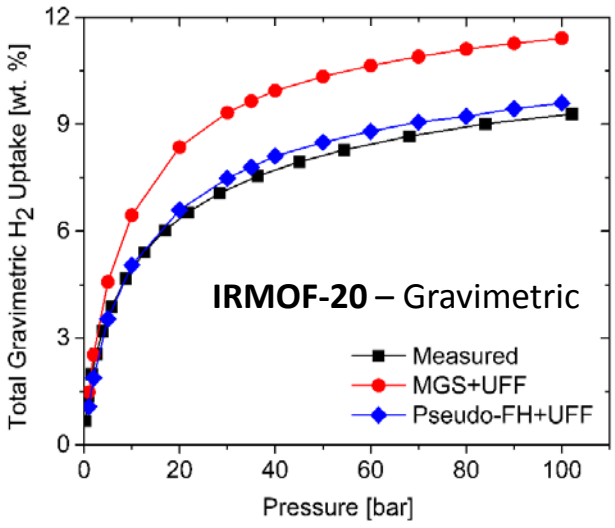
Simulated *vs.* Measured Isotherms

Pseudo-FH force field appears to more accurately reproduce our measurements





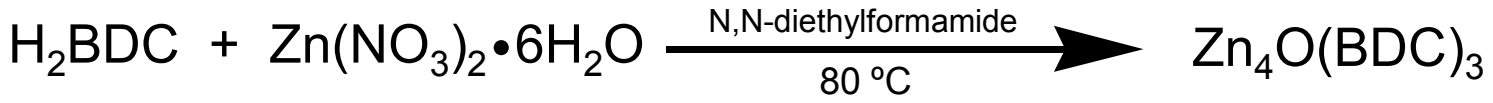


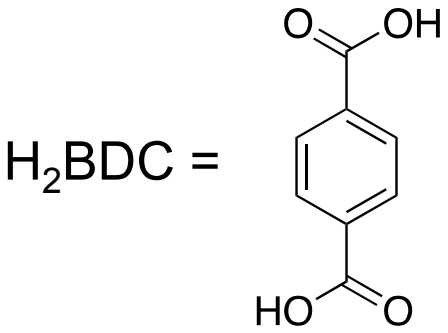


At present our GCMC calculations employ both the p-FH and MGS force fields

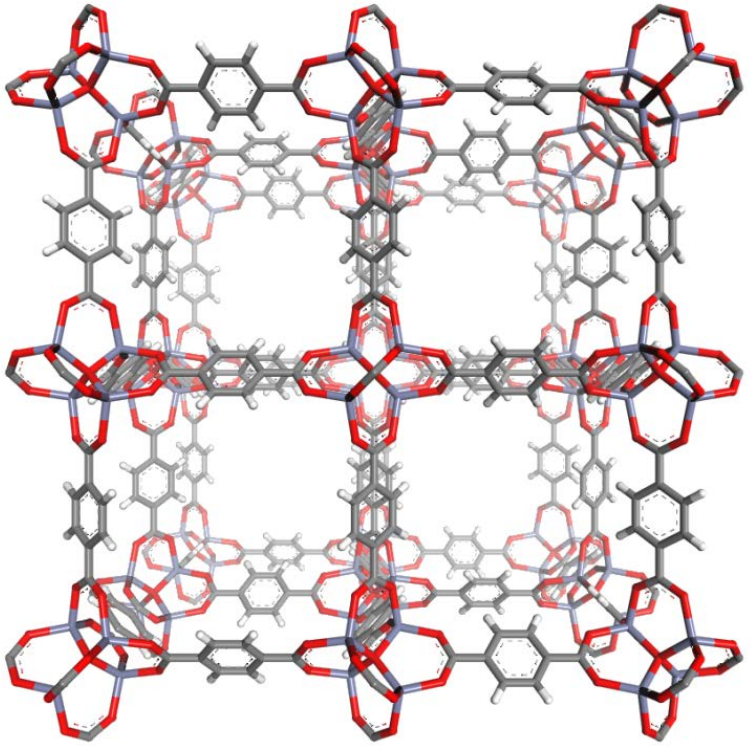
Synthesis of MOF-5

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





Benzenedicarboxylic acid



Activated by:

1) Multiple solvent exchanges
2) RT vacuum drying

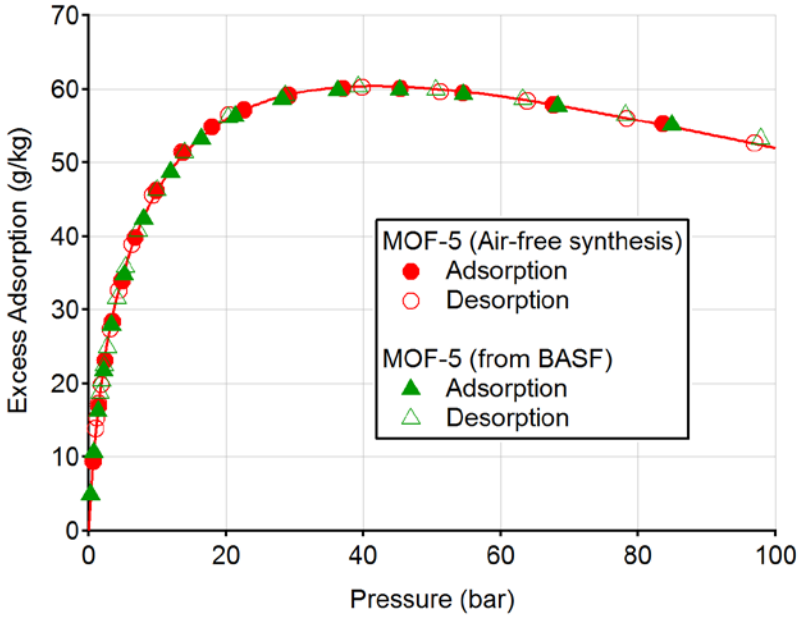
BET S.A. =	3512 m^2/g
Calculated =	3563 m^2/g
Literature =	3800 m^2/g [1]

[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

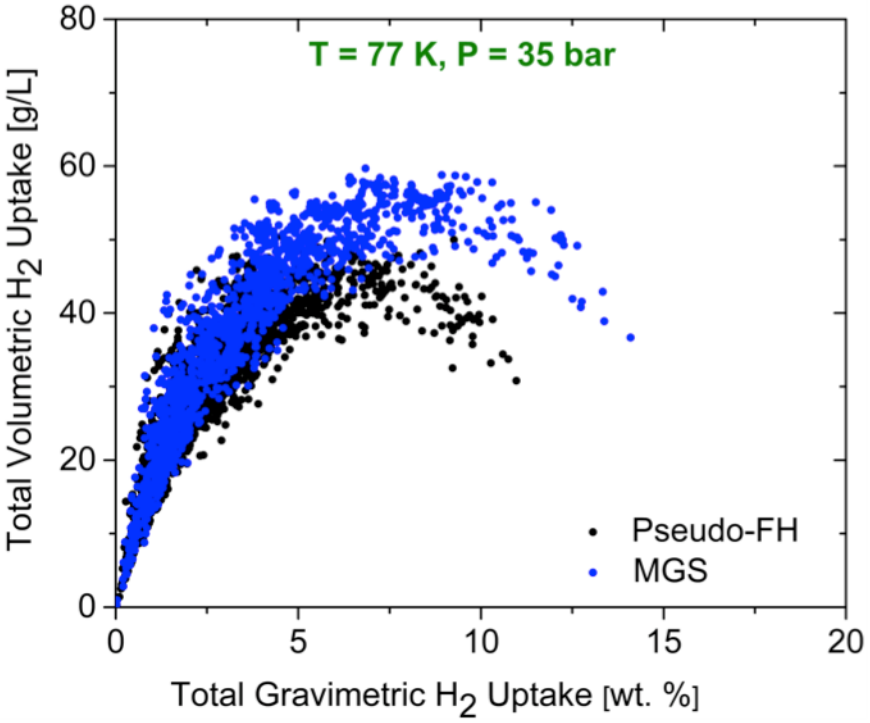


	Total		Usable (P-swing)	
p (bar)	Volumetric (g/L)	Gravimetric (wt.%)	Volumetric (g/L)	Gravimetric (wt.%)
5	22.2	3.5		
35	44.4	6.8	**22.2**	**3.3**
50	47.8	7.3	**25.6**	**3.8**
100	53.3	8.0	**31.1**	**4.5**

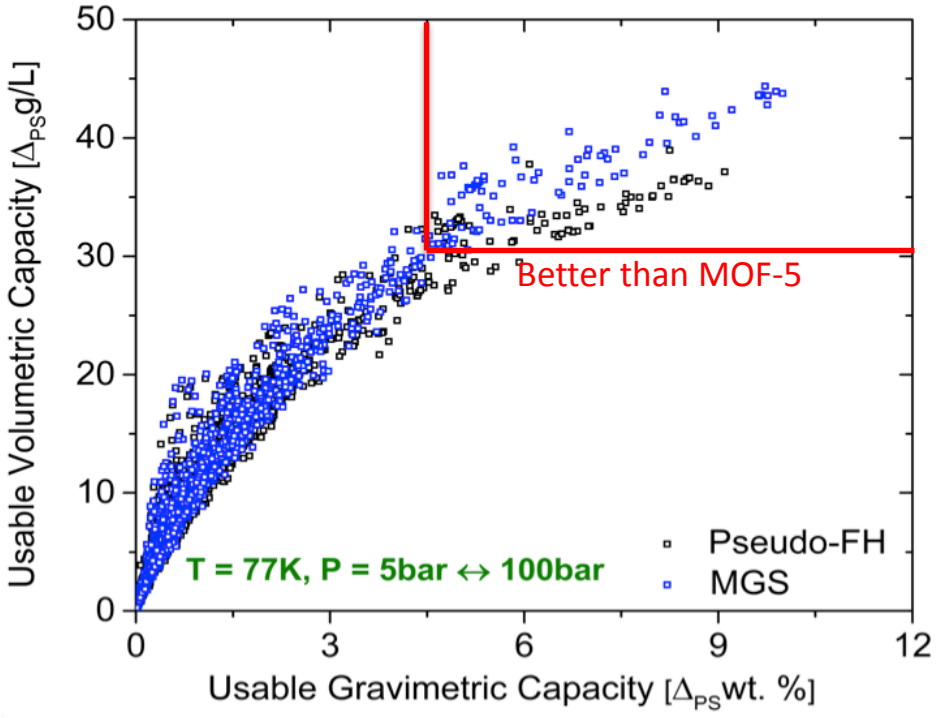
Promising Compounds

Predicted total and usable H_2 capacity for more than 2,000 compounds using GCMC

Total H_2



Usable H_2



- MOFs extracted from UM database, CoRE database, and intuition
- Identified dozens of candidates that exceed MOF-5 on usable (pressure swing) basis

Promising Compounds

Computation has identified ~70 MOFs that are projected to surpass MOF-5 in H_2 capacity

MOF	$SA_{Accessible}$ [m^2/g]	$\rho_{crystal}$ [g/cm^3]	$PV_{Accessible}$ [cm^3/g]	Tot. Grav. 35 bar [wt. %]	Tot. Vol. 35 bar [g/L]	Tot. Grav. 100 bar [wt. %]	Tot. Vol. 100 bar [g/L]	Usable Grav. 35 → 5 bar [wt. %]	Usable Vol. 35 → 5 bar [g/L]	Usable Grav. 100 → 5 bar [wt. %]	Usable Vol. 100 → 5 bar [g/L]
1	4124	0.50	1.61	10.3	57.8	11.6	66.2	4.0	23.8	5.3	32.2
2	3469	0.57	1.45	9.1	57.2	10.6	67.7	4.3	28.8	5.8	39.2
3	4040	0.54	1.46	9.4	56.6	10.6	64.4	3.9	24.6	5.0	32.4
4	4614	0.50	1.63	10.0	55.6	11.5	65.1	4.7	27.6	6.2	37.1
5	3801	0.57	1.42	8.9	55.6	10.2	64.4	4.1	26.6	5.3	35.5
6	3648	0.59	1.36	8.5	55.4	9.8	64.2	3.9	26.8	5.2	35.7
7	3564	0.61	1.32	8.3	55.4	9.5	64.2	3.7	25.8	4.9	34.6
8	4902	0.42	1.92	11.5	55.1	13.2	64.5	5.2	26.6	6.9	35.9
9	3644	0.60	1.35	8.4	55.1	9.6	64.1	3.9	26.8	5.1	35.8
10	4623	0.45	1.77	10.8	55.0	12.3	63.4	4.7	25.3	6.1	33.7
11	4687	0.46	1.75	10.6	54.8	12.2	64.8	5.3	29.1	7.0	39.0
12	3636	0.59	1.37	8.4	54.7	9.7	64.0	4.0	27.1	5.3	36.4
13	3636	0.59	1.37	8.5	54.6	9.7	63.7	4.1	27.6	5.4	36.8
14	3810	0.54	1.50	9.1	54.5	10.5	64.0	4.2	26.7	5.7	36.2
15	4676	0.47	1.76	10.5	54.4	12.1	64.2	5.2	28.4	6.8	38.2
16	4434	0.52	1.54	9.4	54.1	10.7	62.3	4.1	25.2	5.4	33.4
17	5769	0.40	2.06	11.9	54.0	13.8	63.8	6.0	28.8	7.8	38.6
18	3575	0.61	1.32	8.1	53.7	9.4	62.7	3.8	26.2	5.0	35.2
19	3374	0.58	1.35	8.4	53.2	9.6	61.7	3.7	24.3	4.9	32.8
20	5159	0.43	1.88	10.8	52.7	12.6	62.5	5.5	28.4	7.3	38.2
MOF-5	**3512**	**0.60**	**1.14**	**6.8**	**44.4**	**8.0**	**53.3**	**3.3**	**22.2**	**4.5**	**31.1**

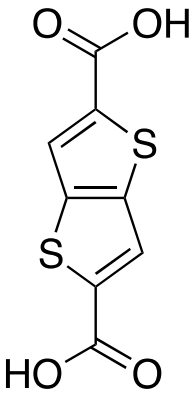
These compounds surpass MOF-5 in total, usable PS, and usable T+PS

A Success Story: IRMOF-20

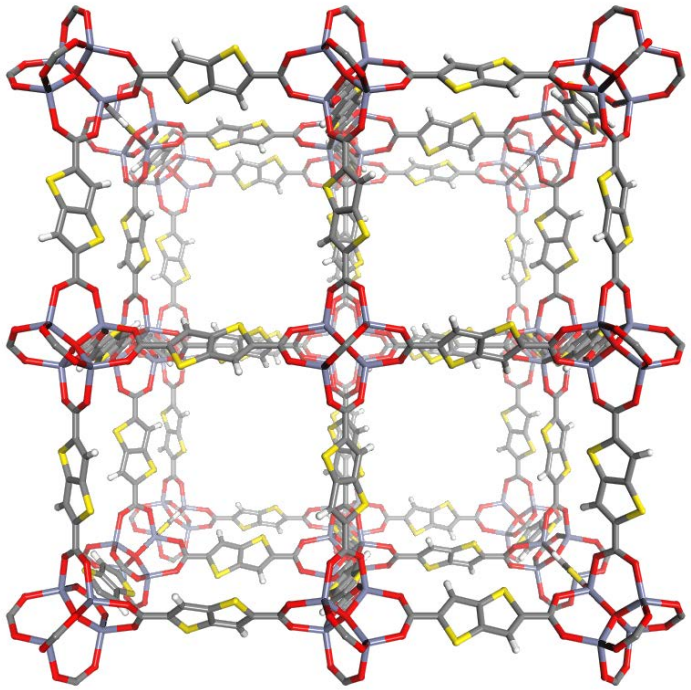
Synthesis of IRMOF-20 was attempted after computation identified it as a promising compound

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

$H_2TTDC =$



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



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

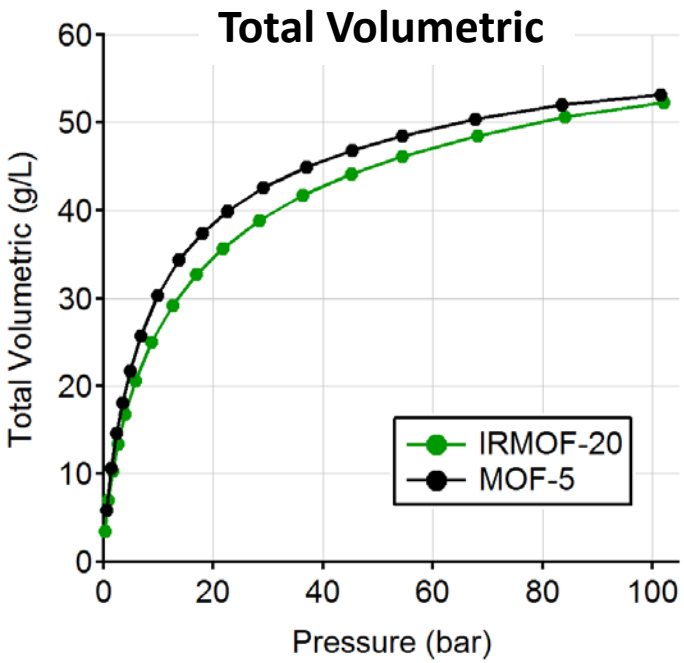
Activated by:

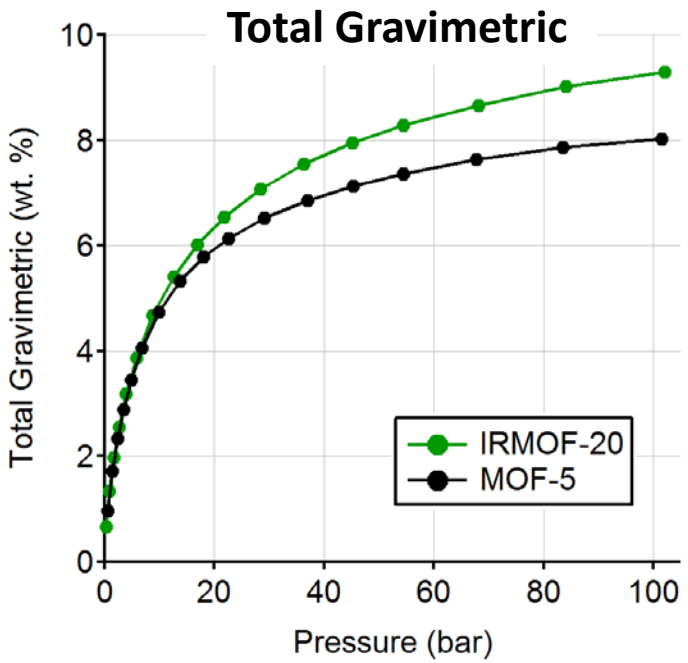
1) Multiple solvent exchanges
2) RT vacuum drying

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

IRMOF-20 H_2 Capacity

Usable capacity of IRMOF-20 surpasses that of MOF-5

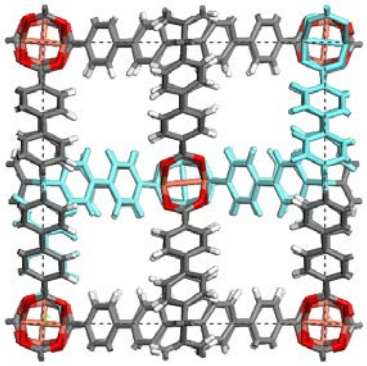




	Usable Volumetric (g H_2/L)		Usable Gravimetric (wt. %)	
p (bar)	MOF-5	IRMOF-20	MOF-5	IRMOF-20
35	22.2	22.2	3.3	3.9
50	25.6	26.1	3.8	4.5
100	31.1	33.1	4.5	5.7

A Few Failures

Several promising MOFs could not be synthesized with high surface area

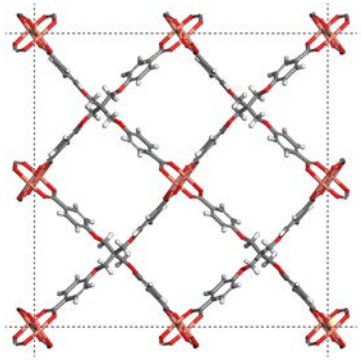


SUKYON

Ma, L. et al., *Angew. Chem. Int. Ed.* **2009**, *48*, 9905.

BET S.A. = 2152 m^2/g (fresh)
[= 2081 m^2/g (6 days under N_2)]
Calculated = 4965 m^2/g
Literature = 1020 m^2/g

Chahine rule capacities:
Total grav. = 11.2 wt. %
Total vol. = 61 g/L

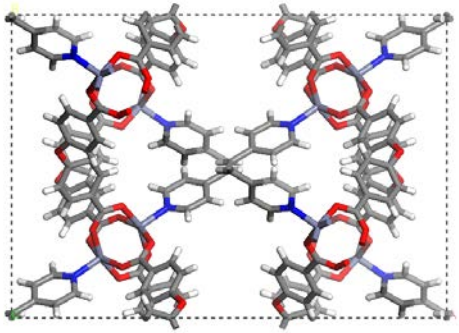


EPOTAF (SNU-21)

Kim, T. K. et al., *Chem. Commun.* **2011**, *47*, 4258.

BET S.A. = 27 m^2/g
Calculated = 5208 m^2/g
Literature = 905 m^2/g

Chahine rule capacities:
Total grav. = 11 wt. %
Total vol. = 71 g/L



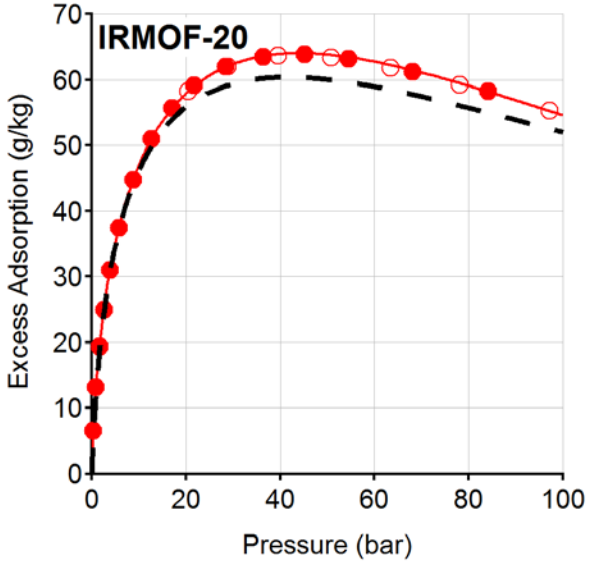
DIDDOK

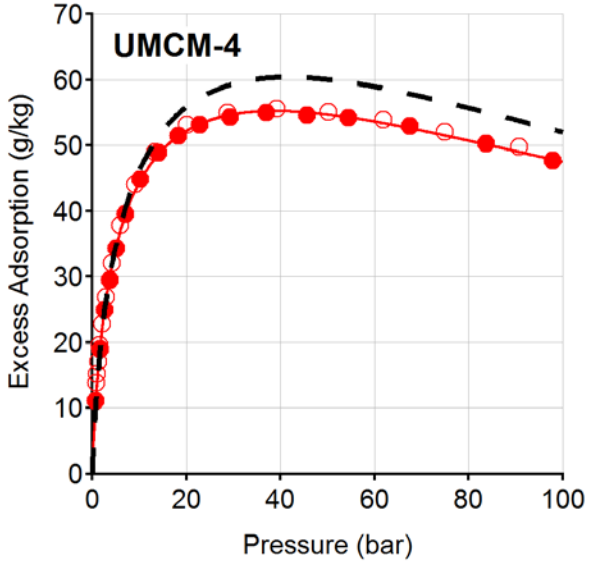
Kondo, M. et al., *J. Organomet. Chem.* **2007**, *692*, 136.

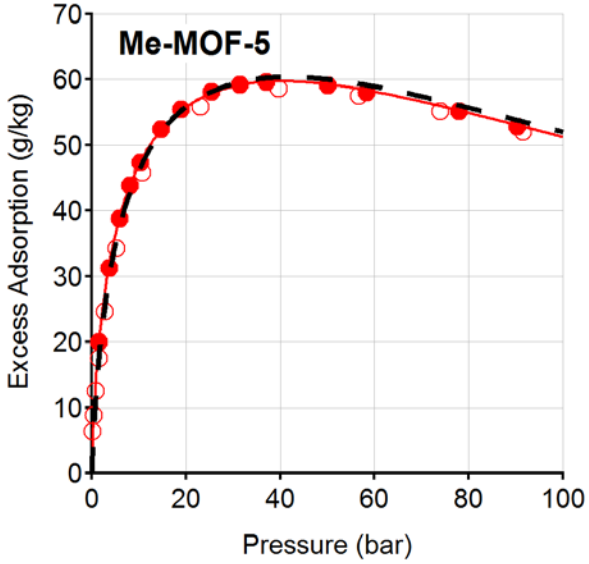
BET S.A. = 578 m^2/g
Calculated = 4652 m^2/g
Literature = not reported

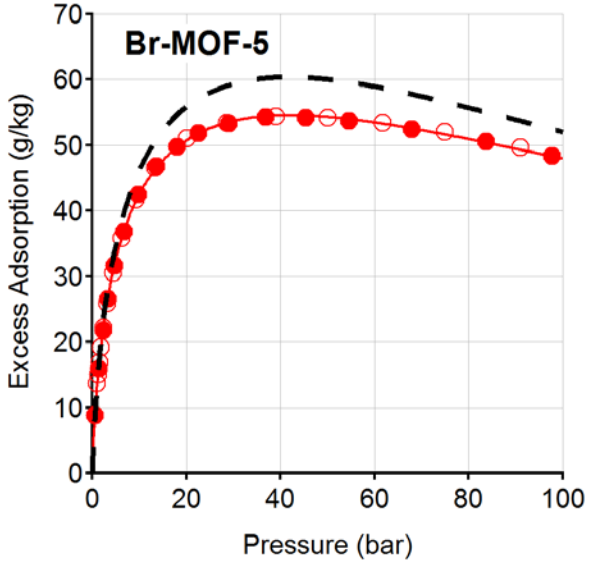
Chahine rule capacities:
Total grav. = 10.2 wt. %
Total vol. = 60 g/L

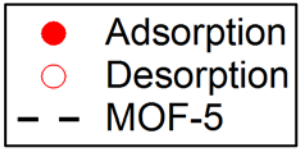
Others MOFs in Pipeline





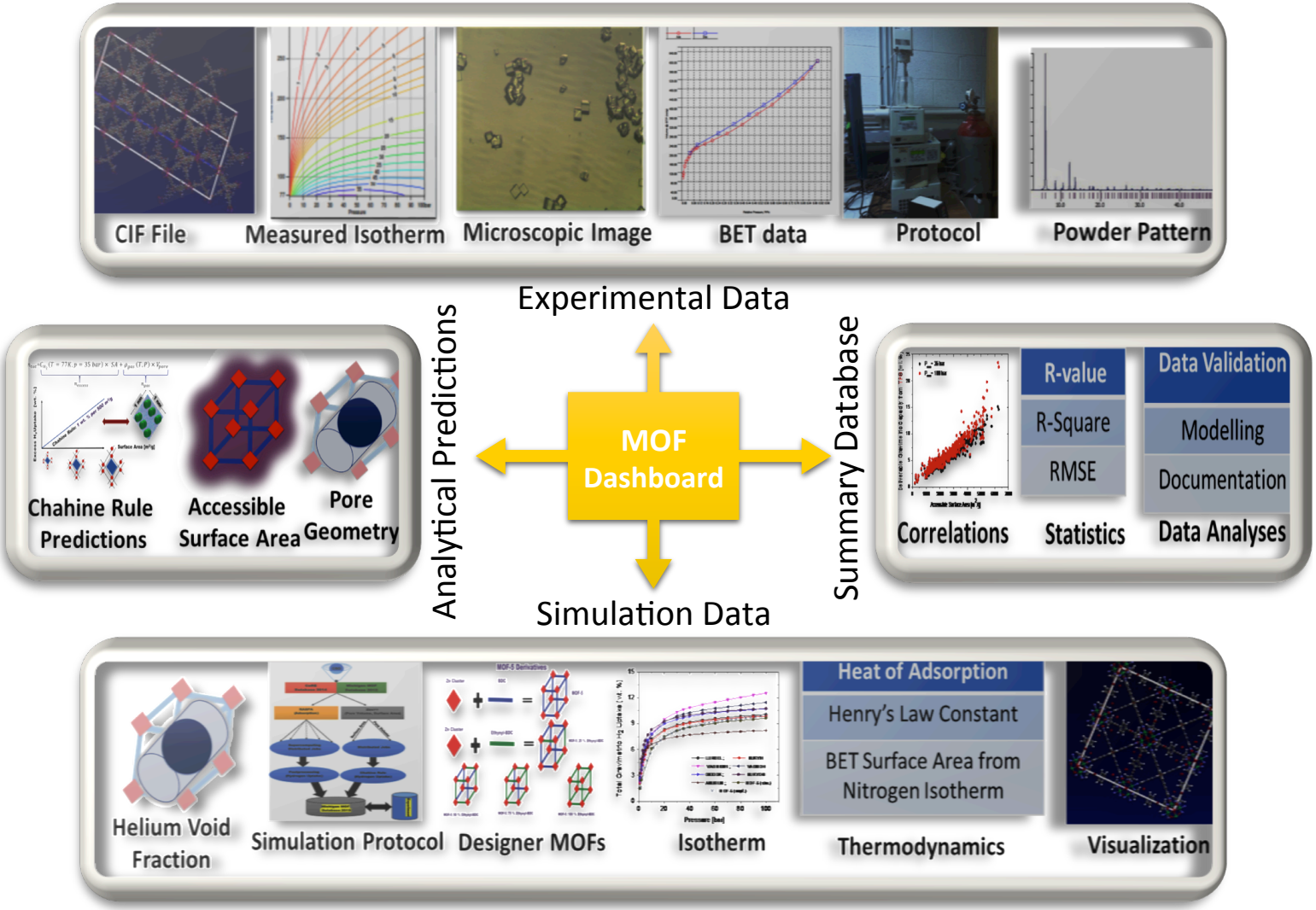






MOF Dashboard

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



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 (unfunded collaborator)

- Assistance with system models

Challenges and Barriers

- Incorrect, incomplete, or disordered crystal structure data
  - Garbage in, garbage out
  - False positives in screening
- Structure collapse or incomplete solvent removal during activation
  - “Can it be made?”
  - Failure to achieve expected surface area and porosity
  - Which features control “pristineness?”
- Achieving absolute accuracy from computed isotherms
  - Trends and surface area appear to be reliable
  - Pseudo-FH force field appears to more accurately reproduce experimental isotherms than does MGS model

Potential Future Work

- Expand screening to additional compounds
- Explore influence of interatomic potential on accuracy of computed isotherms
- Explore strategies for maximizing *volumetric* surface area
- Optimize synthesis/activation of UMCM-4
  - Replicate predicted surface area
- Focus on 2nd go/no-go milestone
  - Identify MOFs with 15% improvement in H_2 capacity over MOF-5

Summary

- **New project**: underway for 8 months
- **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**: High-throughput screening coupled to experimental synthesis, activation, and characterization
- **Accomplishments:**
  - Replicated performance of BASF-supplied MOF-5 with home-made MOF-5
  - 2,000+ MOF capacities screened computationally; several promising compounds identified
  - 7 candidate MOFs synthesized and characterized
  - Demonstrated IRMOF-20: surpasses usable capacity of MOF-5

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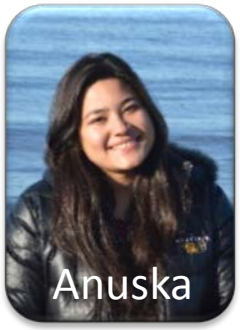
The Team

UNIVERSITY OF MICHIGAN

Ford



Technical Backup Slides

Capacity Definitions

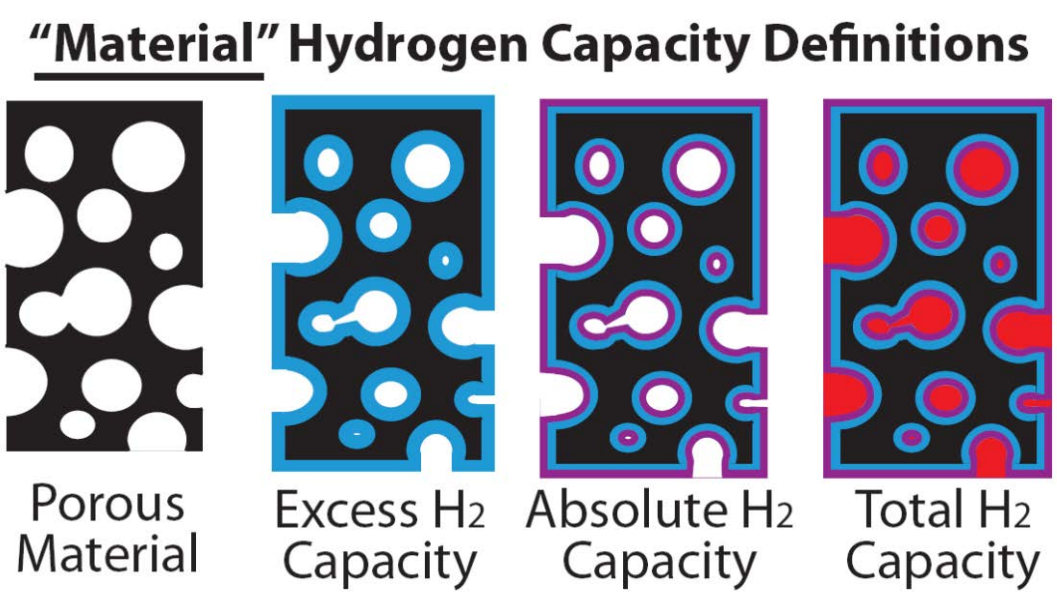
$$C_{tot} = C_{exc} + \frac{100 \times d_g V_{pore}}{1 + d_g V_{pore}}$$

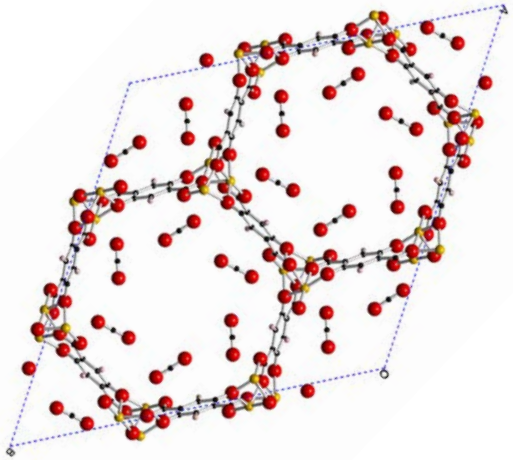
$$V_{pore} = \frac{d_{sk} - d_{bulk}}{d_{sk} d_{bulk}}$$

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

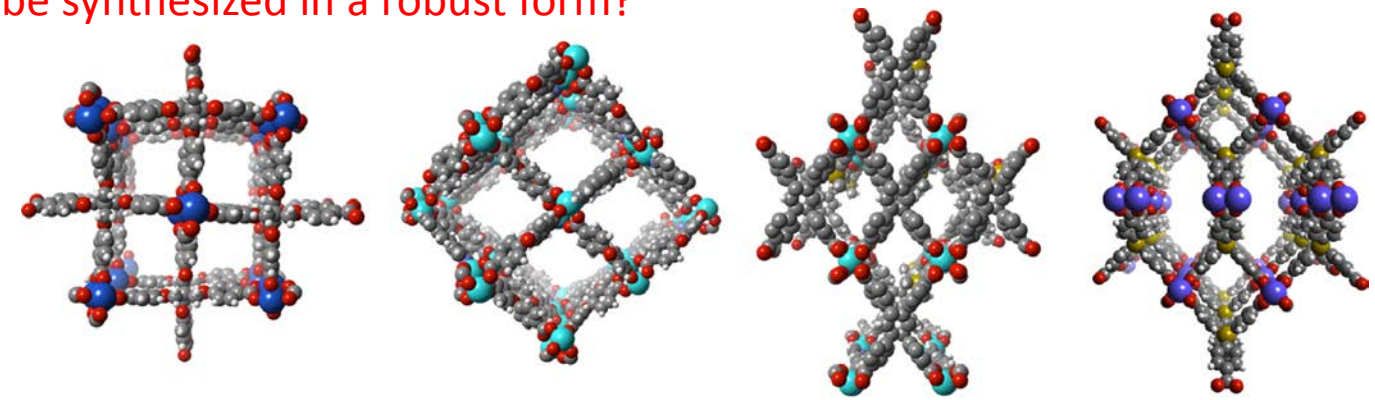




MOFs Identified by Prior Screening

Several MOF "Targets of Opportunity" were identified

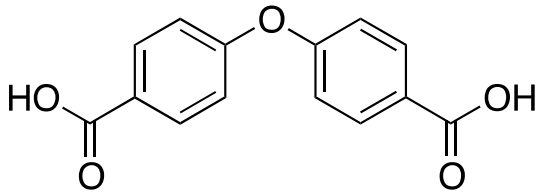
- Combine high gravimetric and volumetric densities
- Overlooked: no/limited experimental evaluation
- Can these be synthesized in a robust form?



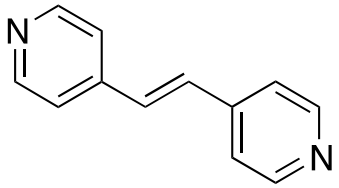
	EPOTAF (SNU-21)	DIDDOK	LURGEL (TO-MOF)	ENITAX (IMP-9)
Total Grav. (wt. %)	11	10.2	9.7	9.3
Total Volumetric (g/L)	71	60	57	59
Crystal Density (g/cm^3)	0.58	0.53	0.53	0.57
Calc'd/Meas. SA (m^2/g)	5208/700-900	4651	4386/680	4162
Notes	Best combination of grav. & vol. density. H_2 uptake measured previously: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

Synthesis of DIDDOK

$H_2oba + bpe + Zn(NO_3)_2 \bullet 6H_2O \xrightarrow[23\ ^oC]{DMF} Zn_2(oba)_2(bpe)$

$H_2oba =$ 

4,4'-Oxybis(benzoic) acid

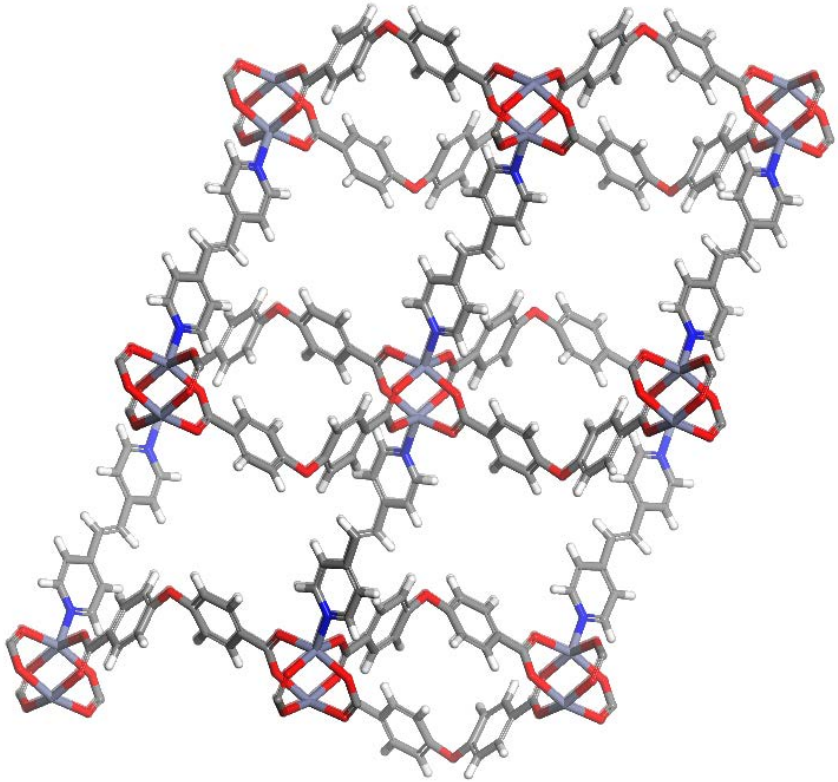
bpe = 

trans-1,2-Bis(4-pyridyl)ethylene

Activated by:

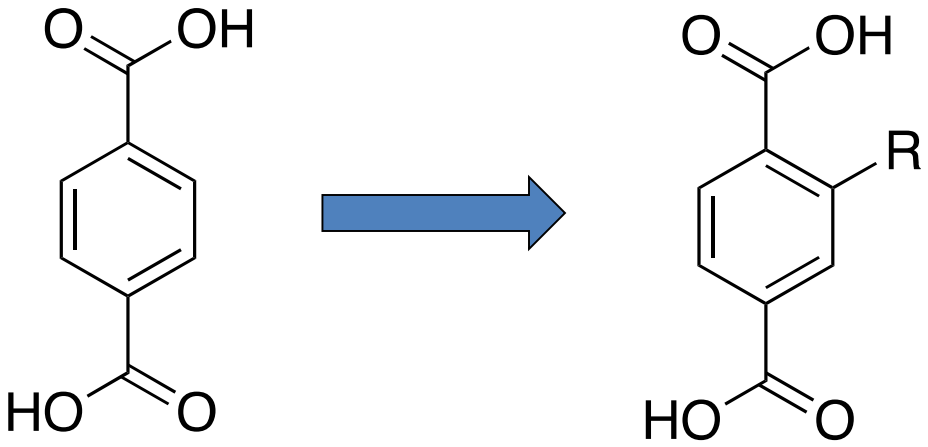
1) Multiple solvent exchanges
2) Flowing $scCO_2$

BET S.A. = 578 m^2/g
Calculated = 4652 m^2/g
Literature = not reported



Kondo, M.; Irie, Y.; Miyazawa, M.; Kawaguchi, H.; Yasue, S.; Maeda, K.; Uchida, F. *J. Organomet. Chem.* **2007**, *692*, 136.

Mixed-Linker MOF-5 Derivatives



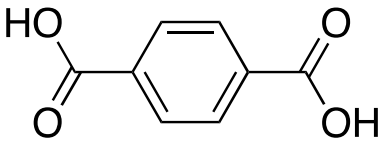
Idea:

1) Partially fill the pores of MOF-5 to increase surface area per volume
2) Maintain the same unit cell size, increase crystal density
3) Aim to increase H_2 volumetric density while keeping gravimetric density

Synthesis of mMe-MOF-5

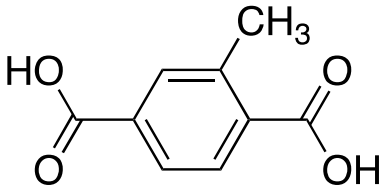
$$H_2BDC + H_2MeBDC + Zn(NO_3)_2 \cdot 6H_2O \xrightarrow[100\ ^oC]{N,N\text{-diethylformamide}} Zn_4O(BDC)_{2.19}(MeBDC)_{0.81}$$

H_2BDC =

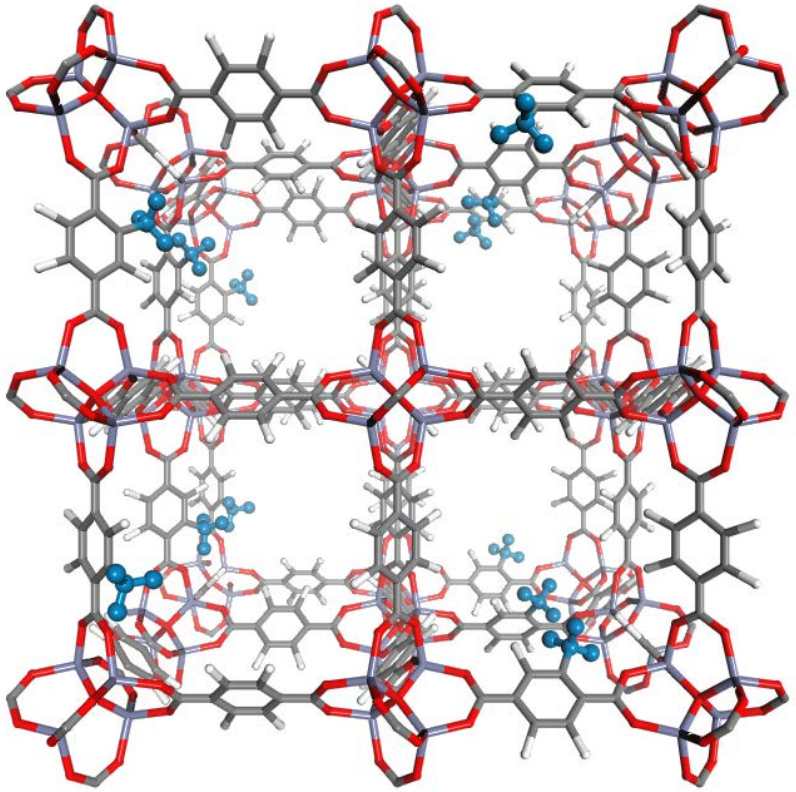


Benzenedicarboxylic acid

H_2MeBDC =



Methylbenzenedicarboxylic acid

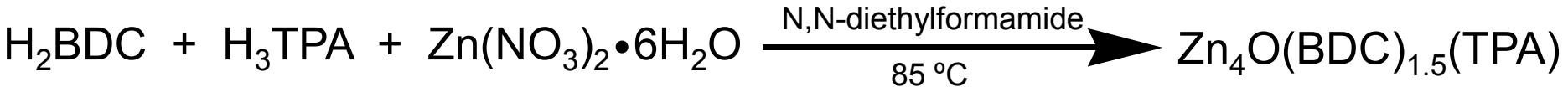


Activated by:

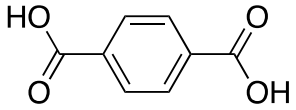
1) Multiple solvent exchanges
2) RT vacuum drying

BET S.A. = 3171 m^2/g

Synthesis of UMCM-4

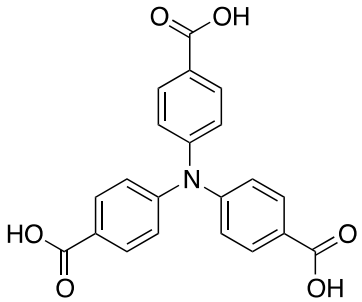


H_2BDC =



Benzenedicarboxylic acid

H_3TPA =

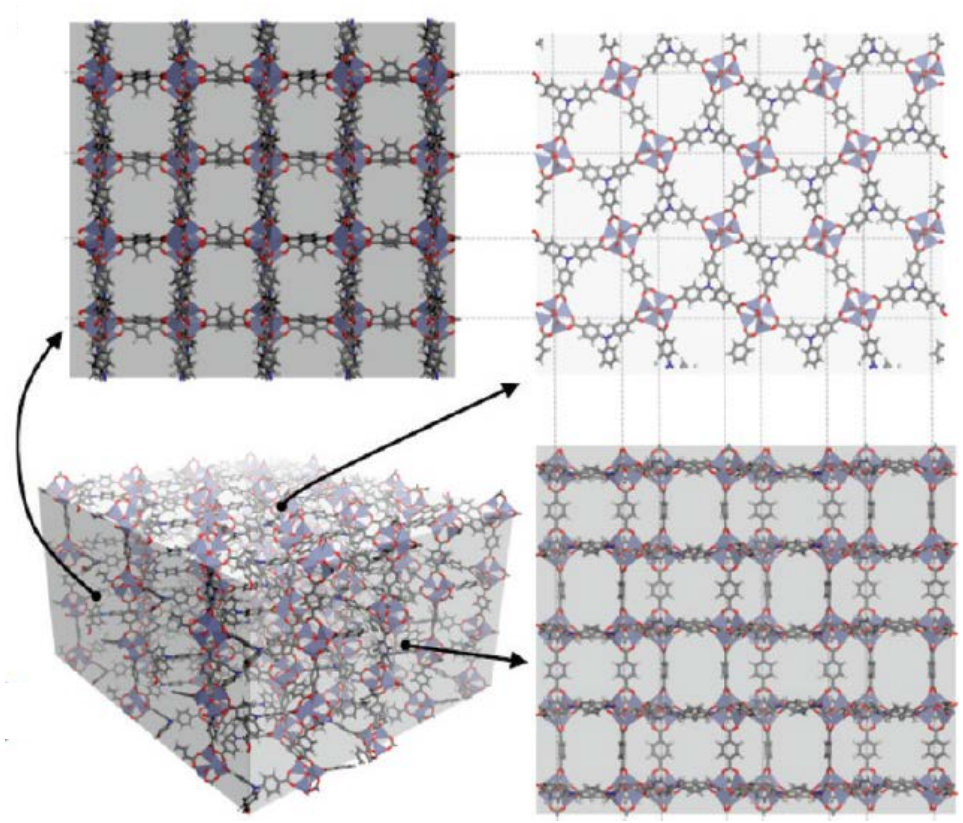


Triphenylaminetricarboxylic acid

Activated by:

1) Multiple solvent exchanges
2) RT vacuum drying

BET S.A. = 3000 m^2/g
Calculated = 3810 m^2/g
Literature = 3500 m^2/g



Koh, K.; Wong-Foy, A. G.; Matzger, A. J.
J. Am. Chem. Soc. **2010**, *132*, 15005.