Project ID: ST122

# Hydrogen Adsorbents with High Volumetric Density:

## *New Materials and System Projections*

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University of Michigan

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

# 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

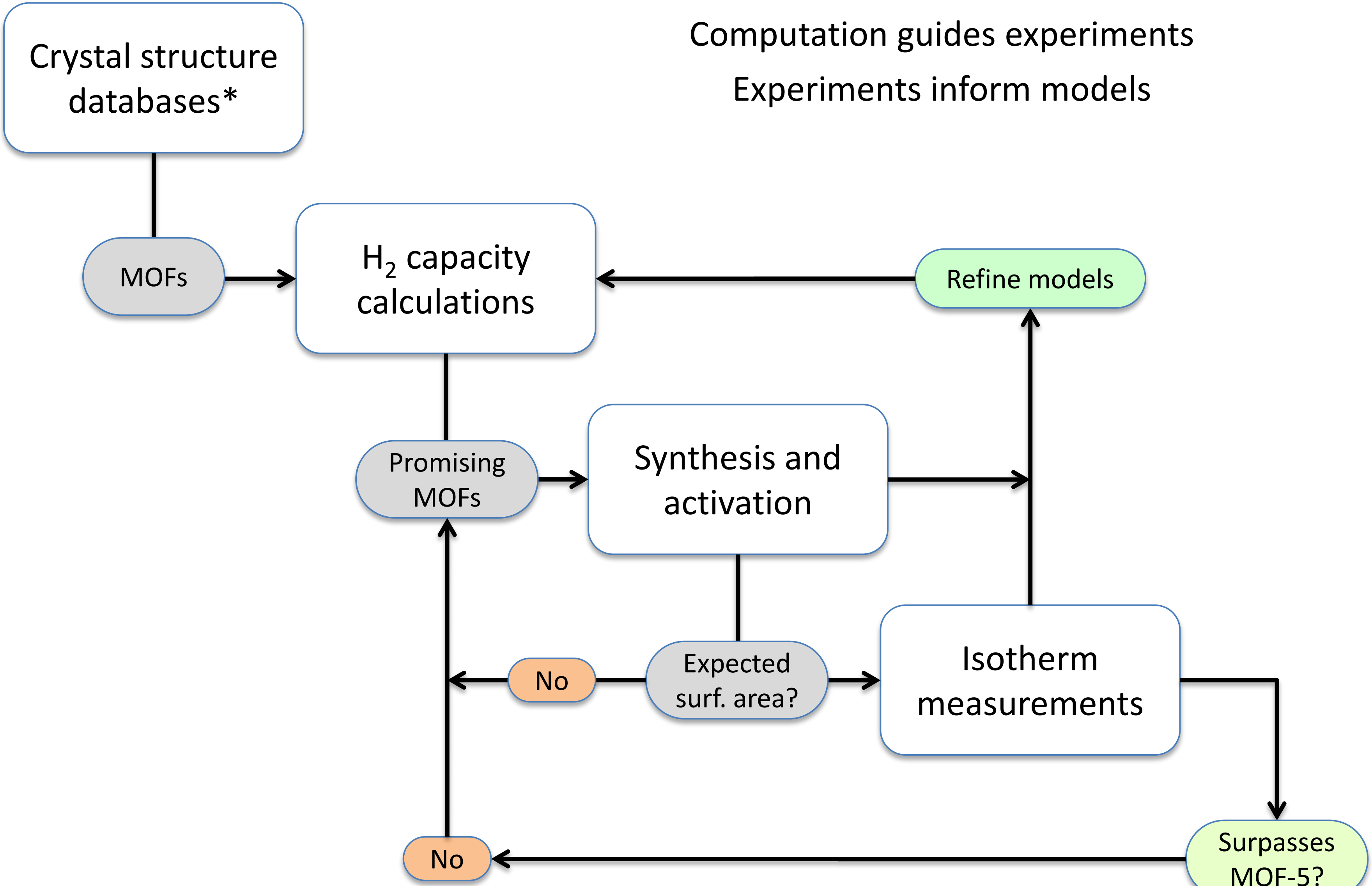
# Approach

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

# Concept

Computation guides experiments

Experiments inform models



Crystal structure databases*

MOFs

$H_2$ capacity calculations

Refine models

Promising MOFs

Synthesis and activation

Expected surf. area?

No

Isotherm measurements

Surpasses MOF-5?

No

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*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

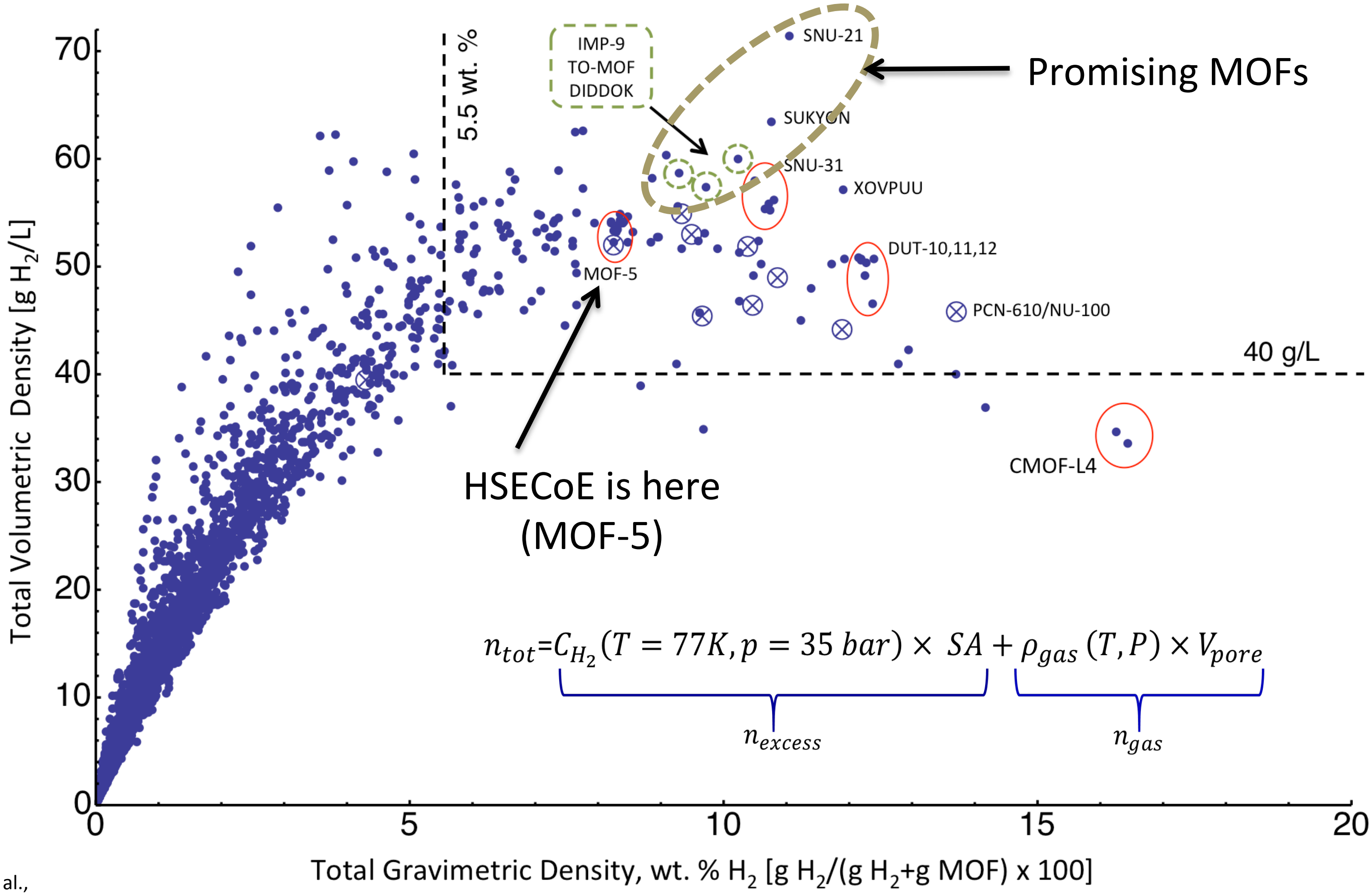
| Year | Milestone or Go/No-Go | Due | Description | Status |
|---|---|---|---|---|
| 1 | Update and validate computational methods | 10/31/15 | • Update screening method to account for impact of adsorbed hydrogen on total volumetric hydrogen density<br>• Validate against experimental capacities for MOF-5 baseline | **Complete**.<br>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**.<br>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** |

| Year | Milestone or Go/No-Go | Due | Description | Status |
|---|---|---|---|---|
| 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** |

| Year | Milestone or Go/No-Go | Due | Description | Status |
|---|---|---|---|---|
| 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



Promising MOFs

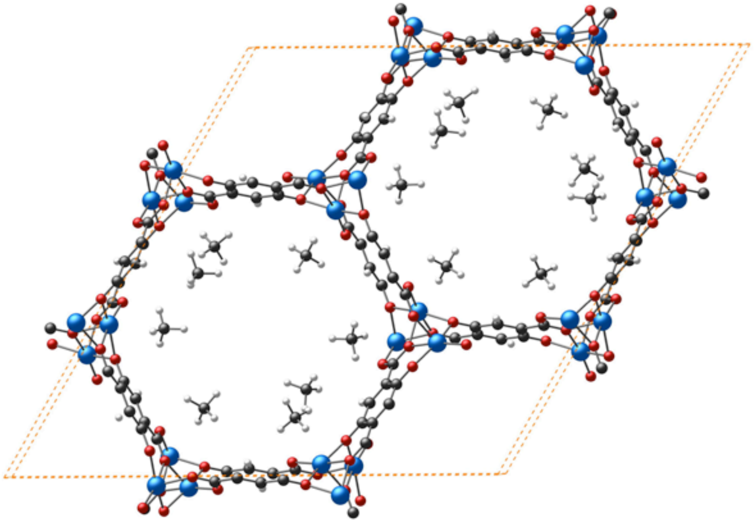
HSECoE is here (MOF-5)

$$n_{tot}=\underbrace{C_{H_2}(T=77K, p=35\ bar)\times\ SA}_{n_{excess}}+\underbrace{\rho_{gas}(T,P)\times V_{pore}}_{n_{gas}}$$

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

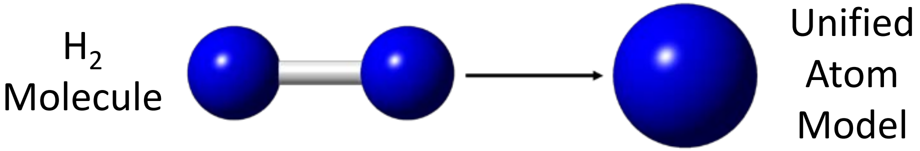
# Grand Canonical Monte Carlo

- 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



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

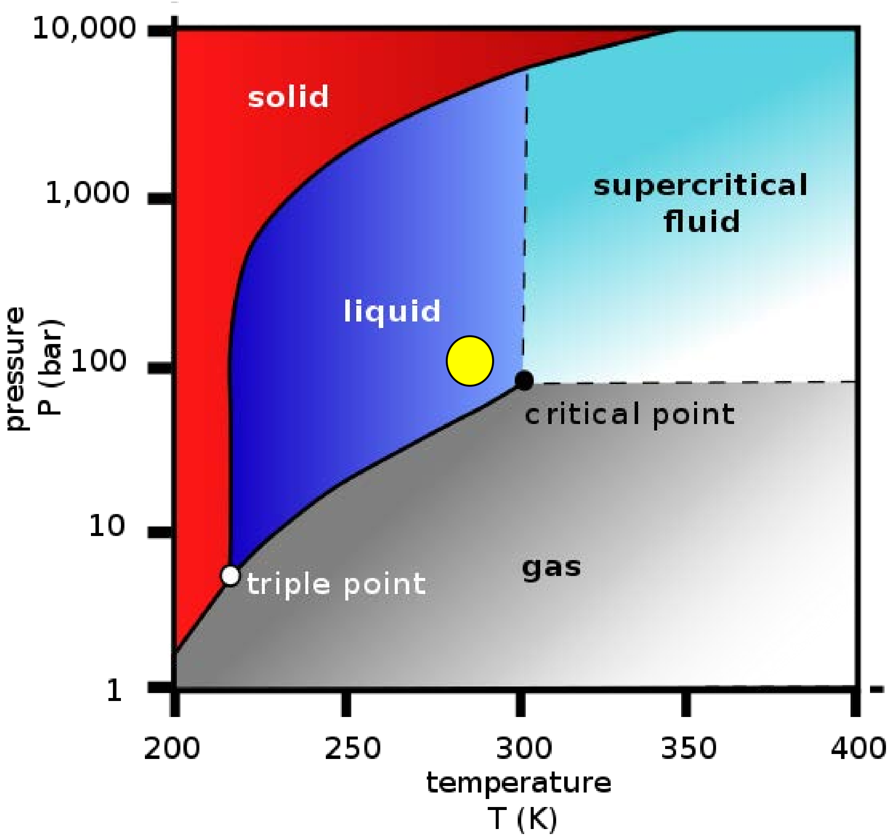
| Force Field | Sigma (Å) | Epsilon/$k_B$ (K) |
|---|---|---|
| MGS | 2.958 | 36.7 |
| Pseudo-FH | 3.064 | 30.1 |

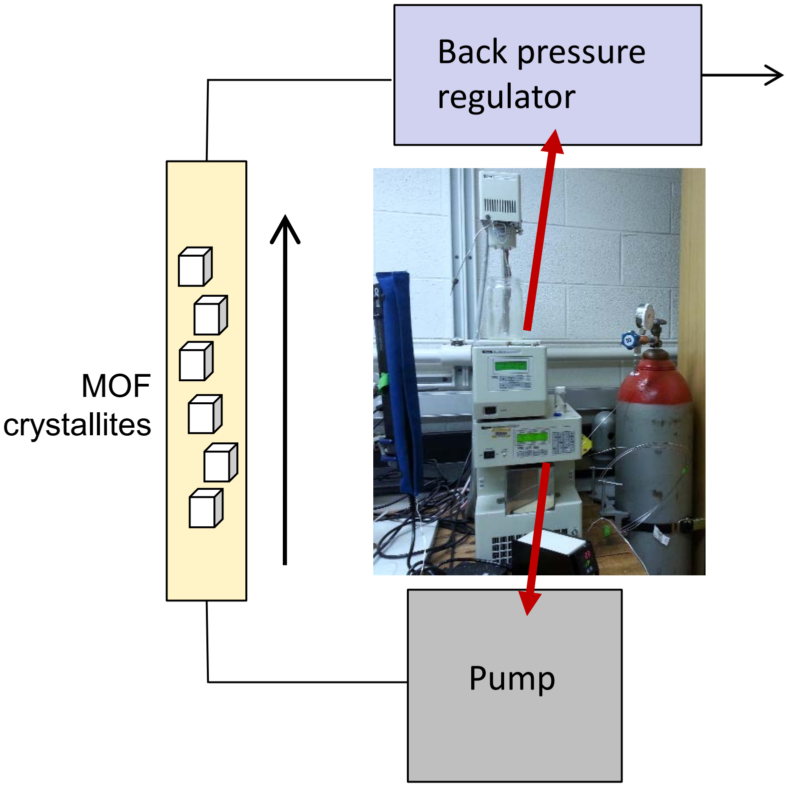
*Michels, de Graaff and Seldam, *Physica*, **1960**, 26, 393; Ryan, Broadbelt, and Snurr, *Chem. Comm*. 2008, 4134

**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

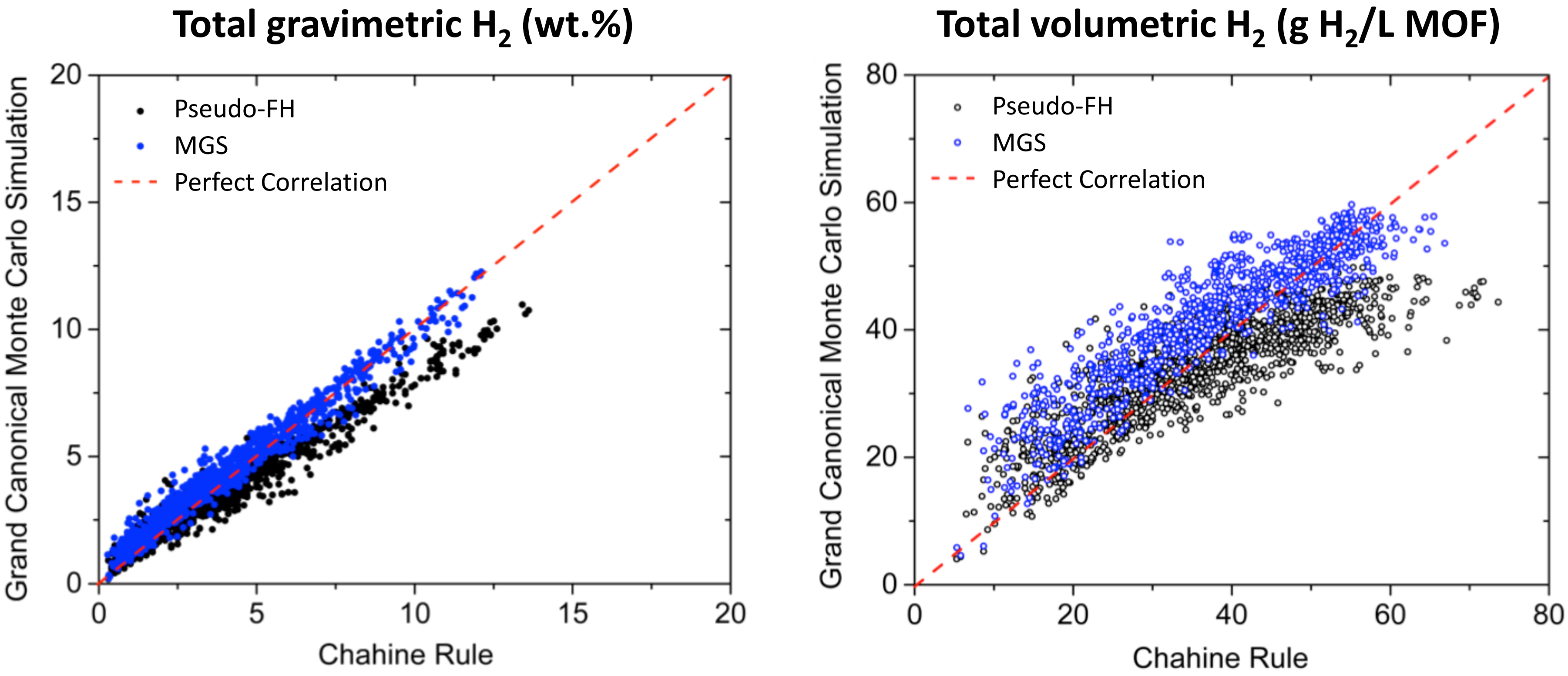
| Material | Surface area (flow Sc-$CO_2$ activation) | Surface area (vacuum/batch Sc-$CO_2$ activation) |
|---|---|---|
| UMCM-9 | 5357 $m^2/g$ | 1330 $m^2/g$ (vac) |
| FJI | 4813 $m^2/g$ | 4043 $m^2/g$ (batch) |
| MOF-74 (Zn/DOBDC) | 1108 $m^2/g$ | 750-950 $m^2/g$ (vac) |
| UMCM-10 | 4001 $m^2/g$ | 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

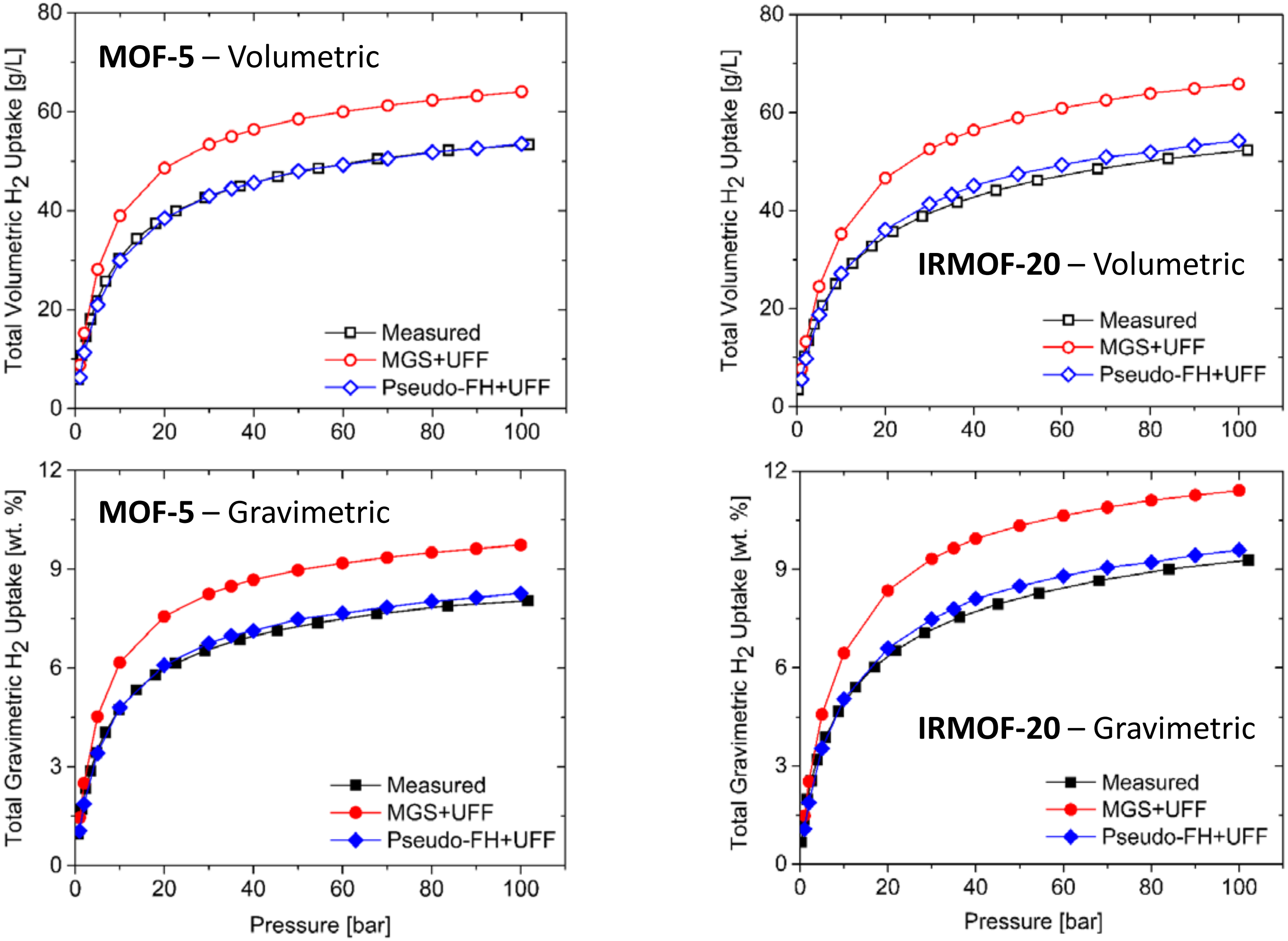
“Quick and dirty” Chahine-rule predictions of $H_2$ uptake in MOFs correlate strongly with GCMC calculations



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



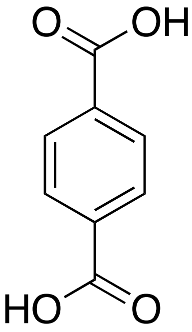
At present our GCMC calculations employ both the p-FH and MGS force fields

# Synthesis of MOF-5

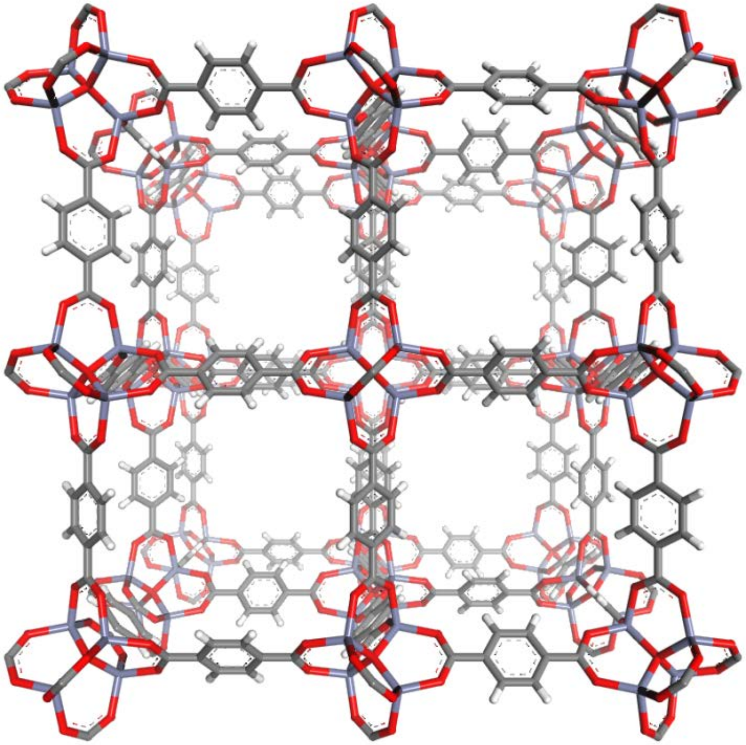
Performed air-free synthesis[1] of the benchmark compound MOF-5

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

$H_2BDC$ =



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] |

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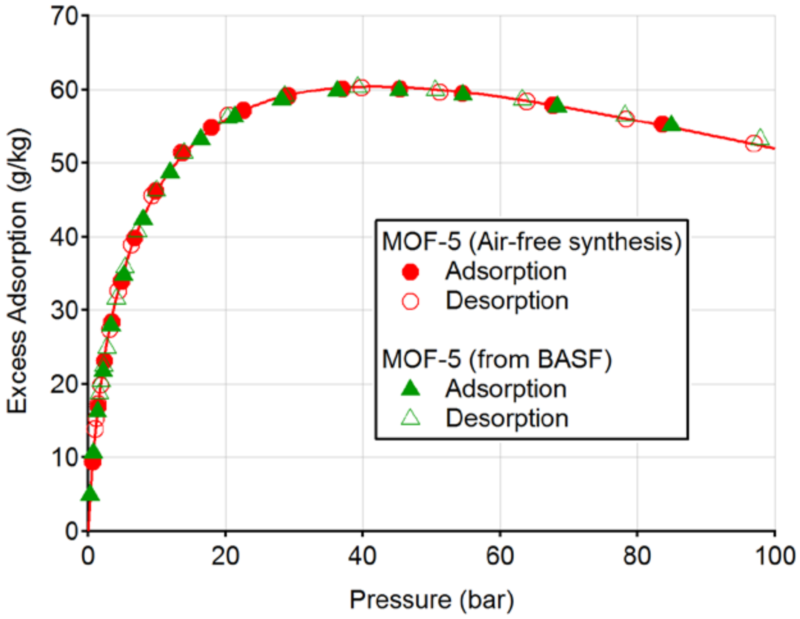
[1] Kaye, Dailly, Yaghi, and Long, 2007. JACS, 129,14176: 8.4 wt.%, 54 g/L at 35 bar/77K

# 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

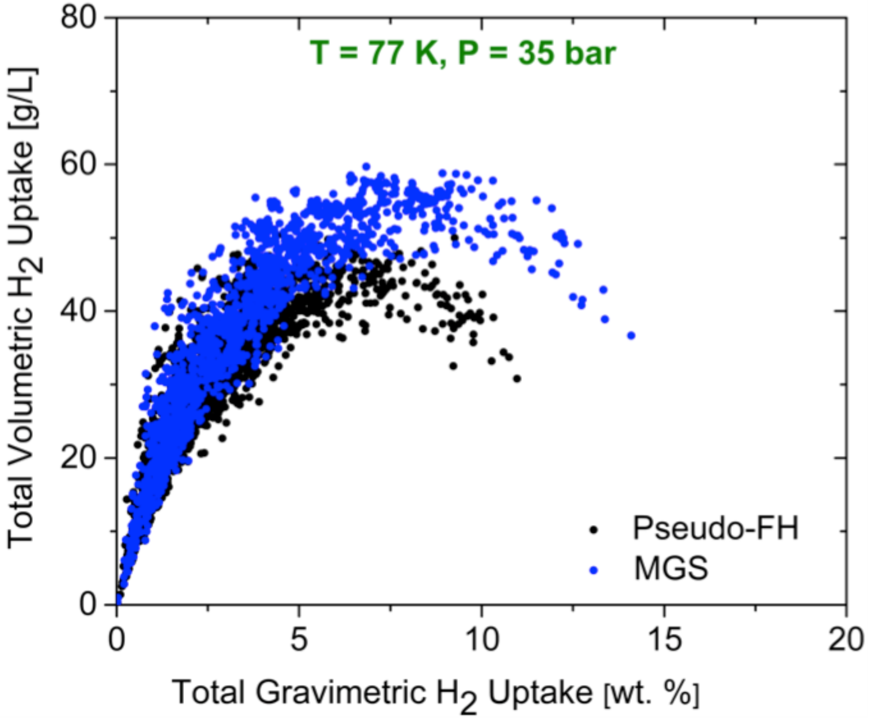


|  | **Total** |  | **Usable** (P-swing) |  |
|---|---|---|---|---|
| **p (bar)** | **Volumetric (g/L)** | **Gravimetric (wt.%)** | **Volumetric (g/L)** | **Gravimetric (wt.%)** |
| 5 | 22.2 | 3.5 |  |  |
| 35 | 44.4 | 6.8 | **22.2** | **3.3** |
| 50 | 47.8 | 7.3 | **25.6** | **3.8** |
| 100 | 53.3 |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

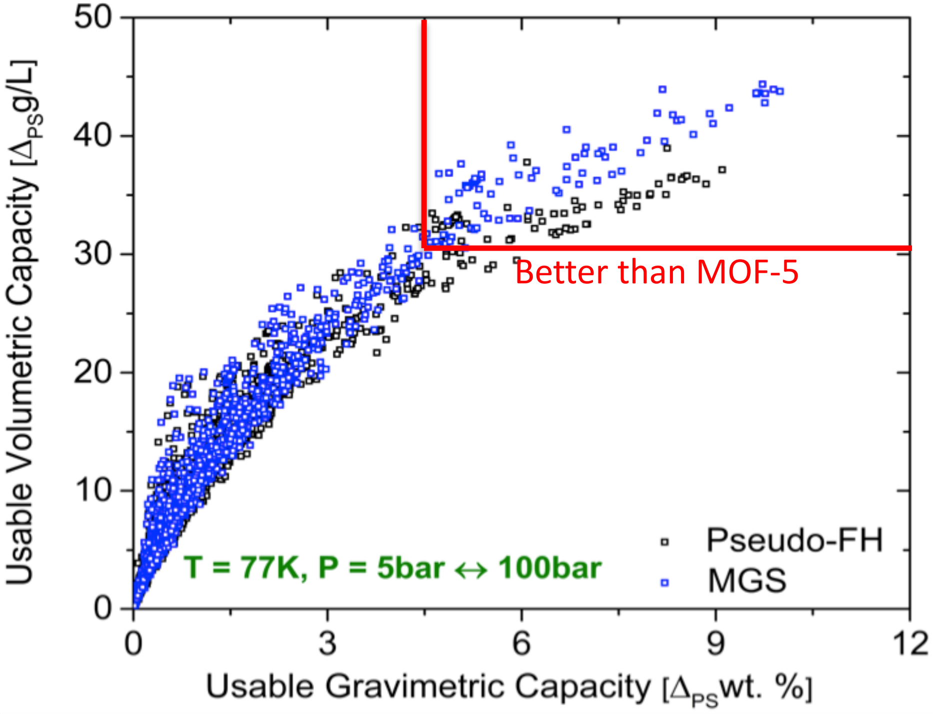
# Promising Compounds

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

**Total $H_2$**



**Usable $H_2$**



Better than MOF-5

- 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** |

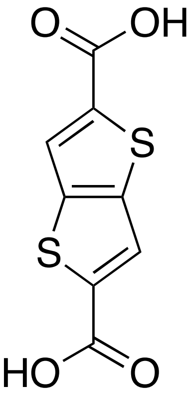
These compounds surpass MOF-5 in total, usable PS, and usable T+PS

# A Success Story: IRMOF-20

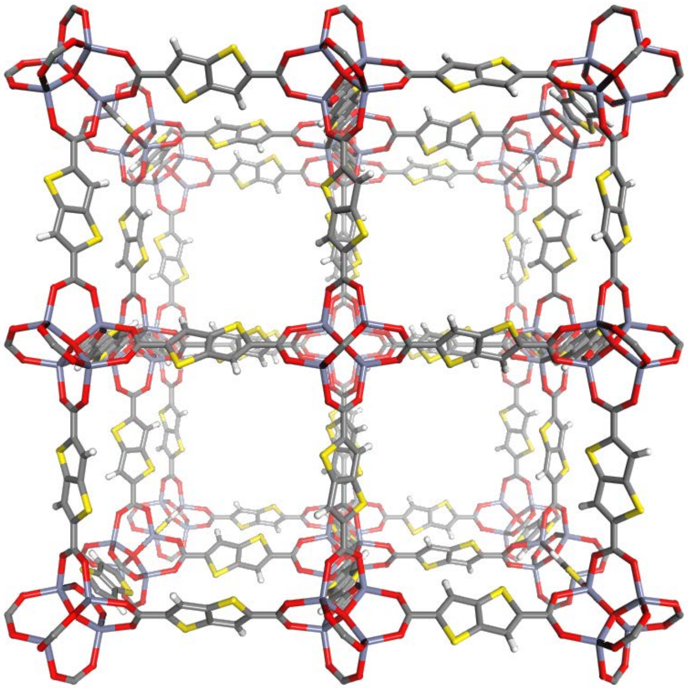
Synthesis of IRMOF-20 was attempted after computation identified it as a promising compound

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

$H_2TTDC$ =



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



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

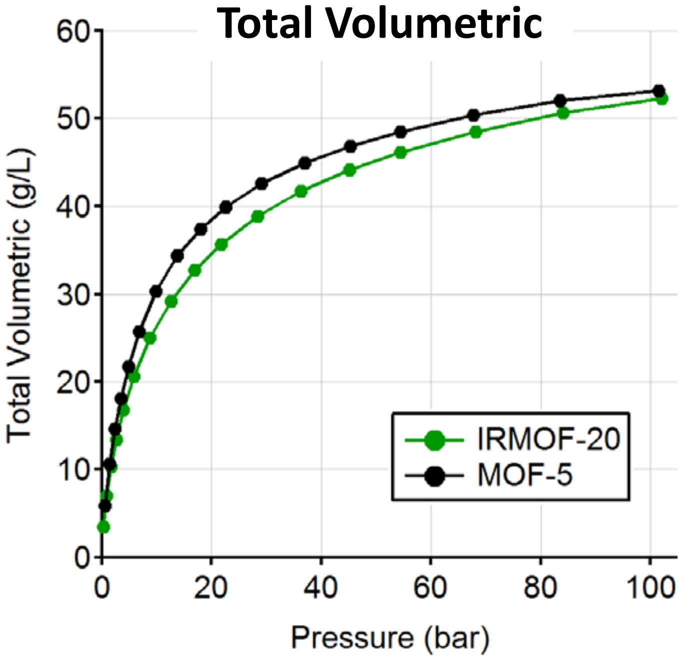
Activated by:

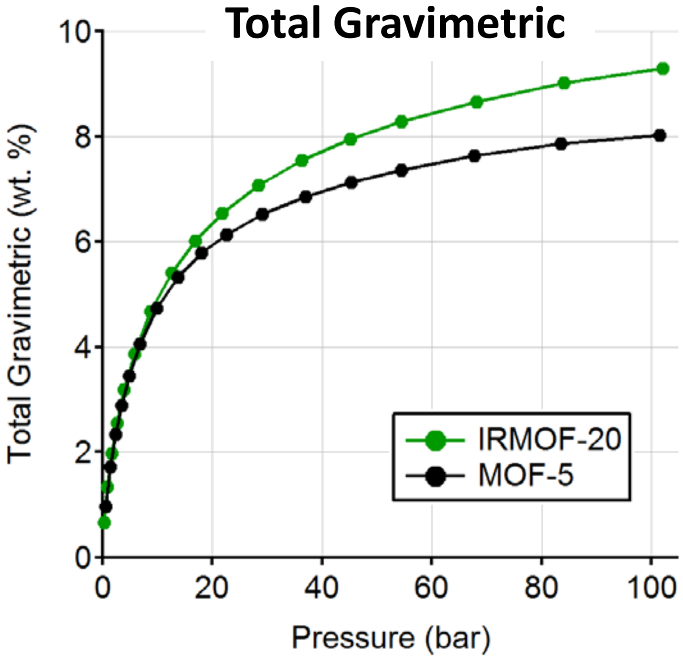
1) Multiple solvent exchanges
2) RT vacuum drying

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

# IRMOF-20 $H_2$ Capacity

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

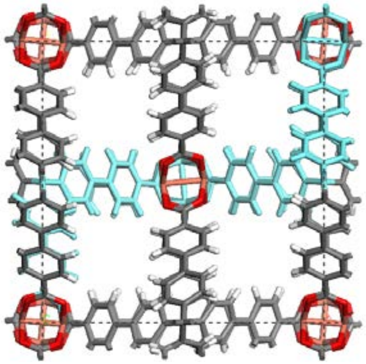




| | Usable Volumetric ($g\ H_2/L$) | | Usable Gravimetric (wt. %) | |
|---|---|---|---|---|
| **p (bar)** | **MOF-5** | **IRMOF-20** | **MOF-5** | **IRMOF-20** |
| 35 | 22.2 | 22.2 | 3.3 | 3.9 |
| 50 | 25.6 | 26.1 | 3.8 | 4.5 |
| 100 | 31.1 | 33.1 | 4.5 | 5.7 |

# A Few Failures

Several promising MOFs could not be synthesized with high surface area

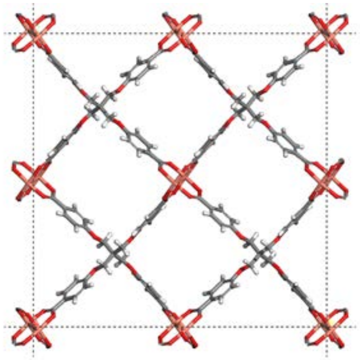


**SUKYON**

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

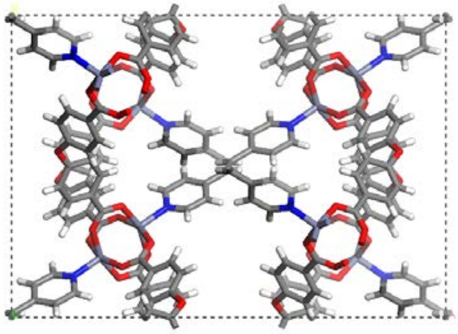


**EPOTAF (SNU-21)**

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



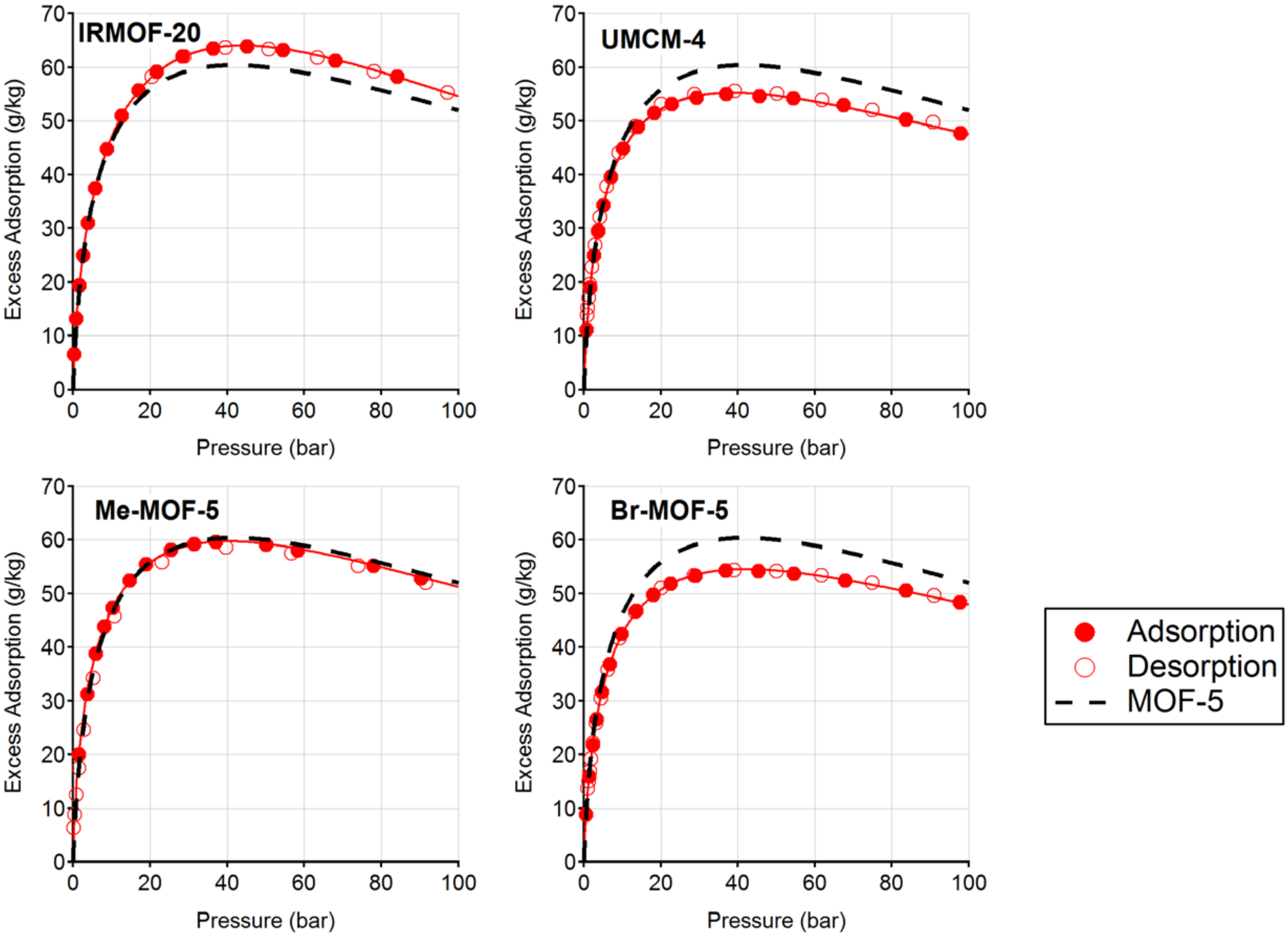
**DIDDOK**

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

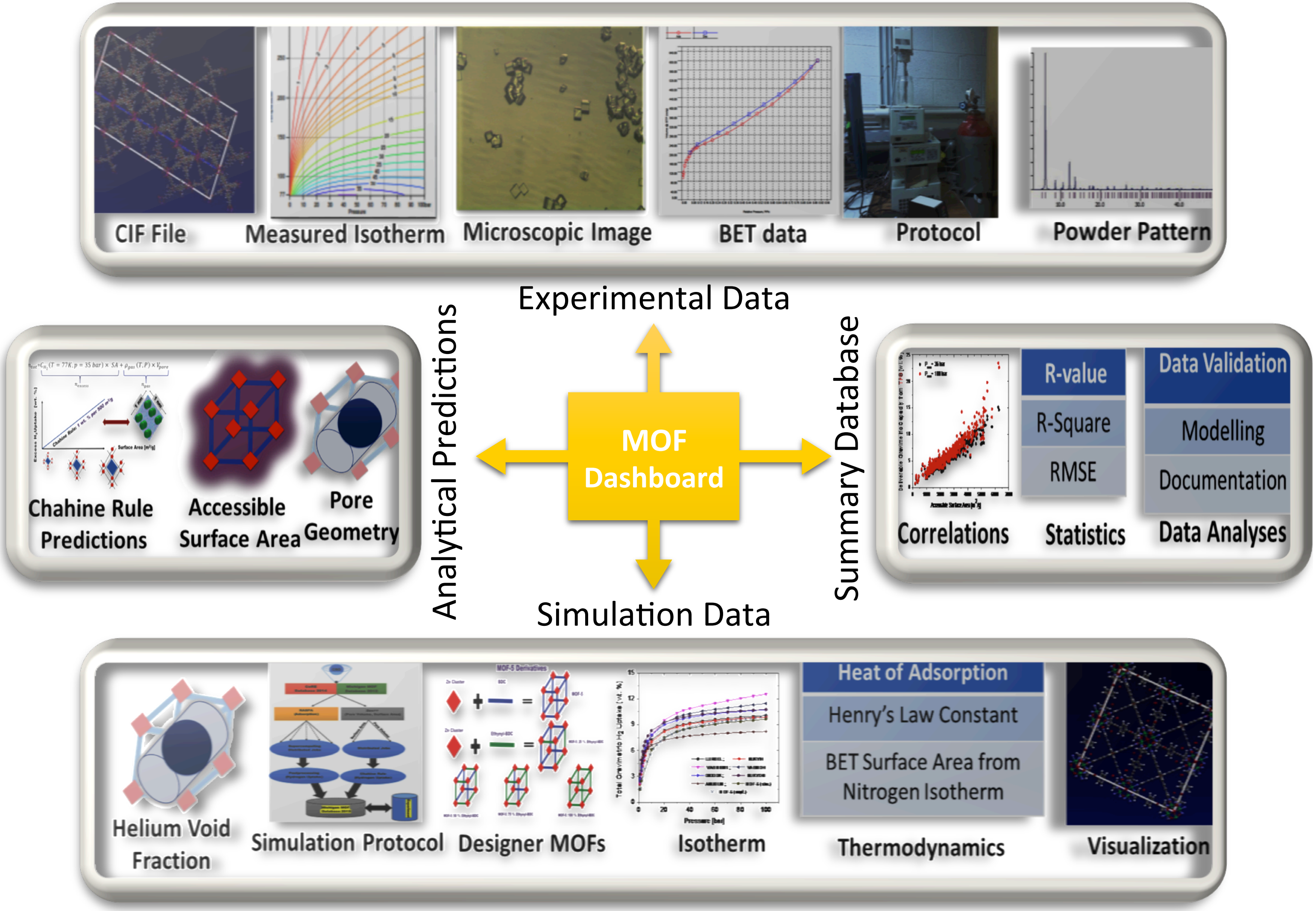
Chahine rule capacities:
Total grav. = 10.2 wt. %
Total vol. = 60 g/L

# Others MOFs in Pipeline



# MOF Dashboard

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



CIF File

Measured Isotherm

Microscopic Image

BET data

Protocol

Powder Pattern

Experimental Data

Analytical Predictions

MOF Dashboard

Summary Database

Chahine Rule Predictions

Accessible Surface Area

Pore Geometry

Correlations

R-value

R-Square

RMSE

Statistics

Data Validation

Modelling

Documentation

Data Analyses

Simulation Data

Helium Void Fraction

Simulation Protocol

Designer MOFs

Isotherm

Heat of Adsorption

Henry's Law Constant

BET Surface Area from Nitrogen Isotherm

Thermodynamics

Visualization

# 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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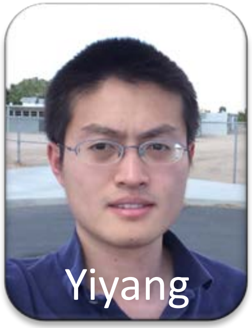
# The Team


Justin


Mike

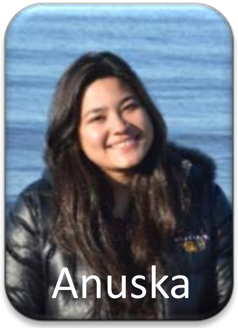

Antek

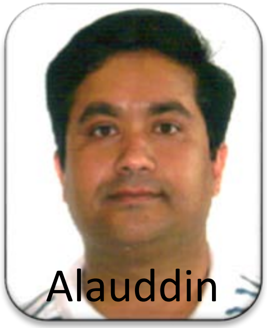

Yiyang

UNIVERSITY OF MICHIGAN

Ford


Adam


Anuska


Alauddin


Don

# Technical Backup Slides

# Capacity Definitions

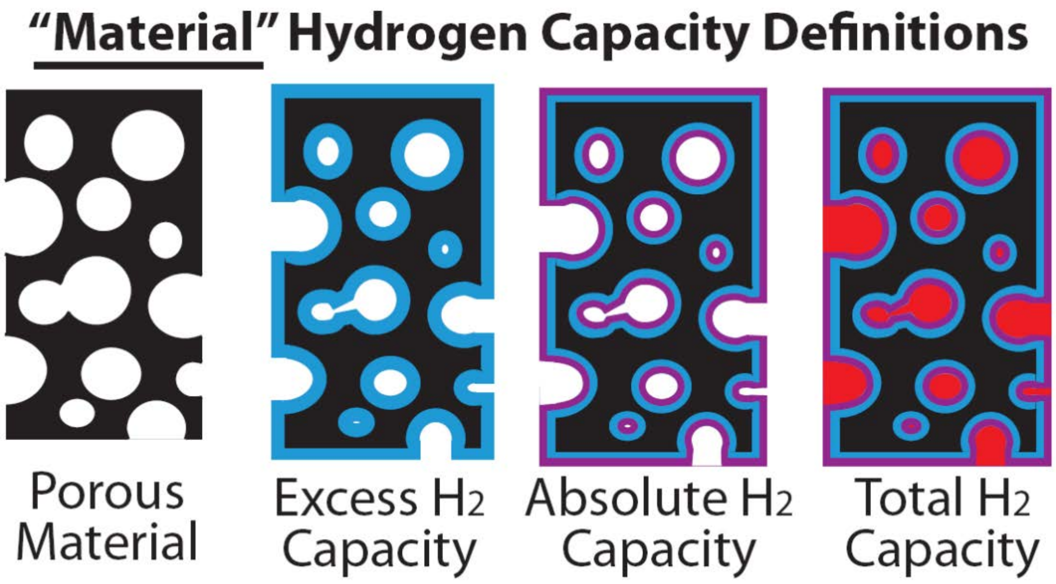
$$C_{tot} = C_{exc} + \frac{100 \times d_g V_{pore}}{1 + d_g V_{pore}}$$

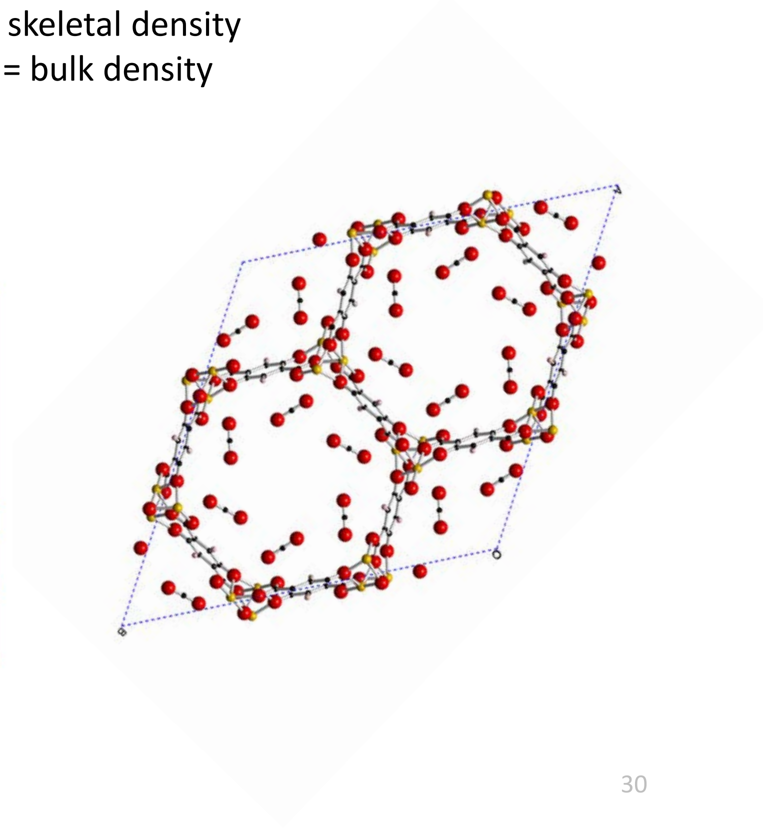
$$V_{pore} = \frac{d_{sk} - d_{bulk}}{d_{sk} d_{bulk}}$$

*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

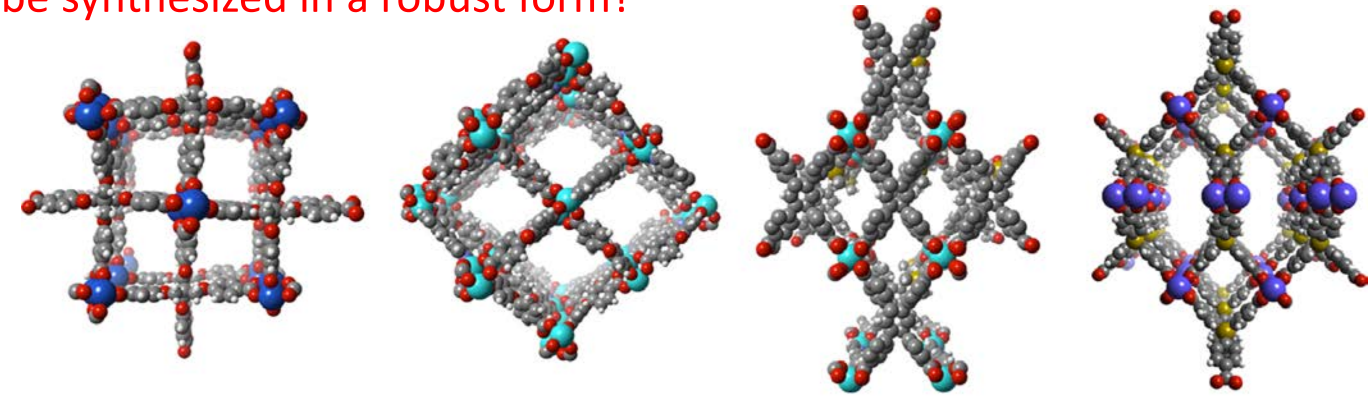




# MOFs Identified by Prior Screening

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?

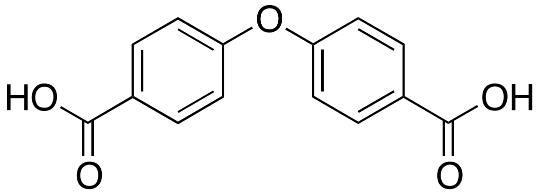


| | EPOTAF (SNU-21) | DIDDOK | LURGEL (TO-MOF) | ENITAX (IMP-9) |
|---|---|---|---|---|
| **Total Grav. (wt. %)** | 11 | 10.2 | 9.7 | 9.3 |
| **Total Volumetric (g/L)** | 71 | 60 | 57 | 59 |
| **Crystal Density (g/cm$^3$)** | 0.58 | 0.53 | 0.53 | 0.57 |
| **Calc’d/Meas. SA (m$^2$/g)** | 5208/700-900 | 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

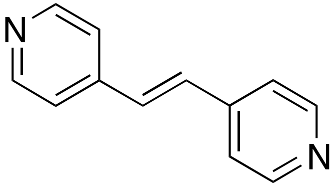
$$H_2oba + bpe + Zn(NO_3)_2\bullet 6H_2O \xrightarrow[23\ ^\circ C]{DMF} Zn_2\,(oba)_2(bpe)$$

$H_2oba$ =



4,4'-Oxybis(benzoic) acid

bpe =

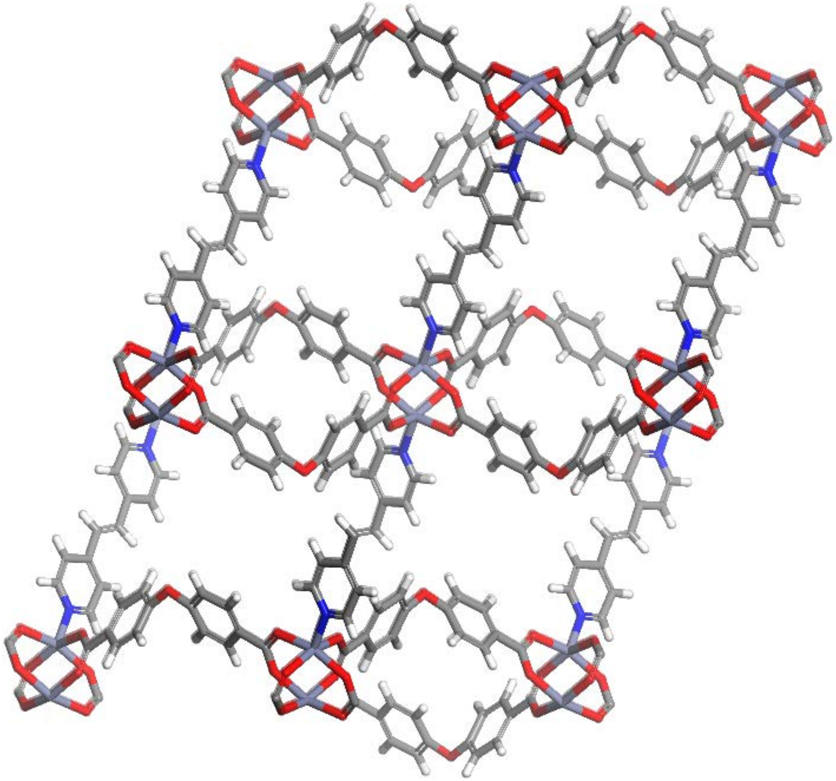


*trans*-1,2-Bis(4-pyridyl)ethylene

Activated by:

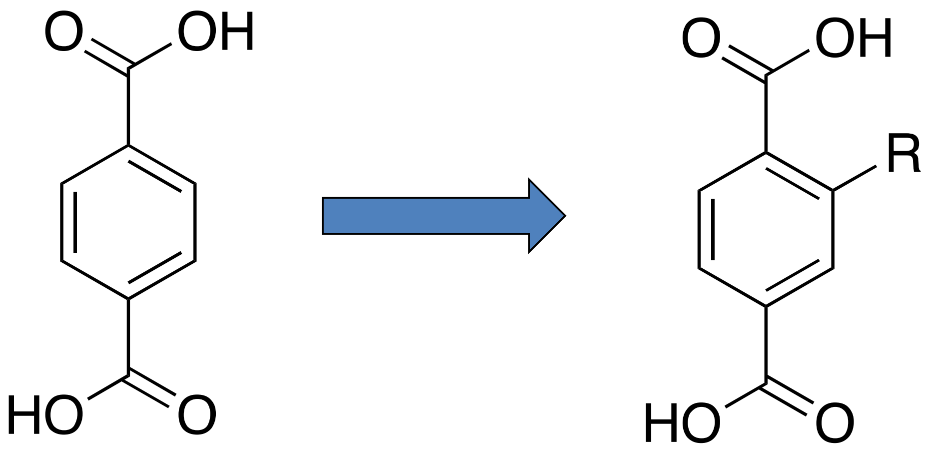
1) Multiple solvent exchanges
2) Flowing $scCO_2$

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



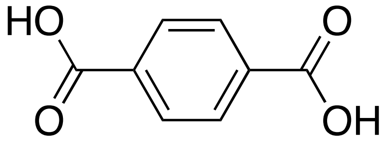
Idea:

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

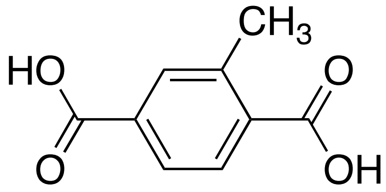
$$H_2BDC + H_2MeBDC + Zn(NO_3)_2\bullet 6H_2O \xrightarrow[100\ ^{o}C]{\text{N,N-diethylformamide}} Zn_4O(BDC)_{2.19}(MeBDC)_{0.81}$$

$H_2BDC$ =

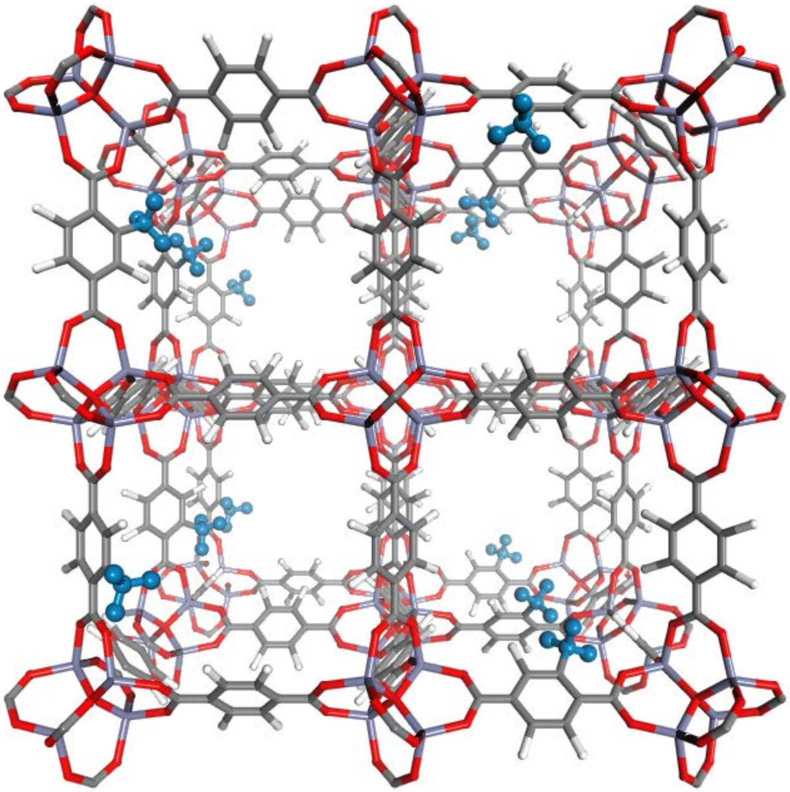


Benzenedicarboxylic acid

$H_2MeBDC$ =



Methylbenzenedicarboxylic acid



Activated by:

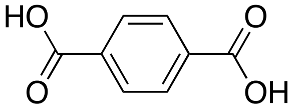
1) Multiple solvent exchanges
2) RT vacuum drying

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

# Synthesis of UMCM-4

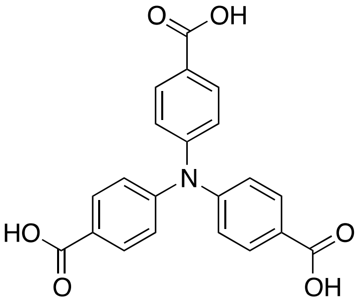
$$H_2BDC + H_3TPA + Zn(NO_3)_2{\bullet}6H_2O \xrightarrow[85\ ^{o}C]{\text{N,N-diethylformamide}} Zn_4O(BDC)_{1.5}(TPA)$$

$H_2BDC$ =



Benzenedicarboxylic acid

$H_3TPA$ =

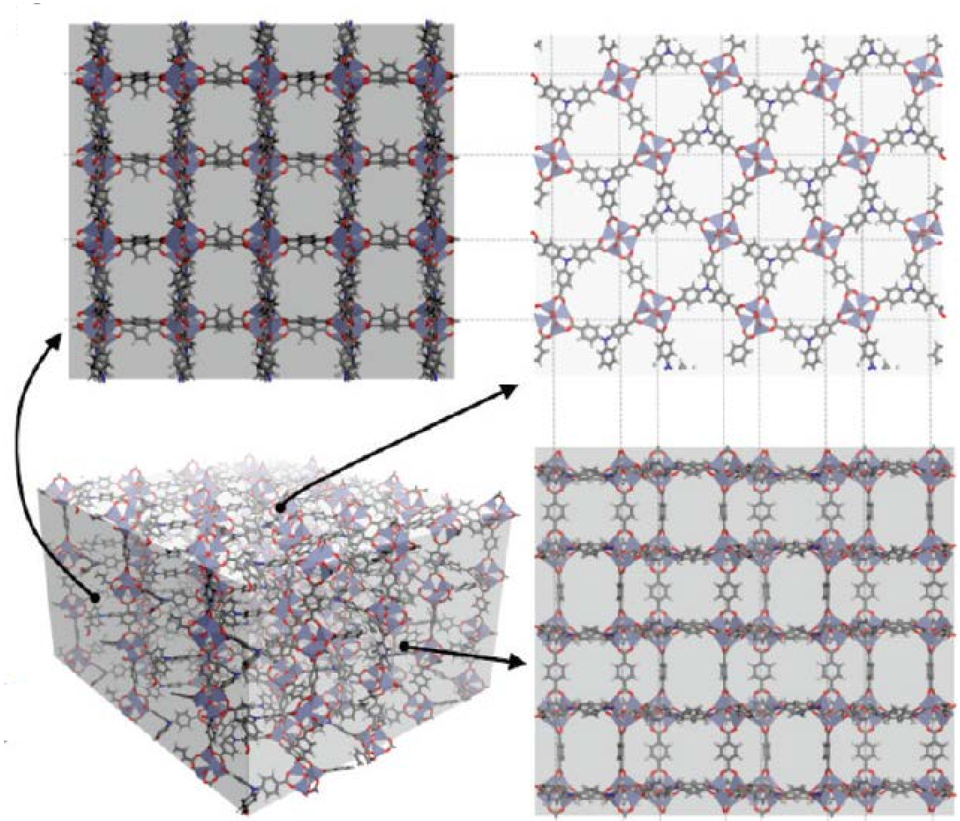


Triphenylaminetricarboxylic acid

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.