Hydrogen Trapping through Designer Hydrogen Spillover Molecules with Reversible Temperature and Pressure-Induced Switching

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stp_34_lueking

Overview

Timeline

- Start - Jan 2009
- End - Dec 2013
- ~7% Complete

Barriers

- Barriers addressed
  - Gravimetric Capacity
  - Min/max delivery temperature
  - Max delivery pressure from tank

Budget

- Total project funding
  - DOE - $1,512,922
  - PSU – $262,151
  - RU - $229,028
- $75K in FY08
- $275K FY09

Partners

- Prof. Angela D. Lueking (Penn State)
- Prof. Jing Li (Rutgers) Co-PI
- Prof. Milton W. Cole (Penn State), Co-PI

Objectives - Relevance

The **overarching objective** is to synthesize designer microporous metal-organic frameworks (MMOFs) mixed with catalysts to enable H-spillover for H_2 storage at 300K-400K and moderate *P*s.

In 2009 (Jan.-Dec.), we will:

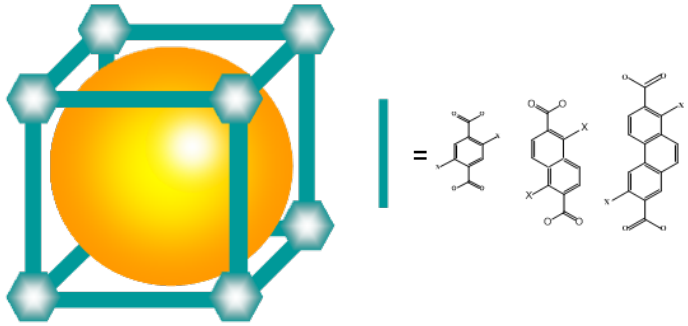
A. Train new users, upgrade and validate H_2 storage measurements -- (PSU) *50% complete*
B. Synthesize new MMOF structures to explore the effect of surface chemistry, porosity, and structure on hydrogen spillover (RU) -- *30% complete*
C. Method Development for Catalyst Studies and MMOF compatibility with catalysts (PSU) – *5% complete*
D. Explore the incorporation of active hydrogen dissociation centers directly into the MMOF framework (PSU & RU) –*5% complete*

The impact your project has on addressing the barriers identified in the Overview slide and other specific targets and milestones.

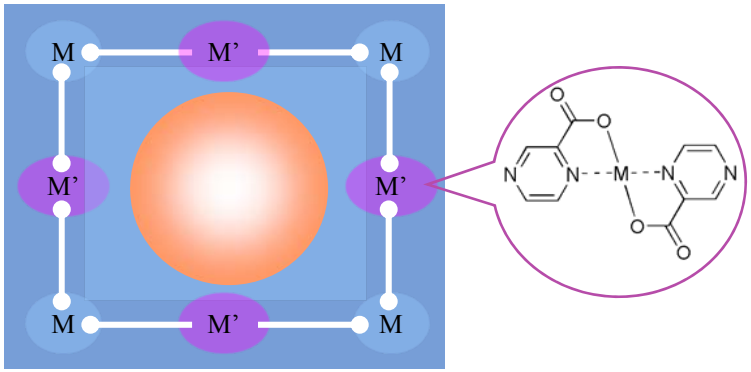
Strategies / Approach

to Maximize H_2 Storage at Moderate T and P

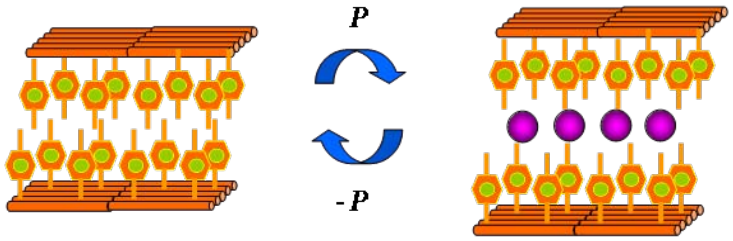
- Optimize Hydrogen Spillover Mechanism utilizing MOF design to maximize receptors of spilled-over H:
  - Surface Chemistry
  - Porosity



- Direct incorporation of catalytic sites



- Explore P-induced and H-induced structural changes for H_2 trapping



Approach

Upcoming Milestones:

- Correlation between spillover and MMOF functional groups, (Yr. 2-- FY10) leading to:
  - H2 uptake > 1 wt% at 20 bar and 300K;
  - Extrapolation suggests > 4 wt% at 100 bar, or
  - Pressure savings of >90% relative to the empty tank
- Incorporation of catalytic entities into MMOF framework (Yr. 2-- FY10) leading to:
  - MMOF catalytic activity H-spillover
  - Improved performance relative to Pt-C catalysts

Go/No-Go Decision Point.

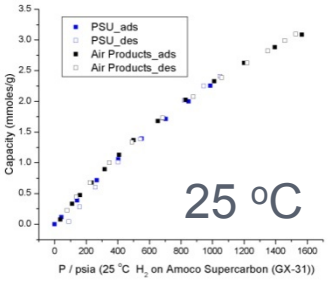
Exceed 5.5 wt% hydrogen storage through the use of the “hydrogen spillover” mechanism, MOF material, or a combination of the two as proposed at moderate temperatures (i.e. 300-400 K) and 100 bar with anticipated system penalties (Go/No Go: 3Q Year 2).

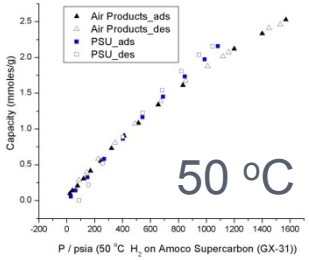
TECHNICAL ACCOMPLISHMENTS

A. TRAIN NEW USERS, UPGRADE AND VALIDATE H_2 STORAGE MEASUREMENTS

High-Pressure Differential Volumetric System (custom-built)

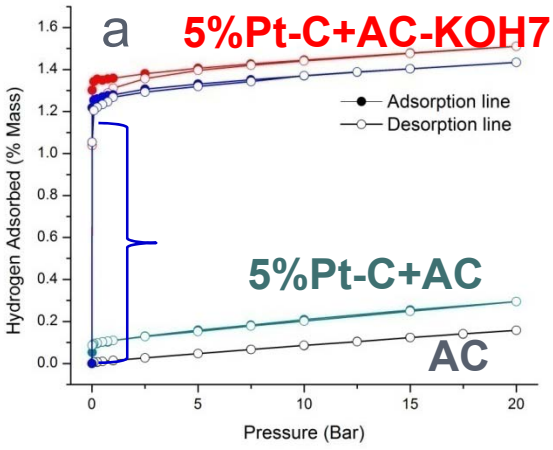
- New students at PSU are trained on custom-built differential Sieverts and required to validate published data for AX-21 activated carbon against published results.
- Multiple *T*s are used in preparation for future catalyst studies

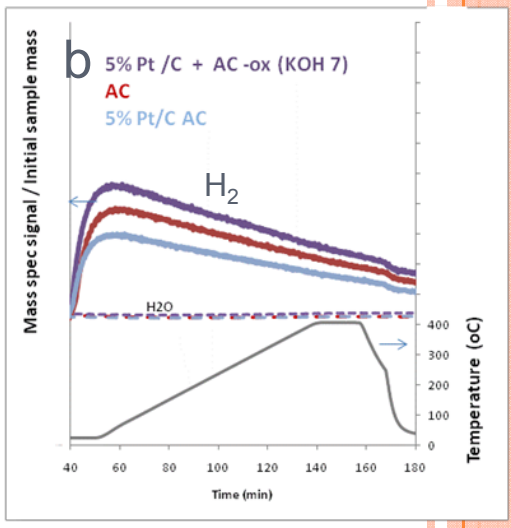




High-Pressure TG-MS (Mass spec upgrade)

- A mass spectrometer was incorporated into an existing high P TGA in Mar 09
- MS validation shown below:



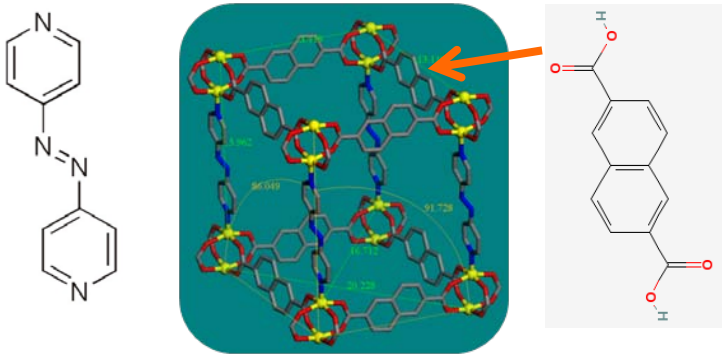


(a) Adsorption-Desorption Isotherm showed 1.0 wt% chemisorbed H_2, which (b) desorbed with subsequent heating.

TECHNICAL ACCOMPLISHMENTS

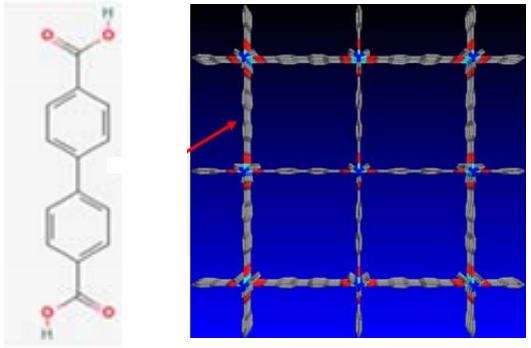
B. SYNTHESIZE NEW MMOF STRUCTURES TO EXPLORE THE EFFECT OF SURFACE CHEMISTRY, POROSITY, AND STRUCTURE ON HYDROGEN SPILLOVER

MMOF-1-Zn

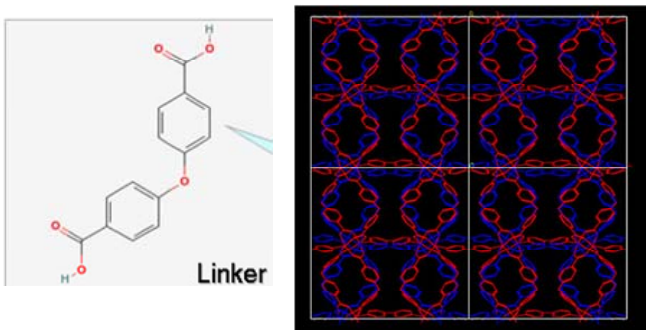


MMOF-2-M

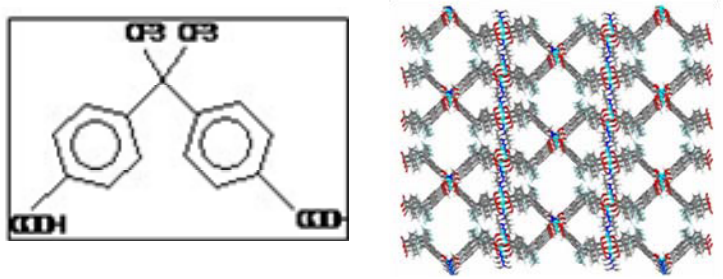
(M = Ni, Cu, Zn)



MMOF-3-Zn



MMOF-4-Zn



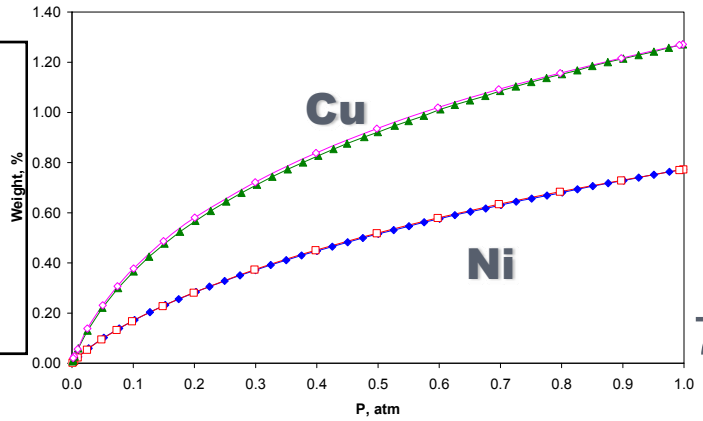
Technical Accomplishments

Baseline Physisorption Data for As-Synthesized MMOFs

MMOF-2-M

(M = Ni, Cu, Zn)

Properties	Ni	Cu
Pore Volume (Total)	0.64	0.80
Surface Area (BET)	1661	1332
Surface Area (Lang)	1801	1790
Hydrogen wt%	1.16	1.27
Isosteric Heats	4.4-5.4	4.5-5.5



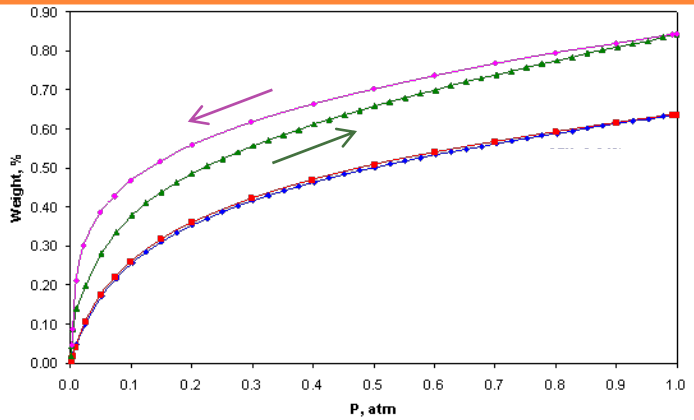
1.3% (1 atm)

0.77% (1 atm)

q_{st} ~5 kJ/mol

77K

MMOF-3-Zn



0.84% (1 atm, 77K)

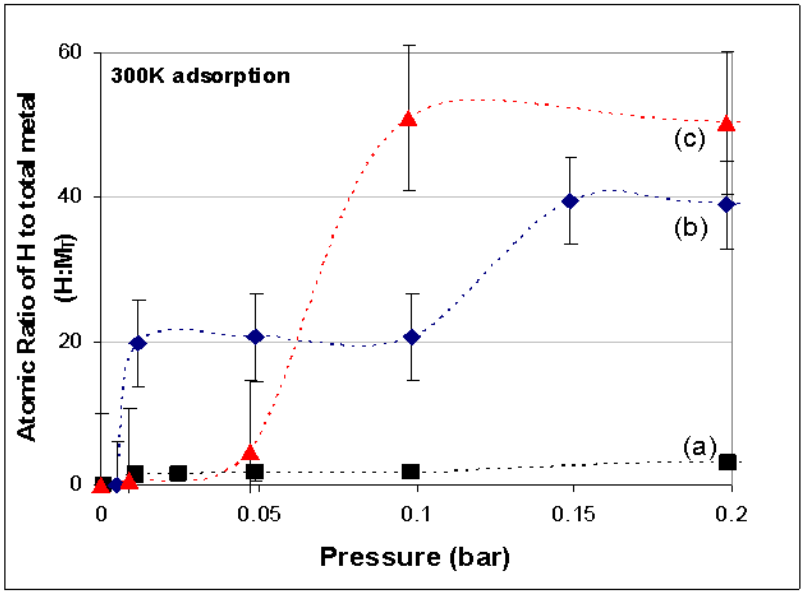
0.64% (1 atm, 87K)

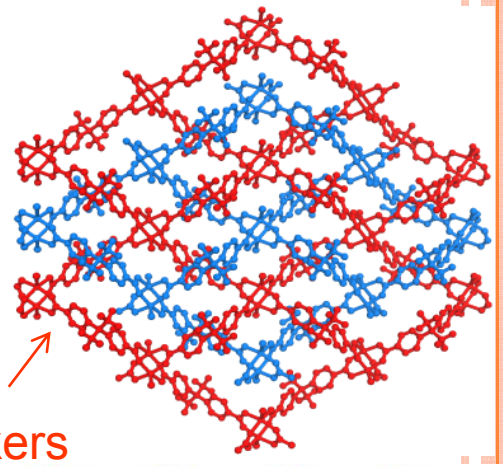
q_{st} ~6.5 kJ/mol

TECHNICAL ACCOMPLISHMENTS

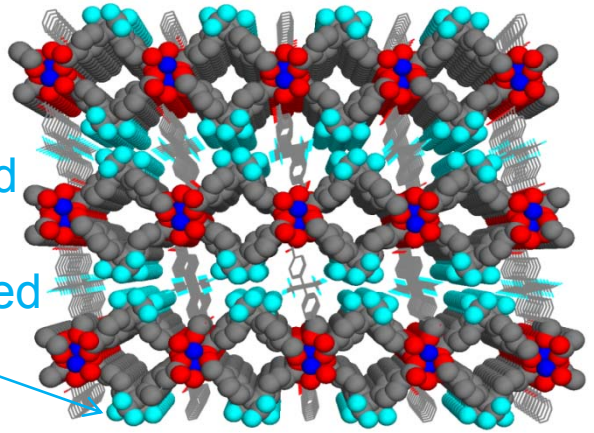
B. EXPLORE THE EFFECT OF SURFACE CHEMISTRY, POROSITY, AND STRUCTURE ON HYDROGEN SPILLOVER

Mixing MMOFs with 5% Pt/C for 300K adsorption





(c) Carbon-based linkers



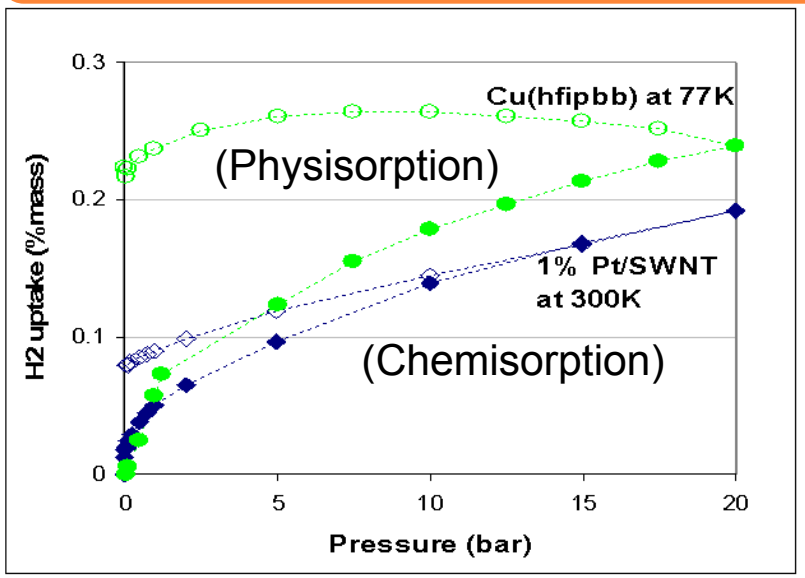
(b) Incorporated surface sites for increased H-bonding

(a) 5% Pt/C catalyst

Use of a spillover catalyst increases T_{ads} to 300K. MMOFs can increase the uptake by providing specific H-binding sites. Above, (b) surface chemistry may play a role at very low pressure, then (c) enhanced porosity may dominate.

Future Work

Explore P- , T-, and H- induced structural changes for H_2 trapping



KEY HURDLE:
Understanding effects of structure, window size, surface chemistry, gas-surface potential, temperature, and pressure on P-induced hysteresis.

Cole will explore the theory of P-induced hysteresis.

The proposal will explore 'switches' that have the ability to turn on/off hydrogen adsorption/desorption with *T* and *P*.

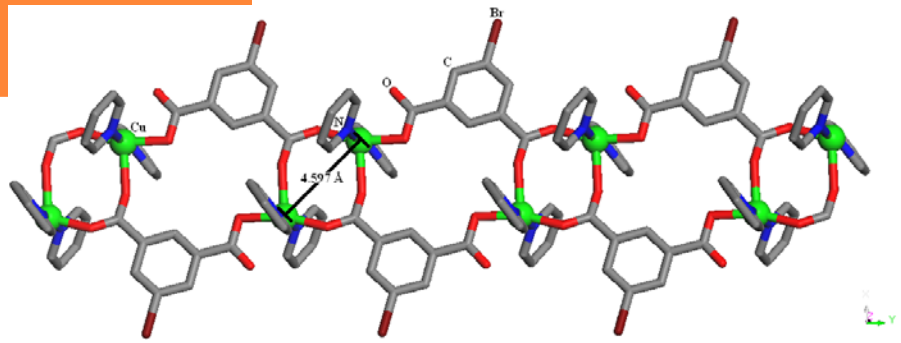
•*For T-switching*: the milestone will be to identify surface functionalities that may strongly bind hydrogen species at T_A, but desorb at T_D <80 °C. The path-dependence of these 'temperature-switch' experiments will be evaluated. (Yr. 2 – FY10)

•*For P-switching*: MMOFs have demonstrated transformations induced by *P* and H-bonding. A milestone will be to observe at least 37.5% trapping due to hysteretic adsorption at moderate temperatures. The milestone will be model validation, and observation of H_2 and H gate-opening pressures in order to serve as a chemical switch for the dilation phenomenon. (Yr. 3 – FY 11)

Future Work

Incorporation of catalyst directly into MMOF Structure

Testing Catalytic Activity of M^{2+} in the MMOF framework.



Heterometallic MMOFs having catalytic metal ions imbedded in the internal wall of the channels/voids may act as the hydrogen spillover source. The unsaturated metals will be cross-referenced with catalysis data to determine expected active catalytic temperature for hydrogen dissociation. Milestones (FY10) include (a) evidence for catalytic activity of incorporated catalysts, based on either H_2-D_2 exchange studies and/or the WO_3 color change test (at left); and (b) superior performance (increased H:M, active T<80 °C) relative to the Pt/C catalysts.

Collaborations

University:

- Prof. Angela D. Lueking (Penn State) PI
- Prof. Jing Li (Rutgers) Co-PI
- Prof. Milton W. Cole (Penn State), Co-PI

Pending Collaborations / On-going discussions

- Prof. Silvina Gatica, Howard University
- Brookhaven National Laboratory

Project Schedule - Future Work

Legend

- i. Synthesis
- ii. Characterization 1
- iii. Characterization 2 (porosity, surface area)
- iv. Characterization 3 (catalysis)
- v. Hydrogen Storage
- vi. Model Development/Refinement (Cole)
- vii. Model Experimental Validation(Lueking)
- viii. Analysis, Writing, Leading to Synthesis Feedback & Refinement
- ix. Overall Optimization; Final Material Design

Goal	Class of Materials	Project Milestone Description	Year 1				Year 2				Year 3				Year 4				Year 5			
			Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Train Users	Rutgers																					
	Penn state																					
1A	i																					
	ii																					
	iii.																					
	iv.																					
1B	i																					
	ii																					
	iii.																					
	iv.																					
1C	i																					
	ii																					
	iii.																					
	iv.																					
2A	TBD (based on 1A, 1B)																					
2B	TBD (based on 1A, 1B)																					
2C	i																					
	ii																					
	iii.																					

Summary

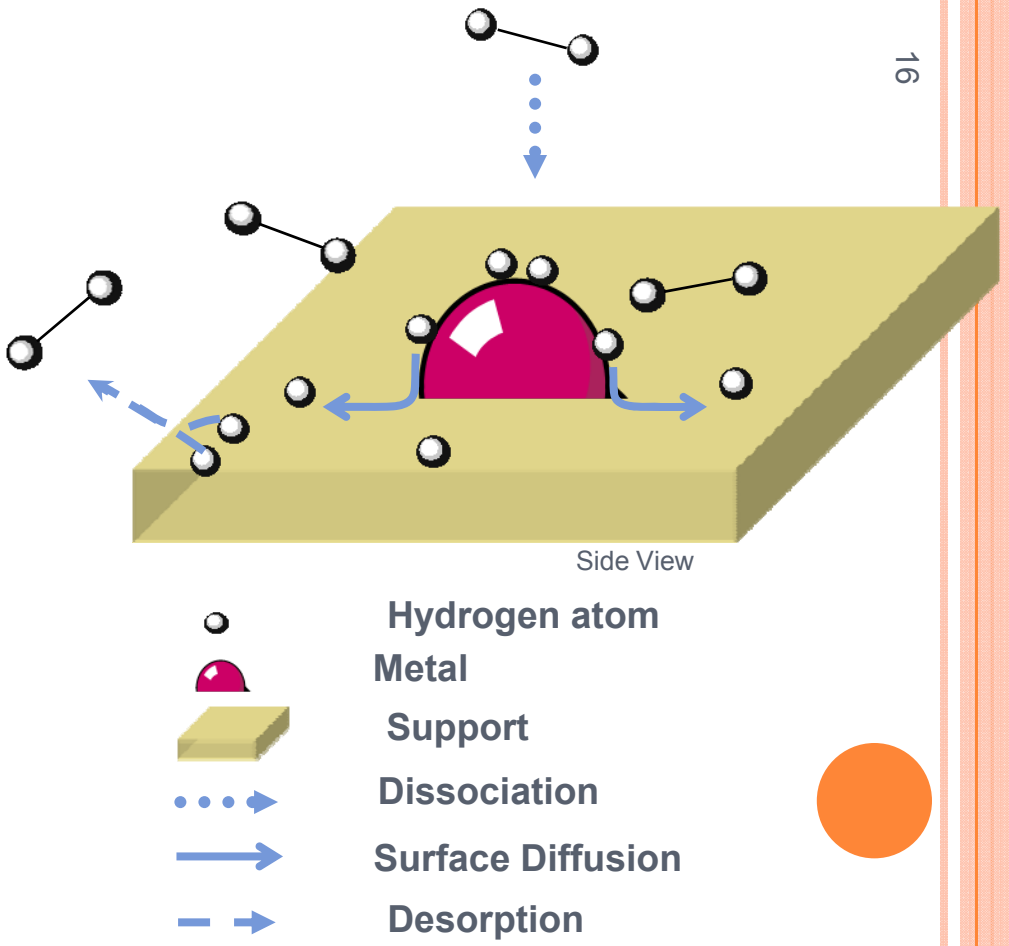
- Incorporation of catalysts to MMOFs increases operative adsorption temperature by activating hydrogen spillover process
- MMOF synthesis allows for tight control over porosity and surface chemistry, factors which are expected to increase hydrogen spillover and corresponding uptake.
- To date, surface chemistry appears to play a role at very low pressure while porosity plays a role at increased pressure.
- In first 3 months of project, focus has been on student training, synthesis, and equipment upgrades and validation.

Supplemental Slides

Background: What is Hydrogen Spillover?

$H_2\,(g) + 2M \rightarrow 2HM$	(i)
$HM + M' \rightarrow M + HM'$	(ii)
$2HM' \rightarrow H_2\,(g) + 2M'$	(iii)
$HM' + S \rightarrow H_{sp}S + M$	(iv)
$H_{sp}S + S' \rightarrow S + H_{sp}S'$	(v)
$2H_{sp}S' \rightarrow H_2\,(g) + 2\,S'$	(vi)
$H_2 + S'' \rightarrow H_2\text{-}S''$	(vii)

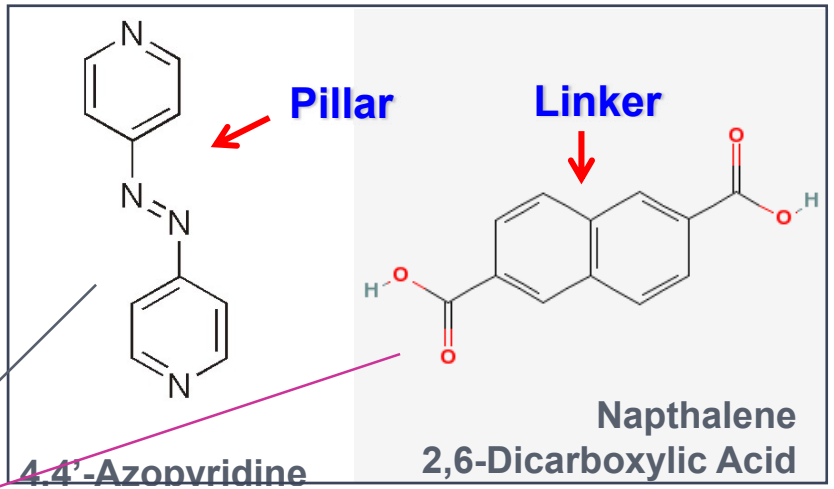
Box 1: Reaction sequence for hydrogen spillover.

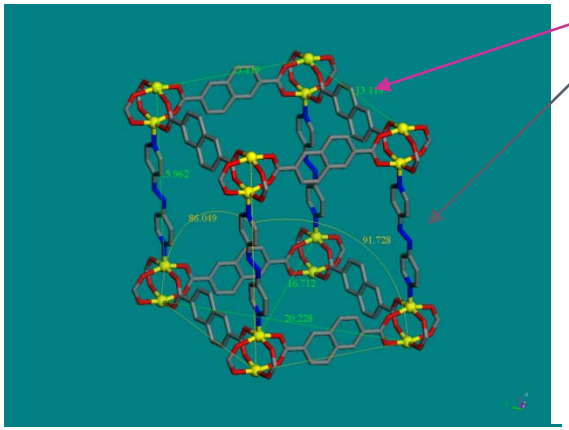


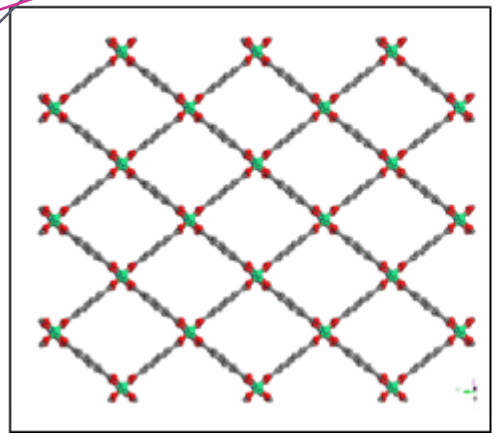
MMOF-1-Zn

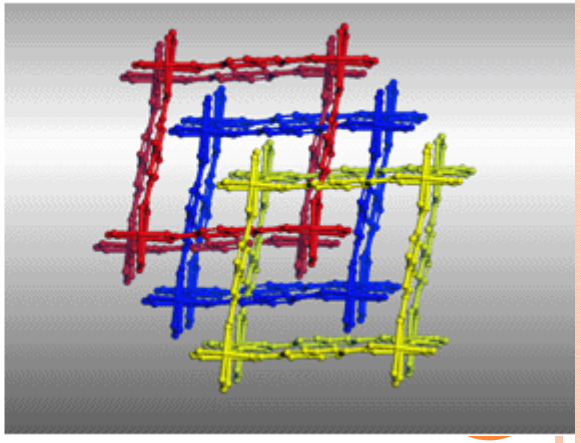
Formula Weight: 816.38 g/mol
Crystal System: Monoclinic
Space Group: *C2/c*
Data Collection Temperature: 100K
Unit Cell Dimensions:
a= 16.7116(14) Å
b = 20.2283(17)Å
c = 11.9471(10) Å
β = 117.367(2)°
V = 3586.7(5) Å^3
Z = 8
Density (Calculated): 1.512 g/cm^3
Solvent Accessible Volume: **23.6 %**

Ligands





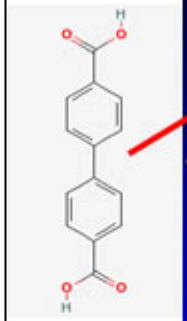


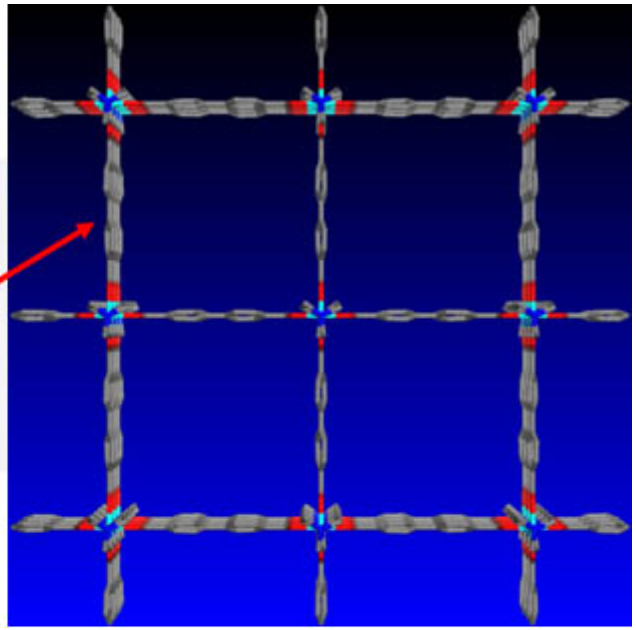


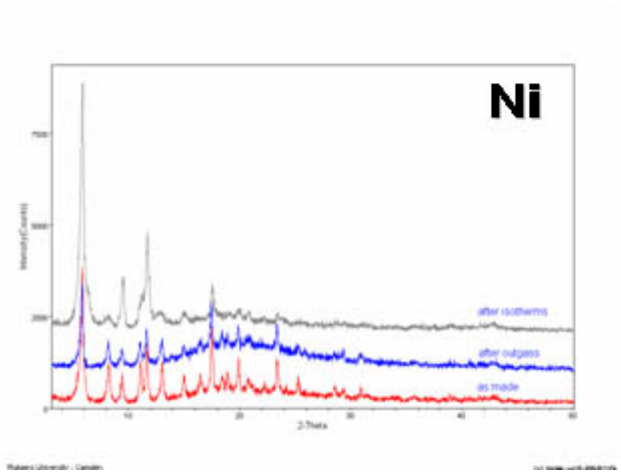
MMOF-2-M (M = Ni, Cu, Zn)

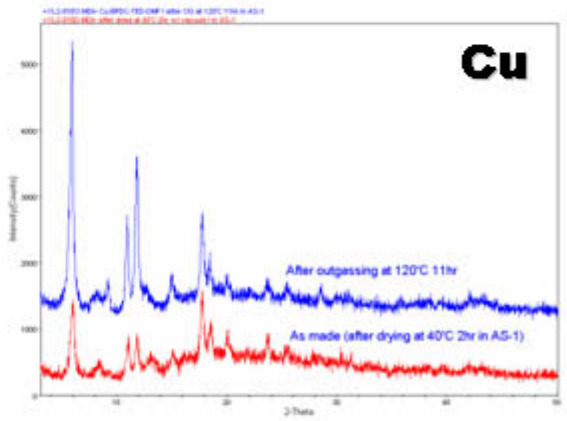
Crystal Data

Evacuated Formula Weight: 355.63 g/mol
Crystal System: Tetragonal
Space Group: *P422*
Unit Cell Parameters:
***a*=15.2312Å**
***b* = 15.2312Å**
***c* = 9.6630 Å**
V = 2241.7 Å^3, Z = 2
Framework Density: 0.5269 g/cm^3
Solvent Accessible Volume: 73.3%

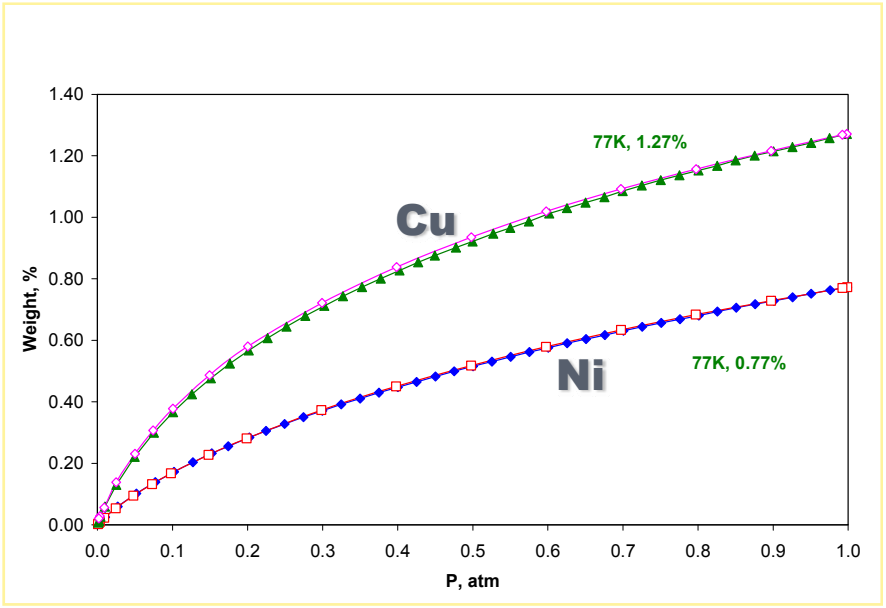


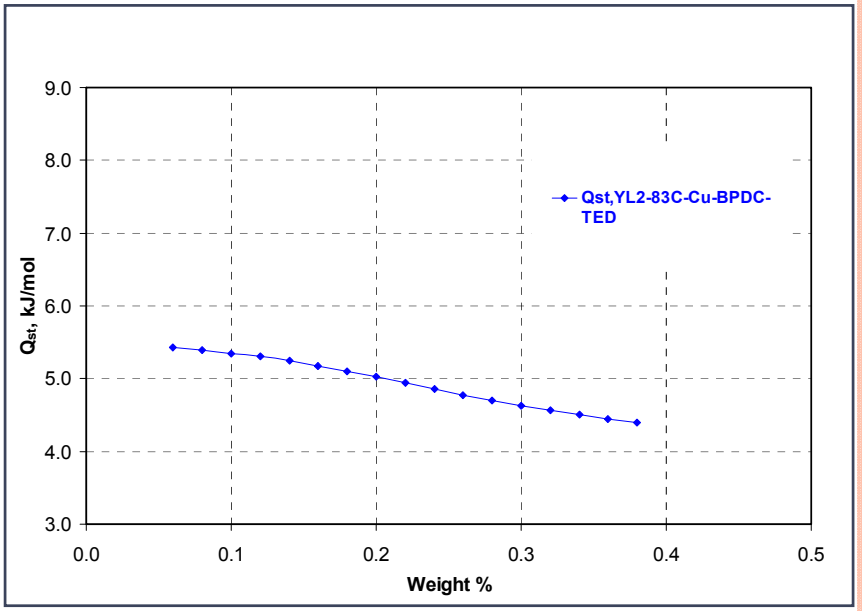




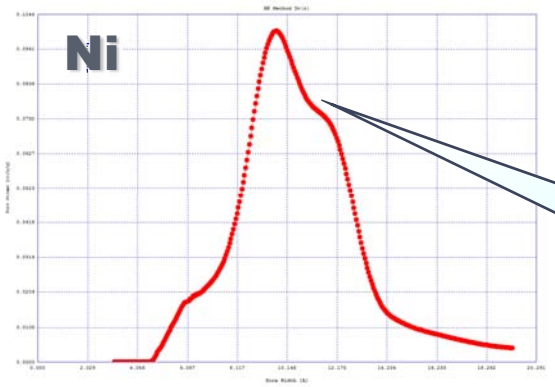


MMOF-2-M (M = Ni, Cu, Zn)





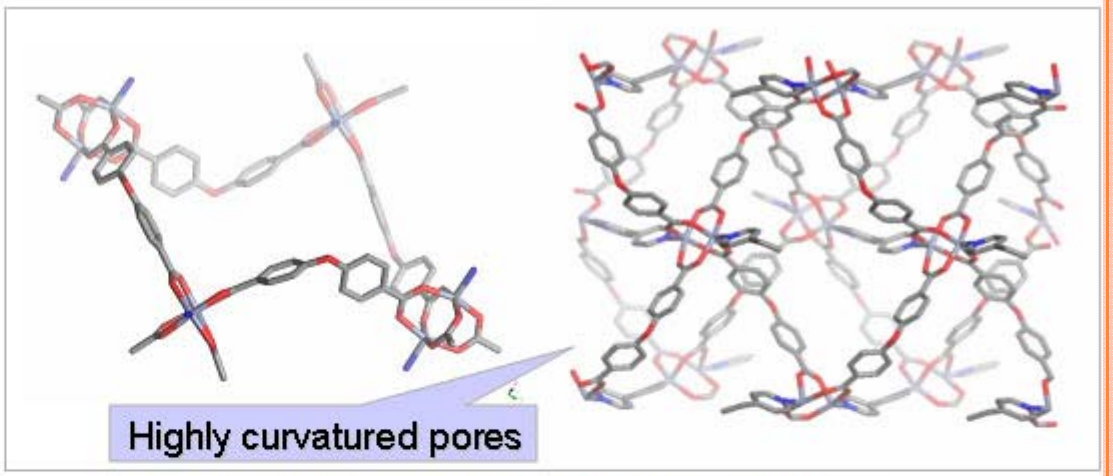
Properties	Ni	Cu
Pore Volume (Total)	0.64	0.80
Surface Area (BET)	1661	1332
Surface Area (Lang)	1801	1790
Hydrogen wt%	1.16	1.27
Isosteric Heats	4.4-5.4	4.5-5.5



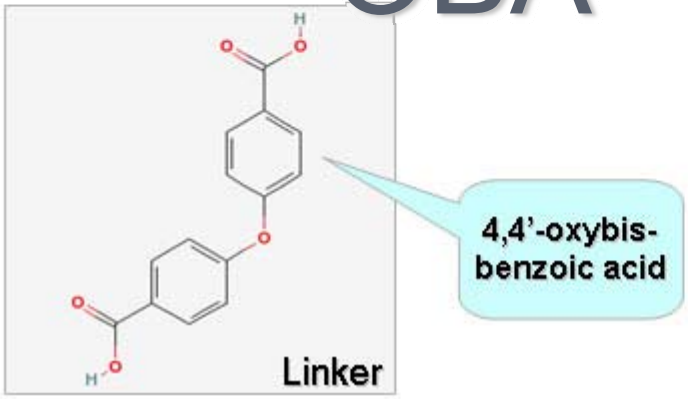
Pore Size Distribution (~8-12Å)

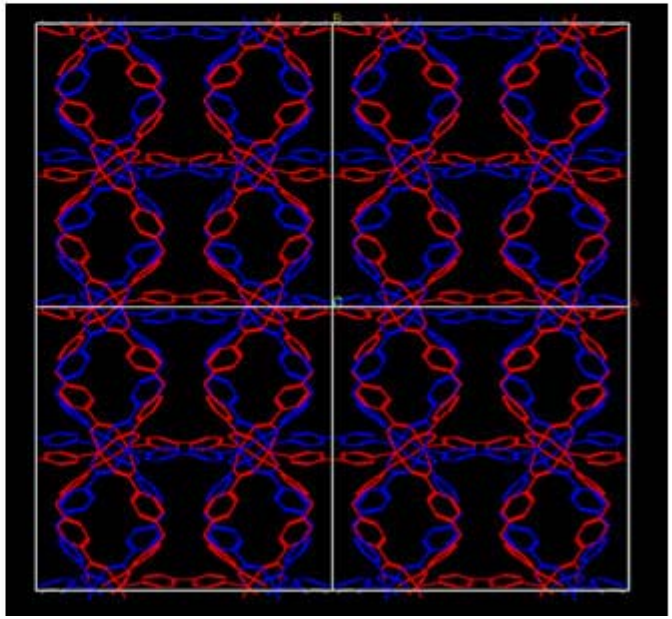
MMOF-3-Zn

Formula Weight: 872.43 g/mol
Crystal System: Orthorhombic
Space Group: *Pbcn*
Unit Cell Dimensions:
a= 22.028(3) Å
b = 22.390(2) Å
c = 16.573(5) Å
V = 8223.1(14) Å^3
Z = 8
Density (Calculated): 1.409 g/cm^3
Solvent Accessible Volume: 24.2 %

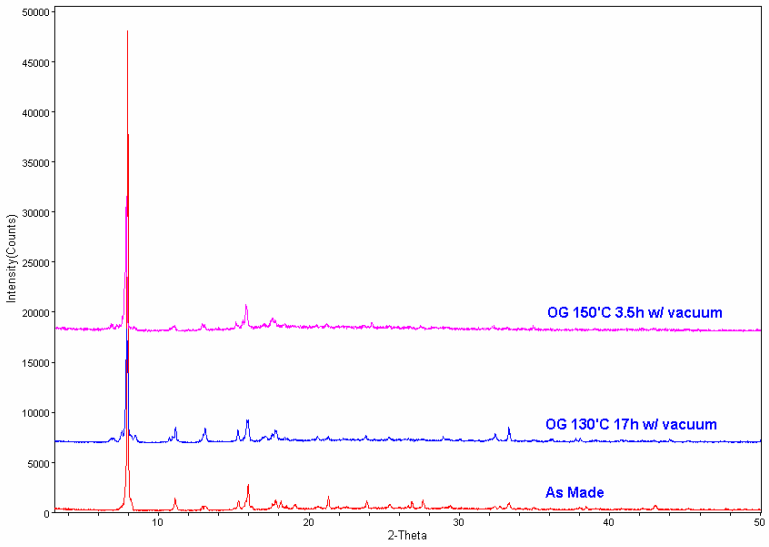


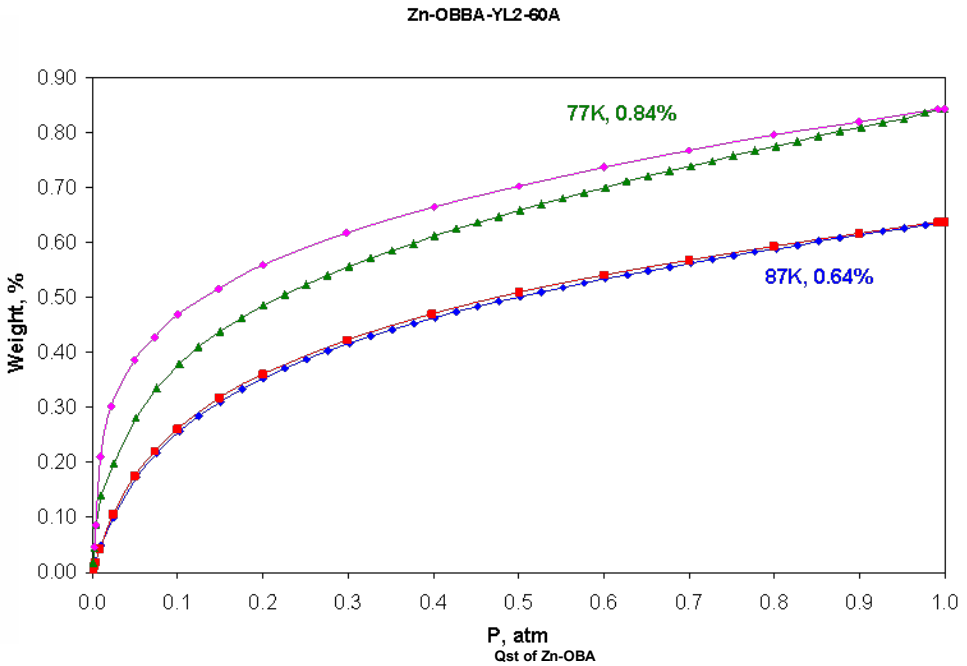
OBA

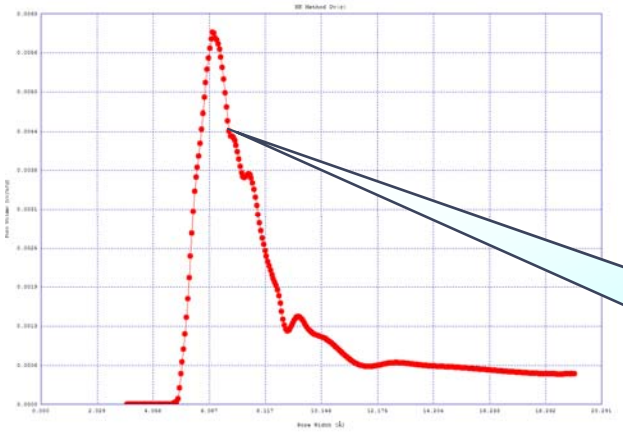




MMOF-3-Zn

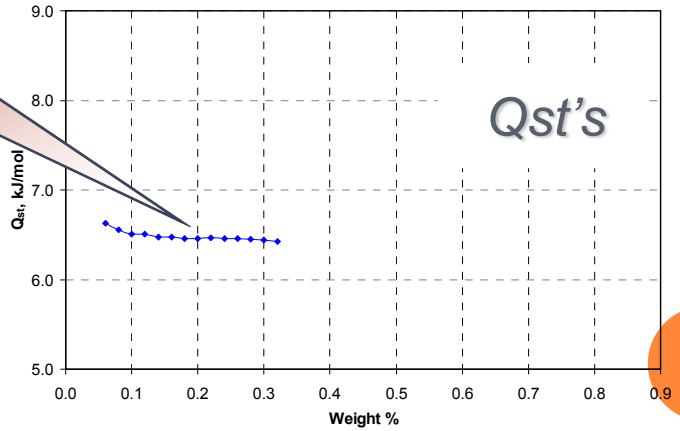






Isosteric Heats (6.5-6.7Å)

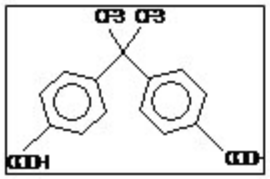
Pore Size Distribution (6-7Å)



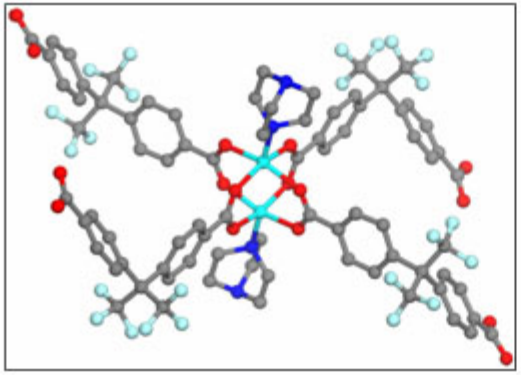
MMOF-4-Zn

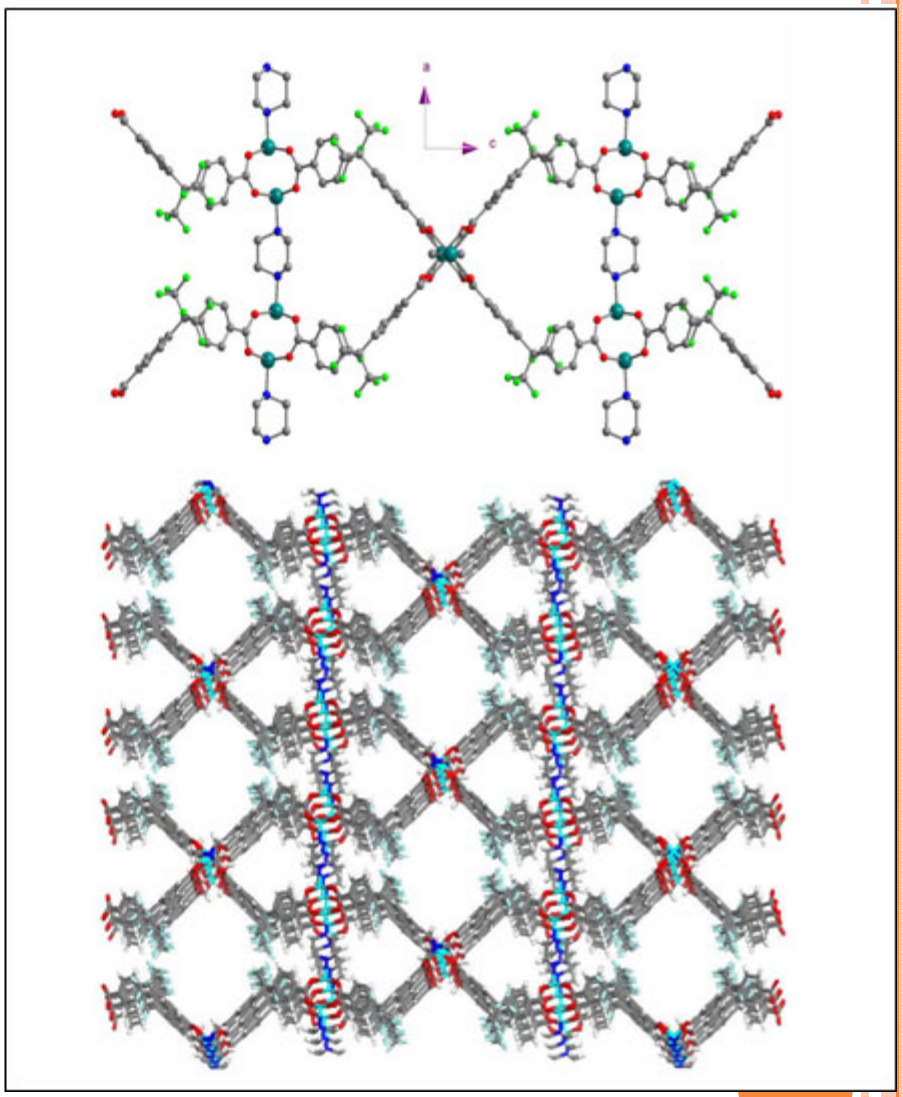
Crystal Data

Formula Weight (g/mol)	580.89
Crystal System	Tetragonal
Space Group	$I4_1/amd$
Unit Cell Dimensions:	
a = 19.0903Å	α = 90.0°
b = 19.0903 Å	β = 90.0°
c = 47.7560 Å	γ = 90.0°
V = 17404.2 Å^3	
Z = 16	
Density (Calculated, g/cm^3)	0.783
Solvent Accessible Volume	64.4%

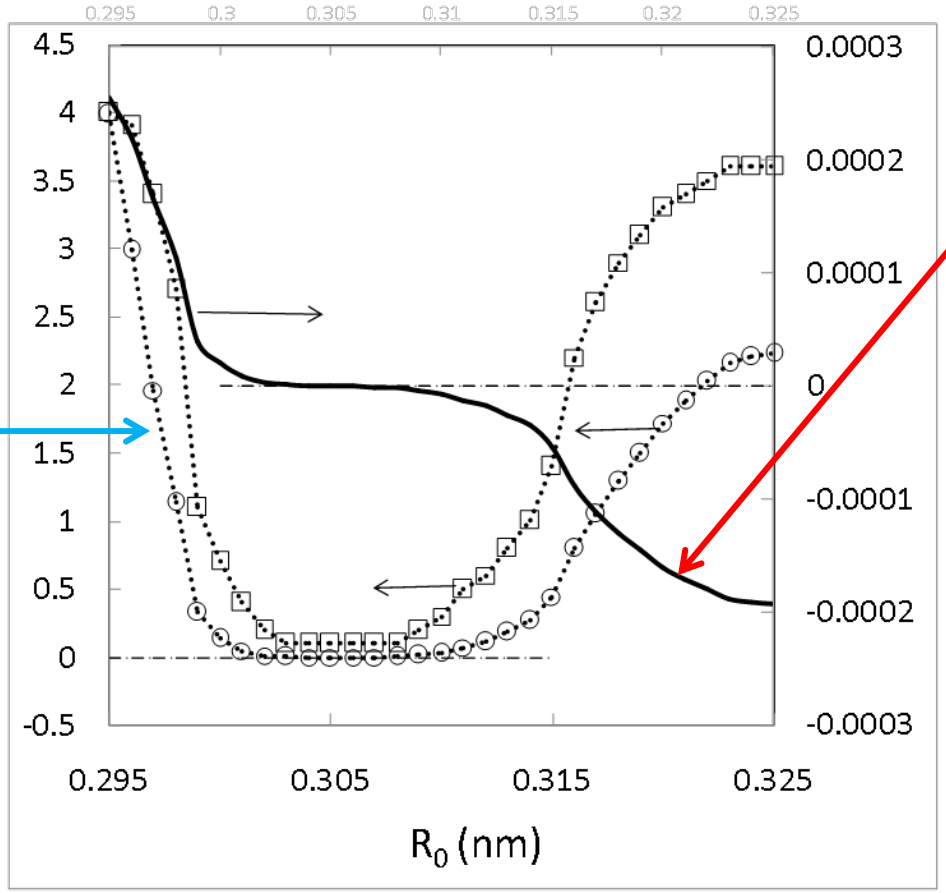


H_2hfipbb = 4,4'-hexafluoroisopropylidene)bis(benzoic acid





Energy change, in Kelvin



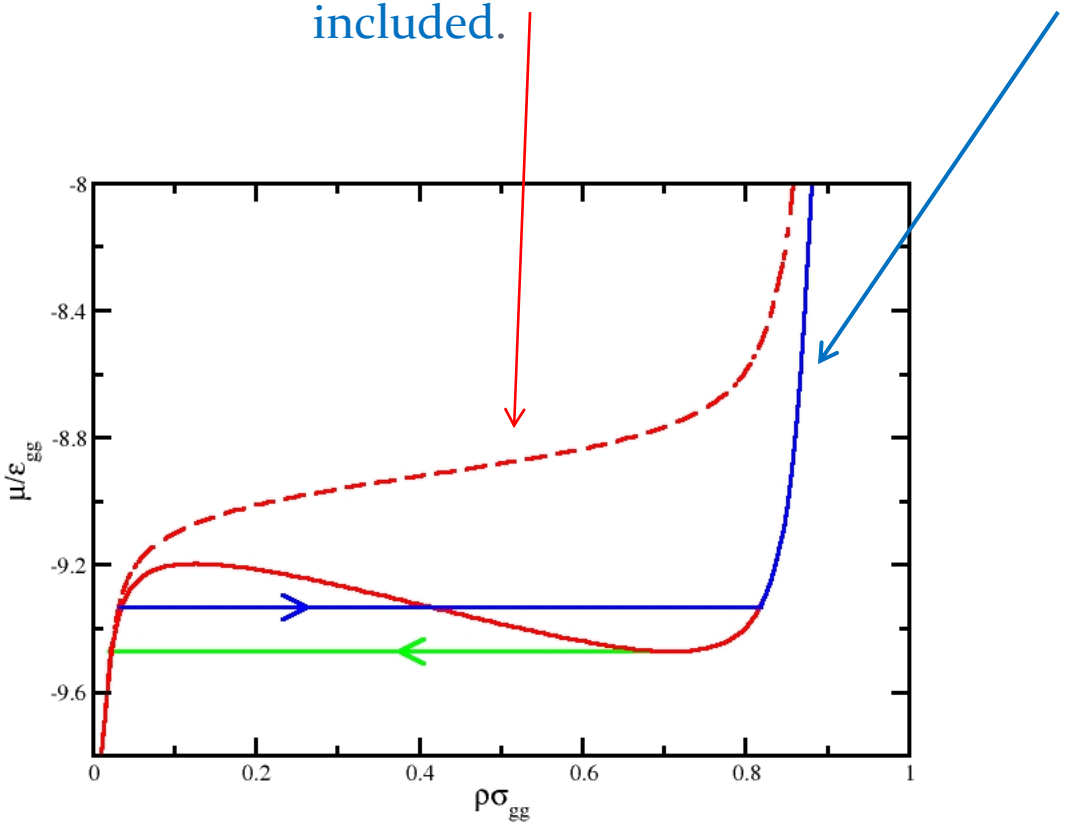
$\Delta R=R_{eq}-R_o$ (in nm).

^{3}He at T=o:

The fluid is not self-bound if no relaxation is included, but becomes strongly self-bound when it is included.

The effect of lattice relaxation is huge!

Example 2: Ar inside a small nanotube, initial radius 0.325 nm, at T=30 K. Chemical potentials vs. fluid density ρ, omitting relaxation, or when included.



Imbibition transition occurs when the fluid enters a pore that is expanded as a consequence of the presence of the fluid. **Qualitative change in the isotherm!**

Note hysteresis, associated with van der Waals loop.