

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

Angela D. Lueking,<sup>1</sup> Jing Li,<sup>2</sup> Milton W. Cole<sup>1</sup>

<sup>1</sup>Penn State University, <sup>2</sup>Rutgers University

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stp\_34\_lueking

# Overview

## Timeline

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

## Budget

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

## Barriers

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

## 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<sub>2</sub> storage at 300K-400K and moderate *P*s.

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

- A. Train new users, upgrade and validate H<sub>2</sub> 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*

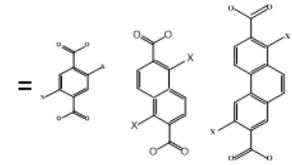
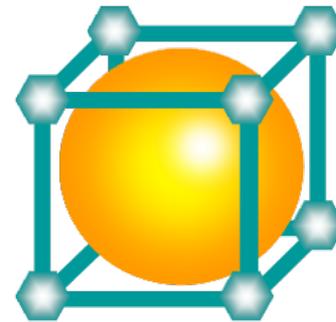
The impact your project has on addressing the barriers identified in the Overview slide and other specific targets and milestones.

# STRATEGIES / APPROACH

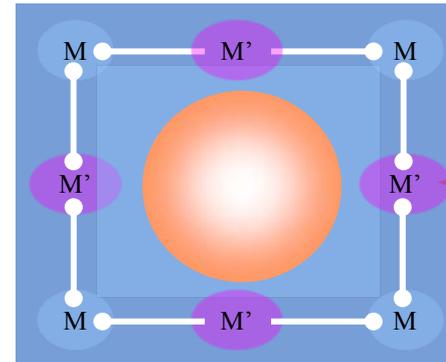
TO MAXIMIZE  $H_2$  STORAGE AT MODERATE  $T$  AND  $P$

- Optimize **Hydrogen Spillover Mechanism** utilizing MOF design to maximize receptors of spilled-over  $H$ :

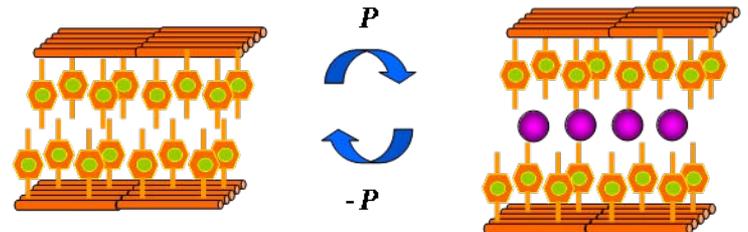
- Surface Chemistry
- Porosity



- 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:
  - H<sub>2</sub> 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.**

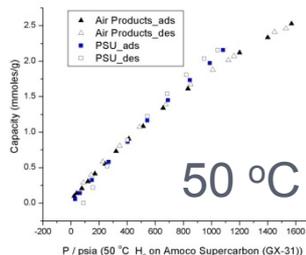
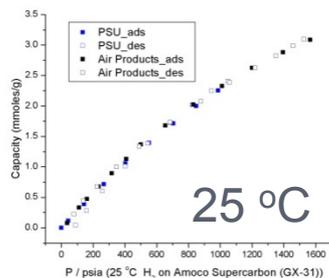
Exceed 5.5 wt% hydrogen storage through the use of the “hydrogen spillover” mechanism, MOF material, or a combination of the two as proposed at moderate temperatures (i.e. 300-400 K) and 100 bar with anticipated system penalties (Go/No Go: 3Q Year 2).

# TECHNICAL ACCOMPLISHMENTS

## A. TRAIN NEW USERS, UPGRADE AND VALIDATE H<sub>2</sub> STORAGE MEASUREMENTS

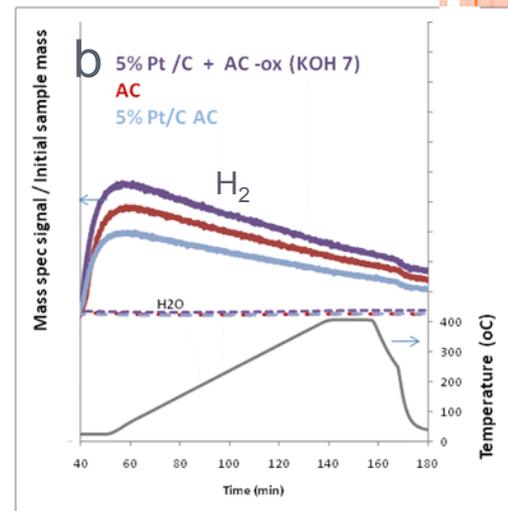
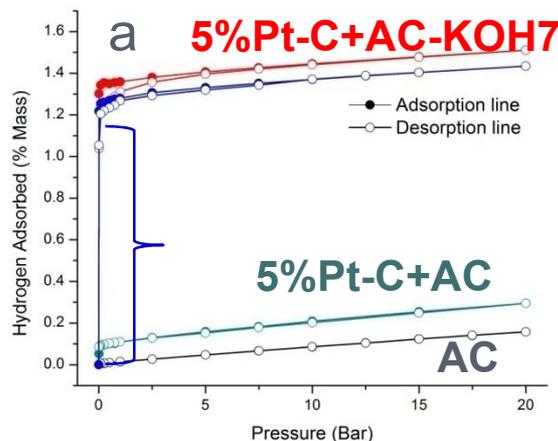
### High-Pressure Differential Volumetric System (custom-built)

- 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:

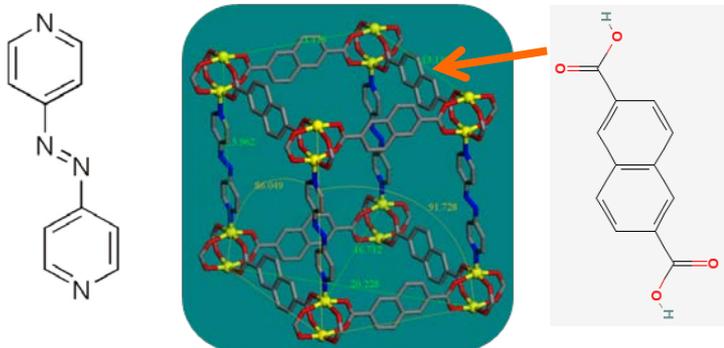


(a) Adsorption-Desorption Isotherm showed 1.0 wt% chemisorbed H<sub>2</sub>, which (b) desorbed with subsequent heating.

# TECHNICAL ACCOMPLISHMENTS

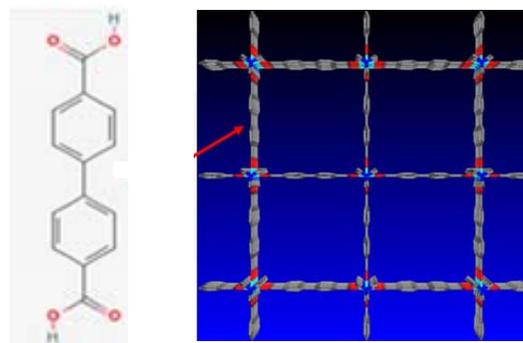
B. SYNTHESIZE NEW MMOF STRUCTURES TO EXPLORE THE EFFECT OF SURFACE CHEMISTRY, POROSITY, AND STRUCTURE ON HYDROGEN SPILLOVER

## MMOF-1-Zn

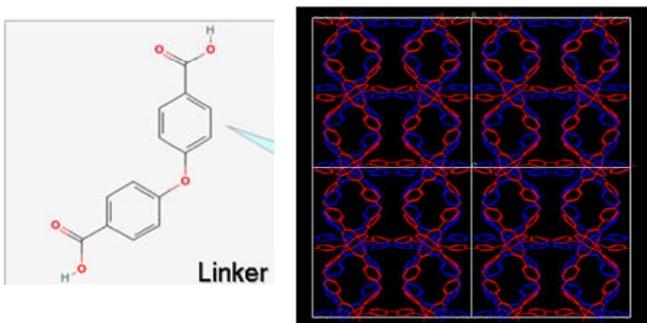


## MMOF-2-M

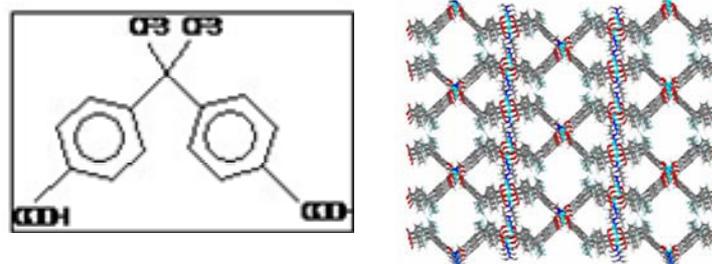
(M = Ni, Cu, Zn)



## MMOF-3-Zn



## MMOF-4-Zn

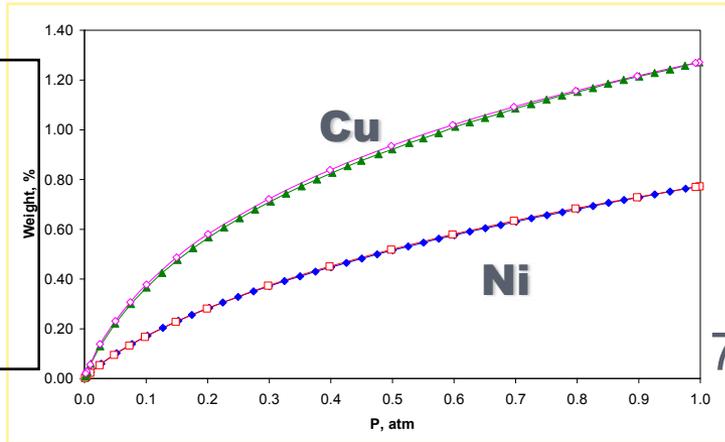


# TECHNICAL ACCOMPLISHMENTS

BASELINE PHYSISORPTION DATA FOR AS-SYNTHEZIZED MMOFs

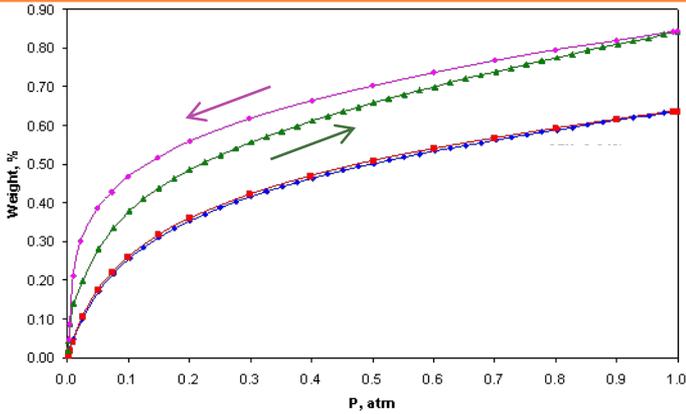
## MMOF-2-M (M = Ni, Cu, Zn)

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)  
 $q_{st} \sim 5$  kJ/mol  
77K

## MMOF-3-Zn

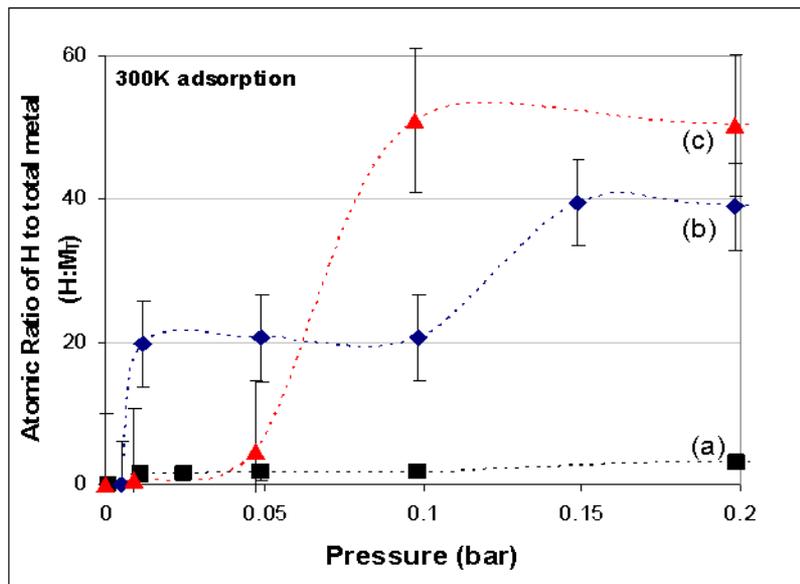


0.84% (1 atm, 77K)  
0.64% (1 atm, 87K)  
 $q_{st} \sim 6.5$  kJ/mol

# TECHNICAL ACCOMPLISHMENTS

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

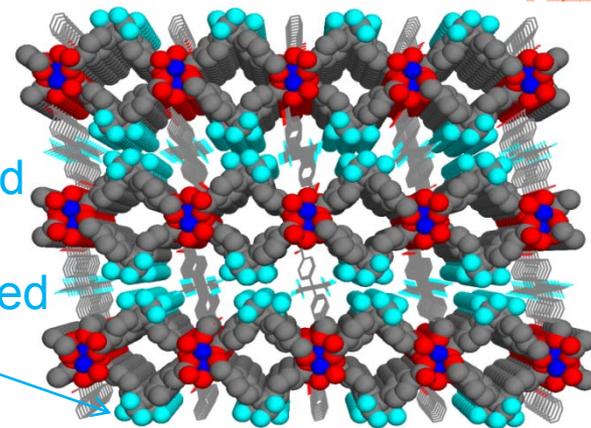
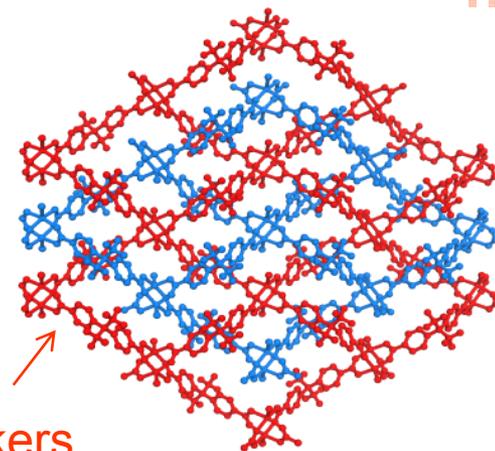
Mixing MMOFs with 5% Pt/C for 300K adsorption



(c) Carbon-based linkers

(b) Incorporated surface sites for increased H-bonding

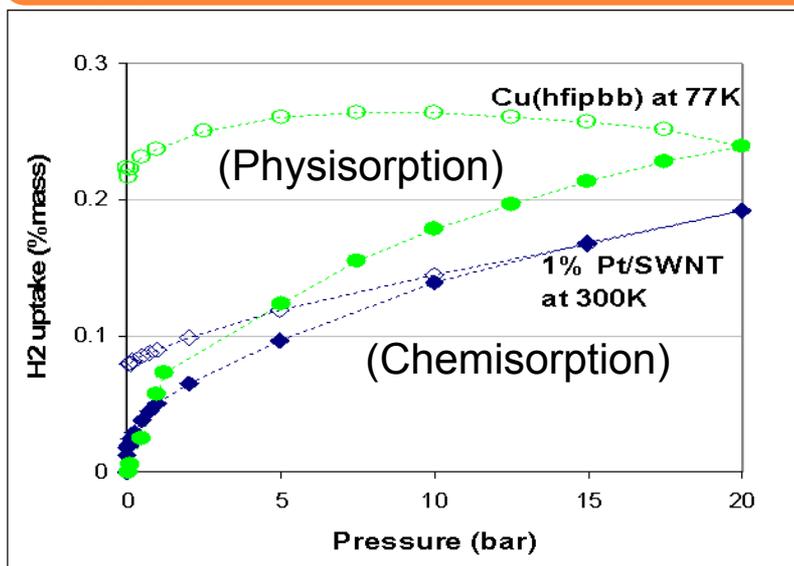
(a) 5% Pt/C catalyst



Use of a spillover catalyst increases  $T_{ads}$  to 300K. MMOFs can increase the uptake by providing specific H-bonding 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<sub>2</sub> 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<sub>2</sub> and H gate-opening pressures in order to serve as a chemical switch for the dilation phenomenon. (Yr. 3 – FY 11)

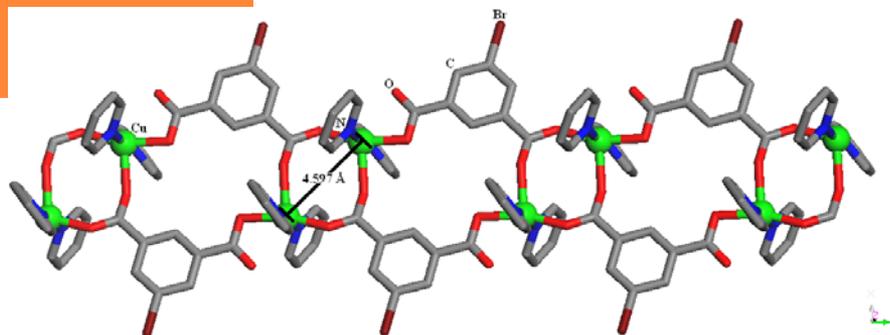
# FUTURE WORK

INCORPORATION OF CATALYST DIRECTLY INTO MMOF STRUCTURE

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

BEFORE

AFTER 200 °C in  $H_2$



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



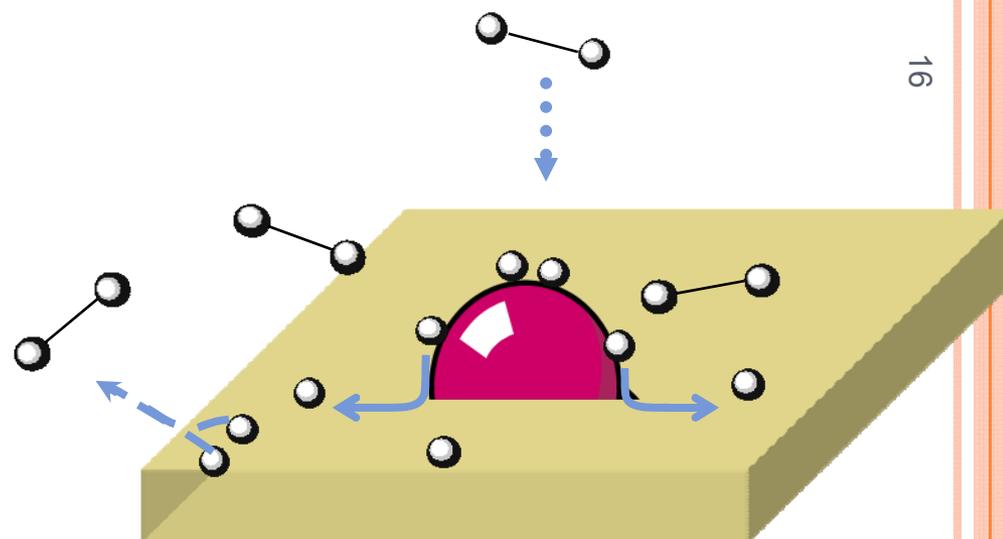
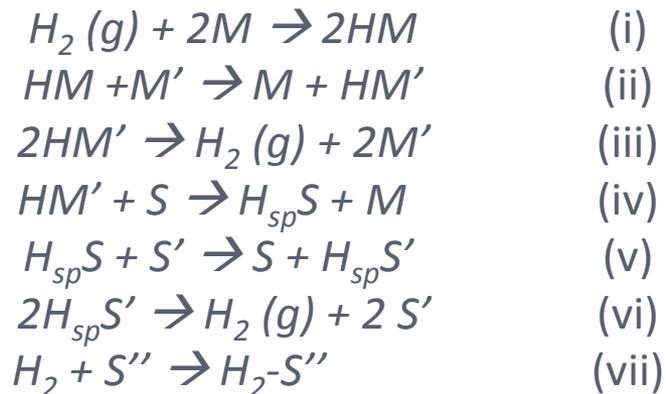
# SUMMARY

- 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

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# BACKGROUND: WHAT IS HYDROGEN SPOILOVER?



Side View

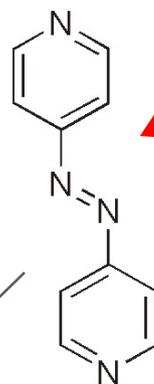


**Box 1: Reaction sequence for hydrogen spillover.**

# MMOF-1-Zn

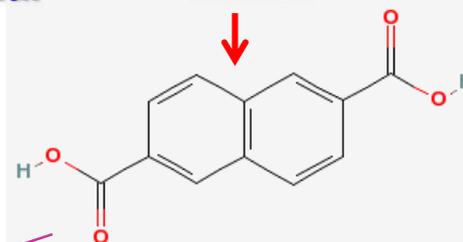
Formula Weight: 816.38 g/mol  
Crystal System: Monoclinic  
Space Group: C2/c  
Data Collection Temperature: 100K  
Unit Cell Dimensions:  
 $a = 16.7116(14) \text{ \AA}$   
 $b = 20.2283(17) \text{ \AA}$   
 $c = 11.9471(10) \text{ \AA}$   
 $\beta = 117.367(2)^\circ$   
 $V = 3586.7(5) \text{ \AA}^3$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

## Ligands



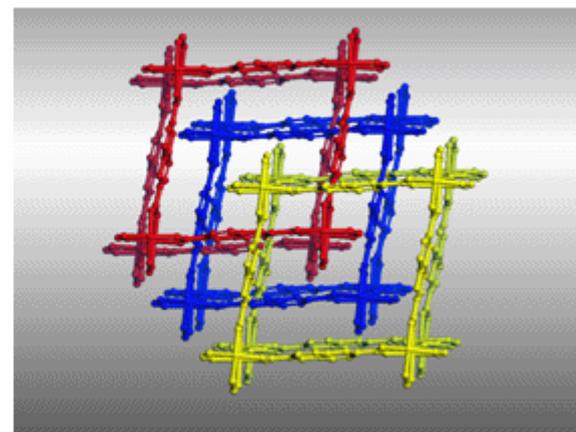
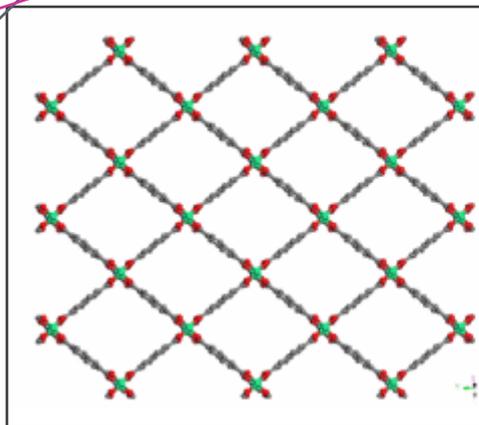
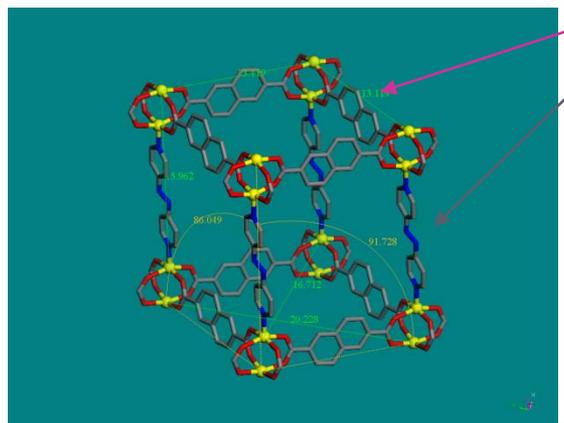
Pillar

Linker



4,4'-Azopyridine

Napthalene  
2,6-Dicarboxylic Acid



# 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:

$a = 15.2312 \text{ \AA}$

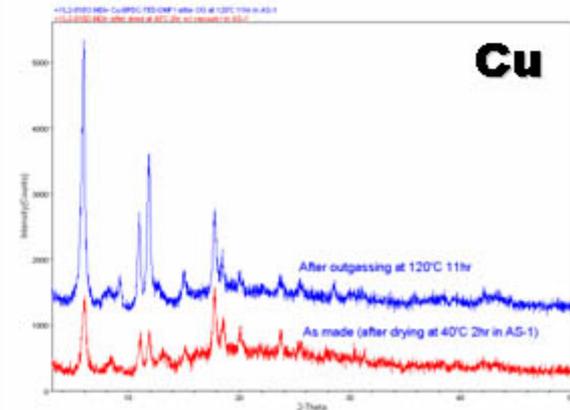
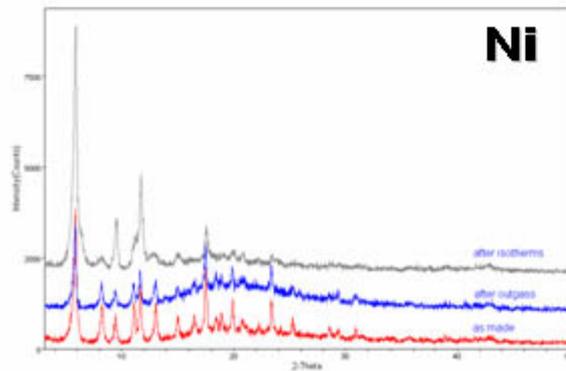
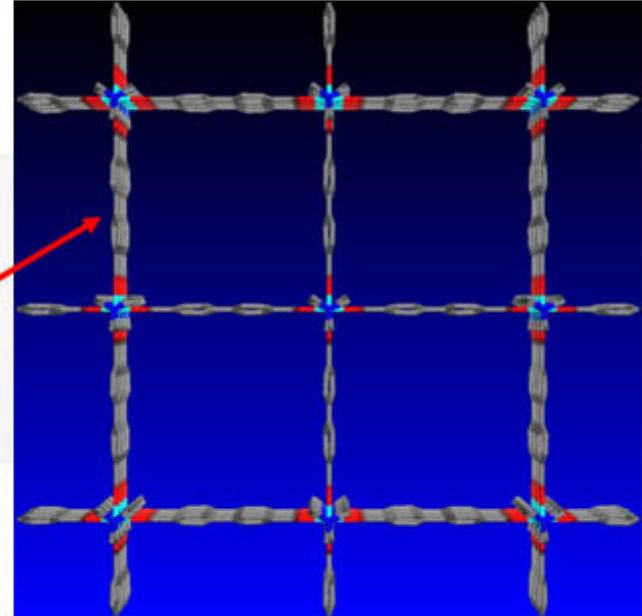
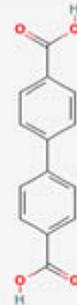
$b = 15.2312 \text{ \AA}$

$c = 9.6630 \text{ \AA}$

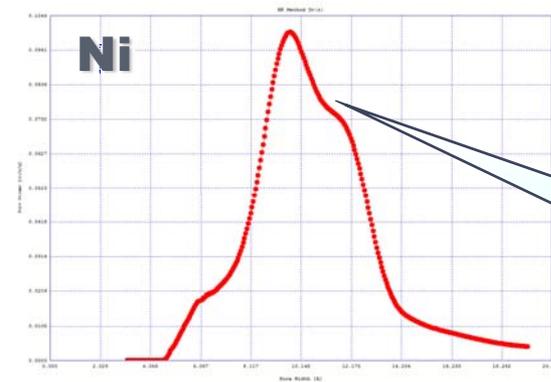
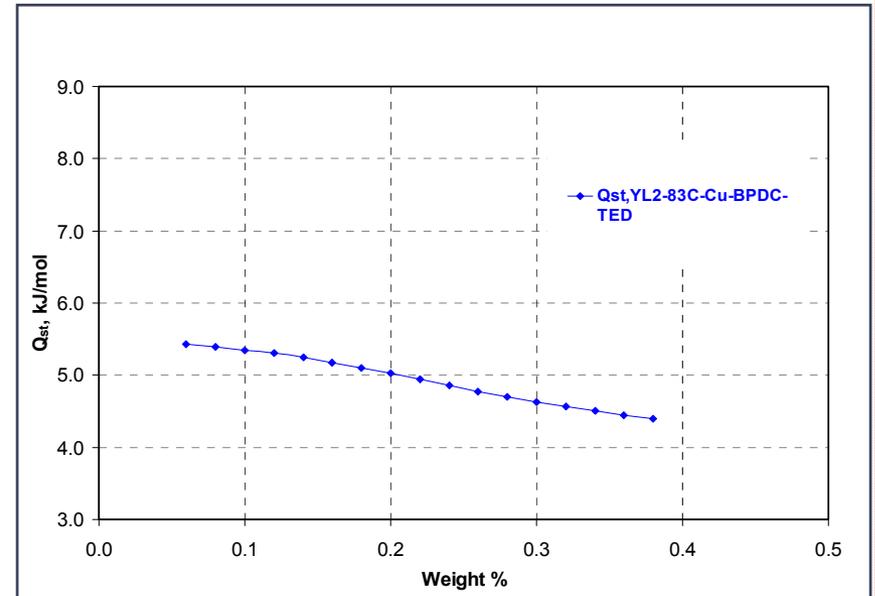
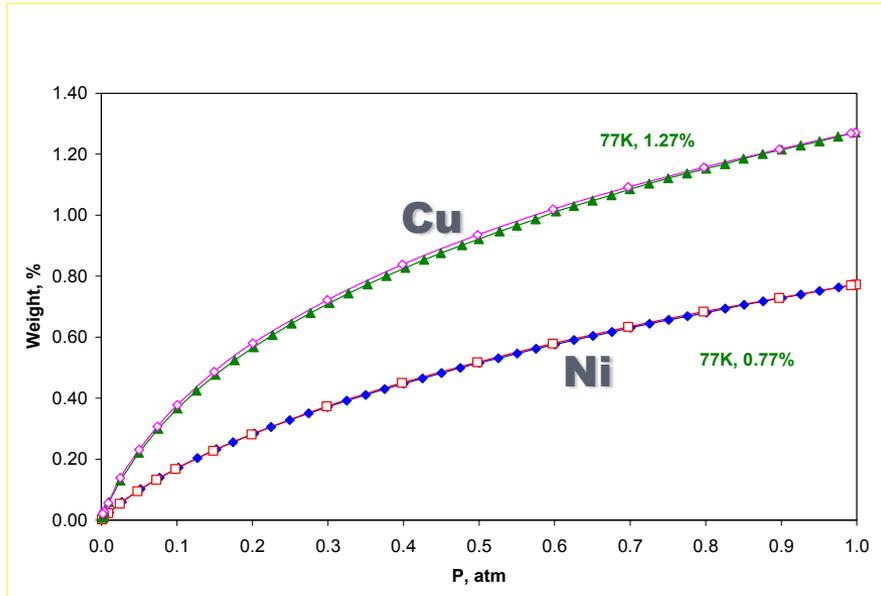
$V = 2241.7 \text{ \AA}^3$ ,  $Z = 2$

Framework Density:  $0.5269 \text{ g/cm}^3$

Solvent Accessible Volume: 73.3%



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

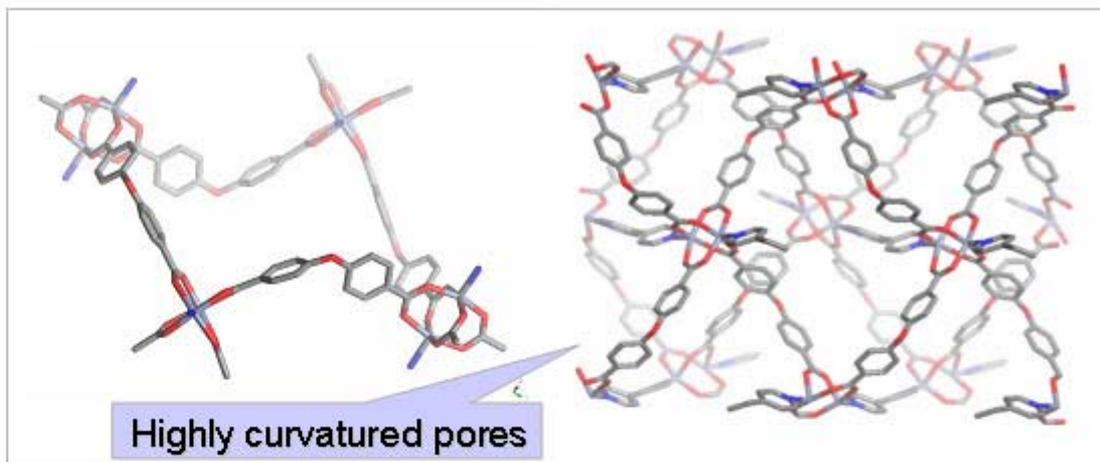


**Pore Size Distribution (~8-12Å)**

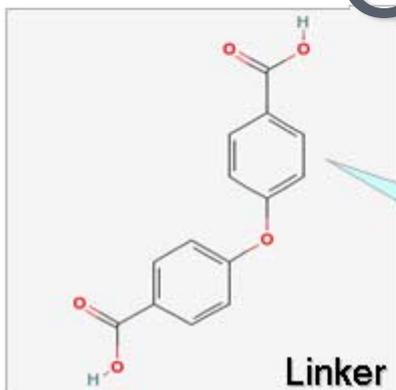
Properties	Ni	Cu
Pore Volume (Total)	0.64	0.80
Surface Area (BET)	1661	1332
Surface Area (Lang)	1801	1790
Hydrogen wt%	1.16	1.27
Isosteric Heats	4.4-5.4	4.5-5.5

# MMOF-3-Zn

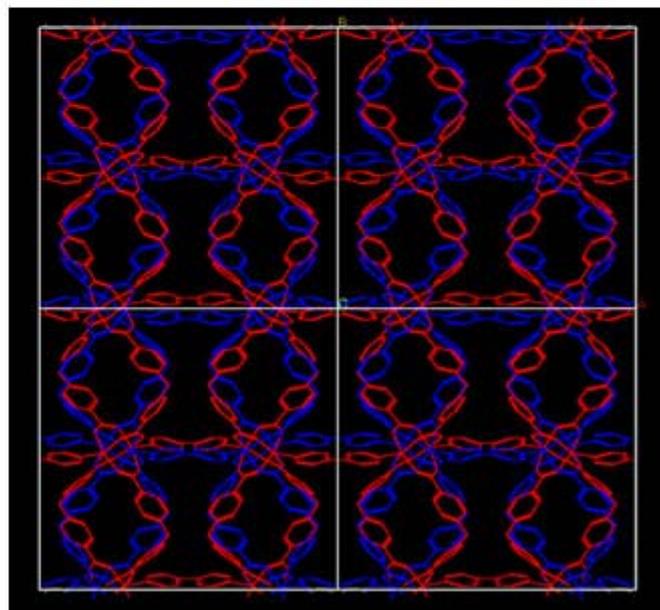
**Formula Weight:** 872.43 g/mol  
**Crystal System:** Orthorhombic  
**Space Group:** *Pbcn*  
**Unit Cell Dimensions:**  
 $a = 22.028(3) \text{ \AA}$   
 $b = 22.390(2) \text{ \AA}$   
 $c = 16.573(5) \text{ \AA}$   
 $V = 8223.1(14) \text{ \AA}^3$   
 $Z = 8$   
**Density (Calculated):** 1.409 g/cm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



## OBA

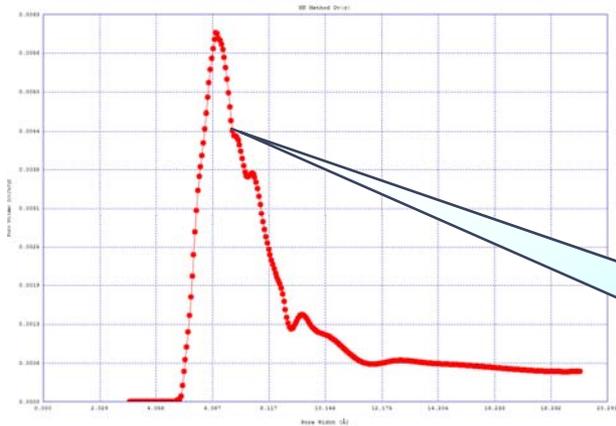
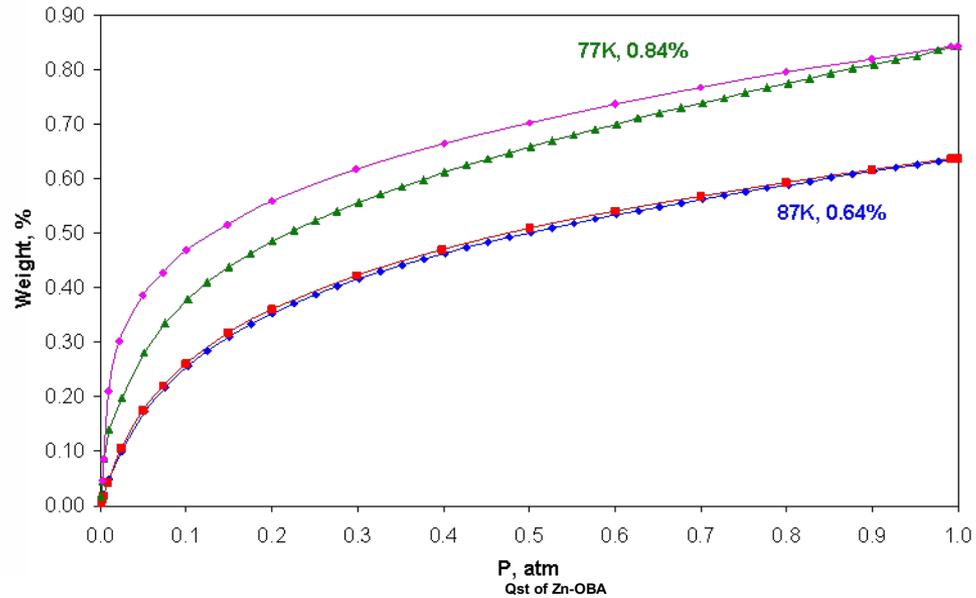
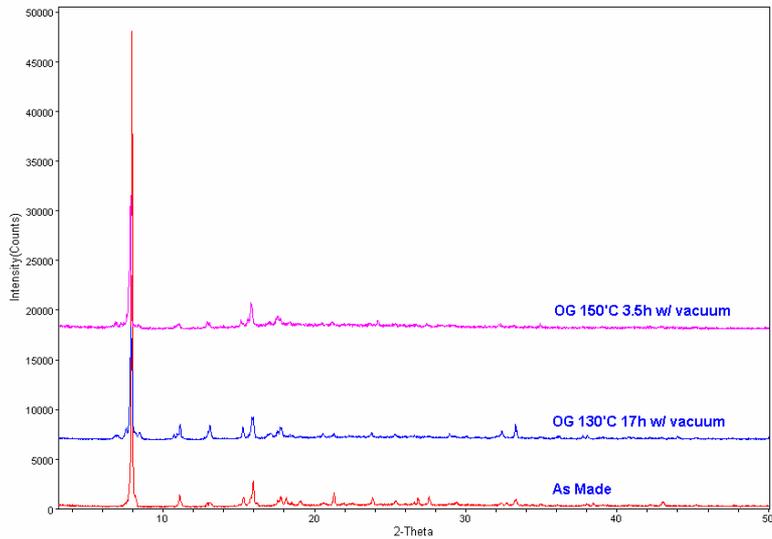


4,4'-oxybis-  
benzoic acid



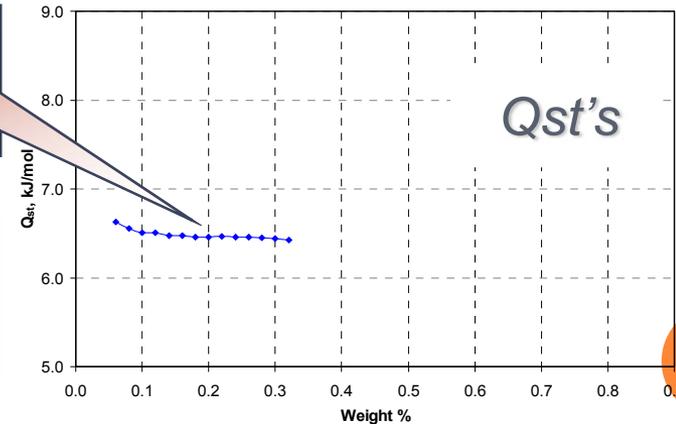
# MMOF-3-Zn

Zn-OBBA-YL2-60A



Isosteric Heats  
(6.5-6.7Å)

Pore Size  
Distribution  
(6-7Å)

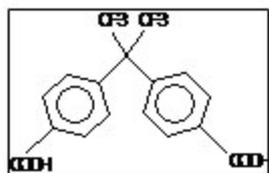


*Qst's*

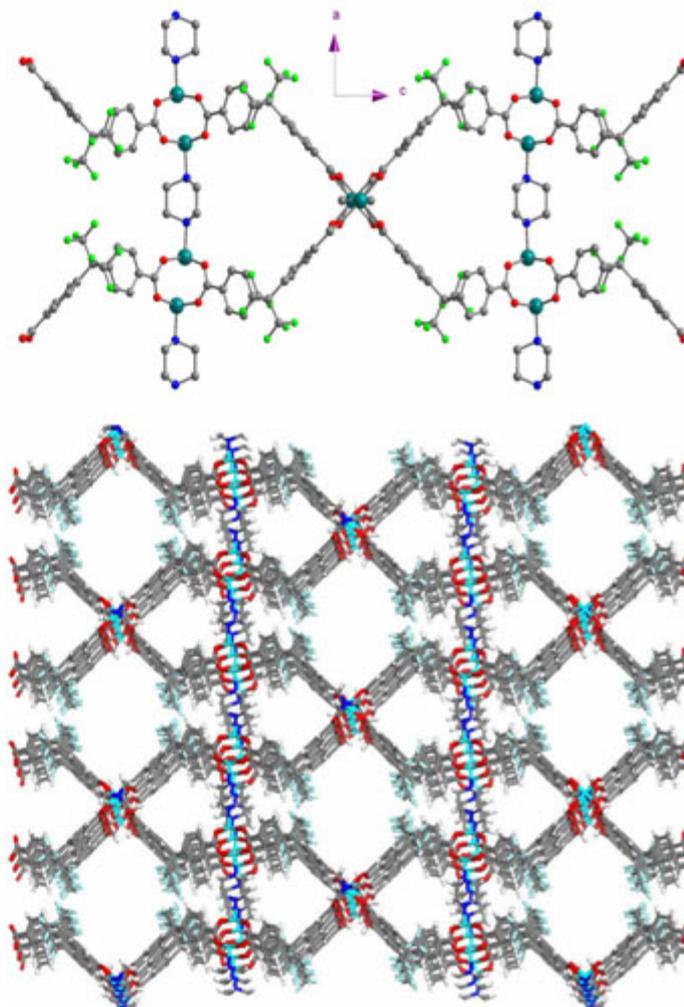
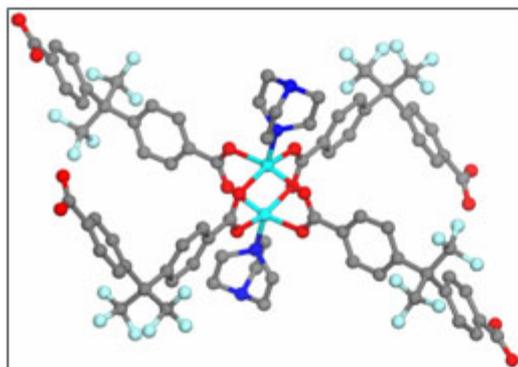
# MMOF-4-Zn

## Crystal Data

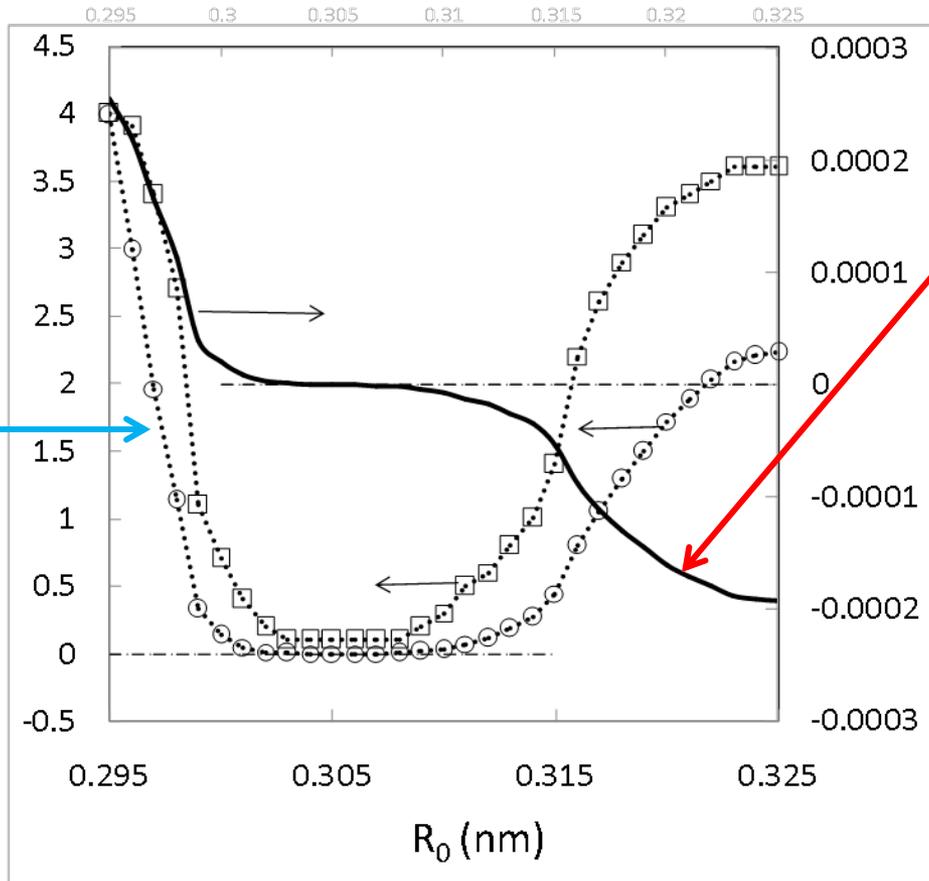
Formula Weight (g/mol)	580.89
Crystal System	Tetragonal
Space Group	$I4_1/amd$
Unit Cell Dimensions:	
$a = 19.0903 \text{ \AA}$	$\alpha = 90.0^\circ$
$b = 19.0903 \text{ \AA}$	$\beta = 90.0^\circ$
$c = 47.7560 \text{ \AA}$	$\gamma = 90.0^\circ$
$V = 17404.2 \text{ \AA}^3$	
$Z = 16$	
Density (Calculated, $\text{g/cm}^3$ )	0.783
Solvent Accessible Volume	64.4%



$\text{H}_2\text{hfipbb} = 4,4'$ -  
hexafluoroisopropyl  
idene)bis(benzoic  
acid



Energy change,  
in Kelvin



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

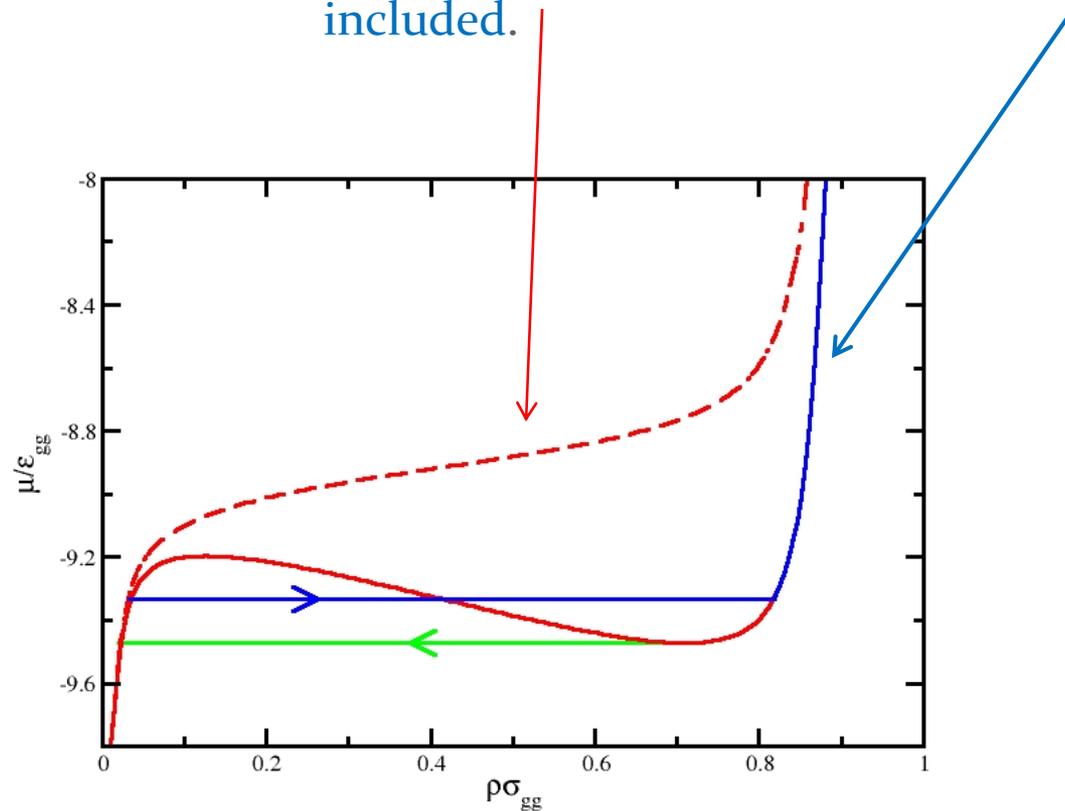
**$^3\text{He}$  at  $T=0$ :**

**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  $\rho$ , 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.