

# 2013 DOE Hydrogen and Fuel Cells Program Review

## Hydrogen Storage in Metal-Organic Frameworks

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Project ID #: ST103

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# Overview

## Timeline

- Start: April 2012
- Finish: March 2015
- 30% complete

## Budget

- Total project funding
  - DOE share: \$2,100k
  - Contractor share: \$525k
- Funding received in FY12:
  - \$500k
- Funding planned for FY13:
  - \$600k

## Barriers

- Barrier addressed
  - A. System Weight and Volume

## Partners

- LBNL: synthesis and modeling
- NIST: neutron diffraction  
(start Oct. 2012)
- GM: high-pressure adsorption  
(start July 2012)
- Project lead: Jeffrey Long (LBNL)



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# Relevance

## Project objectives

- Research and development of on-board systems that allow for a driving range greater than 300 miles.
- Materials sought with the potential for meeting the DOE targets of reversible uptake:
  - 2017 targets: 5.5 % H<sub>2</sub> by mass, volumetric capacity of 40 g/L
  - “ultimate full fleet” targets: 7.5 % H<sub>2</sub> by mass, 70 g/L.
- Synthesize new metal-organic frameworks capable of achieving the –20 kJ/mol adsorption enthalpy required for use as hydrogen storage materials operating under 100 bar at ambient temperatures



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# Approach

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**Task 1:** Synthesis of Metal-Organic Frameworks  
(Jeffrey Long-LBNL)

**Task 2:** Characterization of Framework-H<sub>2</sub> Interactions  
(Craig Brown-NIST)

**Task 3:** First-Principles Calculations of Hydrogen Binding Enthalpies  
(Martin Head-Gordon-LBNL)

**Task 4:** High-Pressure H<sub>2</sub> Adsorption Measurements  
(Anne Dailly-GM)



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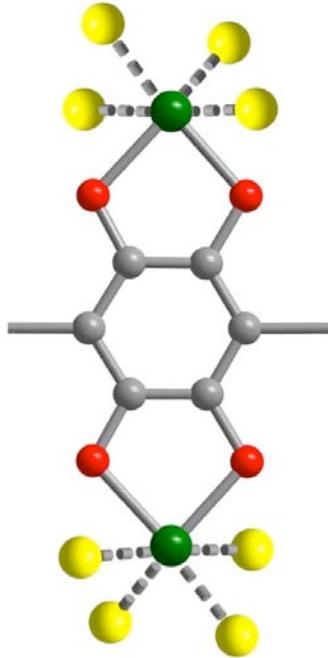


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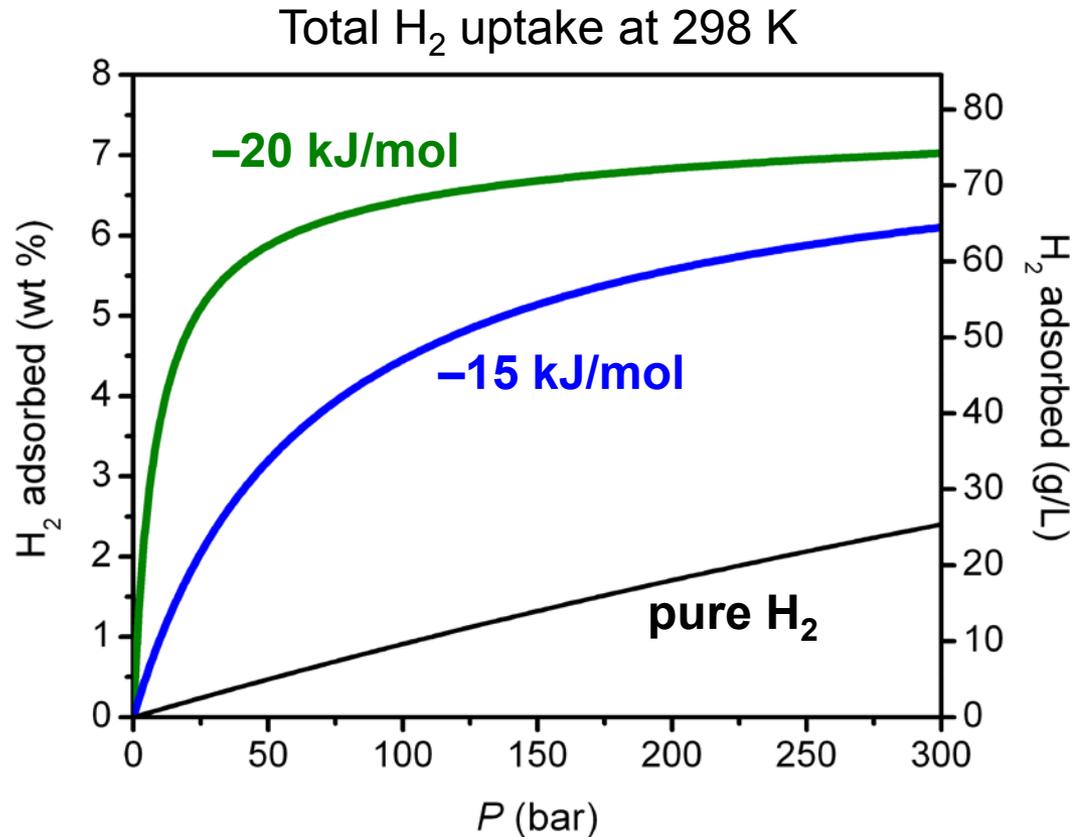
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# Approach

## Multiple H<sub>2</sub> Binding Sites per Metal



Al(OH)(C<sub>14</sub>O<sub>12</sub>Mg<sub>4</sub>)



- Isotherms simulated using dual site Langmuir model with estimated parameters
- Binding enthalpy and associated entropy not yet known for Mg<sup>2+</sup> in this geometry

# Approach: Milestones and Go/No go

Due date	Description	% Comp	Status March 2013
03/13	<b>Go/No-go (Task 1):</b> Demonstration of ability to prepare 5 mixed functionality ligands allowing for post-synthetic insertion of metal cations	100%	7 ligands containing both carboxylate and pyridine/phenol binding sites have been prepared
03/13	<b>Go/No-go (Task 1):</b> Development of in silico screening for calculating opposing pore surface distances	100%	Software completed and manuscript submitted
03/13	<b>Go/No-go (Task 1):</b> Preparation of two new MOFs containing coordinatively-unsaturated high-valent cations.	100%	Frameworks with open Al <sup>3+</sup> and Ti <sup>3+</sup> sites have been synthesized
03/13	<b>Milestone (Task 2):</b> Demonstrated ability to locate and uncover detailed descriptions of high-enthalpy H <sub>2</sub> binding sites in high-valent MOFs via neutron diffraction	30%	Diffraction measurements on pyridine and MOF-74 variants performed. Analysis underway
03/13	<b>Milestone (Task 3):</b> Demonstration of a correlation between calculated and experimentally observed H <sub>2</sub> binding affinities and usefulness in facilitating design of new materials	100%	Calculated H <sub>2</sub> binding parameters agree with experimental values
03/13	<b>Milestone (Task 4):</b> Demonstrate ability to accurately measure H <sub>2</sub> adsorption in MOFs at 298 K and pressures up to 350 bar	30%	High-pressure system installed and some benchmark samples measured



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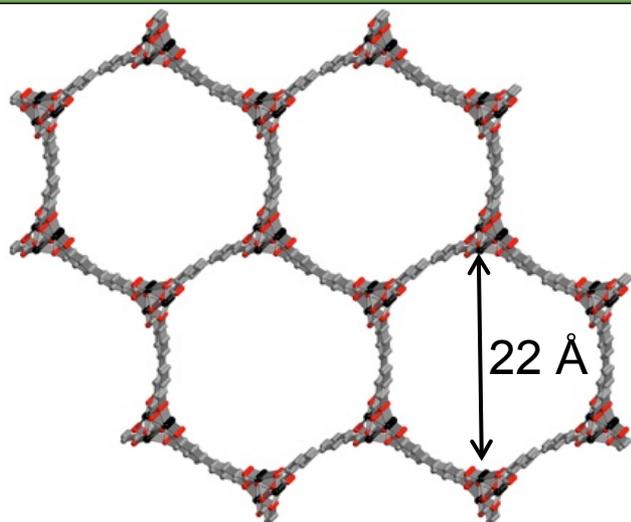


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# Accomplishments: Task 1

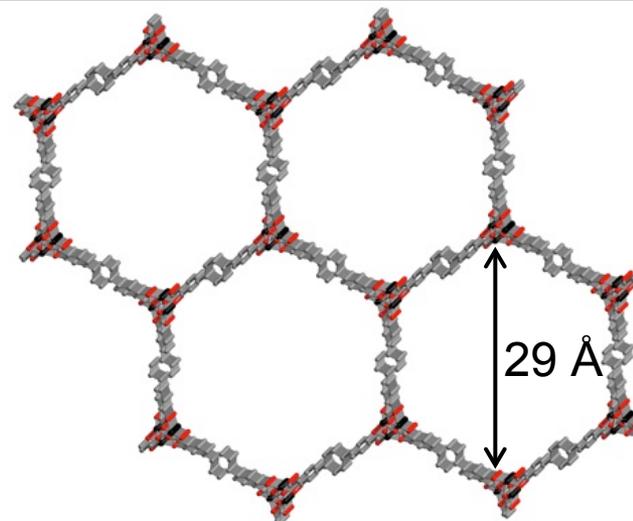
## Synthesis of Expanded MOF-74 Analogues



$M_2(\text{dobpdc})$

(M = Mg, Mn, Fe, Co, Ni, Zn)

$SA_{\text{Lang}} = 2700\text{-}3500 \text{ m}^2/\text{g}$



$M_2(\text{dotpdc})$

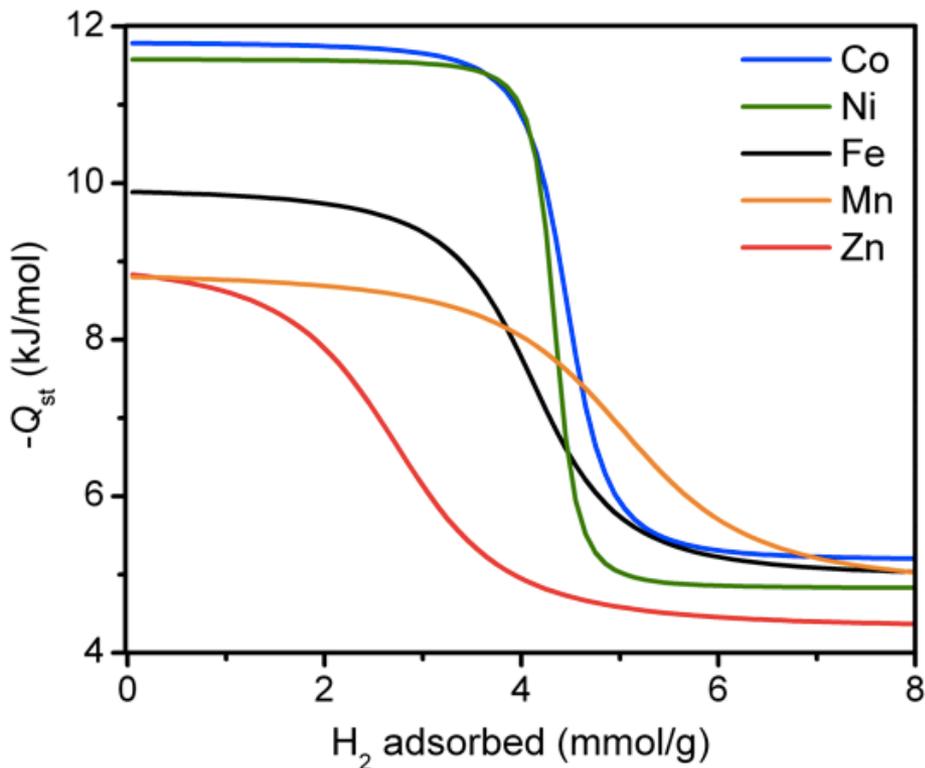
(M = Mg, Mn, Fe, Co, Ni)

$SA_{\text{Lang}} = 3500\text{-}4800 \text{ m}^2/\text{g}$

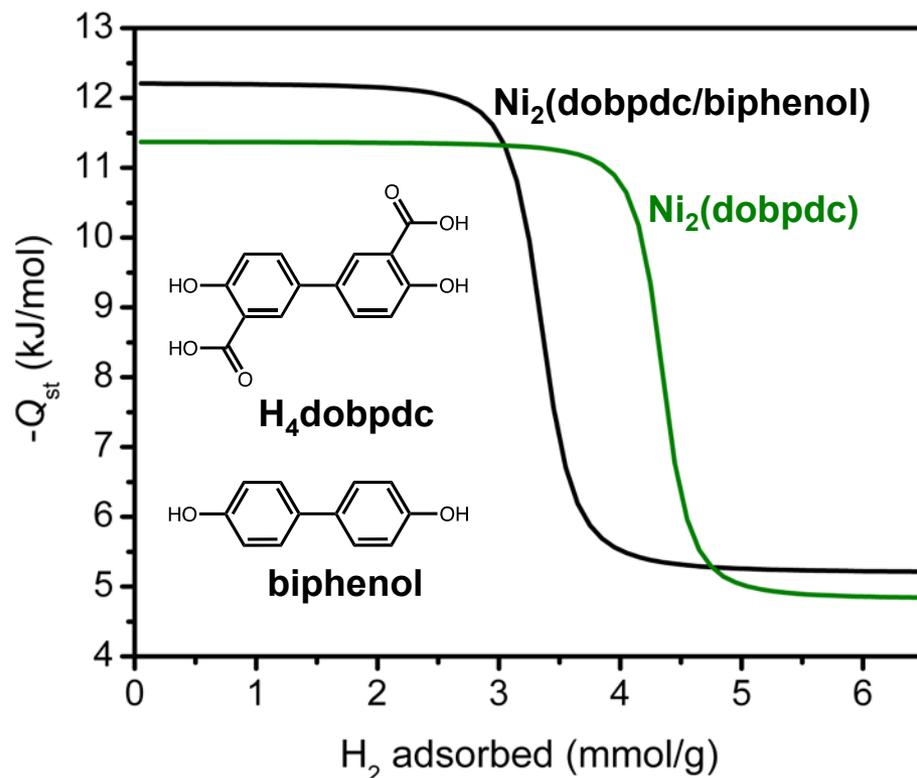
- Higher surface areas and pore sizes will allow systematic study of high-pressure adsorption
- Robust framework and extra volume to accommodate analogous ligands that can support highly exposed metal cations

# Accomplishments: Task 1

## Isosteric Heats of H<sub>2</sub> Adsorption in M<sub>2</sub>(dobpdc)



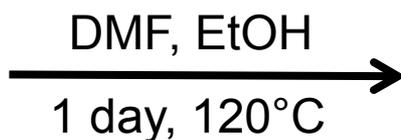
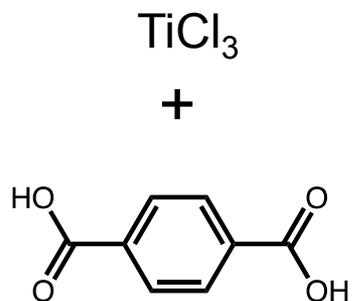
The Co<sup>2+</sup> and Ni<sup>2+</sup> analogues display H<sub>2</sub> binding enthalpies approaching -12 kJ/mol



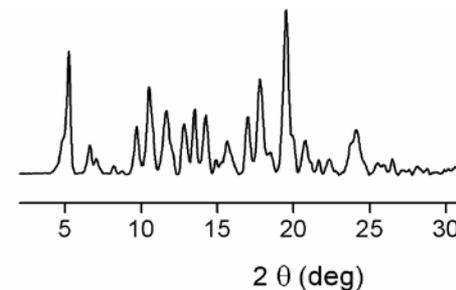
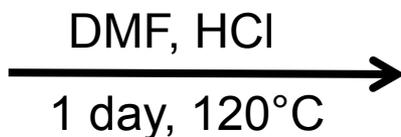
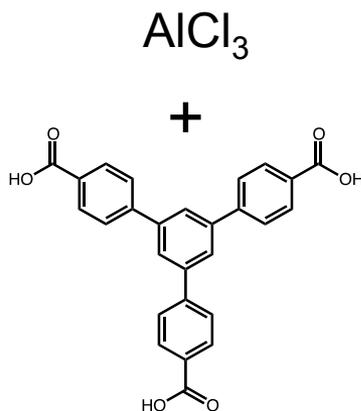
H<sub>2</sub> binding enthalpies can be increased through the introduction of defect sites

# Accomplishments: Task 1

## Synthesis of $M^{3+}$ -Based Metal-Organic Frameworks



$Ti_3O(BDC)_3Cl(DMF)$   
 $SA_{BET} = 2570 \text{ m}^2/\text{g}$



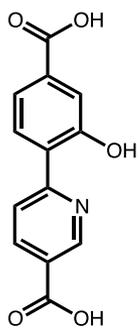
**Al-BTB**  
 $SA_{BET} = 3250 \text{ m}^2/\text{g}$

Two new frameworks displaying the highest reported surface areas for  $Ti^{3+}$  and  $Al^{3+}$  MOFs have been synthesized

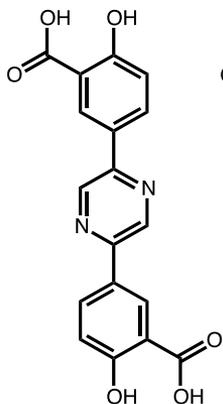
# Accomplishments: Task 1

## Synthesis of Mixed Functionality Ligands

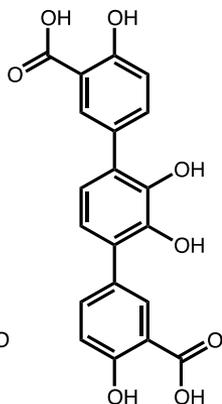
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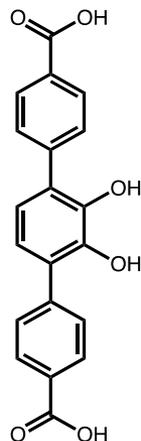
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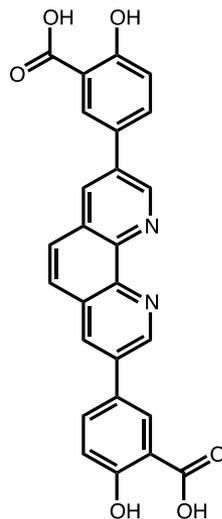
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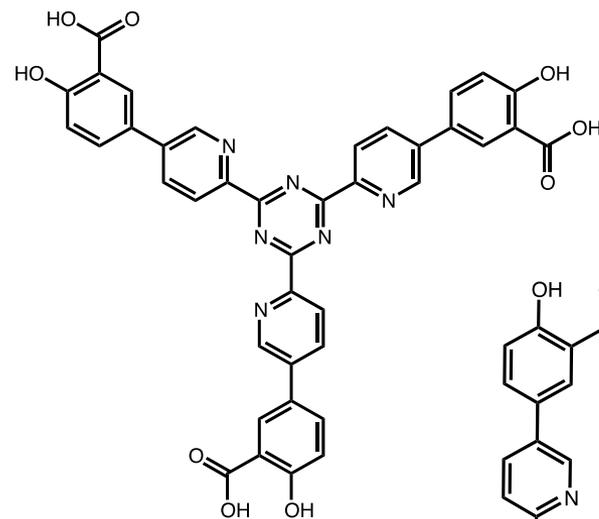
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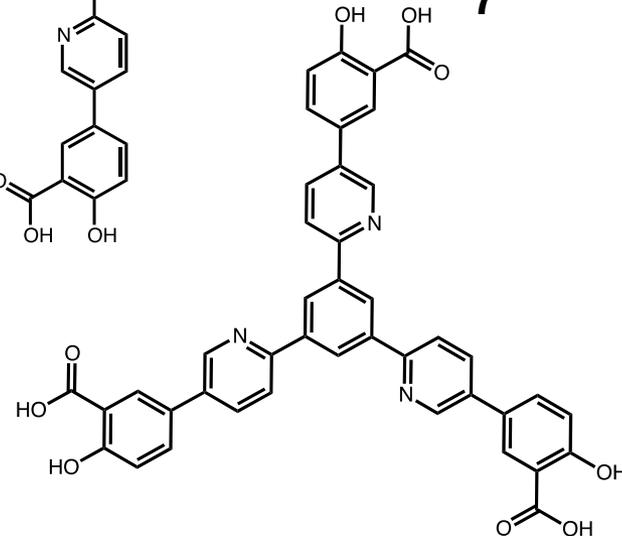
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6



7



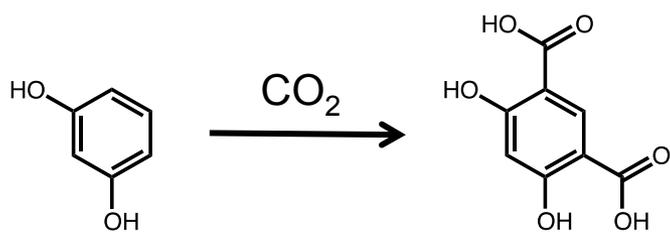
Synthesis of 7 new ligands has been completed

Incorporation of these ligands into metal-organic frameworks is ongoing. Porous, crystalline phases have been identified for 1,2,4,5.

# Accomplishments: Task 2

## Powder Diffraction of Cobalt and Nickel MOFs

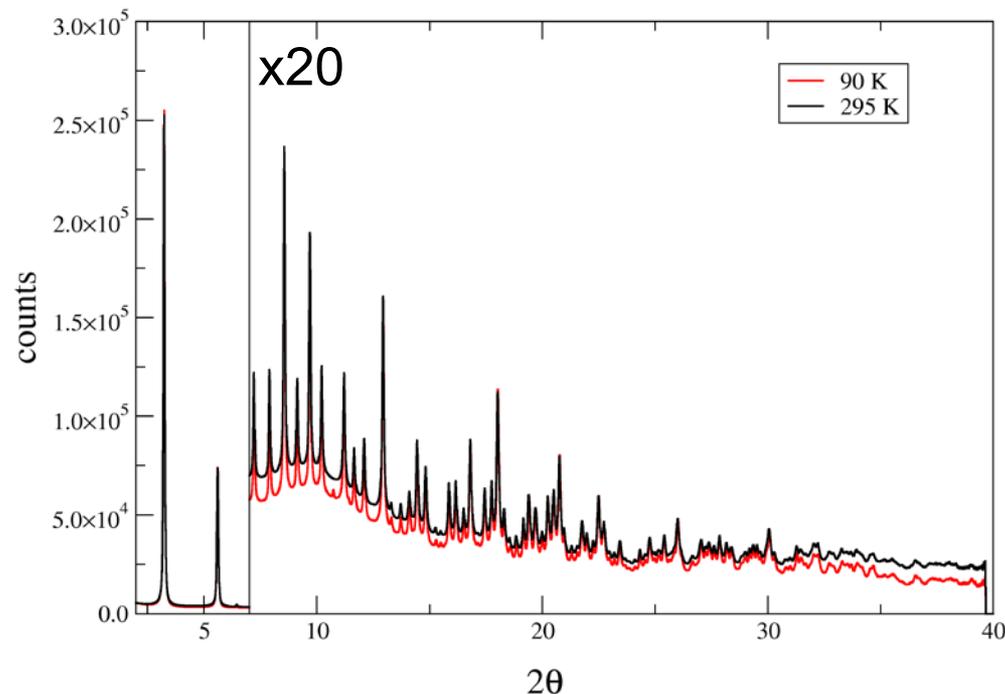
### Newly synthesized cobalt and nickel MOFs



**H<sub>4</sub>dobdc'**

**M<sub>2</sub>(dobdc') (M = Co, Ni)**

**SA<sub>Lang</sub> = 1400-2000 m<sup>2</sup>/g**



X-ray and neutron powder diffraction provides MOF structure and H<sub>2</sub> adsorption sites (determined crystal structure/analysis in progress)

*measurements performed at APS (XRS) and NIST (neutrons)*



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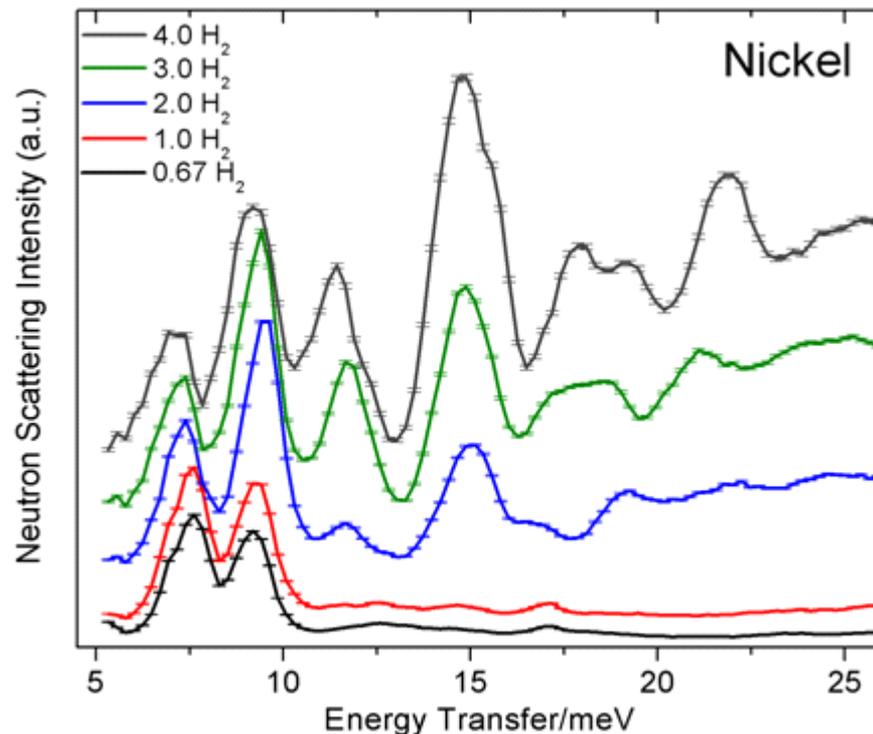
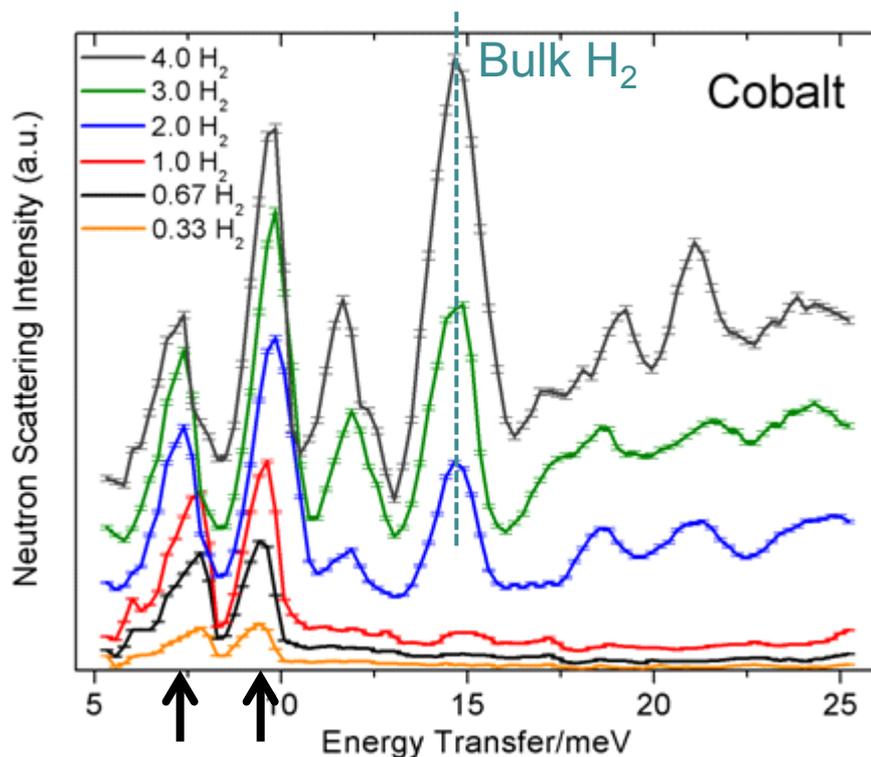


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# Accomplishments: Task 2

## Neutron Inelastic Scattering of Cobalt and Nickel MOFs



- Distribution of highly active sites shifts  $H_2$  rotational lines away from bulk line
- At least three different adsorption sites identified, becoming more 'bulk'-like by  $\sim 3H_2$ :metal loadings.

*measurements performed at NIST*



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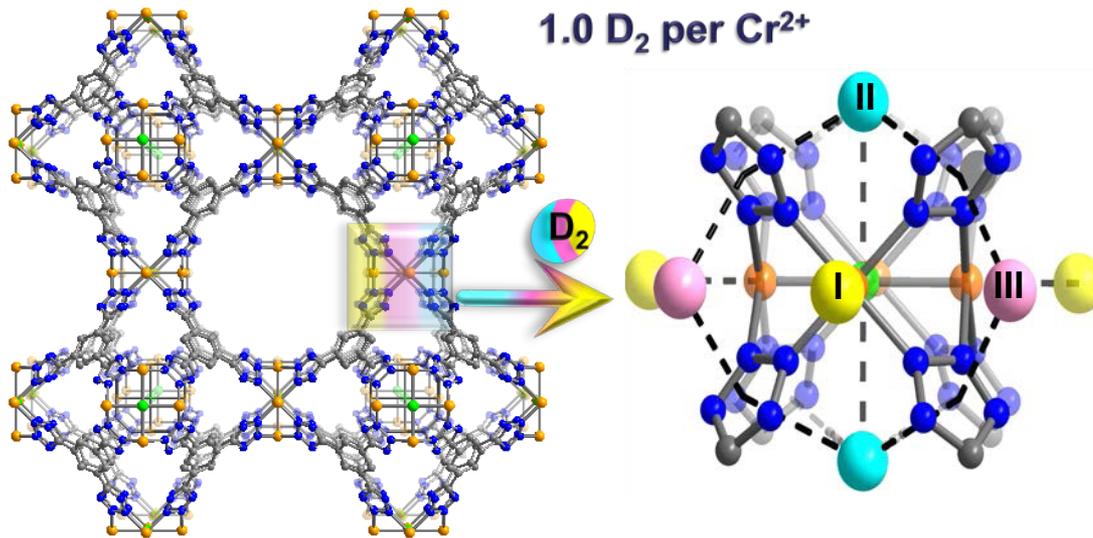


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# Accomplishments: Task 2

## Determination of Cr-BTT structure



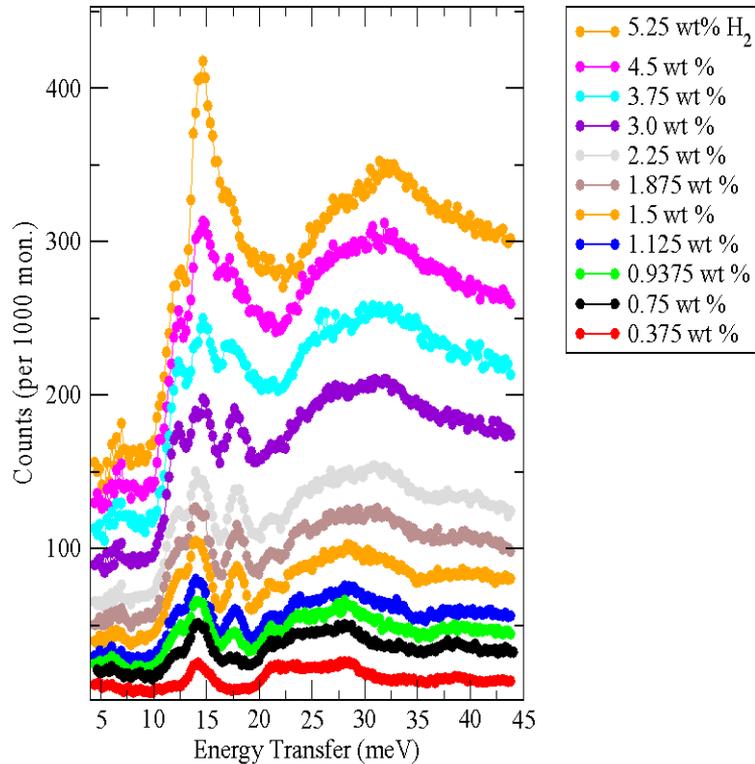
Bond	distance(Å)
Cr-Cl	2.42(4)
Cr-N	2.075(8)
Cr-D(I)	2.64(6)
Cl-D(II)	3.56(3)

### Structure determination

- Correlate enthalpy to structure / electronic configuration of TM
- Feeds into calculations

# Accomplishments: Task 2

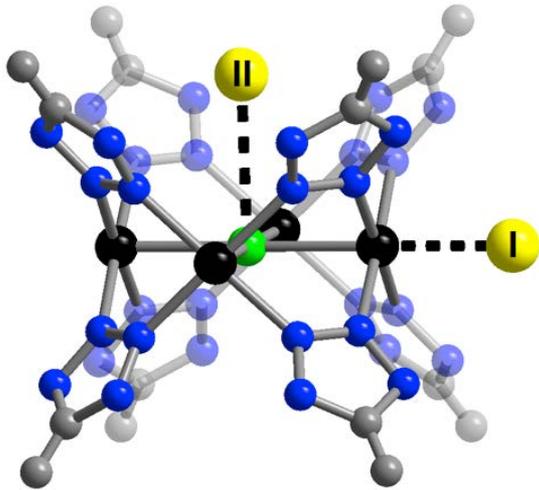
## Determination of Co-BTT:H<sub>2</sub> adsorption potential



- Inelastic neutron scattering of H<sub>2</sub> provides
- Determination of binding strength
  - Loading dependence of different sites
  - Strict comparison for theory

# Accomplishments: Task 3

## Calculations on Cu-BTT: Structure



Structure prediction

- Pre-requisite for H<sub>2</sub> binding

DFT calculations using  $\omega$ B97X-D

- Near-quantitative agreement
- JACS 135, 1083 (2013)

Bond (Å)	<u>exp.<sup>b</sup></u>	<u>calc.</u>
M- <u>Cl</u>	2.504	2.456
M- <u>N(1)</u>	2.007	2.040
<u>N(1)</u> -N(1)	1.344	1.323
N1- <u>N(2)</u>	1.323	1.310
<u>N(2)</u> -C	1.354	1.332

Angle (°)	<u>exp.<sup>b</sup></u>	<u>calc.</u>
<u>Cl</u> -M- <u>N(1)</u>	87.0	89.5
M- <u>N(1)</u> -N(1)	123.2	121.8
M- <u>N(1)</u> -N(2)	127.0	128.2
<u>N(1)</u> -N(2)-C	104.3	103.8
<u>N(2)</u> -C-N(2)	111.7	112.6

# Accomplishments: Task 3

## Calculations on M-BTT: H<sub>2</sub> binding

DFT calculations of H<sub>2</sub> binding are sensitive to functional used

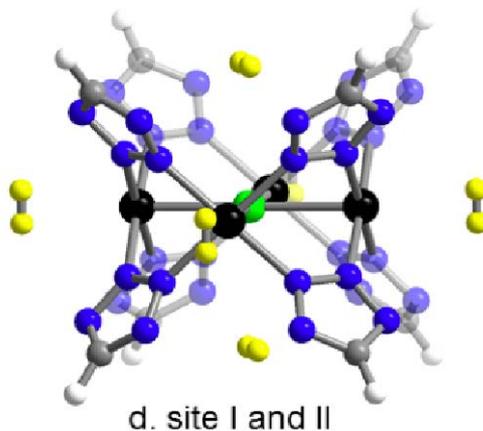
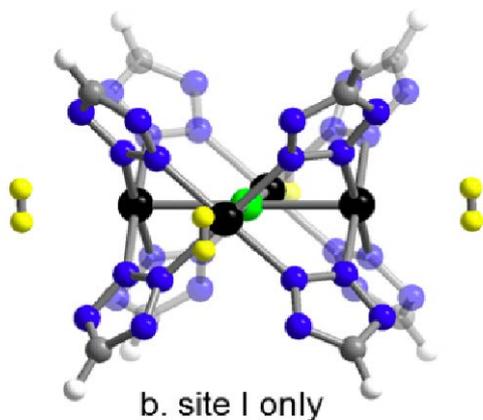
- ZPE and BSSE corrections are used for all calculations
- LDA, GGA (BP86) and hybrid (B3LYP) show large errors
- The range-separated dispersion-corrected functional ( $\omega$ B97X-D) is quite accurate

<u>functional</u>	<u>Mn: HBE</u> ( <u>kJ/mol</u> )	<u>Cu: HBE</u> ( <u>kJ/mol</u> )
LDA	-27.2	-18.9
BP86	-0.7	3.1
B3LYP	-2.7	1.3
$\omega$ B97X-D	-14.9	-9.4
<u>exp.</u>	-11.9	-10.4

*JACS 135, 1083 (2013)*

# Accomplishments: Task 3

## Calculations on M-BTT: M...H<sub>2</sub> & IR



		M = Mn		Cu		Zn
		calc.	exp.	calc.	exp.	calc.
HBE (kJ/mol)	site I only	-14.9	-11.9 <sup>a</sup>	-9.4	-10.4 <sup>a</sup>	-14.0
	site II only	-7.4		-6.9		-7.6
	site I + II	-11.0	-10.3 <sup>b</sup>	-8.5	-9.5 <sup>b</sup>	-11.5
H <sub>2</sub> distance (Å)	M...H <sub>2</sub> (site I)	2.33	2.27 <sup>c</sup>	2.56	2.47 <sup>c</sup>	2.27
	Cl...H <sub>2</sub> (site II)	3.25	3.47 <sup>c</sup>	3.20	3.46 <sup>c</sup>	3.22
Δν (cm <sup>-1</sup> )	site I	-125	-123 <sup>a</sup>	-78	-100 <sup>a</sup>	-129
	site II	-16	-31 <sup>a</sup>	-14	-41 <sup>a</sup>	-16

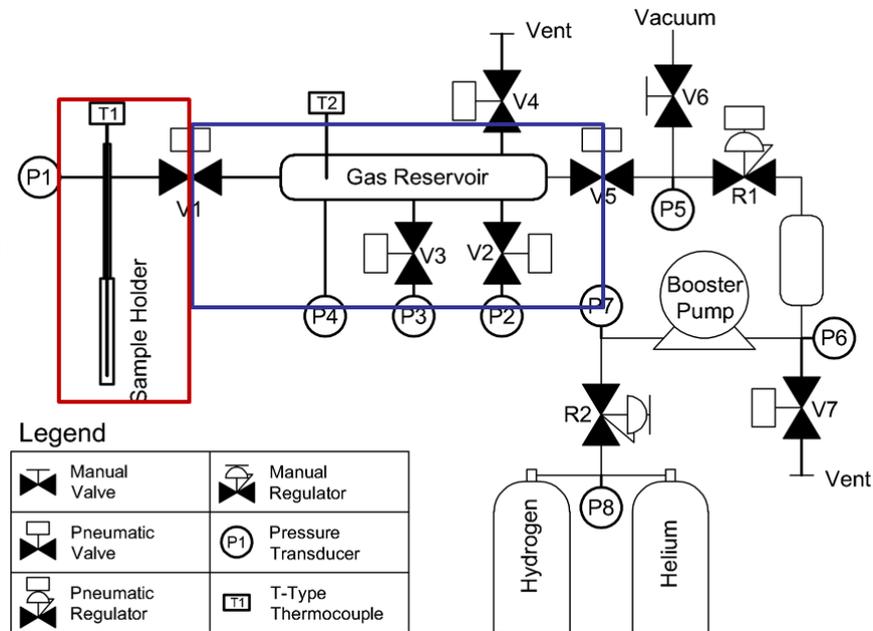
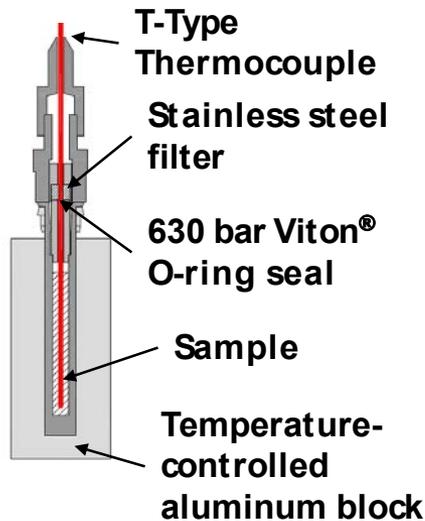
<sup>a</sup>Based on infrared data; <sup>b</sup>Zero-coverage isosteric heat of adsorption;

<sup>c</sup>Based on neutron diffraction data.

Calculated H<sub>2</sub> binding parameters agree with experimental values and can be used to explore possible new materials

# Accomplishments: Task 4

## High-Pressure H<sub>2</sub> Adsorption System



### Challenges of 350 bar H<sub>2</sub> measurements:

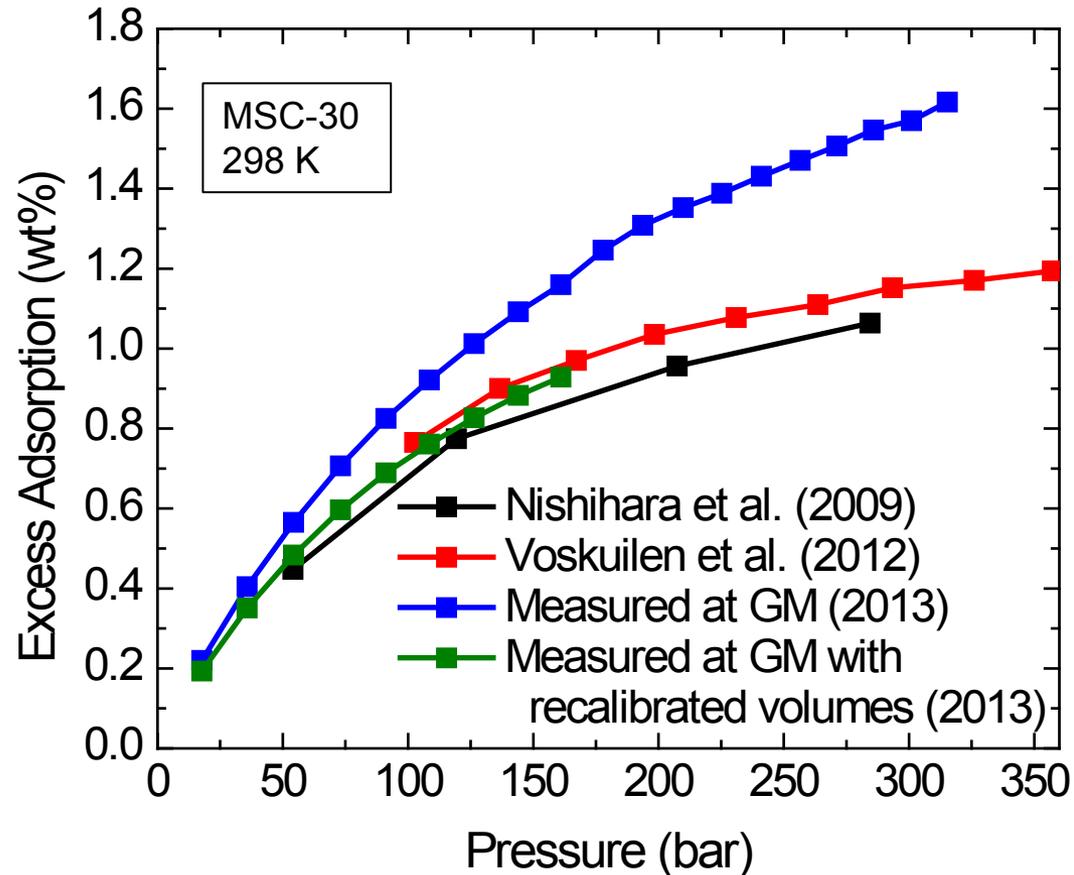
- System needs to be calibrated very well to minimize uncertainty
- 0.05 cm<sup>3</sup> reference volume error  
→ ~500 μmol deviation at 350 bar
- 0.5 g of MSC-30 adsorbs ~3000 μmol at 350 bar and 298 K
- Volumes needed recalibration after installation

- Max operating pressure: 344 bar
- Thermoelectric temperature control
- Large sample capacity (~500 mg)

# Accomplishments: Task 4

## Evaluation of Benchmark Materials

- Benchmark materials MSC-30 & MOF-177 measured for instrument validation
- Measurements taken after recalibration show good agreement with previous results (agreement is within uncertainty)
- High-pressure (>180 bar) range still needs to be recalibrated



# Collaborations

## Project team within DOE Fuel Cell Technologies Office:

- Lawrence Berkeley National Laboratory (prime, National Lab.)/UC Berkeley:
  - Jeffrey Long: Synthesis and basic characterization of MOFs
  - Martin Head-Gordon: Calculation and prediction of H<sub>2</sub> binding energies
- National Institute of Standards and Technology (sub, National Lab.):
  - Craig Brown: Neutron diffraction and neutron spectroscopy
- General Motors Company (sub, Industry):
  - Anne Dailly: Measurement of high-pressure H<sub>2</sub> uptake capacity

## Additional collaborations:

- Oberlin College (University):
  - Stephen Fitzgerald: Infrared spectroscopy
- Purdue University (University):
  - Timothée Pourpoint: Development of high-pressure H<sub>2</sub> adsorption system



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# Proposed Future Work

## Task 1: Synthesis of Metal-Organic Frameworks

- Continue structural characterization of Al-BTB and  $\text{Ti}_3\text{O}(\text{BDC})_3$
- Scale up synthesis of bipyridine containing MOFs and insert metal cations
- Use *in silico* screening technique to discover new materials with optimal opposing surface distances
- Complete synthesis of catechol and biphenol type ligands and prepare new MOFs with these ligands containing post-synthetically inserted ligands

## Task 2: Characterization of Framework- $\text{H}_2$ Interactions

- Solve structure for new Co-MOF74'
- Understand structural loading dependence with  $\text{H}_2$
- Complete Milestone for demonstrating utility of techniques
- Obtain newest MOFs from Long Group
- Perform diffraction measurements on most promising candidates, to give feedback on highest adsorption sites to partners



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# Proposed Future Work

## Task 3: First-Principles Calculations of Hydrogen Binding Enthalpies

- Modifications to Al(OH)bpydc (MOF-253) based on metal insertions at the bpy binding site. Explore H<sub>2</sub> binding in this system as a function of metal and counter ions, and linker modifications
- Exploring metal insertions in deprotonated catechols. What are the solvent binding energies (for desolvation)? Make reliable H<sub>2</sub> binding predictions for complete and partial desolvation
- Design principles for target H<sub>2</sub> binding energies. Identify the relevant descriptors as a basis for rational design

## Task 4: High-Pressure H<sub>2</sub> Adsorption Measurements

- Further validate high-pressure H<sub>2</sub> adsorption in metal-organic frameworks and compare results to theoretical and spectroscopic predictions
- Modify instrument program and test commercially available (benchmark) MOF samples for 20-30 cycles up to 350 bar
- Test high performing MOFs for 100 cycles up to 350 bar



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# Summary

- A variety of expanded MOF-74 analogues, showing high surface area and high H<sub>2</sub> binding enthalpies have been synthesized
- Neutron powder diffraction and inelastic scattering have been utilized to solve new structures and characterize the strength of M<sup>2+</sup>-H<sub>2</sub> interactions
- Calculated H<sub>2</sub> binding enthalpies show excellent agreement with experimental values
- High-pressure adsorption system validated, calibrations are ongoing
- The combination of theoretic predictions, synthetic work, and structural characterization will be used to prepare new frameworks with a larger density of strong H<sub>2</sub> binding sites

Capacity	2012	2013	2017*	Ultimate*
Gravimetric	0.016 kg H <sub>2</sub> /kg adsorbent	0.016 kg H <sub>2</sub> /kg adsorbent	0.055 kg H <sub>2</sub> /kg system	0.075 kg H <sub>2</sub> /kg system
Volumetric	0.011 kg H <sub>2</sub> /L adsorbent	0.011 kg H <sub>2</sub> /L adsorbent	0.040 kg H <sub>2</sub> /L system	0.070 kg H <sub>2</sub> /L system

\*DOE targets



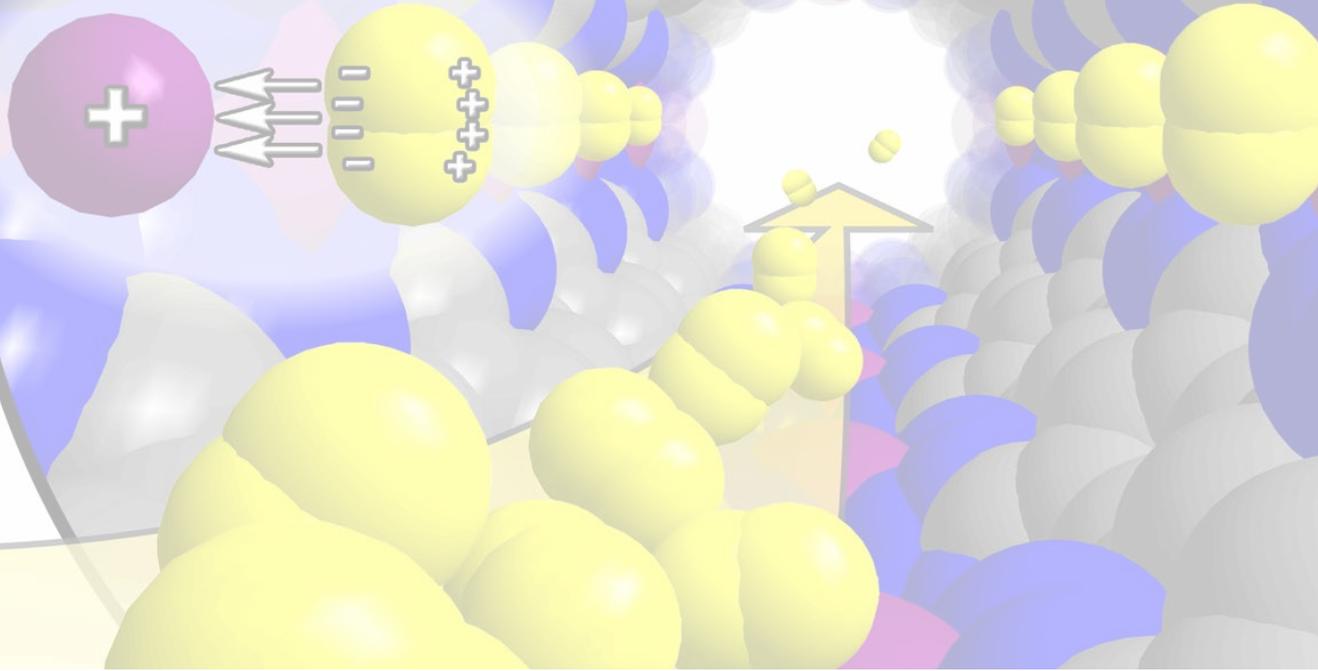
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# Technical Back-Up Slides



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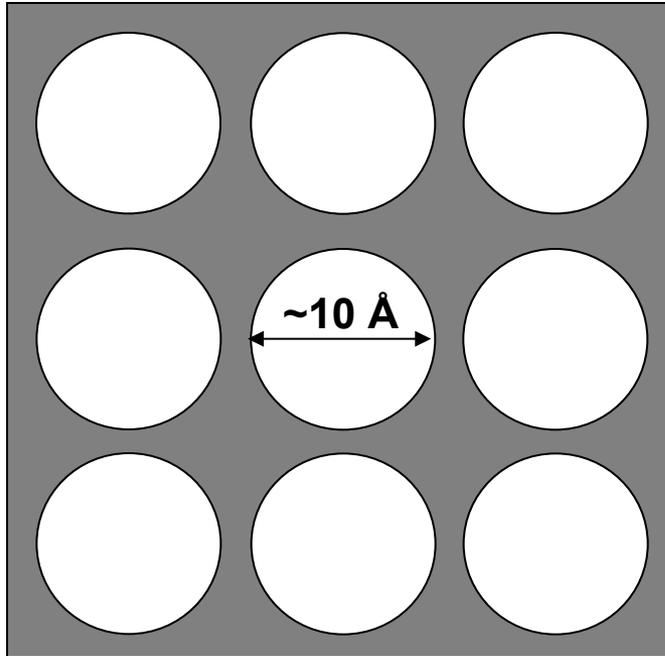


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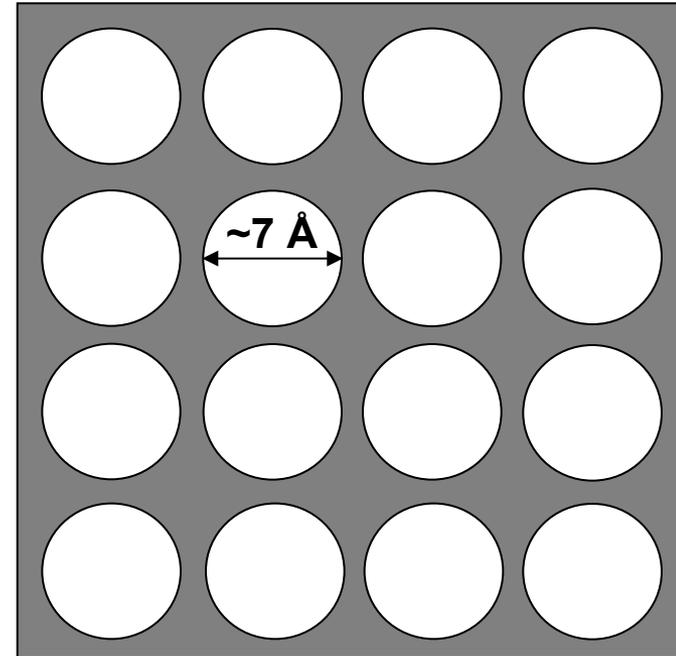
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# Optimum Pore Sizes for Hydrogen Storage

77 K



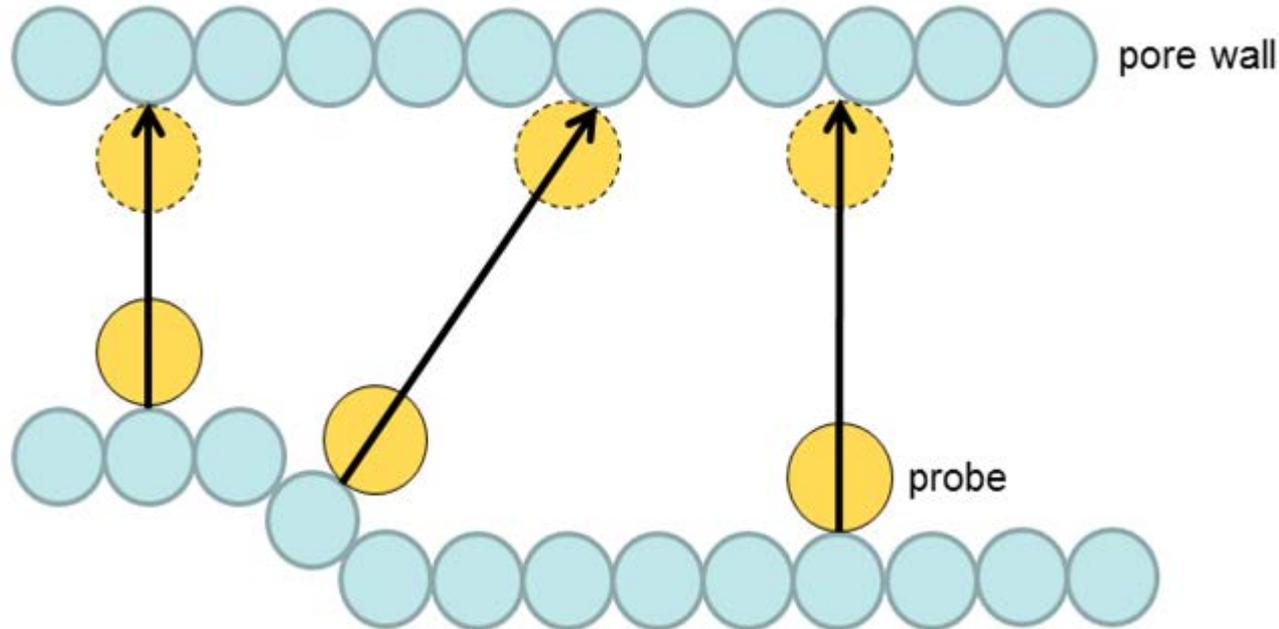
298 K



□ Calculated using Monte Carlo simulations with both cylindrical and slit pores

*Rzepka, Lamp, de la Casa-Lillo J. Phys. Chem. B* **1998**, 102, 10894

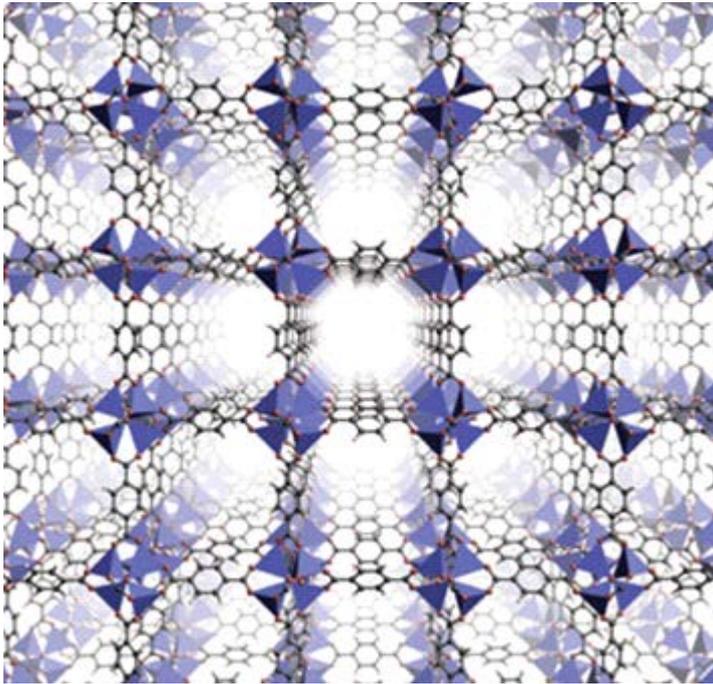
# Geometric Calculation of Opposing Wall Distances



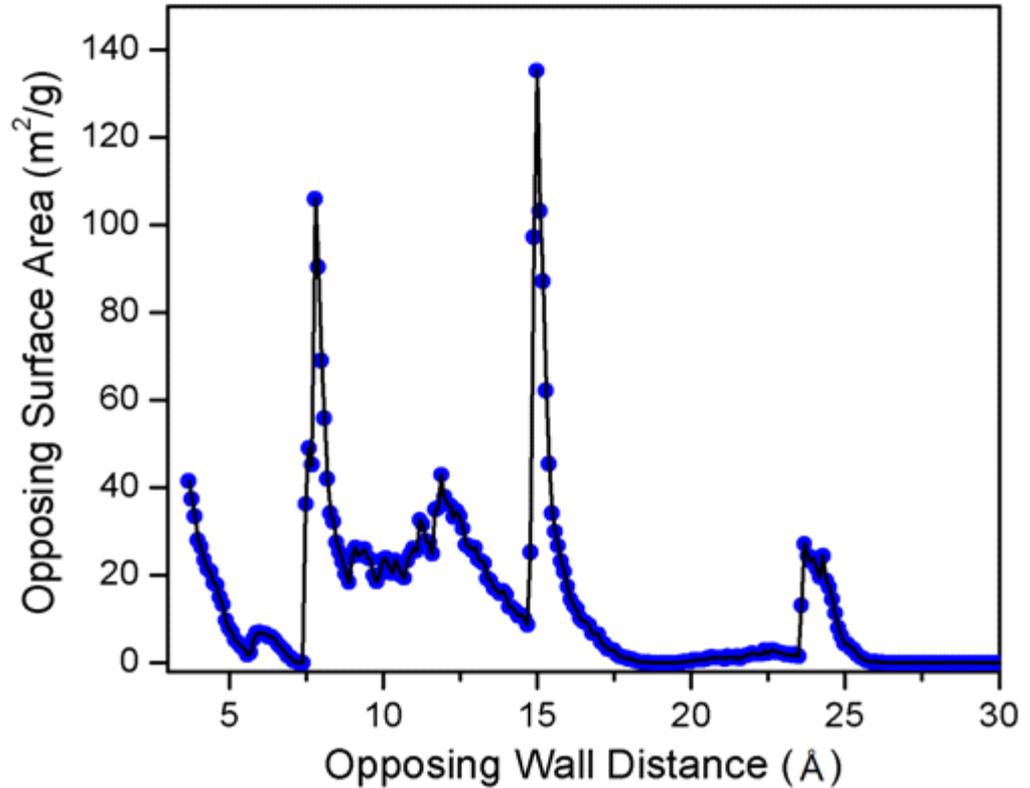
- Probe is inserted on the pore surface, and moved away in a direction normal to the surface until it collides with the opposing wall
- This is repeated until the entire pore surface has been traversed by the algorithm to create a distribution of opposing wall distances

*Sumida, Rogow, Herm, Long, submitted*

# Opposing Surface Area Distribution (OSAD)



MOF-5



*Sumida, Rogow, Herm, Long, submitted*

# Synthesis of $Mg_2(dobpdc)$

