

2016 DoE Hydrogen and Fuel Cells Program Review

Hydrogen Storage Characterization and Optimization Research Effort

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Project ID #: ST133

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Start: October 2015
- Finish: September 2018

Budget

- Project Start Date: 10/01/2015
- FY16 DoE Funding:
 - \$795k
- DoE funding received to date:
 - \$795k
- Matching fellowship support:
 - \$197k

Barriers Addressed

- A. System Weight and Volume

Partners

- LBNL: IR, synthesis, and modeling
- NREL: synthesis and measurements
- PNNL: modeling and NMR
- NIST: neutron diffraction
- Project lead: Thomas Gennett (NREL)

Relevance

Project objectives

- Develop *in situ* infrared spectroscopy as a tool for characterizing emerging H₂ storage materials that may allow for a driving range greater than 300 miles.
- Materials sought with the potential for meeting the DoE targets of reversible uptake:
 - 2020 targets: 5.5 % H₂ by mass, volumetric capacity of 40 g/L
 - “ultimate full fleet” targets: 7.5 % H₂ by mass, 70 g/L.
- Validate new concepts for H₂ storage mechanisms in adsorbents.
- Provide accurate computational modeling for H₂ adsorbed in porous materials.

This reporting period

- Research and development of metal-organic framework materials with high volumetric and gravimetric H₂ capacities (Barrier A).

Role of LBNL within the Effort

Hydrogen Storage Characterization and Optimization Research Effort

Researchers at NREL, LBNL, PNNL, and NIST are tasked with supporting the DoE Hydrogen Storage Program through validation of:

- 1) Properties of emerging hydrogen storage materials
- 2) New concepts for hydrogen storage mechanisms
- 3) Computational methods for predicting hydrogen storage properties

LBNL:

- 1) IR spectroscopy with precise H₂ dosing at $T = 10\text{-}300\text{ K}$, $P \leq 100\text{ bar}$
- 2) Mechanistic validation:
 - Can exposed cations in adsorbents reach target of $\Delta H = -15\text{ kJ/mol}$?
 - Is it possible to adsorb two, three, or four H₂ per metal cation?
- 3) Accurate modeling of H₂ adsorbed within porous materials

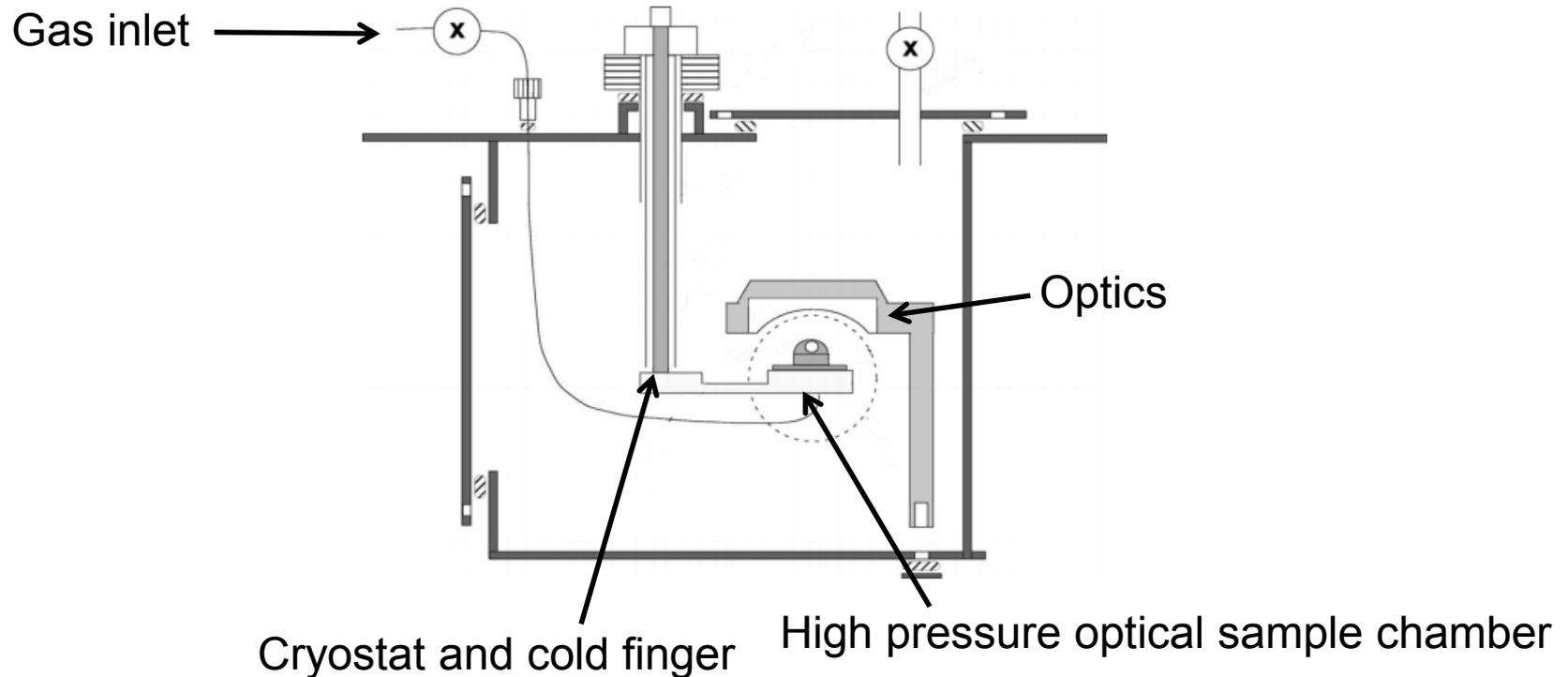
FY16 *In Situ* Infrared Spectroscopy Milestones

Q2: Evaluate choices for various infrared spectrometer setups for *in situ* gas dosing. *100% complete*

Q3: Order DRIFTS instrument that will be best and most functional for the desired *in situ* H₂-dosed experiments over a temperature range of 15-373 K and up to 100 bar hydrogen pressure at 298 K based on experience testing several similar instruments. *100% complete*

Q4: Complete installation of the DRIFTS instrument and demonstrate that the DRIFTS instrument is operating with a resolution of 10 cm⁻¹ by measuring spectra for a sorbent standard and comparing with accepted published data. *0% complete*

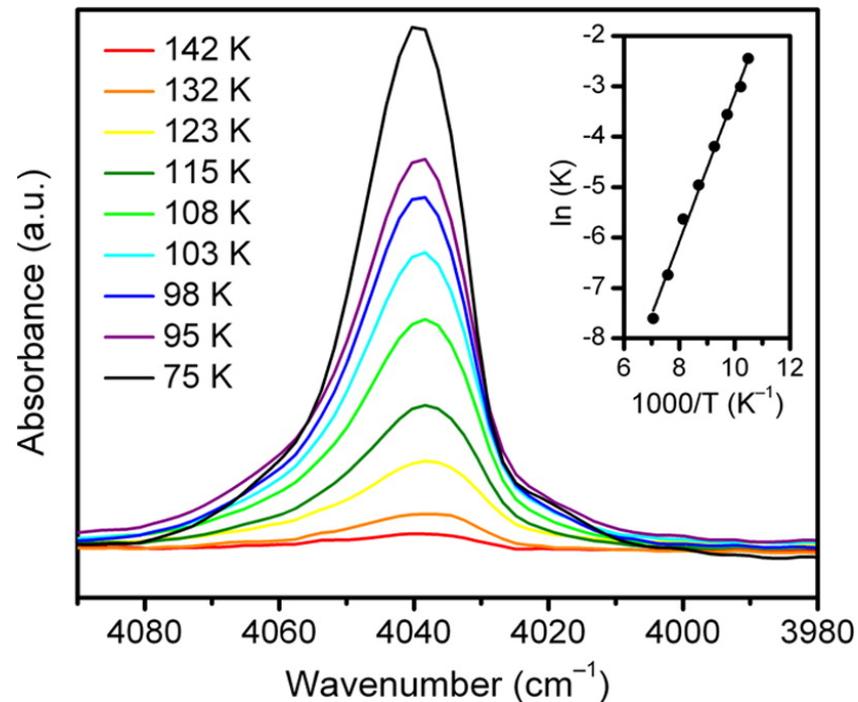
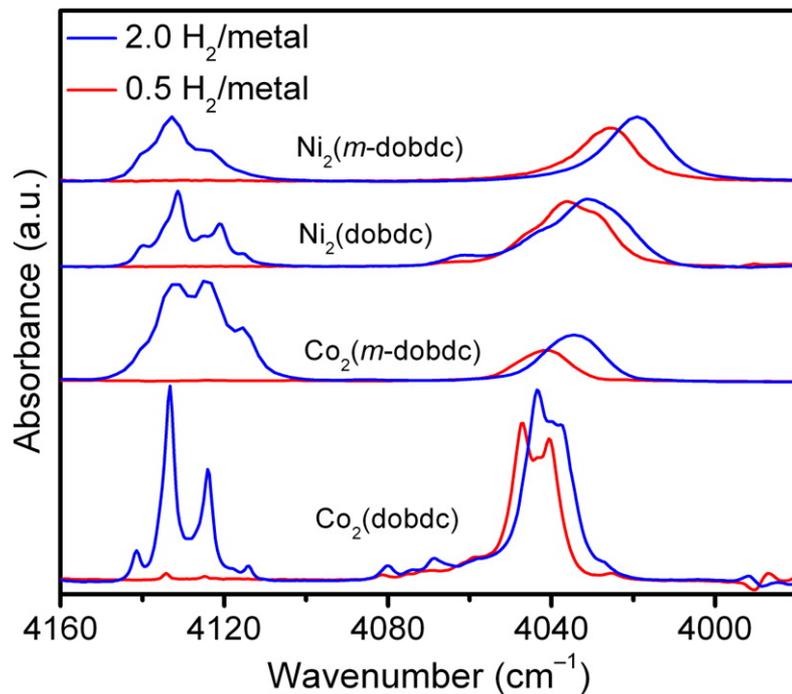
In Situ Infrared Spectroscopy



- Infrared spectroscopy with *in situ* gas dosing probes behavior of adsorbed species
- Allows investigation of adsorption in crystalline and non-crystalline materials

Fitzgerald, Churchill, Korngut, Simmons, Strangas *Rev. Sci. Instrum.* **2006**, 77, 093110

In Situ Infrared Spectroscopy



- H_2 molecules adsorbed on different sites have different infrared energy shifts
- Shift of H_2 signals correlates to changes in isosteric heats of adsorption
- Measurements at multiple temperatures yield site-specific enthalpies of adsorption

Kapelewski, Geier, Hudson, Stuck, Mason, Nelson, Xiao, Hulvey, Gilmour, FitzGerald, Head-Gordon, Brown, Long *J. Am. Chem. Soc.* **2014**, *136*, 12119

Relevance: DoE 2020 Hydrogen Storage System Targets and FY16 Project Targets

DoE 2020 Storage Targets

gravimetric capacity	5.5 wt % H ₂
volumetric capacity	40 g H ₂ /L
operating temperature	-40 to 60 °C
maximum pressure	100 bar (project target)
refueling rate	1.67 kg H ₂ /min
cycle life	1500 cycles
cost	\$333 per kg H ₂

FY16 Targets

Q1: Computational chemists will initiate investigation of the most promising structures for the desired pore domain size and chemistry within porous aromatic frameworks (PAFs) or block copolymer, (BCP) using first-principles electronic structure calculations with range separation and dispersion corrections. *100% complete*

Q2: Synthesize a porous aromatic frameworks material with metal-chelating sites and a Langmuir surface area of at least 1000 m²/g. *100% complete*

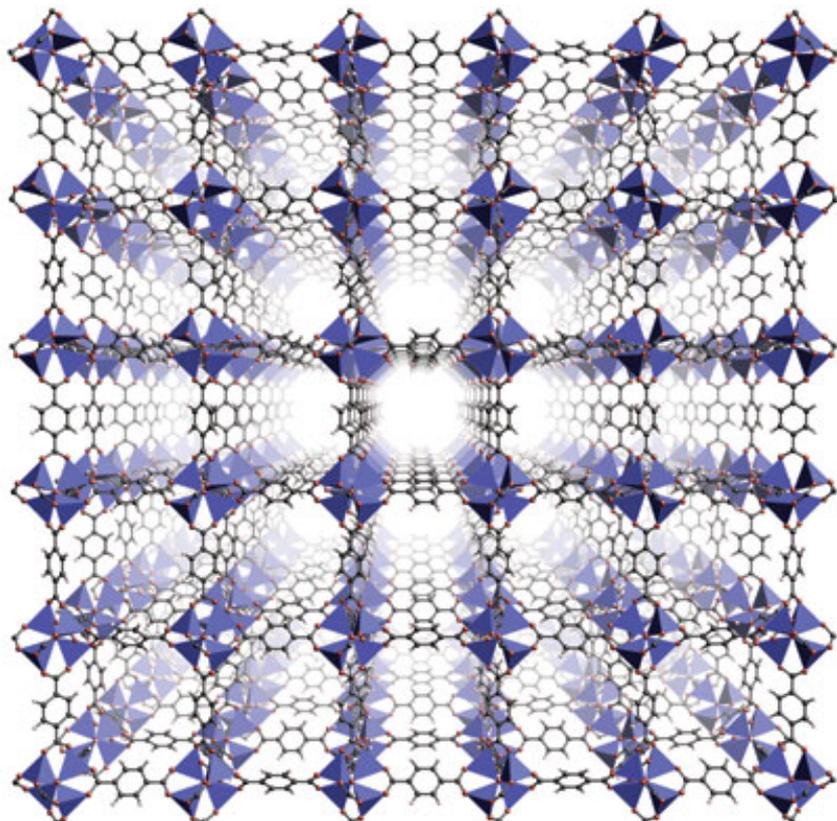
Q3: Synthesize and characterize a carbon based sorbent with catechol functionalized pore domains that contain unsaturated metal centers attached to the materials matrix. *95% complete*

Q4 Go/No-Go: Demonstrate the ability to bind two H₂ molecules to one metal center in a metal-organic framework, porous aromatic framework, or carbon-based material. *100% complete*

- MOFs can meet volumetric capacity in relevant temperature range if multiple H₂ molecules can be bound to each metal center

http://energy.gov/sites/prod/files/2015/05/f22/fcto_myRDD_storage.pdf

Approach: Metal-Organic Frameworks



$\text{Zn}_4\text{O}(1,4\text{-benzenedicarboxylate})_3$

MOF-5

BET surface areas up to 7100 m²/g

Densities as low as 0.13 g/cm³

Tunable pore sizes up to 10 nm

Channels connected in 1-, 2-, or 3-D

Internal surface can be functionalized

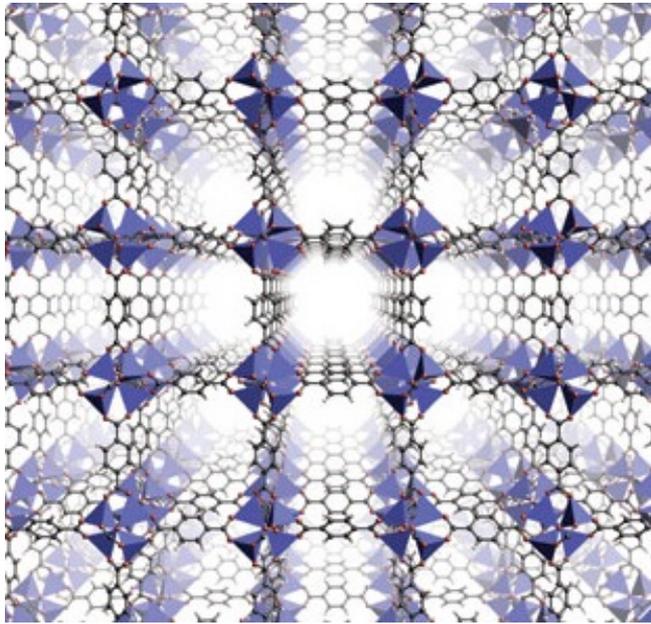
Can these high-surface area materials be used for hydrogen storage at ambient temperatures?

Yaghi et al. *Nature* **2003**, 423, 705

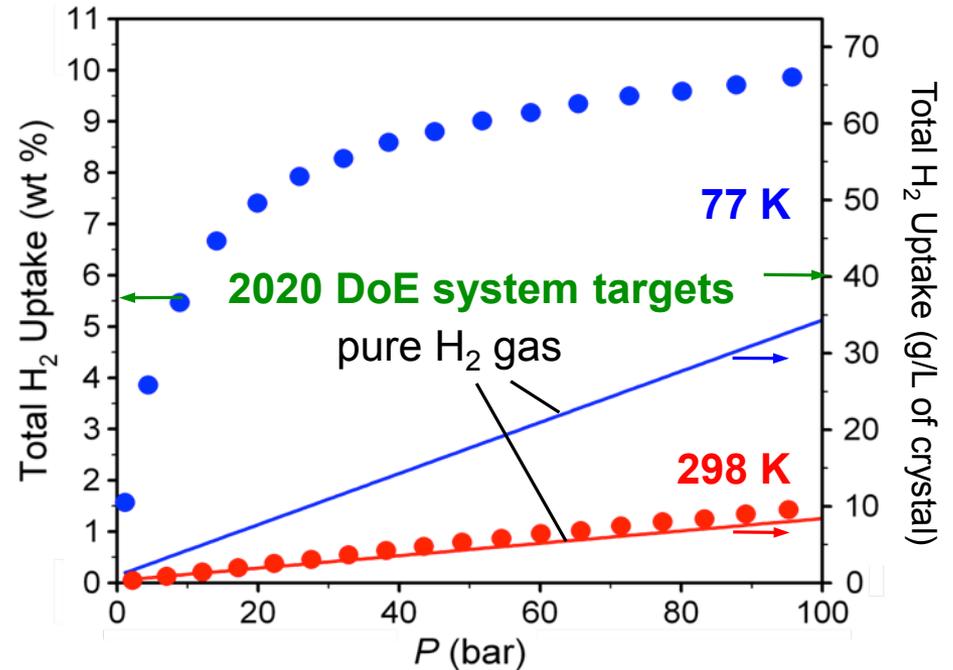
Kitagawa et al. *Angew. Chem., Int. Ed.* **2004**, 43, 2334

Férey *Chem. Soc. Rev.* **2008**, 37, 191

Hydrogen Storage in MOF-5



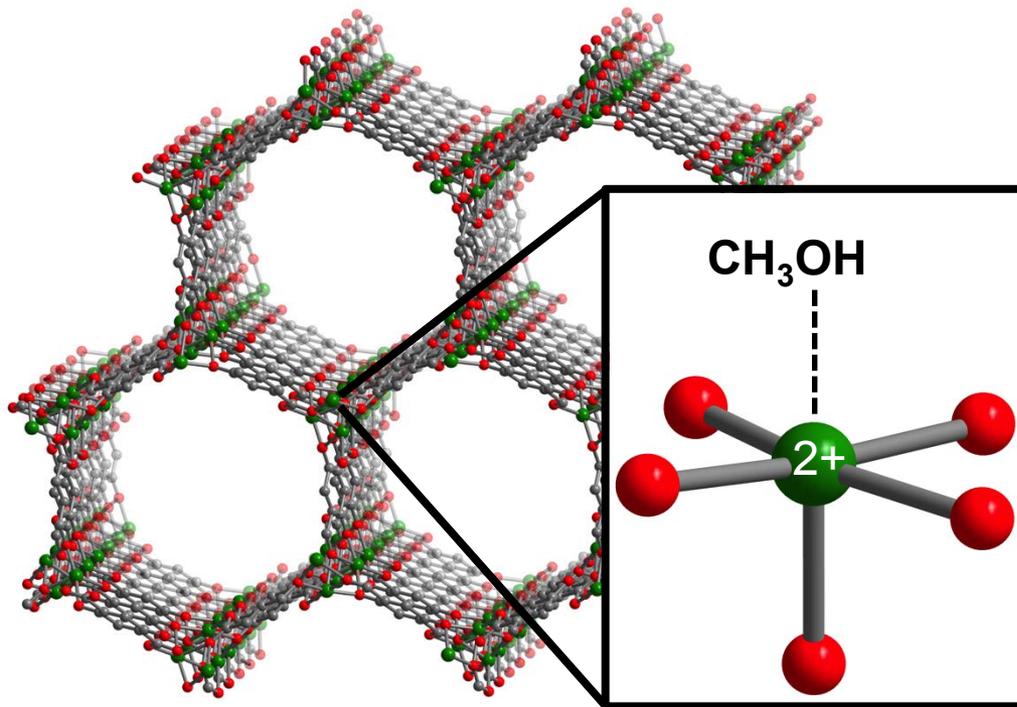
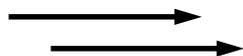
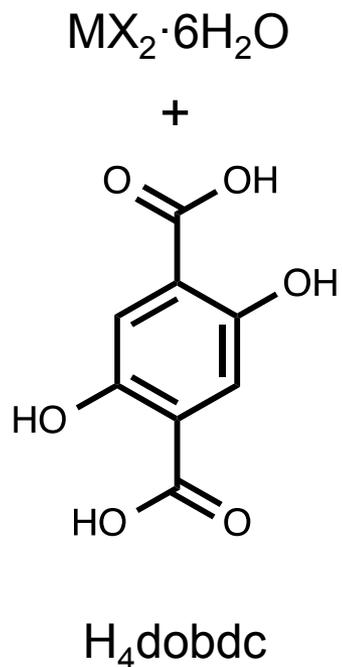
MOF-5



- At 100 bar and 77 K, a record physisorbed storage density of 66 g/L is achieved
- At 298 K, framework offers little improvement over density of pure H₂ gas

Kaye, Dailly, Yaghi, Long *J. Am. Chem. Soc.* **2007**, 129, 14176

A MOF with a High Density of Exposed M^{2+} Sites

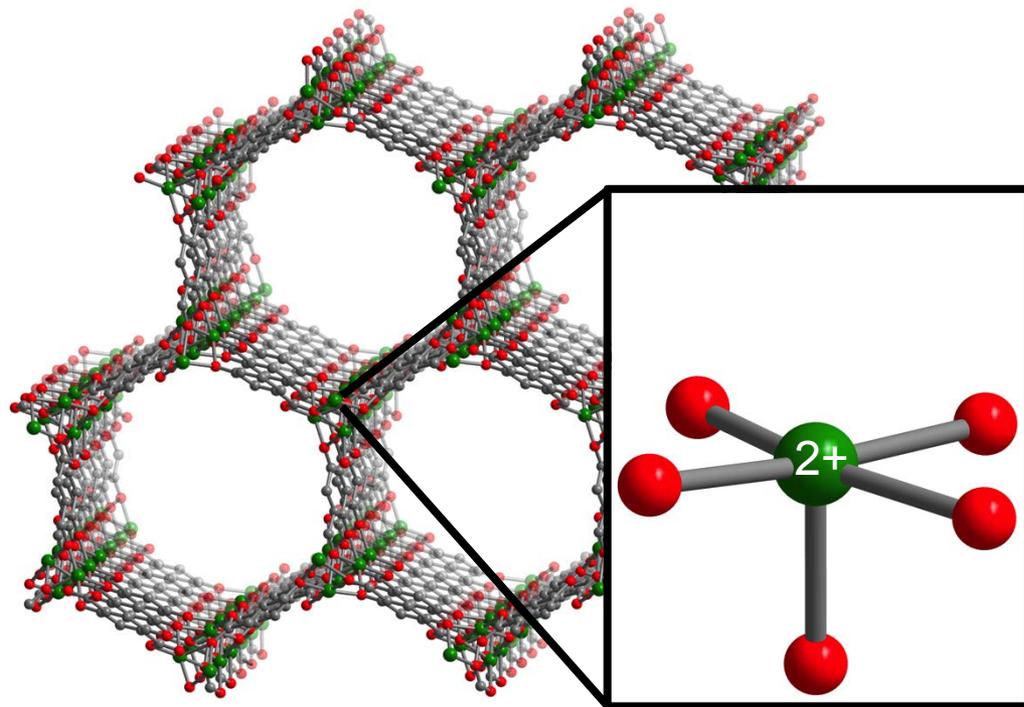
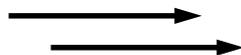
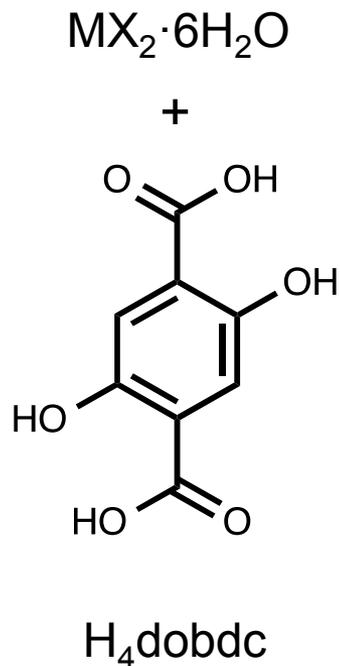


$M_2(dobdc)$, M-MOF-74

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

□ Activated frameworks have Langmuir surface areas of 1277-2060 m^2/g

A MOF with a High Density of Exposed M^{2+} Sites

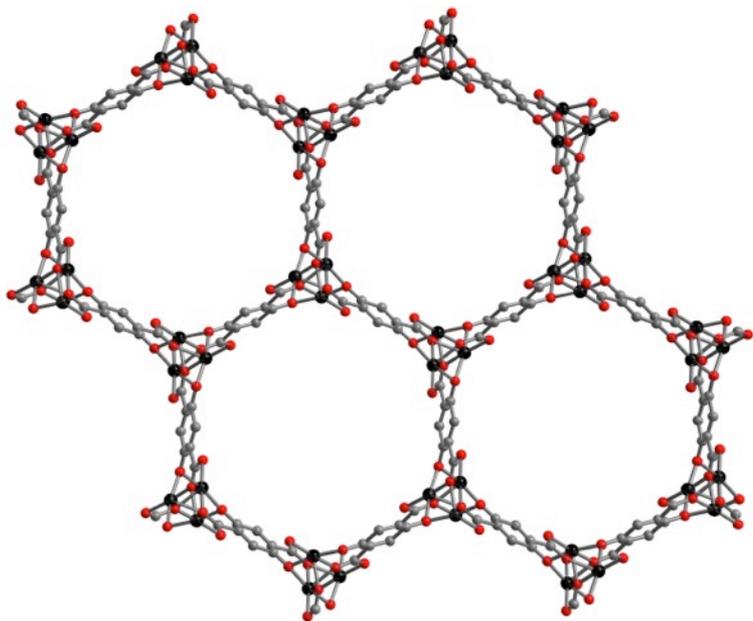


$M_2(dobdc)$, M-MOF-74

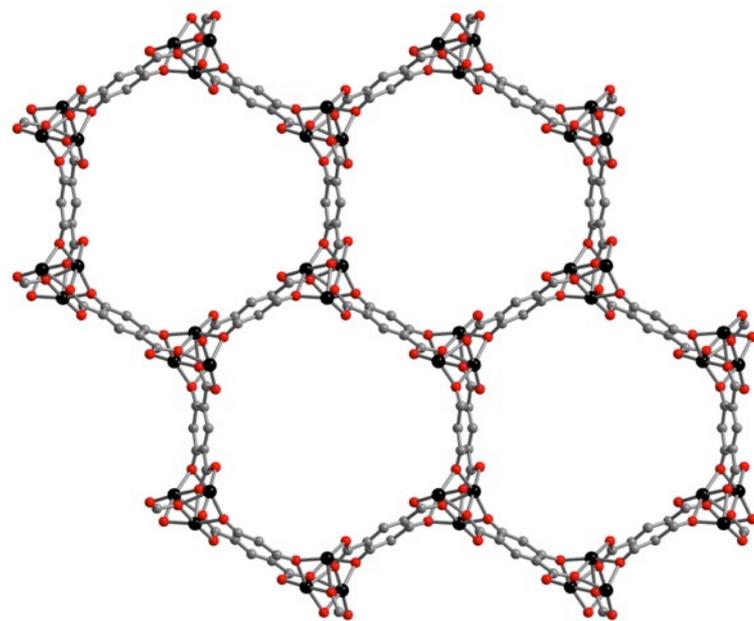
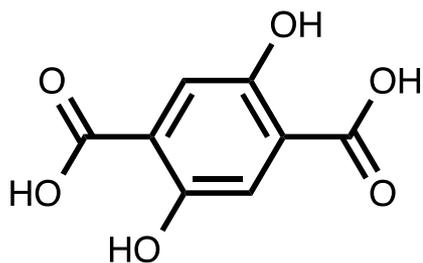
(M = Mg, Mn, Fe, Co, Ni, Cu, Zn)

- Desolvation leads to square pyramidal M^{2+} centers with an open coordination site

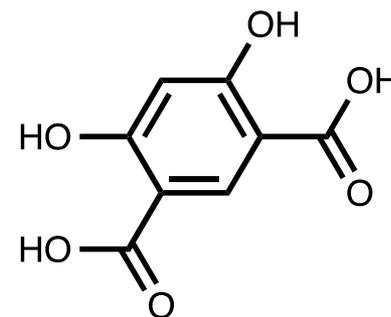
Approach: Synthesis of a Structural Isomer of $M_2(\text{dobdc})$



$H_4(\text{dobdc})$



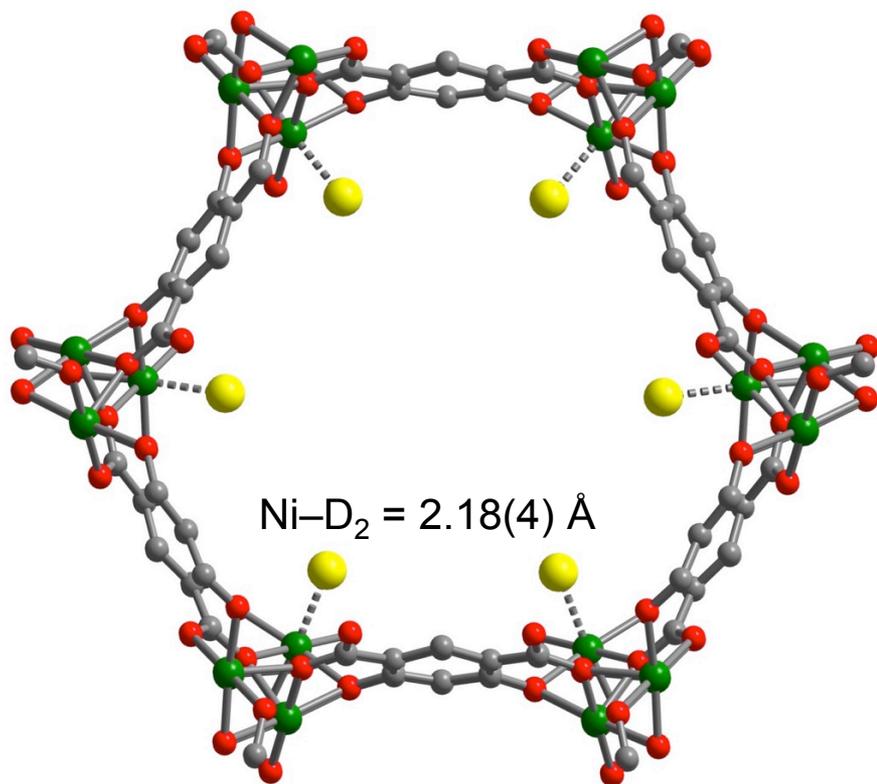
$H_4(m\text{-dobdc})$



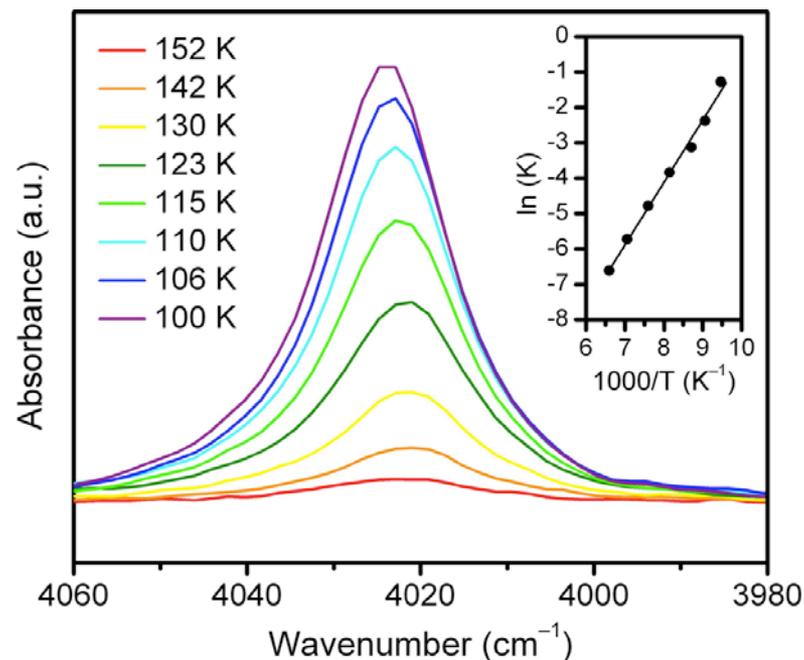
Kapelewski, Geier, Hudson, Stuck, Mason, Nelson, Xiao, Hulvey, Gilmour, FitzGerald, Head-Gordon, Brown, Long *J. Am. Chem. Soc.* **2014**, *136*, 12119

Strong H₂ Binding in Ni₂(*m*-dobdc)

Neutron Diffraction



Infrared Spectroscopy



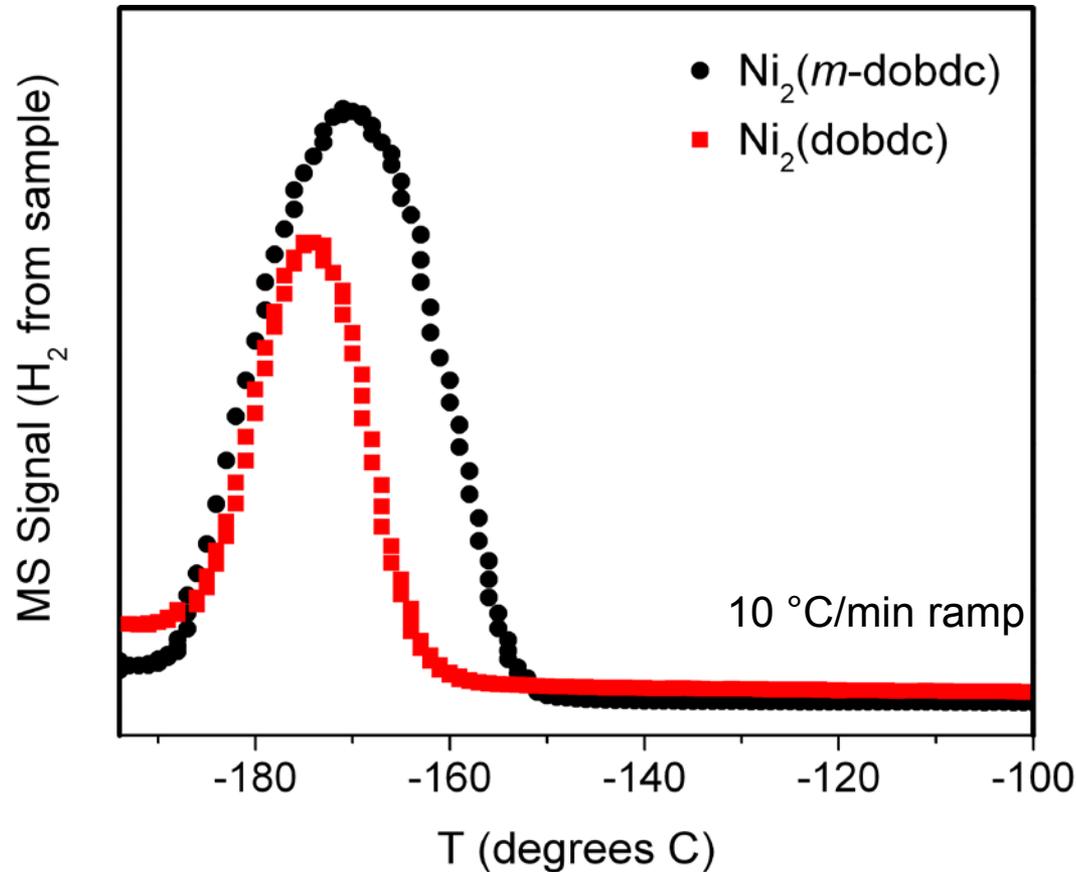
$$\Delta H_{\text{ads}} = -13.7 \pm 0.5 \text{ kJ/mol}$$

(Ni₂(dobdc): -12.3 ± 0.5 kJ/mol)

- High charge density at Ni²⁺ pulls H₂ close and gives record MOF binding energy

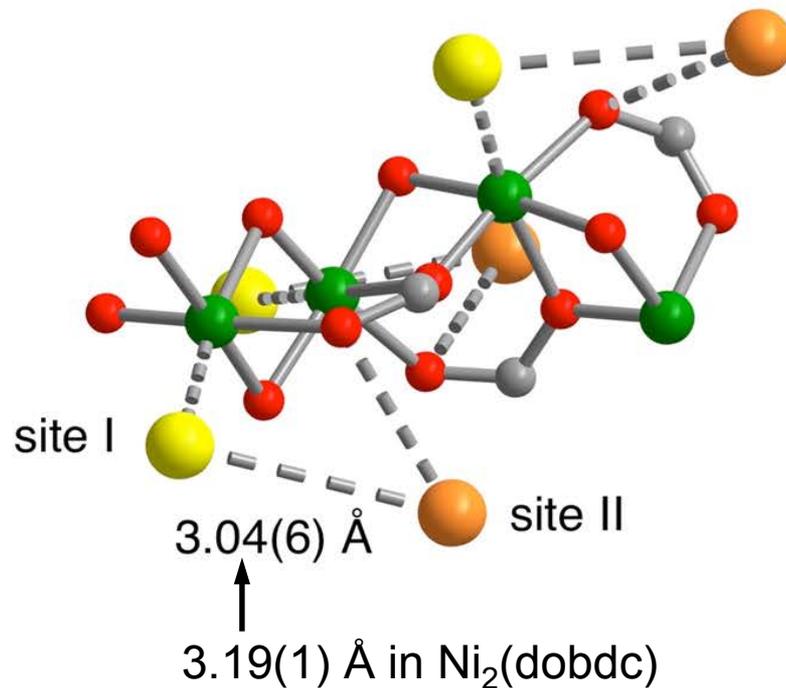
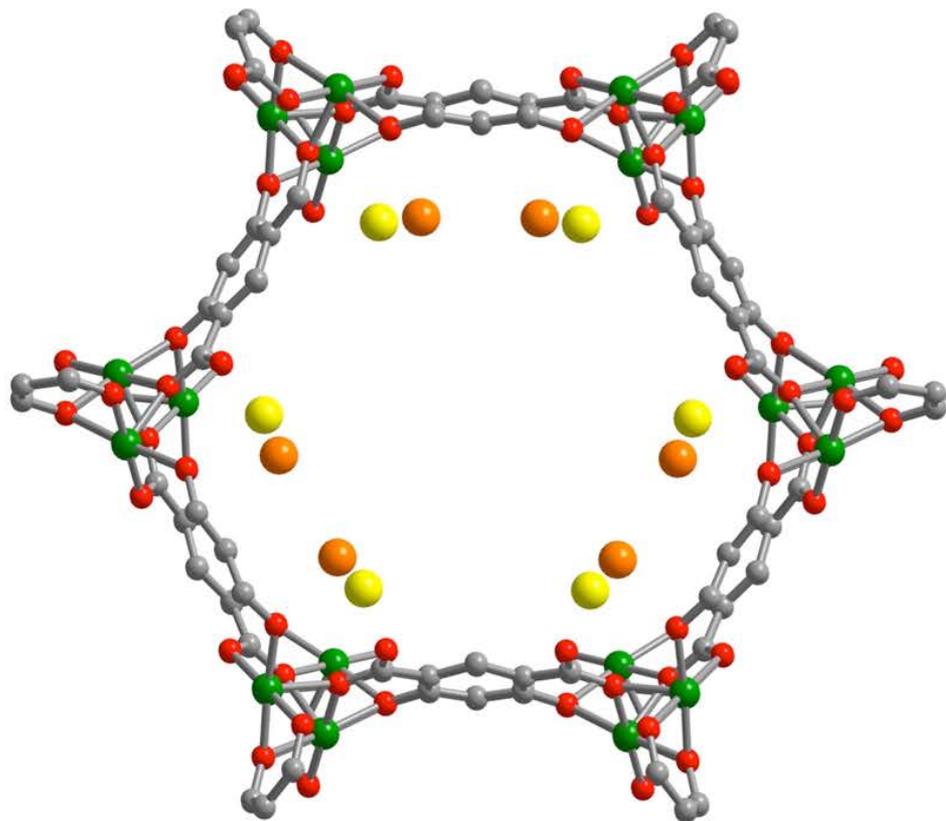
Kapelewski, Geier, Hudson, Stuck, Mason, Nelson, Xiao, Hulvey, Gilmour, FitzGerald, Head-Gordon, Brown, Long *J. Am. Chem. Soc.* **2014**, *136*, 12119

NREL: Temperature Programmed H₂ Desorption



- H₂ desorbs from Ni₂(*m*-dobdc) at higher T , consistent with stronger binding

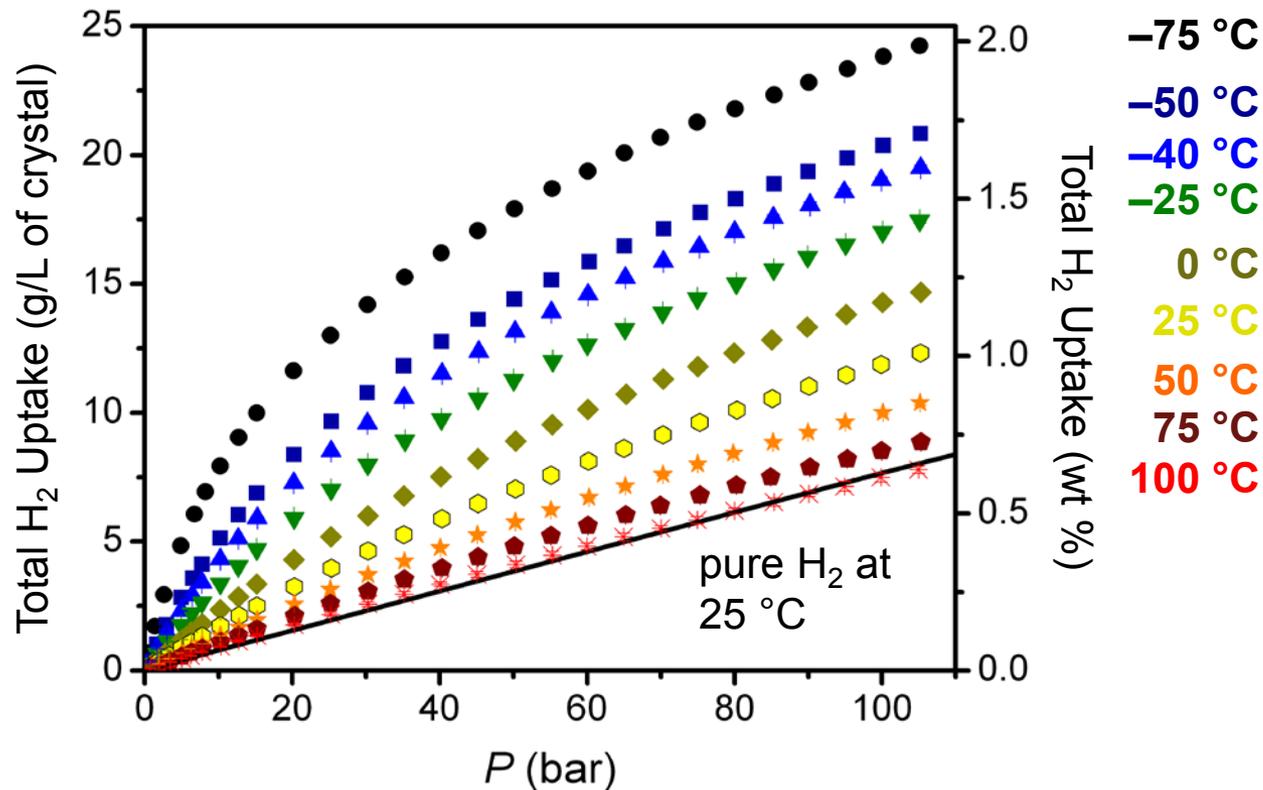
Close D₂ Packing within Ni₂(*m*-dobdc)



□ Greater charge density at Ni²⁺ gives closer packing for secondary adsorption site

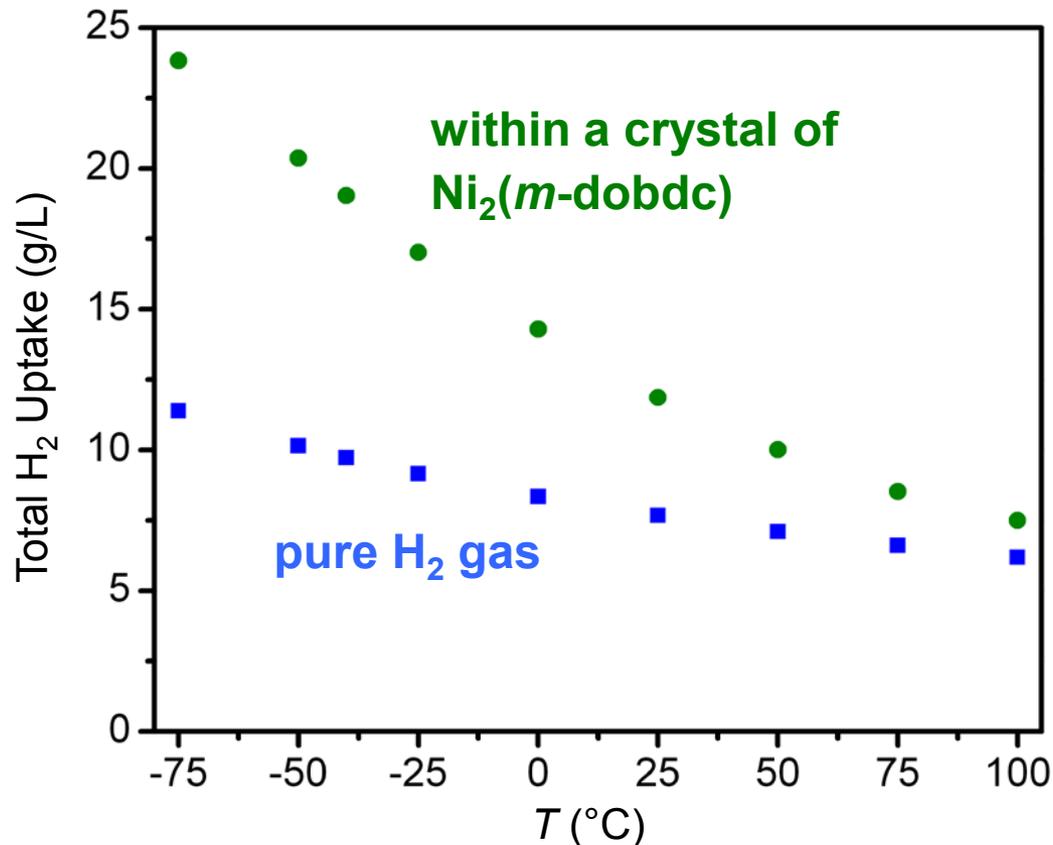
Kapelewski, Geier, Hudson, Stuck, Mason, Nelson, Xiao, Hulvey, Gilmour, FitzGerald, Head-Gordon, Brown, Long *J. Am. Chem. Soc.* **2014**, *136*, 12119

High Pressure H₂ Adsorption in Ni₂(*m*-dobdc)



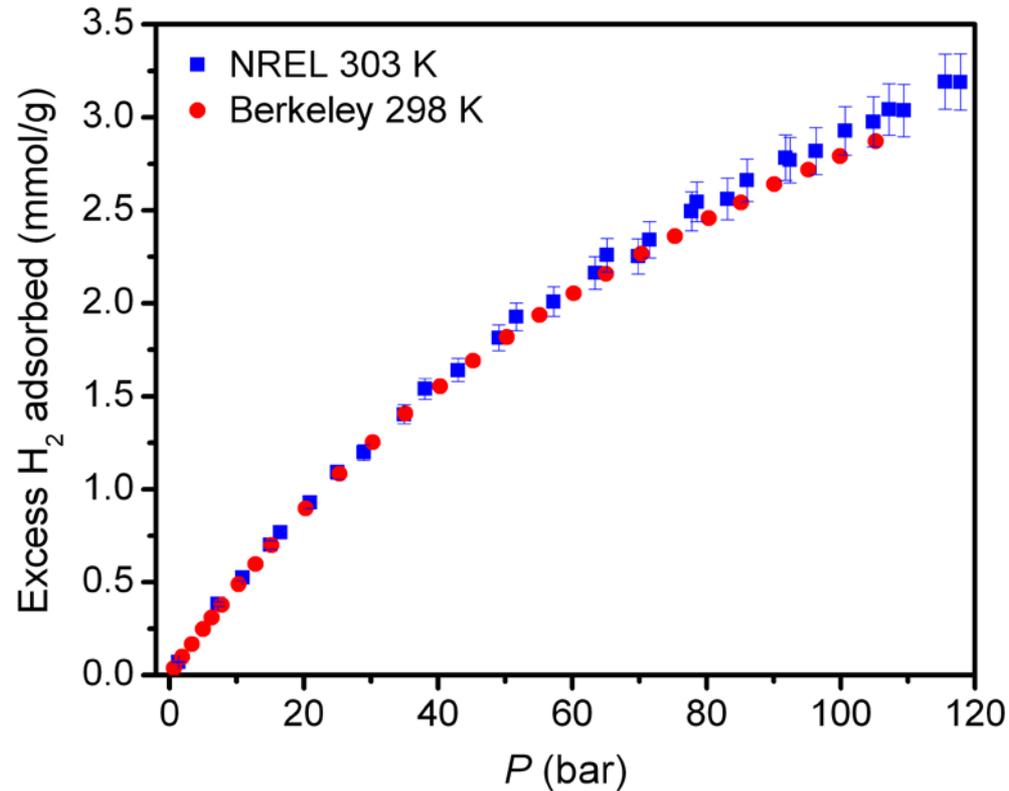
- Below 100 °C, all isotherms show greater capacity than compressed H₂ at 25 °C
- Ni₂(*m*-dobdc) has a total capacity of 24 g/L of crystal at -75 °C and 100 bar

Increased H₂ Density in Ni₂(*m*-dobdc) at 100 bar



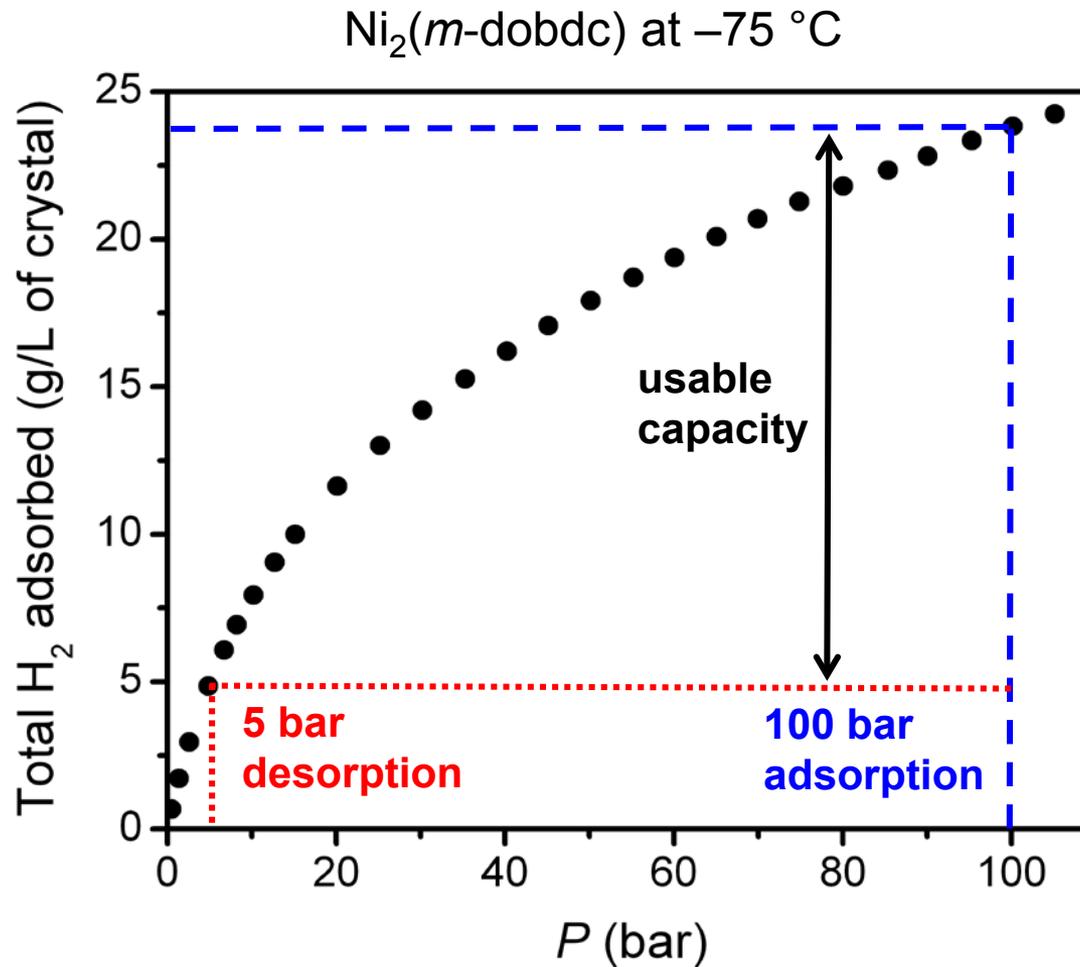
- Ni₂(*m*-dobdc) shows increasing boost in capacity with decreasing temperature

Ni₂(*m*-dobdc) Berkeley/NREL Comparison



- Collaboration with NREL used to verify H₂ isotherms in Ni₂(*m*-dobdc)
- Data matches within error

Accomplishments: H₂ Volumetric Usable Capacity

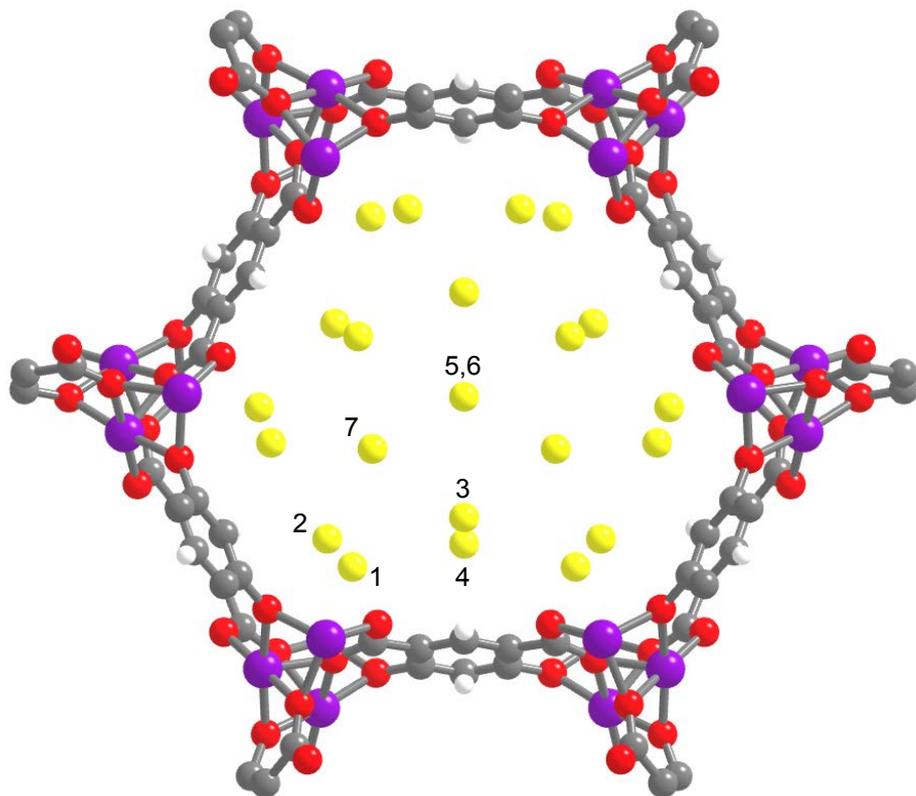


H₂ Usable Capacities in g/L of Crystal

	Ni ₂ (<i>m</i> -dobdc)	Co ₂ (<i>m</i> -dobdc)	Ni ₂ (dobdc)	Co ₂ (dobdc)	MOF-5
25 °C, no swing	11.0	10.5	9.9	8.8	8.8
-75 °C, no swing	19.0	18.2	18.4	16.5	15.8
-40 to 25 °C	18.2	17.3	16.6	14.0	12.8
-75 to 25 °C	23.0	21.9	21.4	18.3	16.5
-75 to 100 °C	23.4	22.3	21.8	18.6	16.7

- Values represent maximum capacity possible and will be reduced depending on packing
- Ni₂(*m*-dobdc) is the top-performing adsorbent for these temperatures
- 23.0 g/L usable capacity for -75 °C to 25 °C swing represents **58% of system target**

High Pressure Neutron Diffraction in $\text{Co}_2(m\text{-dobdc})$



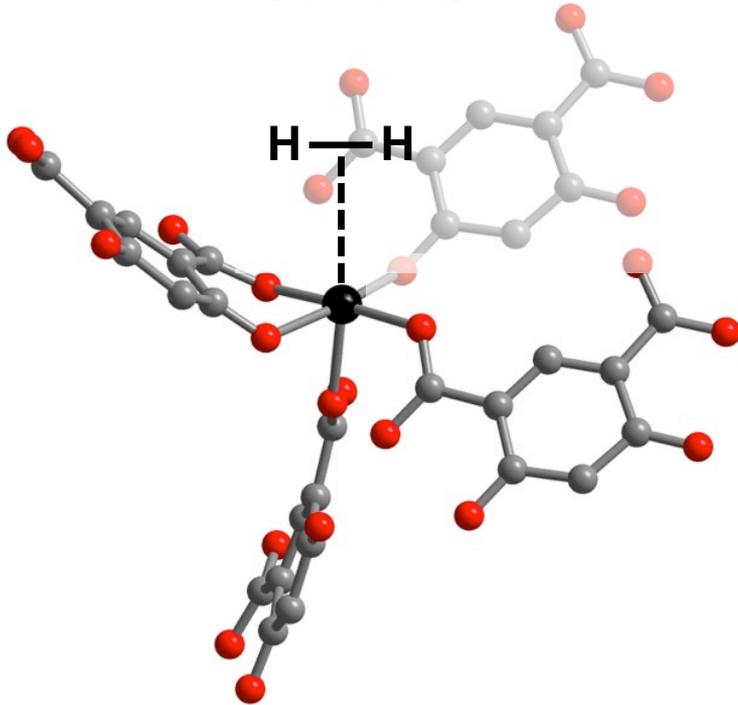
$\text{D}_2 \cdots \text{D}_2$ interaction	distance (Å)
1 \cdots 2	2.82(3)
2 \cdots 2	3.02(3)
3 \cdots 4	3.09(5)
4 \cdots 5	3.48(3)
solid H_2^*	3.20
liquid H_2	3.61

*van Kranendonk, Gush *Phys. Lett.* **1962**, 1, 22

- Seven distinct D_2 adsorption sites are observed at 78 bar and 77 K

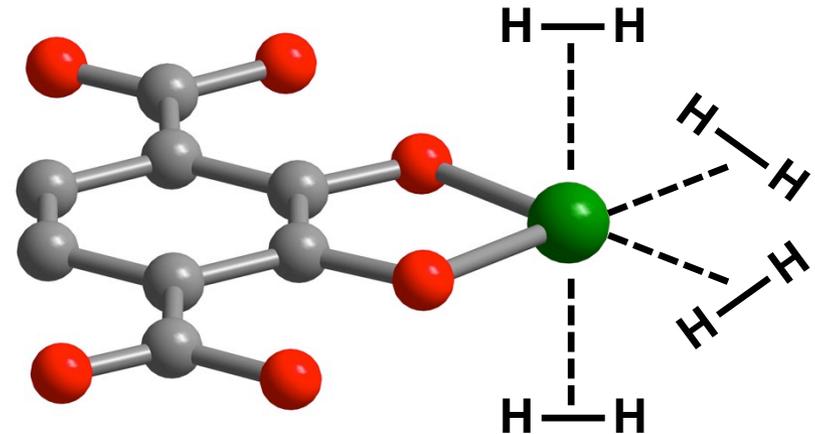
Binding Multiple H₂ Molecules per Metal Cation

Classical



1 H₂ per metal cation

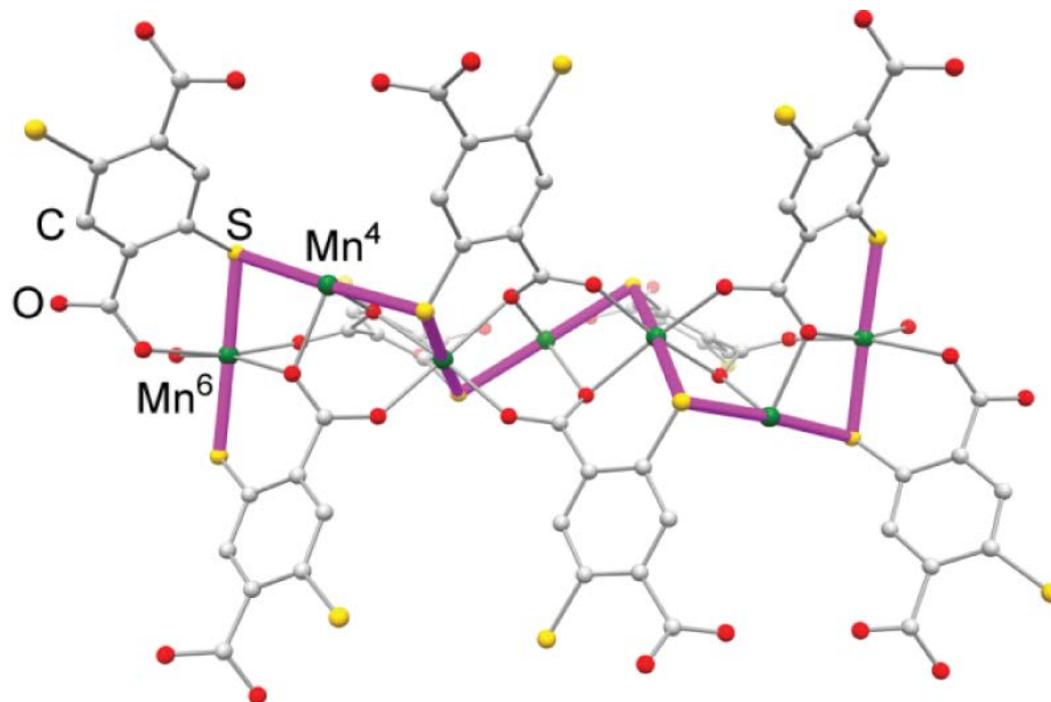
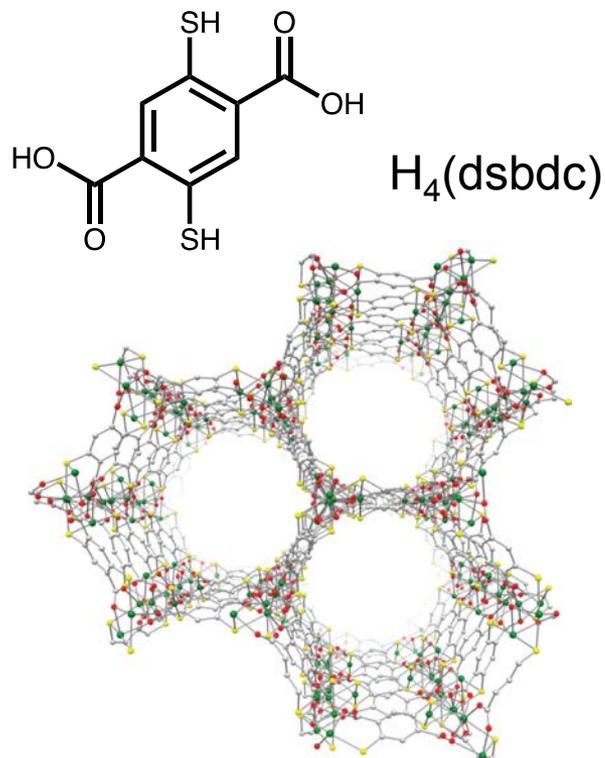
Next-Generation



4 or 5 H₂ per metal cation

- Volumetric capacity can be substantially increased while maintaining strong binding

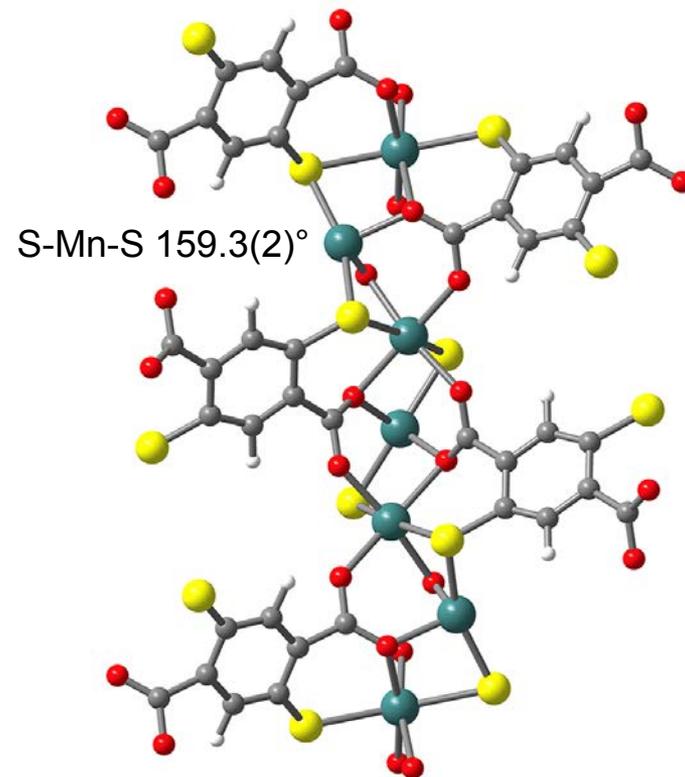
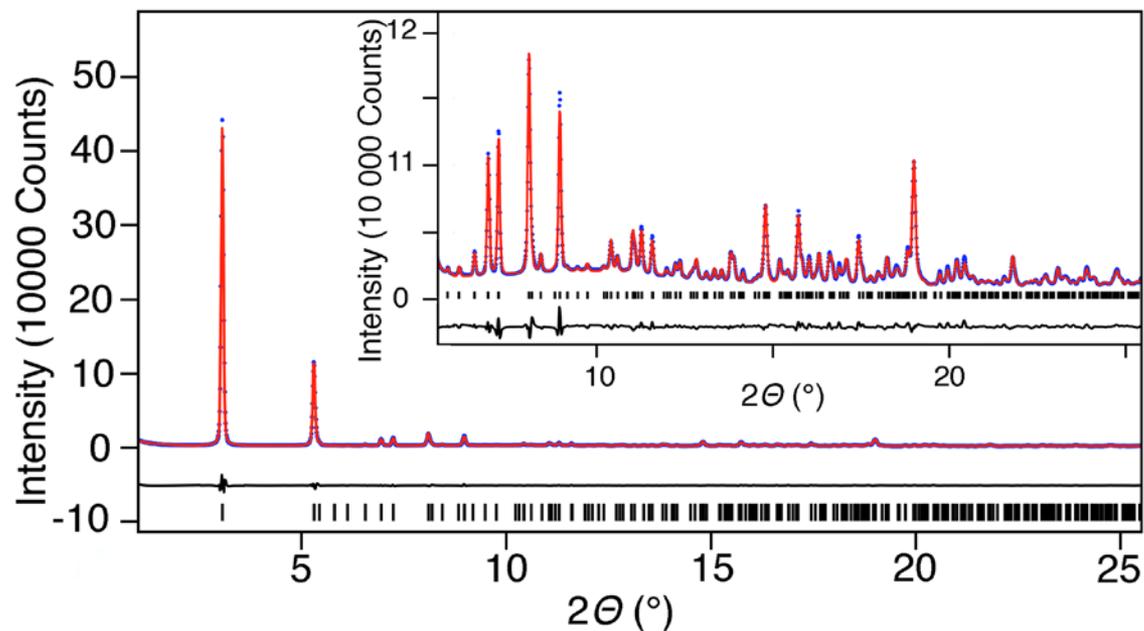
Approach: $\text{Mn}_2(\text{dsbdc})$



- Isomer of $\text{Mn}_2(\text{dobdc})$ structure with sulfido groups in place of oxido
- Crystal structure shows four-coordinate Mn^{2+} ions with two bound DMF molecules

Sun, Miyakai, Seki, Dincă. *J. Am. Chem. Soc.* **2013**, *135*, 8185

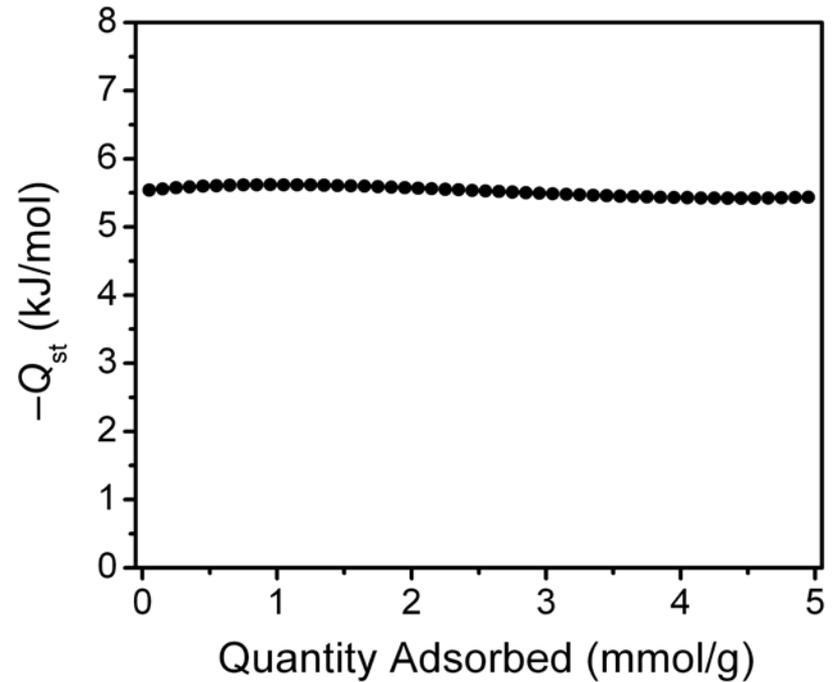
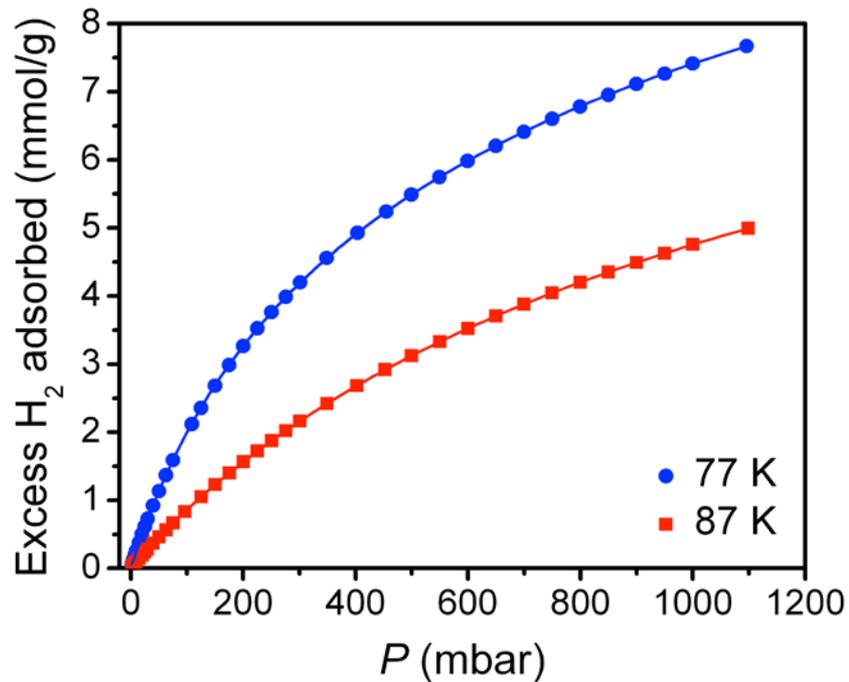
Structure of Desolvated $\text{Mn}_2(\text{dsbdc})$



- Desolvated structure of $\text{Mn}_2(\text{dsbdc})$ determined
- Half of the Mn^{2+} ions exhibit four-coordinate, seesaw geometry

Runčevski, Kapelewski, Torres-Gavosto, Tarver, Brown, Long, submitted

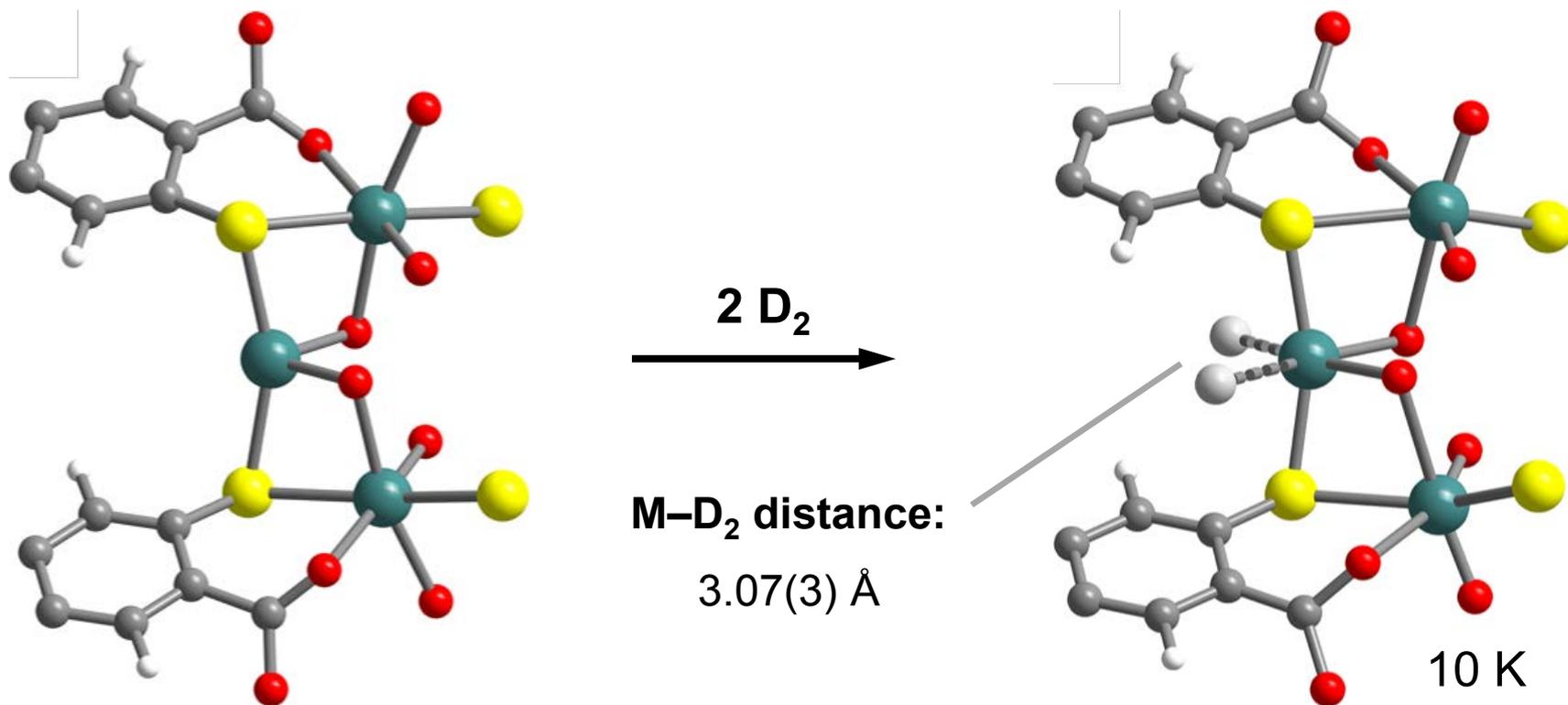
H₂ Adsorption in Mn₂(dsbdc)



- Hydrogen uptake is not steep but has about the same capacity as Mn₂(dobdc)
- Binding enthalpy remains low for entire range of loadings

Runčevski, Kapelewski, Torres-Gavosto, Tarver, Brown, Long, submitted

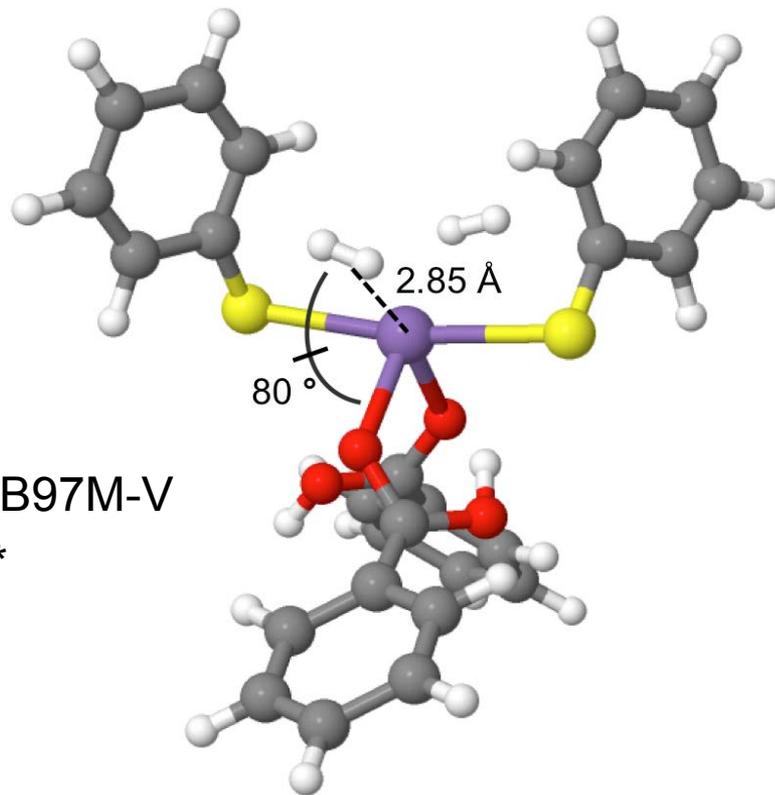
H₂ Adsorption in Mn₂(dsbdc)



□ First demonstration of two H₂ molecules binding to a metal center in a MOF

Runčevski, Kapelewski, Torres-Gavosto, Tarver, Brown, Long, submitted

Computational Results for $\text{Mn}_2(\text{dsbdc})$



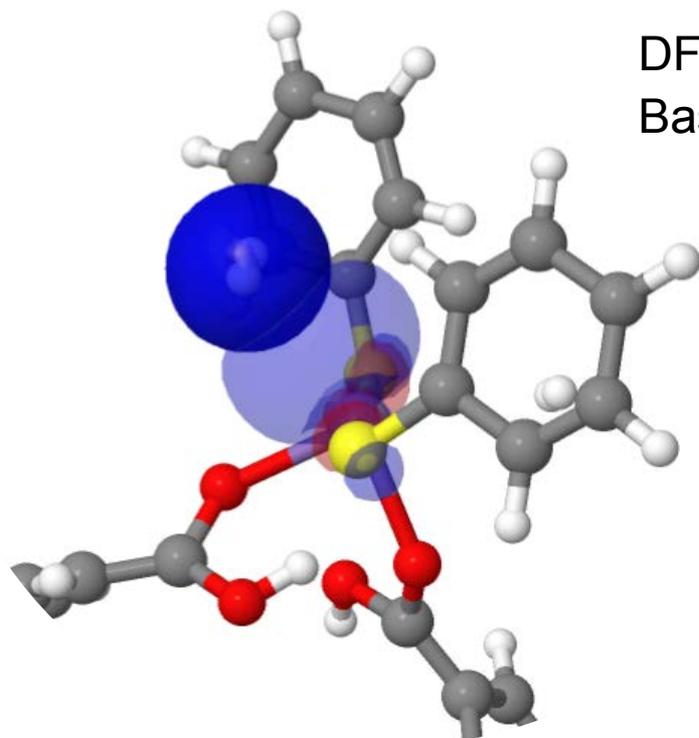
High-Spin Mn(II)

DFT Functional: B97M-V

Basis set: 6-31g*

- Shorter Mn-H₂ distances than observed experimentally
- Modeling electronics of ligand is challenging for this structure type

Mn–H₂ Energy Decomposition Analysis

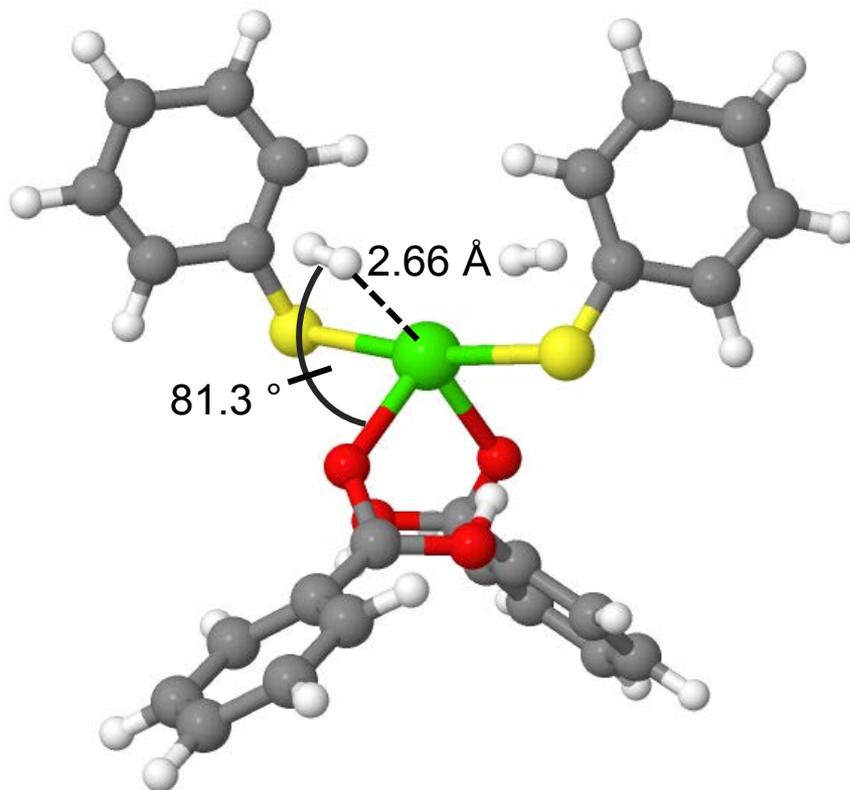


DFT Functional: B97M-V
Basis set: def2-tzvp

Interaction	Energy (kJ/mol)
Frozen	1.0
Polarization	-3.9
Charge Transfer	-8.4
ΔE (per H ₂)	-12.5

- Interaction of H₂ with Mn²⁺ has double the binding enthalpy of experiment
- New calculations are being run with updated crystal structure

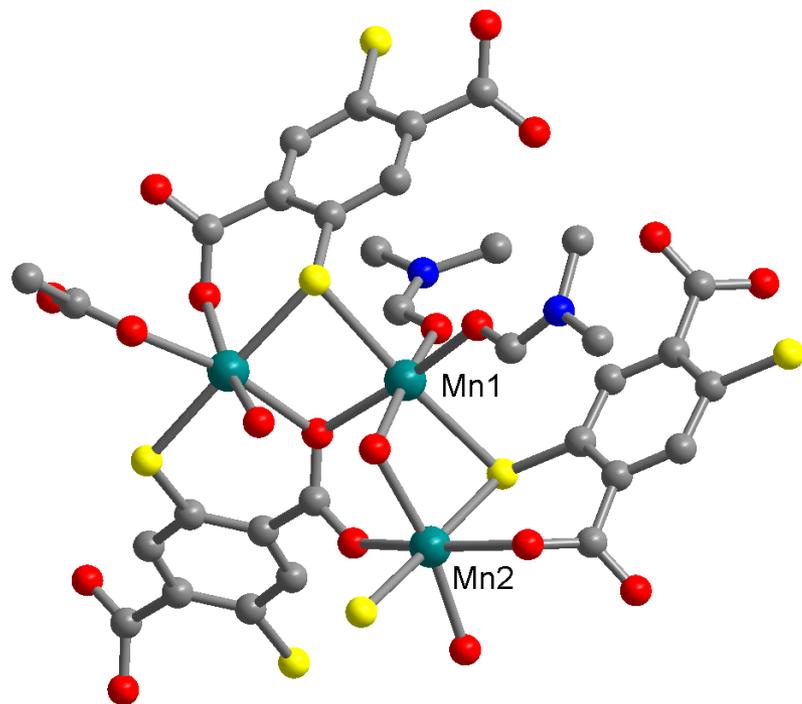
Ca₂(dsbdc) Calculations



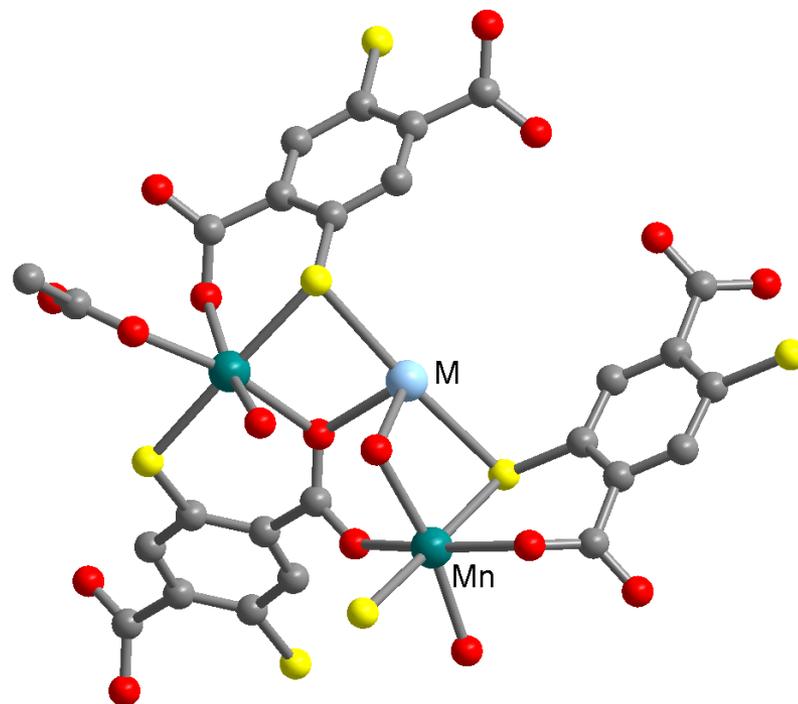
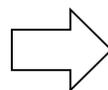
DFT Functional: B97M-V
Basis set: def2-qzvp

- Interaction of Ca²⁺ with H₂ has a shorter H₂ M distance than in Mn₂(dsbdc)
- $\Delta E = -17.9$ kJ/mol

Variations on $\text{Mn}_2(\text{dsbdc})$ for Increased H_2 Capacity



$\text{Mn}_2(\text{dsbdc})$



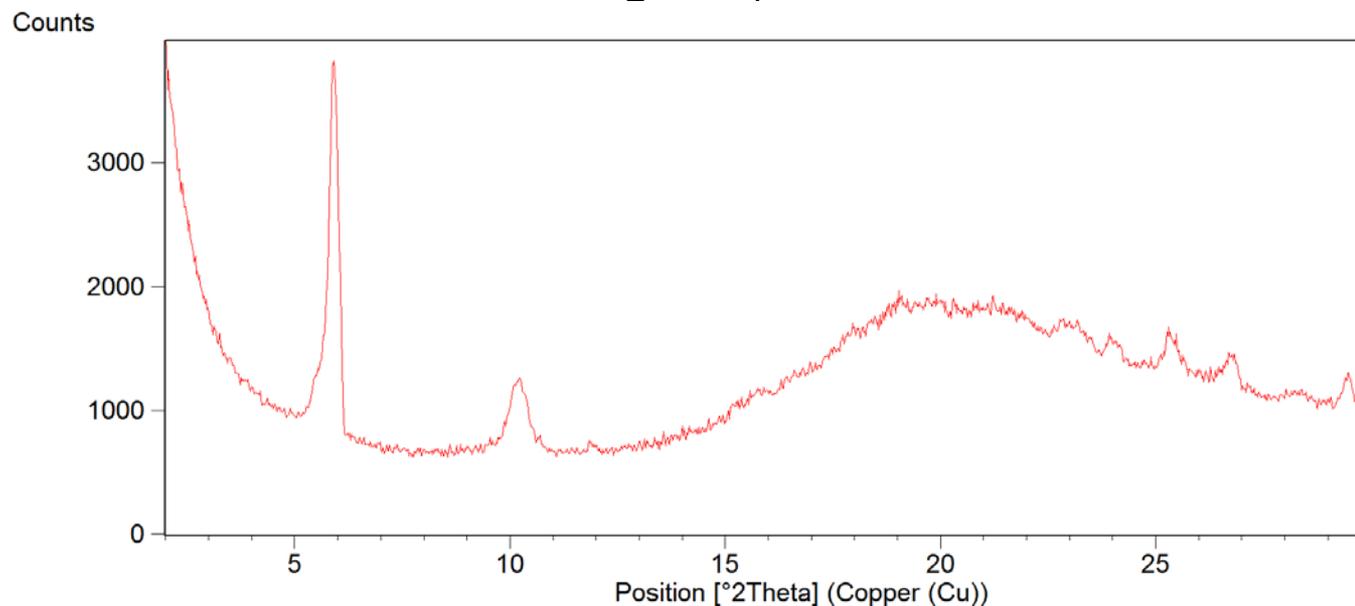
$\text{MnM}(\text{dsbdc})$

$\text{M} = \text{Ca}, \text{Mg}, \text{Co}, \text{Ni}, \text{Zn}$

- Different metals in the four-coordinate sites may bind more H_2 more strongly

Ca₂(dsbdc) Synthesis Attempts

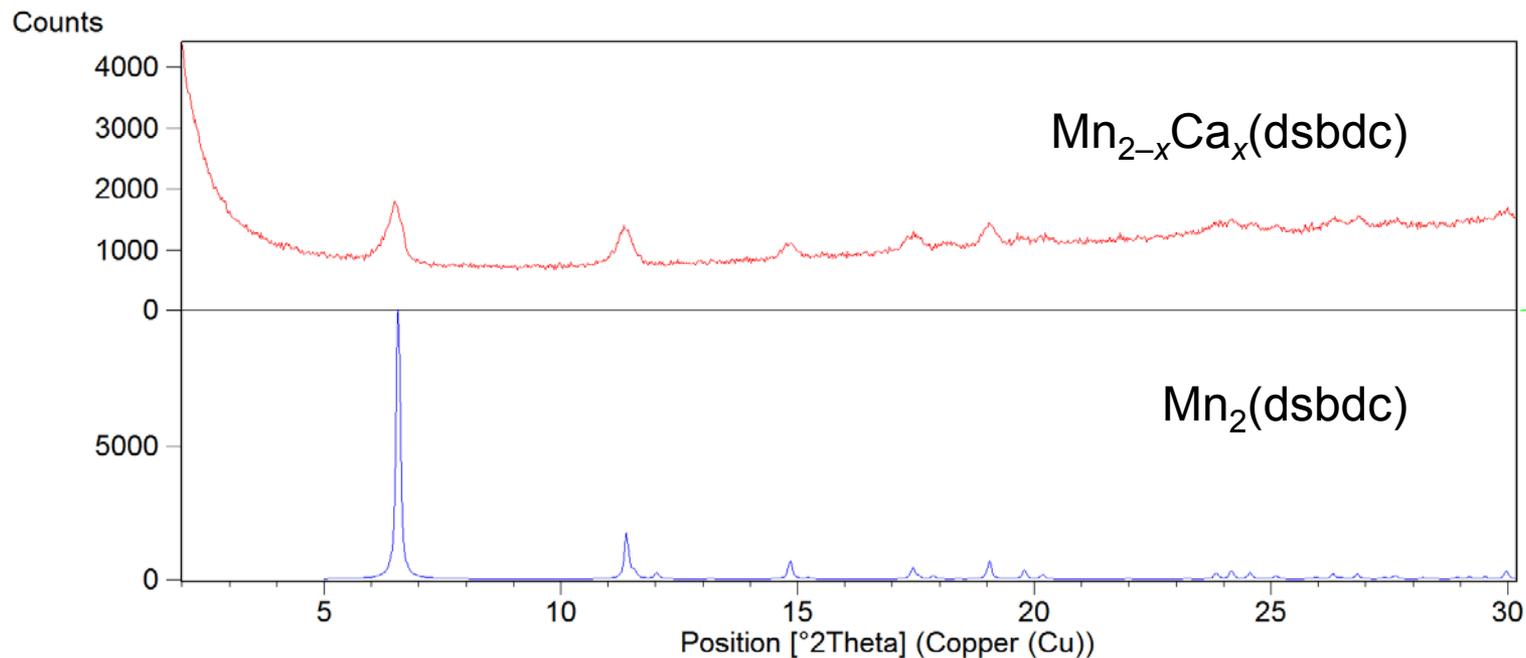
Ca(acac)₂ + H₄(dsbdc) in DMF



- Most promising phase, first two peaks are close to Mn₂(dsbdc)
- Lower angle peaks suggest a larger unit cell, as expected for larger Ca²⁺

Mixed-Metal $\text{Mn}_{2-x}\text{Ca}_x(\text{dsbdc})$ Synthesis

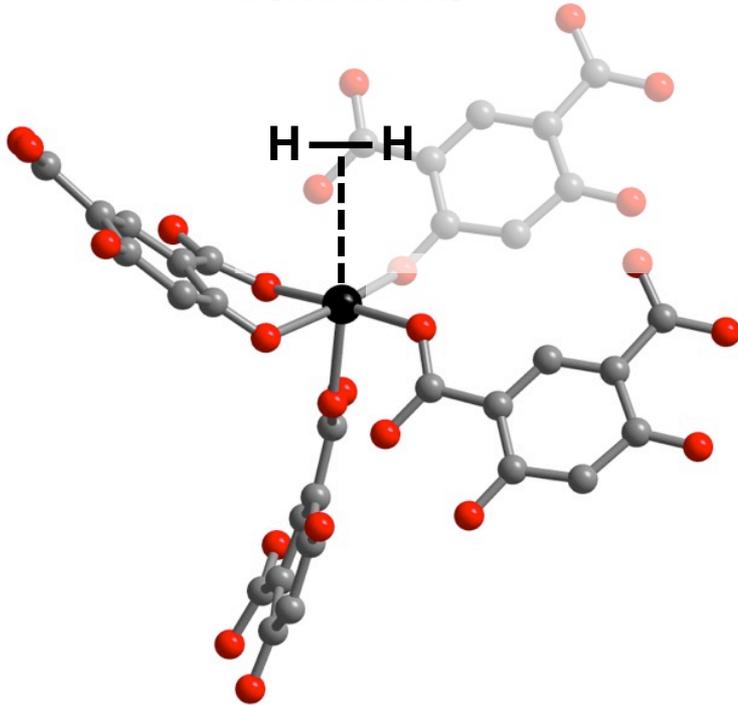
$\text{MnCl}_2 + \text{Ca}(\text{acac})_2 + \text{H}_4(\text{dsbdc})$ in DMF/MeOH



- Peaks match well with $\text{Mn}_2(\text{dsbdc})$, work underway to find Ca location
- 9.2% Ca replacement of Mn according to ICP analysis

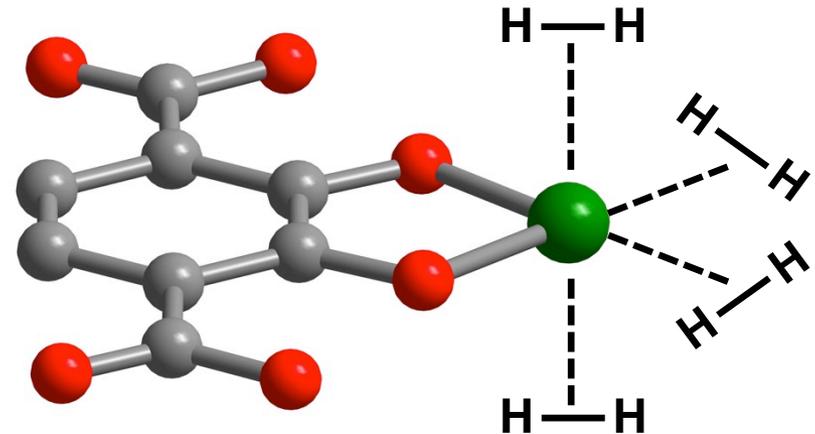
Binding Multiple H₂ Molecules per Metal Cation

Classical



1 H₂ per metal cation

Next-Generation



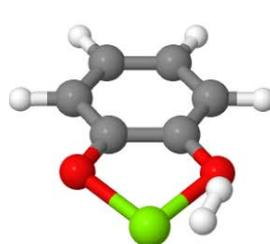
4 or 5 H₂ per metal cation

- Volumetric capacity can be substantially increased while maintaining strong binding

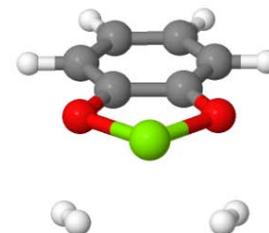
Calculated Adsorption for H₂ at Catechol-M²⁺

Catecholate-Mg²⁺

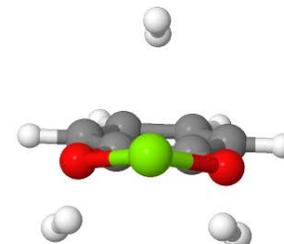
Strong binding for first two H₂ molecules



$$\Delta E_{\text{ads}} = -26.3 \text{ kJ/mol}$$



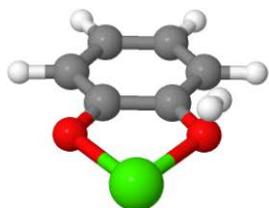
$$\Delta E_{\text{ads}} = -24.4 \text{ kJ/mol}$$



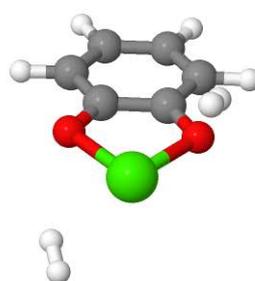
$$\Delta E_{\text{ads}} = -9.4 \text{ kJ/mol}$$

Catecholate-Ca²⁺

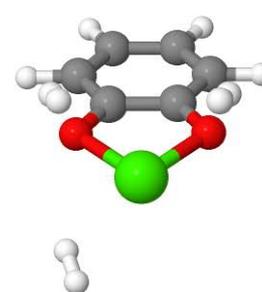
Strong binding for all four H₂ molecules



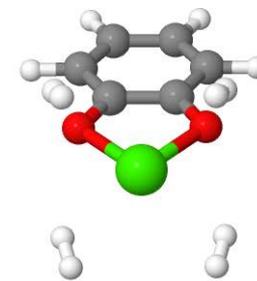
$$\Delta E_{\text{ads}} = -18.5 \text{ kJ/mol}$$



$$\Delta E_{\text{ads}} = -17.1 \text{ kJ/mol}$$



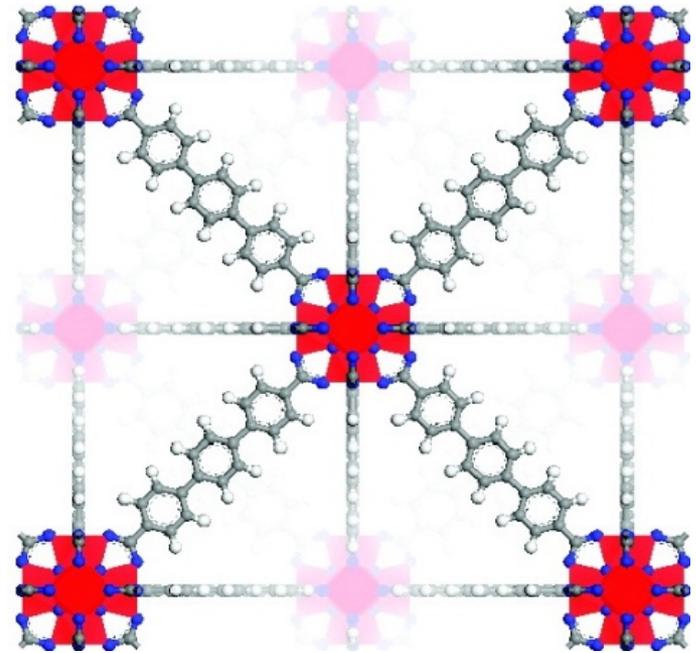
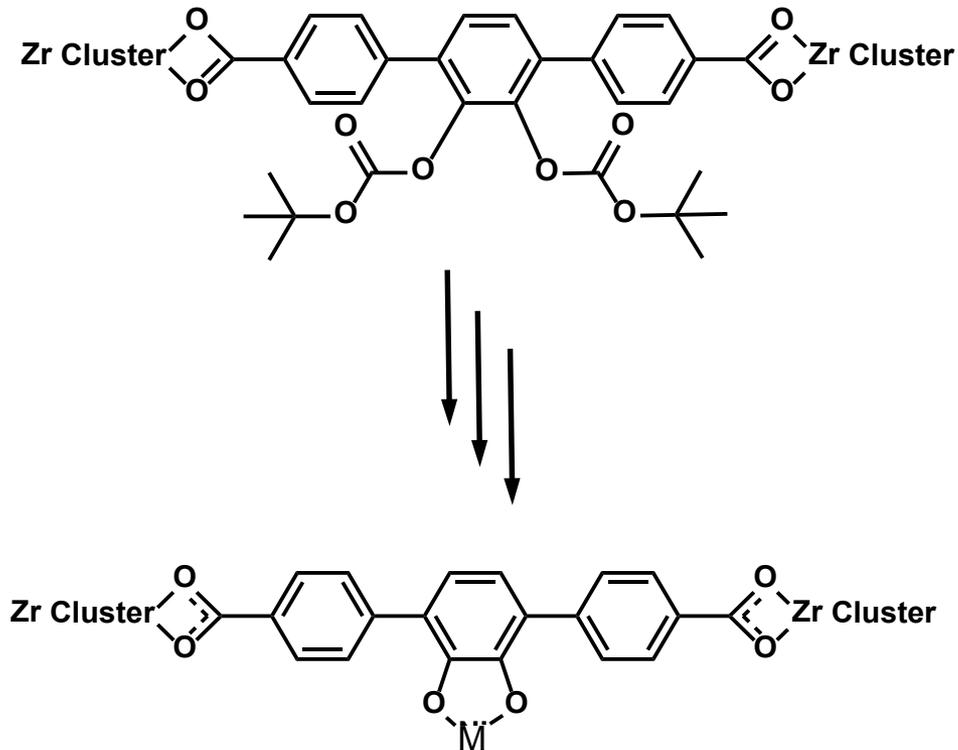
$$\Delta E_{\text{ads}} = -17.4 \text{ kJ/mol}$$



$$\Delta E_{\text{ads}} = -17.0 \text{ kJ/mol}$$

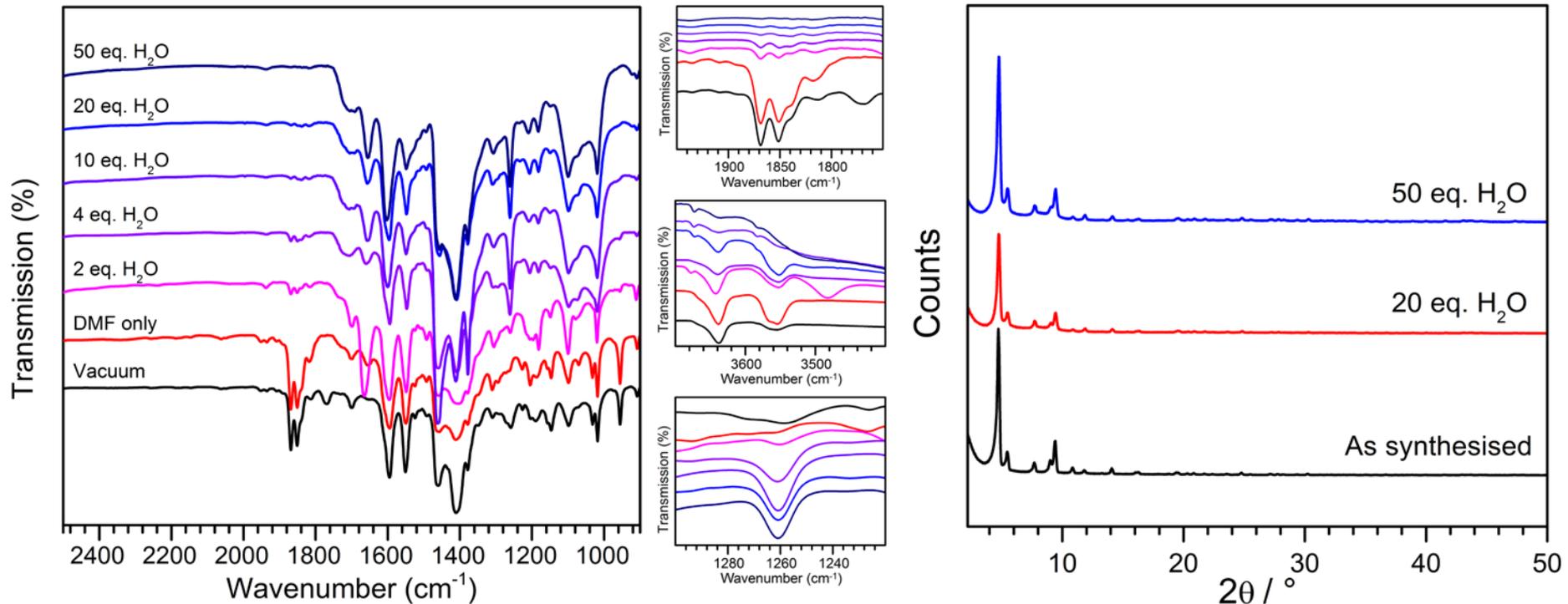
Theory: def2-qzvp/B97M-V

Approach: UiO-68-catecholate- M^{2+}



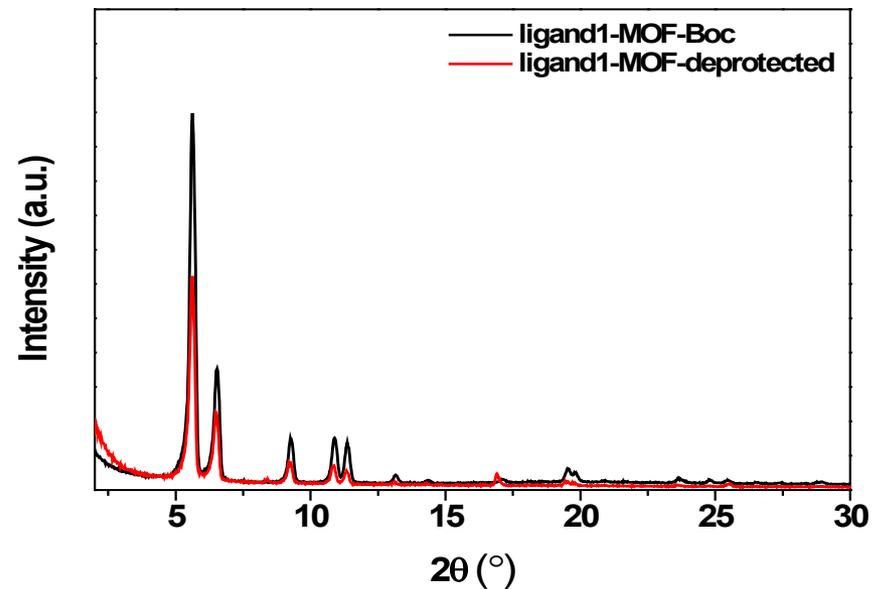
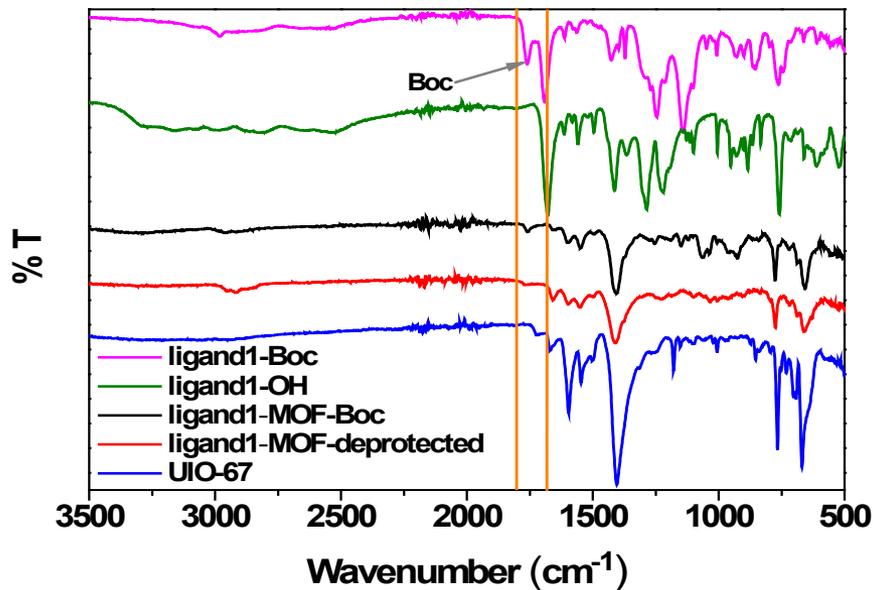
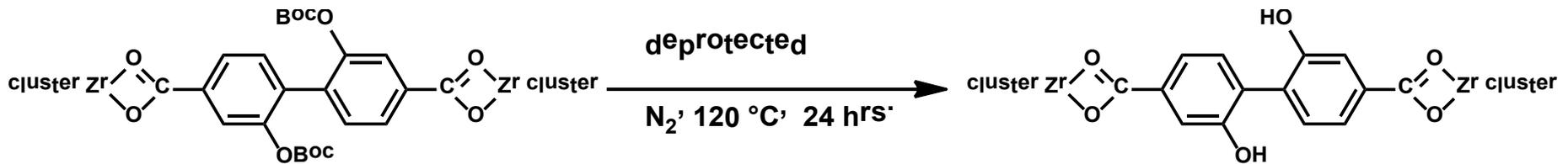
- Deprotection upon MOF synthesis can expose catechols for metal insertion
- Catechol-bound M^{2+} cations can then bind multiple H_2 molecules

Deprotection to form UiO-68-catechol



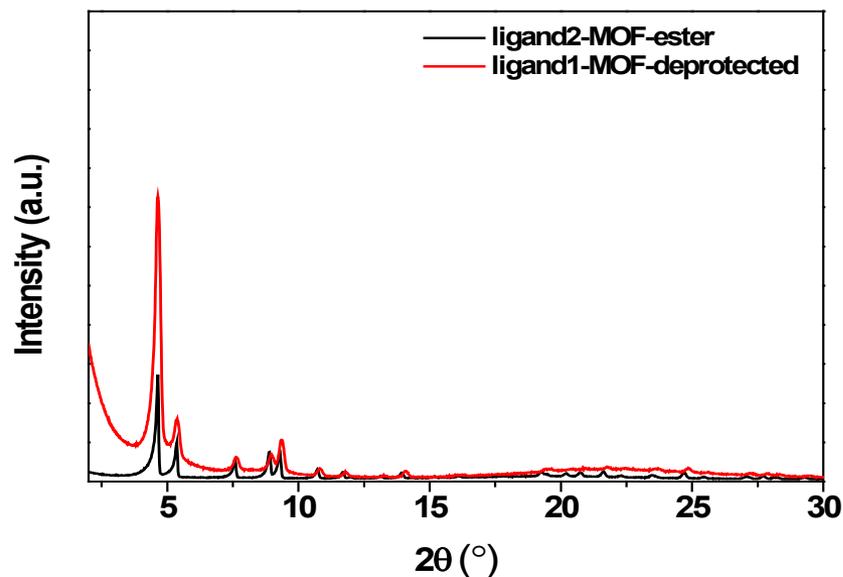
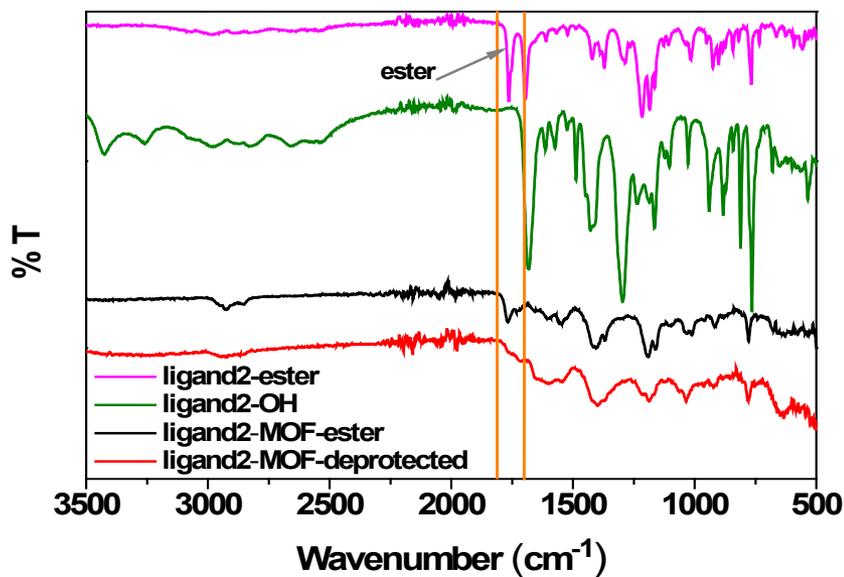
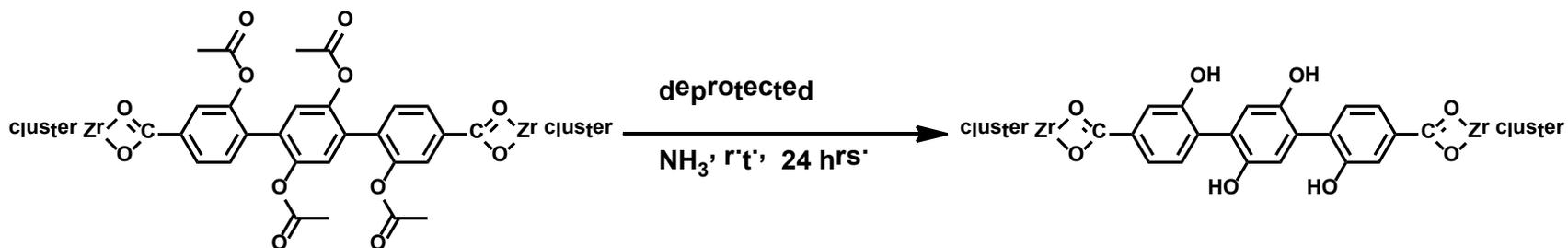
- Addition of water results in clean deprotection with no loss of crystallinity
- Metalation of fully deprotected framework is in progress

Synthesis and Metalation of UiO-67-biphenol



- Successful synthesis of ligand and deprotected MOF exhibiting UiO-67 structure
- Successful metalation with $Mg(C_4H_9)_2$ with $\sim 50\%$ incorporation by ICP

Synthesis of UiO-68-bis(biphenol)



- Successful synthesis of ligand and deprotected MOF exhibiting UiO-68 structure
- Metalation attempts are underway, two metals per ligand are possible

Predicted Capacities Upon Insertion of Ca²⁺

	volumetric (g/L of crystal)	gravimetric (wt %)
UiO-68-catechol	39	6.6
UiO-67-biphenol	42	4.6
UiO-68-bis(biphenol)	48	7.2

- Predicted capacities based on 4 H₂/Ca²⁺ and H₂ packing in pores of Ni₂(*m*-dobdc)
- Proof of principle for H₂ on metal centers and in pores

Responses to Previous Year Reviewers' Comments

This is the first year of this project,
so there are no previous comments.

Collaborations

Project team:

- Lawrence Berkeley National Laboratory/UC Berkeley:
Jeffrey Long: Synthesis and basic characterization of MOFs
Martin Head-Gordon: Calculation and prediction of H₂ binding energies
- National Renewable Energy Laboratory:
Thomas Gennett (Lead): Characterization
- Pacific Northwest National Laboratory:
Thomas Autrey: Calculations and NMR spectroscopy
- National Institute of Standards and Technology:
Craig Brown: Neutron diffraction and neutron spectroscopy

Additional collaborations:

- Variable-temperature infrared spectroscopy with *in situ* H₂ dosing
– *Stephen FitzGerald* (Oberlin College)

Remaining Challenges and Barriers

- Desolvation of catecholate-bound metal cations remains a challenge
- Synthesis of the $\text{Mn}_2(\text{dsbdc})$ analogs with Ca and Ni must be finalized
- Materials with a higher density of open metal cation sites must be identified to meet volumetric and gravimetric capacity targets

Proposed Future Work

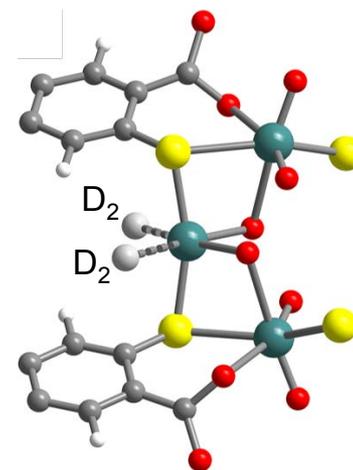
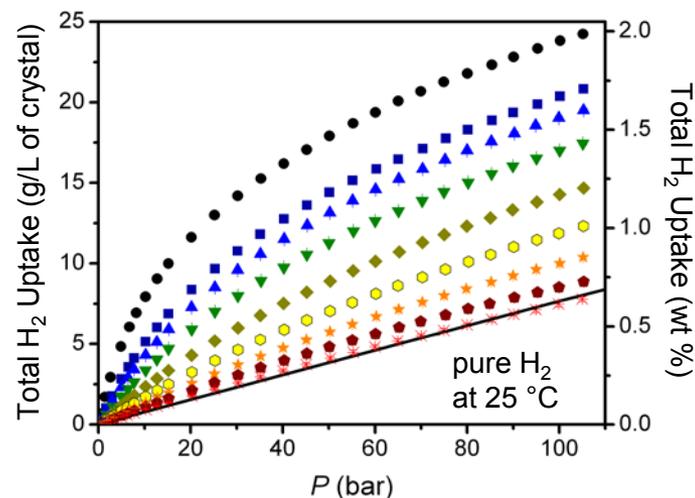
- Test many different metalation and desolvation conditions for the catechol-containing frameworks
- Narrow down synthetic conditions for $\text{Mn}_2(\text{dsbdc})$ analogs
- Metalate the high surface area porous polymers with metal-chelating sites
- Further research into new materials containing metal centers with open metal coordination sites is underway
- Install *in situ* infrared spectrometer and begin testing materials
- Continue to explore metal- H_2 interactions in real systems that have been realized experimentally

Technology Transfer Activities

- The $M_2(m\text{-dobdc})$ patent application was previously submitted
- Mosaic Materials, Inc. has developed an inexpensive, scalable synthesis of $Ni_2(m\text{-dobdc})$ and is looking to commercialize this material

Summary

- $\text{Ni}_2(m\text{-dobdc})$ shows the best volumetric usable capacities of any porous solid for H_2 storage up to 100 bar at ambient temperatures
- $\text{Mn}_2(\text{dsbdc})$ is the first ever example of multiple H_2 molecules binding to a single metal center in a MOF!
- Synthesis of analogs of $\text{Mn}_2(\text{dsbdc})$ with higher binding enthalpies and more H_2 per metal are underway
- MOFs containing ligands with metal chelating sites have been synthesized and metalation is underway



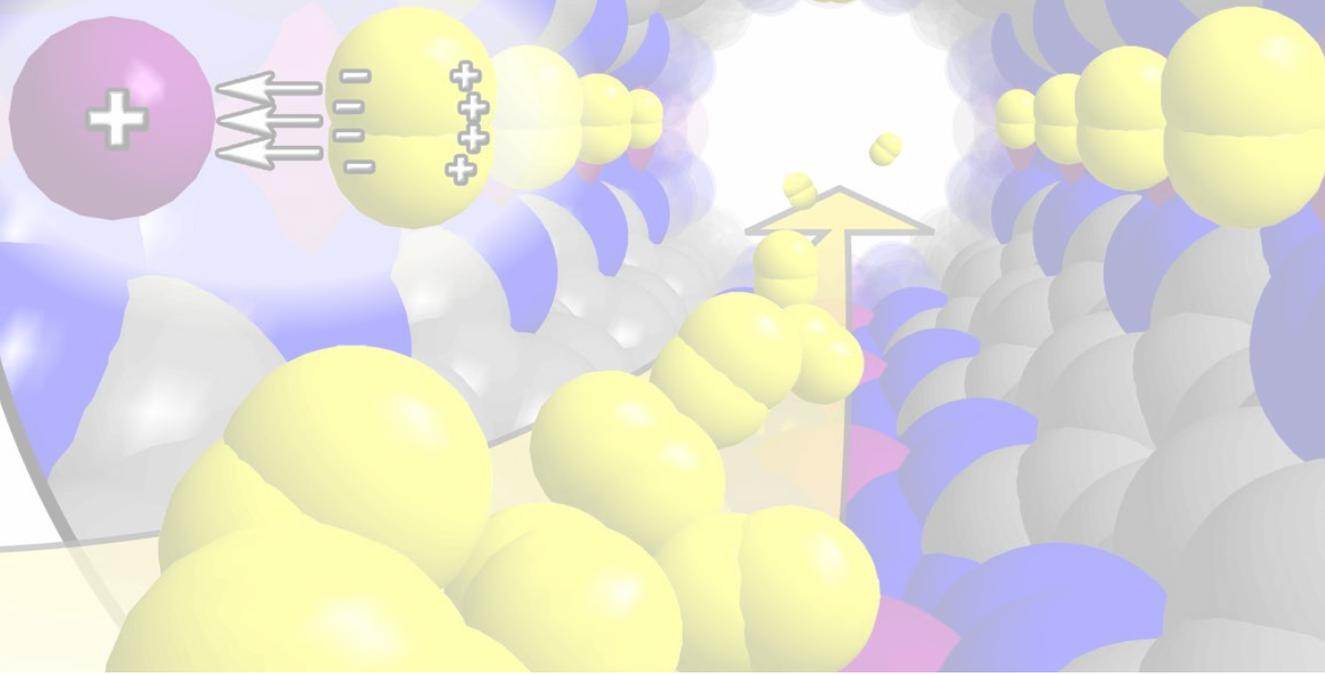
Summary

Milestone	% complete
Q1: Computational chemists will initiate investigation of the most promising structures for the desired pore domain size and chemistry within porous aromatic frameworks (PAFs) or block copolymer, (BCP) using first-principles electronic structure calculations with range separation and dispersion corrections.	100%
Q2: Synthesize a porous aromatic frameworks material with metal-chelating sites and a Langmuir surface area of at least 1000 m ² /g.	100%
Q3: Synthesize and characterize a carbon based sorbent with catechol functionalized pore domains that contain unsaturated metal centers attached to the materials matrix.	95%
Q4 Go/No-Go: Demonstrate the ability to bind two H ₂ molecules to one metal center in a metal-organic framework, porous aromatic framework, or carbon-based material.	100%

Summary

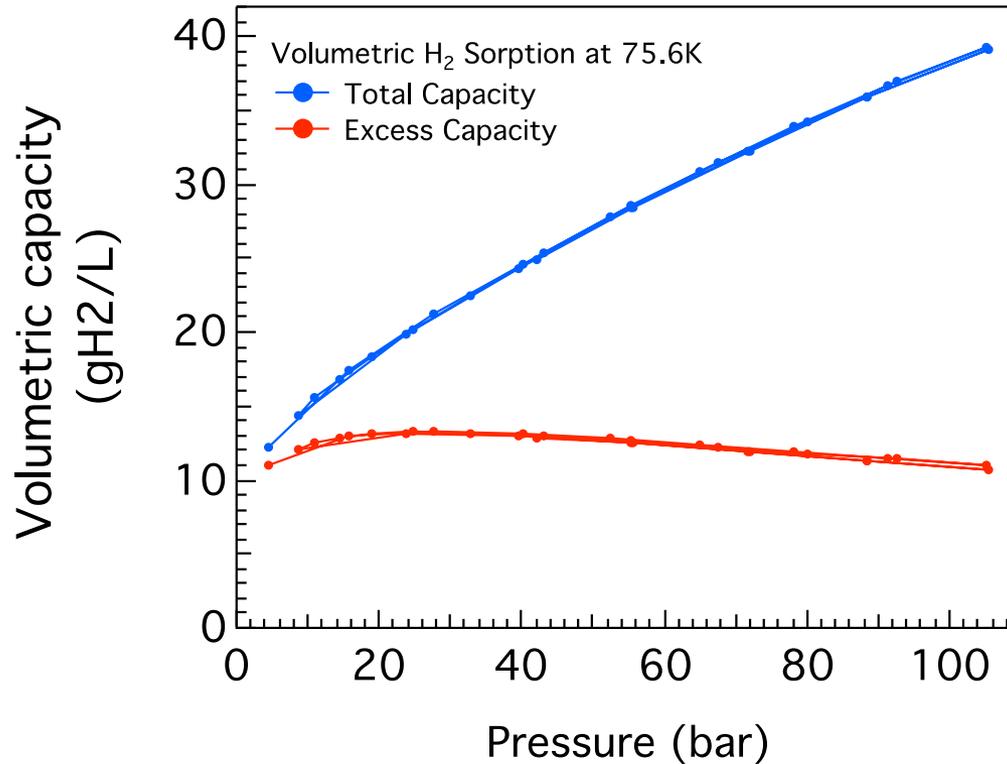
Milestone	% complete
Q2: Evaluate choices for various infrared spectrometer setups for <i>in situ</i> gas dosing.	100%
Q3: Order DRIFTS instrument that will be best and most functional for the desired <i>in situ</i> H ₂ -dosed experiments over a temperature range of 15-373 K and up to 100 bar hydrogen pressure at 298 K based on experience testing several similar instruments.	100%
Q4: Complete installation of the DRIFTS instrument and demonstrate that the DRIFTS instrument is operating with a resolution of 10 cm ⁻¹ by measuring spectra for a sorbent standard and comparing with accepted published data.	0%

Technical Back-Up Slides



Accomplishments: 77 K H₂ Isotherms in Ni₂(*m*-dobdc)

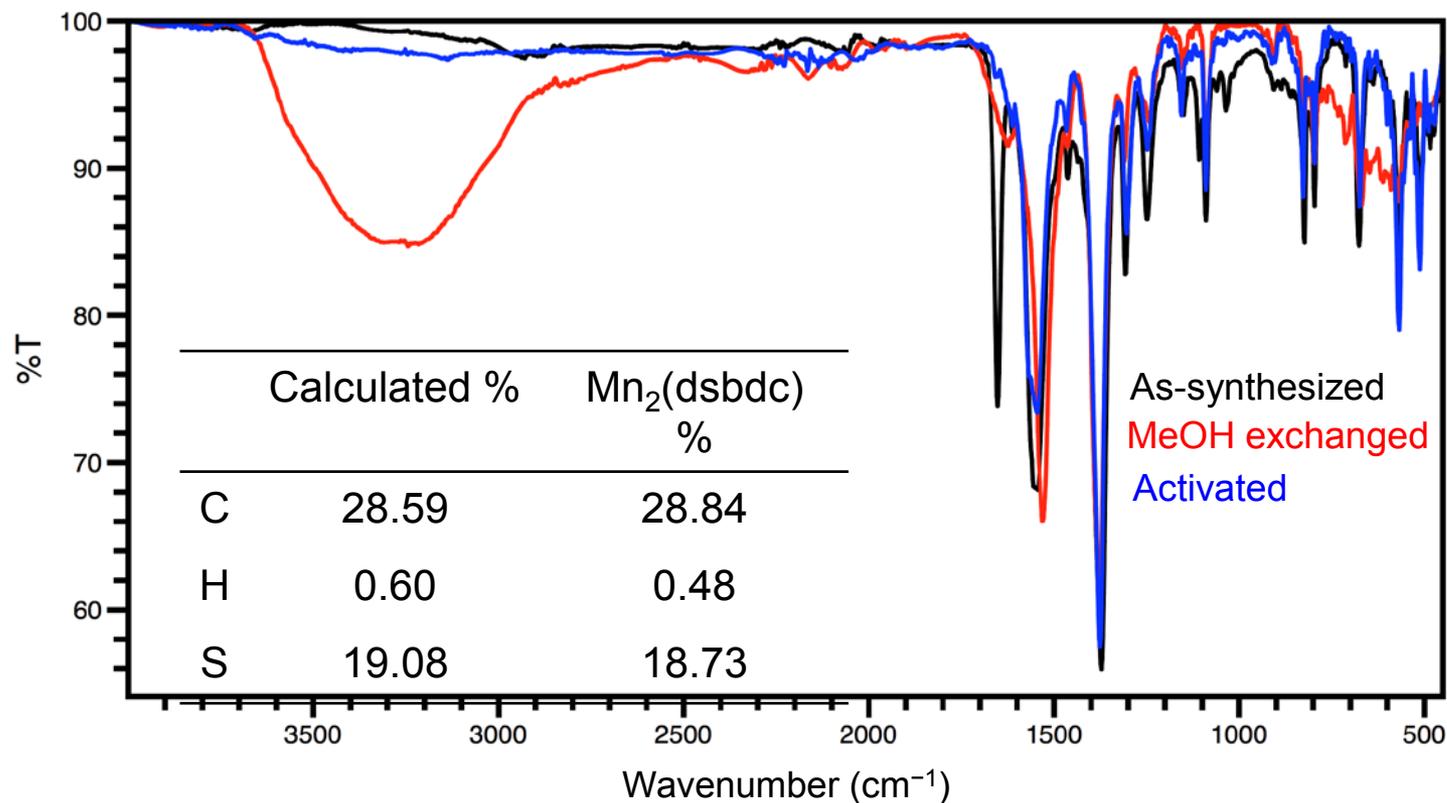
NREL measurements:



*Single crystal density used for volumetric capacity determination

- Data at 77 K shows Ni₂(*m*-dobdc) reaches 38 g/L, very close to system target
- NREL-measured isotherms at other temperatures verified LBNL data

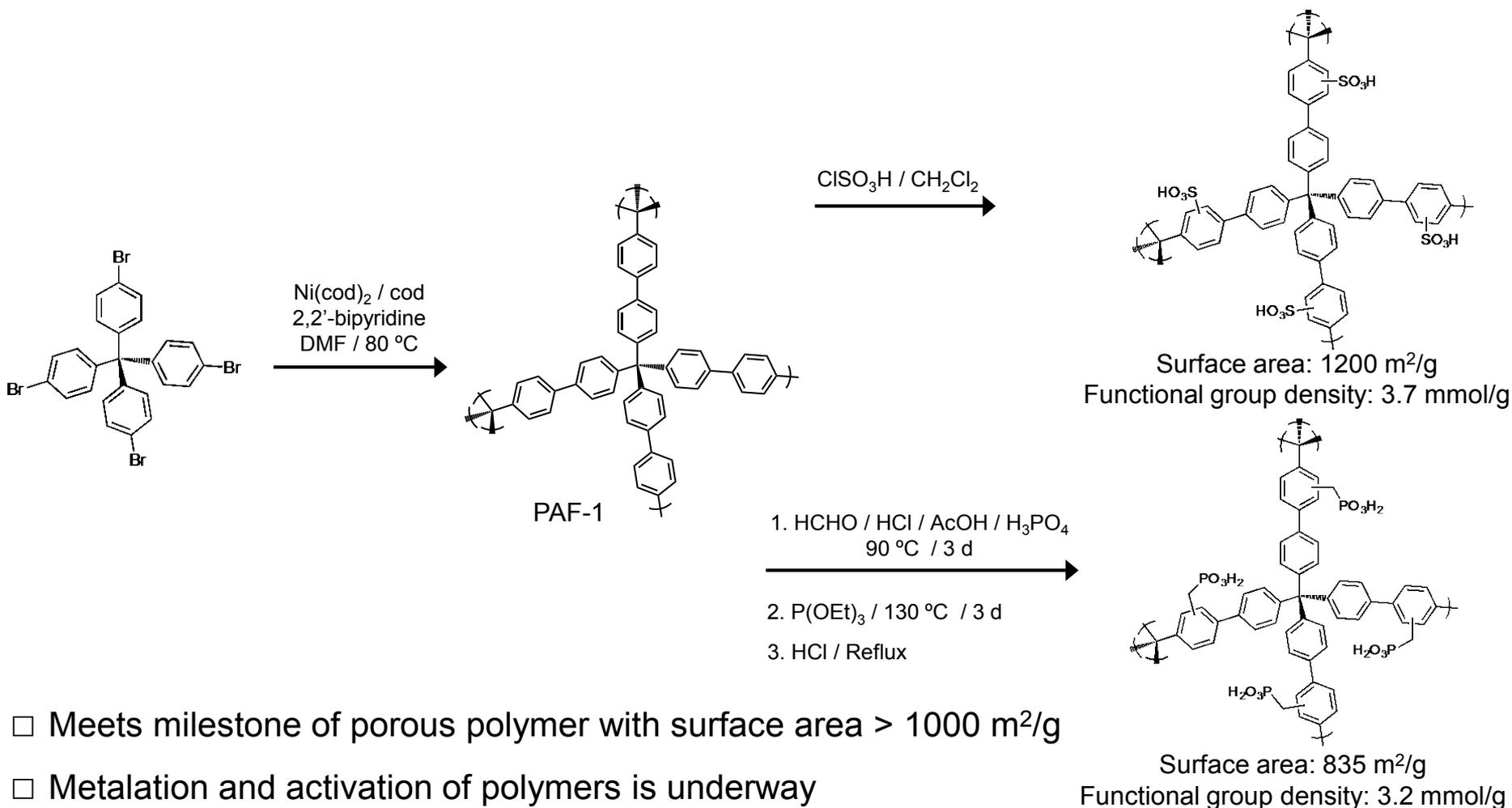
Mn₂(dsbdc) Desolvation and Purity



□ Infrared spectrum indicates successful removal of all DMF in Mn₂(dsbdc)

Runčevski, Kapelewski, Torres-Gavosto, Tarver, Brown, Long, submitted

High-Surface Area Porous Polymers for Metalation



- Meets milestone of porous polymer with surface area > 1000 m^2/g
- Metalation and activation of polymers is underway