2016 DoE Hydrogen and Fuel Cells Program Review

Hydrogen Storage Characterization and Optimization Research Effort

Jeffrey Long and Martin Head-Gordon

Materials Sciences Division

Lawrence Berkeley National Laboratory

June 8, 2016

Project ID #: ST133

NREL — NATIONAL RENEWABLE ENERGY LABORATORY

BERKELEY LAB

UNIVERSITY OF CALIFORNIA 1868

Pacific Northwest NATIONAL LABORATORY

NIST

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 H_2 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 % H_2 by mass, volumetric capacity of 40 g/L
  - "ultimate full fleet" targets: 7.5 % H_2 by mass, 70 g/L.
- Validate new concepts for H_2 storage mechanisms in adsorbents.
- Provide accurate computational modeling for H_2 adsorbed in porous materials.

This reporting period

- Research and development of metal-organic framework materials with high volumetric and gravimetric H_2 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 H_2 dosing at T = 10-300 K, $P \leq$ 100 bar
2) Mechanistic validation:

Can exposed cations in adsorbents reach target of ΔH = –15 kJ/mol?

Is it possible to adsorb two, three, or four H_2 per metal cation?
3) Accurate modeling of H_2 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* 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% 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

Gas inlet →

Optics

Cryostat and cold finger

High pressure optical sample chamber
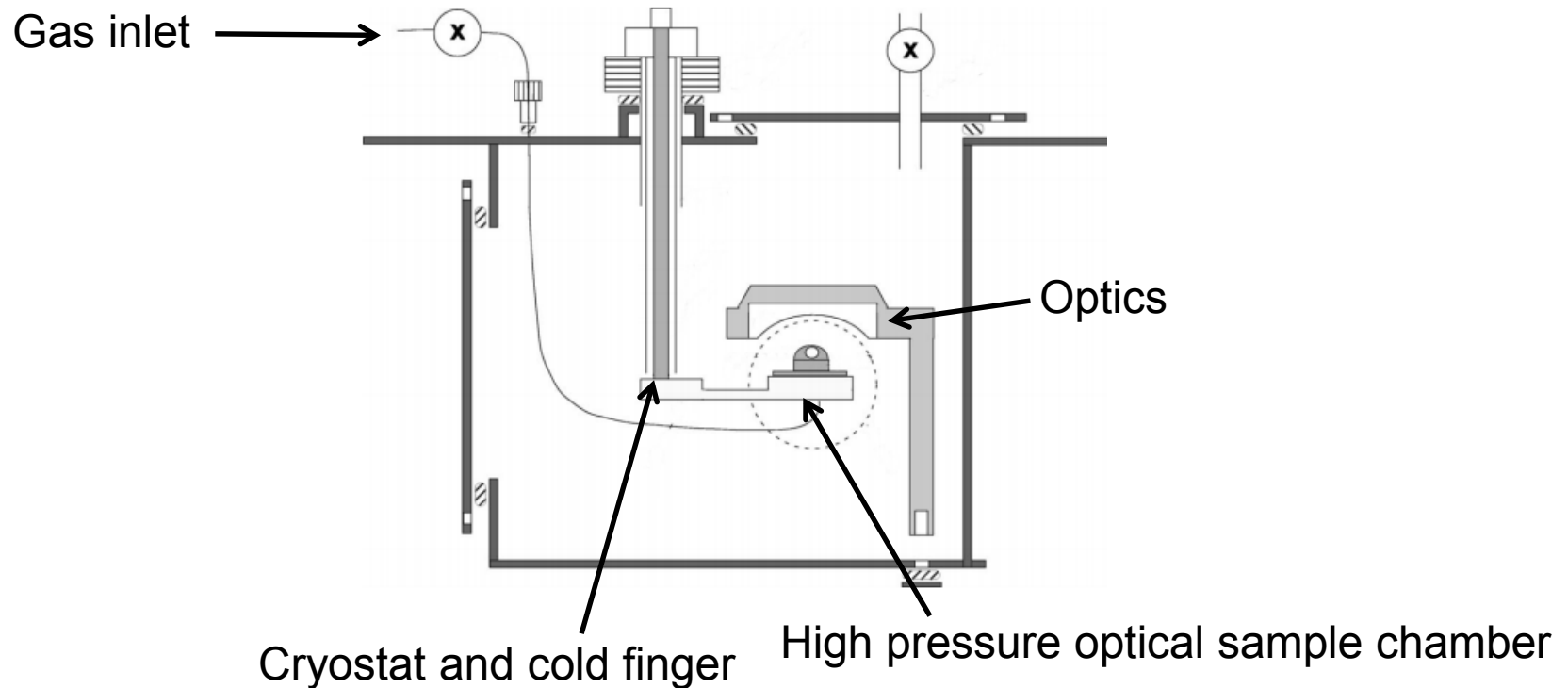
☐ Infrared spectroscopy with *in situ* gas dosing probes behavior of adsorbed species

☐ 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
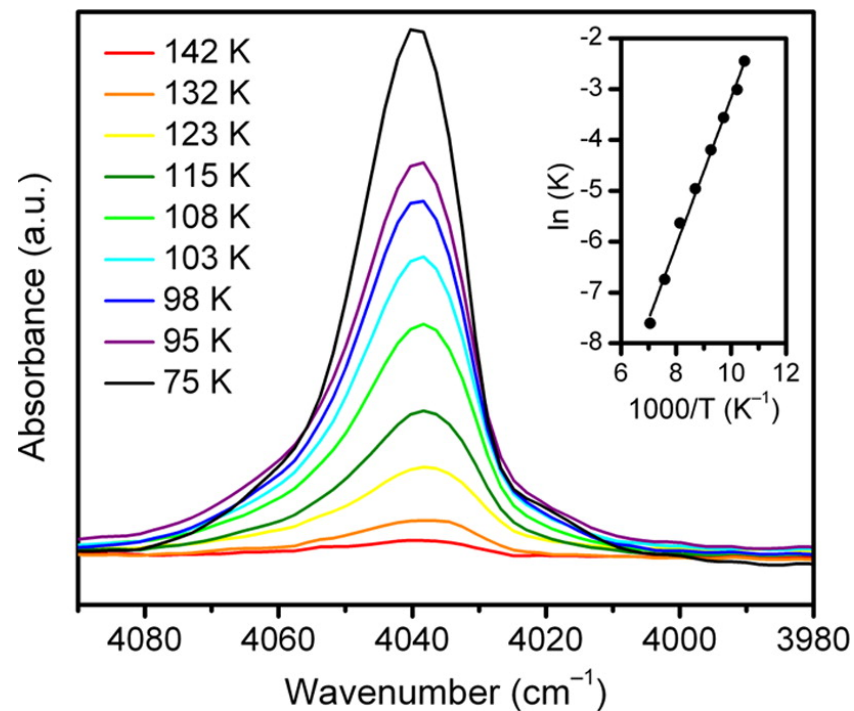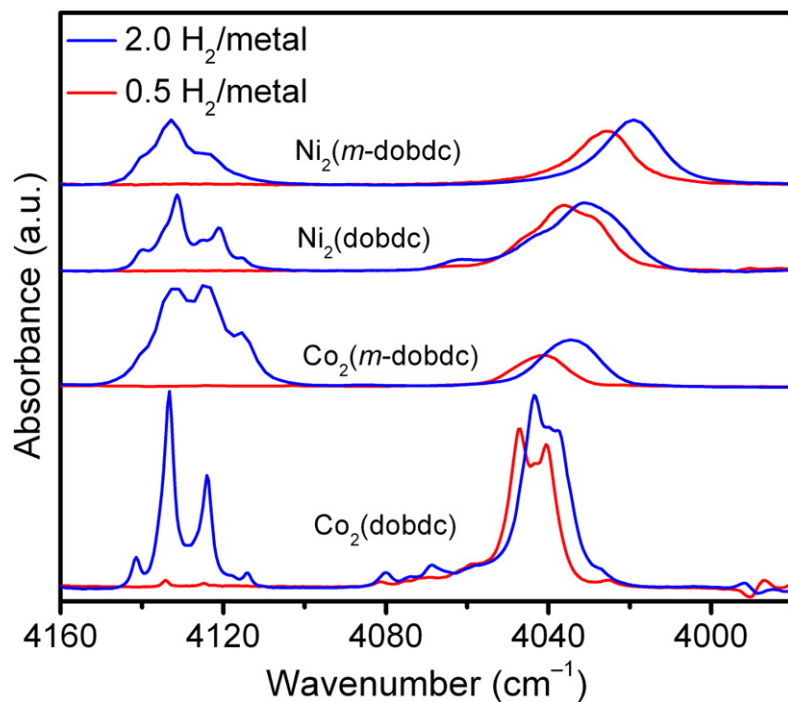
□ H₂ molecules adsorbed on different sites have different infrared energy shifts

□ Shift of H₂ 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 m^2/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 H_2 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 H_2 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
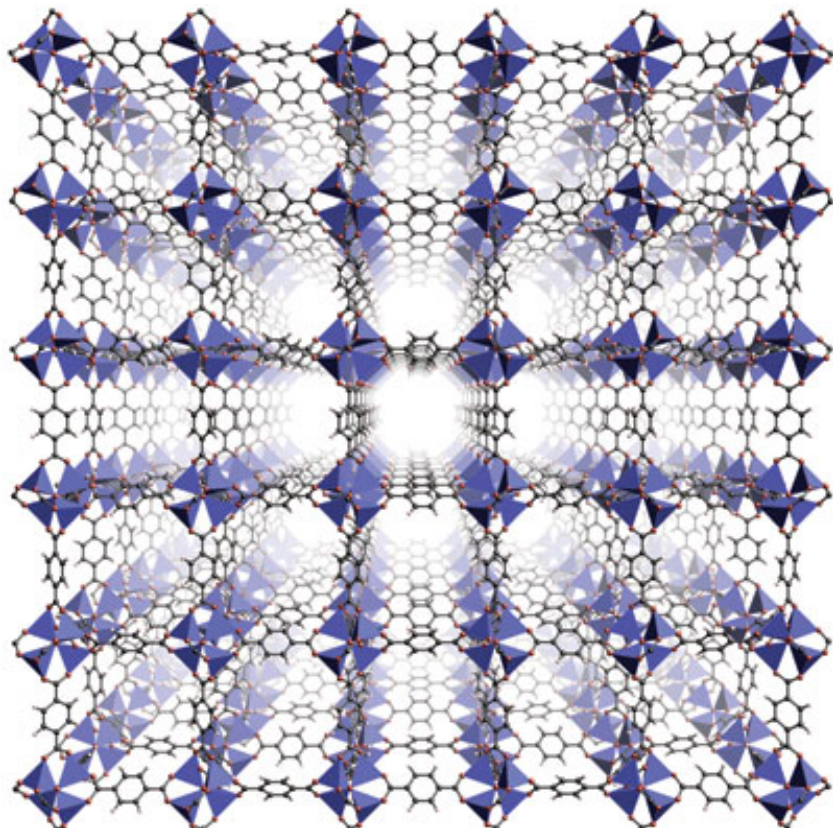
Zn$_4$O(1,4-benzenedicarboxylate)$_3$

MOF-5

BET surface areas up to 7100 m^2/g

Densities as low as 0.13 g/cm^3

Tunable pore sizes up to 10 nm

Channels connected in 1-, 2-, or 3-D
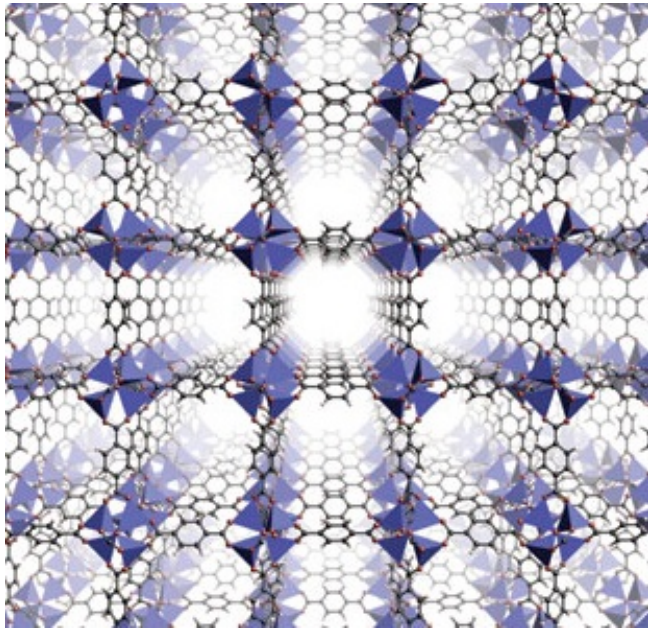
Internal surface can be functionalized

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

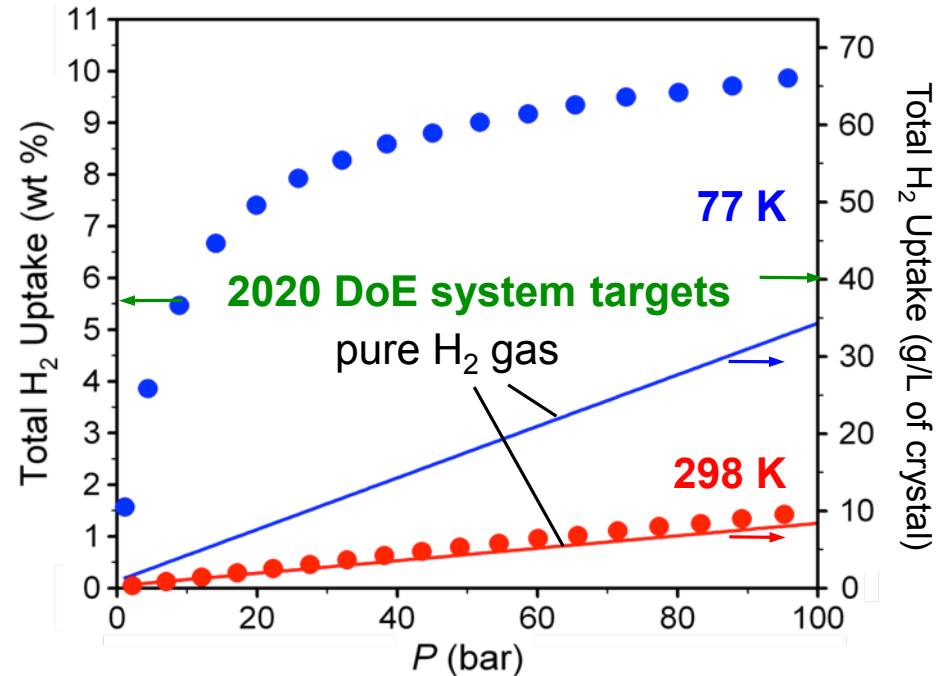Yaghi et al. *Nature* **2003**, *423*, 705
Kitagawa et al. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334
Férey *Chem. Soc. Rev.* **2008**, *37*, 191

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 H_2 gas

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

A MOF with a High Density of Exposed M²⁺ Sites

$MX_2 \cdot 6H_2O$

\+

H_4dobdc
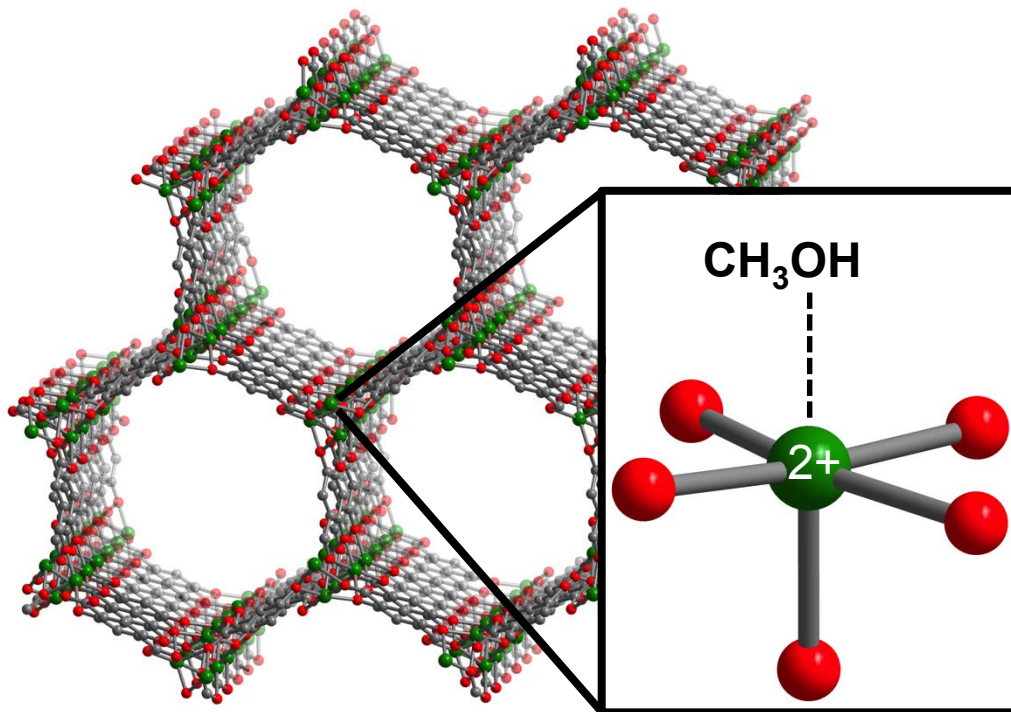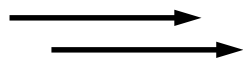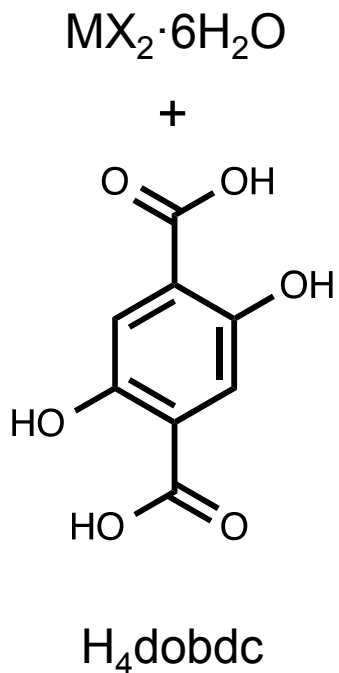
M₂(dobdc), M-MOF-74
(M = Mg, Mn, Fe, Co, Ni, Cu, Zn)

☐ Activated frameworks have Langmuir surface areas of 1277-2060 m²/g

A MOF with a High Density of Exposed M²⁺ Sites

$MX_2 \cdot 6H_2O$

+
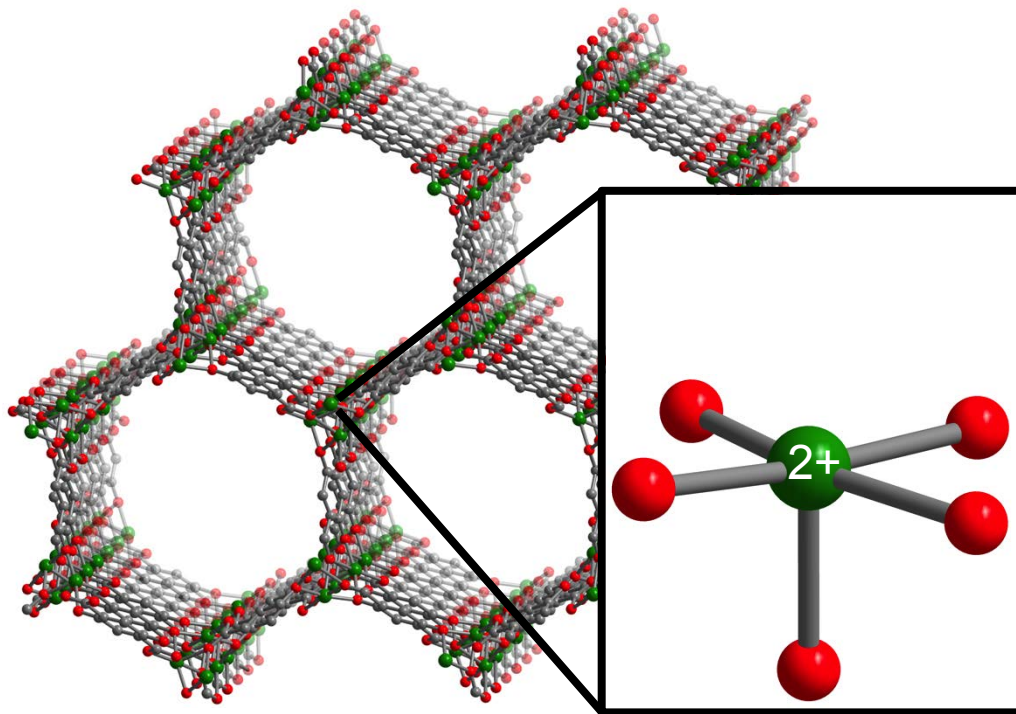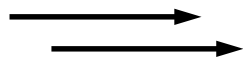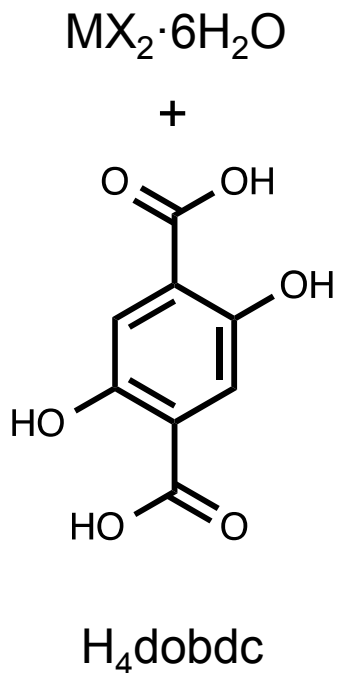
H₄dobdc

M₂(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$_2$(dobdc)
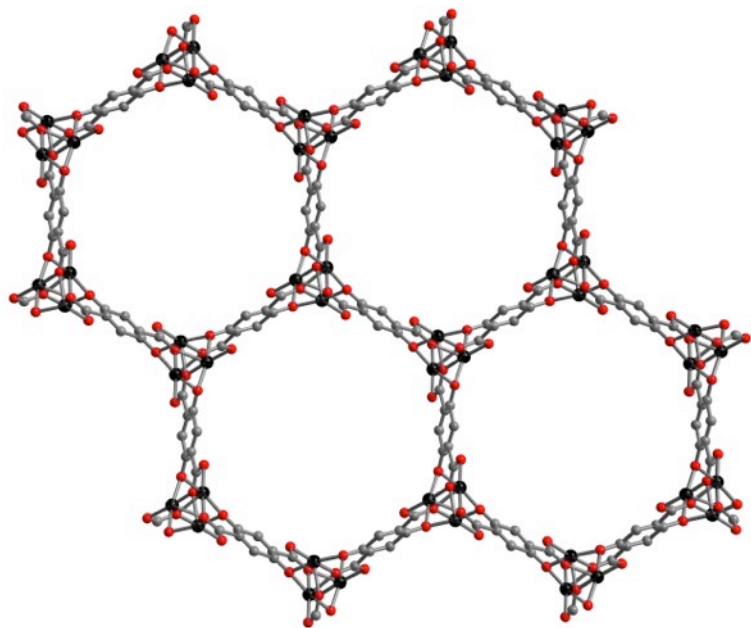
H$_4$(dobdc)
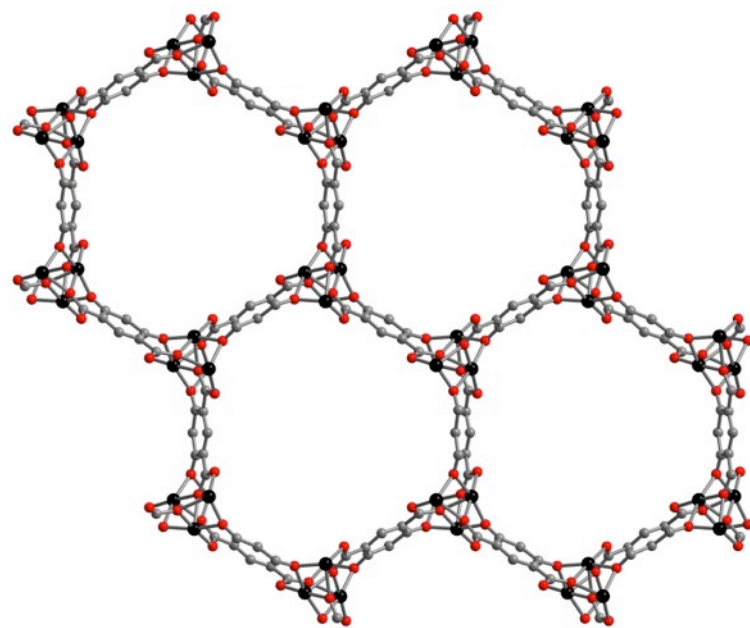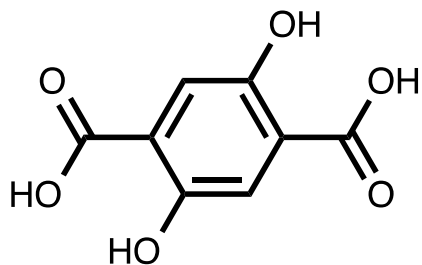
H$_4$(m-dobdc)
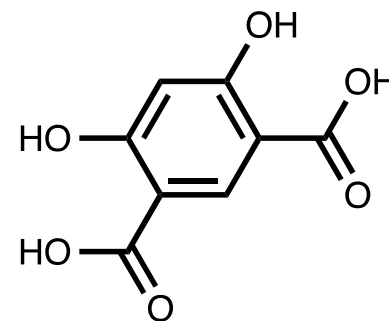
Kapelewski, Geier, Hudson, Stuck, Mason, Nelson, Xiao, Hulvey, Gilmour, FitzGerald, Head-Gordon, Brown, Long *J. Am. Chem. Soc.* **2014**, *136*, 12119

Strong H$_2$ Binding in Ni$_2$(*m*-dobdc)

Neutron Diffraction

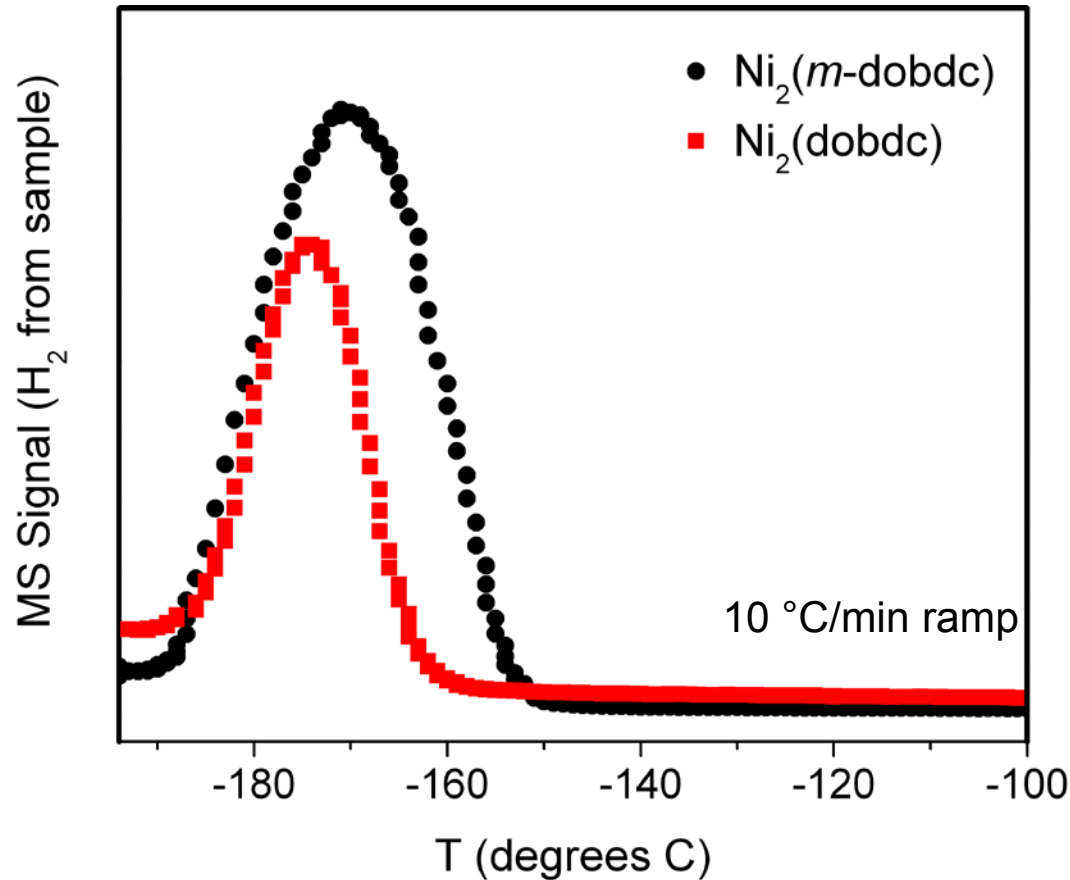Ni–D$_2$ = 2.18(4) Å

Infrared Spectroscopy

- 152 K
- 142 K
- 130 K
- 123 K
- 115 K
- 110 K
- 106 K
- 100 K
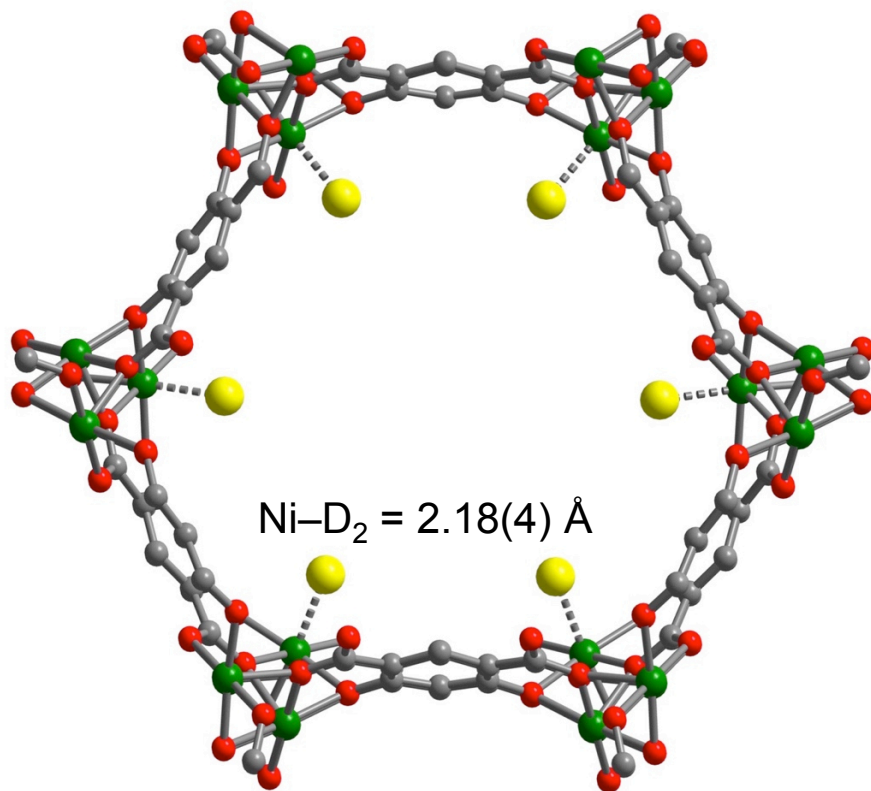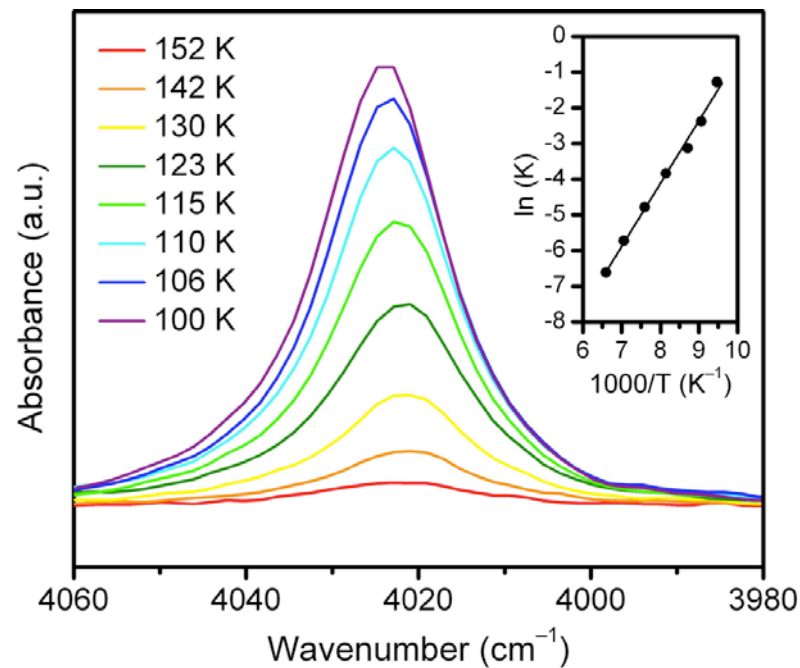
ΔH_{ads} = −13.7 ± 0.5 kJ/mol

(Ni$_2$(dobdc): −12.3 ± 0.5 kJ/mol)

☐ High charge density at Ni^{2+} pulls H$_2$ 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 H$_2$ Desorption

□ H$_2$ desorbs from Ni$_2$(m-dobdc) at higher T, consistent with stronger binding

Close D$_2$ Packing within Ni$_2$(*m*-dobdc)

site I

site II

3.04(6) Å

3.19(1) Å in Ni$_2$(dobdc)
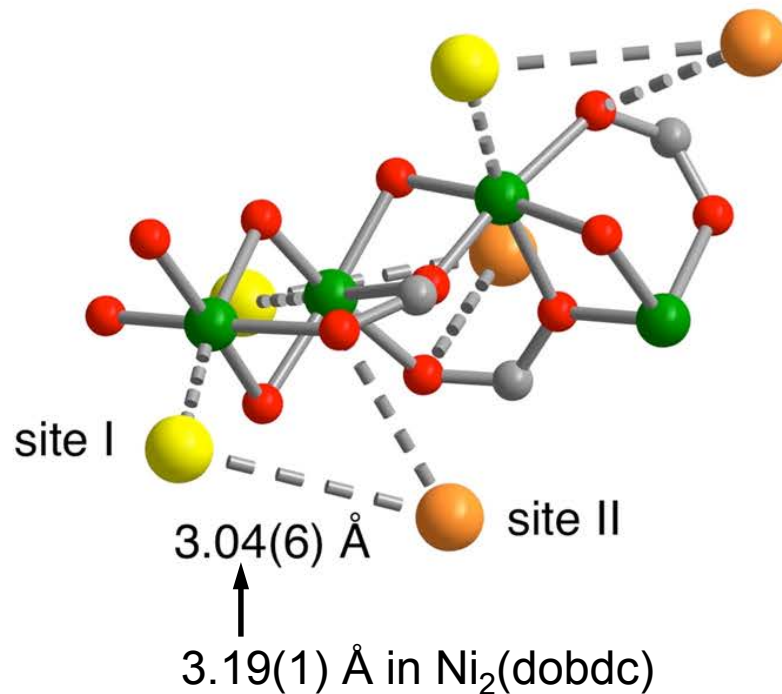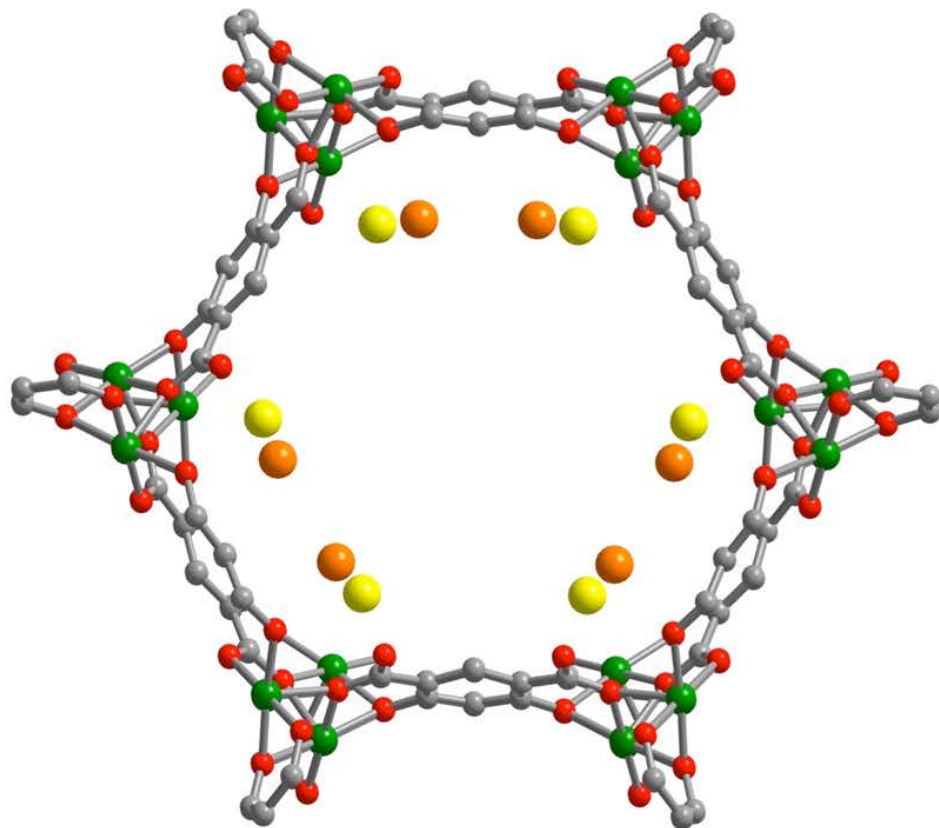
☐ Greater charge density at Ni^{2+} gives closer packing for secondary adsorption site

Kapelewski, Geier, Hudson, Stuck, Mason, Nelson, Xiao, Hulvey, Gilmour, FitzGerald, Head-Gordon, Brown, Long *J. Am. Chem. Soc.* **2014**, *136*, 12119
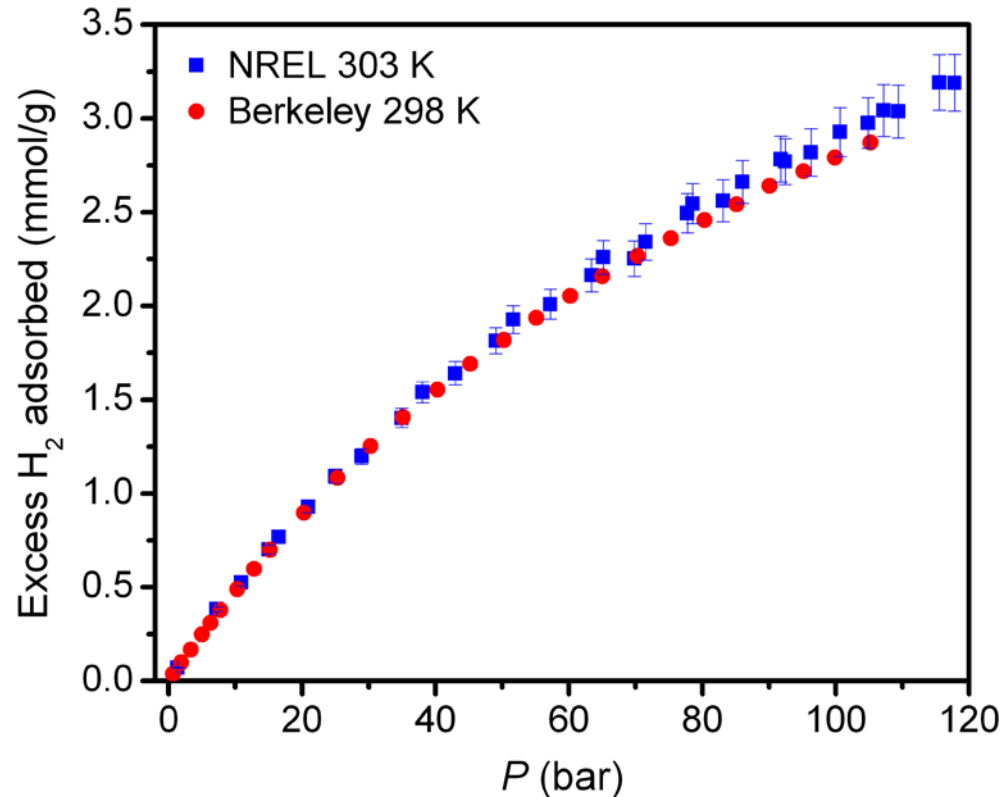
High Pressure H$_2$ Adsorption in Ni$_2$(*m*-dobdc)
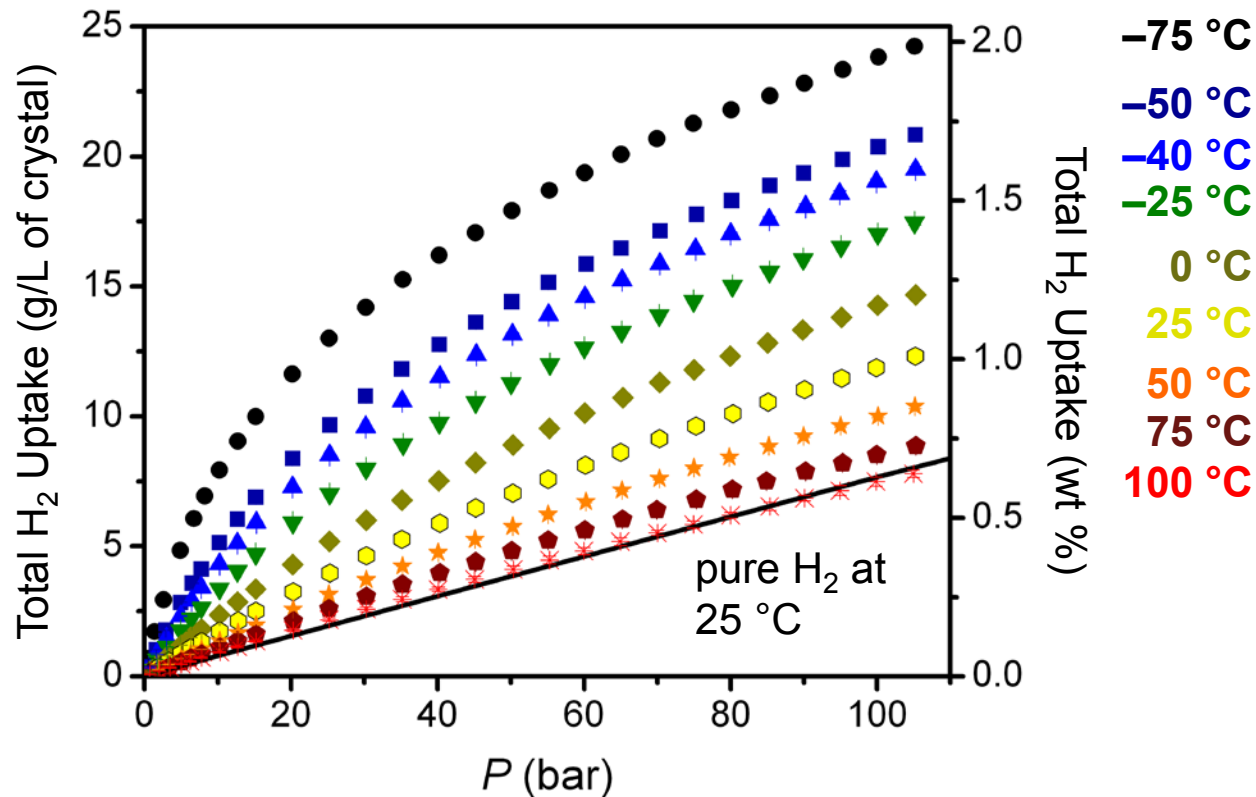
□ Below 100 °C, all isotherms show greater capacity than compressed H$_2$ at 25 °C

□ Ni$_2$(*m*-dobdc) has a total capacity of 24 g/L of crystal at –75 °C and 100 bar

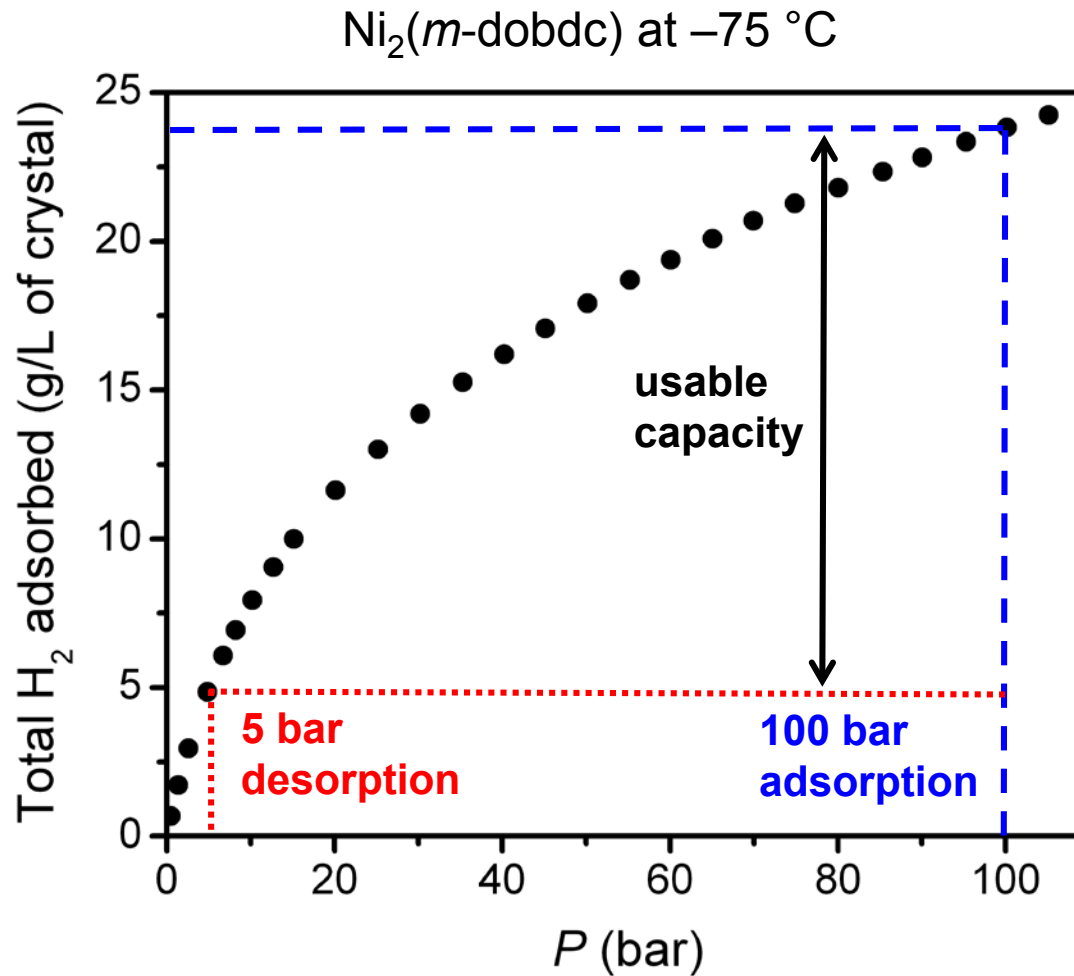# Increased H$_2$ Density in Ni$_2$(*m*-dobdc) at 100 bar
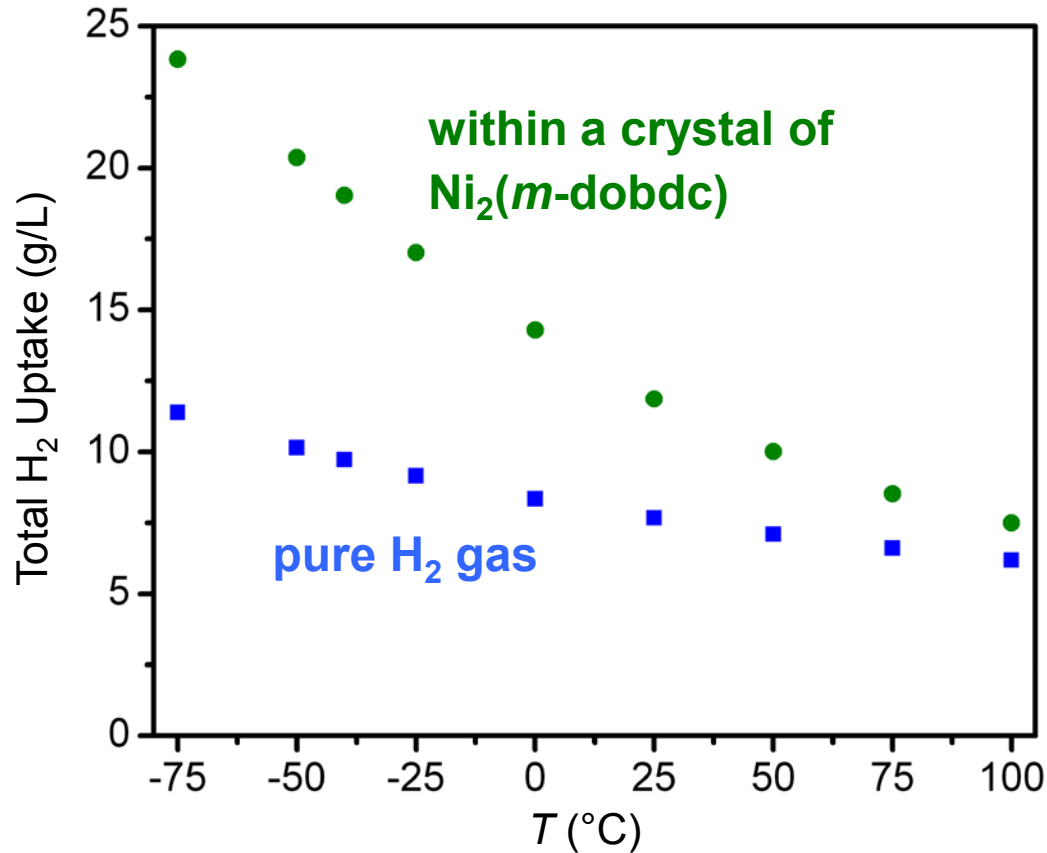
□ Ni$_2$(*m*-dobdc) shows increasing boost in capacity with decreasing temperature

Ni$_2$(*m*-dobdc) Berkeley/NREL Comparison

☐ Collaboration with NREL used to verify H$_2$ isotherms in Ni$_2$(*m*-dobdc)

☐ Data matches within error

# Accomplishments: H₂ Volumetric Usable Capacity

Ni₂(*m*-dobdc) at –75 °C

H$_2$ Usable Capacities in g/L of Crystal

	Ni$_2$(*m*-dobdc)	Co$_2$(*m*-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

☐ Ni$_2$(*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 Co$_2$(*m*-dobdc)
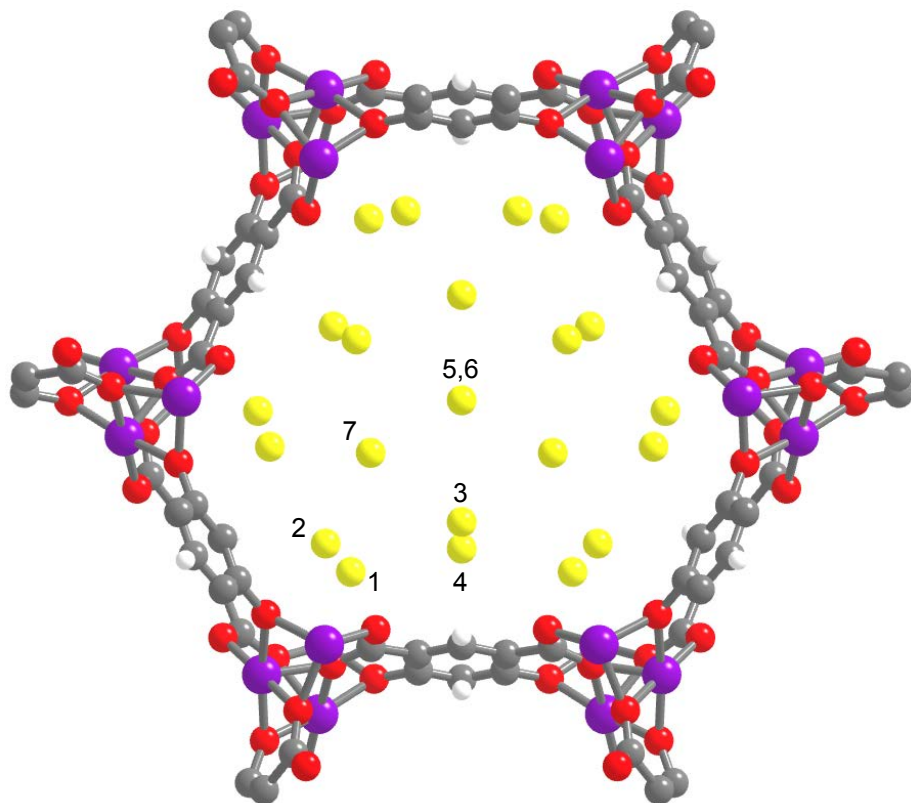
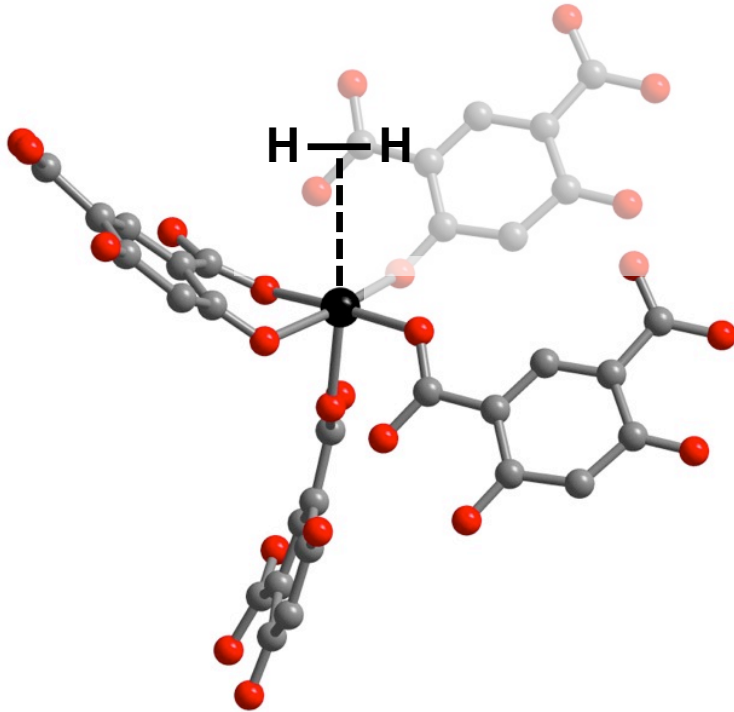| D$_2$···D$_2$ interaction	distance (Å)
1···2	2.82(3)
2···2	3.02(3)
3···4	3.09(5)
4···5	3.48(3)
solid H$_2$*	3.20
liquid H$_2$	3.61

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

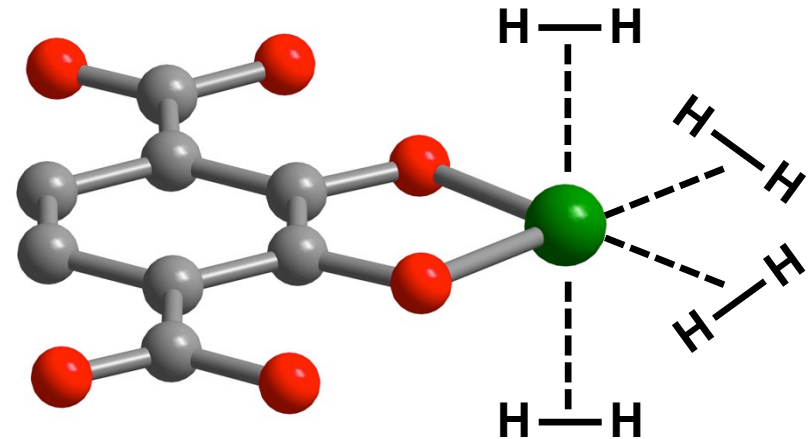☐ Seven distinct D$_2$ adsorption sites are observed at 78 bar and 77 K

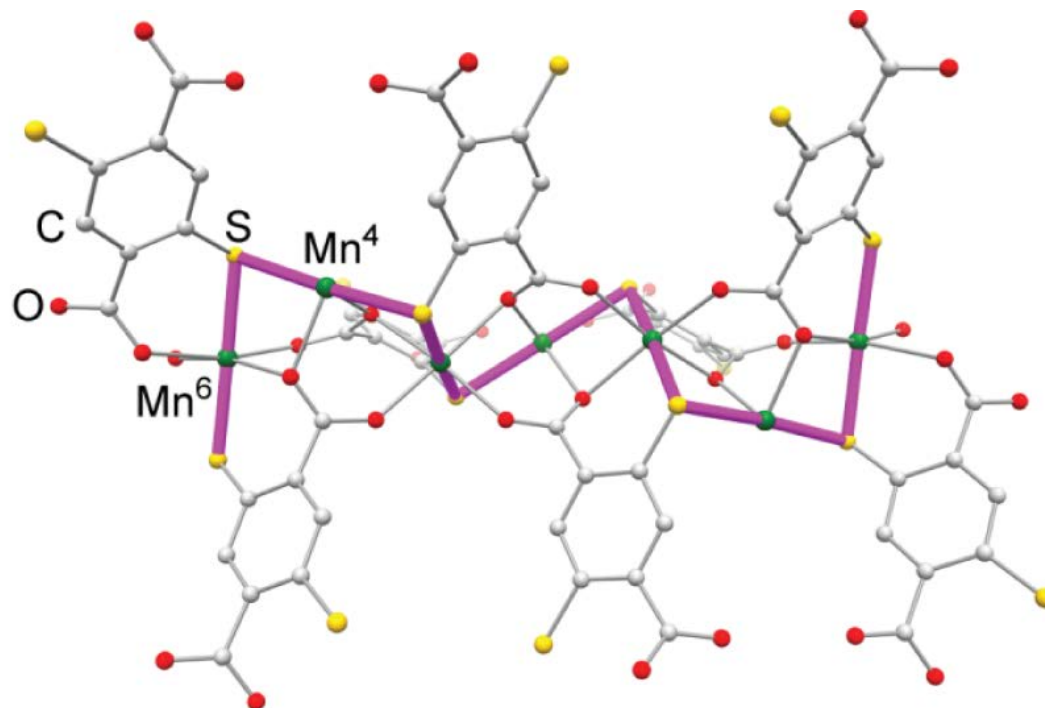# Binding Multiple H₂ Molecules per Metal Cation
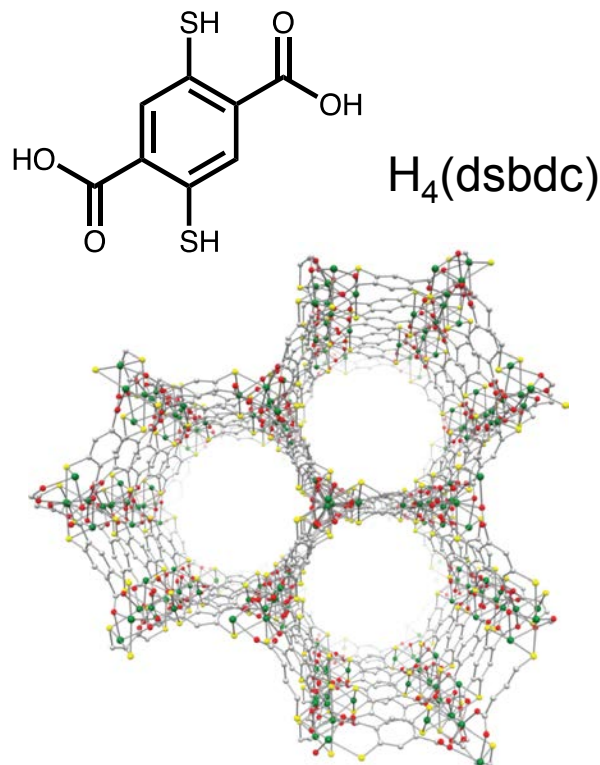
Classical

Next-Generation

1 H$_2$ per metal cation

4 or 5 H$_2$ per metal cation

☐ Volumetric capacity can be substantially increased while maintaining strong binding

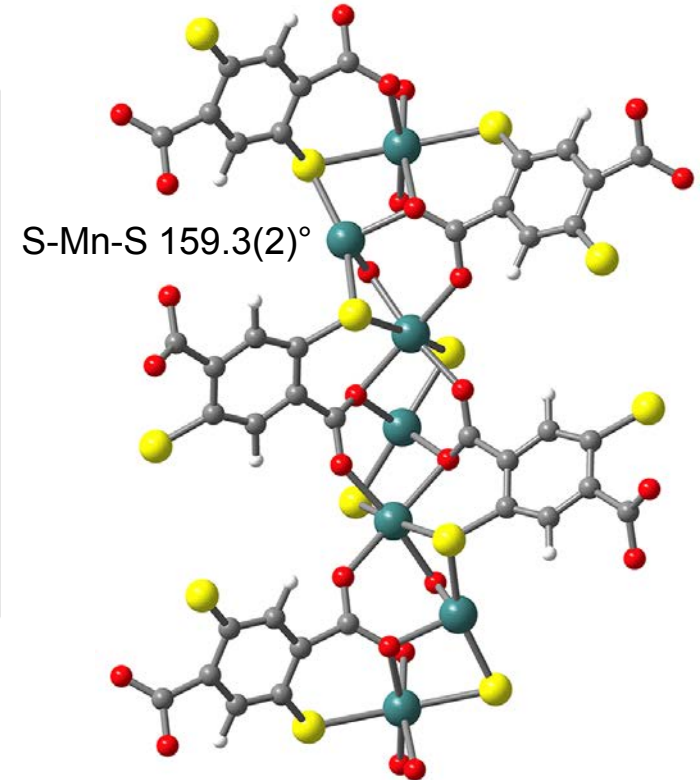# Approach: Mn$_2$(dsbdc)
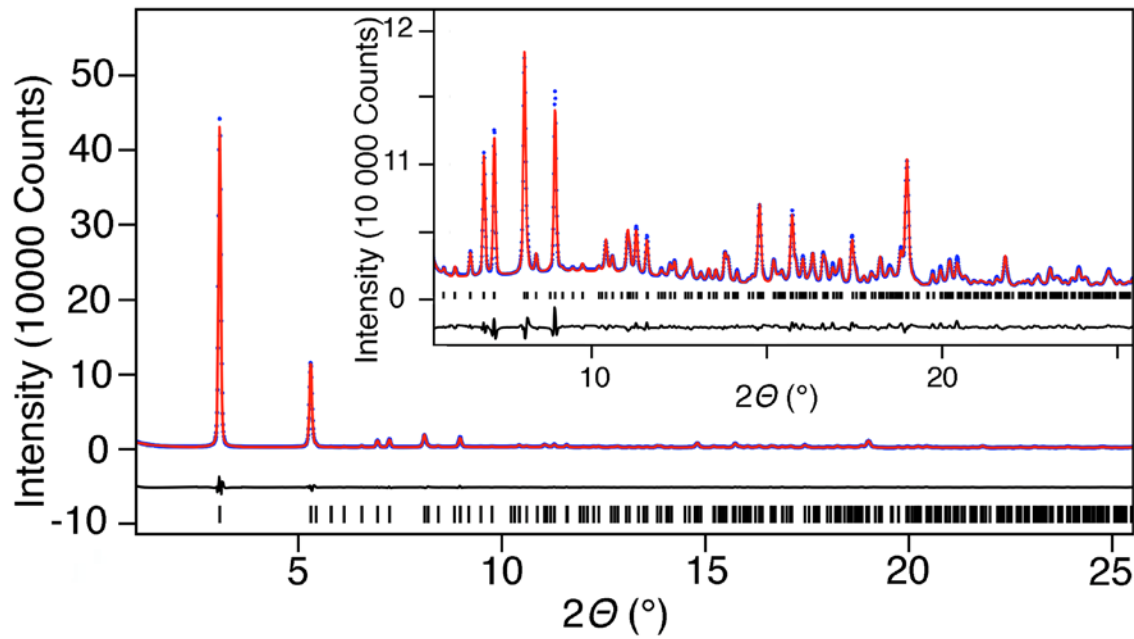

H$_4$(dsbdc)

☐ Isomer of Mn$_2$(dobdc) structure with sulfido groups in place of oxido

☐ Crystal structure shows four-coordinate Mn^{2+} ions with two bound DMF molecules

Structure of Desolvated Mn_2(dsbdc)

S-Mn-S 159.3(2)°

☐ Desolvated structure of Mn_2(dsbdc) determined

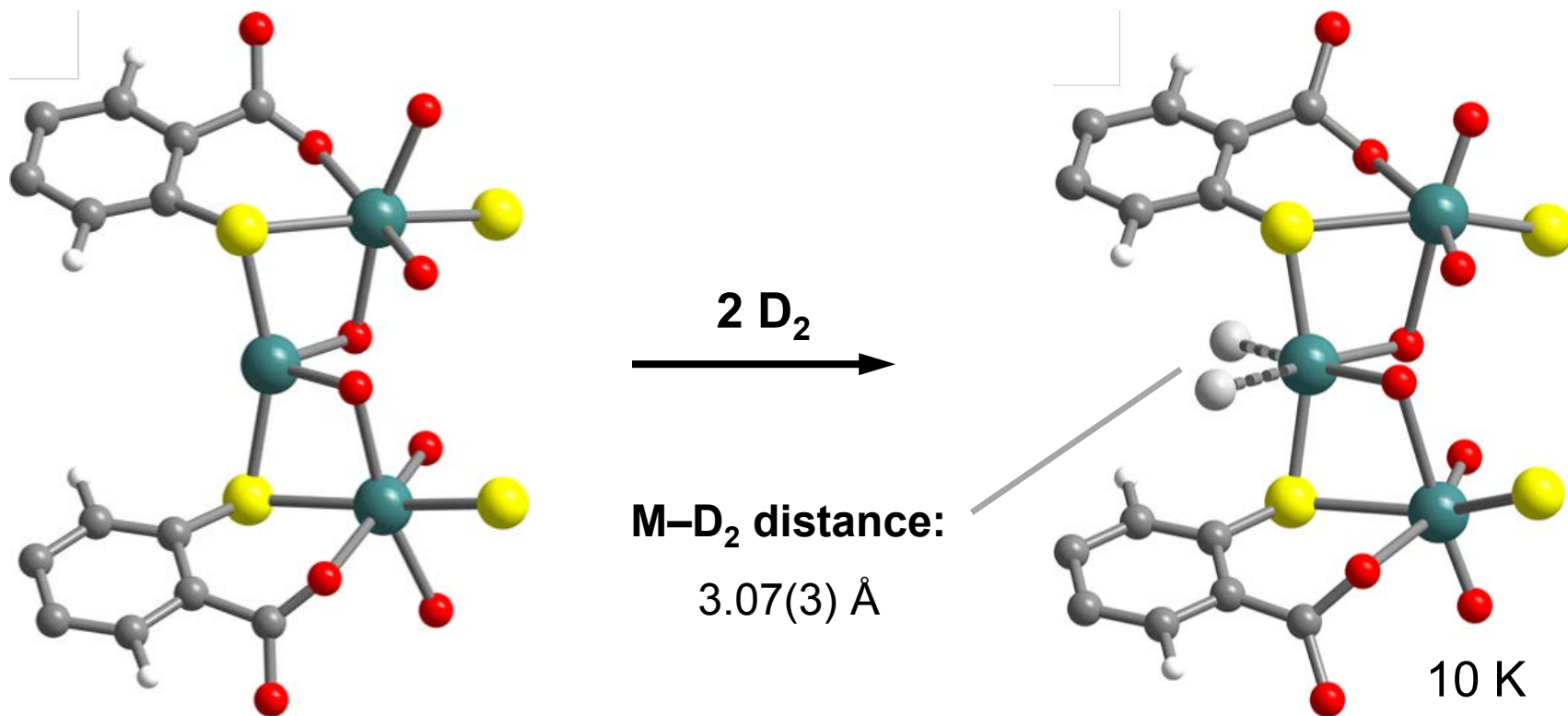☐ Half of the Mn^{2+} ions exhibit four-coordinate, seesaw geometry

H$_2$ Adsorption in Mn$_2$(dsbdc)
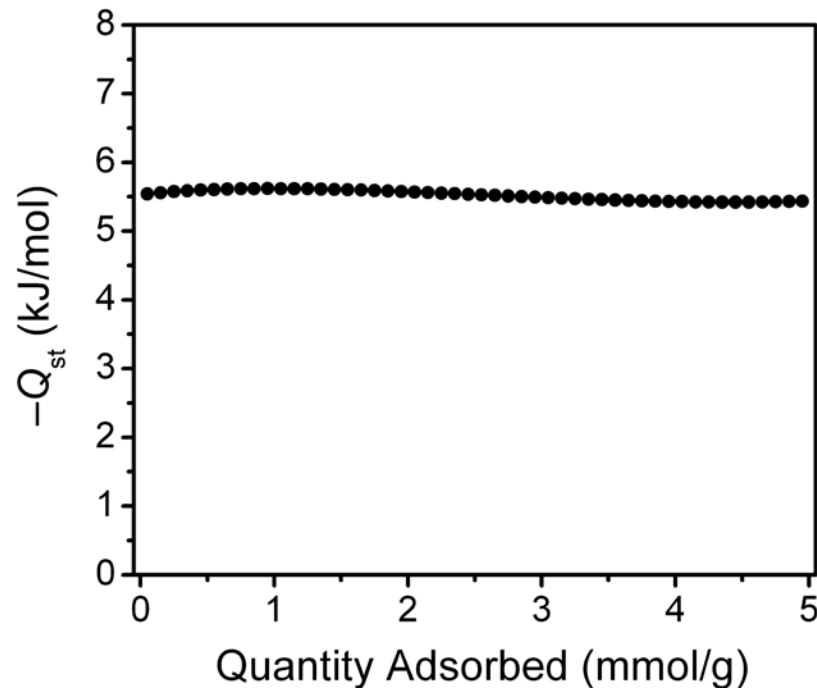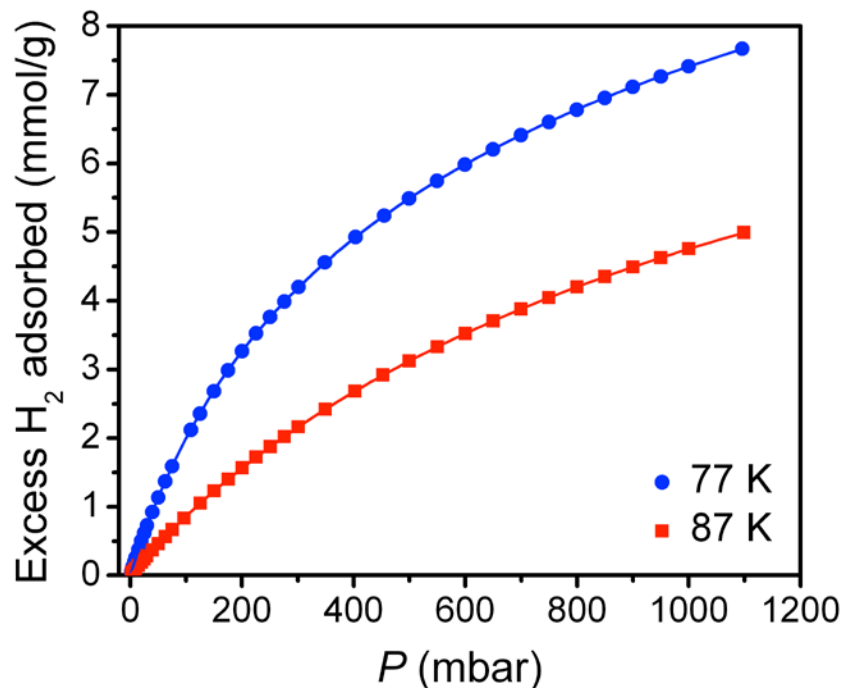
□ Hydrogen uptake is not steep but has about the same capacity as Mn$_2$(dobdc)

□ Binding enthalpy remains low for entire range of loadings

H$_2$ Adsorption in Mn$_2$(dsbdc)

2 D$_2$

M–D$_2$ distance:

3.07(3) Å

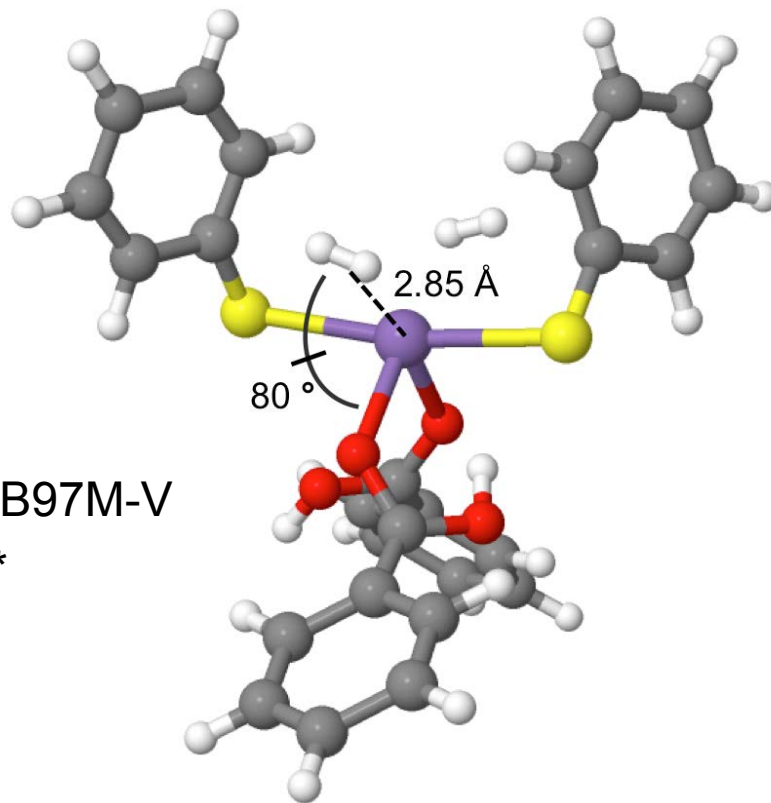10 K

☐ First demonstration of two H$_2$ molecules binding to a metal center in a MOF

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

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

BERKELEY LAB

Pacific Northwest
NATIONAL LABORATORY
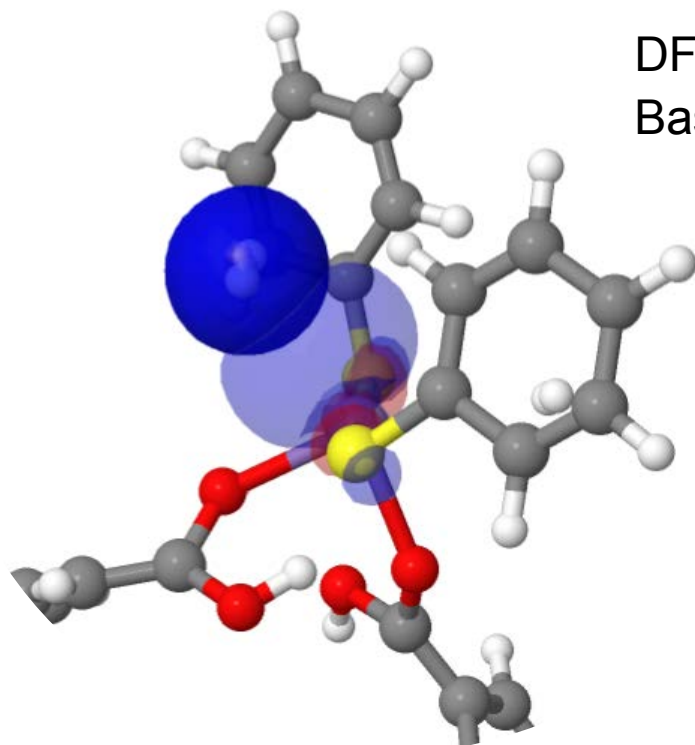
NIST

Computational Results for Mn$_2$(dsbdc)

High-Spin Mn(II)
DFT Functional: B97M-V
Basis set: 6-31g*

2.85 Å

80 °

☐ Shorter Mn–H$_2$ distances than observed experimentally

☐ Modeling electronics of ligand is challenging for this structure type
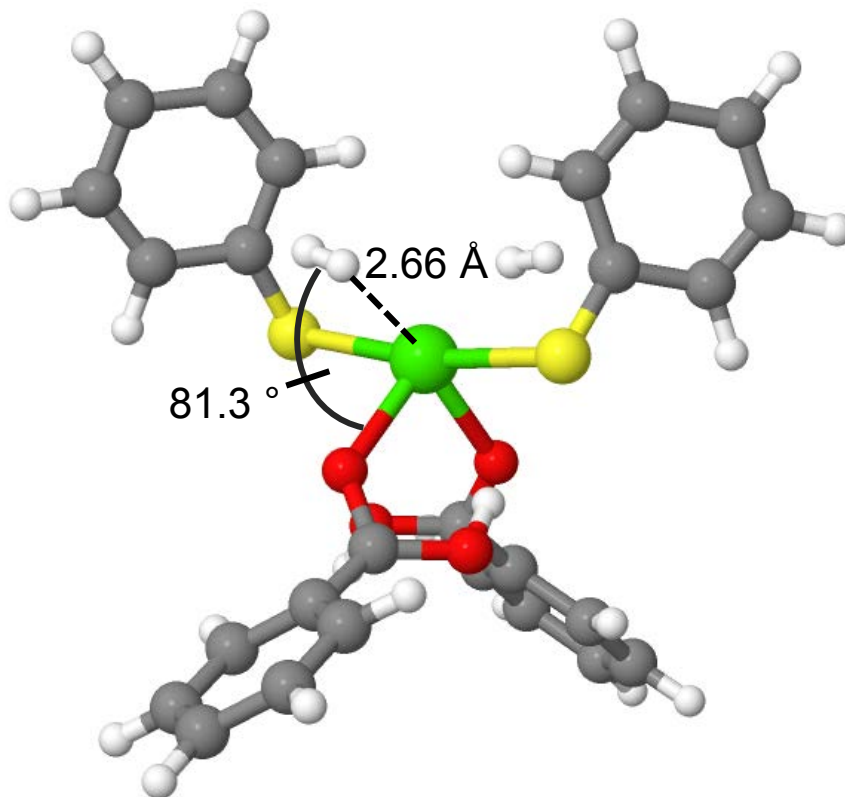
Mn–H$_2$ Energy Decomposition Analysis

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 H$_2$ with Mn^{2+} has double the binding enthalpy of experiment

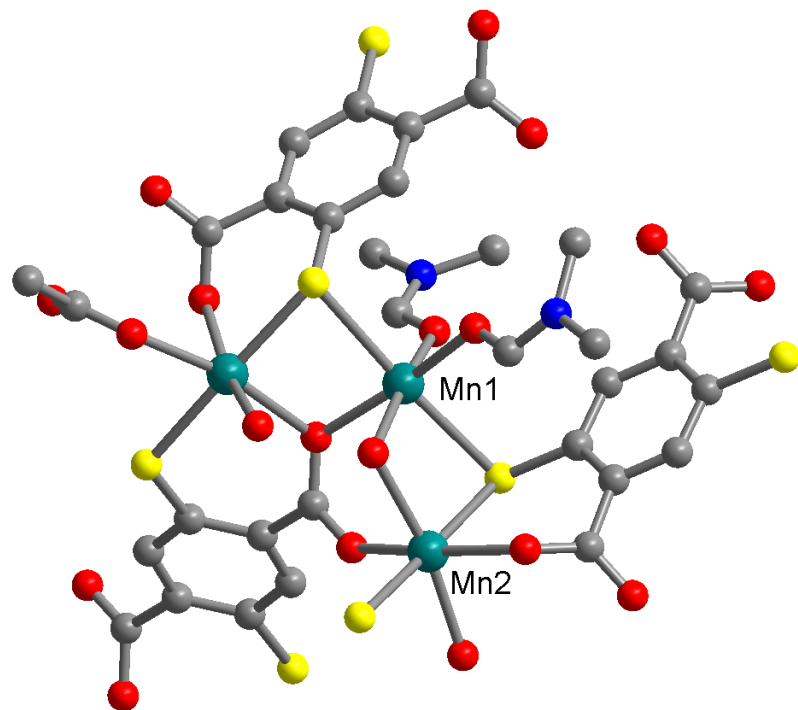☐ New calculations are being run with updated crystal structure
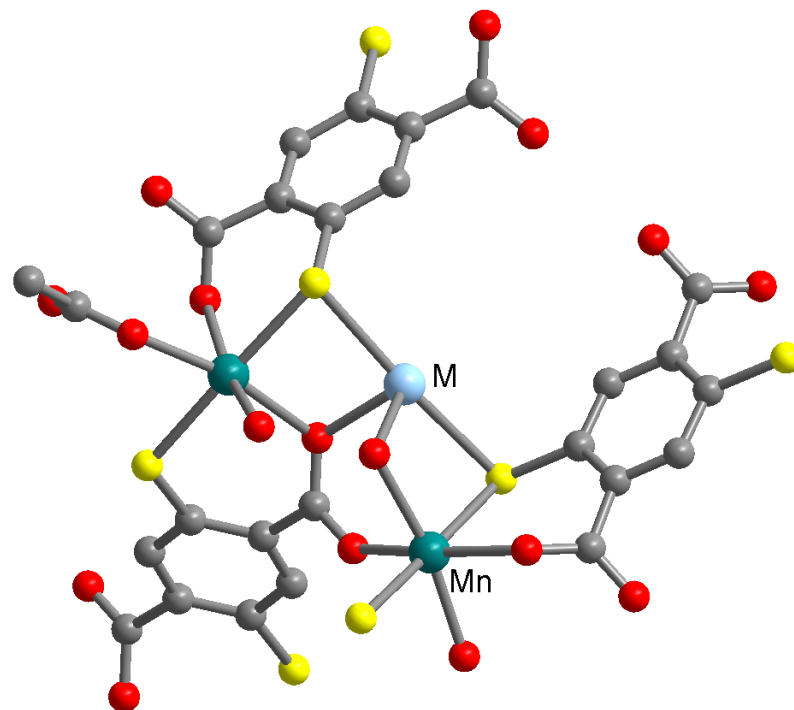
Ca$_2$(dsbdc) Calculations

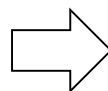DFT Functional: B97M-V
Basis set: def2-qzvp

□ Interaction of Ca^{2+} with H$_2$ has a shorter H$_2$ M distance than in Mn$_2$(dsbdc)

□ ΔE = –17.9 kJ/mol

Variations on Mn$_2$(dsbdc) for Increased H$_2$ Capacity

Mn$_2$(dsbdc)

MnM(dsbdc)

M = Ca, Mg, Co, Ni, Zn

☐ Different metals in the four-coordinate sites may bind more H$_2$ more strongly
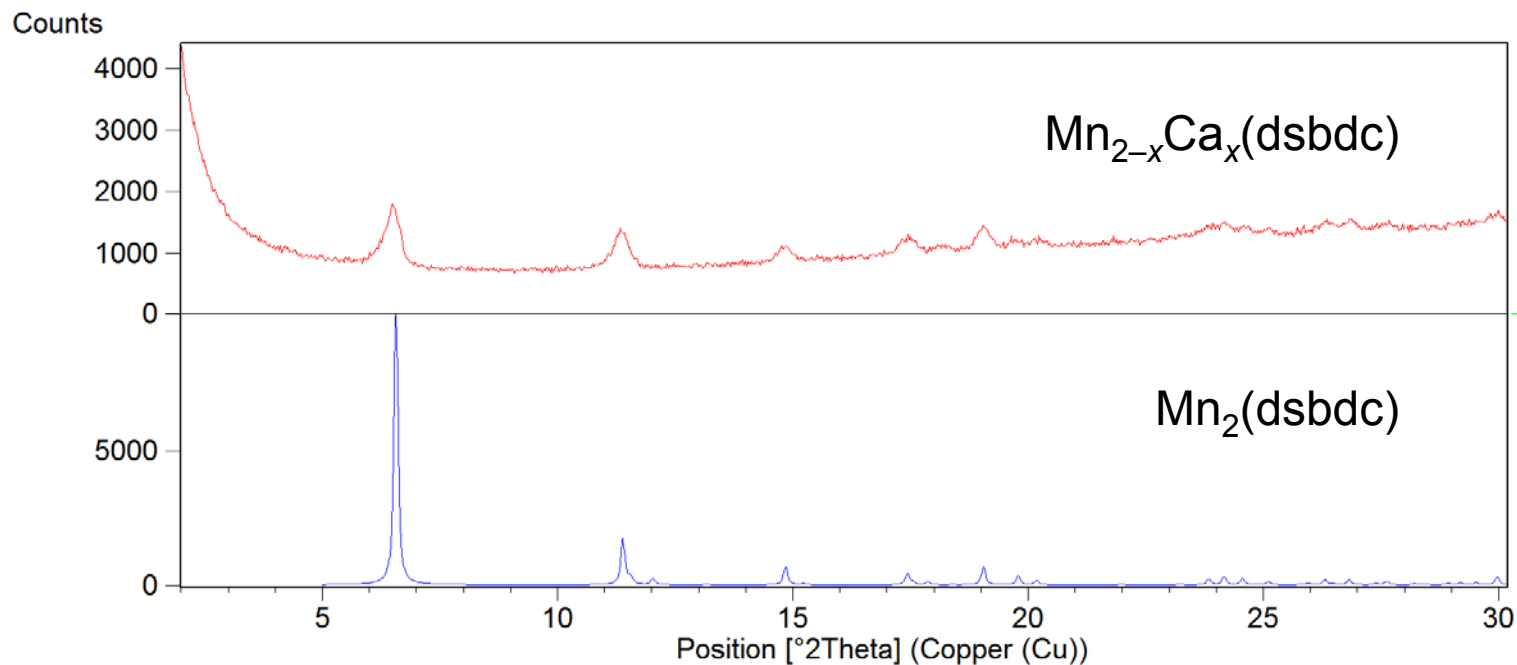
Ca$_2$(dsbdc) Synthesis Attempts

Ca(acac)$_2$ + H$_4$(dsbdc) in DMF

☐ Most promising phase, first two peaks are close to Mn$_2$(dsbdc)

☐ Lower angle peaks suggest a larger unit cell, as expected for larger Ca^{2+}
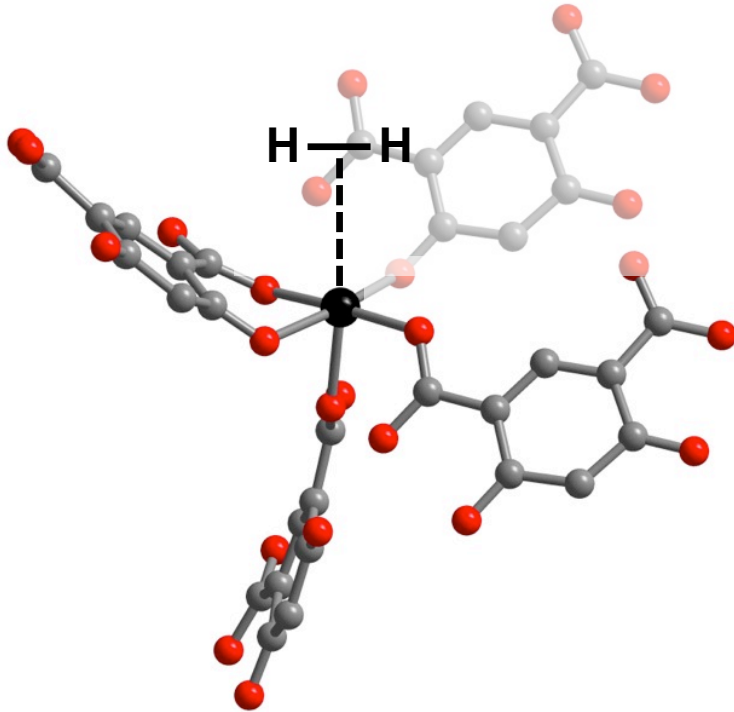
Mixed-Metal $Mn_{2-x}Ca_x(dsbdc)$ Synthesis

$MnCl_2$ + $Ca(acac)_2$ + $H_4(dsbdc)$ in DMF/MeOH

☐ Peaks match well with $Mn_2(dsbdc)$, work underway to find Ca location

☐ 9.2% Ca replacement of Mn according to ICP analysis

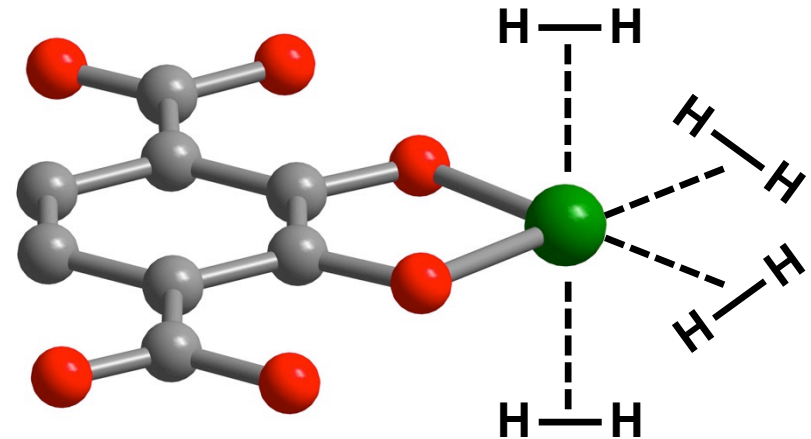# Binding Multiple H$_2$ Molecules per Metal Cation

Classical
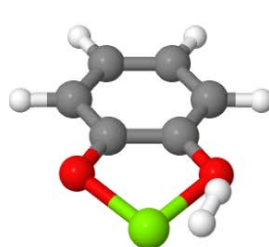
Next-Generation

1 H$_2$ per metal cation

4 or 5 H$_2$ per metal cation

☐ Volumetric capacity can be substantially increased while maintaining strong binding

Calculated Adsorption for H_2 at Catecholate-M^{2+}

Catecholate-Mg^{2+}
Strong binding for first two H_2 molecules
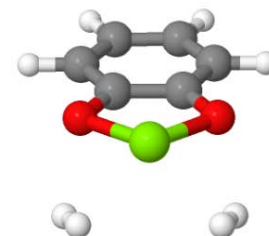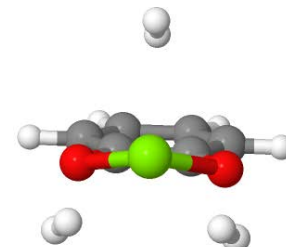
ΔE_{ads} =   −26.3 kJ/mol   −24.4 kJ/mol   −9.4 kJ/mol

Catecholate-Ca^{2+}
Strong binding for all four H_2 molecules
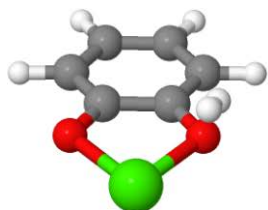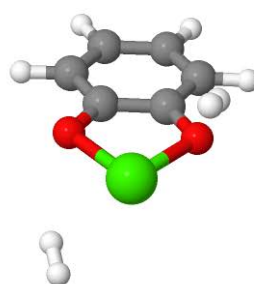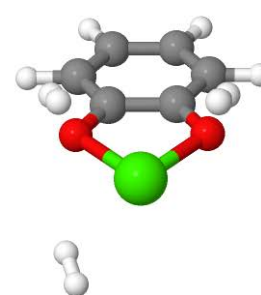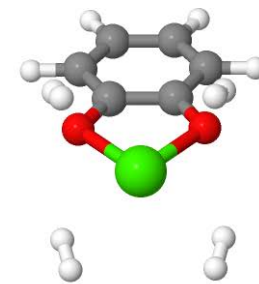
ΔE_{ads} =   −18.5 kJ/mol   −17.1 kJ/mol   −17.4 kJ/mol   −17.0 kJ/mol

Theory: def2-qzvp/B97M-V

Aproach: UiO-68-catecholate-M^{2+}
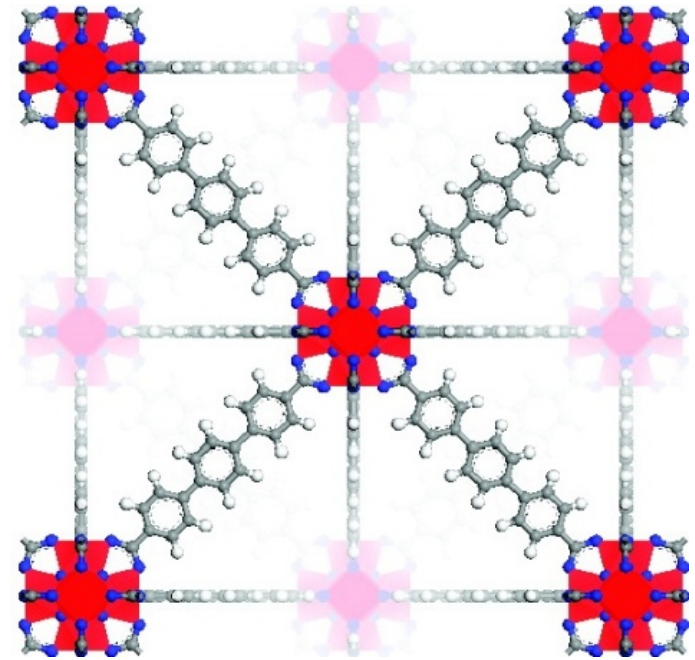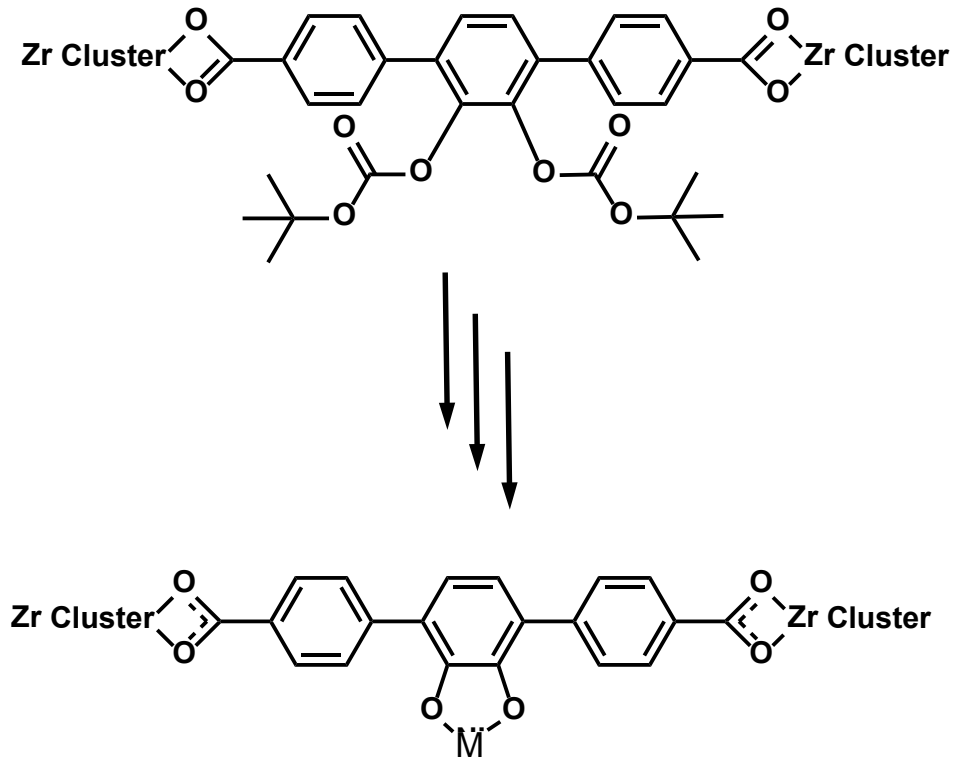
- ☐ Deprotection upon MOF synthesis can expose catechols for metal insertion
- ☐ Catecholate-bound M^{2+} cations can then bind multiple H$_2$ molecules

Deprotection to form UiO-68-catechol
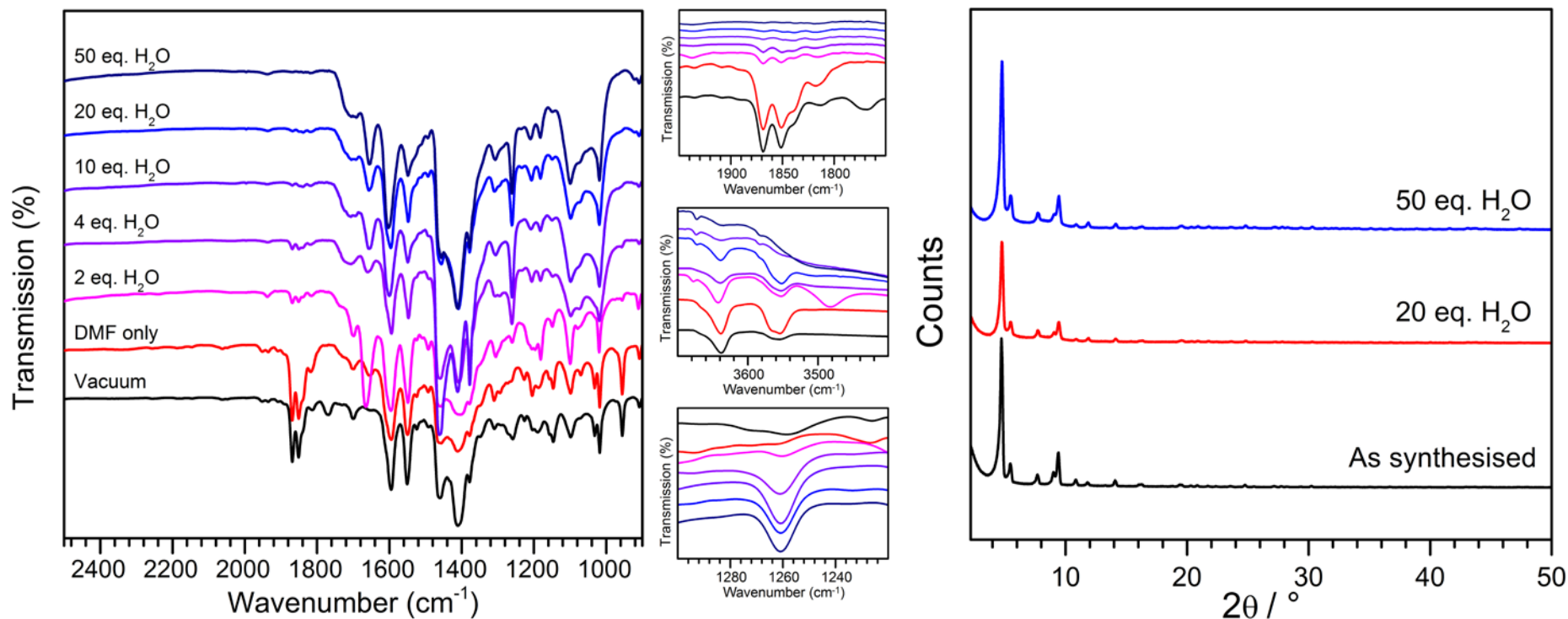
□ Addition of water results in clean deprotection with no loss of crystallinity

□ Metalation of fully deprotected framework is in progress

Synthesis and Metalation of UiO-67-biphenol
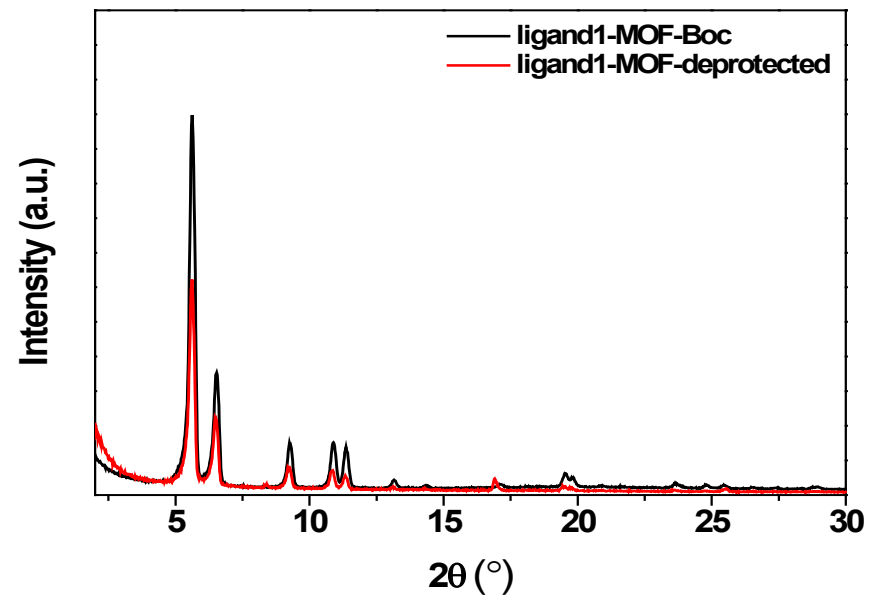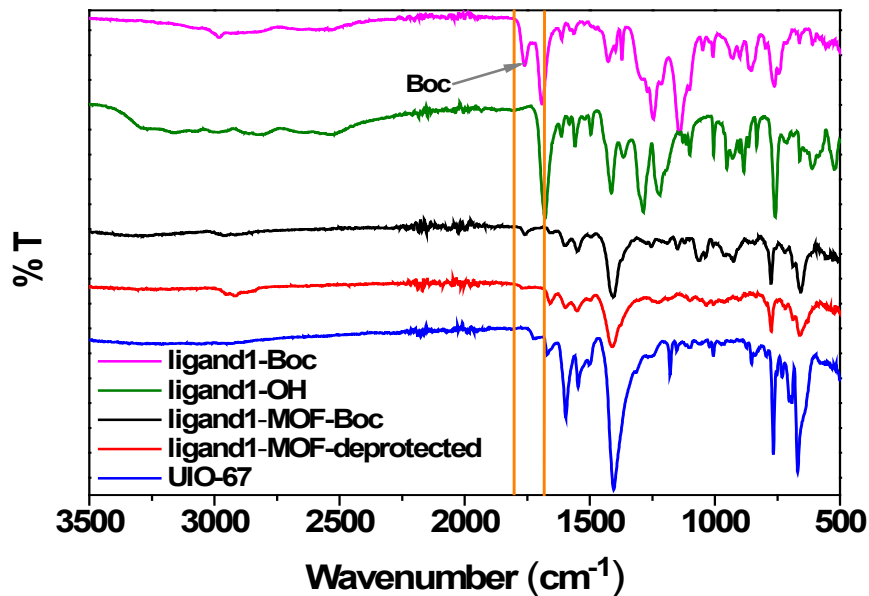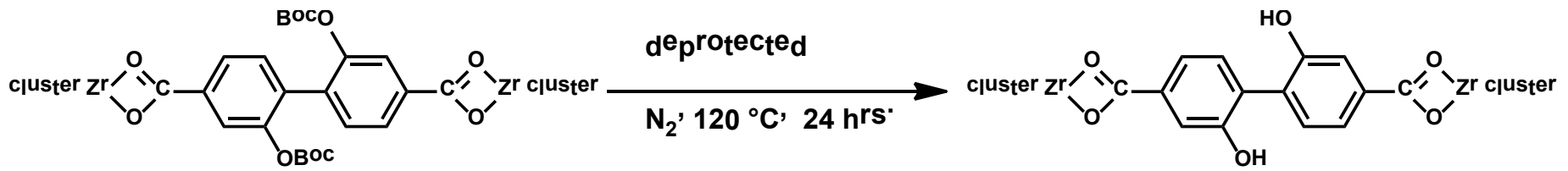
□ Successful synthesis of ligand and deprotected MOF exhibiting UiO-67 structure

□ Successful metalation with $Mg(C_4H_9)_2$ with ~50% incorporation by ICP

Synthesis of UiO-68-bis(biphenol)
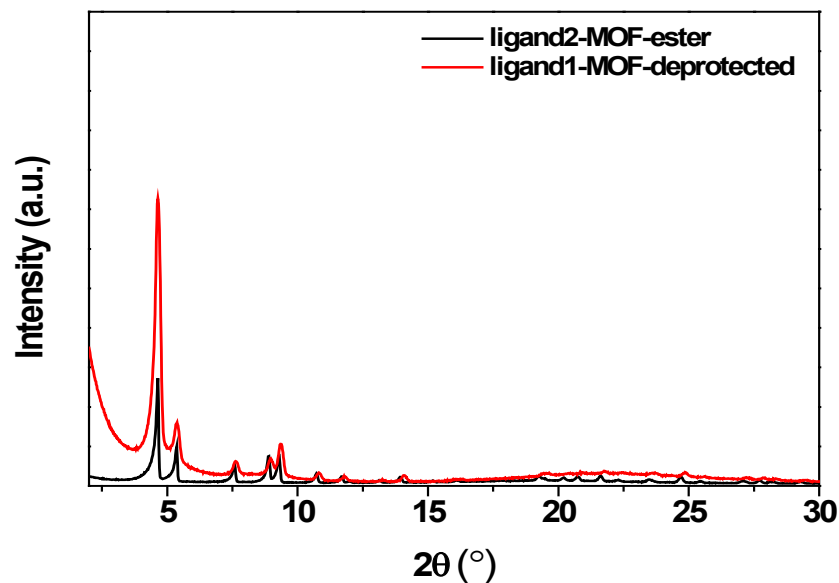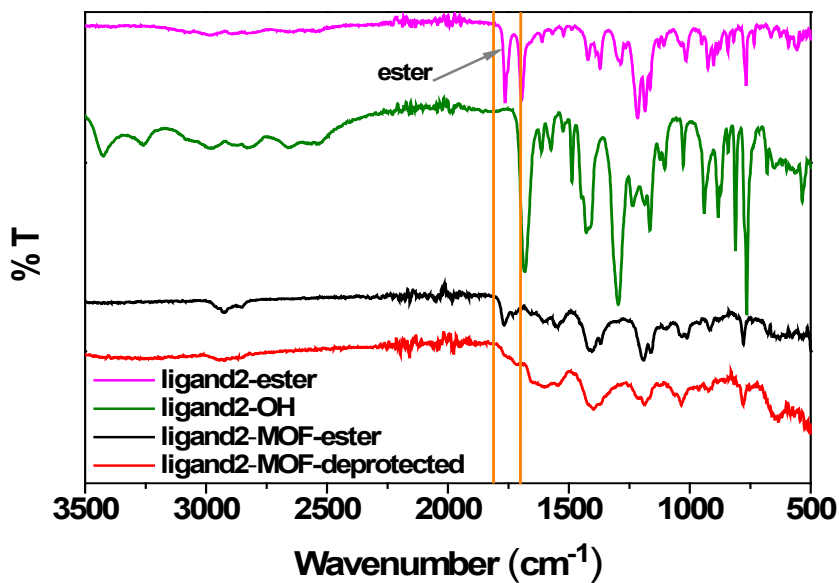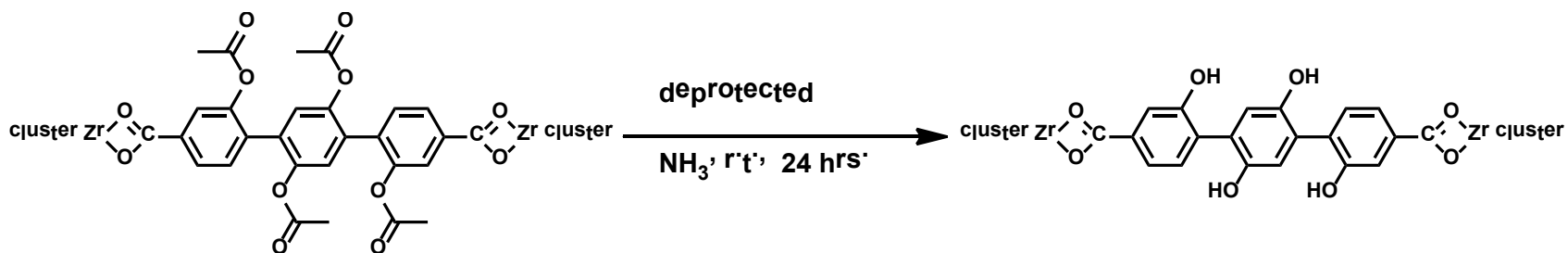
□ Successful synthesis of ligand and deprotected MOF exhibiting UIO-68 structure

□ Metalation attempts are underway, two metals per ligand are possible

Predicted Capacities Upon Insertion of Ca^{2+}

	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 H_2/Ca^{2+} and H_2 packing in pores of Ni_2(*m*-dobdc)

☐ Proof of principle for H_2 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 H_2 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* H_2 dosing
– *Stephen FitzGerald* (Oberlin College)

Remaining Challenges and Barriers

☐ Desolvation of catecholate-bound metal cations remains a challenge

☐ Synthesis of the $Mn_2(dsbdc)$ 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 Mn_2(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*-dobdc) patent application was previously submitted

☐ Mosaic Materials, Inc. has developed an inexpensive, scalable synthesis of Ni_2(*m*-dobdc) and is looking to commercialize this material

Summary

☐ Ni$_2$(*m*-dobdc) shows the best volumetric usable capacities of any porous solid for H$_2$ storage up to 100 bar at ambient temperatures

☐ Mn$_2$(dsbdc) is the first ever example of multiple H$_2$ molecules binding to a single metal center in a MOF!

☐ Synthesis of analogs of Mn$_2$(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

pure H$_2$ at 25 °C

D$_2$

D$_2$
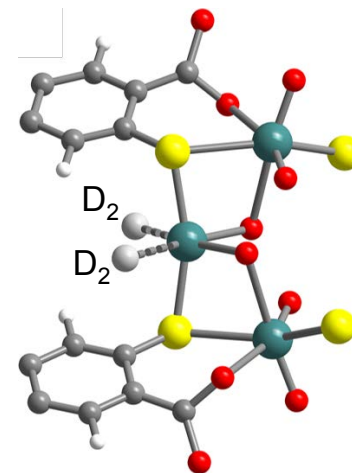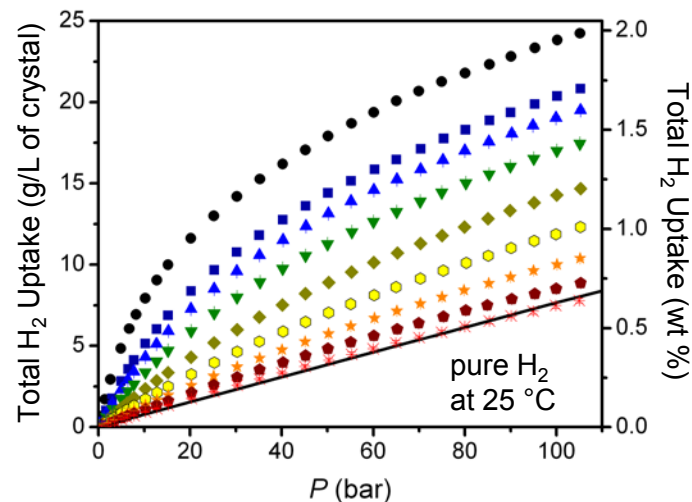
Summary

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 *in situ* gas dosing.	100%
Q3: Order DRIFTS instrument that will be best and most functional for the desired *in situ* 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
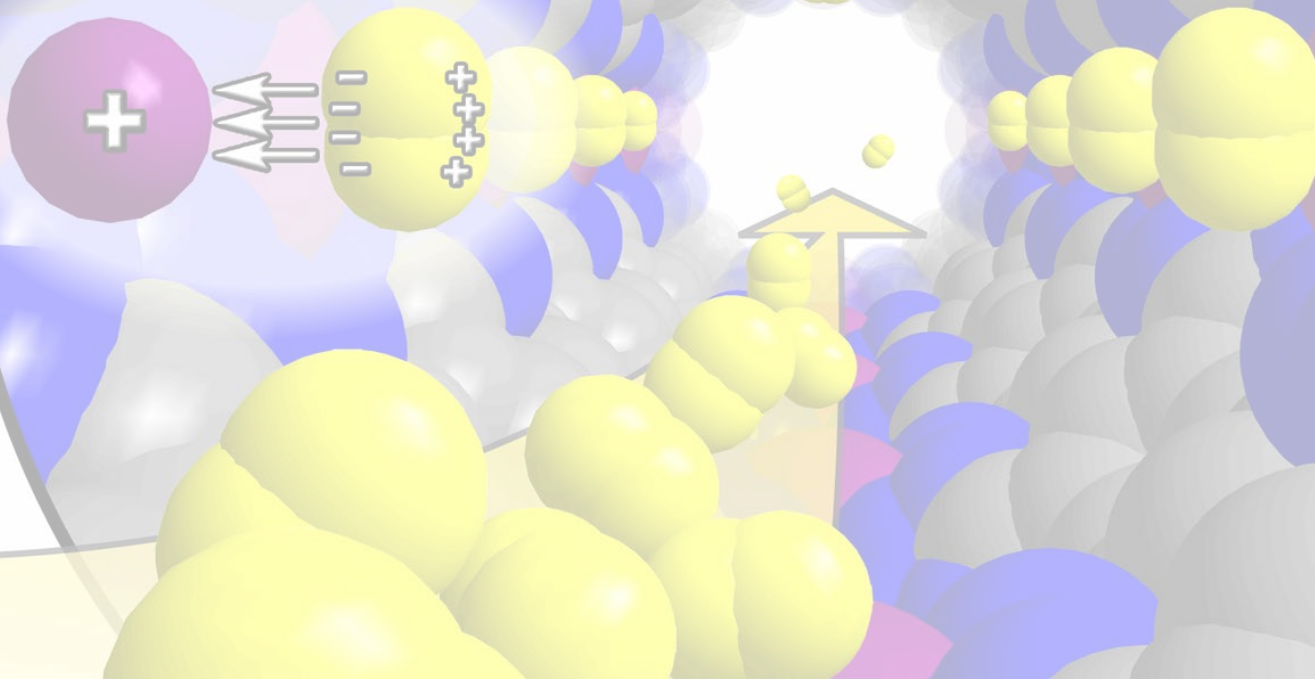
Accomplishments:
77 K H_2 Isotherms in Ni_2(*m*-dobdc)

NREL measurements:

Volumetric H_2 Sorption at 75.6K
— Total Capacity
— Excess Capacity
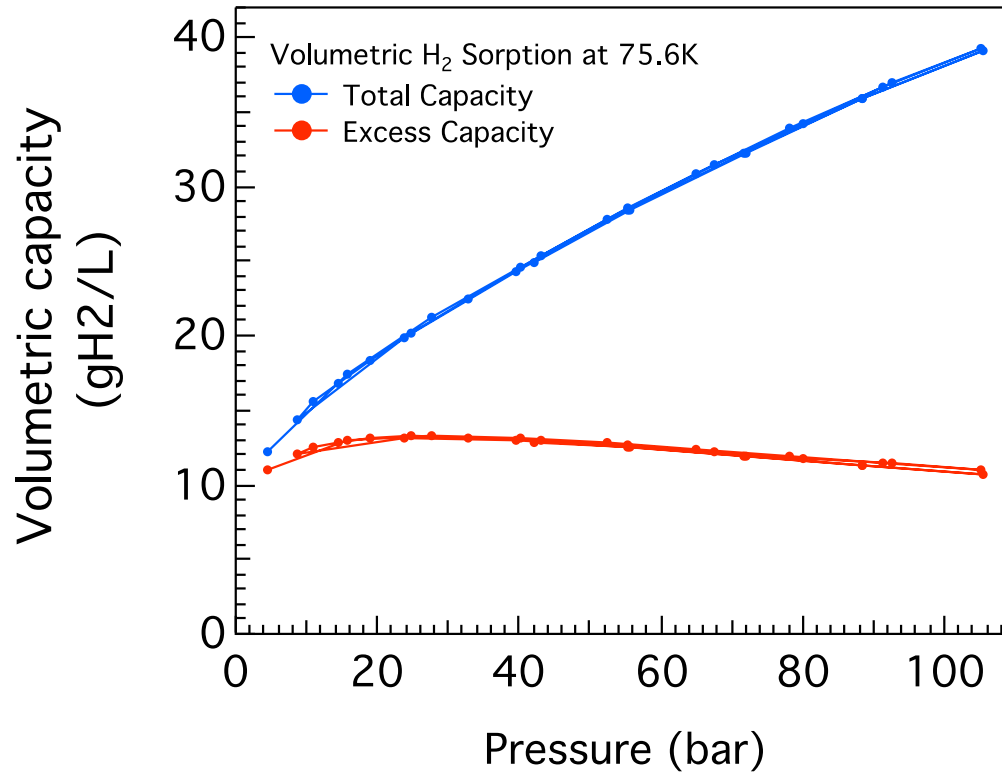
*Single crystal density used for volumetric capacity determination

☐ Data at 77 K shows Ni_2(*m*-dobdc) reaches 38 g/L, very close to system target

☐ NREL-measured isotherms at other temperatures verified LBNL data

Mn$_2$(dsbdc) Desolvation and Purity

	Calculated %	Mn$_2$(dsbdc) %
C	28.59	28.84
H	0.60	0.48
S	19.08	18.73

As-synthesized
MeOH exchanged
Activated
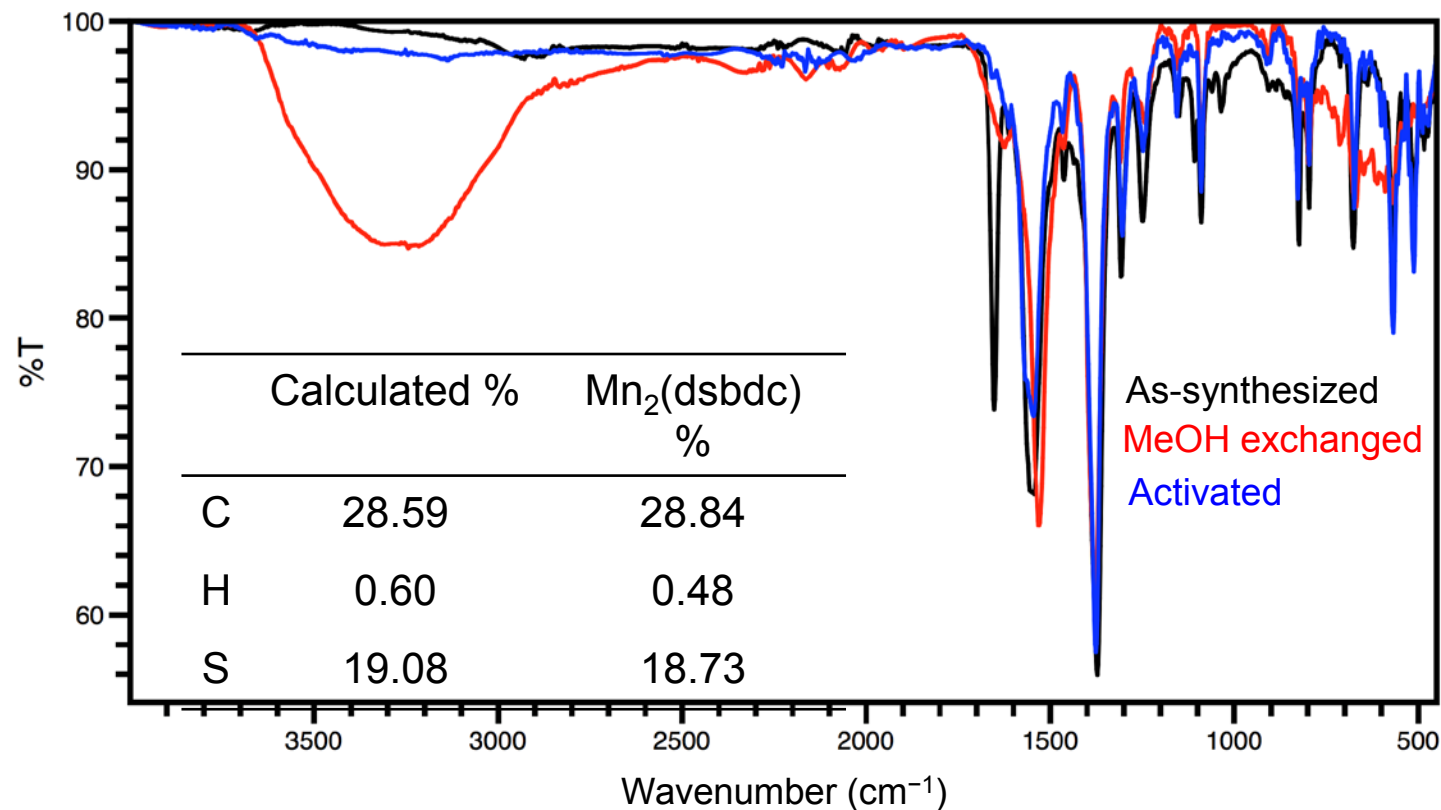
☐ Infrared spectrum indicates successful removal of all DMF in Mn$_2$(dsbdc)

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

High-Surface Area Porous Polymers for Metalation

Ni(cod)$_2$ / cod
2,2'-bipyridine
DMF / 80 °C

PAF-1

ClSO$_3$H / CH$_2$Cl$_2$

Surface area: 1200 m^2/g
Functional group density: 3.7 mmol/g

1. HCHO / HCl / AcOH / H$_3$PO$_4$
   90 °C / 3 d

2. P(OEt)$_3$ / 130 °C / 3 d

3. HCl / Reflux

Surface area: 835 m^2/g
Functional group density: 3.2 mmol/g

☐ Meets milestone of porous polymer with surface area > 1000 m^2/g

☐ Metalation and activation of polymers is underway