2015 DOE Hydrogen and Fuel Cells Program Review

Hydrogen Storage in Metal-Organic Frameworks

P. I. Jeffrey Long

Lawrence Berkeley Nat. Lab., University of California, Berkeley
Nat. Inst. of Standards and Technology, General Motors Co.

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Project ID #: ST103

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

Overview

Timeline

- Start: April 2012
- Finish: May 2015

Budget

- Total project funding
  - DOE share: $2,100k
  - Contractor share: $525k
- DOE funding spent to date*:
  - $1,778k

*as of 3/31/15

Barriers Addressed

- A. System Weight and Volume

Partners

- LBNL: synthesis and modeling
- NIST: neutron diffraction
- GM: high-pressure adsorption (funding ended FY14)
- Project lead: Jeffrey Long (LBNL)

Relevance

Project objectives

- Research and development of onboard systems that 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.

- Synthesize new metal-organic frameworks capable of achieving the –15 to –20 kJ/mol adsorption enthalpy required for use as hydrogen storage materials operating under 100 bar at ambient temperatures

Approach

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

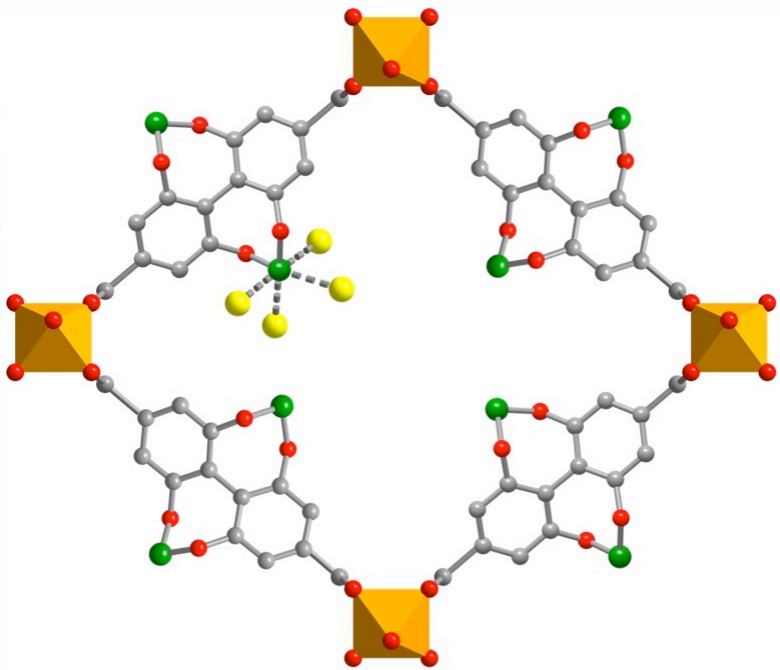
Task 2: Characterization of Framework-H_2 Interactions
(Craig Brown-NIST)

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

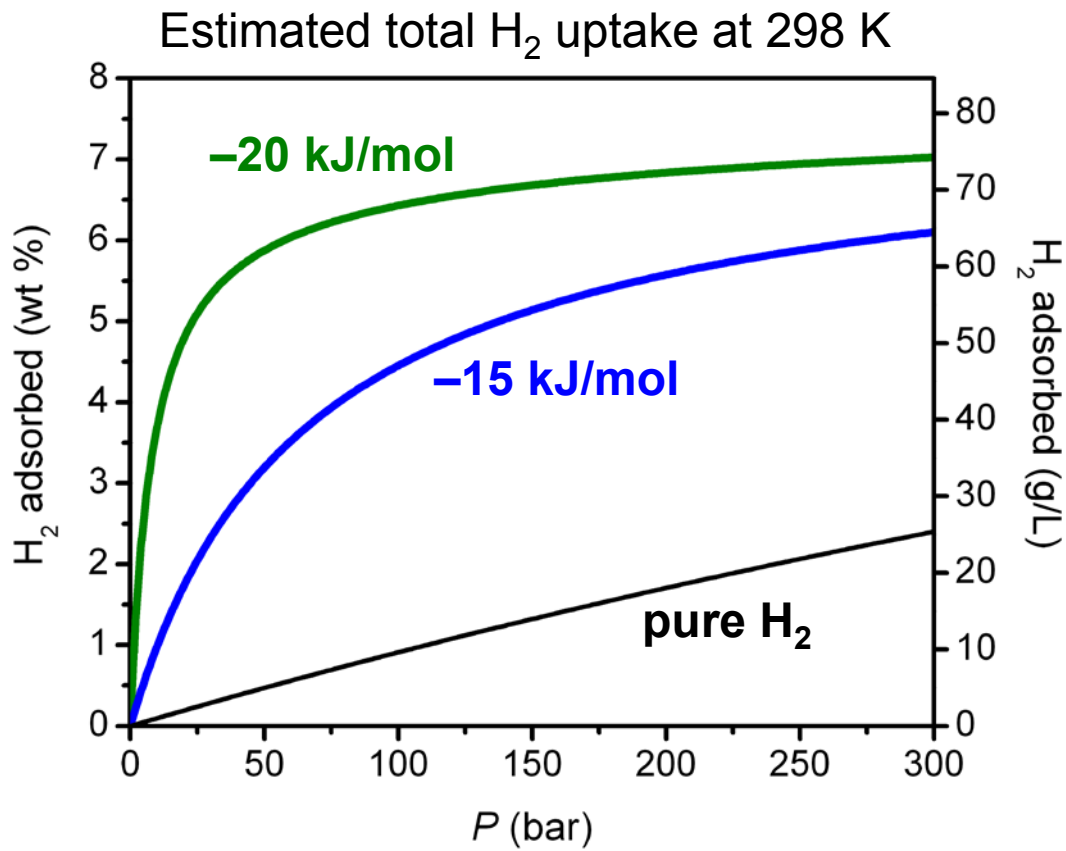
Task 4: High Pressure Hydrogen Adsorption Measurements
(Anne Dailly-GM)

Approach

Multiple H_2 Binding Sites per Metal



$Al(OH)(C_{14}O_{12}Mg_4)$



- ☐ Create MOFs with exposed M^{2+} or M^{3+} cations, each binding 4 or 5 H_2 molecules
- ☐ Hypothetical MOF can meet capacity targets, depending on Mg^{2+} binding enthalpy

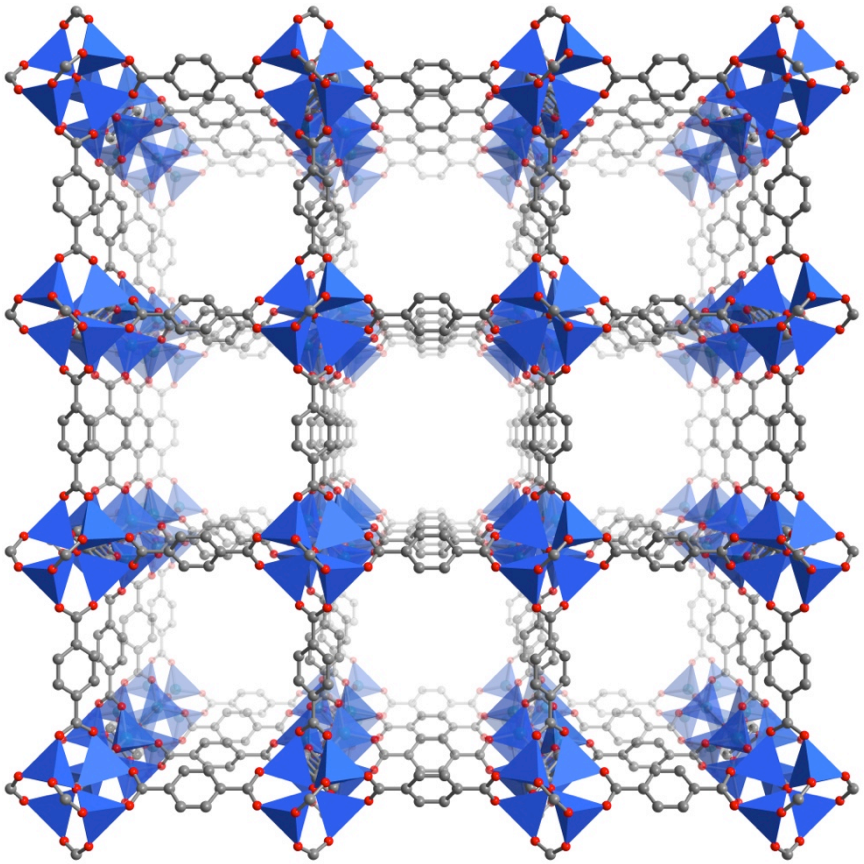
Approach: Milestones Tasks 1 & 2

Due date	Description	%Comp	Status April 2015
03/14	**Task 1 (G/N):** Synthesis of MOFs with reversible H_2 uptake > 2.5 wt %	100%	Completed
03/14	**Task 1 (G/N)**: Preparation of a high-valent MOF with an initial H_2 adsorption enthalpy greater than 12 kJ/mol	100%	Ni_2(*m*-dobdc) displays H_2 binding enthalpy of -12.3 kJ/mol
03/14	**Task 1 (G/N):** Synthesis of MOFs with the ligands prepared in year 1	100%	3 bipyridine-MOFs synthesized
03/14	**Task 1 (G/N):** Demonstration of the post-synthetic insertion of metals into the open chelate sites of these new materials	100%	Single crystal diffractions shows binding of M^{2+} to the bipy sites
03/14	**Task 1 (G/N):** Preparation of at least 2 MOFs with the optimal 7 Å between opposing pore surfaces as predicted with *in silico* screening	100%	3 dicarboxylate MOFs synthesized with optimal pore size
05/15	**Task 1 (G/N):** Demonstration of a MOF with an initial H_2 adsorption enthalpy greater than the current record of 15.1 kJ/mol	90%	On-track
05/15	**Task 1 (G/N):** Synthesis of a metal-organic framework with reversible hydrogen uptake greater than 4.5 wt % at 298 K	50%	On-track
03/14	**Task 2:** Demonstrate that understanding of MOF-H_2 interactions through inelastic neutron scattering experiments provide new insight	100%	Completed
05/15	**Task 2:** Demonstrate the use of quasielastic neutron scattering to help understand the roles of diffusion and entropy in H_2 binding to MOFs	95%	Experiments and analysis underway

Approach: Milestones Tasks 3 & 4

Due date	Description	% Comp	Status April 2015
12/14	**Task 3:** Demonstrate the ability to determine H_2-metal interactions in realistic systems containing low-coordinate metal cations	100%	Completed
05/15	**Task 3:** Pre-screen optimal MOF targets by identification of systems that produce an H_2 binding enthalpy > 20 kJ/mol	100%	Completed
03/14	**Task 4:** Demonstration of a correlation between high-pressure measurements and theoretical and spectroscopic predictions	100%	Correlation demonstrated for several MOF-74 variants
06/14	**Task 4:** Demonstrate the ability to measure H_2 adsorption in a test material up to 10 cycles at 298 K	100%	Completed
09/14	**Task 4:** Demonstrate the ability to measure H_2 adsorption in a test material up to 10 cycles at t° relevant to onboard vehicle applications	100%	Completed
12/14	**Task 4:** Down select 1 or 2 samples for 100 cycles measurement	100%	Completed
05/15	**Task 4:** Demonstrate the ability to measure high-pressure H_2 adsorption in MOFs up to 100 cycles at temperatures relevant to use in onboard vehicle applications	80%	Work stopped 12/2014

Approach: Metal-Organic Frameworks



Zn_4O(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

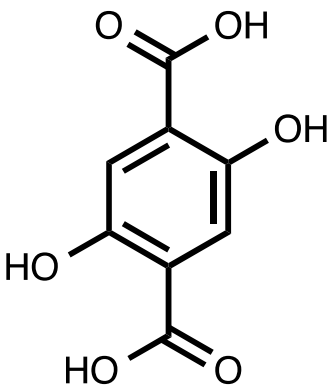
Can these high-surface area materials be used for hydrogen storage at ambient temperatures?

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

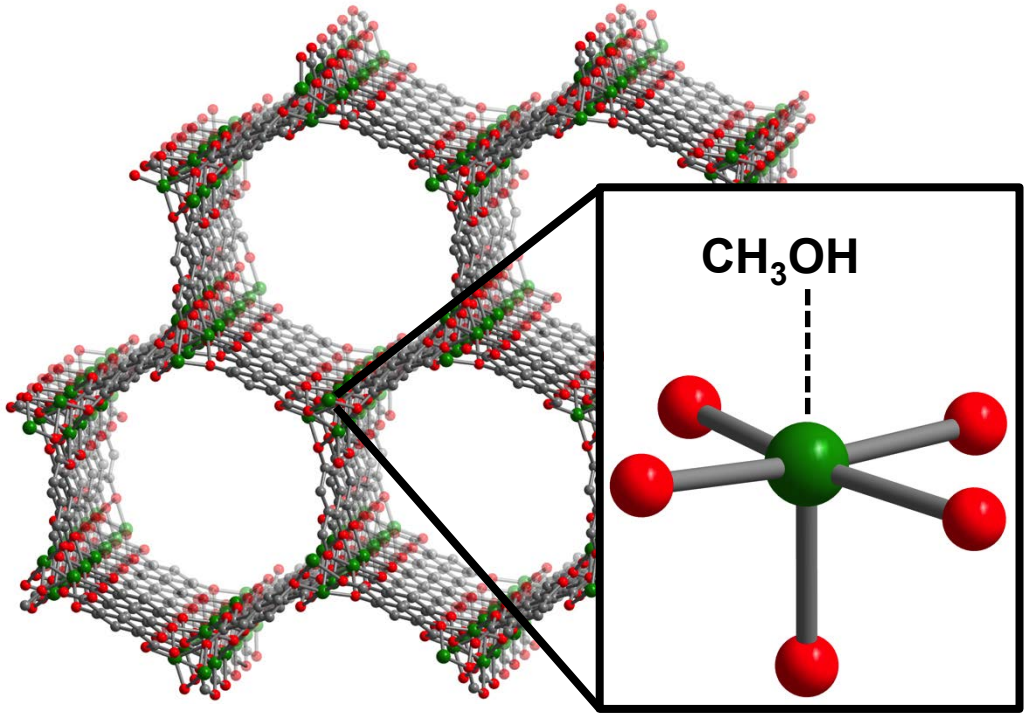
A MOF with a High Density of Exposed M^{2+} Sites

$MX_2 \cdot 6H_2O$

+



H_4dobdc



M_2(dobdc), MOF-74
(M = Mg, Mn, Fe, Co, Ni, Cu, Zn)

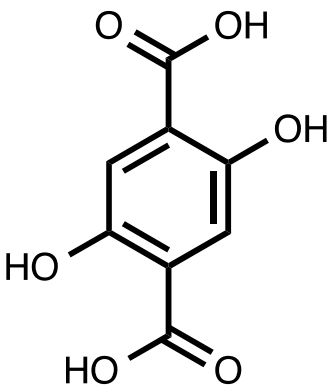
- Activated frameworks have Langmuir surface areas of 1277-2060 m^2/g

Caskey, Wong-Foy, Matzger *J. Am. Chem. Soc.* **2008**, *130*, 10870
Sumida, Brown, Herm, Chavan, Bordiga, Long *Chem. Commun.* **2011**, *47*, 1157

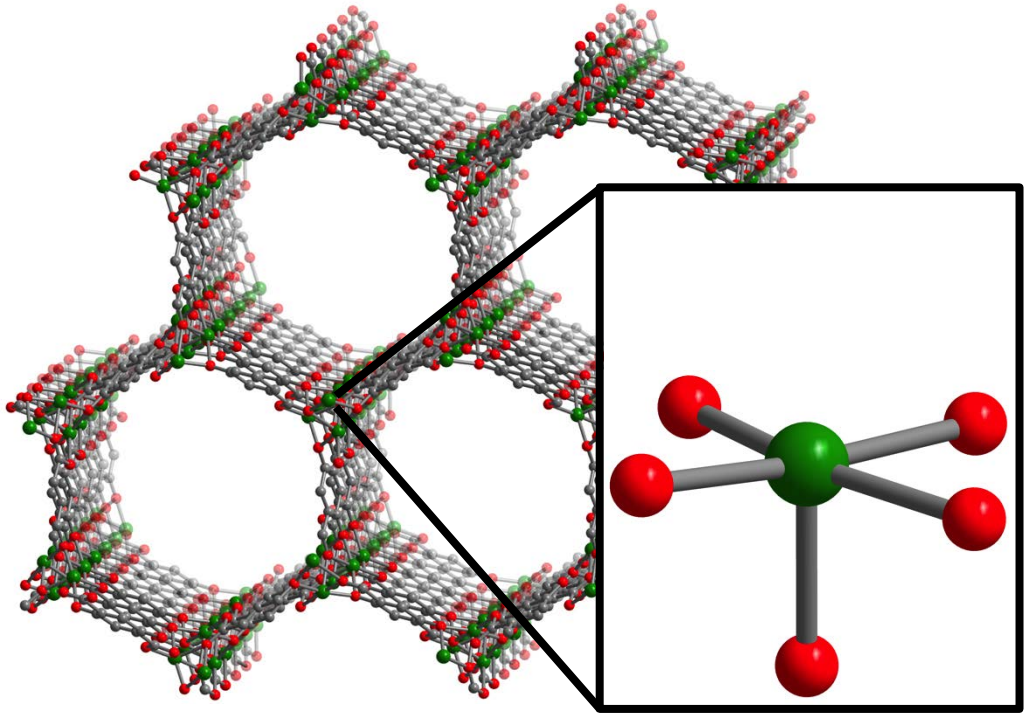
A MOF with a High Density of Exposed M^{2+} Sites

$MX_2 \cdot 6H_2O$

+



H_4dobdc

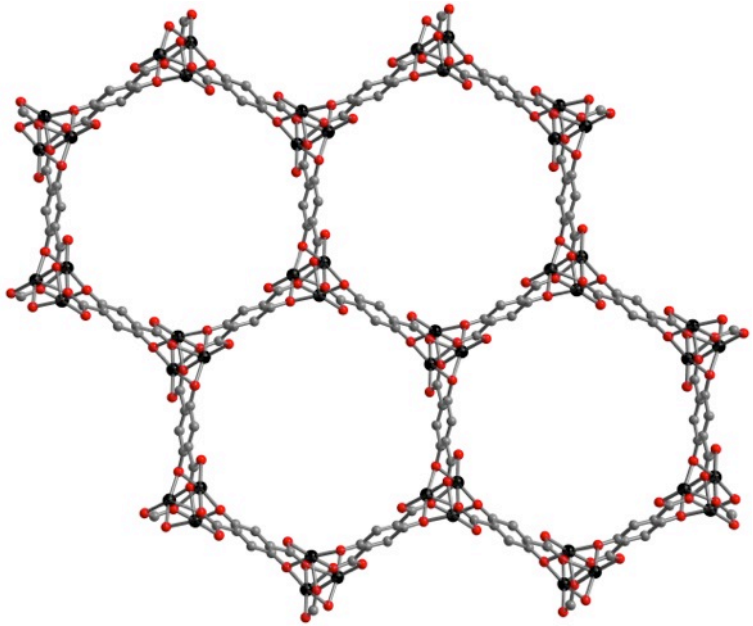


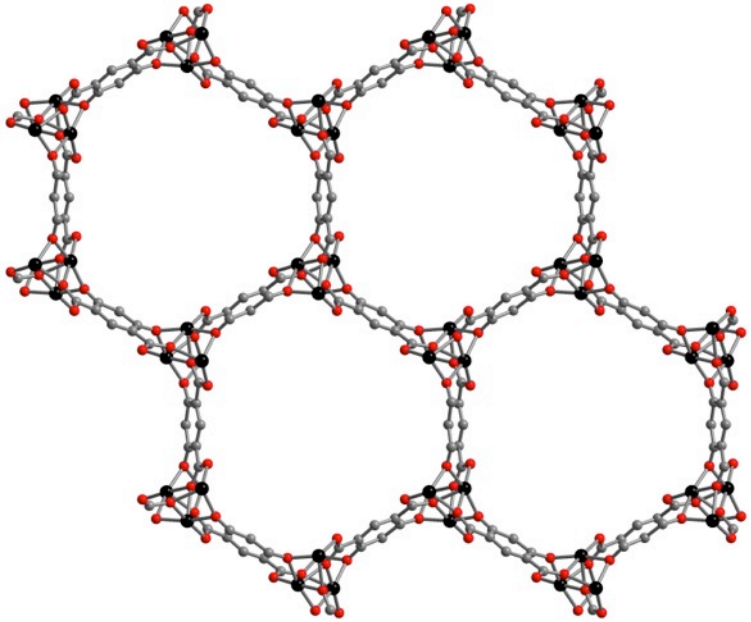
M_2(dobdc), MOF-74
(M = Mg, Mn, Fe, Co, Ni, Cu, Zn)

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

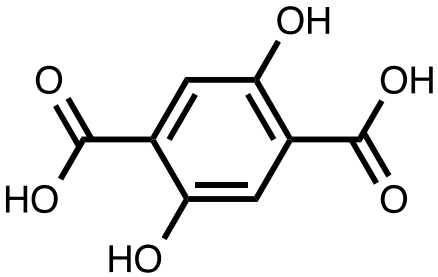
Caskey, Wong-Foy, Matzger *J. Am. Chem. Soc.* **2008**, *130*, 10870
Sumida, Brown, Herm, Chavan, Bordiga, Long *Chem. Commun.* **2011**, *47*, 1157

Accomplishments: Task 1
Synthesis of a Structural Isomer of M_2(dobdc)

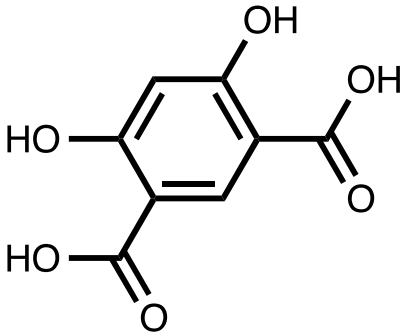




H_4(dobdc)

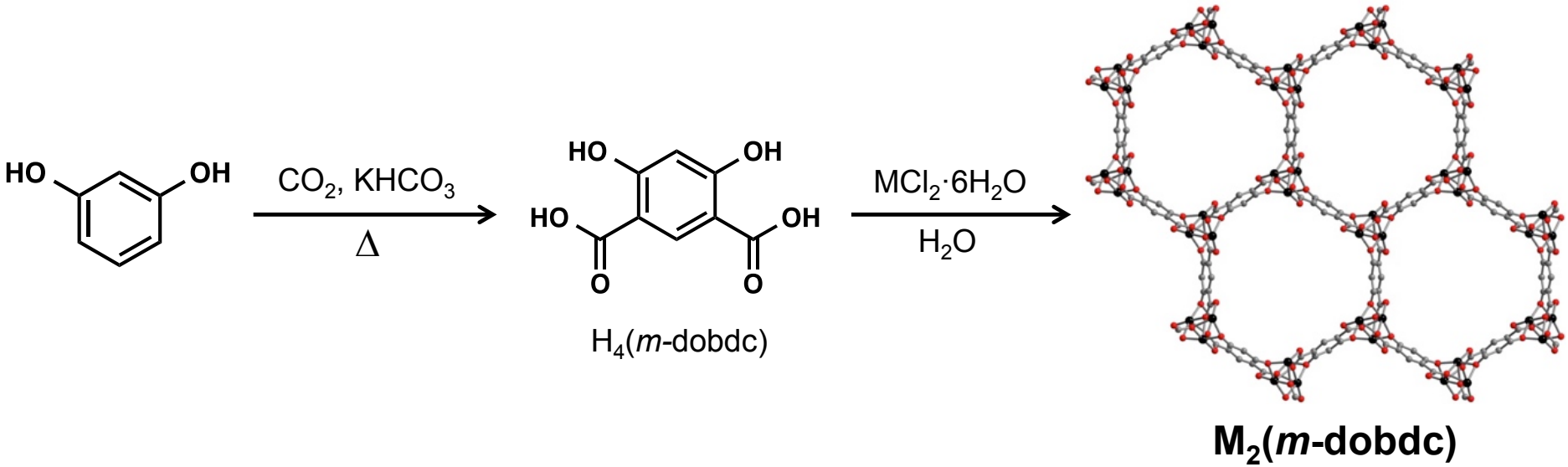


H_4(*m*-dobdc)



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

Low Cost Synthesis of M_2(*m*-dobdc)

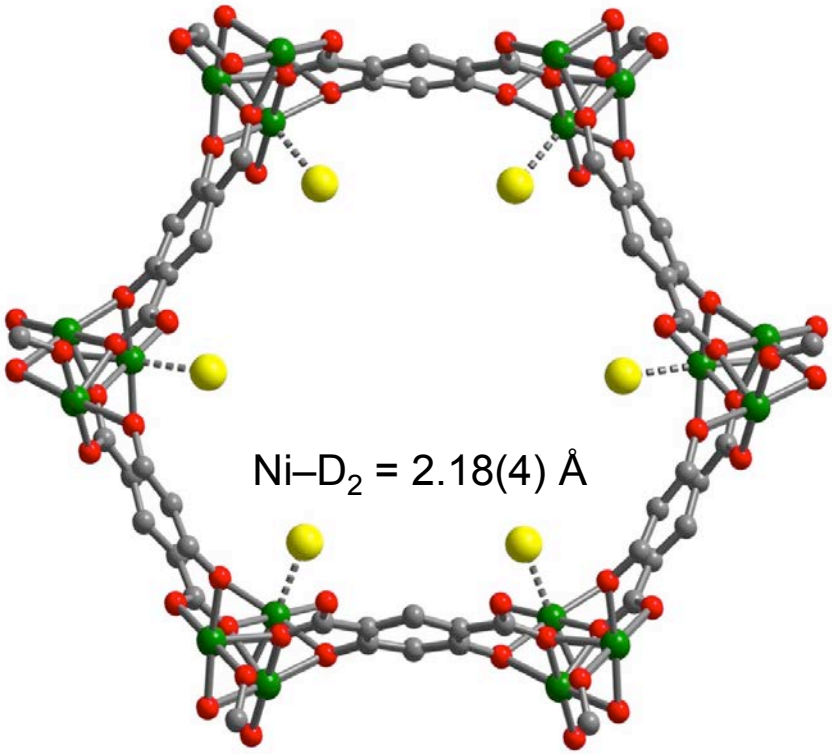


- ☐ Ligand can be synthesized in one step from resorcinol, CO_2, and $KHCO_3$
- ☐ All analogues can be synthesized in high space-time yield using inexpensive solvent
- ☐ Total raw materials cost for making Mg_2(*m*-dobdc) is just $3.10 per kg

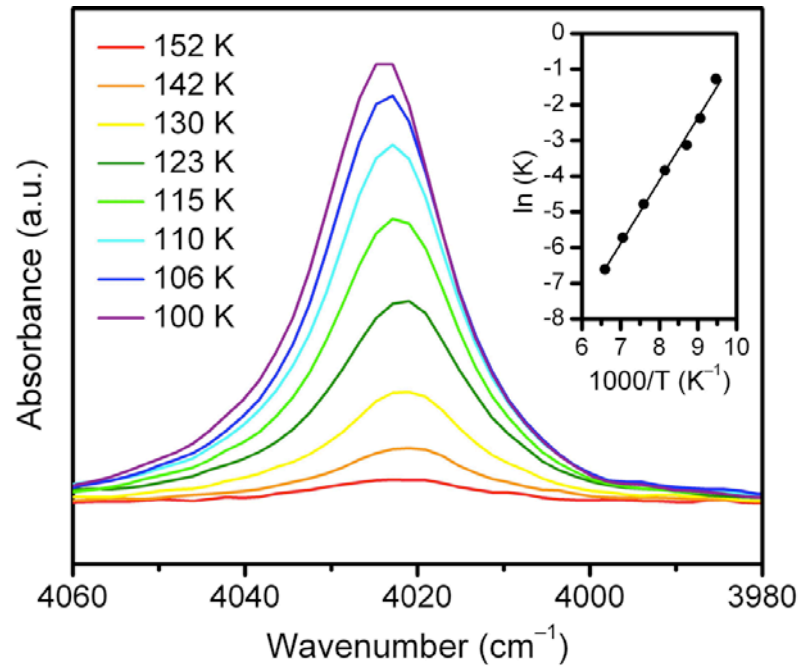
Kapelewski, Geier, Hudson, Stuck, Mason, Nelson, Xiao, Hulvey, Gilmour, FitzGerald, Head-Gordon, Brown, Long *J. Am. Chem. Soc.* **2014**, *136*, 12119

Accomplishments: Task 1
Strong H_2 Binding in Ni_2(*m*-dobdc)

Neutron Diffraction



Infrared Spectroscopy

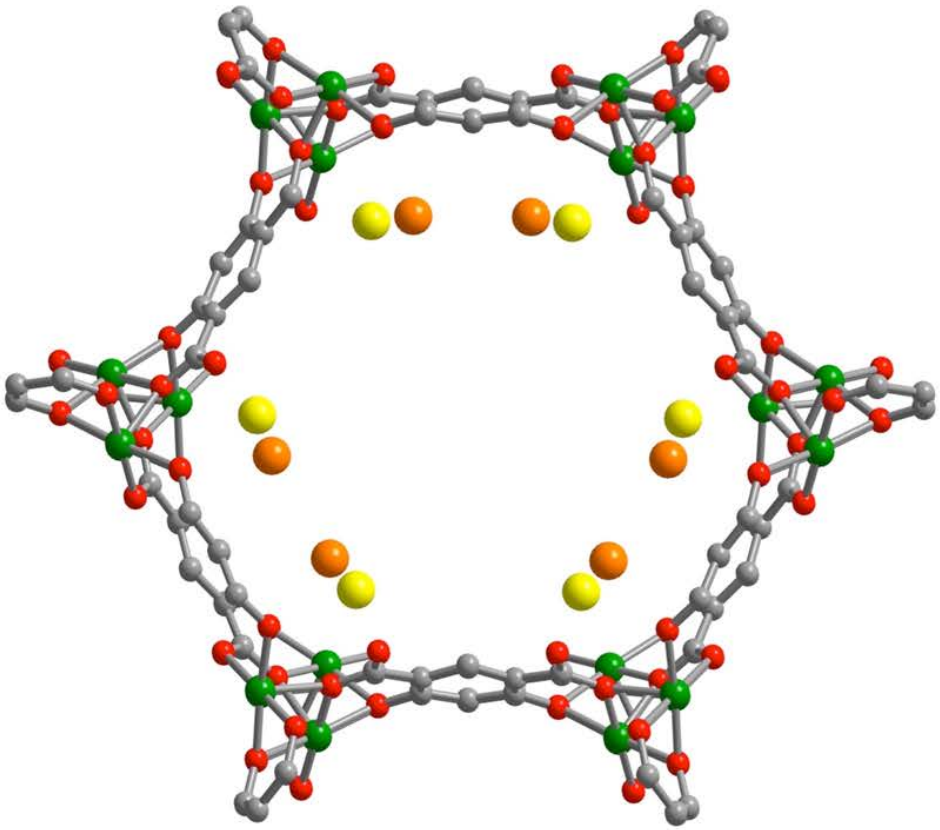


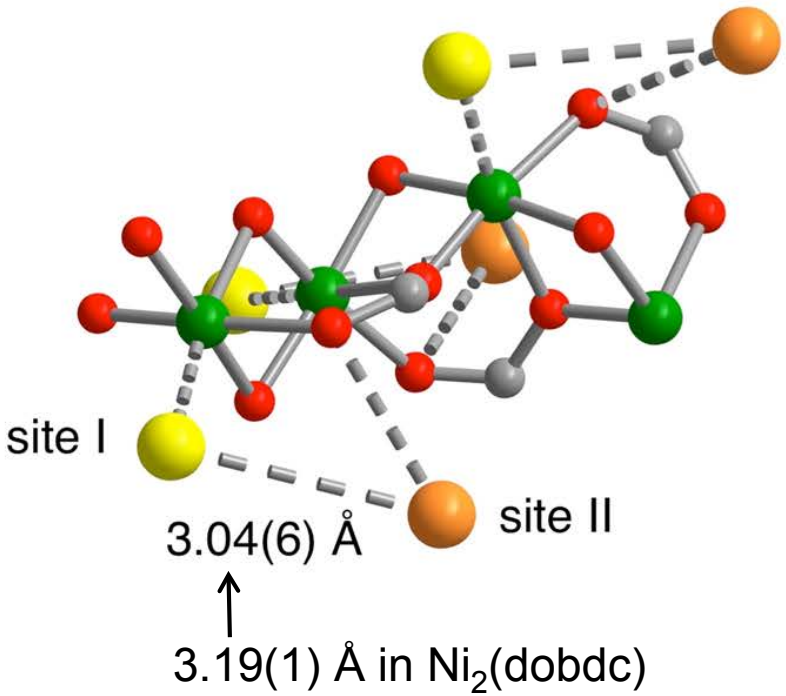
ΔH_{ads} = –13.7 ± 0.5 kJ/mol

☐ 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

Accomplishments: Task 1
Close H_2 Packing within Ni_2(*m*-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

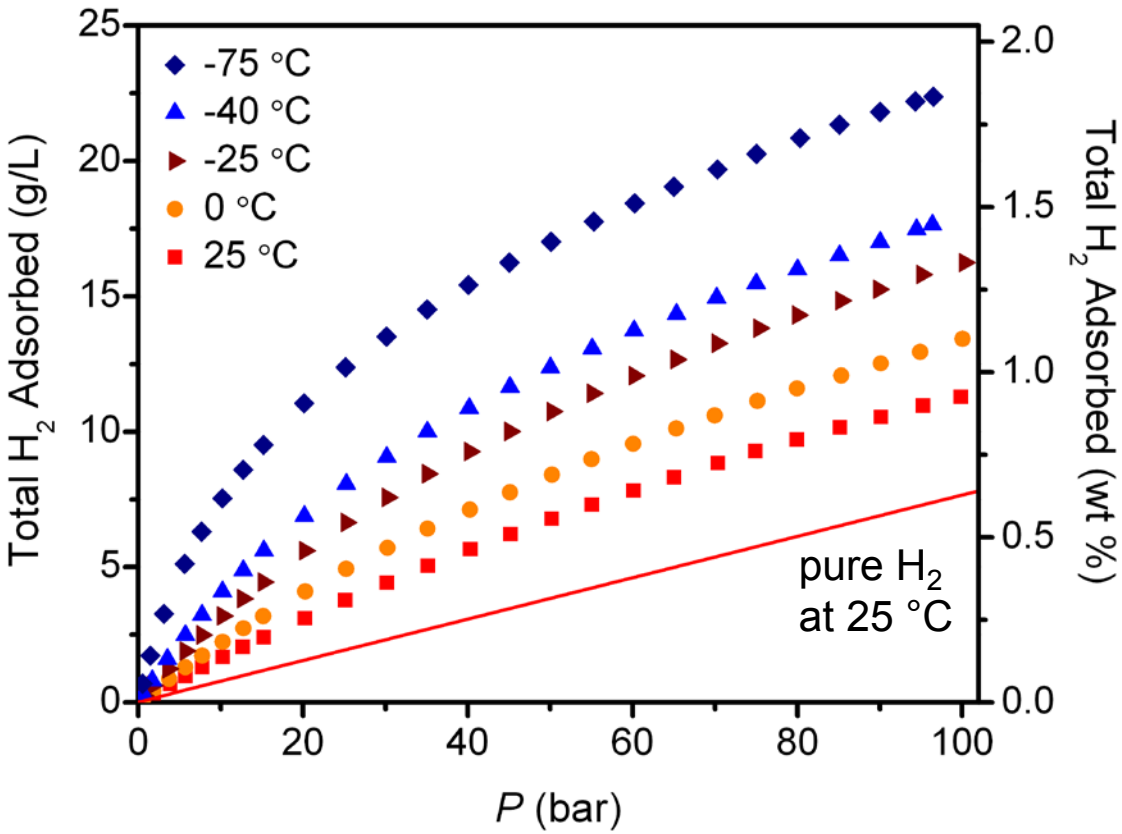
Accomplishments: Task 1
Increased Volumetric Capacity in Ni_2(*m*-dobdc)

	25 °C total capacity (g/L)	*P* (bar)
Ni_2(*m*-dobdc)	12.1 ± 0.2*	100
Ni_2(dobdc)	11.2 ± 0.2	100
Co_2(*m*-dobdc)	10.2±0.2	100
Co_2(dobdc)	9.7	100
Be-BTB	9.1	95
MOF-5	9.0	100
pure H_2	7.7	100

- High density of exposed Ni^{2+} cations that strongly polarize H_2 molecules leads to a record volumetric uptake for a sorbent at 25 °C and 100 bar

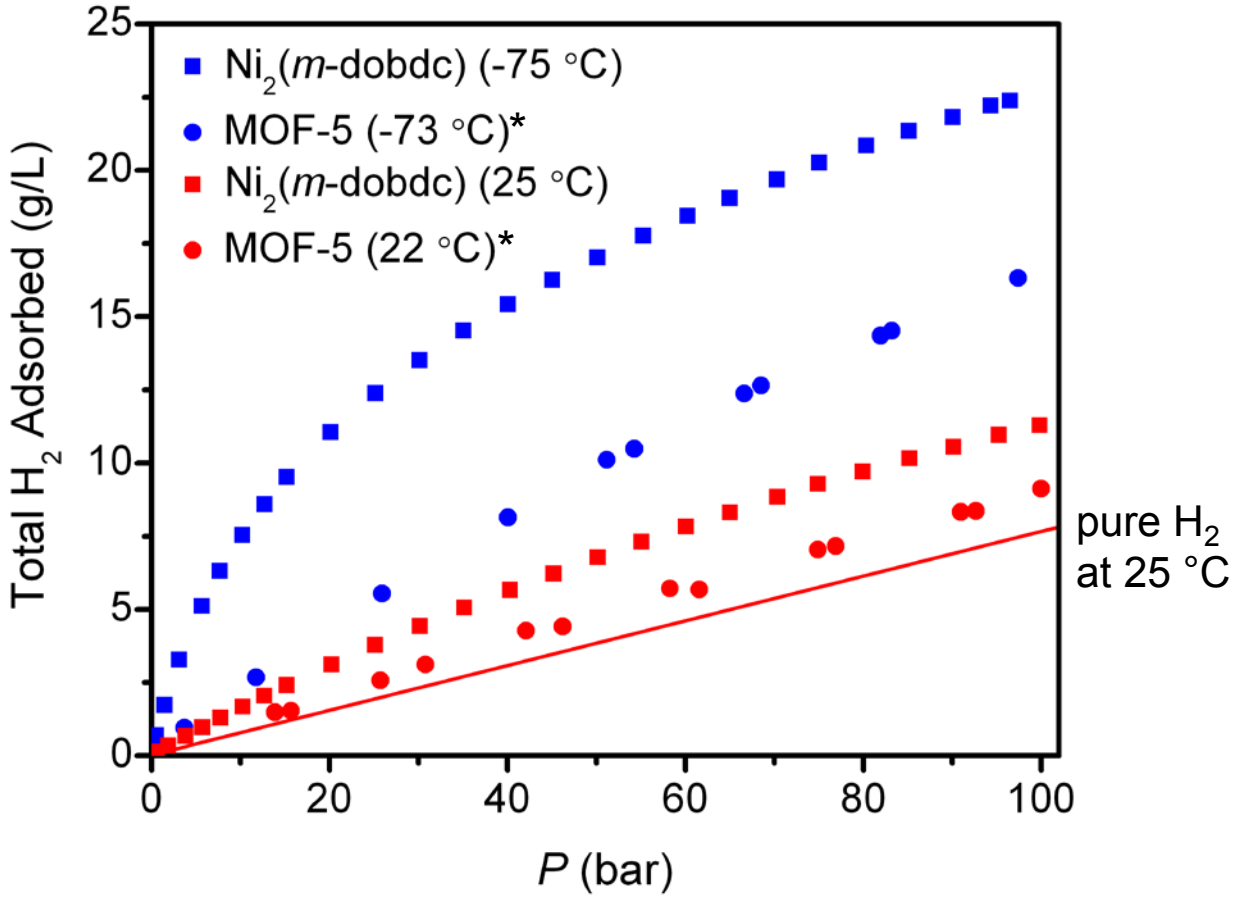
*Value of 11.4 ± 0.1 g/L obtained from sample from repeated large-scale synthesis

Accomplishments: Task 1
High-Pressure H_2 Adsorption in Ni_2(*m*-dobdc)



- All isotherms show capacity greater than compressed H_2 at 25 °C
- Ni_2(*m*-dobdc) has a total capacity of 22.3 g/L at –75 °C and 100 bar

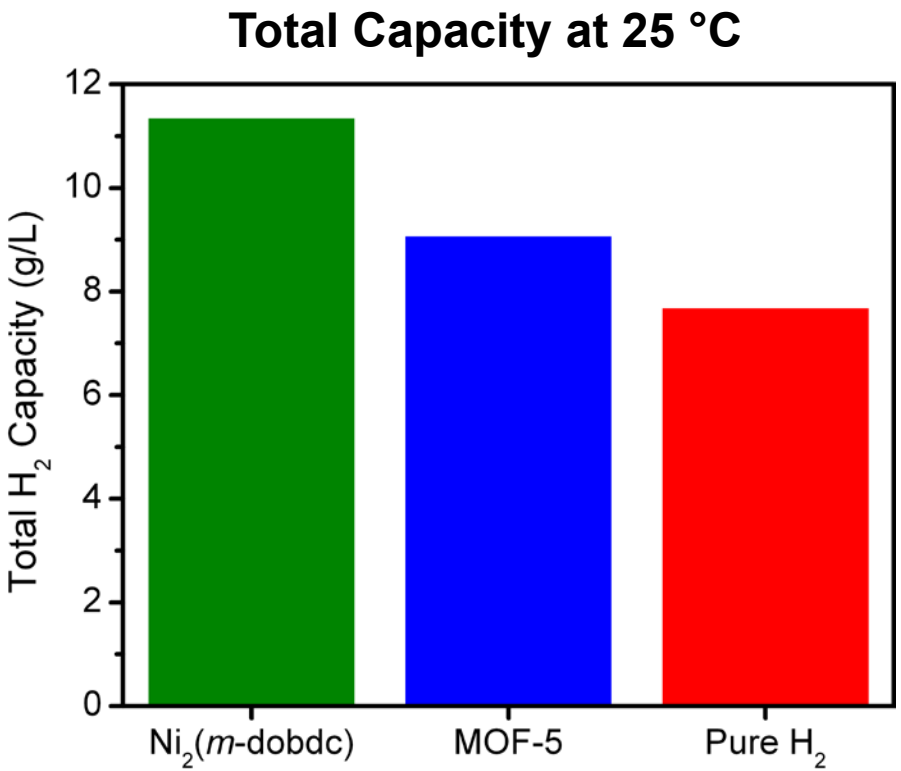
Accomplishments: Task 1
High-Pressure H_2 Adsorption in Ni_2(*m*-dobdc)

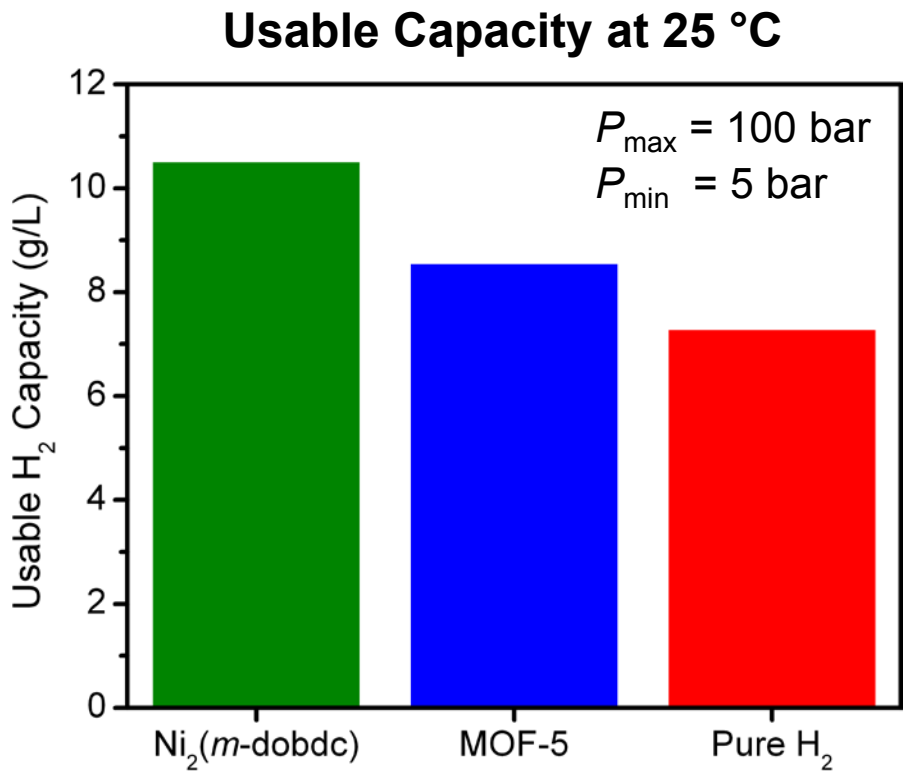


☐ Ni_2(*m*-dobdc) has significantly improved capacity over MOF-5 at –75 °C and 25 °C

*Ming, Purewal, Liu, Sudik, Xu, Yang, Veenstra, Rhodes, Soltis, Warner, Gaab, Müller, Siegel *Microporous Mesoporous Mater.* **2014**, *185*, 235

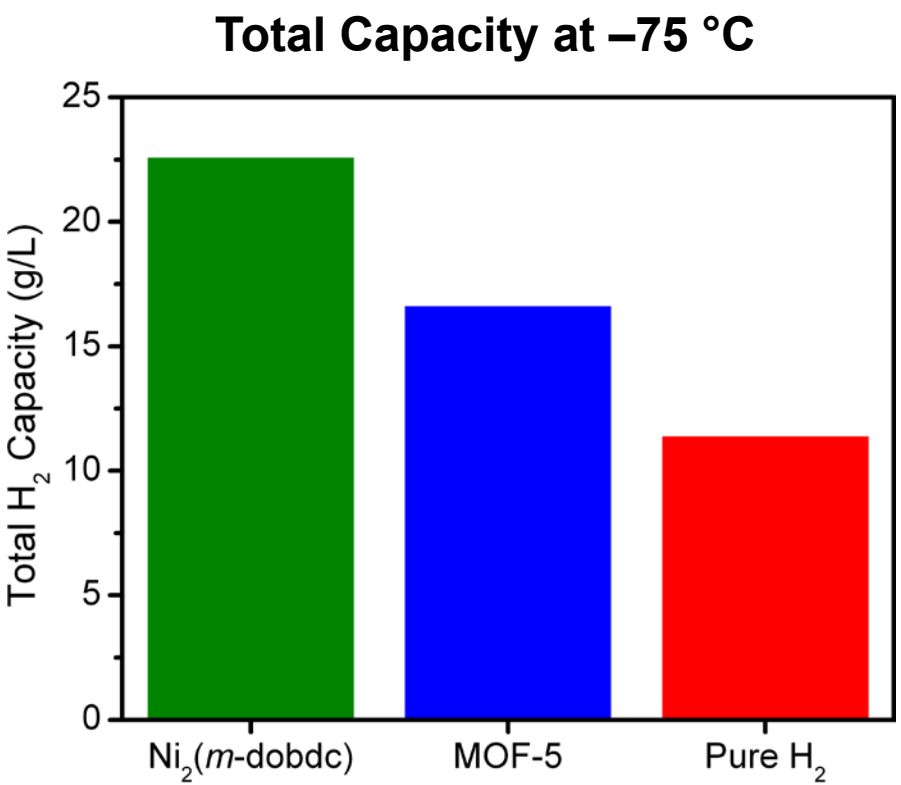
Accomplishments: Task 1
High-Pressure H_2 Adsorption in Ni_2(*m*-dobdc)

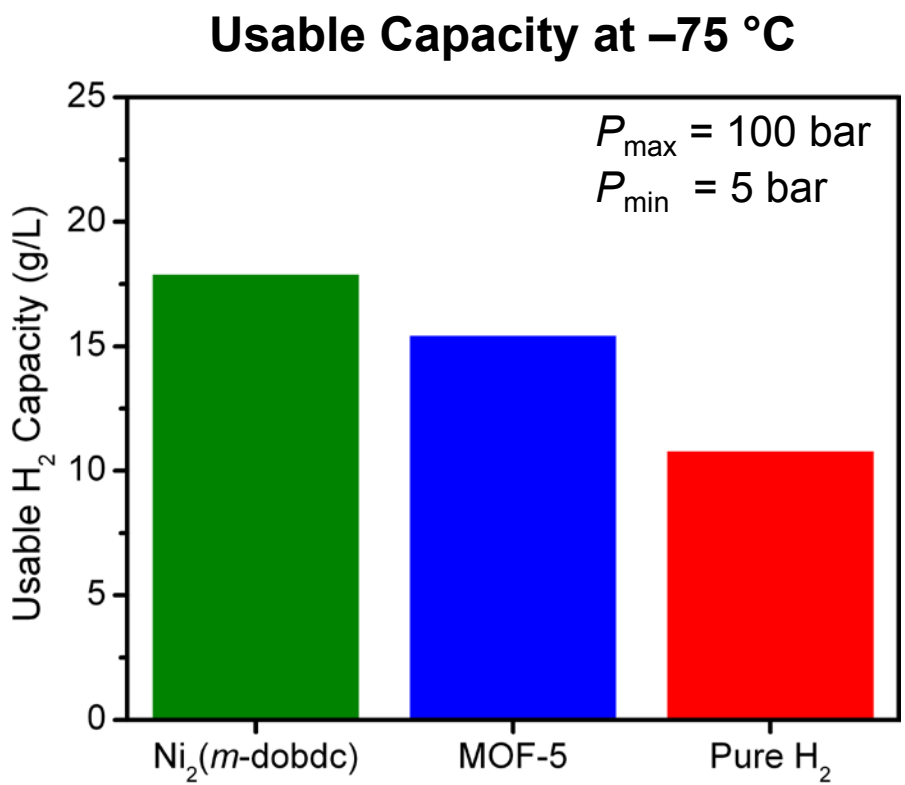




- ☐ Total capacity of Ni_2(*m*-dobdc) is 25% more than MOF-5 and 48% more than pure H_2
- ☐ Usable capacity of Ni_2(*m*-dobdc) is 23% more than MOF-5 and 44% more than pure H_2

Accomplishments: Task 1
High-Pressure H_2 Adsorption in Ni_2(*m*-dobdc)

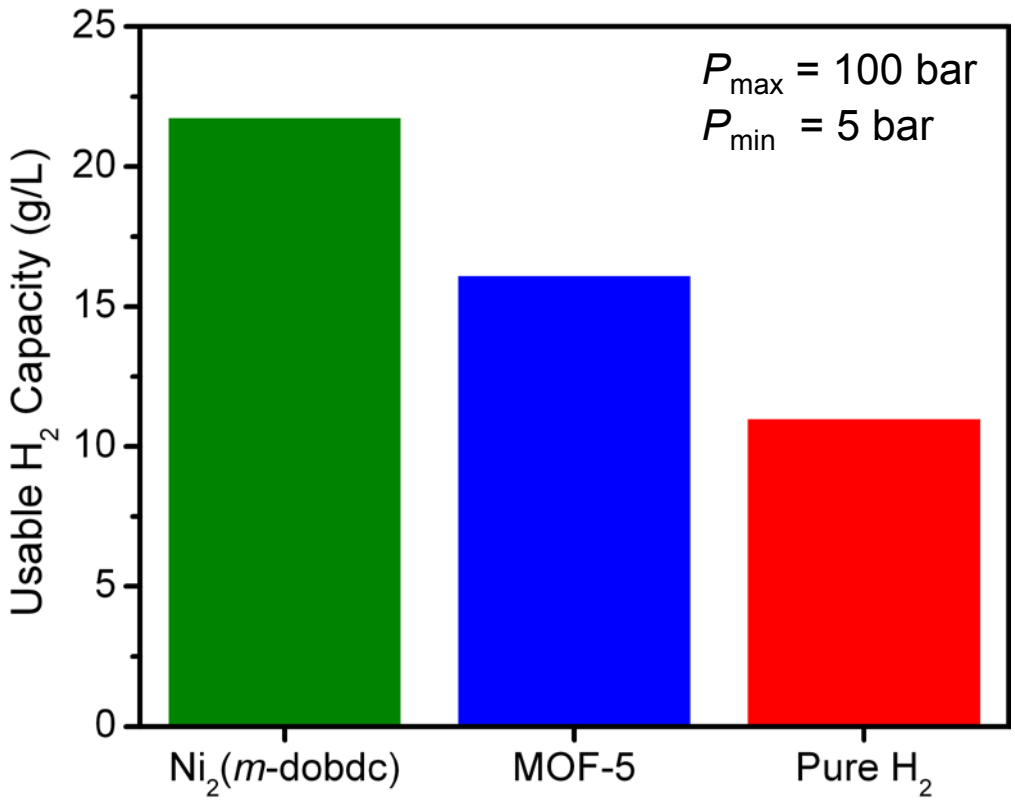




- ☐ Total capacity of Ni_2(*m*-dobdc) is 36% more than MOF-5 and 98% more than pure H_2
- ☐ Usable capacity of Ni_2(*m*-dobdc) is 16% more than MOF-5 and 66% more than pure H_2

Accomplishments: Task 1
High-Pressure H_2 Adsorption in Ni_2(*m*-dobdc)

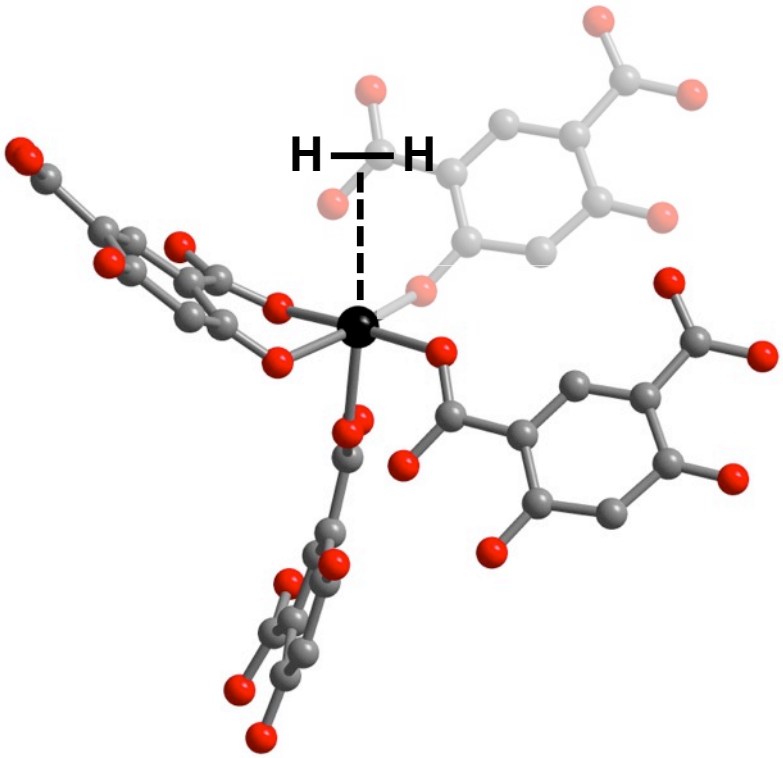
Usable Capacity with Swing from –75 to 25 °C



- Capacity of Ni_2(*m*-dobdc) is 36% more than MOF-5 and 98% more than pure H_2

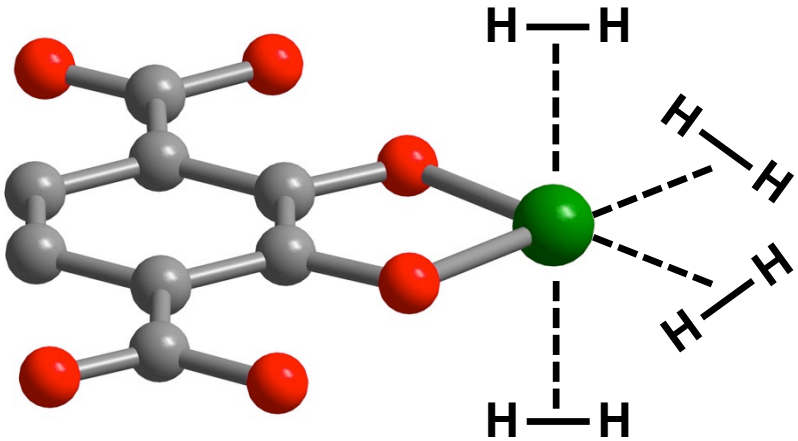
Accomplishments: Task 1
Binding Multiple H_2 Molecules per Metal Cation

Classical



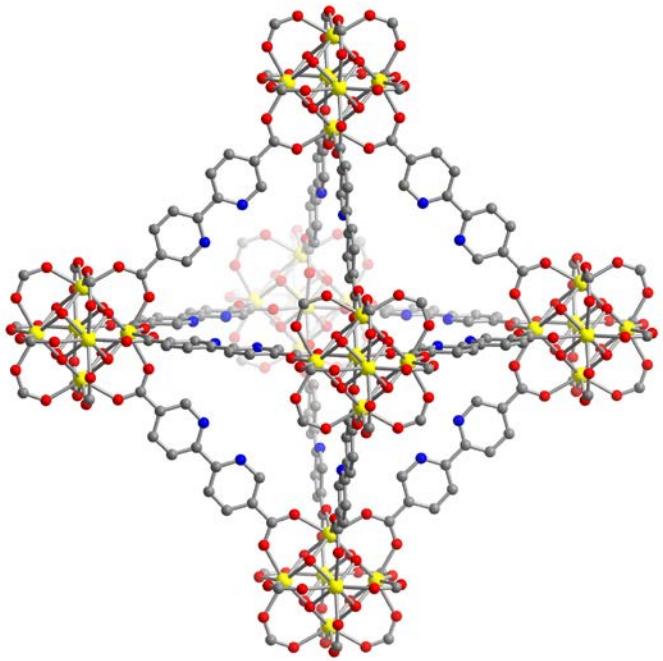
1 H_2 per metal cation

Next-Generation



4 H_2 per metal cation

Accomplishments: Task 1
Insertion of MCl_2 in $Zr_6O_4(OH)_4(bpydc)_6$



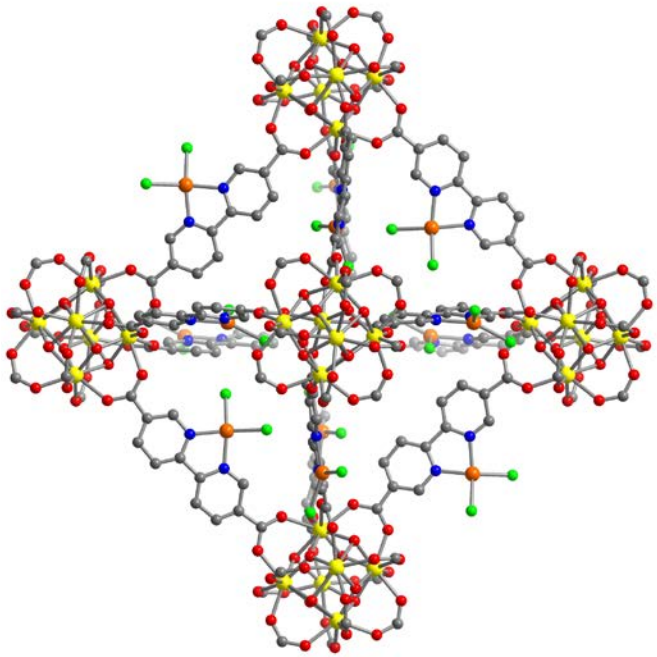
$Zr_6O_6(OH)_4(bpydc)_6$

SA_{BET} = 2645 m^2/g

MX_2, MeCN

1 day, 70 °C

MX_2 = $CoCl_2$, $MnCl_2$, $MnBr_2$, $FeCl_2$, $FeBr_2$, $CuCl_2$, $PdCl_2$



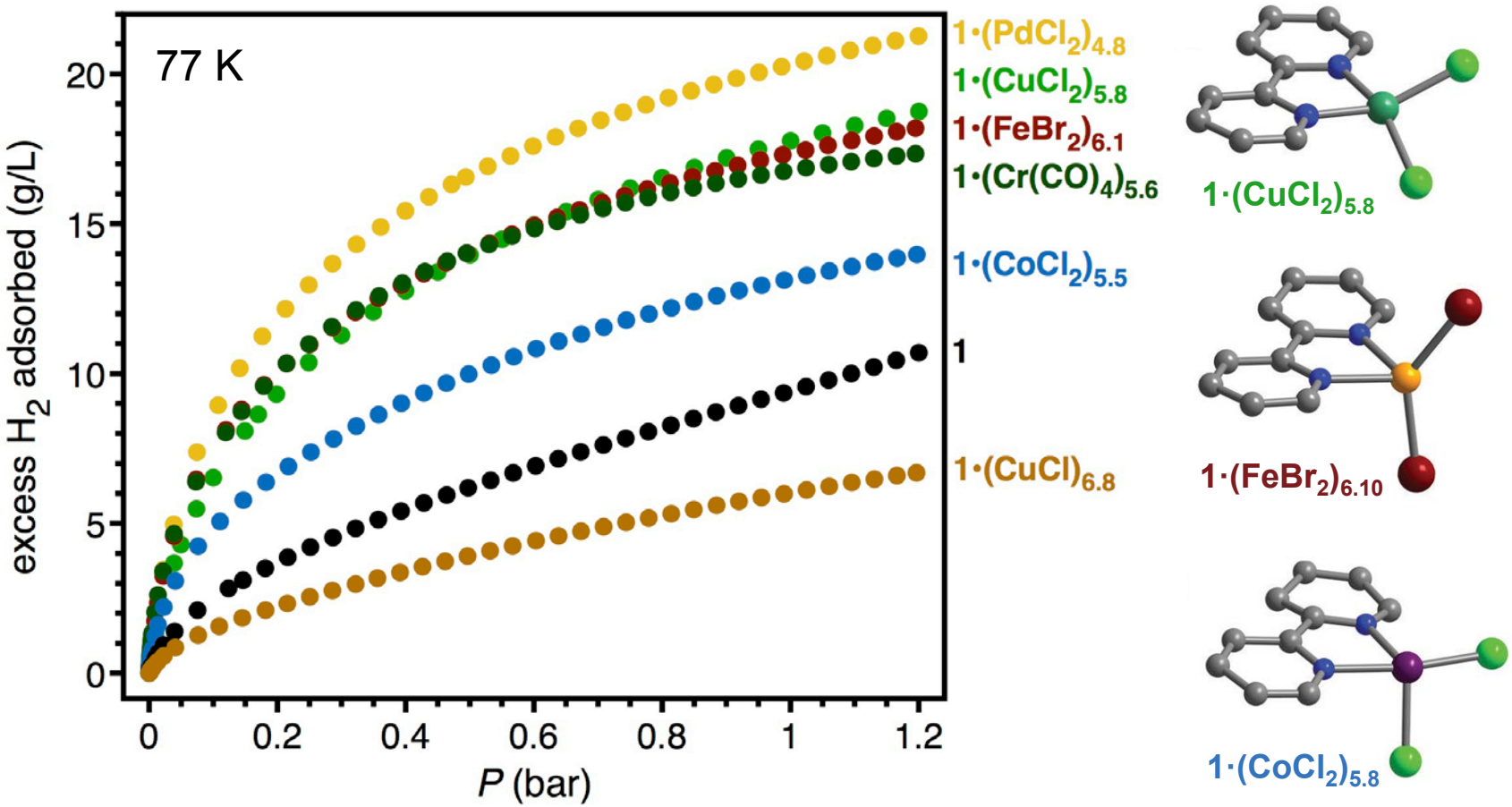
$Zr_6O_6(OH)_4(bpydc)_6(MX_2)_6$

SA_{BET} = 1200-1800 m^2/g

- ☐ Single crystal x-ray diffraction unambiguously confirms metal insertion
- ☐ Inserted metal sites could potentially each bind two H_2 molecules

Gonzalez, Bloch, Mason, Teat, Long. *Inorg. Chem.* **2015**, *54*, 2995

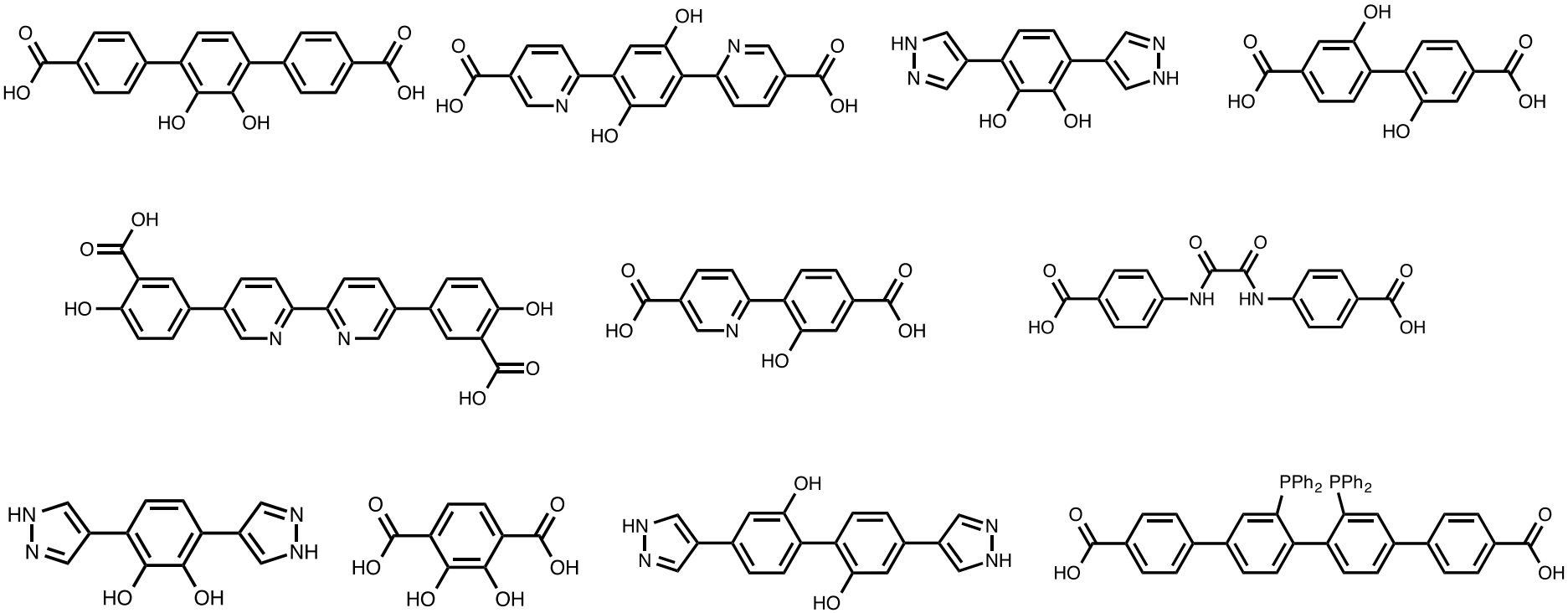
Accomplishments: Task 1
H_2 Adsorption in Metalated $Zr_6O_4(OH)_4(bpydc)_6$



- Metalated frameworks can show increased uptake relative to bare framework

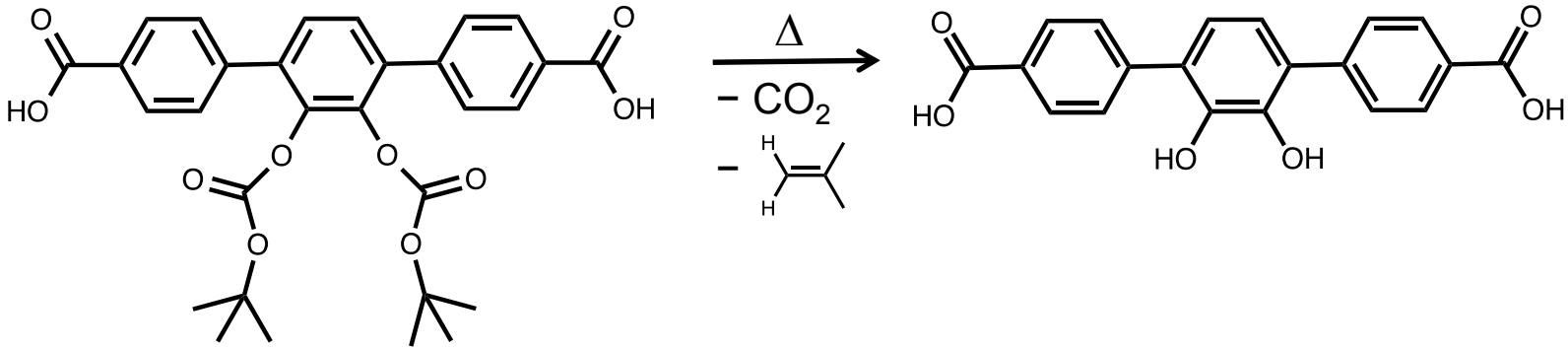
Gonzalez, Bloch, Mason, Teat, Long. *Inorg. Chem.* **2015**, *54*, 2995

Accomplishments: Task 1
Synthesis of New Chelating Ligands

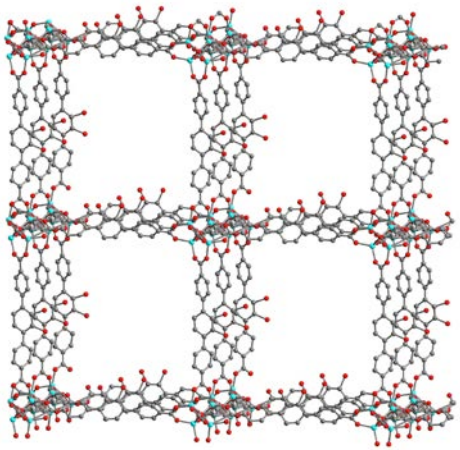


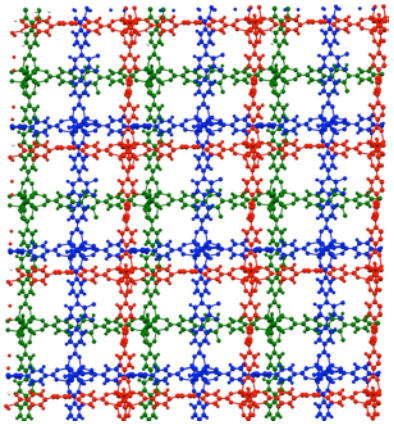
- Seventeen new linkers with (charge-bearing) chelating functionalities have been synthesized, including ones with catechols, biphenols, bipyridines, and oxamides

Accomplishments: Task 1
Development of Protecting Group Strategies



$Zn(NO_3)_2 \cdot 6H_2O$
DEF, 2.5 M NaOH
90 °C



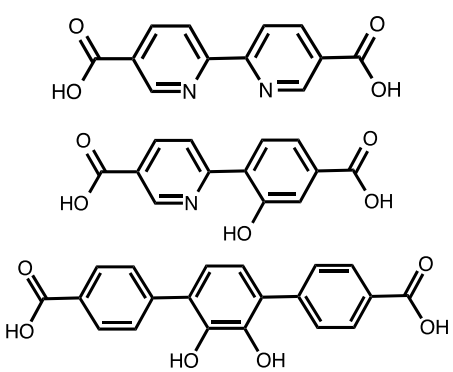


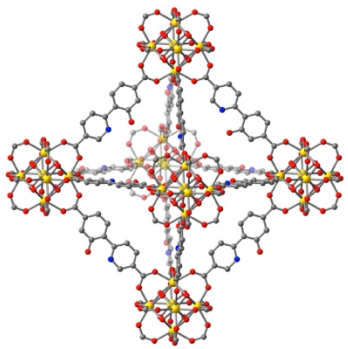
- ☐ Protecting groups needed to block chelate sites during synthesis
- ☐ Bulky protecting groups may be used to control interpenetration

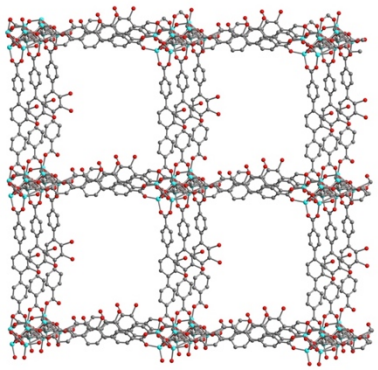
Toward Next-Generation MOFs for H_2 Storage

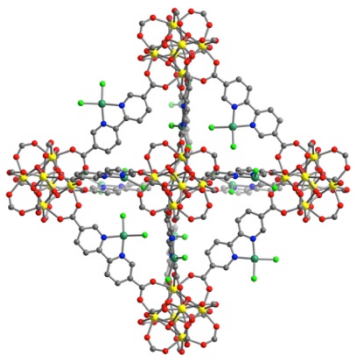
- Eleven different new MOFs synthesized for metal insertion attempts
- More than 50 post-synthetic metal insertions into new MOFs have been performed and tested via H_2 adsorption isotherm measurements

- In particular efforts underway to demonstrate two or more H_2 bound at metals in:

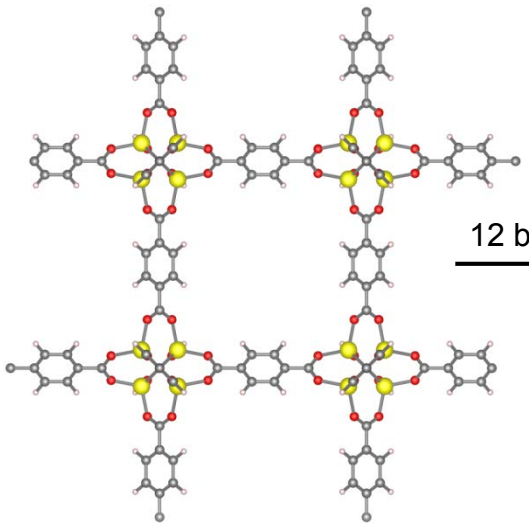






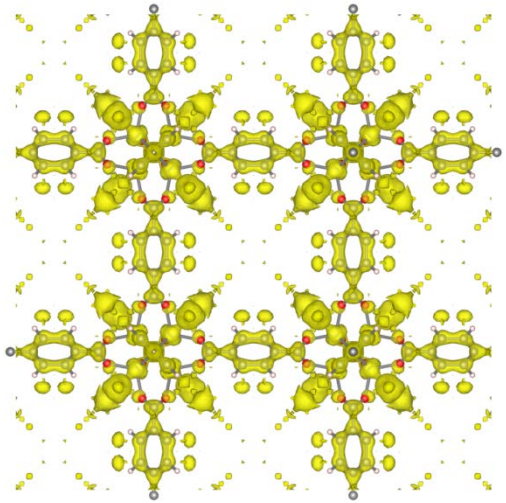


Accomplishments: Task 2
High Pressure Neutron Diffraction



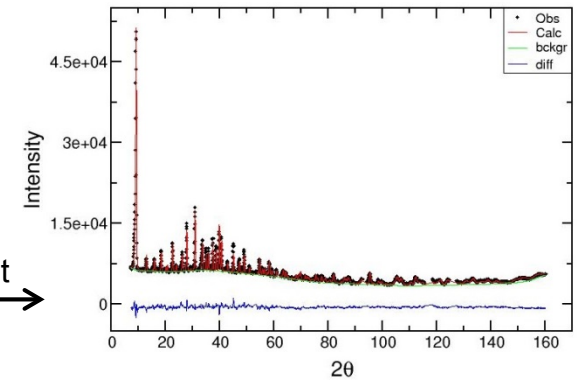
MOF-5

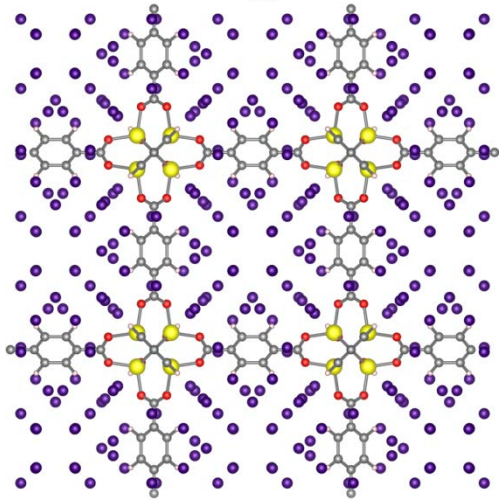
12 bar D_2 →



Difference Fourier plot generated from powder pattern (yellow surface)

Rietveld refinement →



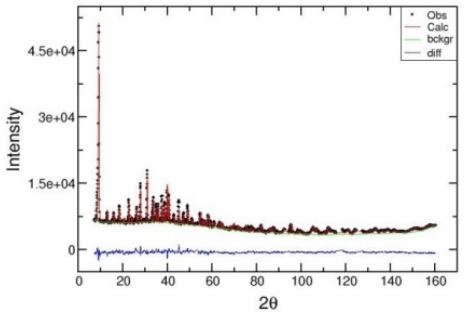


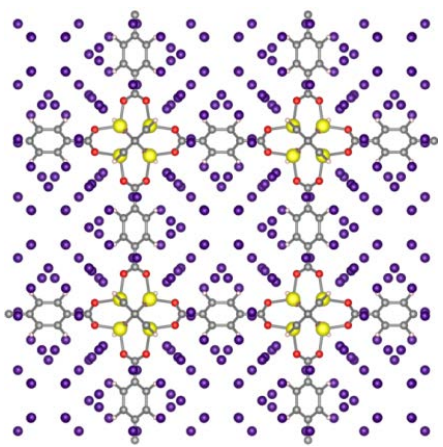
Total refined occupancy at 12 bar: 148 D_2/unit cell, ~4.8 wt % H_2

- ☐ High symmetry MOF-5 chosen for refinement simplicity
- ☐ Data refined with D_2 molecules in several sites; summation of refined fractional occupancies yields values comparable to adsorption isotherm data

Accomplishments: Task 2
High Pressure Neutron Diffraction

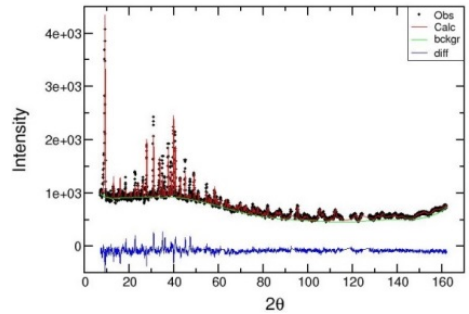
12 bar

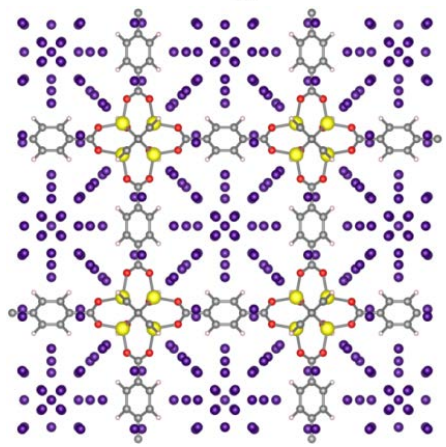




148 D_2/cell or 4.8 wt %

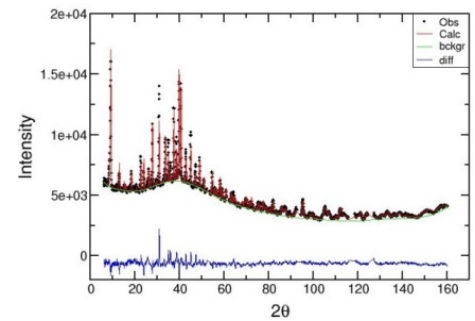
40 bar

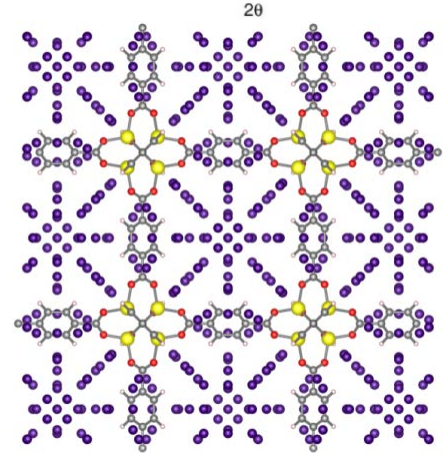




189 D_2/cell or 6.2 wt %

98 bar

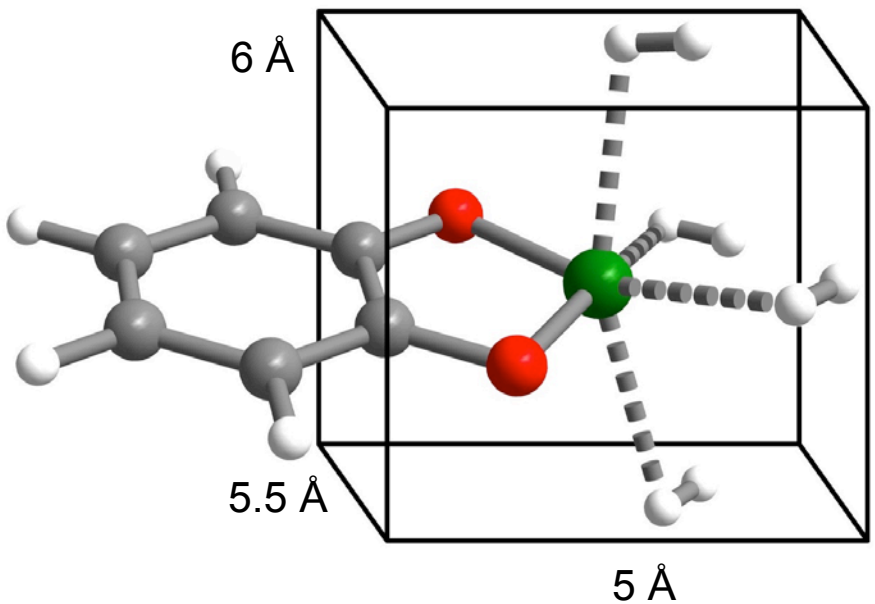




240 D_2/cell or 7.8 wt %

- ☐ Occupancies increase and D_2 site densities increase in expected manner
- ☐ Important step toward understanding density profiles of H_2 at relevant conditions

Accomplishments: Task 3
Binding Multiple H_2 Molecules per Metal

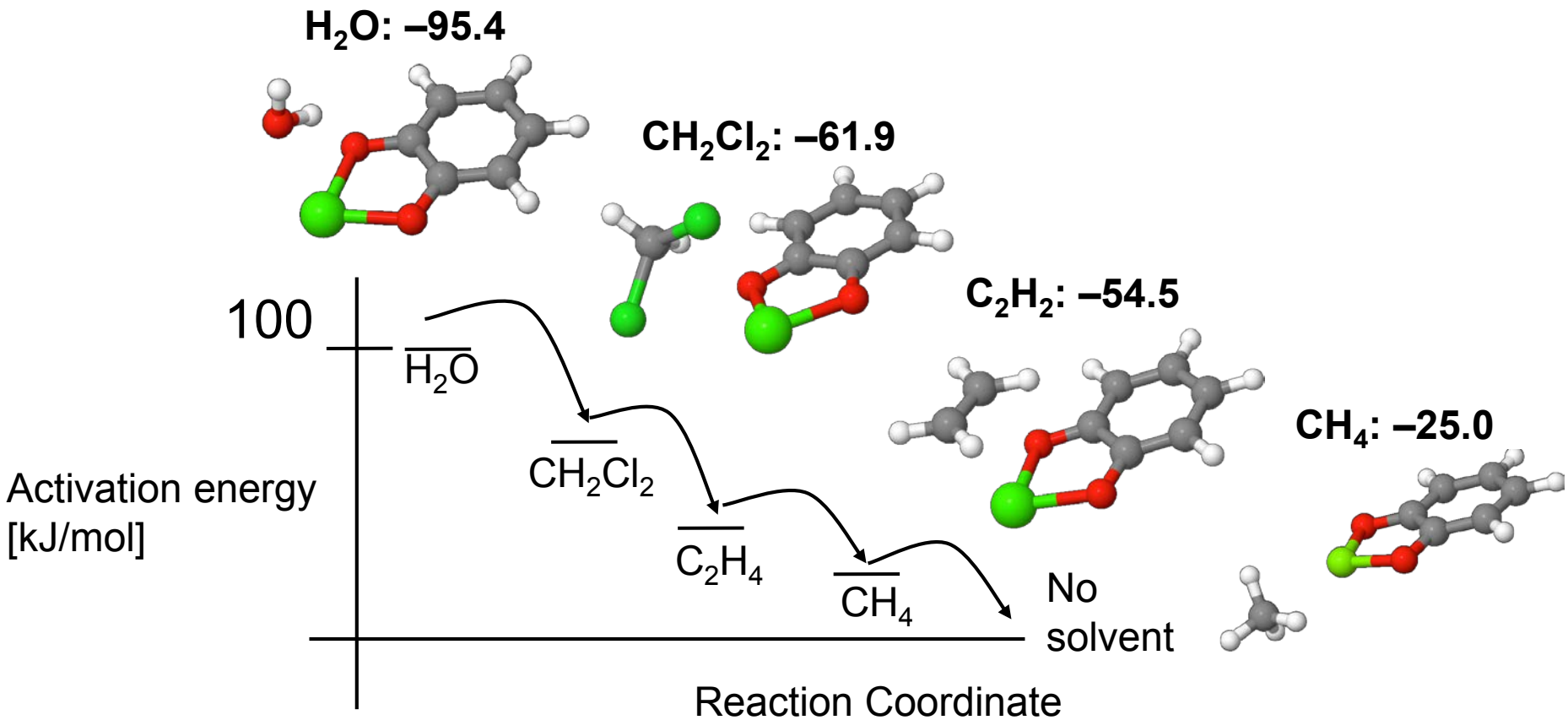


# of H_2 per Mg^{2+}	g/L	wt %
1	20	1.8
2	41	3.5
3	61	5.1
4	81	6.6

- DFT calculated H_2 binding enthalpy is –19 kJ/mol at 25 °C
- Potential for volumetric densities exceeding that of liquid H_2

Tsivion, Long, Head-Gordon *J. Am. Chem. Soc.* **2014**, *136,* 17827

Accomplishments: Task 3
Stepwise Activation Calculations for Metal Cations



- ☐ Sequential ligand exchanges are calculated to lead to low-coordinate metals
- ☐ Can achieve multiple exposed coordination sites on the metal for H_2 binding

Accomplishments and Progress: Responses to Previous Year Reviewers' Comments

- Task 4, high-pressure H_2 measurements at GM, has been eliminated, per previous reviewer comments and with LBNL's ability to measure high-pressure isotherms

- Total volumetric capacity is the most relevant to commercial applications, as total capacity is an intrinsic property of a material that represents the total amount of gas that can be stored in the pores and volumetric capacity is more critical to onboard systems in small motor vehicles than gravimetric capacity

- Our overall strategy, as summarized on Slide 5, is to create materials with a high-density of open M^{2+} or M^{3+} cation sites, each capable of binding 4 or 5 H_2 molecules. This is the only viable route we see to meeting the volumetric capacity target of 40 g/L for a system using an adsorbent

- Our roadmap to accomplishing this involves the synthesis of thermally robust MOFs containing anionic chelating sites that can then be metalated and fully activated

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_2 binding energies
- National Institute of Standards and Technology (sub, National Lab.):
  Craig Brown: Neutron diffraction and neutron spectroscopy

Additional collaborations:

- Variable-temperature infrared spectroscopy with *in situ* H_2 dosing
  - Silvia Bordiga (University of Turin), Stephen FitzGerald (Oberlin College)
- Synthesis and metalation of porphyrin-containing MOFs
  - T. David Harris (Northwestern University)

Remaining Challenges and Barriers

- ☐ Metalation conditions for MOFs containing charge balancing ligands needs to be optimized
- ☐ Desolvation of frameworks containing non-structural metal cations remains a significant challenge; optimal strategies for exposing coordination sites must be determined
- ☐ Ligand syntheses are challenging and time-consuming; shorter synthetic routes would allow for more testing of framework formation, metalation, and desolvation
- ☐ While theoretical predictions have suggested optimal metalation targets, experimental realization must be achieved to confirm theoretical results

Proposed Future Work

Task 1: Synthesis of Metal-Organic Frameworks

- ☐ Scale up synthesis of catechol containing MOFs and insert metal cations
- ☐ Continue synthesis of catechol-based ligands and other charge-balancing ligands and associated MOFs for metal insertion
- ☐ Further variable temperature studies comparing Ni_2(*m*-dobdc) and MOF-5
- ☐ Send Ni_2(*m*-dobdc) sample to NREL for isotherm validation

Task 2: Characterization of Framework-H_2 Interactions

- ☐ Solve neutron structure of $Zr_6O_4(OH)_4(bpydc)_6(PdCl_2)_6$ dosed with D_2, as 2 H_2 molecules per Pd^{2+} should be possible
- ☐ Continue inelastic neutron scattering experiments
- ☐ Perform quasielastic neutron diffraction experiments to study diffusion and entropy effects on H_2 adsorption

Proposed Future Work

Task 3: First-Principles Calculations of Hydrogen Binding Enthalpies

- ☐ Explore H_2-metal interactions in real systems that have been realized experimentally
- ☐ Determine optimal metalation conditions and subsequent desolvation

Technology Transfer Activities

- Patent applications:
  - M. T. Kapelewski, S. J. Geier, J. R. Long. "Metal-Organic Frameworks with a High Density of Highly Charged Exposed Metal Cation Sites. Submitted, patent pending.

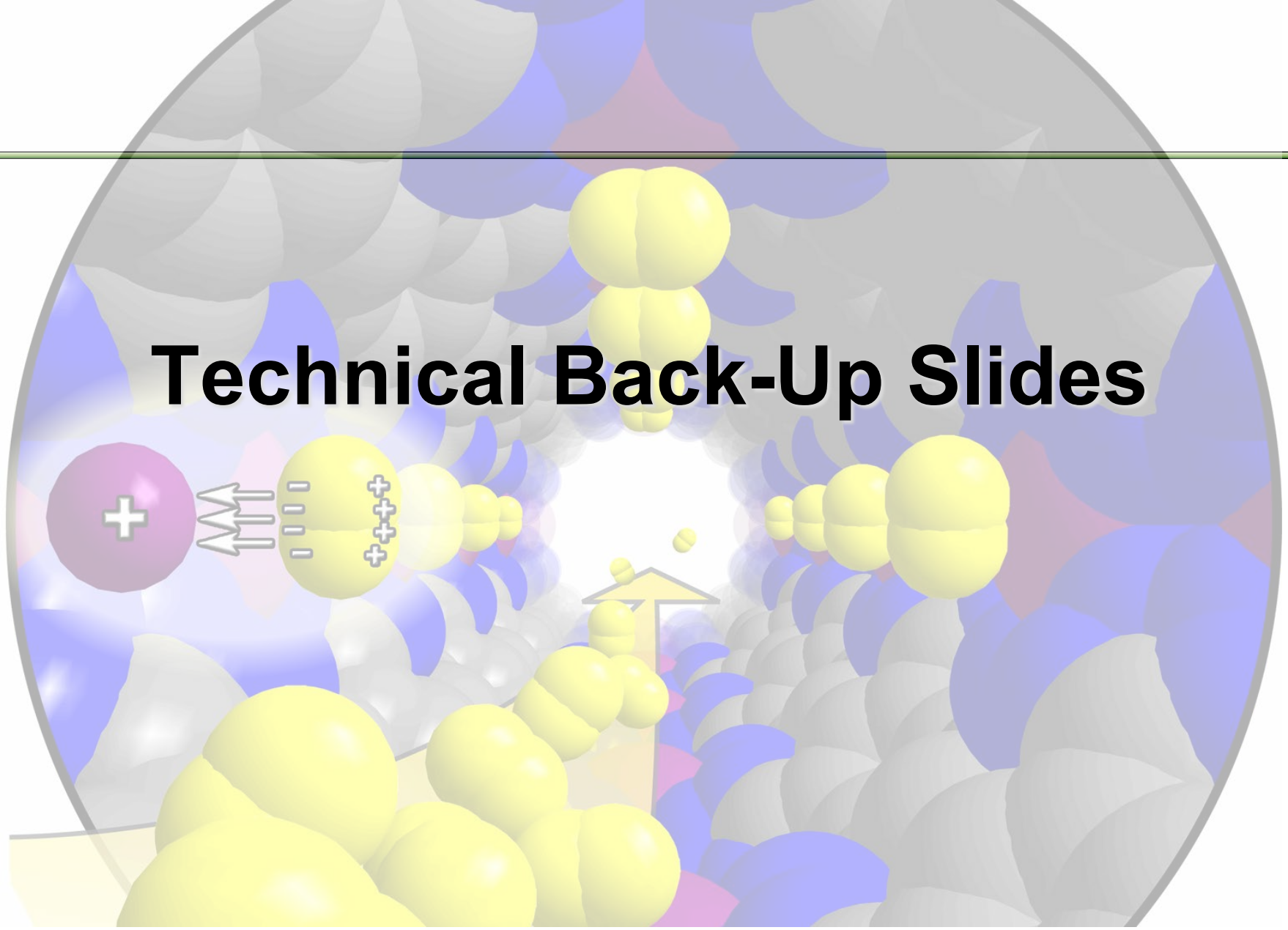
- Applying for follow-up funding to further develop the materials presented here

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

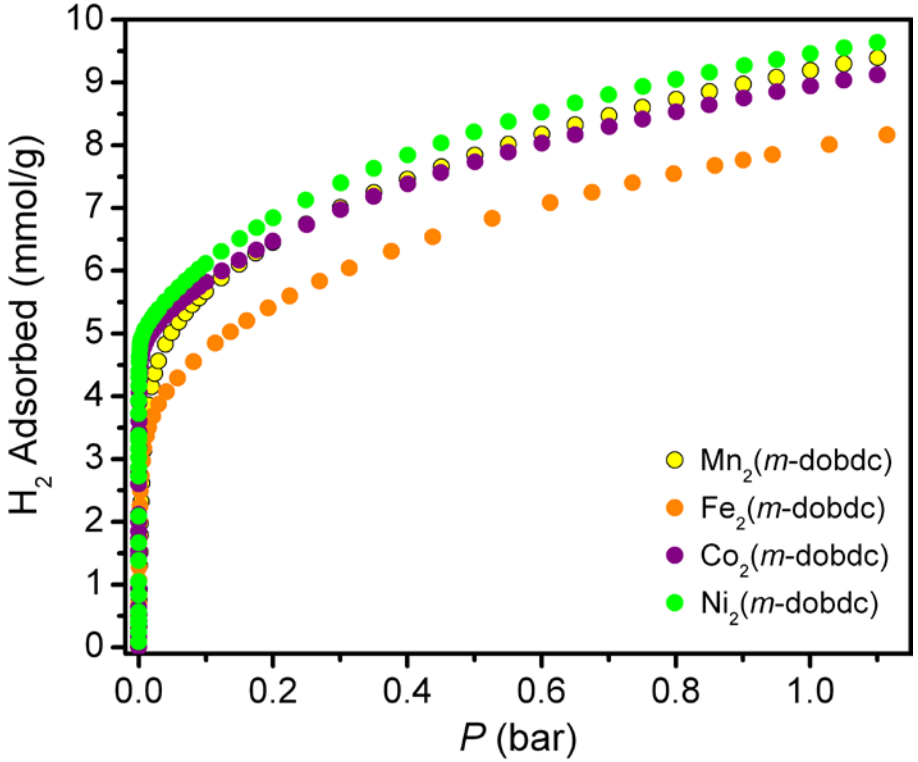
Summary

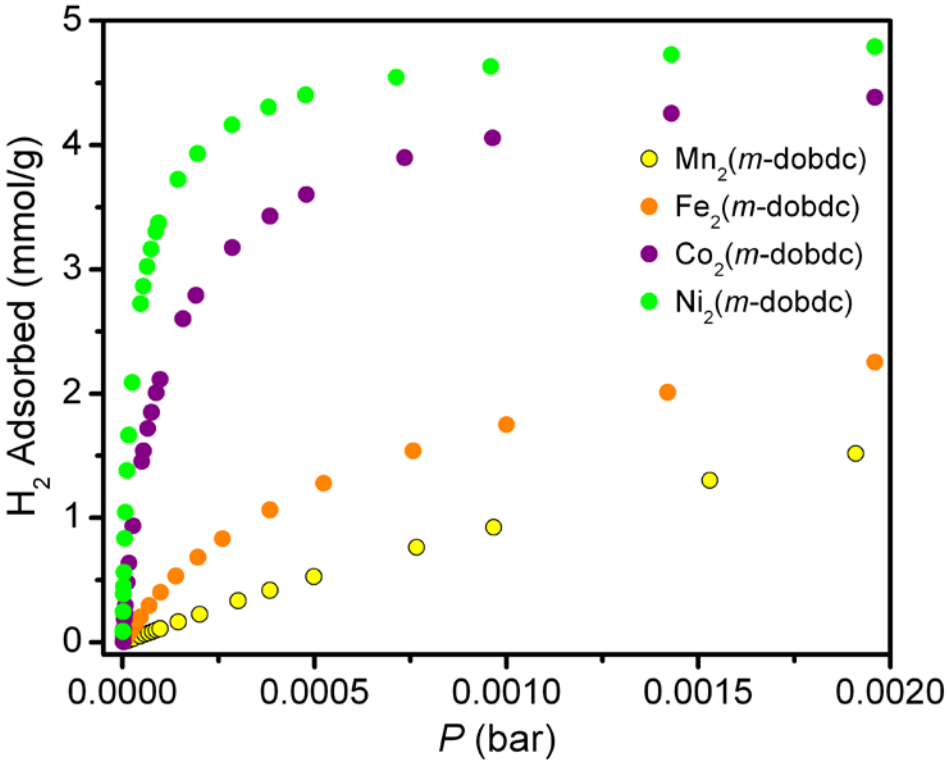
- At 25 °C and 100 bar, Ni_2(*m*-dobdc) exhibits the highest total volumetric storage capacity of any known metal-organic framework
- At –75 °C and 100 bar, a crystal of Ni_2(*m*-dobdc) exhibits double the storage capacity of an equivalent empty volume
- H_2 adsorption was measured in metalated zirconium-based frameworks, with some having substantially greater H_2 uptake over the base material
- A catechol-based ligand has been incorporated into a highly-stable zirconium-based framework on a large scale, allowing for metalation
- Neutron diffraction of MOF-5 was used to determine the density profile of D_2 in the pores with increasing pressure, revealing similar adsorption sites to those occupied at lower temperatures and lower pressure
- Theoretical calculations have been used to predict pathways for desolvating metal cations in MOF pores

Technical Back-Up Slides



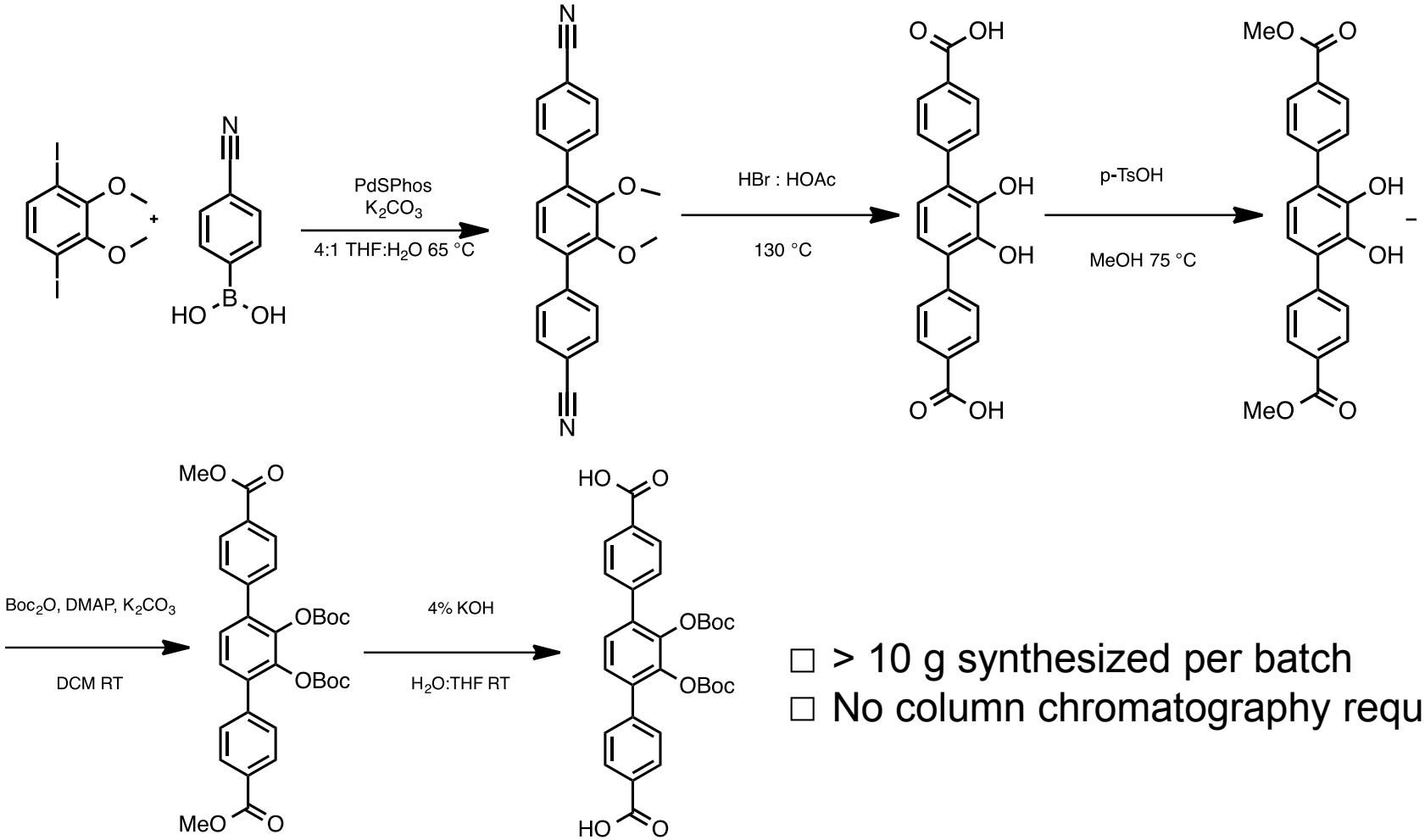
Low-pressure H_2 Isotherms in M_2(*m*-dobdc)





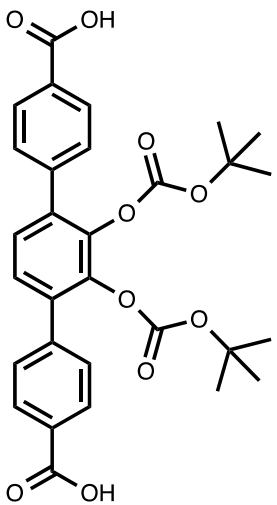
- Although $-Q_{st}$ follows Ni > Co > Fe > Mn, saturation capacity at 77 K and 1.2 bar doesn't follow the trend as surface area factors into total uptake

Synthesis of diboc-cat-dc Ligand



- ☐ > 10 g synthesized per batch
- ☐ No column chromatography required

Synthesis of a MOF with the diboc-cat-tpdc ligand

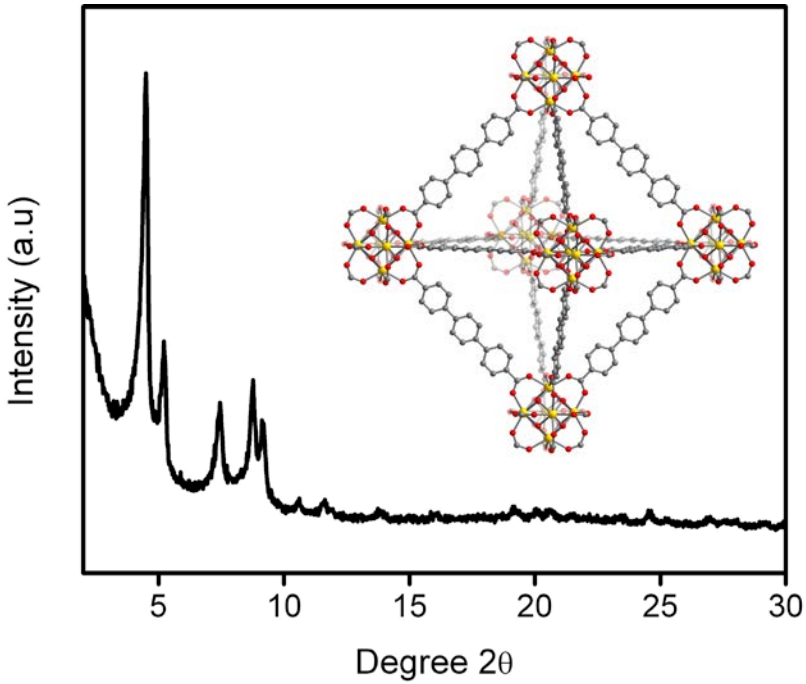


diboc-cat-tpdc

+ $ZrCl_4$

DMF, HCl (23 eq)

1:1.3 (M:L), 80 °C



- ☐ Large-scale synthesis of UIO-68-type material with protected catechol is possible
- ☐ Langmuir surface area: 2768 m^2/g
- ☐ More sample is being prepared for metalation