2018 DoE Hydrogen and Fuel Cells Program Review
June 15, 2018

HySCORE: LBNL Technical Activities

Hydrogen Storage in Metal-Organic Frameworks

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Materials Sciences Division
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Project ID #: ST133

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

Overview

Timeline*

Project Start: 10/1/2015
End: Project continuation determined by DoE. Currently scheduled through 9/30/18
(*previously a component of NREL's materials development program and supported annually since 2006)

Barriers addressed

General: (A) Cost, (B) Weight and Volume, (C) Efficiency, and (E) Refueling Time
Reversible Solid-State Material:
(M) Hydrogen Capacity and Reversibility
(N) Understanding of Hydrogen Physi- and Chemisorption, and
(O) Test Protocols and Evaluation Facilities

Budget

Total Team Budget (HySCORE): $8,855k
Federal Share (LBNL):
- FY17: $1,150k
- FY18: $500k
- Total effort: $2,645k

Partners/Collaborators

NIST – Craig Brown, Terry Udovic
PNNL – Tom Autrey, Mark Bowden
NREL – Tom Gennett, Phillip Parilla
HyMARC – SNL, LLNL, LBNL
LLNL, USA – Brandon Wood
LBNL, USA – David Prendergast
H_2ST^2, USA – H_2 Storage Tech Team

Relevance

Project Objectives

- Determine if adsorbents have a pathway to achieve the binding energies, capacities and kinetics necessary to reach the 2020 DoE targets for H_2 storage by synthesizing and characterizing new porous framework
- 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
- Double H_2 storage energy density (increase from 25 g/L to 50 g/L)
- Provide accurate computational modeling for H_2 adsorbed in porous materials

This Reporting Period

- Research and development of metal-organic frameworks with high volumetric and gravimetric H_2 capacities (Barrier A – C, E).
- DRIFTS characterization (Barrier N,O)

Role of LBNL in the HyMARC/HySCORE Effort

Hydrogen Storage Characterization and Optimization Research Effort

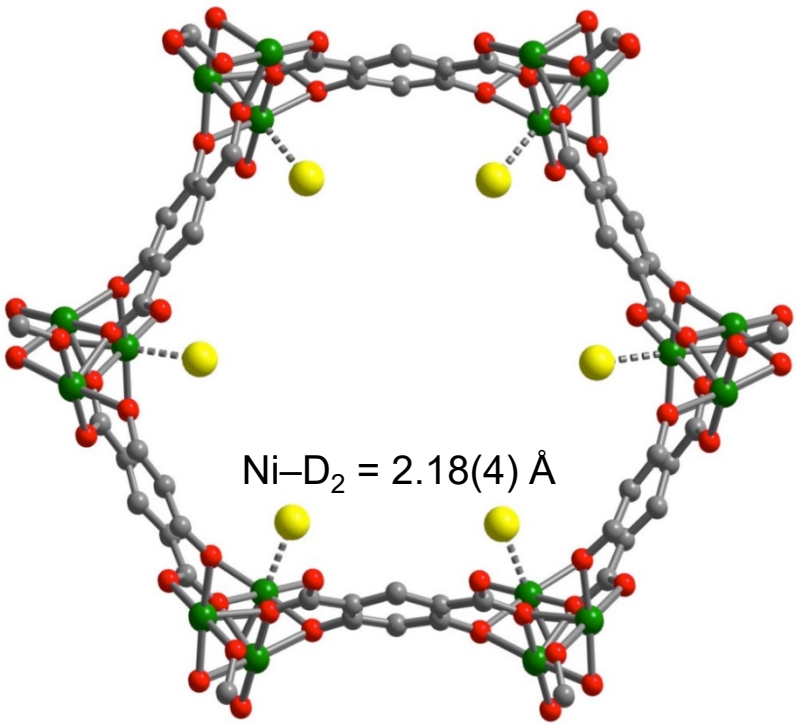
Researchers at NREL, LBNL, PNNL, and NIST are tasked with supporting the DOE Hydrogen Storage Program through validation of:

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

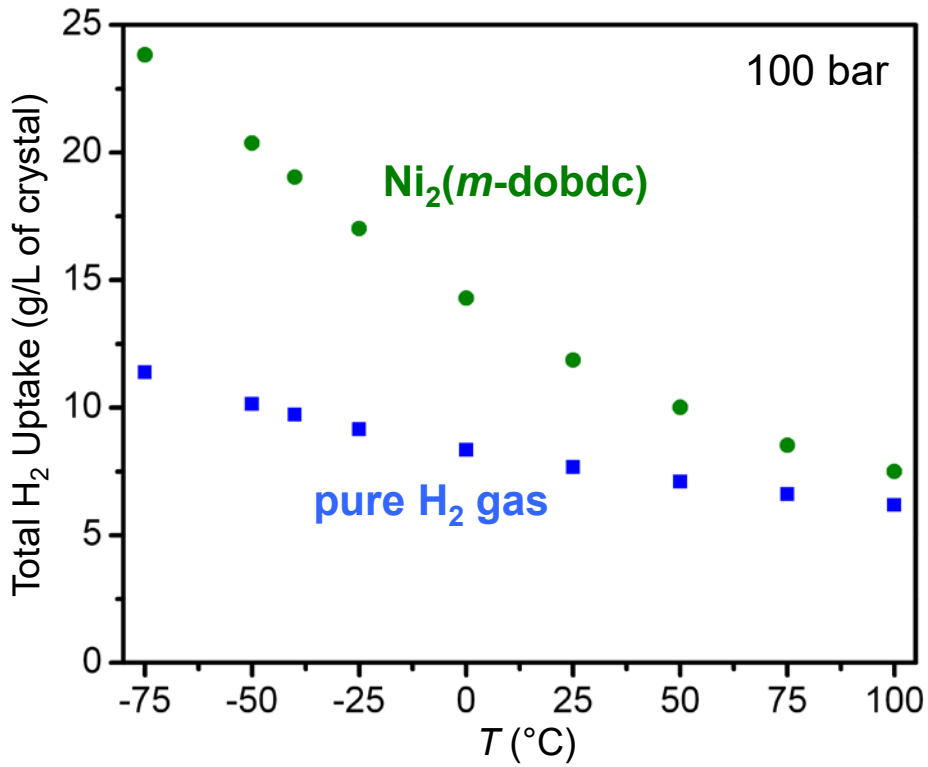
LBNL

1) Mechanistic validation:
   - Can exposed cations in adsorbents reach target of $\Delta H = -15$ kJ/mol?
   - Is it possible to adsorb two, three, or four H_2 per metal cation?
2) IR spectroscopy with precise H_2 dosing at T = 10-300 K, $P \leq 100$ bar
3) Accurate modeling of H_2 adsorbed within porous materials

Approach: Polarization of H_2 with Metal Cations



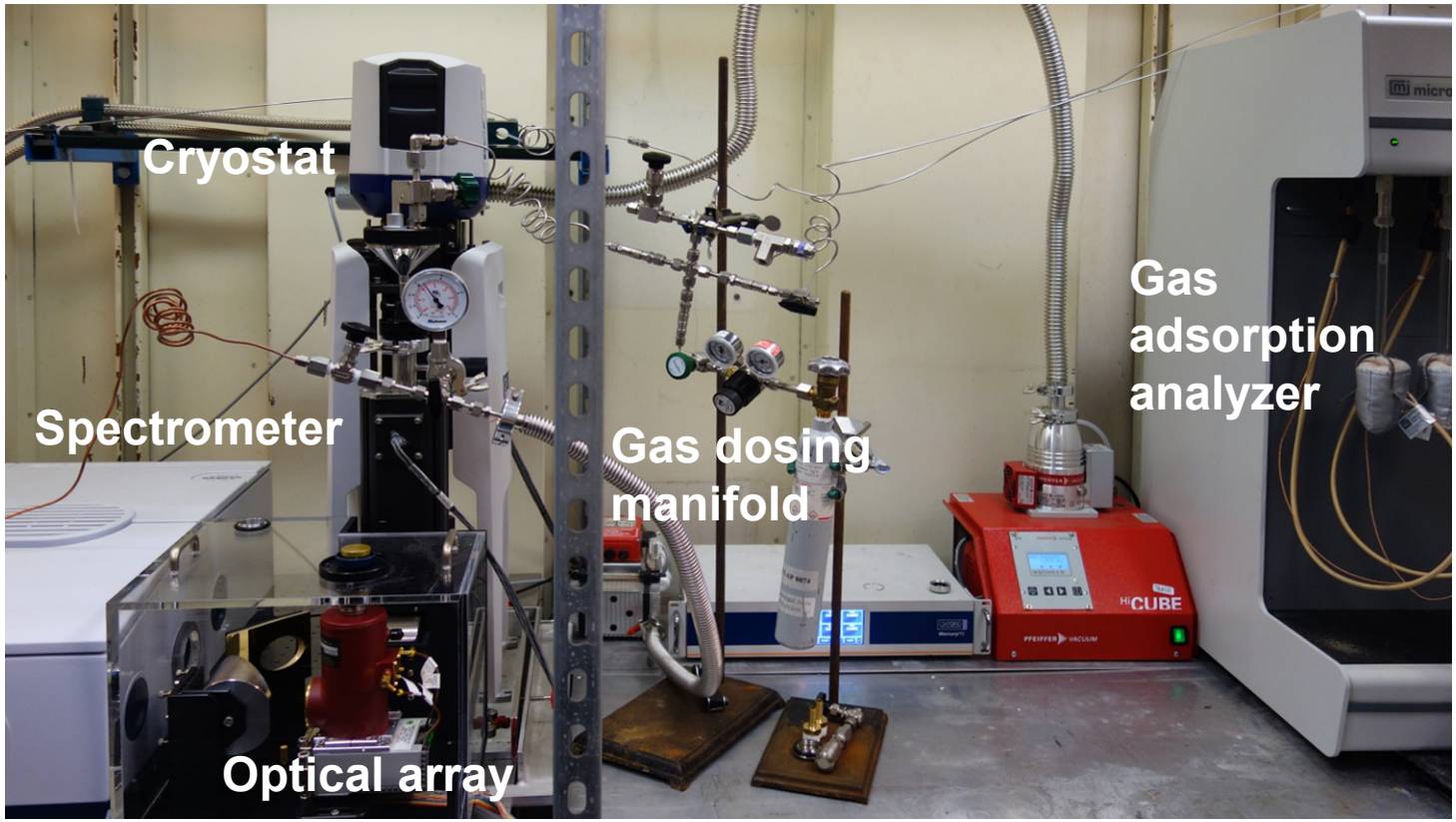
Ni_2(*m*-dobdc)



- High charge density at Ni^{2+} pulls H_2 close, giving binding enthalpy of –13.7 kJ/mol
- Record high adsorbent uptake at ambient temperature and 100 bar fill pressure
- Full characterization provides standards for comparison with new adsorbents

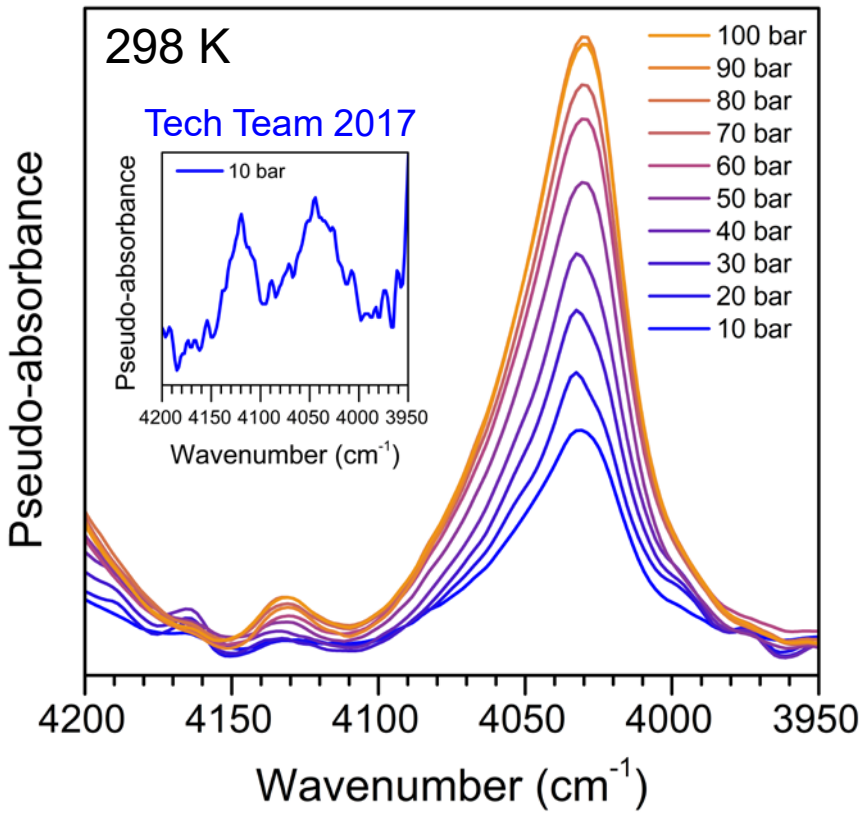
Kapelewski, Runčevski, Tarver, Jiang, Hurst, Ayala, Gennett, FitzGerald, Brown, Long, *manuscript submitted*

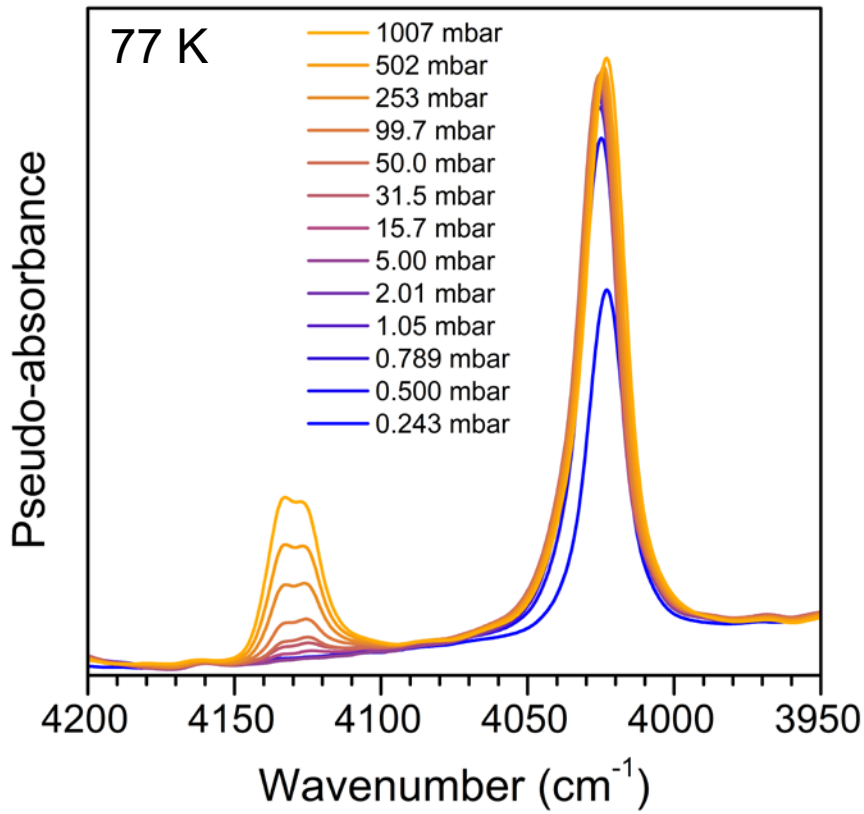
LBNL Core Capability: *In Situ* Infrared Spectroscopy



- Diffuse reflectance system coupled to cryostat and gas adsorption analyzer
- Improved: sample cell, gas dosing manifold, purge of IR beam path
- Can collect data at 15-373 K and 0-100 bar (controlled dosing up to 1.2 bar)

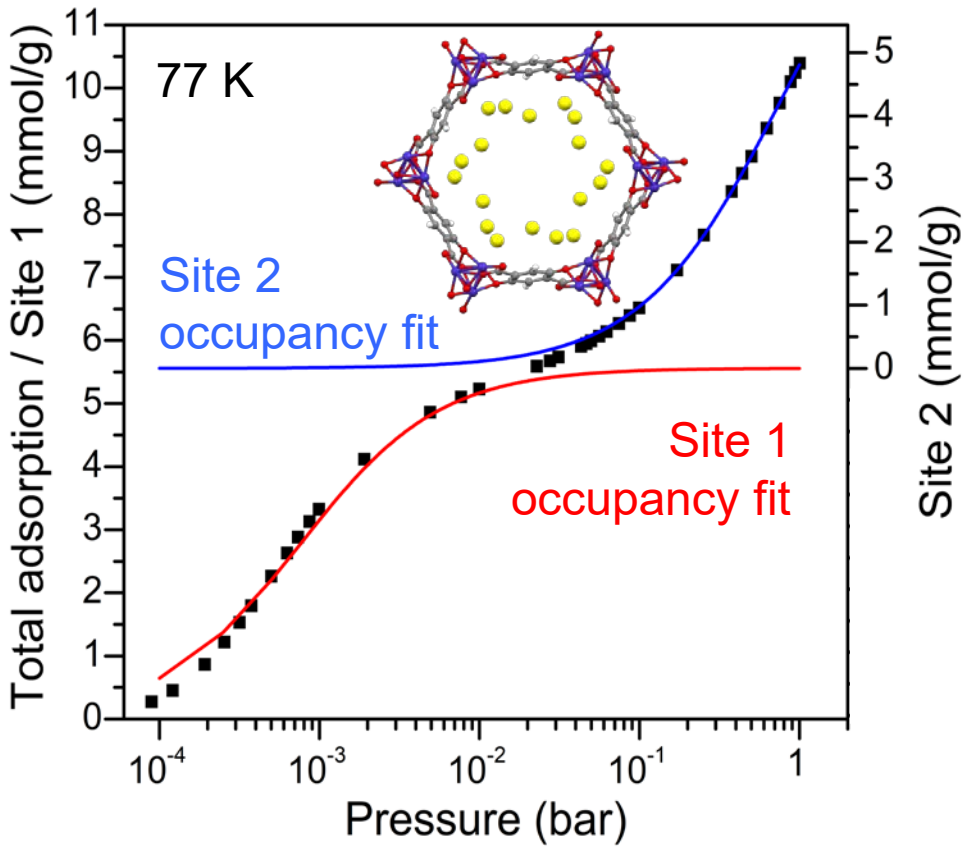
LBNL Core Capability: *In Situ* Infrared Spectroscopy

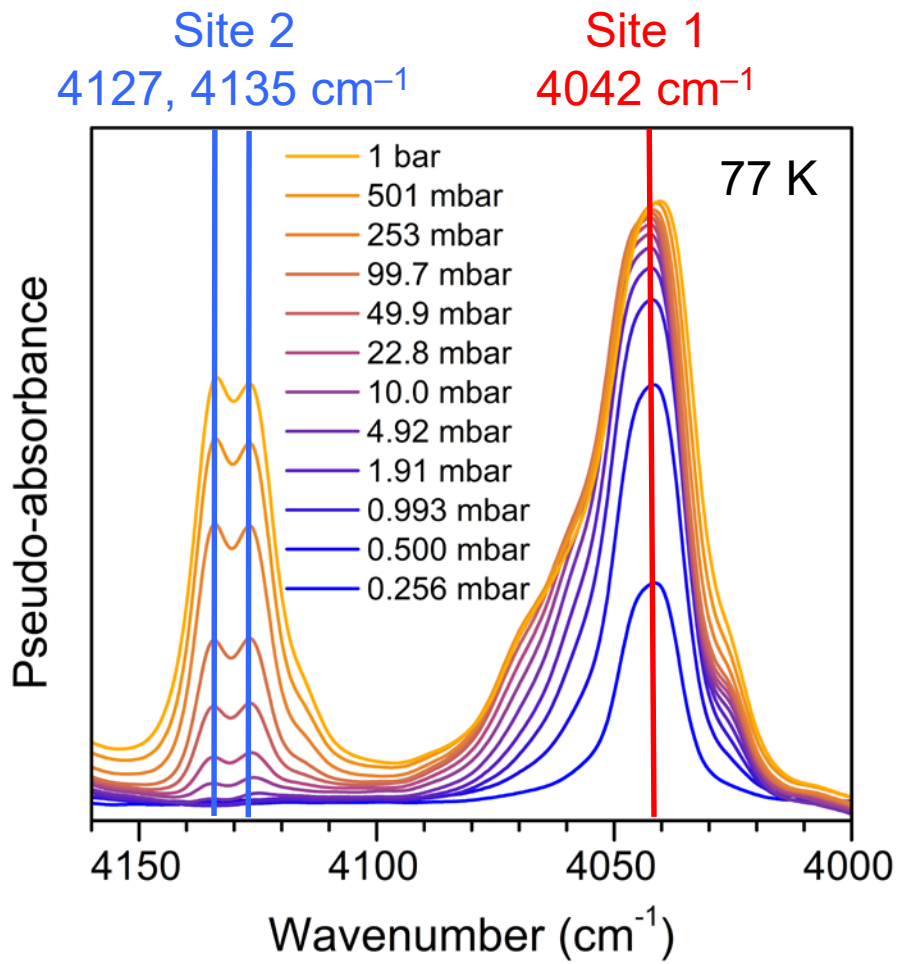




- Cryogenic capability with precise gas dosing now operational
- Clear observation of site-specific H_2 interactions in Ni_2(*m*-dobdc)

Deconvoluting H_2 Isotherm Data for Co_2(dobdc)





- At low pressures spectra indicate only adsorption at Co^{2+} site (Site 1)
- Secondary physisorption sites (Site 2) are populated after Site 1 is filled

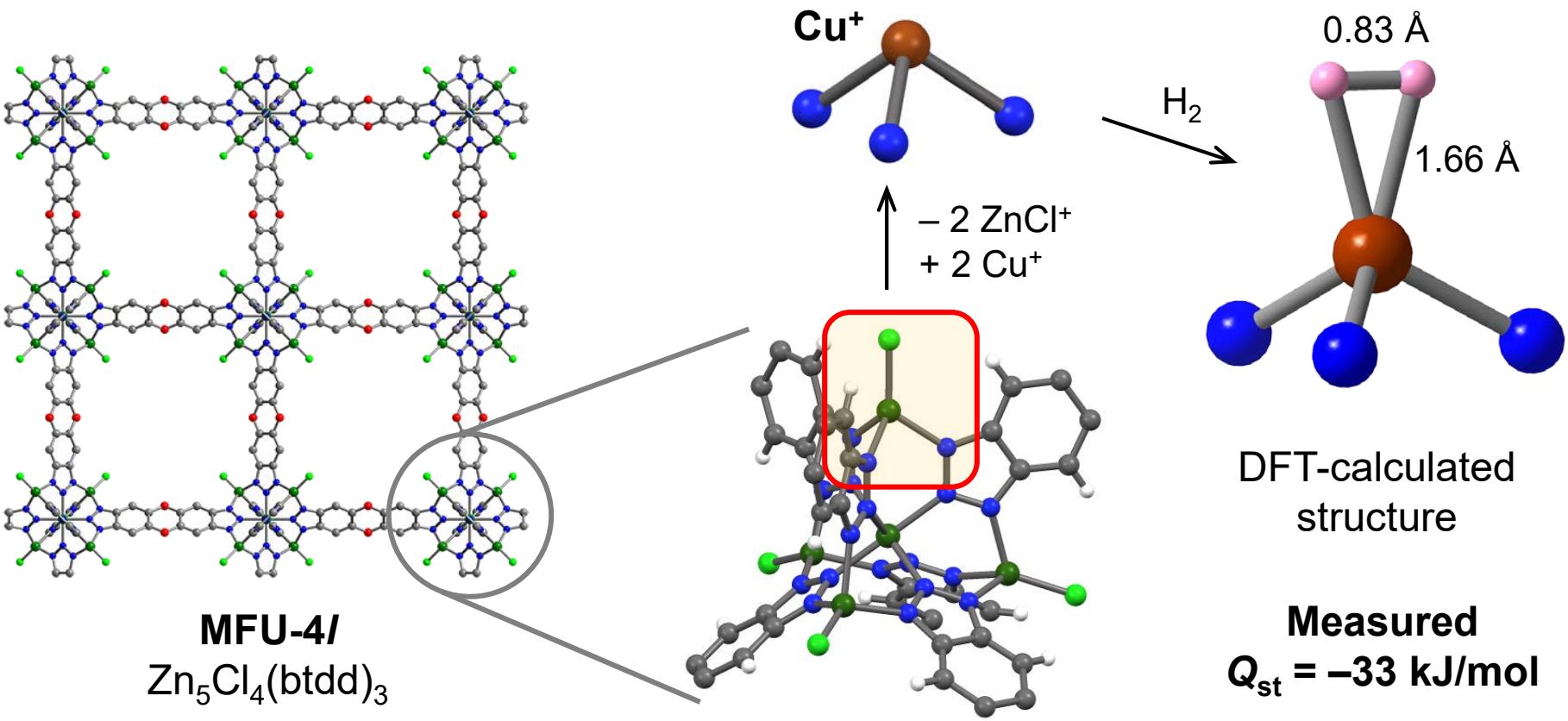
Approach: HySCORE Validation Effort

Is it possible to create MOFs that adsorb H_2 with an enthalpy in the optimal range of –15 to –25 kJ/mol?

- Values are based upon assumptions about the correlation between adsorption enthalpy and entropy
- Are these assumptions even valid? (No: see back-up slides)

Bhatia, Myers *Langmuir* **2006**, *22*, 1688
Garrone, Bonelli, Otero Arean *Chem. Phys. Lett.* **2008**, *456*, 68

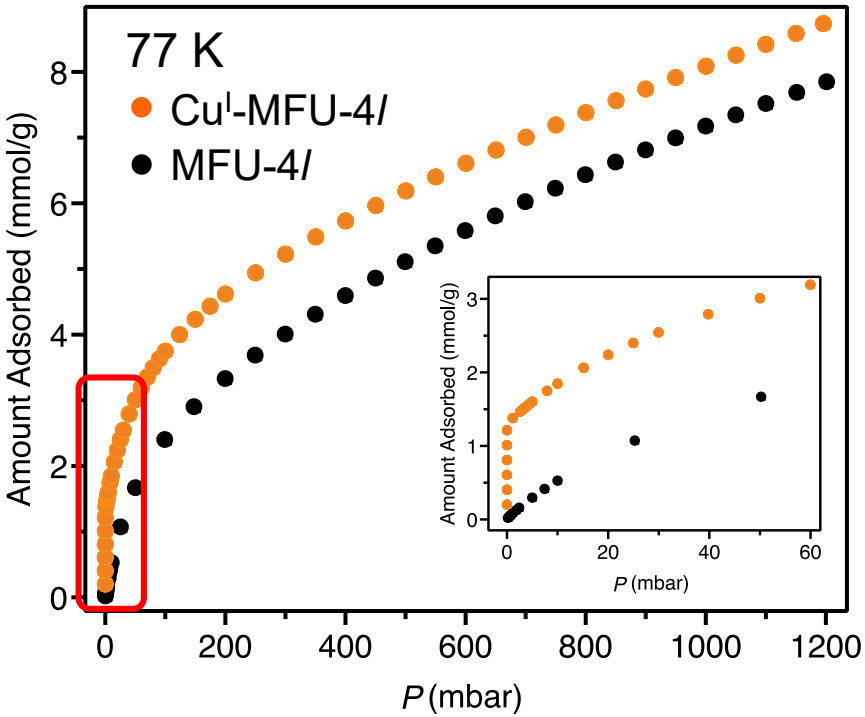
Cu^{I}-MFU-4/: A MOF with Open Cu^{+} Metal Sites

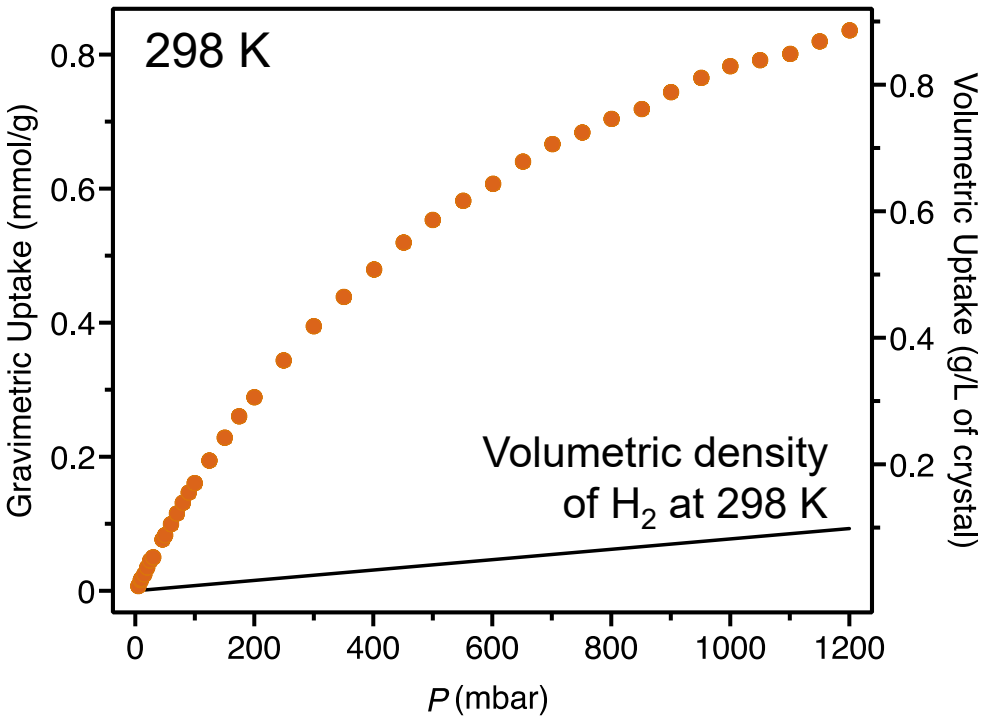


- Only two of the four tetrahedral Zn^{2+} sites can be exchanged with Cu^{+}
- Synthesis was reproduced and we are attempting to increase metal exchange

Denysenko, Jelic, Reuter, Volkmer *Angew. Chem. Int. Ed.* **2014**, *53*, 5832

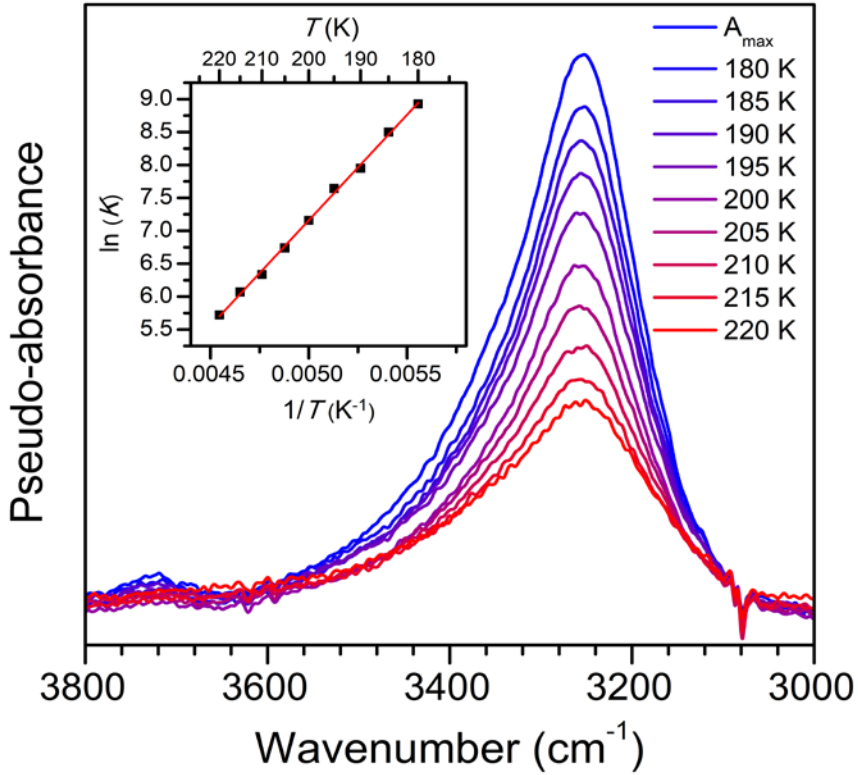
Accomplishments: Strong H_2 Binding in Cu^I-MFU-4*l*

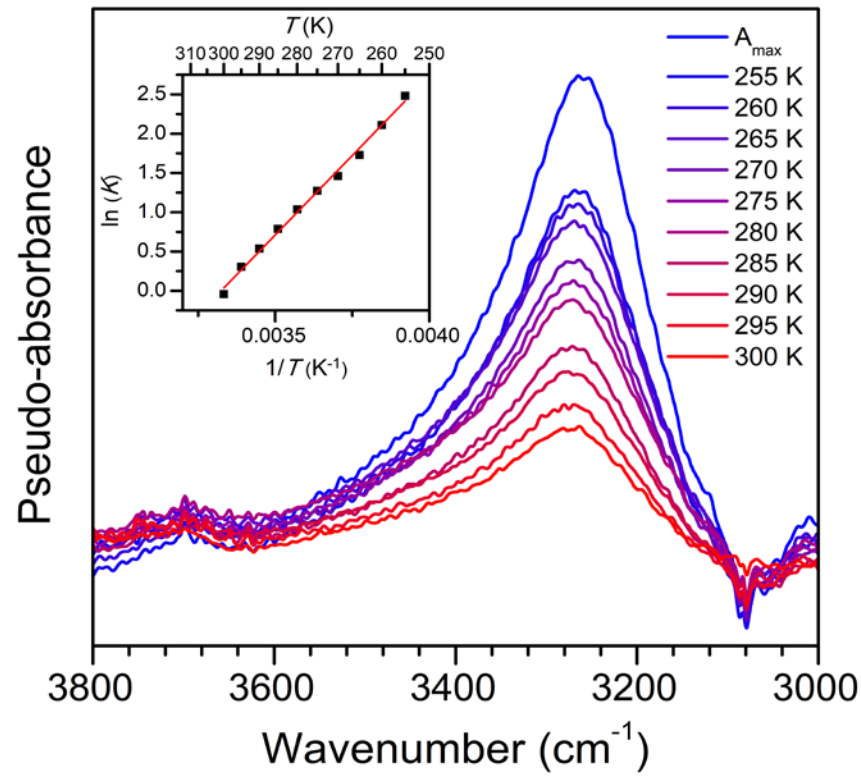




- Steep uptake at low pressures corresponds to adsorption at open Cu^+ sites
- Uptake at 298 K and 1 bar corresponds to filling of ~50% of the Cu^+ sites

Accomplishments: IR Spectra for H_2 in Cu^I-MFU-4/





T range (K)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/mol·K)
180-220	–26.7	–74
255-300	–33.6	–112

- Temperature dependence highlights the importance of measuring data under actual operating conditions: 5-100 bar and –40 to 60 °C

Approach: HySCORE Validation Effort

Is it possible to create MOFs that adsorb H_2 with an enthalpy in the optimal range of –15 to –25 kJ/mol?

- Values are based upon assumptions about the correlation between adsorption enthalpy and entropy
- Are these assumptions even valid? (No: see back-up slides)

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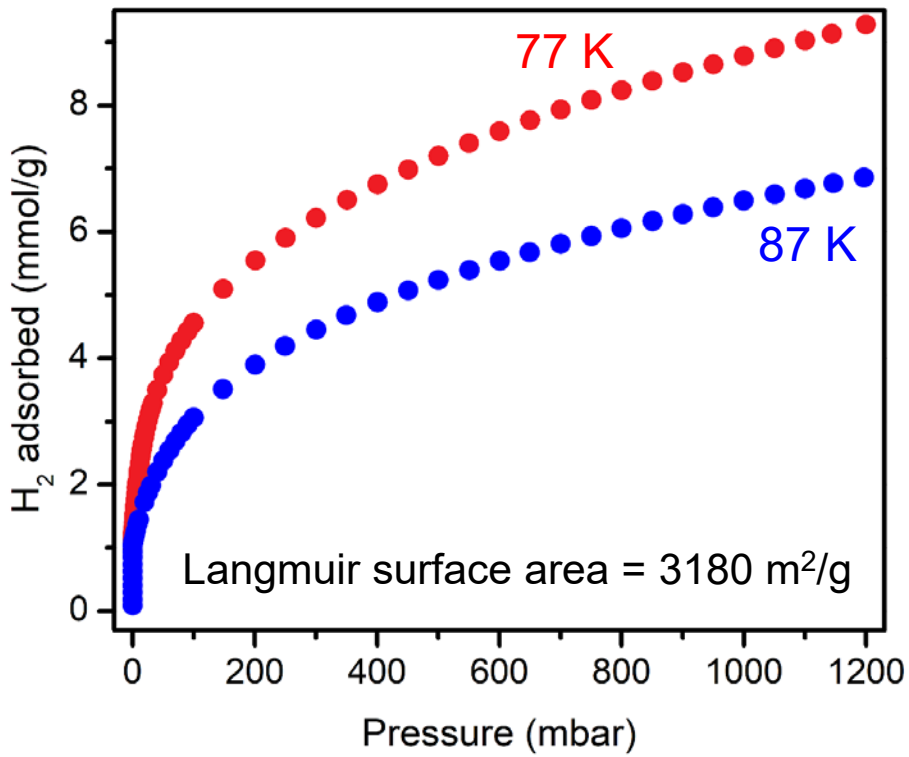
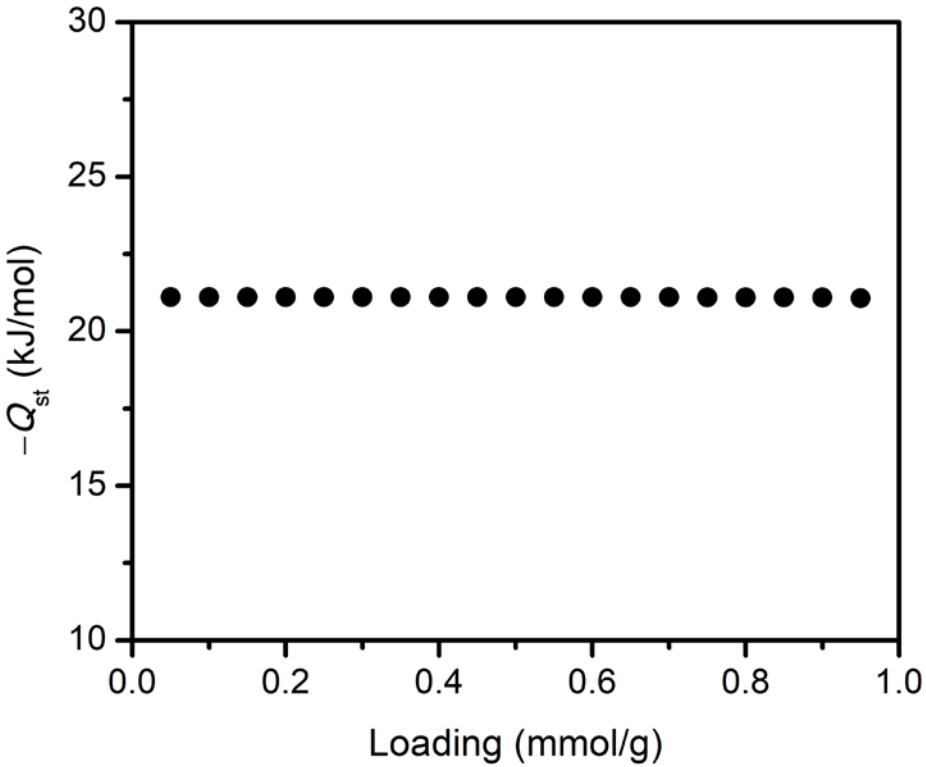
Garrone, Bonelli, Otero Arean *Chem. Phys. Lett.* **2008**, *456*, 68

Hypothesis:
Open V^{2+} coordination sites will place us in this range

- No such MOFs are known, but can we (finally) make one?

Accomplishments: First MOF with Open V^{2+} Sites





- Successful synthesis and structure determination of the first V(II) MOF
- Q_{st} determined from fits to isotherms collected at –78 and –58 °C
- First MOF with Q_{st} in the optimal range between –15 and –25 kJ/mol

Challenges to Address Moving Forward

MOF	Metal ion	H_2 uptake at 77 K, 1 bar (mmol/g)	Q_{st} from isotherms (kJ/mol)	ν(H–H) from DRIFTS* (cm^{-1})	$\Delta H°$ from DRIFTS (kJ/mol)
Ni_2(*m*-dobdc)	Ni^{2+}	11.1	–12.3	4025	–13.7
V-MOF	V^{2+}	9.2	–21	3919	in progress
Cu^I-MFU-4*l*	Cu^+	8.1	–32.7	3252	–33.6

* ν(H–H) for free H_2 = 4161 cm^{-1}

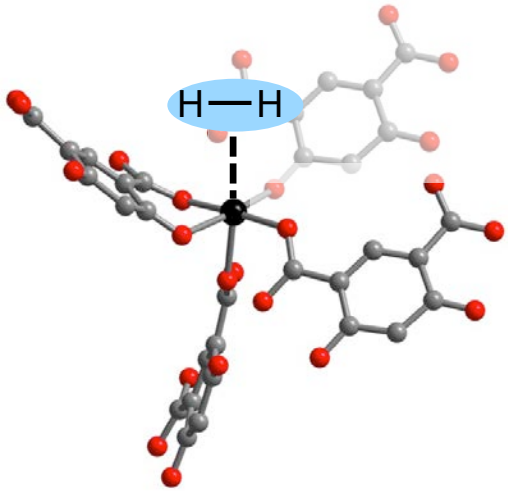
- Gain a complete understanding of H_2 adsorption in V^{II} and Cu^I systems:
  - high-pressure adsorption isotherms and *in situ* spectroscopy
  - neutron diffraction studies (underway for Cu^I-MFU-4*l*)
  - computational studies of H_2 binding mechanisms (in progress)
- Increase the density of the available metal binding sites

Approach: HySCORE Validation Effort

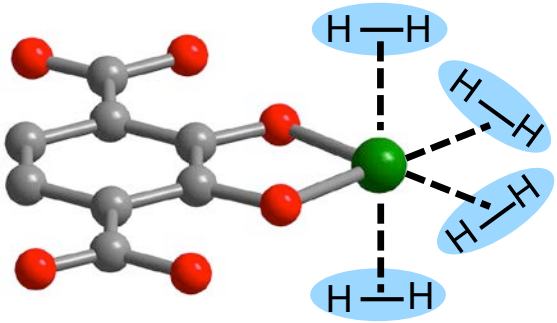
Is it possible to create MOFs with open metal sites that adsorb more than two H_2 molecules?

- This is a long-standing, "holy grail" challenge in MOF chemistry
- Highly complex synthetic challenge

Mn_2(dsbdc) adsorbs two H_2 at a Mn^{2+} site: Runčevski, Kapelewski, Torres-Gavosto, Tarver, Brown, Long *Chem. Commun.* **2016**, *52*, 8351

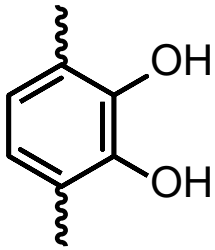


Classical (1 H_2 per metal cation)

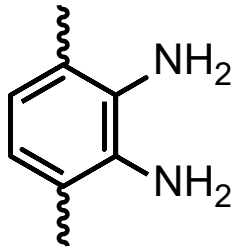


Next-Generation
(4 or 5 H_2 per metal cation)

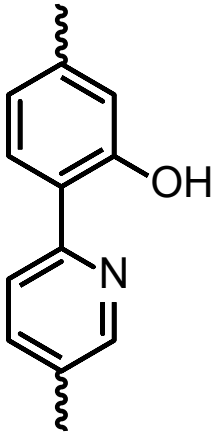
Approach: Anionic Chelating Groups Embedded within MOFs



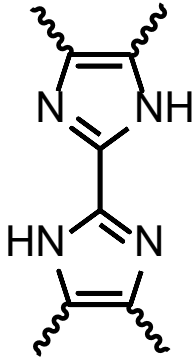
catechol



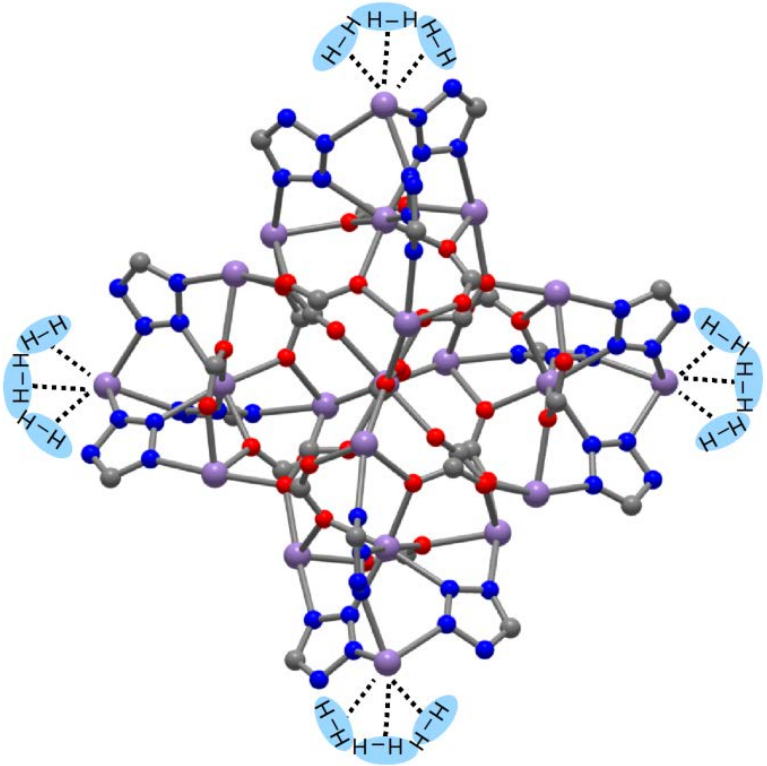
phenylenediamine



pyridinylphenol

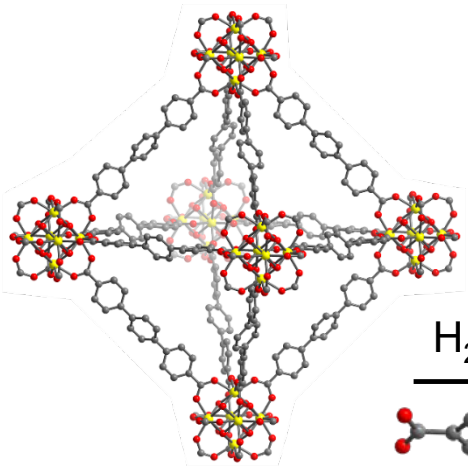


bisimidazole

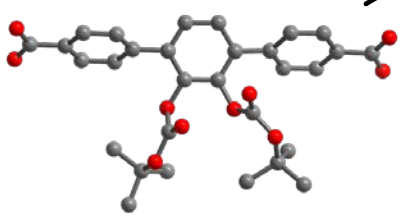


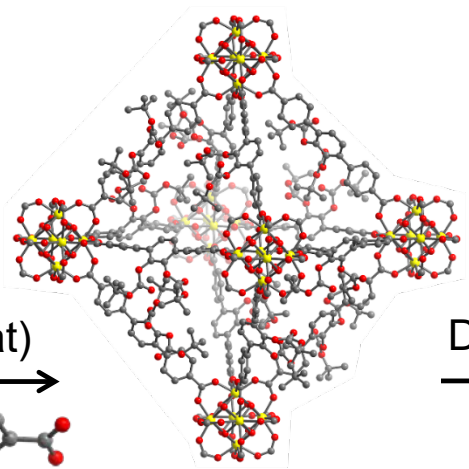
$M_4Mn_{16}(tetrazolate)_{12}(HCO_2)_{12}$ nodes
(like trispyrazolylborate)

Catechol-Functionalized MOF Synthetic Strategy

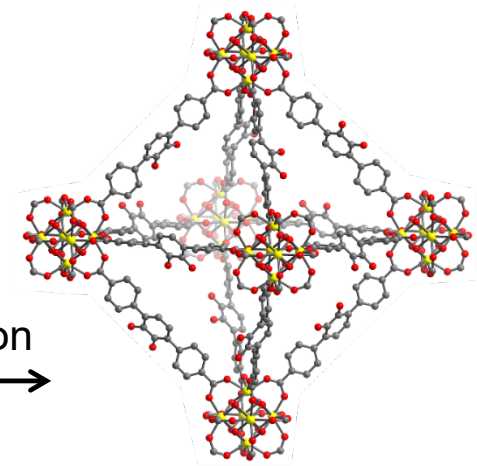


H_2(*Boc*-tpdc-cat) →



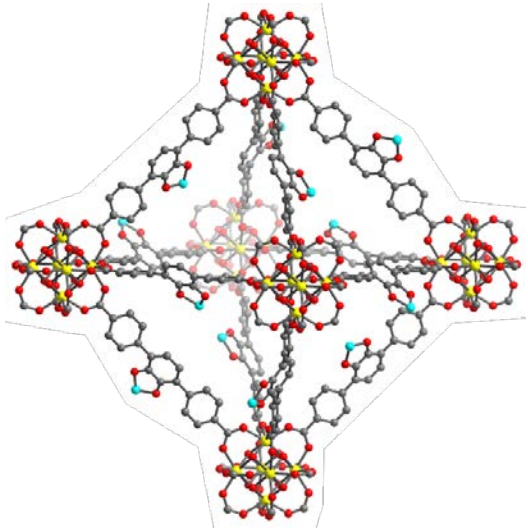


Deprotection →



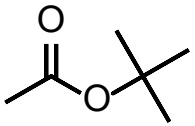
Gram-scale synthesis!

Metalation

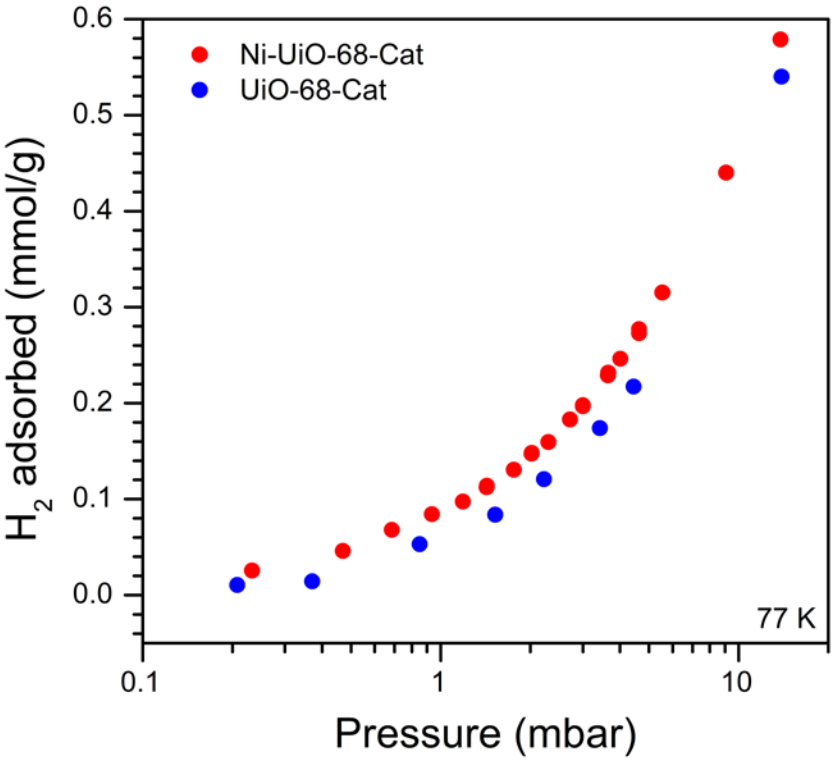


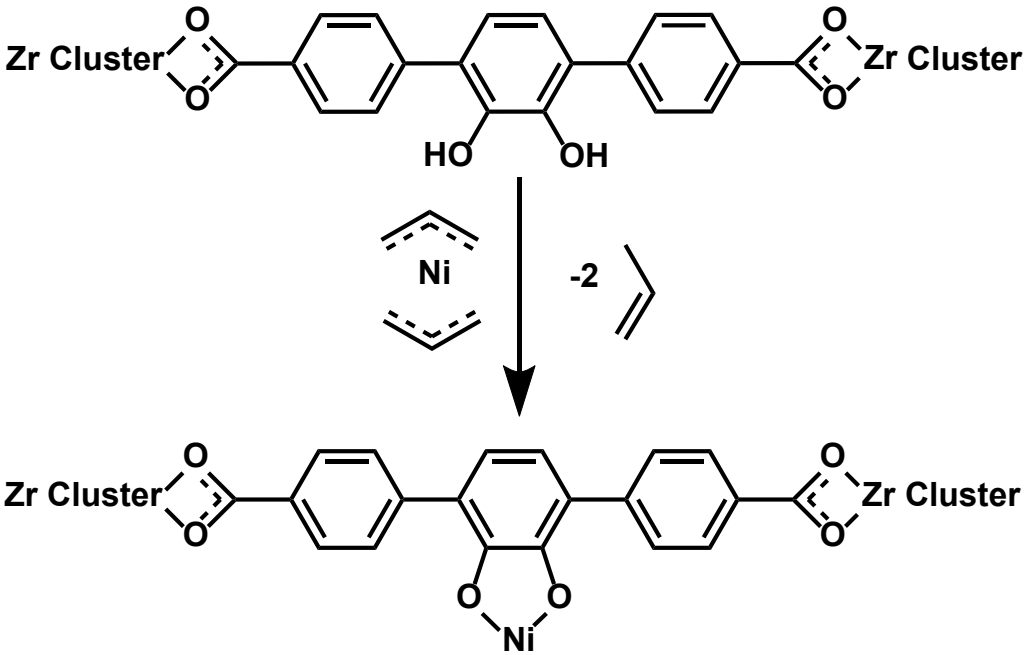
Boc protecting group chosen for its thermal lability

–*Boc* ≡



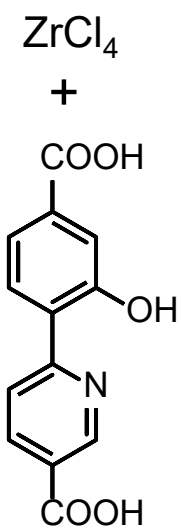
Accomplishments: Partial Metalation with Ni^{2+}



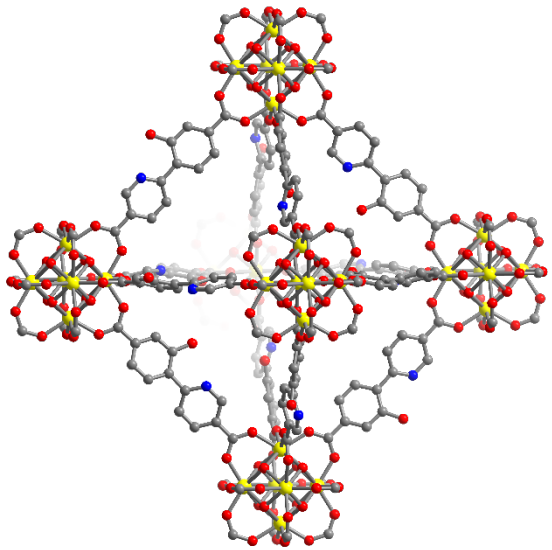


- Crystallinity maintained under metalation conditions
- ICP analysis indicates metalation of only ~13% of catechol sites (need to increase)
- Slight increase in H_2 capacity at low pressures consistent with low level of metalation
- Currently attempting to to improve metalation reactions, including with Mg^{2+} and Ca^{2+}

Accomplishments: A Zr-MOF with *N,O*-Chelating Groups

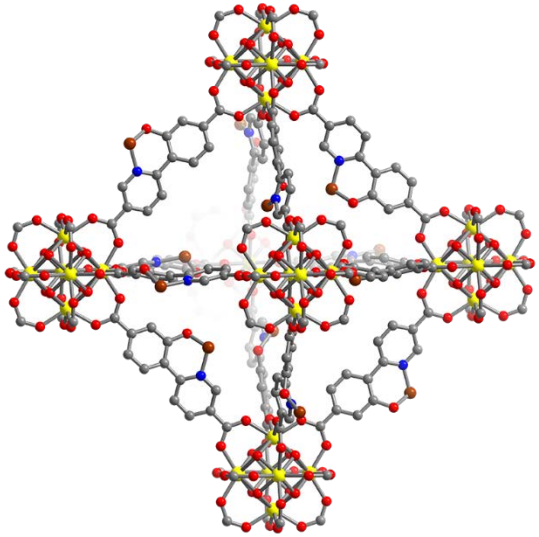


H_2PhOHpydc



$Zr_6O_4(OH)_4$(PhOHpydc)$_6$
"UiO-67-PhOHpydc"

Metalation



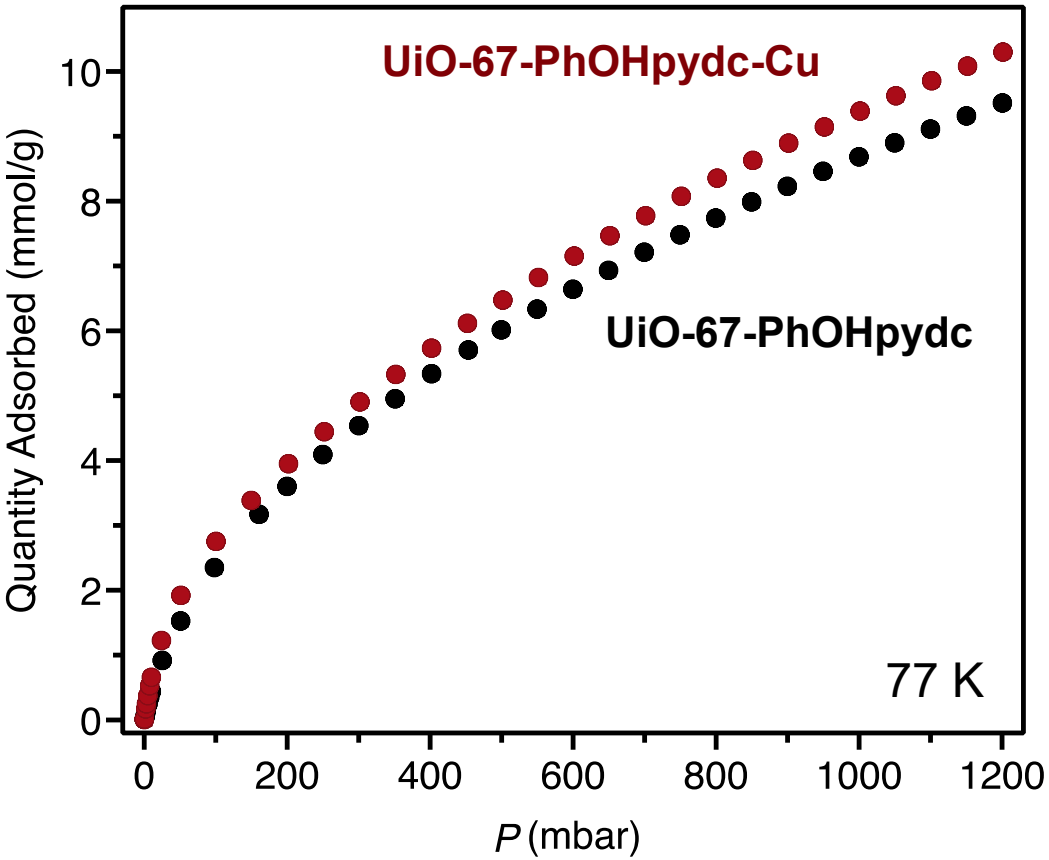
UiO-67-PhOHpydc-Cu^I
(modeled structure)

Predicted total uptake at 298 K, 100 bar

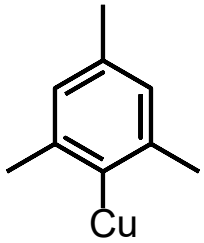
Volumetric (g/L)	Gravimetric (wt %)
17.1	2.2

- Assumes binding of 2 H_2 per Cu and H_2 packing in pores of MOF-5
- Increases over Ni_2(*m*-dobdc) of 40% (volumetric) and 120% (gravimetric)

Accomplishments: Partial Metalation with Cu^+



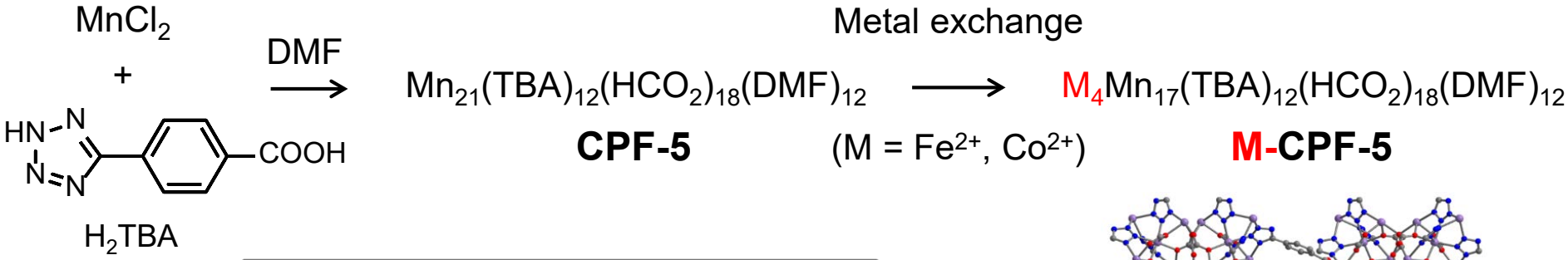
Metalation conditions:
1 eq. CuMes per linker
30 °C for 24 h in C_6H_6
Activated at 120 °C

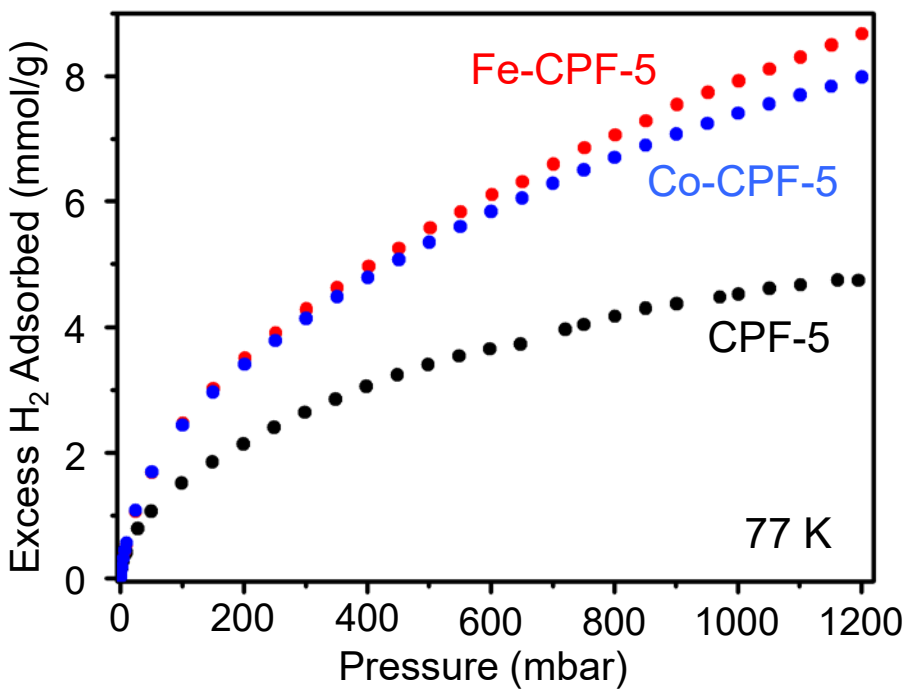


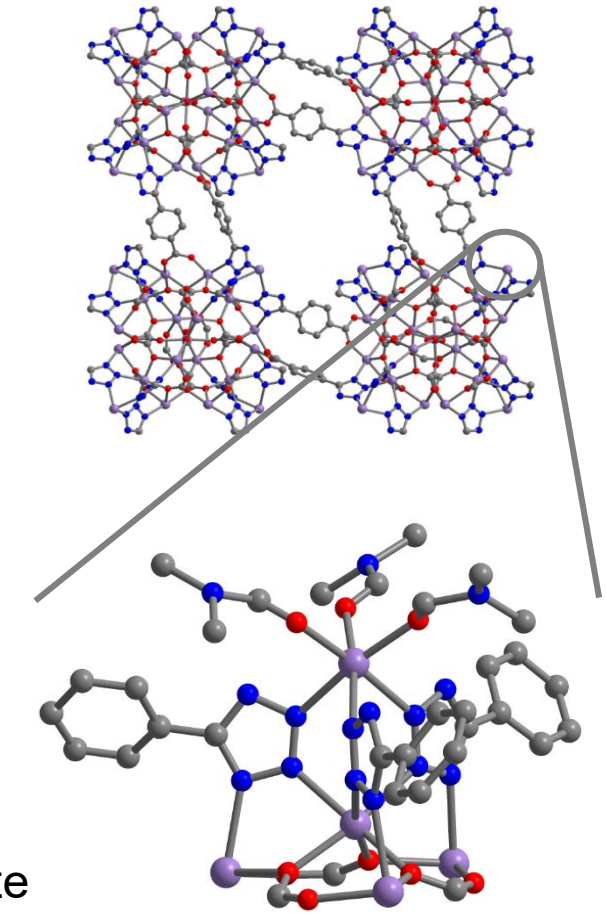
= CuMes

- Langmuir SA shows slight decrease from 2900 m^2/g (pristine) to 2640 m^2/g
- ICP-OES indicates only 9% of linkers have been metalated
- ^1H NMR of digested material shows residual benzene – may be bound to Cu^+

Accomplishments: Tri-Solvento M^{2+} Sites in M-CPF-5







- Increased uptake in Fe- and Co-exchanged CPF-5 may be associated with adsorption of up to 3 H_2 per metal site

Summary of Metalation and Metal Exchange Efforts

Parent MOF	Binding site	Metal precursor	Uptake compared to pristine MOF (1 bar, 77 K)
UiO-68	Catechol	Bis(allyl)Ni(II)	Slight increase
UiO-67	Pyridinyl phenol	(Mesityl)Cu(I)	Slight increase
MOF-74	Phenylenediamine	In progress	
MOF-74	Bisimidazole	In progress	
CPF-5	Tristetrazolate	$FeCl_2$	54% increase (7.9 mmol/g)
CPF-5	Tristetrazolate	$CoCl_2$	65% increase (7.4 mmol/g)

- Initial metalation studies focused on catechol-containing frameworks, and vast majority of metalated frameworks displayed reduced H_2 capacities
- *N,O*- and *N,N*-chelating groups can obviate the need for protecting groups
- Well-suited for metalation with soft metal sources (*e.g.* Cu^I), and attempts to fully activate UiO-67-PhOHpydc-Cu^I are in progress
- Complete activation could yield three H_2 molecules per metal site
- Search for conditions amenable to complete activation is ongoing

Benchmarking Density Functionals for H_2 Storage

- **Features of dataset**

  Creation of dataset specifically for H_2 storage

  Dataset consists of 45 unique binding motifs, and more than 100 data points

  Dataset consists of single and multiple hydrogens bound to a single metal site

- **Reference energies**

  CCSD(T) used for reference – considered the “gold standard”

  Energies extrapolated to complete basis set limit

- **Density functionals**

  40 density functionals chosen based on their performance in non-covalent interactions and previous usage in periodic and non-periodic H_2 adsorption calculations

  def2-QZVPPD basis set used for all calculations

First comprehensive dataset and benchmarks representing the H_2 adsorption problem

Best Performing Density Functionals

Rank	Functional	Type	RMSE (in kJ/mol)
1	ωB97M-V	Range separated hybrid metaGGA	1.50
2	ωB97X-V	Range separated hybrid GGA	1.74
4	B97-D3(BJ)	GGA	1.85
18	PBE	GGA	2.97
24	B3LYP	Hybrid GGA	3.33
32	MN15	Hybrid metaGGA	4.20

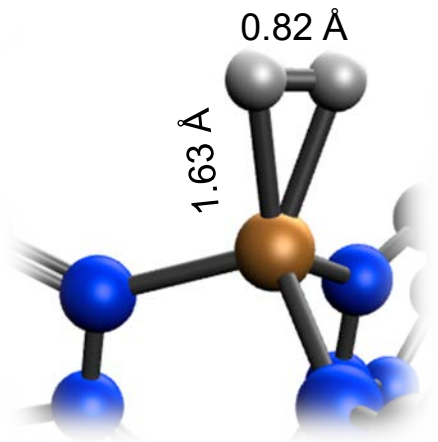
- ωB97M-V has been previously shown to give the best performance for a wide variety of data like thermochemistry, barrier heights and isomerization energies*
- Basis set superposition error: ~0.1 kJ/mol
- More expensive functionals do not necessarily give better interaction energies
- Dispersion corrected density functionals perform significantly better

B97-D3(BJ) functional gives the best tradeoff between accuracy and computation cost

*Mardirossian, Head-Gordon *Mol. Phys.* **2017**, *115*, 2315

Computing Enthalpy of H_2 Binding in Cu^I-MFU-4/

Contribution	Energy (kJ/mol)	
	B3LYP-D3(BJ)	ωB97M-V
Electrostatic	92.0	99.8
Polarization	–62.4	–79.2
Charge-transfer	–56.9	–48.7
Total	**–27.4**	**–28.1**



ωB97M-V optimized geometry

- Theoretical estimates complement VT-IR enthalpy change: **–26.7** kJ/mol (180 to 220 K)
- Binding surface deepens upon considering higher order relaxations: **–31.5 kJ/mol** for B3LYP-D3(BJ)

Responses to Previous Year Reviewers' Comments

FY17 Reviewer Comment	FY18 Response to Comment
Despite last year's important report on binding two H_2 per metal site, this year's presentation made no mention of progress toward extending (or demonstrating) that approach on other MOFs. It is not clear whether any other systems were examined.	In actuality, much of the presentation from last year (slides 13-20) was dedicated to our extensive attempts to create new MOFs capable of binding two or more H_2 per metal site. This challenging synthetic work has continued over the past year, and we have presented initial evidence of exposing low-coordinate Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{+} within various new MOFs (slides 15-22).
There are only a few strong, good collaborations internal to HySCORE, and none external to HySCORE.	We believe we have forged numerous strong collaborations both within HySCORE and external to HySCORE. Some examples: TPD and high pressure H_2 at NREL, NMR at PNNL, neutron diffraction at NIST, XAS with Drisdell and Prendergast at LBNL, computations with Wood at LLNL, IR with FitzGerald at Oberlin.

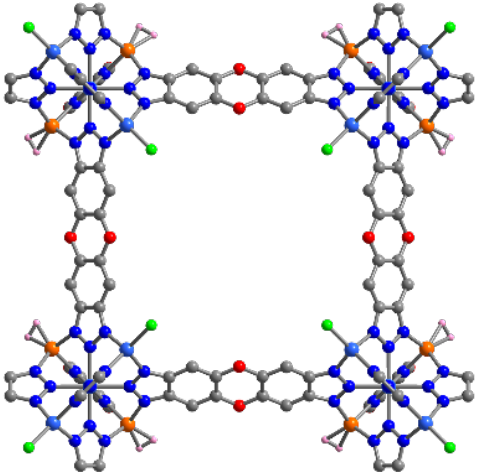
Remaining Challenges and Barriers

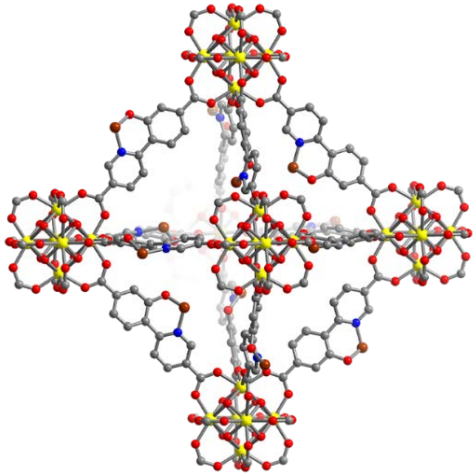
- Design and synthesis of MOFs that adsorb H_2 with an enthalpy in the optimal range of –15 to –25 kJ/mol cations remains a challenge
- Establishing a valid correlation between ΔH and ΔS for H_2 adsorption under target operating conditions: 5-100 bar and –40 to 60 °C
- Can we manipulate ΔS with synthetic chemistry?
- Complete insertion of metal cations into *O*,*O*-, *N*,*O*- or *N*,*N*-chelating groups within MOFs is a key synthetic challenge
- Can we demonstrate adsorption of 3 or more H_2 molecules per metal?
- While accurate computational tools are available for calculating binding energies, the optimal trade-off point between accuracy and expense is still under investigation

Any proposed future work is subject to change based on funding levels

Summary

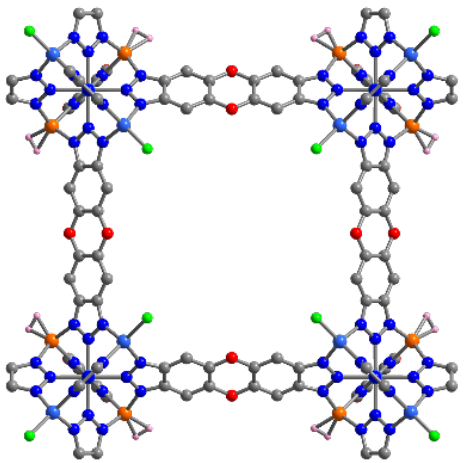
- Extensively studied the thermodynamics of H_2 binding in Cu^I-MFU-4*l* using *in situ* DRIFTS and first-principles computations
- Synthesized a new V-MOF that binds H_2 with an optimal ΔH_{ads} for ambient temperature storage
- Synthesized Fe- and Co-CPF-5 with potential to bind 3 H_2 molecules per open metal site
- Synthesized a pyridinyl phenol-containing variant of UiO-67 and (partially) metalated with Cu^I
- Synthesized two new frameworks of the M_2(dotpdc) (MOF-374) structure type containing *N*,*N*-chelating groups for metalation
- Benchmarked a dataset tailored for hydrogen storage to identify cheap, high-performance density functionals

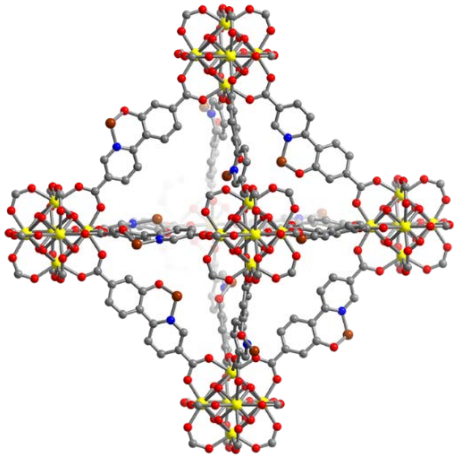




Future Directions

- Find conditions for complete activation of V-MOF
- Synthesize smaller pore analogues of Cu^{I}-MFU-4*l* and V-MOF to increase volumetric H_2 capacities
- Use *in situ* DRIFTS to determine ΔH_{ads} and ΔS_{ads} under target operating conditions—requires buying integrating a high-pressure gas adsorption analyzer
- Continue metalation of frameworks with functionalized linkers to access low-coordinate metal sites
- Pursue flexible MOFs that can maximize H_2 usable capacity through step-shaped adsorption isotherms
- Utilize lattice Boltzmann simulations to model H_2 adsorption and predict storage capacities





Any proposed future work is subject to change based on funding levels

Summary (Milestones)

Milestone	% complete
FY17 Q4: Demonstrate the ability to determine H_2 adsorption enthalpies from variable-temperature spectra collected on the DRIFTS spectrometer.	**100%**
FY18 Q1: Synthesize three low-valent metal precursors and develop a methodology to use these precursors to metalate the cat-UiO-68 MOF.	**100%**
FY18 Q2: Submit a paper to a peer reviewed journal that has Authors from at least three of the four participating laboratories.	**100%**
FY18 Q3: Measure H_2 isotherms for the metalated cat-UiO-68 MOF to estimate their H_2 adsorption enthalpies.	60%

Summary (DRIFTS Milestones)

Milestone	% complete
FY17 Q3: Demonstrate a) that the DRIFTS instrument is operating with a resolution of 10 cm^{-1} by measuring spectra for a mutually agreed upon sorbent standard at 1 bar H_2 in the temperature range 77–373 K and b) the ability to determine H_2 adsorption enthalpies on a mutually agreed upon sorbent standard from variable-temperature spectra collected on the DRIFTS spectrometer to within 10% of the accepted values.	100%
FY17 Q4: Submit DoE report and/or peer reviewed manuscript on the DRIFTS instrument, its capabilities, and the application of the system to hydrogen storage materials characterization.	15%
FY18 Q1: Demonstrate that the DRIFTS instrument is operating with a resolution of 10 cm^{-1} at a temperature of 50 K by measuring spectra for a MOF.	Pending Funding
FY18 Q2: Demonstrate that the DRIFTS instrument is operating with a resolution of 10 cm^{-1} at a temperature of 25 K by measuring spectra for a MOF.	Pending Funding
FY18 Q3: Demonstrate that the DRIFTS instrument is operating with a resolution of 10 cm^{-1} at a temperature of 10 K by measuring spectra for a MOF.	Pending Funding

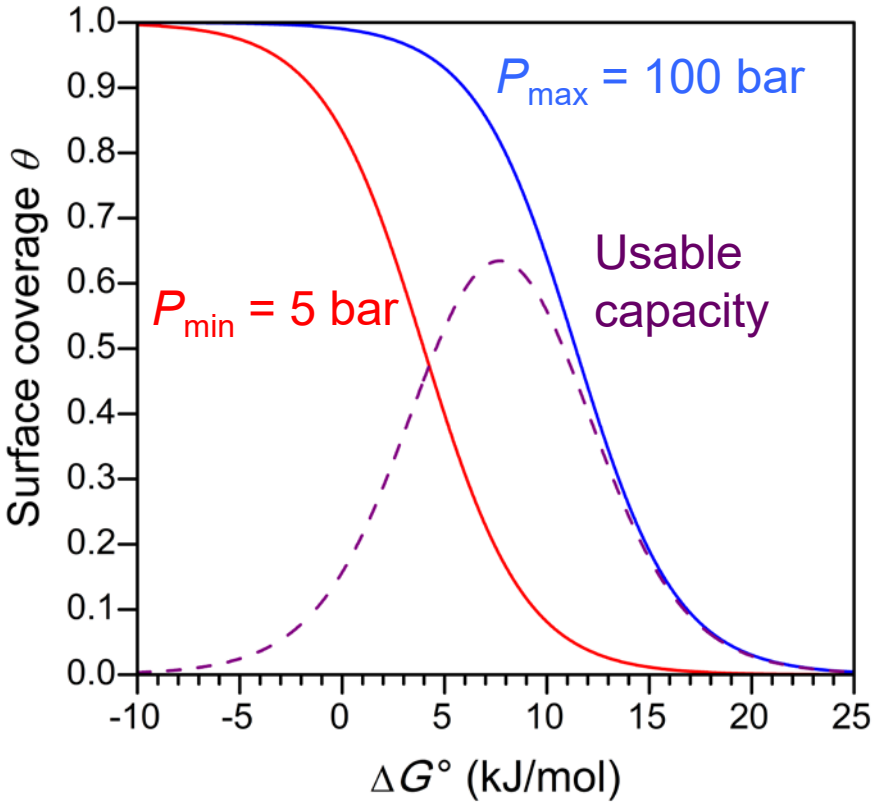
Acknowledgements

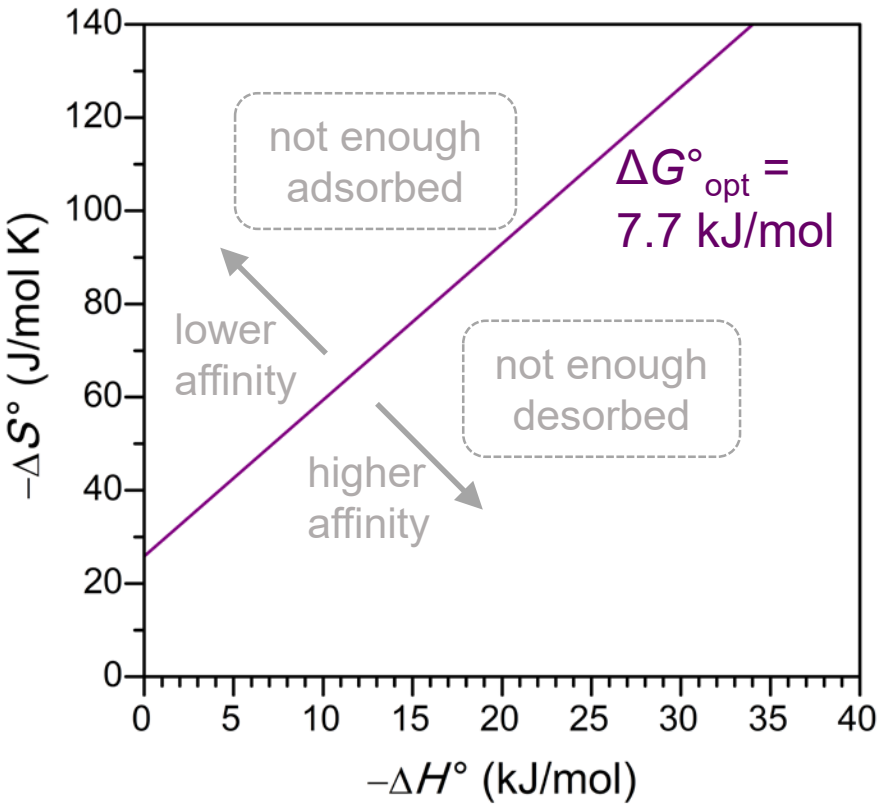
This work was supported by the U.S. Department of Energy (US DOE), Office of Energy Efficiency and Renewable Energy (EERE), Fuel Cell Technologies Office (FCTO), under Contract No. DE-AC02-05CH11231.

Reviewers: Thank you for the constructive feedback.

Technical Back-Up Slides

Optimal ΔG° for a High Usable Capacity at 298 K

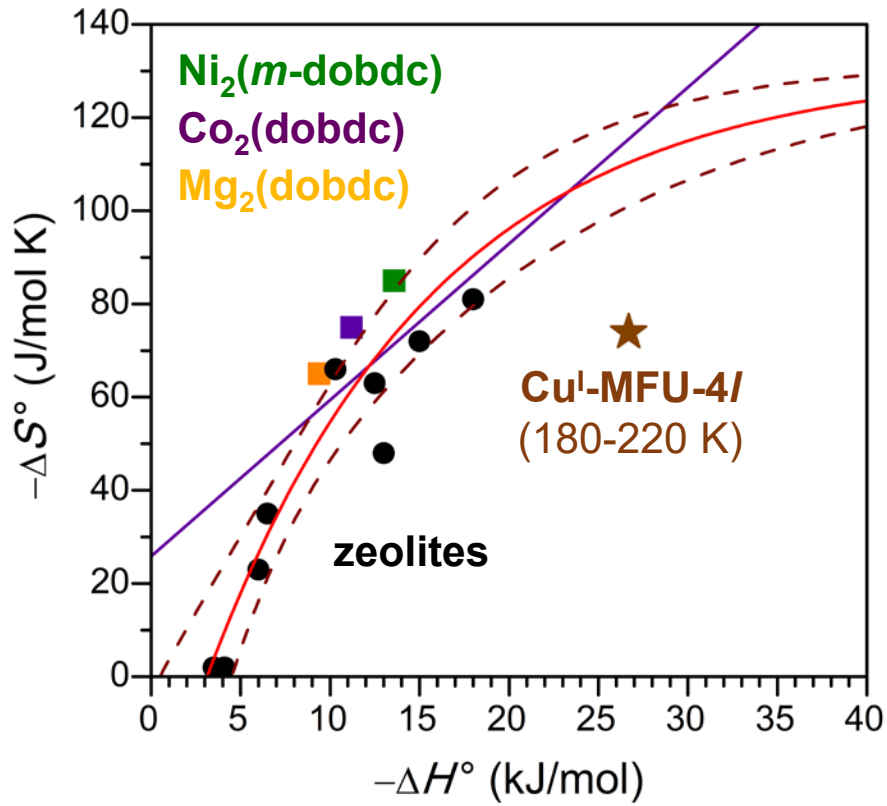




- Usable H_2 storage capacity determined by $\Delta G°$, not $\Delta H°$ alone
- Optimal $\Delta G°$ of 7.7 kJ/mol balances the tradeoff between maximizing capacity during adsorption and minimizing capacity during desorption

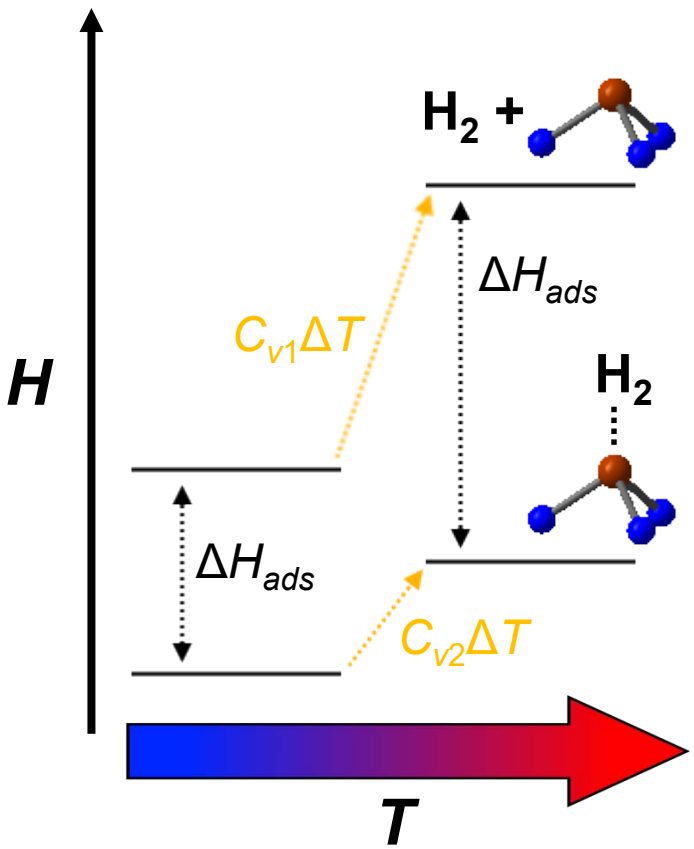
Enthalpy-Entropy Correlations for H_2 Adsorption

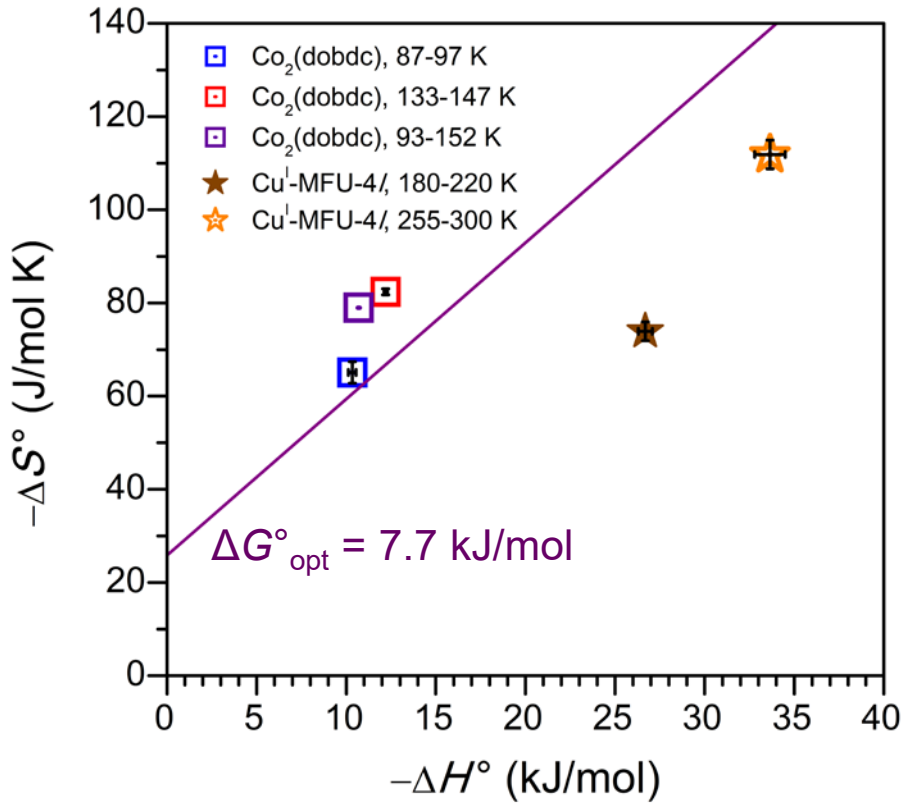
	$-\Delta H°$ (kJ/mol)	$-\Delta S°$ (J/mol·K)
(Mg,Na)-Y	18	81
(Ca,Na)-Y	15	72
Ca-X	13	63
Mg-X	13	48
Li-ZSM-5	6.5	35
Na-ZSM	10	66
Li-FER	4.1	2
Na-FER	6	23
K-FER	3.5	2



- Need a good correlation between $\Delta H°$ and $\Delta S°$ to determine $\Delta H°_{opt}$
- For Cu^I-MFU-4*l* doubling the magnitude of $\Delta H°$ leads to a smaller $\Delta S°$!

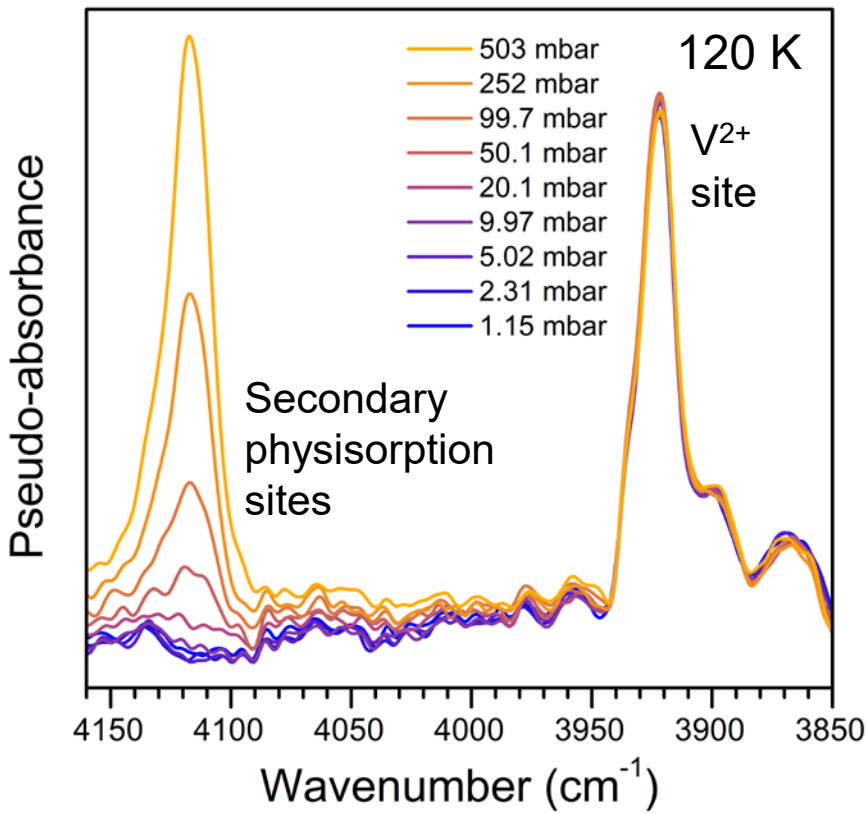
$\Delta H°$ and $\Delta S°$ Must be Determined under Relevant Conditions





- Temperature dependence of heat capacity could be responsible
- We need a system capable of measuring $\Delta H°$ and $\Delta S°$ under the intended operating conditions (ambient temperatures, 5-100 bar)

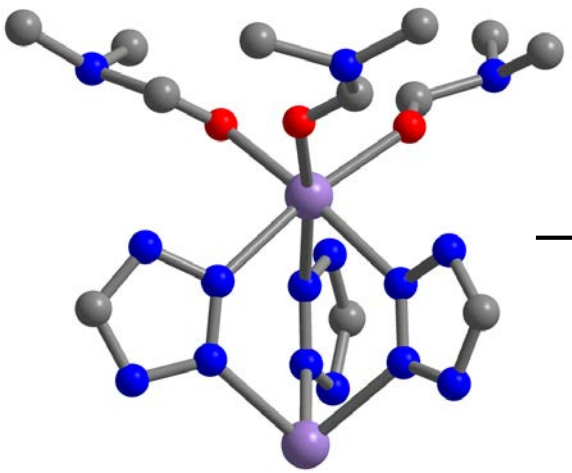
IR Spectrum of V^{II}-MOF Dosed with H_2



	ν(H–H) (cm^{-1})
free H_2	4161
Ni_2(*m*-dobdc)	4025
V^{II}-MOF	**3919**
Cu^{I}-MFU-4*l*	3252

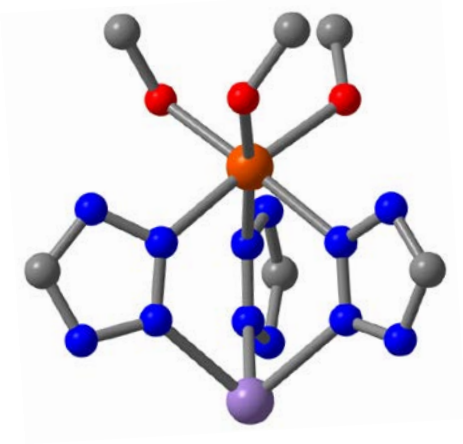
- Open V^{2+} sites capable back donation into the σ^* orbital of H_2
- These sites saturate at extremely low equilibrium pressure at 120 K

Post-Synthetic Metal Exchange in CPF-5



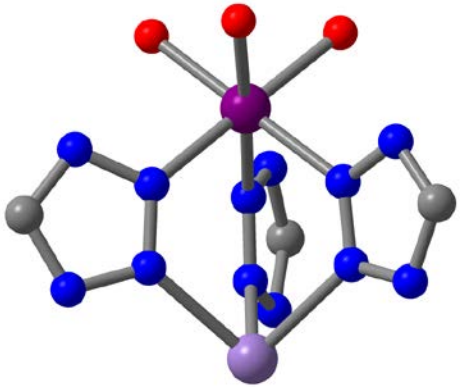
Mn–N = 2.266(4) Å

$FeCl_2$ / CH_3OH



Fe–N = 2.159(8) Å

$CoCl_2 \cdot 6H_2O$ / CH_3OH



Co–N = 2.124(4) Å

- ICP-OES suggests complete and selective Fe/Co incorporation into these sites
- Corroborated by multi-wavelength anomalous dispersion (MAD) crystallography