HyMARC Core Activity: Sorbent

HyMARC
Hydrogen Materials Advanced Research Consortium

Enabling twice the energy density for onboard H_2 storage

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Tom Gennett, National Renewable Energy Laboratory

COVID-19 Pandemic halted all work in February 2020. Milestones to be evaluated after re-opening.

NREL NATIONAL RENEWABLE ENERGY LABORATORY · Sandia National Laboratories · Lawrence Livermore National Laboratory · BERKELEY LAB · ALS ADVANCED LIGHT SOURCE · MOLECULAR FOUNDRY · Pacific Northwest NATIONAL LABORATORY · NIST · SLAC NATIONAL ACCELERATOR LABORATORY

Project ID #: ST202

Overview

HyMARC
Hydrogen Materials Advanced Research Consortium

Timeline*

Phase 1: 10/1/2015 to 9/30/2018
Phase 2: 10/1/2018 to 9/30/2022
Project continuation determined annually by DOE.
(*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,
E. Refueling Time
Reversible Solid-State Material:
M. Hydrogen Capacity and Reversibility
N. Understanding of Hydrogen Physi- and Chemisorption
O. Test Protocols and Evaluation Facilities

Budget

DOE Budget (Entire HyMARC Team)
Total FY19: $4.3M
Total FY20 (Planned): $6.25M

SNL: $1.15M
NREL: $1.5M (covers NIST and SLAC)
PNNL: $1.1M
LLNL: $0.9M
LBNL (Long): $1.1M
LBNL (Prendergast) $0.5M

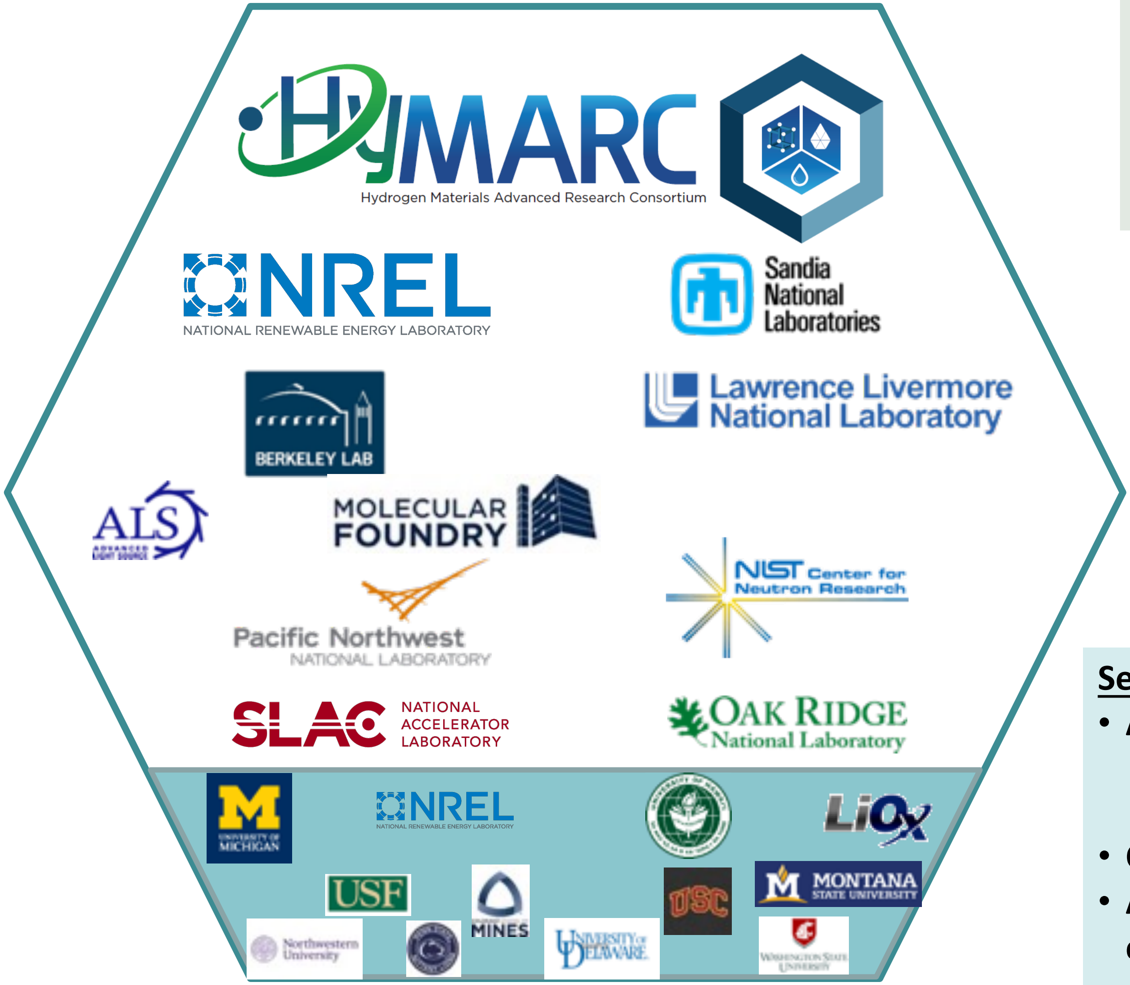
Partners/Collaborators

NIST – Craig Brown, SLAC – Michael Toney
HyMARC – SNL, LLNL, LBNL, PNNL team members
H_2ST^2, USA – Hydrogen Storage Tech Team
Colorado School of Mines - Colin Wolden, Brian Trewyn,
Univ. Hawaii – Craig Jensen, Godwin Severa
Université de Genève – Hans-Rudolf Hagemann, Angelina Gigante

HyMARC Energy Materials Network: enhanced, highly coordinated capabilities to accelerate materials discovery

Enabling twice the energy density for hydrogen storage

- **Foundational R&D**
- **Computational models**
- **Synthetic protocols**
- **Advanced characterization tools**
- **Validation of material performance**
- **Guidance to FOA projects**
- **Database development**



Seedling Projects

- **Applied material development**
  - Novel material concepts
  - High-risk, high-reward
- **Concept feasibility demonstration**
- **Advanced development of viable concepts**

Approach and Relevance (Adsorbents)

Approach

- **1.A** Enthalpy/entropy under practical conditions (with NREL, PNNL)
- **1.B Optimization of sorbent binding energies**
  - **1.B.1** Electronic structure computations (LBNL, LLNL)
  - **1.B.2** Strong-binding sites (LBNL, NREL, NIST)
- **1.C** Sorbent packing: MOF monolith synthesis (LBNL, SNL, NREL)
- **1.D** Dynamic sorbent materials (LBNL, NREL)
- **1.E** Multiple H_2 binding (LBNL, NIST)

Relevance

Research and development of metal–organic frameworks with high volumetric and gravimetric H_2 storage capacities (Barrier A – C, E).

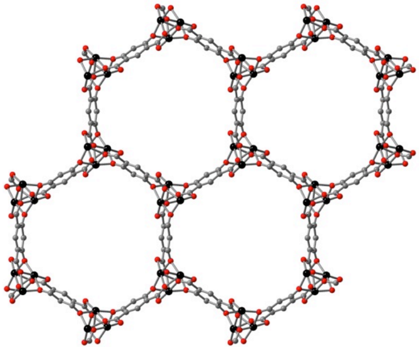
- Adsorption enthalpy in the optimal range of −15 to −25 kJ/mol
- Open metal sites that adsorb more than two H_2 molecules

*Focus Areas discussed in this presentation are in black

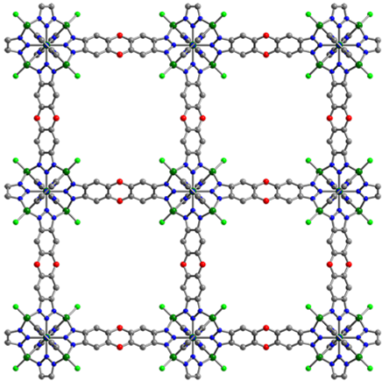
Approach 1.B.2: Sorbents with Optimal Binding Energies

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

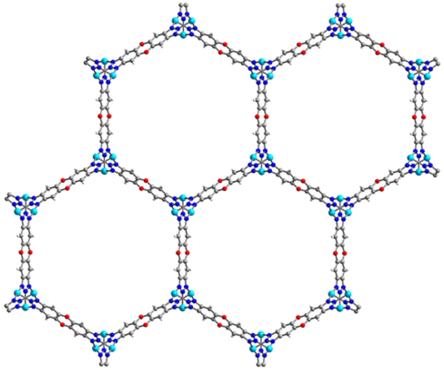
- Values are based upon assumptions about the correlation between adsorption enthalpy and entropy. However, these assumptions are not always valid.



Ni_2(*m*-dobdc)



Cu-MFU-4*l*



$V_2Cl_{2.8}$(btdd)

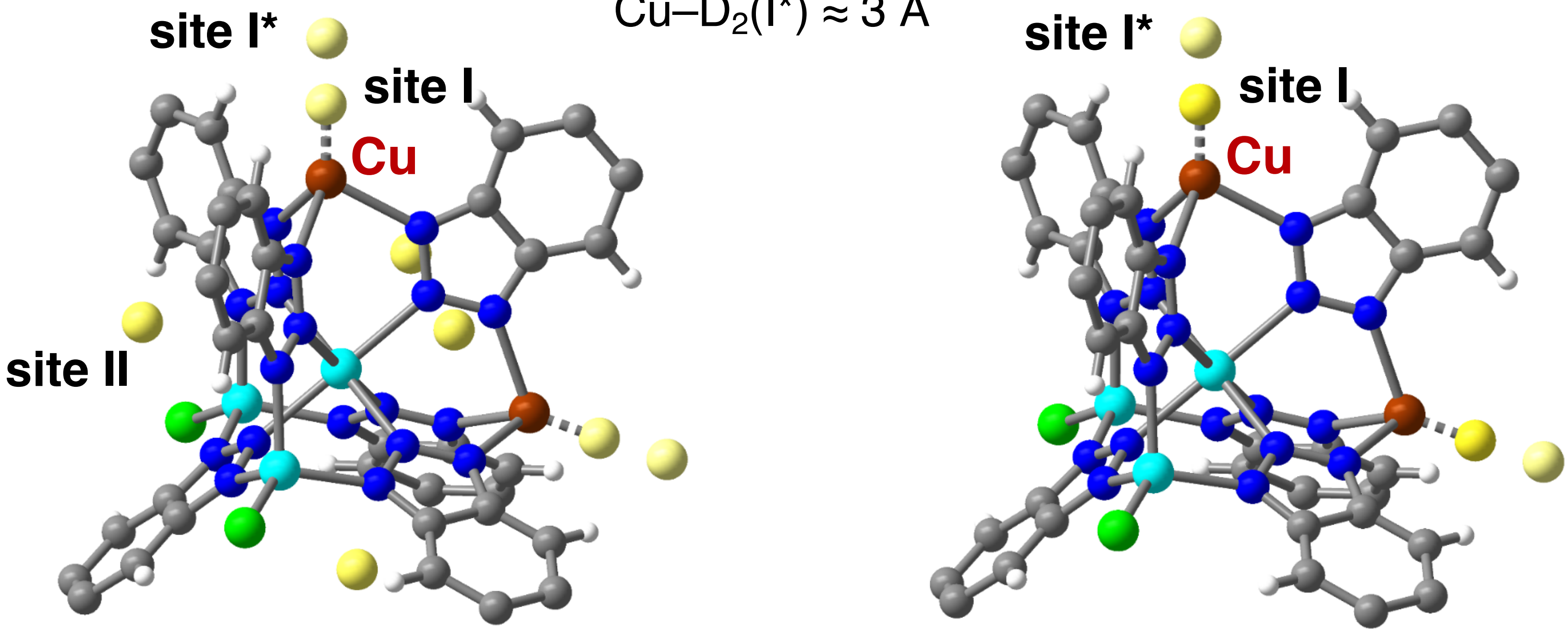
The Lewis-acidic open metal sites are capable of polarizing and accepting electron density from H_2; however, Δ*H* is lower than 15 kJ/mol.

π-Backdonation plays a primary role in strong H_2 binding: therefore, π-basic metals (Cu^I and V^{II}) will be incorporated into frameworks.

Accomplishment 1.B.2: *In situ* Powder Neutron Diffraction of Cu-MFU-4*l*

$Cu–D_2(I) \approx 1.6$ Å

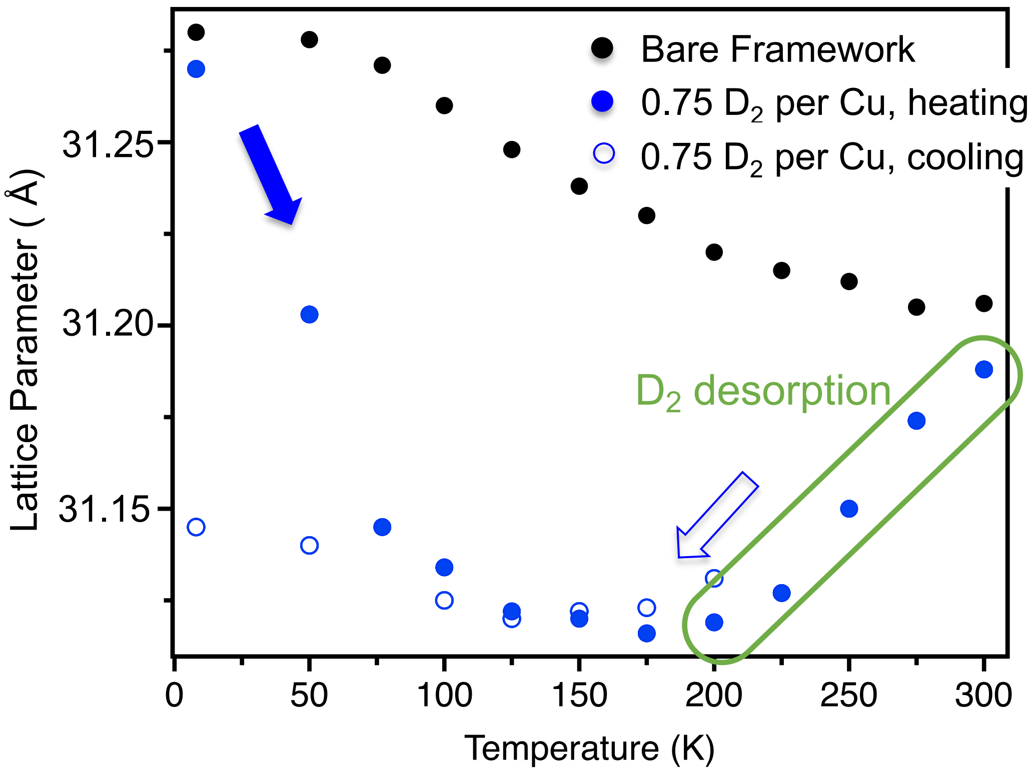
$Cu–D_2(I^*) \approx 3$ Å



- Sample dosed with 0.75 D_2/Cu at 40 K and then cooled to 7 K
- Occupation of two distinct D_2 sites near Cu^+ is apparent
- Occupancy of site I increases upon dosing at successively higher *T*

Barnett, Evans, Su, Jiang, Chakraborty, Banyeretse, Martinez, Trump, Tarver, Dods, Drisdell, Hurst, Gennett, FitzGerald, Brown, Head-Gordon, Long, *Submitted.*

Activated D_2 Binding in Cu^I-MFU-4*l*

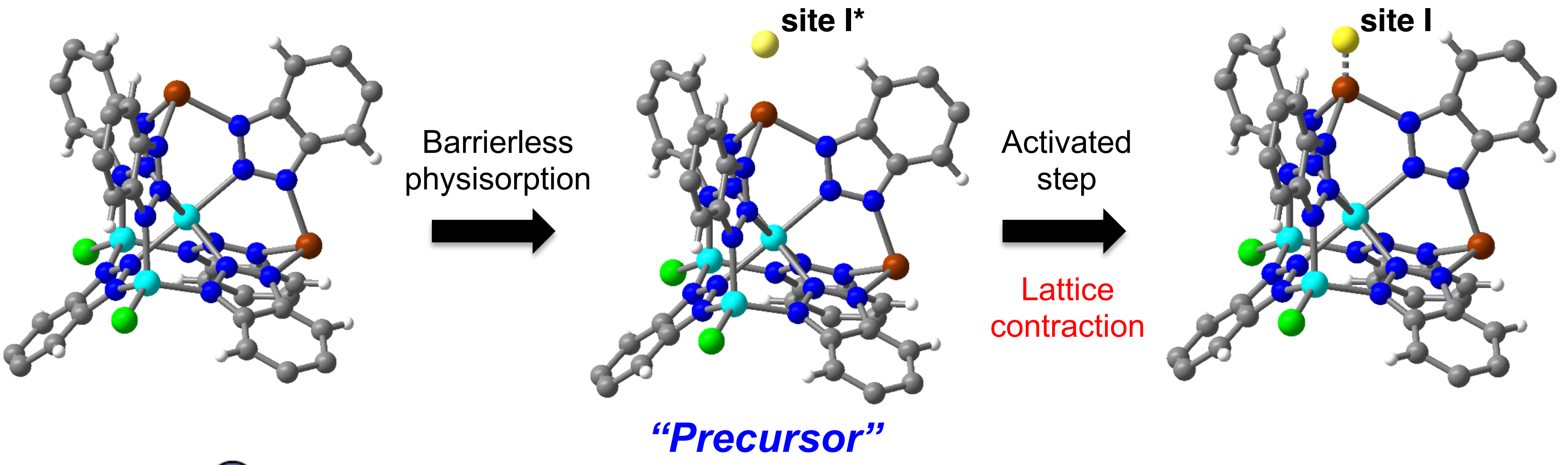


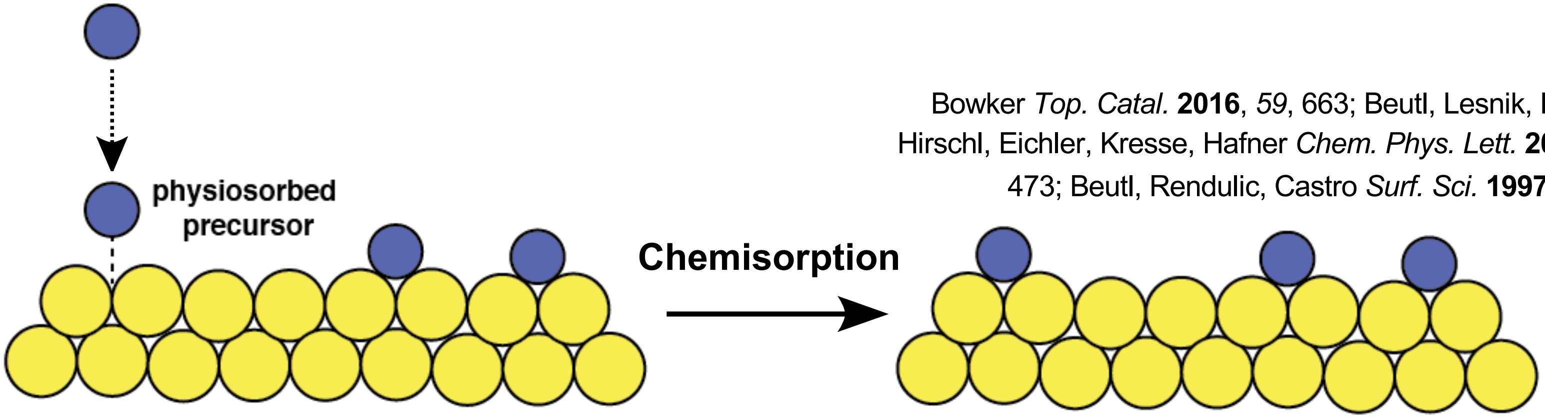
Dosing temp.	Site I occ. (D_2 per Cu)	*a* (Å)
none (bare MOF)	–	31.2744(14)
40 K	0.10(2)	31.2174(10)
77 K	0.48(2)	31.1652(10)
300 K	0.602(14)	31.1505(6)

- Significant lattice contraction with strong D_2 binding
- Spontaneous desorption begins around 200 K
- Hysteresis observed on cooling below 100 K

Barnett, Evans, Su, Jiang, Chakraborty, Banyeretse, Martinez, Trump, Tarver, Dods, Drisdell, Hurst, Gennett, FitzGerald, Brown, Head-Gordon, Long, *Submitted.*

Elucidating the Mechanism of H_2 Chemisorption

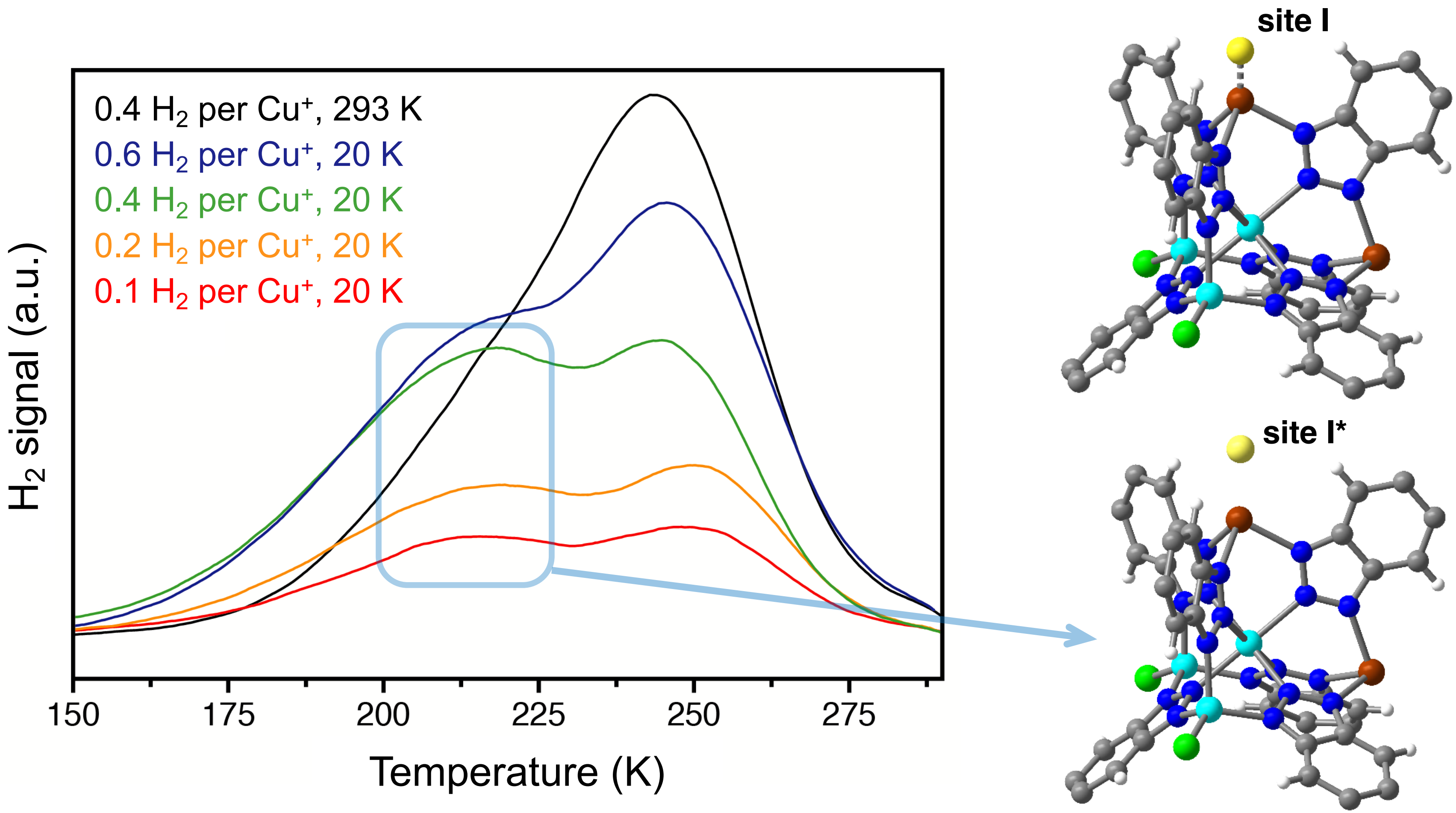




Bowker *Top. Catal.* **2016**, *59*, 663; Beutl, Lesnik, Rendulic, Hirschl, Eichler, Kresse, Hafner *Chem. Phys. Lett.* **2001**, *342*, 473; Beutl, Rendulic, Castro *Surf. Sci.* **1997**, *385*, 97

- Precursor state corresponds to local energy minimum en route to chemisorption
- Such states have been observed for dissociative and non-dissociative adsorption of various substrates (*e.g.*, H_2, N_2, O_2, CO)

Direct Observation of Precursor Using TPD

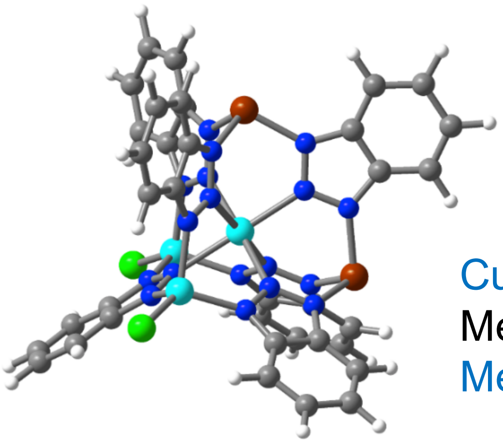


- New desorption peak around 200 K can be assigned to precursor state

Barnett, Evans, Su, Jiang, Chakraborty, Banyeretse, Martinez, Trump, Tarver, Dods, Drisdell, Hurst, Gennett, FitzGerald, Brown, Head-Gordon, Long, *Submitted.*

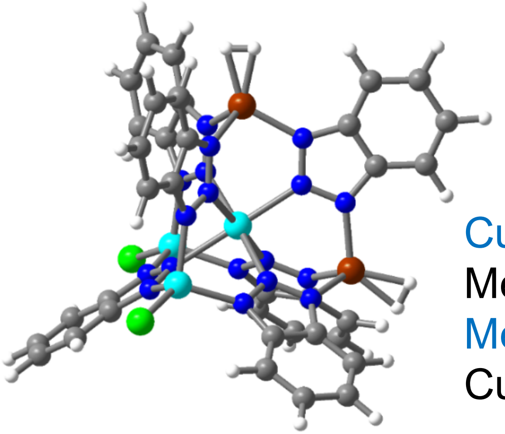
DFT Optimizations of Cu^{I}-MFU-4*l* Cluster Models

Question: Why is there an activation barrier to adsorption at an open metal site?



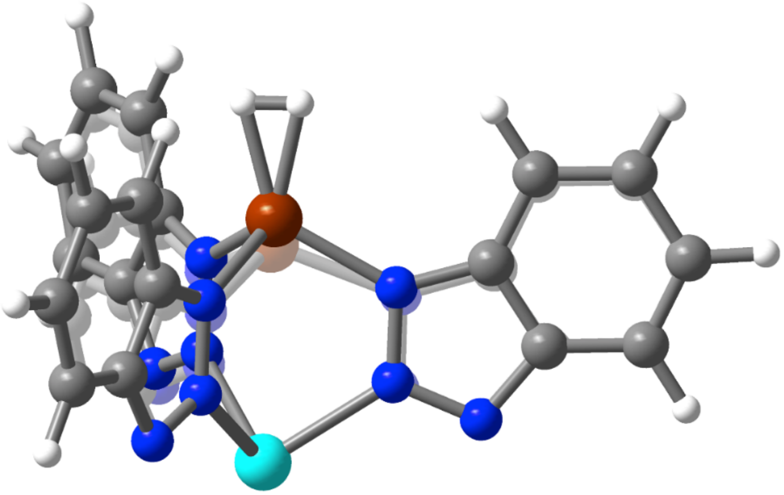
Bare cluster

Cu–Zn(O_h) = 3.27 Å
Mean Cu–N = 1.96 Å
Mean N–Cu–N = 108.6°



Cu–Zn(O_h) = 3.49 Å
Mean Cu–N = 2.00 Å
Mean N–Cu–N = 101.2°
Cu–H_2 = 1.70 Å

Cluster with adsorbed H_2



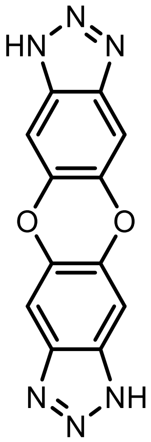
Significant Structural Distortions upon H_2 Adsorption

- Cu moves away from center of cluster upon binding H_2
- Bonds between N and central Zn shorten by a mean value of 0.03 Å

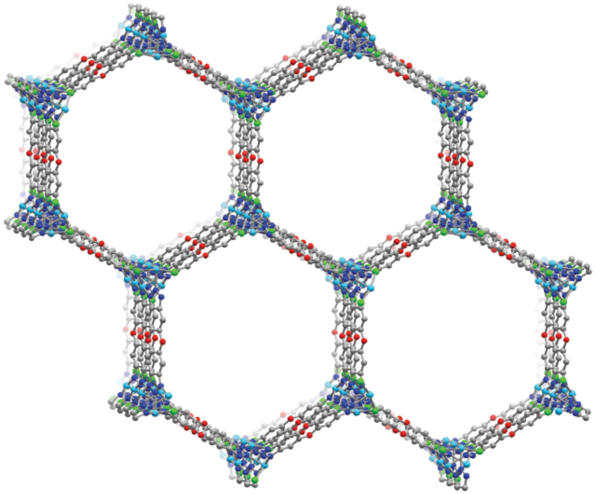
Previous Results: $V_2Cl_{2.8}$(btdd) Contains Open V^{2+} sites

Hypothesis: Increasing orbital interactions with H_2 will allow us to access this range

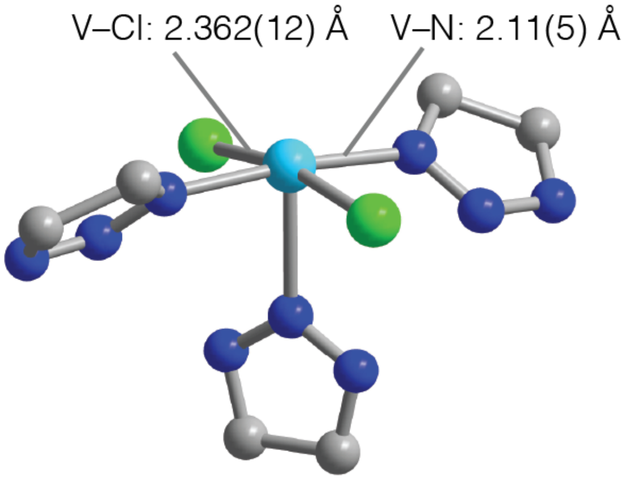
- Square pyramidal V^{2+} sites exhibit appropriate electronic structure



H_2btdd



$V_2Cl_{2.8}$(btdd)



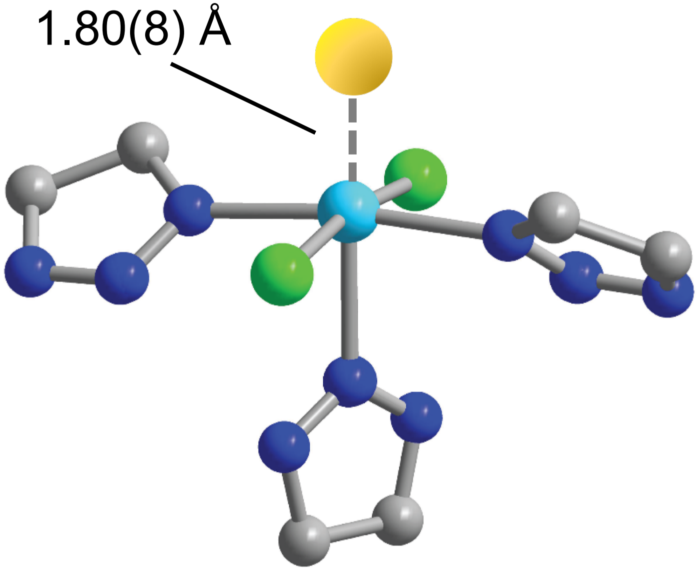
5-coordinate V^{II} site

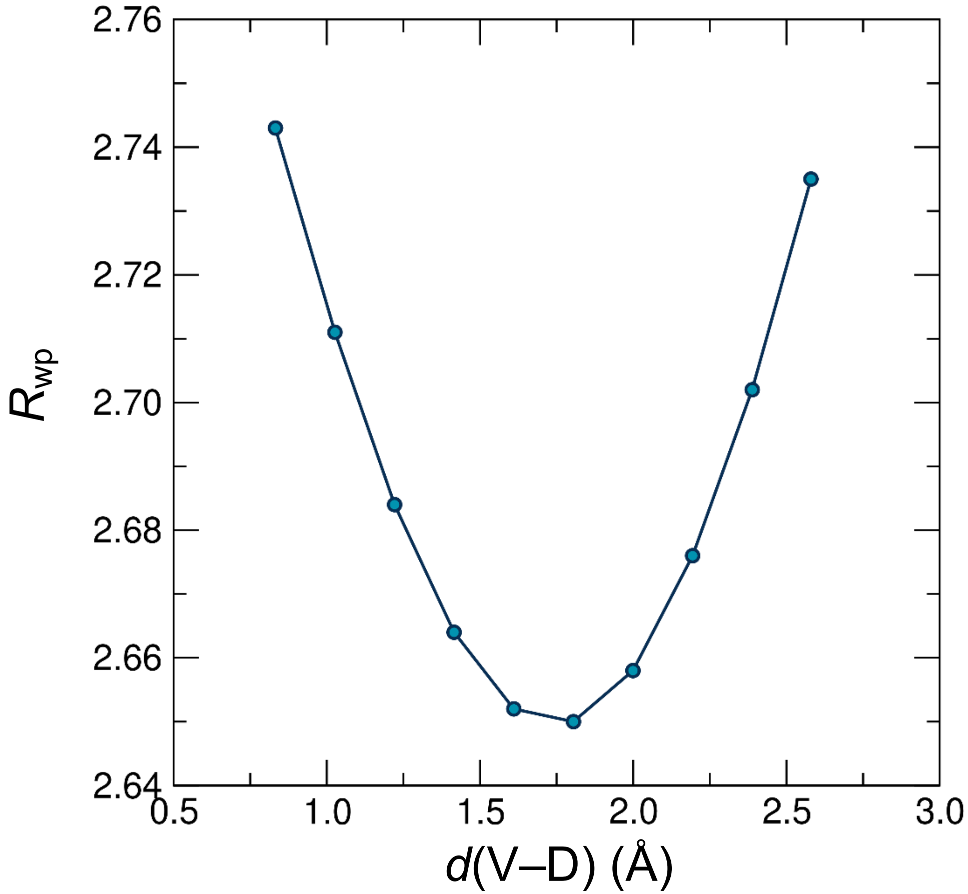
- Triazolate linker stable to the highly reducing V^{2+} (unlike carboxylate linkers)
- $SA_{Langmuir}$ = 3290 m^2/g, SA_{BET} = 1930 m^2/g

Jaramillo, Reed, Jiang, Oktawiec, Mara, Forse, Lussier, Murphy, Cunningham, Colombo, Shuh, Reimer, Long. *Nat. Mater.* **2020**, DOI: 10.1038/s41563-019-0597-8

Accomplishment: Neutron Diffraction Characterization of V–D_2

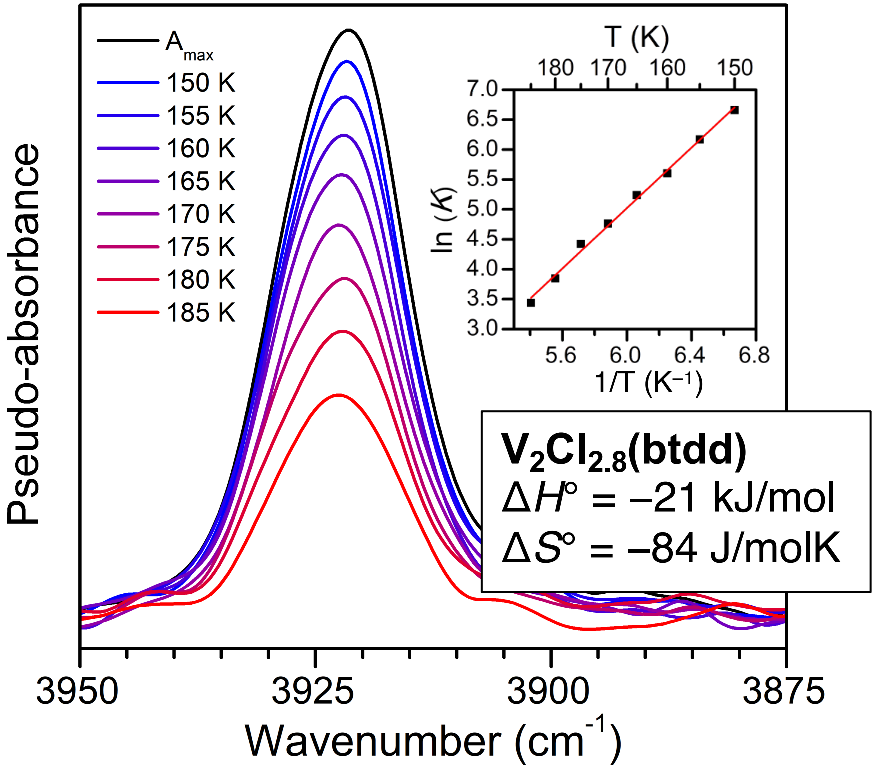
$V_2Cl_{2.8}$(btdd) + 0.75 equiv. D_2

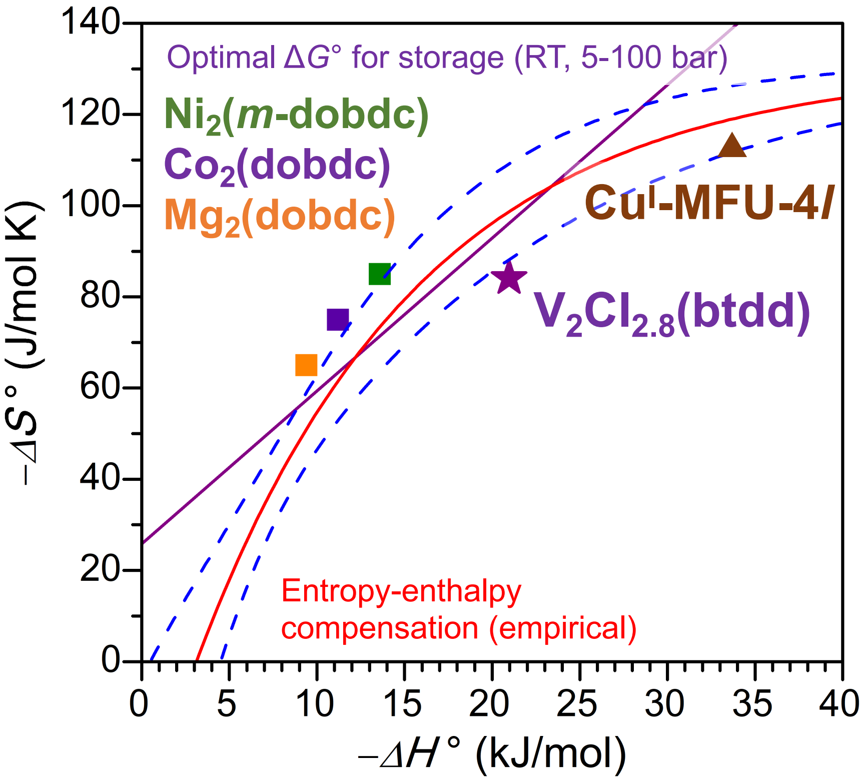




- V–D_2 can be resolved despite disorder with V^{III}–Cl sites
- d(Cu–D_2) = 1.60(3) Å in Cu^I–MFU-4*l*; d(Ni–D_2) = 2.18(4) Å

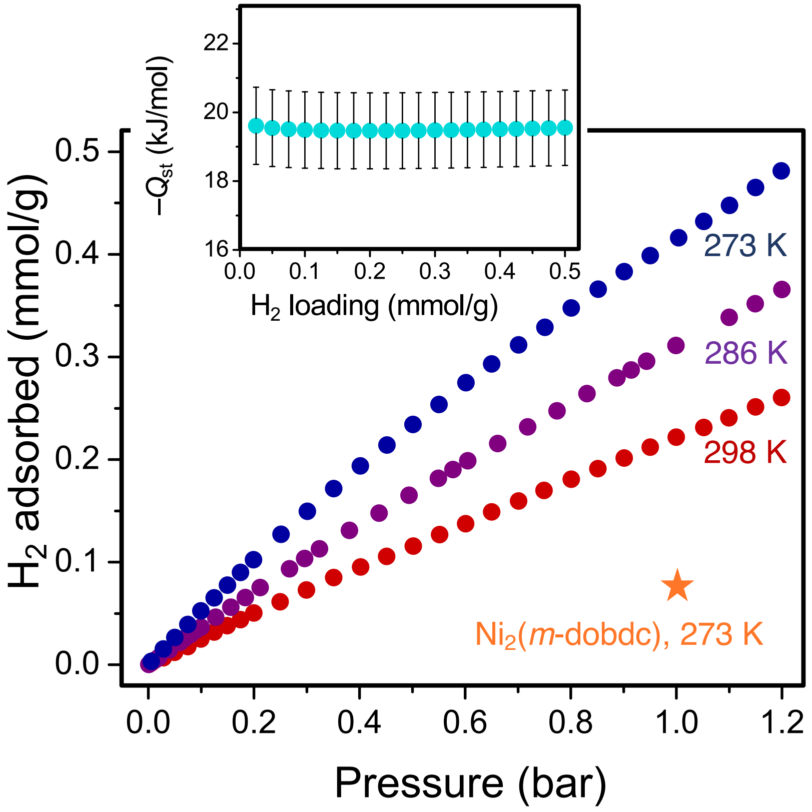
Variable-Temperature IR Spectra of H_2

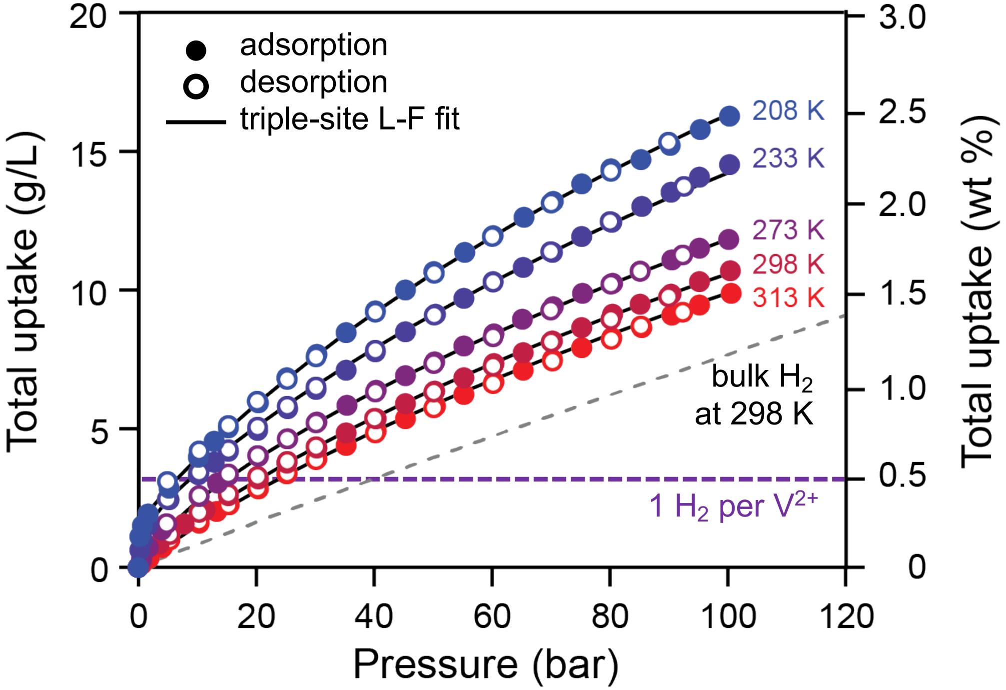




- First example of a MOF with ΔH in the optimal range between –15 and –25 kJ/mol
- Enthalpy-entropy relation distinct from M_2(dobdc) family

Low- and High-Pressure Ambient H_2 Isotherms





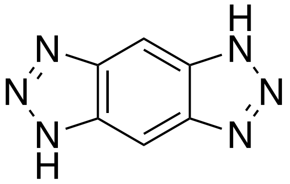
- Gravimetric total uptake for $V_2Cl_{2.8}$(btdd) surpasses Ni_2(*m*-dobdc) at 298 K and 100 bar (1.64 *vs.* 0.98 wt %)
- Initial steep uptake can be observed below 233 K where V^{2+} sites do not contribute to usable capacity

Future Plans (Task 1.B)

MOF	**Δ*H* from DRIFTS**[a] (kJ/mol)	**Q_{st} from isotherms** (kJ/mol)	**Total H_2 uptake at 298 K, 100 bar** (g/L)	**Usable capacity at 298 K, 5–100 bar** (g/L)
Comp. H_2	—	—	7.7	7.3
Ni_2(*m*-dobdc)	−13.7	−12.3	11.9[b]	11.0[b]
Cu^I-MFU-4*l*	−33.6	−32.7	11.0[b]	9.3[b]
$V_2Cl_{2.8}$(btdd)	−21.0	−19.5	10.7[b]	9.6[b]
HKUST-1[c]	n.d.	−6.9	9.8	9.0

[a]Diffuse reflectance infrared Fourier transform spectroscopy, [b]Applied single crystal density,
[c]HKUST-1 monolith prepared in Task 1.C.1

- Gain a complete understanding of H_2 adsorption in these V^{II} and Cu^I systems
- Post-synthetically reduce $V_2Cl_{2.8}$(btdd) to access an all vanadium(II) framework (vanadium density of 4.4 mmol/g)
- Synthesis of V_2Cl_2(bbta): greater gravimetric capacity (6 mmol/g) with likely binding enthalpy ~20 kJ/mol



H_2bbta

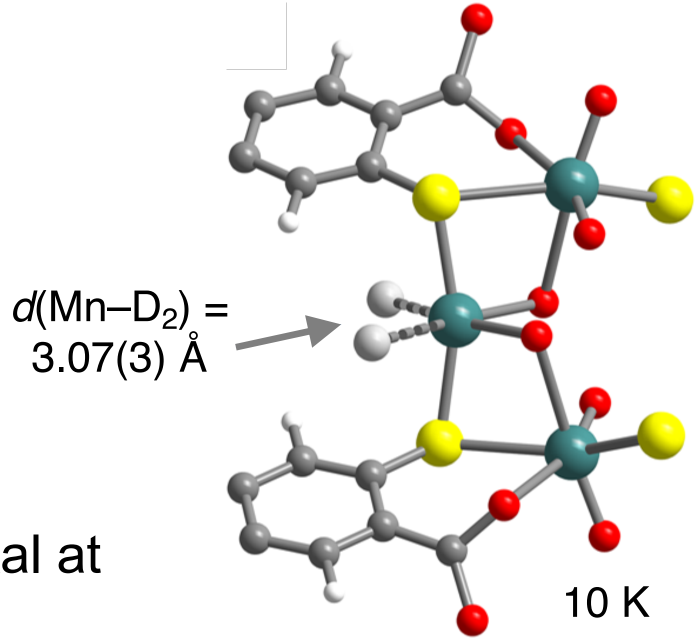
Any proposed future work is subject to change based on funding levels

Approach 1.E: Binding of Multiple H_2 per Metal Cation

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" in MOF chemistry
- Highly complex synthetic challenge

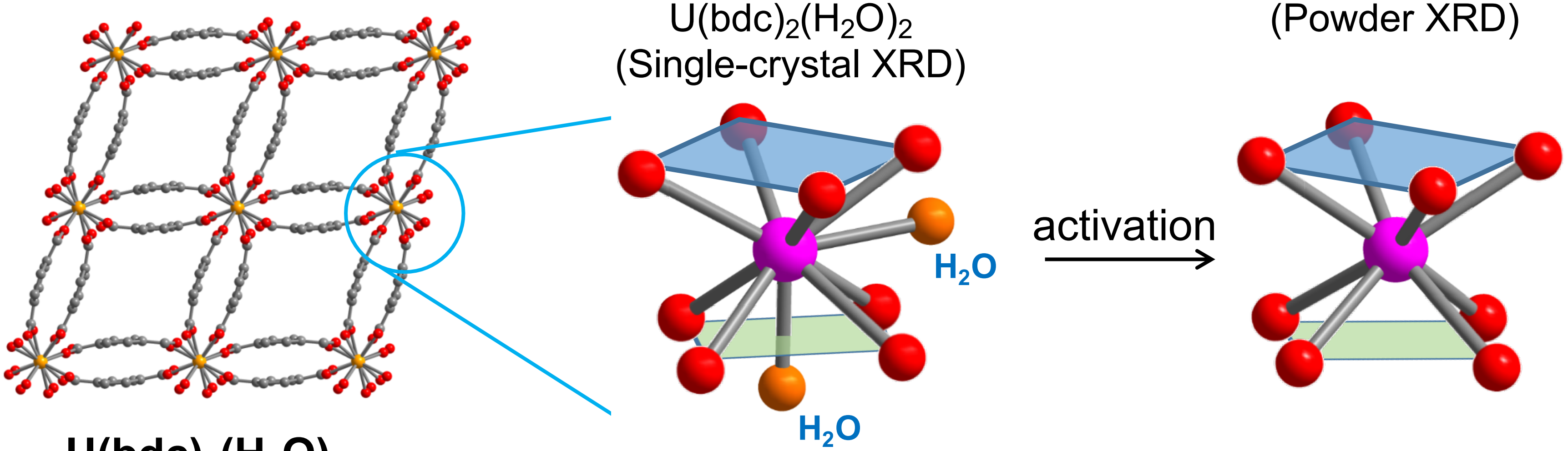
Mn_2(dsbdc) adsorbs two H_2 at a Mn^{2+} site: Runčevski, Kapelewski, Torres-Gavosto, Tarver, Brown, Long *Chem. Commun.* **2016**, *52*, 8351.



Questions:

- Can we access multiple open sites per metal at secondary building units in MOFs?
- Can MOFs with the f-elements (coordination numbers up to 15) bind multiple H_2 per metal?

Accomplishment 1.E: A New 3-Dimesional Uranium MOF—$U(bdc)_2(H_2O)_2$



$U(bdc)_2(H_2O)_2$

As-synthesized
$U(bdc)_2(H_2O)_2$
(Single-crystal XRD)

Bi-capped square antiprism

activation →

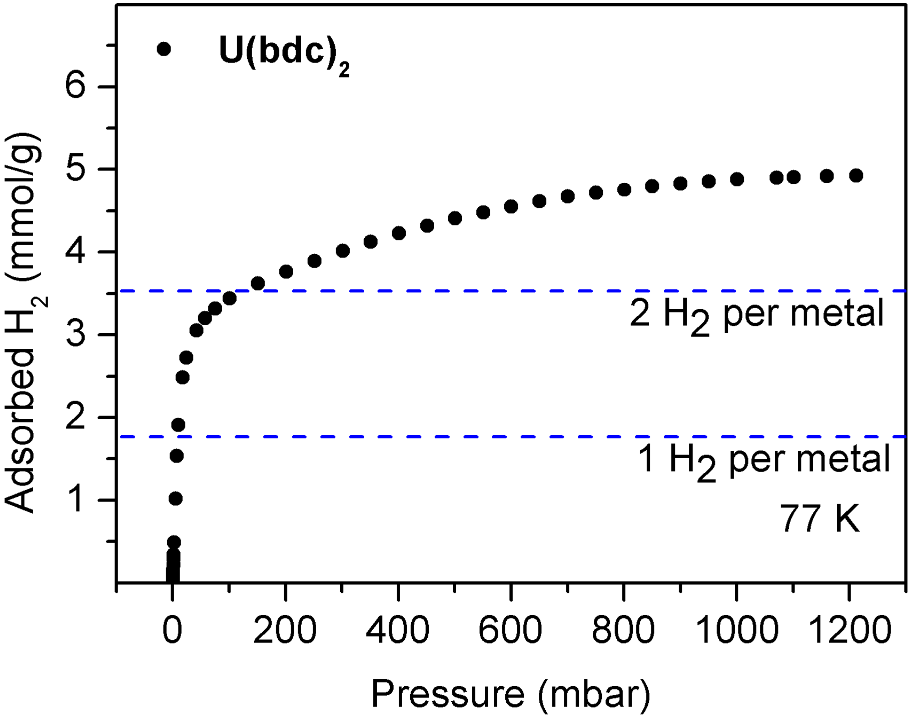
Activated $U(bdc)_2$
(Powder XRD)

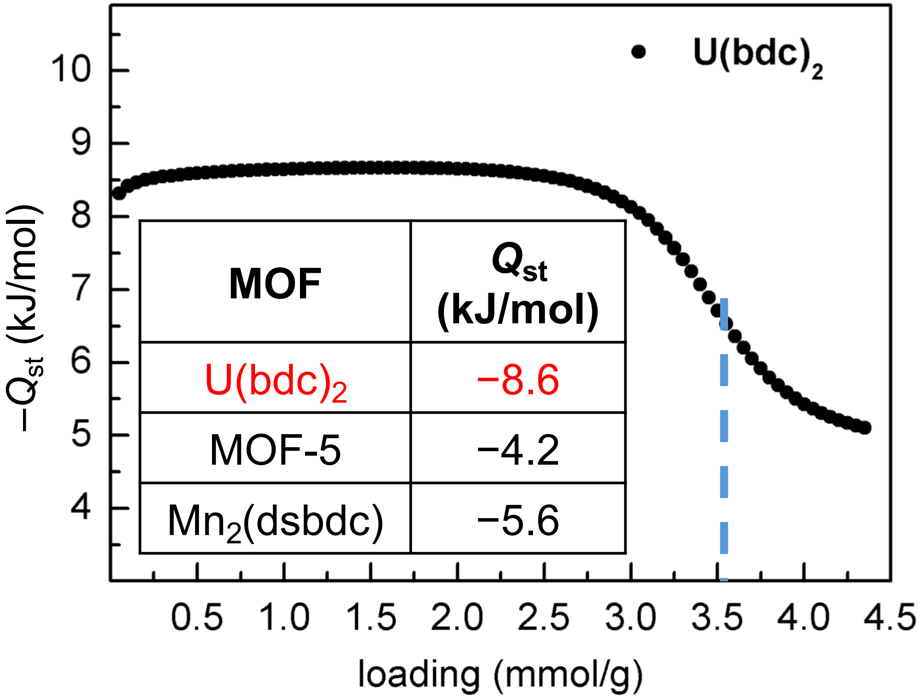
Square antiprism

- Langmuir surface area = 570 m²/g
- Each uranium is coordinated by two H_2O (TGA shows desolvation step at 130 °C)
- Can we access two open metal sites for H_2 binding in activated $U(bdc)_2$?

Halter, D. P.; Klein, R. A.; Boreen, M. A.; Trump, B. A.; Brown, C. M.; Long, J. R. *Angew. Chem. Int. Ed.*, submitted.

Low-Pressure H_2 Adsorption in $U(bdc)_2$



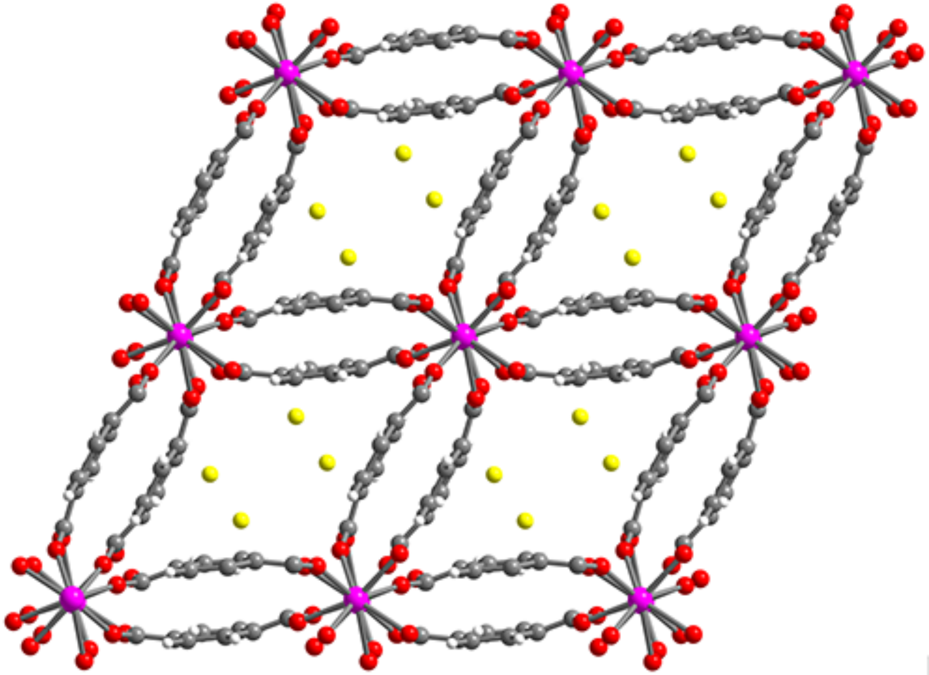


MOF	**Q_{st} (kJ/mol)**
$U(bdc)_2$	−8.6
MOF-5	−4.2
$Mn_2(dsbdc)$	−5.6

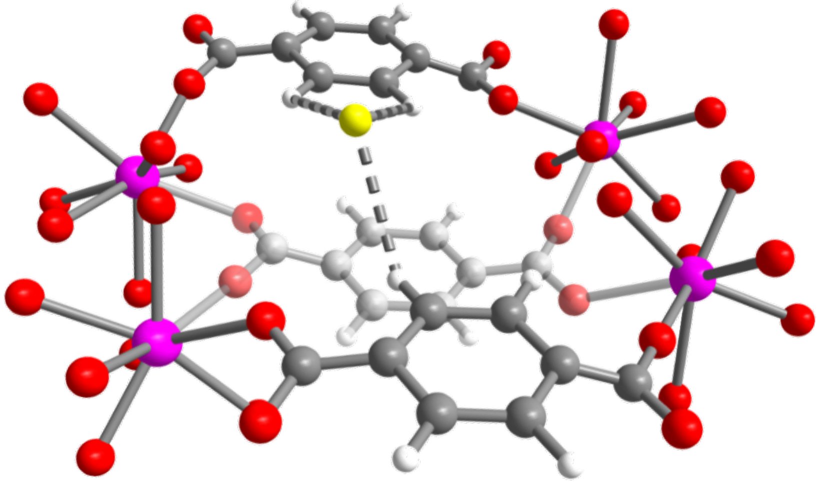
- Strong H_2 binding to theoretical capacity of 2 H_2 per metal
- Inflection point matches theoretical capacity of 2 H_2 per metal

Halter, D. P.; Klein, R. A.; Boreen, M. A.; Trump, B. A.; Brown, C. M.; Long, J. R. *Angew. Chem. Int. Ed.*, submitted.

In situ Neutron Diffraction Studies of $U(bdc)_2$ with D_2



4 D_2 per pore = 2 D_2 per U



Binding pocket: 3 C–H bonds

- Loading from neutron diffraction data is consistent with that observed in H_2 isotherms
- Unexpectedly there are no D_2–U interactions

Halter, D. P.; Klein, R. A.; Boreen, M. A.; Trump, B. A.; Brown, C. M.; Long, J. R. *Angew. Chem. Int. Ed.*, submitted.

Accomplishments in FY20 (Adsorbents)

- **Mechanism of H_2 chemisorption in Cu^I-MFU-4*l*:** Used powder neutron diffraction and temperature-programmed desorption to characterize a metastable, adsorbed precursor intermediate in Cu^I-MFU-4*l*
- ***In situ* powder neutron diffraction:** Resolved V–D_2 bond distance in $V_2Cl_{2.8}$(btdd) despite disorder with V^{III}–Cl sites. Bond distance is compatible with strong binding
- **Multiple H_2 per metal:** Synthesized MOFs with multiple open sites per metal by harnessing larger ionic radii and high coordination numbers of the *f*-elements

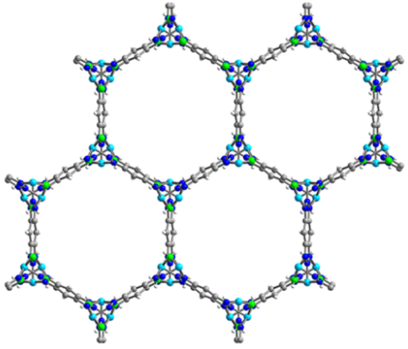
- Obtained valuable insight into the mechanistic pathway of activated H_2 chemisorption in Cu^I-MFU-4*l* from DFT simulations of the Cu^I nodes
- Measured high-pressure H_2 adsorption isotherms for $V_2Cl_{2.8}$(btdd), which corroborated binding enthalpy within an optimal operation range
- Demonstrated N_2-induced flexibility at 77 K in two new Zn(bdp) derivatives
- Confirmed photochemical release of CO from Mn carbonyl complexes ligated by bipyridine (bpy) in the zirconium framework UiO-67-bpy
- Verified the synthesis of HKUST-1 monolith, which exhibits volumetric H_2 uptake 50% greater than the powder form

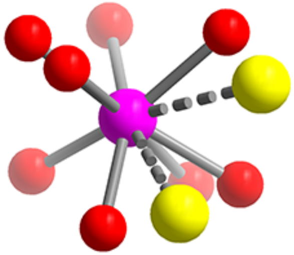
Summary (FY20 Internal Adsorbents Milestones)

Task	Milestone	Due	Status
1.B.1	**Electronic structure computations:** Develop a computational protocol to asses thermochemical effects (enthalpy and entropy) in hydrogen adsorption.	9/2020	30%
1.B.2	**Optimal binding energies:** Synthesize a derivative of Cu^I-MFU-4*l* or V_2Cl_2(btdd) with a modified ligand and measure H_2 heat of adsorption.	9/2020	30%
1.C.1	**MOF monoliths:** Synthesize at least 2 monolith MOFs that outperform the volumetric storage capacity of monolith HKUST-1 at temperatures above 150 K and < 100 bar.	9/2020	30%
1.D.1	**Flexible MOFs:** Synthesize at least 2 different M(bdp) (M other than Co) frameworks and locate step pressures at 77 K.	9/2020	50%
1.E	**Multiple H_2s per metal:** Demonstrate either (a) binding of three H_2 to a single metal center, or (b) binding of multiple H_2 to a single metal center, with a maximum heat of adsorption of at least 8 kJ/mol.	9/2020	25%

Future Directions (Adsorbents)

- Use ^{65}Cu solid-state NMR to investigate whether thermodynamic or kinetic cooperativity between proximal Cu^{I} centers influences H_2 binding in Cu^{I}-MFU-4*l*
- Synthesize V-based MOFs with shorter linkers for greater volumetric H_2 storage capacities and a target binding enthalpy of ~20 kJ/mol
- Explore functionalized M(bdp) variants to tune the step pressure at ambient temperatures
- Explore new MOFs with *f*-elements featuring multiple accessible metal binding sites
- Optimize synthetic conditions of MOF-74-type monoliths to increase volumetric H_2 storage capacities
- Predict usable capacities from anharmonic free energy estimates in MOFs





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

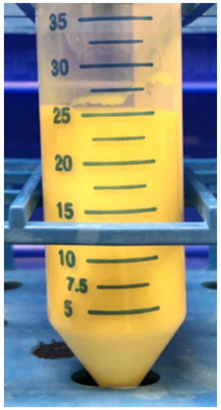
Additional slides

Task 1.C.1. COF Monolith Synthesis

Relevant technical target improve volumetric capacity

Project success – Synthesis of first COF monolith

Colloidal Suspension

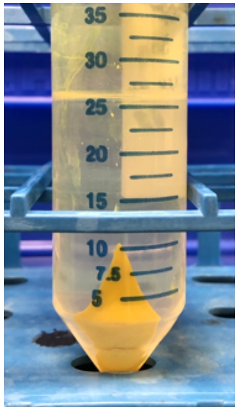


Centrifuge

Purify Colloids

Decant, resuspend

Packed 'Gel'



'Regrowth' (colloids fused)

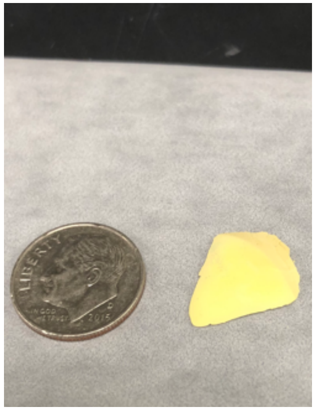
Framework-Monomer Equilibrium Re-established

Wet Monolith

Soxhlet Extraction

Slow drying

Dried Monolith



Colloidal Powder
500 m²/g
~0.1 g/cm³

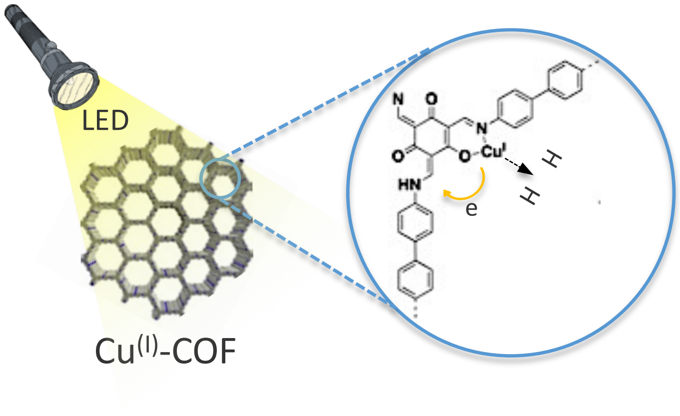
COF Monolith
400 m²/g
~0.5 g/cm³

Task 1.D.2. Thermal/photo-responsive sorbent matrices

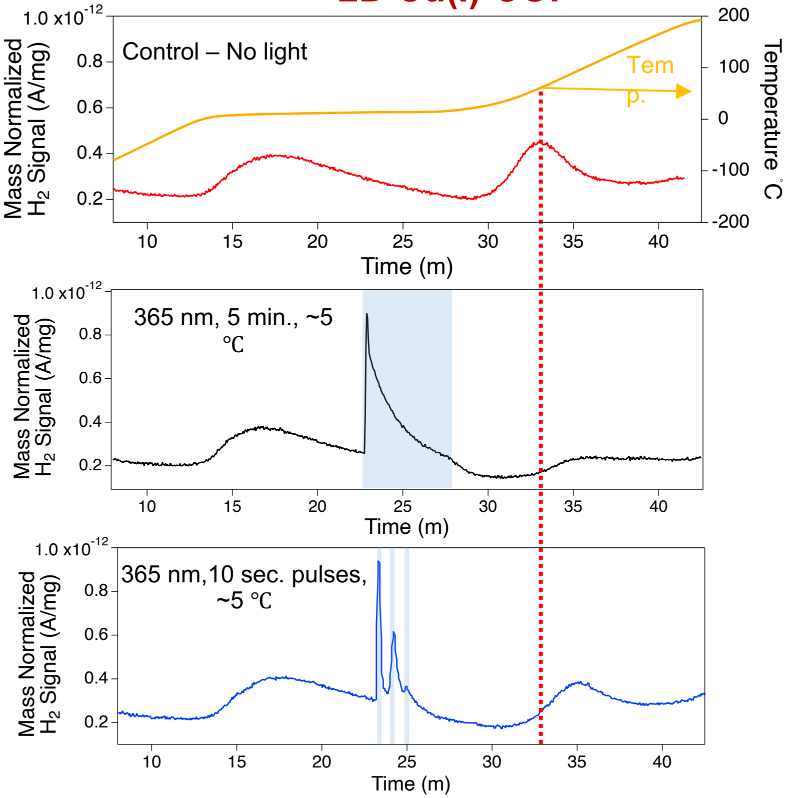
Relevant technical target: ‘Tuning’ isosteric heats of H_2 adsorption

Approach:

- Cu loaded into a framework, heat treatment to generate open $Cu^{(I)}$ binding site, enthalpy of H_2 desorption ~15 k/mol
- Photoinduced metal-ligand charge transfer from $Cu^{(I)}$ to Frameworke generates ‘transient’ $Cu^{(II)}$ with decreased π-backbonding
- H_2 evolves when exposed to light



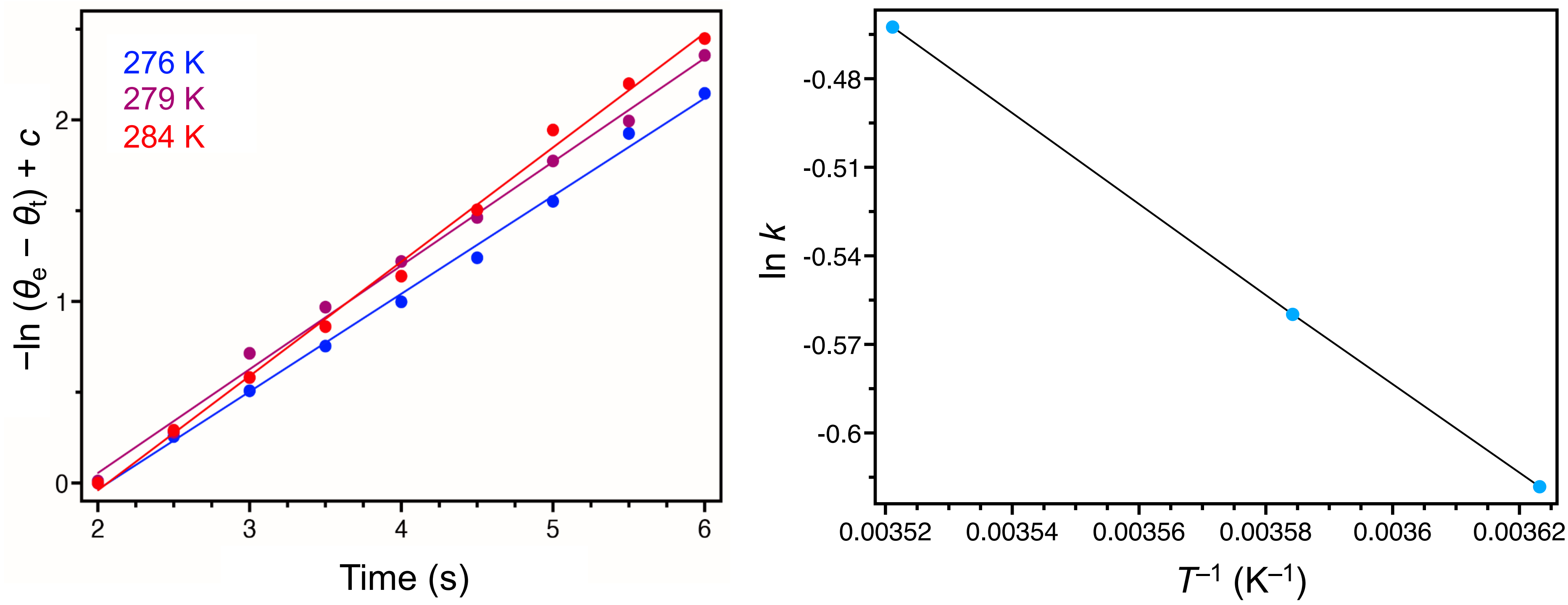
2D Cu(I)-COF



Accomplishment: Successfully demonstrated ‘on demand’ release of H_2 from sorbent

Project success → ‘On demand’ ambient temperature H_2 delivery

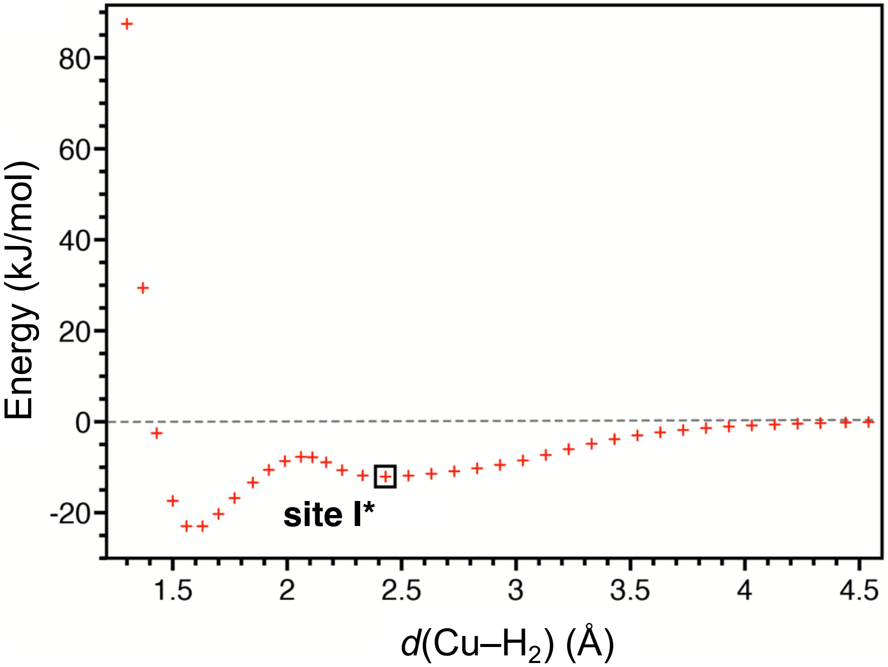
Ambient Temperature Adsorption Kinetics of Cu-MFU-4*l*

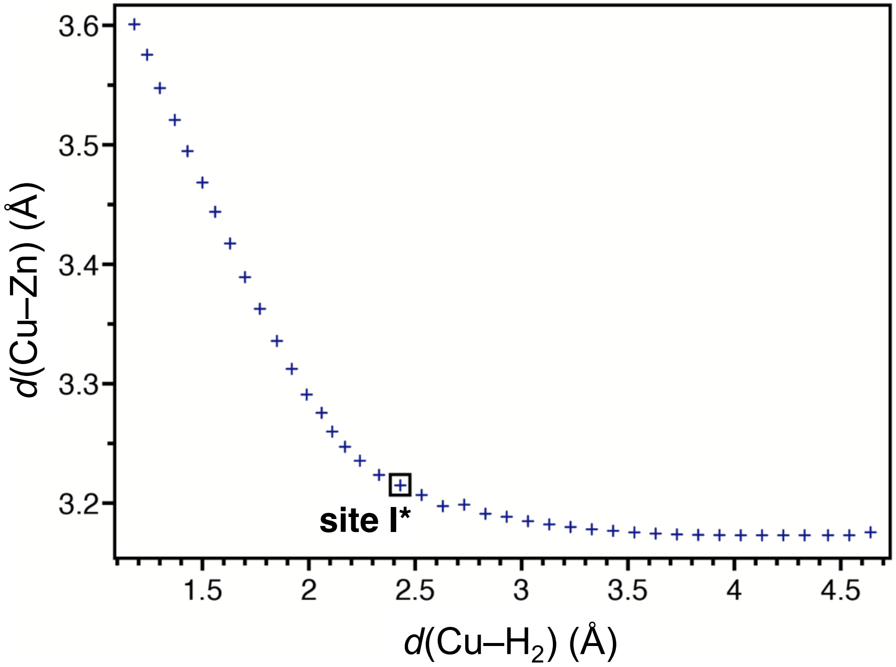


- Transient uptake measurements performed between 276–284 K
- Data were fit to first-order Langmuir-derived rate law
- Arrhenius equation gives an apparent activation barrier E_a = **12.7 kJ/mol**
- Value most reasonably represents lower bound of actual E_a

Liu, Shen, *Langmuir* **2008**, *24*, 11625

Chemisorption Potential Energy Surface of Cu-MFU-4*l*



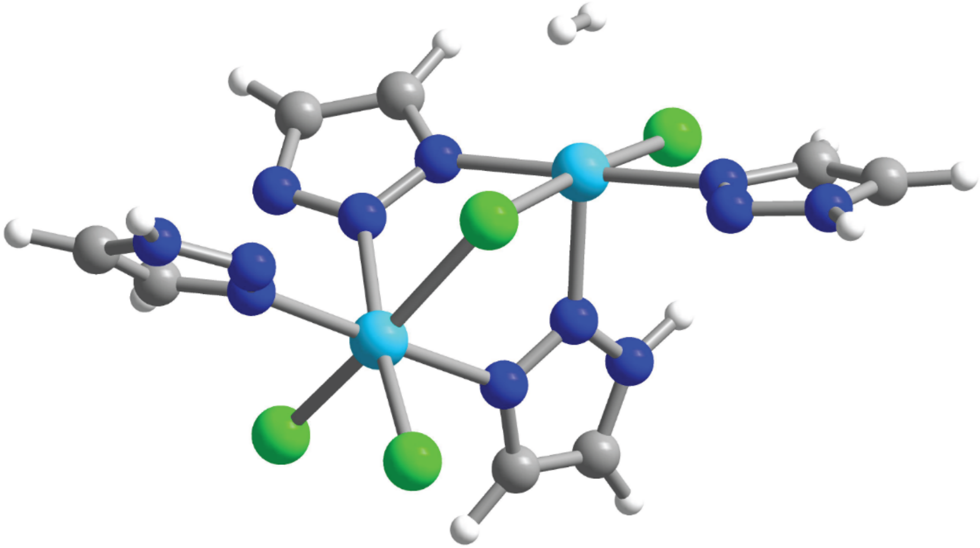


- Calculations are able to reproduce the presence of a local energy minimum
- Results are highly basis set dependent
- Activation barrier in these calculations is 4.4 kJ/mol

Barnett, Evans, Su, Jiang, Chakraborty, Banyeretse, Martinez, Trump, Tarver, Dods, Drisdell, Hurst, Gennett, FitzGerald, Brown, Head-Gordon, Long, *Submitted.*

Calculations Show High Orbital Contribution

H_2 binding to V(II)V(III) model



V–H 2.118 Å $\Delta\nu_{HH}$ (cm^{-1}) = 240 cm^{-1}

Energy decomposition analysis

Component	Energy (kJ/mol)
Frozen	11.4
Polarization	–3.8
Charge transfer	–34.1
Total	–26.9

σ H_2 → V(II)	–22.7
π V(II) → H_2	–5.4

- 70% of total binding contributions come from CT

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