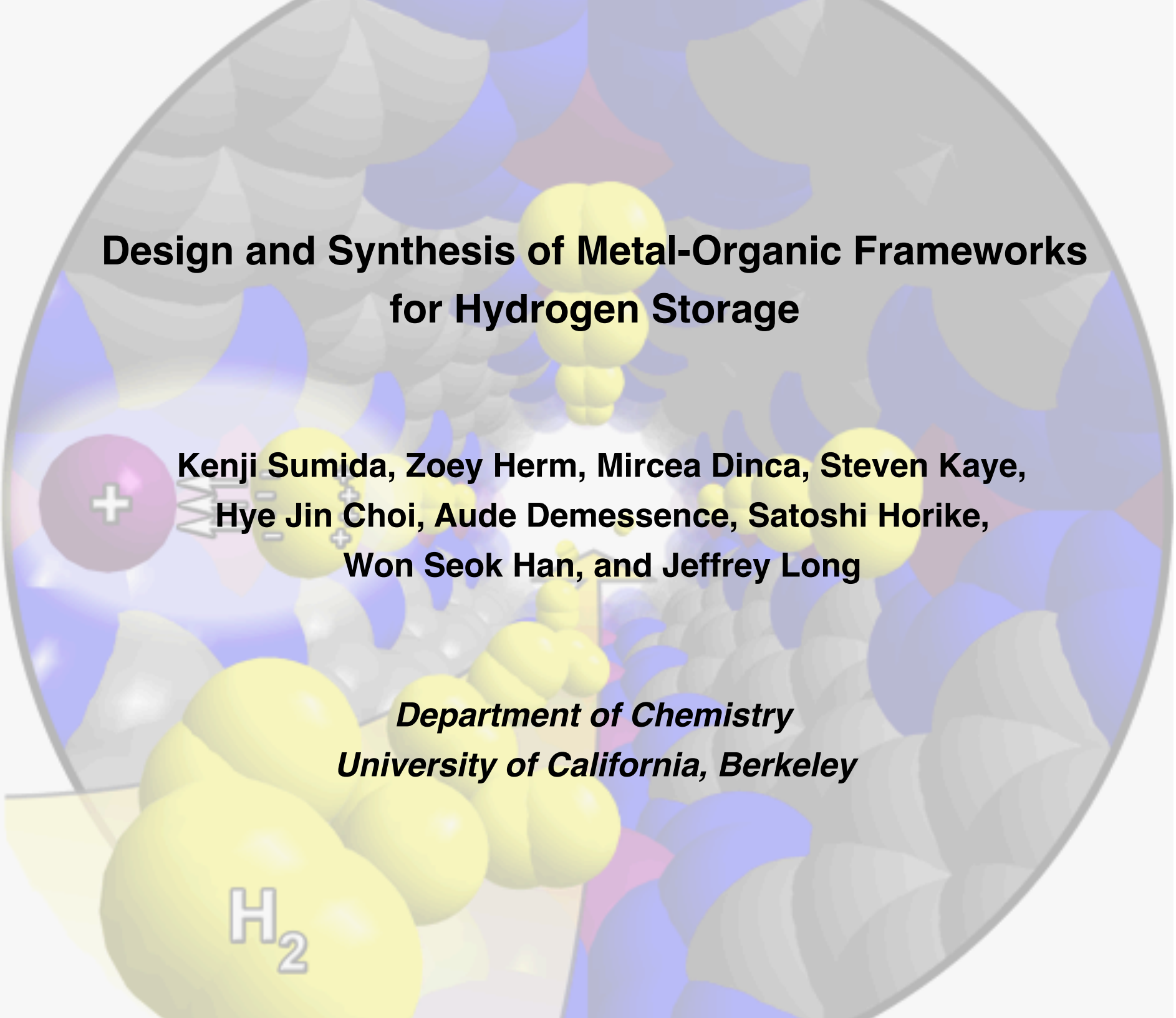


Design and Synthesis of Metal-Organic Frameworks for Hydrogen Storage

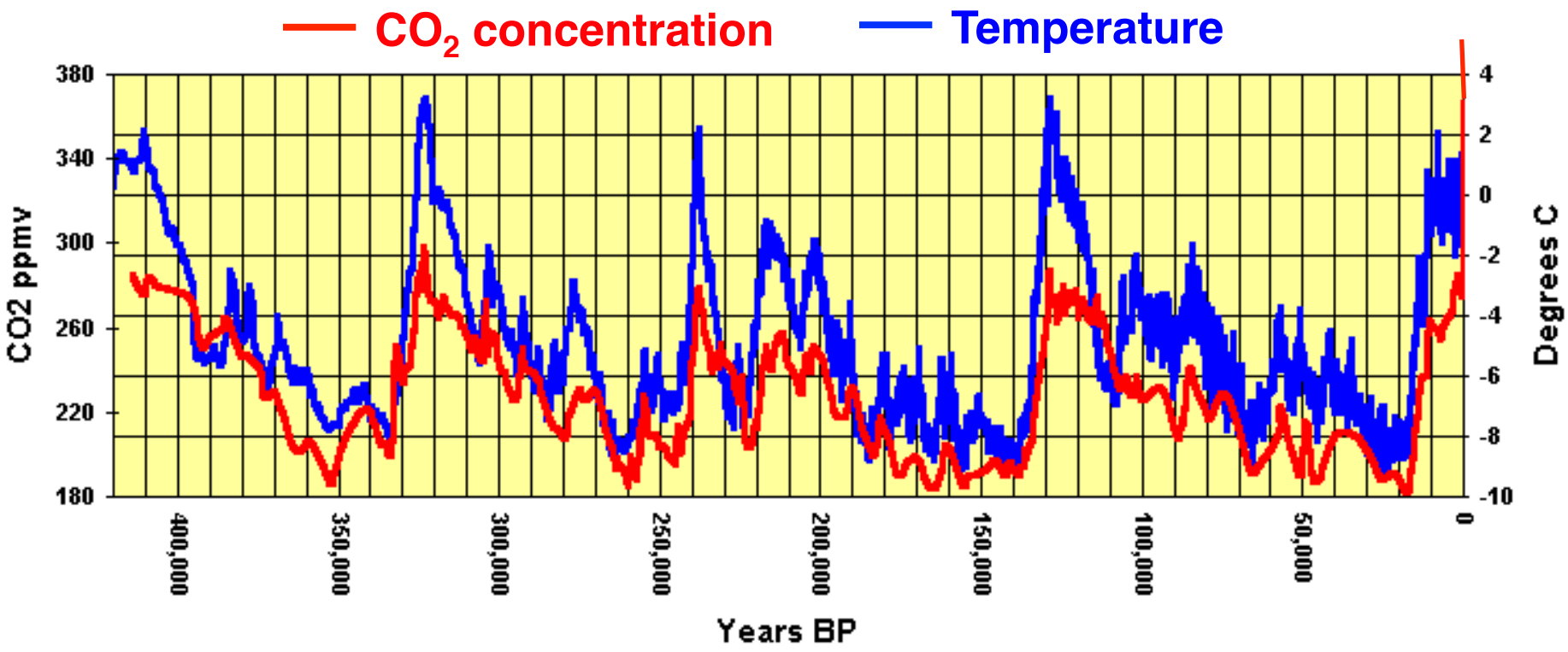
Kenji Sumida, Zoey Herm, Mircea Dinca, Steven Kaye, Hye Jin Choi, Aude Demessence, Satoshi Horike, Won Seok Han, and Jeffrey Long

Department of Chemistry
University of California, Berkeley

Los Angeles, December 2007

Atmospheric CO_2 at Mauna Loa Observatory

Ice Core Data from Vostok, Antarctica



Petit, Jouzel, Raynaud, Barkov, Barnola, Basile, Bender, Chappellaz, Davis, Delaygue, Delmotte, Kotlyakov, Legrand, Lipenkov, Lorius, Pépin, Ritz, Saltzman, Stievenard *Nature* **1999**,*399*, 429

CO_2 Emissions in the United States

electricity and heat

47%

3.4 Gtons/year

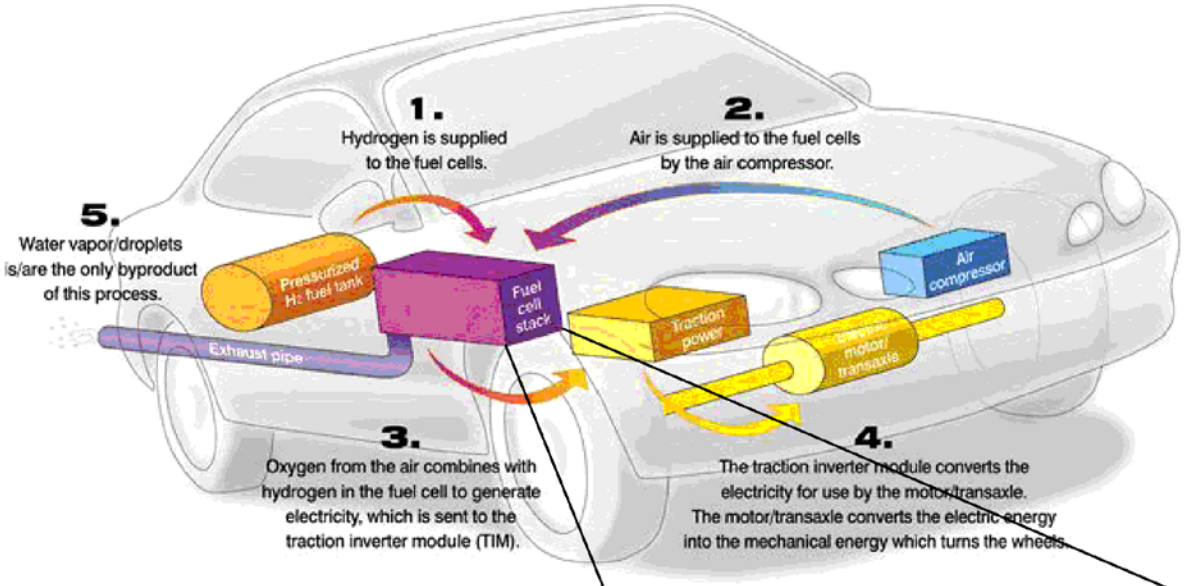
transportation

29%

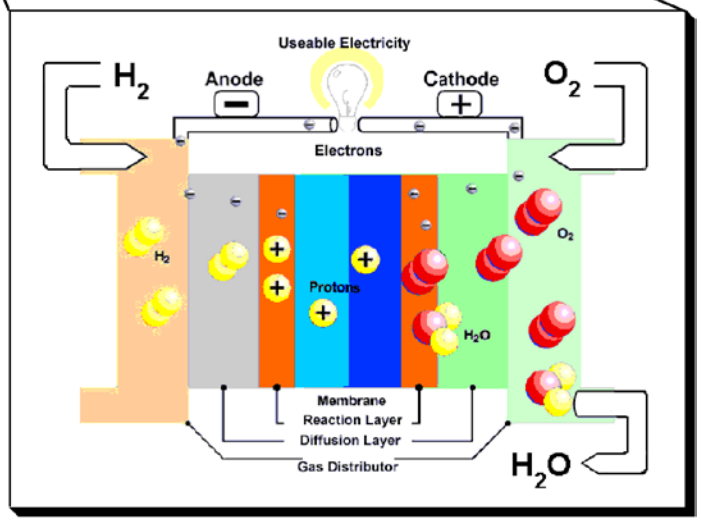
2.1 Gtons/year

Source: McKinsey & Co *Reducing US GHG Emissions* **2007**

The Hydrogen Fuel Cell-Powered Car



fuel	lower heating value (kW·h/kg)
hydrogen	33.6
gasoline	12.4
methane	13.9
methanol	5.6



Hydrogen Production

Currently 95% is produced by natural gas reforming:

$$CH_4 + H_2O \xrightarrow{\sim 800\ ^\circ C} CO + 3H_2$$

$$CO + H_2O \longrightarrow CO_2 + H_2$$

- $4-8/kg and can include **CO_2 sequestration**
- Overall greenhouse emissions 60% lower with CH_4 consumption 5% higher
- Nonrenewable energy source

Alternative sources via H_2O splitting:

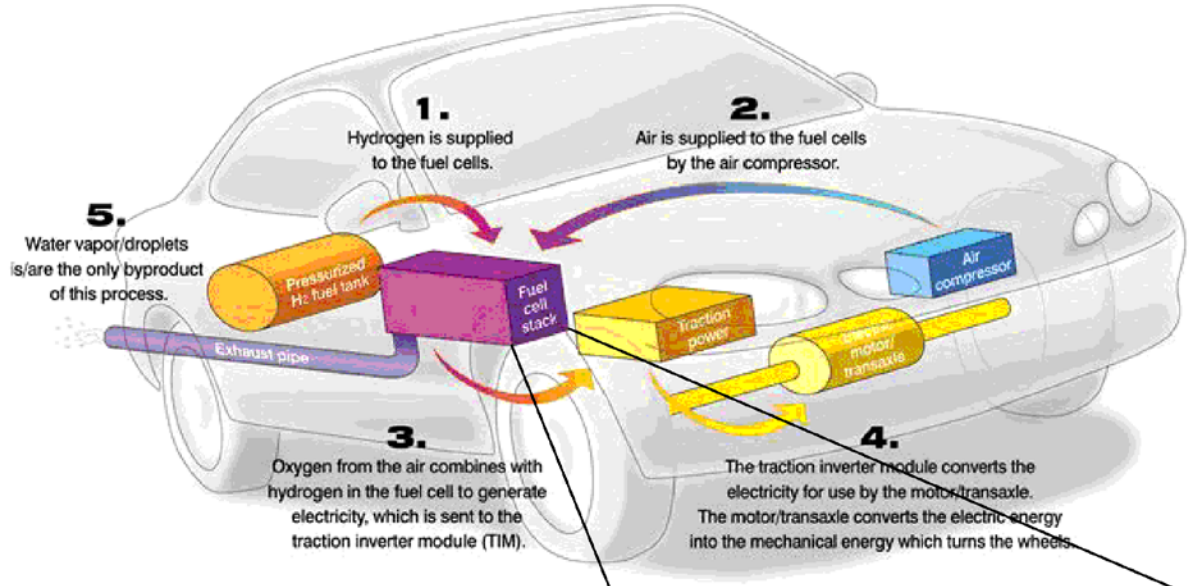
- $1.5/kg with nuclear power via thermal processes, but concerns over waste
- Electrolysis, photolysis, or thermal processing using a renewable energy source:

  solar, biomass, geothermal, hydroelectric, wind, ocean waves

Honda Solar Hydrogen Refueling Station

Torrance, CA

The Hydrogen Fuel Cell-Powered Car



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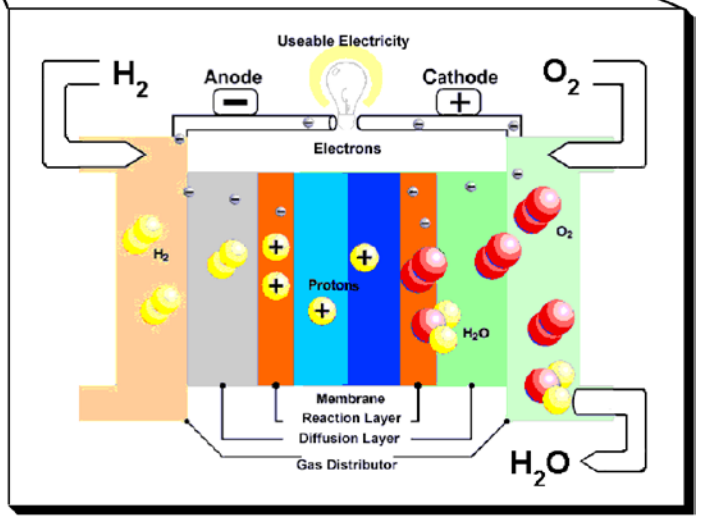
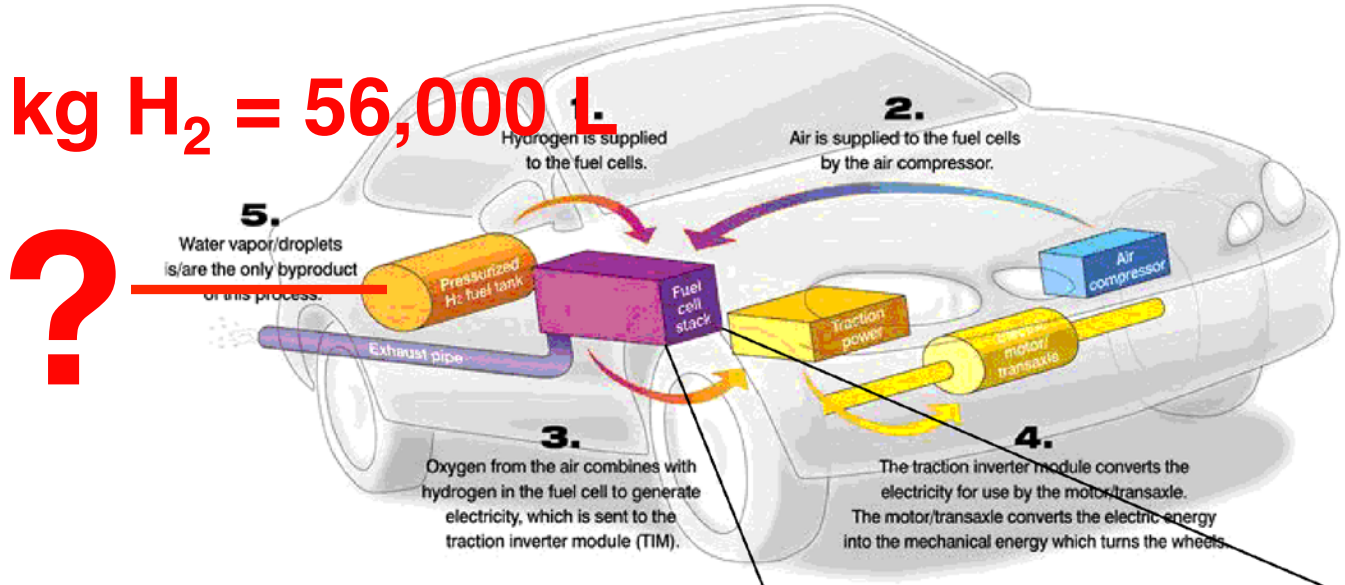


The Hydrogen Fuel Cell-Powered Car

5 kg H_2 = 56,000 L

?



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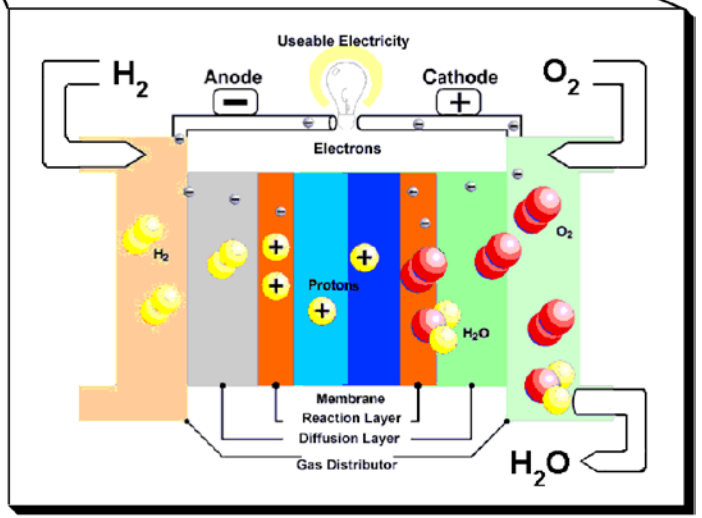


Automobile Industry Initiatives

BMW is now leasing a 7-series vehicle with an ICE that can run on gas or H_2

Honda FCX fuel cell vehicle became available for lease in US and Japan in 2008

General Motors tested a fleet of 100 new HydroGen4 cars in 2008

Toyota: 500-1000 people working on hydrogen car for 2013 “Prius scale release”

Currently 80 hydrogen filling stations in the US; 53 more will open soon

Current Hydrogen Storage Options

Compressed Hydrogen Gas (used in most current vehicles)

Very high pressures (500-700 atm) entail expensive cylinders with undesirable shape

Compression cost is significant fraction of energy content (18% for 200 atm)

Liquid Hydrogen (used in some current vehicles)

Requires expensive, heavy cooling system, and still lose ~1% H_2 per day to evaporation

Significant energy cost associated with liquefaction process

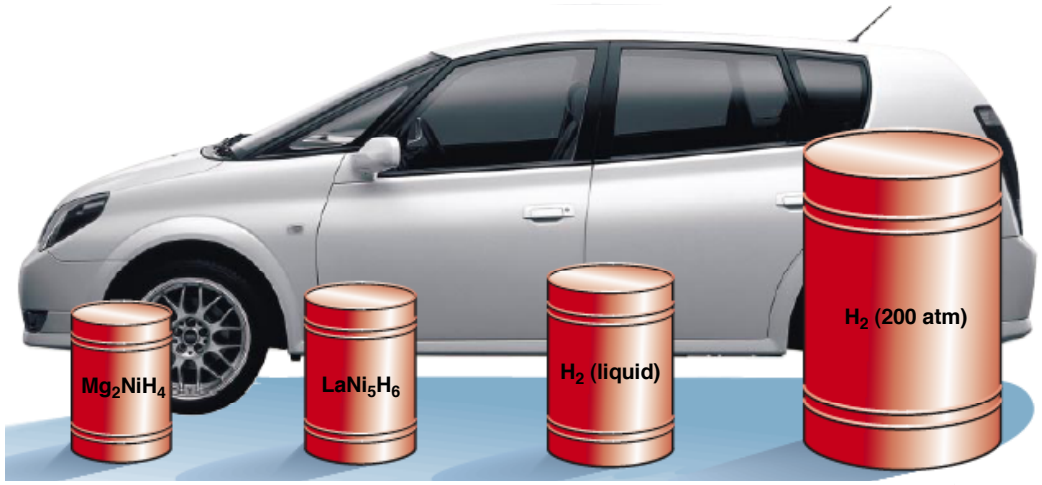
Complex and Metal Hydrides (e.g. 4.5 wt. % in $NaAlH_4$ with 2% $TiCl_3$ catalyst)

Poor reversibility and kinetics (typically require >100 °C and >100 atm)

Carbon Nanotubes

Actual capacity is very low

Schlapbach, Züttel
Nature **2001**, *414*, 353

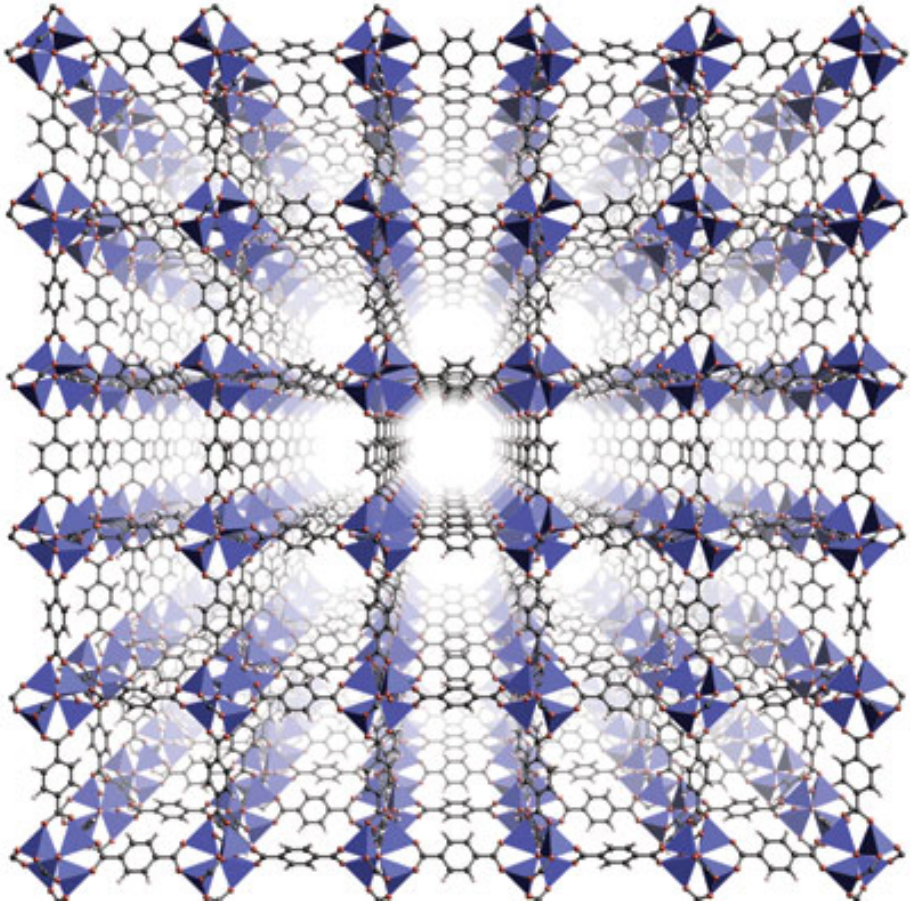


DoE 2015 H_2 Storage System Targets

gravimetric capacity	5.5 wt % H_2
volumetric capacity	40 g H_2/L
operating temperature	-40 to 60 °C
maximum pressure	100 bar
refueling rate	1.5 kg H_2/min
cycle life	1500 cycles
cost	$67 per kg H_2

http://www1.eere.energy.gov/hydrogenandfuelcells/storage/pdfs/targets_onboard_hydro_storage.pdf

Metal-Organic Frameworks



Zn_4O(1,4-benzenedicarboxylate)$_3$

MOF-5

BET surface areas up to 6000 m^2/g

Density as low as 0.4 g/cm^3

Tunable pore sizes up to 5 nm

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

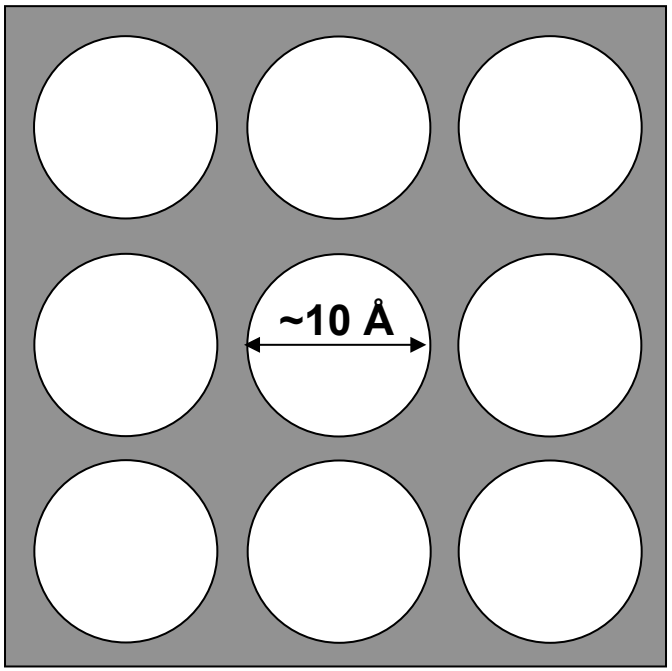
Internal surface can be functionalized

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

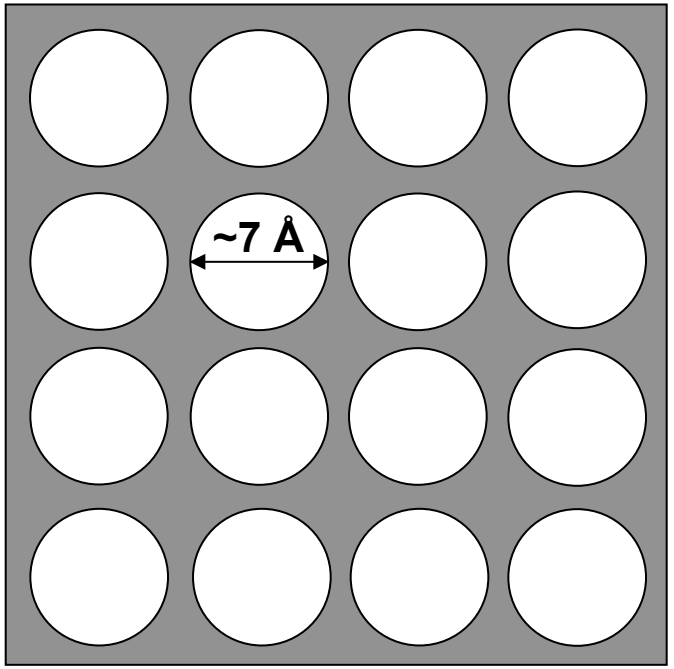
Yaghi et al. *Nature* **2003**, *423*, 705
Kitagawa et al. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334
Férey *Chem. Soc. Rev.* **2008**, *37*, 191

Optimum Pore Sizes for Hydrogen Storage

77 K



298 K



- Calculated using Monte Carlo simulations with both cylindrical and slit pores

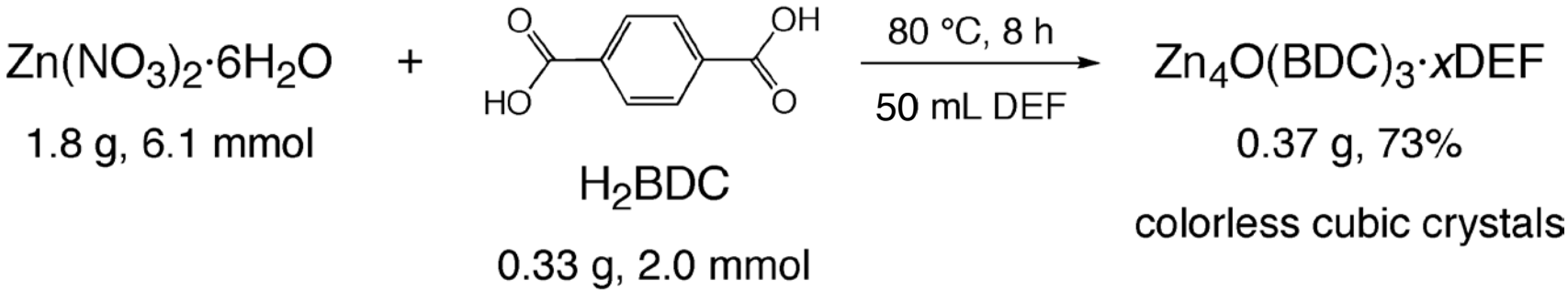
Rzepka, Lamp, de la Casa-Lillo *J. Phys. Chem. B* **1998**, *102*, 10894

Variation of N_2 Uptake in $Zn_4O(BDC)_3$

preparation	N_2 uptake (mmol/g)	SA_{BET} (m^2/g)	$SA_{Langmuir}$ (m^2/g)
1	11.8	570	1010
2	14.5	950	1250
3	29.7		2900
4	31.6		3080
5	34.4		3360
6		3530	4170

(1) Panella, Hirscher *Adv. Mater.* **2005**, *17*, 538
(2) Yan, *et al. Microporous Mesoporous Mater.* **2003**, *58*, 105
(3) Li, Eddaoudi, O'Keeffe, Yaghi *Nature* **1999**, *402*, 276
(4) Dailly, Vajo, Ahn *J. Phys. Chem.* **2006**, *110*, 1099
(5) Rowsell, Millward, Park, Yaghi *J. Am. Chem. Soc.* **2004**, *126*, 5666
(6) Wong-Foy, Matzger, Yaghi *J. Am. Chem. Soc.* **2006**, *128*, 3494

Synthesis of $Zn_4O(BDC)_3$ (MOF-5)



- Heating too high or too long gives yellow-brown crystals with reduced storage capacity

Evacuation procedure

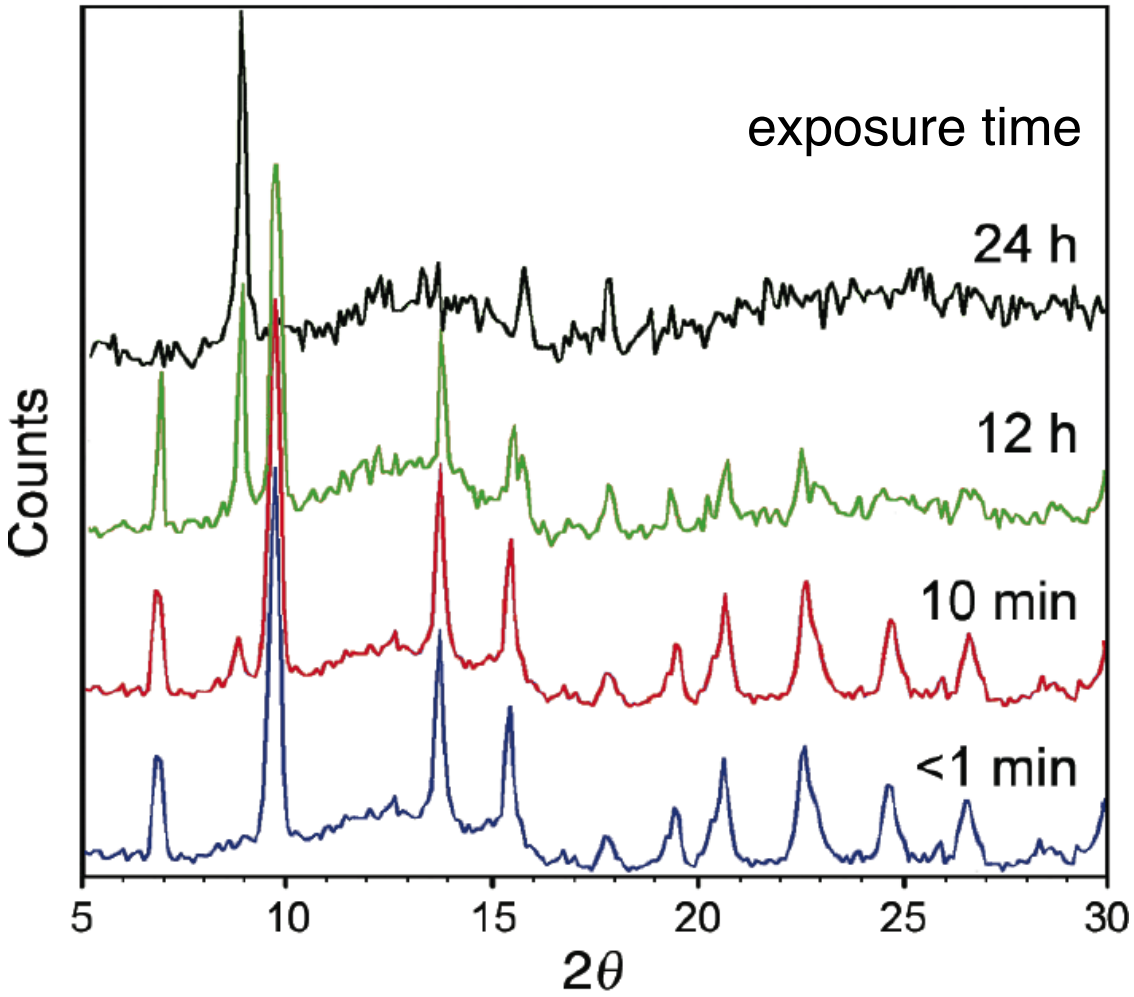
Soak crystals in 10 mL DMF for 8 h (6 times)

Soak crystals in 10 mL CH_2Cl_2 for 8 h (6 times)

Evacuate crystals at 25 °C under dynamic vacuum until an outgas rate of <1 mtorr/min is achieved

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

Decomposition of $Zn_4O(BDC)_3$ in Air



$Zn_3(OH)_2(BDC)_2$ + **?**
(nonporous)

$Zn_4O(BDC)_3$

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

Variation of N_2 Uptake in $Zn_4O(BDC)_3$

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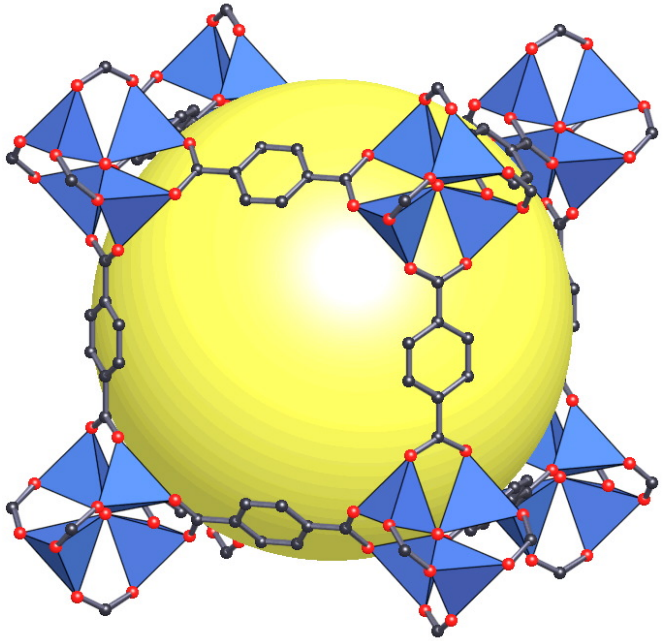
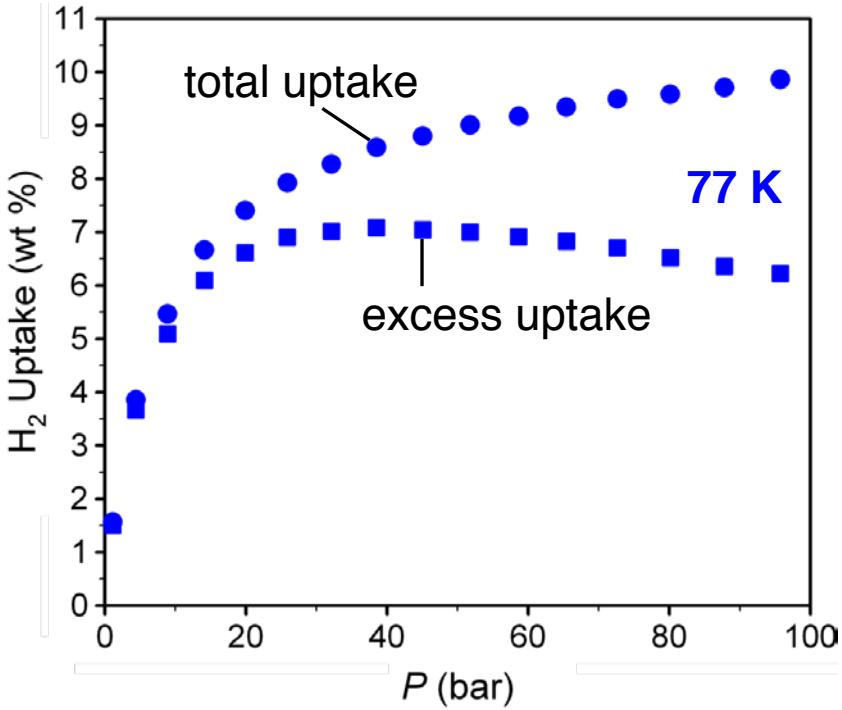
4	31.6		3080
5	34.4		3360
6		3530	4170
air-free	**44.5**	**3800**	**4400**

(1) Panella, Hirscher *Adv. Mater.* **2005**, *17*, 538
(2) Yan, *et al. Microporous Mesoporous Mater.* **2003**, *58*, 105
(3) Li, Eddaoudi, O'Keeffe, Yaghi *Nature* **1999**, *402*, 276
(4) Dailly, Vajo, Ahn *J. Phys. Chem.* **2006**, *110*, 1099
(5) Rowsell, Millward, Park, Yaghi *J. Am. Chem. Soc.* **2004**, *126*, 5666
(6) Wong-Foy, Matzger, Yaghi *J. Am. Chem. Soc.* **2006**, *128*, 3494
(7) Kaye, Dailly, Yaghi, Long *J. Am. Chem. Soc.* **2007**, *129*, 14176

Hydrogen Storage in a Metal-Organic Framework



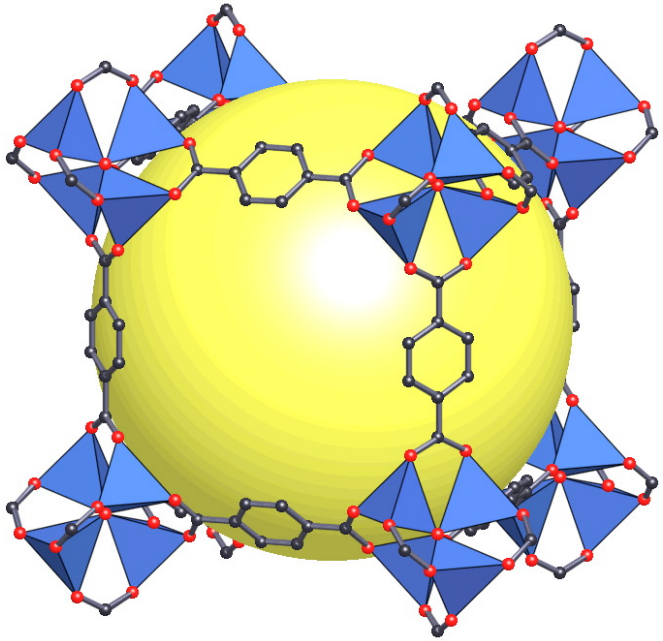
$Zn_4O(BDC)_3$



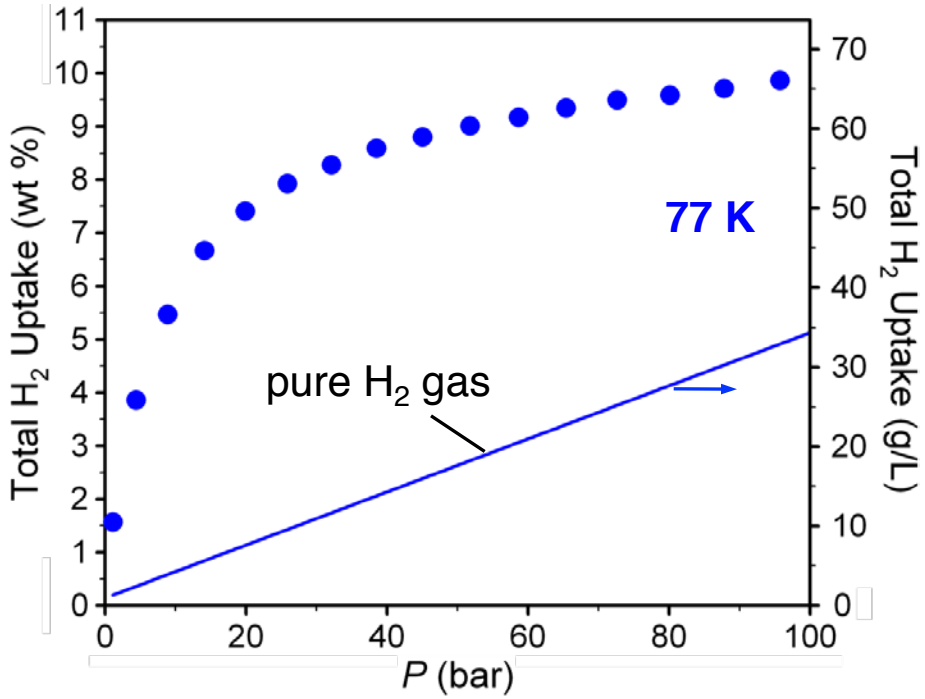
- Excess uptake is the amount of gas adsorbed beyond available pore volume
- Total uptake is the amount of gas contained within the volume of the crystals

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

Hydrogen Storage in a Metal-Organic Framework



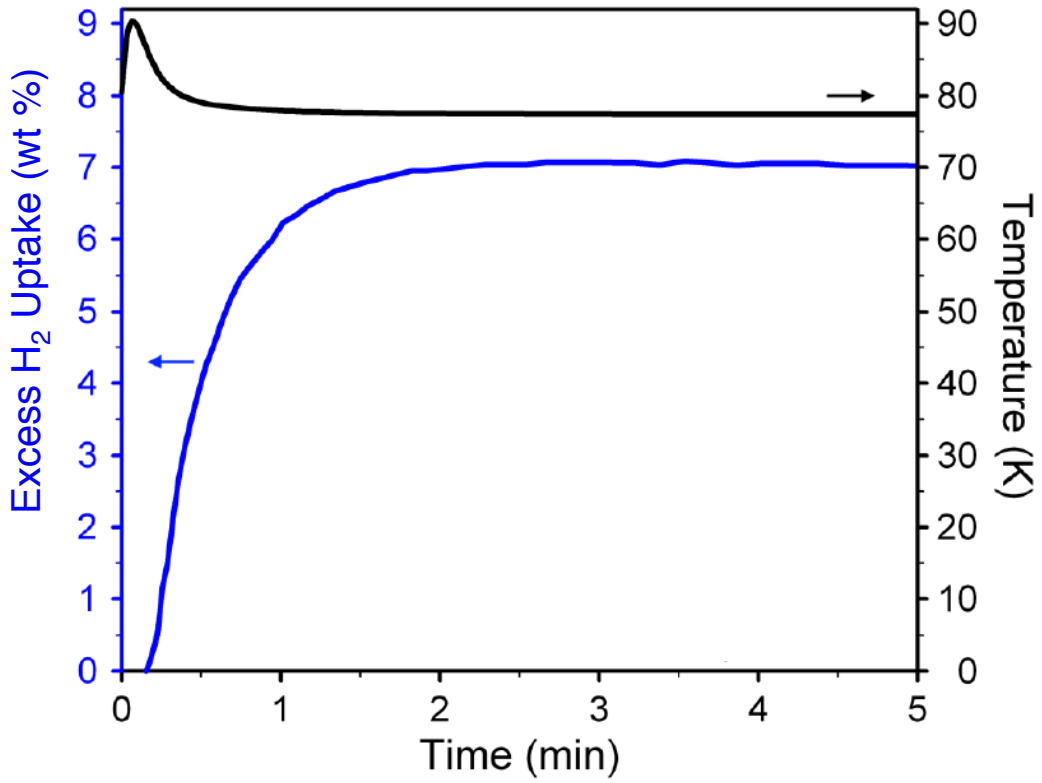
$Zn_4O(BDC)_3$



- Knowledge of total uptake permits calculation of the volumetric storage density
- At 100 bar and 77 K, a record physisorbed storage density of 66 g/L is achieved

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

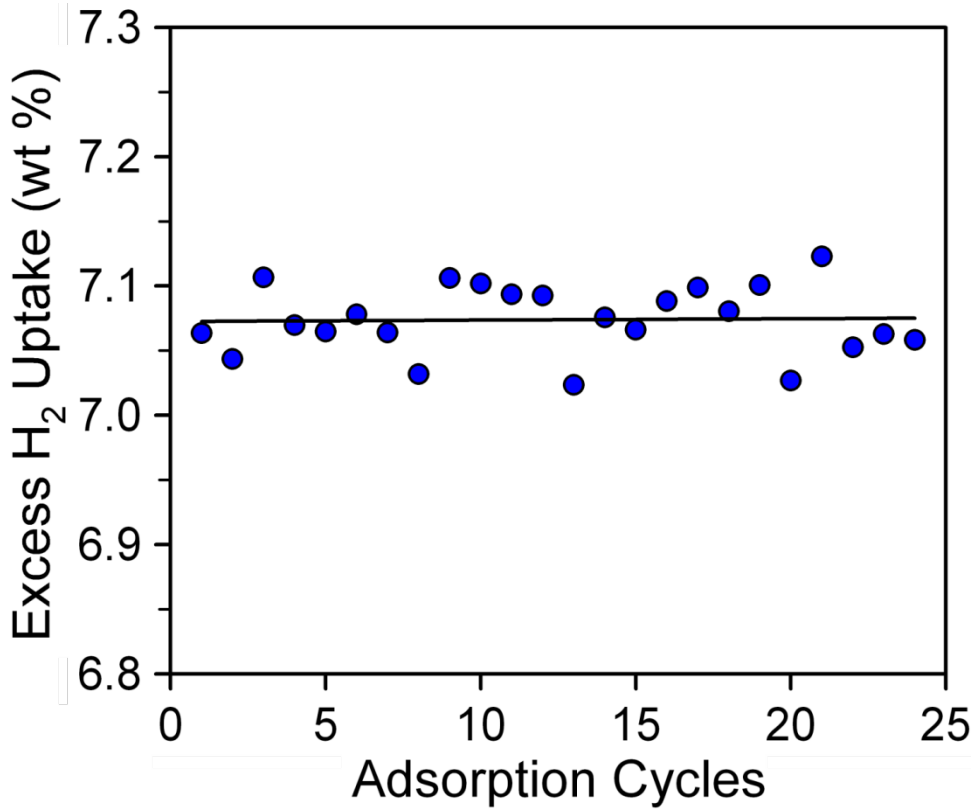
Kinetics of H_2 Uptake in $Zn_4O(BDC)_3$



- Results are upon exposure to a manifold of H_2 gas at 45 bar and 298 K
- Saturation is achieved in approximately 2 min

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

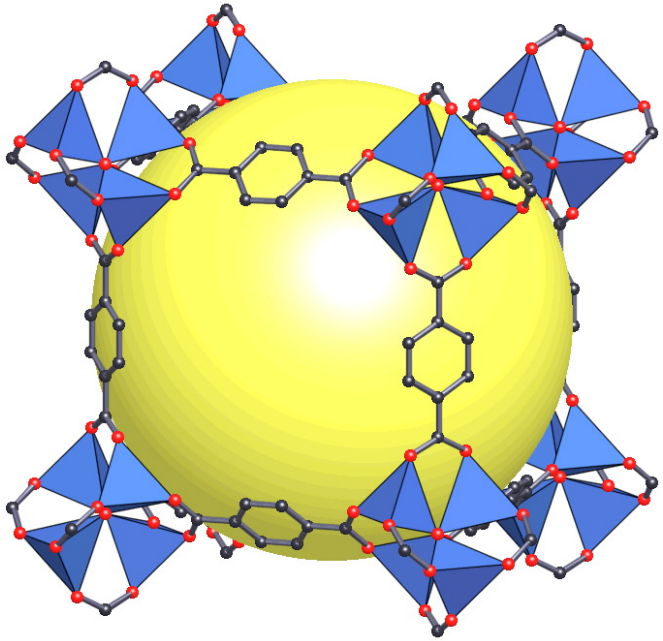
H_2 Adsorption-Desorption Cycling in $Zn_4O(BDC)_3$



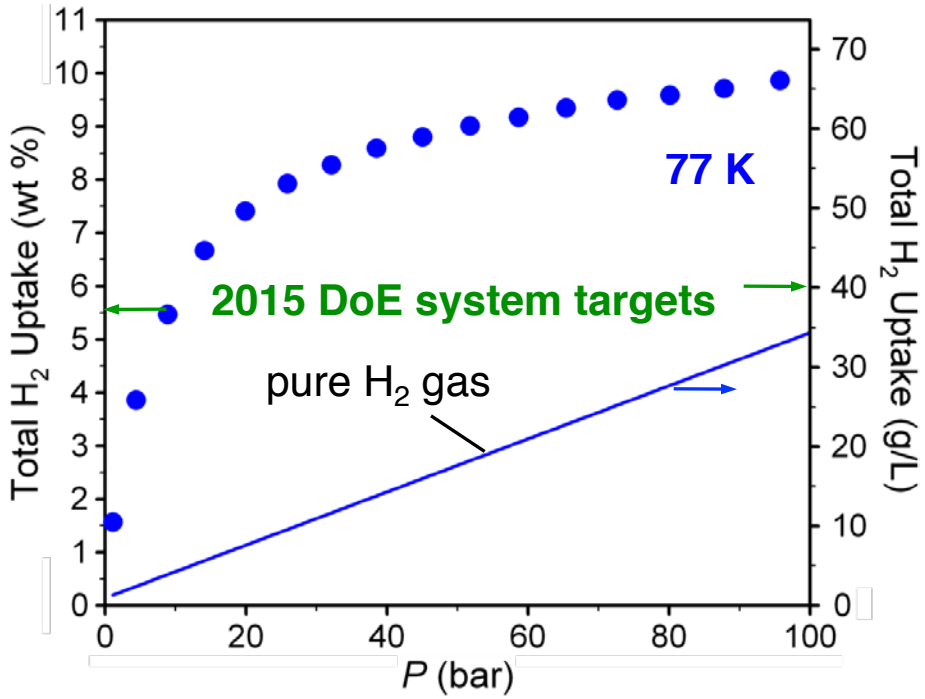
- No detectable loss in capacity or kinetics after 24 adsorption-desorption cycles

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

Hydrogen Storage in a Metal-Organic Framework



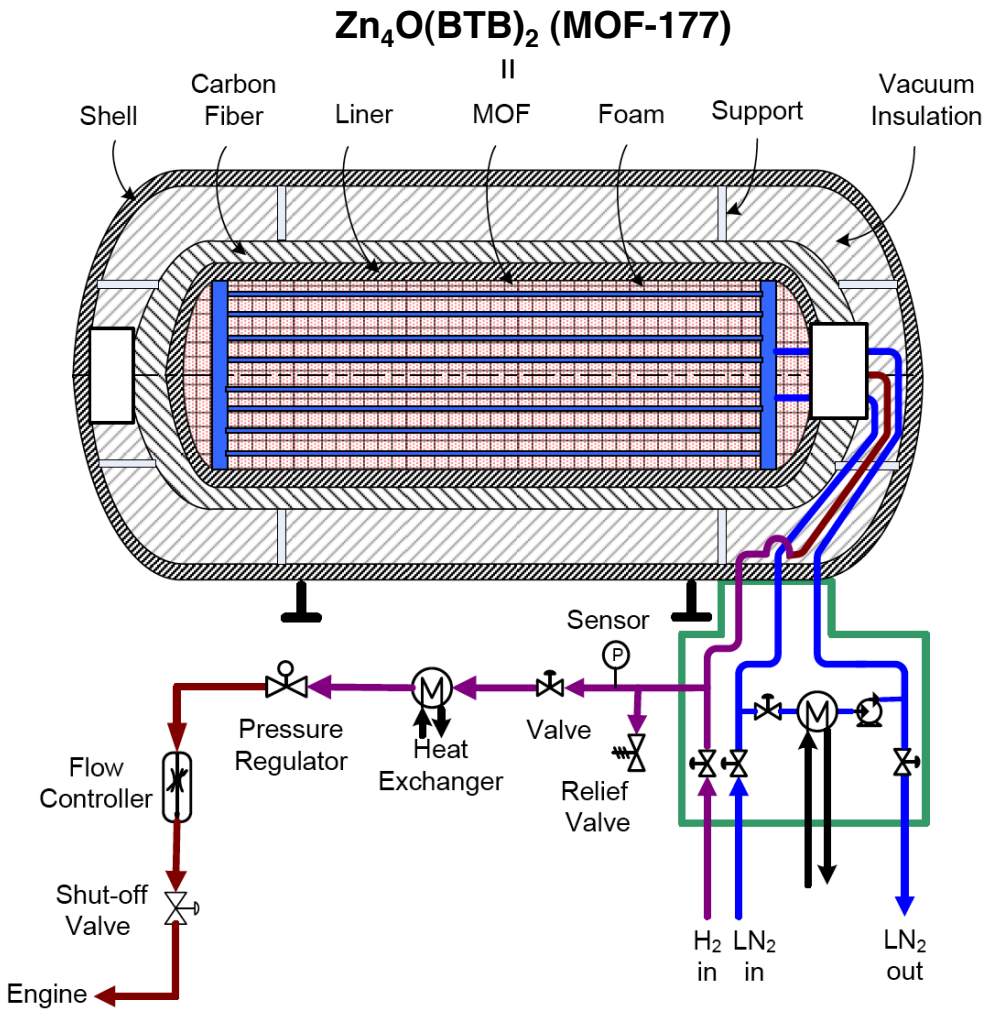
$Zn_4O(BDC)_3$

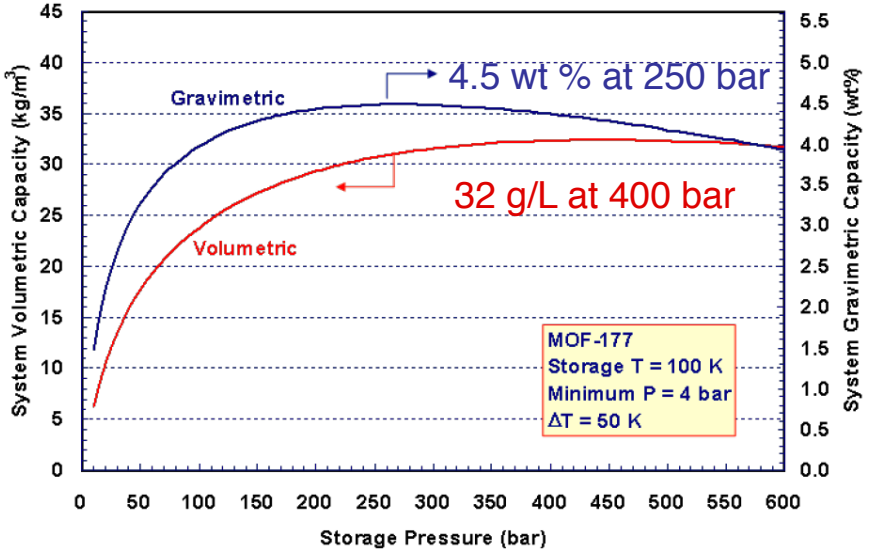


- At 100 bar and 77 K, a record physisorbed storage density of 66 g/L is achieved
- Best medium available for storing H_2 at 77 K and pressures below 100 bar

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

A MOF-Based Cryo-Compressed H_2 Storage Tank





- Filling uses 50 kg of liquid N_2
- Adiabatic refueling with liquid H_2 also possible
- For $Zn_4O(BDC)_3$ (MOF-5) expect: same gravimetric capacity volumetric capacity of > 40 g/L

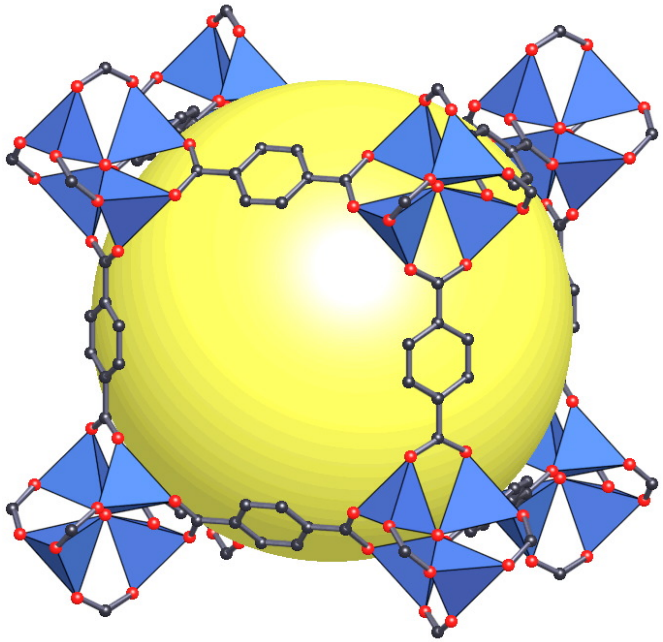
Ahluwalia, Hua, Peng, Argonne National Laboratory

DoE 2015 H_2 Storage System Targets

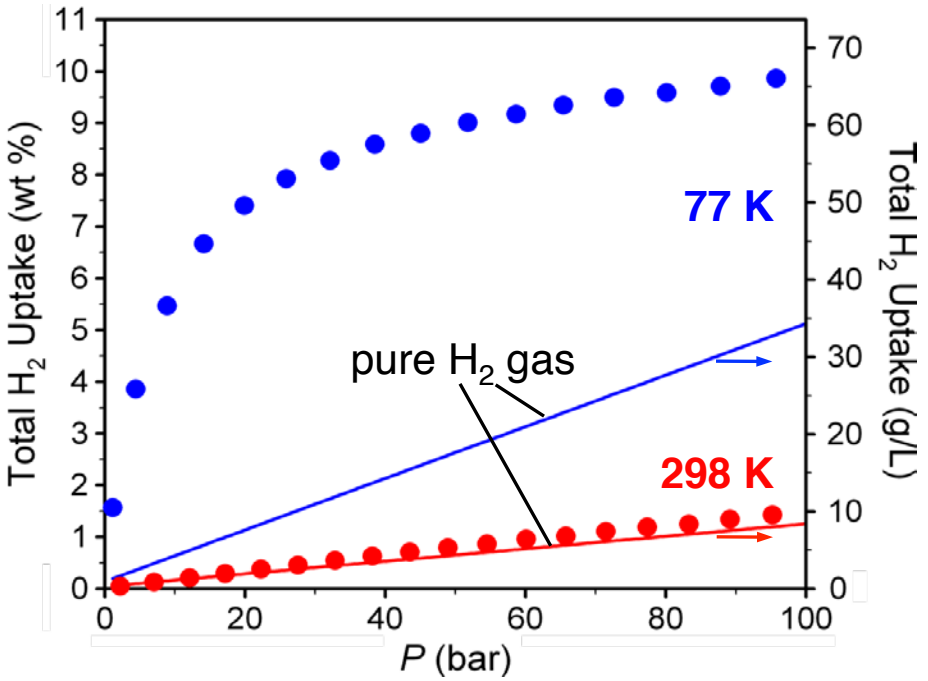
gravimetric capacity	5.5 wt % H_2
volumetric capacity	40 g H_2/L
operating temperature	-40 to 60 °C
maximum pressure	100 bar
refueling rate	1.5 kg H_2/min
cycle life	1500 cycles
cost	$67 per kg H_2

http://www1.eere.energy.gov/hydrogenandfuelcells/storage/pdfs/targets_onboard_hydro_storage.pdf

Hydrogen Storage in a Metal-Organic Framework



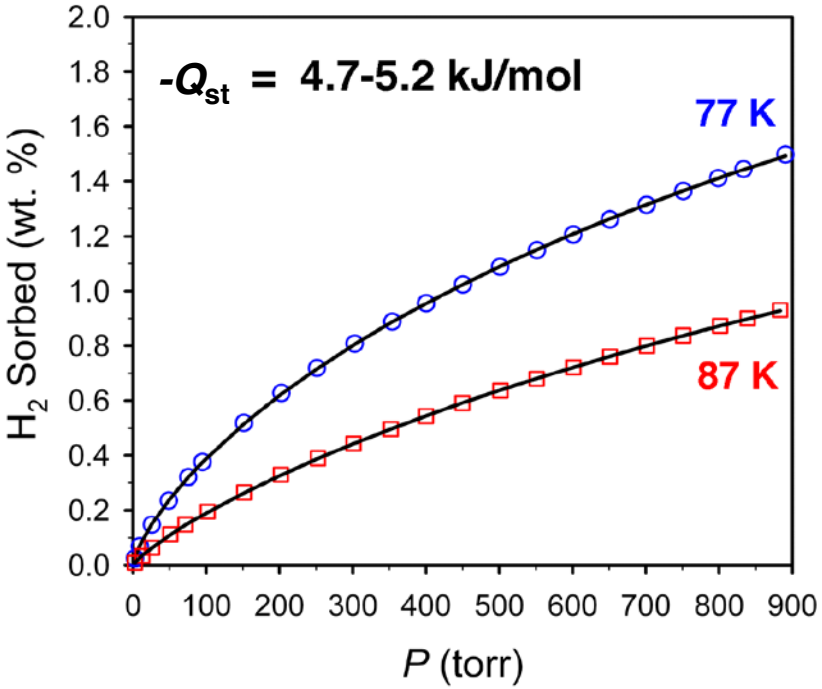
$Zn_4O(BDC)_3$



- At 298 K, framework offers little improvement over density of pure H_2 gas
- Strength of H_2 interaction with framework is too weak

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

Assessing H_2 Adsorption Enthalpy in $Zn_4O(BDC)_3$



Sorption isotherms can be fit using the Langmuir-Freundlich equation:

$$\frac{Q}{Q_{sat}} = \frac{B \cdot P^{(1/t)}}{1 + B \cdot P^{(1/t)}}$$

where: Q = moles adsorbed

Q_{sat} = moles adsorbed at saturation

P = pressure

B and t = fit constants

The binding enthalpy associated with a given quantity of H_2 adsorbed can then be determined using a variant of the Clausius-Clapeyron equation:

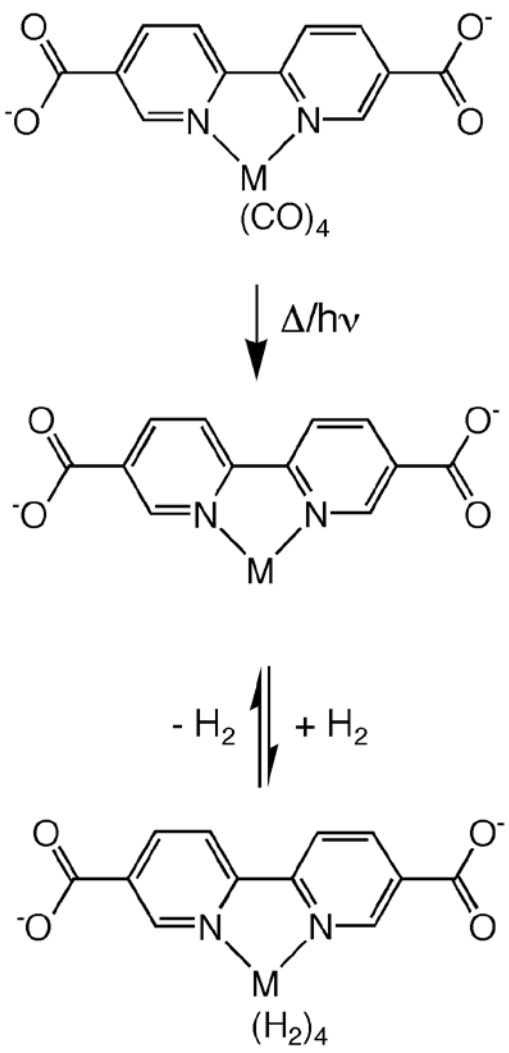
$$\ln\left(\frac{P_1}{P_2}\right) = \Delta H \cdot \frac{T_2 - T_1}{R \cdot T_1 \cdot T_2}$$

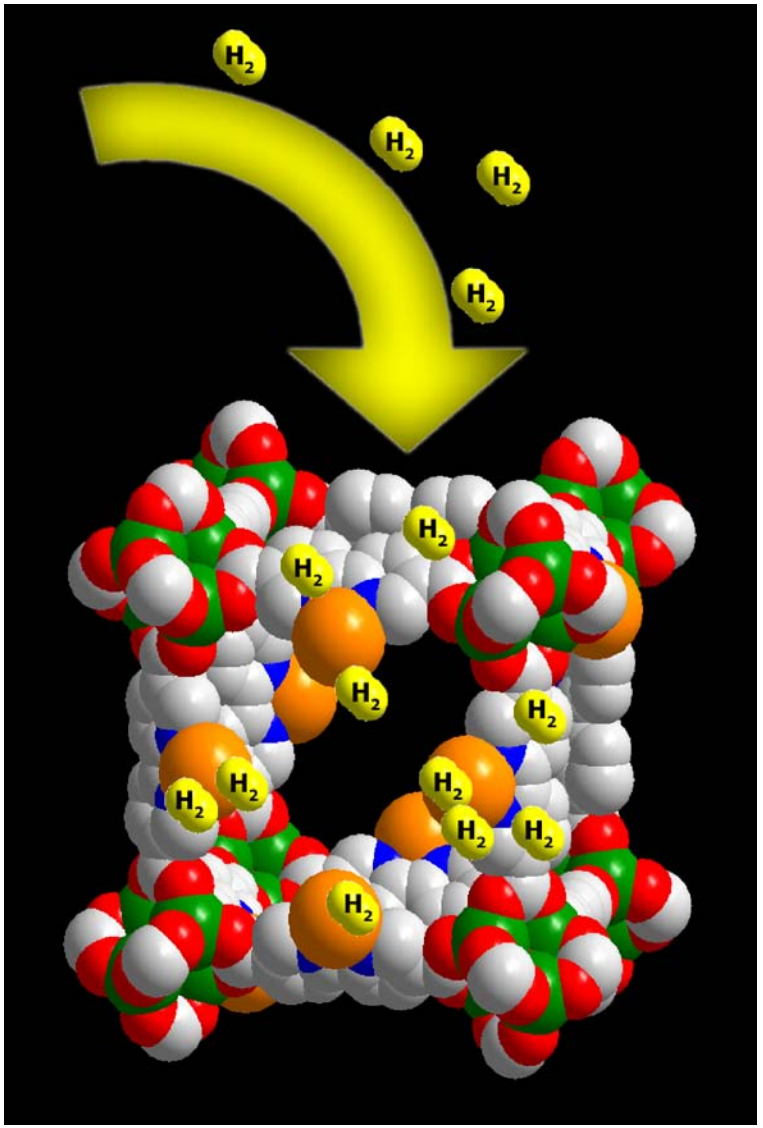
where: P_n = pressure for isotherm n

T_n = temperature for isotherm n

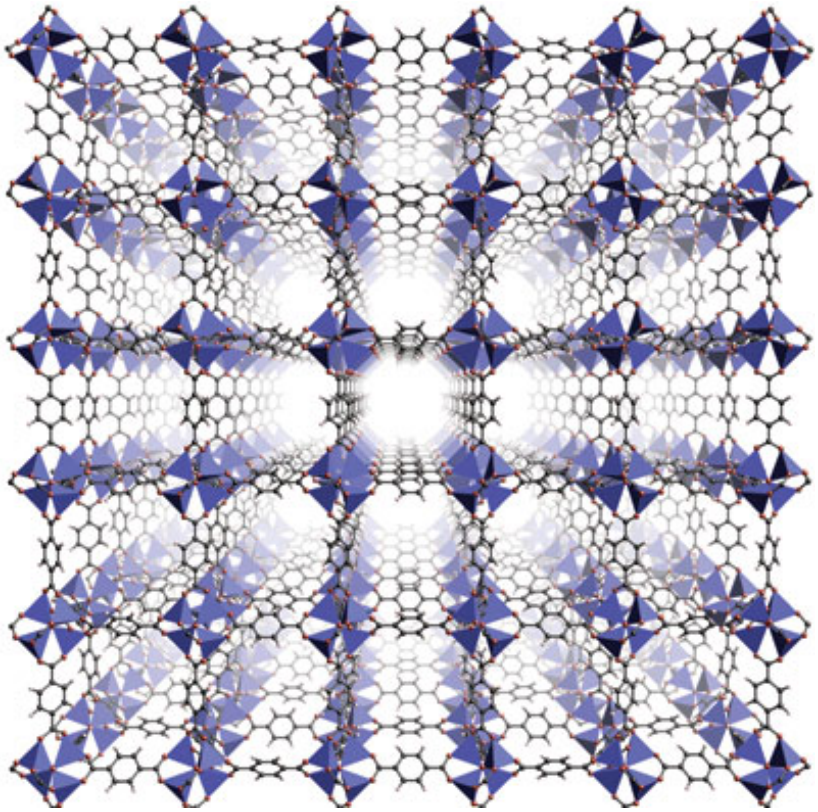
R = 8.315 J/K·mol

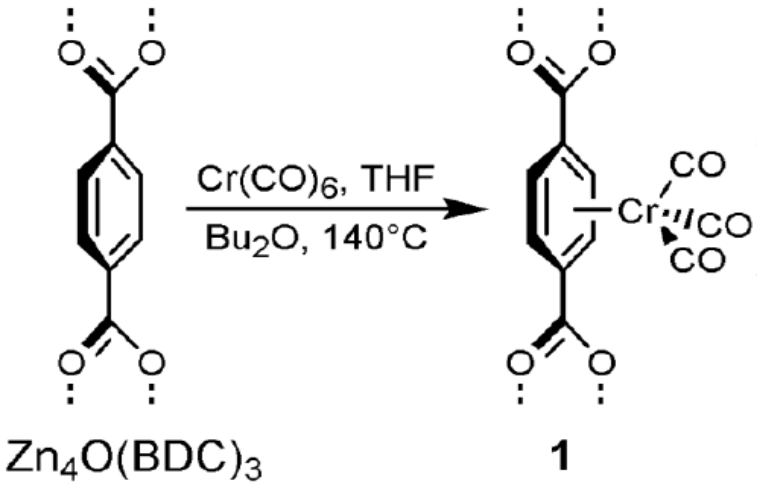
Incorporating Metal Binding Sites





Coating the Surfaces with $Cr(CO)_3$ Units

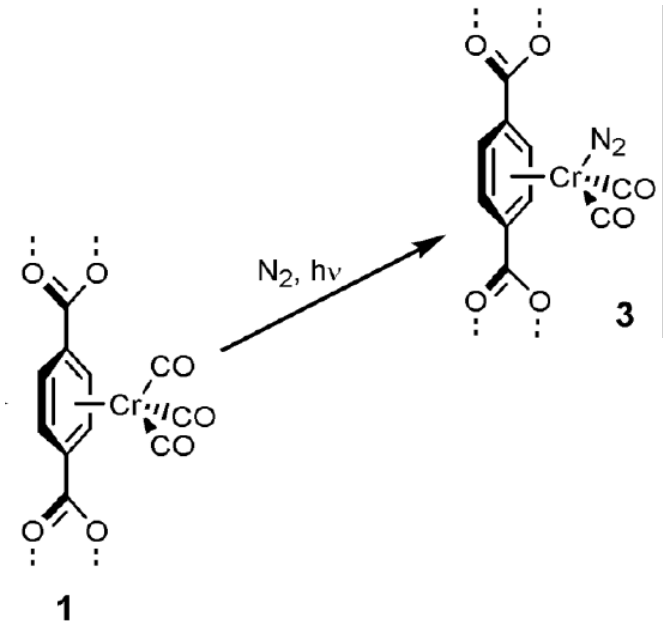


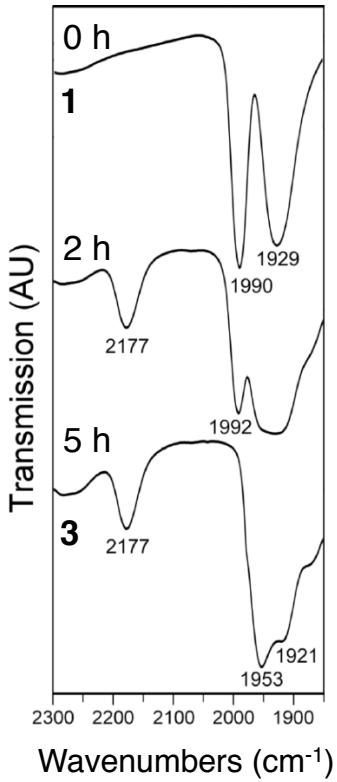


- Infrared spectrum matches that observed for molecular analogue
- Elemental analysis and NMR spectroscopy indicate attachment to all rings

Kaye, Long *J. Am. Chem. Soc.* **2008**, *130*, 806

N_2 Binding at Cr^0 Centers

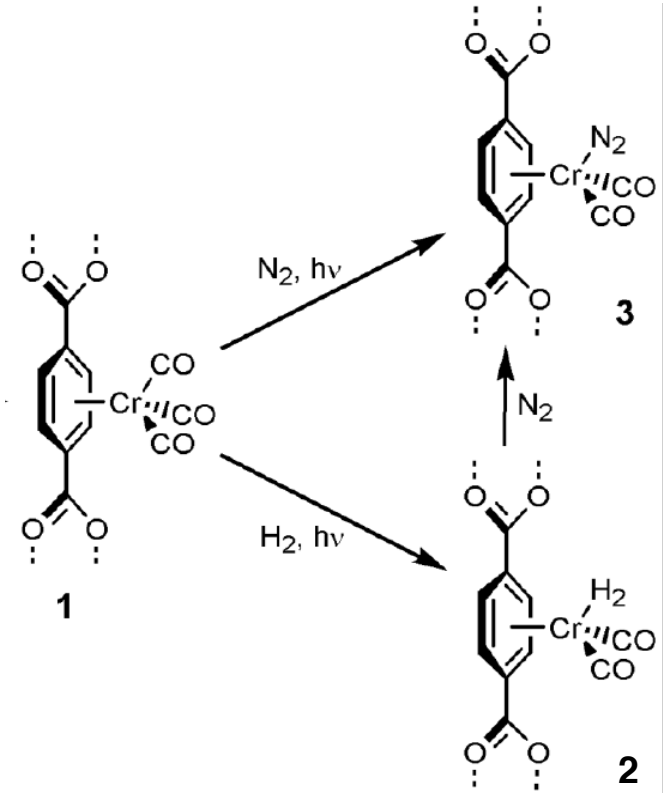


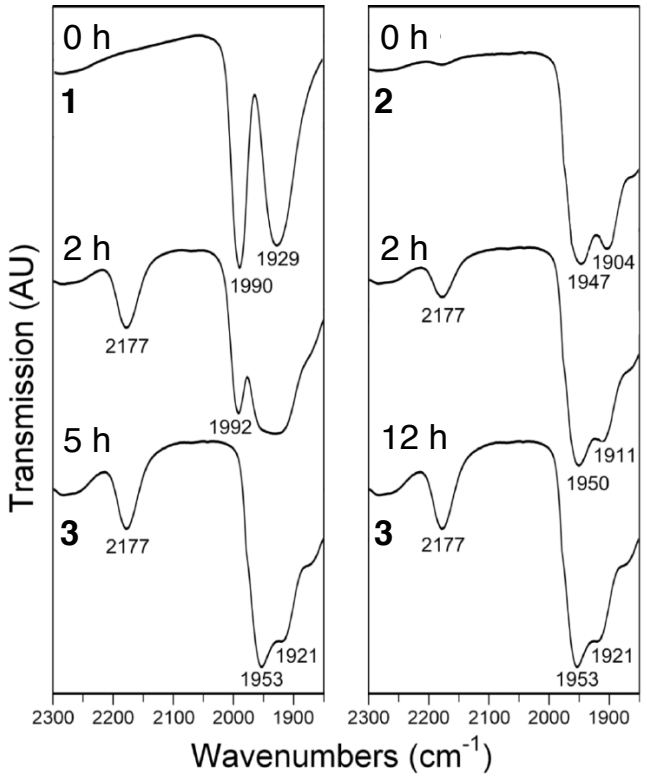


- Infrared spectrum matches that observed for molecular analogue
- Cr^0-N_2 complex in compound **3** is stable indefinitely at room temperature

Kaye, Long *J. Am. Chem. Soc.* **2008**, *130*, 806

Strong H_2 Binding at Cr^0 Centers

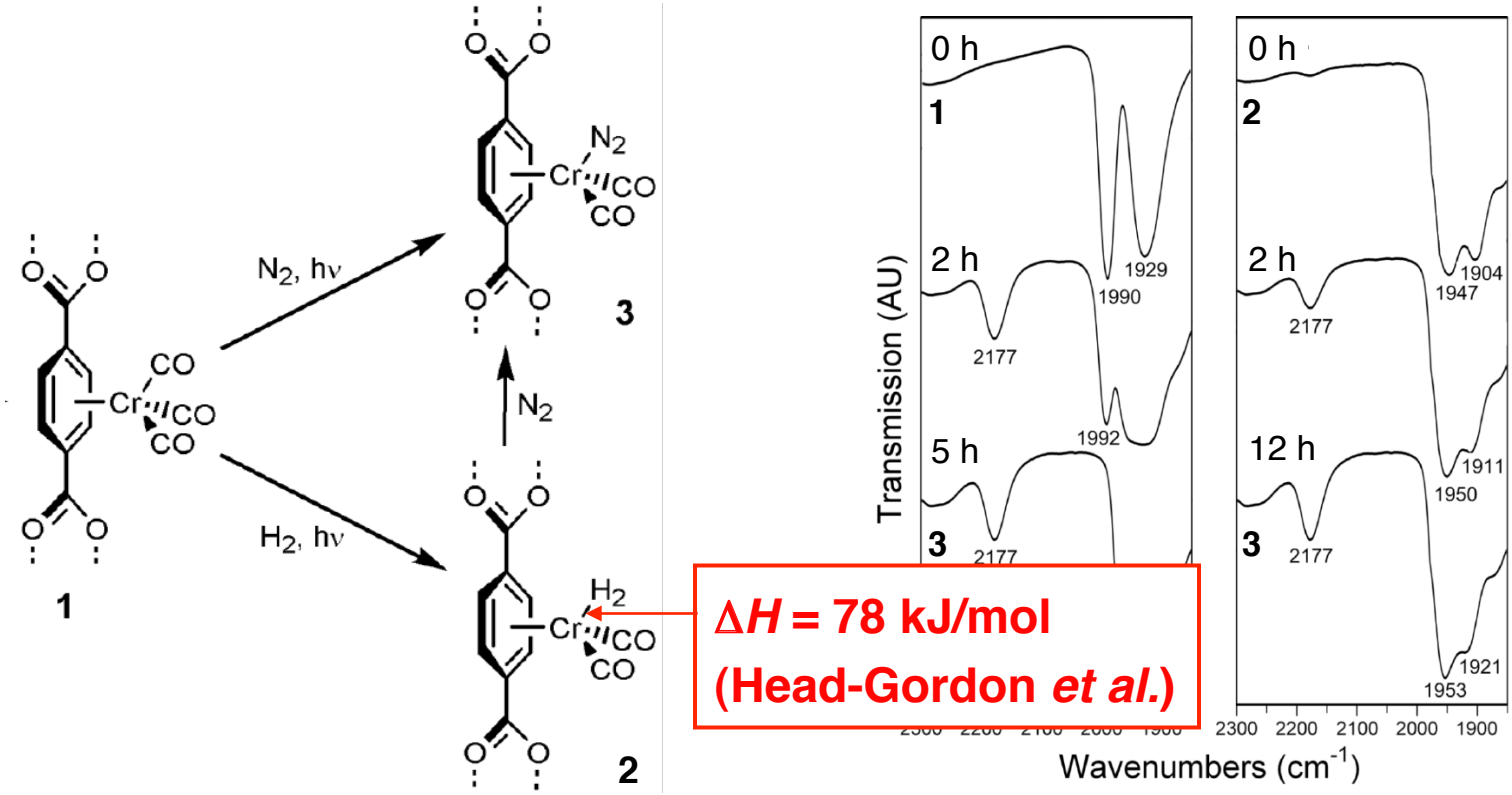




- Infrared spectra match those observed for molecular analogues
- Cr^0-H_2 complex in compound **2** is stable indefinitely at room temperature!

Kaye, Long *J. Am. Chem. Soc.* **2008**, *130*, 806

Strong H_2 Binding at Cr^0 Centers



ΔH = 78 kJ/mol
(Head-Gordon *et al.*)

- Infrared spectra match those observed for molecular analogues
- Cr^0-H_2 complex in compound **2** is stable indefinitely at room temperature!

Kaye, Long *J. Am. Chem. Soc.* **2008**, *130*, 806

H_2 Binding Enthalpies

$$MH_2 \rightleftharpoons M + H_2 \qquad \Delta H$$

- Ideally, fuel cells will operate with storage pressures of 1.5-100 bar
- For operation in this pressure range at 298 K, applying a Langmuir adsorption model affords:*

target ΔH = 14 kJ/mol

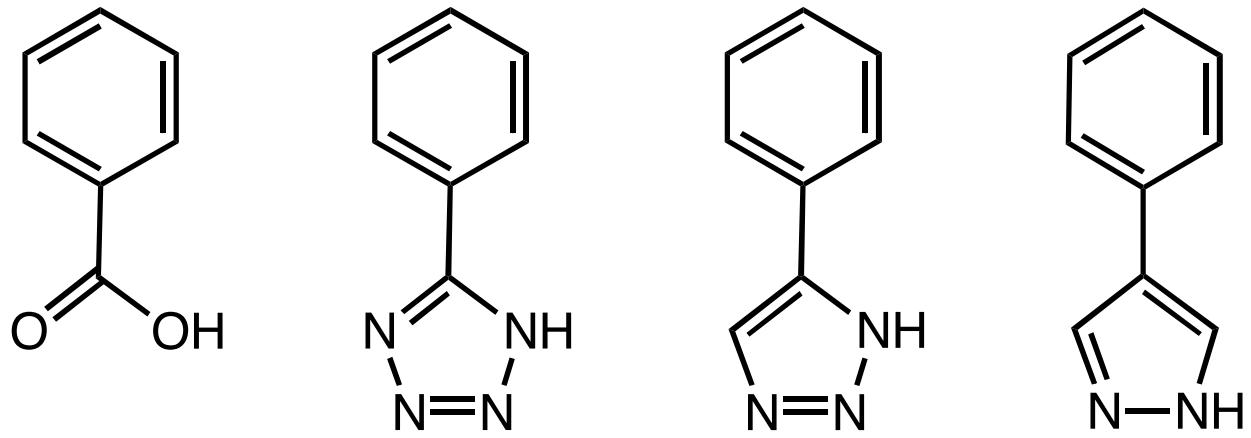
*Bhatia, Myers *Langmuir* **2006**, *22*, 1688

- Need to expose lightweight metal centers that can provide this enthalpy

Dinca, Long *Angew. Chem., Int Ed.* **2008**, *47*, 6766

M	ΔH (kJ/mol)
$Li^+_{(g)}$	21
$Na^+_{(g)}$	10
$K^+_{(g)}$	6
$Ti^+_{(g)}$	37
Cu^+ in chabazite	56
CuCl surface	93
$Cr(CO)_5$	78
$Mo(CO)_5$	81
$Cr(CO)_3(PCy_3)_3$	31
$Mo(CO)_3(PCy_3)_3$	27
$W(CO)_3(PCy_3)_3$	42
$OsH_2(CO)(P^iPr_3)_2$	82

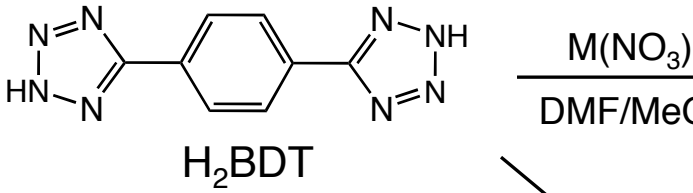
Comparison of pK_a Values



pK_a: **4.2** **4.5** **8.4** **14**

increasing metal-ligand bond strength

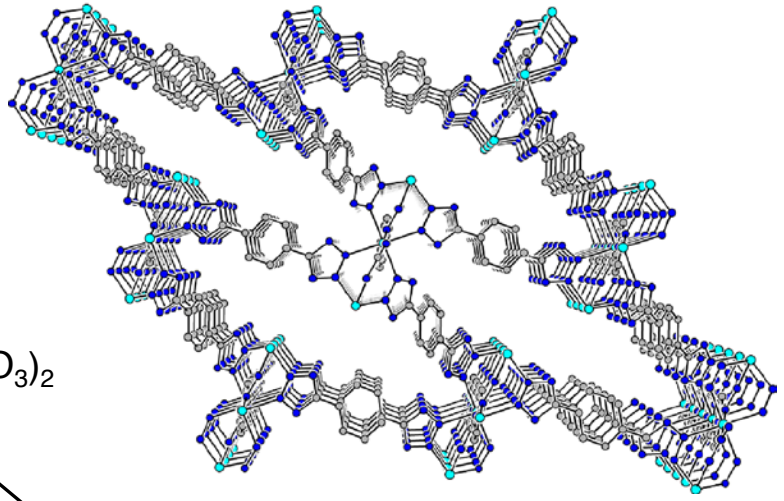
Porous 1,4-Benzeneditetrazolate-Bridged Frameworks



H_2BDT

$M(NO_3)_2$

DMF/MeOH

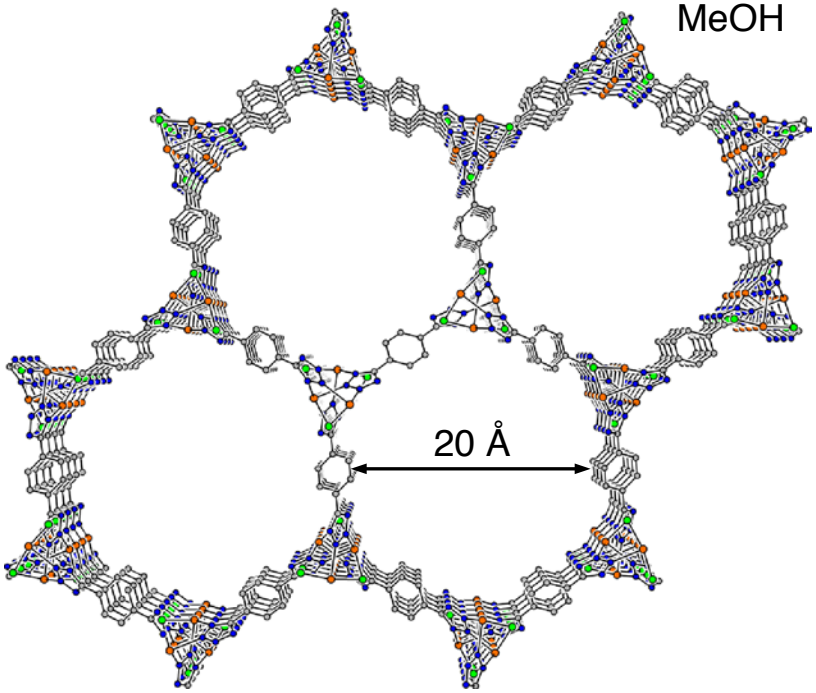


$M_3(BDT)_3$ (M = Mn, Zn)

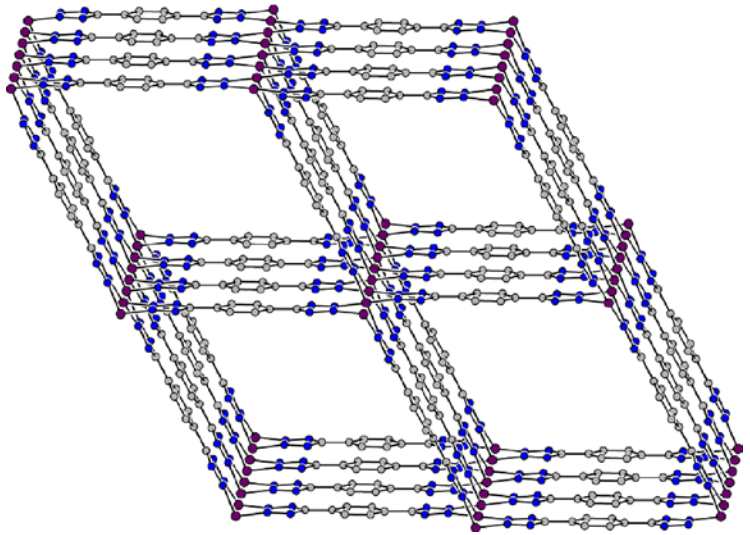
$MnCl_2$ DMF/MeOH

DMF/
MeOH

$Cu(NO_3)_2$



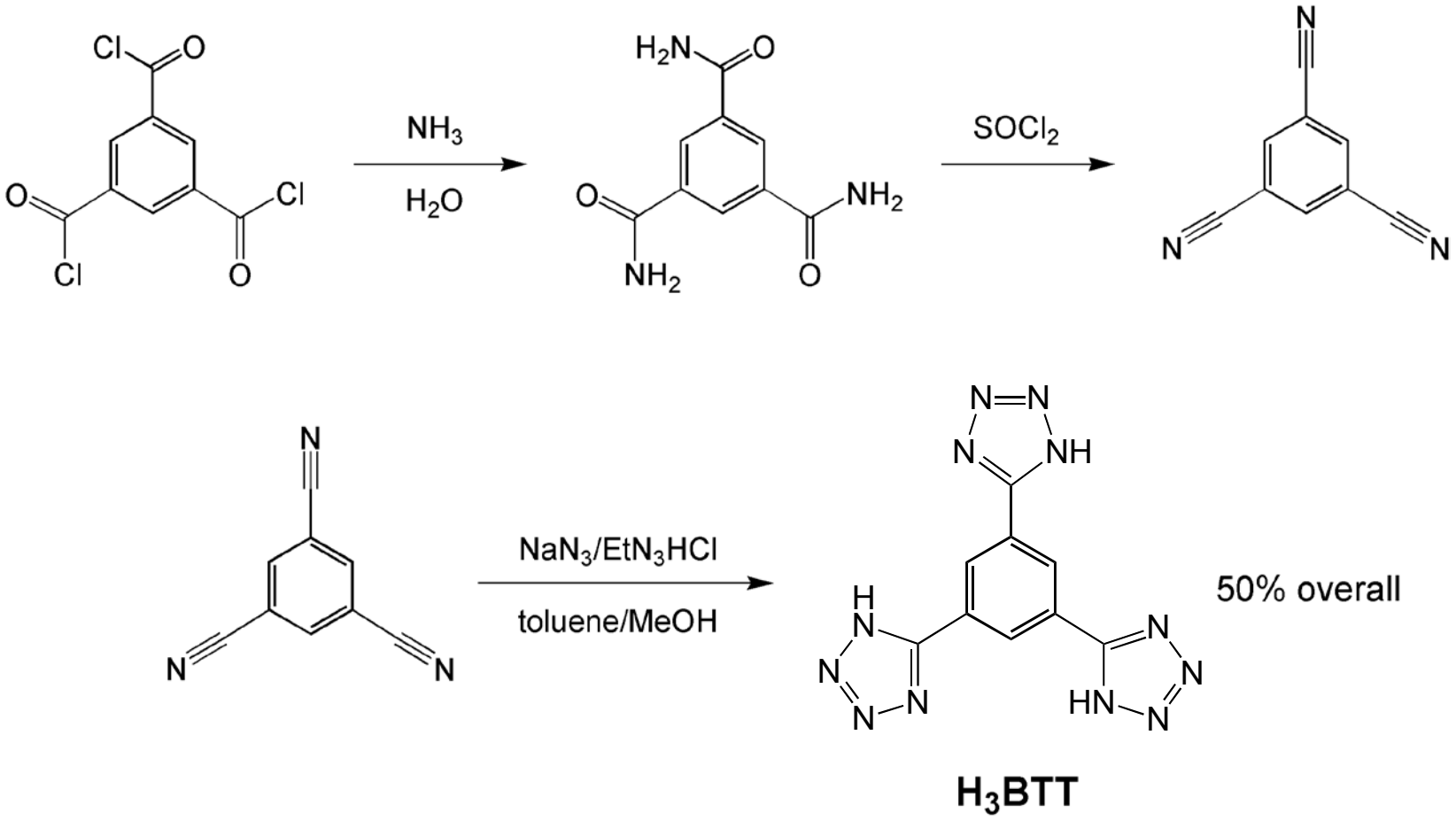
$Mn_2Cl_2(BDT)$



$Cu(BDT)$

Dinca, Long *J. Am. Chem. Soc.* **2006**, *128*, 8904

Synthesis of a Tritopic Tetrazole

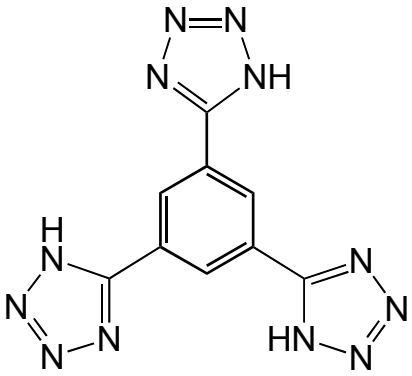


Dinca, Dailly, Liu, Brown, Neumann, Long *J. Am. Chem. Soc.* **2006**, *128*, 16876

A Framework with Exposed Mn^{2+} Coordination Sites

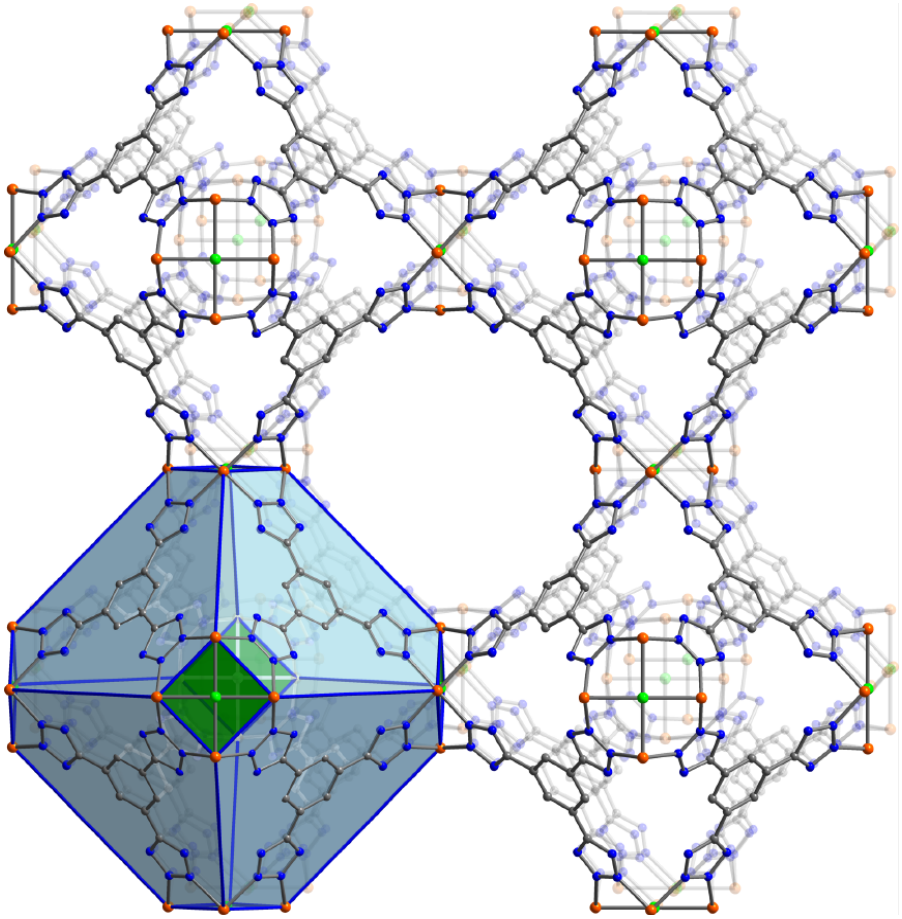
$MnCl_2$

+



H_3BTT

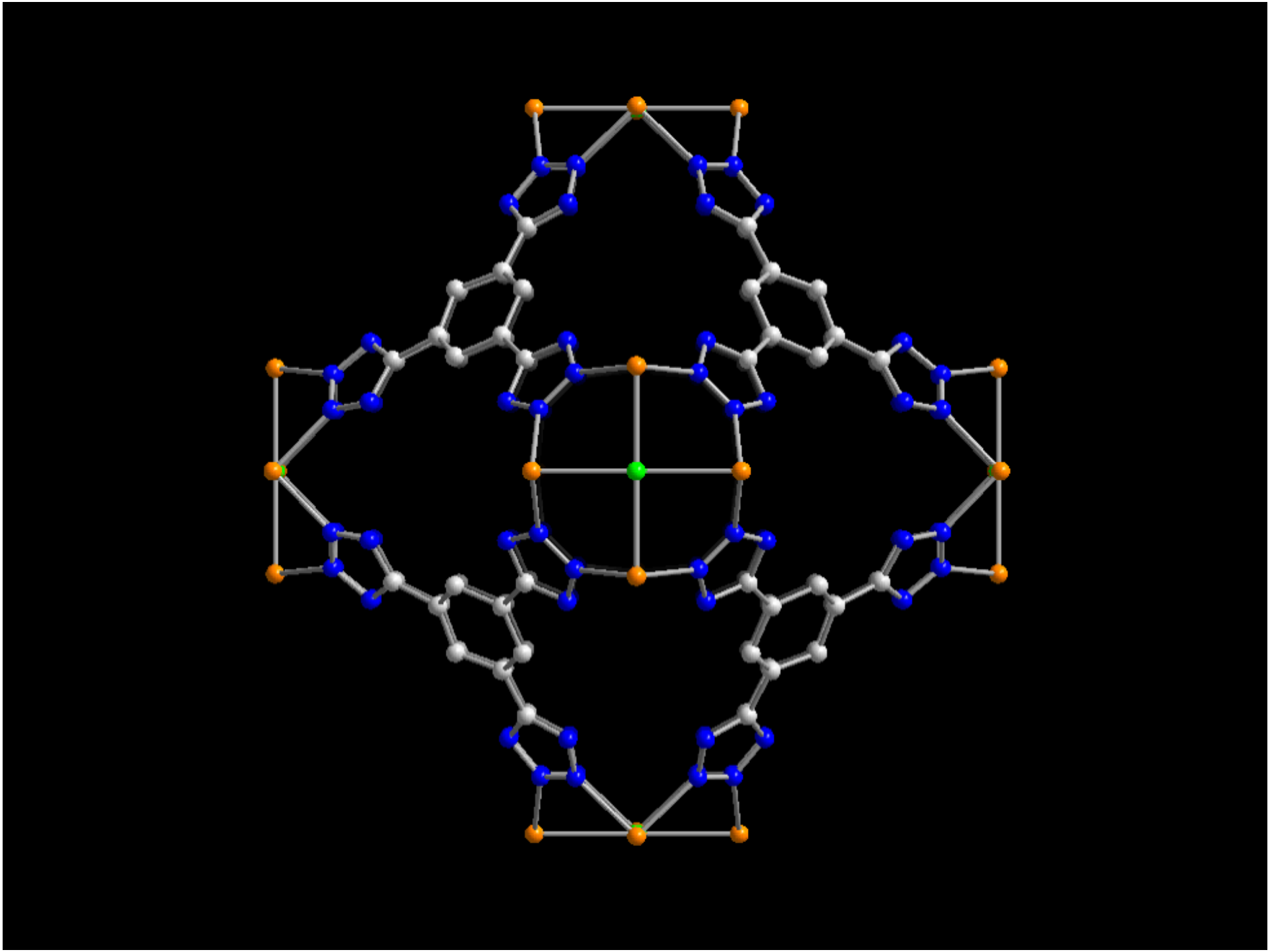
1) 70 °C, DMF/MeOH
2) MeOH soak
3) 150 °C, *in vacuo*



$Mn_3[(Mn_4Cl)_3(BTT)_8]_2 \cdot 20MeOH$

- N_2 adsorption isotherm indicates a BET surface area of 2100 m^2/g

Dinca, Dailly, Liu, Brown, Neumann, Long *J. Am. Chem. Soc.* **2006**, *128*, 16876



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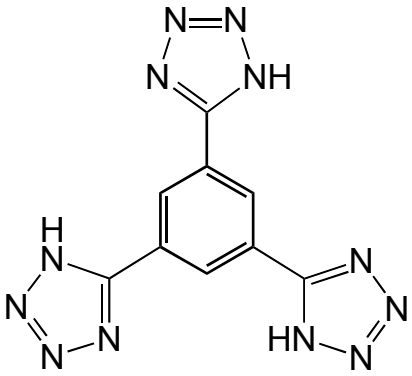
+



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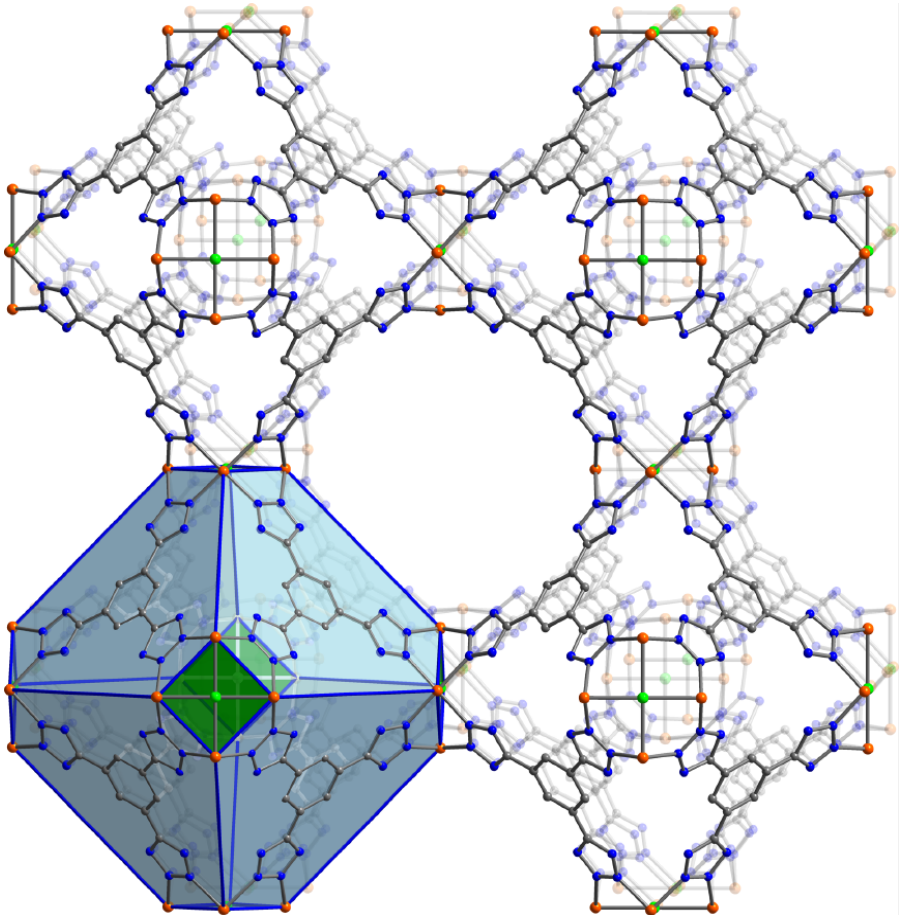

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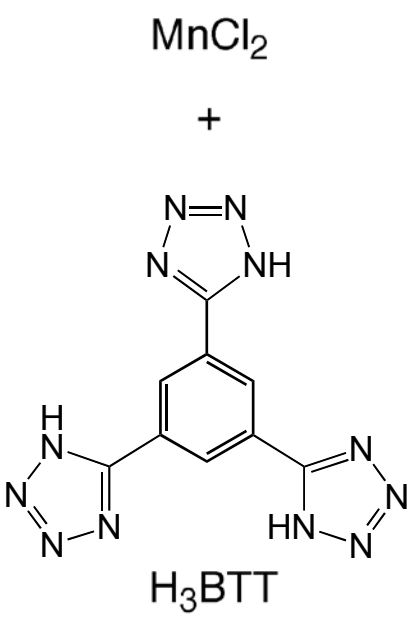
Dinca, Dailly, Liu, Brown, Neumann, Long *J. Am. Chem. Soc.* **2006**, *128*, 16876

A Framework with Exposed Mn^{2+} Coordination Sites



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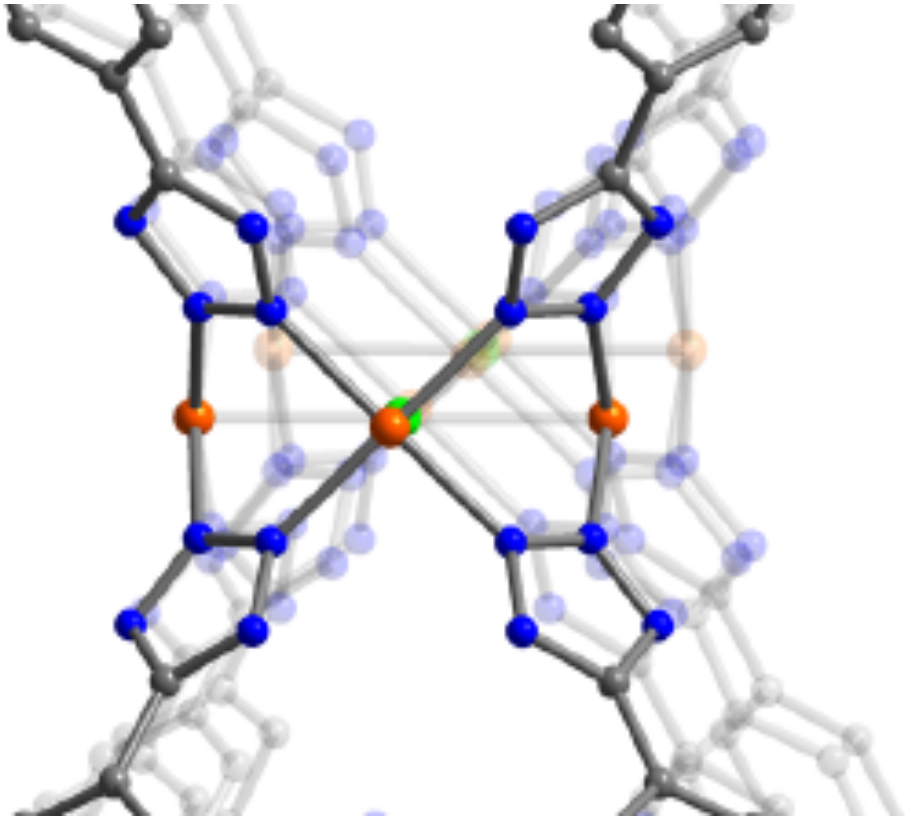
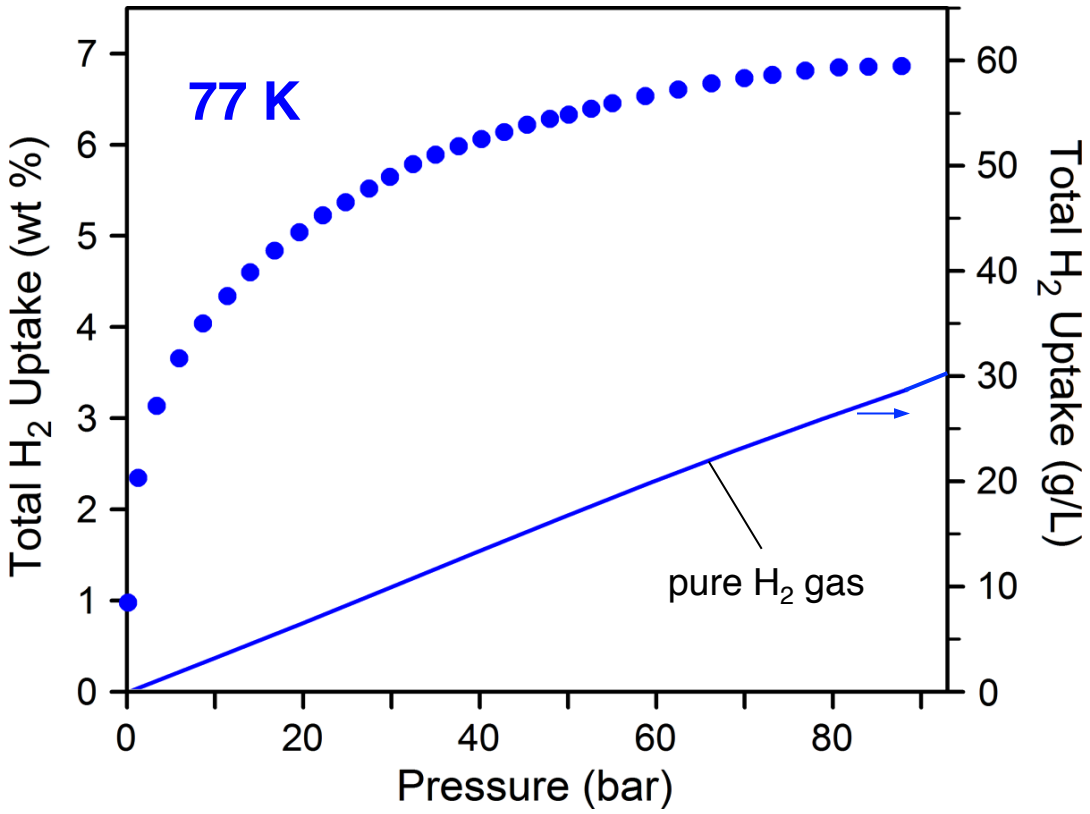


$Mn_3[(Mn_4Cl)_3(BTT)_8]_2 \cdot 20MeOH$

- N_2 adsorption isotherm indicates a BET surface area of 2100 m^2/g

Dinca, Dailly, Liu, Brown, Neumann, Long *J. Am. Chem. Soc.* **2006**, *128*, 16876

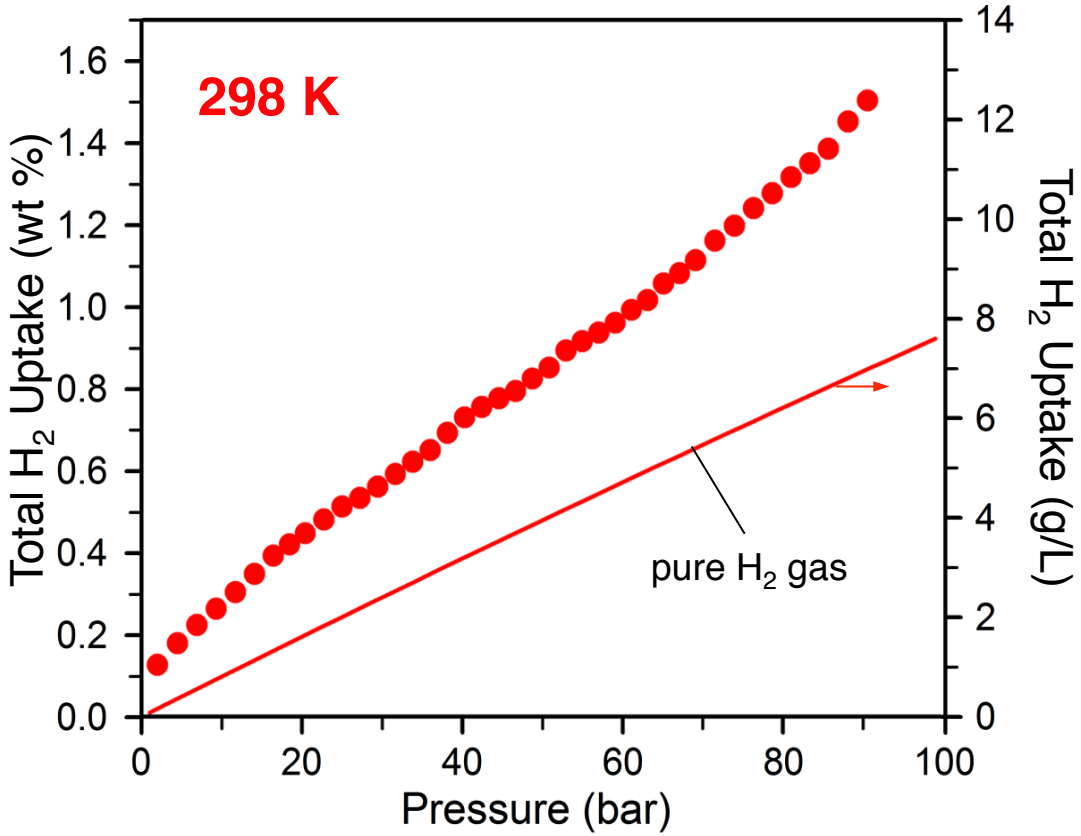
H_2 Uptake in $Mn_3[(Mn_4Cl)_3(BTT)_8]_2 \cdot 20MeOH$



- Adsorption isotherm is fully reversible
- At 90 bar, storage capacity is 6.9 wt % with a density of 60 g/L

Dinca, Dailly, Liu, Brown, Neumann, Long *J. Am. Chem. Soc.* **2006**, *128*, 16876

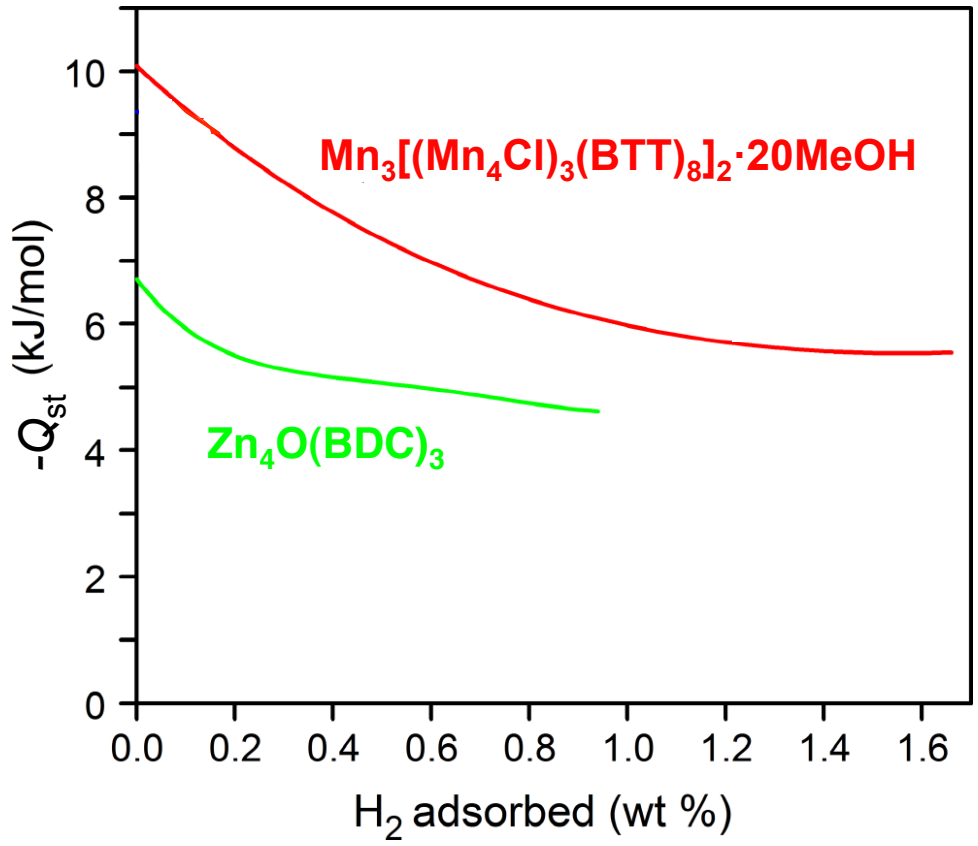
H_2 Uptake in $Mn_3[(Mn_4Cl)_3(BTT)_8]_2 \cdot 20MeOH$



- Expect that approximately twice as much H_2 can be stored in a cylinder at the usual loading pressure of ca. 120 bar

Dinca, Dailly, Liu, Brown, Neumann, Long *J. Am. Chem. Soc.* **2006**, *128*, 16876

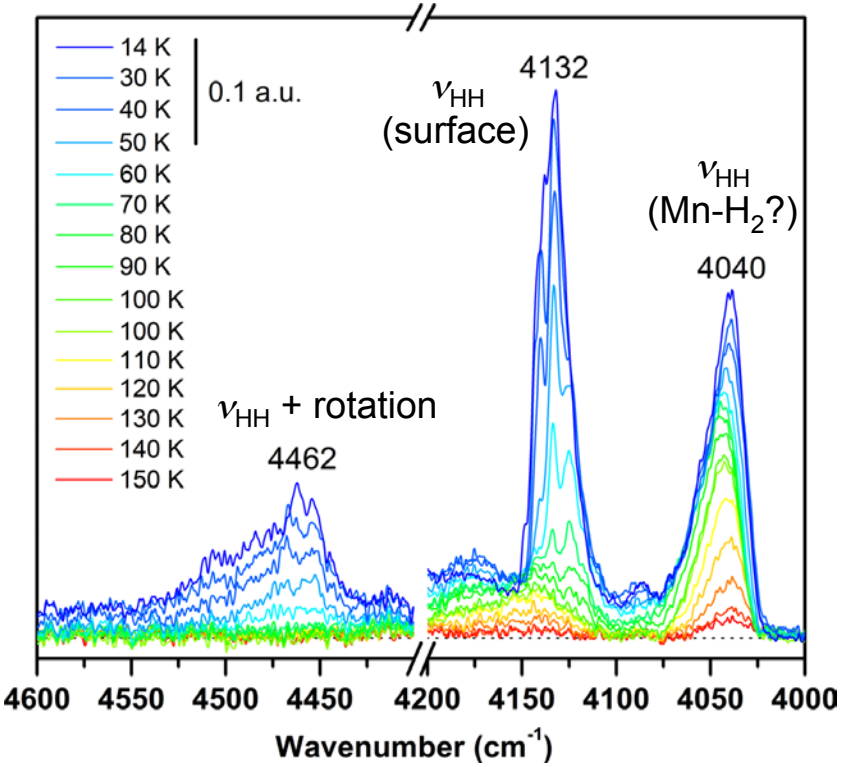
Increased H_2 Adsorption Enthalpy

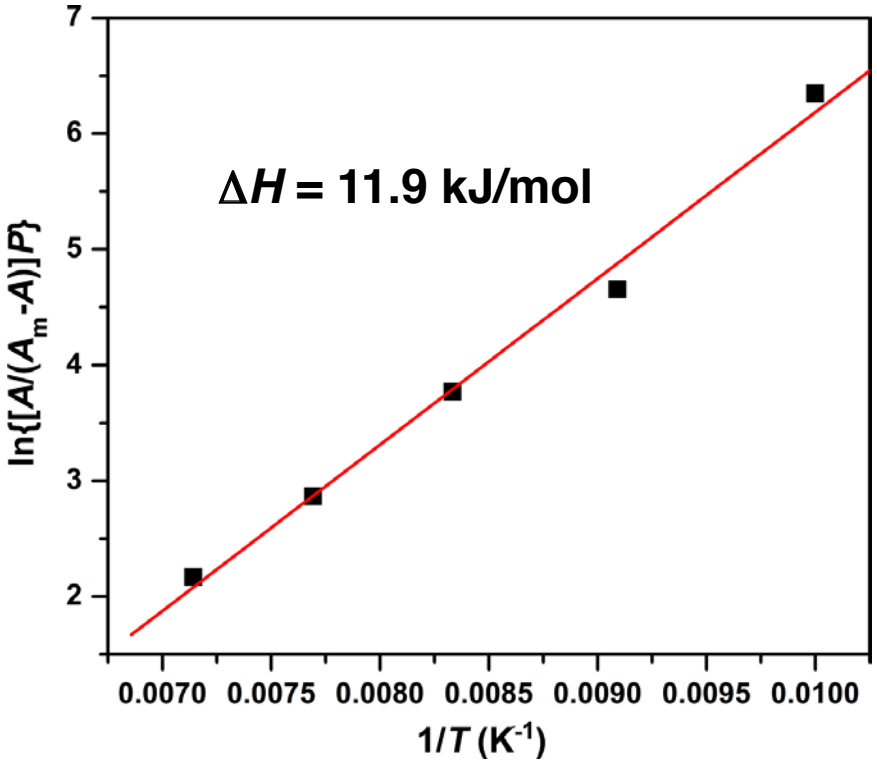


- Higher initial binding enthalpy is likely due to exposed Mn^{II} sites
- Average adsorption enthalpy is still well below target value of 14 kJ/mol

Dinca, Dailly, Liu, Brown, Neumann, Long *J. Am. Chem. Soc.* **2006**, *128*, 16876

Assessing ΔH via Infrared Spectroscopy

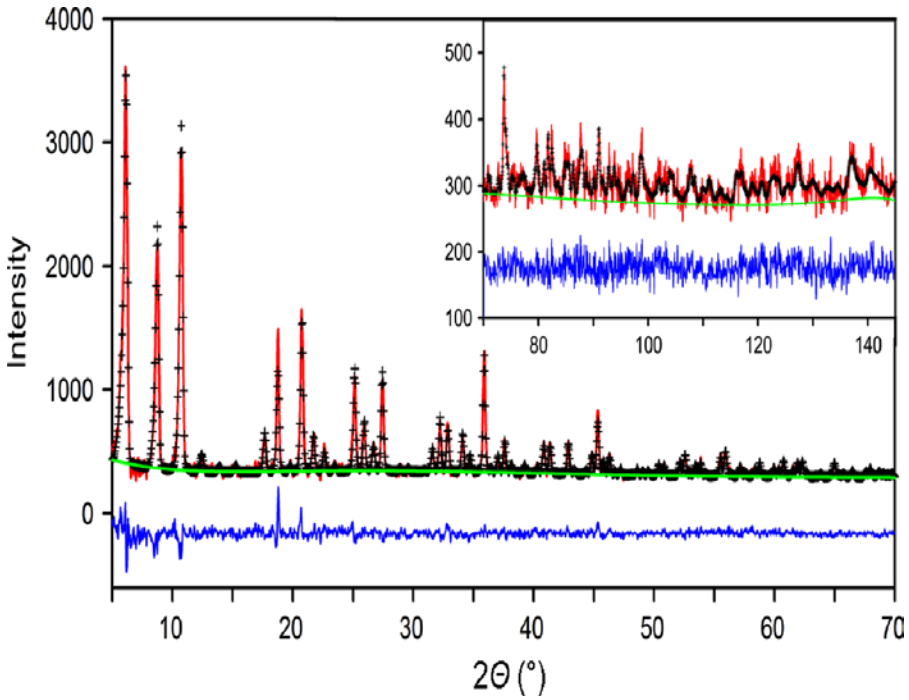


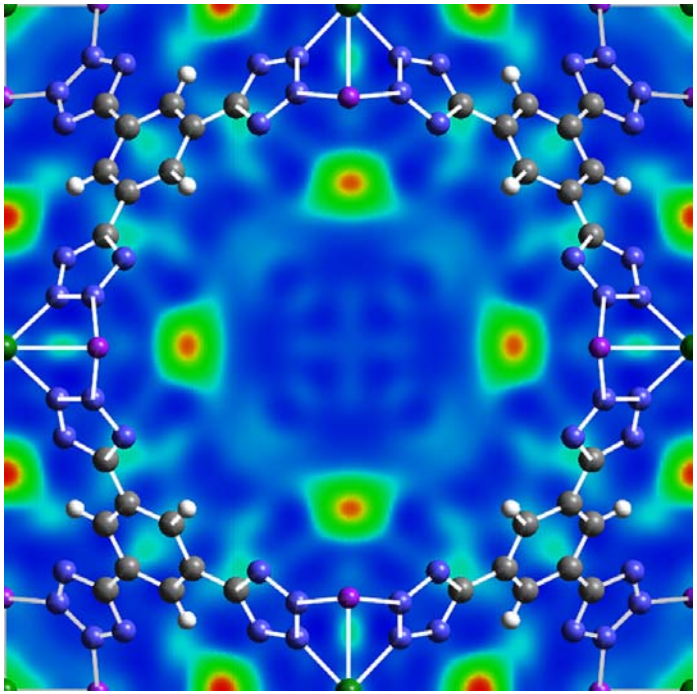


- Peak at 4040 cm^{-1} is the most prominent peak at higher temperatures
- Integration of peak area *A* enables evaluation of ΔH via the Langmuir equation

with O. Zavorotynska and S. Bordiga

Neutron Diffraction Study of D_2 Adsorption at 4 K

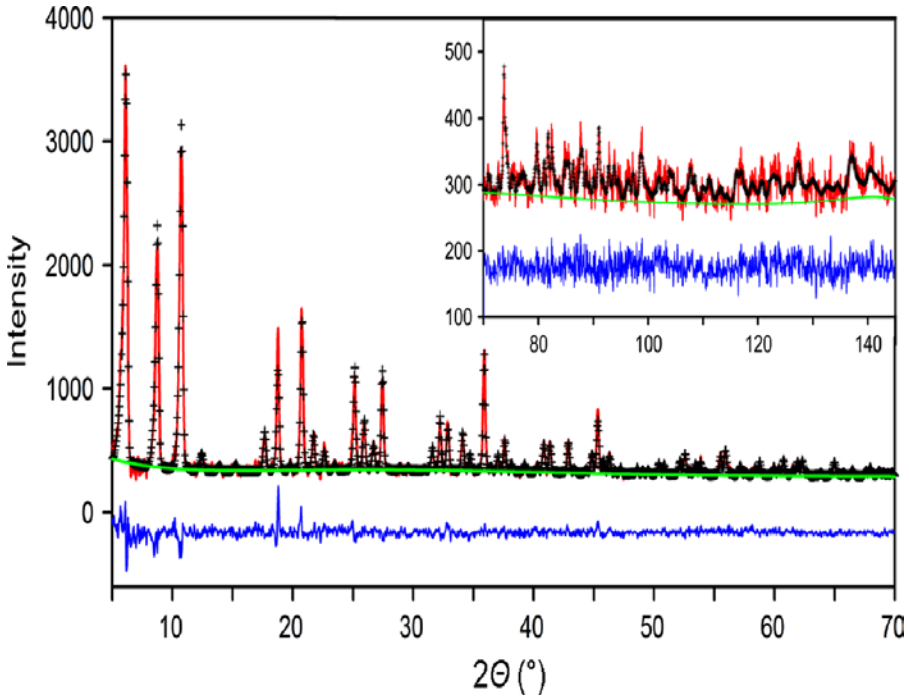


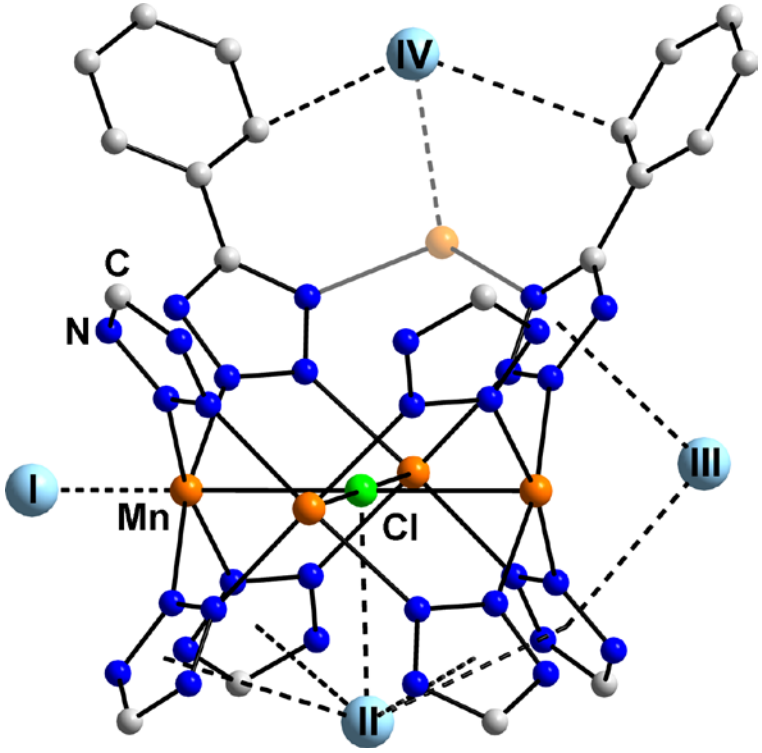


- Strongest D_2 binding occurs at sites I (Mn-D_2 = 2.2 Å) and II (Cl···D_2 = 3.5 Å)
- First direct observation of metal-D_2 interaction in a metal-organic framework

Dinca, Dailly, Liu, Brown, Neumann, Long *J. Am. Chem. Soc.* **2006**, *128*, 16876

Neutron Diffraction Study of D_2 Adsorption





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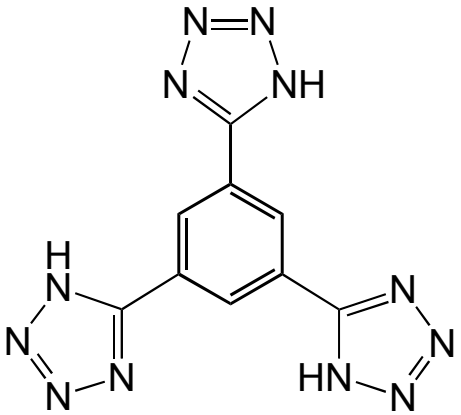
Dinca, Dailly, Liu, Brown, Neumann, Long *J. Am. Chem. Soc.* **2006**, *128*, 16876

Variation of the Metal Center?

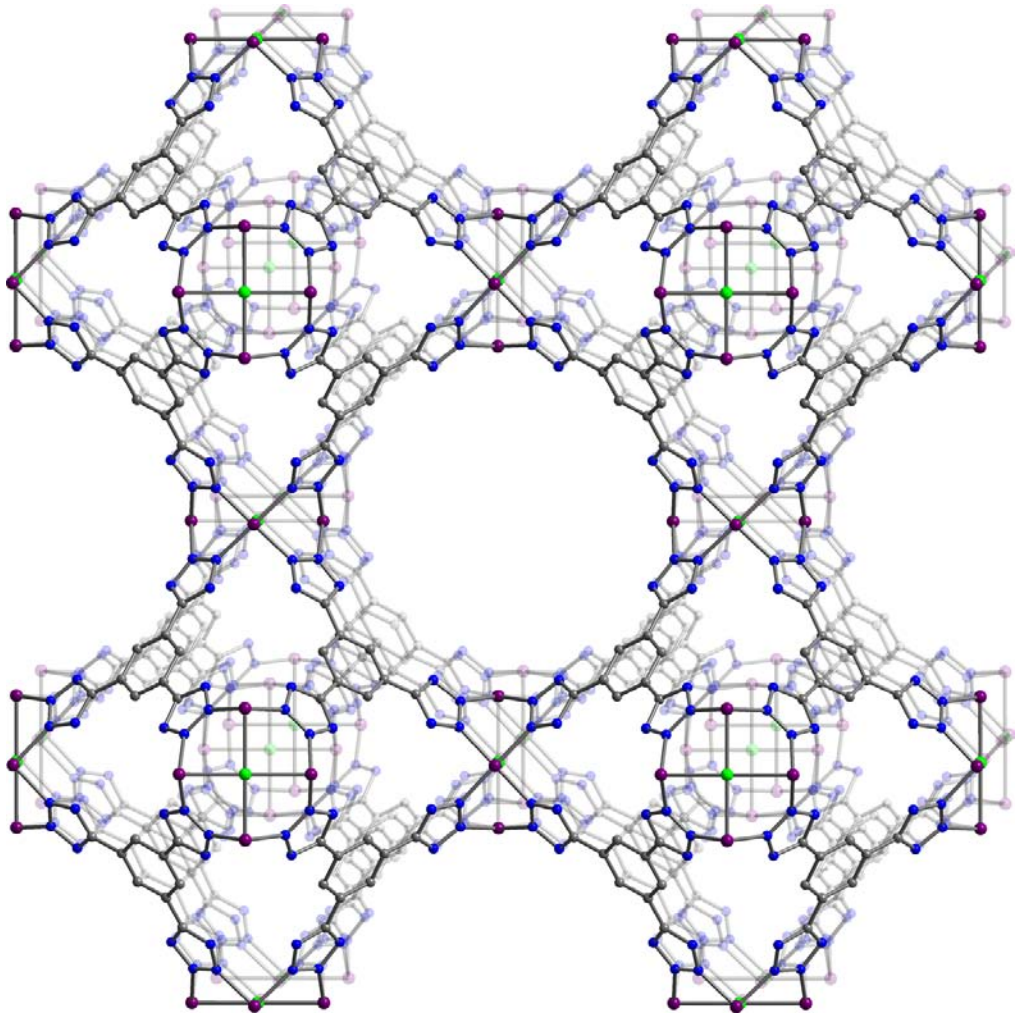
MCl_2

+



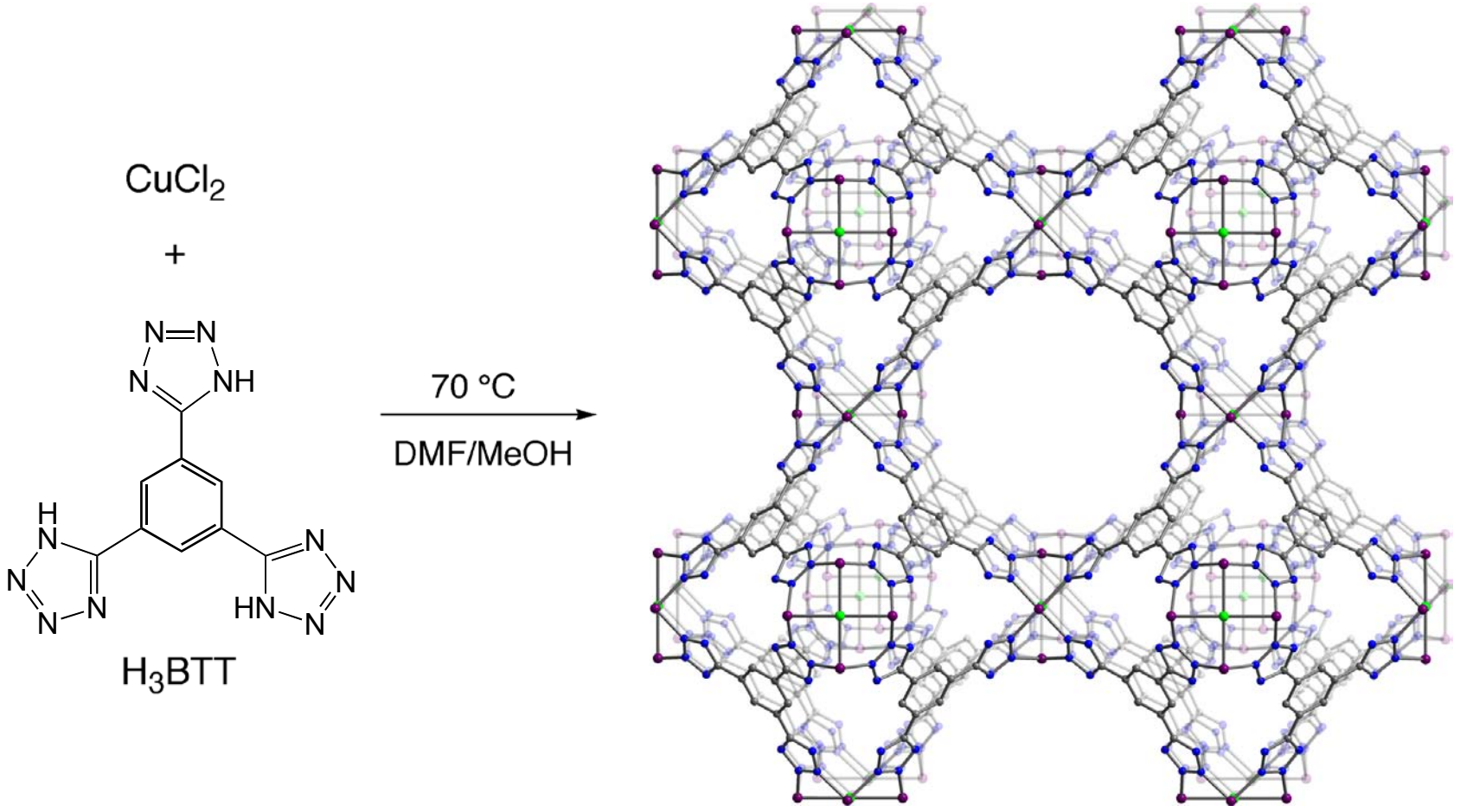
H_3BTT

?



$M_3[(M_4Cl)_3(BTT)_8]_2 \cdot x$solvent

A Copper-Based Sodalite Framework

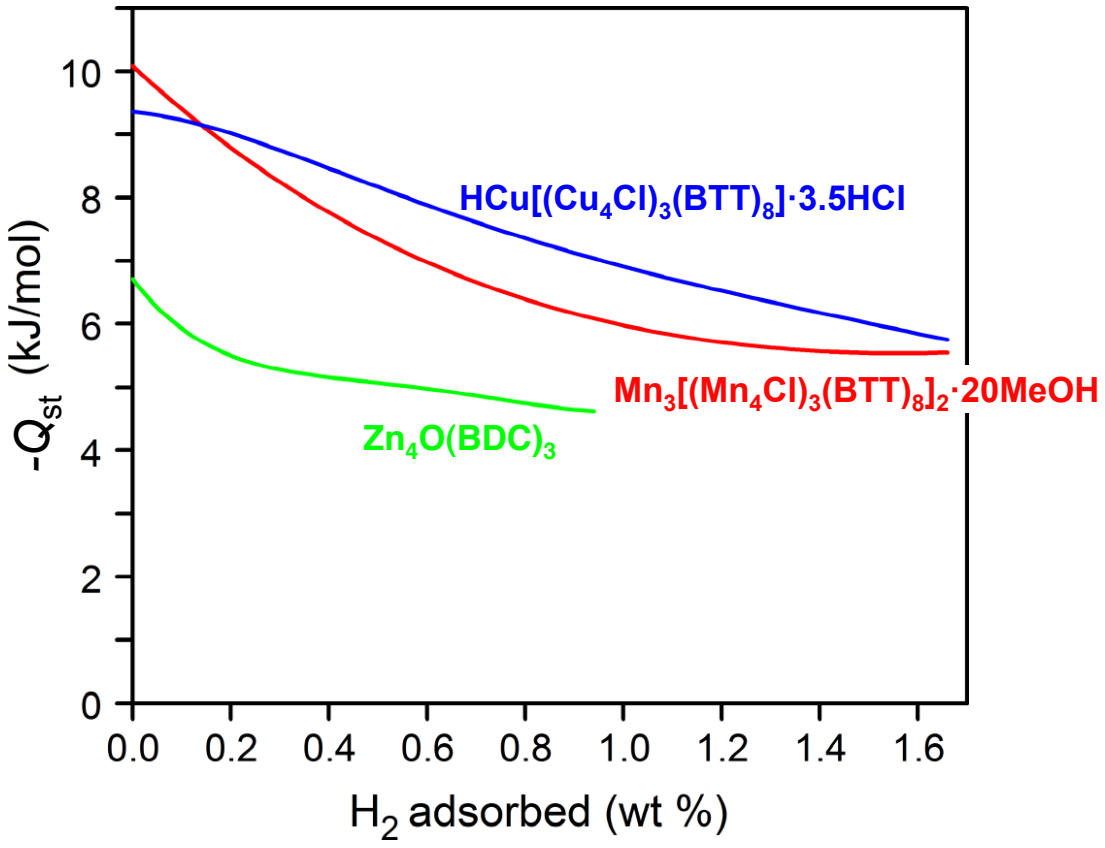


$HCu[(Cu_4Cl)_3(BTT)_8]\cdot 3.5HCl\cdot 12DMF\cdot 24H_2O\cdot 16MeOH$

- Washing with methanol and heating under dynamic vacuum gives **fully desolvated** material

Dinca, Han, Liu, Brown, Dailly, Long *Angew. Chem. Int. Ed.* **2007**, *46*, 1419

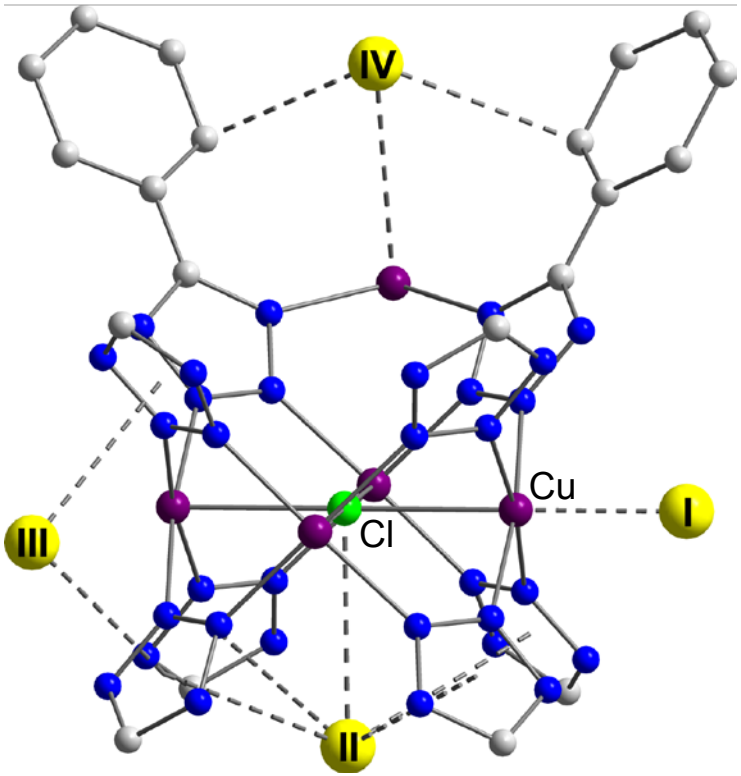
Comparison of H_2 Adsorption Enthalpies



- H_2 storage capacity for Cu phase is similar to that of Mn analogue
- Infrared spectra indicate a site-specific binding enthalpy of -10.4 kJ/mol

Dinca, Han, Liu, Brown, Dailly, Long *Angew. Chem. Int. Ed.* **2007**, *46*, 1419

Neutron Study of D_2 Adsorption in Cu-BTT Framework



D_2 loading	site I	site II	site III	site IV
6	4.4(1)	3.1(1)	0	0
12	7.8(1)	5.2(1)	0	0
18	10.7(1)	5.7(1)	1.2(1)	0
30	11.1(2)	5.5(1)	8.0(2)	4.3(2)
sat.	12	6	24	24

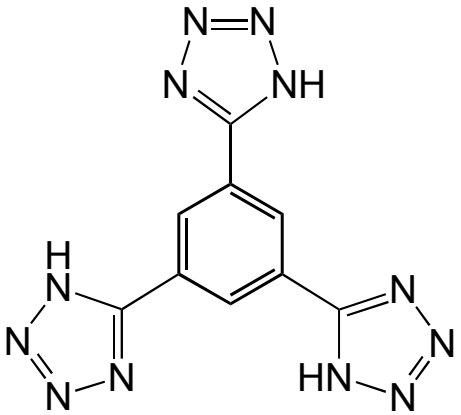
- Strongest D_2 binding occurs at sites I (Cu-D_2 = 2.5 Å) and II (Cl···D_2 = 3.5 Å)
- Site I nearly saturates at the highest loadings, indicating complete desolvation

Dinca, Han, Liu, Brown, Dailly, Long *Angew. Chem. Int. Ed.* **2007**, *46*, 1419

Variation of the Metal Center?

MCl_2

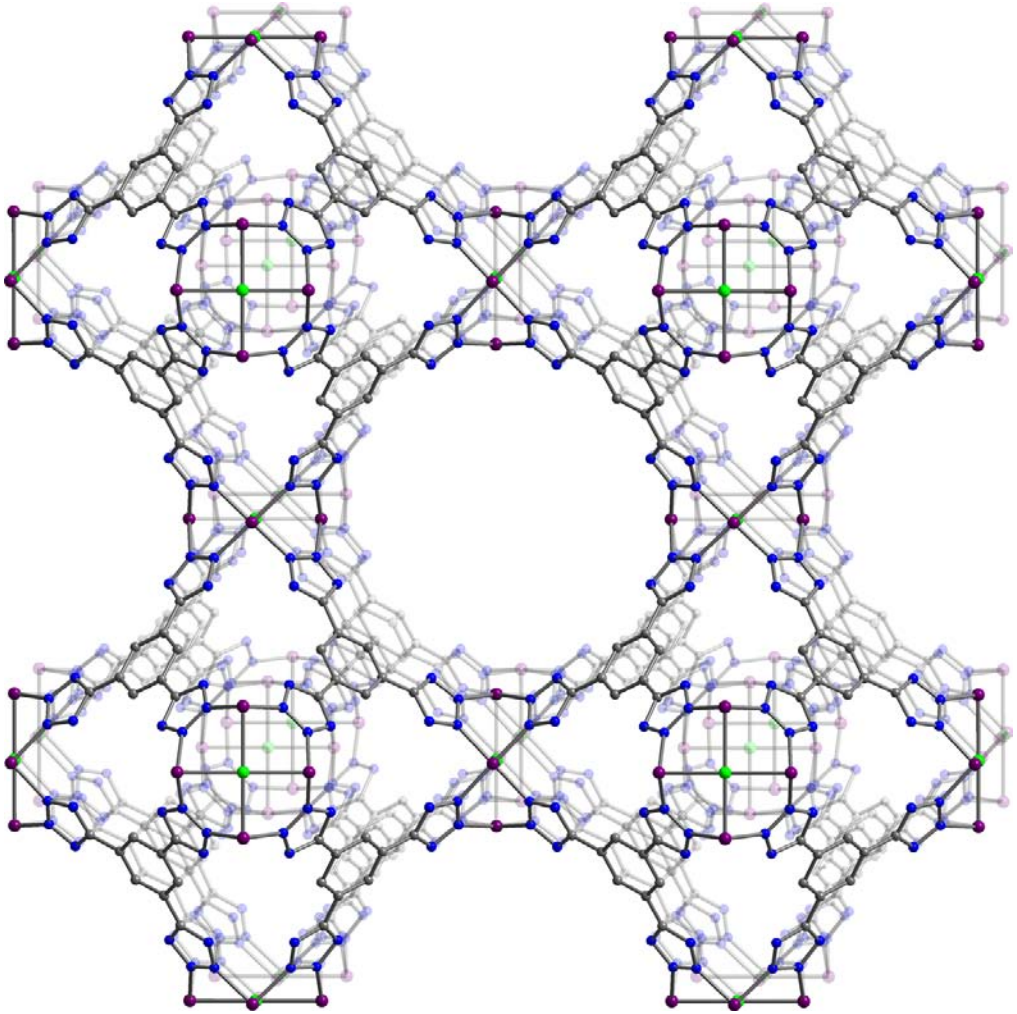
+



H_3BTT

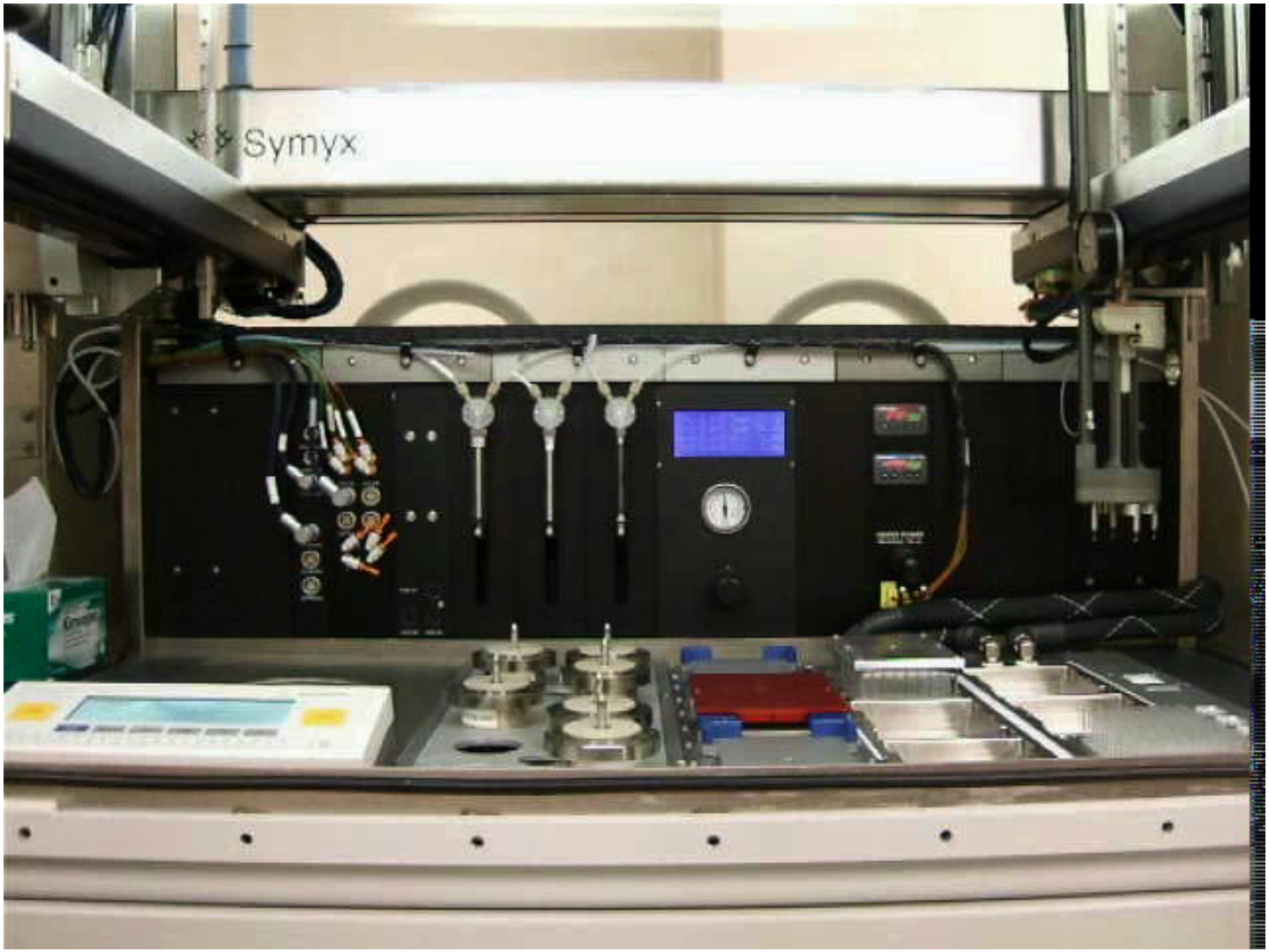
?

reactant ratio?
solvent?
cosolvent?
acid?

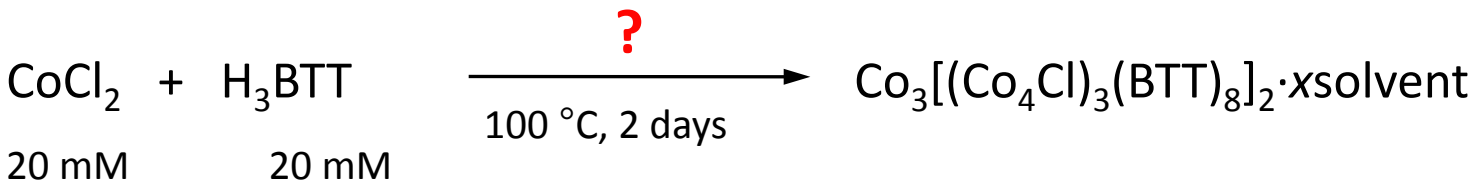


$M_3[(M_4Cl)_3(BTT)_8]_2 \cdot x$solvent

High-Throughput Synthesis and Screening



Screening Acid Concentration and Solvent



100 mM $HCl_{(MeOH)}$

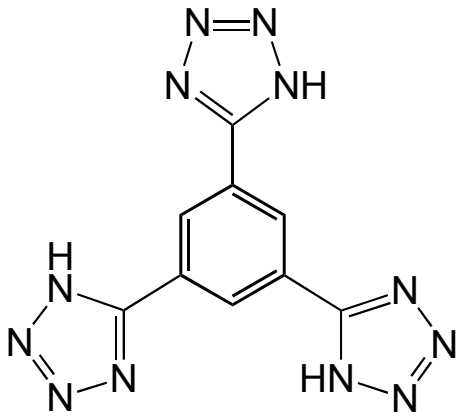
total of 0.55 mL of solvent per vial

$CoCl_2$	No HCl	DMF	DMF/ DEF	DMF/ DMSO	DMF/ MeOH	DMF/ EtOH	DMF/ 1-PrOH	DMF/ Acetone	DMF/ H_2O	DMF/ Dioxane	DMF/ CH_3CN
$CoCl_2$	HCl 0.02mL	DMF	DMF/ DEF	DMF/ DMSO	DMF/ MeOH	DMF/ EtOH	DMF/ 1-PrOH	DMF/ Acetone	DMF/ H_2O	DMF/ Dioxane	DMF/ CH_3CN
$CoCl_2$	HCl 0.05mL	DMF	DMF/ DEF	DMF/ DMSO	DMF/ MeOH	DMF/ EtOH	**DMF/ 1-PrOH**	DMF/ Acetone	DMF/ H_2O	DMF/ Dioxane	DMF/ CH_3CN
$CoCl_2$	HCl 0.1mL	DMF	DMF/ DEF	DMF/ DMSO	DMF/ MeOH	DMF/ EtOH	DMF/ 1-PrOH	DMF/ Acetone	DMF/ H_2O	DMF/ Dioxane	DMF/ CH_3CN
$CoCl_2$	No HCl	DEF	DEF/ DMSO	DEF/ MeOH	DEF/ EtOH	DEF/ 1-PrOH	DEF/ Acetone	DEF/ H2O	DEF/ Dioxane	DEF/ CH_3CN	
$CoCl_2$	HCl 0.02mL	DEF	DEF/ DMSO	DEF/ MeOH	DEF/ EtOH	DEF/ 1-PrOH	DEF/ Acetone	DEF/ H2O	DEF/ Dioxane	DEF/ CH_3CN	
$CoCl_2$	HCl 0.05mL	DEF	DEF/ DMSO	DEF/ MeOH	DEF/ EtOH	DEF/ 1-PrOH	DEF/ Acetone	DEF/ H2O	DEF/ Dioxane	DEF/ CH_3CN	
$CoCl_2$	HCl 0.1mL	DEF	DEF/ DMSO	DEF/ MeOH	DEF/ EtOH	DEF/ 1-PrOH	DEF/ Acetone	DEF/ H2O	DEF/ Dioxane	DEF/ CH_3CN	

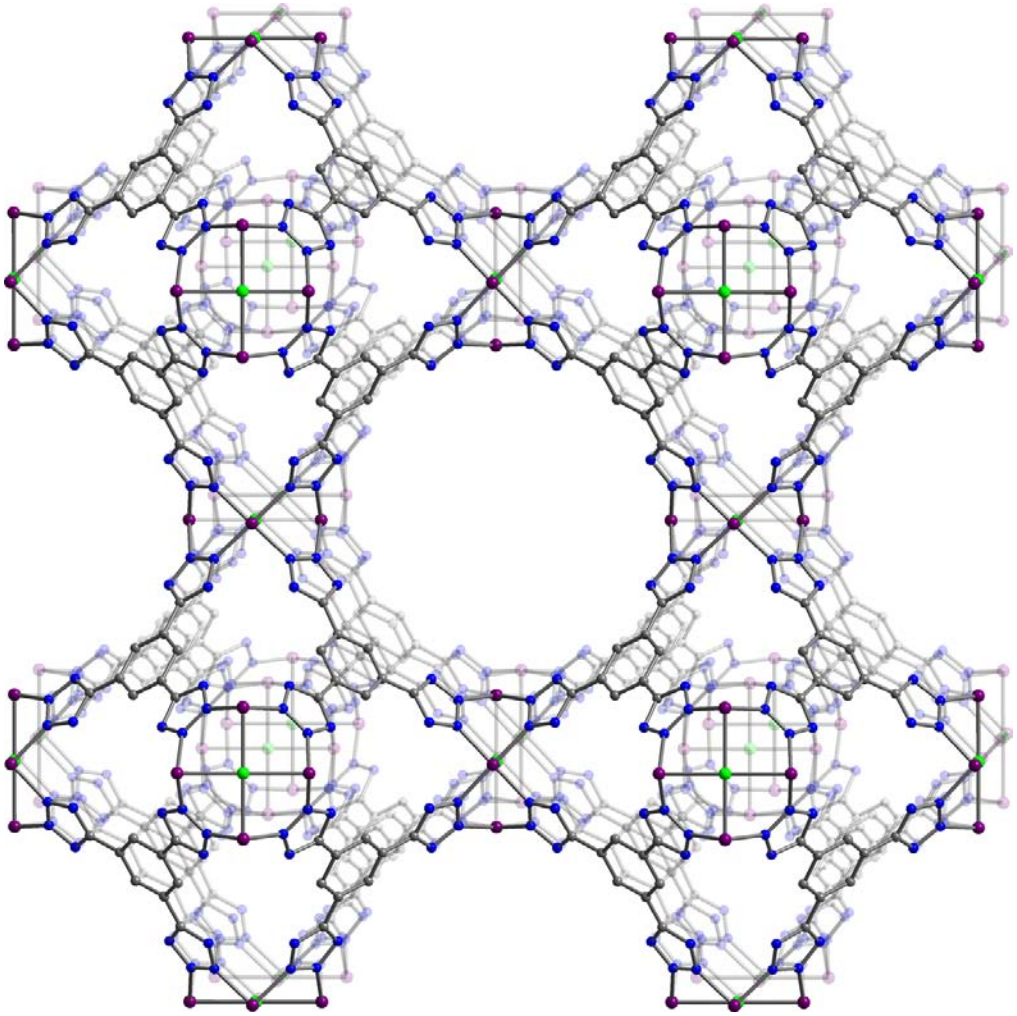
Variation of the Metal Center

MCl_2

+



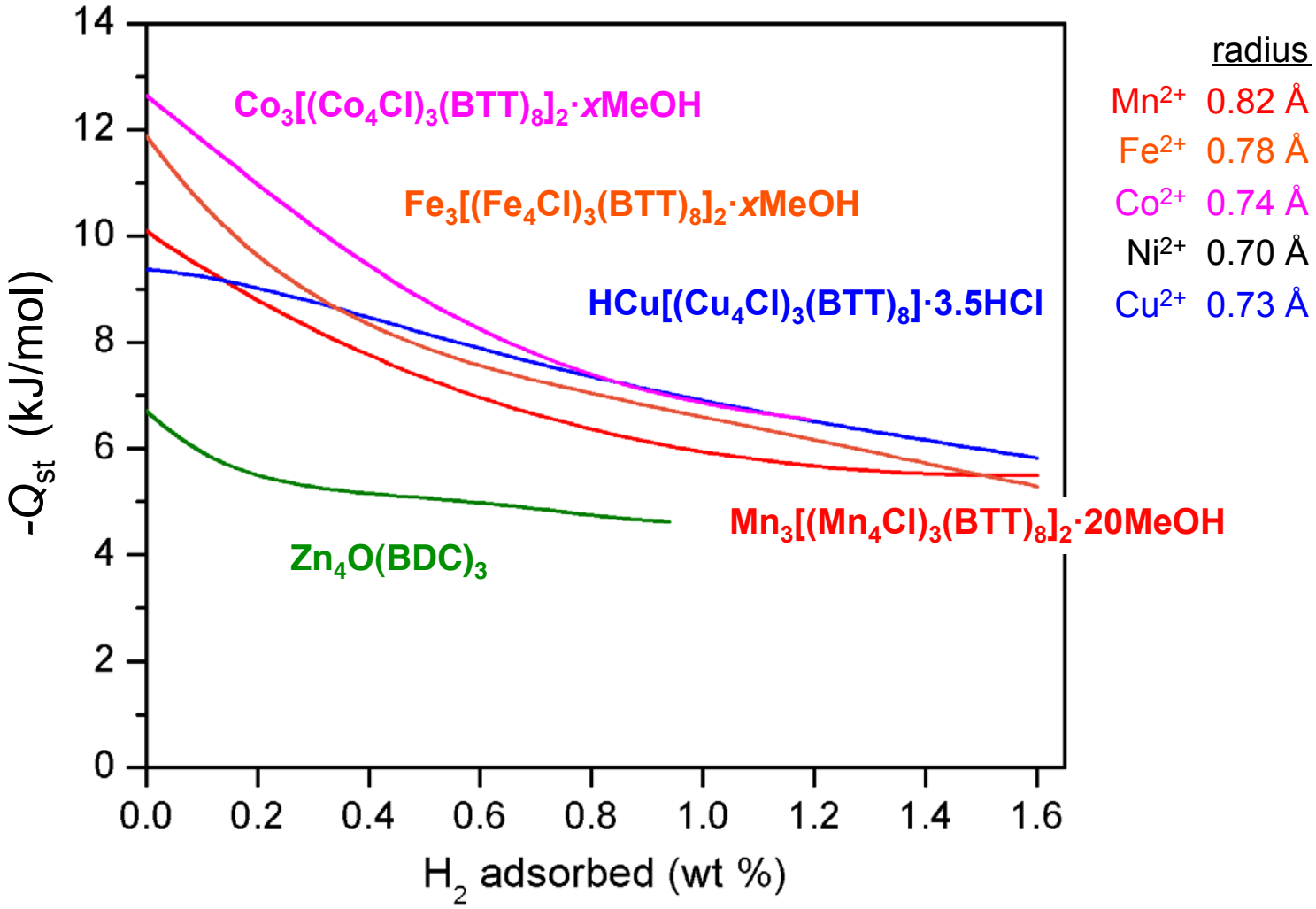
H_3BTT



$M_3[(M_4Cl)_3(BTT)_8]_2 \cdot x$solvent

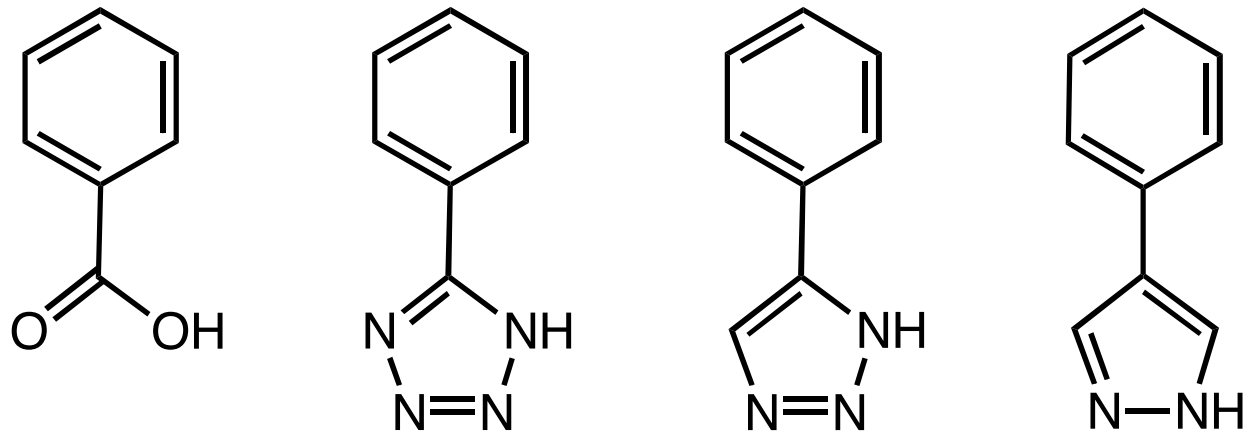
(M = Mg, Ca, Cr, Mn, Fe, Co, Ni, Cu, Cd)

Variation of Heat of H_2 Adsorption with Metal



- More complete solvent evacuation should increase -Q_{st} at higher H_2 loading

Comparison of pK_a Values



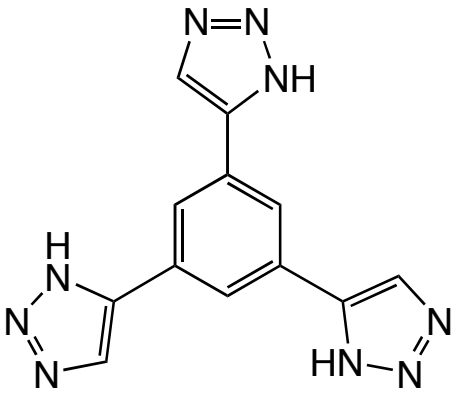
pK_a: **4.2** **4.5** **8.4** **14**

increasing metal-ligand bond strength

A Triazolate-Bridged Sodalite Framework

$CuCl_2$

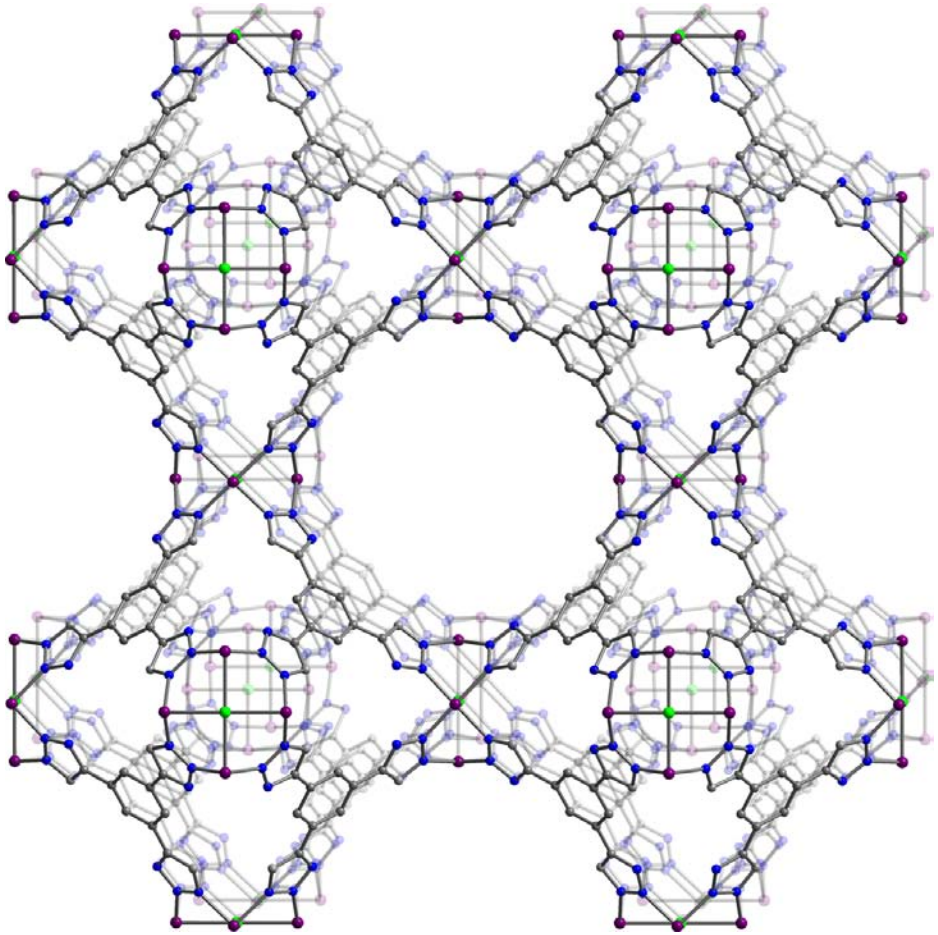
+



H_3BTTri

100 °C

$DMF/HCl_{(aq)}$



$HCu[(Cu_4Cl)_3(BTTri)_8]\cdot 33DMF\cdot 40H_2O$

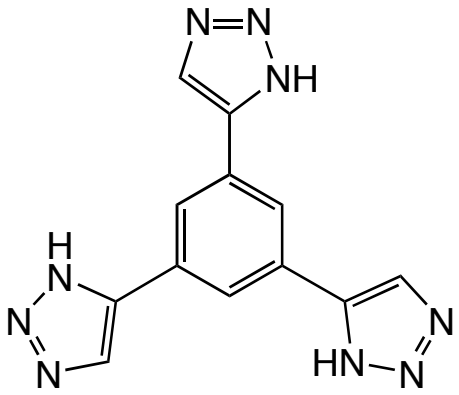
- Unlike the teztrazolate analogue, the triazolate framework is **air- and water-stable**

Demessence, D'Alessandro, Foo, Long *J. Am. Chem. Soc.* **2009**, *131*, 8784

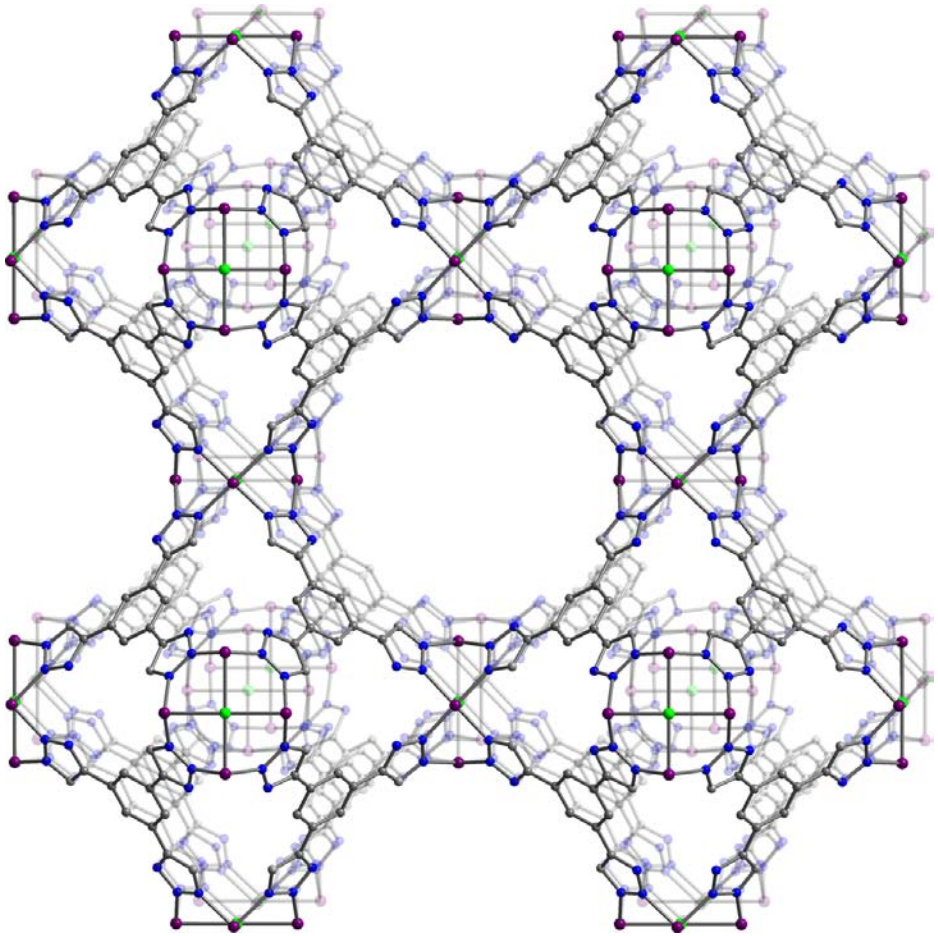
Variation of the Metal Center

MCl_2

+



H_3BTTri

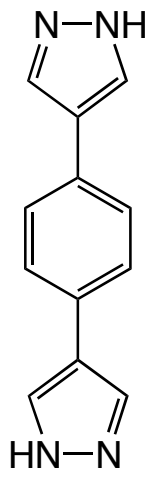


$M_3[(M_4Cl)_3(BTTri)_8]_2 \cdot x$solvent
(M = Mn, Fe, Co, Ni, Cu)

A 1,4-Benzenedipyrazolate-Bridged Framework

$Co(CF_3SO_3)_2$

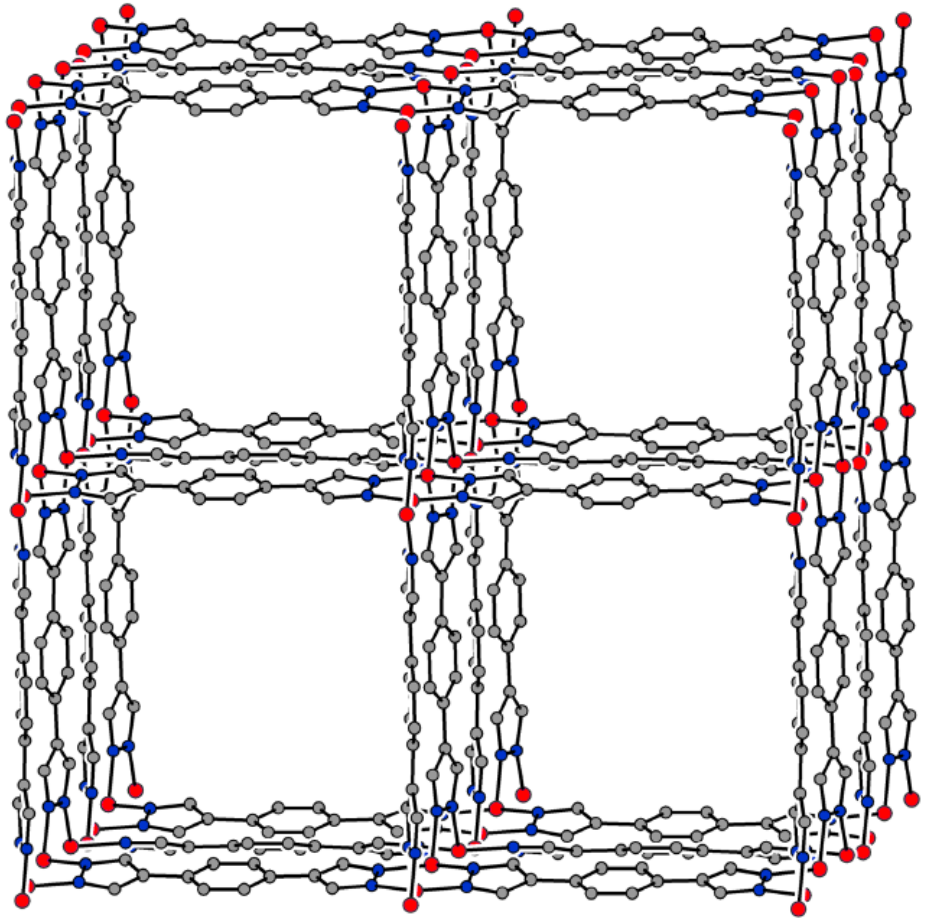
+



H_2BDP

130 °C, 6 days

DEF

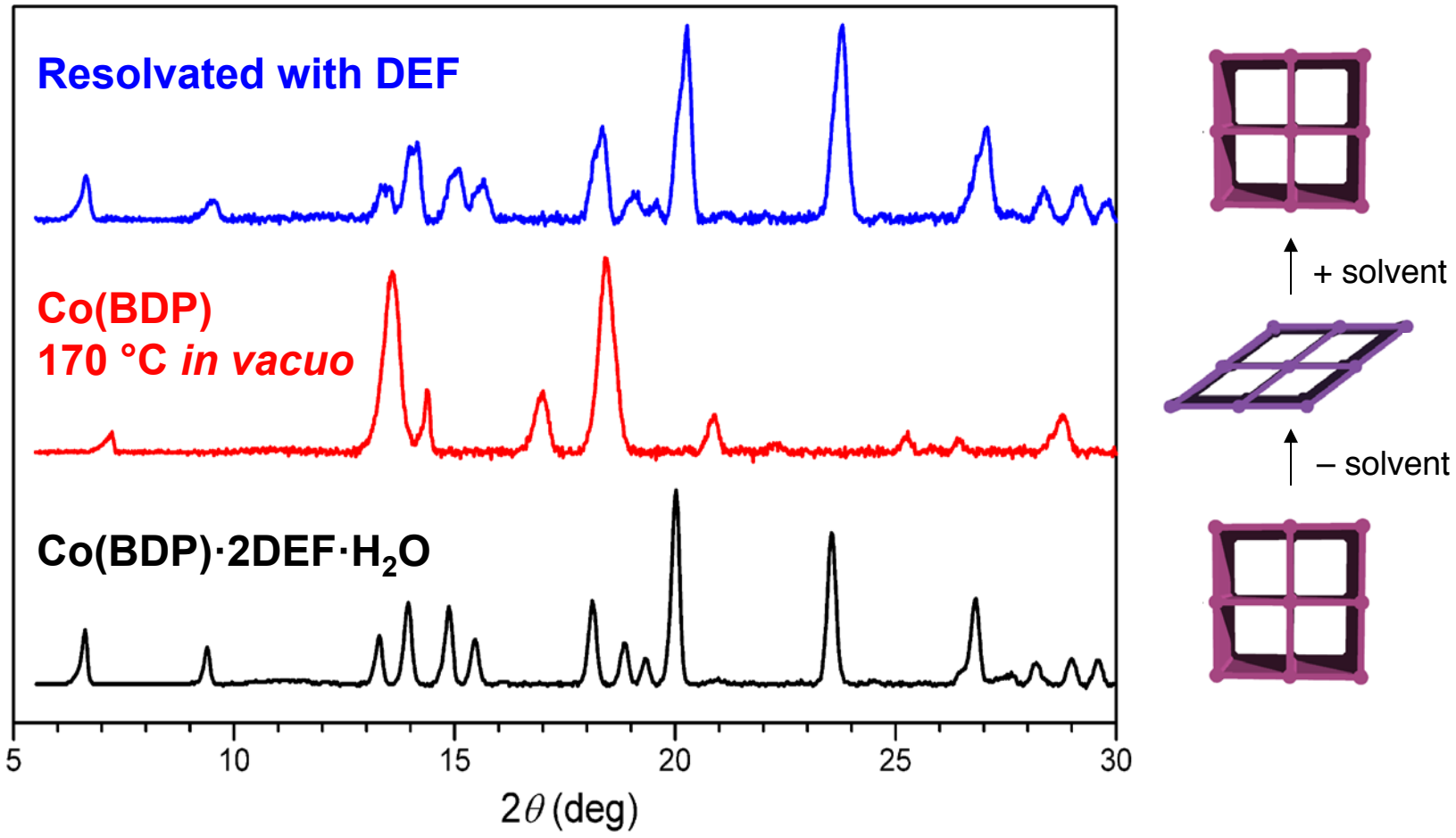


$Co(BDP)\cdot 2DEF\cdot H_2O$

- Extreme conditions required for obtaining pure crystalline product

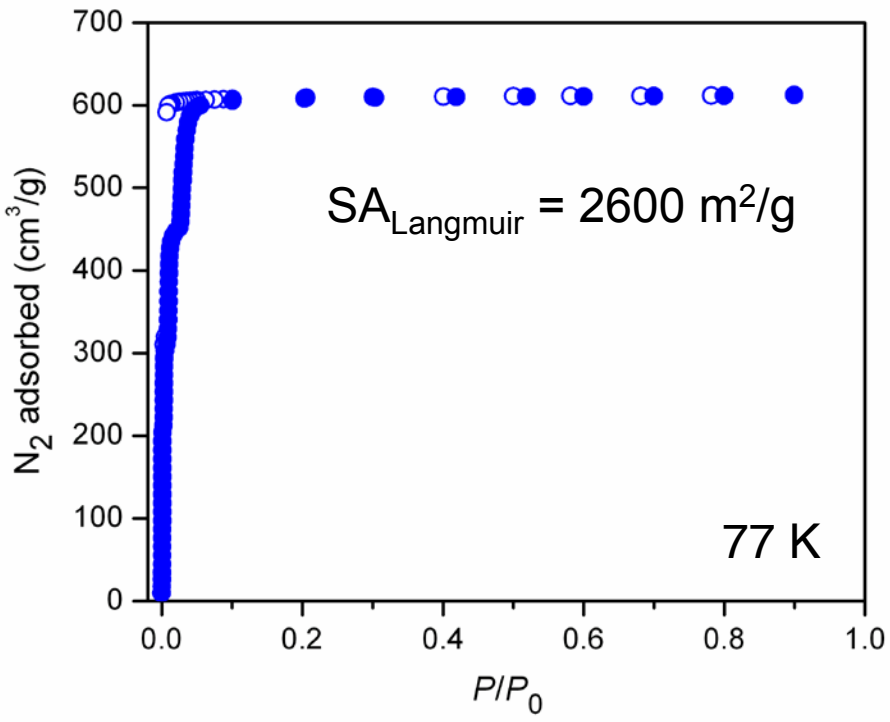
Choi, Dinca, Long *J. Am. Chem. Soc.* **2008**, *130*, 7848

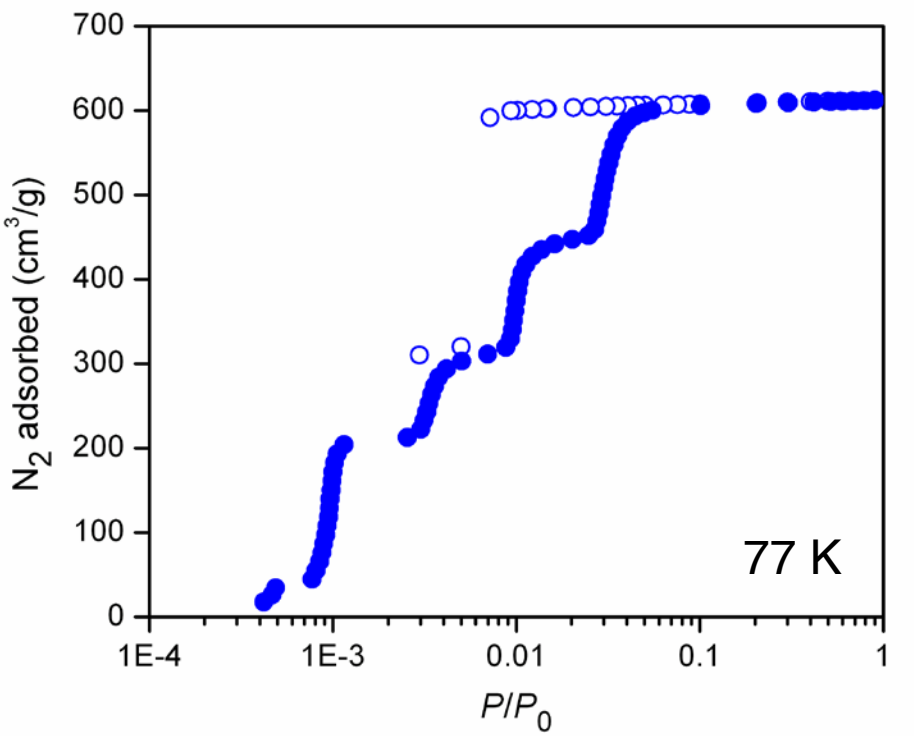
Reversible Structure Change Upon Desolvation



- Results indicate accordion-style flexing of framework, similar to observations by Férey and coworkers for carboxylated-bridged frameworks

Stepwise N_2 Adsorption in Co(BDP)





- Highest surface area yet observed for a flexible metal-organic framework
- Five distinct steps observed, suggesting activated pore opening

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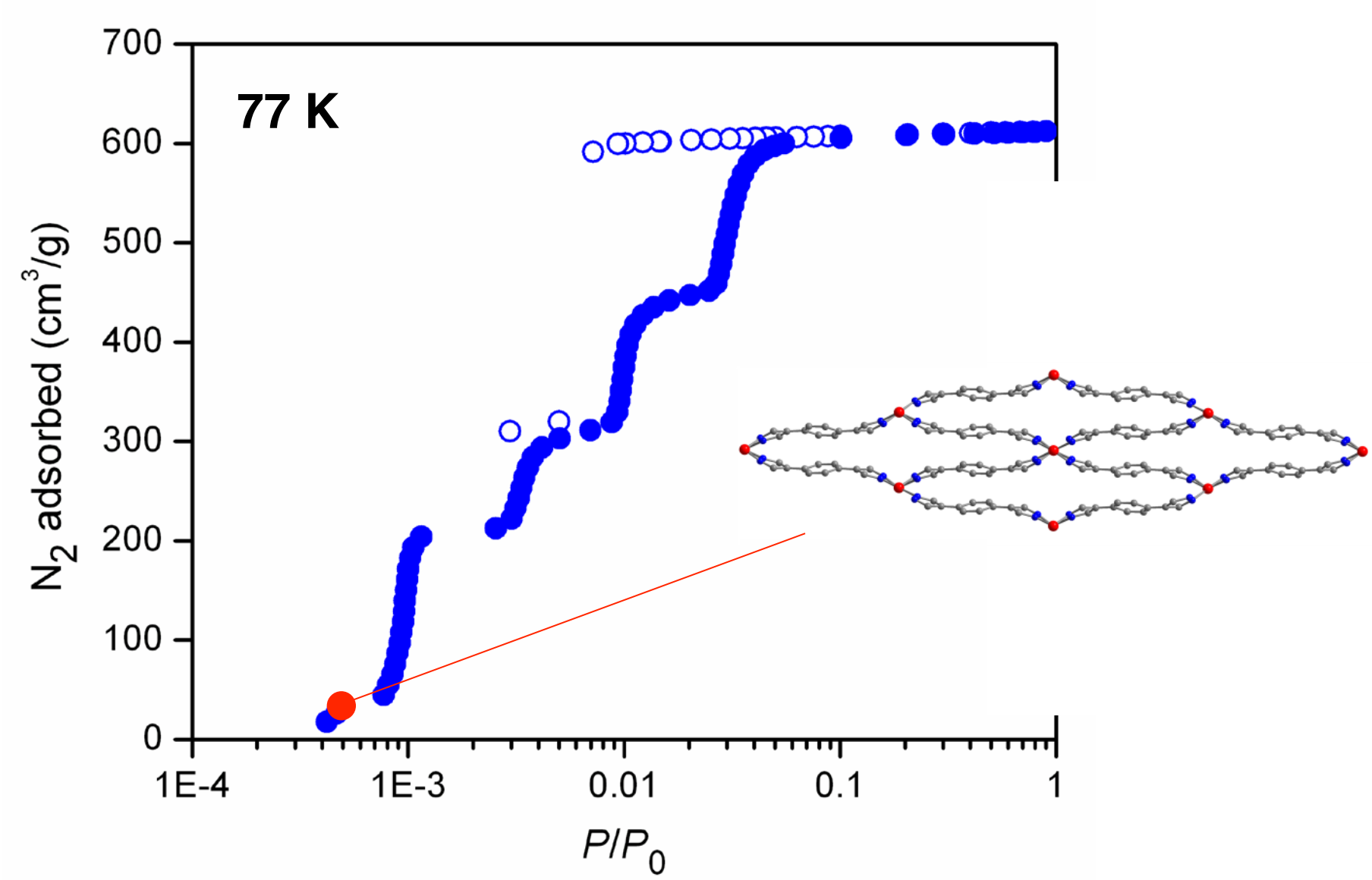
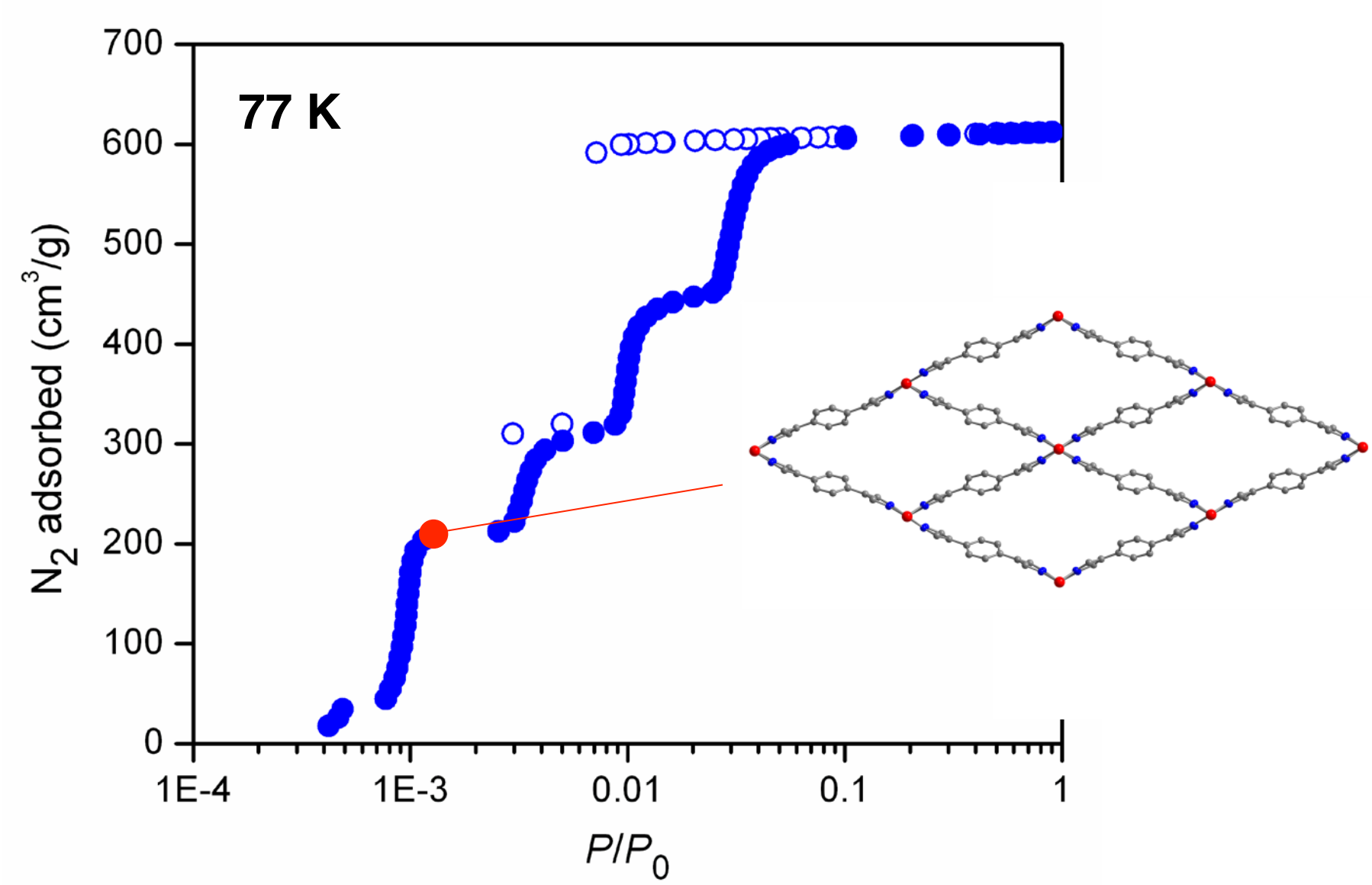
Structural Changes via Powder X-Ray Diffraction



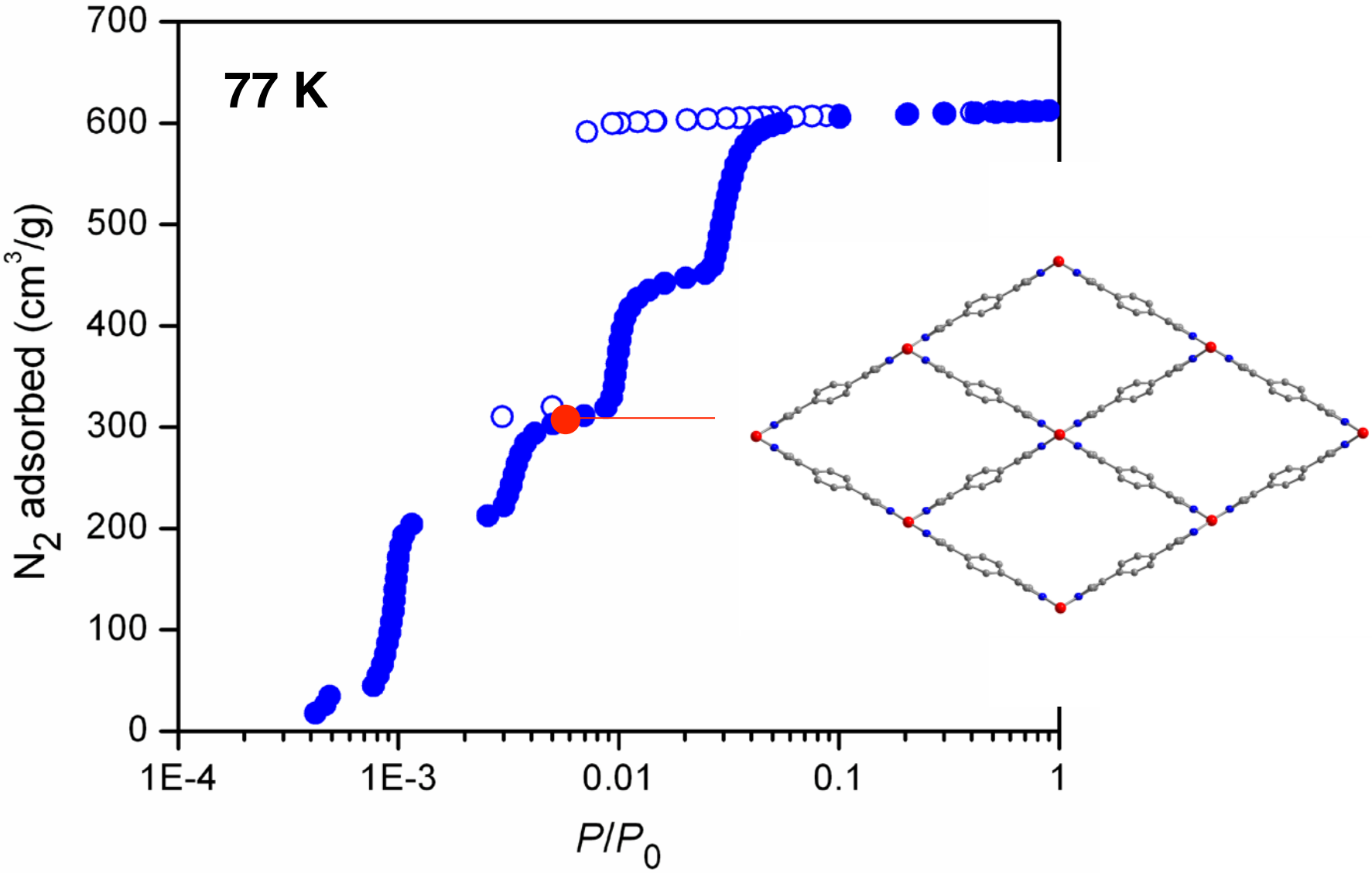
Salles, Maurin, Serre, Llewellyn, Knöfel, Choi, Filinchuk, Oliviero, Vimont, Long, Férey *J. Am. Chem. Soc.*, in press

Structural Changes via Powder X-Ray Diffraction



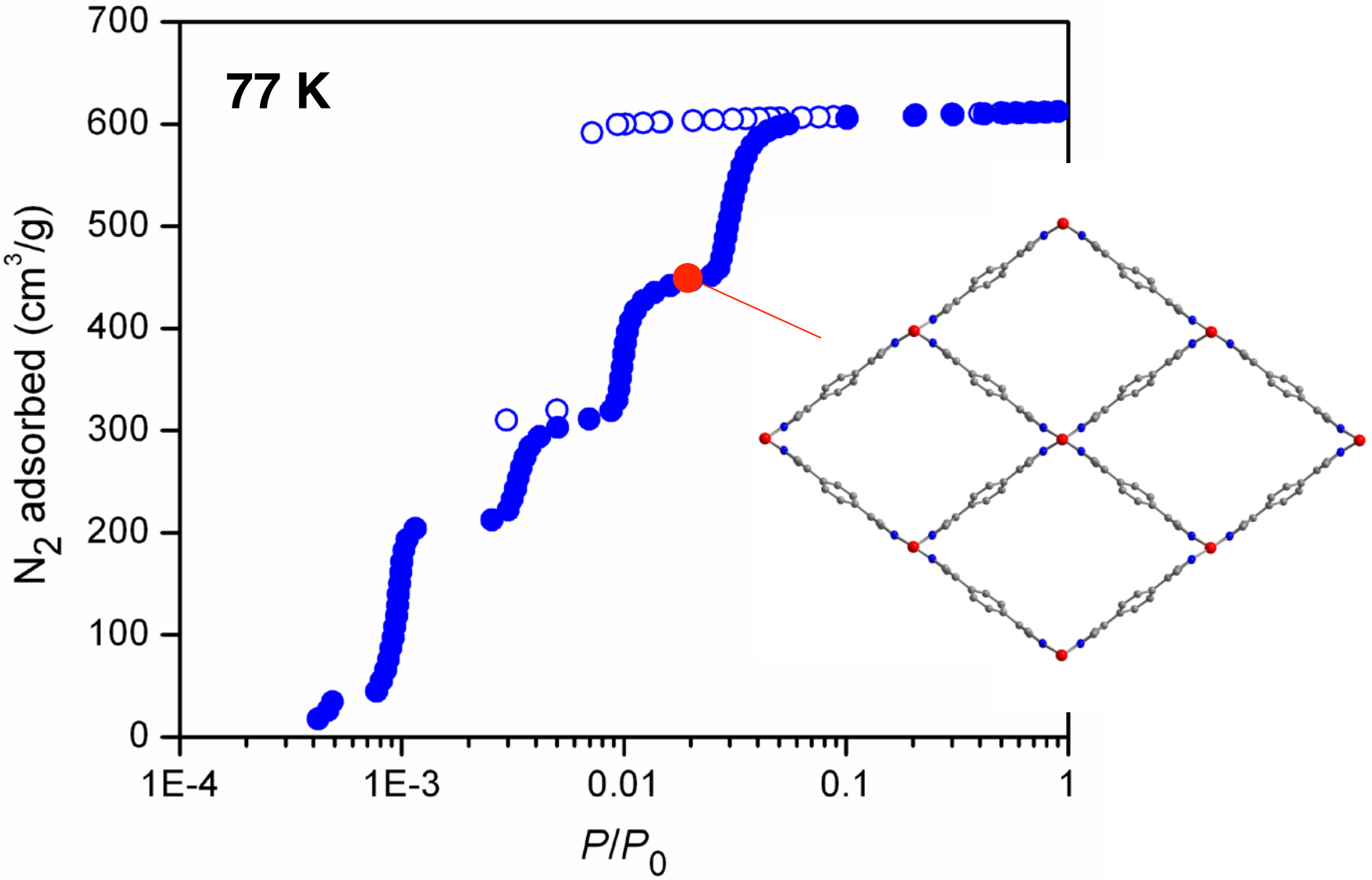
Salles, Maurin, Serre, Llewellyn, Knöfel, Choi, Filinchuk, Oliviero, Vimont, Long, Férey *J. Am. Chem. Soc.*, in press

Structural Changes via Powder X-Ray Diffraction



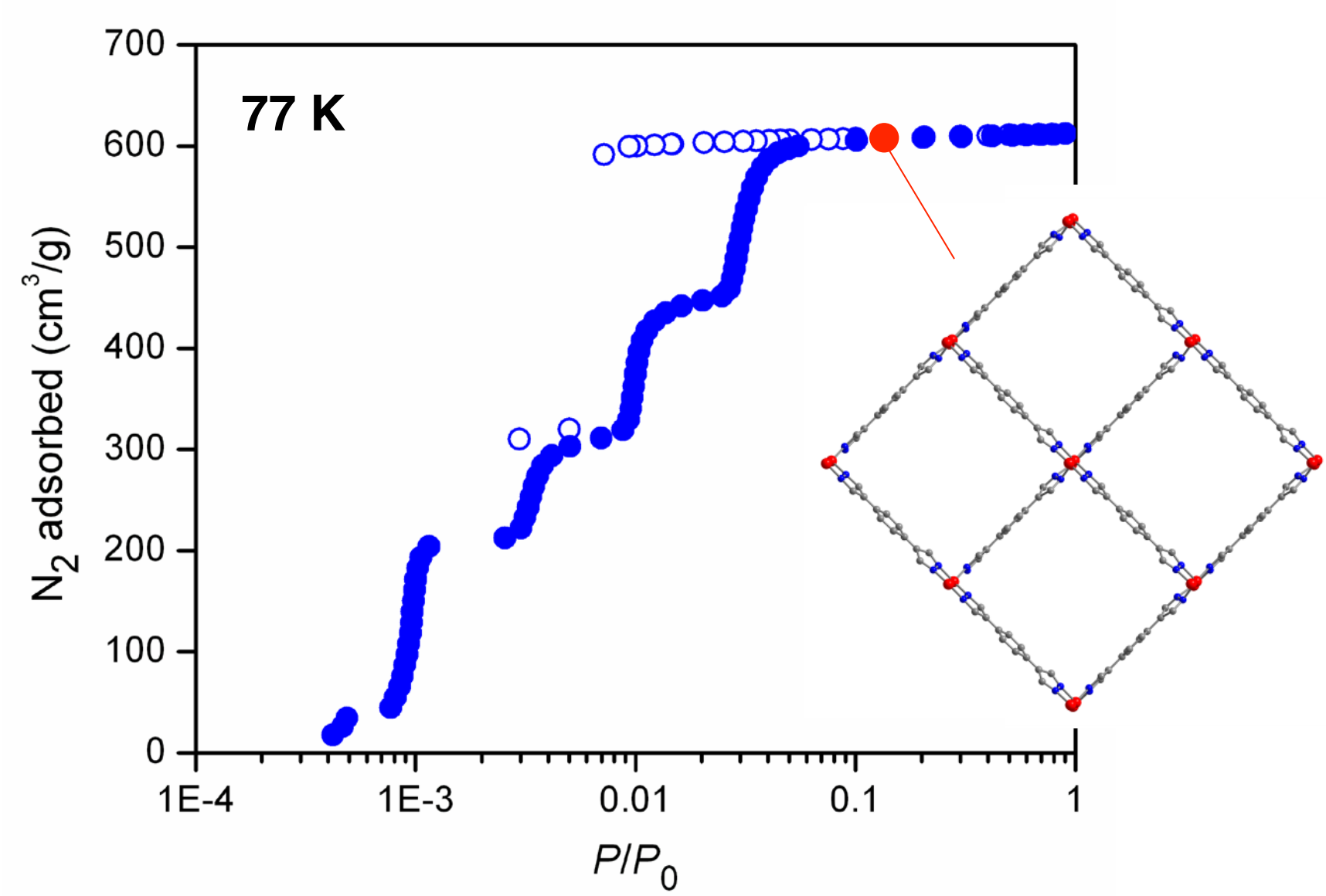
Salles, Maurin, Serre, Llewellyn, Knöfel, Choi, Filinchuk, Oliviero, Vimont, Long, Férey *J. Am. Chem. Soc.*, in press

Structural Changes via Powder X-Ray Diffraction



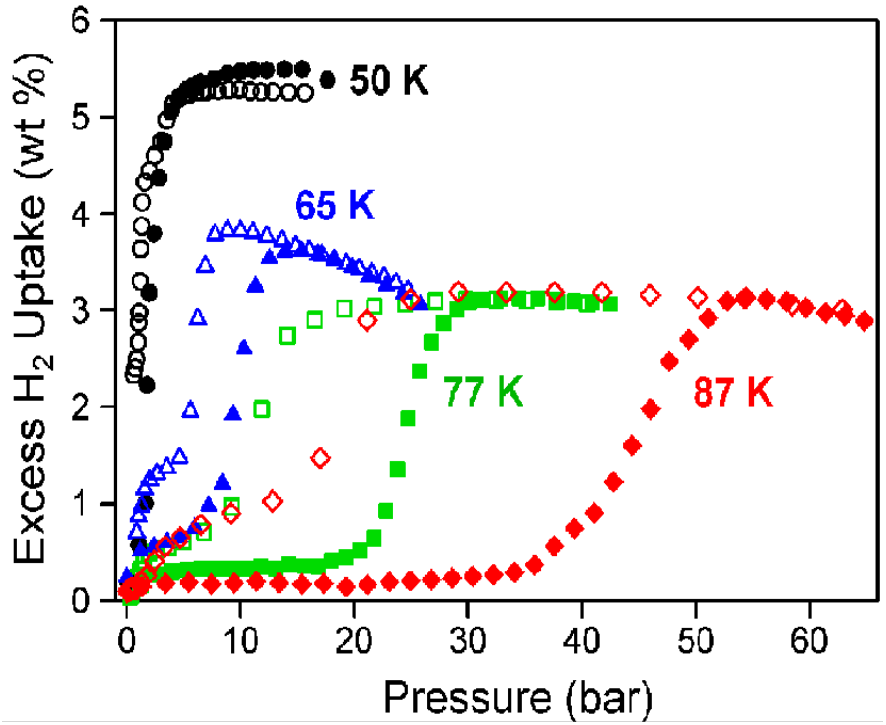
Salles, Maurin, Serre, Llewellyn, Knöfel, Choi, Filinchuk, Oliviero, Vimont, Long, Férey *J. Am. Chem. Soc.*, in press

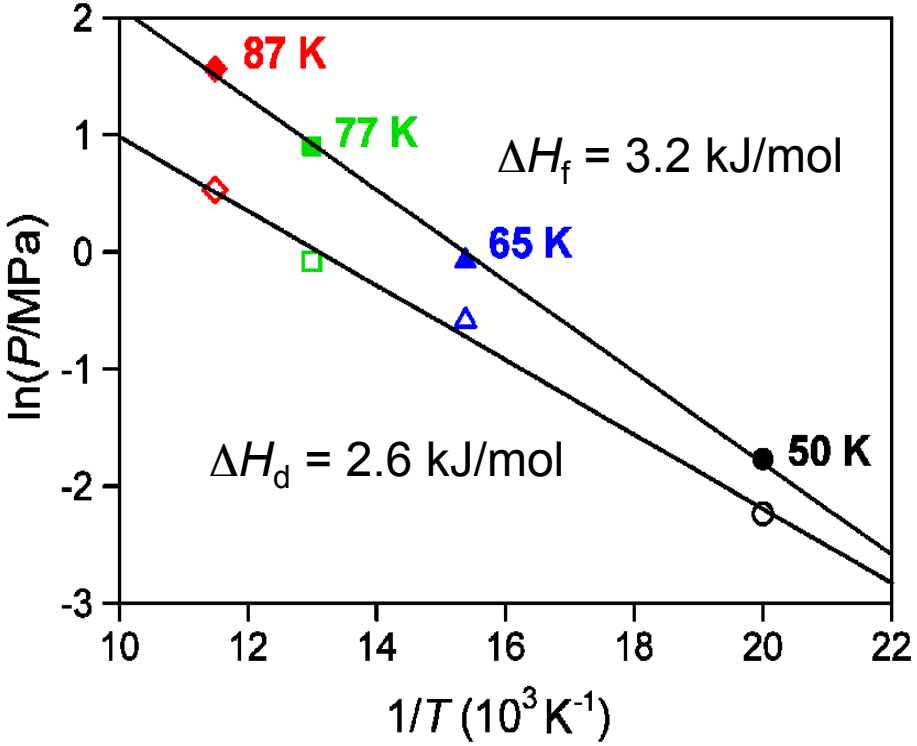
Structural Changes via Powder X-Ray Diffraction



Salles, Maurin, Serre, Llewellyn, Knöfel, Choi, Filinchuk, Oliviero, Vimont, Long, Férey *J. Am. Chem. Soc.*, in press

Temperature-Dependence of Hysteresis





- Formation and dissociation enthalpies for "clathrate" Co(BDP):H_2 determined using Clausius-Clapeyron equation
- Extrapolation to 298 K suggests pore opening at 1100 bar and closing at 220 bar

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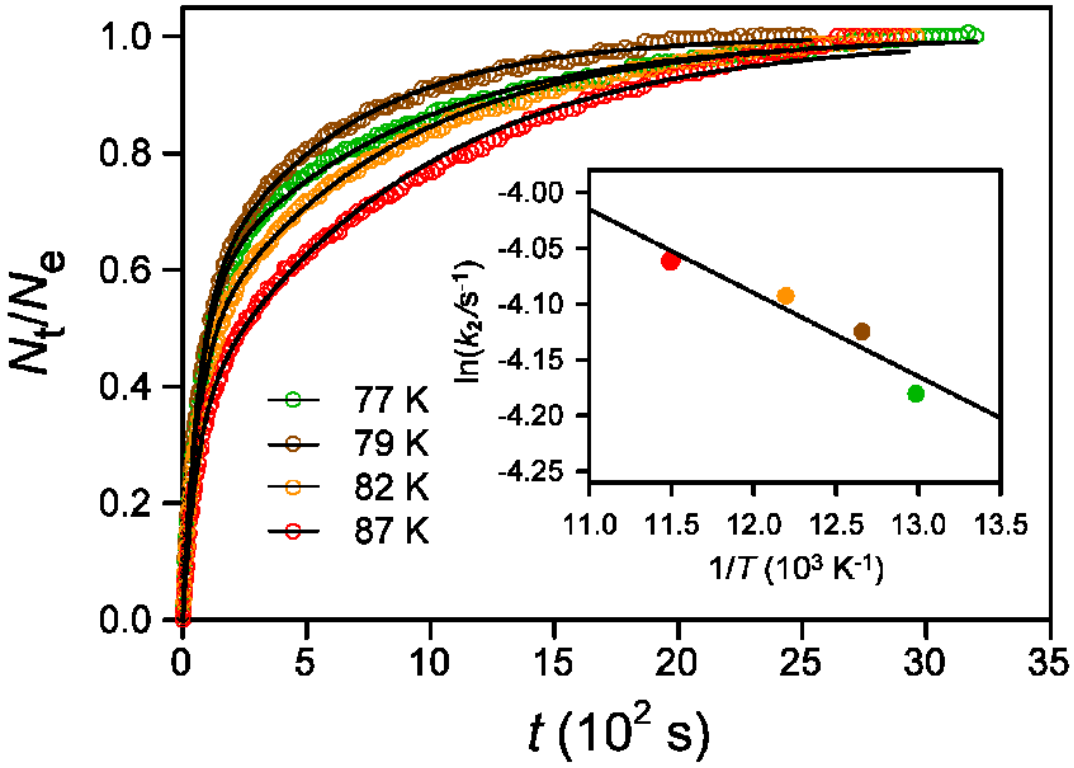
H_2 Adsorption Kinetics in Co(BDP)



- Data fit with a double exponential model: $N_t/N_e = \underbrace{A_1(1 - e^{-k_1 t})}_{\text{pore opening}} + \underbrace{A_2(1 - e^{-k_2 t})}_{\text{diffusion in pores}}$

- Rates associated with faster term indicate an H_2 diffusion barrier of 0.62 kJ/mol

Choi, Dinca, Long *J. Am. Chem. Soc.* **2008**, *130*, 7848

Summary

- Microporous metal-organic frameworks such as $Zn_4O(BDC)_3$ can exhibit excellent H_2 storage characteristics, but only at 77 K
- Use of tetrazolate-based bridging ligands can lead to high-surface area frameworks with exposed Mn^{2+} and Cu^{2+} sites, and increased storage capacity at 298 K
- Neutron diffraction and infrared spectroscopy experiments indicate binding at Mn^{2+} with an enthalpy as high as 12 kJ/mol
- Use of triazolate- and pyrazolate-based bridging ligands can lead to improved thermal stability, as well as air- and water-stability

Review articles: Dinca, Long *Angew. Chem., Int. Ed.* **2008**, *47*, 6766

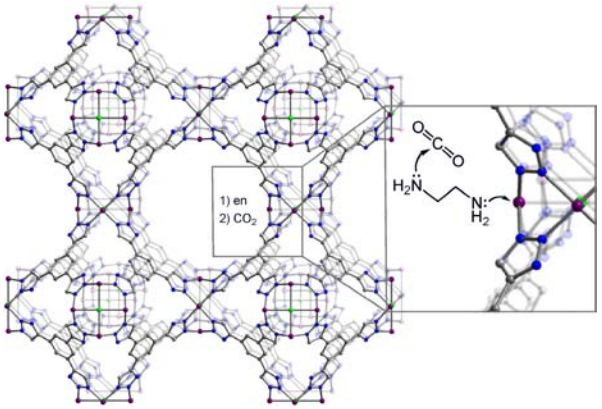
Murray, Dinca, Long *Chem. Soc. Rev.* **2009**, *38*, 1294

Other Potential Applications

CO_2 Capture from Flue Gas:

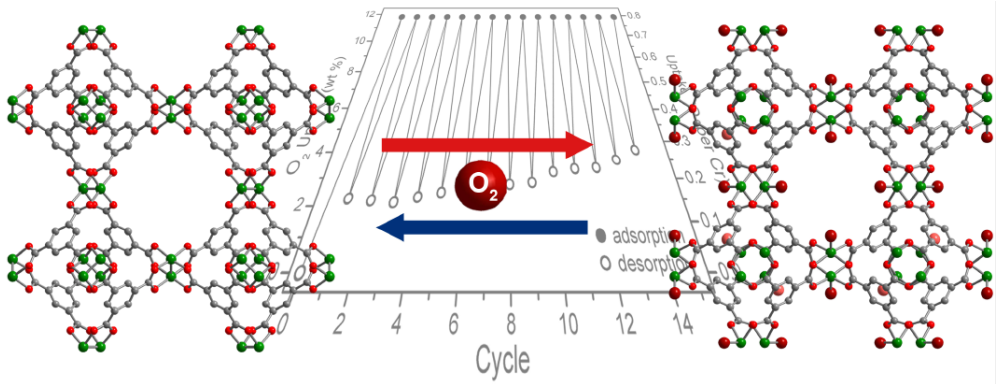
Demessence, D'Alessandro, Foo, Long
J. Am. Chem. Soc. **2009**, *131*, 8784

Sumida, Horike, Kaye, Herm, Queen,
Brown, Grandjean, Long, Dailly, Long
Chem. Sci. **2010**, *1*, 184



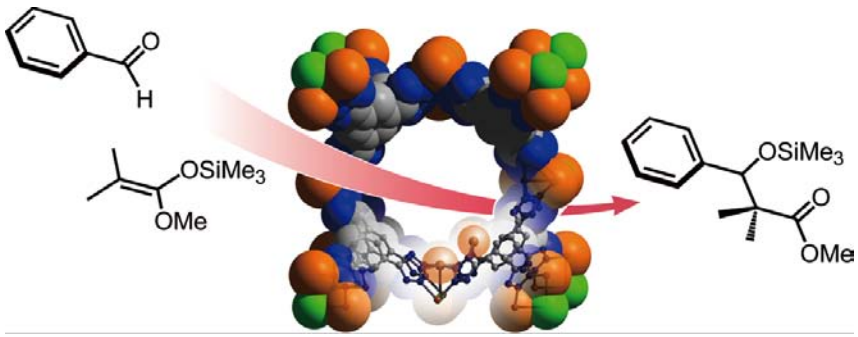
O_2 Capture from Air:

Murray, Dinca, Yano, Chavan,
Bordiga, Brown, Long
J. Am. Chem. Soc. **2010**, *132*, 7856



Heterogeneous Catalysis:

Horike, Dinca, Tamaki, Long
J. Am. Chem. Soc. **2008**, *130*, 5854



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