Hydrogen Storage in Metal-Organic Frameworks

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Project ID # **ST103**

Overview

Timeline

- Project start date: 01/01/12
- Project end date: 12/31/14
- Percent complete: 5%

Budget

- Total project funding $2.625M
  - DOE share: $2.1M
  - Contractor share: $0.525M
- Funding received in FY11: $0
- Planned Funding for FY12: $0.5M

Barriers

- Identify new metal-organic frameworks enabling a hydrogen storage system achieving:
  - 1.8 kWh/kg (5.5 wt %)
  - 1.3 kWh/L (0.040 kg/L)
  - -40/60 °C operating temperature

Partners

- National Institute of Standards and Technology
- General Motors
- Project lead-Jeffrey Long, LBNL

The H_2 Powered Car – Current Technologies

About 4-5 kg of H_2 required for a 300 mi range

Compressed Hydrogen Gas (most common)

Significant energy spent in compression process

Liquid Hydrogen

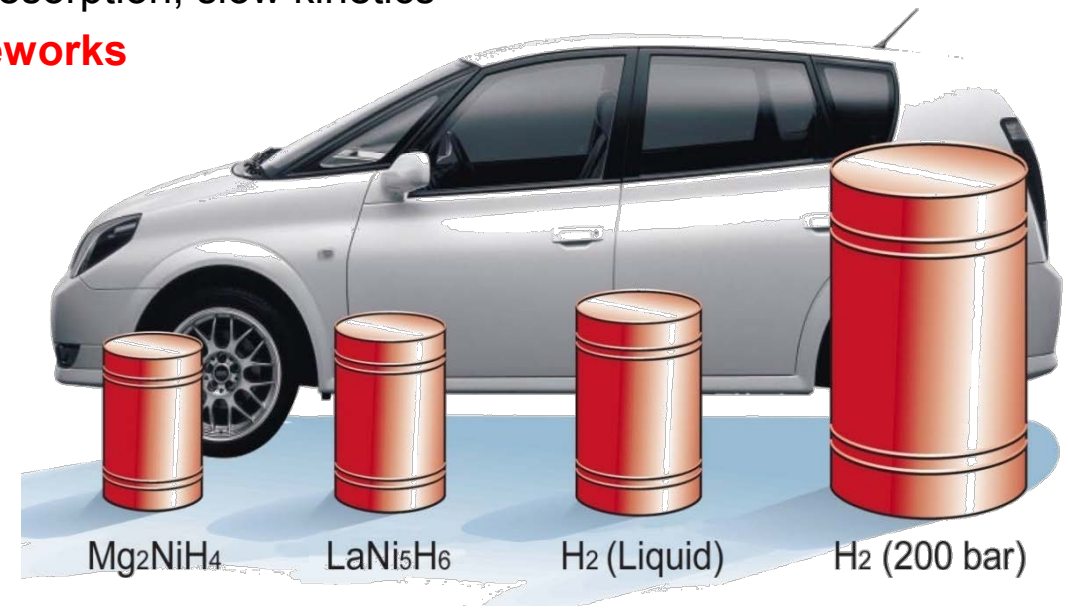
Large energy input for liquefaction

Heavy and expensive cooling unit required

Chemical and Metal Hydrides

High temperatures required for desorption, slow kinetics

Adsorbed on Metal-Organic Frameworks



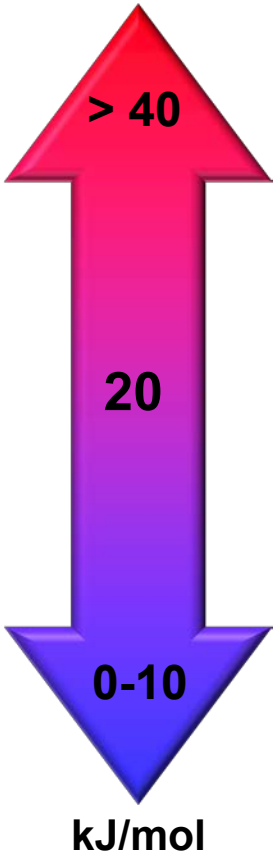
Schlapback, Züttel, *Nature*, **2001**, *414*, 353.

Optimal Binding Enthalpy for H_2

Chemisorption
Strong binding in chemical bonds
High desorption temperature, ΔH

Ideal ΔH_{ads} for storage at RT

Physisorption
Readily reversible storage
H_2 liberated too easily at RT



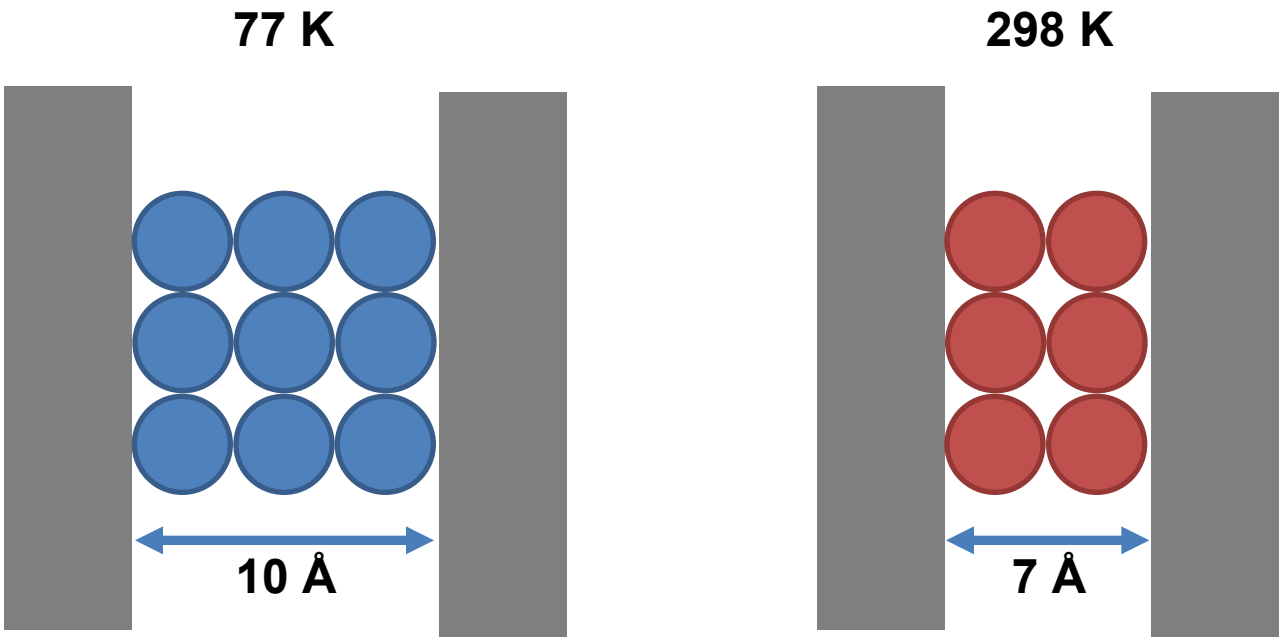
Metal hydrides
Ammonia, ammonia-borane
Amine complexes

Hybrid system
High surface area
Stronger binding of H_2

Metal-organic frameworks
Carbons
Zeolites

Garrone, *et al.Chem. Phys. Lett.*, **2008**, *456*, 68.

Ideal Pore Size for H_2 Storage

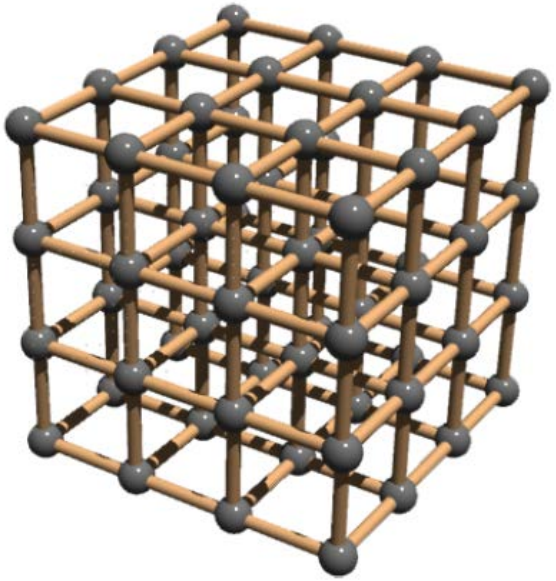


- Shorter-range influence of pore walls at higher temperatures
- Design of a room temperature sorbent requires careful consideration of both chemical and structural properties

Patchkovskii, *et al. Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 10439.

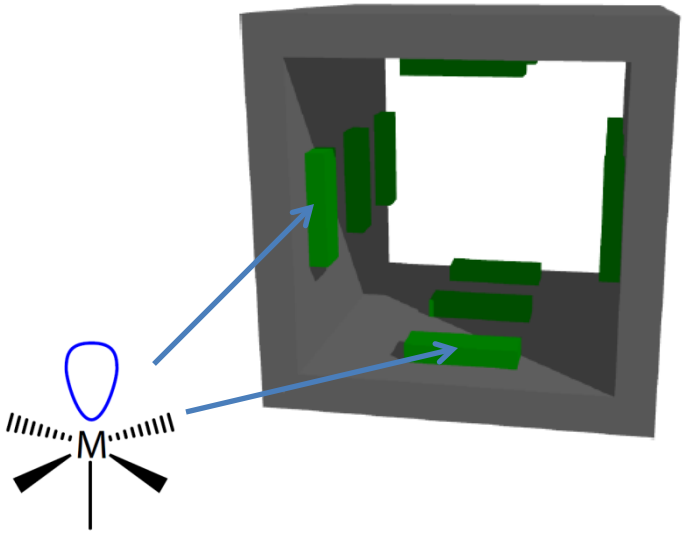
Strategies for Improving H_2 Storage Performance

Lightweight Materials



- Lightweight metal ions (Be^{2+}, Mg^{2+}, Al^{3+})
- Improve gravimetric capacity
- New structure types (particularly with main group elements)

Unsaturated Coordination Sites

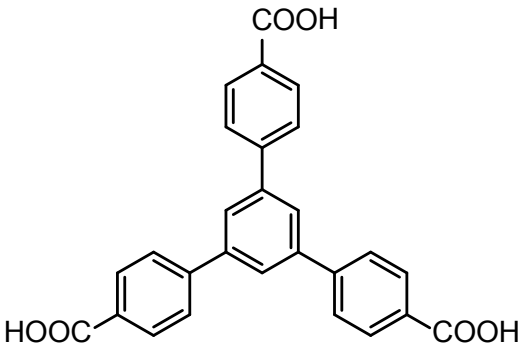


- Charge-dense, polarizing binding sites
- M-H_2 interactions at the right enthalpy for reversible storage at 298 K
- Close approach to metal center increases packing density of H_2

Synthesis of a Be-based Metal-Organic Framework

$Be^{2+}_{(aq)}$

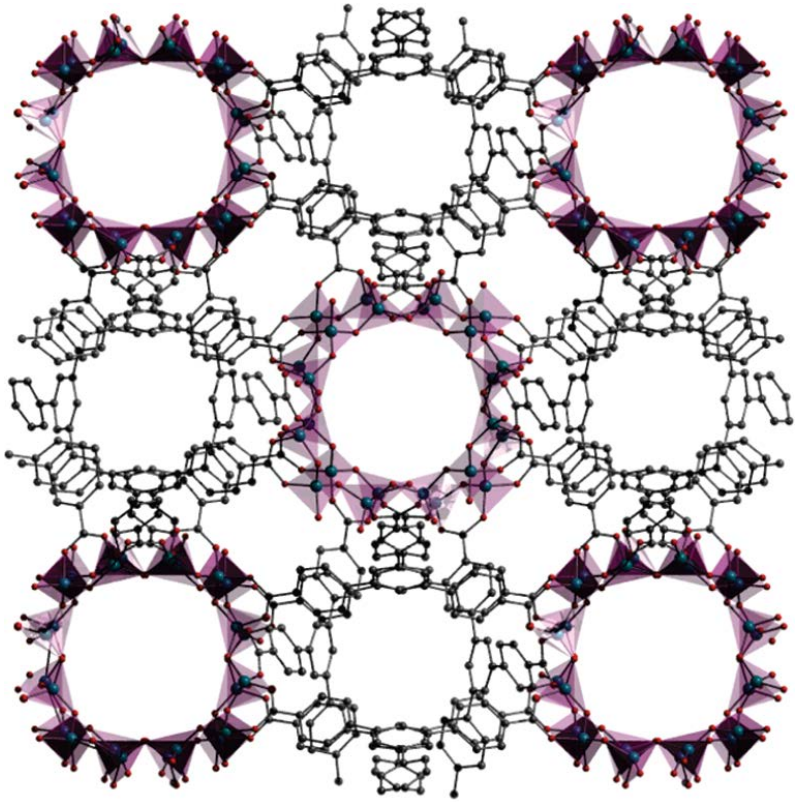
+



1,3,5-benzenetribenzoic acid
H_3BTB

DMF/DMSO/H_2O

130 °C, 10 days

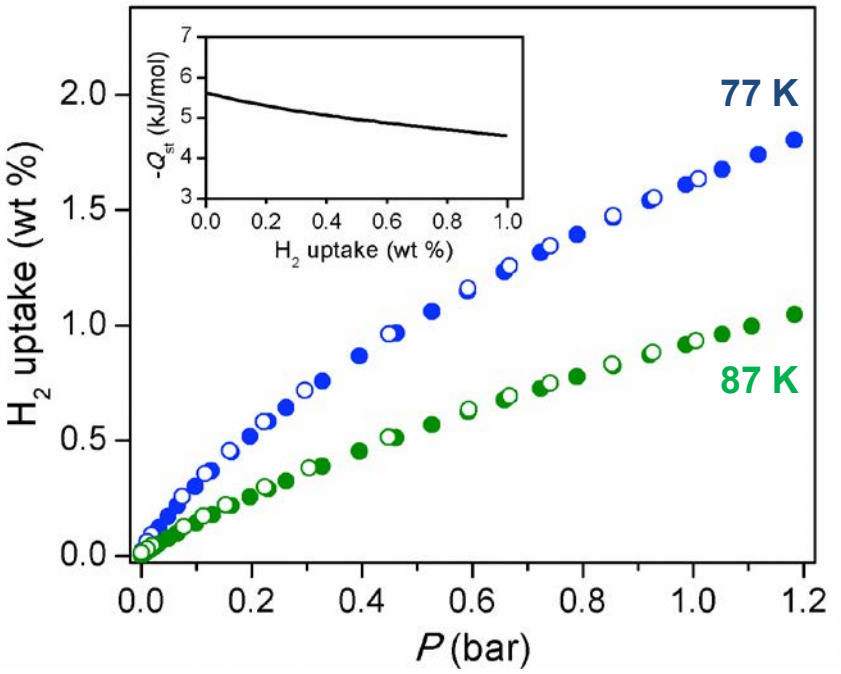


$Be_{12}(OH)_{12}$(1,3,5-benzenetribenzoate)$_4$
Tetragonal, *P*-4*c*2
SA_{BET} = 4030 m^2/g

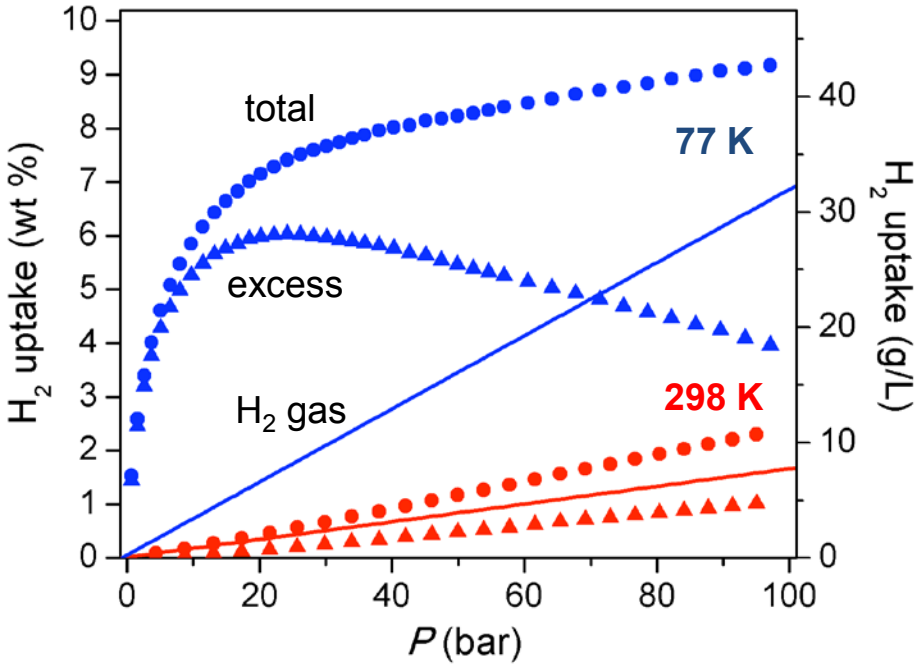
Sumida, K.; Hill, M. R.; Horike, S.; Dailly, A.; Long, J. R. *J. Am. Chem. Soc.* **2009**, *131*, 15120.

H_2 Storage Properties of Be-BTB

Low-Pressure H_2 Isotherm



High-Pressure H_2 Isotherm



- High surface area coupled with low isosteric heat of adsorption (Q_{st}) facilitates excellent cryogenic storage properties

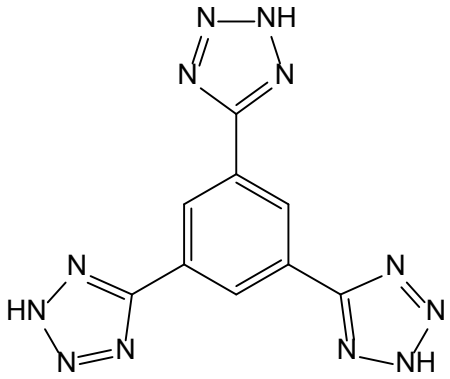
- Multiple pore apertures of ca. 6-7 Å leads to record gravimetric uptake in a metal-organic framework at 298 K

Sumida, K.; Hill, M. R.; Horike, S.; Dailly, A.; Long, J. R. *J. Am. Chem. Soc.* **2009**, *131*, 15120.

Synthesis of Fe-BTT – Exposed Fe^{2+} Cation Sites

$FeCl_2$

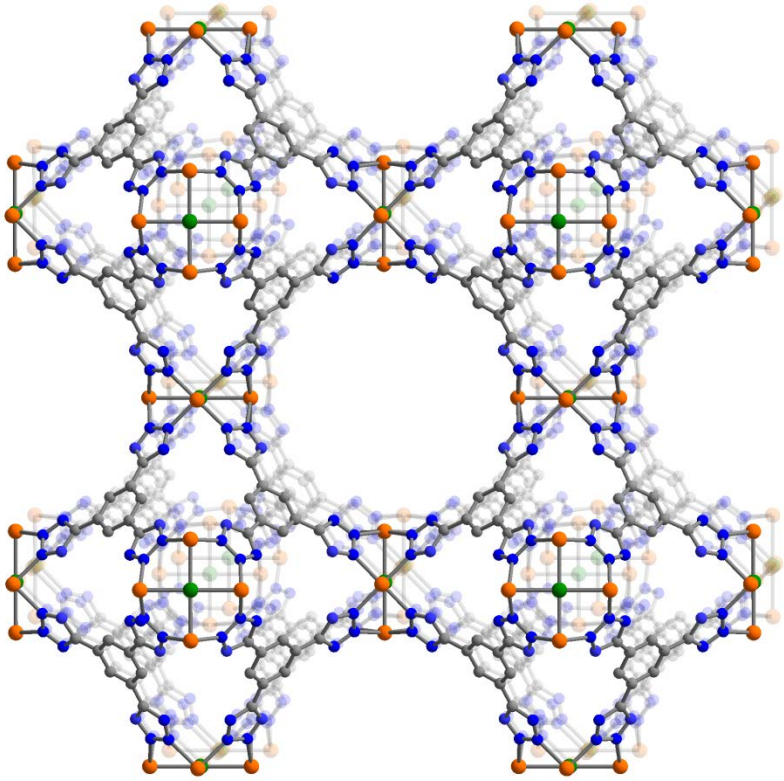
+



1,3,5-benzenetristetrazolate
H_3BTT

DMF/DMSO

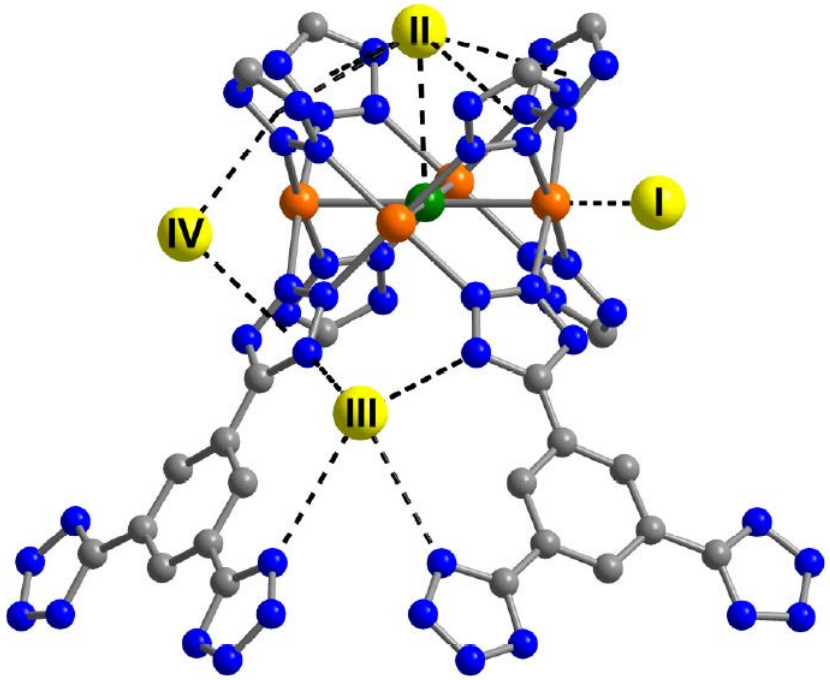
110 °C, 48 h

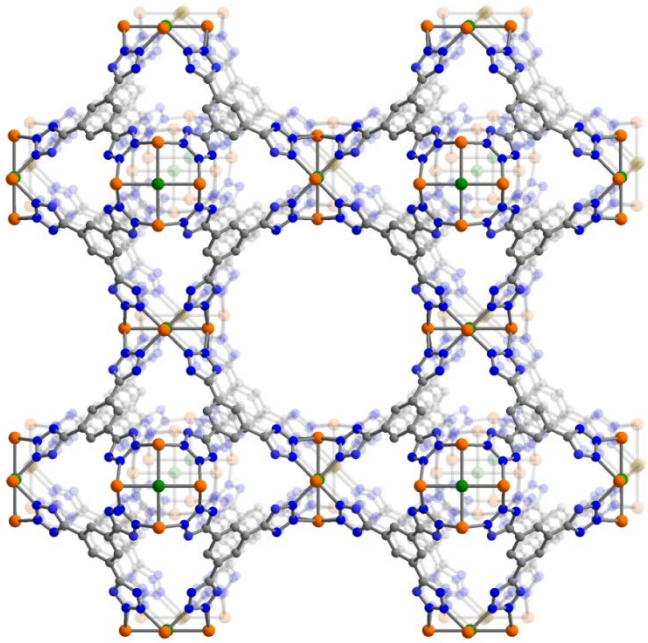


$Fe_3[(Fe_4Cl)_3(BTT)_8]_2$
Cubic, *Pm*-3*m*
a = 18.82 Å

Sumida, K; Horike, S.; Kaye, S. S.; Herm, Z. R.; Queen, W. L; Brown, C. M.; Grandjean, F.; Long, G. J.; Dailly, A.; Long, J. R. et al. *Chem. Sci.* **2010**, *1*, 184.

D_2 Loading Experiments within Fe-BTT



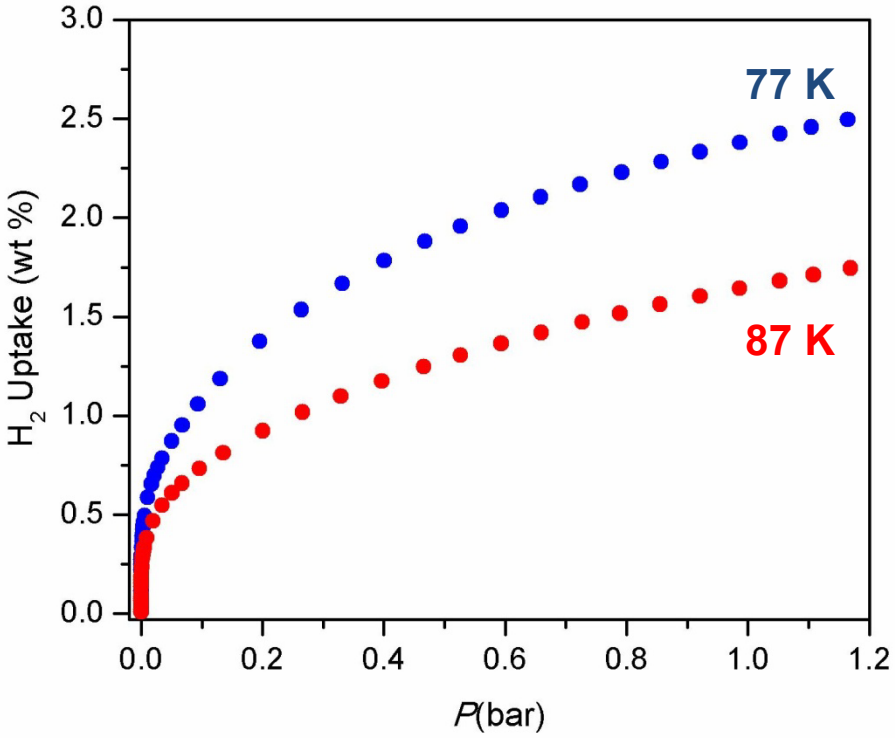


- At higher loadings, up to 10 binding sites identified within unit cell

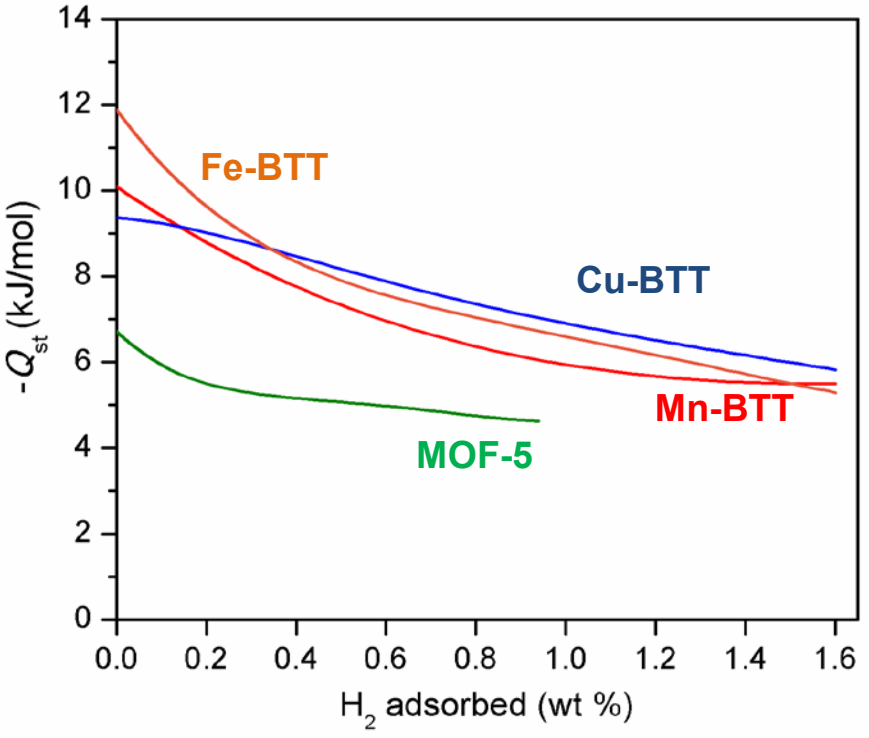
Sumida, K; Horike, S.; Kaye, S. S.; Herm, Z. R.; Queen, W. L; Brown, C. M.; Grandjean, F.; Long, G. J.; Dailly, A.; Long, J. R. et al. *Chem. Sci.* **2010**, *1*, 184.

H_2 Storage Properties of Fe-BTT

H_2 Isotherms



Enthalpy of Adsorption



- Enthalpy of adsorption consistent with the high charge density on Fe^{2+} metal center

Sumida, K; Horike, S.; Kaye, S. S.; Herm, Z. R.; Queen, W. L; Brown, C. M.; Grandjean, F.; Long, G. J.; Dailly, A.; Long, J. R. et al. *Chem. Sci.* **2010**, *1*, 184.

Collaborations

Martin Head-Gordon, UC Berkeley/LBNL(Academic)

-Calculations of H_2 Binding Energies

Theoretical calculations will be utilized to aid in the prediction of key new metal-organic frameworks that may meet DOE H_2 storage targets.

Craig M. Brown, NIST (National Lab)

-Characterization of Framework-H_2 Interactions

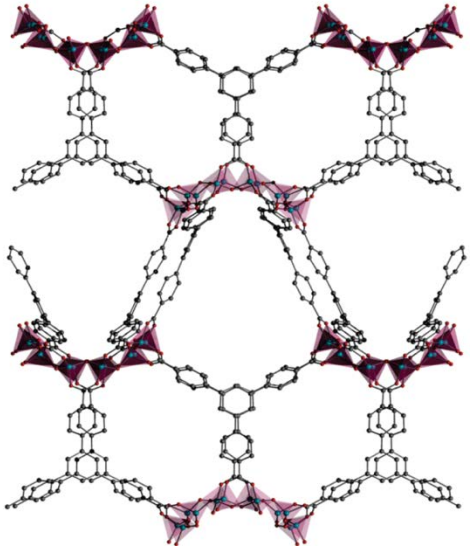
Neutron methods will give insight into the adsorption of H_2 in newly synthesized porous frameworks.

Anne Dailly, GM (Industry)

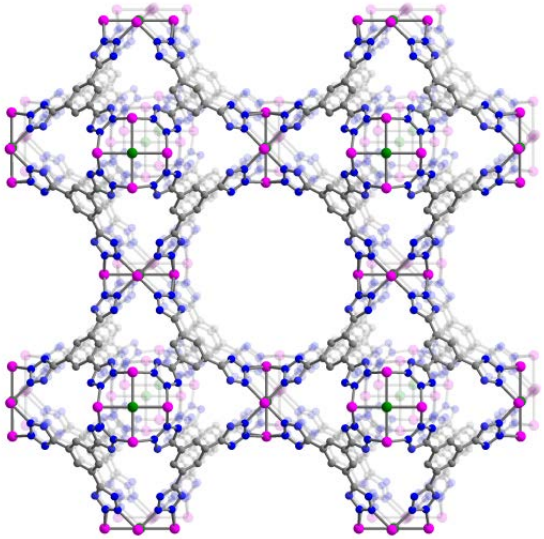
-High Pressure H_2 Adsorption Measurements

The most promising H_2 storage materials will be further investigated in collaboration with GM by measuring high-pressure (up to 350 bar) adsorption at relevant temperatures.

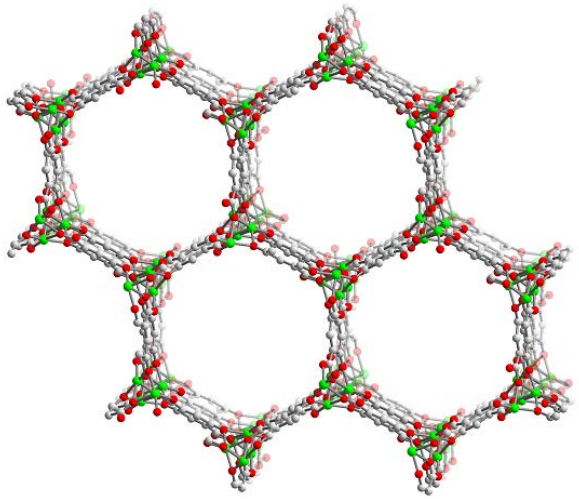
Opposing Surface Area as a Characterization Tool



Be-BTB
large egg-shaped pores



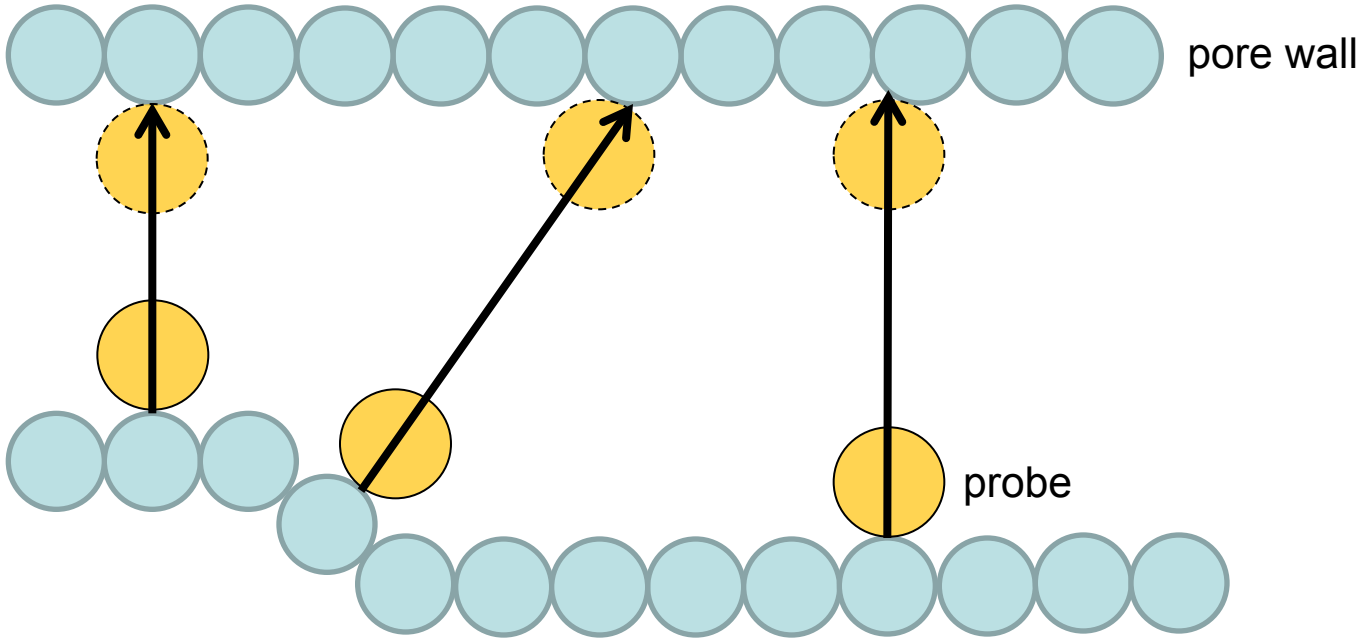
Co-BTT
small octahedral cages
three-dimensional channels



Mg_2(dobdc)
one-dimensional channels

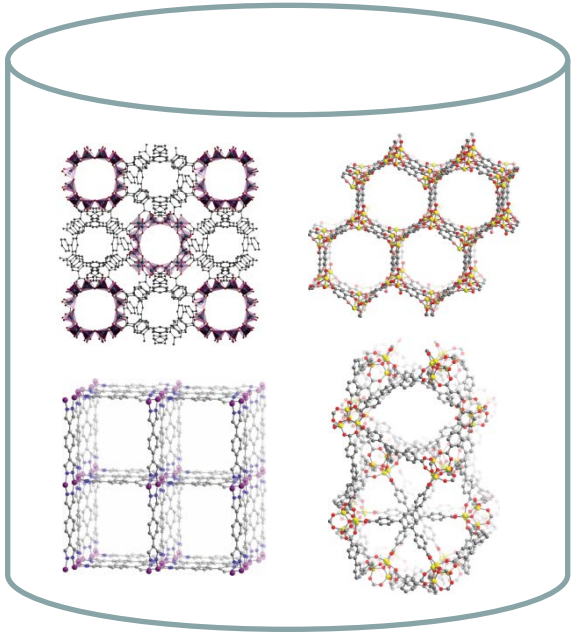
- Metal-organic frameworks feature a rich diversity in the shape and connectivity of their pores, giving a distribution of opposing wall distances
- Need an algorithm that surveys these distances using the crystal structure

Geometric Calculation of Opposing Wall Distances



- Probe is inserted on the pore surface, and moved away in a direction normal to the surface until it collides with the opposing wall
- This is repeated until the entire pore surface has been traversed by the algorithm to create a distribution of opposing wall distances

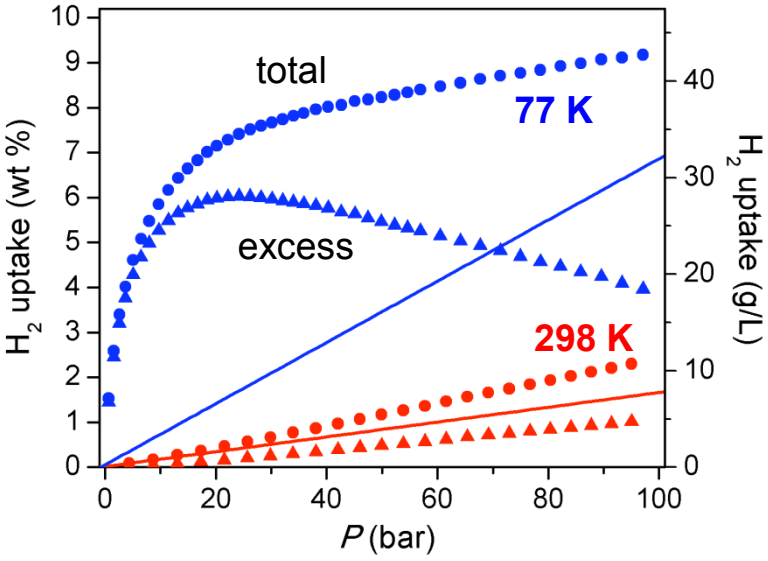
Rapid Screening of Structure Types for H_2 Storage



structural database

select best candidates

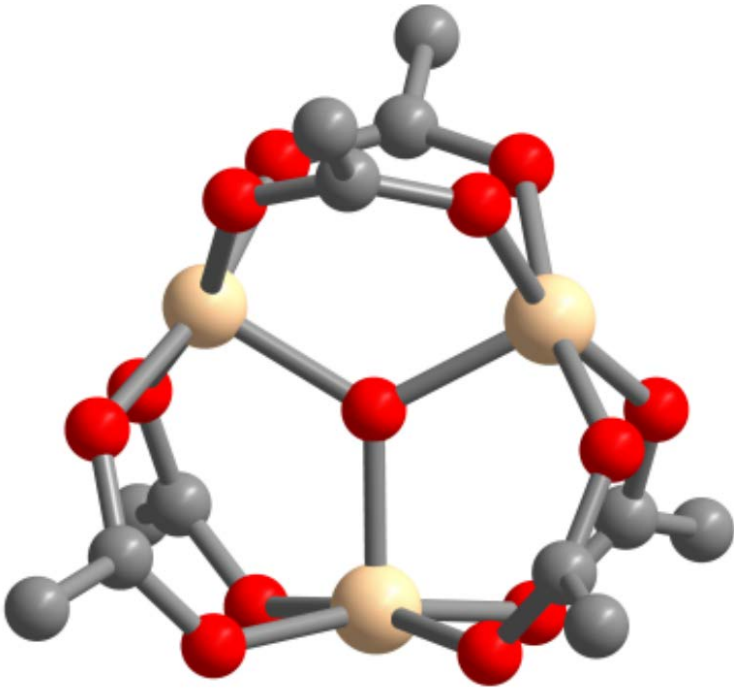
opposing surface algorithm



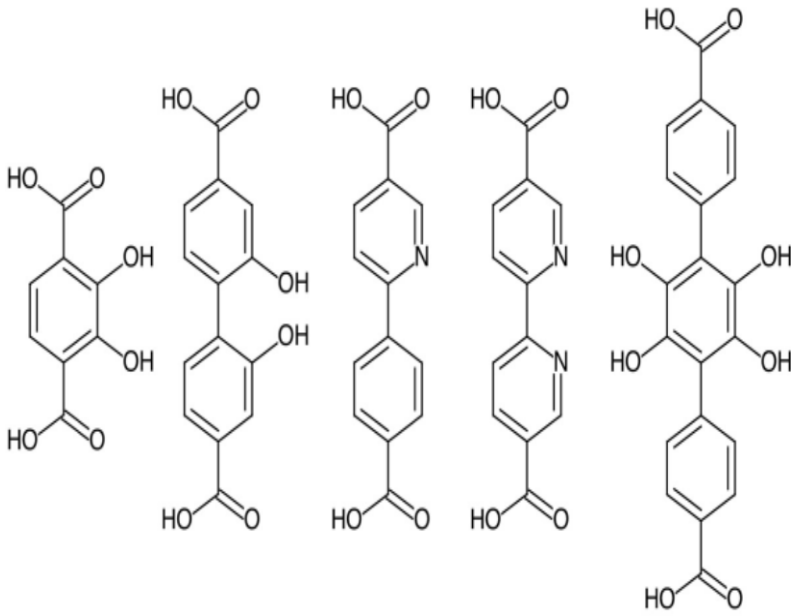
experimental isotherms

- Algorithm could be deployed for rapid examination of a vast database of existing and theoretical structure types
- Structure types exhibiting narrow distributions at 7 Å and 10 Å can then be experimentally tested for H_2 storage performance

Strategies for Increasing H_2 Binding Enthalpy and Capacity

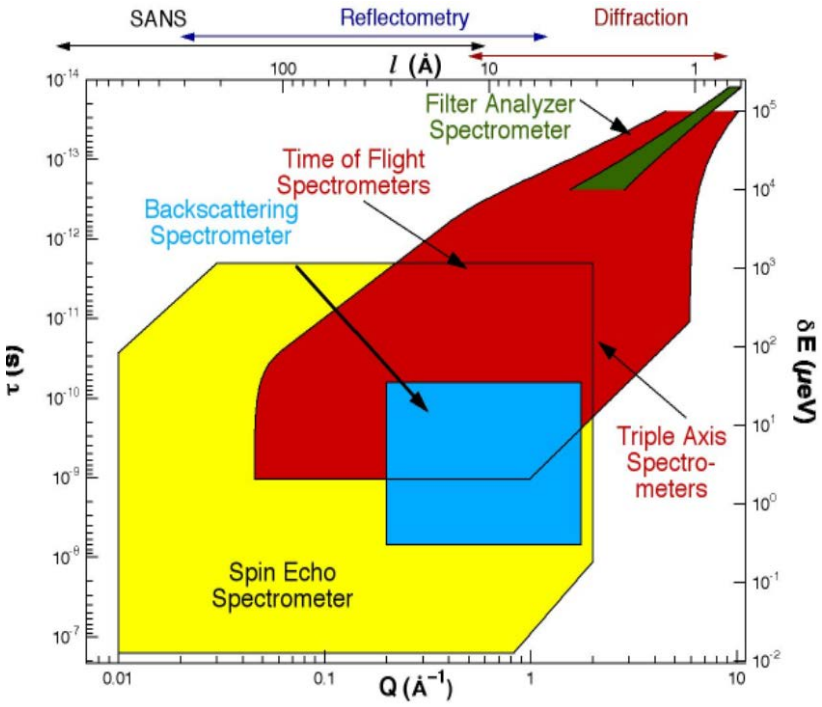


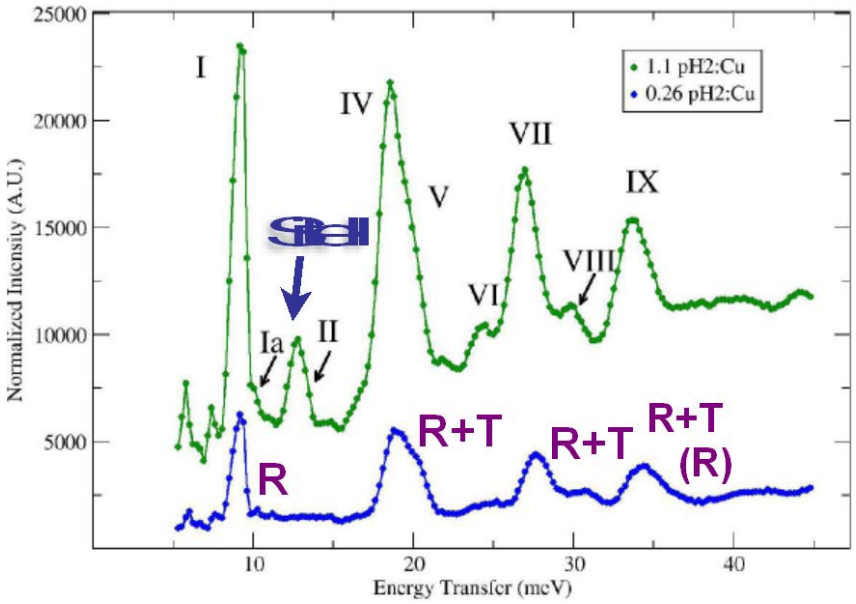
- Incorporation of high-valent metal cations
- Increase M-H_2 binding enthalpy
- Allows for high metal:ligand ratio



- Multiple metal binding sites for post-synthetic insertion of metal cations
- Potential charge balance offered by –OH containing ligands may lead to increased H_2 uptake

Characterization of Metal-H_2 Interactions

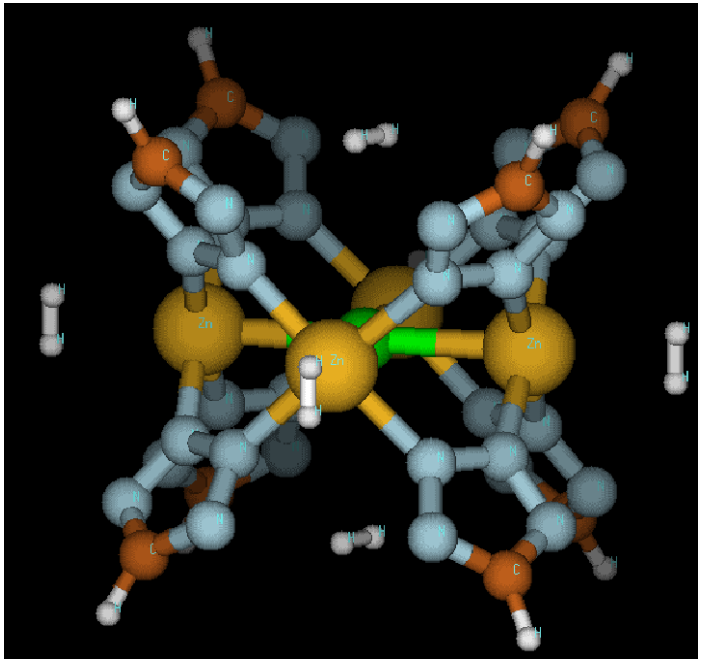


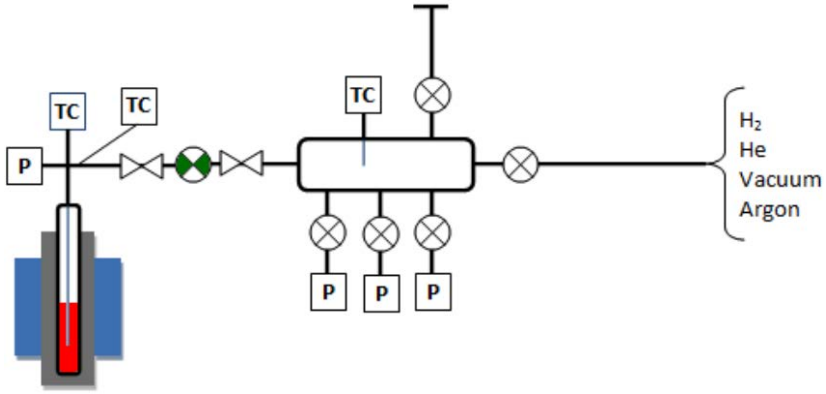


- Neutron methods at NIST encompass a range of seven orders in time- and appropriate storage length-scales

- Inelastic neutron scattering spectra of hydrogen adsorbed at the first (lower curve) and second sites in Cu-BTC. Assignments of rotations (R) and translations (T) are made through DFT calculations.

First-Principles Calculations of Hydrogen Binding Enthalpies and High Pressure Hydrogen Adsorption Experiments.





- Calculated optimized geometry for hydrogen binding in $Mn_3[(Mn_4Cl)_3(BTT)_8]_2$.
- Theoretical calculations will be utilized to predict optimal H_2 storage materials
- A custom-made Sieverts apperatus will be used to measure H_2 adsorption at various temperatures up to 350 bar in promising metal-organic frameworks.

Summary

- A synergistic approach to the development of new metal-organic frameworks for hydrogen storage has recently (January 2012) been started.

- The combination of synthesis (Long), theoretical calculations (Head-Gordon), characterization (Brown), and H_2 adsorption measurements (Dailly) will aide in the efficient design and preparation of next-generation storage materials.