

Hydrogen Storage Materials with Binding Intermediate between Physisorption and Chemisorption

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Project ID:
STP_05_Eckert

Overview

Timeline

- Project start date: 4/1/2005
- Project end date: 3/31/2010

Budget

- Total project funding
 - DOE share: \$1,199,073
 - Contractor share: \$299,674
- Funding received in FY08
\$ 320,000 (appr.)
- Funding expected in FY09
\$??

Barriers

- Barriers addressed: Hydrogen Storage
 - (B) System Weight and Volume
 - (F) Efficiency

Partners

- A. K. Cheetham (co-P.I.) Cambridge, UK
- G. J. Kubas, LANL
- University of California, Santa Barbara (host site)

Collaborators

- A. Albinati (U. di Milano, Italy)
- M. Eddaoudi (USF)
- M. Sodupe Roure (UA Barcelona, Spain)
- P. Dietzel (U. of Oslo, Norway)
- P. Forster (UNLV)

Overall Objective

Develop hydrogen storage materials for reversible on-board applications with hydrogen binding energies intermediate between physisorption and (dissociative) chemisorption

- Sorption based storage materials **have a several factors*** in their favor - but we must

Improve Hydrogen Binding - without loss of capacity
(but not too much: preserve ease of desorption)
to reduce RT operating pressures
(but not too low: 2 atm ~ empty)

- **Goal is to reach binding energies of 15 - 25 kJ/mol**

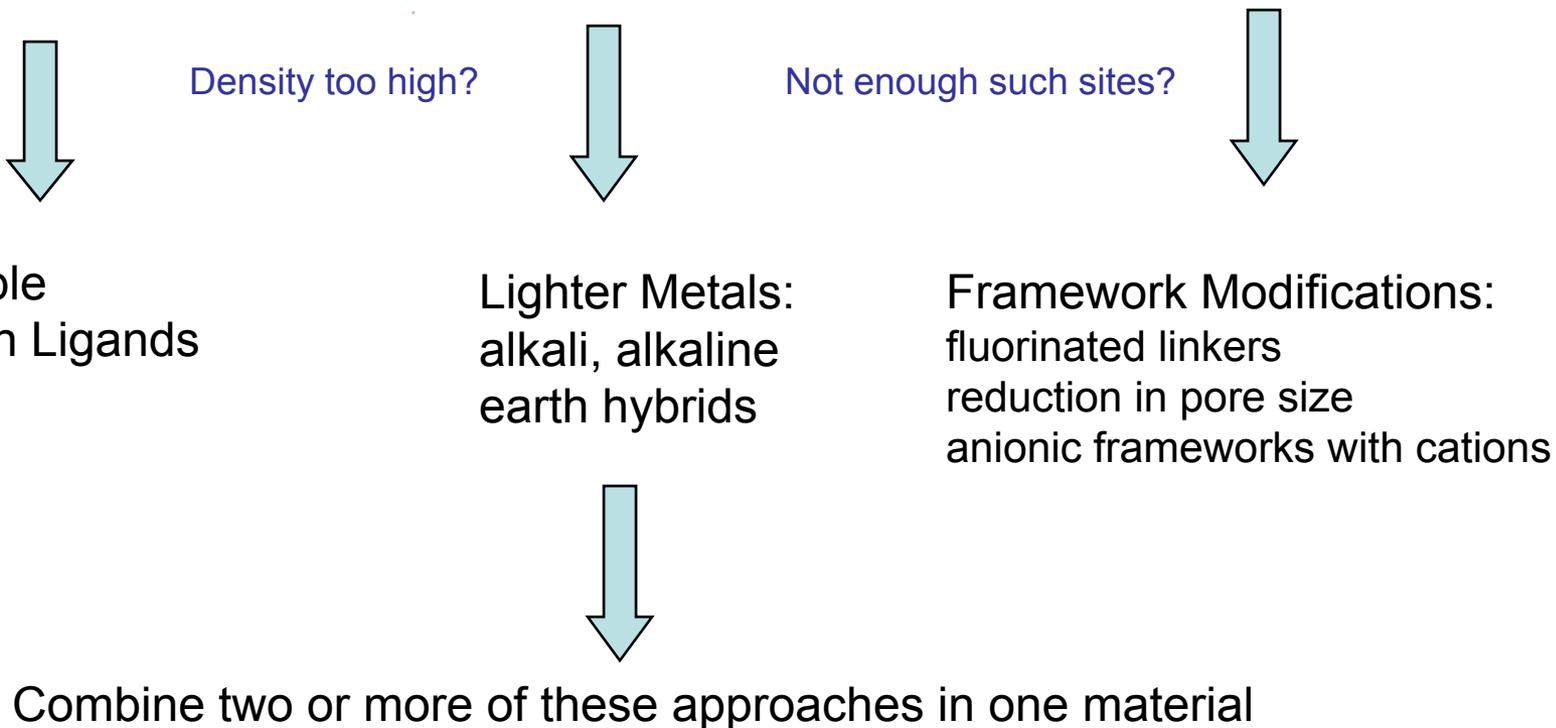
1. Appropriate thermodynamics (favorable enthalpies of hydrogen absorption and desorption)
2. Fast kinetics (quick uptake and release)
3. High storage capacity (at low temperature)
4. Effective heat transfer
5. Long cycle lifetime for hydrogen absorption/desorption

Path to Sorption-based Material with greater H₂ binding Energy

Molecular Chemisorption at Unsaturated (Transition) Metal Binding Sites

(part of the framework, or extraframework)

⇒ binding energies can easily reach >> 20 kJ/mol



Approach

(1) Focus **first** on **synthesis** of materials, which bind **molecular H₂ more strongly** than most MOF's, using the following approach:

- (a) Materials with unsaturated metal binding sites **combined with**
- (b) Framework modifications

(2) Then synthesize analogs with larger surface areas

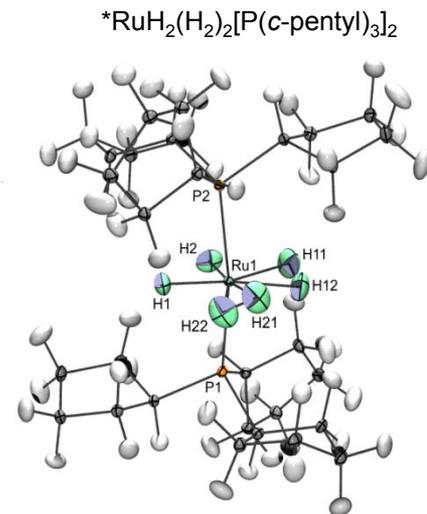
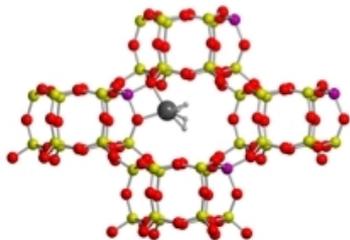
1a. Demonstrate possibility of molecular chemisorption of hydrogen in porous materials (as in organometallic complexes)

create porous material with large numbers of unsaturated and accessible metal sites, as part of the framework, or extraframework cations, or post-synthesis insertion)

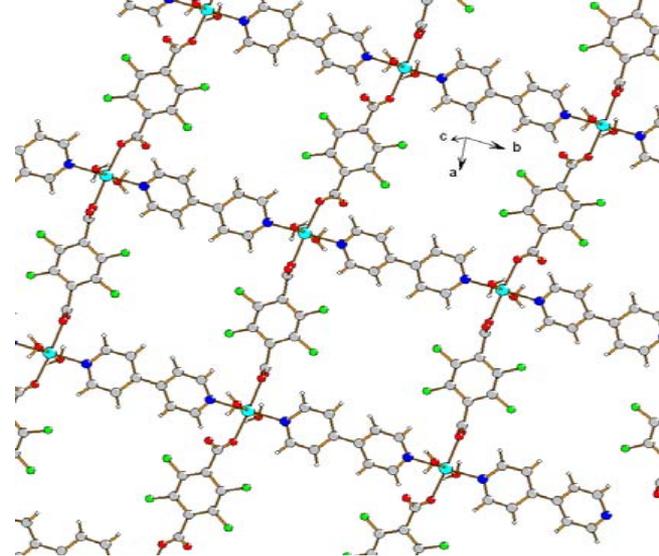
address 'weight penalty' by binding multiple dihydrogen ligands to the open metal sites

OR

hybrid materials with lighter metals instead of transition metals



Approach

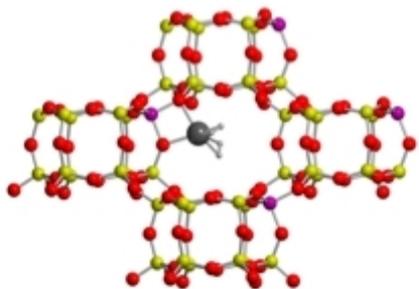


1b. Use **fluorinated organic** linkers and reduce pore size:
increases H₂ binding by **> 50%**

1c. Characterize Binding of Hydrogen by Bulk Measurements and Inelastic Neutron Scattering

1. Adsorption isotherms, porosity, TPD, etc.
2. Structural studies: sorption sites,
3. Computational work (in collaboration)
4. **Extensive use of Inelastic Neutron Scattering** from the hindered rotations of the sorbed hydrogen molecule: **THE most sensitive probe of H₂ interactions** with host

(**BUT:** QENS spectrometer w/IPNS/ANL was **SHUT DOWN** - must use mainly **European Neutron Sources in the near term**)



Technical Accomplishments Progress/Results

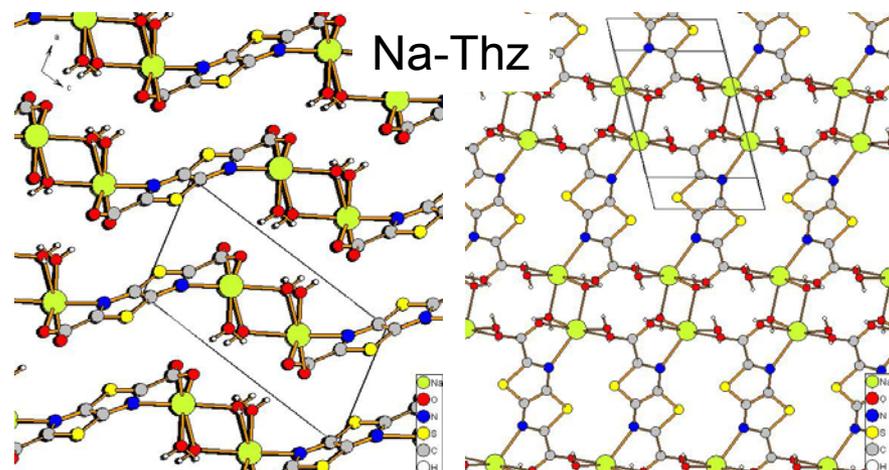
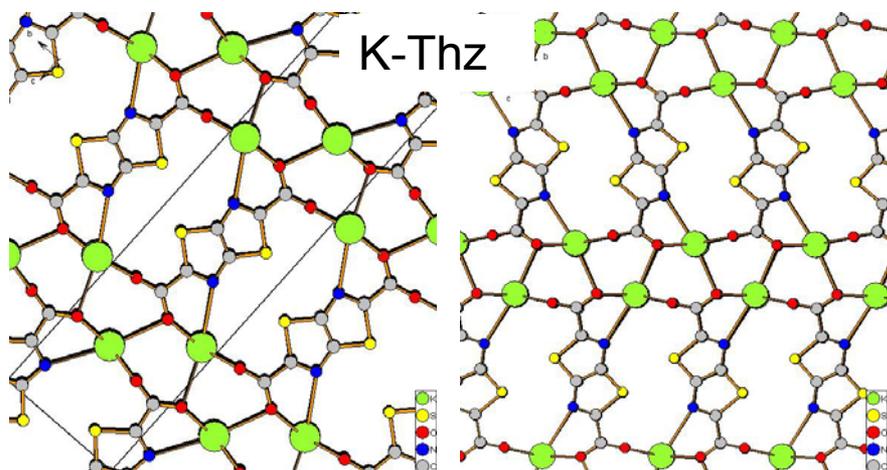
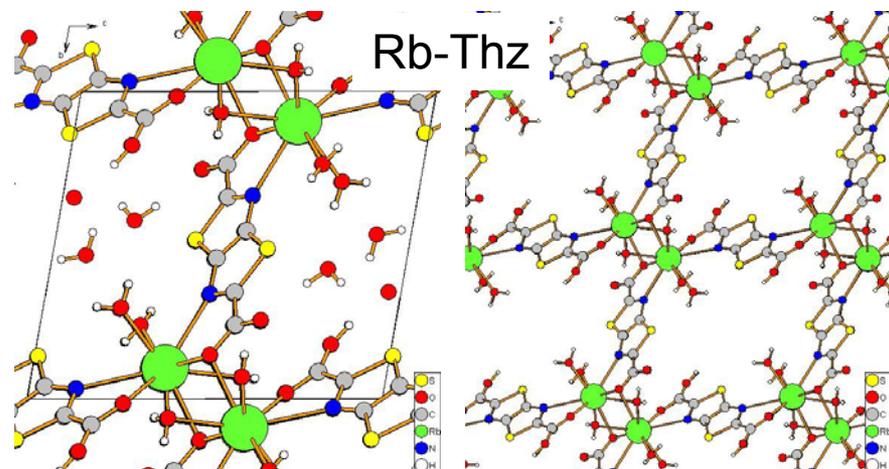
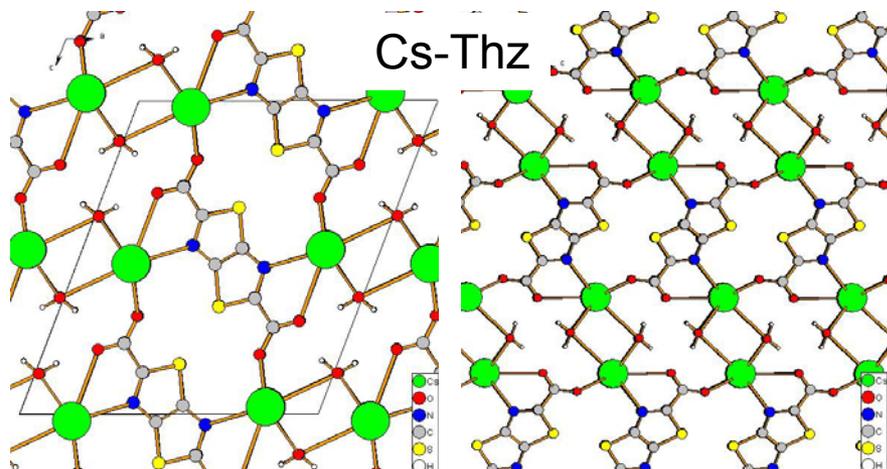
- Experimental observation of the existence of MOLECULAR chemisorption of hydrogen in several porous materials, including possibly the presence of **multiple dihydrogen ligands on one metal site**
- Synthesized and characterized structures of a series of hybrid materials using alkaline earths and alkali metals with a highly functionalized organic link
- Synthesized and characterized several novel hybrids with mixed **fluorinated** and normal organic **links**
- Demonstrated a ~50% increase in binding energies for fluorinated linkers
- Synthesized an analog of $\text{Zn}(\text{Im})_2$: $\text{LiB}(\text{Im})_4$ or $\text{LiB}(\text{C}_3\text{N}_2\text{H}_3)_4$ with the dense zni structure
- Showed that H_2 interactions with extraframework cations are nearly always greater than with “open” metal sites that are part of the framework
- Computational studies on H_2 binding at Fe and Cu inserted into ZSM-5 show formation of true dihydrogen coordination, binding energies from 13.5 to 74 kJ/mol

Accomplishment: Synthesis of Hybrid Materials with Alkali Metal Centers and a Highly Functionalized Organic Link:

Cs-Thz, Rb-Thz, K-Thz: 3D structures; Na-Thz is 2-D (H-bonds keep the layers together).

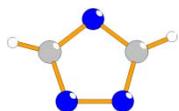
K-Thz is anhydrous.

Water molecules in Rb-Thz: coordinating, coordinating/ cation-bridging, and “free” (H-bonded).

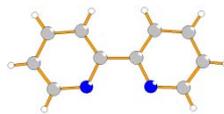


Accomplishment: development of novel, partially fluorinated hybrids

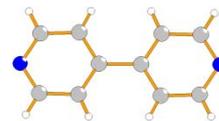
- our earlier attempts to make porous perfluorinated hybrids* were unsuccessful
- attempt make partially fluorinated hybrids with open metal sites
- explore this “ligand-metal space”:



1,2,4-triazole



2,2'-bipyridine



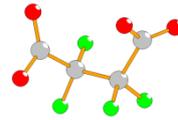
4,4'-bipyridine



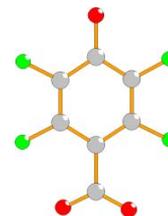
F₄-isophthalate



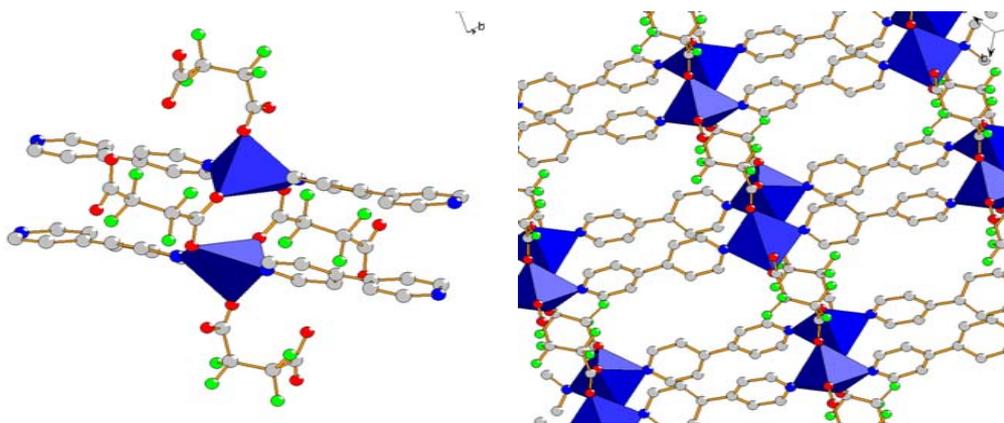
F₄-terephthalate



F₄-succinate



F₄-hydroxybenzoate

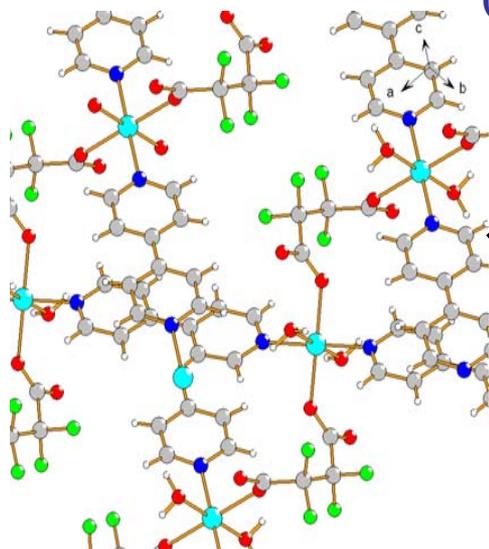


Example: Cu(F₄-succinate)(4,4'-bpy)

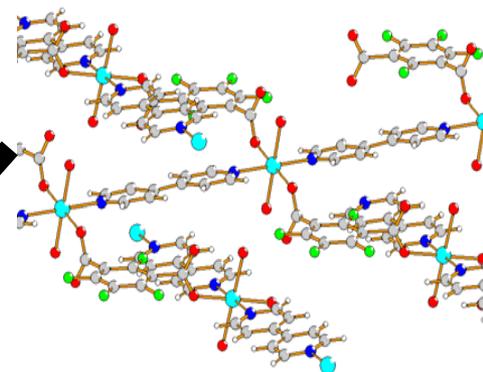
2-D layered structure

Dimer of Cu²⁺ trigonal bipyramids
connects four
F₄-succinate ligands

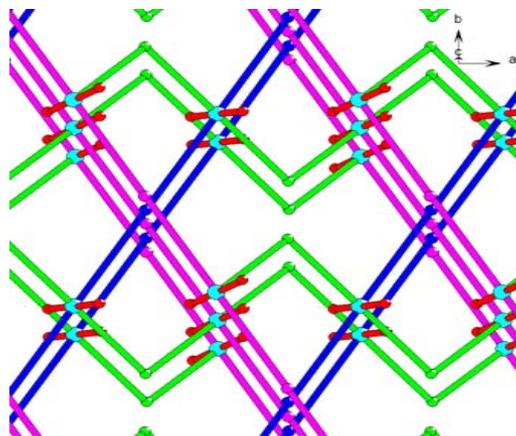
Accomplishment: partially fluorinated structures with 4,4'-bpy



Structures have same basic connectivity

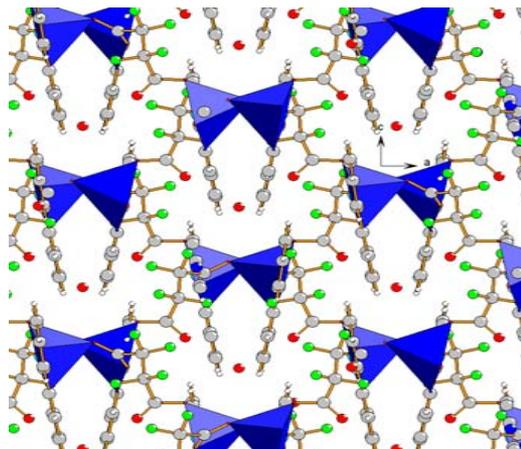
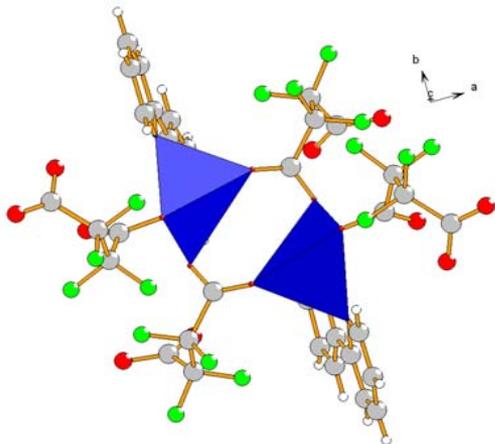


Pink/blue = 4,4'-bpy
Green = F₄-succinate or F₄-isophthalate
Aqua = Metal
Red = Water



Interesting and complicated 3-D structure built up from two different 1-D metal-bpy chains and one 1-D zig-zag F₄-succ/ipa chain

Accomplishment: partially fluorinated structures with 2,2'-bpy



Polar 3-D structure

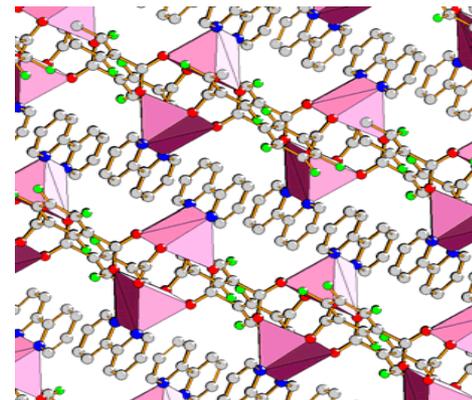
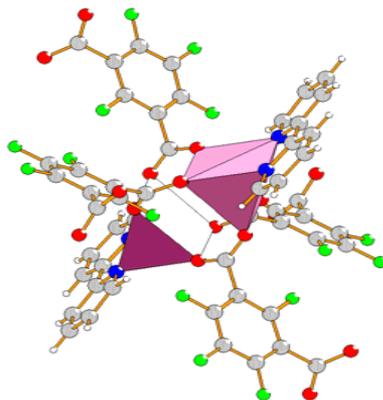
Dimer of Cu^{2+} square pyramids connects to four F_4 -succinate ligands

Potential for porosity, problem with purity

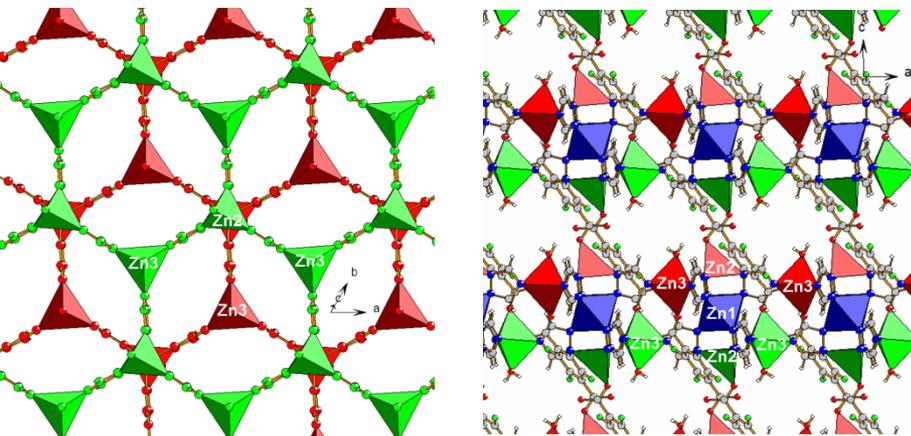


2-D layered structure

Dimer of Mn^{2+} trigonal prisms connects through four F_4 -isophthalate ligands



Accomplishment '08: $\text{Zn}_{2.5}(1,2,4\text{-triazole})_3(\text{tetrafluoroterephthalate})(\text{H}_2\text{O}) \cdot 2\text{H}_2\text{O}$



Zn-triazolate

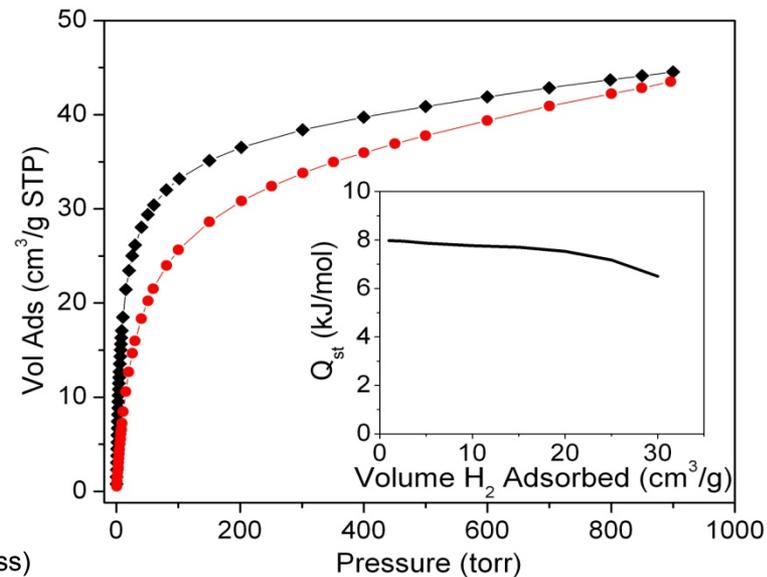
layers composed of two hexagonal arrays (left)

Layers connected by F_4 -terephthalate to give porous 3-D structure

Desolvated structure contains $4 \text{ \AA} \times 7 \text{ \AA}$ channel;
adsorbs 0.4 wt% H_2 at 77 K, 1 atm

Adsorption enthalpy $\sim 8 \text{ kJ/mol}$, among highest reported for
purely physisorptive interaction

Binding energies increased by more than 50% relative to
conventional MOF's: result of fluorinated surface, small pores



Accomplishment:

Demonstration of the Existence of **True Molecular** Chemisorption of Molecular Hydrogen with large binding energies

New computational studies of H₂ in Fe - and in Cu-ZSM-5:

- binding energies in Fe-ZSM-5 are much lower (13.5 kJ/mol - FeO species) than in Cu-ZSM-5 (70 kJ/mol, Cu(I)).
- Second H₂ can bind at Cu site

Follow-up on our previous observations:

-Room temperature H₂ isotherms in Cu-ZSM-5

(P. A. Gregoriev, A. Albinati and J. Eckert, Chemical Physics Letters **449**, 182, 2007).

-Hydrogen in Cu-ZSM-5

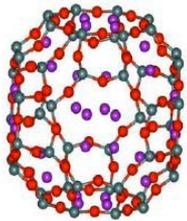
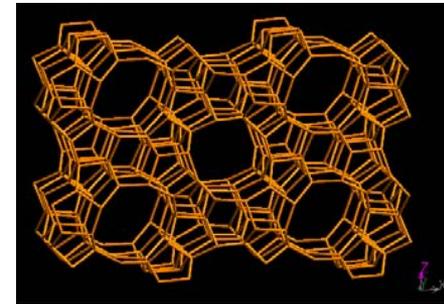
(P. A. Georgiev, A. Albinati, B. L. Mojet, J. Olivier and J. Eckert, J. Am. Chem. Soc. **129**, 8086, 2007)

- **THE FIRST** observation: Hydrogen adsorbed in “over-exchanged” Fe-ZSM-5

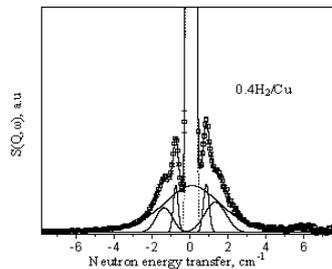
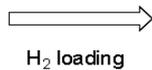
(B. L. Mojet, J. Eckert, R. van Santen, A. Albinati and R. Lechner, J. Am. Chem. Soc. **123**, 8147 2001)

-Unsaturated Ni binding sites in the Nickel Phosphate VSB-5 and in Nickel-5-Sulfoisophthalate

(P. M. Forster, J. Eckert, J.-S. Chang, S.-E. Park, G. Ferey and A. K. Cheetham J. Am. Chem. Soc. **125**, 1309, 2003; P. M. Forster, J. Eckert, B. D. Heiken, J. B. Parise, J. W. Yoon, S. H. Jung, J.-S. Chang, and A. K. Cheetham J. Am. Chem. Soc. **128**, 16846, 2006)

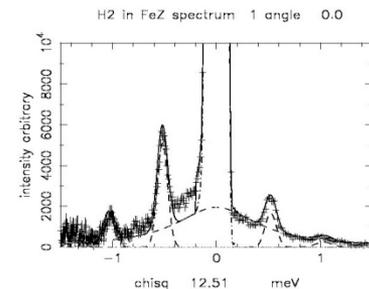


Cu-ZSM-5



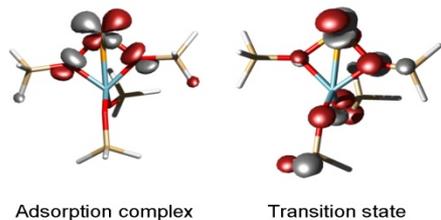
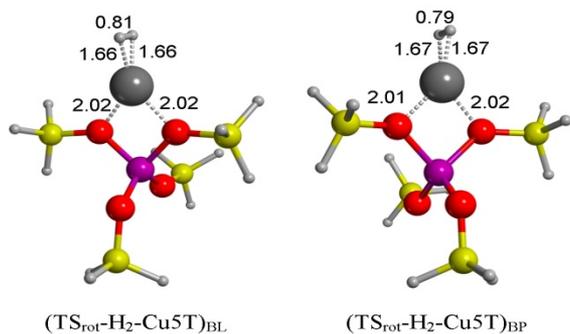
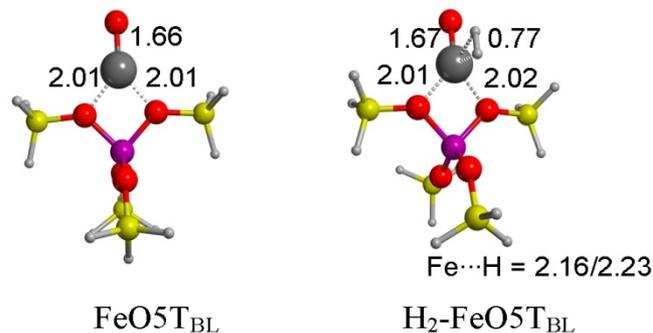
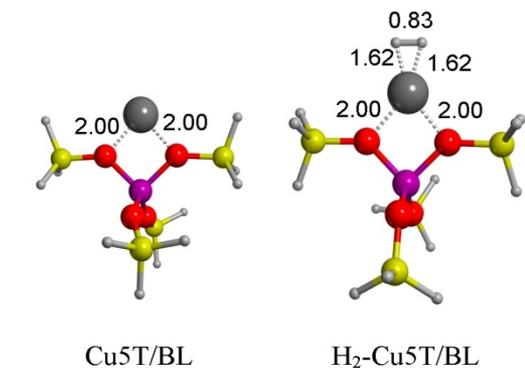
“Cu(η²-H₂)” Complex

H₂ rotational tunneling Spectra(INS)

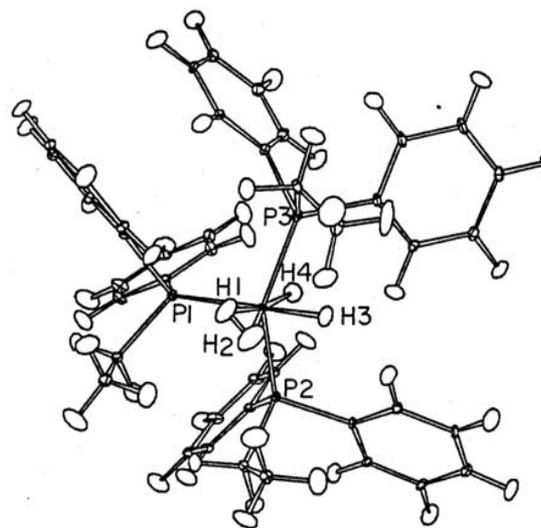


Note: Tunnel splitting in Fe-ZSM-5 >> Cu-ZSM-5 ⇒ Binding energy in Fe-ZSM-5 lower

Accomplishment: Cluster models for H₂ binding at Fe and Cu sites in ZSM-5

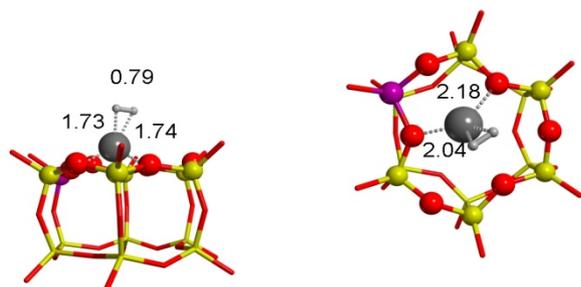


Comparison with Fe-dihydrogen complex
(single crystal neutron diffraction)

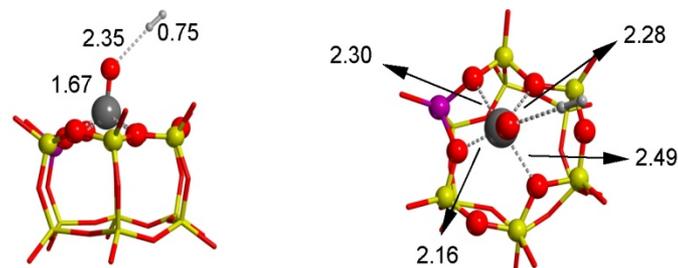


Fe-H = 1.57, 1.61 Å
H-H = 0.82 Å

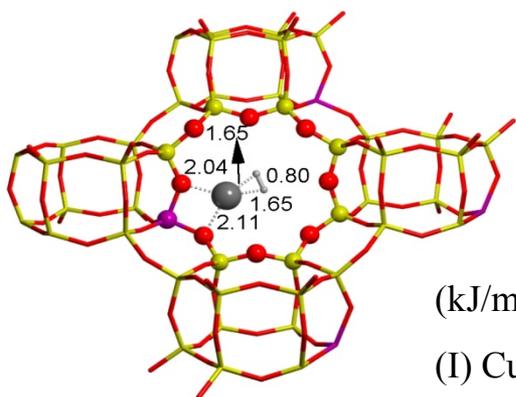
Accomplishment: Periodic models for H₂ binding at Fe and Cu sites in ZSM-5



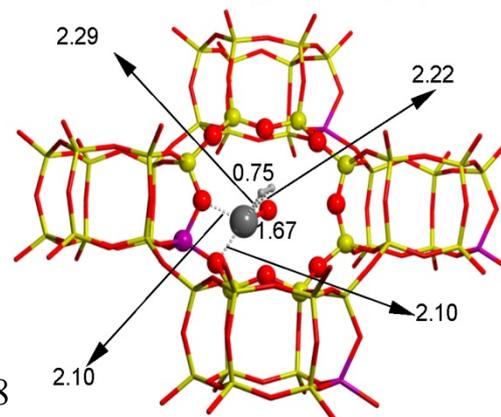
H₂-CuCHA(I)



H₂-FeO-CHA(I)FeO-CHA(IV)



H₂-CuCHA(IV)



H₂-FeO-CHA(IV)

	(kJ/mol)	E_{ads}	E_{INT}	D
(I) Cu	-15.0	-7.2	-7.8	
(I) Fe	-8.7	-0.7	-8.0	
(IV) Cu	-69.9	-58.2	-11.7	
(IV) Fe	-13.0	-2.3	-10.7	

CRYSTAL 03, DFT, with dispersion added according to Grimme

Xavier Solans-Montford and Mariona Sodupe Roure, Universitat Autònoma de Barcelona, Spain

Accomplishment: Rotational Barriers for H₂ in Fe- and Cu-ZSM-5 - Comparison of Calculations with Experiment

INS results

$$\omega_t = 1 \text{ cm}^{-1}$$

$$V_2 \sim 9 \text{ kJ/mol}$$

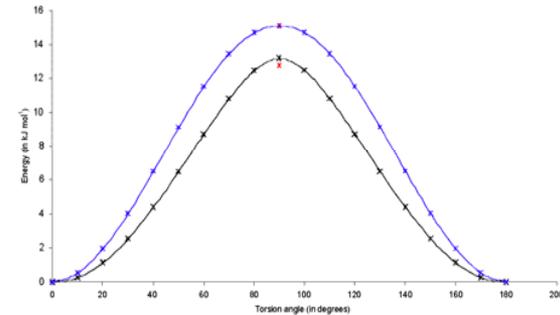
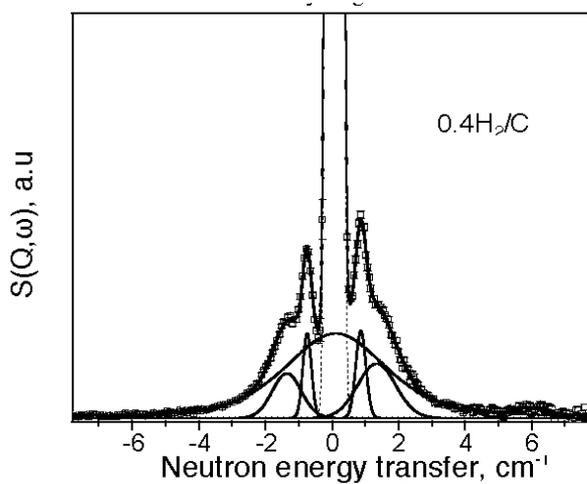
$$\omega_t = 4 \text{ cm}^{-1}$$

$$V_2 \sim 4 \text{ kJ/mol}$$

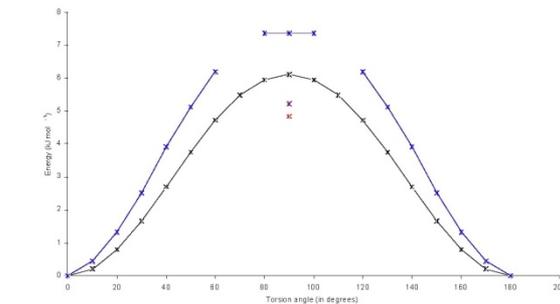
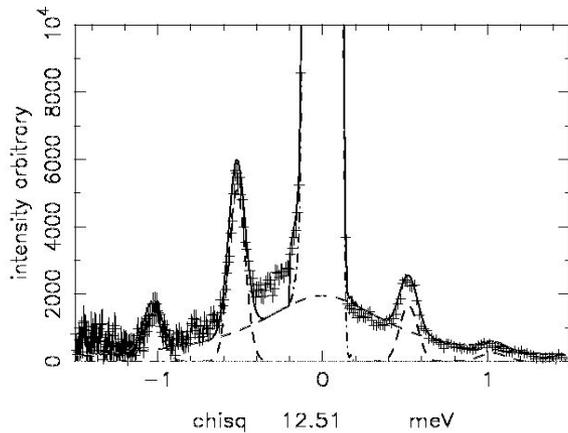
Calculation

$$V_2 \sim 13 \text{ kJ/mol}$$

$$V_2 \sim 6.5 \text{ kJ/mol}$$

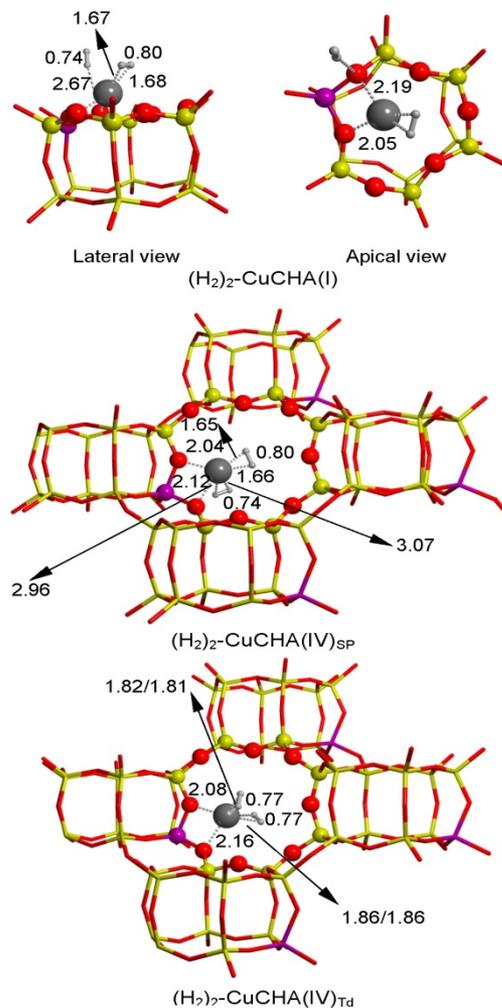
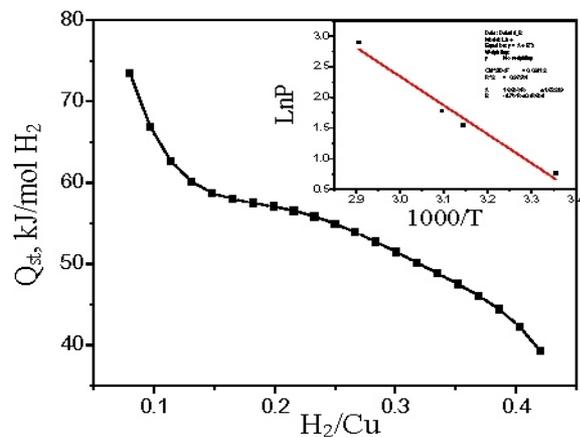


H2 in FeZ spectrum 1 angle 0.0



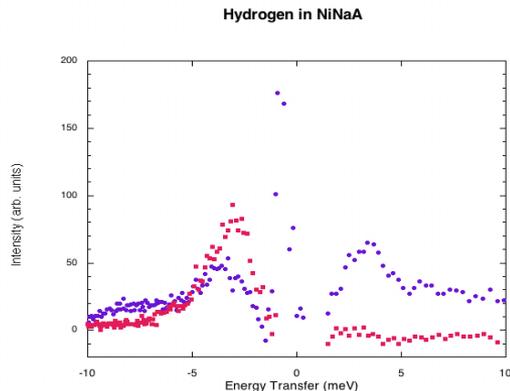
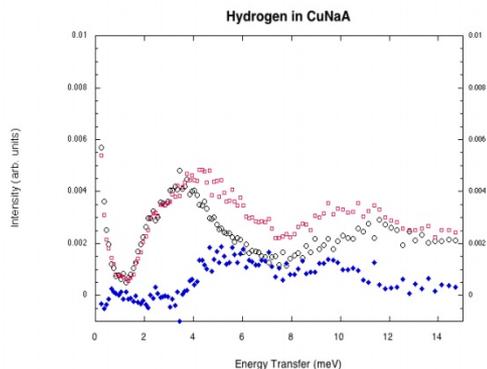
Accomplishment: Investigation of the Origin of the Loading dependence of Q_{st} in Cu-ZSM-5

Population of different sites?
Binding of multiple H_2 ligands?



Second H_2 binds only with dispersive forces, ~ 9 kJ/mol

Accomplishment: INS studies of H₂ adsorption at “open” metal sites - in-framework vs. extraframework(zeolite) metal sites



“0-1” rotational transition* for H₂ at

Cu in

Cu-ZSM-5 ~0.15 meV

CuNaA ~ 3 meV

Cu-ATC (MOF-11) ~ 8 meV

Cu-BTC (HKUST-1) ~ 9 meV

Ni in

VSB-5 ~ 1.5 meV

NiNaA ~ 2.9 meV

Ni-SIPA ~ 4, 5.5 meV

Ni-CPO-27 ~ 6.6 meV

Q_{st} values

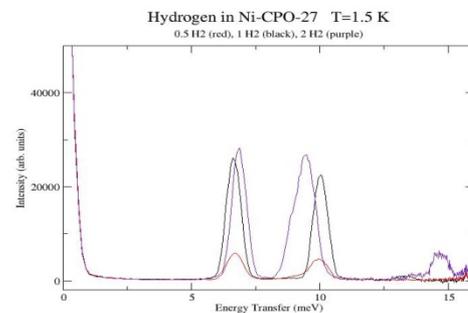
HKUST-1 : 6.8 to < 6 kJ/mol

Cu-ZSM-5: 74 to < 40 kJ/mol (on Cu)

Why the big differences?

⇒ location, location !! (M-H₂ distance):

2.39 Å in HKUST-1*, ~ 1.7 Å for coordinated H₂



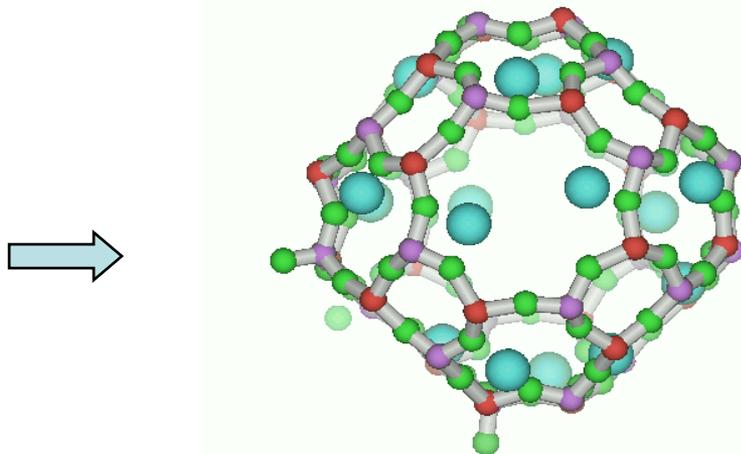
* Smaller value = larger barrier

Accomplishment: INS studies of Li^+ in zeolites

Li^+ is effective for H_2 binding - BUT ONLY when highly undercoordinated and exposed

Li^+ locations are similar as for NaA, except that Site III is not occupied by Li^+

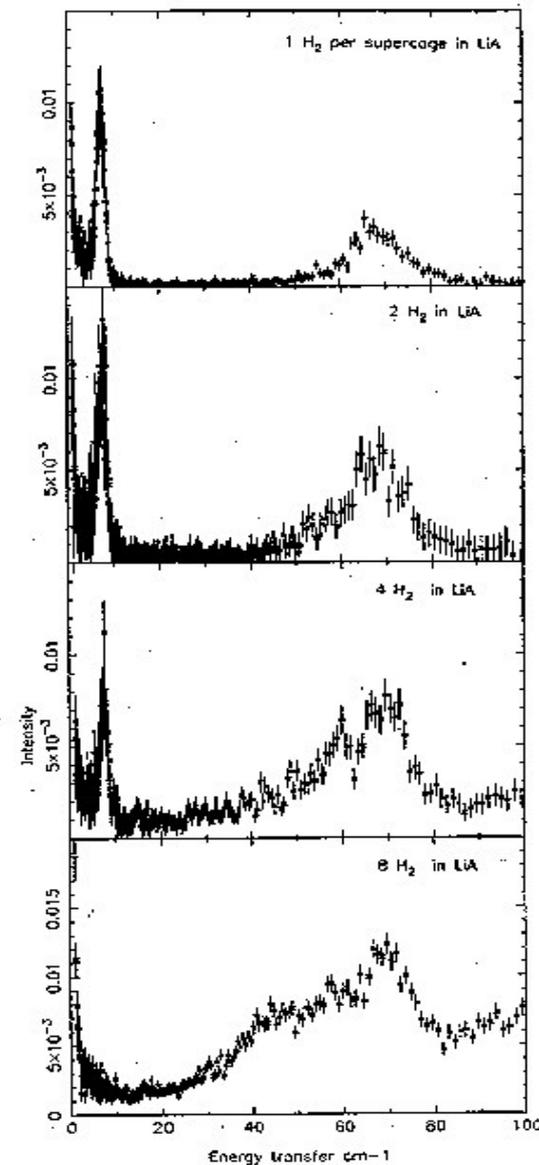
Instead: One or two cations offset in 8-ring window (site II):



Li^+ in six-ring window (site I) is NOT very effective ($\sim \text{Na}^+$, etc.), ~ 8 meV

One or two EXPOSED cations (sites II) make for much stronger interaction: H_2 rot. transition at ~ 1 meV

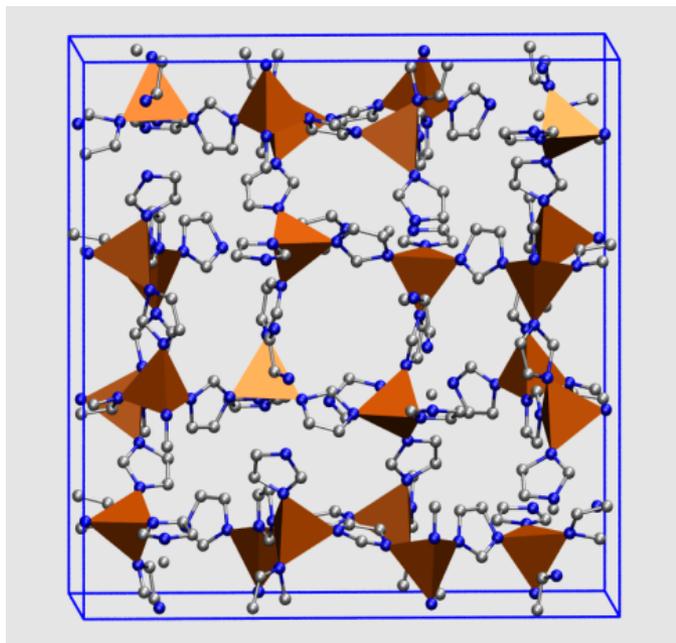
(IPNS)



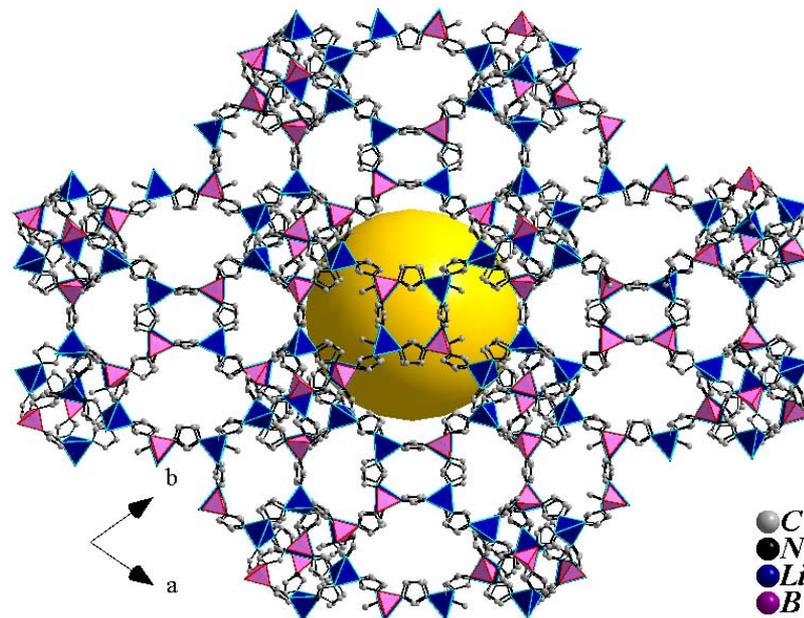
Accomplishment: Synthesis of Ultra Lightweight ZIFs

I-III Analogues of $Zn(\text{Im})_2$: $\text{LiB}(\text{Im})_4$

We have synthesized $\text{LiB}(\text{C}_3\text{N}_2\text{H}_3)_4$ with the dense zni structure; DFT calculations show that the sodalite and zeolite-A analogues should also be accessible (SOD recently confirmed by Feng & Bu, Angew. Chem. 2009)



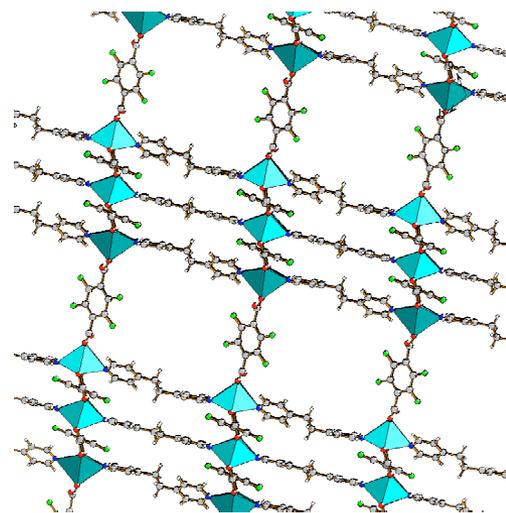
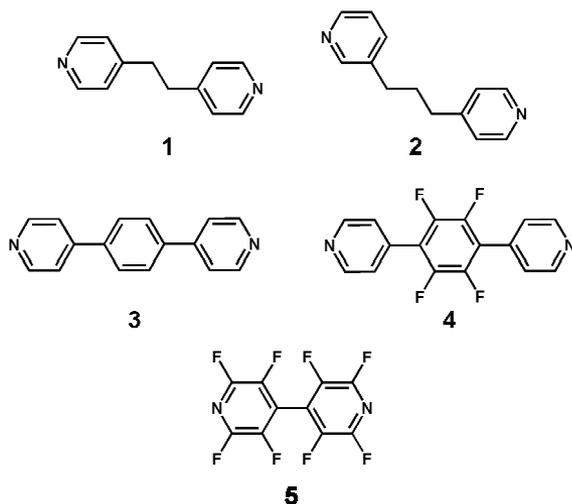
LiB-ZIF with zni structure



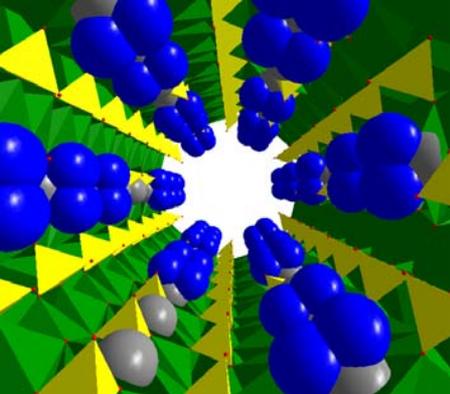
Computation: LiB-ZIF with LTA structure (+10 kJ/mol)

Future Work: Phase 2

- **Improvements in Ni-SIPA*** to raise binding energies from the current 10-11 kJ/mol
 - use metals other than Ni; will effect pore size as well
 - substitute Li, K, or Rb for Na
- **Create highly undercoordinated metal binding sites in MOF's by insertion**
 - use approaches similar to that in ZSM-5 in high-T stable MOF's (e.g. CuCl vapor)
 - may require prior modification of surface to bind metal, metal-oxide
- **Fluorinated linkers in hybrid materials**
 - synthesize materials with open metal sites other than Zn
 - achieve greater porosity (larger links - see below)
 - demonstrate the expected increase in H₂ binding to well above 10 kJ/mol



* our first hybrid to exceed 10 kJ./mol binding energy



Summary

- **Demonstrated the Presence of True Molecular Chemisorption of Hydrogen in a number of porous materials \Rightarrow higher binding energies than physisorption**
 - from 10 kJ/mol (Ni-SIPA), to 13.5 kJ/mol (Fe-ZSM-5) to well over 70 kJ/mol (Cu-ZSM-5)
- **Synthesized a large number of new hybrids with mixed fluorinated and organic linkers and decreased pore size**
 - binding energies increase by some 50% vs. typical MOF's
- **Utilization of INS on the H₂ hindered rotor: most sensitive technique for the study of H₂/host interactions at specific binding sites**
- **Open metal sites must very closely accessible by H₂; this is much more likely at extra-framework metal sites, and difficult for in-framework “open” metal sites**
- **Transition metal sites in porous materials \Rightarrow weight penalty may be addressed by**
 - Use of lightweight frameworks
 - Investigated the possibility of binding multiple dihydrogen ligands
 - requires highly undercoordinated metal sites
- **Combination of the above should make it possible to reach ~ 20 kJ/mol or better**
- **Practical materials of this type need increased surface area**