

Hydrogen Storage Materials with Binding Intermediate between Physisorption and Chemisorption

Juergen Eckert

University of California Santa Barbara

June 9, 2010

Project ID: ST074

Overview

Timeline

- Project start date: 4/1/2005
- Project end date: 9/30/2010

Budget

- Total project funding
 - DOE share: \$1,170,998.00
 - Contractor share: \$301,996.00
- Funding received in FY09
\$ 346,000.00
- Funding expected in FY10
\$ 0.0

Barriers

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

Partners

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

Collaborators

- M. Eddaoudi (USF)
- M. Sodupe Roure (UA Barcelona, Spain)
- P. Dietzel (U. of Oslo, Norway)
- I. Matanovic (LANL)

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

Relevance

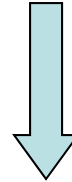
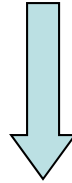
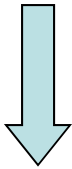
- Objectives for this review period: combine two or more factors known to enhance H₂ binding affinity in one material for greater overall gain
 - “open” metal sites in a charged (anionic) framework
 - Fluorinated organic linkers in frameworks with small pores
- Expected increase(*) in binding energies:
 - charged framework: + 4 kJ/mol, “open” in-framework metal sites +8kJ/mol
 - F substitution for: H 1 - 2 kJ/mol, reduction in pore size: 2 -3 kJ/mol
- Combination of several of these factors in one material:
 - Increase H₂ binding energies to around 20 kJ/mol (or more) as is needed for operation of a sorption based storage system under ambient conditions

(*) relative to a neutral framework, no open metal sites, such as MOF-5

Approach

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

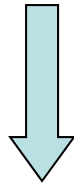


Framework Modifications

Reduction in Pore Size

Fluorinated
Linkers

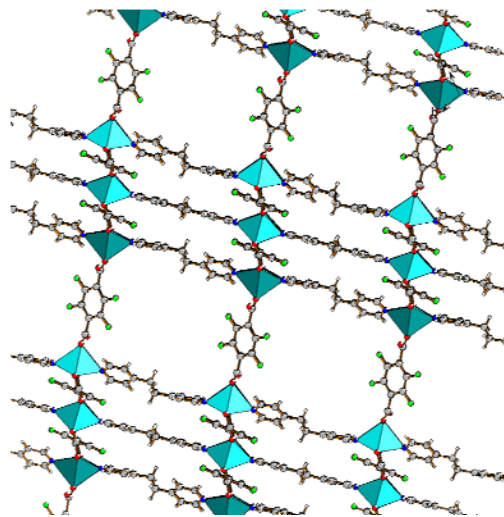
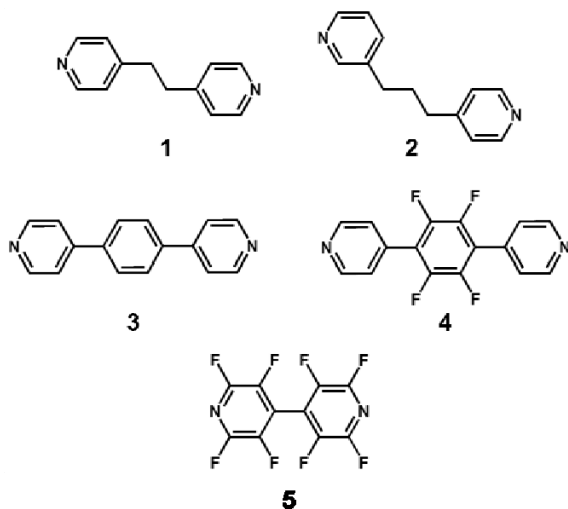
Charged Frameworks



Combine two or more of these approaches in one material

Approach -2

- Create highly undercoordinated metal binding sites in anionic ZMOF's by insertion of transition metal cations post synthesis
 - use approaches similar to that in ZSM-5 in high-T stable ZMOF's (e.g. CuCl vapor)
 - combine with anionic frameworks
- Utilize Fluorinated linkers in hybrid materials*
 - combine with small pores and (potentially), open metal sites
 - achieve greater porosity (larger links - see below)



*Initial result: zinc, **1**, and tetrafluoroterephthalate

Approach - 3

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)
 - Binding sites
 - Ab-initio potential energy surfaces for adsorbed H_2
 - 5-D rotation-translation quantum dynamics
 - Transitions for comparison with INS studies
4. **Extensive use of Inelastic Neutron Scattering** from the hindered rotations of the sorbed hydrogen molecule: **THE most sensitive probe of H_2 interactions** with host

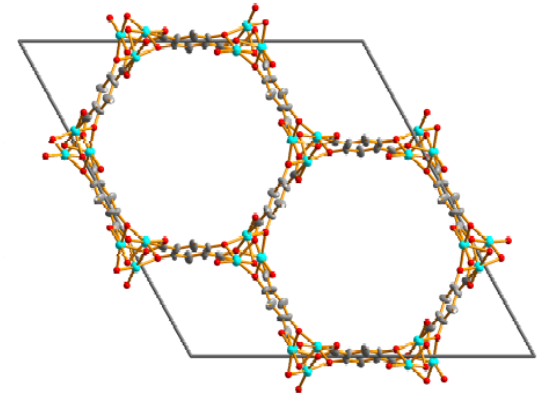
Instruments, Neutron Sources used:

NEAT, Helmholtz Zentrum Berlin, Germany

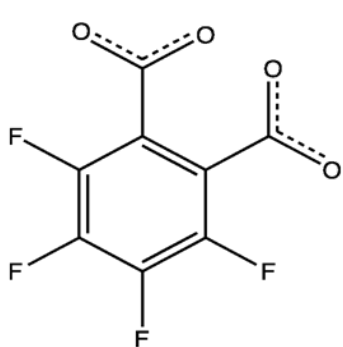
FOCUS, SINQ, Switzerland

TOFTOF, FRM-II, Technische Universität München, Germany

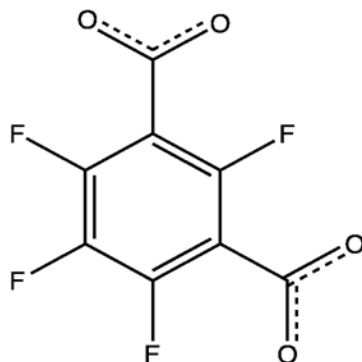
IN-5, Institut Laue-Langevin, Grenoble, France



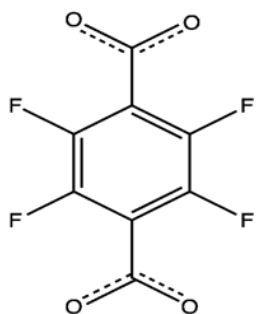
Accomplishment: Synthesis of a Large Number of Partially Fluorinated Hybrids



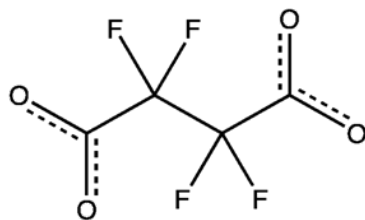
phtalate (tfpha)



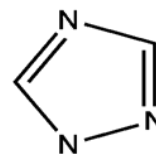
isophthalate (tfipa)



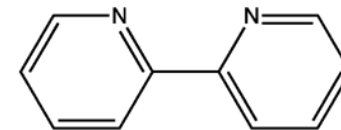
terephthalate (tftpa)



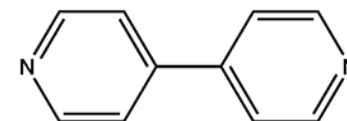
succinate (tfsuc)



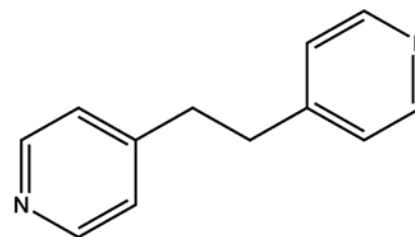
triazolate (trz)



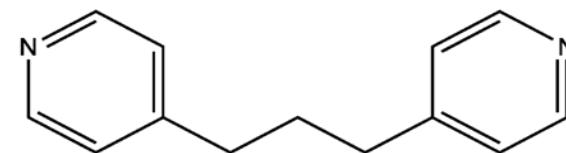
2,2'-bipyridine



4,4'-bipyridine



1,2-bis(4-pyridyl)ethane (bpe)



1,3-bis(4-pyridyl)propane (bpp)

- Perfluorinated analogues of commonly used carboxylate ligands
- Lots of known structures for comparison
- Acids are readily available

List of Partially Fluorinated Hybrids Synthesized

Zn₅(trz)₆(tftpa)₂(H₂O)₂ · 4H₂O
Zn₅(trz)₆(tfsuc)₂(H₂O)₃ · H₂O
Co₂(2,2'-bpy)₂(tftpa)₂(H₂O)
Mn₂(2,2'-bpy)₂(tftpa)₂(H₂O)
Mn(2,2'-bpy)(tfipa) · 0.5 H₂O
Cu(2,2'-bpy)(tfipa)
Cu(2,2'-bpy)(tftpa)
Cu(2,2'-bpy)(tfsuc) · 0.5 H₂O
Cu(2,2'-bpy)(tfsuc)(H₂O) · H₂O
Zn(2,2'-bpy)(tfipa)(H₂O)
Co(4,4'-bpy)(tftpa)(H₂O)₂
Zn(4,4'-bpy)(tftpa)(H₂O)₂
Co(4,4'-bpy)(tfpha)(H₂O)₂
Zn(4,4'-bpy)(tfpha)(H₂O)₂
Co(4,4'-bpy)(tfsuc)(H₂O)₂
Co(4,4'-bpy)(tfipa)(H₂O)₂
Zn(4,4'-bpy)(tfipa)(H₂O)₂

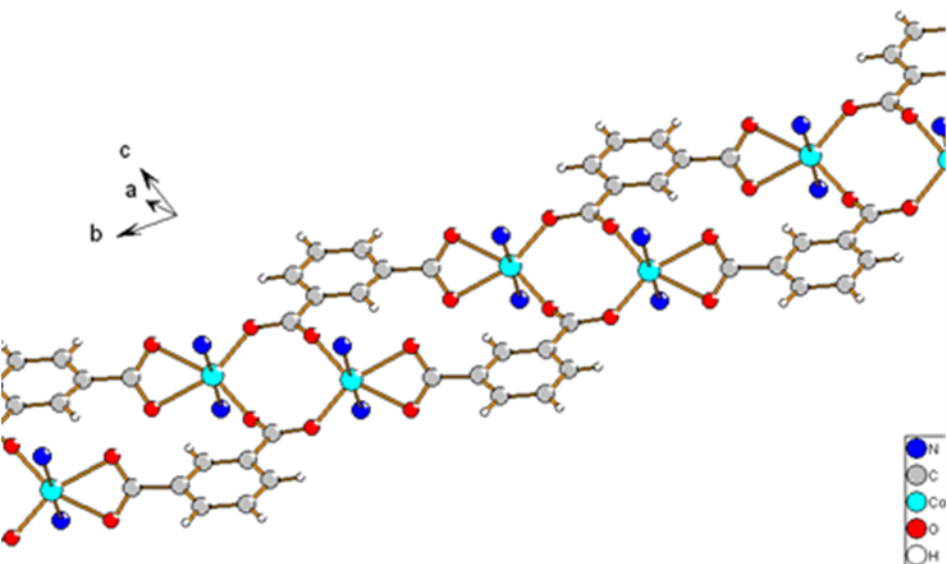
Co₂(4,4'-bpy)(tfhba)₂ · 4,4'-bpy
Zn₂(4,4'-bpy)(tfhba)₂ · 4,4'-bpy
Cu₂(bpe)(tfipa)₂(H₂O)
Co₂(bpe)₃(tfipa)₂
Co(bpe)(tftpa)
Co₂(bpe)₃(tfhba)₂(H₂O)₄ · bpe · 2H₂O
Ni₂(bpe)₃(tfipa)₂
Zn₂(bpe)₃(tfipa)₂
Zn(bpe)(tftpa)
Zn(bpe)(tfpha)
Co(bpp)(tftpa)(H₂O)₂
Cu(bpp)(tfipa)(H₂O)
Cu(bpp)(tftpa)
Cu₂(bpp)(tftpa)₂(H₂O)
Cu(bpp)(tfpha)
Co₂(bpp)₃(tfpha)₂(H₂O)₂
Zn(bpp)(tfpha) · H₂O

Hulvey, Z.; Ayala, E.; Furman, J. D.; Forster, P. M.; Cheetham, A. K. *Cryst. Growth Des.* **2009**, *9*, 4759.

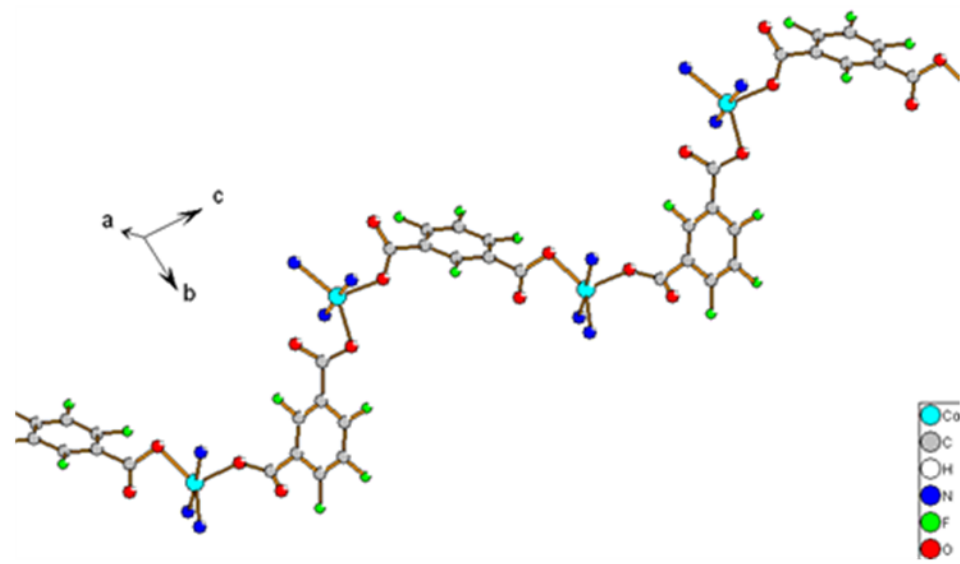
Hulvey, Z.; Ayala, E.; Cheetham, A. K. *Z. Anorg. Allg. Chem.* **2009**, *635*, 1753.

Hulvey, Z.; Furman, J. D.; Turner, S. A.; Tang, M.; Cheetham, A. K. *Submitted*.

Partially Fluorinated Hybrids: Examples - 1



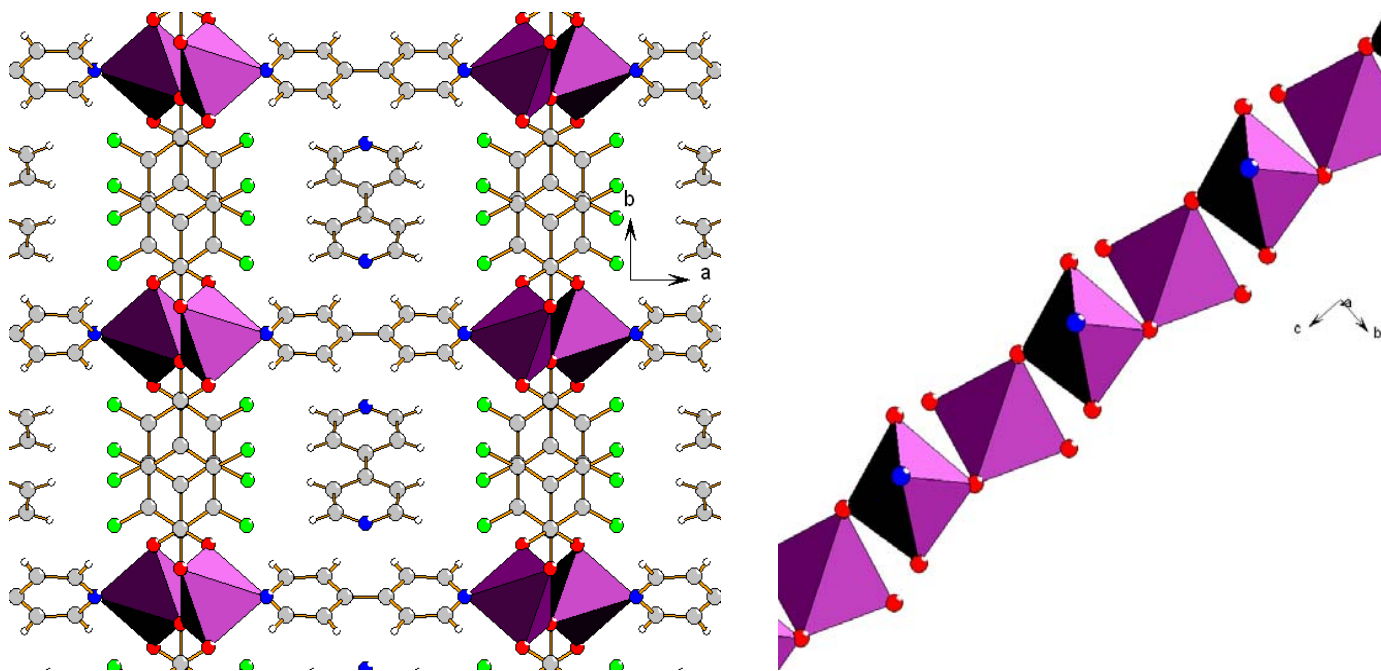
Co^{2+} + bis-pyridyl ethane + isophthalate



Co^{2+} + bis-pyridyl ethane + tetrafluoroisophthalate

- Ligand planarity leads to ribbon-like motif (left)
- Twisting of carboxylates (right) causes canting of adjacent metal polyhedra and additional dimensions of connectivity

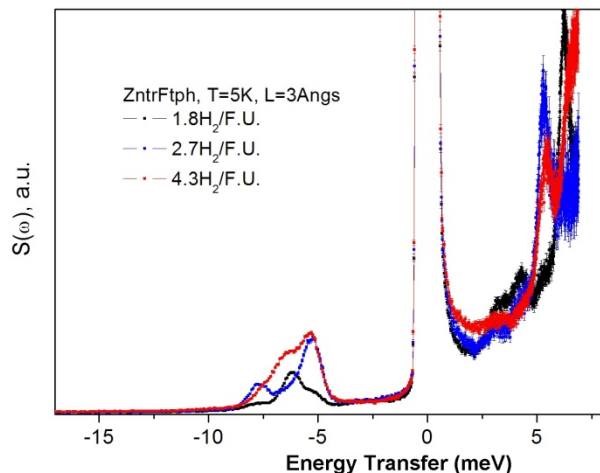
Partially Fluorinated Hybrids: Example -2: Magnetism in $\text{Co}(4,4'\text{-bpy})(\text{tfhba})$



- Chain of corner-sharing CoO_4N trigonal bipyramids
- Ferromagnetic along chains, weak AFM between

Accomplishment: Inelastic Neutron Scattering Studies* of H₂ in Zn_{2.5}(1,2,4-triazole)₃(tetrafluoroterephthalate)(H₂O) · 2H₂O

(Hindered) rotational transitions of adsorbed H₂



First few transitions:

ZnTrFtph: 5.5, 6.5, 8 meV

MOF-5: 10.3, 12 meV

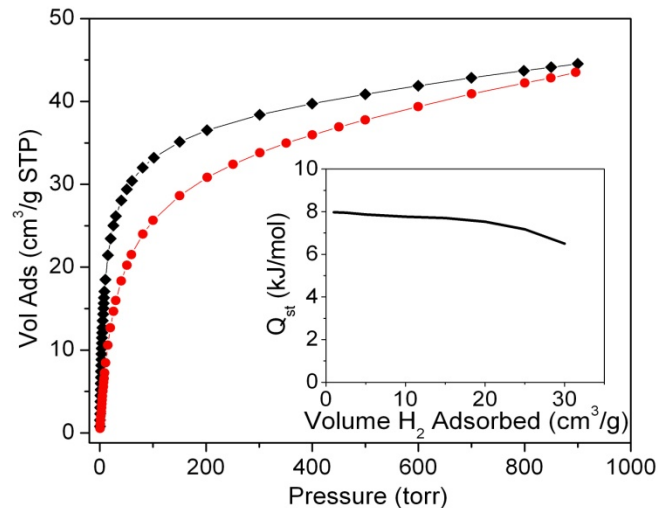
For comparison:

typical Carbons: 14.5 meV

“free” rotor 14.7 meV

Lower transition frequency = higher barrier ~ stronger binding

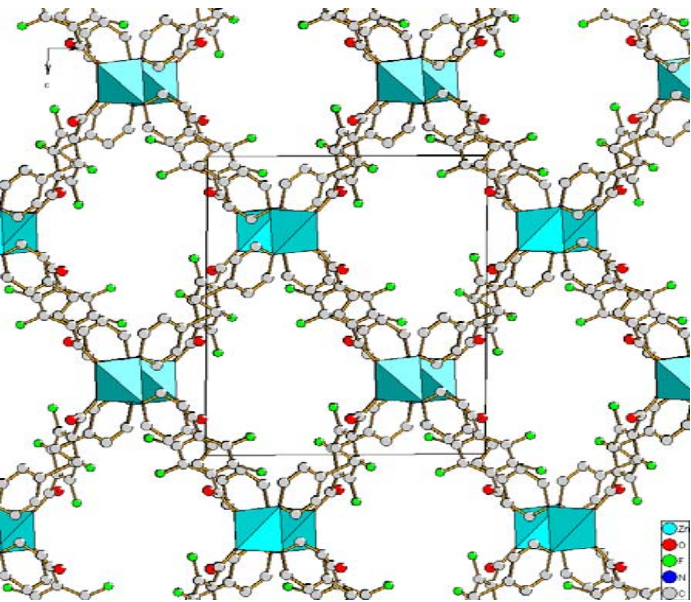
Adsorption enthalpy ~ **8 kJ/mol**: increase
 by more than 50% relative to
 conventional MOF's: result of **fluorinated surface + small pores**



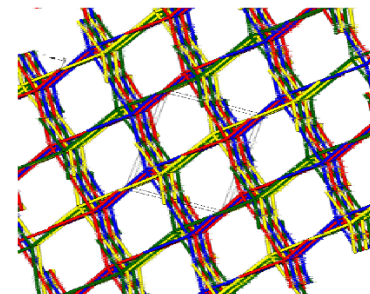
*TOFTOF, FRM-II, Technical University Munich, Germany

Differentiate Effect of Pore Size from F/H substitution

Zn(bpe)(tftpa)·cyclohexanone (bpe = 1,2-bis(4-pyridyl)ethane; tftpa = tetrafluoroterephthalate)



Larger pores; interpenetration of lattices prevented by cyclohexanone template can be removed $T \geq 150^\circ\text{C}$

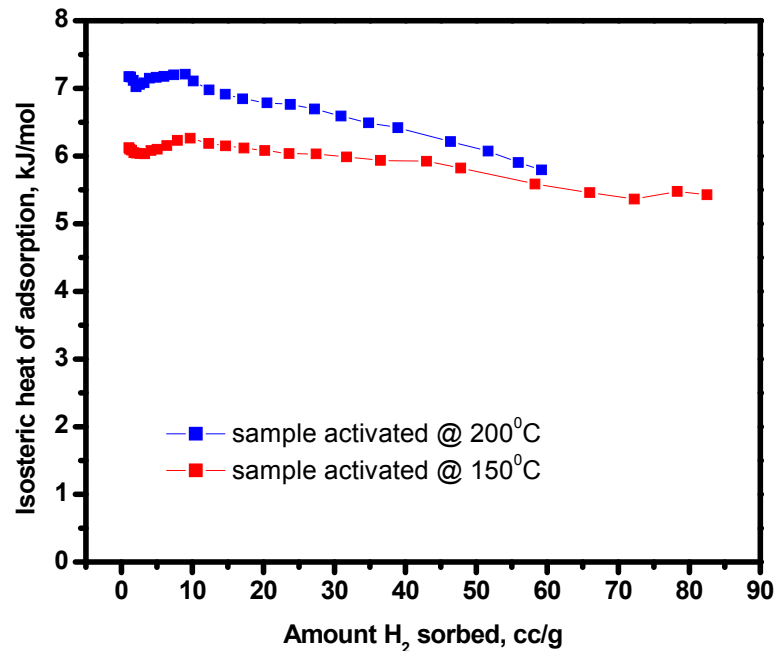


H_2 capacity, Q_{st} (max)

1.03 wt %	6.3 kJ/mol	150°C
0.73 wt %	7.2 kJ/mol	200°C

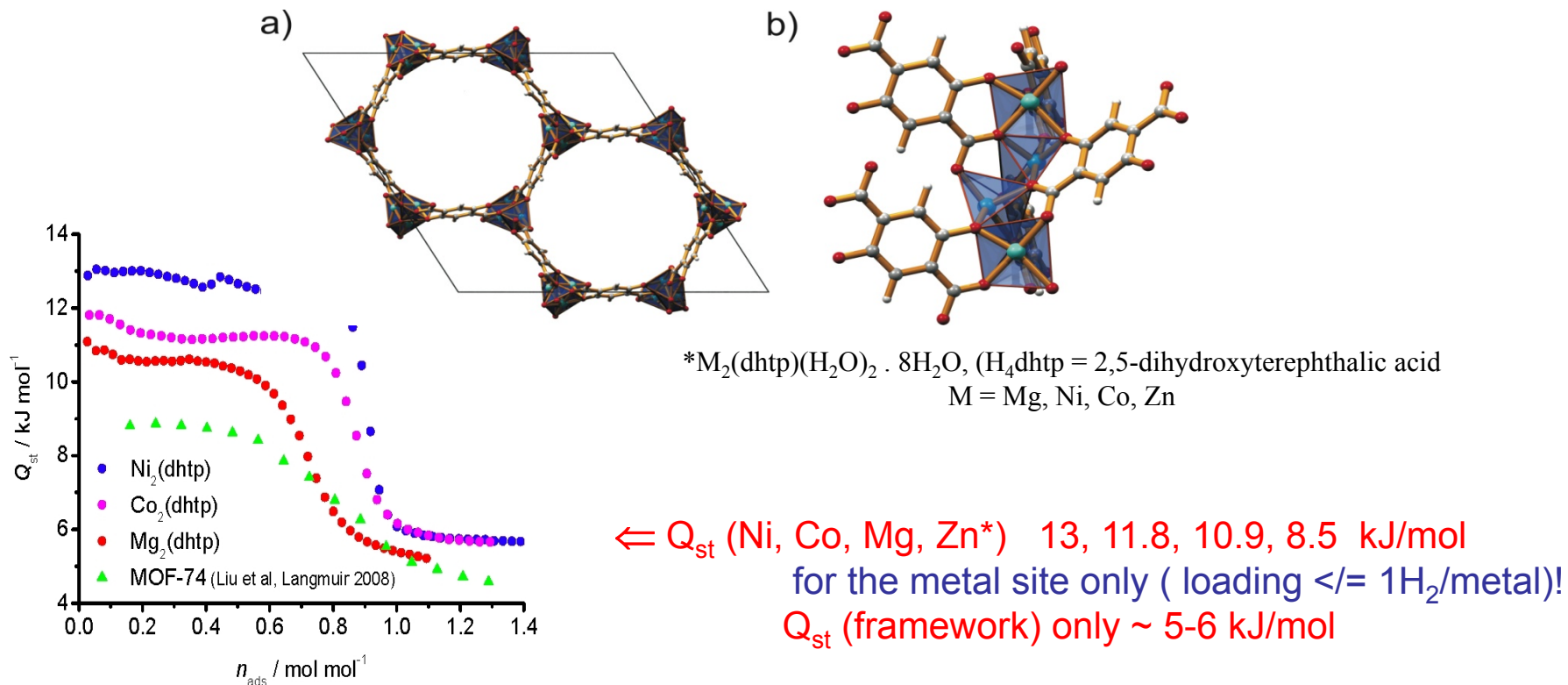
**Higher activation T leads to smaller pores:
greater Q_{st} , lower capacity**

Isosteric heat of adsorption



Accomplishment: Systematic study of “open” metal sites in a series of isostructural compounds CPO-27 (analog of MOF-74)

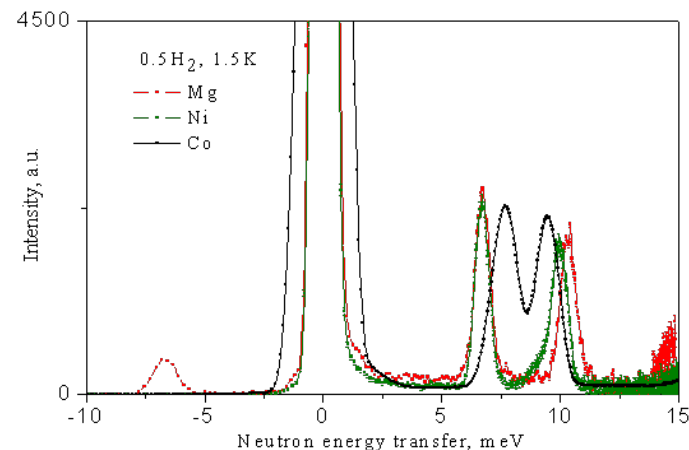
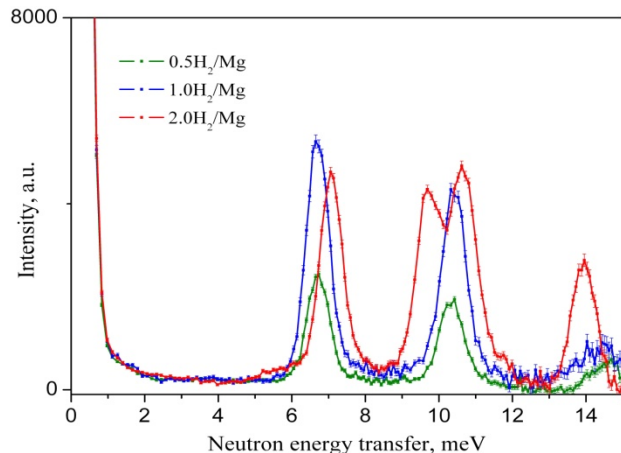
Pascal Dietzel, Peter Georgiev, Juergen Eckert, Thierry Strässle and Tobias Unruh (Chem. Comm., in press, 2010)



“Open” metal sites in CPO-27* - 2

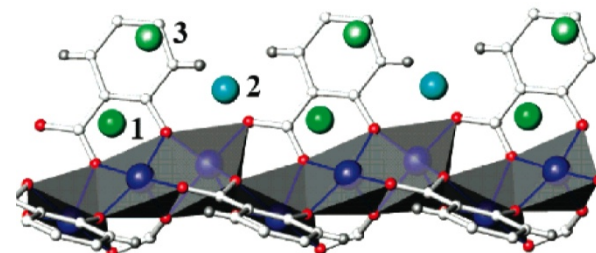
*M₂(dhtp)(H₂O)₂ · 8H₂O, (H₄dhtp = 2,5-dihydroxyterephthalic acid
M = Mg, Ni, Co, Zn

Pascal Dietzel, Peter Georgiev, Juergen Eckert, Thierry Strässle and Tobias Unruh (Chem. Comm., in press, 2010)



Lowest INS peak (Ni, Co, Mg, Zn): 6.6, 7.7, 6.7, 8 meV
: Rotational PES not sensitive to the type of metal

INS spectrum: Loading dependence:
Two low energy peaks ~ metal site

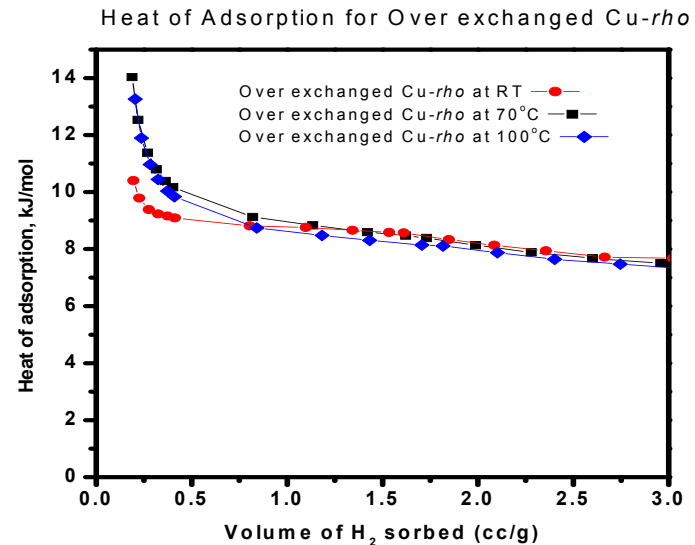
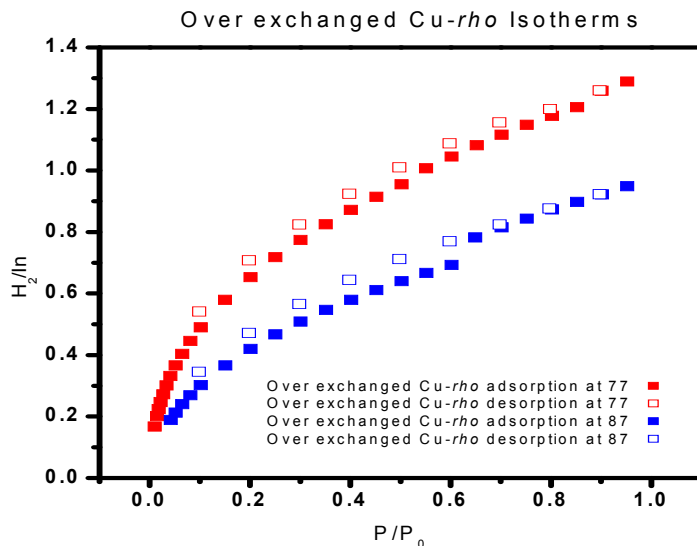


: H₂ is NOT coordinated: (MOF-74) Site 1 D₂ to Zn distance ~ 2.6 Å *

Accomplishment

Large numbers of Cu cations in a charged framework: Overexchanged, Anionic *rho*-ZMOF's (Hasnaa Mouttaki, Ina Sava, USF)

- 2 days in a solution of 0.075M $\text{Cu}(\text{NO}_3)_2 \cdot 2.5(\text{H}_2\text{O})$
- Atomic absorption shows **48 Cu^{2+} for 48 In**, as opposed to **24 Cu^{2+} for 48 In** expected

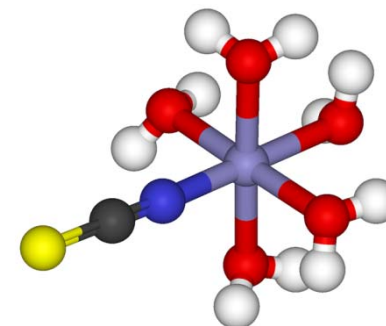
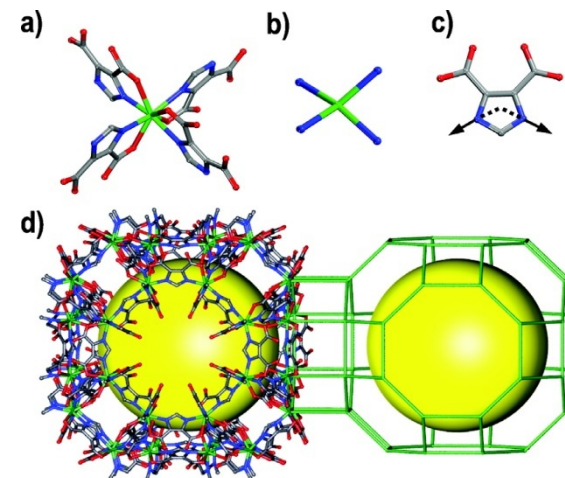


Perhaps a small number of Cu, which are not fully hydrated?

⇒ Must increase thermal stability to make removal of aqua ligands on Cu possible - as in zeolites

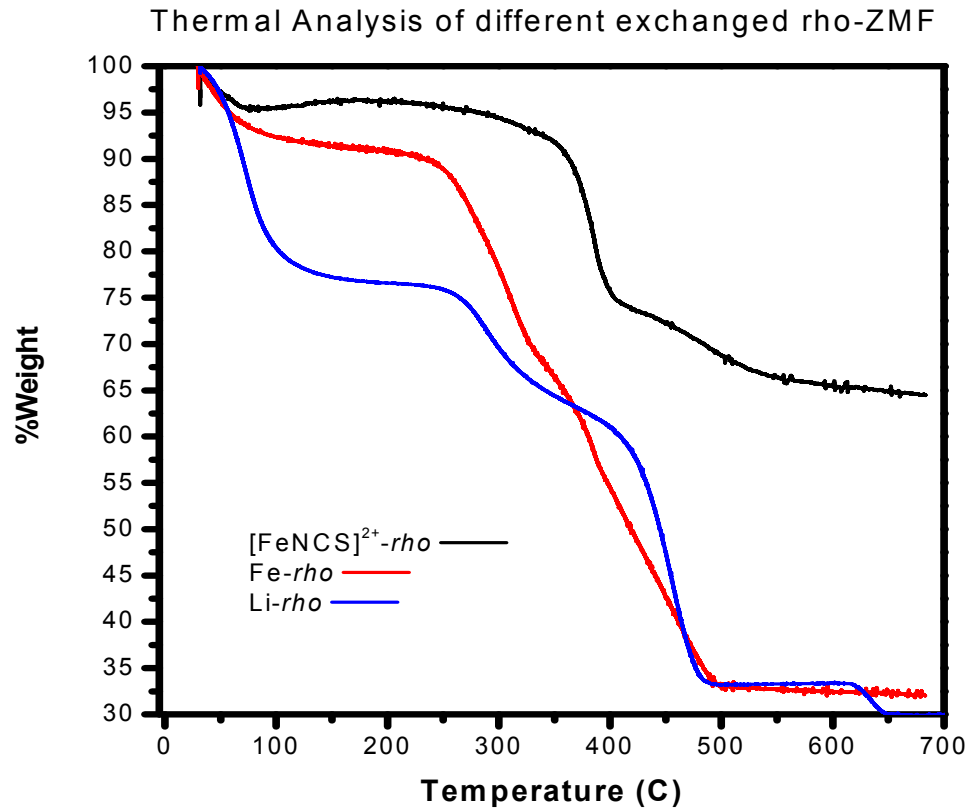
Accomplishment:
Iron Thiocyanate Complex Cation
 in *rho*-ZMOF by ion exchange

Cation exchange in *rho*-ZMOF



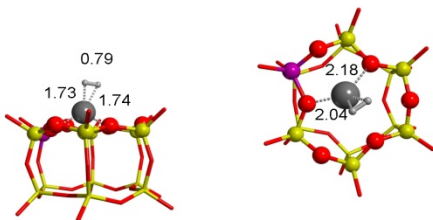
Accomplishment:

MUCH improved thermal stability of overexchanged rho-ZMOF's



Possibility of removing ligands on the cations ⇒ open up metal sites

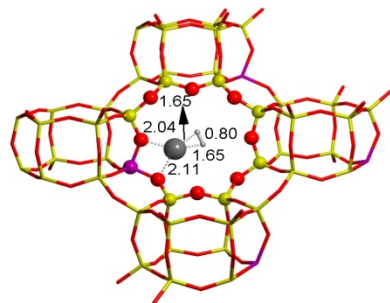
Accomplishment: INS and Computational Study on the Effect on Binding Strength of Site Accessibility By H₂



H₂-CuCHA(I)

Cu-ZSM-5, site I

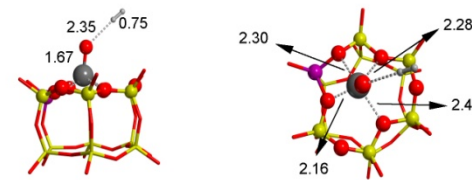
Rotational Transition: 2.3 meV, Binding Energy: **15 kJ/mol***



H₂-CuCHA(IV)

Cu-ZSM-5, site IV

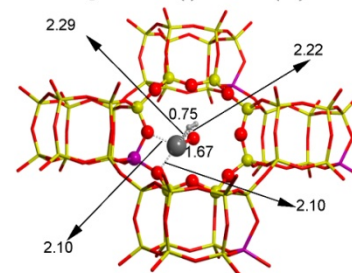
0.08 meV, **70 kJ/mol**



H₂-FeO-CHA(I)FeO-CHA(IV)

(FeO)-ZSM-5, site IV

0.5 meV, **13.5 kJ/mol**



H₂-FeO-CHA(IV)

Significant direct electronic interaction (H₂ coordination) only for highly undercoordinated Cu in site IV

Collaborations

- (1) Mohamed Eddaoudi*, Mike Zaworotko* (USF)
Subcontract: synthesis of new materials
- (2) Xavier Solans-Montfort and Mariona Sodupe Roure (Universidad Autonoma, Barcelona Spain)
Computational support
- (3) Pascal Dietzel (SINTEF, Oslo, Norway)
Materials with “open” metals sites
- (4) Peter Georgiev (Universita di Milano, Italy)
Neutron Scattering Experiments
- (5) Paul Forster (UNLV)
(Micro-) single crystal X-ray diffraction
- (6) Ivana Matanovic (LANL), Zlatko Bacic (NYU),
Kaido Sillar and Joachim Sauer (Humboldt Universität, Germany)
Jonathan Belof* and Brian Space* (USF)
Computational support: ab-initio potential energy surfaces for adsorbed H₂ combined with 5-D rotation-translation quantum dynamics energy levels for comparison with INS experiments

Summary from INS Characterization

Rotational tunneling spectroscopy is an **extraordinarily sensitive measure of local H₂/binding site interactions**:

observed transitions: 1 cm⁻¹ to 120 cm⁻¹

computational developments (in progress) will make it more quantitative

Lessons from zeolites:

Interaction with **EXTRAframework** cation typically is stronger than with a metal that is part of the framework (**INframework**)

Accessibility of metal sites:

metal needs to be highly undercoordinated and accessible (e.g. SIII' in zeolite X):

M-(H₂) distance ≤ 1.8 , NOT 2.3+ !

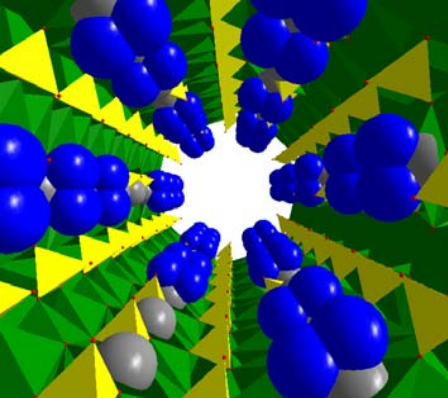
Approximate gains in hydrogen binding from:

framework modifications:	+ 1 to 3 kJ/mol
charged framework:	+ < 4 kJ/mol
“open” metal sites	+ < 8 kJ/mol
molecular chemisorption	+ 8 to ~ 75 kJ/mol

Future Work: Remainder of FY10

- Create highly undercoordinated metal binding sites into anionic ZMOF's by insertion of transition metal cations post-synthesis
 - characterize sorption characteristics
 - structural studies
 - INS studies (TOFTOF, FRM-II) September 20 - 25, 2010
- Fluorinated linkers in hybrid materials
 - Computer "experiment" of the effect of F/H substitution vs. pores size

Thereafter: The End ?



Summary

Demonstrated the potential for **overexchanging anionic ZMOF's** with Cu, Fe and other (hydrated) cations, with perhaps a few open metal sites.

Greatly **improved thermal stability** of ion-exchanged ZMOFS - ligand removal should be possible

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

appr. 1/3 of the increase is from F/H substitution, 2/3 from pores size reduction

Demonstrated the presence of **true molecular chemisorption of hydrogen** in a number of porous materials \Rightarrow much higher binding energies than physisorption

Systematic studies of “open” metal sites in zeolites and MOF's:

effectiveness of in-framework open metal sites are very limited

metal sites have to be highly undercoordinated and accessible: extraframework

Road map to RT sorption based material involves some combination of the factors that have been determined in this (and other) studies.