DOE Hydrogen Program

A Biomimetic Approach to Metal-Organic Frameworks with High H_2 Uptake

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Overview

Timeline

- Project start date: July 2007
- Project end date: July 2011
- Percent complete: 15%

Budget

- Total project funding
  - DOE share: $1.4 M
  - Contractor share: $0.9 M
- FY07 $122,000
- FY08 $350,000

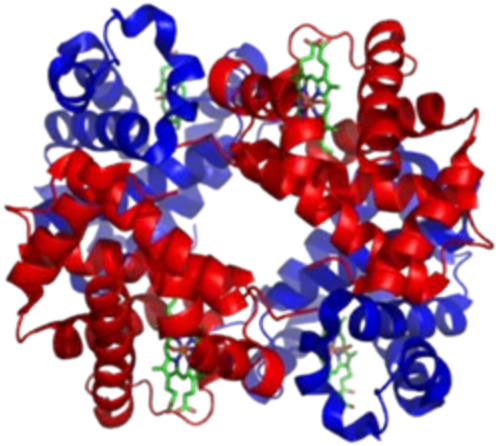
Barriers

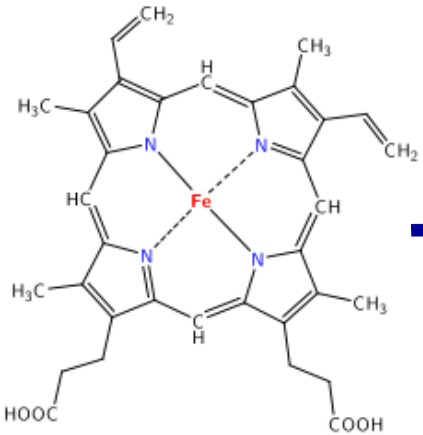
- H_2 uptake at room temperature is low despite high uptake at 77 K
- Current heat of adsorption for common sorbents is around 5 kJ/mol
- To reach high storage capacity at ambient temperature, ΔH needs to be in the range of 15 to 30 kJ/mol

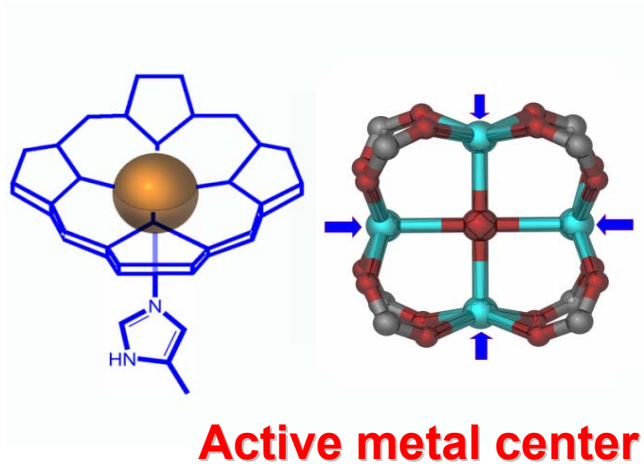
Partners

- Air Product
- NREL
- NIST
- KRICT, Korea
- U of Michigan
- Universität Göttingen, Germany
- Stony Brook U
- UNLV
- UC Santa Barbara

The Biomimetic Approach







- Use concepts evident in metalloproteins to guide the synthesis of metal-organic frameworks (MOFs) with enhanced gas-adsorption affinity
- The approach is analogous in many ways to oxygen transport protein such as hemoglobin (reversible, cooperative, and with active metal centers)
- The effects of interpenetration, coordinatively unsaturated metal centers (UMCs), and alignment of UMCs on hydrogen uptake of MOFs will be explored

Objectives

- Design, synthesis, and characterize MOFs with active metal centers aligned in porous channels and accessible by H_2 molecules
- Through optimized, cooperative binding, the MOFs are expected to have enhanced affinity to H_2
- These MOFs can help to reach the DOE 2010 and ultimately 2015 hydrogen storage goal

Align Coordinatively Unsaturated Metal Centers for Stronger H_2-framework Interaction

Barriers:

The heat of hydrogen-adsorption of MOFs is still limited within the 5 to 10 kJ/mol range.

Reason:

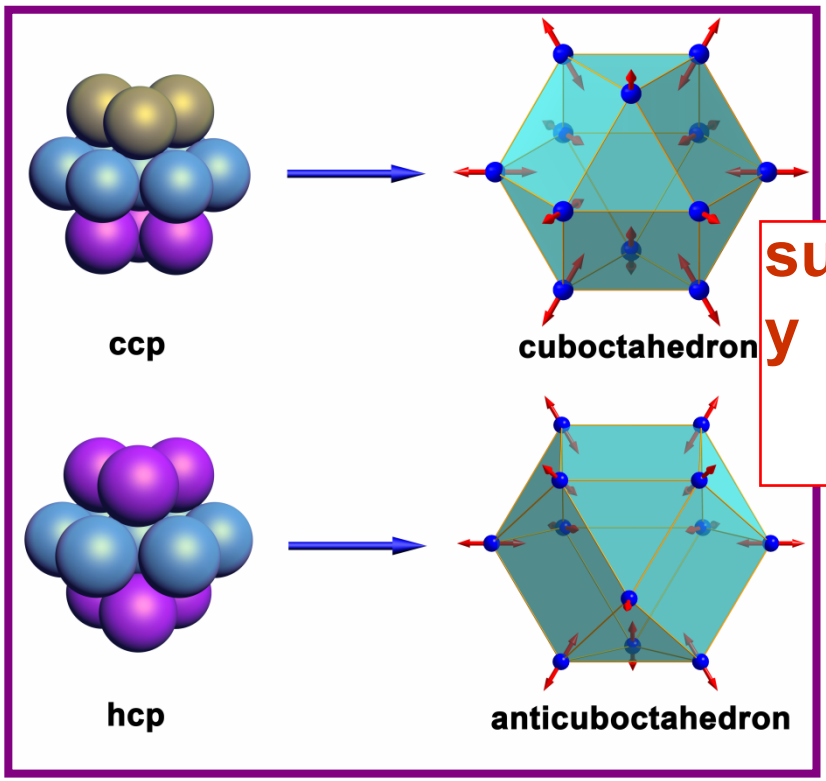
- Dihydrogen, as simple as two protons and two electrons, holds its electrons tightly and is difficult to polarize
- The H_2 molecule is also a poor acid and a weak base and the energy levels of its frontier orbitals prevent the direct interaction between dihydrogen and other non-metals
- Transitional metal can interact with H_2 molecule but Kubas-type binding may be too strong. Coordinatively unsaturated metal centers can moderately increase the enthalpy of hydrogen adsorption in MOFs

Strategy:

strengthen the MOF-H_2 interaction

- Maximize the number of nearest neighboring UMCs (Unsaturated Metal Centers) of each H_2-hosting void in a 3D framework and to align the UMCs so that they can interact directly with the guests (H_2 molecules) inside the void
- In close-packing of spheres, such as ccp or hcp, each sphere has 12 nearest neighbors. Connecting the 12 neighbors gives rise to a cuboctahedron (ccp) or an anticuboctaheddron (hcp).

Formation of Anticuboctahedral or Cuboctahedral cage



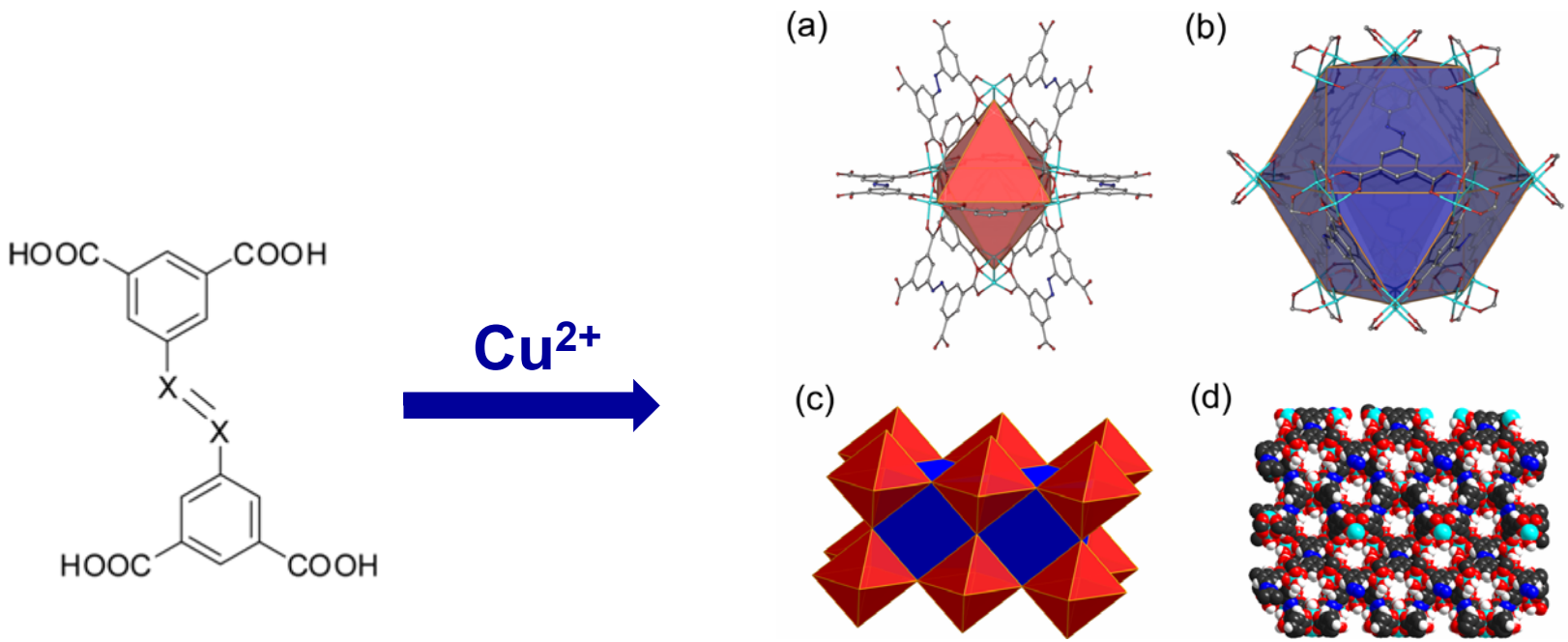
Vectors in red represent open metal-coordination sites.

summary

- For H_2-storage MOFs, using close-packing pattern can strengthen H_2-MOF interaction
- In close-packing of spheres, a sphere maximum of 12 neighbors. cting the 12 spheres form a ahedron for cubic close-packing nd an anticuboctahedron for onal-close packing (ccp)
- If the cages are used for hydrogen storage, the interaction of the H_2 molecules and the open metal centers placed on the 12 corners of a cage can be strengthened

These cages can be formed using isophthalate derivatives.

First Attempt to Align Coordinatively Unsaturated Metal Centers

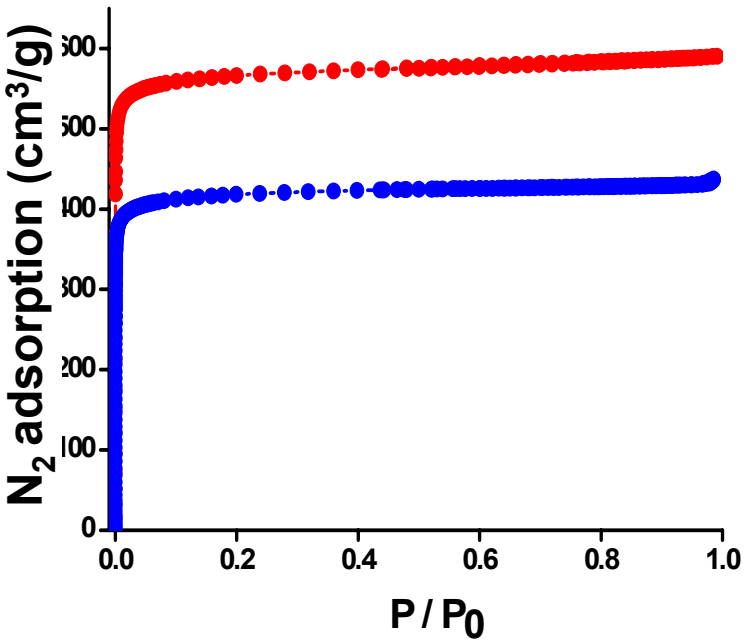


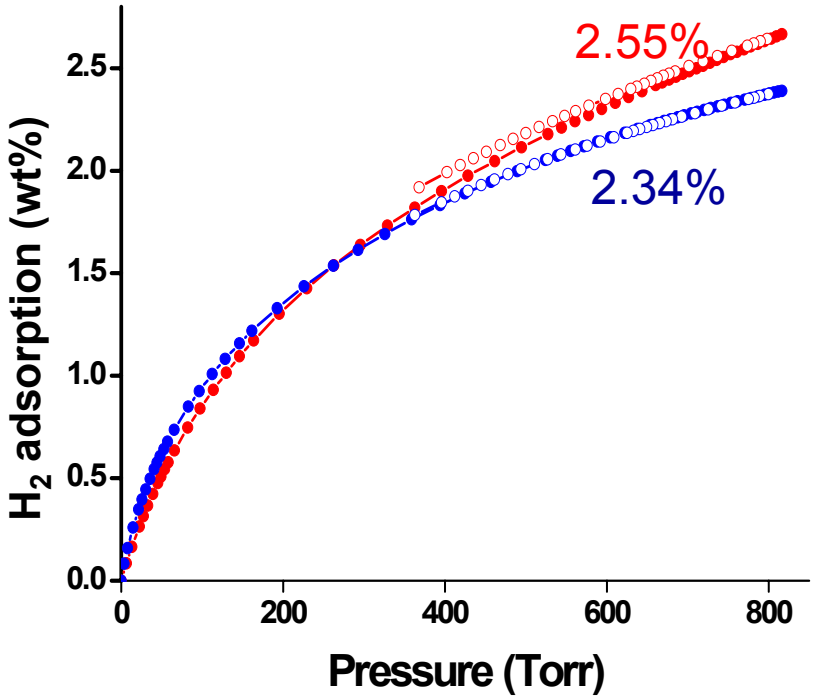
PCN-10 (Porous Coordination Network, X=N)
PCN-11 (X=C*)

- (a) Cuboctahedral cages (18.80 Å) were formed but the open Cu sites are misaligned
- (b) The open Cu centers around the octahedral cage (12.47 Å) are aligned
- (c) The crystal structure and (d) a space-filling model of the MOFs

*Acknowledgements: Karsten Rauch and Armin de Meijere, Universität Göttingen, Germany

Gas Adsorption Properties





Langmuir surface area:

- PCN-11: 2442 (BET 1931) m^2/g
- PCN-10: 1779 (BET 1779) m^2/g
- PCN-10 is partially decomposed

Gas adsorption isotherms for PCN-10 (blue) and PCN-11 (red)

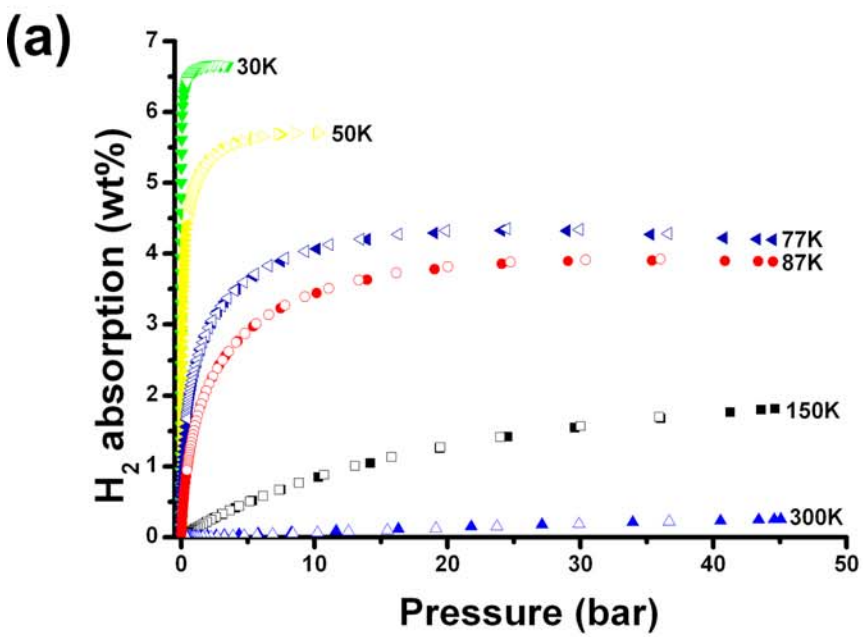
All volumetric capacities have been estimated using crystallographic density

At 760 Torr and 77 K:

- PCN-11 adsorbs 2.55 wt % hydrogen (20.5 g/L)
- PCN-10 adsorbs 2.34 wt % hydrogen (19.3 g/L)

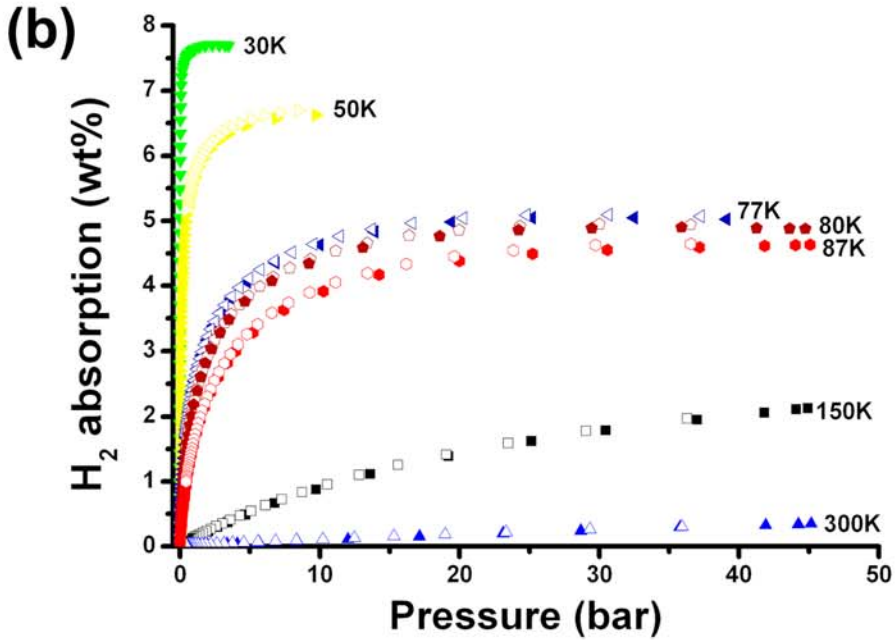
Hydrogen Adsorption of PCN-10 and PCN-11

PCN-10



4.33% (35.7 g/L)

PCN-11

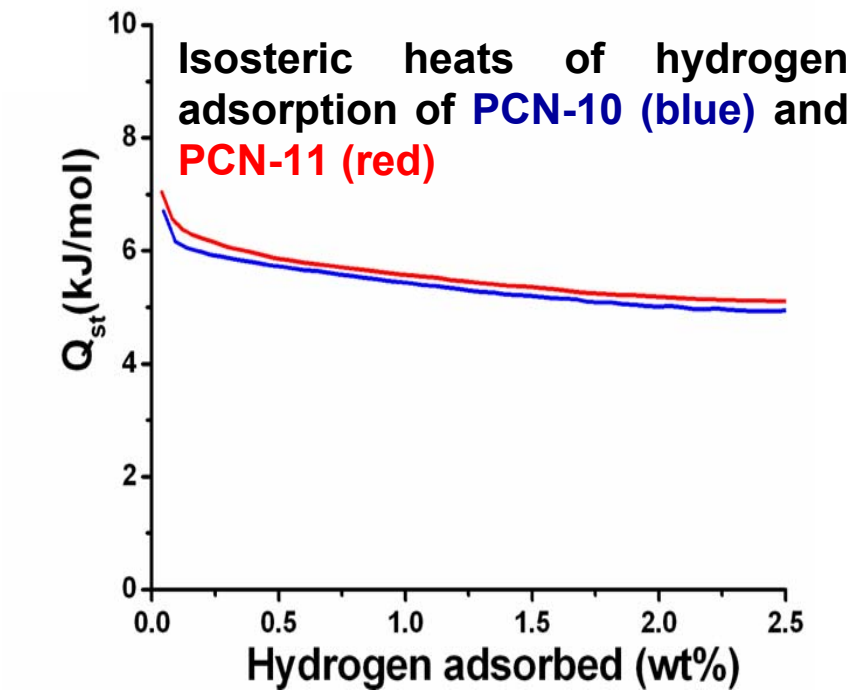


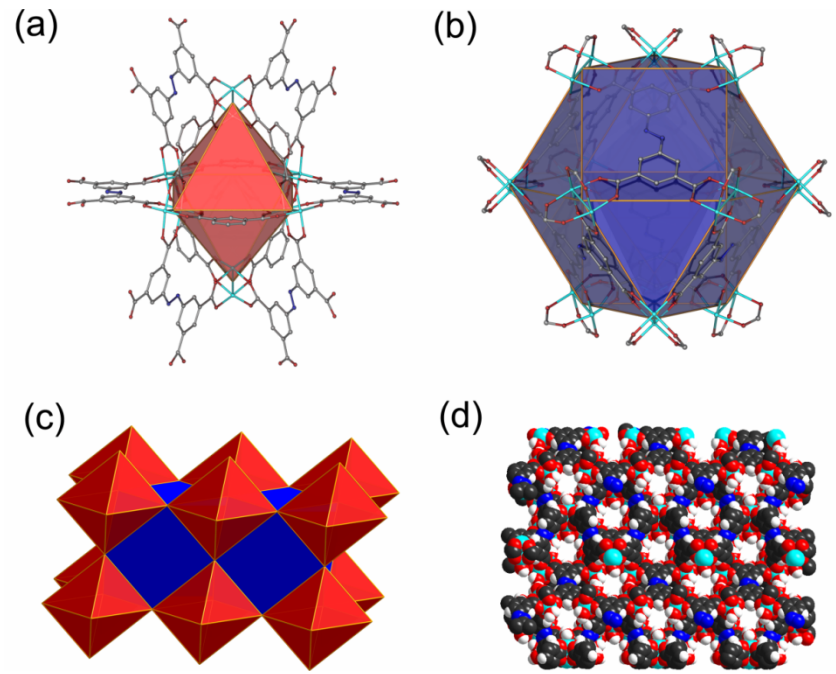
5.05% (40.6 g/L)

The coordinatively unsaturated metal centers are partially aligned.

Acknowledgements: Jason Simmons and Taner Yildirim, NIST

Heats of Hydrogen-Adsorption of PCN-10 and PCN-11

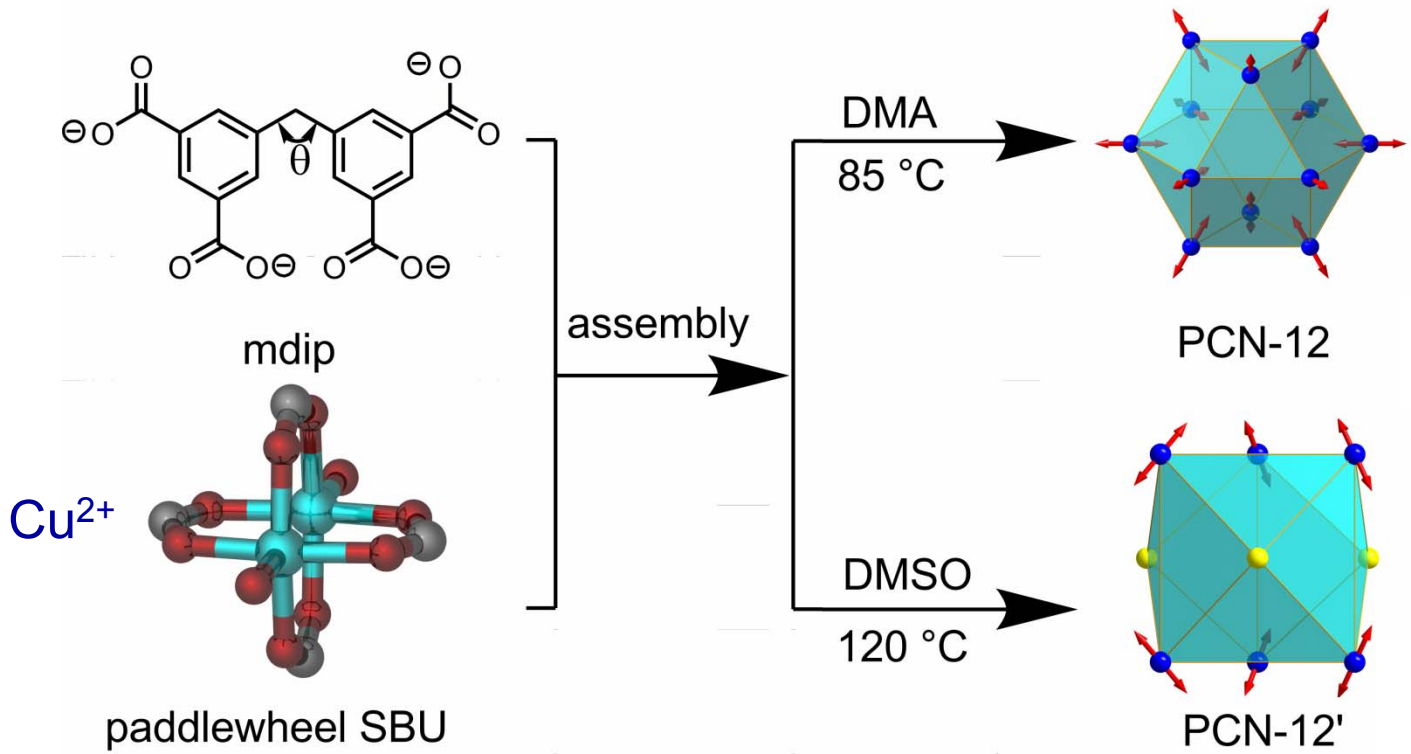




The enthalpies of hydrogen adsorption of PCN-10 and PCN-11 decrease from low coverage to high coverage in the range of 4-7 kJ/mol .

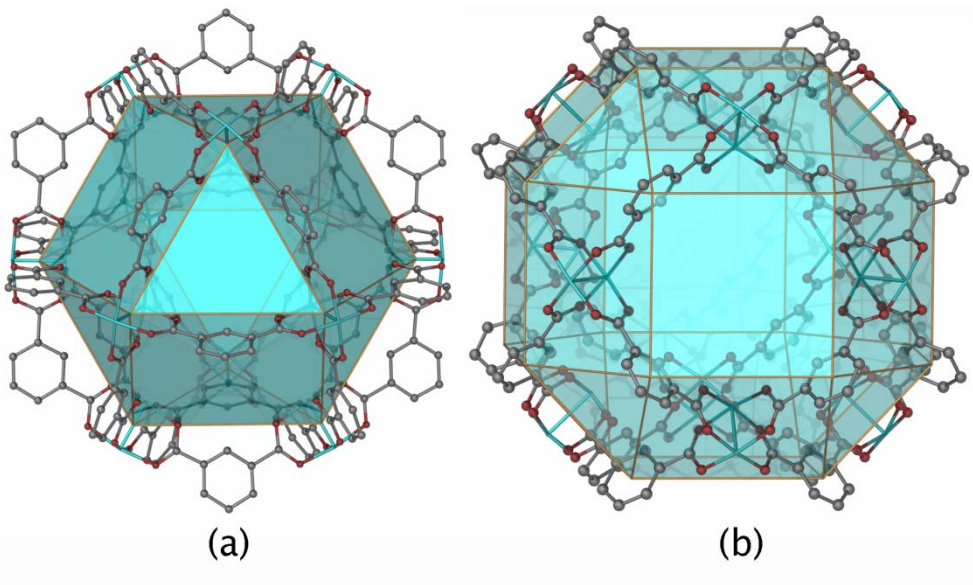
The alignment of the metal atoms is not optimized.

Optimization of the Alignment of the Coordinatively Unsaturated Metal Centers

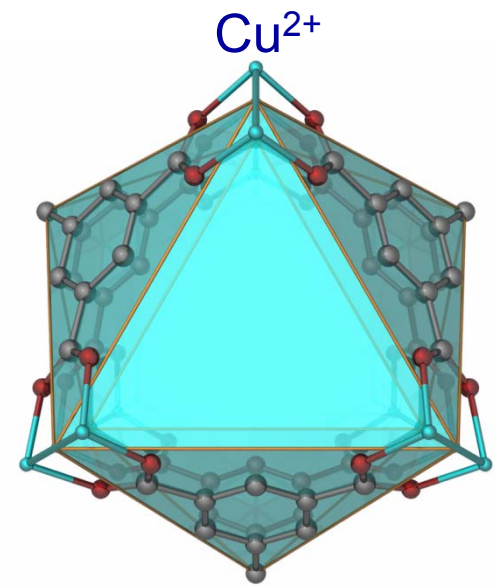


Two polymorphs with different metal alignments were obtained.

Cuboctahedral (PCN-12) and Tricapped-Trigonal-Prism (PCN-12') Cages



PCN-12

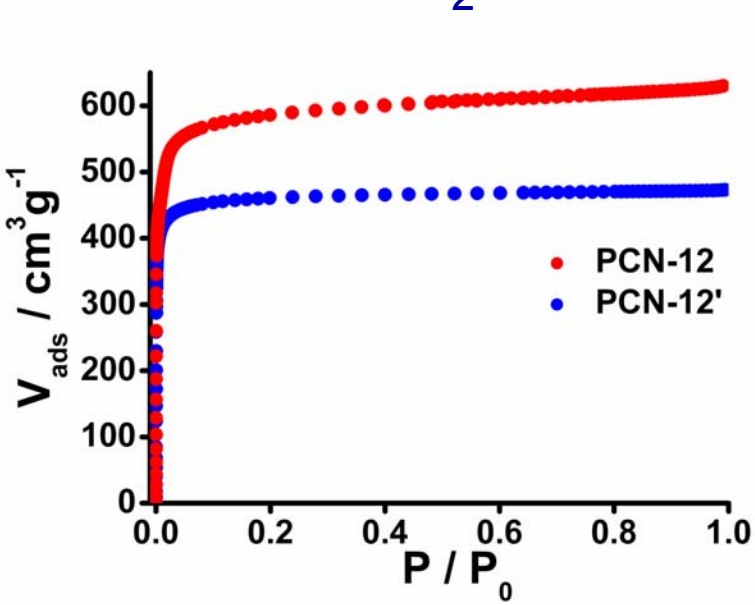


PCN-12'

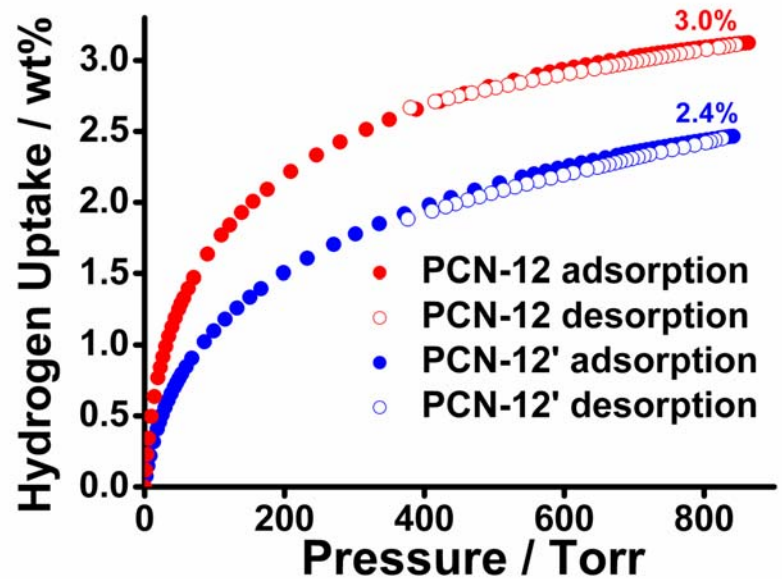
- **Each cuboctahedral (or rhombi-cuboctahedral) cage contains 12 aligned coordinatively unsaturated Cu centers in PCN-12**
- **In PCN-12′ , the Cu centers around the cage are misaligned**

Gas Adsorption Isotherms of PCN-12 and PCN-12'

N_2



H_2

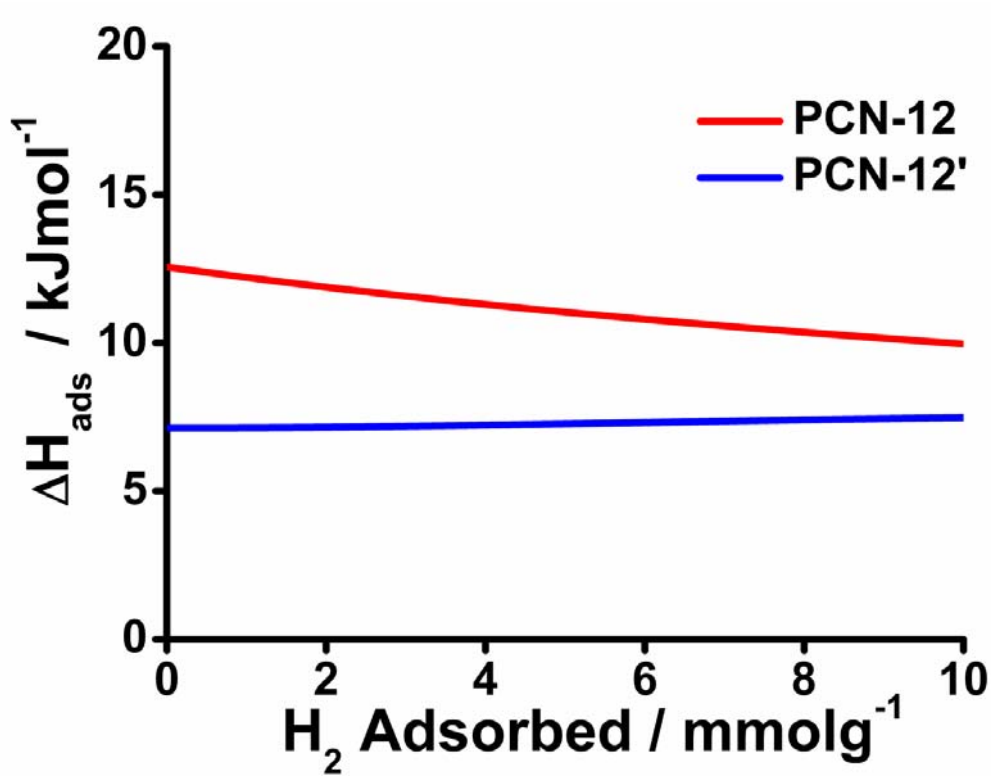


Langmuir surface area:
PCN-12: 2425 (BET 1962) m^2/g
PCN-12': 1779 (BET 1577) m^2/g

PCN-12 exhibits an **exceptionally high** hydrogen uptake of **3.0 wt%** (24.6 mg/cm^3) at 77 K and 1 atm.

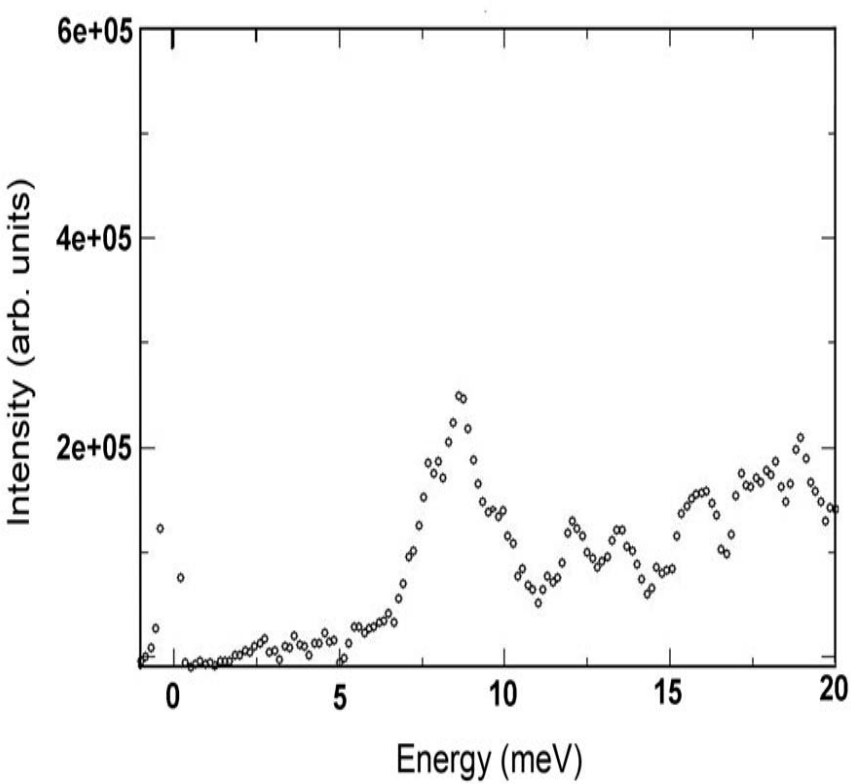
It has been well documented that the hydrogen uptake at 77 K and 1 atm is not proportional to the surface area of the MOF.

Heats of Hydrogen-adsorption of PCN-12 and PCN-12'



The heat of adsorption of PCN-12' is 7.13 kJ/mol at lower coverage. However, the H_2-adsorption heat of PCN-12 can reach as **high** as **12.5 kJ/mol** at low coverage, higher than those of other reported MOFs such as MIL-100(10 kJ/mol), PCN-9 (10.1 kJ/mol), a manganese MOF (10.1 kJ/mol), and NiSIP (10.4 kJ/mol).

Inelastic Neutron Scattering Spectrum

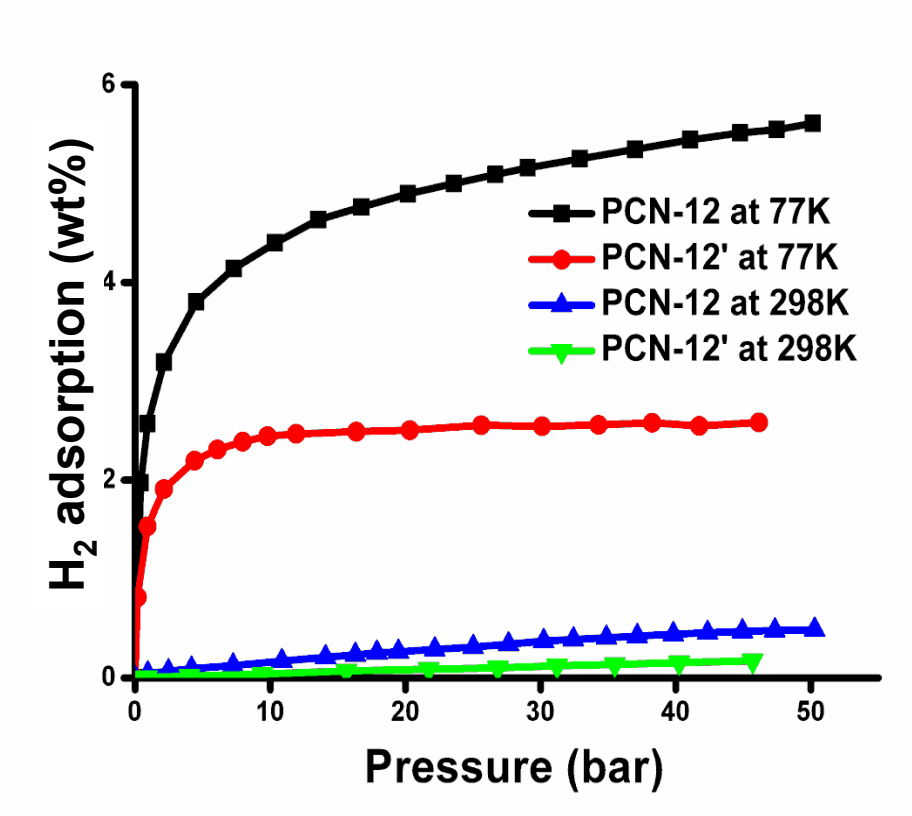


- The bands at 11 meV and 14.5 meV are associated with dihydrogen adsorbed on or near the organic linker, while the transitions in the range of the strong peak (8 meV) are attributed to H_2 molecules at the open Cu(II) sites
- These Cu sites correspond to about 1 wt % of the total uptake if Cu and H_2 are matched one on one
- Under 1 atm and 77 K, overall PCN-12 adsorbs three to four H_2 per metal center, although there is no direct experimental evidence found for multiple H_2-binding on a single metal or cooperative H_2-binding between two metal-centers

Acknowledgements: Paul Forster, UNLV and Juergen Eckert, UC Santa Barbara

INS spectrum showing strong H_2-MOF interaction

Hydrogen Uptake of PCN-12 and PCN-12'



- At 50 bar and 77 K, the excess volumetric (gravimetric) adsorption in PCN-12' is 23.6 g/L (2.58 wt %)
- The excess volumetric (gravimetric) adsorption of PCN-12 is as high as 44.9 g/L (5.51 wt %)
- However, the expected usable capacity between charging (50 bar) and low use pressure (2 bar) is only 2.5 wt% (about 20 g/L)

Acknowledgements: Jong-San Chang, KRICT

Accomplishments

Demonstrated through experiments that :

- **MOFs containing UMCs or entatic metal centers (just like the Fe centers in hemoglobin) tend to have high hydrogen affinity**
- **MOFs containing well-aligned UMCs posses high heat of hydrogen adsorption**
- **MOFs constructed based on close-packing patterns have high hydrogen uptake**
- **Nanoscopic cages such as cuboctahedral cages are particularly suitable for hydrogen storage**

Milestones Reached

FY07

- Synthesized thirty new ligands containing hierarchical donor atoms with the primary donors supporting the metal-organic framework and the secondary ones anchoring hydrogen-philic metal atoms
- Optimized the open channel size and open-metal-center alignment in metal-organic frameworks for hydrogen adsorption based on van der Waals interaction
- Approaching the 15 kJ/mol hydrogen-adsorption heat

Future Plan

FY08

- Further enhancement of H_2-MOF interaction by the introduction of higher density of coordinatively unsaturated metal centers (heat of adsorption 15 kJ/mol)
- Improvement of H_2 uptake at temperatures higher than 77 K by ligand and MOF design.
- Increase MOF thermal stability while maintain its porosity
- Preparation of MOFs with high surface area and optimized cage size (4,500 m^2/g)
- Improve the usable storage capacity of MOFs

FY09

- Show that hydrogen-philic metal-incorporation improves the hydrogen-adsorption heat. Achieve a hydrogen-adsorption heat significantly higher than those of traditional adsorptive materials
- Achieve the DOE 2010 volumetric and gravimetric goals of 0.045 kg H_2/L and 6 wt%, respectively at conditions approaching ambient temperature and applicable pressures
- The Go/No-Go decision (3rd Quarter) will be made primarily on whether or not the DOE 2010 gravimetric and volumetric storage goals are achievable via the proposed approach

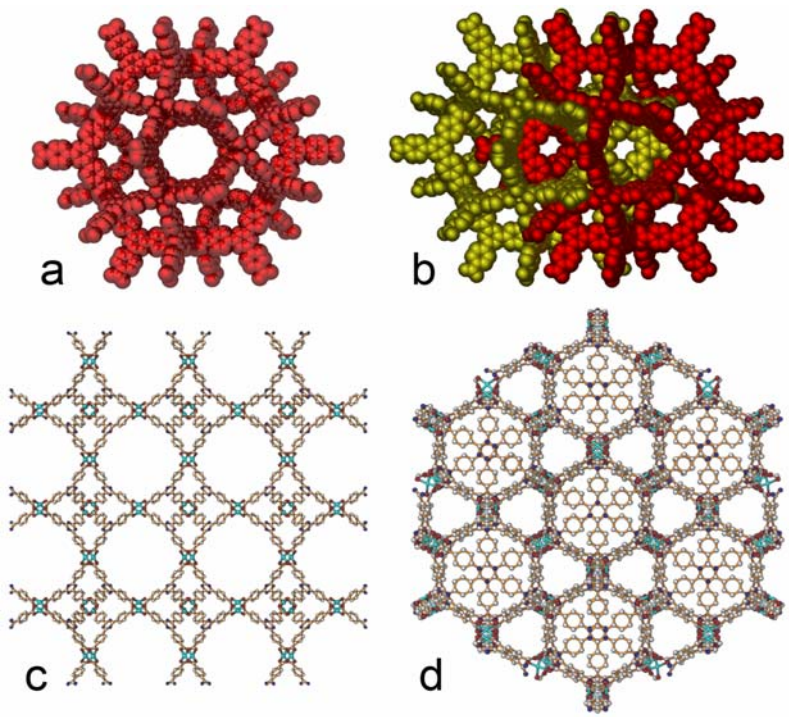
Summary Table

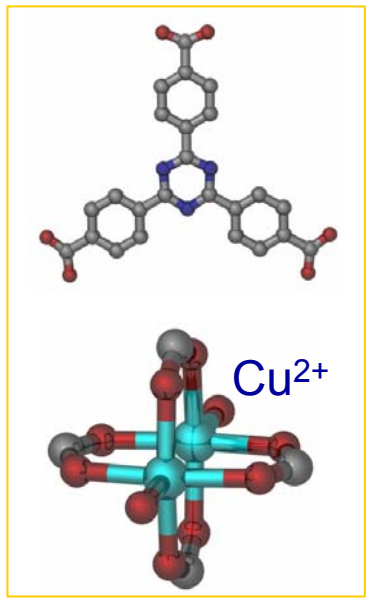
Comparison of Hydrogen Storage of PCN-10,11,12,12'					
Material	ΔH_{ads} (kJ/mol)	H_2 Adsorption			
		Gravimetric H_2 uptake (Wt%)	Volumetric H_2 uptake (g/L)	T (K)	P (bar)
PCN-10	4~7	4.20 (1.3)*	34.65 (10.73)*	77	45
		2.34	19.30	77	1.0
		0.31	2.56	300	45
PCN-11	4~7	5.04 (2.0)*	40.60 (16.11)*	77	45
		2.55	20.53	77	1
		0.57	4.59	300	45
PCN-12	~12.5	5.51 (2.5)*	44.90 (20.37)*	77	50
		3.0	24.45	77	1
		0.49	4.00	303	45
PCN-12′	~7.1	2.58 (0.7)*	23.61 (6.41)*	77	50
		2.4	21.95	77	1
		0.17	1.55	303	45

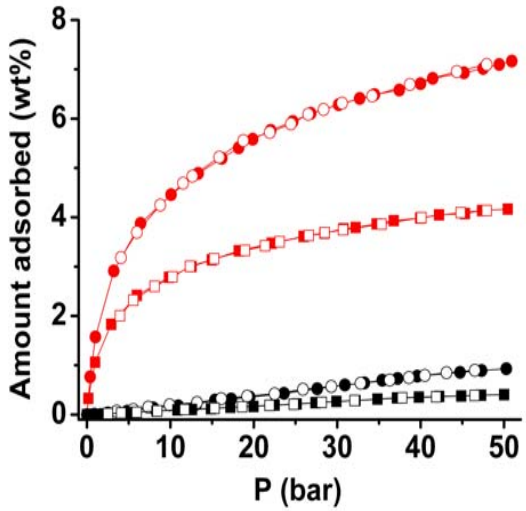
* The expected usable capacity assuming that recharge starts under a pressure of 2 bar.

Expected Usable Capacity should be reported for future research in adsorptive hydrogen storage.

Increase the Expected Usable Capacity by Framework Interpenetration







a. PCN-6′ b. PCN-6

c. Packing of PCN-6′ along *a* axis

d. Packing of PCN-6 along *c* axis

- Interpenetrated PCN-6: 7.2 (EUC: 5.2) wt % H_2 at 77 K, 50 bar and 0.93 wt % at 298 K, 50 bar
- Non-interpenetrated PCN-6′ 4.2 (EUC: 2.4) wt % H_2 at 77 K, 50 bar and 0.40 wt % at 298 K, 50 bar

Acknowledgements: Jong-San Chang, KRICT

Implications of the Expected Usable Capacity (EUC) for Future Research

- High hydrogen uptake (excess or absolute) doesn't necessarily mean high EUC if the main contribution of the high uptake is from the initial stage of the isotherm when the pressure is low (less than 1.5 bar)
- High hydrogen-heat of adsorption implies a steep increase in hydrogen uptake at the initial portion of the isotherm; it may not necessarily lead to high EUC