DOE Hydrogen Program

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

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May 21, 2009

ST_23_Zhou

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Overview

Timeline

- Project start date: 7/1/2007
- Project end date: 6/30/2012
- Percent complete: 38%

Budget

- Total project funding (DOE: $1,342,819; Contractor: $771,856)
- FY07 $122,000
- FY08 $0
- FY09 $525,000

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 and surface area needs to be around 5000 to 9000 m^2/g

Partners

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

Framework Catenation, High surface area, and Unsaturated Metal Centers for High H_2-Uptake

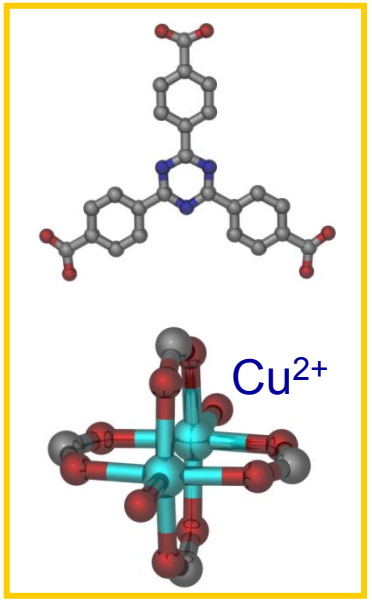
Difficulties:

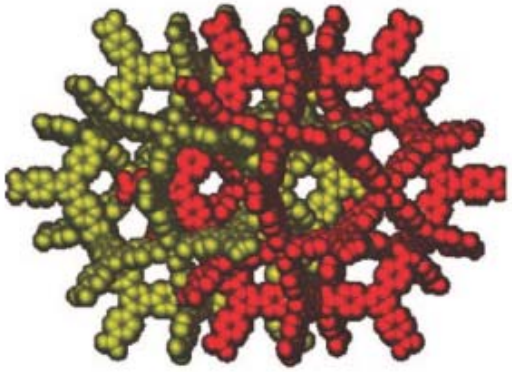
- Dihydrogen, as simple as two protons and two electrons, holds its electrons tightly and is difficult to polarize
- The H_2 molecule is also a poor acid and a weak base and the energy levels of its frontier orbitals prevent the direct interaction between dihydrogen and other non-metals
- Transition metals can interact with H_2 molecule but Kubas-type binding may be too strong.

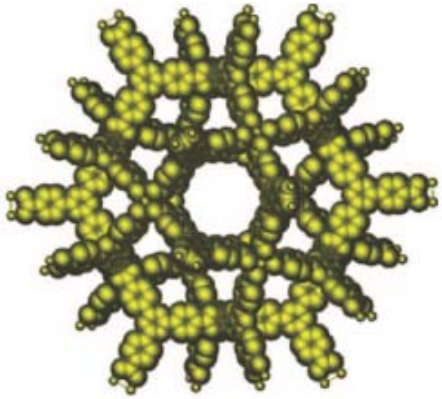
Strategy:

- Catenation can lead to higher hydrogen uptake in MOFs
- Constructing MOFs containing mesocavities with microwindows may serve as a general approach towards stable MOFs with higher and higher surface areas
- MOFs with multiple open metal sites per metal atom may improve hydrogen sorption affinity

The Effect of Framework Catenation on Hydrogen Uptake in Metal-Organic Frameworks



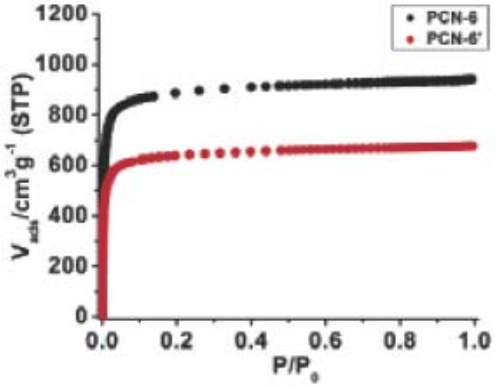


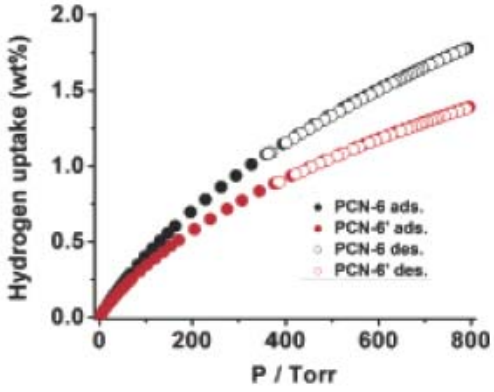


(a) (b)

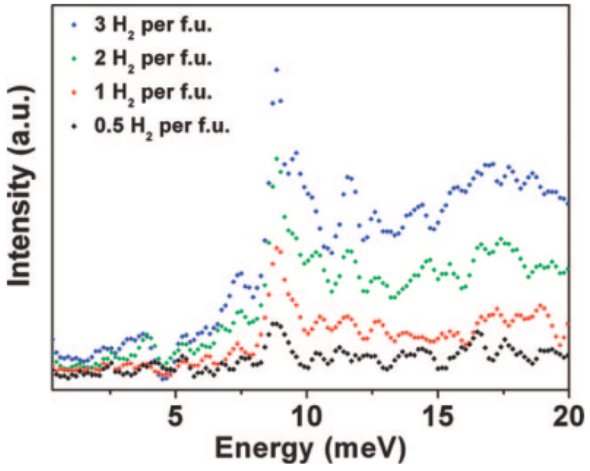
a. PCN-6 b. PCN-6'

At high H_2 loadings, where the H_2 molecules adsorb mainly on or around the organic linkers, the interaction is found to be substantially stronger in catenated PCN-6 than in noncatenated PCN-6', leading to much higher H_2 uptake in the isomer with catenation.

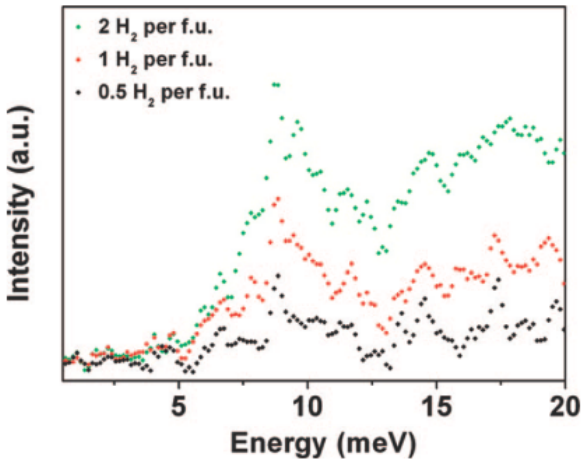




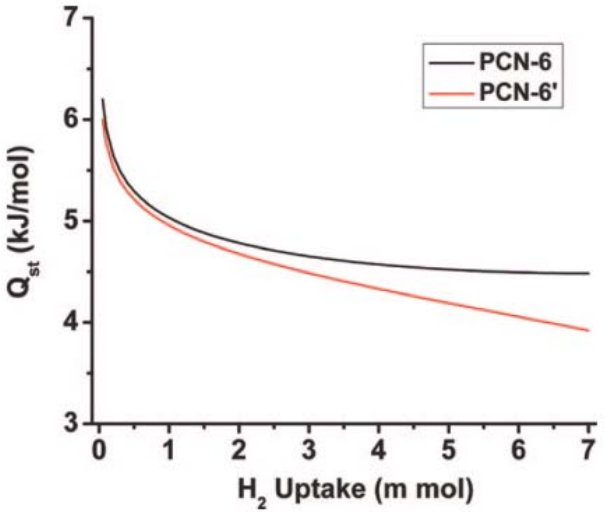
INS, Heats of H_2-adsorption, and H_2-adsorption of PCN-6 and PCN-6'

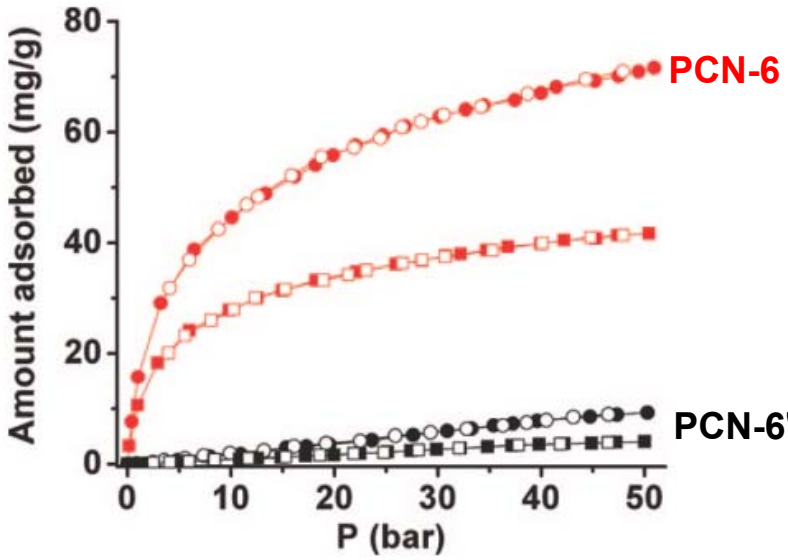


PCN-6



PCN-6'





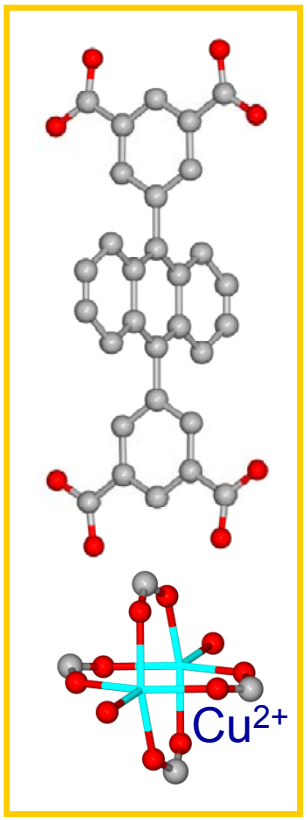
PCN-6

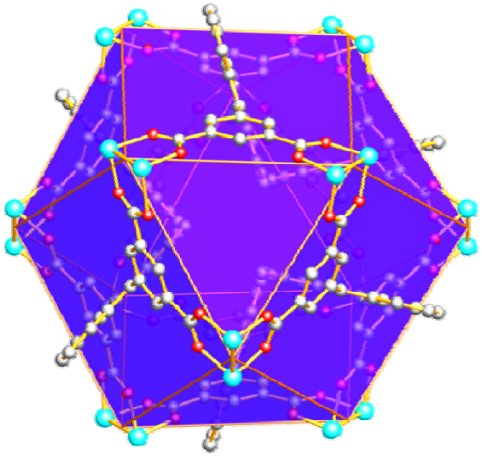
PCN-6'

- The expected usable capacity of PCN-6 is as high as 75 mg/g (or 41.9 g/L) at 77 K
- 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

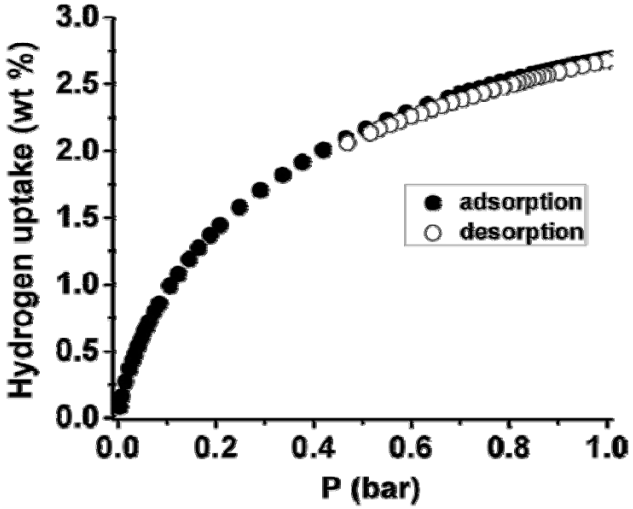
Acknowledgements: Jong-San Chang, KRICT, Paul Forster, UNLV and Juergen Eckert, UC Santa Barbara

Porous Metal-Organic Frameworks Containing a Large Number of Aromatic Rings

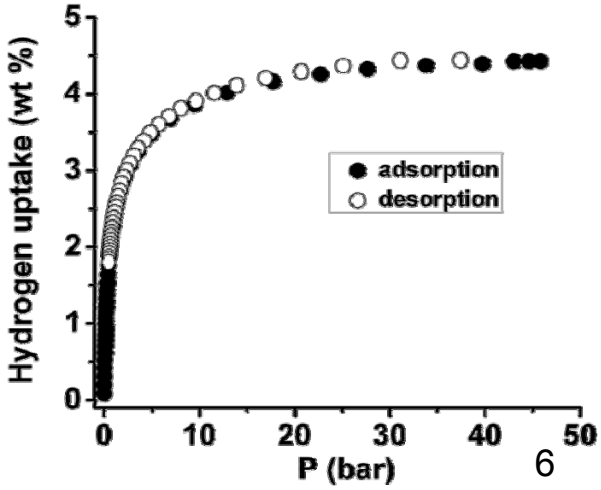




PCN-14



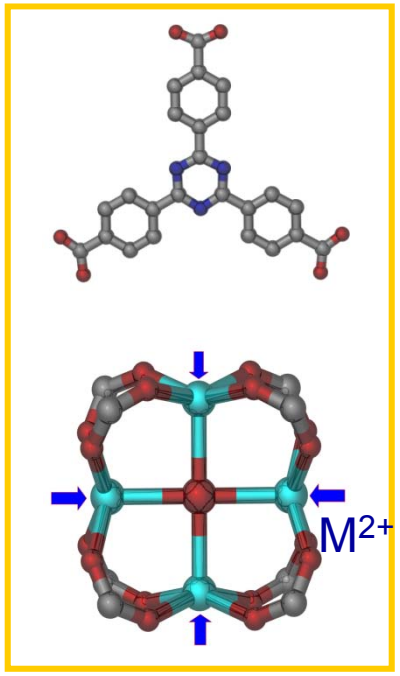
At 77 K and 1 bar, the hydrogen uptake capacity of PCN-14 can reach 2.70 wt% (22.5 g/L) and reaches saturation with a value of 4.42 wt% (36.6 g/L) at 45 bar.



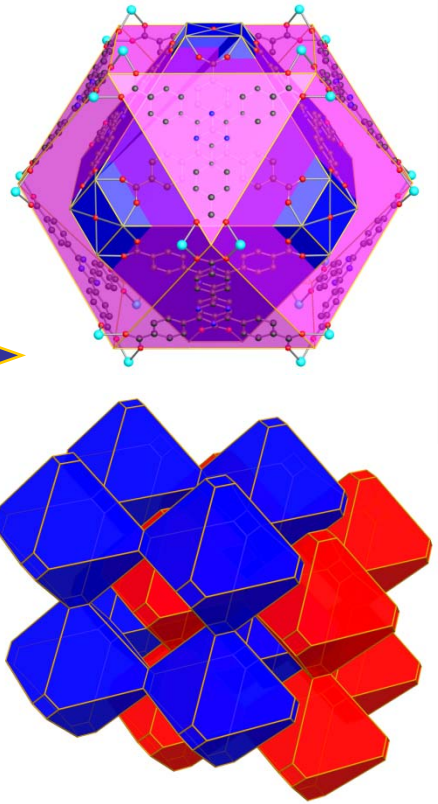
Hydrogen affinity of the ligand

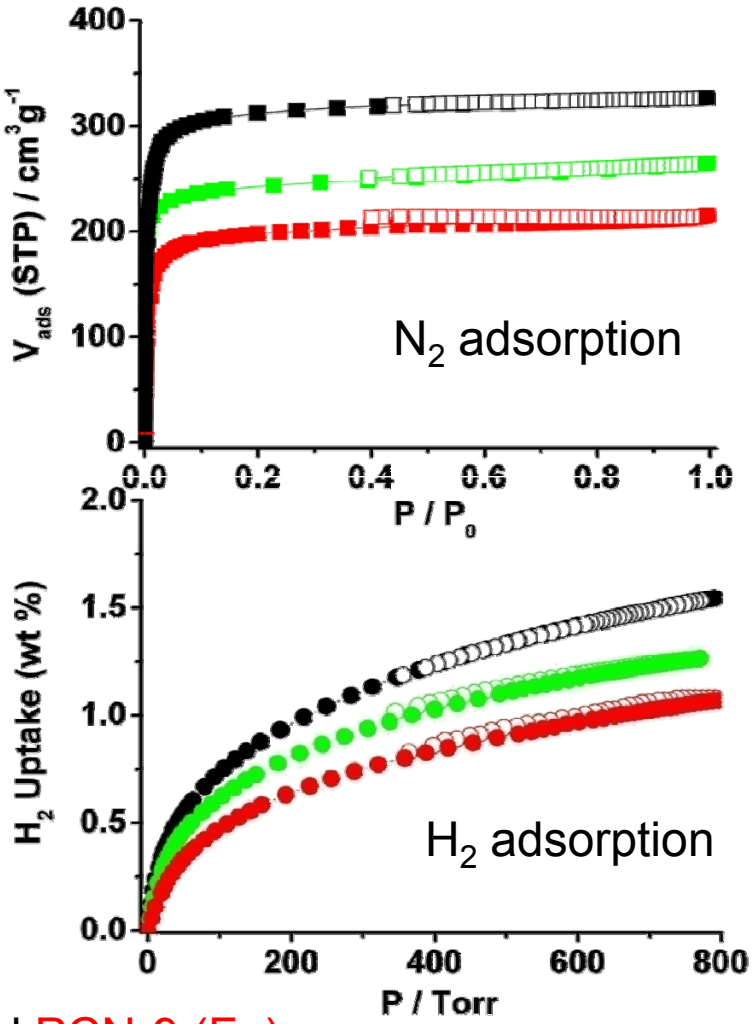
Interpenetrated Metal-Organic Frameworks with Entatic Metal Centers

Open coordination sites without the need of ligand removal



M = Co, Fe, Mn

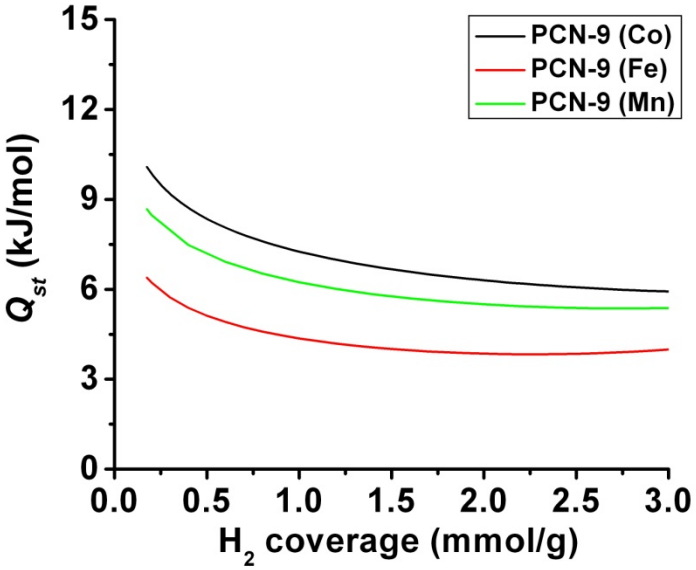




PCN-9 (Co), PCN-9 (Mn), and PCN-9 (Fe)

H_2 Affinities of PCN-9 with Different Entatic Metal Centers

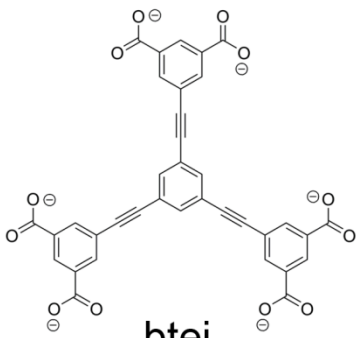
	BET surface area (m^2/g)	Langmuir Surface area (m^2/g)	Pore volume (cm^3/g)	H_2 uptake (wt %, at 77K, 760 Torr)	Isosteric heats of adsorption (Q_{st}) at low H_2 coverage (kJ/mol)
PCN-9 (Co)	1064	1355	0.51	1.53	10.1
PCN-9 (Fe)	682	848	0.33	1.06	6.4
PCN-9 (Mn)	836	1057	0.41	1.26	8.7



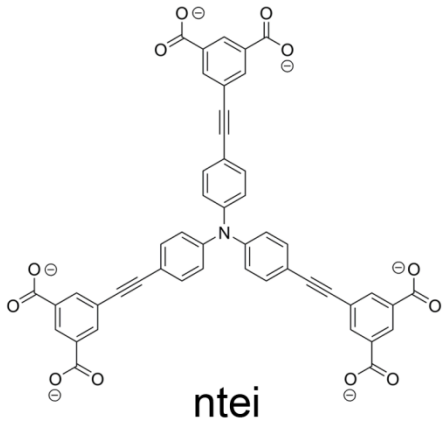
The implementation of open Co centers into porous MOFs may be a promising way to enhance hydrogen adsorption enthalpies.

Fe (II) and Mn (II) oxidation under solvothermal conditions?

Stabilization of Metal-Organic Frameworks with High Surface Areas by the Incorporation of Mesocavities with Microwindows

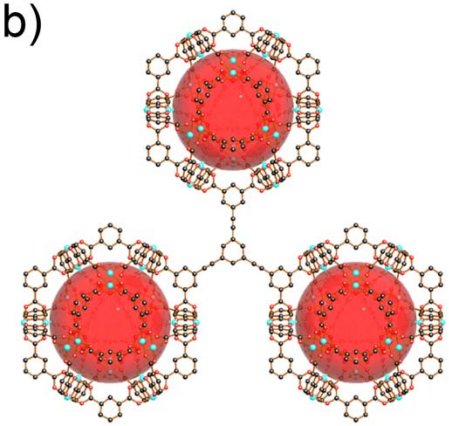


btei

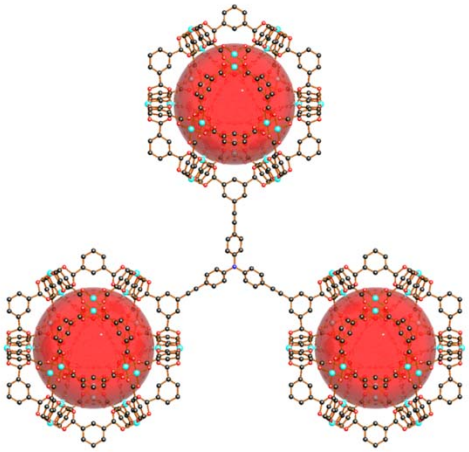


ntei

(b)



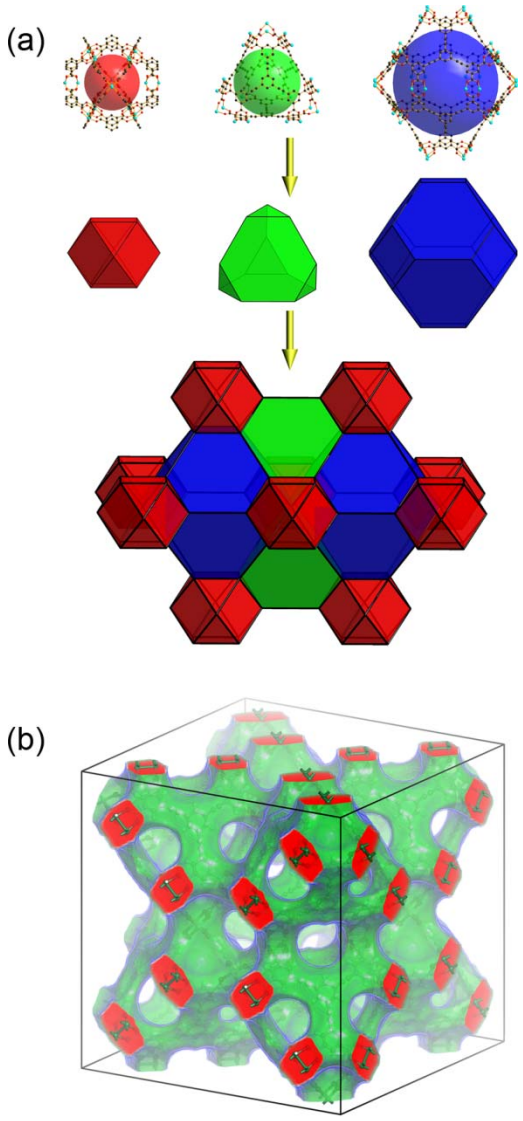
PCN-61

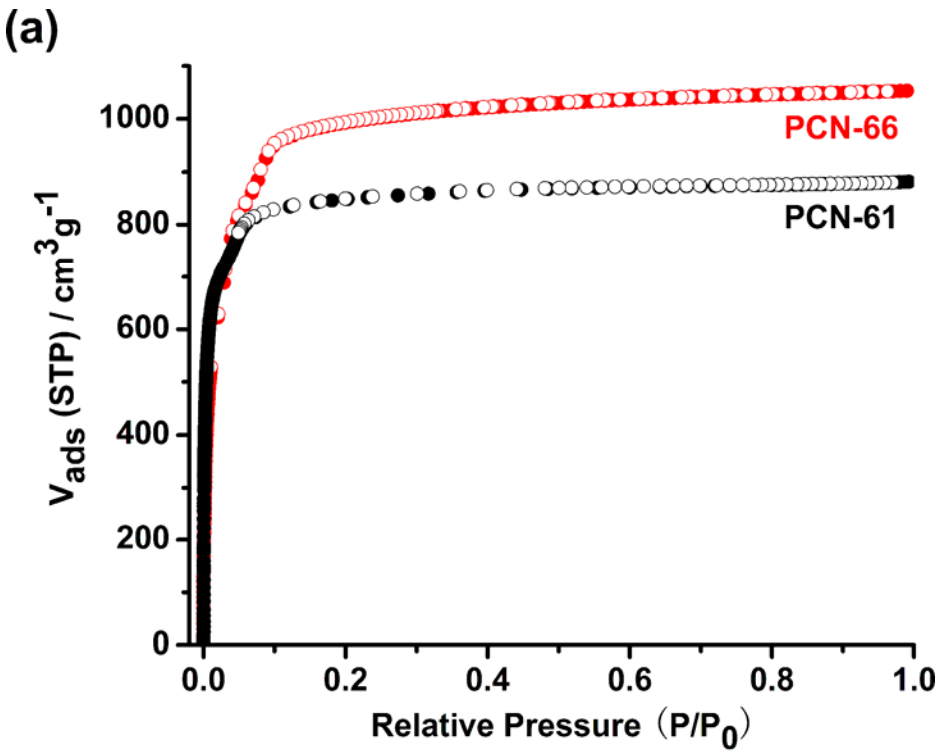


PCN-66

- The stability of these MOFs was strengthened by the in-situ formation of coordination cuboctahedra building units, which limit the open window sizes of the mesocavities
- The surface area of the activated MOF has been increased remarkably by ligand extension, presumably due to the increased size of the mesocavities
- The pore walls of the mesocavities can be modified by post-synthetic reactions

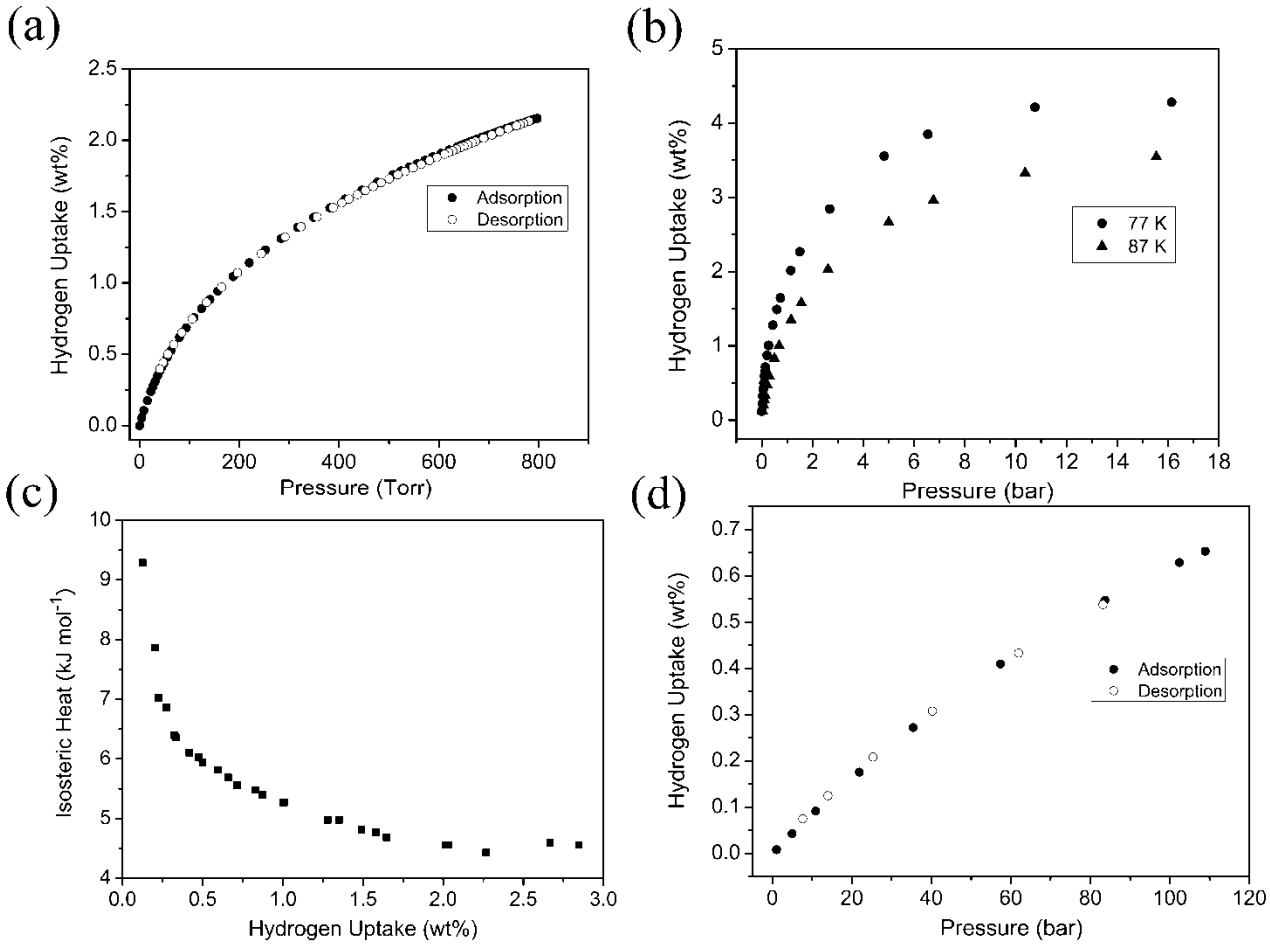
N_2 Adsorption Properties





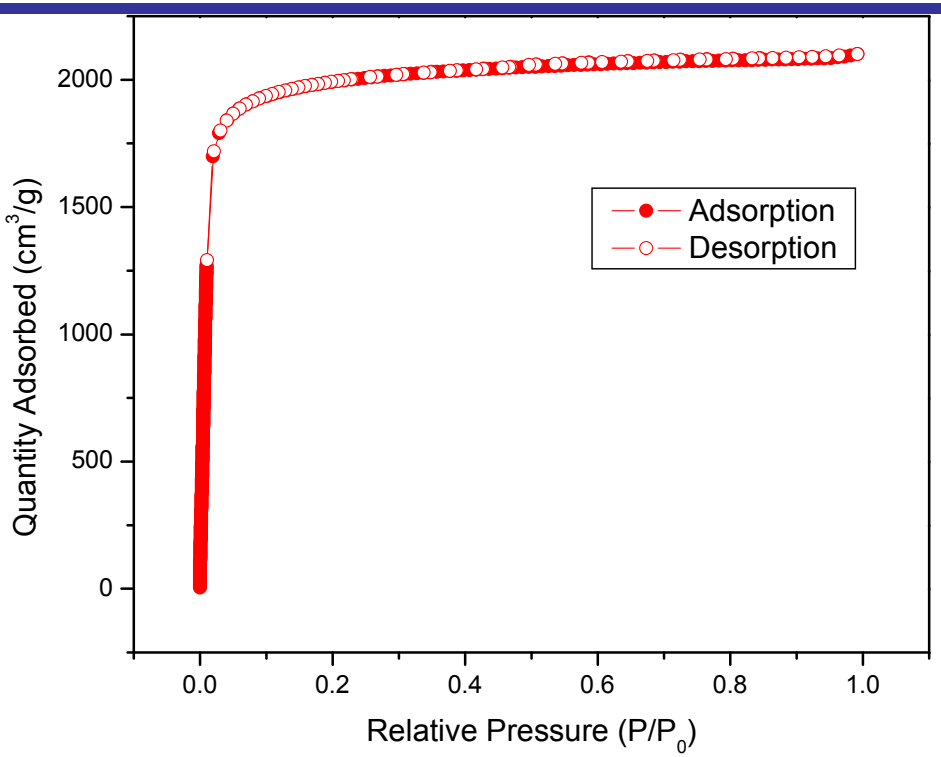
Langmuir surface area:
PCN-61: 3500 (BET 3000) m^2/g
PCN-66: 4600 (BET 4000) m^2/g

Heats of H_2-adsorption and H_2-adsorption of PCN-61



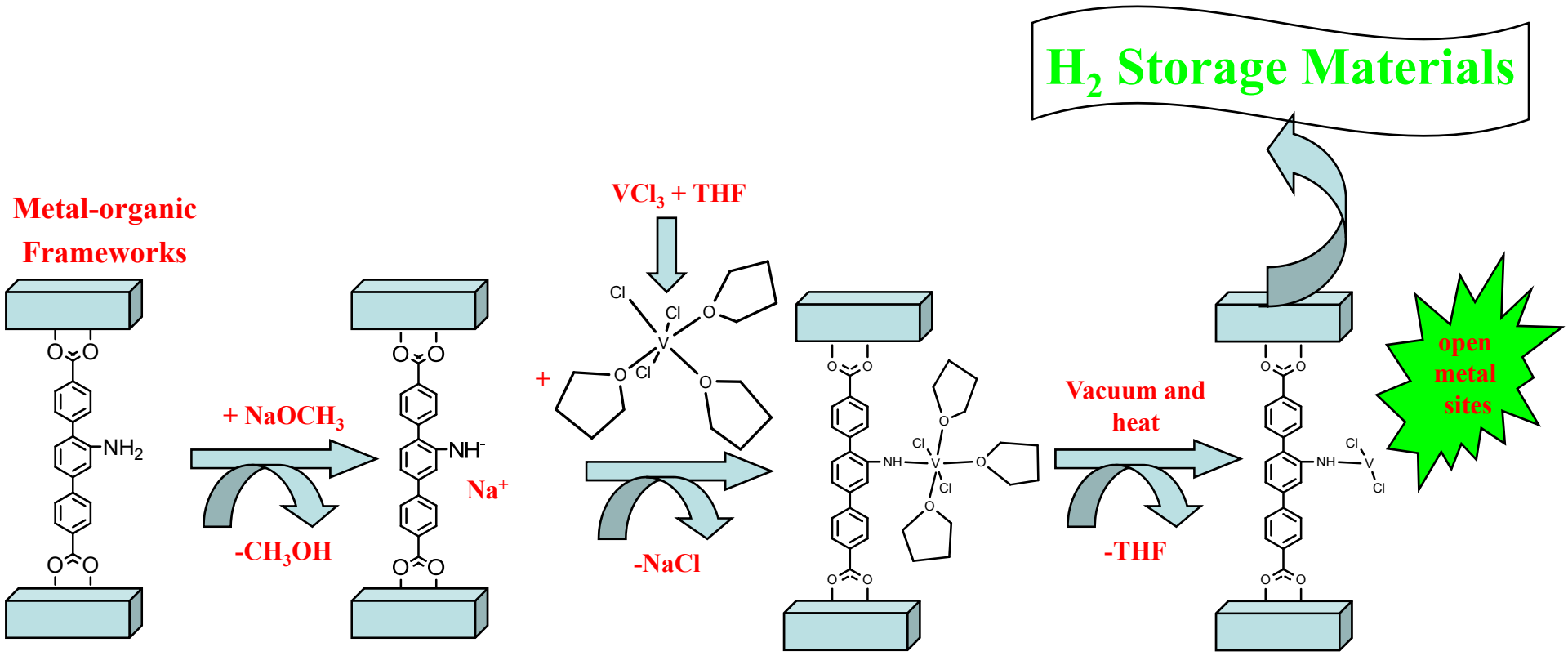
Acknowledgements: Alan C. Cooper, Air Products and Chemicals

N_2 Adsorption Study of PCN-103 Shows the Highest Surface Area



	MOF-5	IRMOF-20	MOF-177	MIL-101	UMCM-1	UMCM-2	PCN-103
BET (m^2/g)	3800	4024	4746	4100	4160	5200	7200
Langmuir (m^2/g)	4400	4590	5640	5900	6500	6060	9000
Pore Volume (mL/g)	0.28	1.53		1.9			3.26

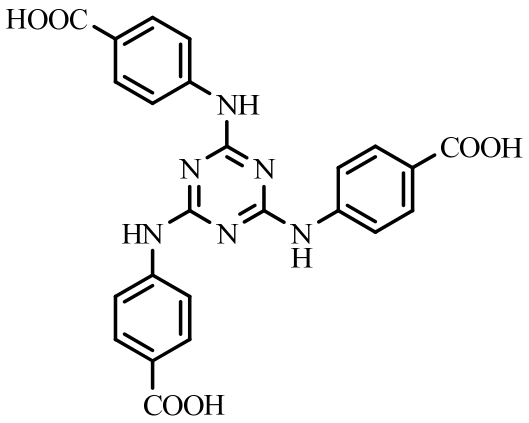
H_2 Storage MOFs with Multiple Open Metal Sites



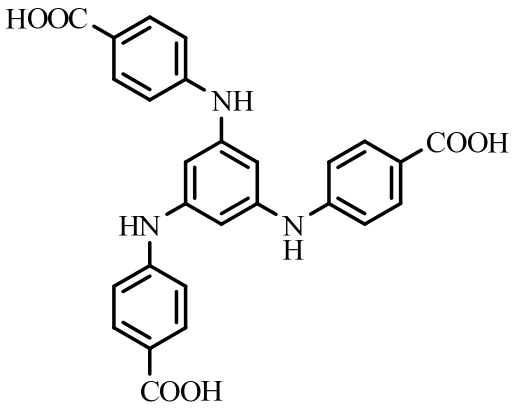
V^{3+} can be replaced by Ti^{4+}, Cr^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Sc^{3+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mg^{2+} .....

Confirmed by calculation (Hansong Cheng, Air Products).

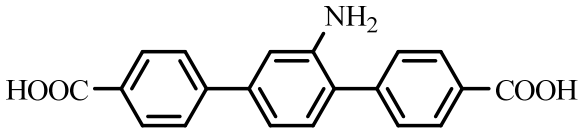
Selected Organic Ligands with Secondary Functional Groups



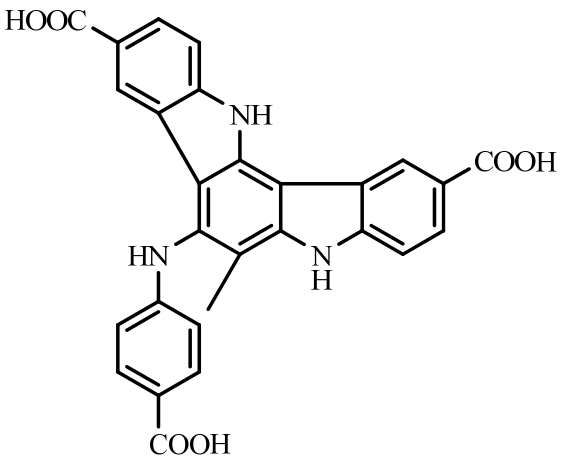
H_3TATAB



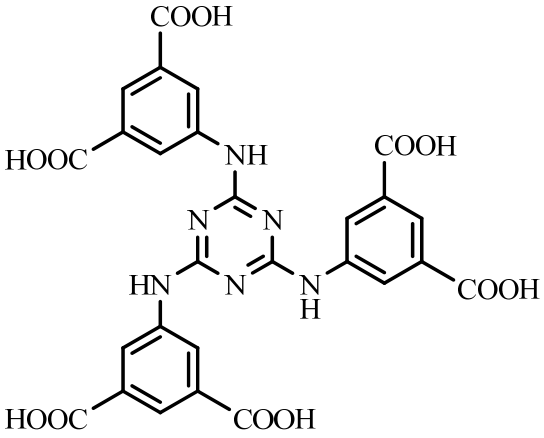
H_3BTATA



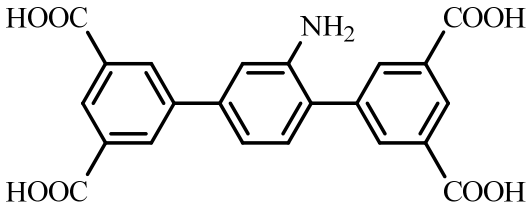
H_2DBDCA



H_3DCTA



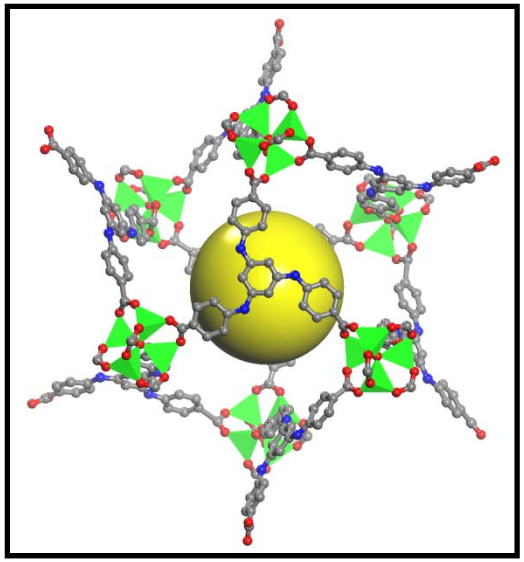
$H_6TATABHC$

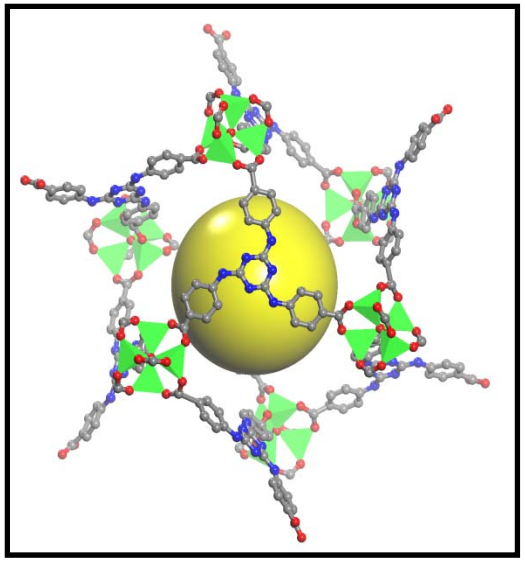


H_2DBTCA

Selected MOFs with Secondary Functional Groups

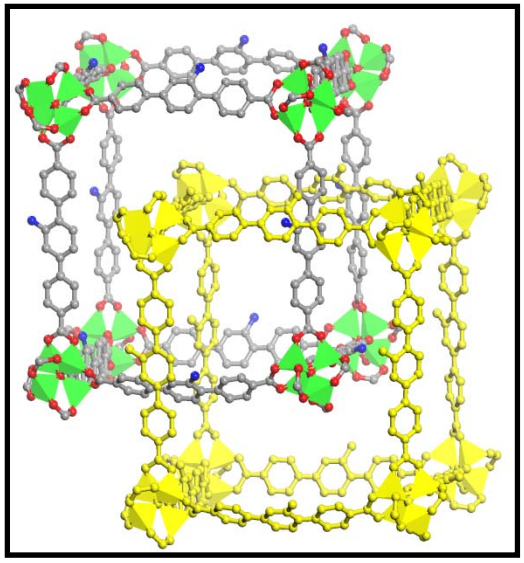
PCN-100

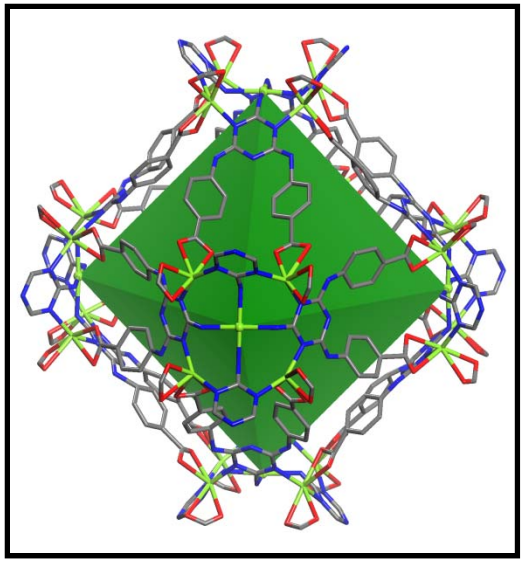




PCN-101

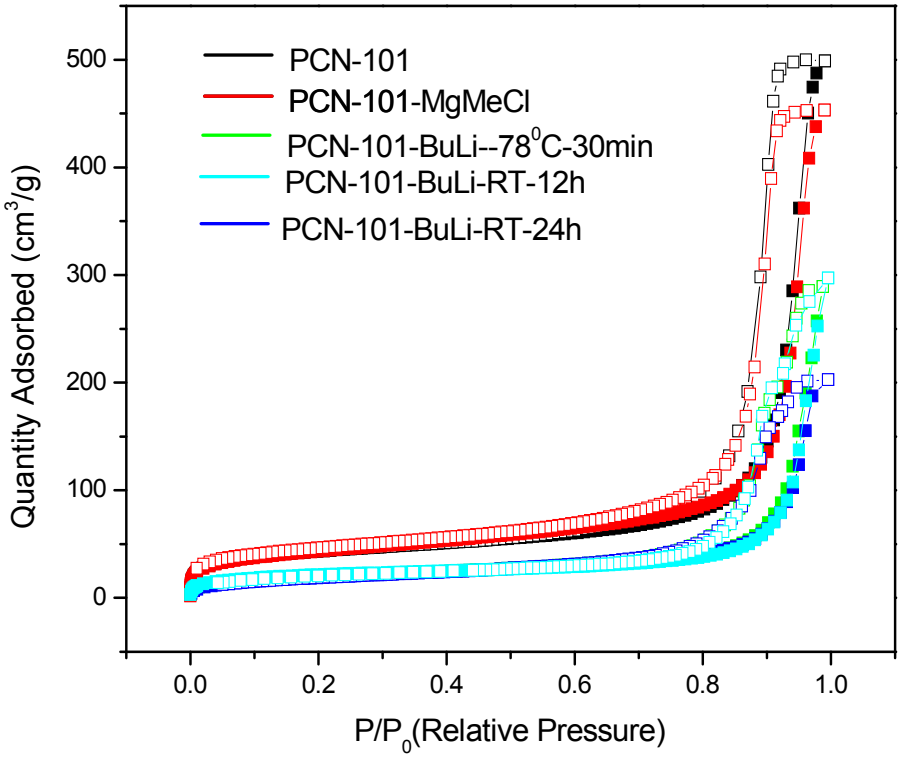
PCN-104



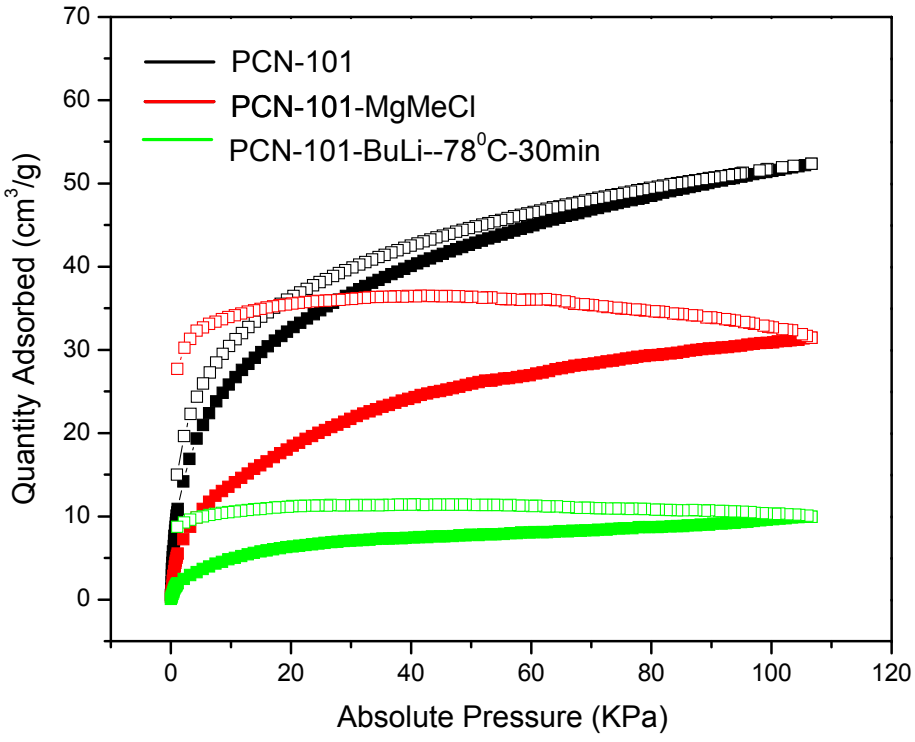


PCN-105

Post-synthetic Modification of MOFs



N_2 adsorption of PCN-101 reacted with different bases



H_2 adsorption of PCN-101 reacted with different bases

Accomplishments

Demonstrated through experiments that :

- **Interpenetrated MOFs have high hydrogen affinity and uptake**
- **MOFs with nanoscopic cages posses high hydrogen uptake**
- **MOFs containing UMCs or entatic metal centers (just like the Fe centers in hemoglobin) tend to have high hydrogen affinity. Among Mn, Fe, and Co, Co has the highest hydrogen affinity**
- **MOFs containing mesocavities with microwindows tend to have high surface area and stability**
- **A MOF with a Langmuir surface area of 9000 m^2/g, which is 50% higher than that of MOF-177, has been obtained**

Milestones Reached

FY08

- 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
- MOFs with surface area more than 6000 m^2/g have been obtained

Future Plan

FY09

- Further enhancement of H_2-MOF interaction by introducing a 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 maintaining its porosity
- Preparation of MOFs with high surface area and optimized cage size (5000 m^2/g)
- Improve the usable storage capacity of MOFs

FY10

- Show that hydrogen-philic metal-incorporation improves the heat of hydrogen-adsorption. Achieve a heat of hydrogen-adsorption 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 the degree of improvements achieved

Summary Table

Comparison of Hydrogen Uptakes of PCNs-6,6',9,14,61,66					
Material	ΔH_{ads} (kJ/mol)	H_2 Adsorption			
		Gravimetric H_2 uptake (Wt%)	Volumetric H_2 uptake (g/L)	T (K)	P (bar)
PCN-6	6.2~4.5	7.2	40.2	77	50
		1.90	10.6	77	1.0
		0.92	5.14	298	50
PCN-6'	6.0~3.9	4.2	11.8	77	50
		1.62	4.73	77	1
		0.40	1.12	298	50
PCN-9 (Co)	10.1	1.53	14.1	77	1
PCN-9 (Fe)	6.4	1.06	9.60	77	1
PCN-9 (Mn)	8.7	1.26	11.3	77	1
PCN-14	5.9-5.0	2.70	22.5	77	1
		4.42	36.6	77	45
PCN-61	9.3~4.5	4.28	14.8	77	16
		2.11	7.32	77	1
		0.65	2.25	298	109
PCN-66	7.2~4.5	1.69	4.26	77	1