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

Hong-Cai (Joe) Zhou
Texas A&M University
June 7, 2010

ST018

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Project start date: 7/1/2007
- Project end date: 6/30/2012
- Percent complete: 48%

Budget

- Total project funding (DOE: $1,342,819; Contractor: $771,856)
- FY07 $100,000
- FY08 $0
- FY09 $742,260
- FY10 $ 300,308

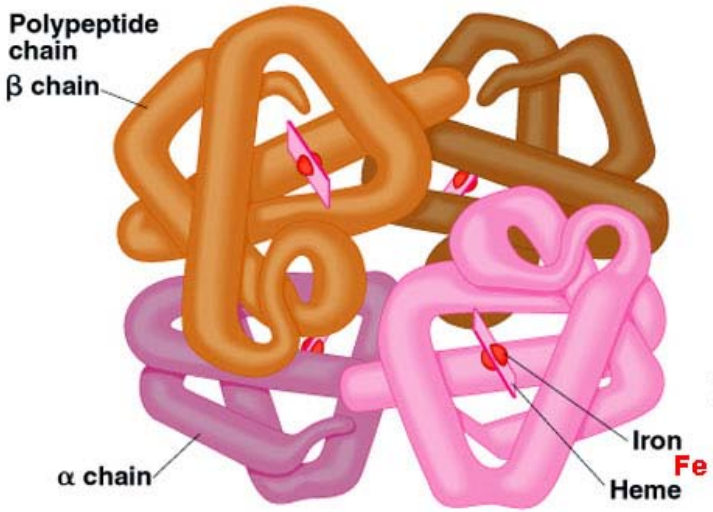
Barriers

- 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
- Surface area needs to be around 5000 to 9000 m^2/g for additional metal incorporation

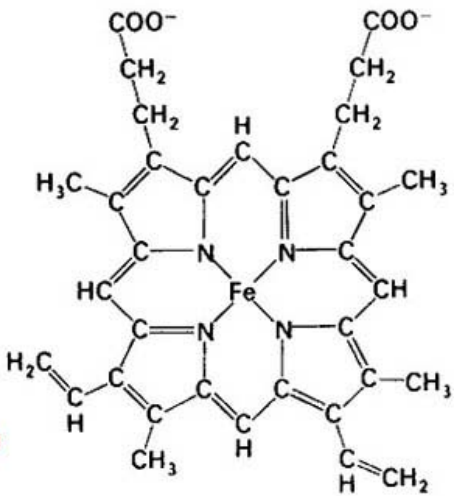
Partners

- Air Product, GM
- NREL, ANL (APS)
- NIST, ORNL, LLNL
- KRICT, Korea
- Dept. of Chem. Eng., TAMU
- KIT, Germany
- RPI

Entatic State



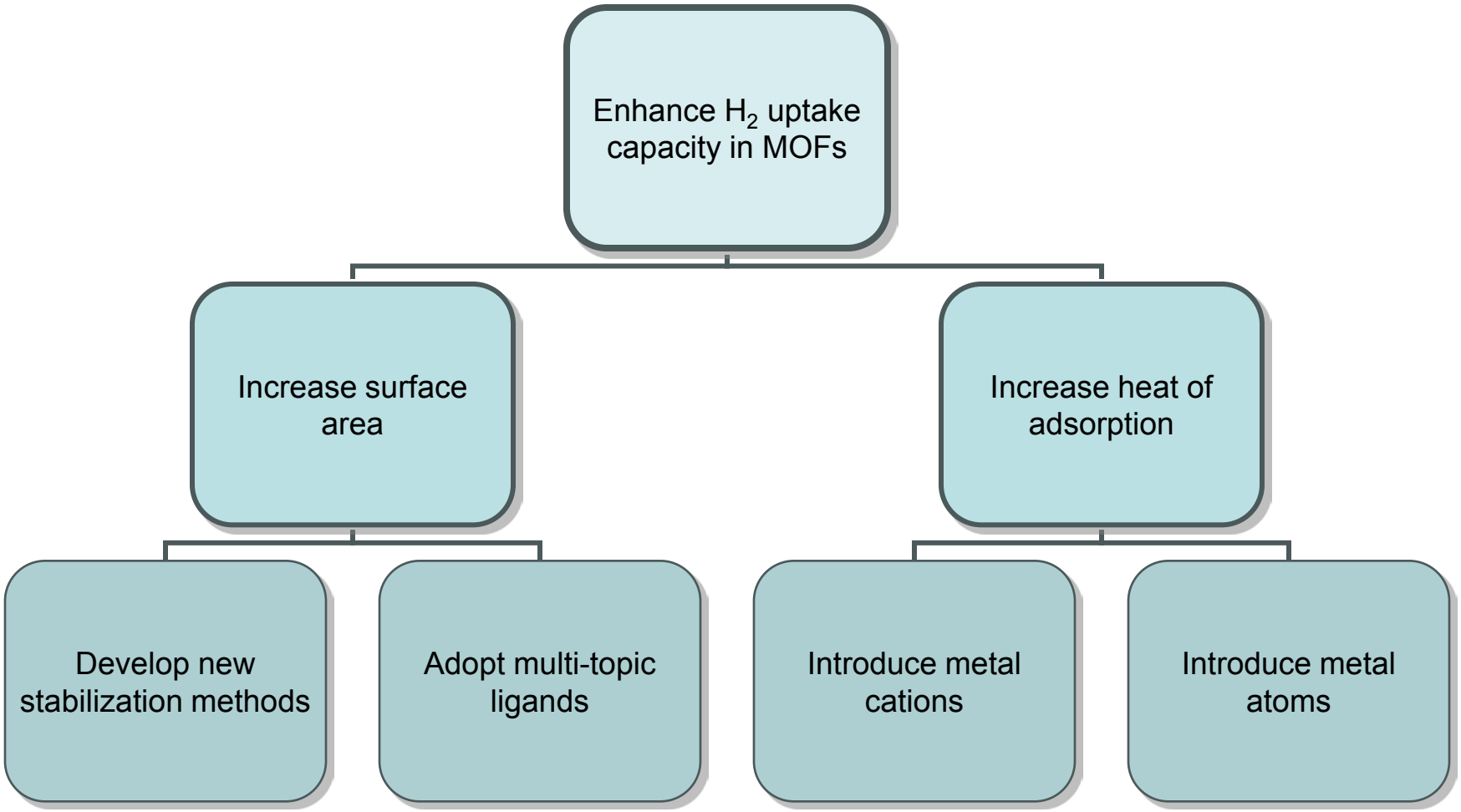
Hemoglobin



Heme
(Fe-protoporphyrin IX)

•In bioinorganic chemistry, an entatic state occurs when an unusual geometry is imposed on a metal center by the protein polypeptides. This subsequently enhances its reactivity in electron transfer, substrate binding, or catalysis

•Similarly, in a MOF, the metal centers can be forced into an entatic state to enhance their affinity toward H_2

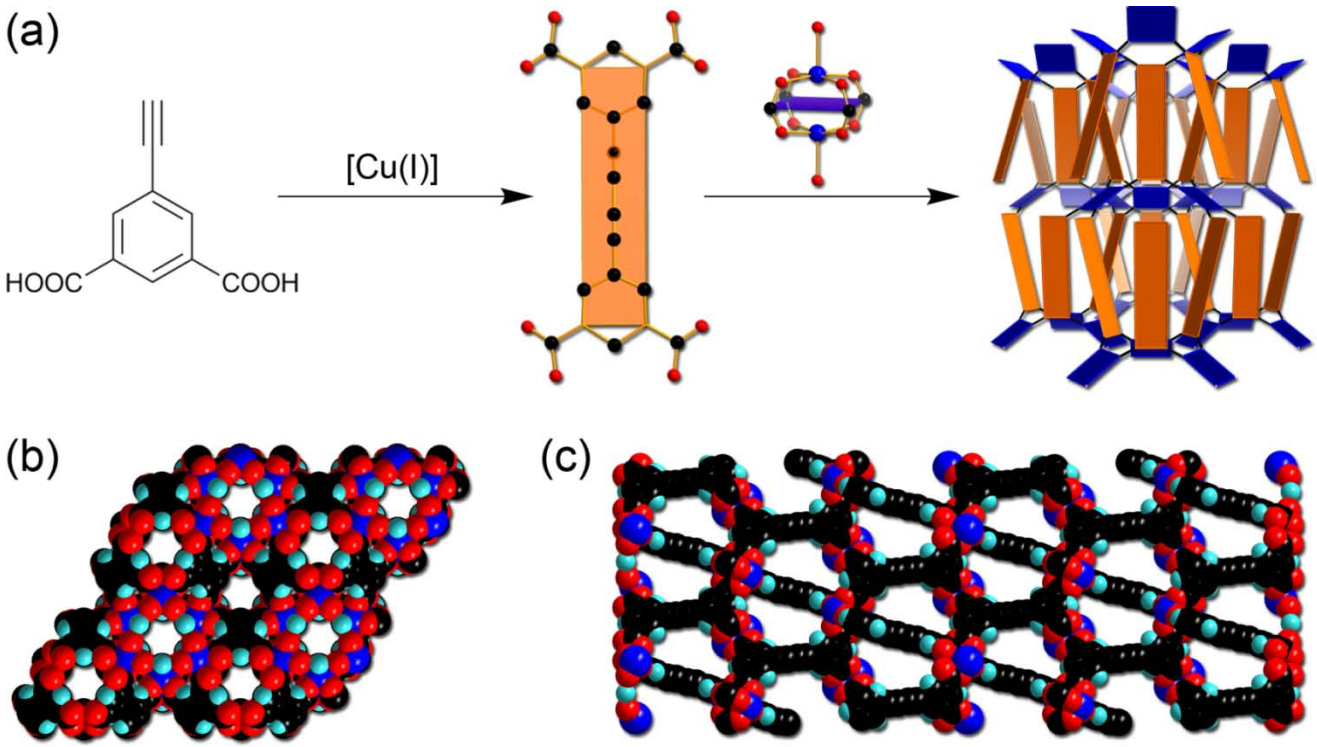


•Ultimate goal: prepare a MOF with both high surface area and high hydrogen-affinity

Approach/Milestone

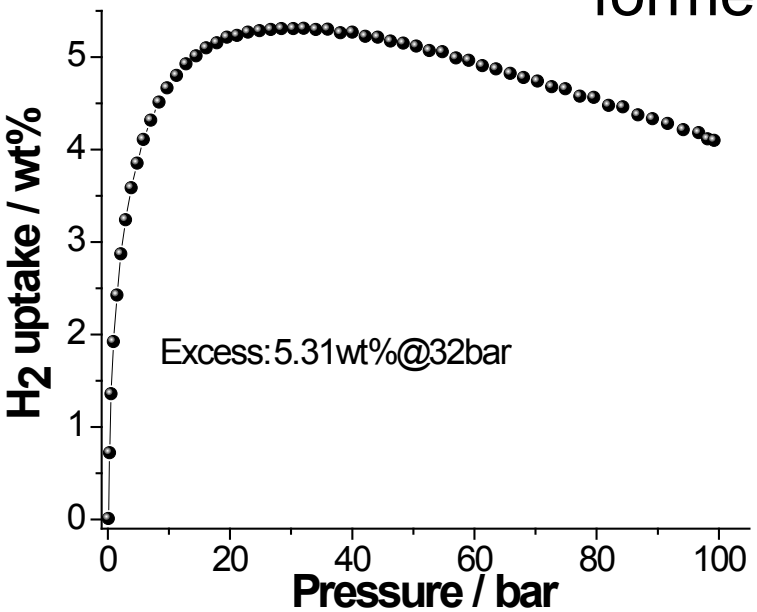
Month/Year	Approach and Milestone
Nov-07	Approach: Complete design of ligand library including above 40 novel ligands for construction of metal-organic frameworks (MOFs). Synthesize 15 new liagnds, and construct and optimize MOF structure. Determine surface area and H_2 adsorption and heat of H_2-adsorption of obtained MOFs. (Status – 100 complete)
Nov-08	Milestone: Optimize the alignment of the coordinatively unsaturated metal centers of MOFs and construct a new MOF, PCN-12, which exhibits an exceptionally high H_2 uptake of 3.0 wt% (24.6 mg/cm^3) at 760 Torr and 77 K. The H_2-adsorption heat of PCN-12 can reach as high as 12.5 kJ/mol at low coverage. (Status – 90% complete)
Nov-09	Milestone: Construct the catenation isomer pairs of PCN-6 and PCN-6'. H_2 sorption measurements at pressures up to 50 bar demonstrate that framework catenation can be favorable for the enhancement of hydrogen adsorption. The excess hydrogen uptake of PCN-6 is 6.7 wt % at 77 K/50 bar. Inelastic neutron scattering (INS) studies reveal that the interaction is found to be substantially stronger in catenated PCN-6 than in noncatenated PCN-6'. This provides information that catenation leads to increase in volumetric hydrogen uptake and strengthens the MOF-H_2 interaction. (Status – 90%)
Nov-10	Milestone: Construct MOFs containing mesocavities with microwindows may serve as a general approach towards stable MOFs with higher and higher surface areas. Incorporation of entatic-state metal sites into the high surface area MOFs. Design and synthesize porous organic frameworks (POF) for hydrogen storage with high surface area, tunable pore size, and flexibility. Determine H_2 adsorption of POFs doped by metal, such as Li and Ni. (Status – planned)

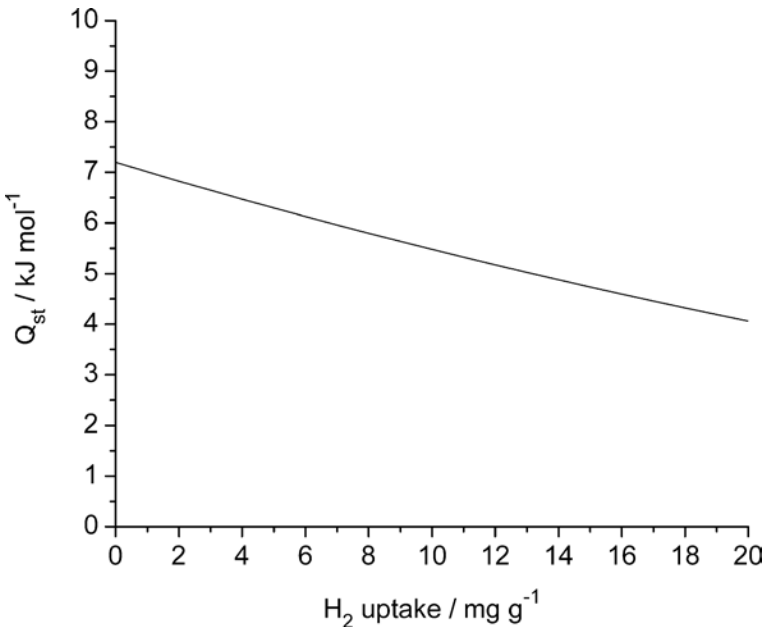
MOF derived from a polyyne-coupled di-isophthalate linker formed *in situ* (PCN-46)

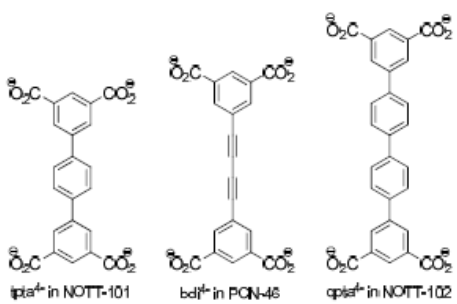


- PCN-46, a NbO-type metal–organic framework, has been synthesized through an *in situ* formed polyyne-coupled di-isophthalate ligand via Cu(I)-catalyzed oxidative coupling of terminal acetylenes

MOF derived from a polyyne-coupled di-isophthalate linker formed *in situ* (PCN-46)





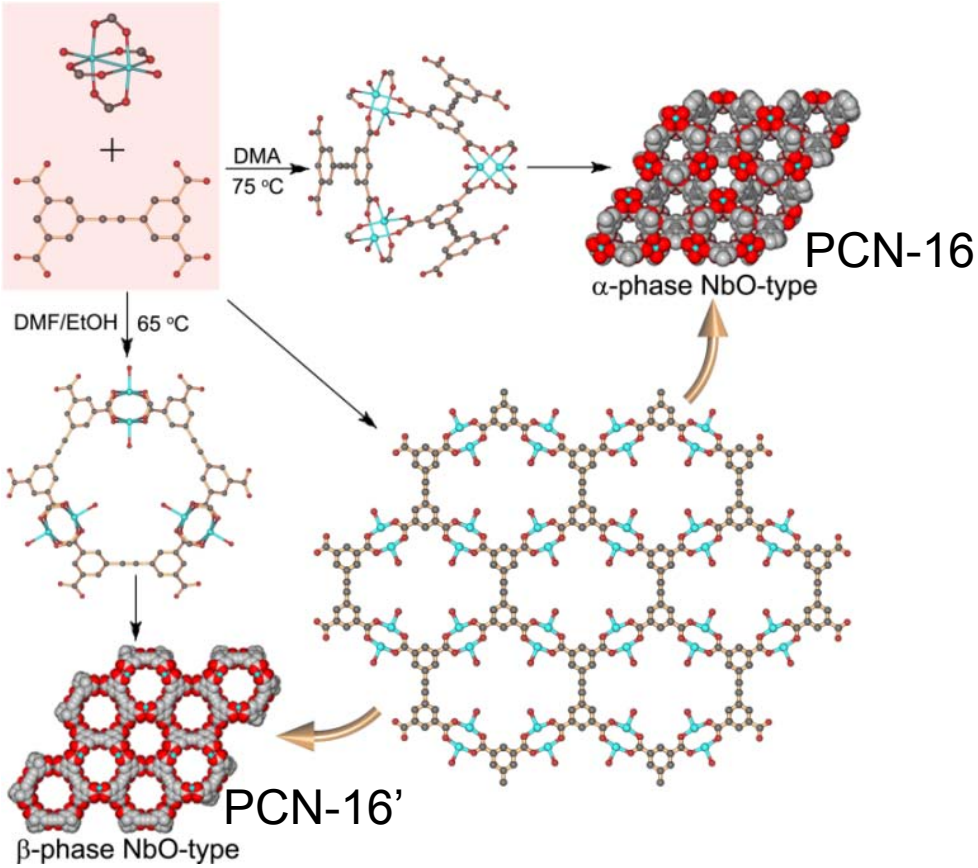


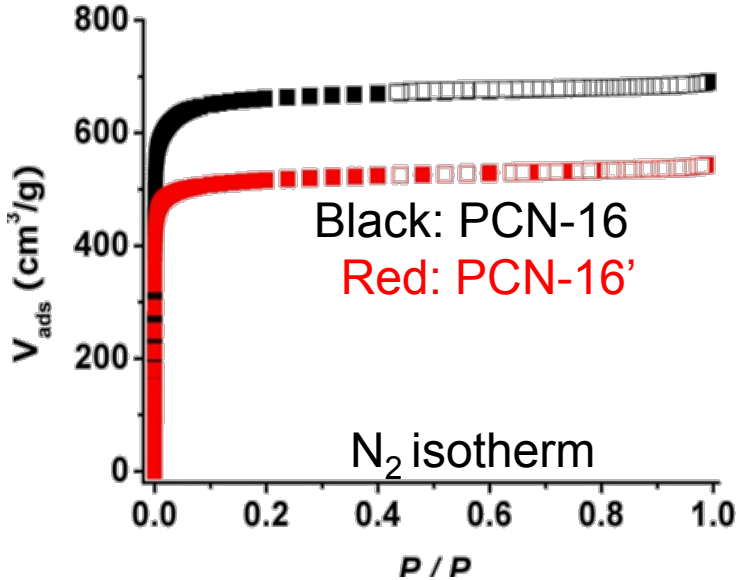
MOFs	Ligand length (Å)[a]	BET surface area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)[b]	H_2 uptake (mg/g)[c] 60bar	Q_{st} at low coverage (kJ mol^{-1})
NOTT-101	5.773	2316	0.886	66.0	<5.5
PCN-46	6.484	2500	1.012	71.6	7.20
NOTT-102	10.098	2942	1.138	72.0	<5.5

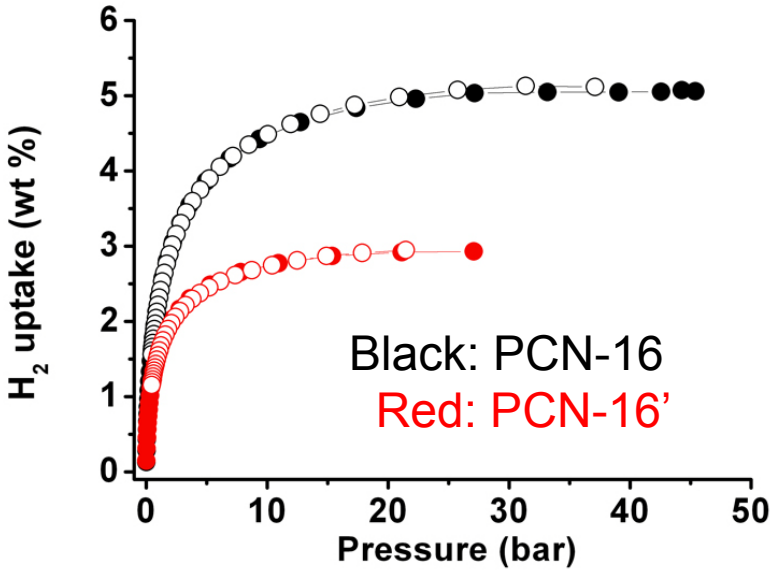
[a] Distance between 5-position of two isophthalate moieties. [b] Calculated from N_2 isotherms at 77 K. [c] Total uptake at 77 K.

- At 77 K and 760 Torr, PCN-46 can reversibly adsorb 1.95 wt% of H_2
- The excess H_2 uptake is 5.31 wt% (56.1 mg/g) at 32 bar
- The H_2 isosteric adsorption enthalpy of PCN-46 reaches 7.20 kJ/mol at low coverage
- The polyyne chain has stronger H_2 affinity than the phenyl rings

Symmetry-Preserving Isomer Pair (PCN-16,16')



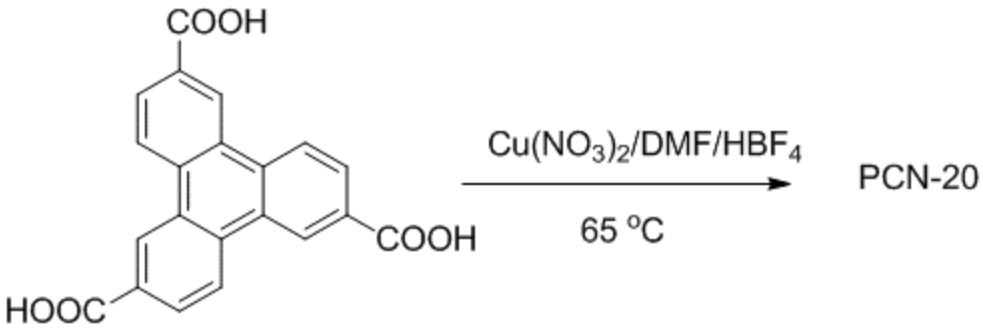


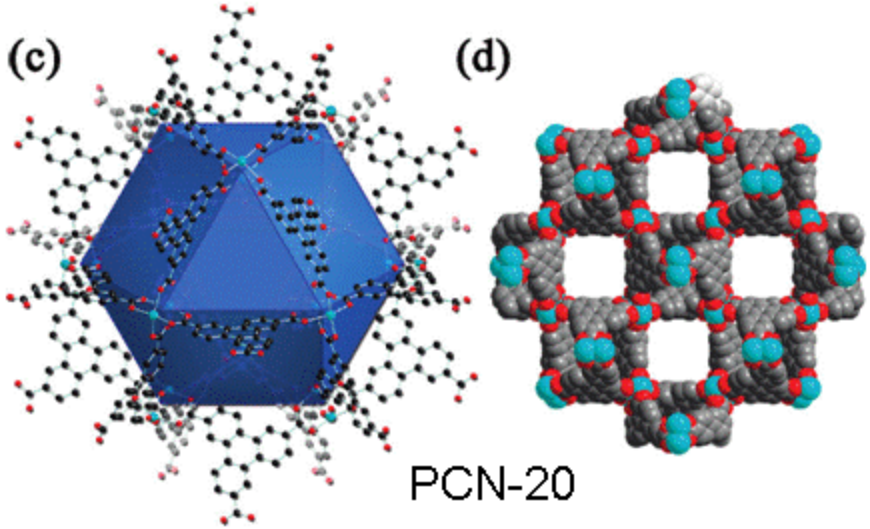


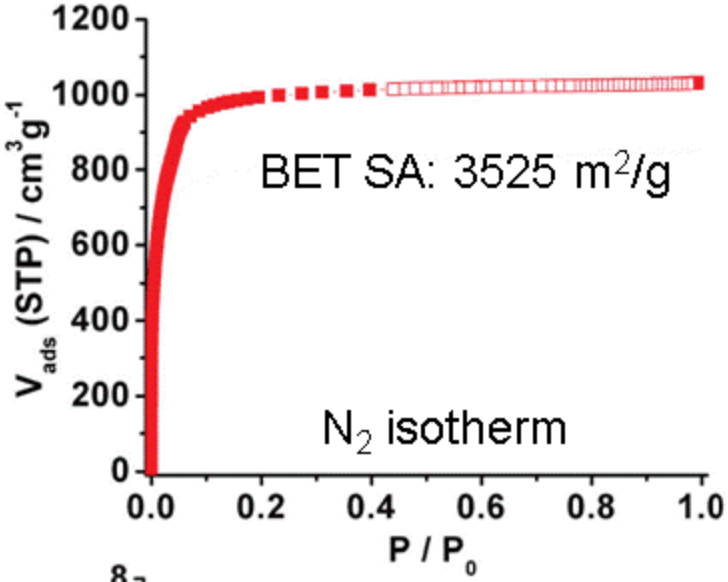
❑This is the first example that two crystals identical in chemical formula, atom-to-atom connectivity, and **symmetry**, differ dramatically in their hydrogen adsorption capacity. The finding hints that there may be a previously unknown class of crystals that would be useful for gas storage or catalysis

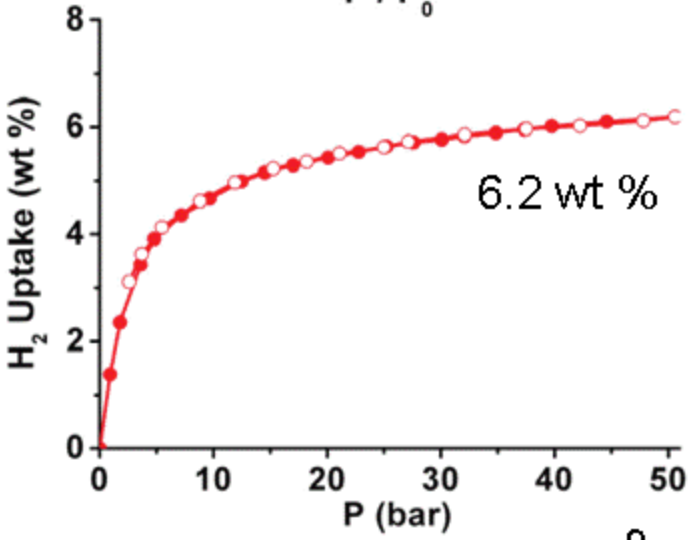
ST018

MOFs Containing Fused Aromatic Rings (PCN-20)



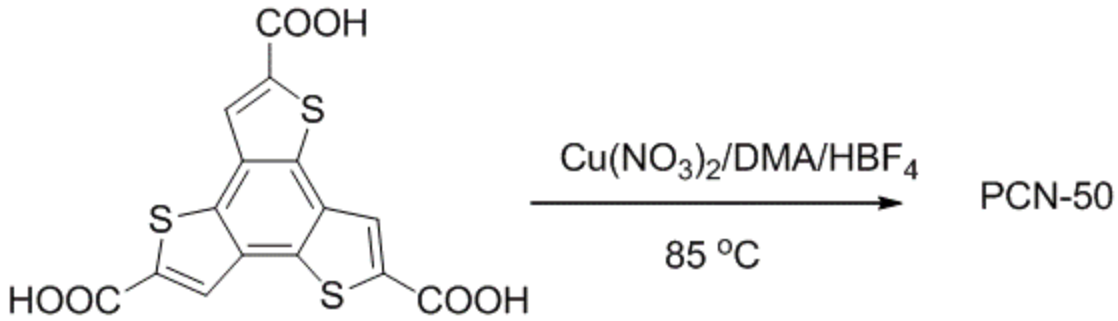




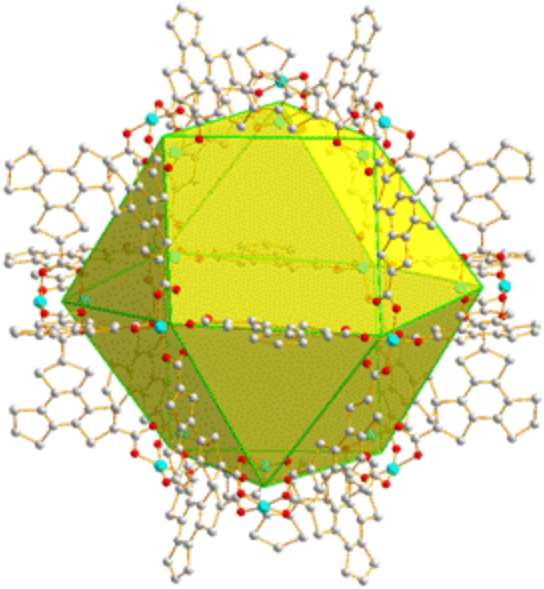


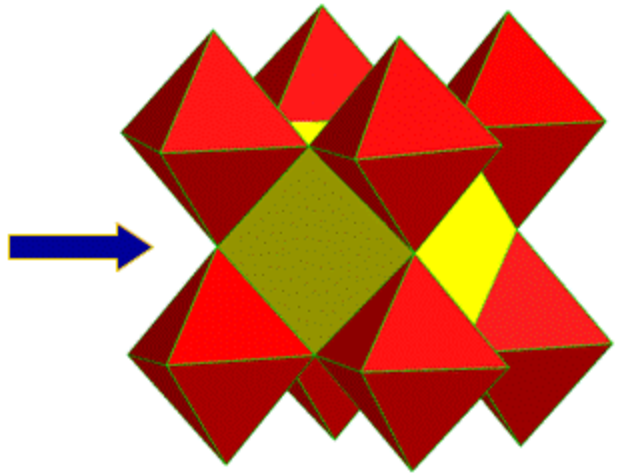
- PCN-20 was constructed from a highly conjugated planar tricarboxylate ligand.
- It possesses a large Langmuir surface area of over 4200 m^2/g and demonstrates a H_2 adsorption capacity of 6.2 wt% at 77 K and 50 bar

MOFs Containing Fused Rings (PCN-50)

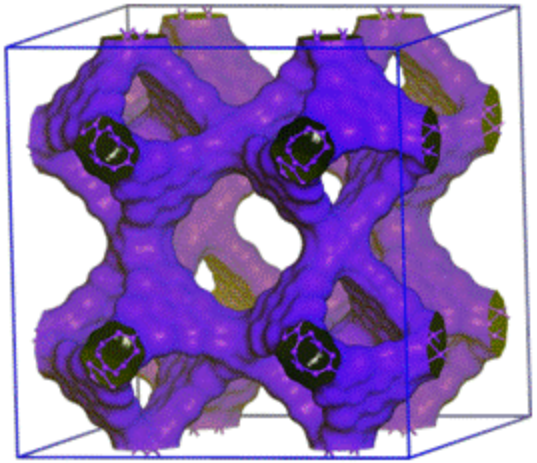


BTTC





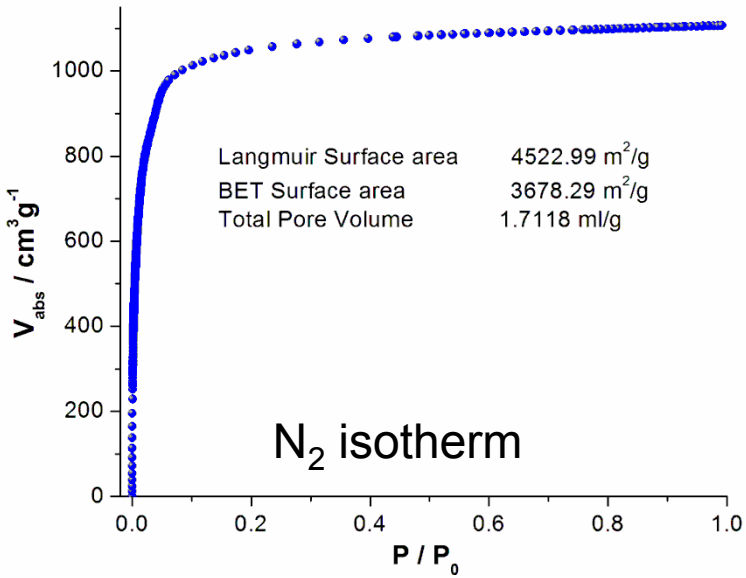
=

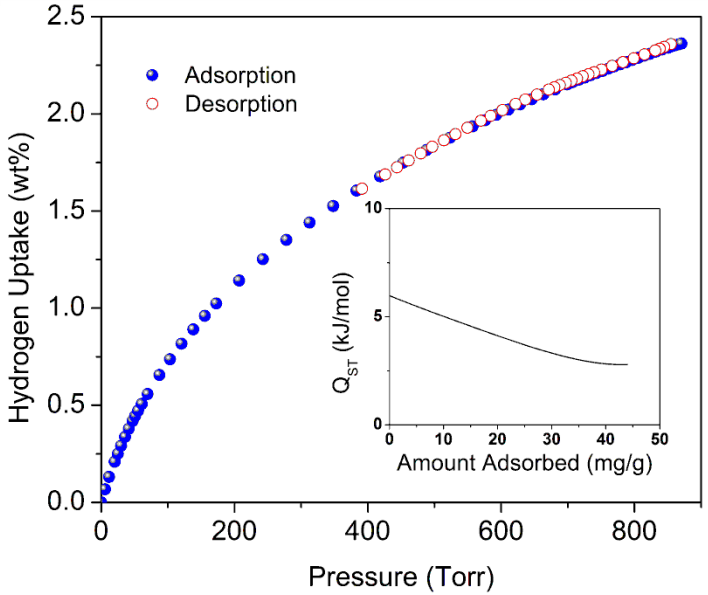


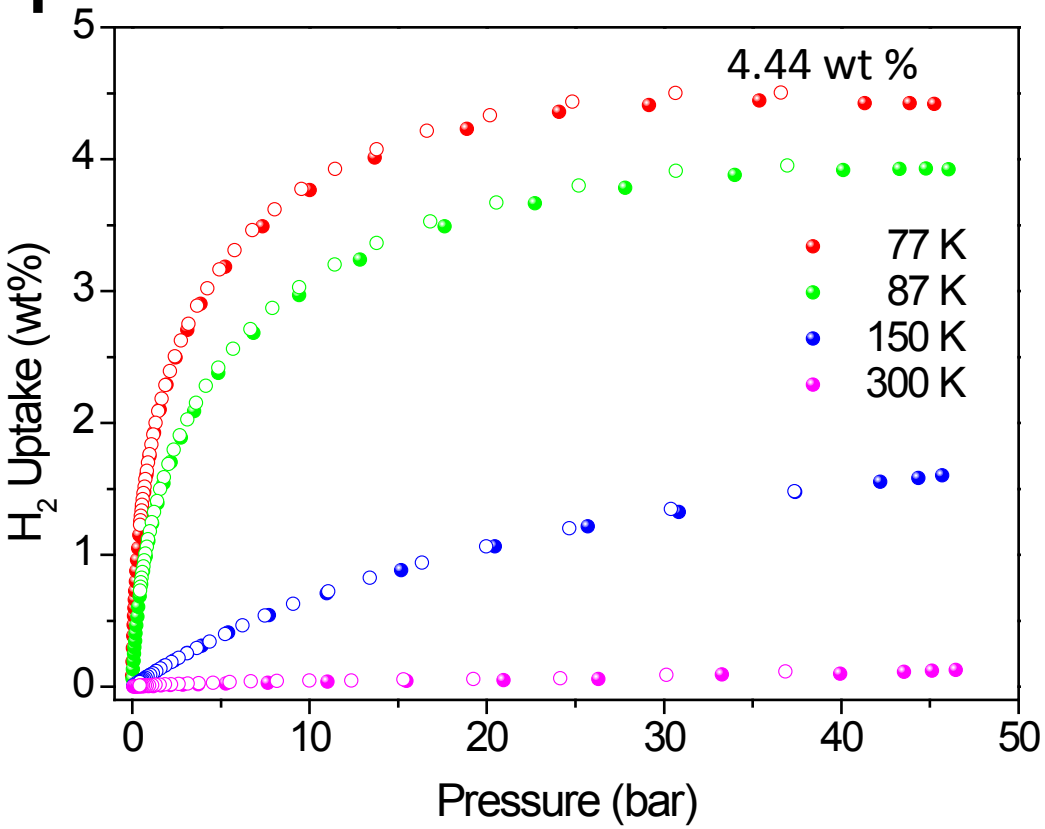
PCN-50

- PCN-50 was constructed based on a highly conjugated planar tricarboxylate BTTC ligand

Gas Adsorption of PCN-50

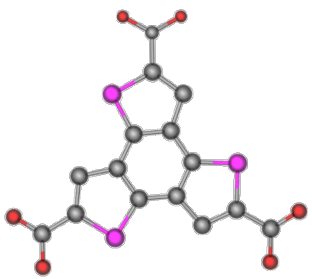




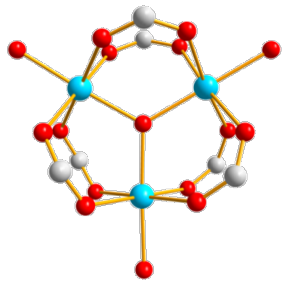


- The highly conjugated fused aromatic ring of the BTTC ligand renders PCN-50 with an exceptionally high Langmuir surface area of 4522 m^2/g and high H_2 adsorption capacity of 4.4 wt % with full reversibility at 77 K and 50 bar

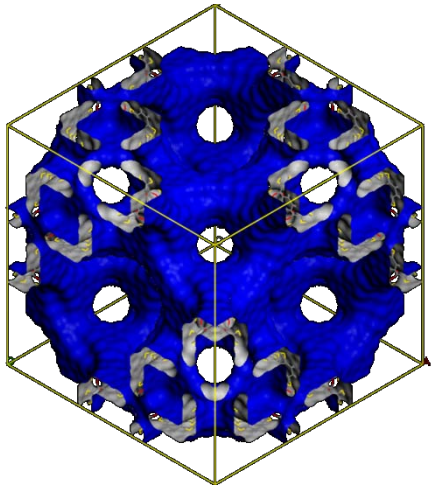
MOFs Containing Highly Conjugated Ligand (PCN-54)



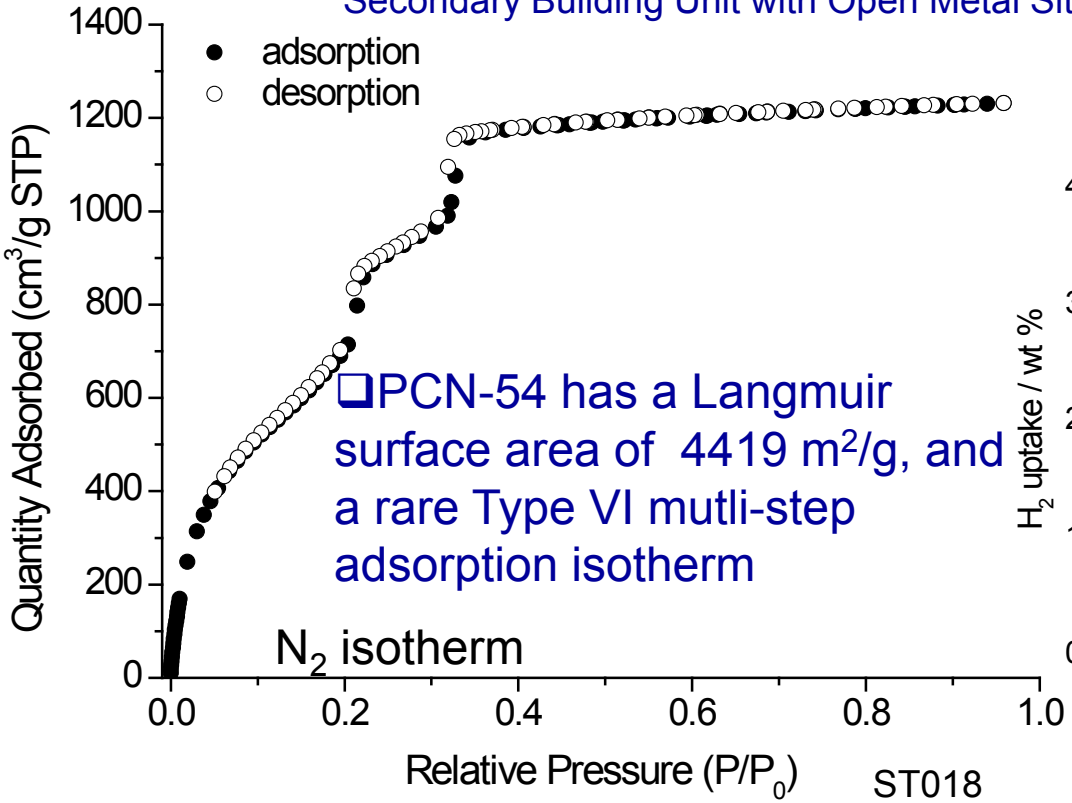
+



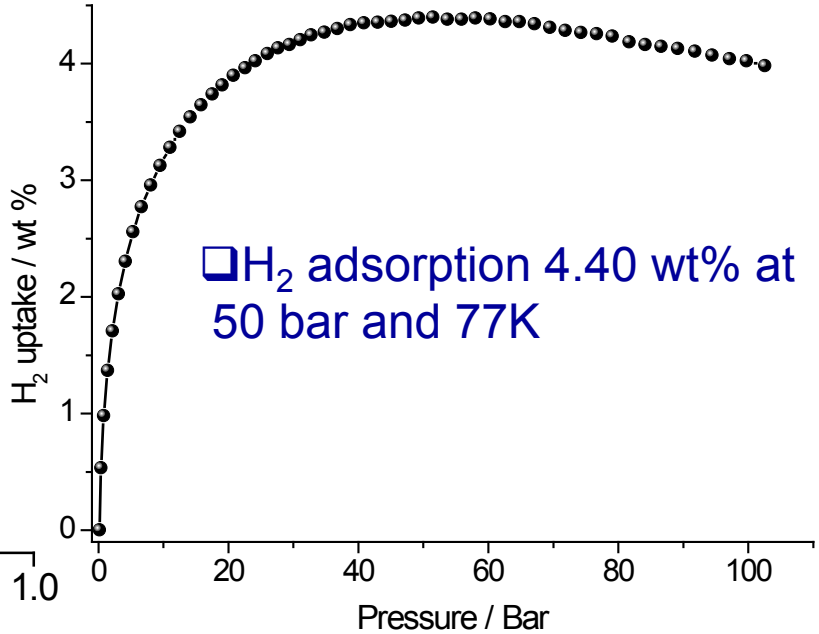
Secondary Building Unit with Open Metal Sites



PCN-54



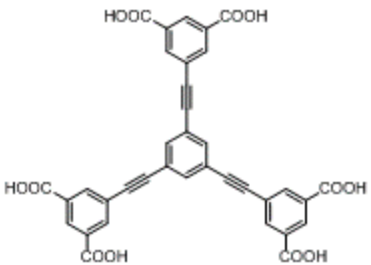
- PCN-54 has a Langmuir surface area of 4419 m^2/g, and a rare Type VI mutli-step adsorption isotherm



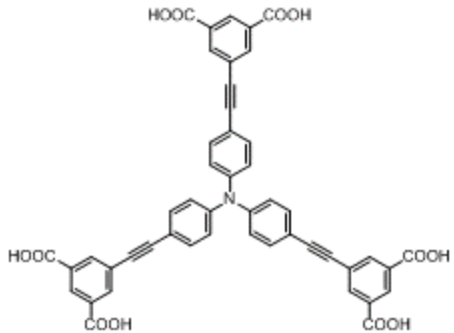
- H_2 adsorption 4.40 wt% at 50 bar and 77K

ST018

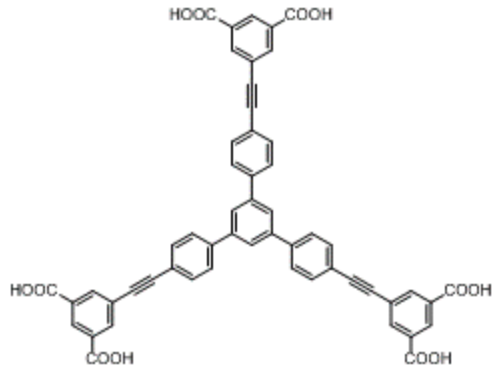
MOFs with Record High Surface Area and Hydrogen Uptake



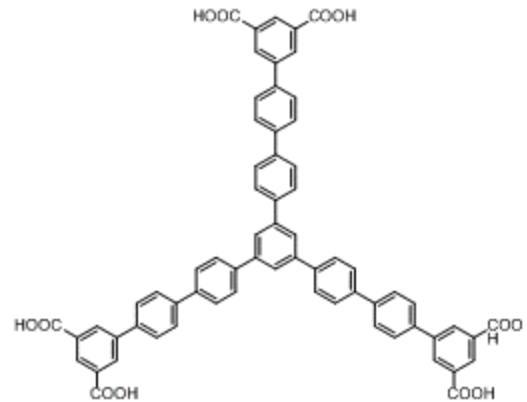
PCN-61



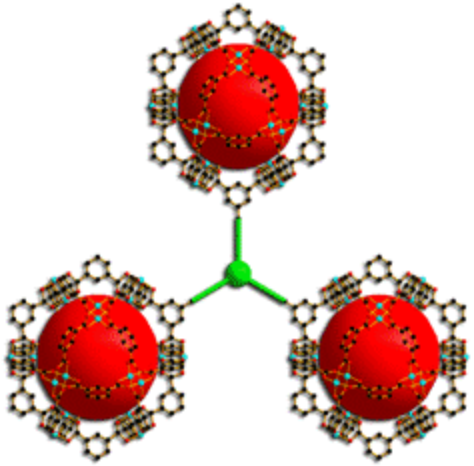
PCN-66



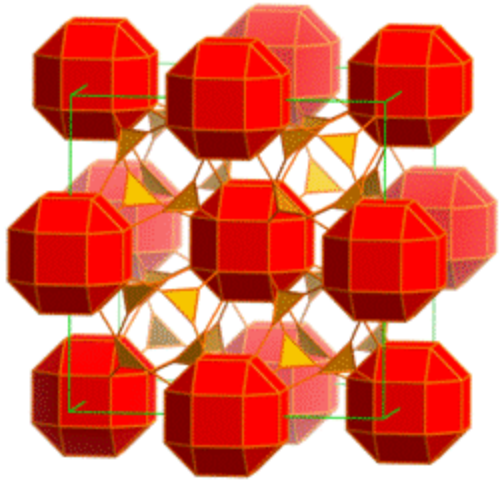
PCN-68



PCN-69

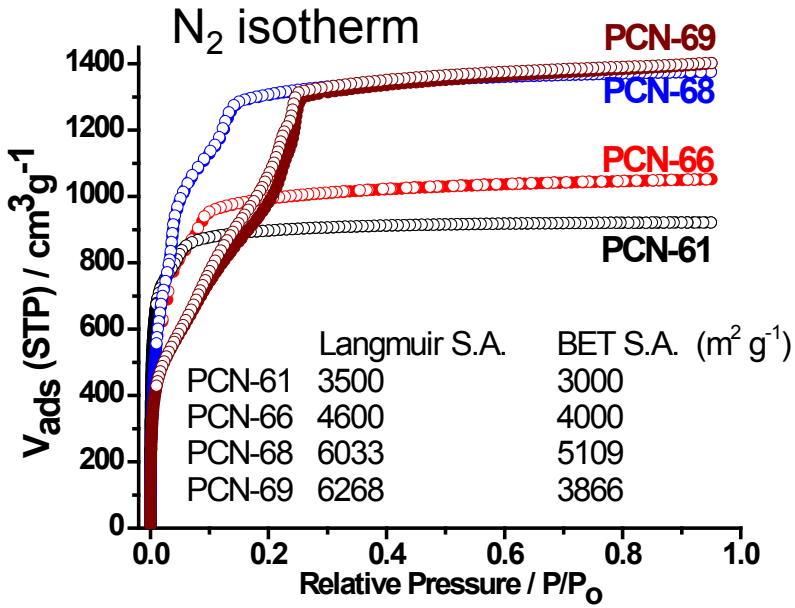


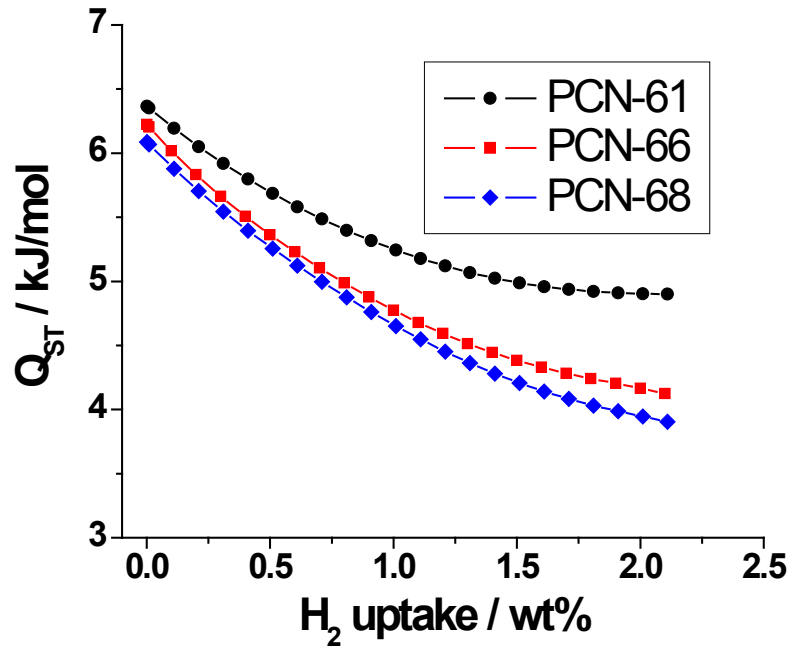
(3,24)-connected network

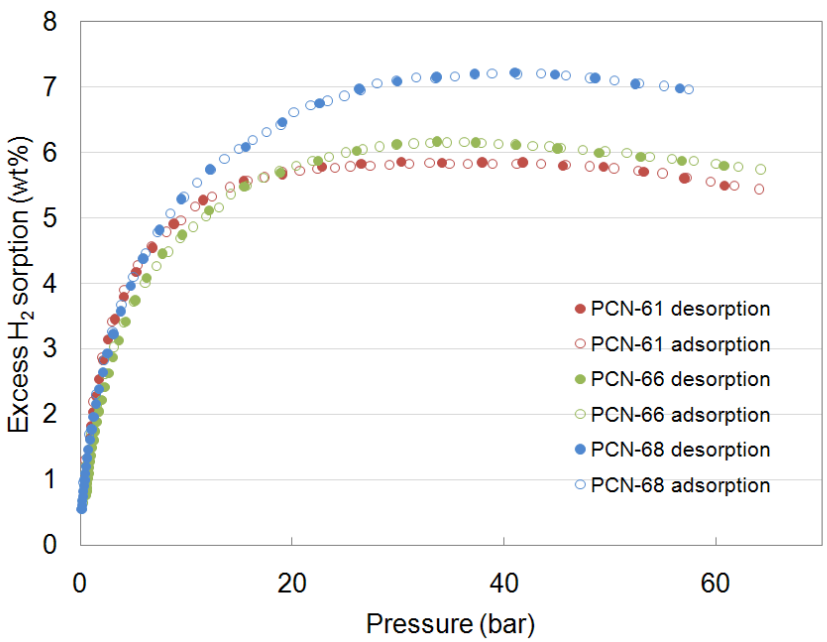


- An isoreticular MOF series with the (3,24)-connected network topology has been synthesized by using a series of dendritic hexa-carboxylate ligands.
- The framework is stabilized by incorporating microwindows, whose size is fixed by the formation of cuboctahedra supported by the isophthalate moieties throughout the framework.

MOFs with Record High Surface Area and Hydrogen Uptake



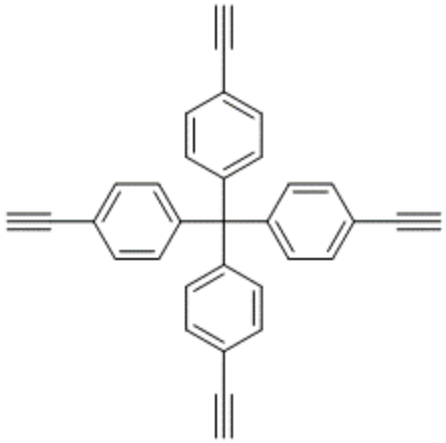




- PCN-69: MOF with the highest Langmuir surface area 6268 m^2/g (3866 m^2/g BET)
- PCN-68: 6033 m^2/g Langmuir (5109 m^2/g BET) and 7.2 wt% excess H_2 adsorption capacity. The data are confirmed by GM
- The excess gravimetric H_2 uptake is the highest (MOF-177 is ~7.0 wt%)

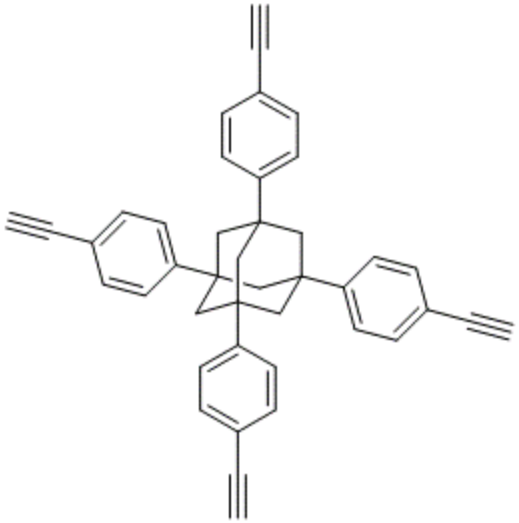
Porous Organic Framework (POF) for Hydrogen Storage

T-0



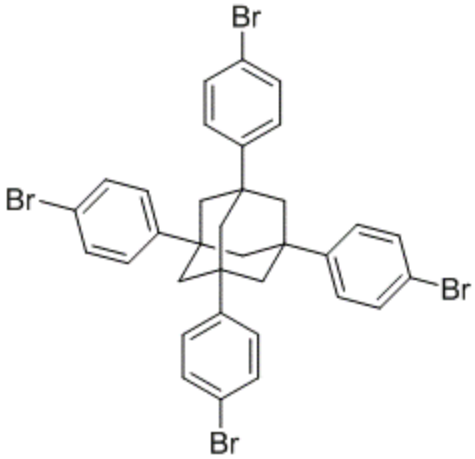
T-1

POF-1



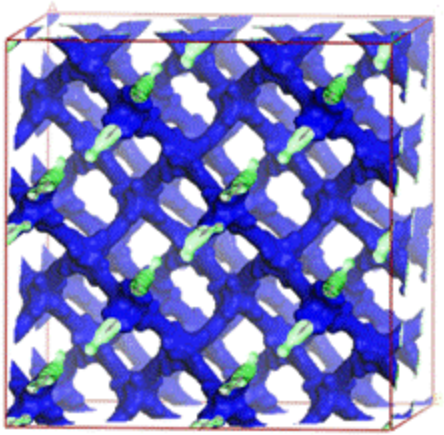
T-2

POF-2



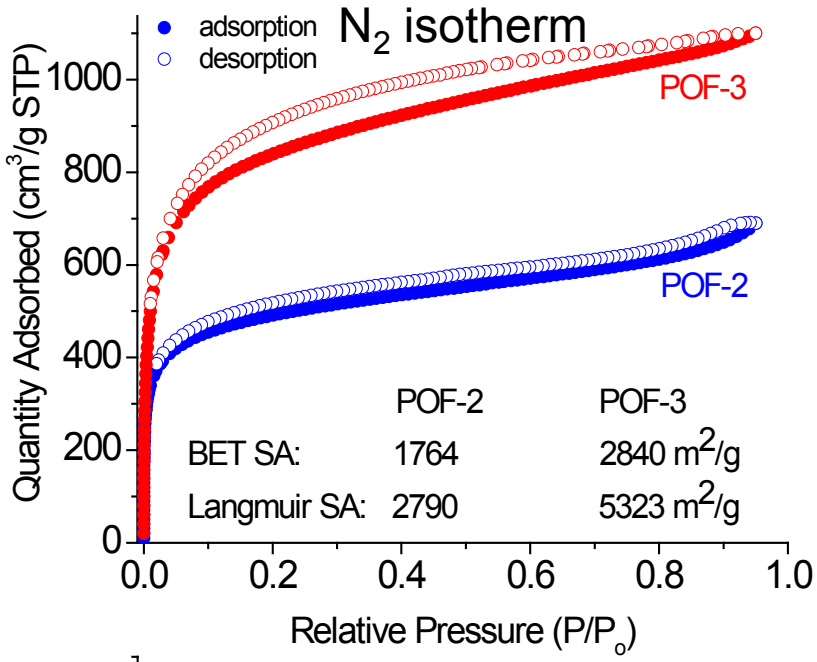
T-2

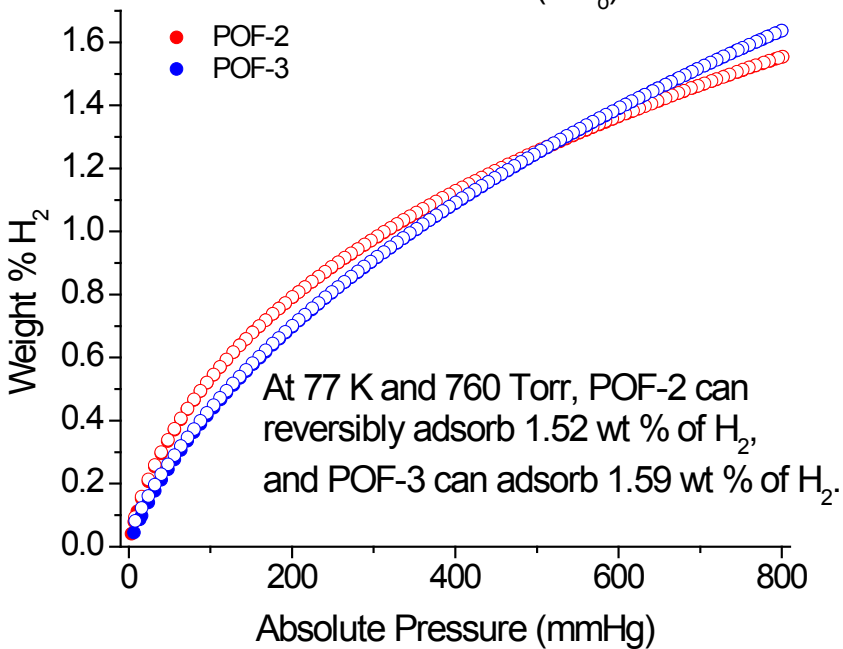
POF-3

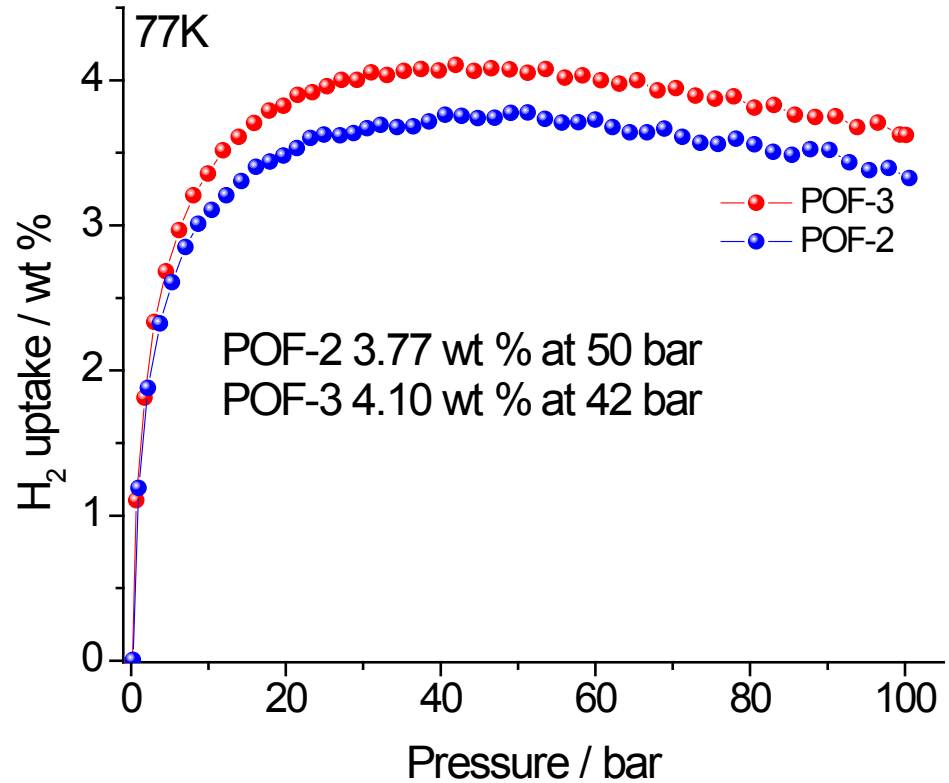


- The framework of POF-1 is constructed and optimized by using the Forcite Plus module in Material Studio
- Diamond-type net
- The POFs with T-2 structural units are first examples

Adsorption Properties of POFs







- The POFs with the possibility of incorporation of additional metal atoms or ions will be explored, which will increase the heat of H_2 adsorption
- POFs are stable toward reactive reagents

Collaborations

Partners

- Air Product, Gas Adsorption Measurement
- NREL, Gas Adsorption Screening
- NIST, Gas Adsorption Measurement, Theoretical Calculations
- KRICT, Korea, Gas Adsorption Measurement
- Dept. of Chem. Eng., TAMU, Theoretical Calculation
- KIT, Germany, Ligand Synthesis
- RPI, Theoretical Calculation
- LLNL, Critical Point Activation
- ANL, APS, Crystal Structure Determination
- GM, Gas Adsorption Measurement

Technology Transfer

- Working with industrial partners closely
- Ready to work with the Engineering CoE

Accomplishments

Demonstrated through experiments that :

- Crystal twins with two isomeric phases have been first discovered, and gas sorption studies revealed that the α-phase possesses a larger surface area, leading to higher hydrogen capacity as compared to the β-phase. This symmetry-preserving isomerization strategy can be applied to other MOFs
- A novel MOF was constructed based on a polyyne-coupled di-isophthalate linker formed *in situ.* The polyyne chains showed improved hydrogen affinity compared to phenyl rings
- An Isoreticular Series of Metal-Organic Frameworks with Dendritic Hexa-Carboxylate Ligands tend to have high surface area and stability. PCN-69 have the highest Langmuir surface area of 6268 m^2/g, while PCN-68 has the highest excess gravimetric H_2 uptake of 7.2 wt% at 77K and 50 bar
- POFs based on T-2 units with high surface area and tunable pore size were designed and synthesized

Future Work

FY10

- Further enhancement of H_2-MOF interaction by doping coordinatively unsaturated metal centers (heat of adsorption 15 kJ/mol). Based on theoretical calculations, main group metals such as Mg and Ca will be tested
- Working with partners, test H_2 uptake at temperatures higher than 77 K
- Preparation of MOFs with high surface area and optimized cage size with newly designed ligands based on theoretical calculations
- Incorporation of entatic-state metals based on theoretical guidance
- Preparation of POFs containing active metals.
- The Go/No-Go decision (3rd Quarter)

FY11 (TBD)

- Show that entatic-state-metal incorporation improves the heat of hydrogen-adsorption. Achieve a heat of hydrogen-adsorption significantly higher than those of traditional adsorptive materials
- Discover a MOF with both high surface area and high hydrogen-affinity. 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

Summary Table

Material	ΔH_{ads} (kJ/mol)	H_2 Adsorption Uptake			
		Gravimetric (wt%)	Volumetric (g/L)	T (K)	P (bar)
PCN-61	6.36	5.87	35.0	77	33
		1.70	9.63	195	90
		0.66	3.74	298	90
PCN-66	6.22	6.23	29.6	77	45
		1.60	7.27	195	90
		0.77	3.50	298	90
PCN-68	6.09	7.20	29.6	77	50
		1.70	6.10	195	90
		1.00	4.10	298	90
PCN-20	5.47	6.20	29.0	77	50
		0.65	3.04	298	50
PCN-16	_	5.10	36.9	77	30
PCN-16'	_	2.90	22.2	77	30
PCN-46	7.20	5.31	34.7	77	32
PCN-50	5.97	4.44	23.2	77	45
		1.60	8.37	150	45
PCN-54	_	4.40	24.5	77	50
POF-2	6.89	3.74	_	77	50
POF-3	5.51	4.10	_	77	42