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

Joe Zhou
Texas A&M University
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ST018

Overview

Timeline

- Project start date: 7/1/2007
- Project end date: 6/30/2013
- Percent complete: 95%

Barriers

- H_2 uptake at room temperature is low despite high uptake at 77 K
- ΔH needs to be in the range of 15 to 30 kJ/mol to reach high storage capacity at ambient temperature
- Materials with high surface areas generally have low volumetric uptake

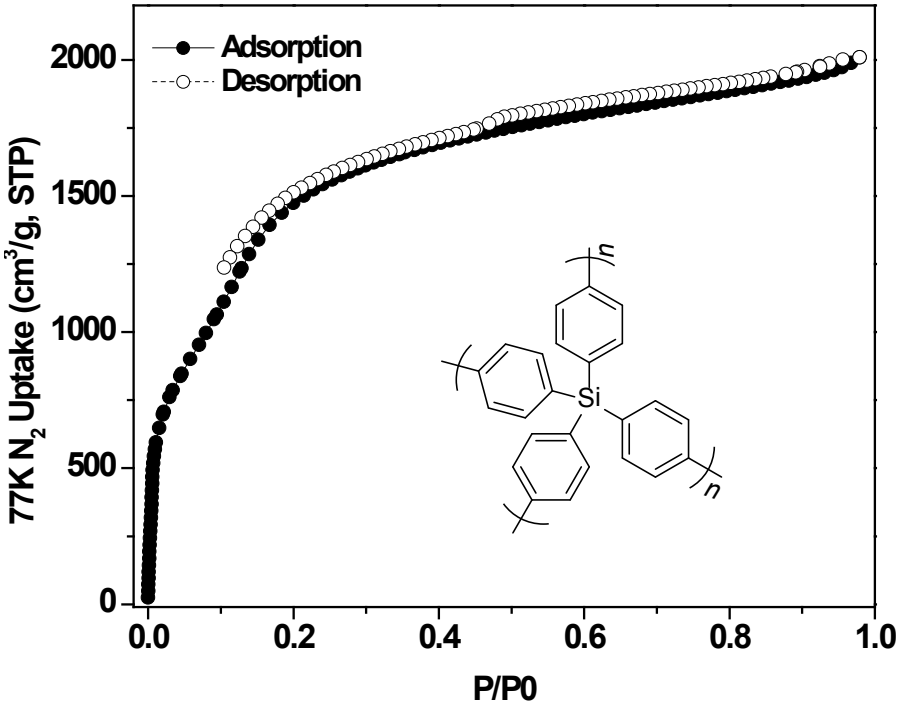
Budget

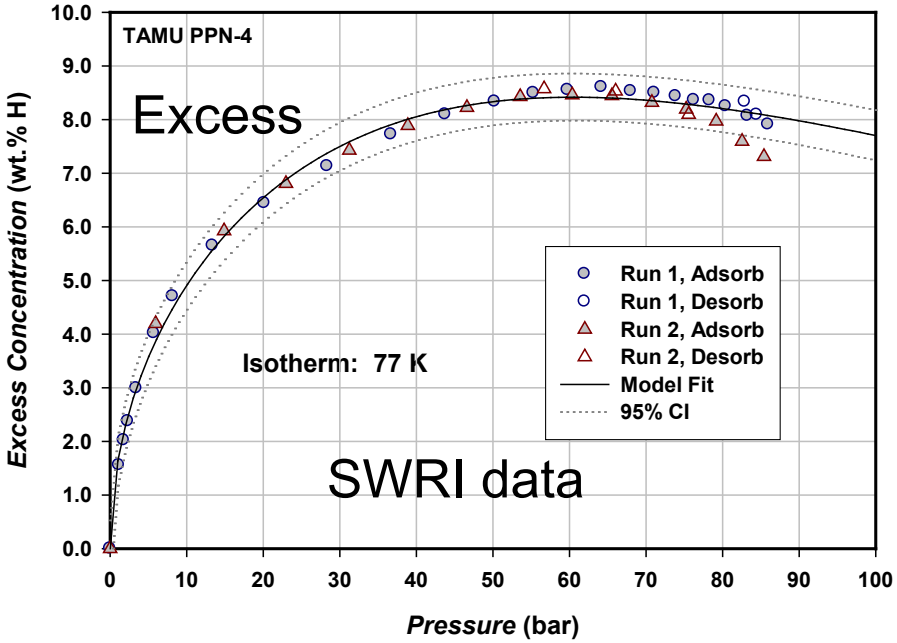
- Total project funding (DOE: $1,342,819; Contractor: $771,856)
- FY07 $ 100,000 (Miami)
- FY08 $ 0
- FY09 $ 742,260 (TAMU)
- FY10 $ 300,000 (TAMU)
- FY11 $ 0
- FY12 $ 200,559 (TAMU)
- FY13 $ 0

Partners

- ANL (APS)
- ORNL, LLNL, LBNL
- Seoul National University
- Dept. of Chem. Eng., TAMU
- KIT, Germany
- GM
- SWRIÈ
- RTI

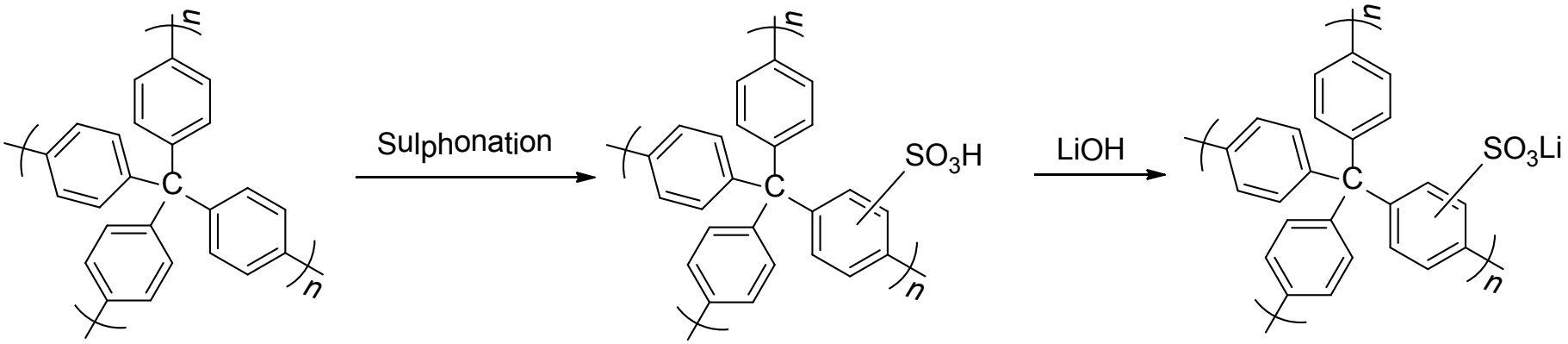
Impact of Ultra-high Surface Area on H_2 Uptake Capacity



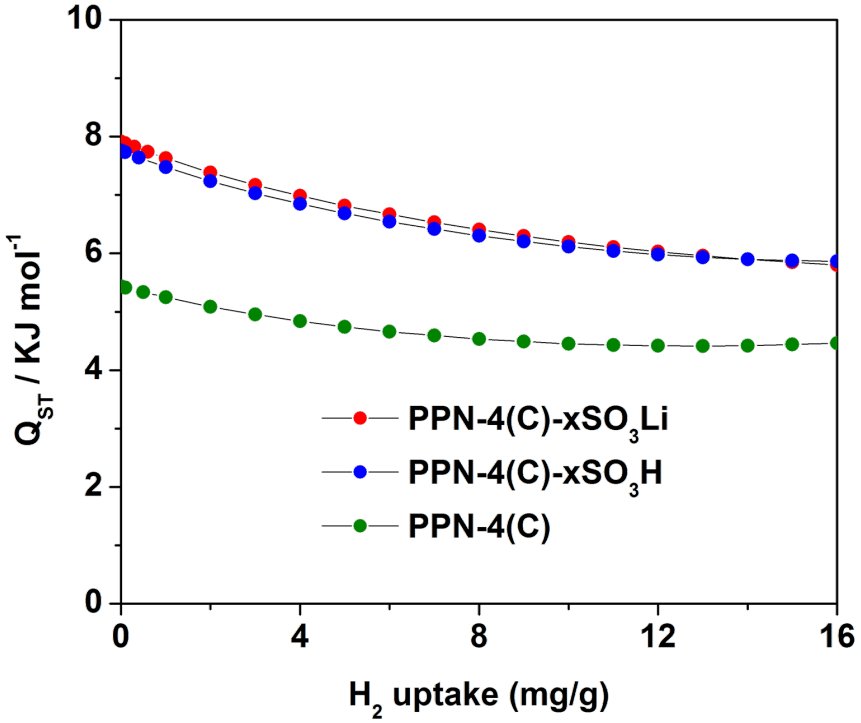


PPN-4(Si) has ultrahigh surface area (S_{BET} = 6470 m^2/g) and is very stable. This surface area is one of the highest reported to date for any porous material. Yet, volumetric uptake (28 g/L) is low due to extremely low framework density (0.284 g/cm^3) and lack of strong H_2-binding sites.

Functionalized PPNs for H_2 Adsorption

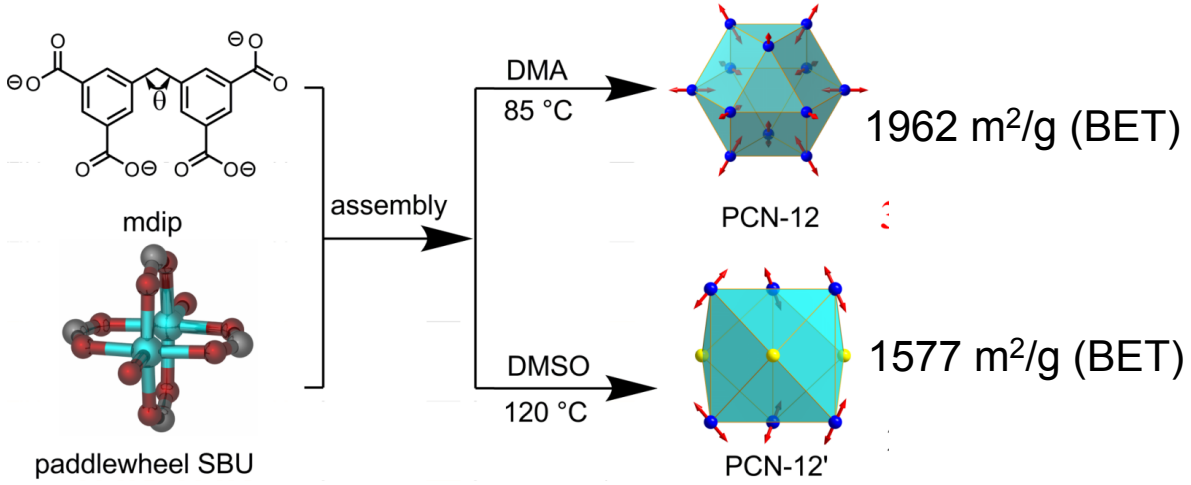


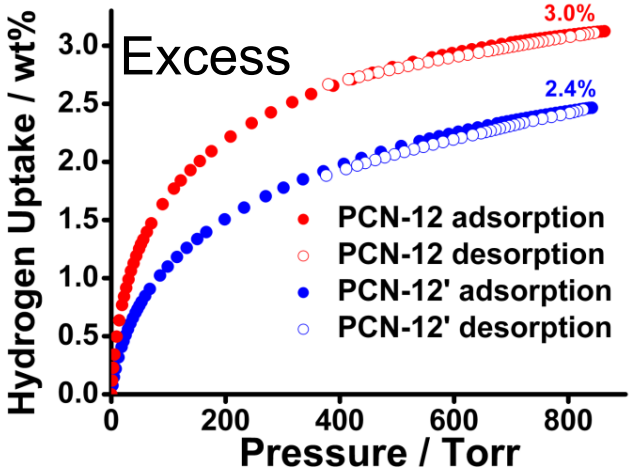
PPN-4(C) PPN-4(C)-xSO_3H PPN-4(C)-xSO_3Li

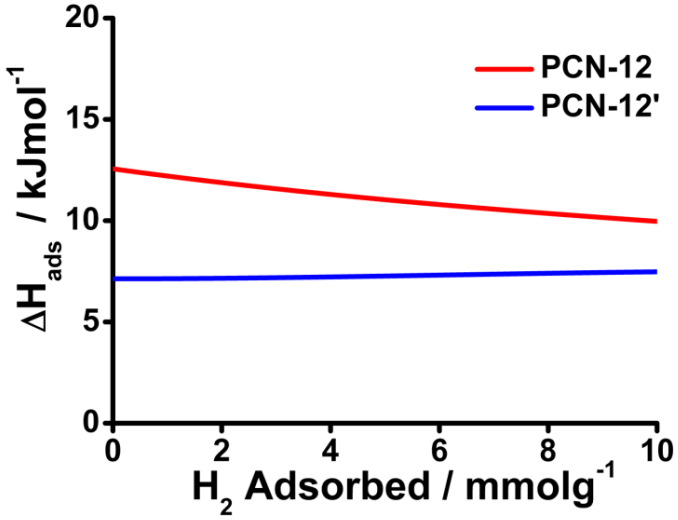


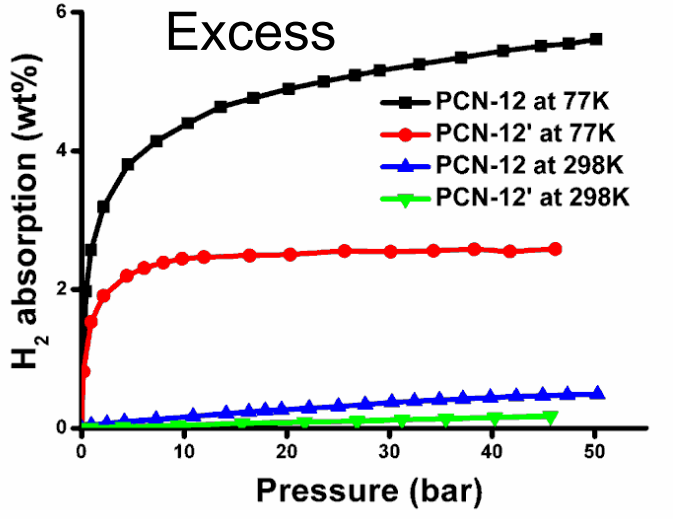
Isosteric heats of adsorption obtained from isotherms at 77 and 87 K. H_2 heat of adsorption has improved by 47% upon post-synthetic modification.

Optimization of the alignment of the coordinatively unsaturated metal centers for high heat of adsorption









At 50 bar and 77 K, PCN-12: 5.51 wt% (44.90 g/L, DOE 2017 goal: 40 g/L).

Relevance

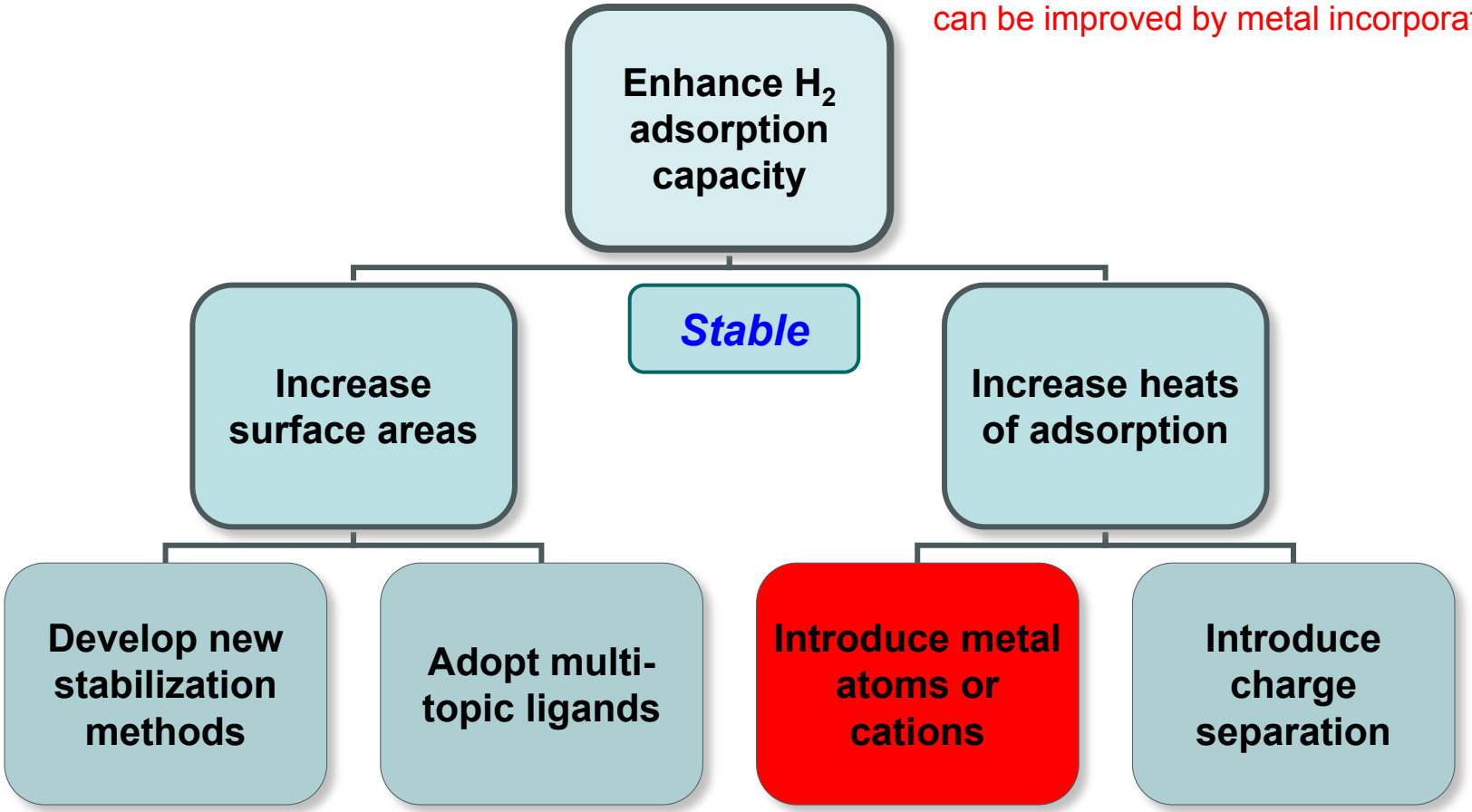
(Technical Challenges)

Dihydrogen affinity

- 15 kJ/mol < Q_{st} < 30 kJ/mol for ambient temperature application
- For most materials, Q_{st} < 10 kJ/mol

Surface area

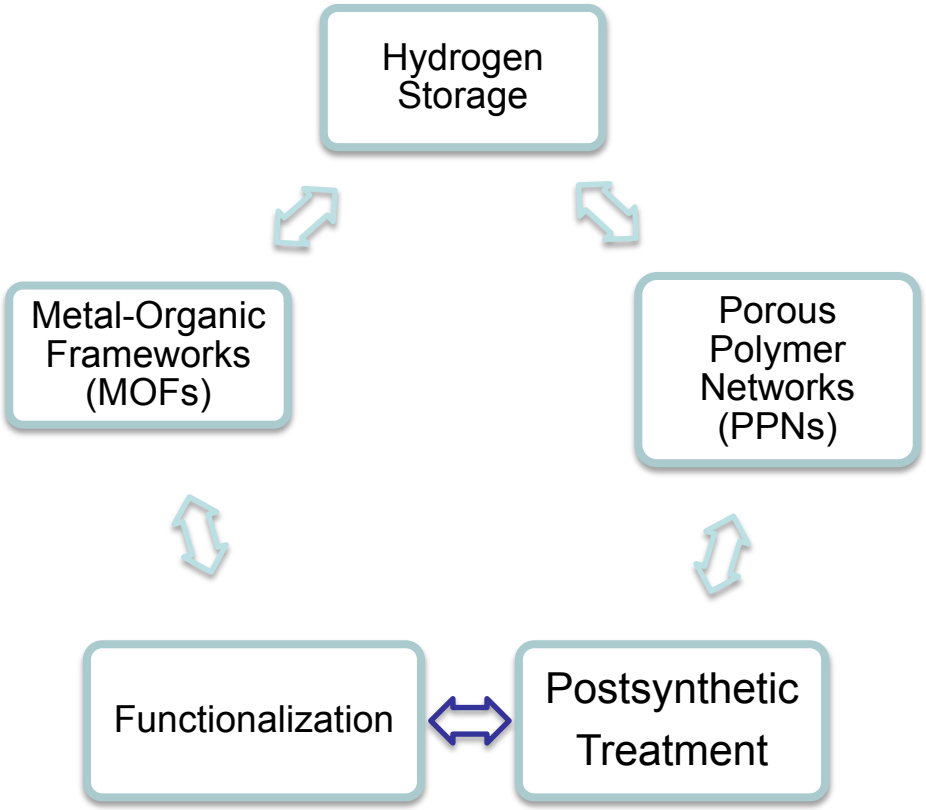
- High surface area is beneficial for gravimetric H_2 uptake
- Volumetric uptake and heat adsorption can be improved by metal incorporation



Approach/Milestone

Month/Year	Approach and Milestone
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 Hydrgeon adsorption heat of PCN-12 can reach as high as 12.5 kJ/mol at low coverage. (Status – 100% complete)
Nov-09	Milestone: Construct the catenation isomer pairs of PCN-6 and PCN-6'. H_2 sorption measurements demonstrate that framework catenation can be favorable. 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 substantially stronger in catenated PCN-6. The catenation leads to increase in volumetric H_2 uptake and the MOF-H_2 interaction. (Status – 100% complete)
Nov-10	Milestone: Construct MOFs containing mesocavities with microwindows may serve as a general approach towards stable MOFs with higher surface areas. Design and synthesize porous polymer networks (PPNs) for hydrogen storage with high surface area, tunable pore size, and flexibility. Determine H_2 adsorption of PPNs with metal incorporation. (Status – 100% complete)
Nov-11	Milestone: Construct PPNs with ultrahigh surface area. Explore the possibility of incorporation of charge and additional light metal ions such as Li^+, Na^+ or Mg^{2+} into PPNs. The modified PPNs show improved hydrogen affinity and volumetric hydrogen uptake due to the increased density. (Status – 100% complete)
Jun-13	**Milestone: Synthesize 20 stable and high-surface-area materials with incorporated metal atoms or cations. Demonstrate multiple dihydrogen bonded to a single open metal site with Zr-porphyrin-MOFs. Approach heat of adsorption15 kJ mol^{-1}. (Status – underway)**

Approach



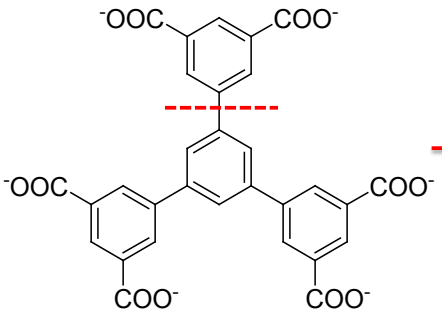
Enhance H_2 uptake

- Framework functionalization
- Framework post-synthetic modification
- Introducing metal ions

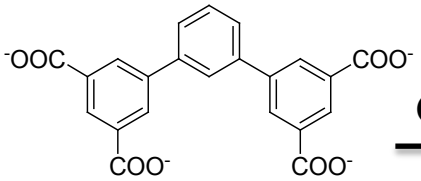
New Achievements

- A series of MOFs (PCN-30X) with new topology have been synthesized through Ligand Truncation Strategy, the H_2 uptakes (77 K and 1 atm) of there MOFs are among the highest (2.2 ~ 2.7 wt%, 17 ~ 21 g L^{-1}). PCN-305 exhibits very high H_2 total storage capacity (7.0 wt% at 60 bar and 77 K, which is 54 g/L calculated with crystal density)
- A MOF (PCN-309) with free carboxylic acid was synthesized; H_2 uptake was improved by metathesis (Zn to Cu), more importantly, the heat of adsorption was constant with the increasing of H_2 adsorption
- Metal-Ligand-Fragment Coassembly Strategy was successfully implemented to introduce functionalities, and heat of adsorption was much improved
- Highly stable Zr-MOFs were synthesized and initial metal-insertion study was carried out, these materials exhibit high surface area and high heat of adsorption
- Three strategies were applied to synthesize PPNs with anchors for metal insertion

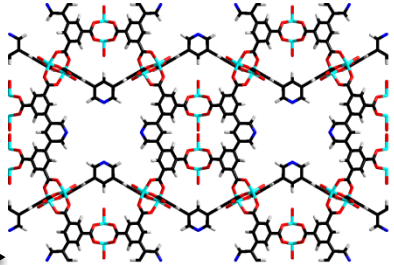
Ligand Truncation Strategy



Ligand Truncation



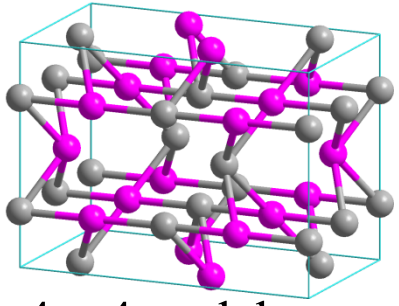
$Cu(NO_3)_2$/DMA



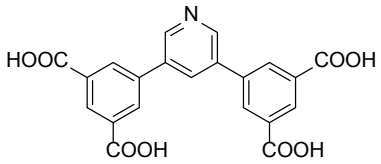
Reduced Symmetry

C_3

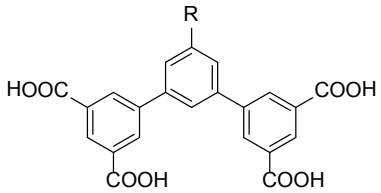
C_2



4-*c* 4-nodal net



PCN-305

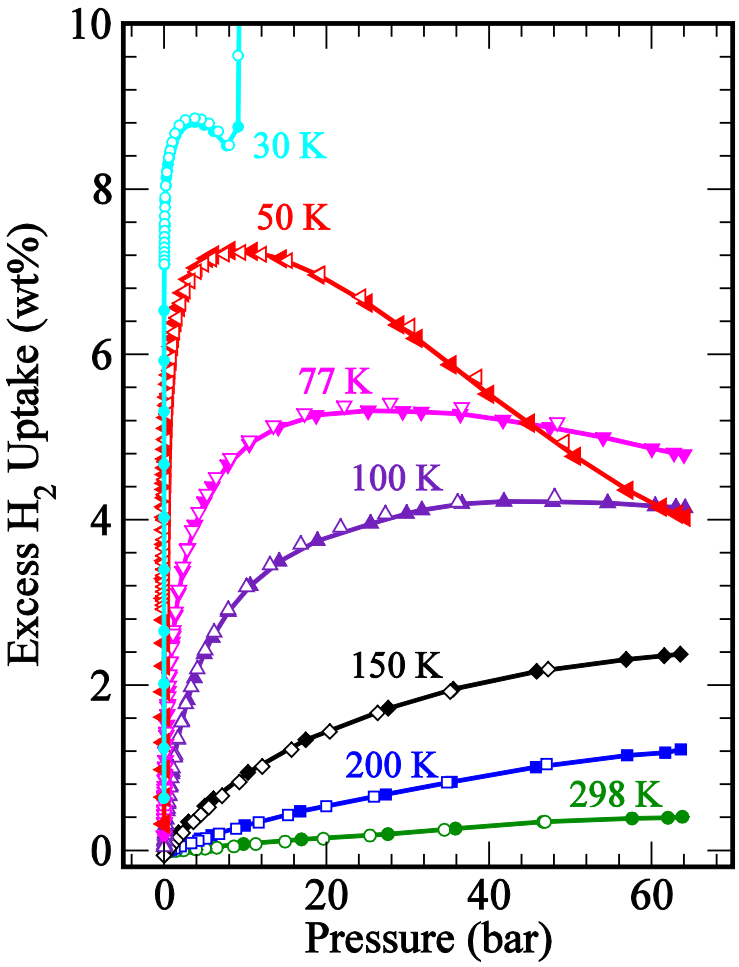


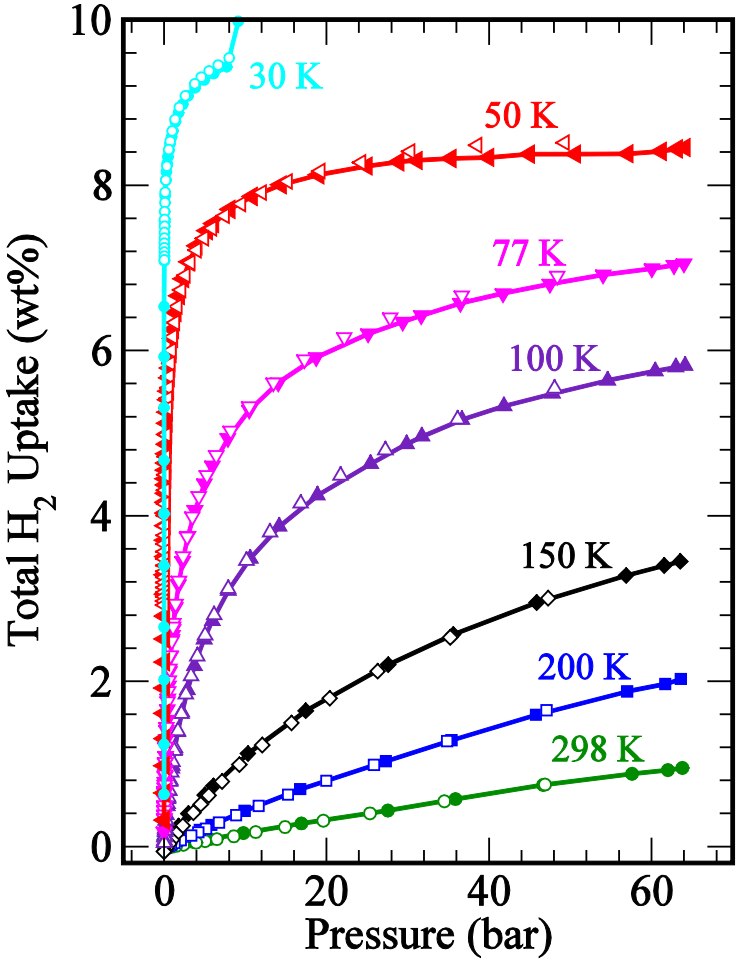
PCN-306: R = H
PCN-307: R = CH_3
PCN-308: R = CF_3

	PCN-305	PCN-306	PCN-307	PCN-308
S_{BET} (m^2 g^{-1})	1651	1927	1377	1419
H_2 uptake (wt%) at 77 K and 1 bar	2.2	2.5	2.6	2.7
H_2 uptake (g L^{-1}) at 77 K and 1 bar	17	19	20	21
Q_{st} (kJ mol^{-1})	6.5	6.4	6.2	6.5

Computer simulation is underway

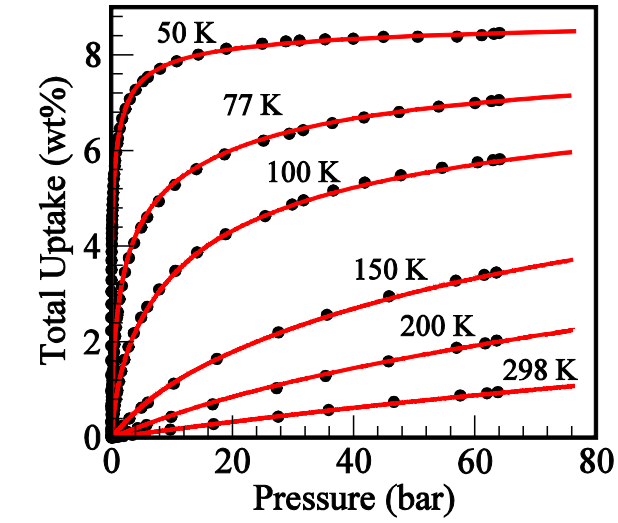
High Pressure Data for PCN-305



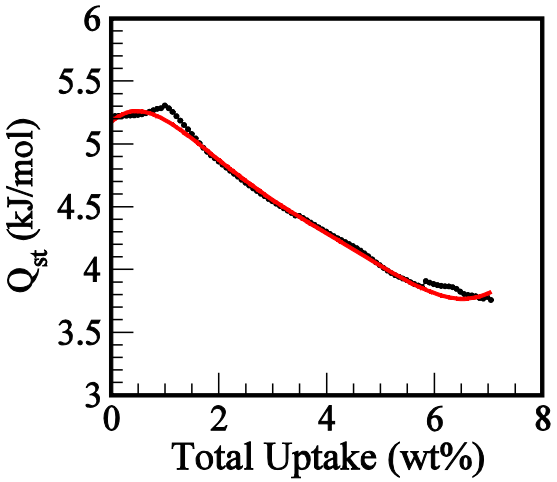


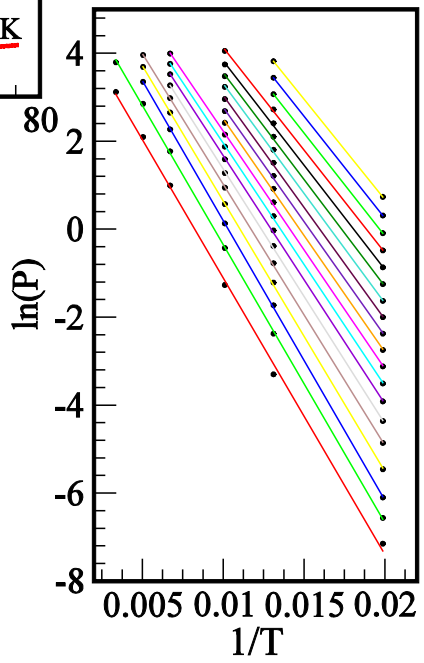
Collaboration with Dr. Taner Yildirim (NIST)

High Pressure Data for PCN-305



a_i	b_i
-622.36	6.1468
-47.947	0.25431
64.224	-0.044604
-20.764	-0.031678
2.7254	0.01643
-0.020391	-0.0024516
-0.024328	9.4172e-05
0.0013794	4.8235e-06

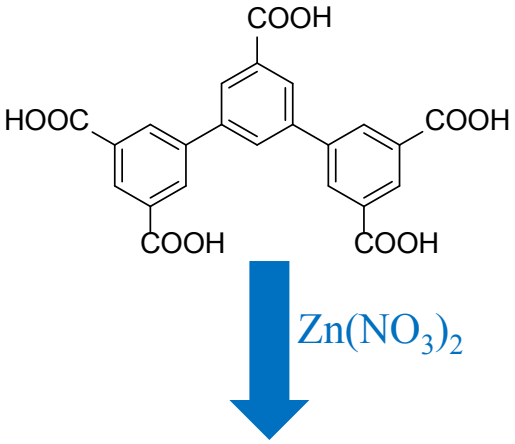


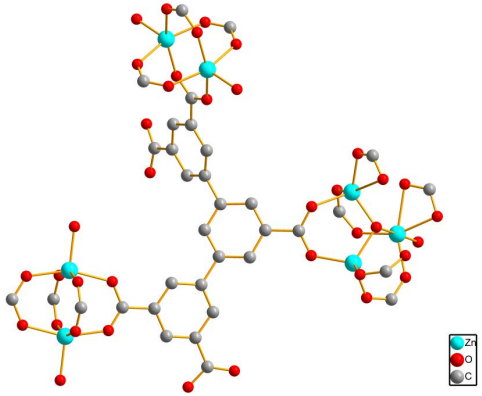


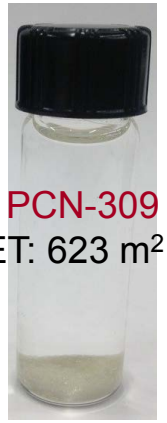
On the left, we show the isotherm data and the corresponding virial-fits. Q_{st} is around 5.2 kJ/mol initially and then start to decrease down to 4 kJ/mol. These numbers are typical for copper-paddle wheel MOFs. **The initial flat Qst is a sign that the main adsorption sites are copper sites!**

Collaboration with Dr. Taner Yildirim (NIST)

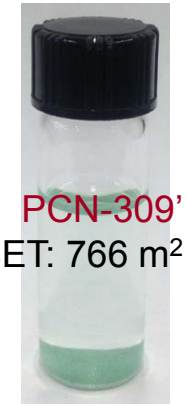
Improved hydrogen uptake through metathesis





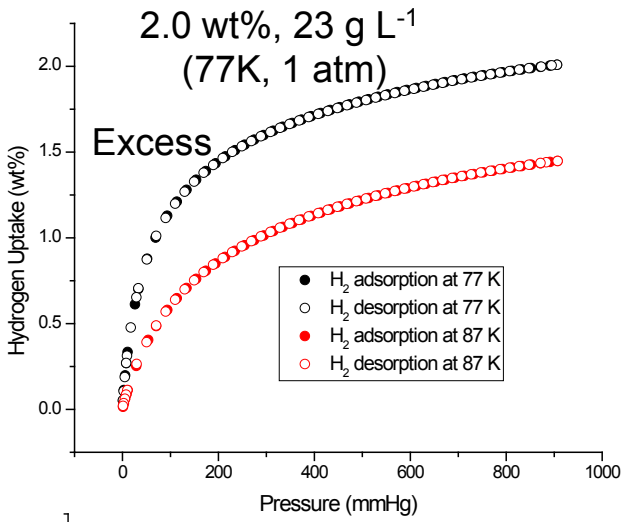


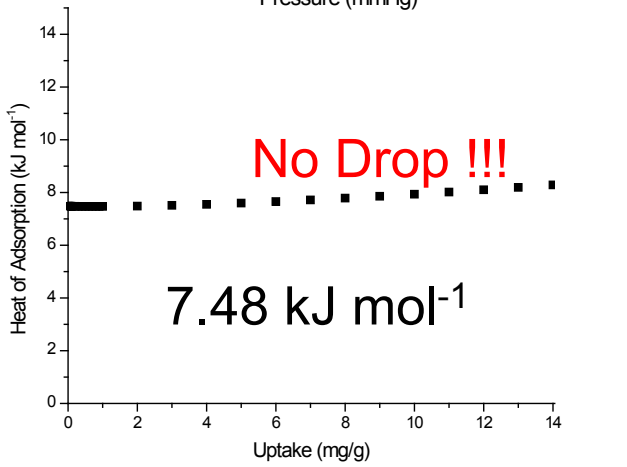
PCN-309
(BET: 623 m^2 g^{-1})



PCN-309'
(BET: 766 m^2 g^{-1})

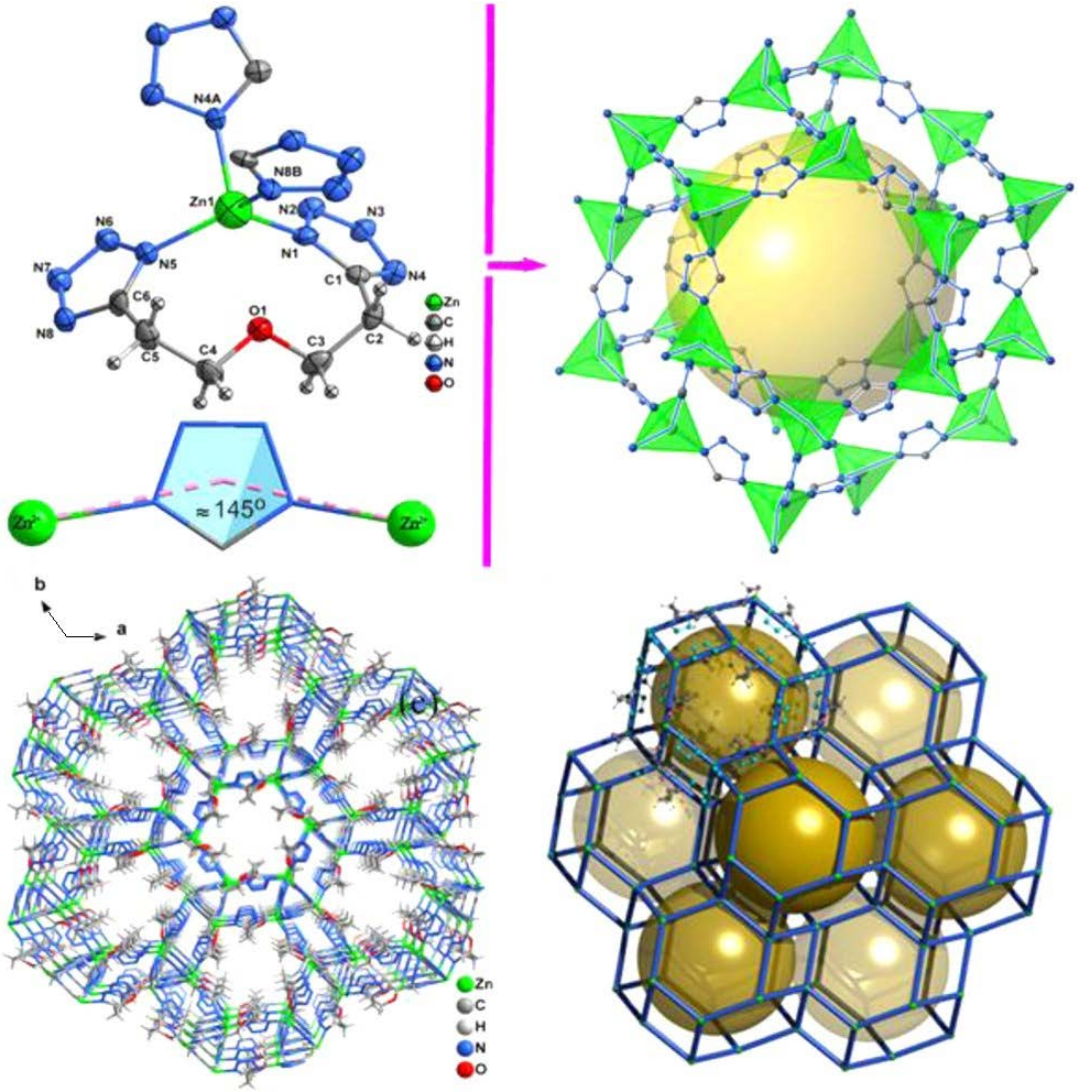
Soaked in $Cu(NO_3)_2$/DMF

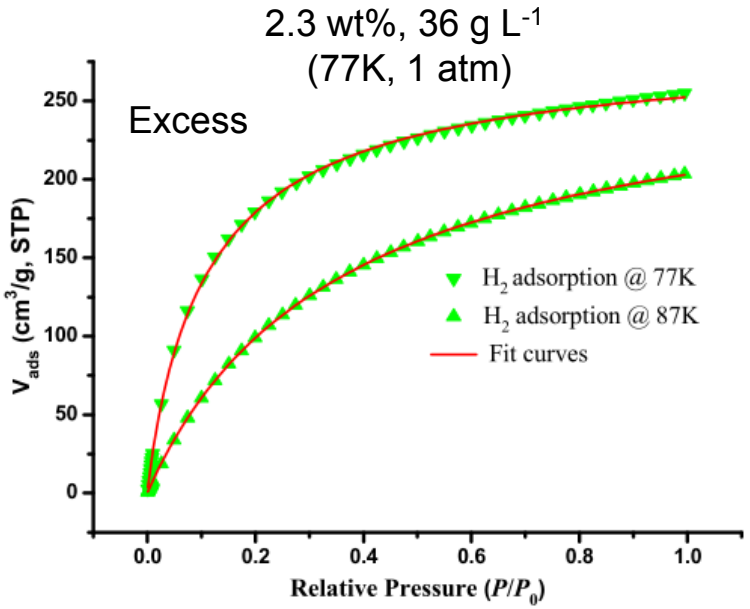




- Could be synergetic effect of unsaturated Cu, Zn sites
- Computer simulation is underway

A Zeolite-*like* Tetrazole Framework with 24-Nuclear Zinc-Cages





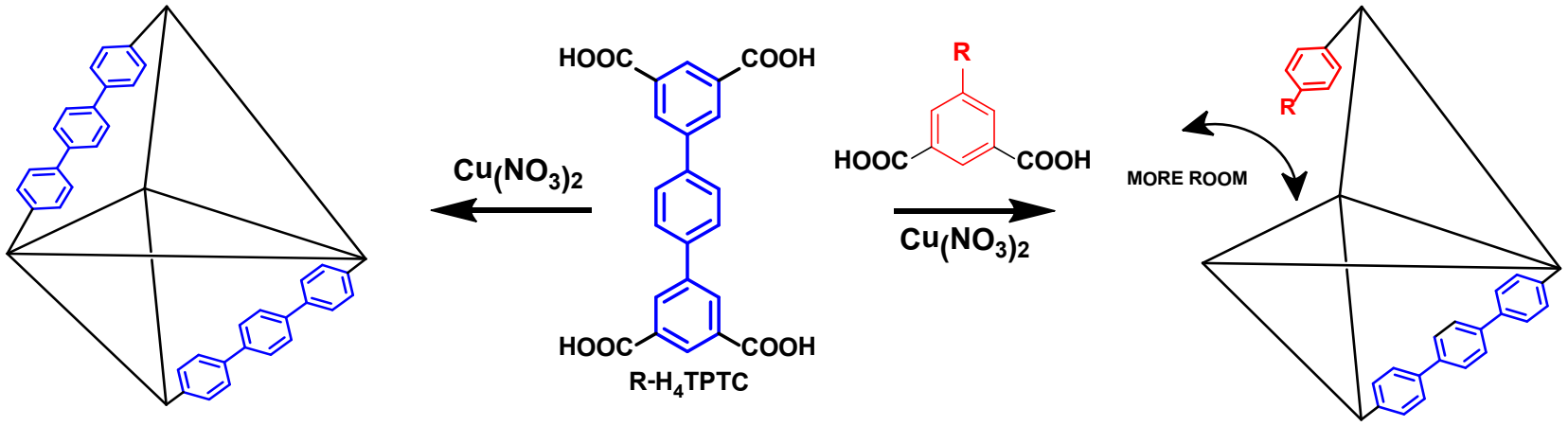
Q_{st} = 8.1 kJ mol^{-1}

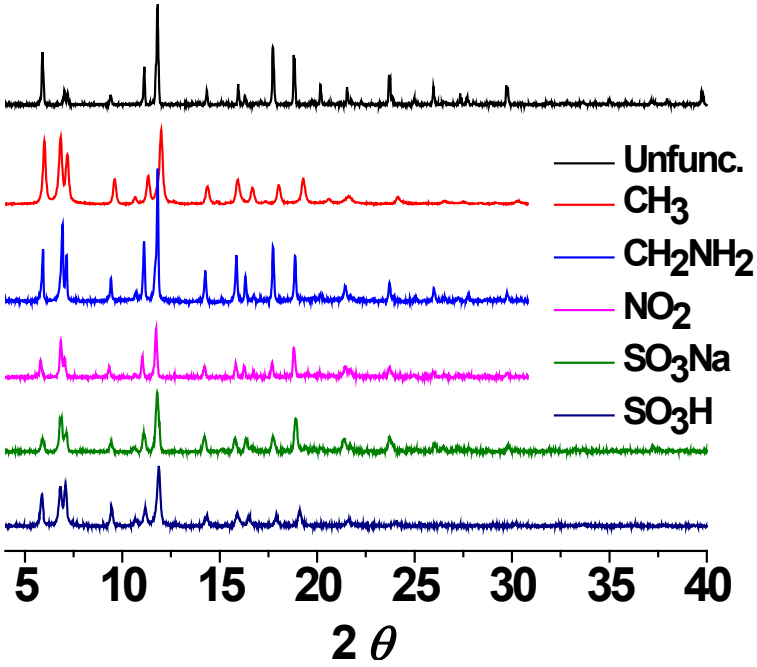
BET: 1151 m^2 g^{-1}

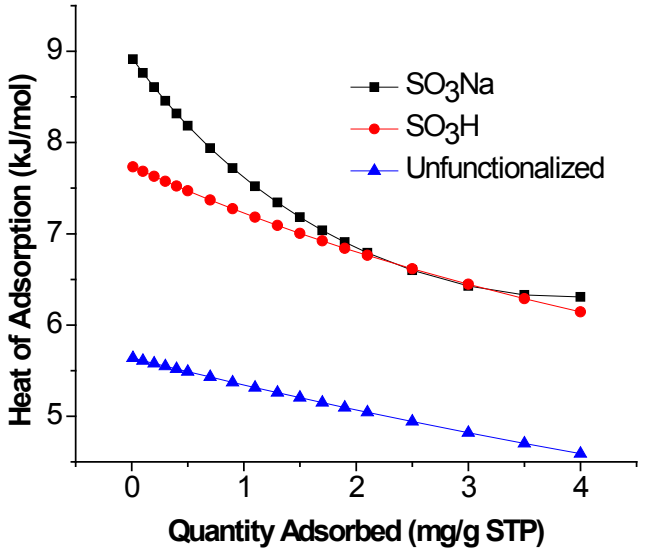
Pore size is ~ 5.5 Å

Density: 1.507 g/cm^3

Metal-Ligand-Fragment Coassembly (PCN-25)

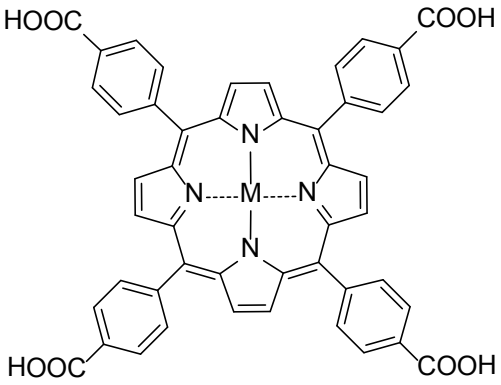




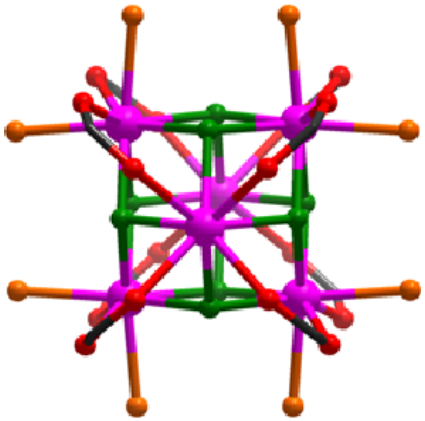


Other metal ions will be introduced

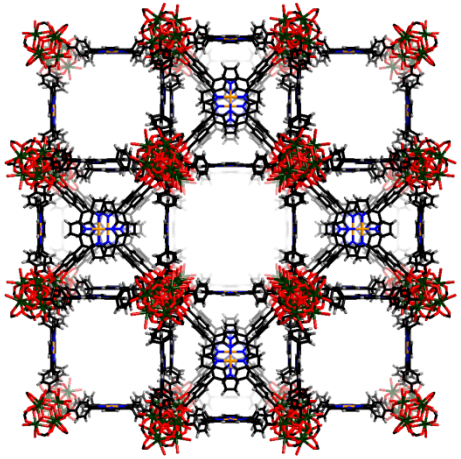
Ultra-stable Metalloporphyrin-Zirconium MOF (PCN-224)

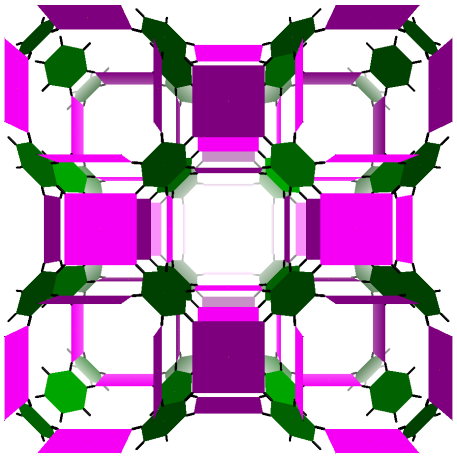


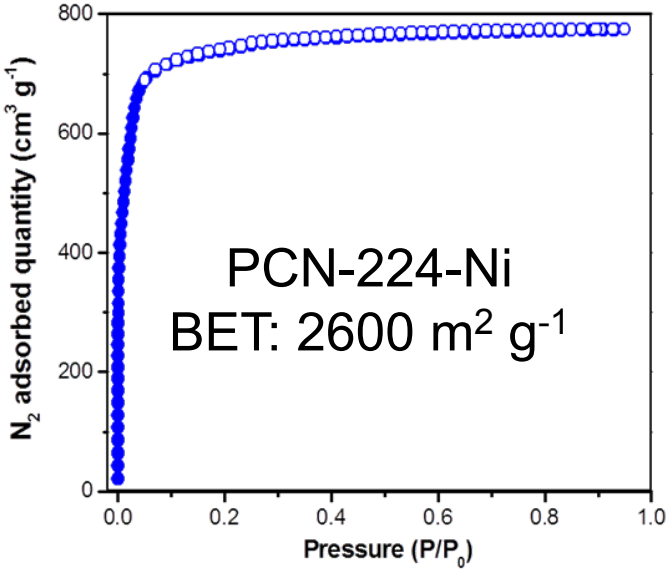
Metalloporphyrin ligand

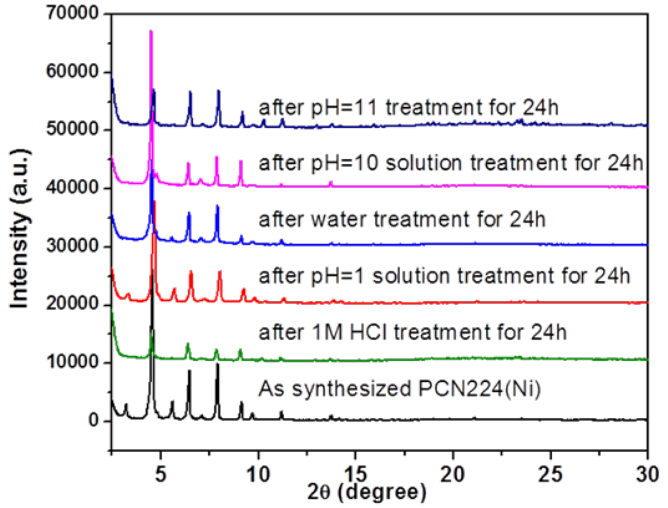


Zr_6 cluster



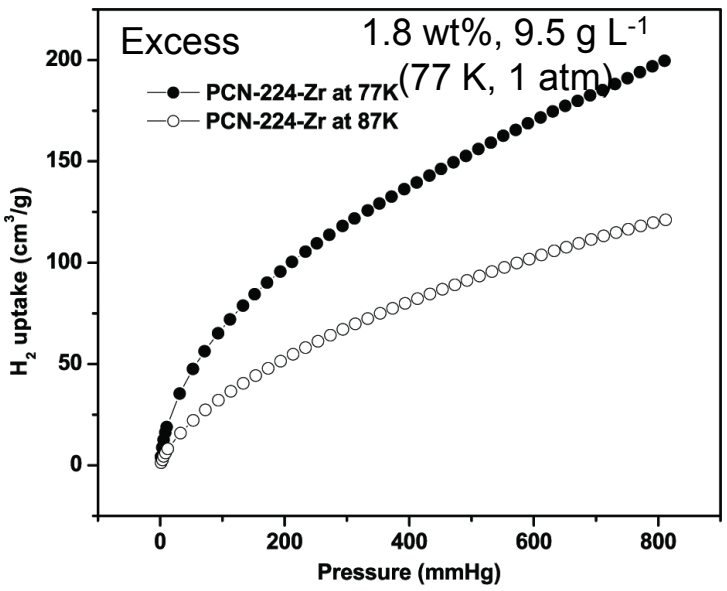


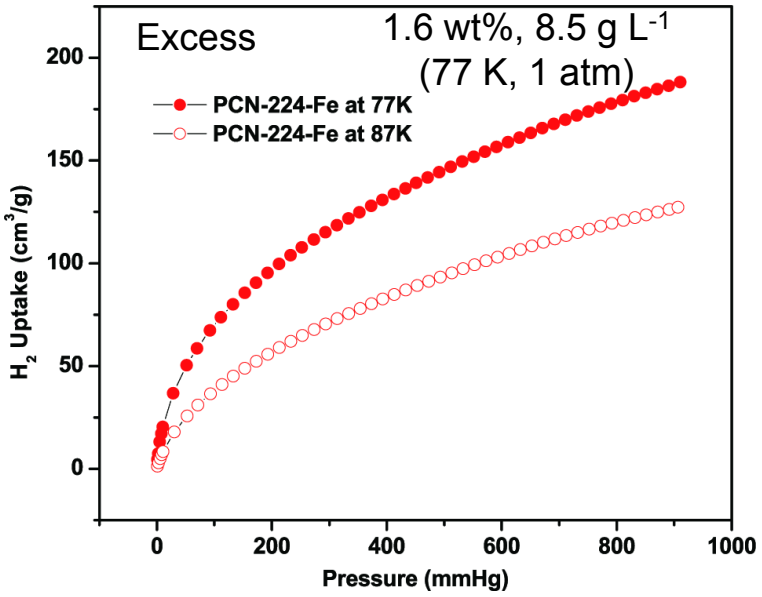


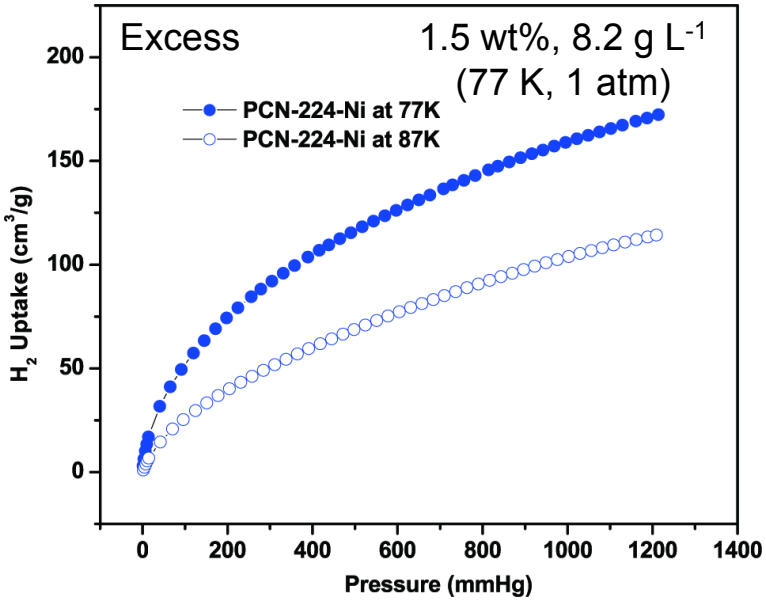


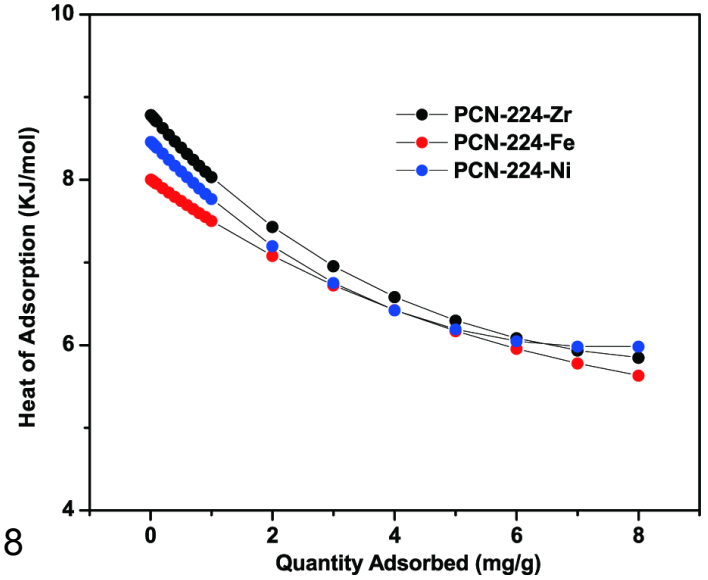
!!! A very promising system to show evidence of multiple H_2's bonded to a single open metal site

Ultra-stable Metalloporphyrin-Zirconium MOF (PCN-224)

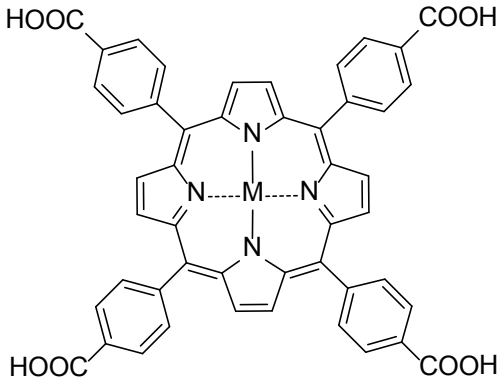




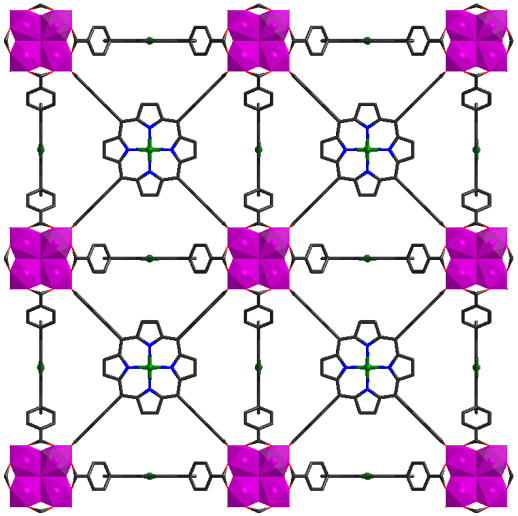


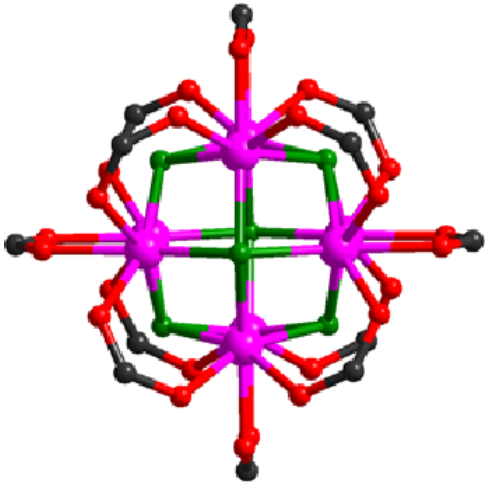


Ultra-stable Metalloporphyrin-Zirconium MOF (PCN-221)



Metalloporphyrin ligand

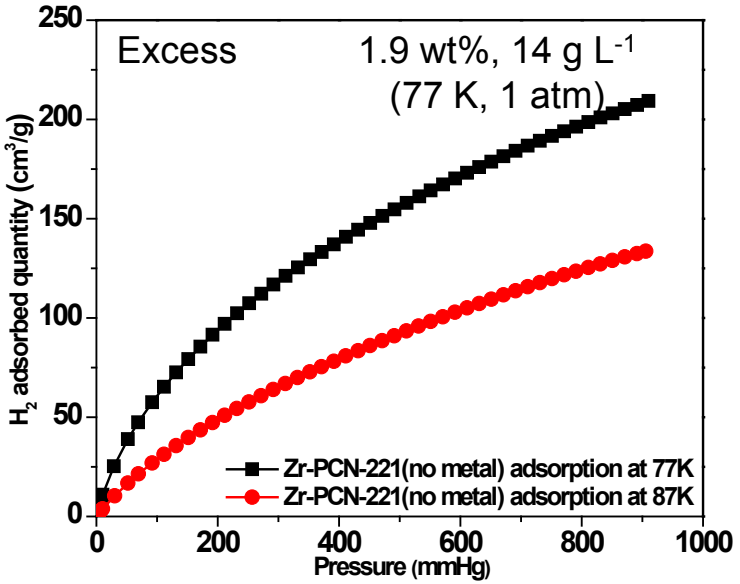


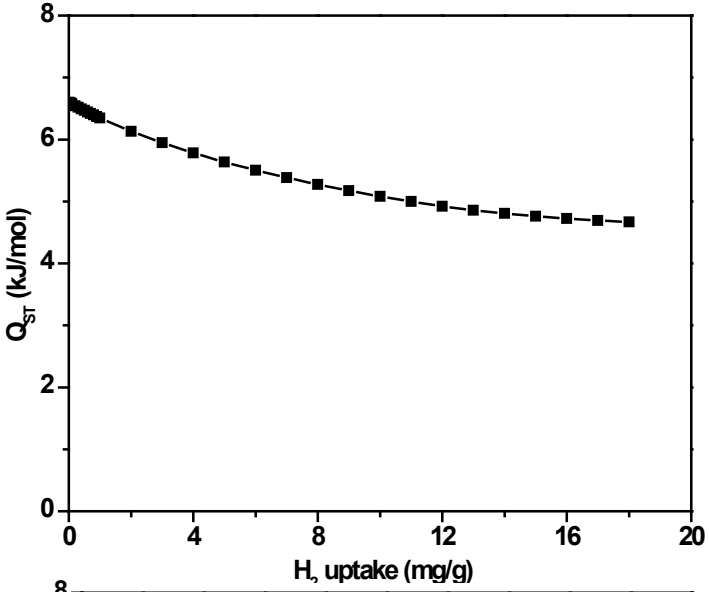


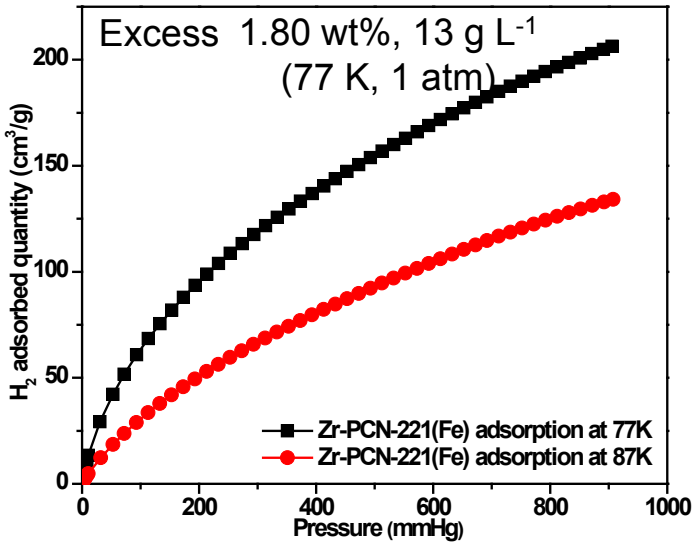
Zr_8O_6 inner core

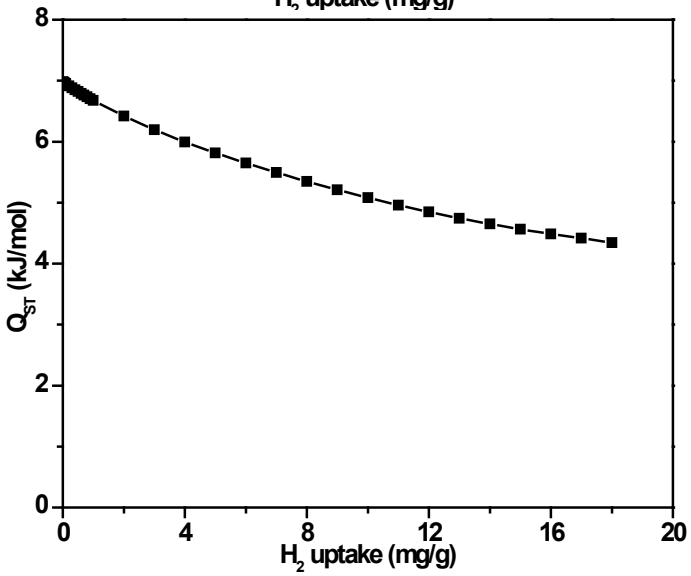
MOFs	BET surface area (m^2 g^{-1})	Langmuir surface area (m^2 g^{-1})	N_2 uptake (cm^3 g^{-1})	Pore volume (m^3 g^{-1})
Zr-PCN-221(no metal)	1936	2660	627	0.76
Zr-PCN-221(Fe)	1549	2149	507	0.61

Ultra-stable Metalloporphyrin-Zirconium MOF (PCN-221)

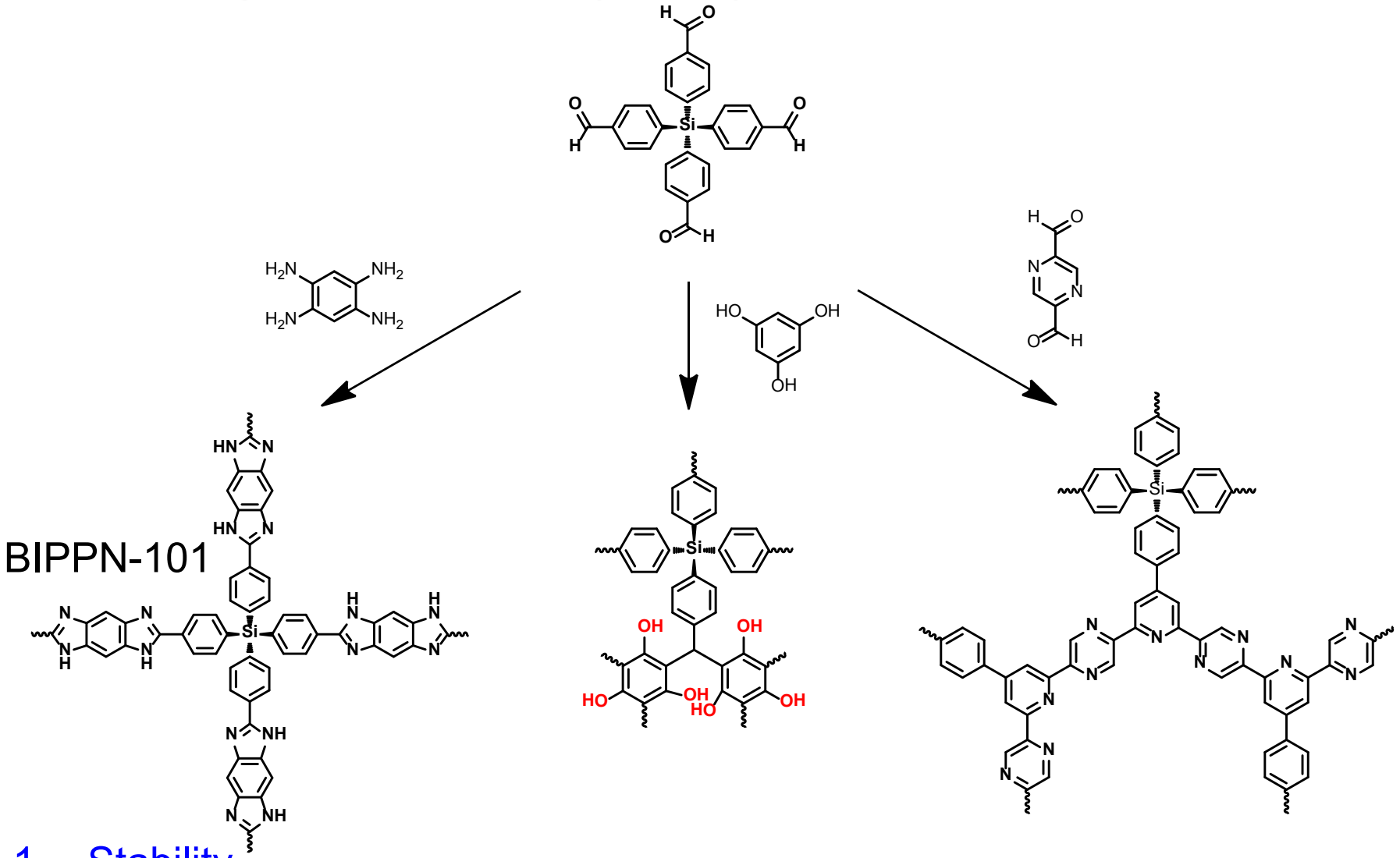








Porous Polymer Networks (PPNs) with Anchors for Metal Insertion



1. Stability
2. Easy synthesis
3. Anchors for metal insertion

Collaborations

Partners

- Dept. of Chem. Eng., TAMU, Theoretical Calculation
- KIT, Germany, Ligand Synthesis
- SWRI, Gas adsorption measurements
- LLNL, Critical Point Activation
- ANL, APS, Crystal Structure Determination
- GM, High Pressure Gas Adsorption Measurements
- LBNL, Structure and Gas Adsorption Simulations
- RTI, Material Scale-up

Technology Transfer

- Working with industrial partners closely
- Ready to work with the Engineering CoE
- Working with a start-up company

Accomplishments

Demonstrated through experiments that :

- A series of MOFs (PCN-30X) with new topology have been synthesized through Ligand Truncation Strategy; the ligands for these MOFs are relatively easy to synthesize, and the H_2 uptakes (77 K and 1 atm) of there MOFs are among the highest (2.2 ~ 2.7 wt%, 17 ~ 21 g L^{-1}). PCN-305 exhibits very high H_2 total storage capacity (7.0 wt%, 54 g/L at 60 bar and 77 K) compared to other MOFs with similar surface area possibly due to the open metal site and suitable pore size.

- A MOF (PCN-309) with free carboxylic acid has been designed and synthesized; the H_2 uptake can be improved by metathesis (Zn to Cu), more importantly, the heat of adsorption (7.5 kJ mol^{-1}) is constant with the increasing of H_2 adsorption.

- Metal-Ligand-Fragment Coassembly Strategy has been successfully implemented to introduce functionalities, heat of adsorption can be much improved.

- Highly stable Zr-porphyrin-MOFs has been designed and synthesized and initial metal-insertion study shows these materials exhibit high surface area and high heat of adsorption

- Three strategies have been successfully applied to synthesize PPNs with anchors for metal insertion

Future Work

- Incorporate different metal cations (such as Fe^{2+}) into porphyrin center of Zr-MOF. Perform elastic diffuse neutron-scattering studies to demonstrate more than one H_2 per open metal site in MOF.
- Measure H_2 storage capacity at high pressure for obtained high-surface-area and metal-incorporated materials.
- Closer investigation into PCN-309 for its constant heat of adsorption for H_2, theoretical calculation to verify the result.
- Continue to implement Ligand Truncation Strategy and Metal-Ligand-Fragment Coassembly Strategy with elongated ligands with different functionalities.
- Optimize the procedure for PPNs for higher surface area, then incorporate multivalent metals, such as V^{3+}, Fe^{3+},Ti^{3+}, etc.

Summary Table (New Materials)

Material	S_{BET} (m^2/g)	ΔH_{ads} (kJ/mol)	V_{ads} at 77 K and 1 atm (wt%)	V_{ads} at 77 K and 1 atm (g L^{-1})	V_{ads} at 77 K and 60 bar (wt%)	V_{ads} at 77 K and 60 bar (g L^{-1})	Slide
PCN-305, -306, -307, -308	1651, 1927, 1377, 1419	6.5, 6.4, 6.2, 6.5	2.2, 2.5, 2.6, 2.7	17, 19, 20, 21	7.0	54	9,10,11
PCN-309’	766	7.5	2.0	23			12
Zeolite-*like* Tetrazole MOF	1151	8.1	2.3	36			13
PCN-224-Zr, -224-Fe, -224-Ni	2200 2300 2600	8.7, 8.0, 8.5	1.8, 1.6, 1.6	9.5, 8.5, 8.2			15,16
PCN-221, -221-Fe	1936, 1549	6.6, 7.0	1.9, 1.8	14, 13			17,18
PCN-25-SO_3H, -SO_3Na	940, 1798	7.8, 9.0	0.89, 0.61				14
BIPPN-101	1096	7.8	1.8				19