

# **A Biomimetic Approach to Metal-Organic Frameworks with High H<sub>2</sub> Uptake**

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# Overview

## *Timeline*

- Project start date: 7/1/2007
- Project end date: 6/30/2012
- Percent complete: 85%

## *Barriers*

- H<sub>2</sub> 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,  $\Delta H$  needs to be in the range of 15 to 30 kJ/mol
- Materials with high surface areas generally have low volumetric uptake

## *Budget*

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

## *Partners*

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

# Ultimate Goal

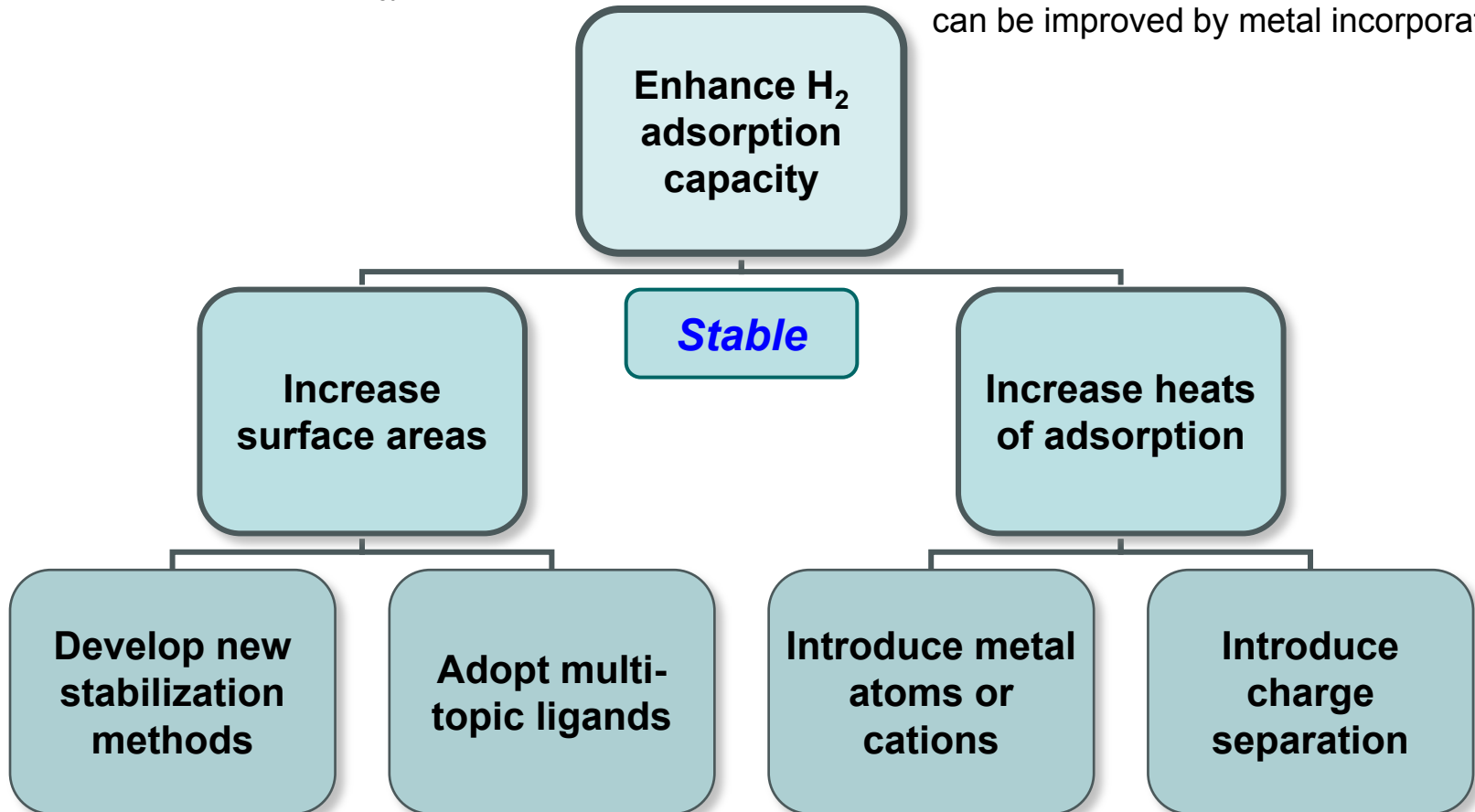
## (Technical Challenges)

### Dihydrogen affinity

- $15 \text{ kJ/mol} < Q_{\text{st}} < 30 \text{ kJ/mol}$  for ambient temperature application
- For most MOFs,  $Q_{\text{st}} < 10 \text{ kJ/mol}$

### Surface area

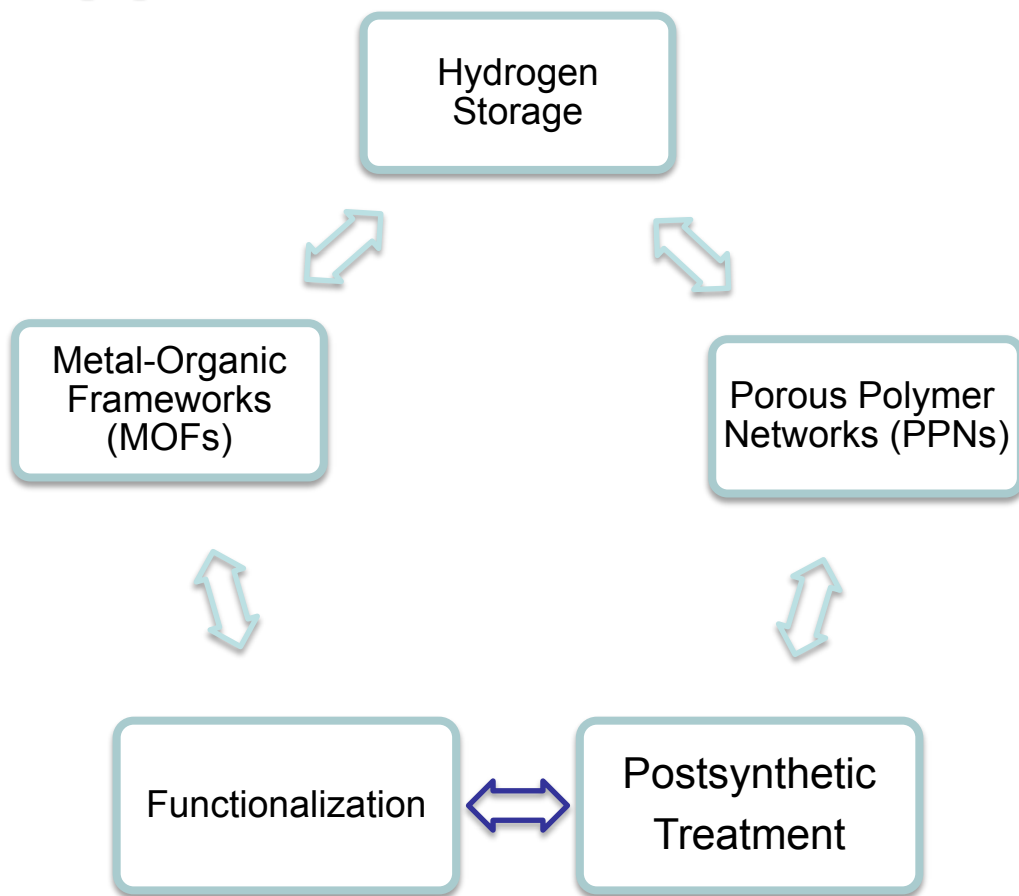
- High surface area is beneficial for gravimetric  $\text{H}_2$  uptake
- Volumetric uptake and heat adsorption can be improved by metal incorporation



# Approach/Milestone

Month/Year	Approach and Milestone
Nov-08	Milestone: Optimize the <b>alignment of the coordinatively unsaturated metal centers</b> of MOFs and construct a new MOF, PCN-12, which exhibits an exceptionally high H <sub>2</sub> uptake of 3.0 wt% (24.6 mg/cm <sup>3</sup> ) at 760 Torr and 77 K. The H <sub>2</sub> -adsorption heat of <b>PCN-12</b> can reach as high as <b>12.5 kJ/mol</b> at low coverage. (Status – 100% complete)
Nov-09	Milestone: Construct the <b>catenation</b> isomer pairs of PCN-6 and PCN-6'. H <sub>2</sub> 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 <b>PCN-6 is 6.7 wt % at 77 K/50 bar</b> . 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 <b>volumetric hydrogen uptake</b> and <b>strengthens the MOF-H<sub>2</sub> interaction</b> . (Status – 100% complete)
Nov-10	Milestone: Construct <b>MOFs containing mesocavities with microwindows</b> 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 <b>porous polymer networks (PPNs)</b> for hydrogen storage with high surface area, tunable pore size, and flexibility. Determine H <sub>2</sub> adsorption of PPNs with <b>metal incorporation</b> . (Status – 90% complete)
Nov-11	Milestone: Construct <b>PPNs with ultrahigh surface area</b> (finished). Explore the possibility of <b>incorporation of charge and additional light metal ions</b> such as Li <sup>+</sup> , Na <sup>+</sup> or Mg <sup>2+</sup> into PPN-4. The modified PPN-4 should have improved hydrogen affinity and improved volumetric hydrogen uptake due to the increased density. (Status – underway)

# Approach



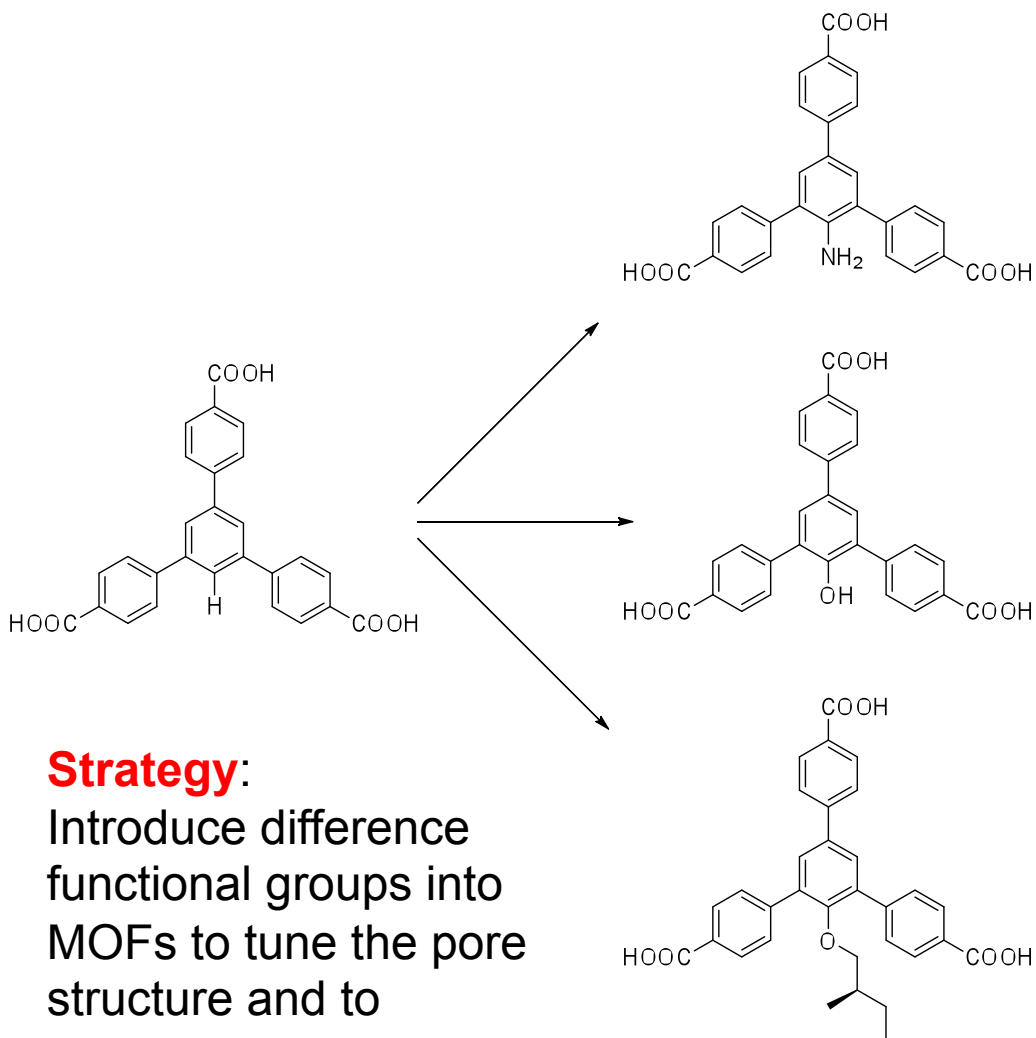
## Enhance H<sub>2</sub> uptake

- Framework functionalization
- Framework postsynthetic modification
- Introduce charge-separation
- Introduce metal ions

# New Achievements

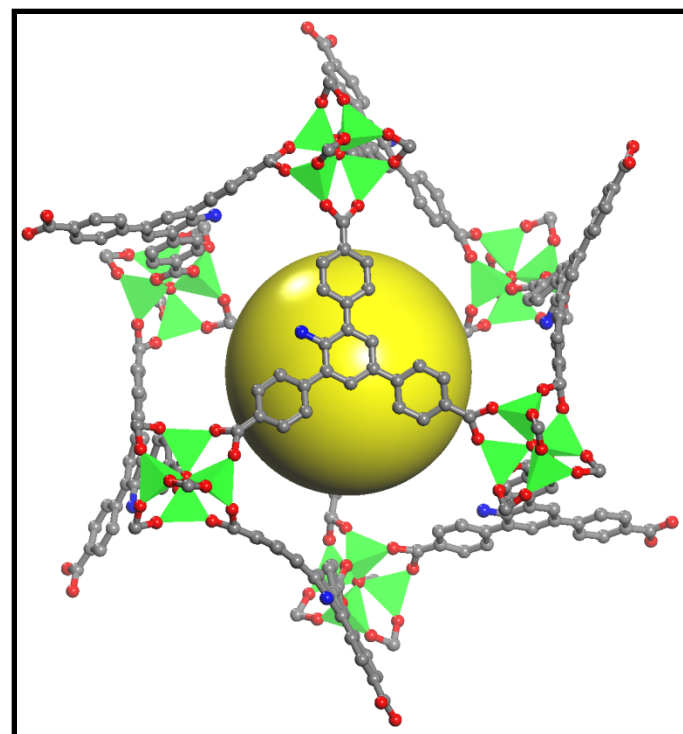
- Air and moisture stable PPNs with ultra-high surface area (BET SA: 6470 m<sup>2</sup>/g, new record)
- Excess gravimetric H<sub>2</sub> uptake of 8.5 wt% (new benchmark validated by SWRI<sup>®</sup>)
- Metal-incorporated PPNs with 8.0 kJ/mol isosteric heats of H<sub>2</sub> adsorption for PPNs
- Introduction of charge-separation into MOFs
- Introduction of different functional groups and large cavities into MOFs for metal-incorporation

# Organic Ligands with functional groups



## Strategy:

Introduce difference functional groups into MOFs to tune the pore structure and to determine the effect on H<sub>2</sub> uptake

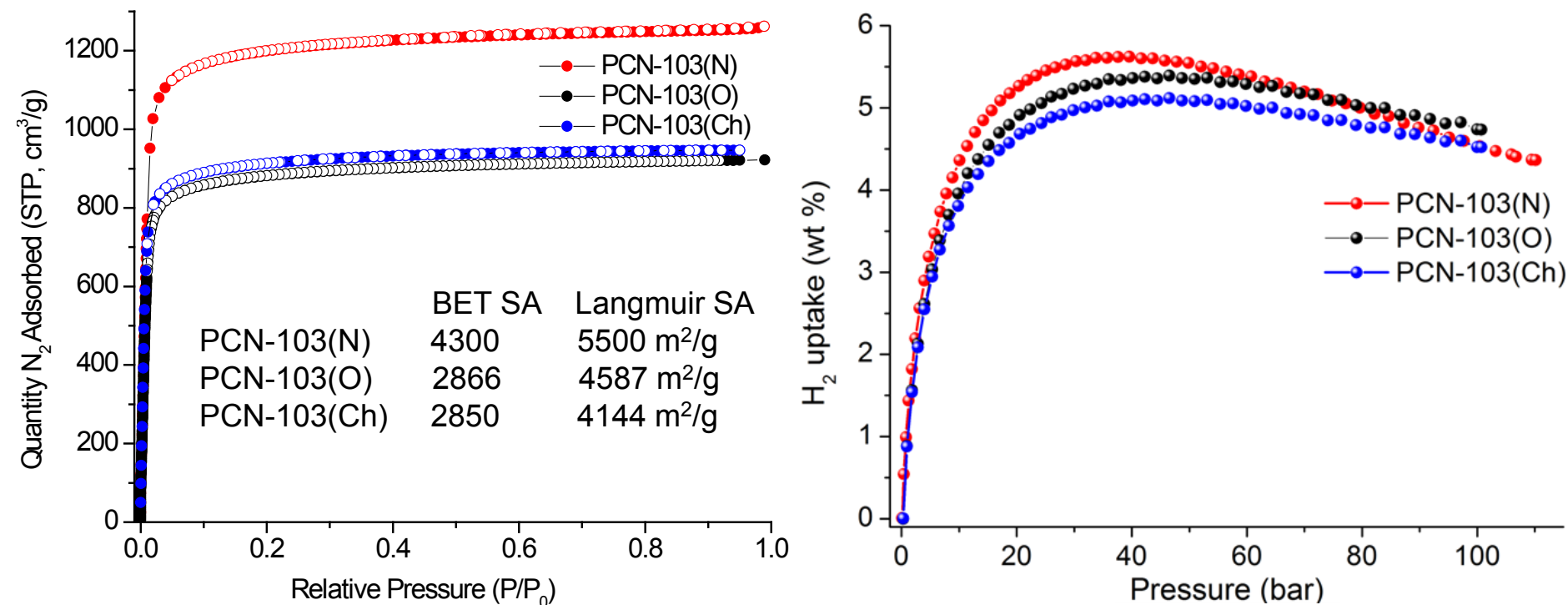


PCN-103(N,O,Ch)

PCN-103x are isostructural with MOF-177

The -NH<sub>2</sub> and -OH groups can be used as anchors for additional metal ions.

# Gas adsorption of PCN-103



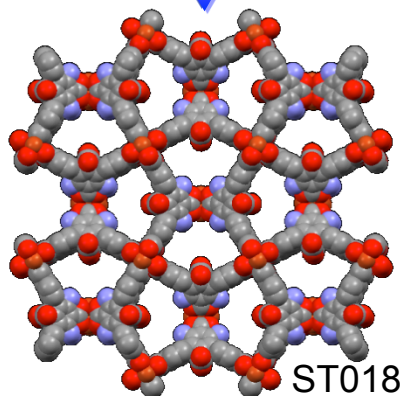
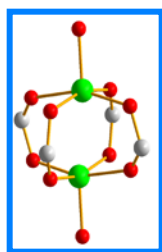
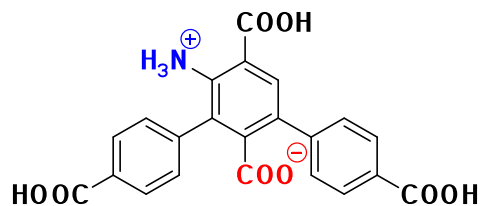
At 77 K, the saturated excess gravimetric  $H_2$  uptake of PCN-103(N) is 5.6 wt % at 40 bar; PCN-103(O) is 5.4 wt % at 45 bar; PCN-103(Ch) is 5.1 wt% at 50 bar. The functional groups exert a weak influence to  $H_2$  uptake.

# Introduce charge-separation into MOF (PCN-35)

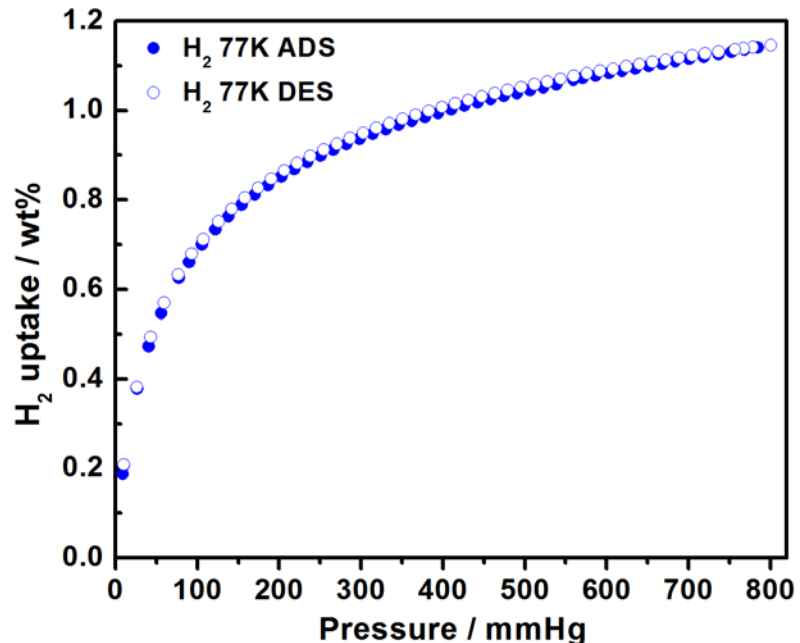
## Rationale:

Charge separation will form an electrostatic field inside of MOFs, which may induce polarization of dihydrogen and enhance the interaction of dihydrogen with MOFs.

Heats of adsorption and High pressure measurements are underway.



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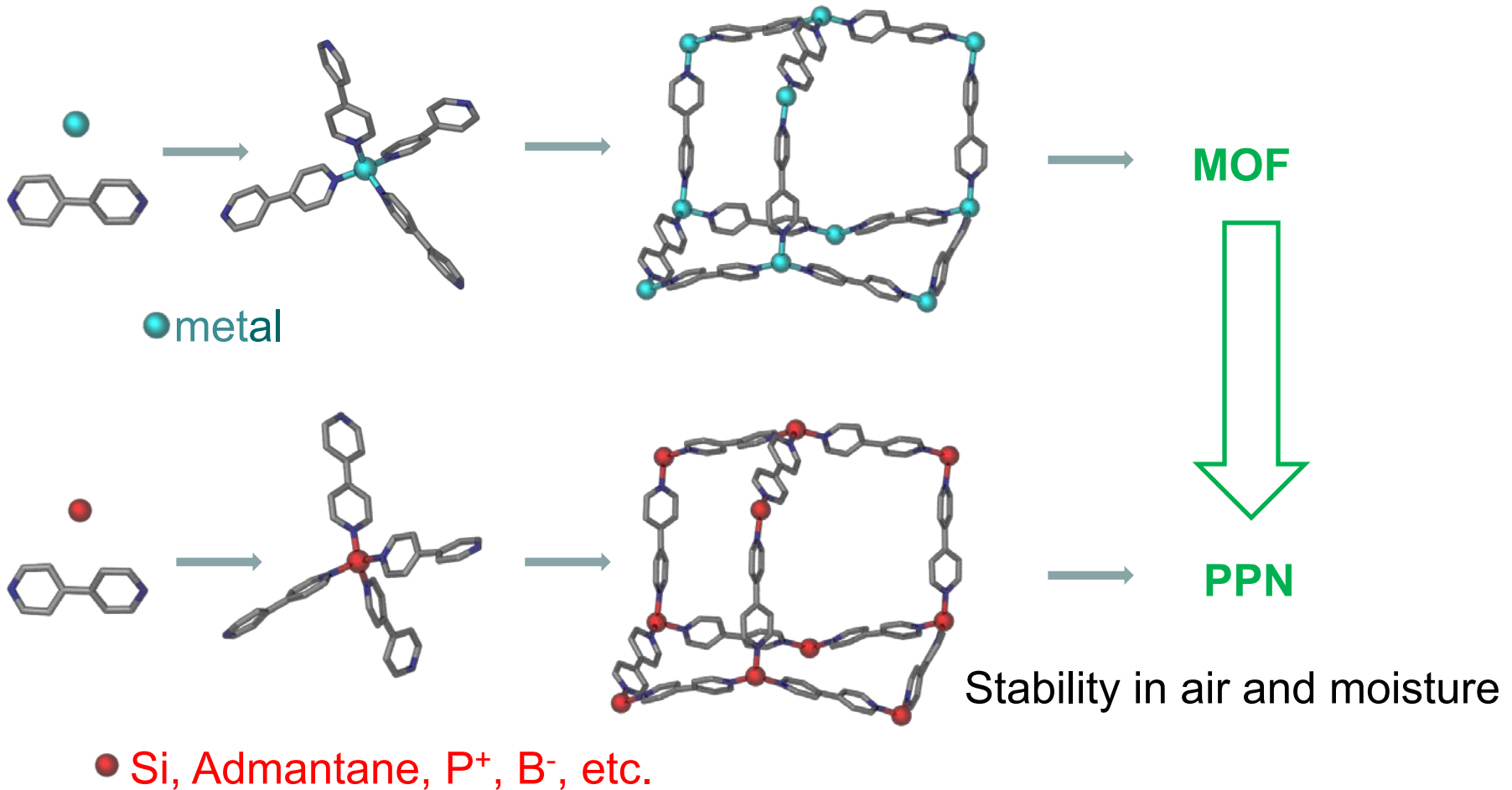


PCN-35 can adsorb 1.1 wt %  $\text{H}_2$  at 77 K and 1 bar.

Collaborator: Theodore F. Baumann  
Lawrence Livermore National Laboratory

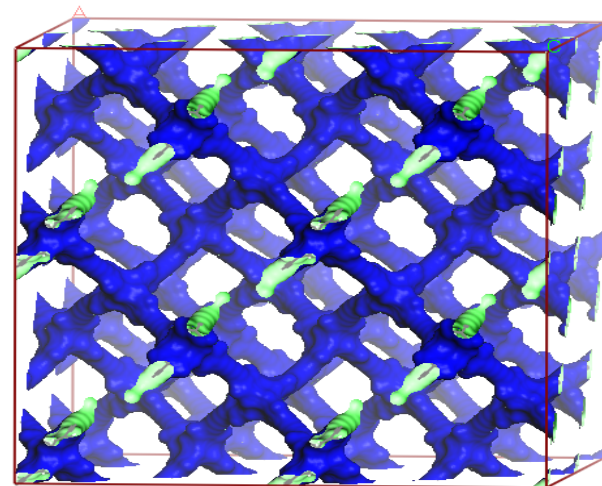
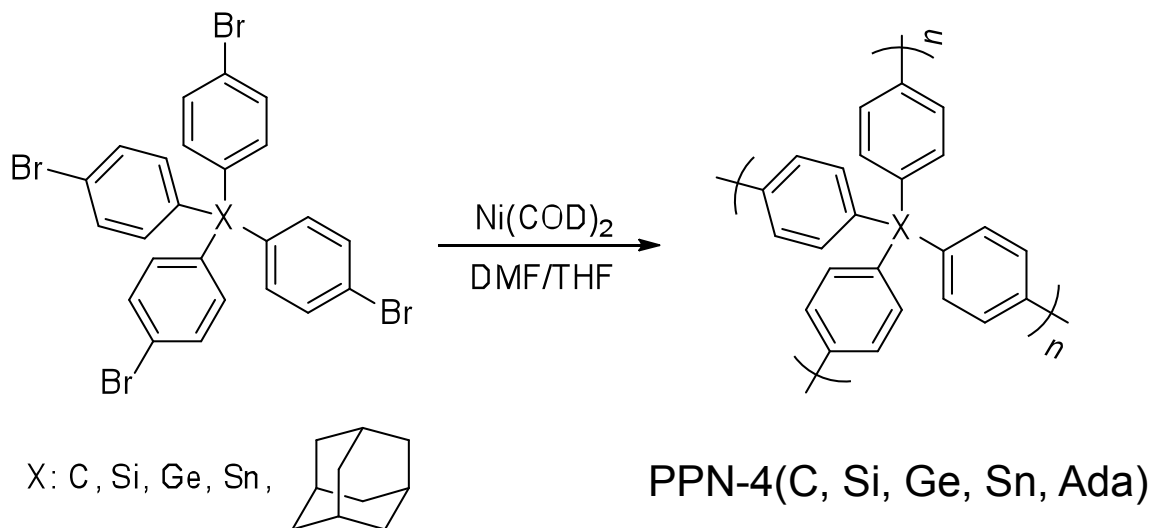


# Porous materials stable in air and moisture for H<sub>2</sub> storage



**Stability** is an important factor for H<sub>2</sub> storage in application.

# Porous Polymer Networks (PPNs) with Ultra-high Surface Area



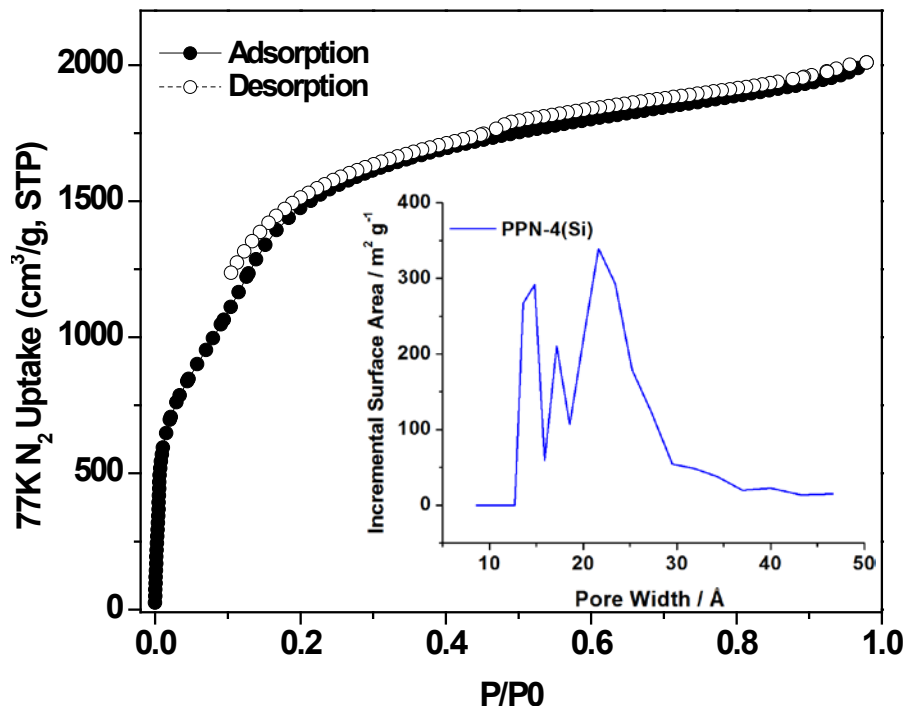
## Diamond-type net

The framework of PPN-4 is constructed and optimized by using the Forcite Plus module in Material Studio.

### Advantages:

- Stability toward air and moisture
- Robust for postsynthetic modification

# Porosity and Stability Tests of PPN-4(Si)



Stability test:

Test condition	Surface area loss (%)
1 H <sub>2</sub> O, 100 °C, 3days	10
2 H <sub>2</sub> O, 60 °C, 3days	12

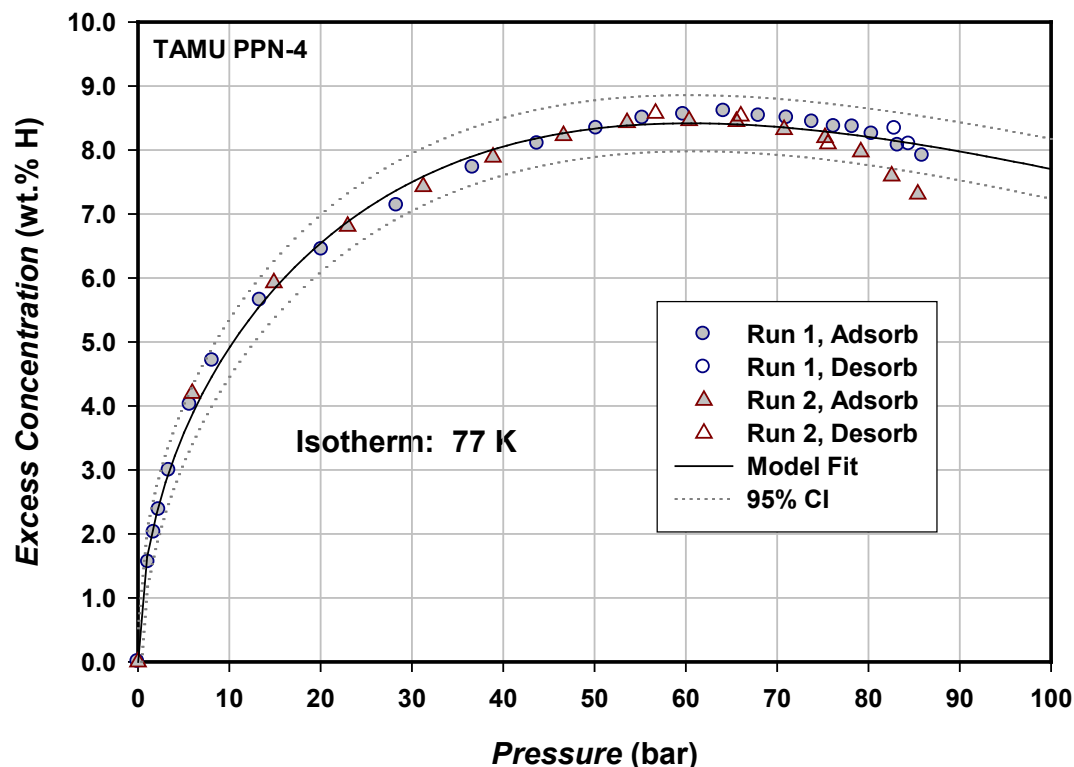
PPN-4(Si) has ultrahigh surface area ( $S_{\text{BET}} = 6470 \text{ m}^2/\text{g}$ ) and is very stable. The N<sub>2</sub> isotherms for PPN-4(Si) has mixed type-I and type-IV sorption behavior, which is typical for materials with both micropores and mesopores. This surface area is one of the highest reported to date for any porous material, which is larger than MOF-210 ( $S_{\text{BET}} = 6240 \text{ m}^2/\text{g}$ ,  $S_{\text{Langmuir}} = 10400 \text{ m}^2/\text{g}$ ) (*Science* **2010**, 329, 424) or NU-100 (or PCN-610,  $S_{\text{BET}} = 6143 \text{ m}^2/\text{g}$ ) (*Nature Chem.*, **2010**, 2, 944.).

# Porosity of PPN-4 (Simulated vs. Experimental)

Material	Density (Cal.) g/cm <sup>3</sup>	Unit Cell	Pore volume cm <sup>3</sup> /g	SA (Cal.) m <sup>2</sup> /g	SA (Exp.) m <sup>2</sup> /g
PPN-4(C)	0.325	I-42d C <sub>100</sub> H <sub>64</sub> a = b = 15.4818 Å c = 26.9655 Å V = 6463.24 Å <sup>3</sup>	2.46	6173	4130
PPN-4(Si)	0.284	I-42d C <sub>96</sub> H <sub>64</sub> Si <sub>4</sub> a = b = 17.0578 Å c = 26.6865 Å V = 7764.97 Å <sup>3</sup>	2.90	6530	6470
PPN-4(Ge)	0.310	I-42d C <sub>96</sub> H <sub>64</sub> Ge <sub>4</sub> a = b = 17.4114 Å c = 26.6453 Å V = 8077.68 Å <sup>3</sup>	2.67	5881	4230
PPN-4(Sn)*	0.313	I-42d C <sub>96</sub> H <sub>64</sub> Sn <sub>4</sub> a = b = 18.3602 Å c = 26.5982 Å V = 8966.21 Å <sup>3</sup>	2.69	5557	N.A.
PPN-4(ADA)	0.196	I-42d C <sub>136</sub> H <sub>112</sub> a = b = 21.5513 Å c = 31.8504 Å V = 14793.2 Å <sup>3</sup>	4.48	6940	3000

\* Except PPN-4(Sn), all the PPN materials have been synthesized.

# SWRI<sup>®</sup> Hydrogen adsorption data for PPN-4(Si)

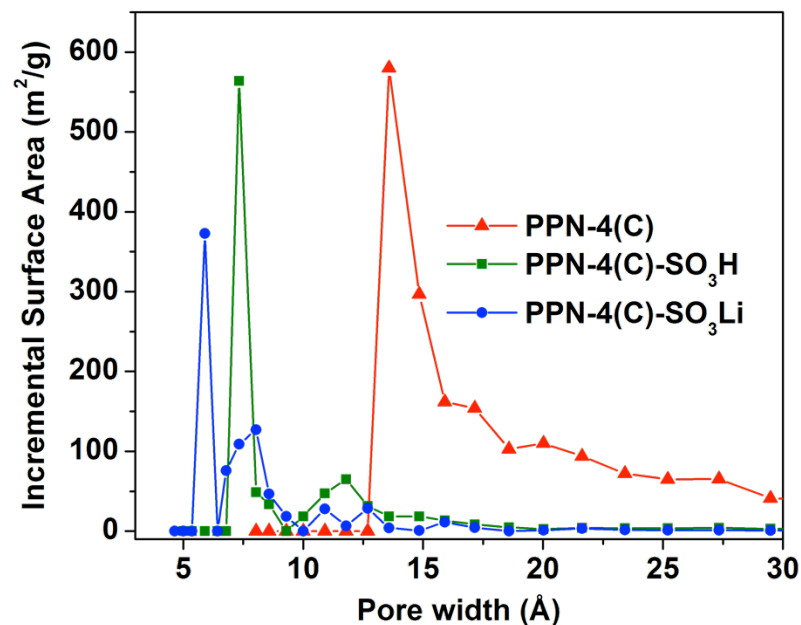
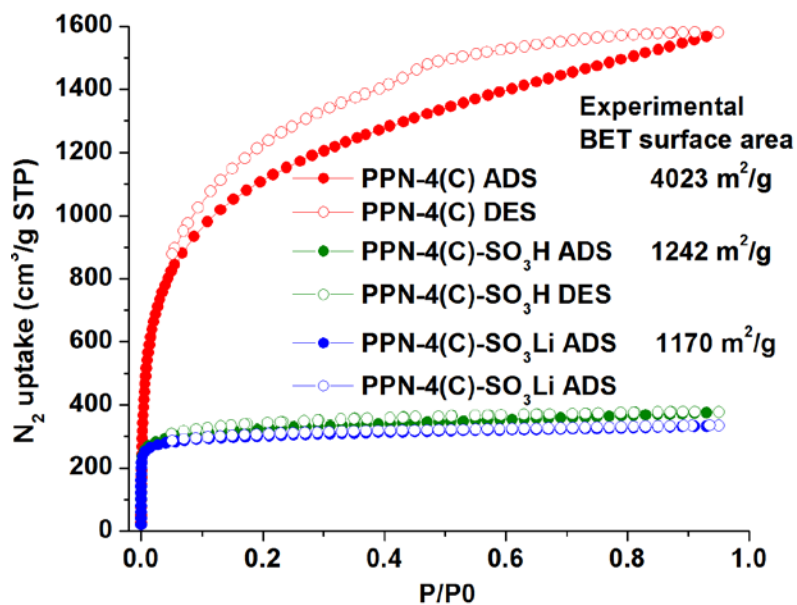
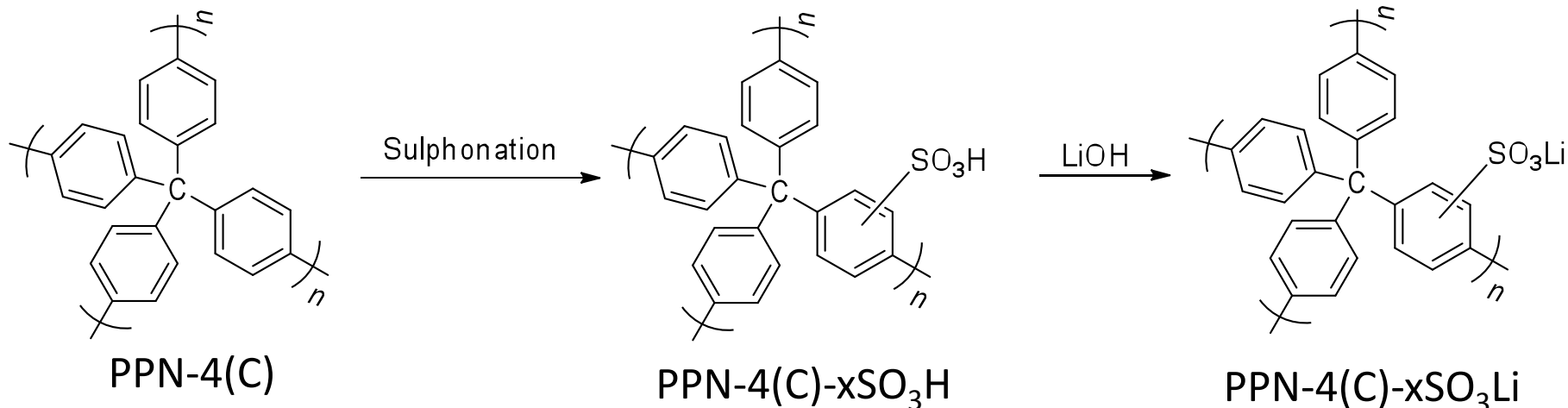


➤ At 77 K, the maximum Gibbs-excess concentration was 8.5 wt.% at 60.4 bar, higher than that of MOF-177.

➤ Compressed PPN-4(Si) kept its surface area and gravimetric uptake. The volumetric uptake doubles when volume is reduced to a half.

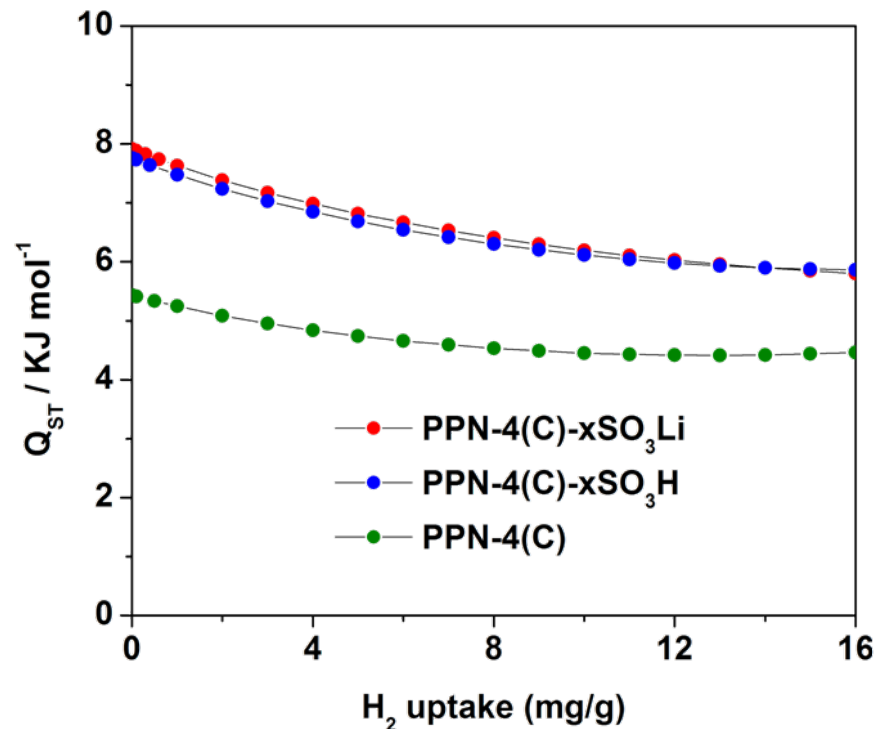
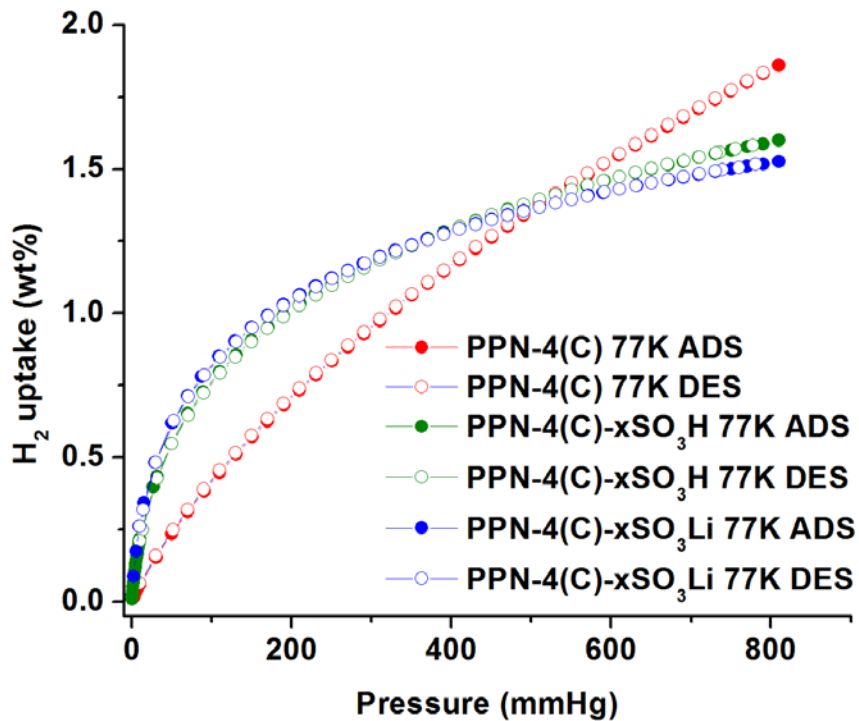
Collaborator: Mike Miller (SWRI<sup>®</sup>)

# Functionalized PPNs for H<sub>2</sub> Adsorption



PPN-4(C) is the same type of material as PPN-4(Si). PPN-4(C) can be postsynthetic modified and metal Li<sup>+</sup> incorporation has been performed. Though the experimental BET surface area (4023 m<sup>2</sup>/g) decreased, the H<sub>2</sub> isosteric heat of adsorption increased.

# Functionalized PPNs for H<sub>2</sub> Adsorption

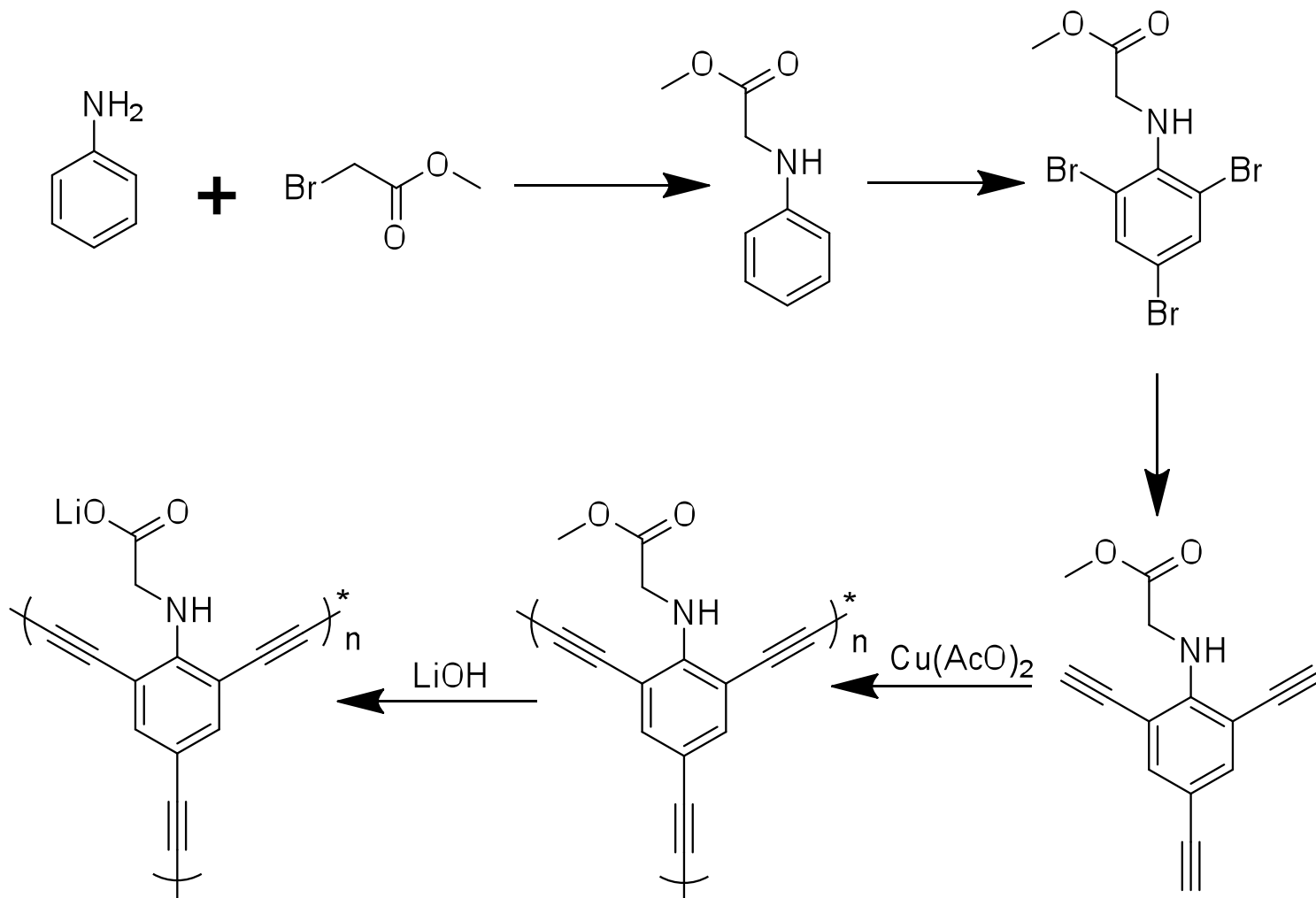


Introduction of H<sup>+</sup> and Li<sup>+</sup> enhance the interaction of PPNs with H<sub>2</sub>

Other metals will be introduced.

Isosteric heats of adsorption obtained from isotherms at 77 and 87 K. H<sub>2</sub> heat of adsorption has improved by 47% upon postdynthetic modification.

# Functionalization of PPN-7 for H<sub>2</sub> Adsorption

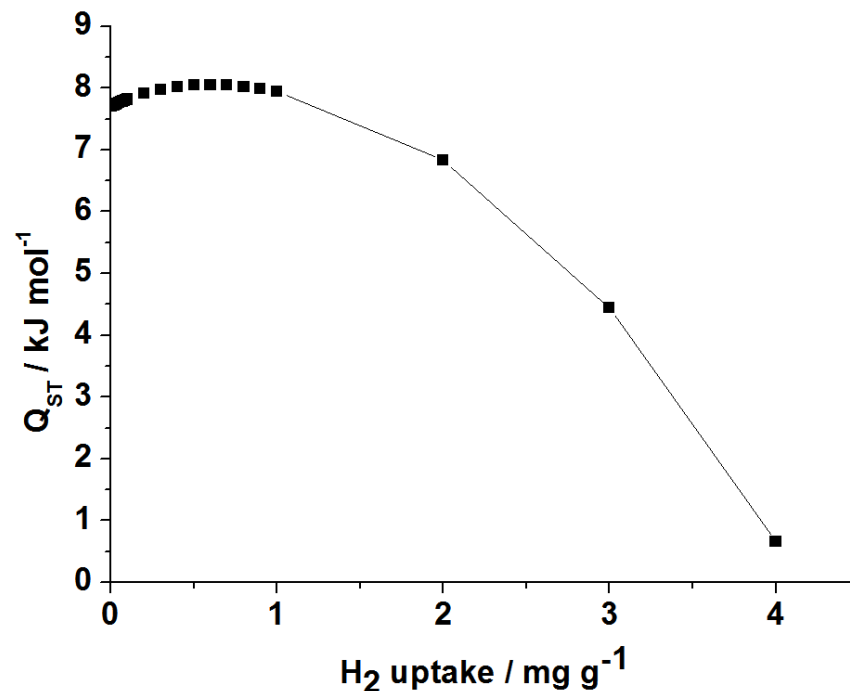
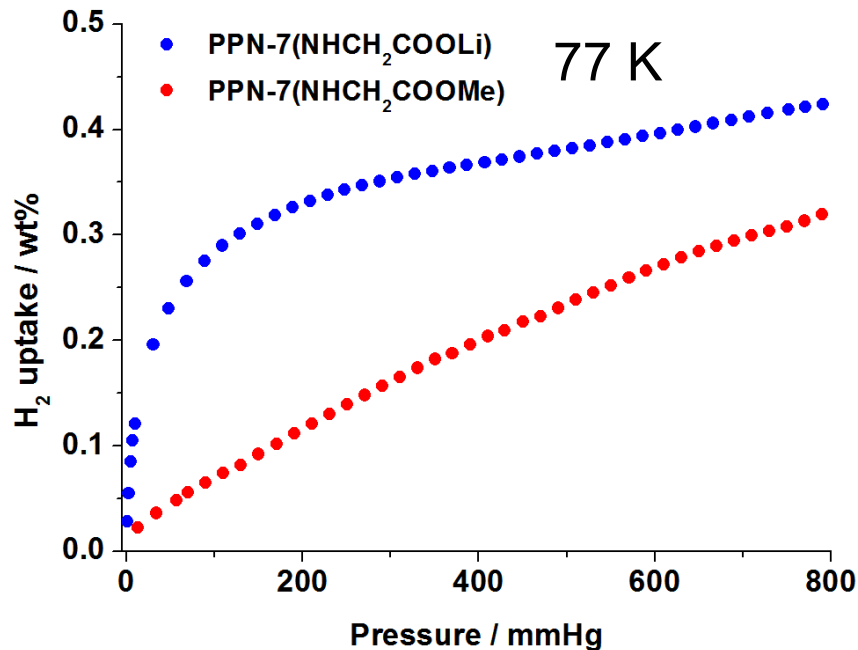


**PPN-7(NHCH<sub>2</sub>COOLi)** **PPN-7(NHCH<sub>2</sub>COOMe)**

**Strategy:** Direct introduction of metal ions in PPNs



# Functionalized PPNs for H<sub>2</sub> Adsorption

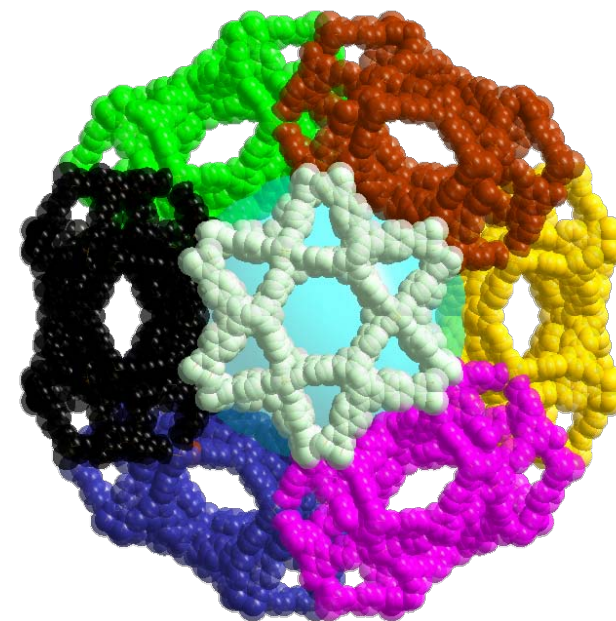
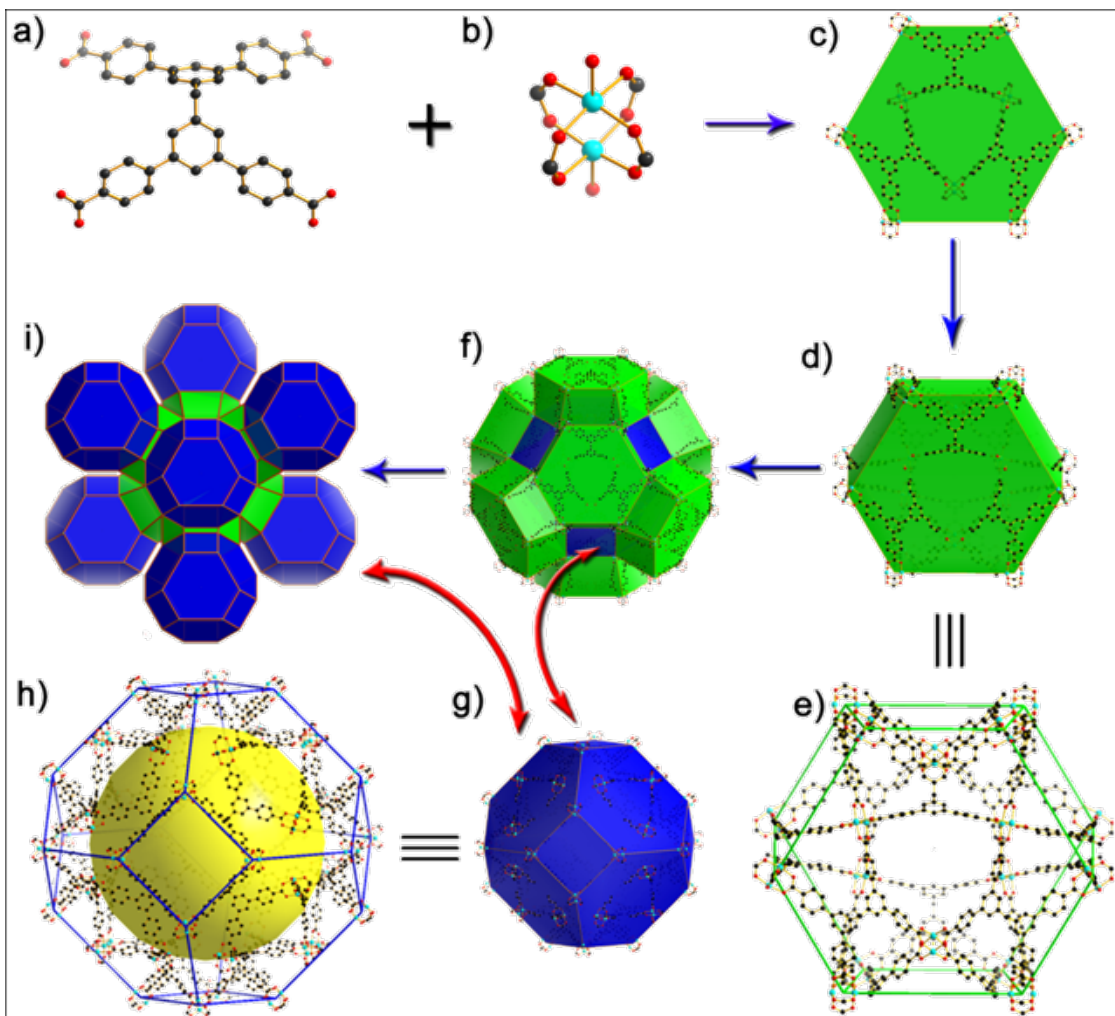


The incorporation of H<sup>+</sup> and Li<sup>+</sup> enhanced H<sub>2</sub> uptake and the interaction of PPNs with H<sub>2</sub>

Isosteric heats of adsorption obtained from isotherms at 77 and 87 K.

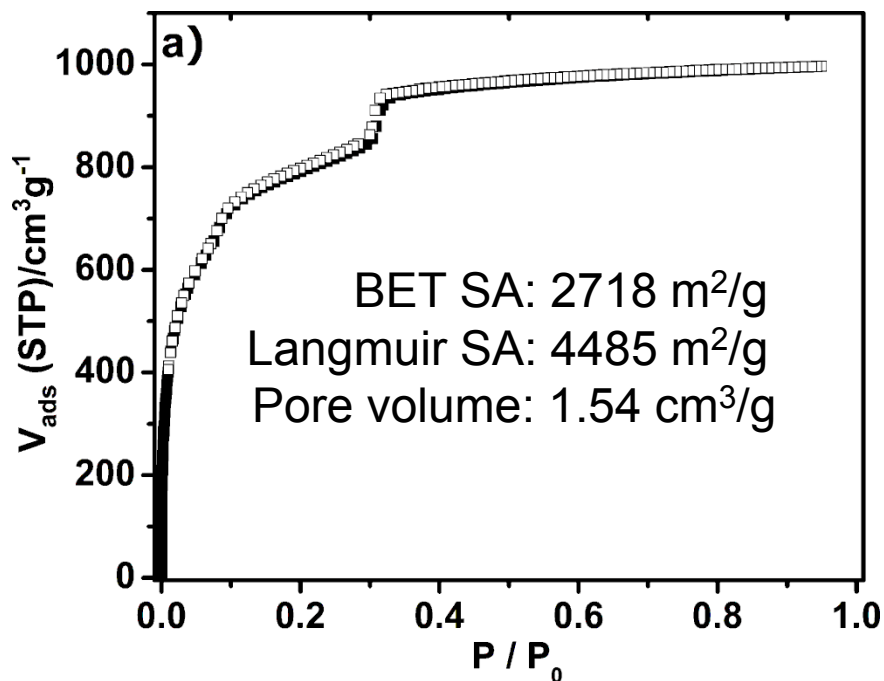
Metal-incorporation has lead to blocked cavities. A prerequisite for metal incorporation is to make porous materials with large cavities.

# MOF with Large Cavity (PCN-21)

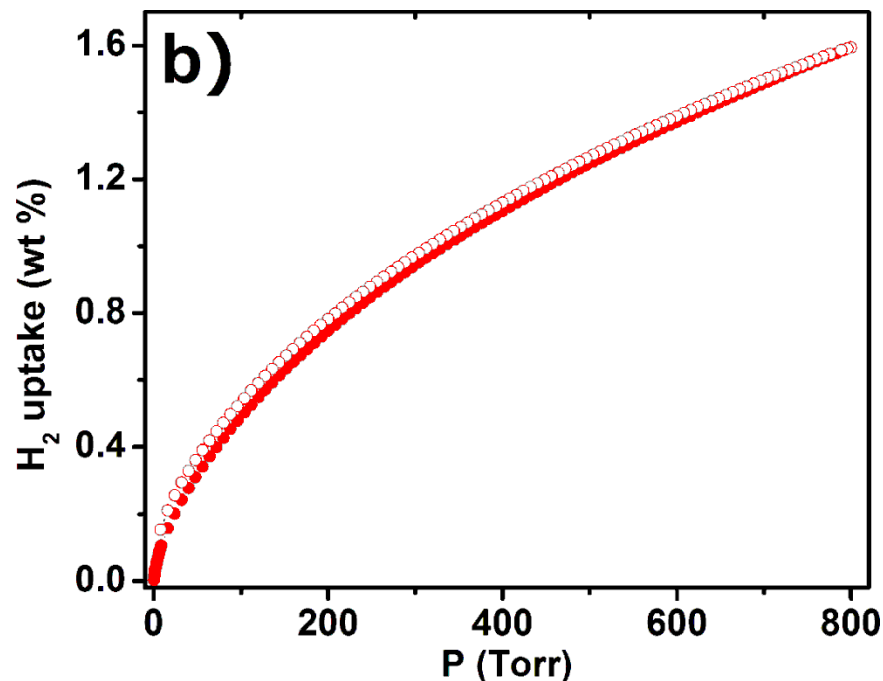


Cavities up to 4 nm have been introduced to a hierarchically-assembled metal-organic framework by adopting an angular, semi-flexible tetratopic ligand.

# Gas Adsorption of PCN-21



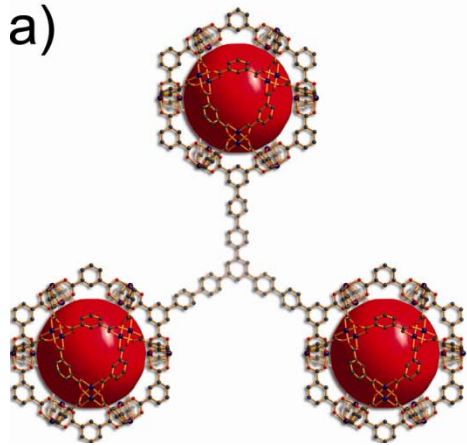
PCN-21 possesses permanent porosity and exhibits stepwise N<sub>2</sub> sorption isotherms.



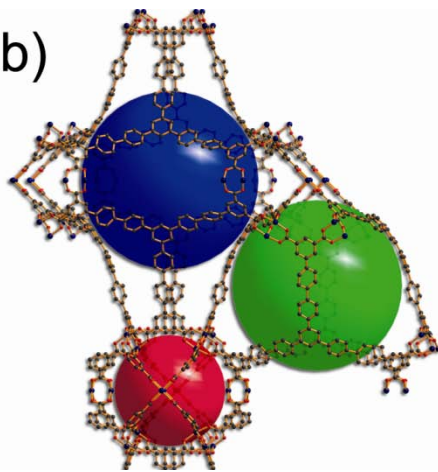
At 77 K and 1 bar, PCN-21 can adsorb 1.6 wt% H<sub>2</sub> gas.

# Other MOFs with Large Cavity (PCN-69)

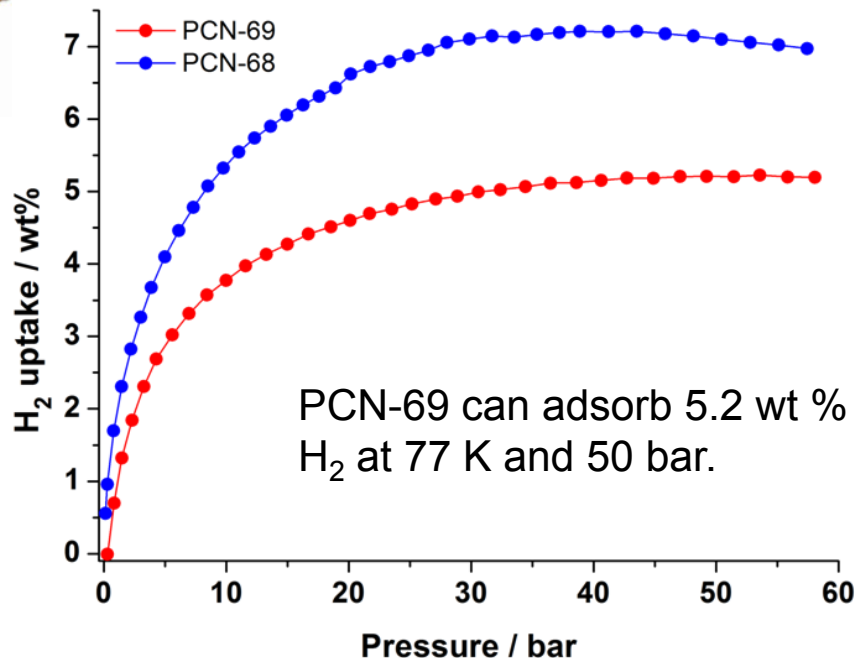
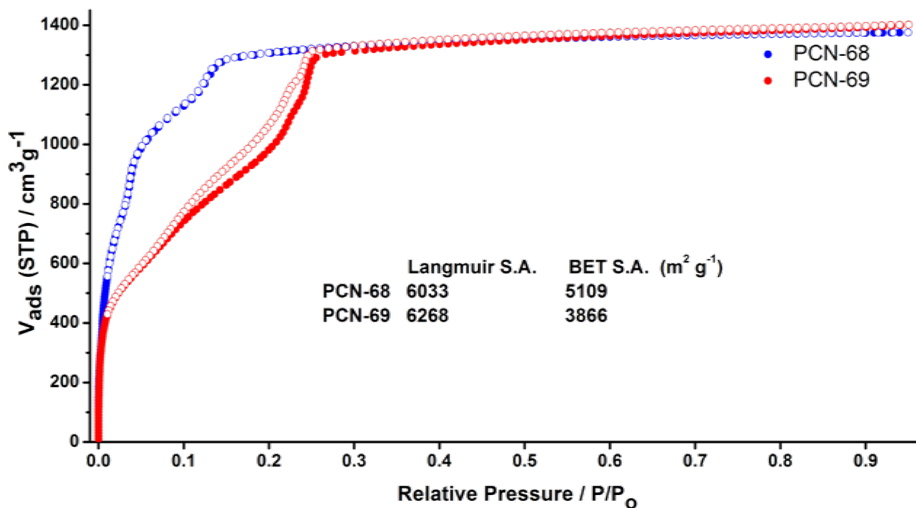
a)



b)



- a) Three fold ligand btti and 24-connected cuboctahedral building blocks in PCN-69;
- b) 3D polyhedra packing in PCN-69



Metal incorporation is underway!

# Collaborations

## Partners

- Dept. of Chem. Eng., TAMU, Theoretical Calculation
- KIT, Germany, Ligand Synthesis
- SWRI<sup>®</sup>, Gas adsorption measurements
- LLNL, Critical Point Activation
- ANL, APS, Crystal Structure Determination
- GM, High pressure Gas Adsorption Measurements

## 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 :

- PPNs with ultra-high surface area have been designed and synthesized. PPN-4(Si) has record high BET surface area of  $6470 \text{ m}^2 \text{ g}^{-1}$  and Langmuir surface area of  $10380 \text{ m}^2 \text{ g}^{-1}$ . The gravimetric excess hydrogen uptake of PPN-4(Si) was 8.5 wt% at 77 K and 60.4 bar. This material is stable in air and moisture and can be compressed without losing its porosity
- Functional MOFs (PCN-103) based on MOF-177 for metal ion incorporation were constructed, which possess BET surface area of over  $4100 \text{ m}^2/\text{g}$  and hydrogen uptake capacity of 5.6 wt% at 77 K
- MOFs containing mesocavities with microwindows tend to have high surface area and stability. PCN-69 with a Langmuir surface area of  $6268 \text{ m}^2/\text{g}$  and high hydrogen uptake capacity of 5.20 wt% at 77K and 50 bar has been obtained
- PPN postsynthetic modification and metal incorporation were performed

# Future Work

- Further enhancement of H<sub>2</sub>-MOF interaction by incorporation of coordinatively unsaturated metal ions and neutral metal atoms
- Preparation of MOFs with high surface area and functional groups for metal incorporation
- Preparation of PPNs containing active metal atoms or metal ions
- Show that metal incorporation improves the heat of hydrogen-adsorption significantly. Achieve a heat of hydrogen-adsorption significantly higher than those of traditional adsorptive materials
- Discover a MOF with high surface area, high hydrogen-affinity, and high volumetric capacity, keeping in mind the DOE 2015 goal of system gravimetric capacity of 0.055 Kg H<sub>2</sub>/Kg and volumetric capacity of 0.040 Kg H<sub>2</sub>/L

# Summary Table

Material	$\Delta H_{\text{ads}}$ (kJ/mol)	H <sub>2</sub> Adsorption Uptake			
		Gravimetric (wt%)	Volumetric (g/L)	T (K)	P (bar)
PCN-26	6.81	2.86	24.7	77	32
PCN-69	8.14	5.20	19.5	77	50
PCN-103(N)	6.60	5.60	25.6	77	40
PCN-103(O)	-	5.40	24.6	77	45
PCN-103(Ch)	-	5.10	26.0	77	50
PCN-80	5.20	4.80	29.0	77	44
PCN-46	7.20	5.31	32.3	77	32
PPN-4(Si)	4.63	8.5	*28.0 X 2	77	60.4

\*If compressed.