Improving Porosity and H_2-Affinity of Porous Framework Materials

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ST018

Overview

Timeline

- Project start date: 7/1/2007
- Project end date: 6/30/2013
- Percent complete: 90%

Budget

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

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

Partners

No formal partners, collaborators are

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

Relevance

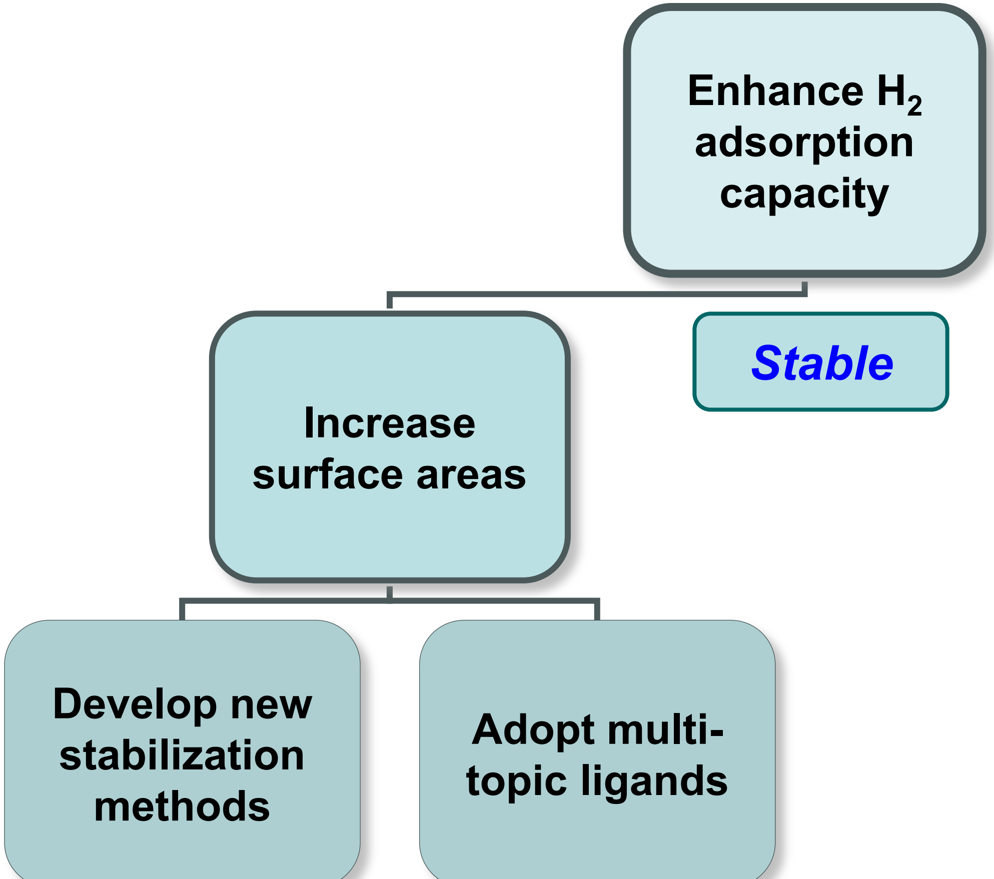
(Technical Challenges)

Dihydrogen affinity

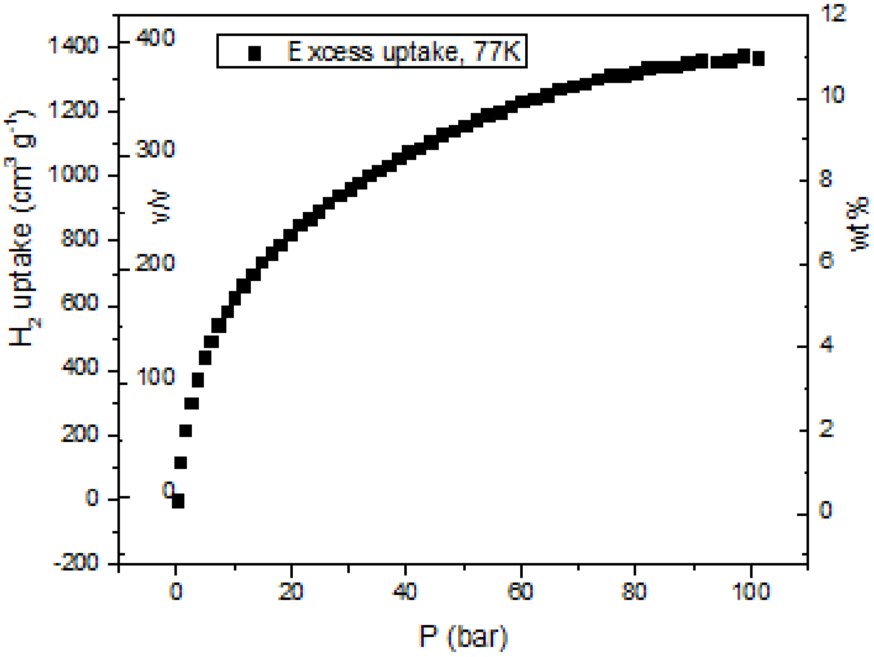
- 15 kJ/mol < Q_{st} < 30 kJ/mol for ambient temperature application
- For most materials, Q_{st} < 10 kJ/mol

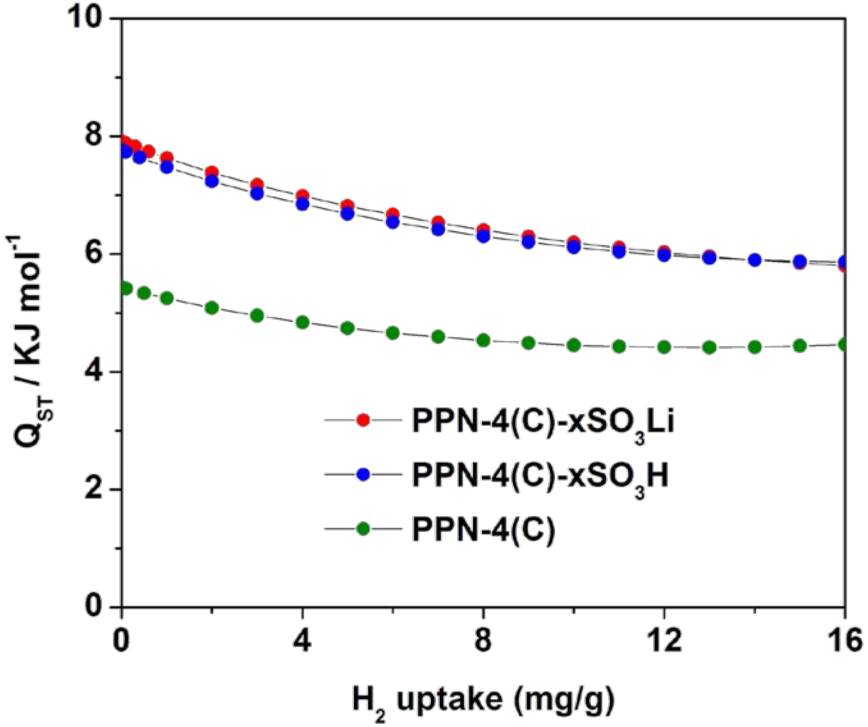
Surface area

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



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 is low due to extremely low framework density and lack of strong H_2-binding sites.

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.

Relevance

(Technical Challenges)

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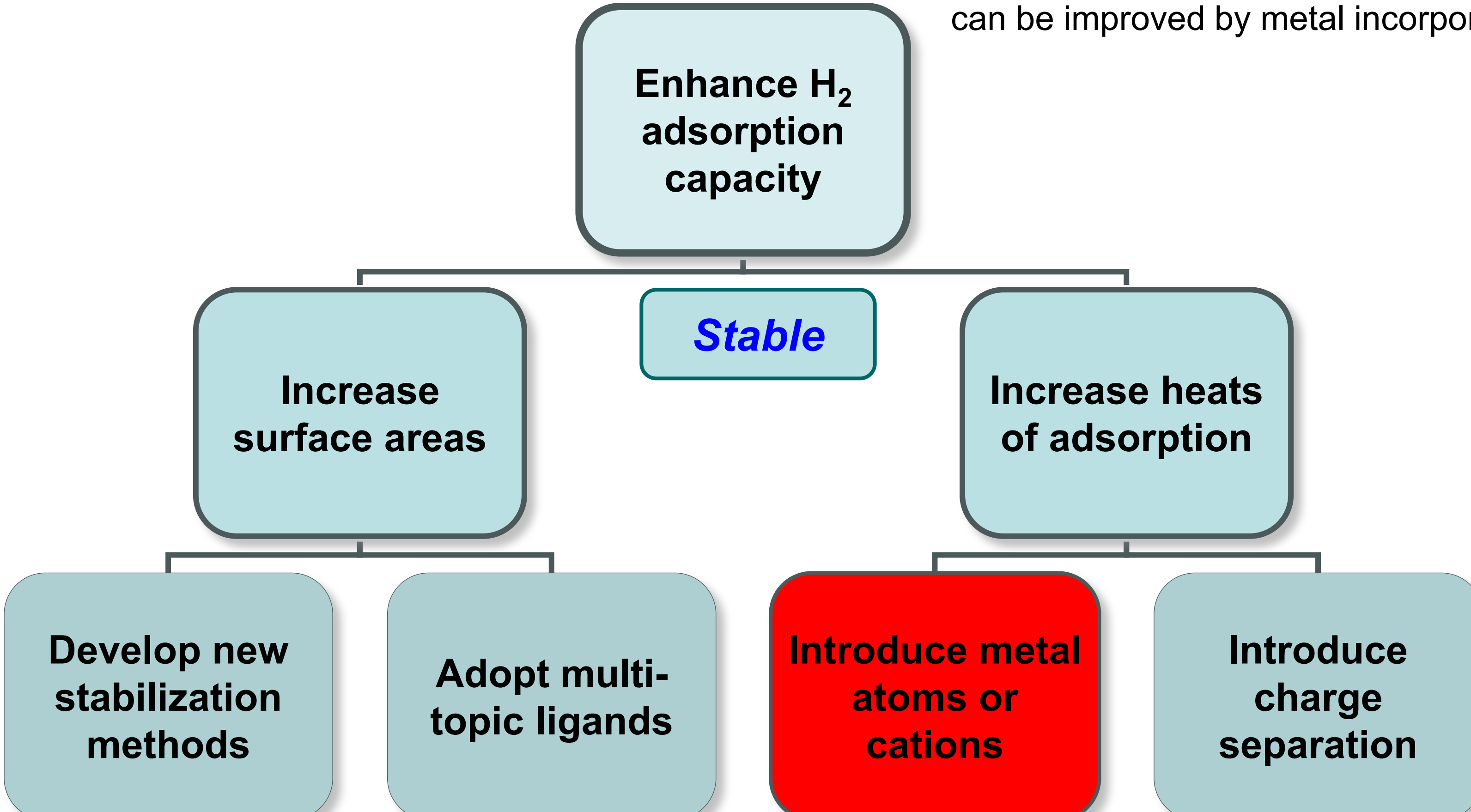
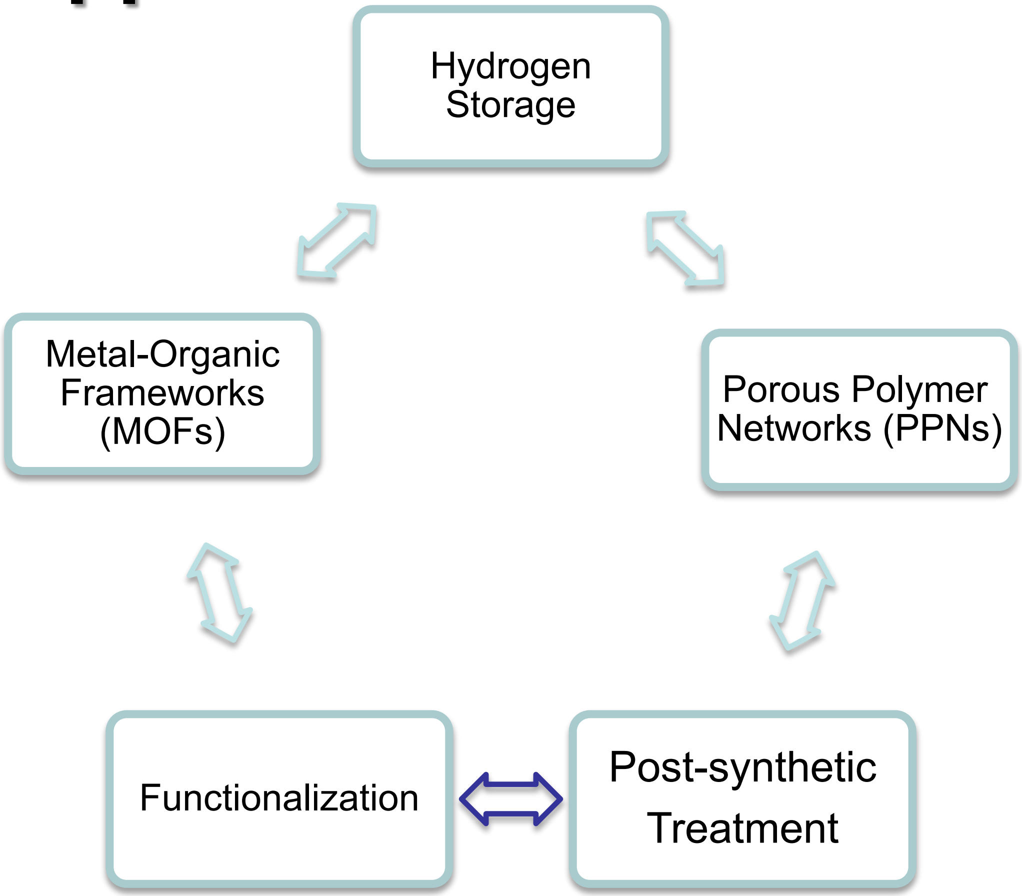


Approach/Milestone

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 Hydrogen 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-12	Milestone: Construct PPNs with high density of functional groups. Synthesize 10 porous materials with incorporated multivalent metal ions such as V^{3+}, Fe^{3+} or Ti^{3+}. Approach ΔH_{ads} of 15 kJ mol^{-1}. Construct series of 10 stable and high-surface-area Zr-MOFs based on porphyrin ligand, study the effect on gas uptake by introducing different metals into their porphyrin linkers. (Status – underway)

Approach



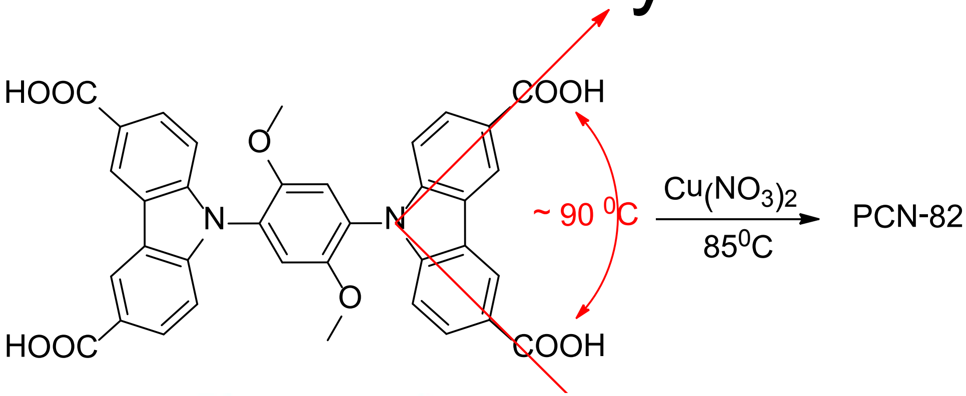
Enhance H_2 uptake

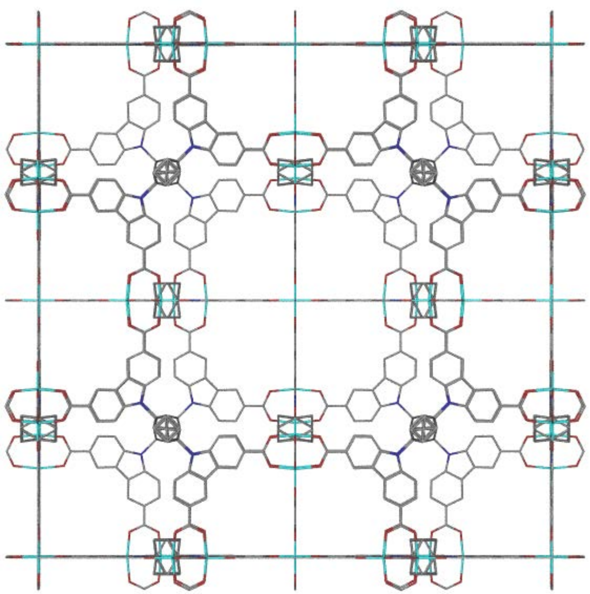
- Framework functionalization
- Framework post-synthetic modification
- Introducing metal ions

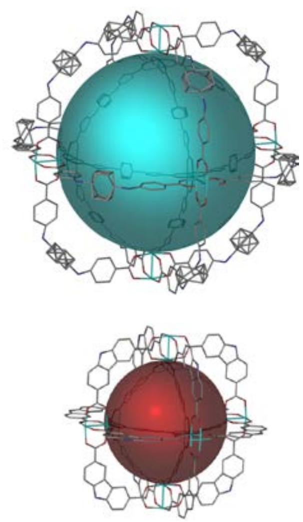
New Achievements

- High-surface-area PCNs (PCN-82 and PCN-88) with potential anchors for metal incorporation
- Highly stable Zr-MOFs with porphyrin ligand (PCN-41) was synthesized and initial metal-insertion study was carried out, these materials exhibit high surface area and high heat of adsorption for H_2
- PPN enriched with phenol groups (PPN-43-OH) was synthesized, phenol group can be served as anchor for metal incorporation
- Design and synthesis of a series of biphenyl ring PPNs, these materials are relatively low cost, and exhibit high surface areas and high heats of adsorption for H_2

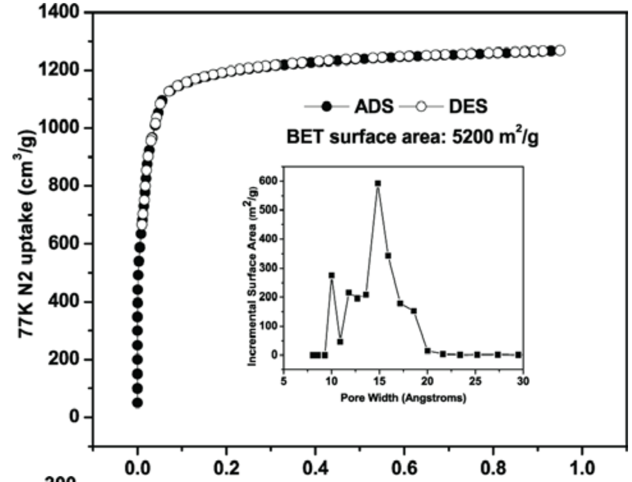
High-Surface-Area MOF with Anchors for Post-synthetic Modification

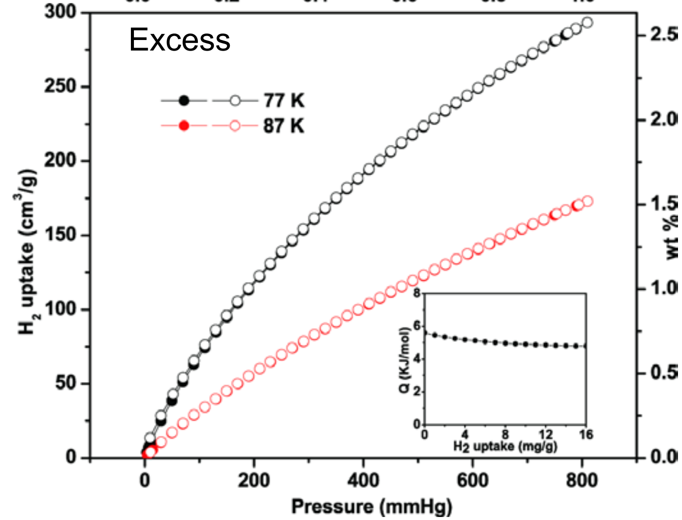






cubic, space group Fm3m
a = 40.026(2), V = 64124 Å^3





Strategy:
To expose phenol group and use it as anchor for binding metal ions

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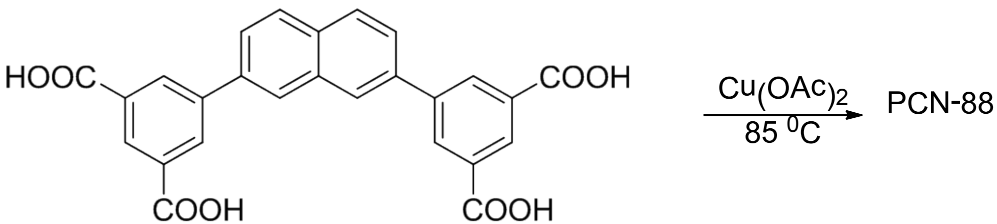
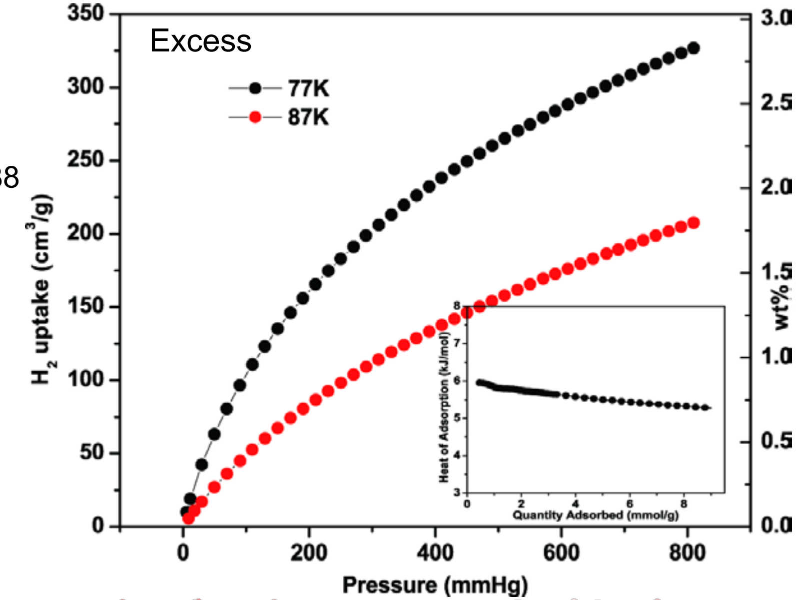
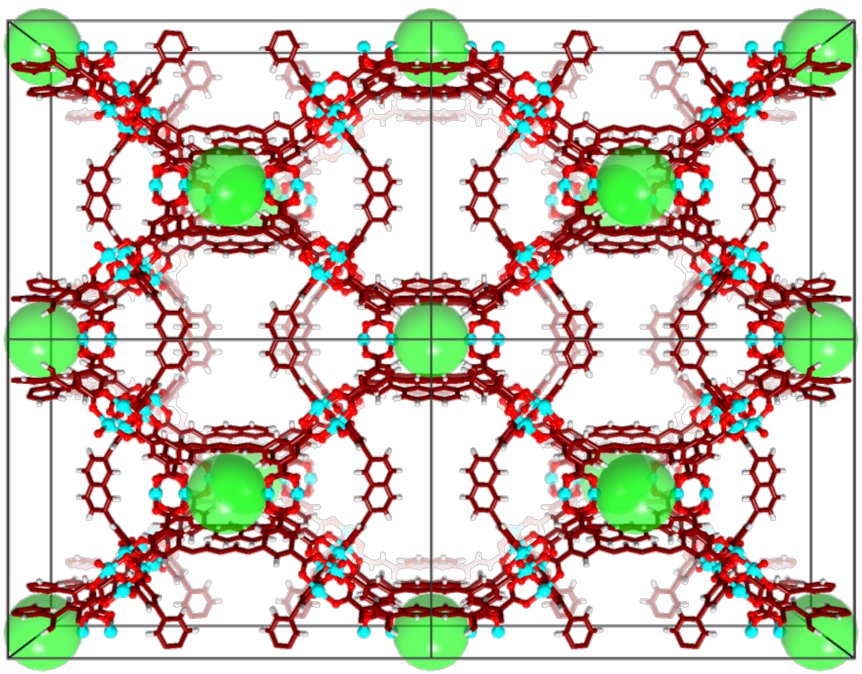
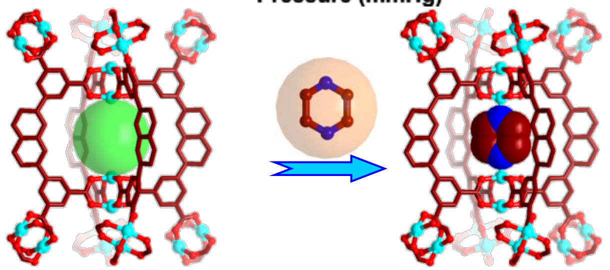
High-Surface-Area MOF with Anchors for Post-synthetic Modification





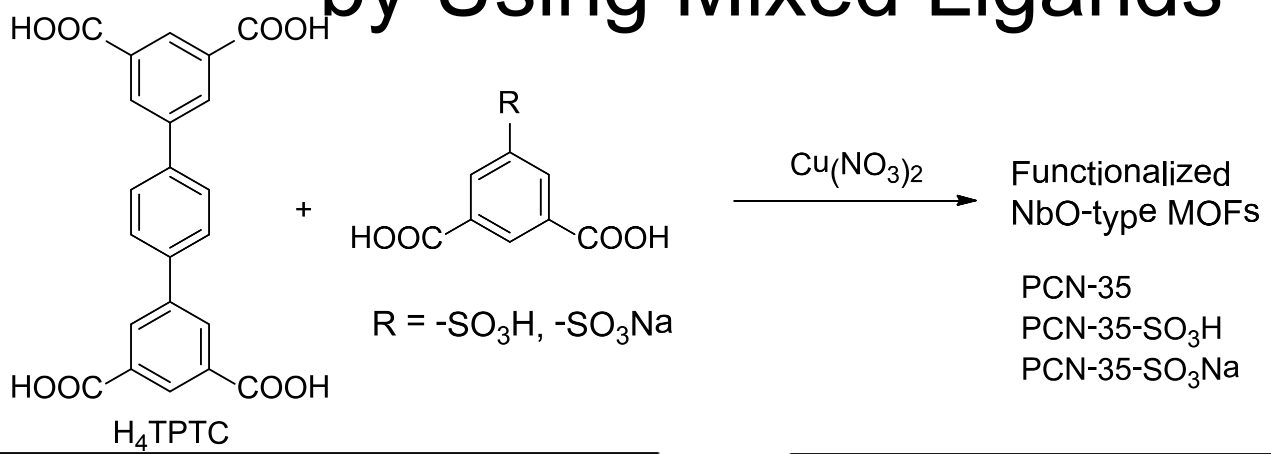


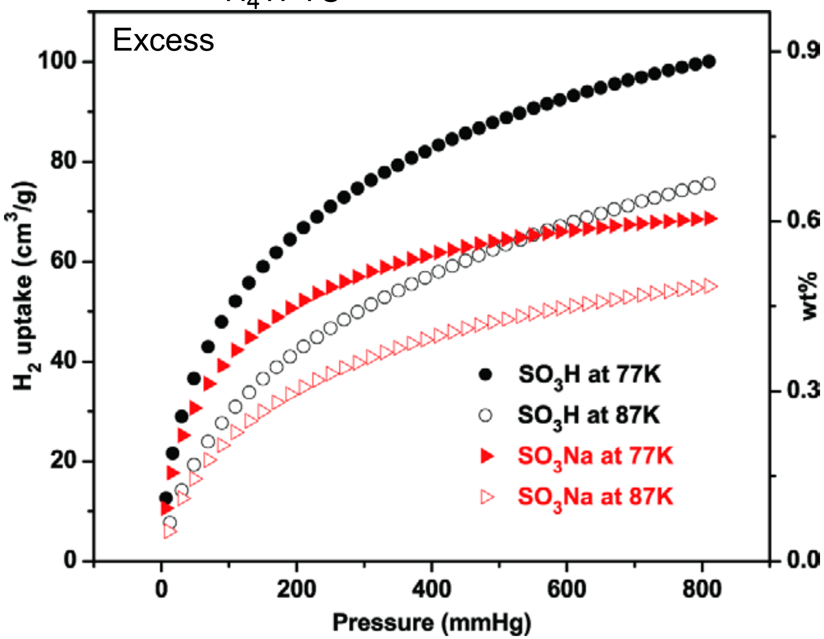
S_{BET}: *3300 m²/g*

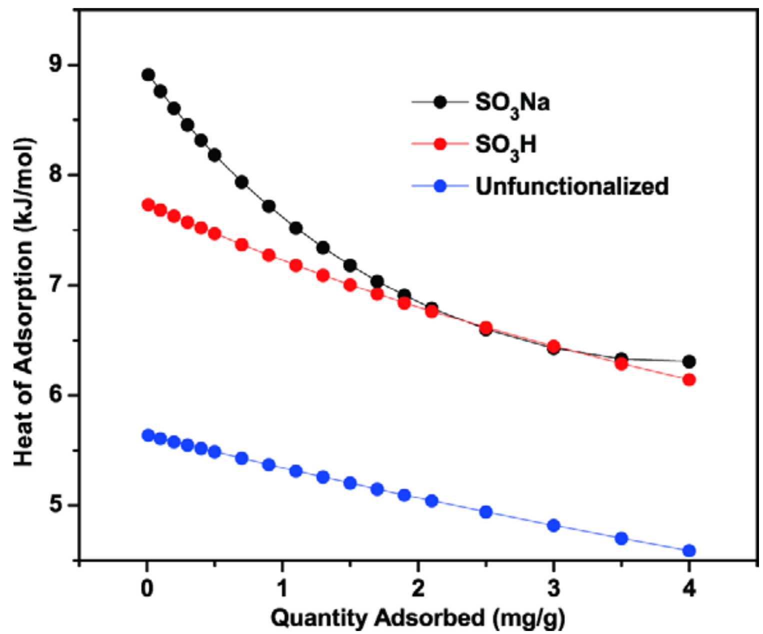


Strategy:
To introduce metal-binding anchors by using pyrazine derivatives

Introduction of Functional Groups into MOFs by Using Mixed Ligands

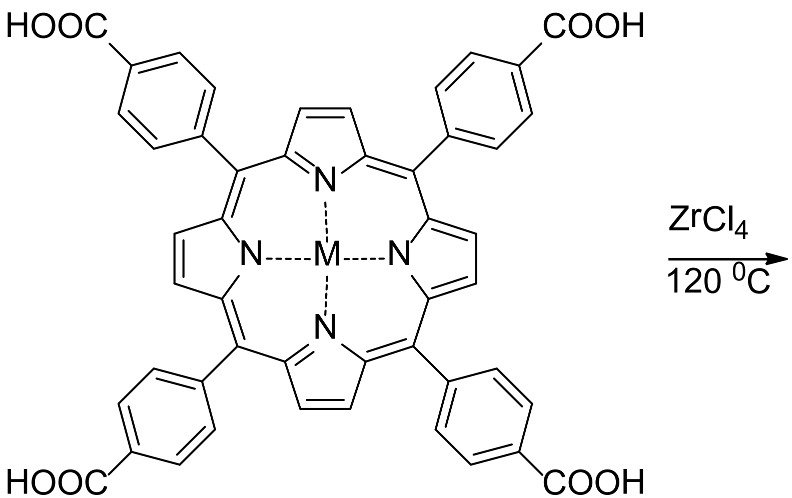






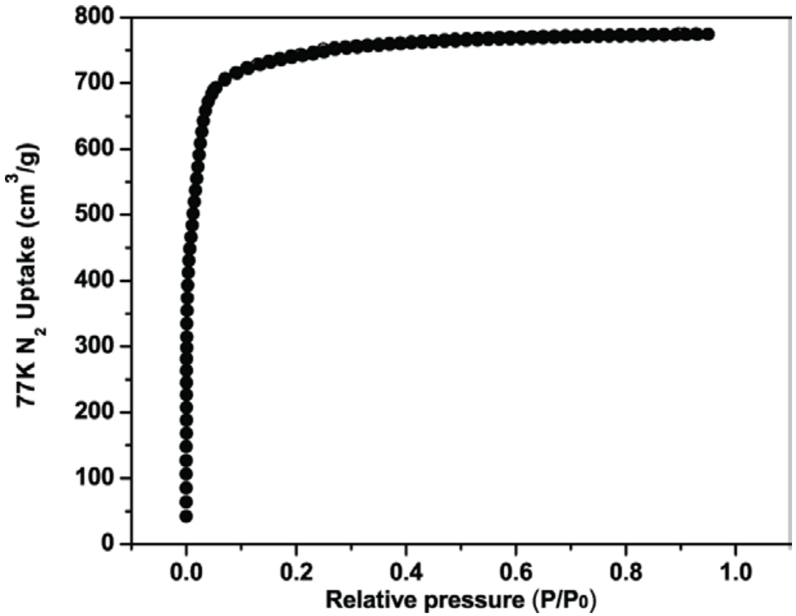
The SO_3H group can be used as anchor for other metal incorporation

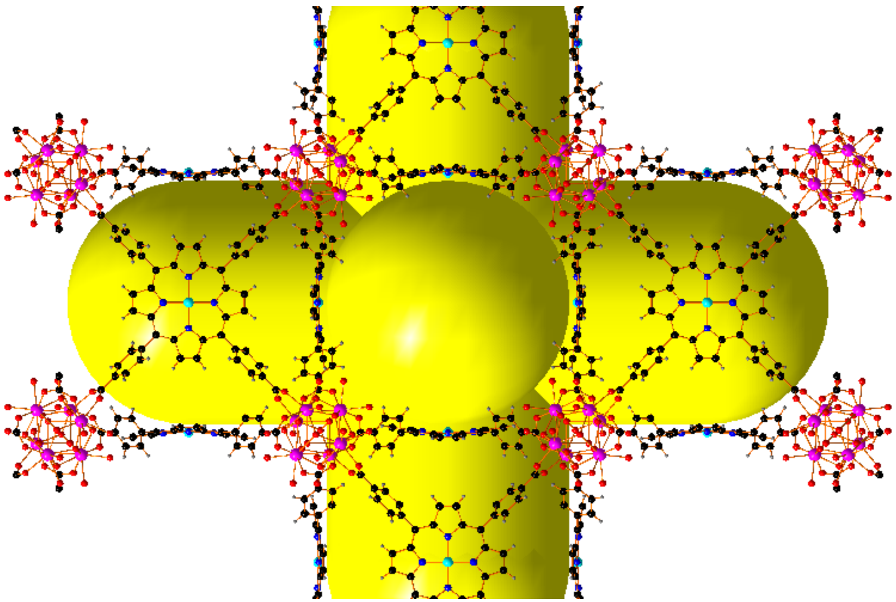
Stable Zr-MOFs



PCN-41-Zr; PCN-41-Fe; PCN-41-Ni

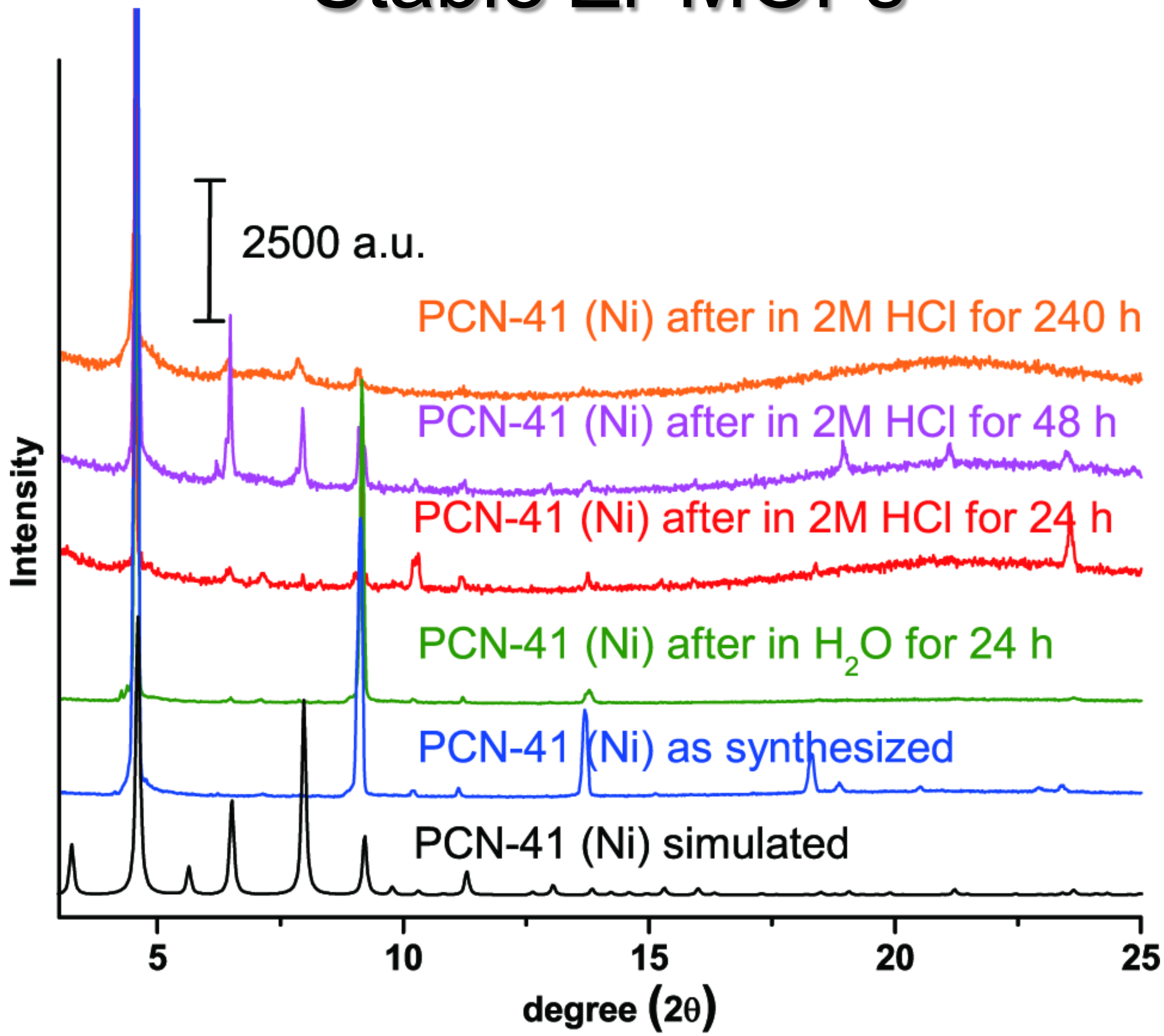
Strategy:
To introduce multivalent metals through porphyorin ligand





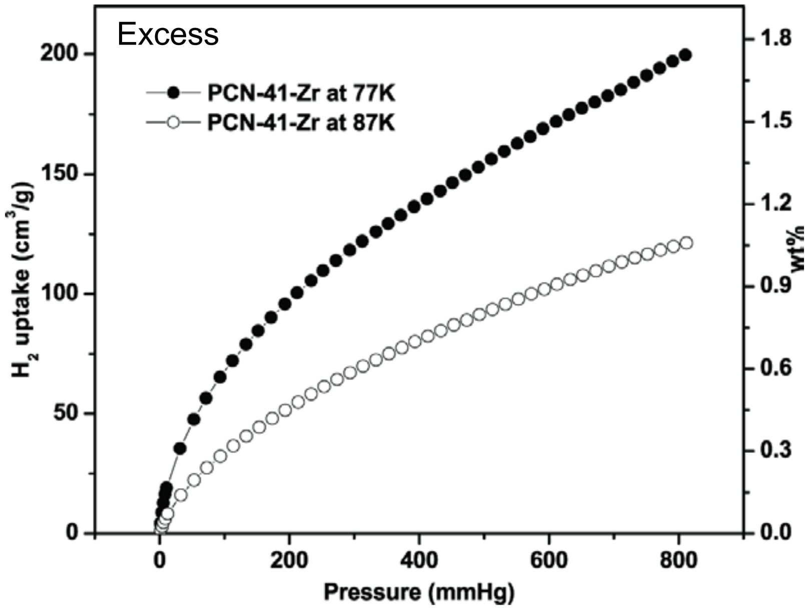
S_{BET}: *2600 m²/g (PCN-41-Ni)*

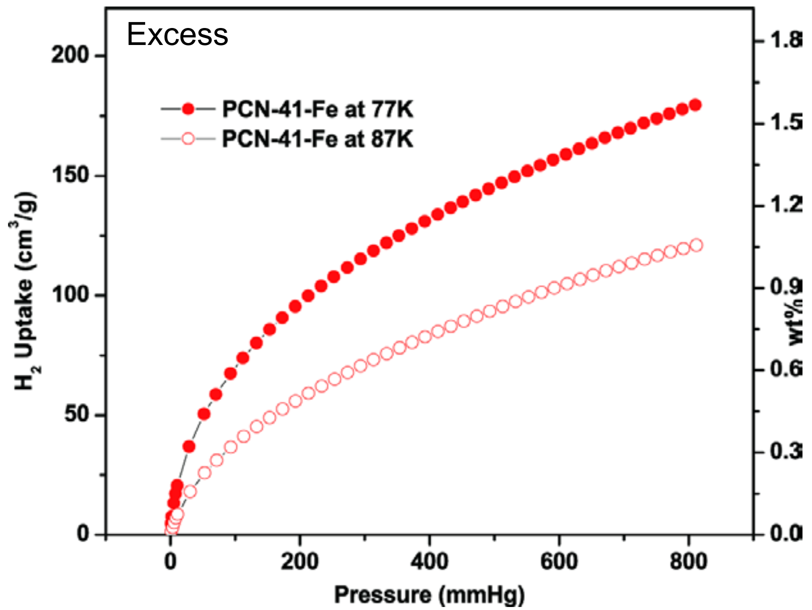
Stable Zr-MOFs

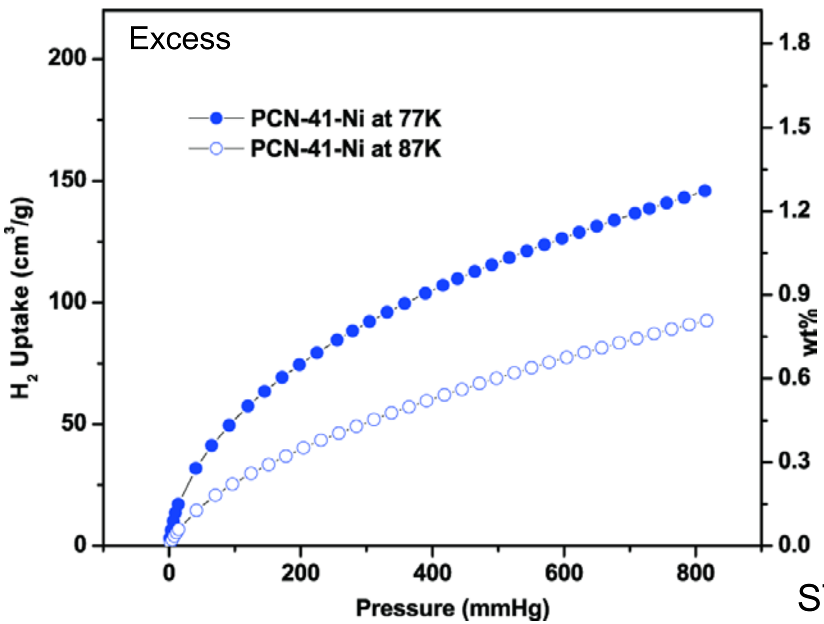


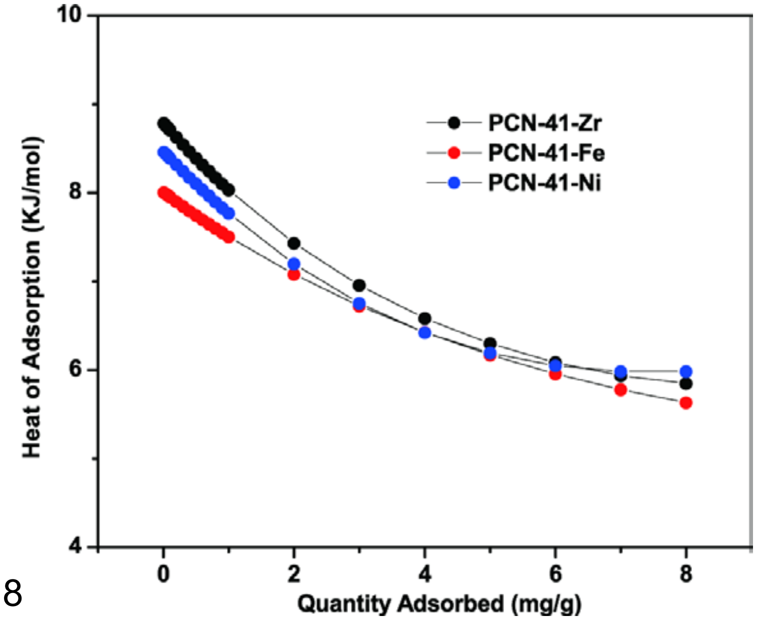
Strength of Zr-O coordination bonds prevents protonation of ligand under acidic conditions typically observed in MOFs.

Stable Zr-MOFs

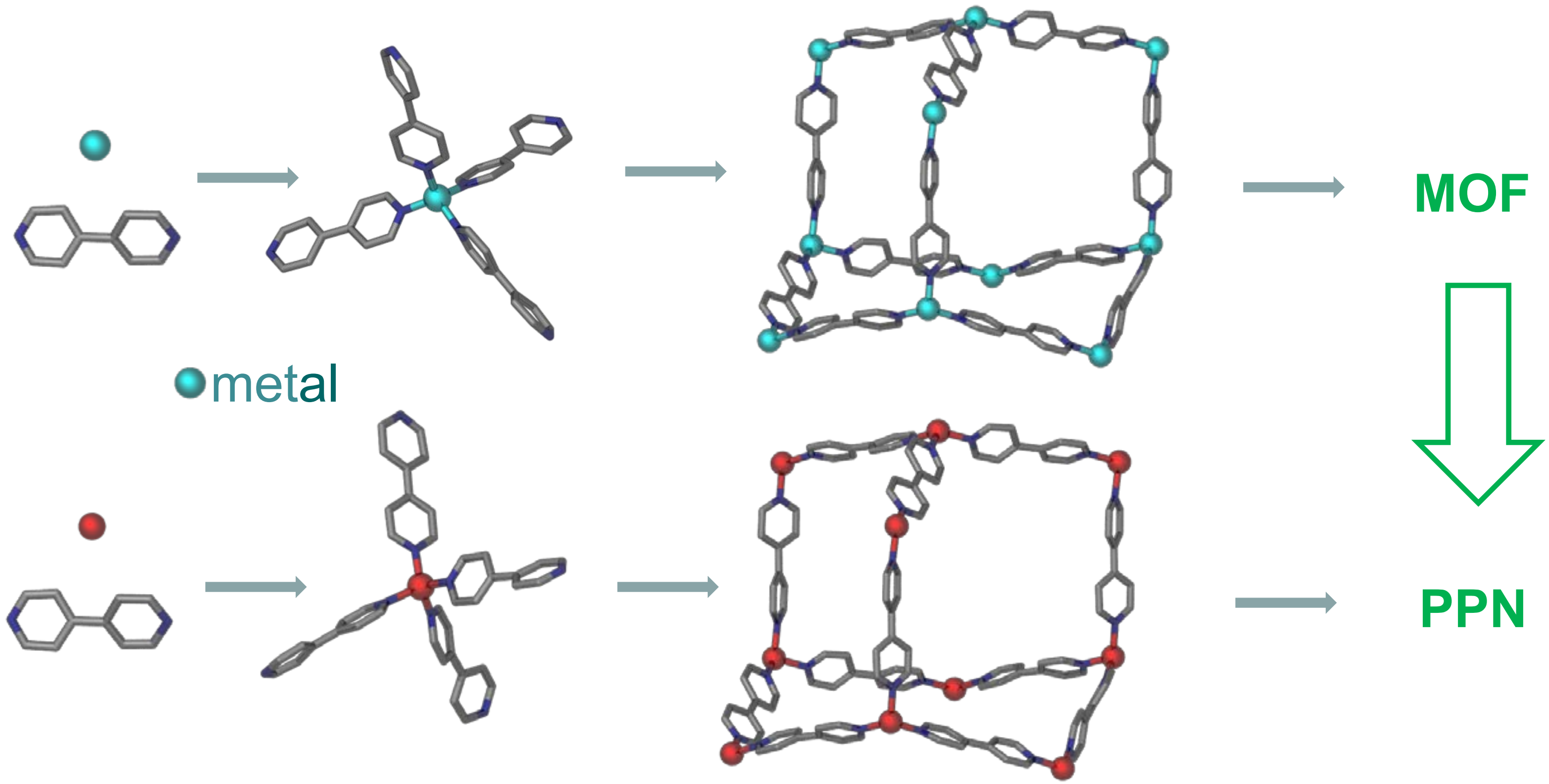








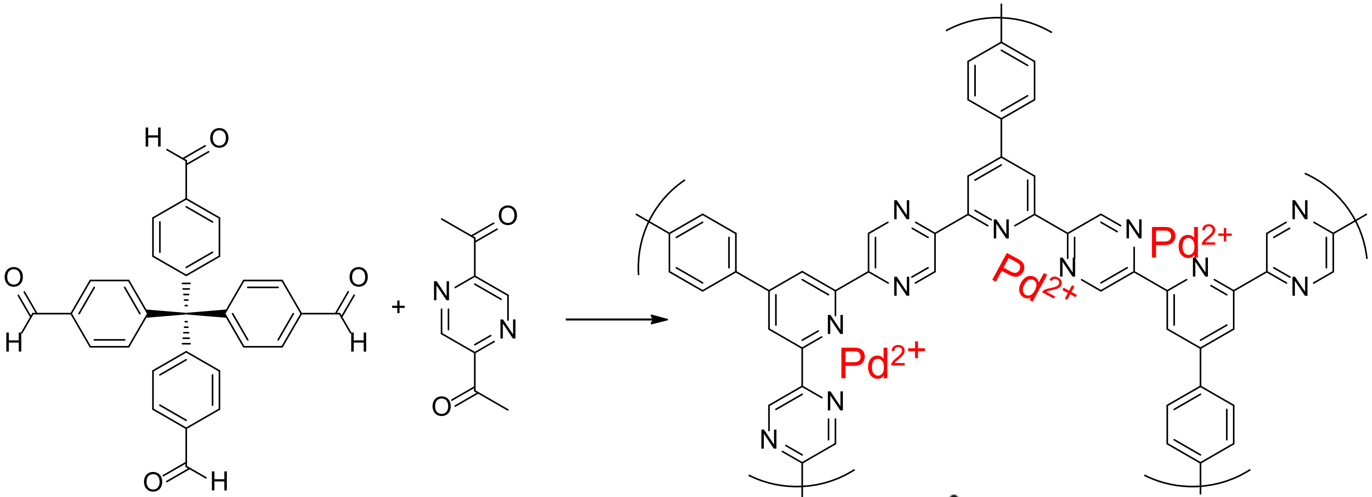
Porous Materials Stable in Air and Moisture for H_2 Storage

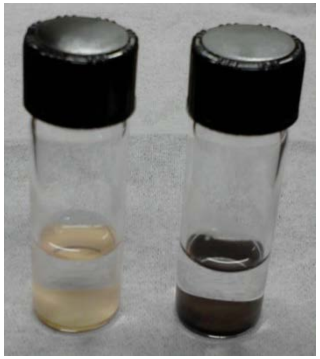


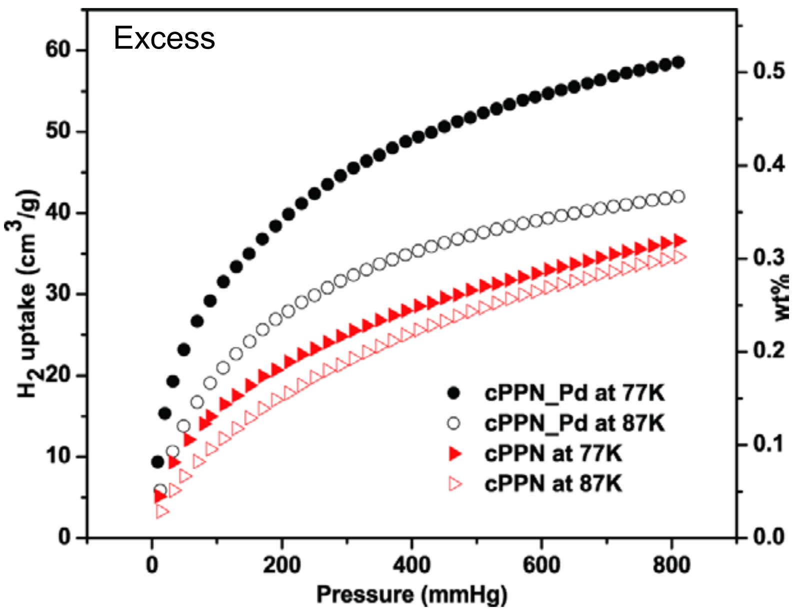
C, Si, Admantane, P^+, B^-, etc.

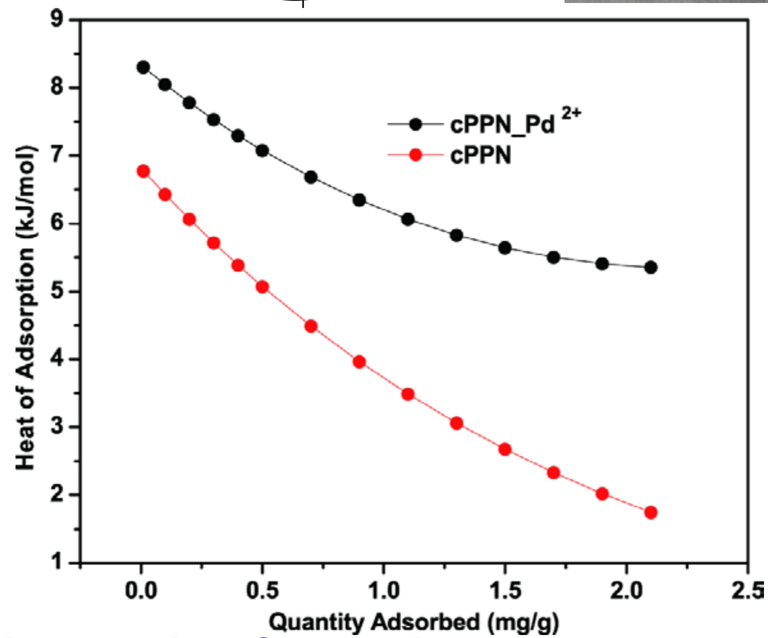
Stability is important for H_2 storage in application.

Introduction of Metal Ions into PPNs



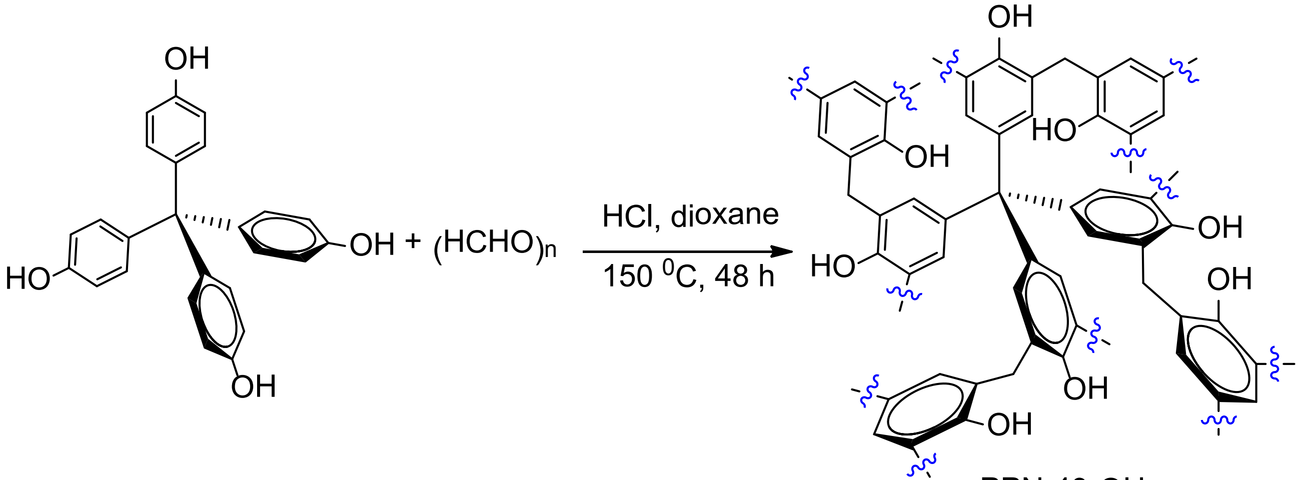


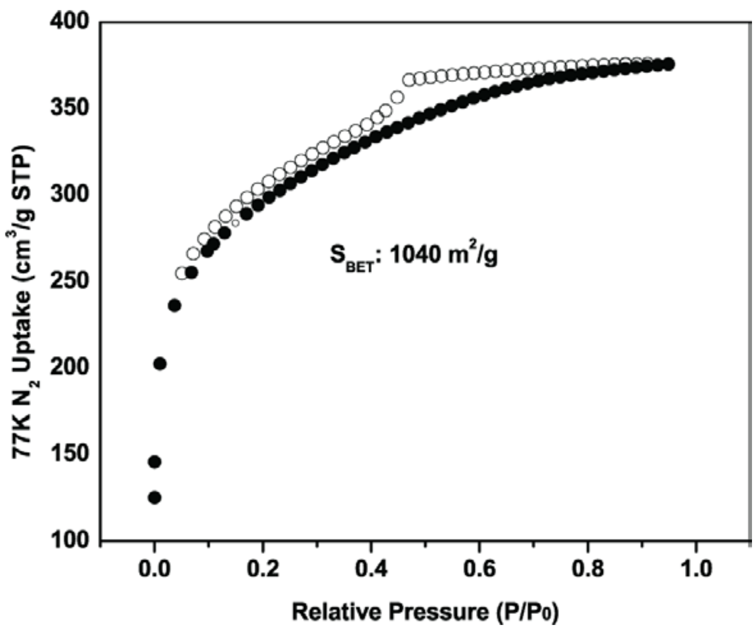


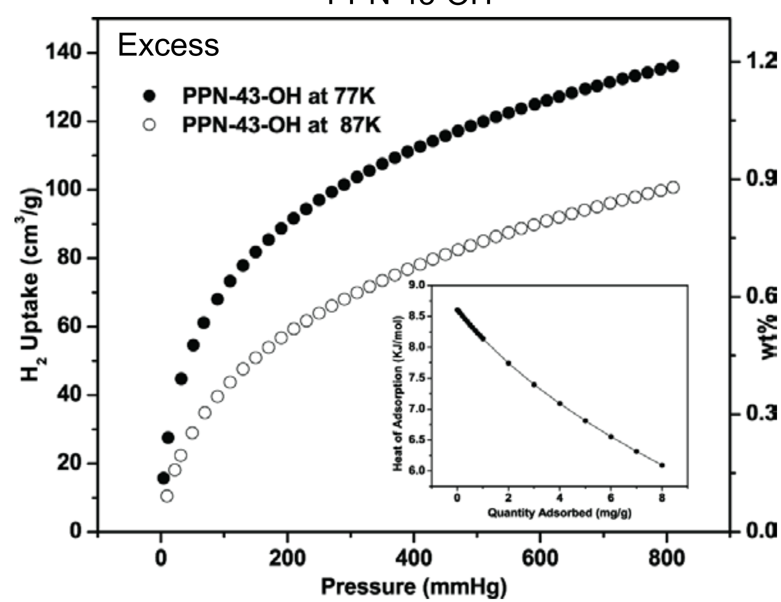


The 2,2'-bipy group can be used as anchor for multivalent metals insertion

Phenolic PPN

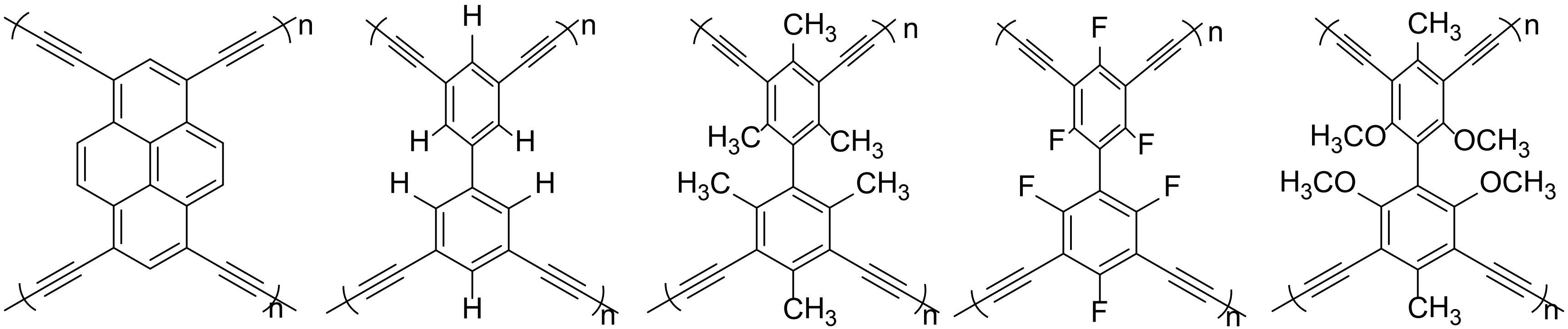






The phenol group can be used as anchor for multivalent metals incorporation

Functionalized Biphenyl Ring PPNs



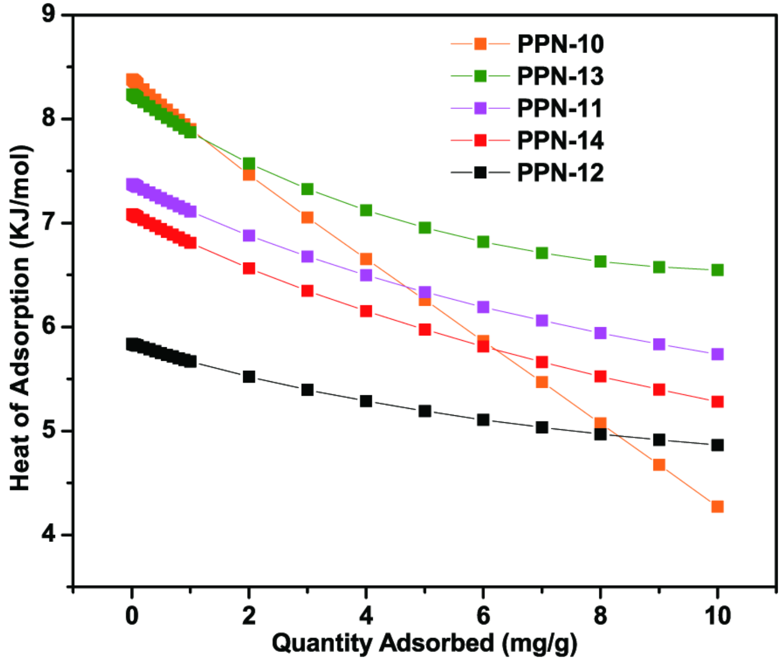
PPN-10
S_{BET}: 1128 m^2/g

PPN-11
SBET: 1551 m2/g

PPN-12
S_{BET}: 3420 m^2/g

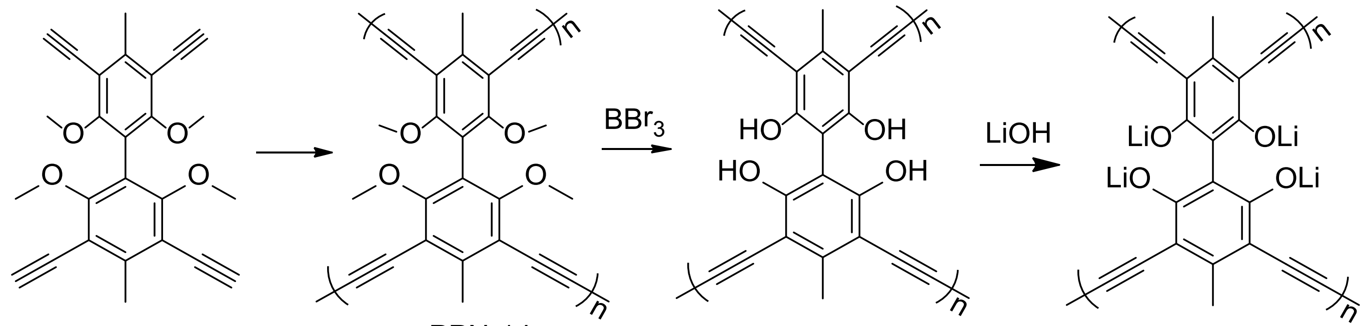
PPN-13
S_{BET}: 1062 m^2/g

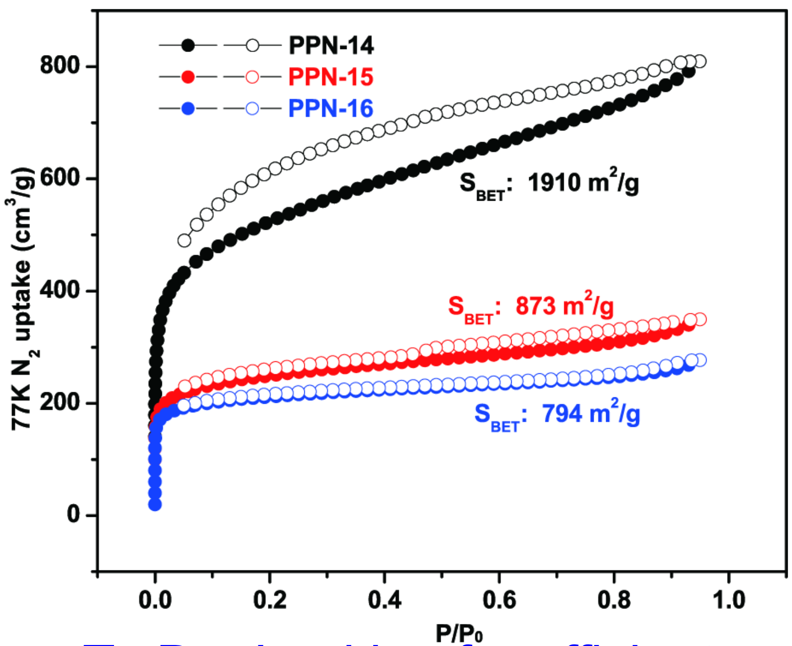
PPN-14
S_{BET}: 1910 m^2/g

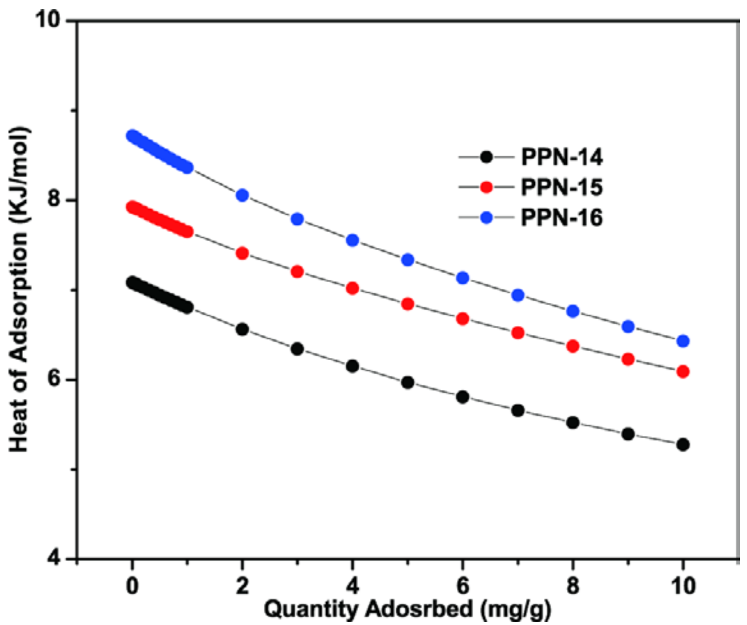


Strategy:
To "lock" the biphenyl ring by introducing functional groups at 2 & 2' positions, therefore construct high surface area PPNs

Functionalized Biphenyl Ring PPNs







To-Do: Looking for efficient method to remove methyl group or using other phenol protecting group instead

Collaborations

Collaborators

- 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

Technology Transfer

- Working with industrial partners closely
- Presented in Tech Team Meeting. Provided relevant parameters for the Engineering CoE on PPN-4
- Working with a start-up company

Accomplishments

Demonstrated through experiments that :

- Two PCNs (PCN-82 and PCN-88) with exceptionally high surface areas (5200 and 3300 m^2/g)have been designed and synthesized. They all have potential anchors for metal incorporation.
- A series of high-surface-area Zr-MOFs were synthesized by using porphyrin ligand, these MOFs are stable even in strong acidic conditions. Initial study shows that metal incorporation leads to high heat of adsorption for H_2.
- A phenolic PPN was synthesized, the phenol group can serve as anchor for multivalent metal incorporation.
- A series of biphenyl PPNs were designed and synthesized by using triple bond coupling reaction, the biphenyl ring is “locked” by introducing functional groups at 2 & 2’ positions, therefore leading to high surface area PPNs, and high heat of adsorption for H_2.

Future Work

- To expose phenol group of PCN-82 and use it as anchor for metal incorporation to study its effect on heat of adsorption for H_2.
- Systematic study Zr-MOFs by incorporating different multivalent metals, such as V^{3+}, Ti^{3+}, etc.
- Optimize the procedure for phenolic PPN-43-OH for higher surface area, then incorporate multivalent metals, such as V^{3+}, Fe^{3+},Ti^{3+}, etc.
- To expose the phenol group of PPN-14 by optimizing the demethylation procedure, and use it as anchor for metal incorporation.
- Measure H_2 storage capacity at high pressure for obtained high-surface-area materials, such as, PCN-82, 88, 41 and PPN-12.

Summary Table

Material	ΔH_{ads} (kJ/mol)	S_{BET} (m^2/g)
PCN-82	5.6	5200
PCN-88	6.0	3300
PCN-35, 35-SO_3H, 35-SO_3Na	5.6, 7.7, 8.9	-
PCN-41-Zr, 41-Fe, 41-Ni	8.7, 8.0, 8.5	2600 (Ni)
CPPN, CPPN-Pd	6.8, 8.3	-
PPN-43-OH	8.6	1040
PPN-10	8.4	1128
PPN-12	5.8	3420
PPN-13	8.2	1026
PPN-14, 15,16	7.1, 7.9, 8.7	1910, 873, 794