2008 DOD Hydrogen Program (Texas A&M and NREL)

Combinatorial Synthesis and High Throughput Screening of Biomimetic Metal-Organic Materials for Military Hydrogen-Storage Applications

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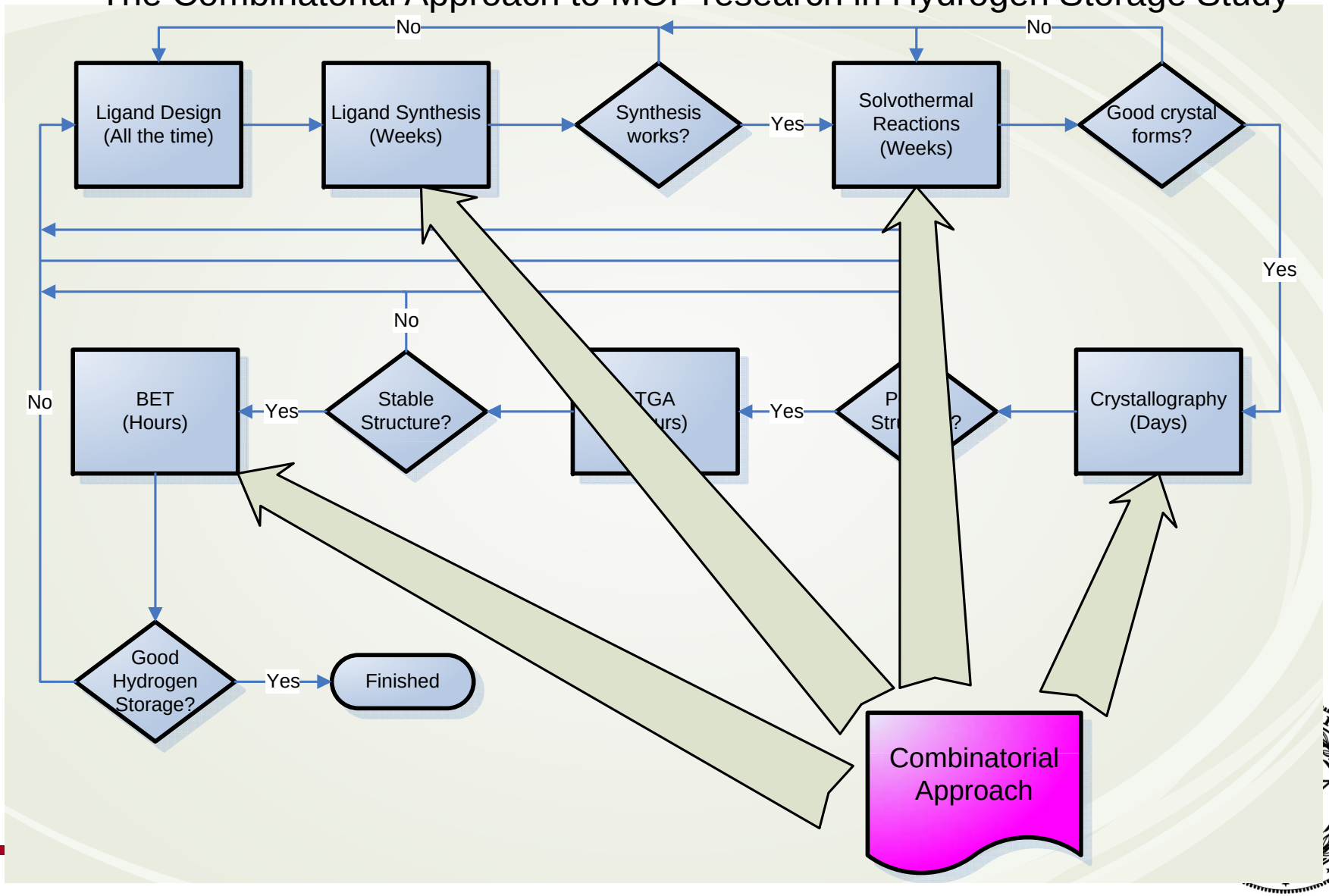
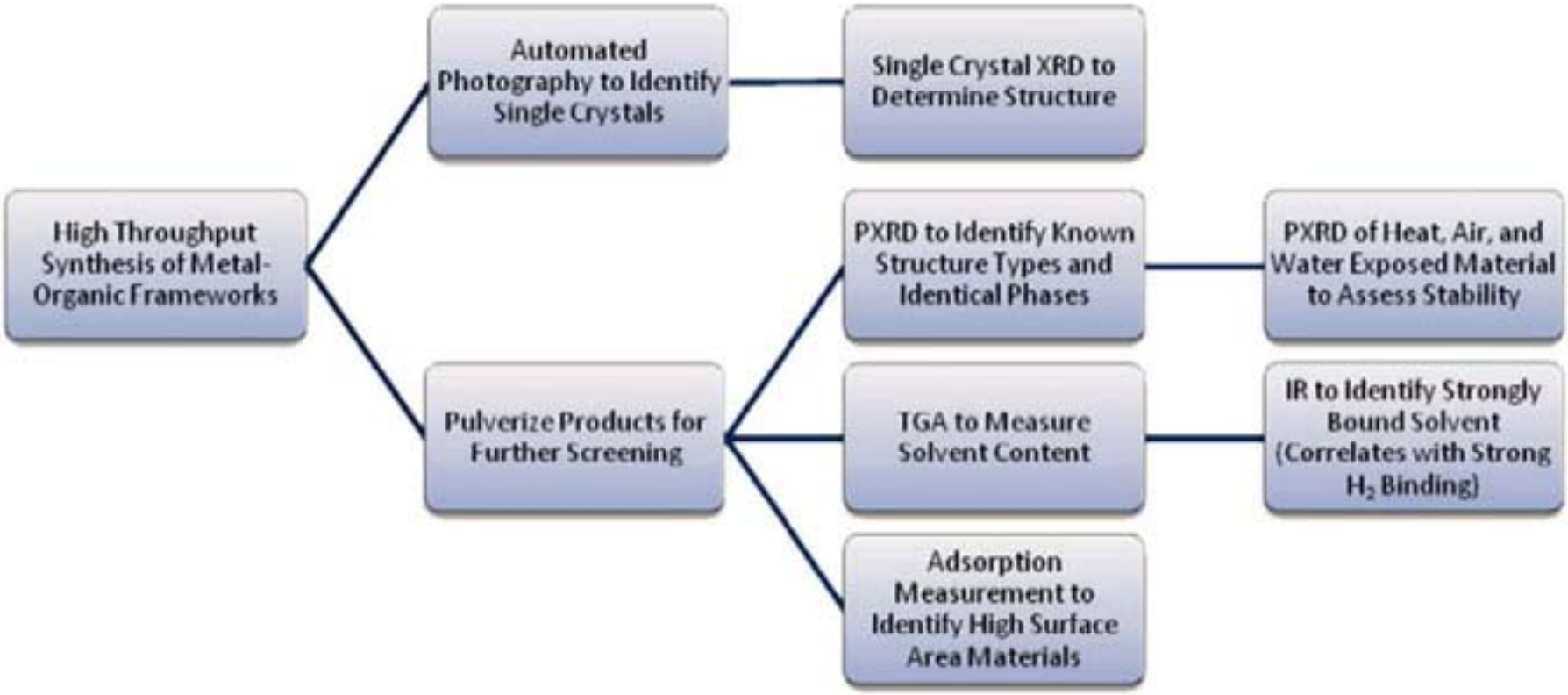
Technical Concepts

The Combinatorial Approach to MOF research in Hydrogen Storage Study



High-Throughput Synthesis and Screening Process



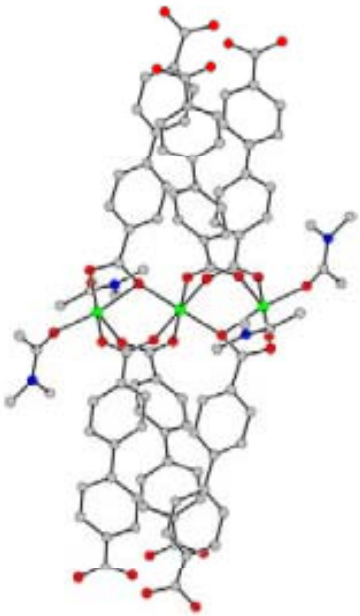
From Prof. Jeffrey Long @ UC Berkeley

Synthesis Depends Critically on Reaction Conditions

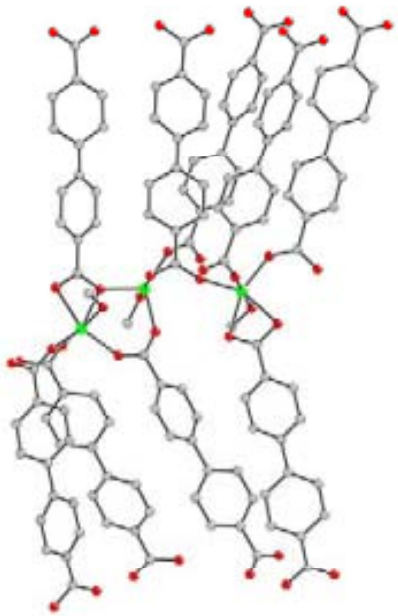
$Mg(NO_3)_2 \cdot 6H_2O$ + H_2BPDC

Δ | DMA/MeOH

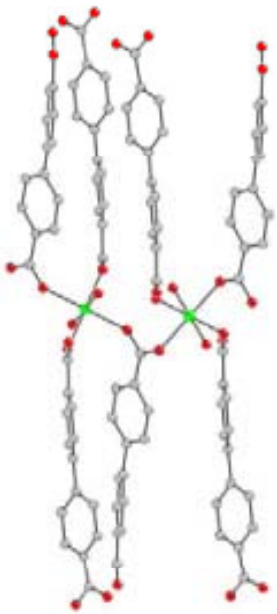
1% H_2O | 2% H_2O | 4% H_2O



$Mg_3(BPDC)_3(DMA)_4$



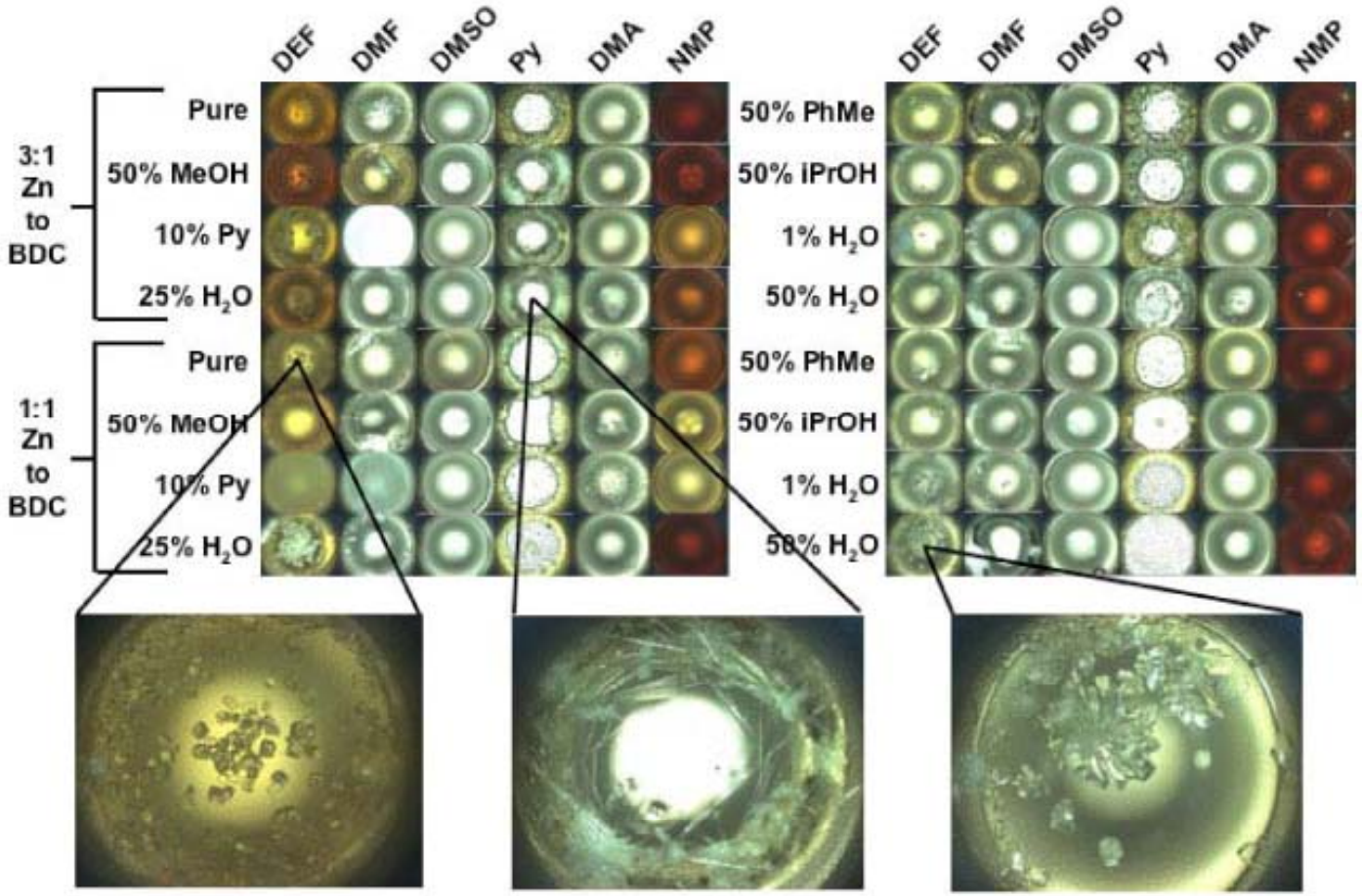
$Mg(BPDC)(MeOH)$



$Mg(BPDC)(H_2O)_2$

From Prof. Jeffrey Long @ UC Berkeley

Test: $Zn(NO_3)_2 \cdot 6H_2O$ + 1,4-Benzenedicarboxylic Acid



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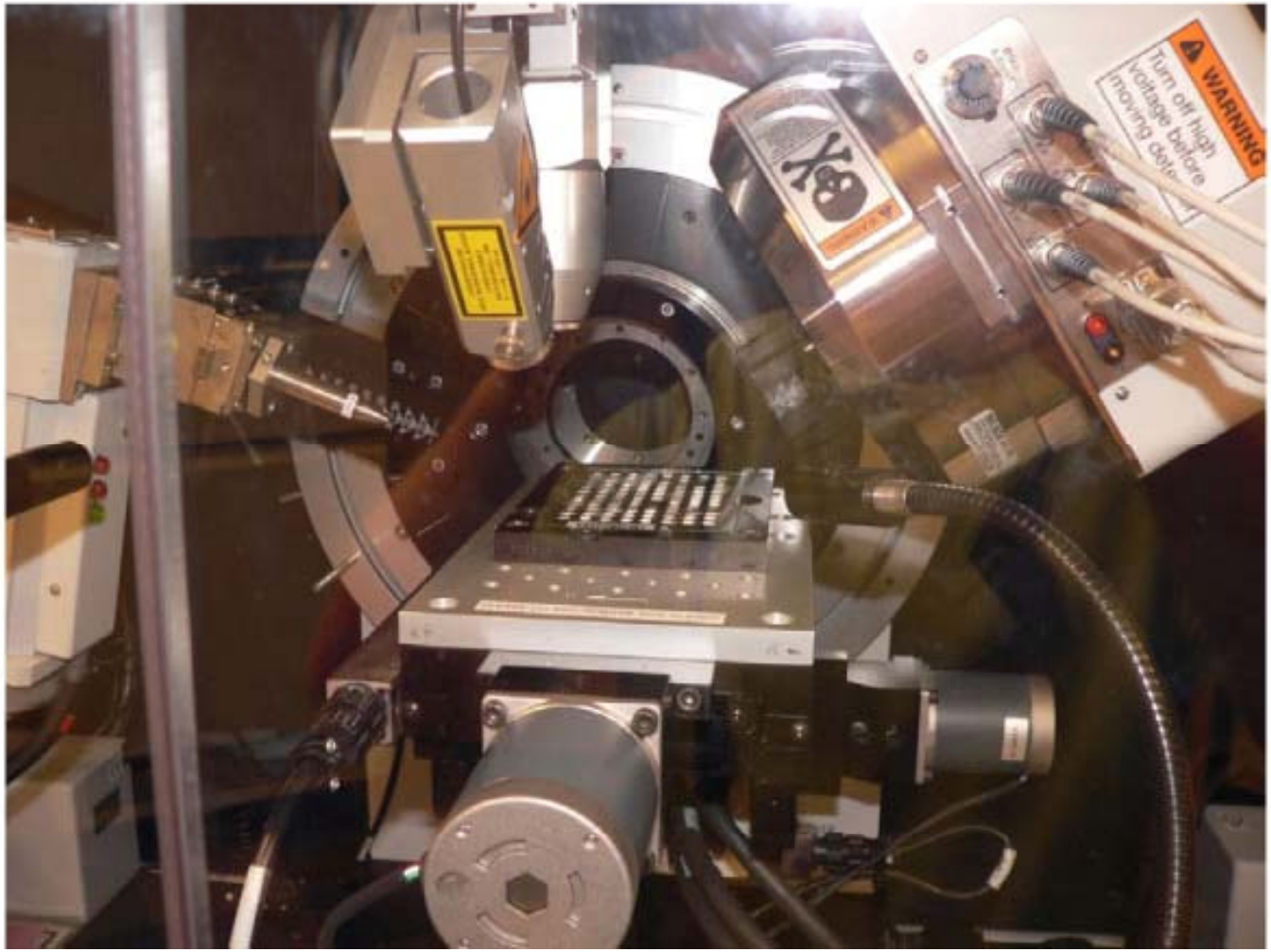
High-Throughput Powder X-Ray Diffraction



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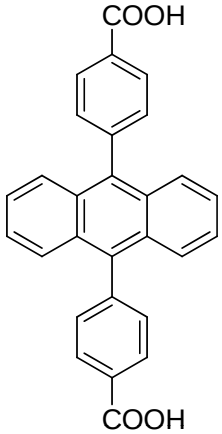
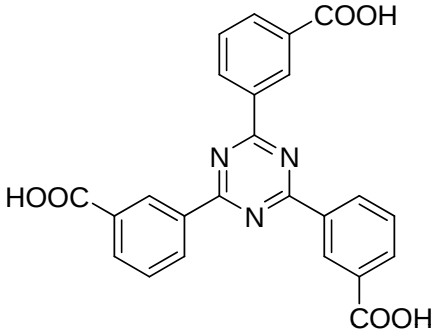
Objectives

- Design and synthesis of ligands for combinatorial screening
- MOF synthesis, characterization using combinatorial approach
- Hydrogen storage measurement and screening potential candidate

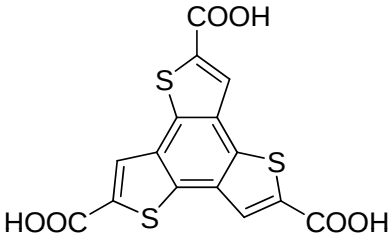
Six new ligands



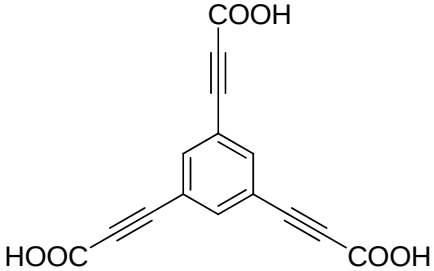
ADB



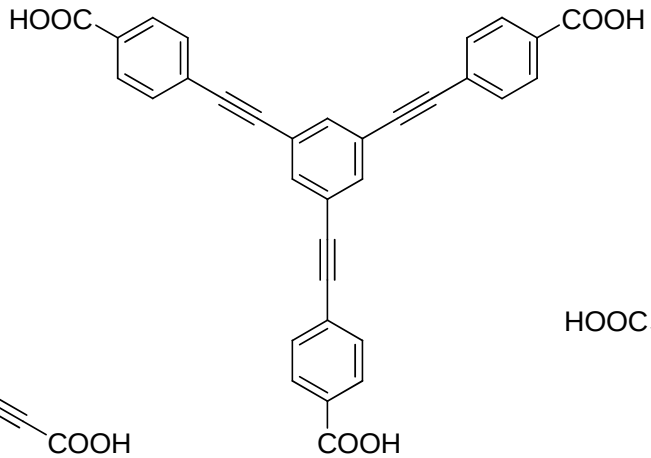
MTATB



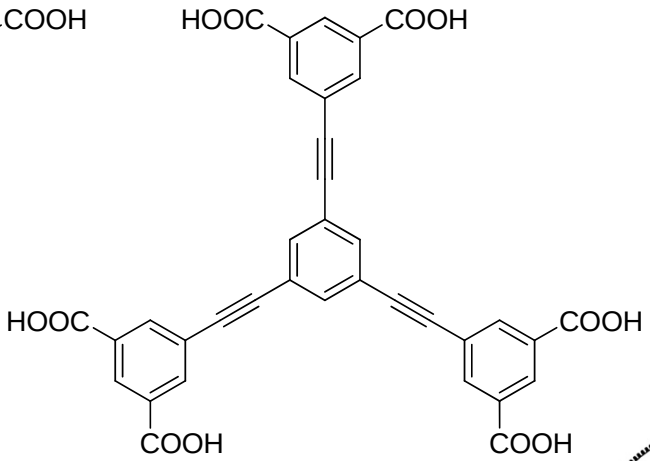
BTTC



BTTP

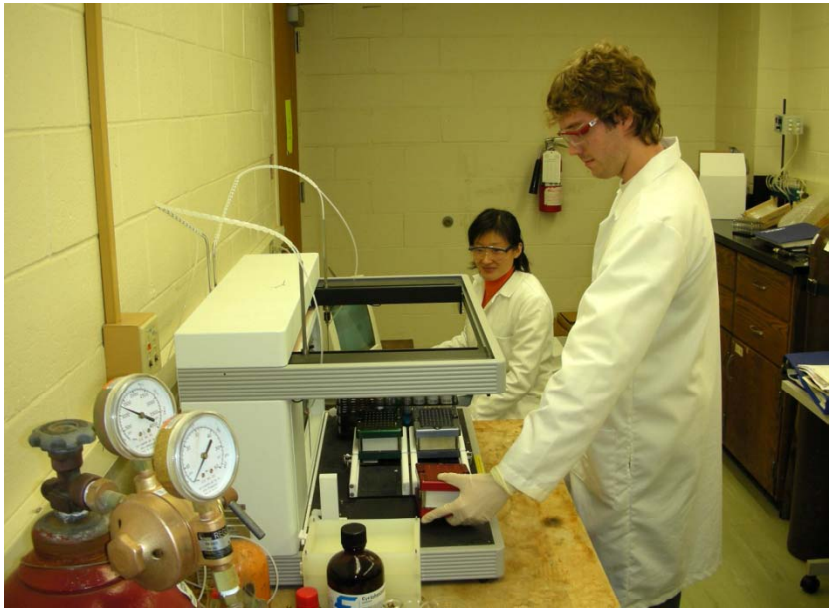


BETC



BYP

Process of combinatorial approach in the synthesis of MOFs



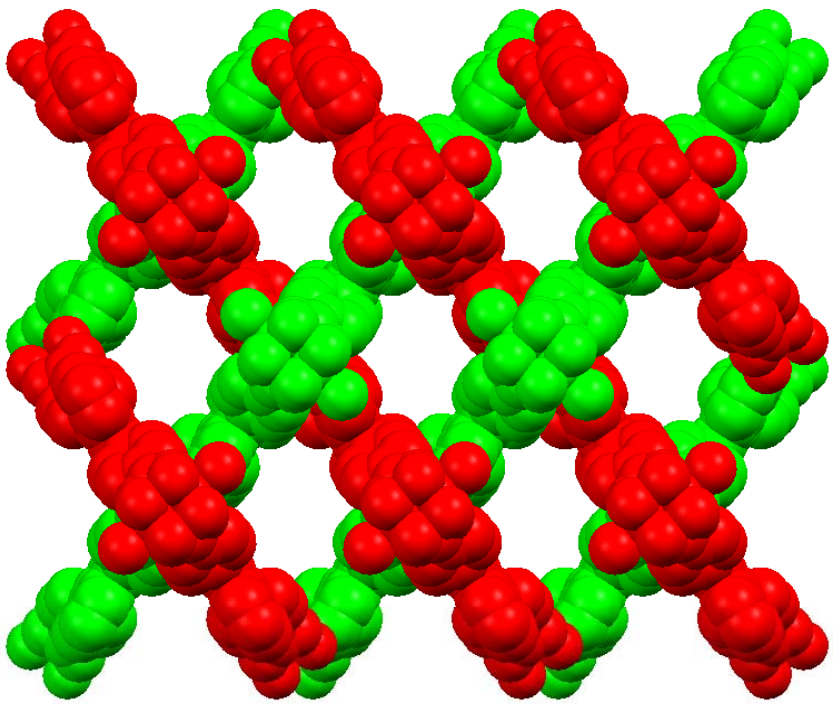
Robot working station for combinatorial chemistry

Obtained products in reaction rack

New MOFs synthesized

- BTTP + M(II) → decompose
- MTABT + Cu(II) → Cu-MOF (unstable)
- BETC + Cu(II) → Cu-MOF (unstable)
- ADB + Cu(II) → PCN-25
- BTTC + Cu(II) → PCN-50
- BTTC + Cd(II) → PCN-51
- BYP + Cu(II) → PCN-61

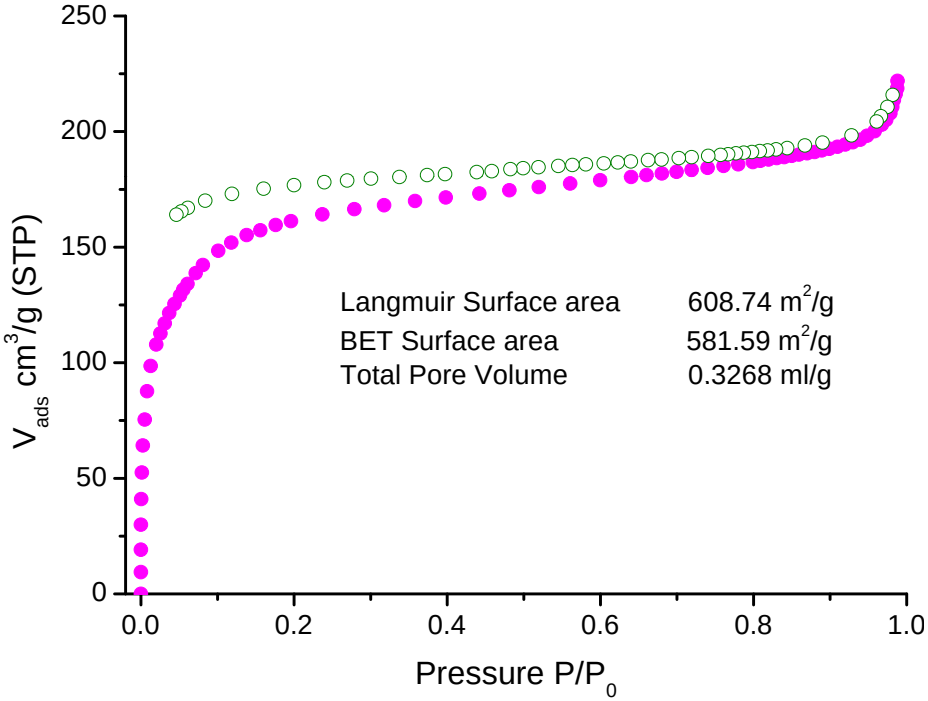
Crystal structure of PCN-25

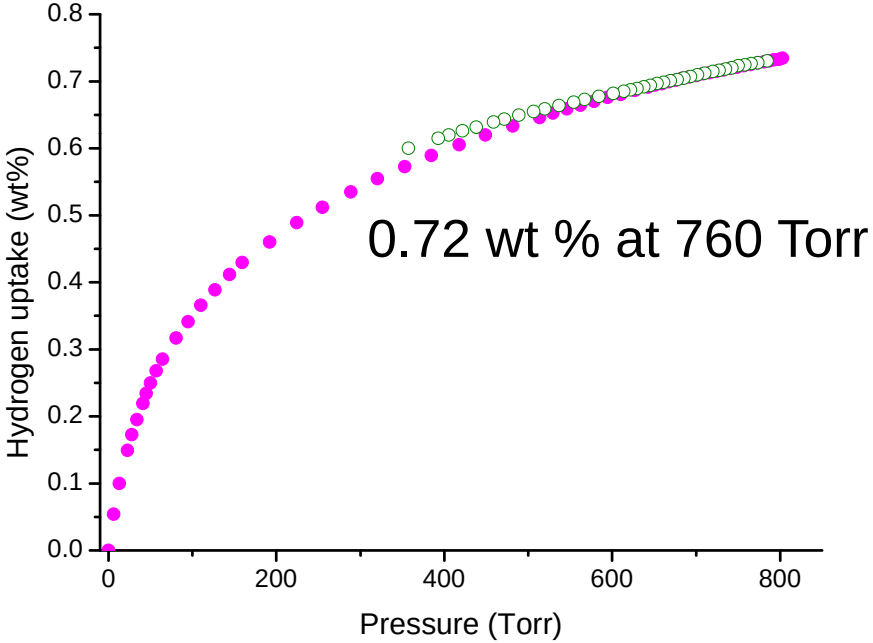


packing model

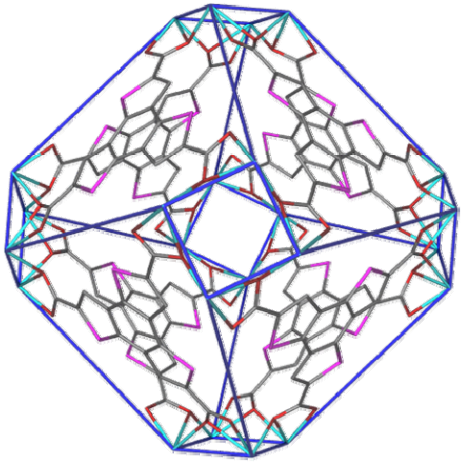
PCN-25 possesses a two-fold interpenetrated (4,4) topology structure.

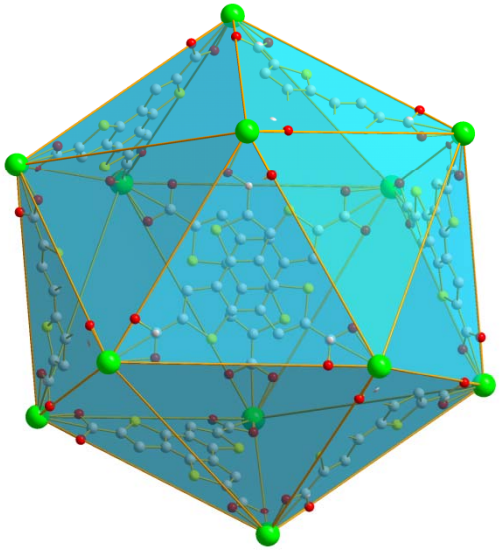
Gas Adsorption Properties of PCN-25

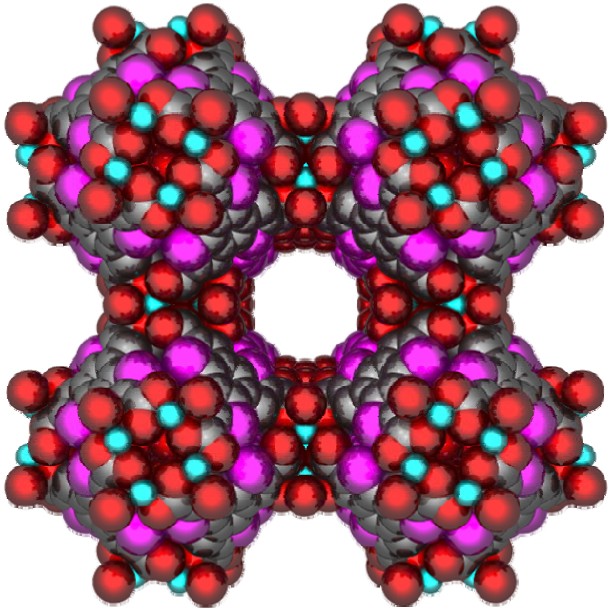




Crystal structure of PCN-51

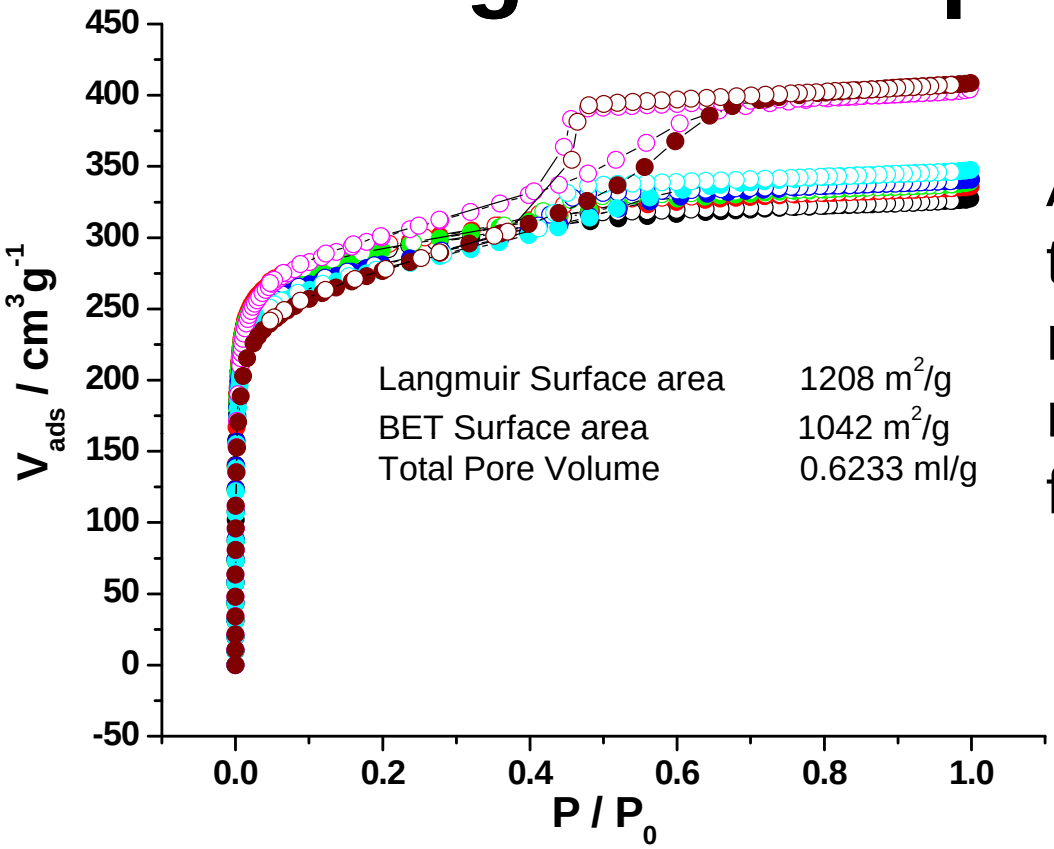






PCN-51 is a stable meso-MOF. Every 12 tritopic ligands connect 6 tetranuclear SBUs to form a twisted truncated octahedral cage. Every cage connects 6 other cages through sharing tetranuclear SBU vertexes, forming a large icosahedron leading to a MOF with 3D channels.

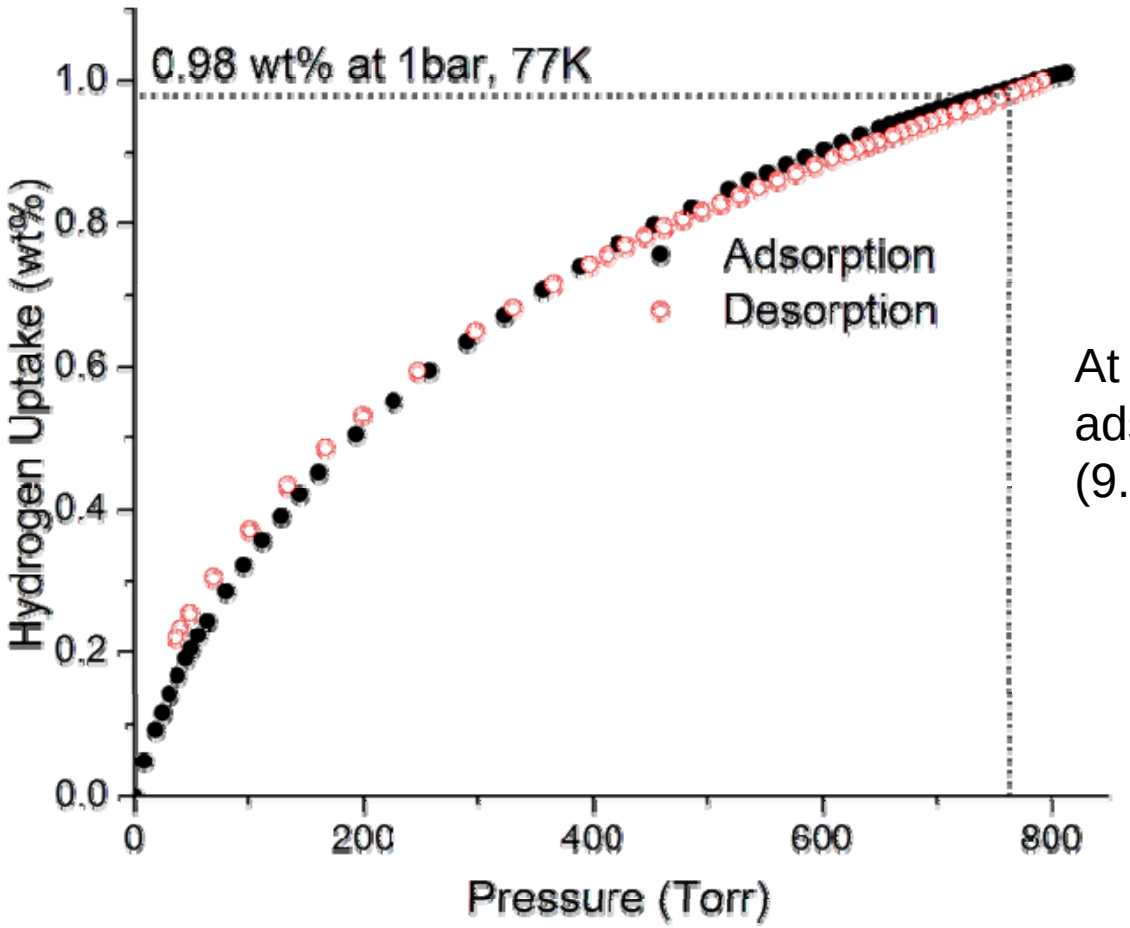
Nitrogen Adsorption of PCN-51



A step by step transformation from microporous to mesoporous metal-organic framework.

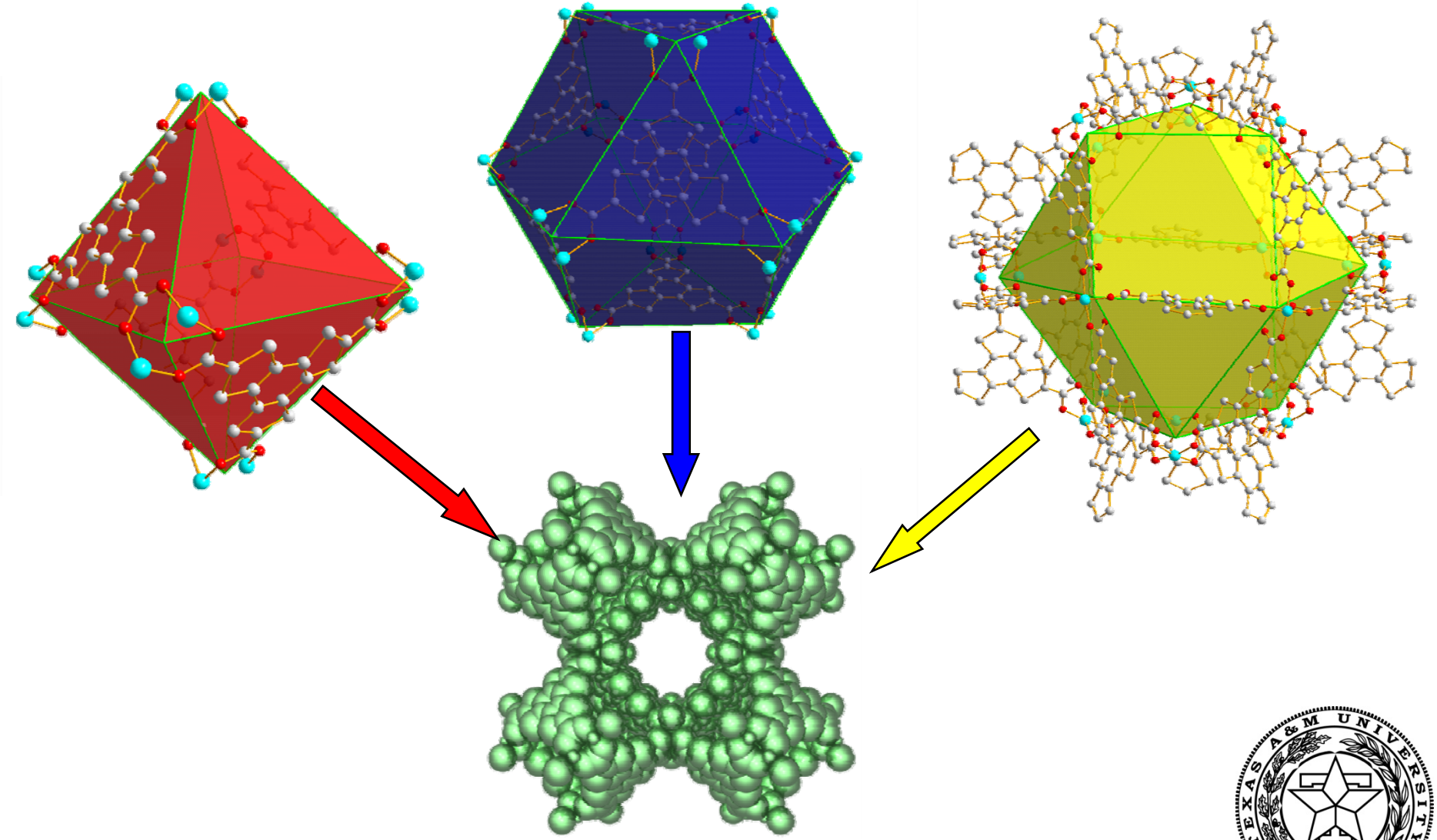
Nitrogen sorption isotherm of PCN-51 at 77 K (solid: adsorption; empty: desorption) in difference activation temperatures. (• 80 °C, • 100 °C, • 120 °C, • 150 °C, • 180 °C, • 200 °C, • 230 °C)

Hydrogen Adsorption of PCN-51

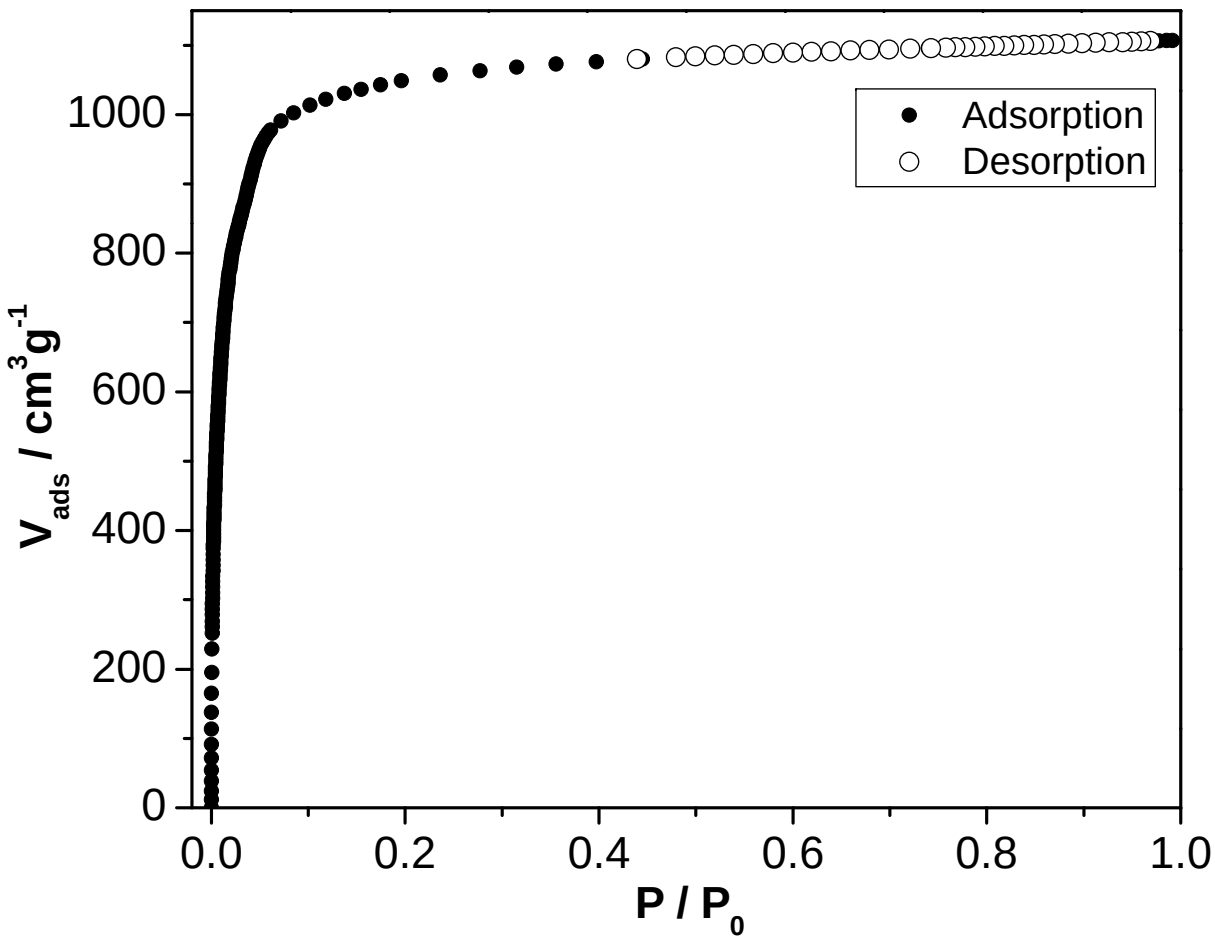


At 760 Torr and 77 K, PCN-51 adsorbs 0.98 wt % hydrogen (9.88 g/L)

Crystal structure of PCN-50



Nitrogen Adsorption of PCN-50

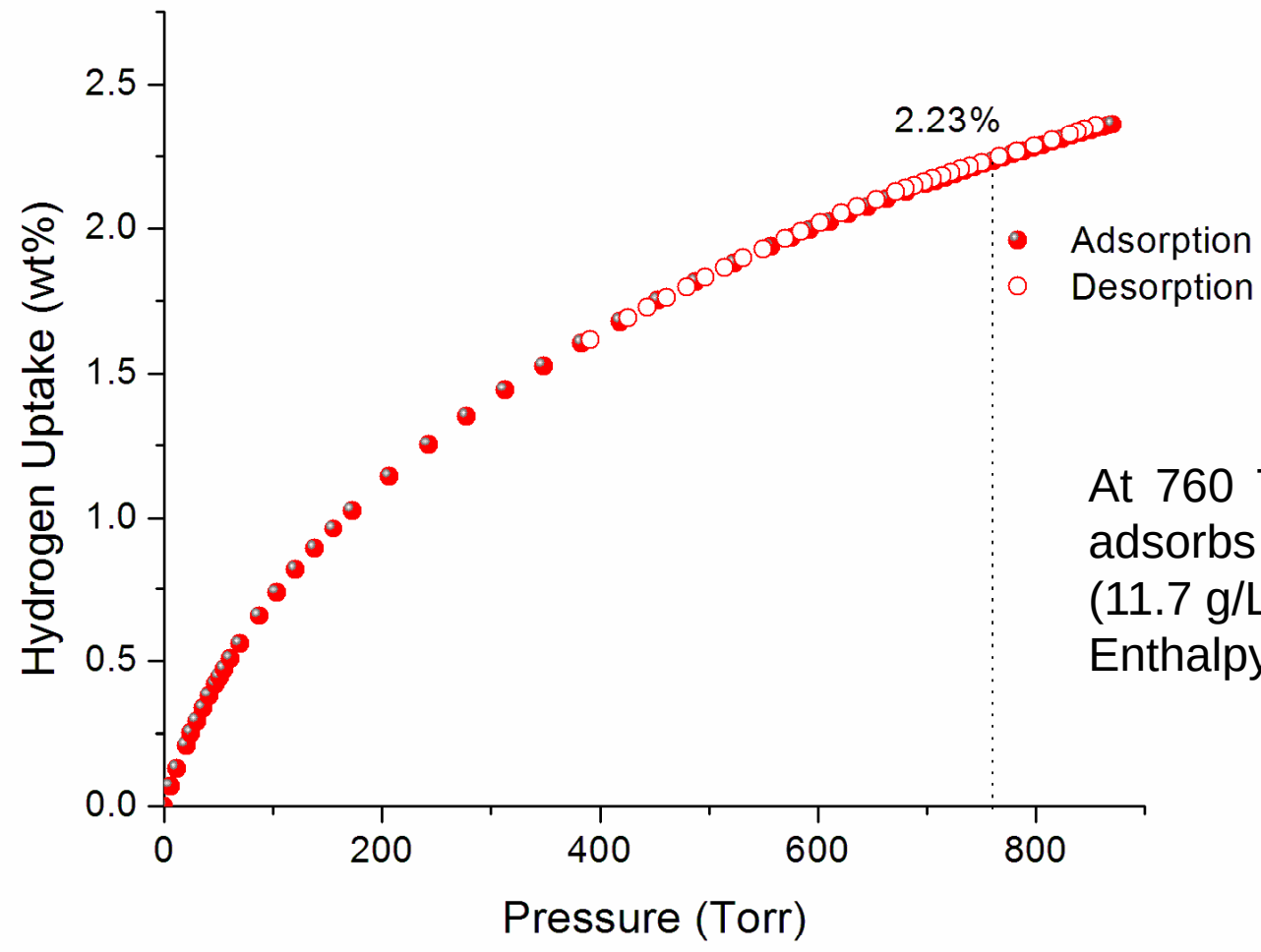


Langmuir surface area
4520 m^2/g

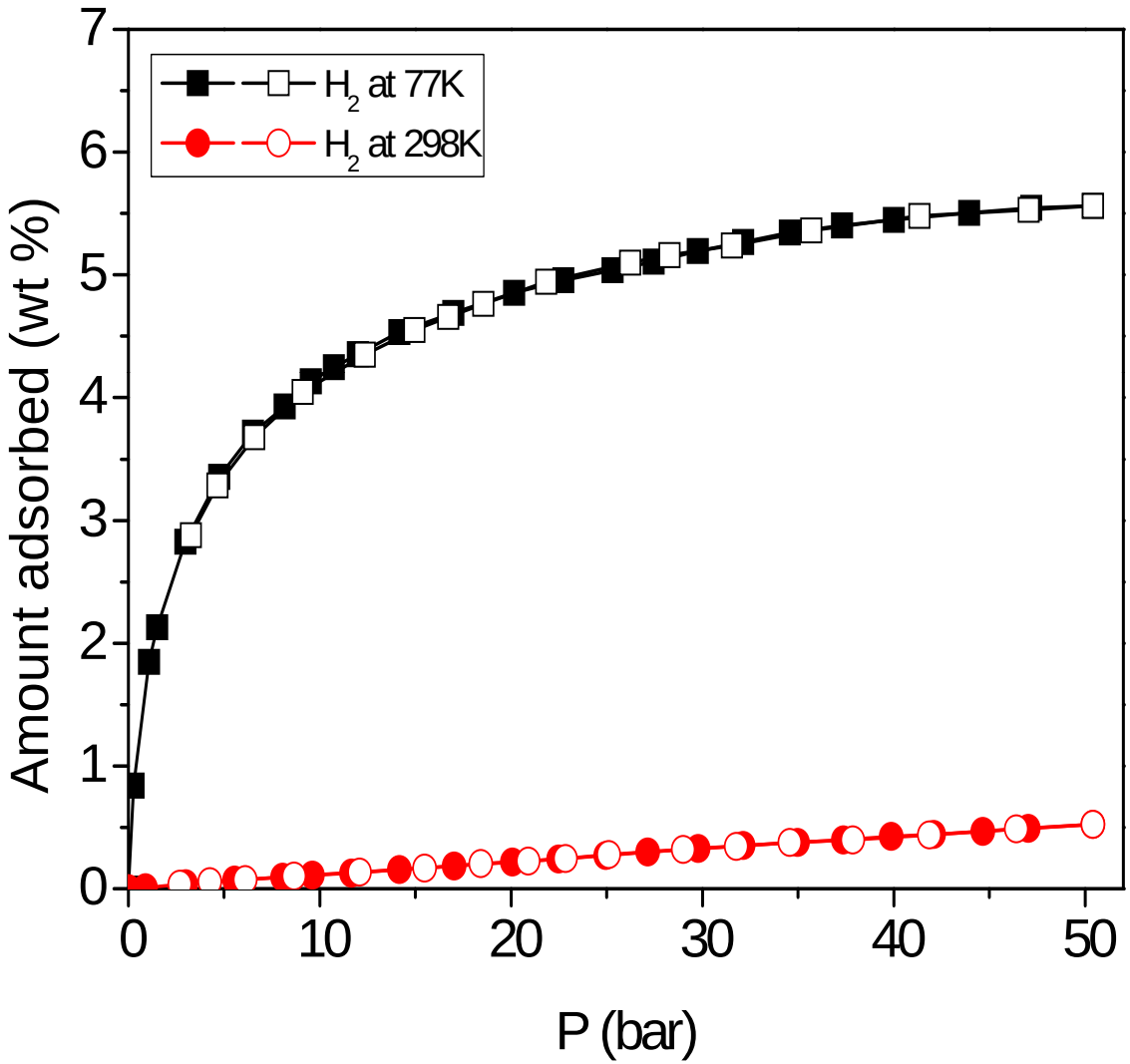
BET surface area
3678 m^2/g

Total Pore Volume
1.71 ml/g

Hydrogen Adsorption of PCN-50



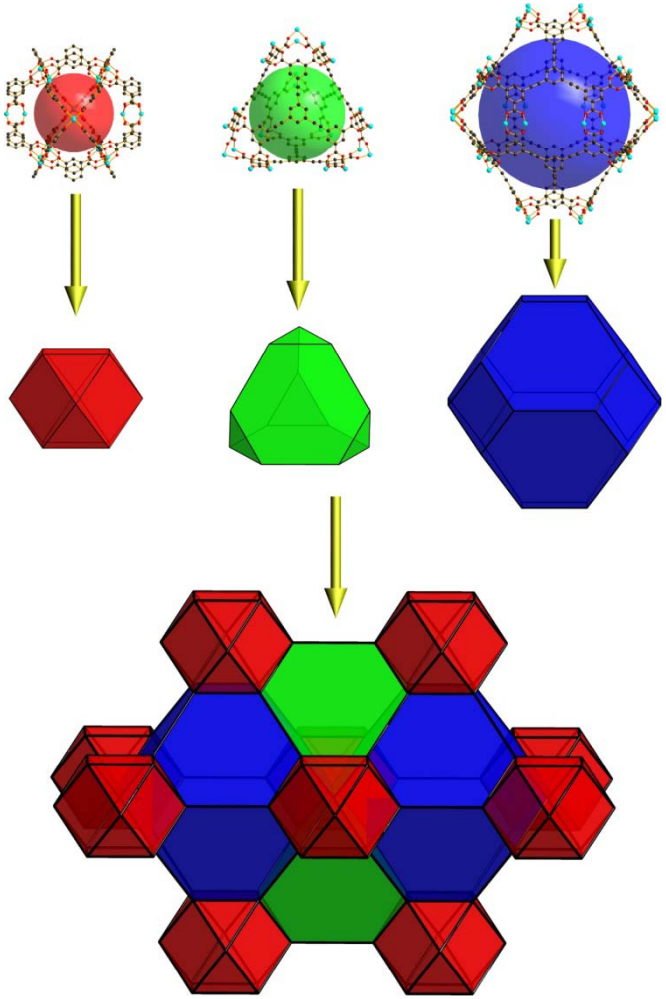
At 760 Torr and 77 K, PCN-50 adsorbs 2.23 wt % hydrogen (11.7 g/L)
Enthalpy ~6 kJ/mol

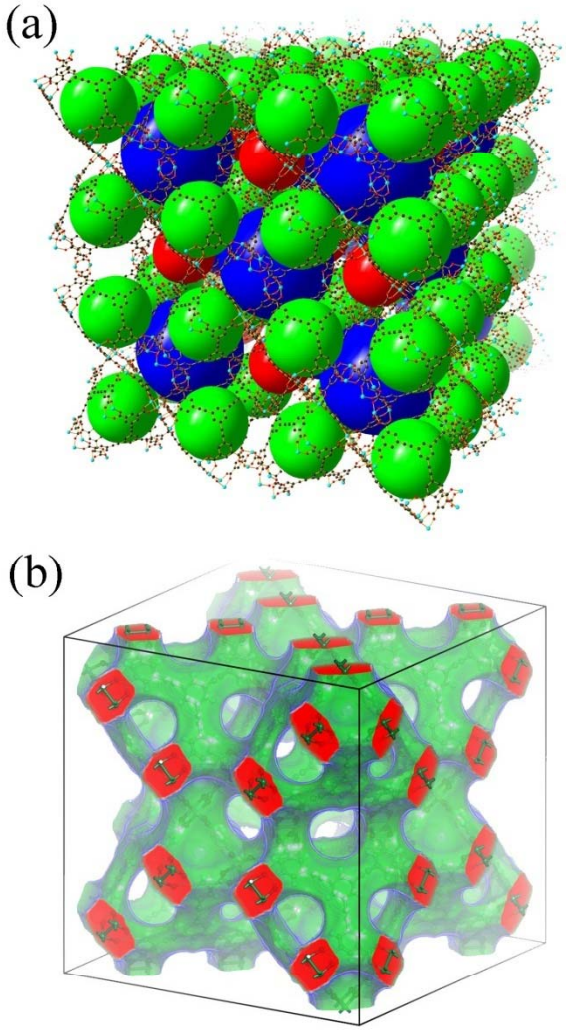


At 50 bar and 77 K, PCN-50 adsorbs 5.56 wt % hydrogen (29.1 g/L)

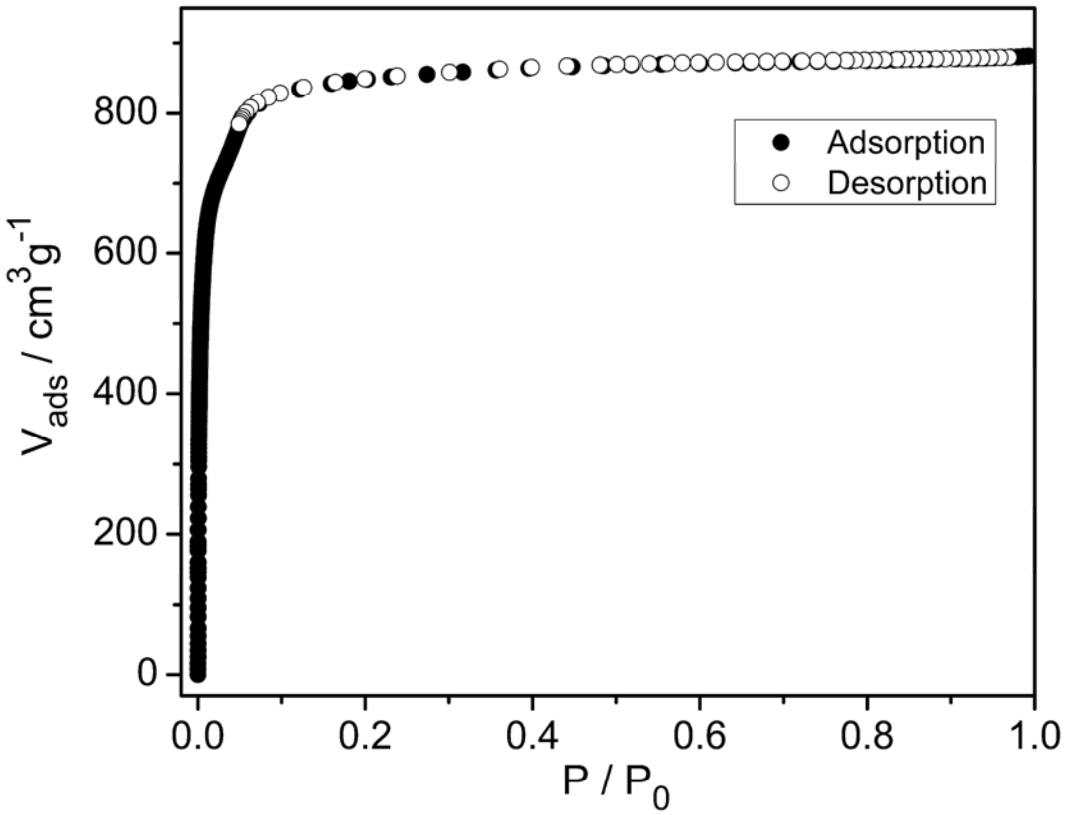
At 50 bar and 298 K, PCN-50 adsorbs 0.53 wt % hydrogen (2.7 g/L)

Crystal structure of PCN-61





Nitrogen Adsorption of PCN-61

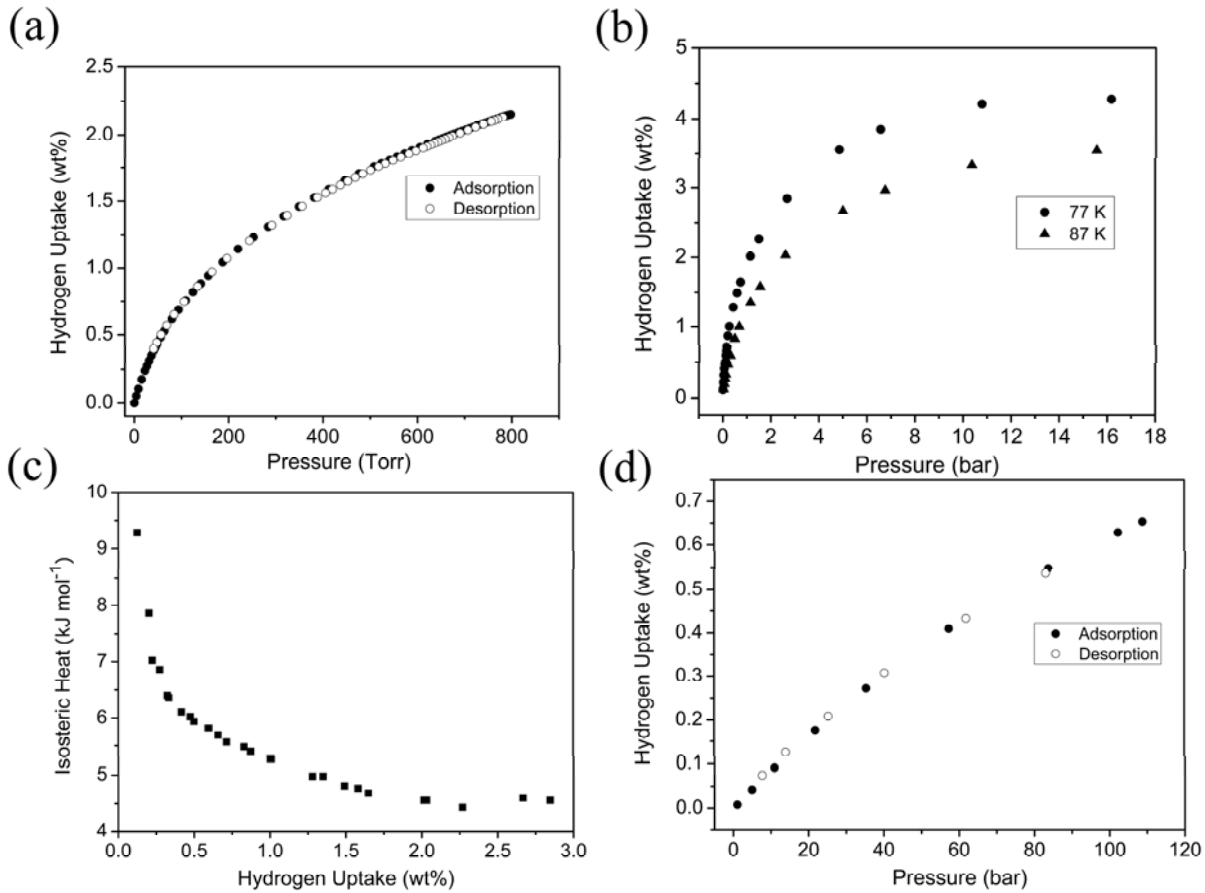


Langmuir surface area: 3509 m^2 g^{-1}

BET surface area: 2936 m^2 g^{-1}

Total pore volume: 1.36 mL g^{-1}

Hydrogen Adsorption of PCN-61



2.11 wt% at 77 K, 760 Torr

4.28 wt% at 77 K, 16 bar

0.65 wt% at 298 K, 109 bar

Isosteric heat of sorption: 4.5-9.3 kJ mol^{-1}

Hydrogen uptake and isosteric heat of sorption in PCN-61 (a: low pressure hydrogen sorption isotherms at 77 K; b: high pressure hydrogen adsorption isotherms at 77 and 87 K; c: isosteric heat of sorption based on data in b; d: high pressure hydrogen sorption isotherms at 298 K)

Vibrational Spectroscopy of Hydrogen

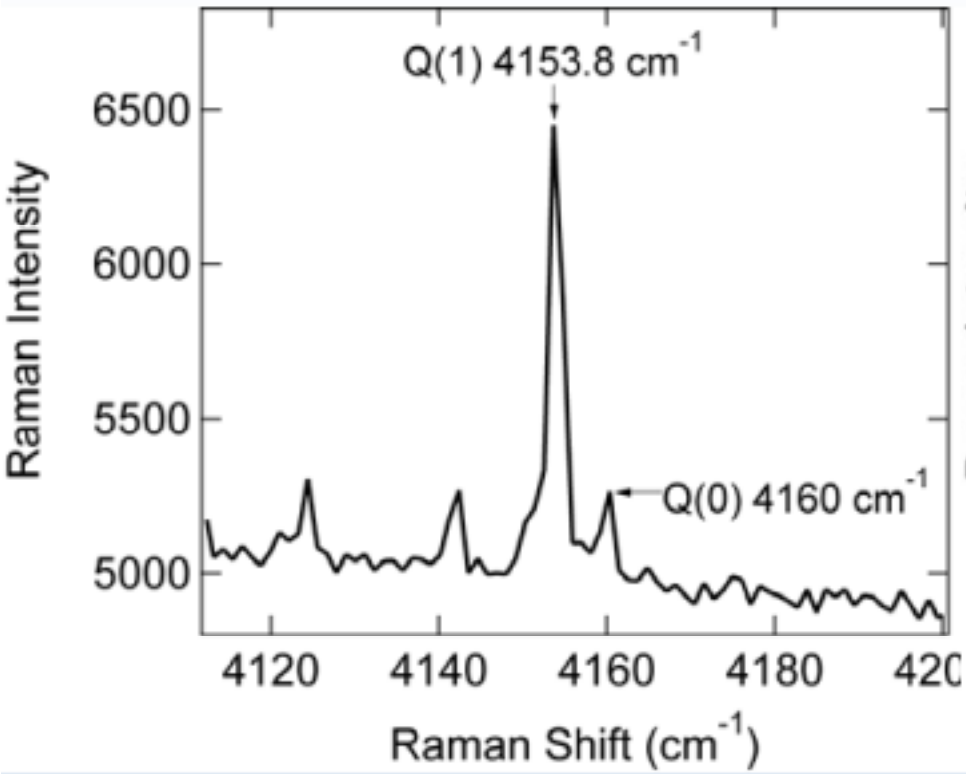
Raman

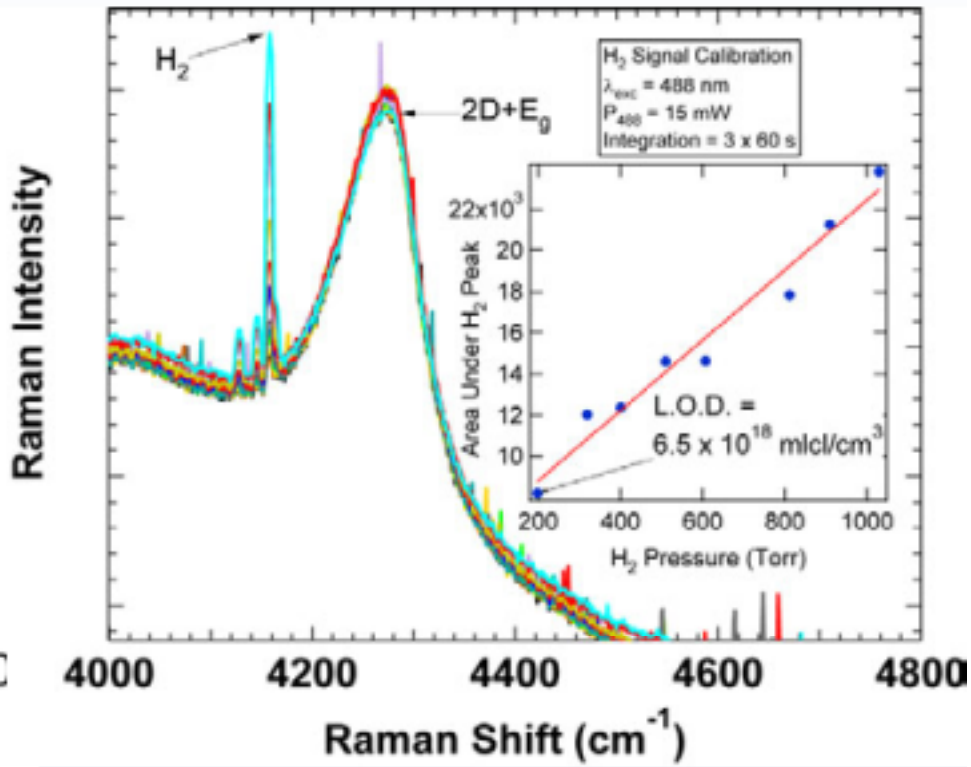
- H_2 in gas phase is Raman active due to large polarizability
- Vibration-rotation spectrum:
  - Q branch: $\Delta\nu = +1$, $\Delta J = 0$
  - S branch: $\Delta\nu = +1$, $\Delta J = 2$
- Spin information:
  - Ortho H_2 – spins parallel, $J = 1$ ($Q(J) = Q(1)$)
  - Para H_2 – spins paired, $J = 0$ ($Q(J) = Q(0)$)
- Strength of adsorption inferred from shifts relative to gas-phase H_2
  - Because of overlap with gas-phase peak, deconvolution often needed

Infrared

- Homo-nuclear diatomic molecules, e.g. gas-phase H_2 are IR-inactive
- IR absorption induced by inter-molecular interactions
  - Collision-induced (high P or near T_c)
  - Adsorbent interactions create a bond dipole
- ΔE_{ad} from shifts relative to H_2 gas
  - Because no gas peak, no deconvolution necessary
  - Metal sites, carbon sites, Lewis sites, etc. give well-separated shifts

Gas-phase H_2 and SWNTs



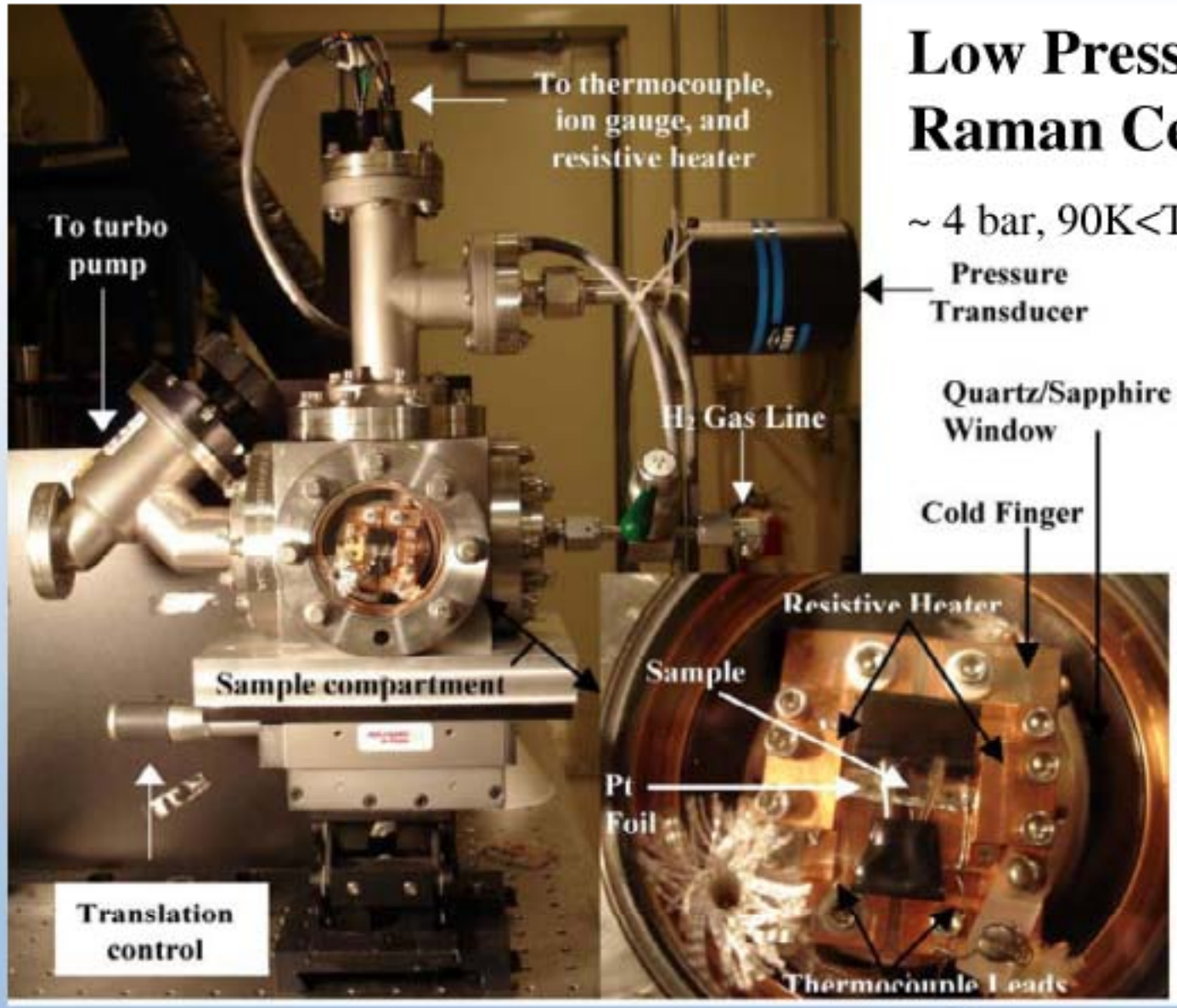


a) Raman spectrum of H_2 gas in the Q branch region at room temperature.

b) Raman spectra of hydrogen gas over a SWNT sample with increasing hydrogen gas pressure; inset – Area under H2 Q(1) peak as a function of hydrogen gas pressure.

L.O.D. determined by calibrated volume

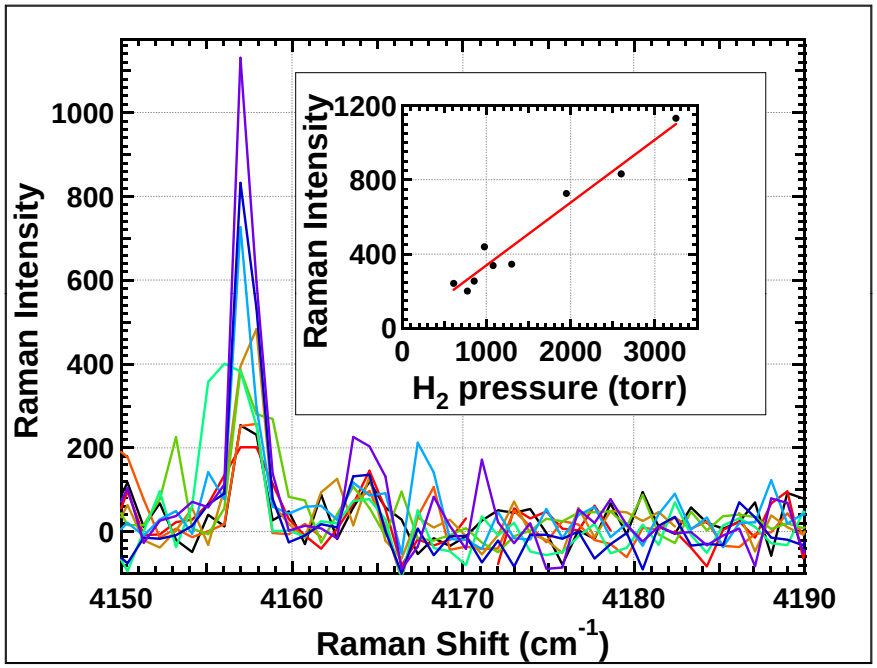
Pressurizable in-situ Raman cell

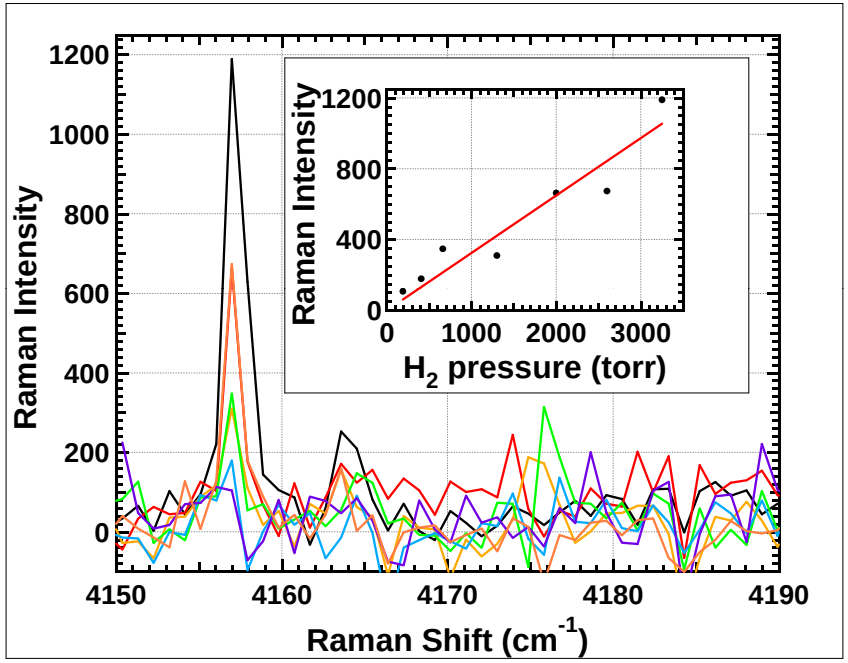


Low Pressure Raman Cell

~ 4 bar, 90K<T<500K

Peak Raman intensity for H2 Q(1) peak as function of pressure





(LEFT) HKUST-1 Raman spectra of H2 Q(1) peak for increasing hydrogen pressures at ~300 K. (inset) Peak Raman intensity for H2 Q(1) peak as function of pressure. (RIGHT) Same as LEFT, taken at ~90 K.

Summery Table

Comparison of Hydrogen Uptakes of PCN-25,50,51,61					
Material	ΔH_{ads} (kJ/mol)	H_2 Adsorption			
		Gravimetric H_2 uptake (wt %)	Volumetric H_2 uptake (g/L)	T (K)	P (bar)
PCN-25	-	0.72	5.9	77	1.0
PCN-51	-	0.98	9.9	77	1
PCN-50	~6.0	2.23	11.7	77	1
		3.6	18.8	77	2
		5.56	29.1	77	50
		0.1	0.5	298	2
		0.53	2.7	298	50
PCN-61	~4.5-9.3	2.11	11.8	77	1
		4.28	23.9	77	16.1
		0.65	3.6	298	108.9

Results for Combinatorial Synthesis

- Six new ligands have been synthesized
- Four stable new MOFs based on those ligands have been synthesized through combinatorial method
- The hydrogen uptake capacity of four MOFs samples have been measured
- A spectroscopic method for fast recognition/screening of potential hydrogen storage materials is under investigation in NREL

Acknowledgments

- Collaborators
  - Guido Pez, Alan Cooper (Air Products)
  - Mike Heben, Philip Parilla (NREL)
  - Jeff Long (Berkeley)

- Funding
  - NSF (NER, CAREER)
  - ACS PRF
  - Res Corp (RI, Cottrell)
  - DOE
  - DOD
  - Air Products
  - Ohio Board of Regents
  - Miami University
  - Texas A&M Research Foundation