Synthetic Design of New Metal-Organic Framework Materials for Hydrogen Storage

Pingyun Feng

Department of Chemistry
University of California at Riverside

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Project ID: BES007

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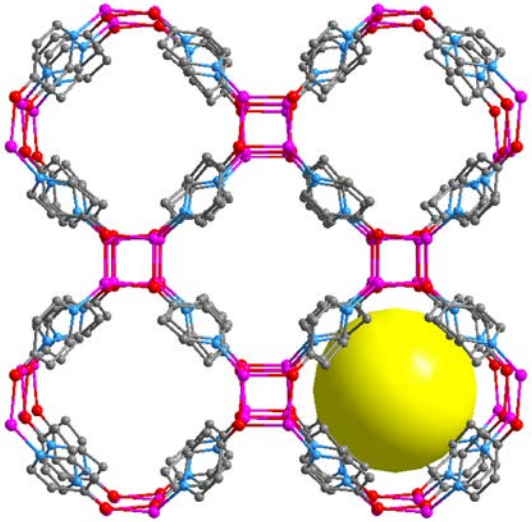
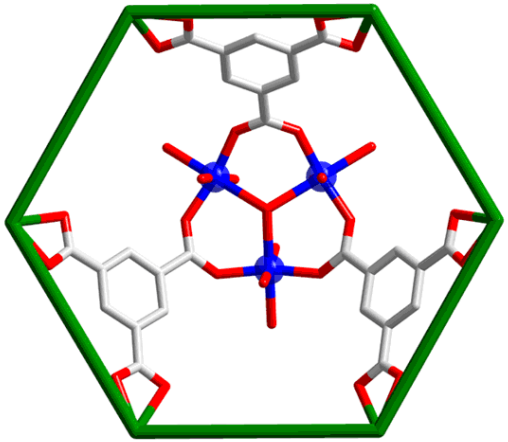
Overall Objective

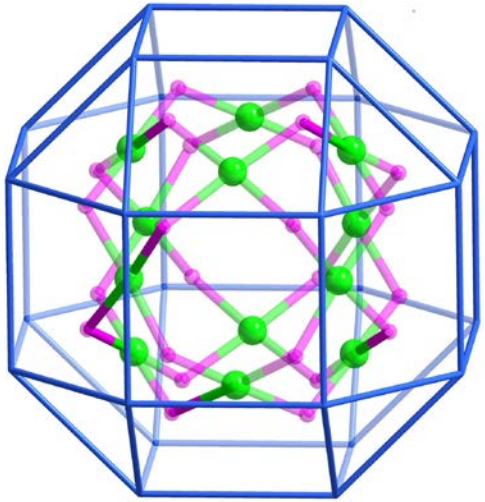
Synthesize new metal-organic framework materials (MOF) with desirable chemical and geometric features as hydrogen storage materials.



Porous materials from lightweight elements



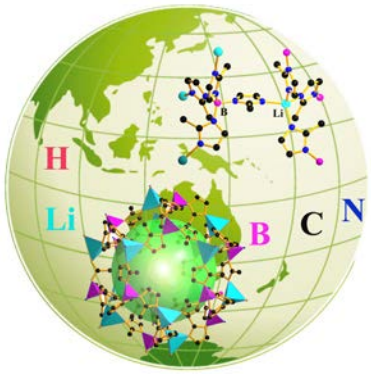
Porous materials with exotic active binding sites

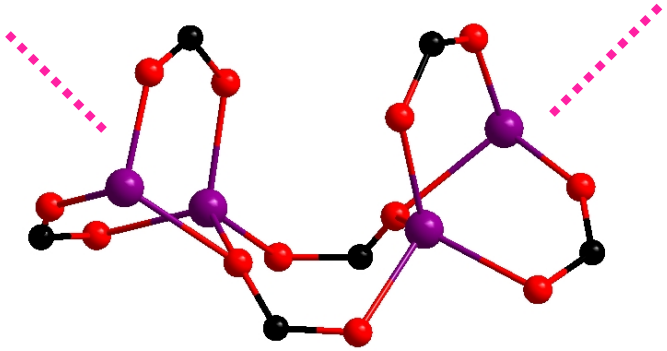


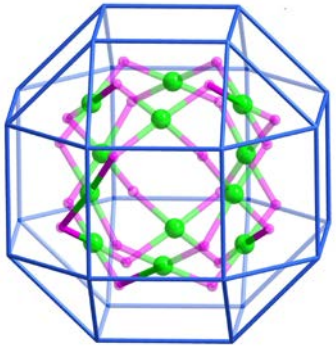
Nested cages with partitioned pore space

Strategies and Specific Goals

- Using lightweight elements (Li, B…) to help with gravimetric storage capacity.





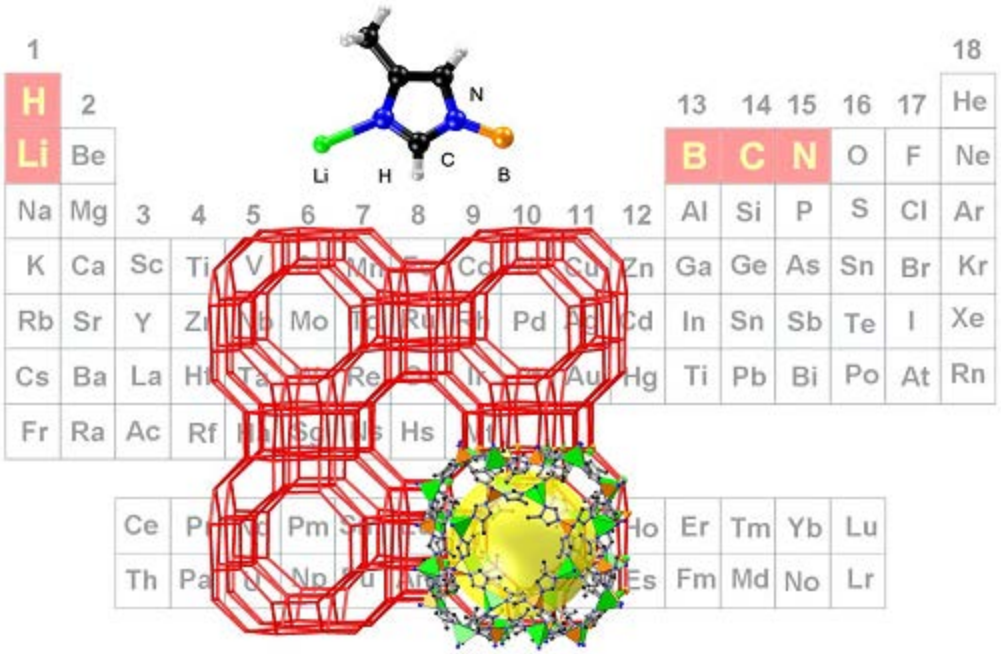


- Creating active binding sites on metals and ligands to increase solid-gas interactions to enhance gas uptake.

- Partitioning the pore space to create multiple domains with pore size commensurate with that of gas molecules for enhanced solid-gas interactions.

How to Get Lighter?

- MOFs are mostly made from group 12 (Zn, Cd), 3d- and 4f-elements.



- Some examples of MOFs with lightweight elements such as Mg^{2+} (especially MOF-74-Mg) and Al^{3+}.

- Few crystalline porous materials based on lightweight elements from Period 2 (Li and B) are known prior this project.

Porous Materials from Lightweight Elements

- Lithium Boron Imidazolate Frameworks (BIF)

  Based on the concept of charge-complementary nodes

- Lithium Imidazolate Frameworks (Li-ZIF)

  Based on the concept of charge-complementary links

- Lithium Aryloxide Cluster Frameworks (Li-PhO)

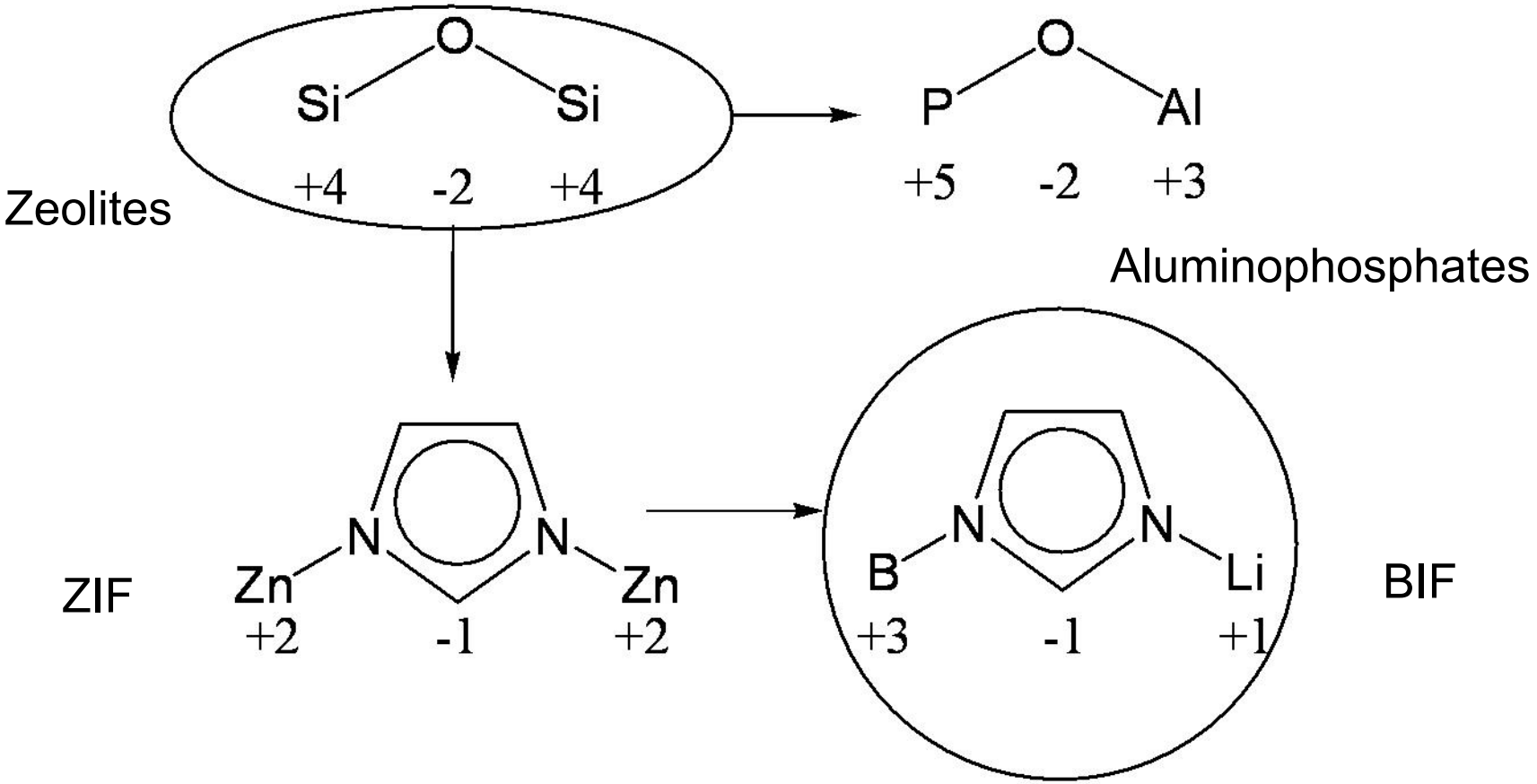
  Based on a ligand with complementary and synergistic binding sites

- Lithium Carboxylate Frameworks

- Magnesium Carboxylate Frameworks

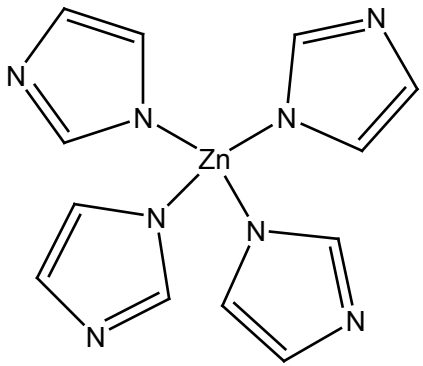
How to Get Lighter?
Boron Imidazolate Framework (BIF)

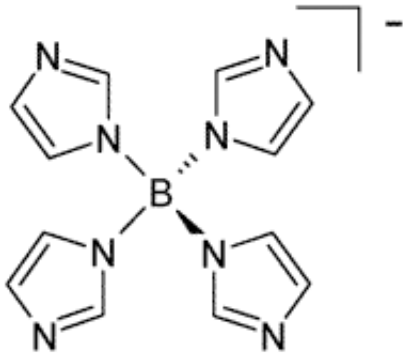
- Using Charge-Complementary Tetrahedral Cations

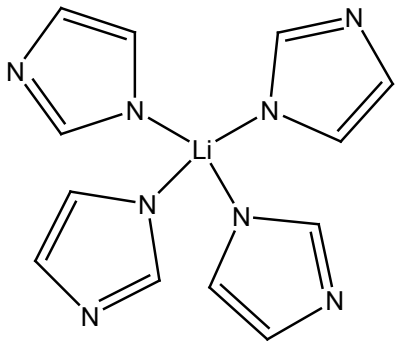


ZIF = Zeolitic Imidazolate Frameworks (Yaghi et al)

Major Difference between $LiB(im)_4$ (**BIF**) and $Zn(im)_2$ (**ZIF**)







ZIF: One bond type:
Zn-N coordination bond only

BIF: Two bond types:

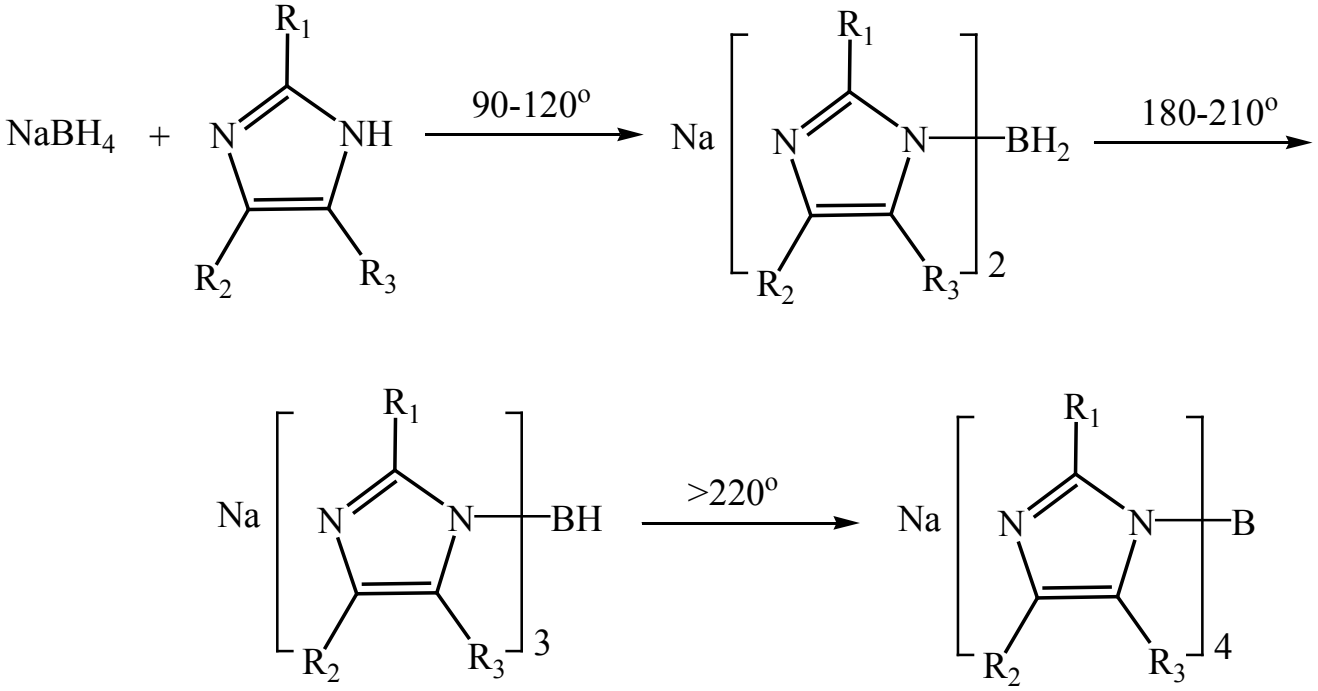
B-N	Li-N
covalent bond	coordination bond

$$Zn^{2+} + \text{imidazole} \xrightarrow{\text{solvent}} Zn(im)_2$$

$$B^{3+} + Li^{+} + \text{imidazole} \xrightarrow{\text{solvent}} \text{No Reaction}$$

Solid State Synthesis before Self-Assembly

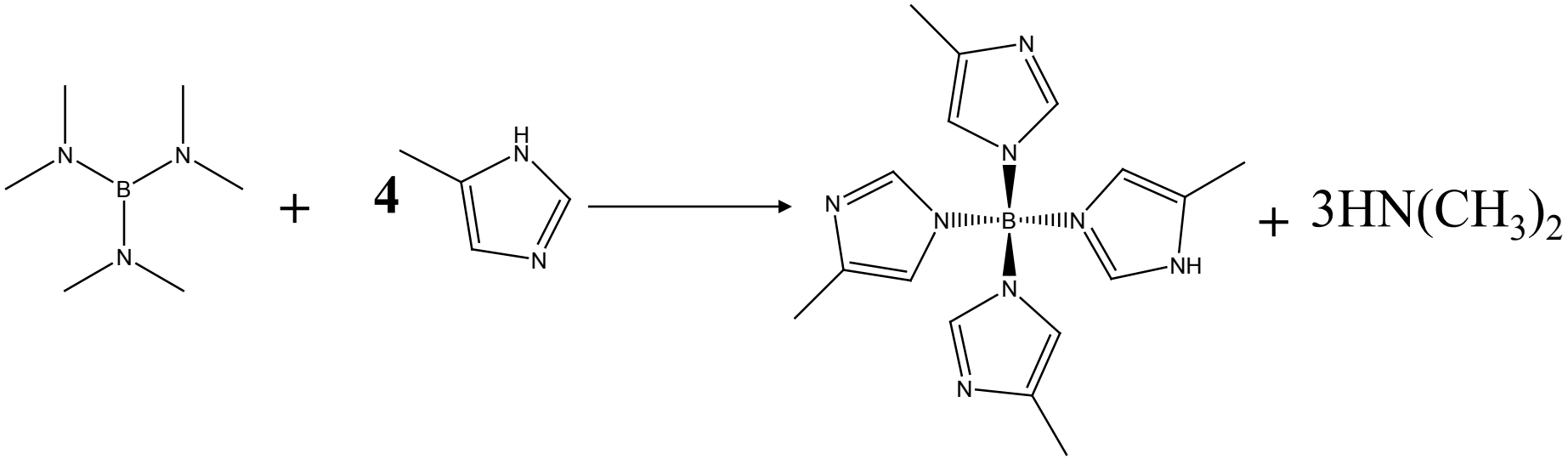
- $[B(im)_4]^-$ complexes can be made by substituting hydride anion H^- in in borohydride BH_4^- with imidazolate anions.



- Depending on the temperature, both tri-substituted $Na[BH(im)_3]$ and tetra-substituted $NaB(im)_4$ can be made (sodium form).

Solution Synthesis before Self-Assembly

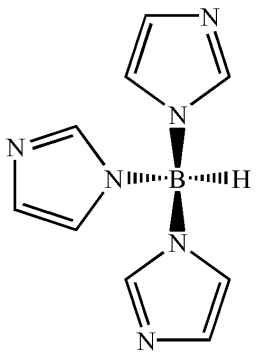
- The acidic form, $HB(im)_4$, can also be synthesized using a solution method by reaction between tris(dimethylamino)borane and imidazole.



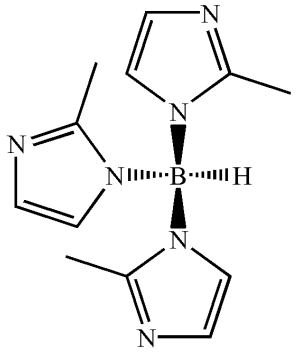
New Tripodal and Tetrahedral Boron Building Blocks

- A large number of boron imidazolate complexes have been made in this work.

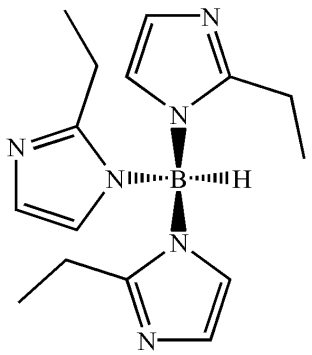
tripodal



$BH(im)_3^-$

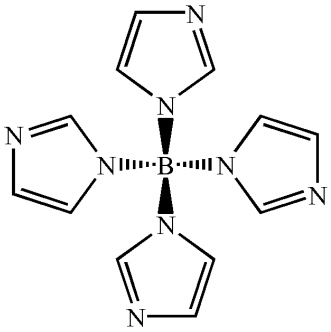


$BH(mim)_3^-$

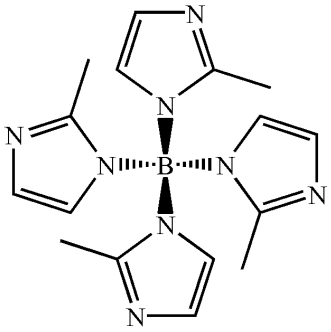


$BH(e\text{-}im)_3^-$

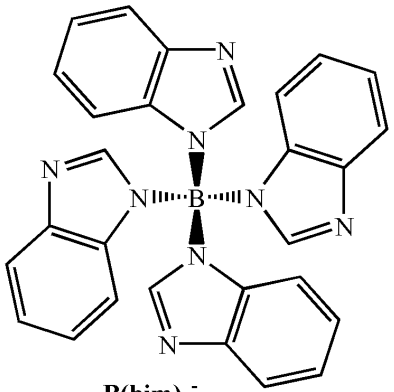
tetrahedral



$B(im)_4^-$



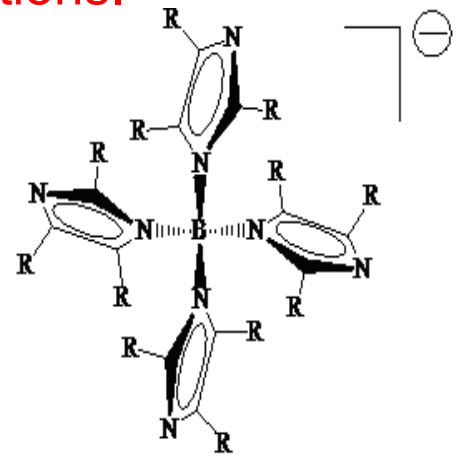
$B(mim)_4^-$



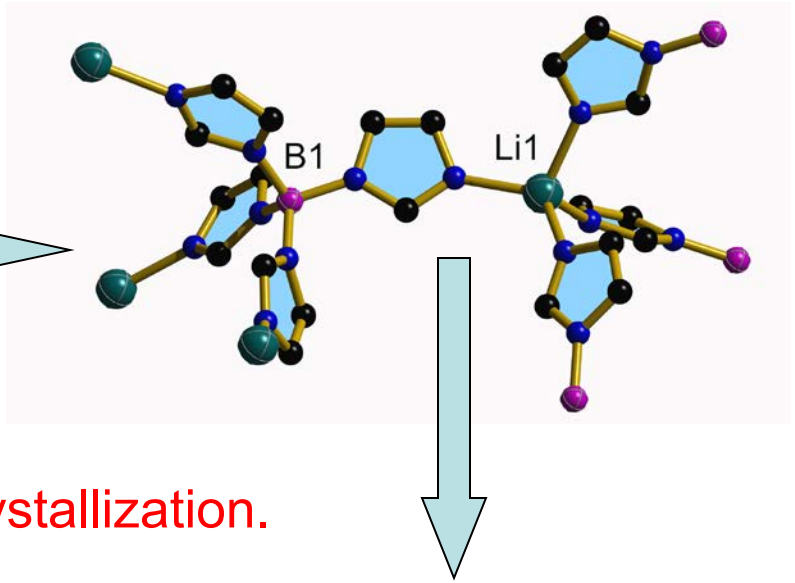
$B(bim)_4^-$

Solvothermal Assembly with Li^+

- During the second step, $[B(im)_4]^-$ complexes are assembled with selected metal cations into porous frameworks under solvothermal conditions.



Li^+ or Cu^+



- Solvents are also very critical for the crystallization.

◊ 2-amino-1-butanol/CH_3CN

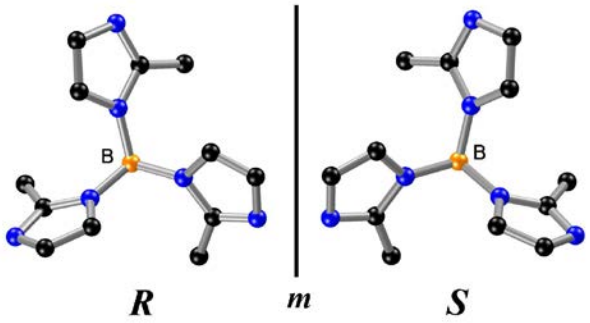
◊ 2-amino-1-butanol/C_6H_6

◊ DMF/CH_3CN

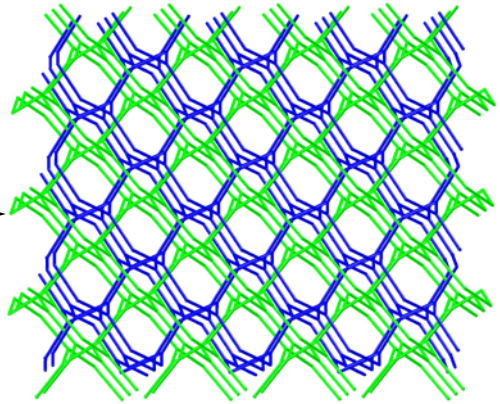
Angew. Chem. Int. Ed. 2009, 48, 2542

J. Am. Chem. Soc. 2009, 131, 6111

Potential Open Lithium Sites in 3-Connected 3-D Frameworks

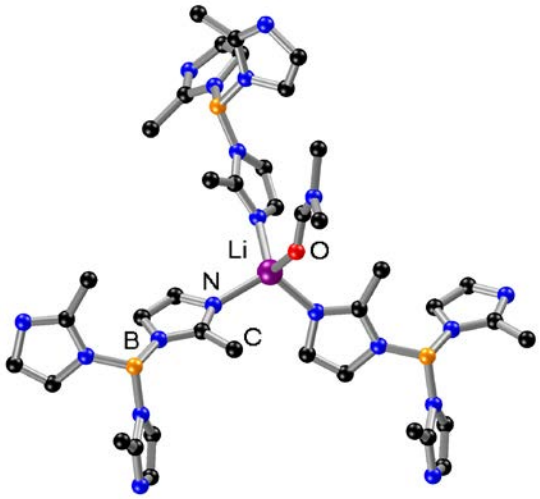


Li_2S

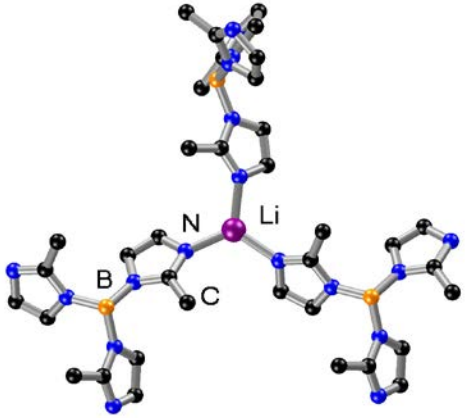


BIF-10

Interpenetrating ths-type net



Tetrahedral Li^+ with one terminating DMF

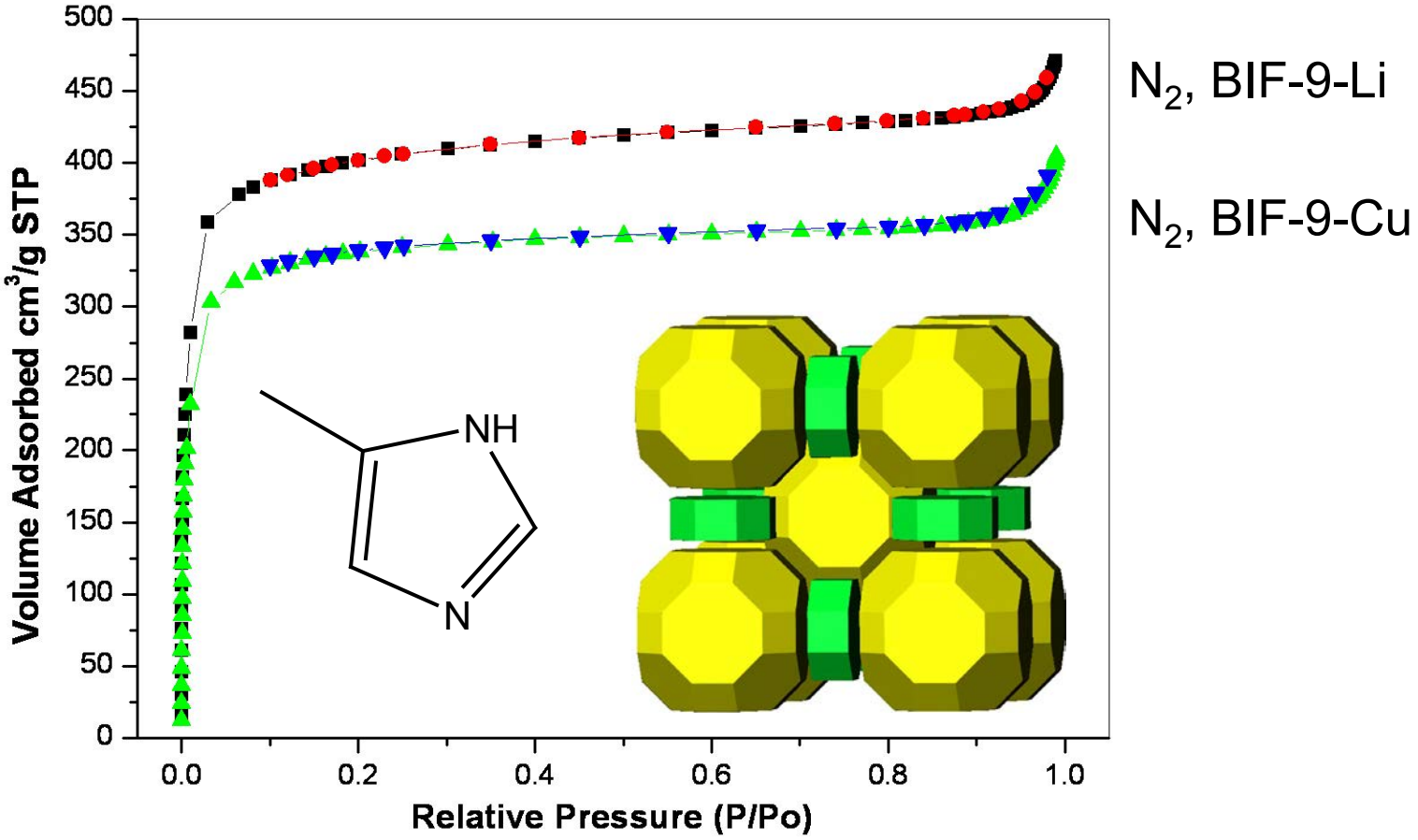


Trigonal-planar Li^+

Chem. Mater. 2009, 21, 3830

Gas Sorption Properties of BIF-9

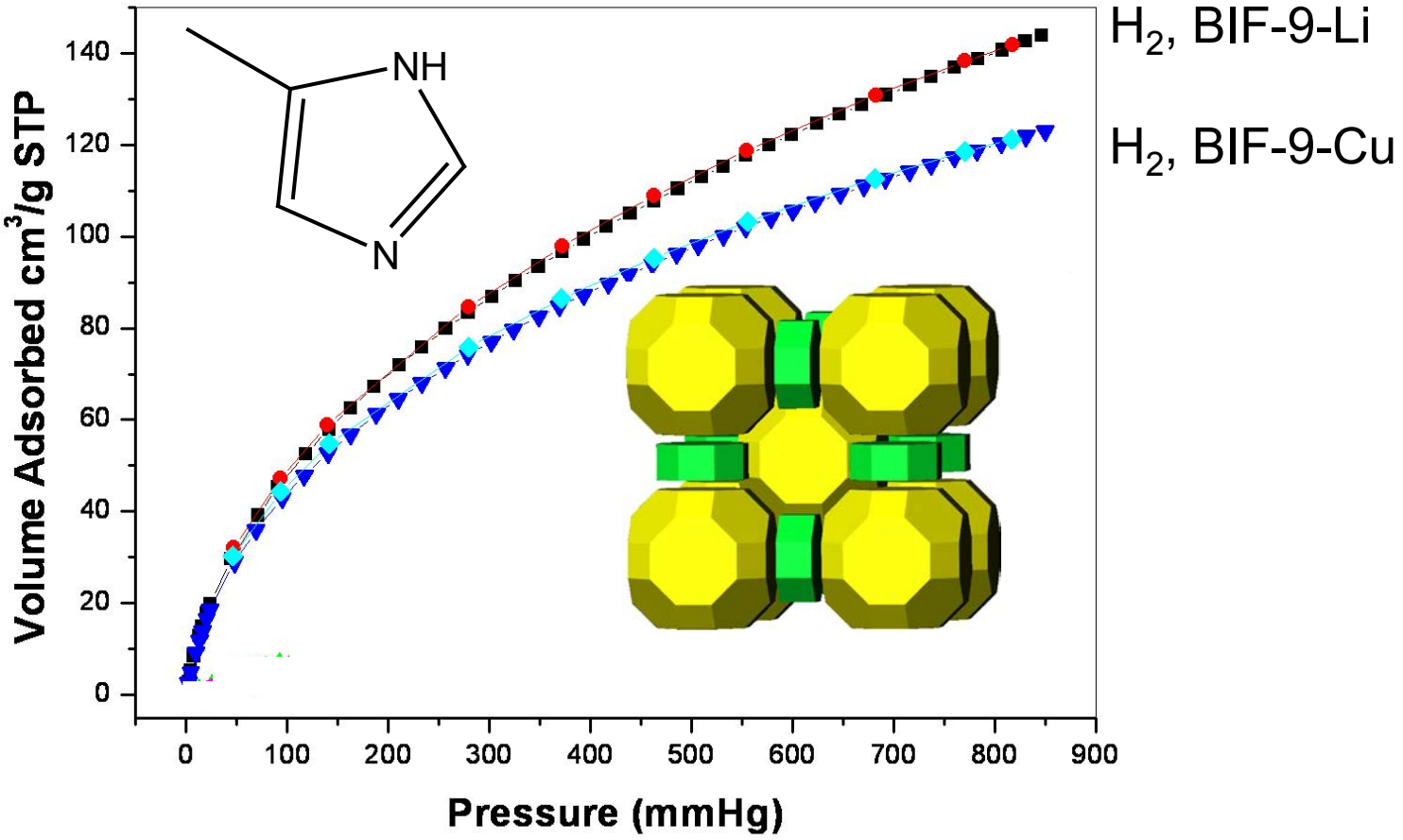
- BIF-9, $LiB(4\text{-mim})_4$ (mim=4-methylimidazolate)



Langmuir surface area for BIF-9-Li: 1818 m^2/g

Gas Sorption Properties of BIF-9

- BIF-9, $LiB(4\text{-mim})_4$ (mim=4-methylimidazolate)



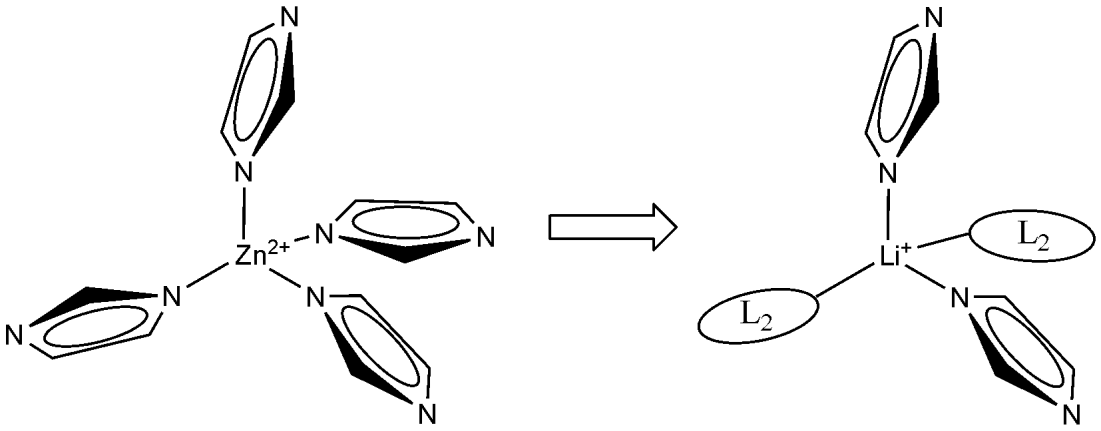
H_2, BIF-9-Li

H_2, BIF-9-Cu

H_2 Uptake at 77K-1atm: 1.4wt%

How to Get Lighter?
Lithium Imidazolate Framework

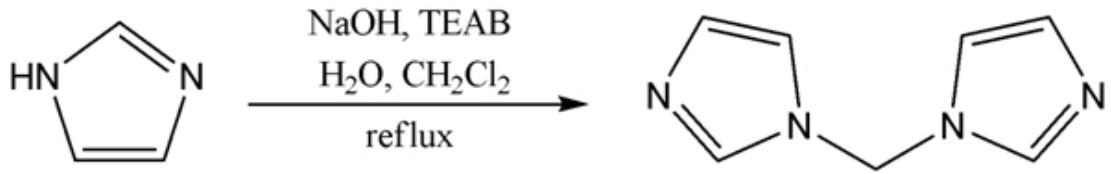
- Using Charge Complementarity of Imidazole Ligands



$Zn^{2+} + 2L_1^-$ $\qquad$ $Li^+ + L_1^- + L_2^0$

(L_1 = imidazole $\qquad$ L_2 = neutral ditopic ligand)

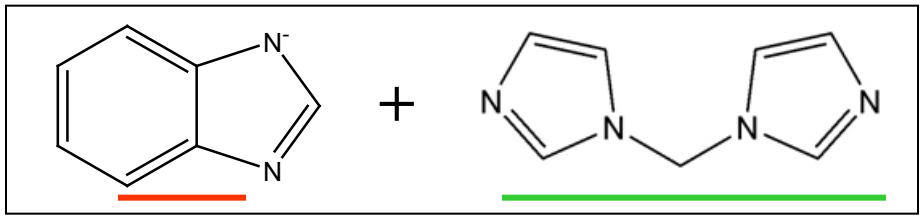
- Both L1 and L2 ligands can be varied.

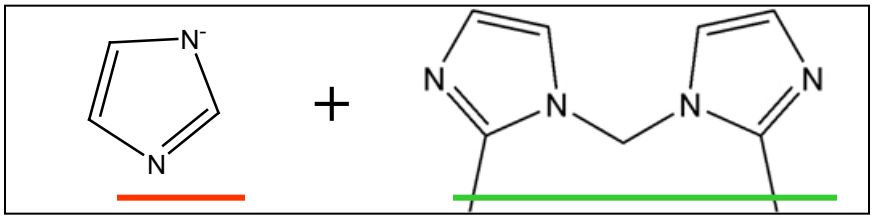


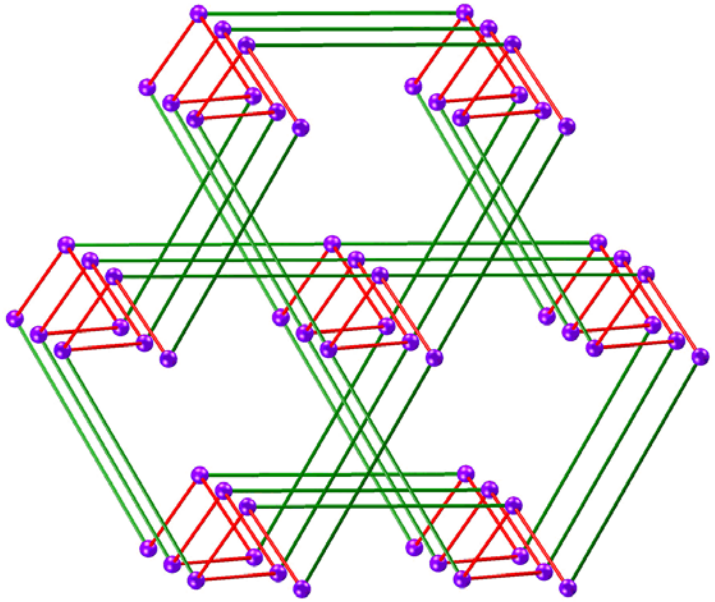
Dalton Trans. 2011, 40, 8072

Chem. Eur. J. 2010, 16, 13035

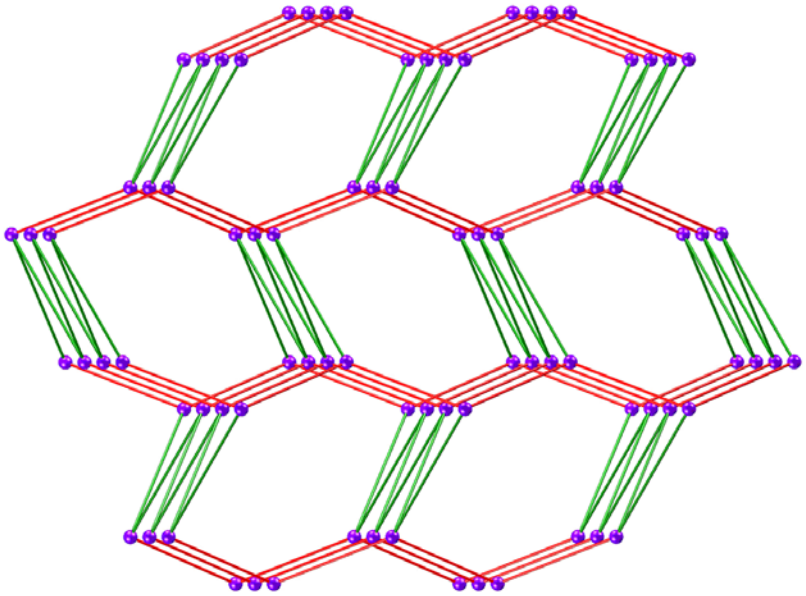
Lithium Imidazolate Framework from Charge Complementary Links







Quartz dual net

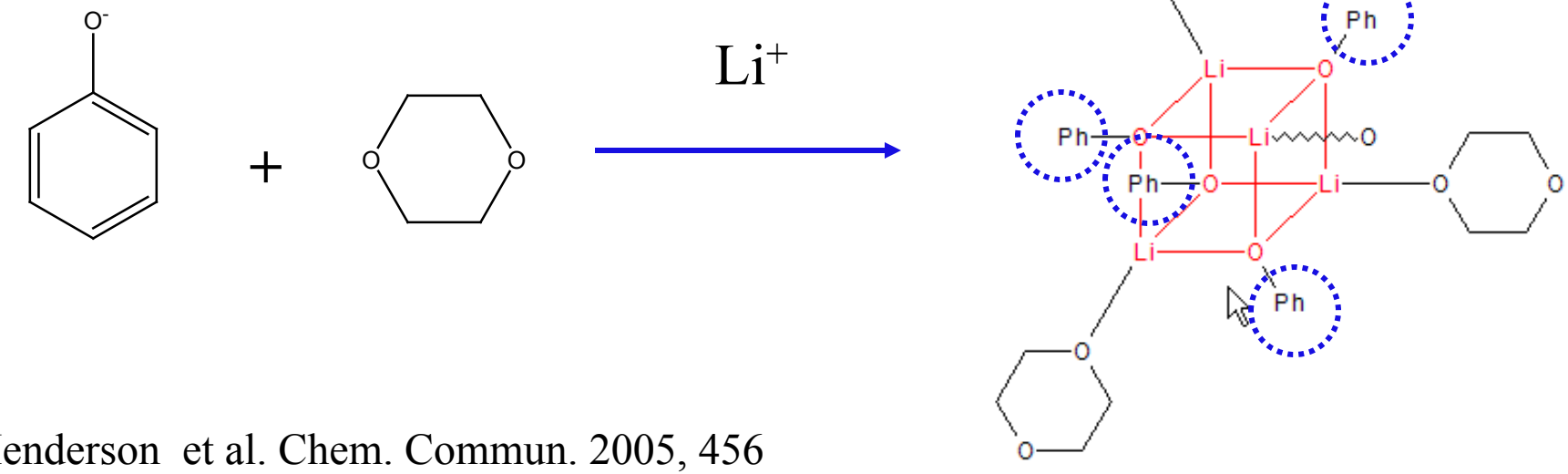


diamond net

Enhancing Stability Using Clusters: Lithium Aryloxide Clusters

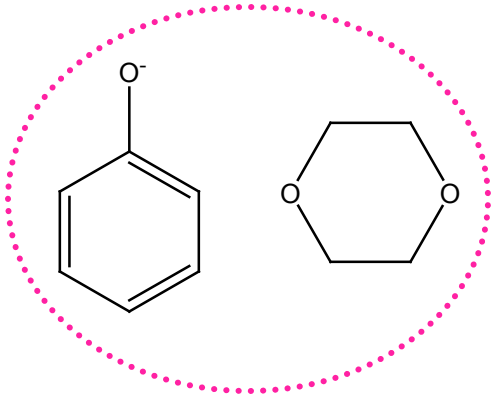
- Why literature examples not porous?

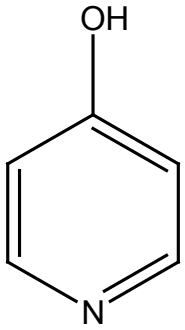
Two ligands with different roles are used:
(1) Negative phenolate to form the clusters;
(2) Neutral 1,4-dioxane to crosslink

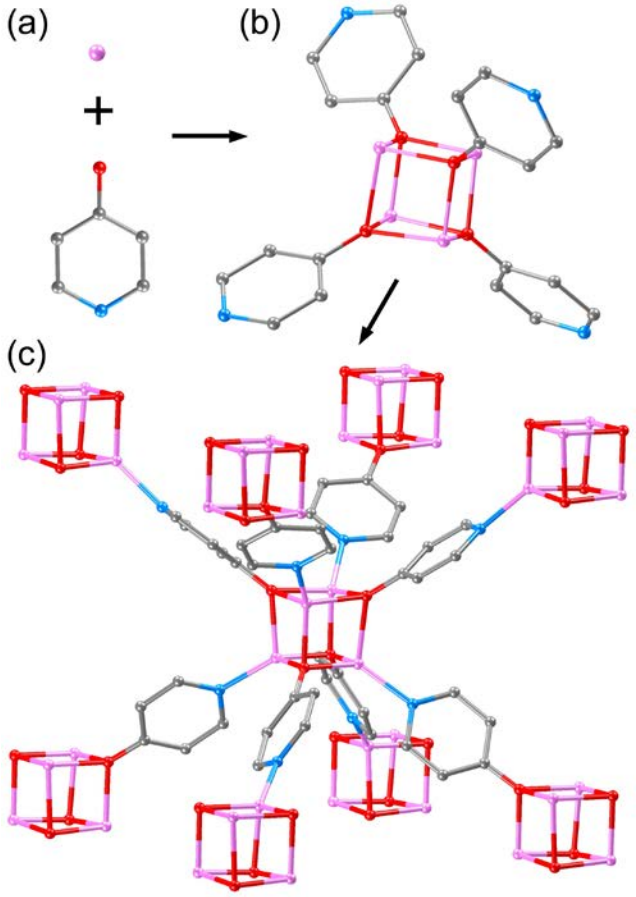


Henderson et al. Chem. Commun. 2005, 456

Enhancing Stability and Generating Porosity: One Ligand and Two Roles







- 4-pyridinol is both cluster-forming and crosslinking.

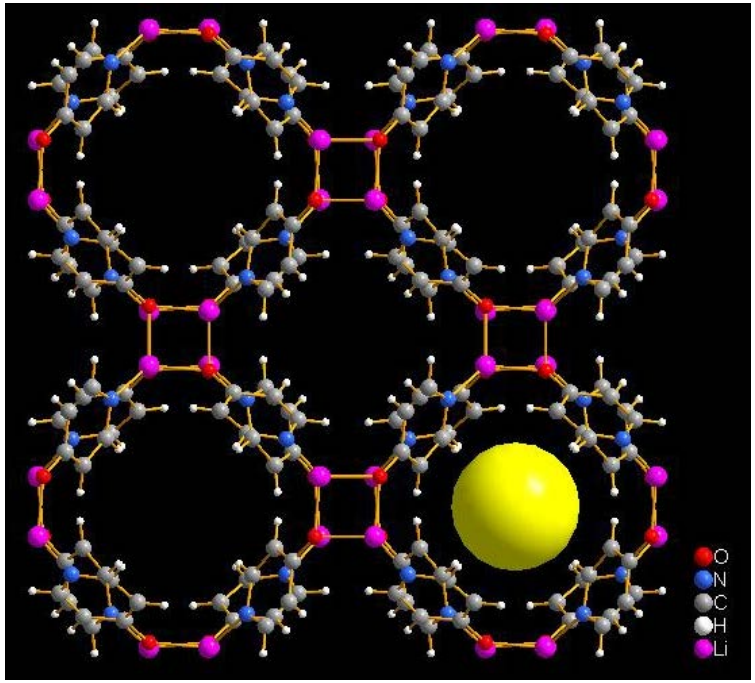
- Two advantages:

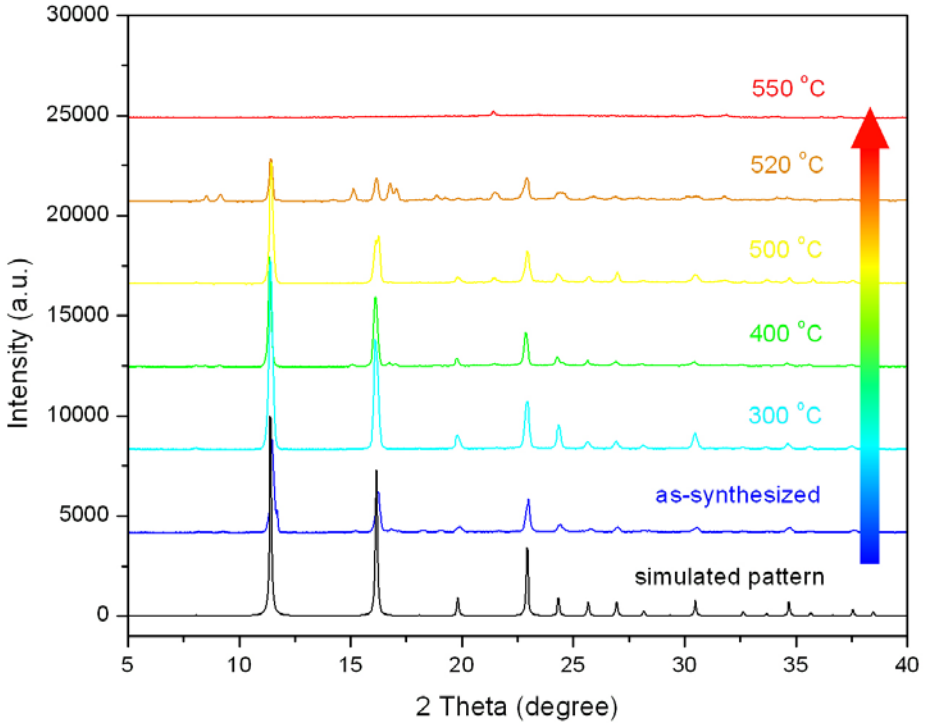
(1) No pore-blocking pendant ligand, leading to a porous material;

(2) The crosslinker is also embedded into the cluster, leading to high stability.

$[Li_4(C_5H_4NO)_4]\cdot x(solv)$

The Most Thermally Stable Lithium Porous Framework



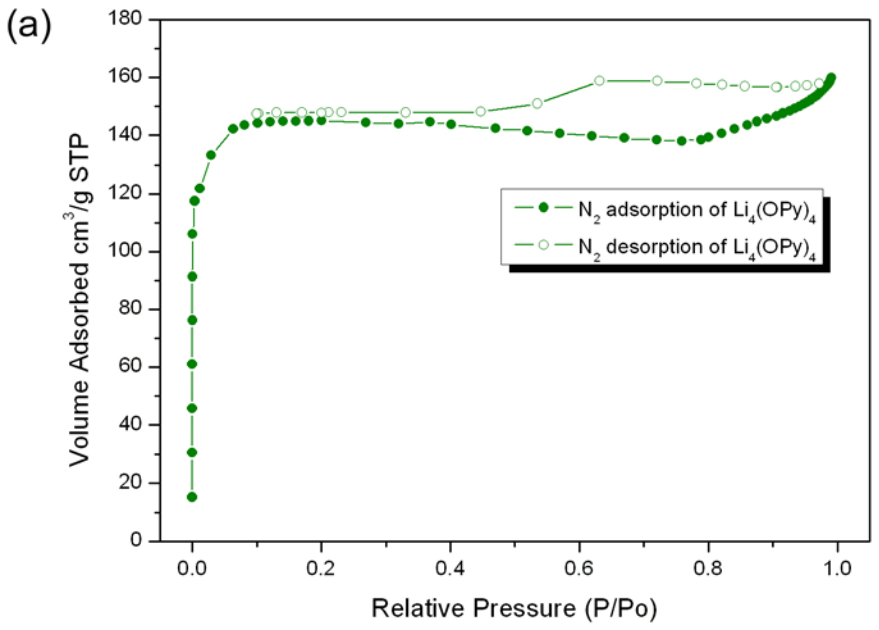


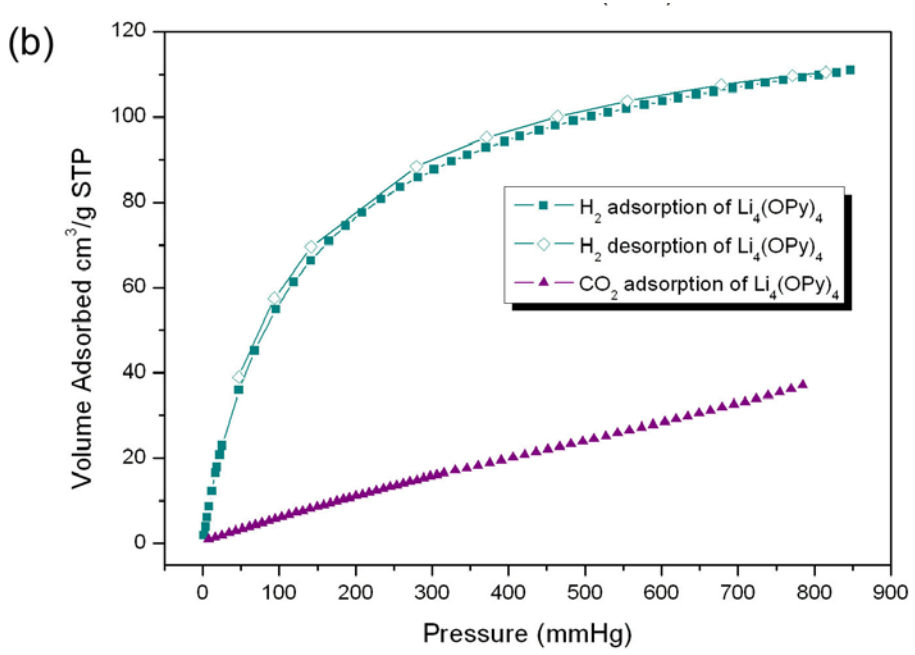
Zeolite ACO-Type Framework

- Only a small number of MOFs with thermal stability >500°C, few based on low-valent metal ions (Li^+, Cu^+…).

Chem. Commun. 2011, 47, 5536

Gas Sorption Properties of Li-ACO Framework





Langmuir surface area: 633 m^2/g

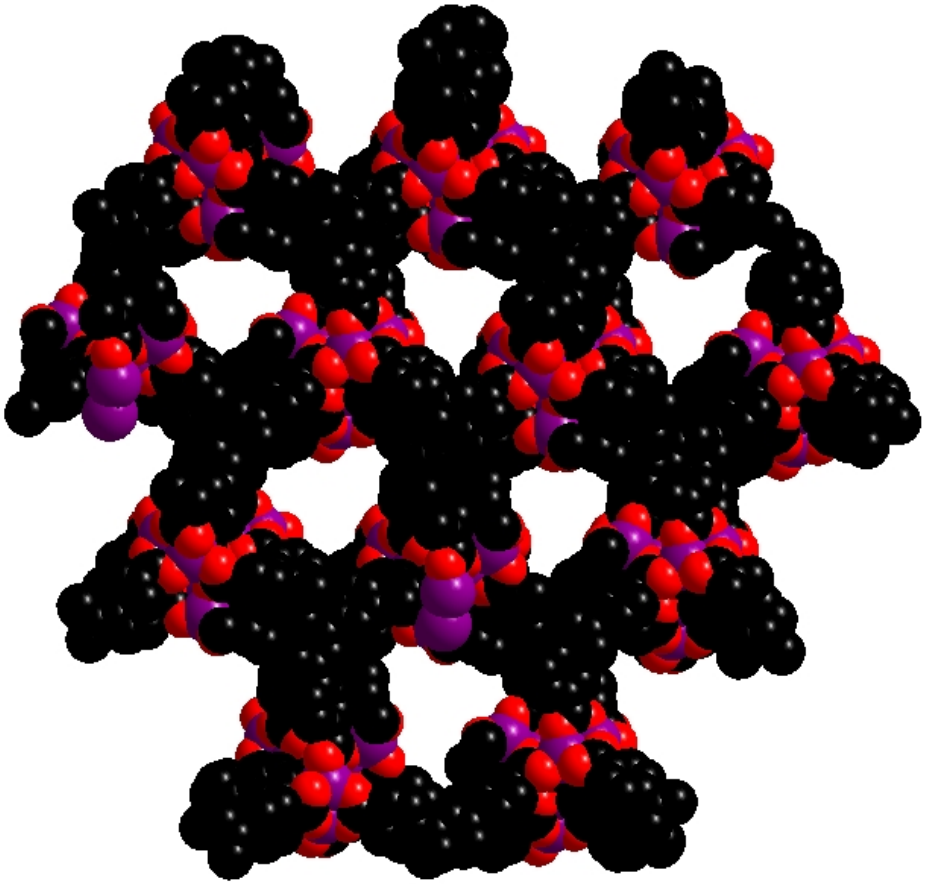
H_2 Uptake at 77K-1atm: 1.0wt%

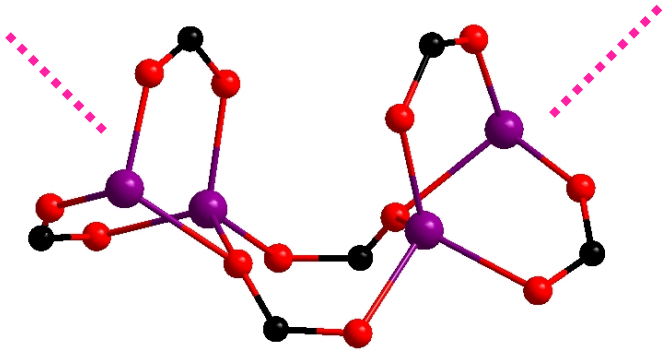
CO_2 Uptake at 273K-1atm: 36cm^3/g

- Limitations to be overcome with BIF, Li-ZIF, and Li-PhO:

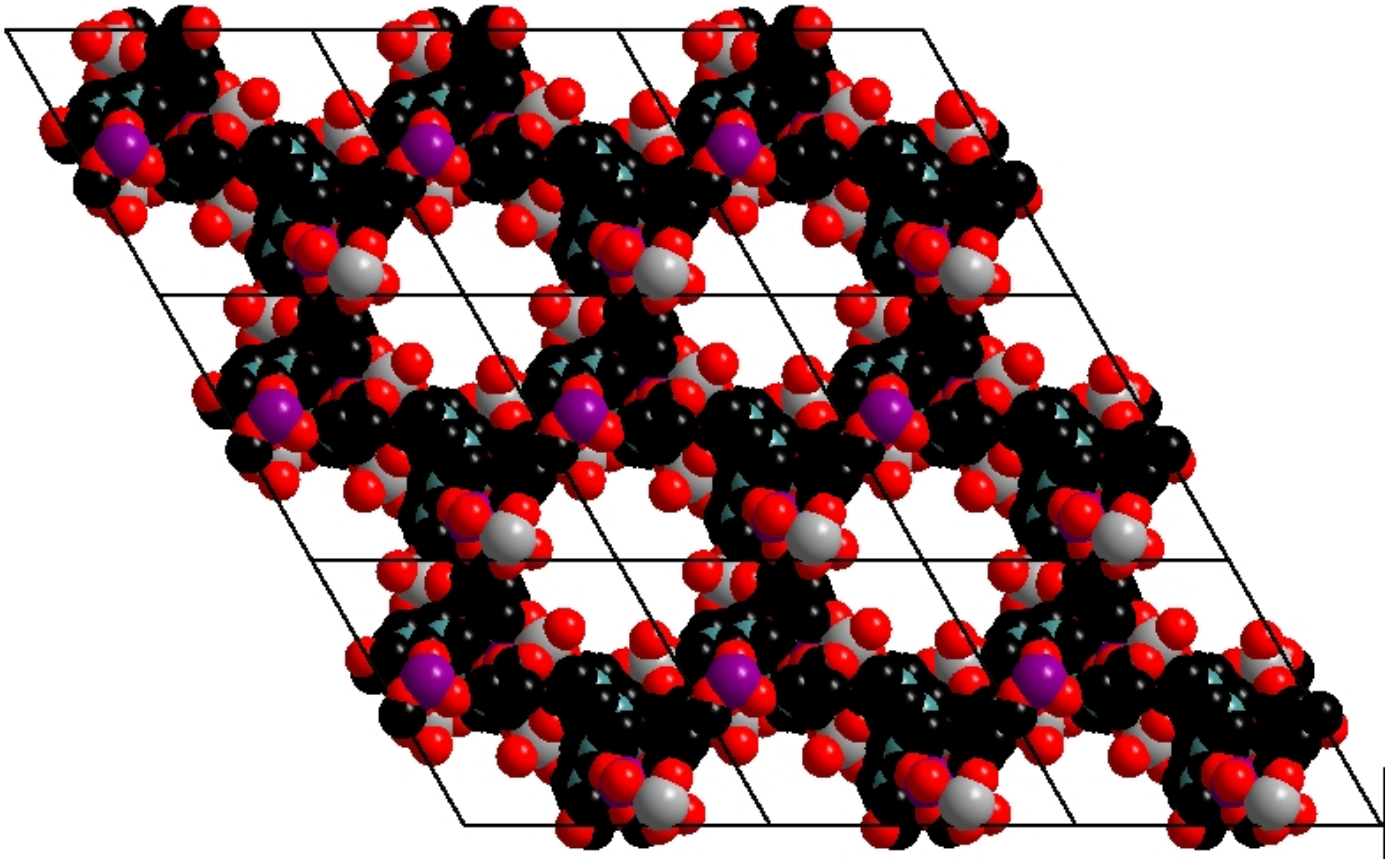
No active metal binding sites.

How to Make Active Metal Binding Sites?
Porous Carboxylate Frameworks

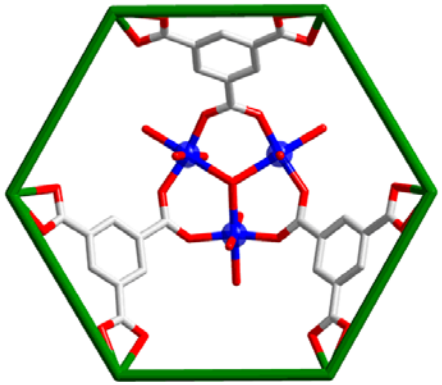


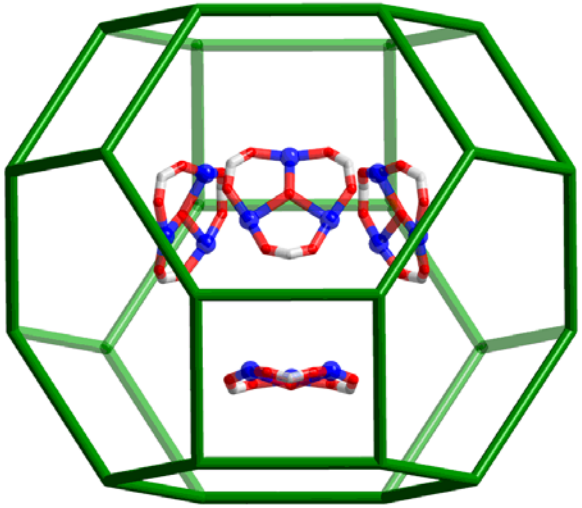


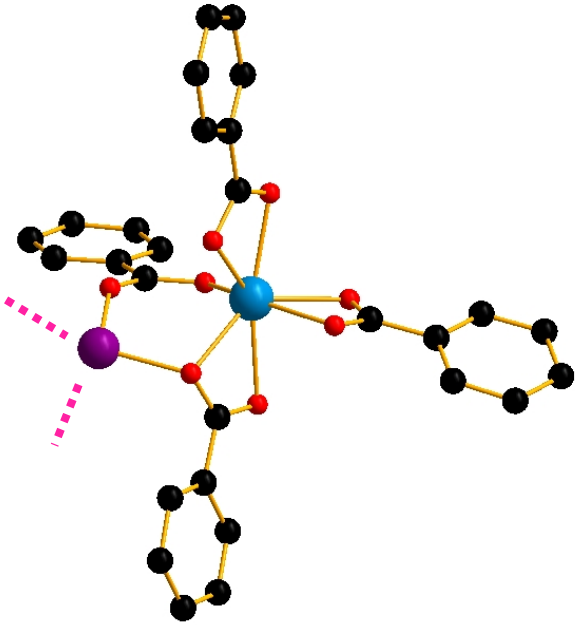
How to Make Active Metal Binding Sites?
Synergistic Porous Systems



How to Make Active Metal Binding Sites? Supported and Templated Porous Systems



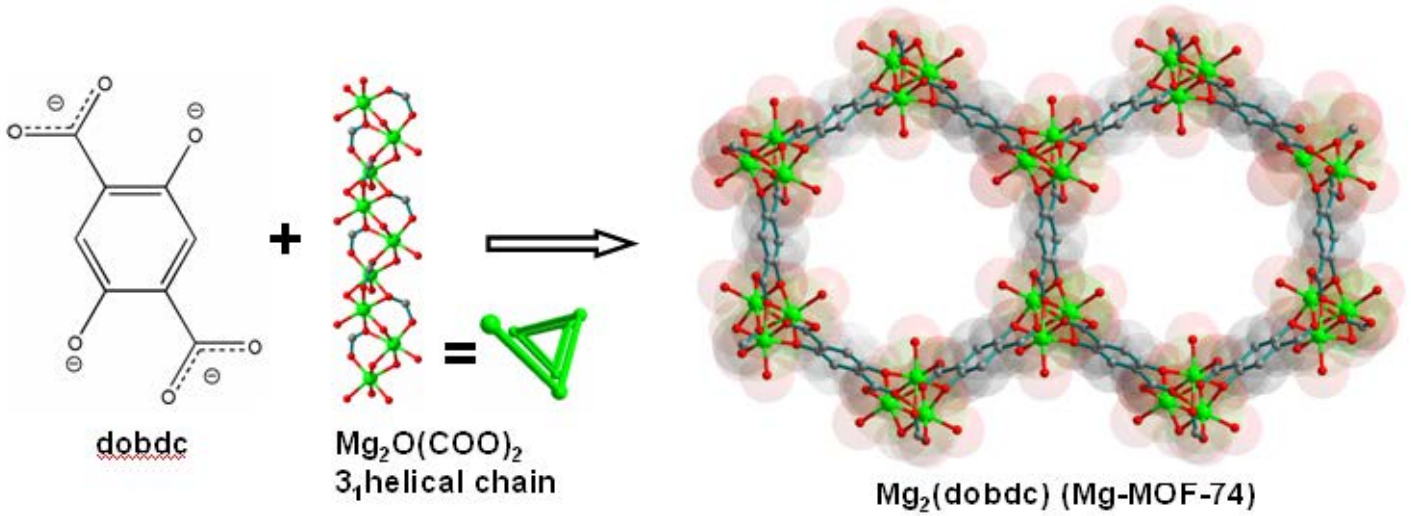




J. Am. Chem. Soc. 2012, 134, 1934

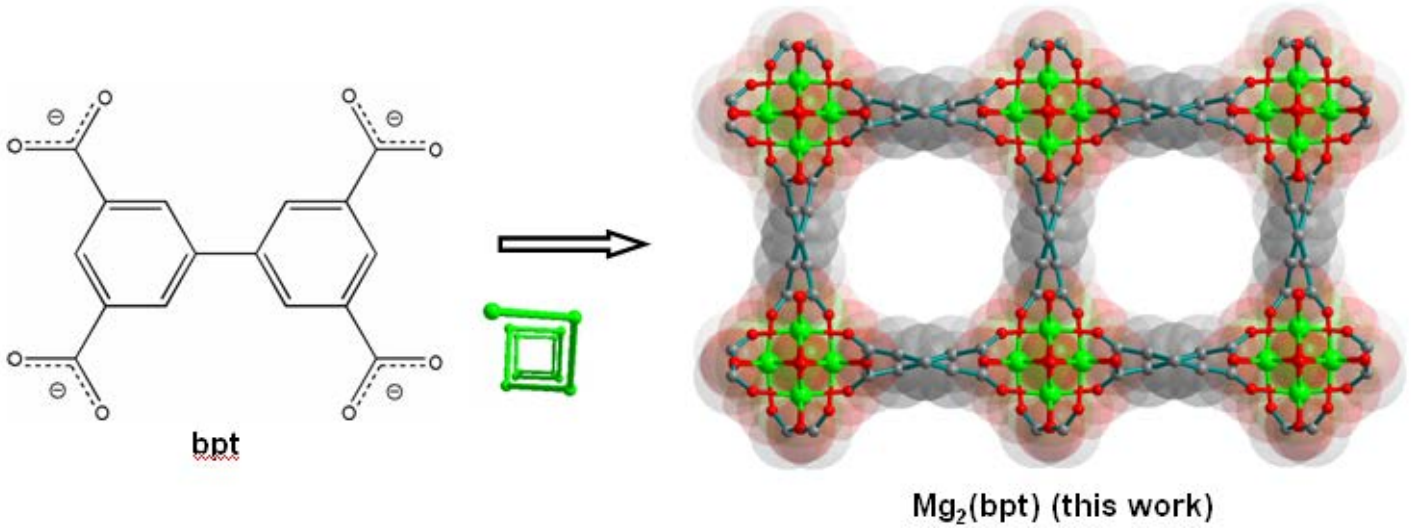
- Templated systems may convert into the supported system upon solvent removal.

How to Make Active Metal Binding Sites: Magnesium Carboxylate Frameworks



MOF-74

Yaghi et al

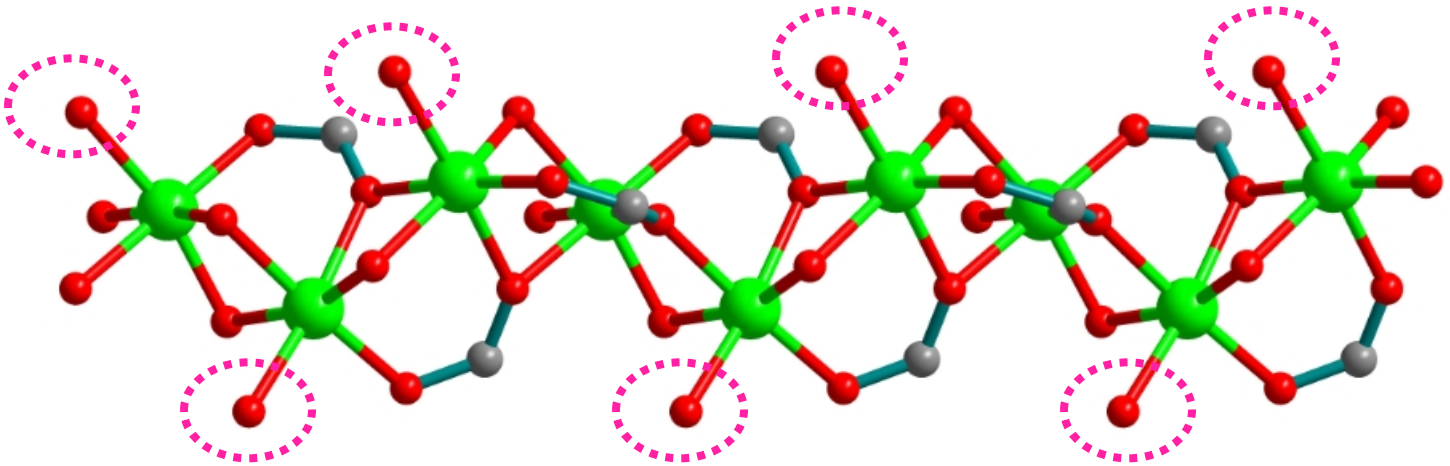


CPF-1

Chem. Commun. 2011, 47, 11852

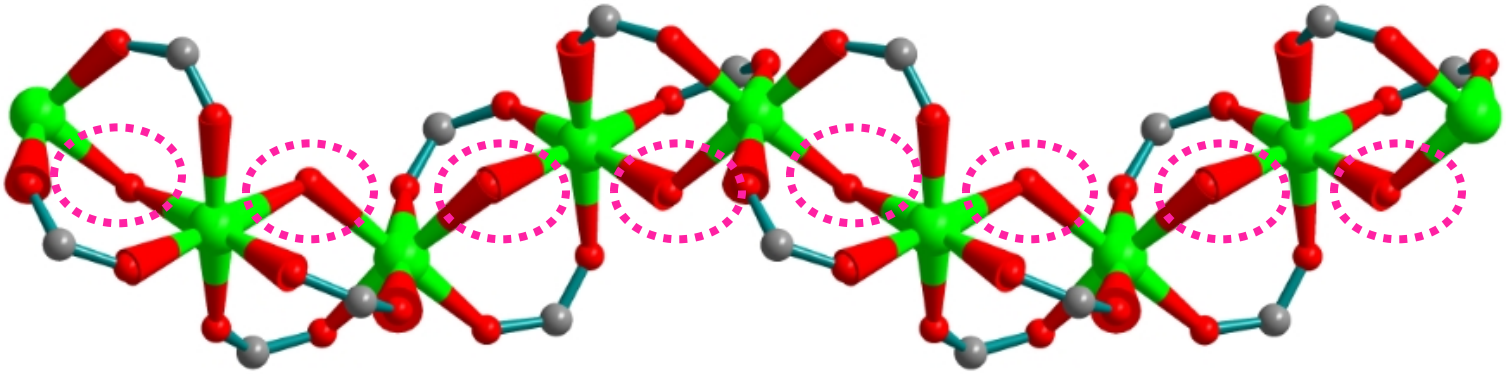
Orientation of Solvent Coordination Sites: Comparison between MOF-74 and CPF-1

- MOF-74, (1) one solvent per Mg^{2+}, (2) non-adjacent (3) non-bridging



MOF-74

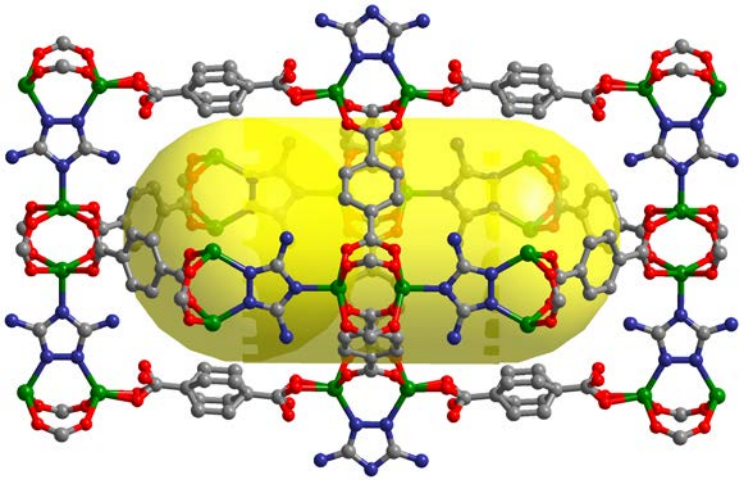
- CPF-1, (1) two solvents per Mg^{2+} *cis* to each other, (2) Oriented toward each other on two adjacent Mg^{2+} sites, (3) bridging.



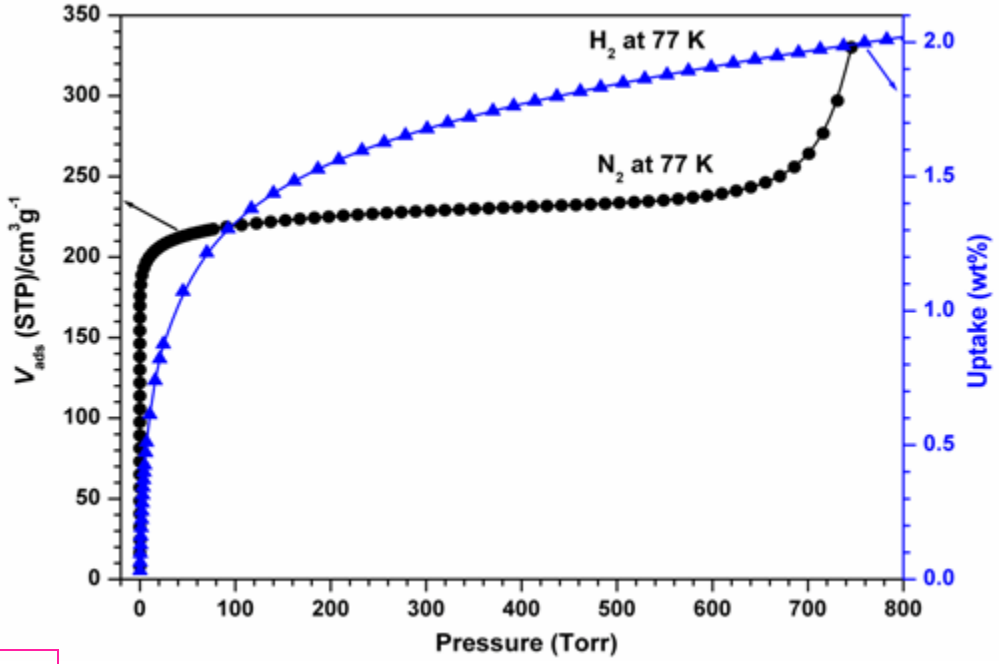
CPF-1

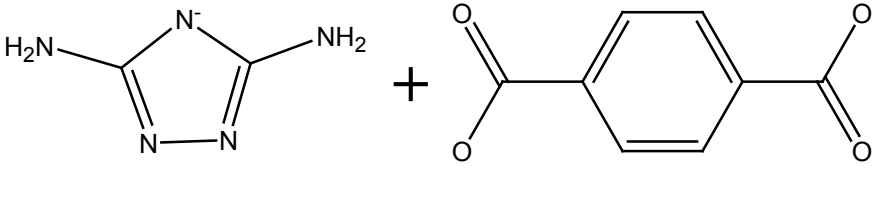
H_2: 1.3 wt% at 77K-1atm, CO_2: 84cm^3/g at 273K-1atm

Toward Active Ligand Binding Sites: Porous Anionic Frameworks with Amino-Decorated Cages



Zn^{2+}





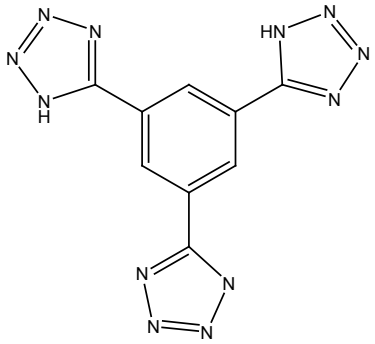
DATRZ BDC

$[(CH_3)_2NH_2][Zn_3(DATRZ)(BDC)_3]$

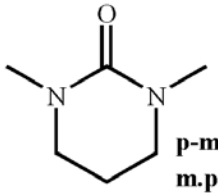
Langmuir surface area: 1008 m^2/g

H_2: 2.0 wt% at 77K-1atm, CO_2: 116cm^3/g at 273K-1atm

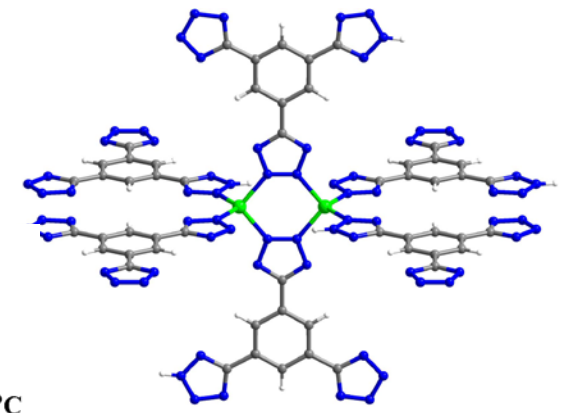
Synthetic Use of Urea Derivatives and Active Donor Sites

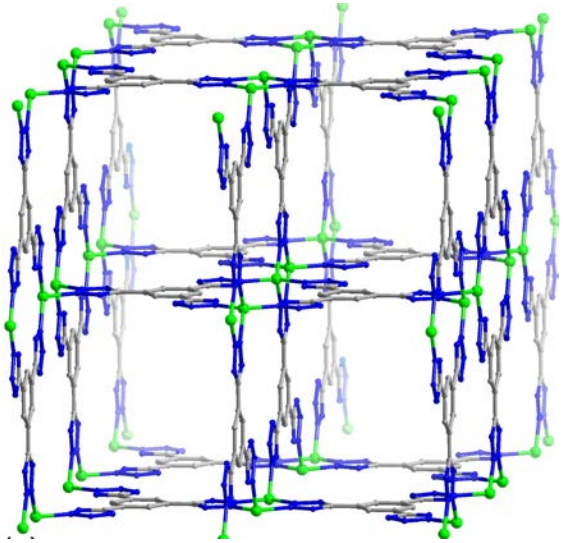


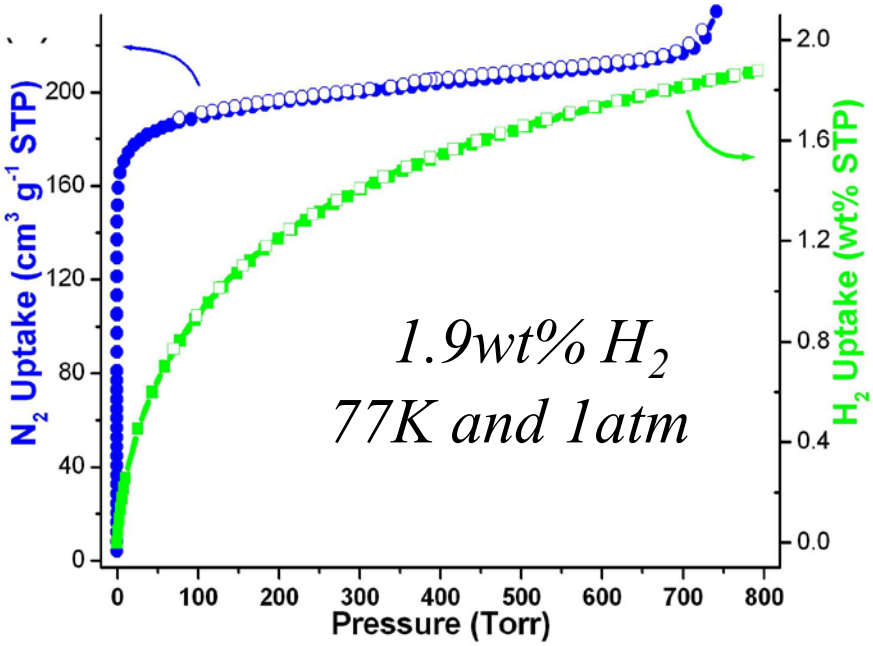
Zn^{2+}

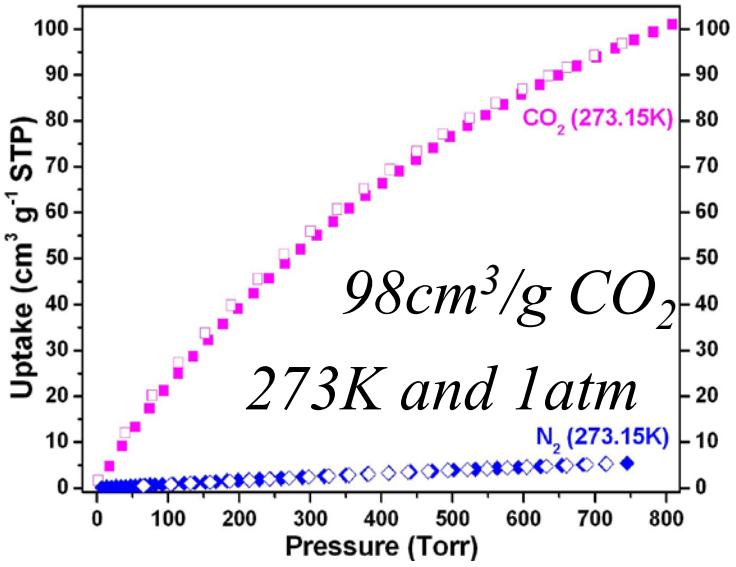


p-murea
m.p.: -23°C
b.p.: 246°C





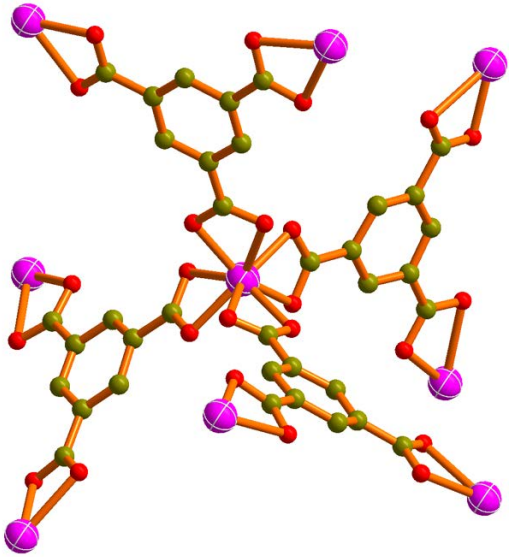


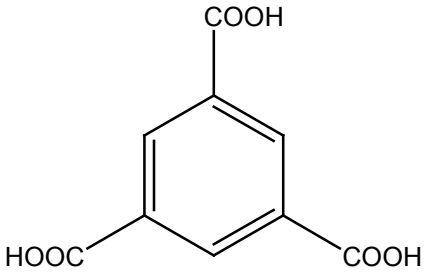


Langmuir surface area: 883 m^2/g

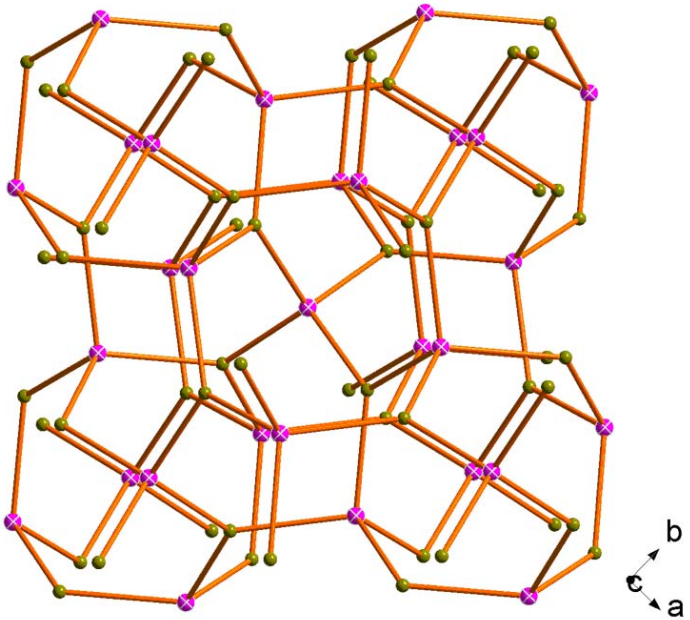
J. Am. Chem. Soc. 2012, 134, 784

Pore Space Engineering:
Control of Pore Space Using Charge-Balancing Ions





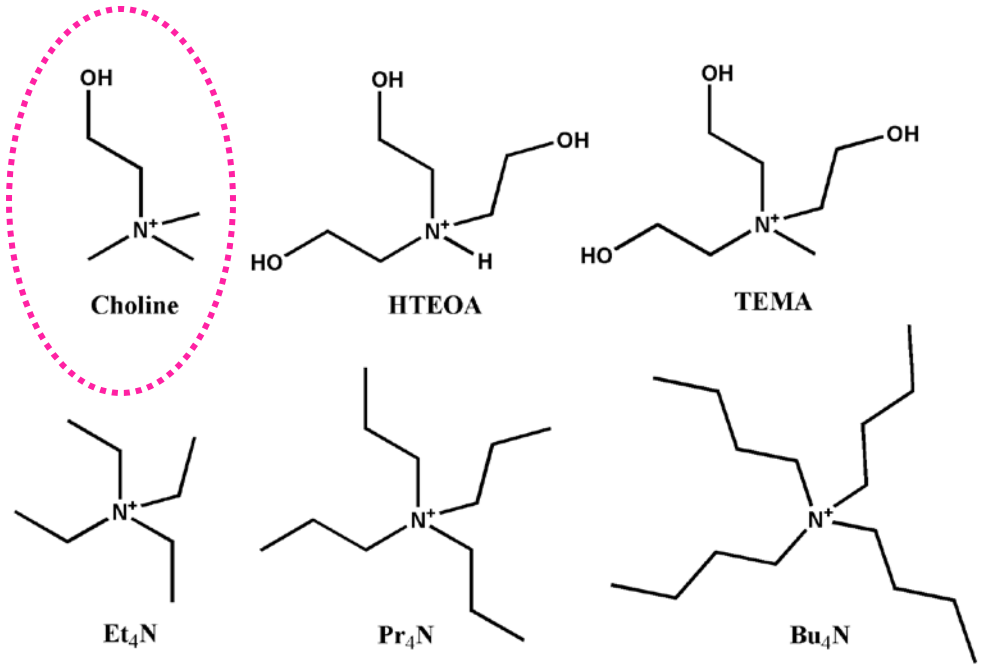
BTC

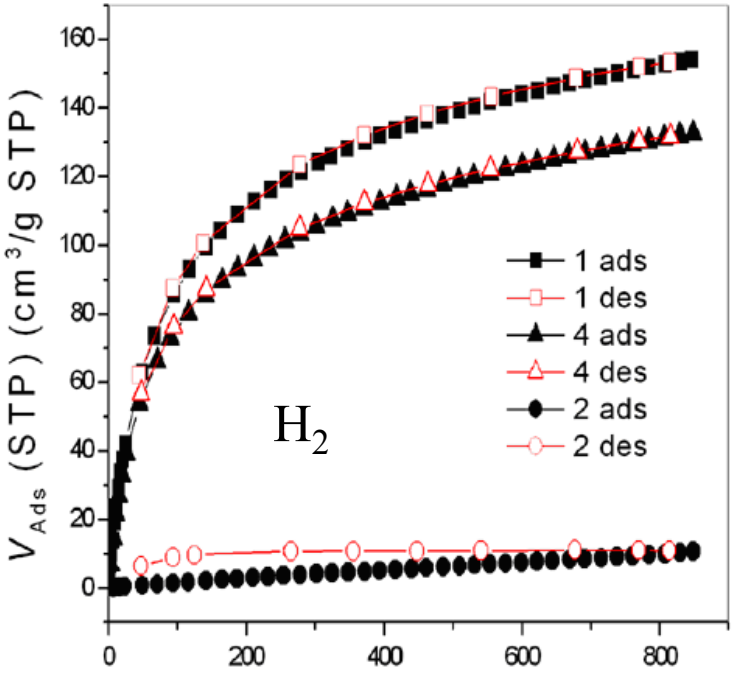


$[In_3(btc)_4]^{3-}$

Cubic C_3N_4-Type 3D Negative Framework

Pore Space Engineering:
Control of Pore Space Using Charge-Balancing Ions





Direct synthesis, not by ion-exchange

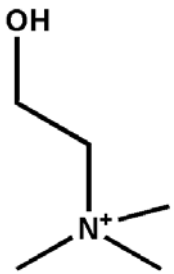
Compound 1: $(Choline)_3[In_3(btc)_4].2(DMF)$

Compound 4: $(Et_4N)_3[In_3(btc)_4].DEF$

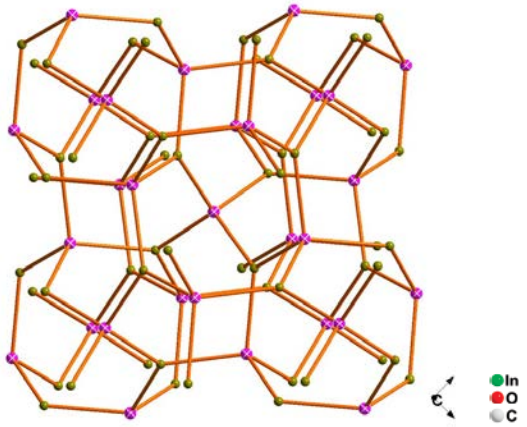
Compound 2: $(Pr_4N)_3[In_3(btc)_4].DEF$

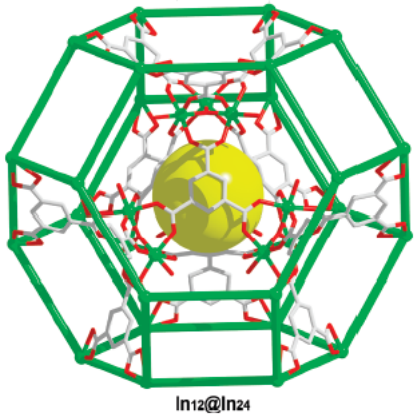
J. Am. Chem. Soc. 2009, 131, 16027

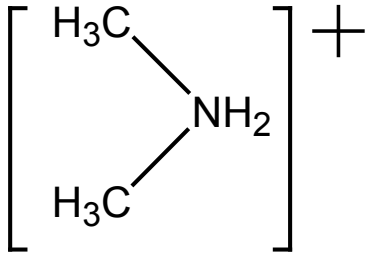
Pore Space Engineering:
Control of Pore Space Using Charge-Balancing Ions



Choline







	CPM-1 (Pure C_3N_4 Net)	*CPM-5 (Stuffed Sodalite Net)*
Building blocks	***Monomer only***	***Monomer & Trimer***
Guest space	***66%***	***48%***
CO_2 at 273K-1atm	***71cm^3/g***	***81cm^3/g***

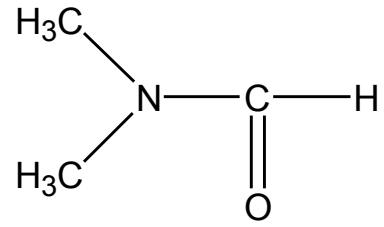
J. Am. Chem. Soc. 2009, 131, 16027

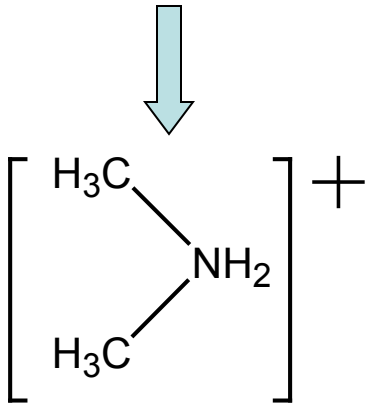
J. Am. Chem. Soc. 2010, 132, 17062

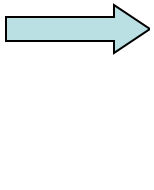
Pore Space Engineering:
What is the smallest organic cation?

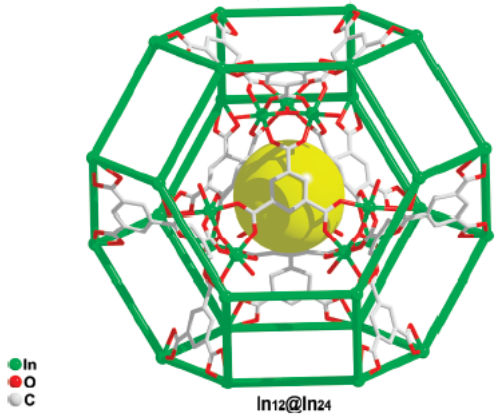
CPM-5

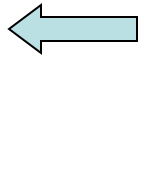
DMF

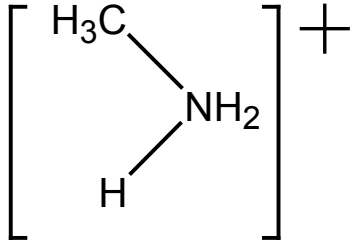






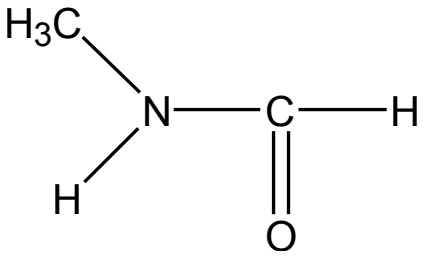






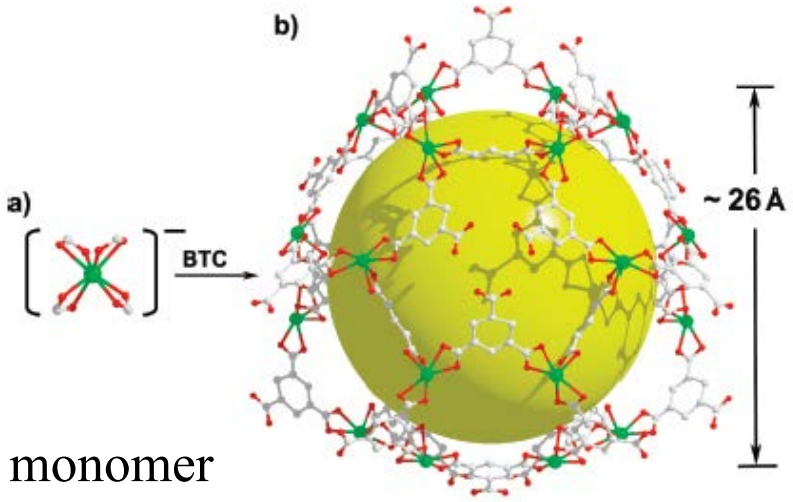
CPM-6

NMF



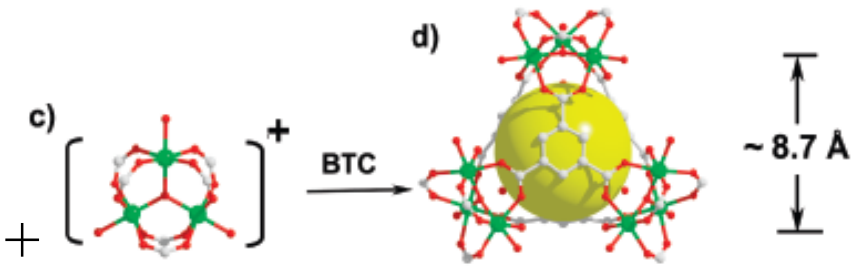
	CPM-1	*CPM-5*	*CPM-6*
CO_2 at 273K-1atm	71cm^3/g	81cm^3/g	107cm^3/g
H_2 at 77K-1atm	1.36wt%	1.24wt%	1.88wt%
Langmuir SA	712m^2/g	733m^2/g	931m^2/g

Pore Space Partition:
Nested Cage-in-Cage Structure



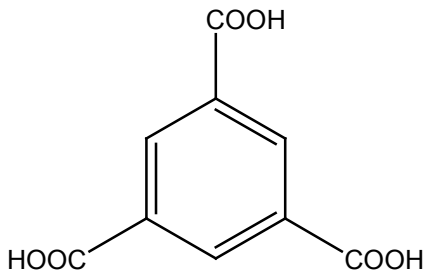
monomer

In_{24} cage

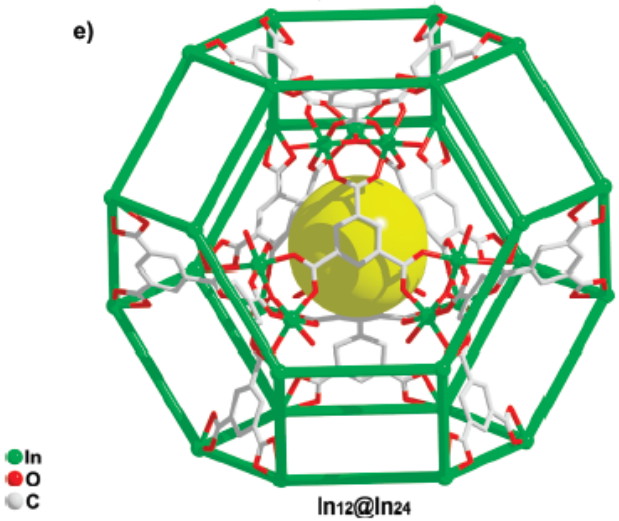


trimer

In_{12} cage



BTC

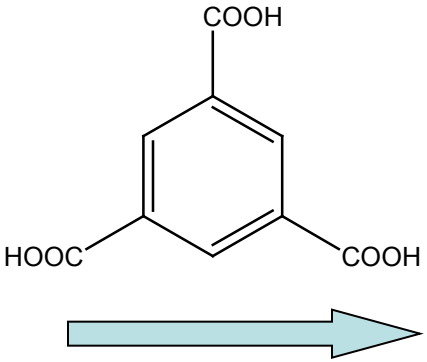


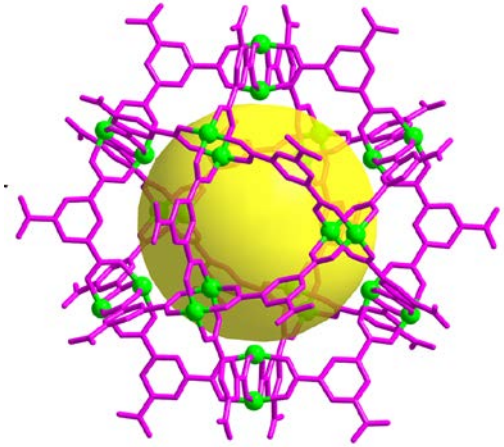
CPM-5 or CPM-6

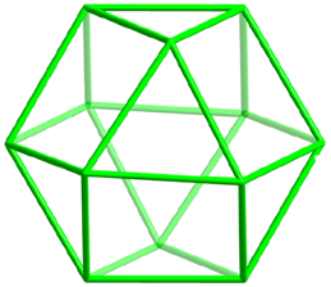
J. Am. Chem. Soc. 2010, 132, 17062

Pore Space Partition:
Nested Cage-in-Cage Structure

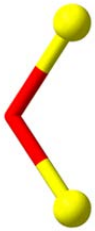
Co_2



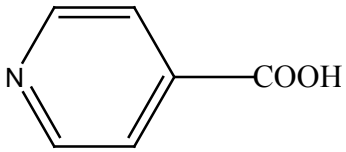


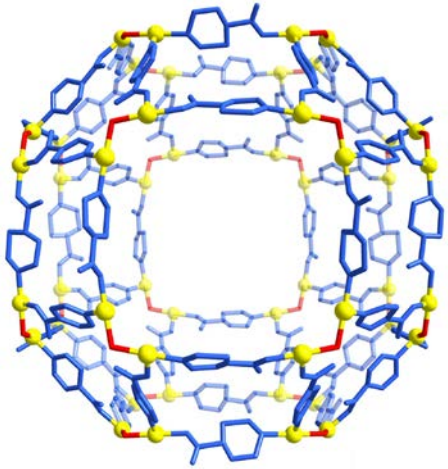


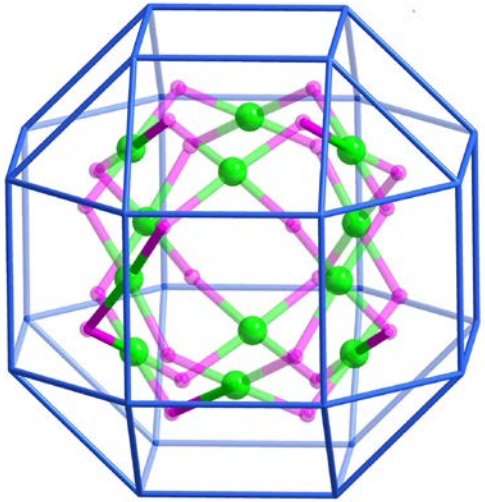
Cuboctahedron



$Co_2(OH)$



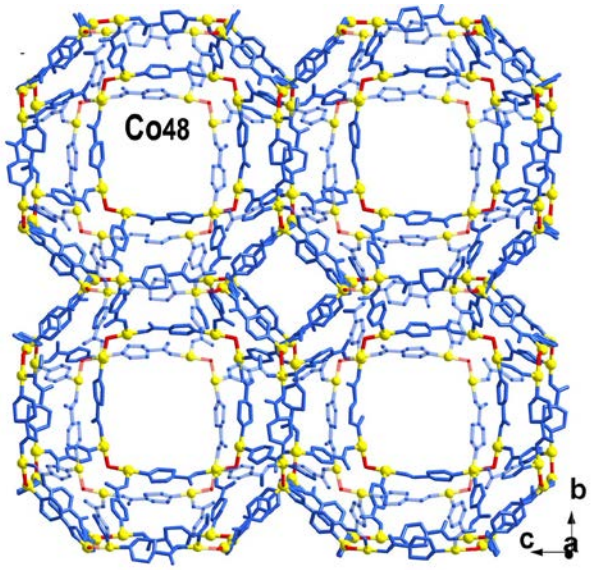


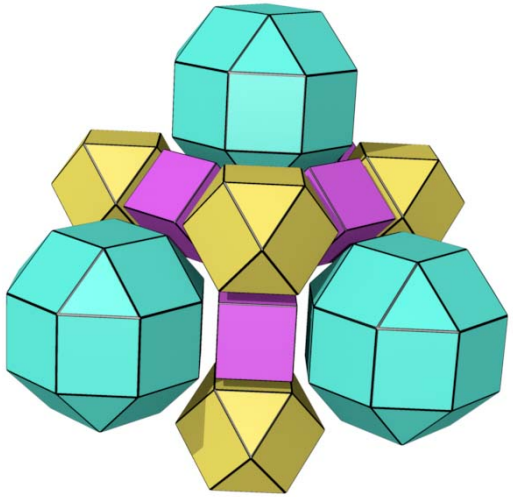


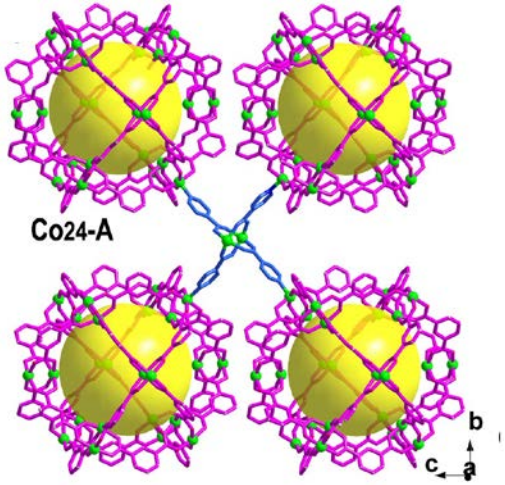
Rhombicuboctahedron

Angew. Chem. Int. Ed. 2011, 50, 8034

Pore Space Partition:
Nested Framework-in-Framework Structure





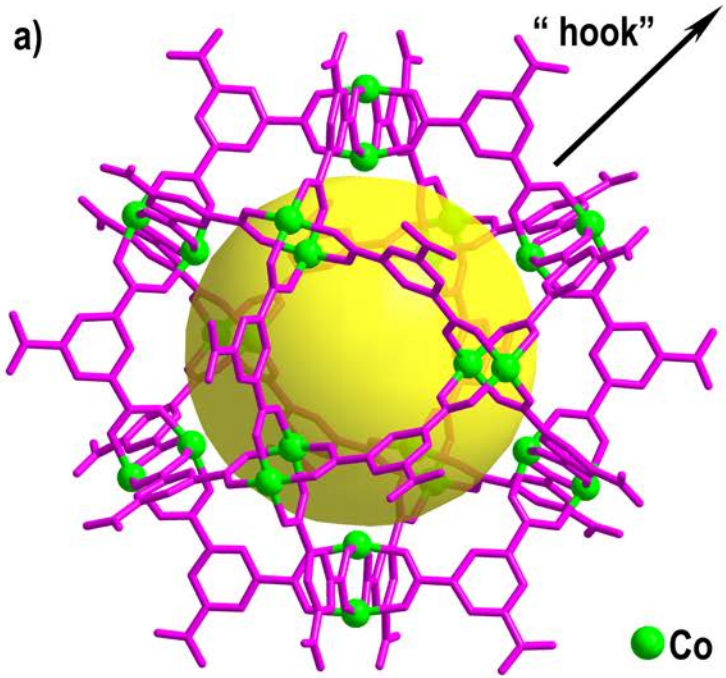


Outside framework based on Rhombicuboctahedron

reo net

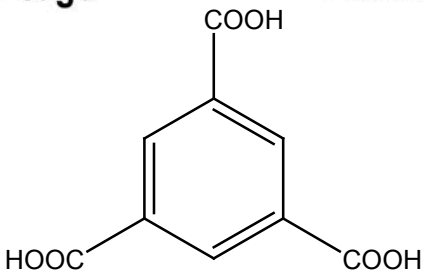
Inside framework based on Cuboctahedron

Pore Space Partition:
"Mechanism" for Cage-to-Cage Communication



From the inner cage onto the outer cage

CPM-24



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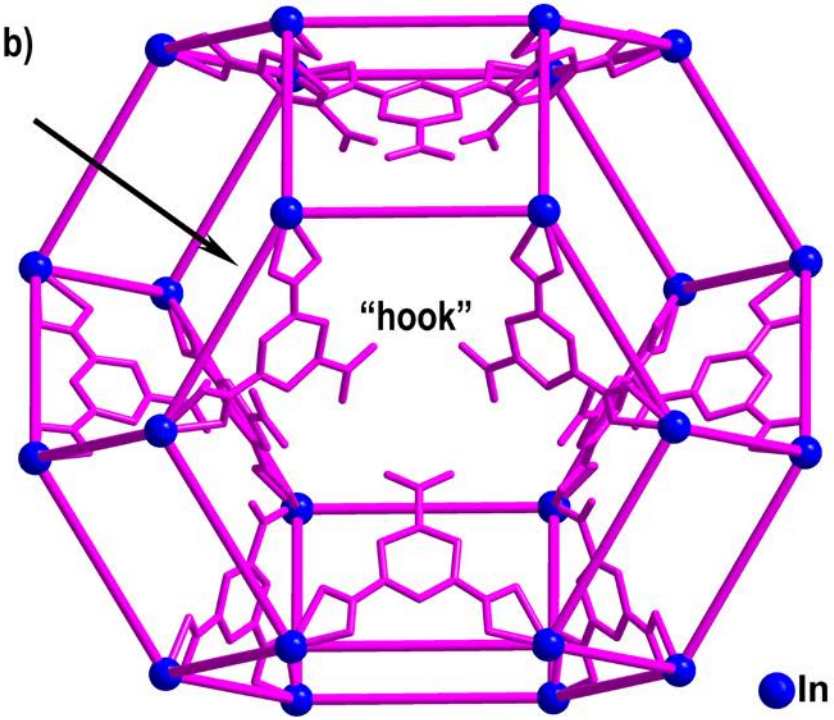
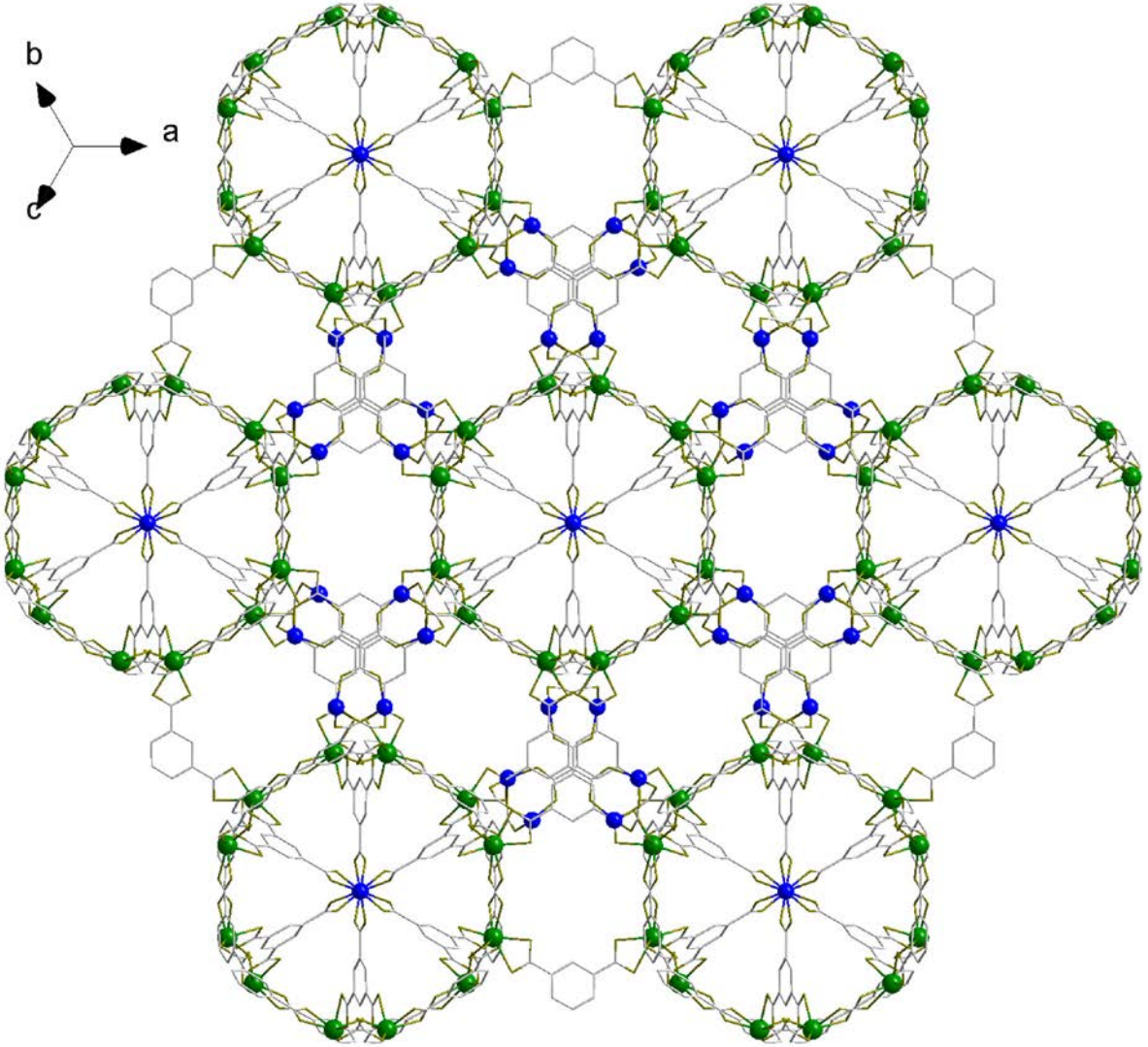


From the outer cage onto the inner cage

CPM-5

Pore Space Partition in Channel-based Materials