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

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This presentation does not contain any proprietary, confidential, or otherwise restricted information.
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 Aryloxiide 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 covalent bond
- Li-N coordination bond

Zn$^{2+}$ + imidazole $\rightarrow$ Zn(im)$_2$

B$^{3+}$ + Li$^+$ + imidazole $\rightarrow$ No Reaction
Solid State Synthesis before Self-Assembly

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

\[ \text{NaBH}_4 + \begin{array}{c} \text{N} \\ \text{R}_1 \\ \text{R}_2 \\ \text{R}_3 \end{array} \xrightarrow{90-120^\circ} \text{Na} \begin{array}{c} \text{N} \\ \text{R}_1 \\ \text{N} \\ \text{R}_2 \\ \text{R}_3 \end{array} \xrightarrow{180-210^\circ} \begin{array}{c} \text{R}_1 \\ \text{R}_2 \\ \text{R}_3 \end{array} \text{BH}_2 \]

- $\begin{array}{c} \text{N} \\ \text{R}_1 \\ \text{N} \\ \text{R}_2 \\ \text{R}_3 \end{array} \text{BH} \xrightarrow{>220^\circ} \begin{array}{c} \text{N} \\ \text{R}_1 \\ \text{N} \\ \text{R}_2 \\ \text{R}_3 \end{array} \text{B} \text{Na} \begin{array}{c} \text{N} \\ \text{R}_1 \\ \text{N} \\ \text{R}_2 \\ \text{R}_3 \end{array} \text{BH} \xrightarrow{>220^\circ} \begin{array}{c} \text{N} \\ \text{R}_1 \\ \text{N} \\ \text{R}_2 \\ \text{R}_3 \end{array} \text{B} \]

- Depending on the temperature, both tri-substituted $\text{Na[BH(im)}_3]$ and tetra-substituted $\text{NaB(im)}_4$ 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.

\[
\begin{align*}
\text{HN(C}_\text{H}_3\text{)}_2 & + 4 \text{im} & \rightarrow & & \text{HB(im)}_4 + 3\text{HN(C}_\text{H}_3\text{)}_2
\end{align*}
\]
New Tripodal and Tetrahedral Boron Building Blocks

- A large number of boron imidazolate complexes have been made in this work.
Solvothermal Assembly with Li⁺

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

- Solvents are also very critical for the crystallization.

- 2-amino-1-butanol/CH$_3$CN
- 2-amino-1-butanol/C$_6$H$_6$
- DMF/CH$_3$CN

Angew. Chem. Int. Ed. 2009, 48, 2542
J. Am. Chem. Soc. 2009, 131, 6111
Potential Open Lithium Sites in 3-Connected 3-D Frameworks

Chem. Mater. 2009, 21, 3830
Gas Sorption Properties of BIF-9

- BIF-9, LiB(4-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-mim)_4 (mim=4-methylimidazolate)

H₂ Uptake at 77K-1atm: 1.4wt%
How to Get Lighter?
Lithium Imidazolate Framework

- Using Charge Complementarity of Imidazole Ligands

\[ \text{Zn}^{2+} + 2L_1^- \leftrightarrow \text{Li}^+ + L_1^- + L_2^0 \]

(L1 = imidazole  L2 = neutral ditopic ligand)

- Both L1 and L2 ligands can be varied.

Dalton Trans. 2011, 40, 8072
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

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.

\[
\text{[Li}_4\text{(C}_5\text{H}_4\text{NO})_4]\cdot x(\text{solv})
\]
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

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

How to Make Active Metal Binding Sites:
Magnesium Carboxylate Frameworks

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

- **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.

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

H₂: 2.0 wt% at 77K-1atm, CO₂: 116 cm³/g at 273K-1atm

\[
\left[\left(\text{CH}_3\text{NH}_2\right)[\text{Zn}_3(\text{DATRZ})(\text{BDC})_3]\right]
\]

DATRZ + BDC

Langmuir surface area: 1008 m²/g

H₂: 2.0 wt% at 77K-1atm, CO₂: 116 cm³/g at 273K-1atm
Synthetic Use of Urea Derivatives and Active Donor Sites

![Chemical structures and diagrams](image)

- **Zn²⁺**
- p-murea
  - m.p.: -23°C
  - b.p.: 246°C

**Graphs**

- **N₂ Uptake (cm³ g⁻¹ STP)**
  - 1.9wt% H₂
  - 77K and 1atm

- **H₂ Uptake (wt% STP)**

- **Uptake (cm³ g⁻¹ STP)**
  - 98cm³/g CO₂
  - 273K and 1atm

**Langmuir surface area:** 883 m²/g

**References:**

J. Am. Chem. Soc. 2012, 134, 784
Pore Space Engineering:
Control of Pore Space Using Charge-Balancing Ions

Cubic C$_3$N$_4$-Type 3D Negative Framework

BTC

$[\text{In}_3(\text{btc})_4]^{3-}$
Direct synthesis, not by ion-exchange

Compound 1: \((\text{Choline})_3[\text{In}_3(\text{btc})_4].2(\text{DMF})\)

Compound 4: \((\text{Et}_4\text{N})_3[\text{In}_3(\text{btc})_4].\text{DEF}\)

Compound 2: \((\text{Pr}_4\text{N})_3[\text{In}_3(\text{btc})_4].\text{DEF}\)

J. Am. Chem. Soc. 2009, 131, 16027
Pore Space Engineering: Control of Pore Space Using Charge-Balancing Ions

<table>
<thead>
<tr>
<th>Building blocks</th>
<th>CPM-1 (Pure C$_3$N$_4$ Net)</th>
<th>Monomer only</th>
<th>CPM-5 (Stuffed Sodalite Net)</th>
<th>Monomer &amp; Trimer</th>
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<tbody>
<tr>
<td>Guest space</td>
<td>66%</td>
<td>48%</td>
<td></td>
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<tr>
<td>$CO_2$ at 273K-1atm</td>
<td>71cm$^3$/g</td>
<td>81cm$^3$/g</td>
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</tr>
</tbody>
</table>

What is the smallest organic cation?

Pore Space Engineering:

**CPM-5**

DMF

\[
\begin{align*}
&\text{H}_3\text{C} \\
&\text{H}_3\text{C} \\
&\text{N} \\
&\text{C} \\
&\text{O} \\
\end{align*}
\]

\[
\begin{align*}
&\text{H}_3\text{C} \\
&\text{NH}_2 \\
&\text{H}_3\text{C} \\
\end{align*}
\]

**CPM-6**

NMF

\[
\begin{align*}
&\text{H}_3\text{C} \\
&\text{N} \\
&\text{C} \\
&\text{O} \\
\end{align*}
\]

\[
\begin{align*}
&\text{H}_3\text{C} \\
&\text{NH}_2 \\
&\text{H} \\
\end{align*}
\]

<table>
<thead>
<tr>
<th></th>
<th>CPM-1</th>
<th>CPM-5</th>
<th>CPM-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO\textsubscript{2} at 273K-1atm</td>
<td>71cm\textsuperscript{3}/g</td>
<td>81cm\textsuperscript{3}/g</td>
<td>107cm\textsuperscript{3}/g</td>
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<tr>
<td>H\textsubscript{2} at 77K-1atm</td>
<td>1.36wt%</td>
<td>1.24wt%</td>
<td>1.88wt%</td>
</tr>
<tr>
<td>Langmuir SA</td>
<td>712m\textsuperscript{2}/g</td>
<td>733m\textsuperscript{2}/g</td>
<td>931m\textsuperscript{2}/g</td>
</tr>
</tbody>
</table>
Pore Space Partition: Nested Cage-in-Cage Structure

monomer

In$_{24}$ cage

BTC

trimer

In$_{12}$ cage

CPM-5 or CPM-6

J. Am. Chem. Soc. 2010, 132, 17062
Pore Space Partition:
Nested Cage-in-Cage Structure

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

From the outer cage onto the inner cage

CPM-24

BTC

CPM-5
Pore Space Partition in Channel-based Materials