Porous solids: hydrogen-bonded networks

Molecular tectonics: 3D organic superlattices based on hydrogen bonding

Wuest and coworkers, *JACS* **1997**, 119, 2737

8 HB's per molecule–can remove up to 63% of solvent molecules before structural integrity is affected
Porous solids: hydrogen-bonded networks

Molecular tectonics: Guanidinium-sulfonate networks

Porous solids: Metal-organic frameworks (MOFs)


**Reticular synthesis of MOFs** (Yaghi and O’Keeffe): *Nature* 2003, 423, 705-714; also see CSR review (2009)

Key design element to non-interpenetrating frameworks: Secondary building units (SBUs) based on “decorated” metal-ligand clusters as framework vertices + rigid polydentate ligands (carboxylates)

Molecular Complexes                  Extended Solids

**a**

\[
\begin{align*}
\text{d\text{inuc\text{ular}}} & \quad \text{“paddle wheel”} \\
(M_2C_4)L_2 & \quad (M_3OC_3)L_3 \\
\end{align*}
\]

μ-oxo polynuclear carboxylate clusters:

\[
\begin{align*}
(M_4OC_6) & \\
(M_3OC_6) & \\
\end{align*}
\]

**b**

Expanded Framework

Decorated-Expanded Framework
Secondary building units (SBUs) in MOF synthesis

Tetrahedron (neutral)

Square pyramidal (fractional charge)

Polynuclear clusters (e.g., Zn₄O)

Nature 2003, 423, 705-714
MOF synthesis is driven by network topologies

Growth is directed by cluster geometries and rigid framework components

Some common networks observed in traditional crystalline materials:

- **a** Si net of SrSi₂
- **b** Si net of ThSi₂
- **c** $\delta^3$ Honeycomb
- **d** Pt₃O₄
- **e** NbO
- **f** Diamond (C)
- **g** Cooperite (PIS)
- **h** $4^4$ Square lattice
- **i** Primitive cubic

Example of reticular MOF synthesis:

**Isoreticular metal-organic frameworks (IRMOFs)**

Reticular assembly is modular; permits growth of MOFs with unprecedented porosity


<table>
<thead>
<tr>
<th>MOF</th>
<th>Pore Size (Å)</th>
<th>Sphere Size (Å)</th>
<th>Free Vol.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>11.2</td>
<td>18.5</td>
<td>79%</td>
</tr>
<tr>
<td></td>
<td>15.4</td>
<td>24.5</td>
<td>87%</td>
</tr>
<tr>
<td></td>
<td>19.1</td>
<td>28.8</td>
<td>91%</td>
</tr>
<tr>
<td>B</td>
<td>7.4</td>
<td>n/a</td>
<td>&lt;50%</td>
</tr>
</tbody>
</table>

Structural characteristics of natural zeolite (faujasite): pore: 7.4 Å, sphere: n/a, free vol.: <50%


**Note:** MOF syntheses are highly dependent on experimental parameters: proper stoichiometry; rapid and even heating (microwave); poor, bulky solvents (e.g., diethylformamide); nucleation conditions (e.g., slow addition of base). Many MOFs are non-interpenetrating, but not all.
Applications of nanoporous MOFs

- Bonding enthalpy of carboxylates to Zn₄O clusters on the order of 100 kcal/mol
- Rigid organic “struts” enable MOFs to withstand evacuation of solvent at high temperatures, producing mesoporous solids with very high surface areas

MOF-5 storage capacity:

MOF-5 capacity for H₂ storage:

![Graph showing MOF-5 storage capacity](image)

Reversible storage of (excess) H₂ up to 7 wt%
