

Representative MOF materials

1. MIL-101, firstly synthesized by Férey and coworkers, possesses accessible open metal sites (coordinatively unsaturated sites).¹ Its zeotype cubic structure has a giant cell volume ($\sim 702,000 \text{ \AA}^3$), a hierarchy of extra-large pore sizes (~ 29 to 34 \AA), and a Langmuir surface area for N_2 of $\sim 5900 \text{ m}^2 \text{ g}^{-1}$. The framework delimits two types of mesoporous cages filled with guest molecules, which are present in a 2:1 ratio. The smaller cages exhibit pentagonal windows with a free opening of $\sim 12 \text{ \AA}$, while the larger cages possess both pentagonal and larger hexagonal windows with a $\sim 14.5 \text{ \AA}$ by 16 \AA free aperture.

2. MIL-53(Al), known as a flexible structure, consists of Al^{3+} metal ions, terephthalate ligands and -OH groups.²⁻⁴ Its 3D framework is built up of infinite trans chains of corner-sharing $\text{AlO}_4(\text{OH})_2$ octahedra. The chains are interconnected by the 1,4-benzenedicarboxylate groups, creating 1D rhombic-shaped tunnels. MIL-53(Al) can be divided into MIL-53*as* (Al) (as-synthesized), MIL-53*ht* (Al) (high-temperature) and MIL-53*t* (Al). Evacuation of disordered 1,4-benzenedicarboxylic acid molecules trapped inside the tunnels upon heating leads to a nanoporous open-framework (MIL-53*ht* (Al) or $\text{Al}(\text{OH})[\text{O}_2\text{C-C}_6\text{H}_4\text{CO}_2]$) with empty pores of diameter 8.5 \AA . The material exhibits a Langmuir surface area of $1590 \text{ m}^2 \text{ g}^{-1}$ together with remarkable thermal stability.

3. UiO-66 is a Zr-based MOF with 1,4-benzene-dicarboxylate (BDC) as linker.⁵⁻⁷ The inorganic brick in the series of structures, $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{CO}_2)_{12}$, is 12 coordinated, which is the coordination of metal atoms in closed packed metal structures; the Zr-MOF structures formed with linear ligands are therefore all expanded versions of the cubic close packed (CCP) structure. The inorganic brick consists of an inner $\text{Zr}_6\text{O}_4(\text{OH})_4$ core in which the triangular faces of the Zr_6 -octahedron are alternatively capped by $\mu_3\text{-O}$ and $\mu_3\text{-OH}$ groups.

4. MOF-5 ($\text{Zn}_4\text{O}(\text{BDC})_3$, $\text{BDC}^{2-} = 1,4\text{-benzenedicarboxylate}$) has a face-centered cubic crystal structure in which each corner is formed by $[\text{Zn}_4\text{O}]^{6+}$ metal cluster, while each edge is linked by 1,4-benzenedicarboxylate (BDC).⁸ Isoreticular MOFs (IRMOFs) are a group of cubic networks derived from the prototypic MOF-5, in which four Zn atoms bond to a single O atom, forming regular Zn_4O tetranuclear clusters that are connected by rigid dicarboxylate linkers to form

$\text{Zn}_4\text{O}(\text{dicarboxylate})_3$.⁹ The pore size can be expanded with the long molecular struts biphenyl, tetrahydropyrene, pyrene, and terphenyl. The open space of the isoreticular series crystalline represented up to 91.1% of the crystal volume, as well as homogeneous periodic pores that can be incrementally varied from 3.8 to 28.8 Å.

5. HKUST-1 is a porous open-framework metal coordination polymer $[\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_3]_n$.¹⁰ It has interconnected $[\text{Cu}_2(\text{O}_2\text{CR})_4]$ units (where R is an aromatic ring), which forms face-centered-cubic crystals that contain a three-dimensional (3D) system of channels with a pore size of 1 nm and a window diameter of ~0.9 nm. The material has a reasonable degree of thermal stability (up to 240°C) and a capacity for chemical functionalization of the channel linings arising from the presence of coordinatively unsaturated Cu^{2+} sites.

6. Zeolitic imidazolate frameworks (ZIFs) consist of tetrahedral metal ions (Zn^{2+} or Co^{2+}) bridged by imidazolate linkers.^{11,12} ZIF structures are based on the nets of seven distinct aluminosilicate zeolites, and the tetrahedral Si(Al) and the bridging O are replaced with transition metal ion and imidazolate link, respectively. The imidazolate bridges make an M-IM-M angle close to 145°, which is preferred and commonly found in many zeolites. ZIF-8 and ZIF-7 are two of the most well-known ZIF materials. ZIF-8 has a formula of $\text{Zn}(\text{2-methylimidazole})_2$ and a sodalite (SOD) topology with a space group of *I*-43m, containing large cages (11.6 Å in diameter) connected through 6-ring windows (3.4 Å), while ZIF-7 has a formula of $\text{Zn}(\text{benzimidazole})_2$ and a rhombohedral *R*-3 SOD topology.

Representative COF materials

1. COF-5, produced from boronic ester condensation reaction between 1,4-benzenediboronic acid and 2,3,6,7,10,11-hexahydroxytriphenylene, is highly crystalline with expanded porous eclipsed layers. COF-5 contains 1D rigid mesopores with pore size of 2.7 nm. COF-5 exhibit high thermal stability (to temperatures up to 500 to 600 °C), permanent porosity, and high surface areas ($1590 \text{ m}^2 \text{ g}^{-1}$).¹³

2. COF-LZU1, produced from imine condensation reaction between 1,3,5-triformylbenzene and

1,4-diaminobenzene, has a two-dimensional layered-sheet structure and possesses regular microporous channels with diameter of ~ 1.8 nm.¹⁴ It is a microcrystalline material with a long-range structure. The formation of eclipsed structure originates from the strong tendency for the hexagonal units to form coplanar aggregates which stabilize the $\pi\cdots\pi$ stacking interactions between adjacent layers (distance of ~ 3.7 Å). The 2D layered-sheet structure together with the eclipsed imine bonds renders COF-LZU1 as an ideal porous scaffold for various applications.

References

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