Rational Design of Porous Metal-Organic Frameworks

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Metal-organic frameworks (MOFs) are hybrid crystalline compounds in which inorganic clusters are connected with polytopic organic linkers by strong bonds to form extended structures[1]. Some MOFs can exhibit much higher porosity (~6,000 m^2/g) than found in any traditional crystalline material (Figure 1). This remarkable property of porous MOFs makes them attractive for a range of applications, such as gas storage, catalysis, and drug delivery[2].

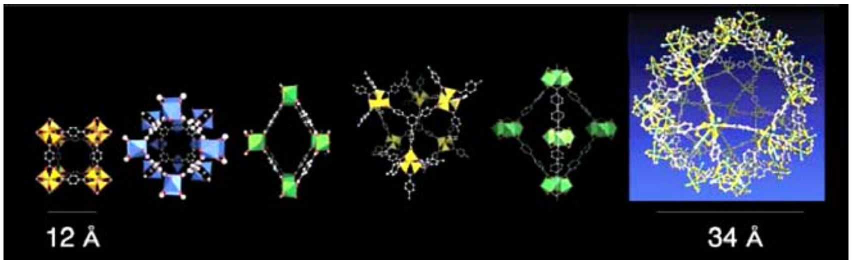

Figure 1: A series of most-cited MOFs with different cages displayed on the same scale. From left to right: MOF-5, HKUST-1, MIL-53, MOF-177, MIL-88, MIL-101. Adapted from ref. 2.

The properties of MOFs are easier to tune synthetically than those of other porous compounds. Crystal structures of most compounds are very difficult to predict a priori, but the structures of MOFs are controllable to certain degree by the choice of the molecular building blocks. This great advantage provides an opportunity to obtain target porous materials with predetermined structures and tailored properties such as size, shape, and chemical functionalities of the pores. Therefore, a general methodology for rational design of porous MOFs has been pursued for past two decades[2].

In the early 1990s, pioneering work was done by R. Robson and coworkers[3]. They applied a conventional strategy, the "node and spacer" approach, to guide the design of porous coordination polymers. This approach was first introduced by A. F. Wells in 1979 for the interpretation of zeolite structures[4], and is now considered as the foundation of today's design strategies of crystalline materials[5]. In this method, metal ions and ditopic organic ligands serve as nodes and linear spacers for the construction of infinite frameworks. By using as nodes metals ions with different coordination numbers the topology of the framework is controlled[5] (Figure 2).

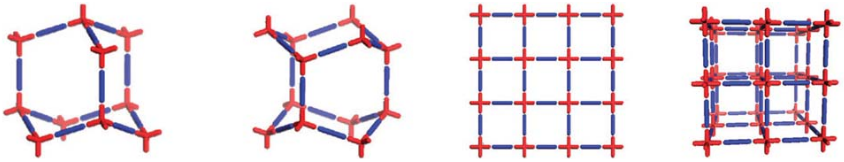

Figure 2: Representative frameworks accessible with the "node and spacer" approach. Red: metal ions; Purple: linear organic spacer. Adapted from ref. 5.

The “node and spacer” approach guided the design of coordination polymers through the 1990s. By using this approach, Robson and coworkers formed a single diamond-like $[Cu^{I}\{C(C_6H_4CN)_4\}]^+$ porous structure in which guest anions could be reversibly exchanged in the pores[3]. Another iconic example came from Fujita’s group, which in 1994 were first to demonstrate shape-specific catalytic activity in the presence of porous 2-periodic $[Cd(NO_3)_2(4,4'\text{-bpy})_2]_n$ material[6].

Around 2000, a breakthrough was made by O. M. Yaghi and others[7]. They replaced metal ions with inorganic clusters – known as the secondary building units (SBUs), which enabled them to greatly expand the range of rigid ligands that could be used as linkers. They called this strategy reticular chemistry[8]. Yaghi and coworkers further demonstrated how diverse linkers yield the same framework topology, which formed the basis of isoreticular principle. This principle has been used to systematically generate series of MOFs with varying pore sizes and to tune other properties of the framework. The prototypical example of materials designed by this method is MOF-5 and its isoreticular congeners (Figure 3), built of Zn_4O SBUs linked by different linear dicarboxylates in cubic lattice[9].

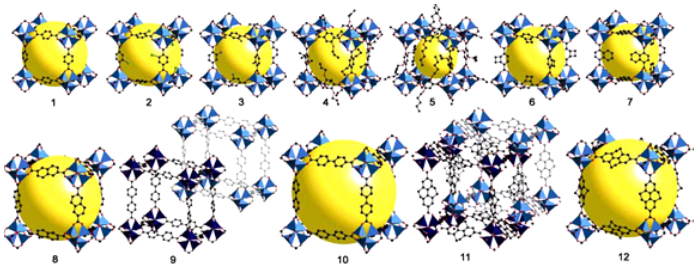

Figure 3: Examples of isoreticular MOFs based on Zn_4O clusters. Adapted from ref. 9.

SBUs offer distinct advantages over simple metal ions as nodes. Their larger size and higher rigidity makes large pores accessible by preventing collapse of highly porous structures and by destabilizing interpenetrated frameworks[10]. Up to now, a large number of SBUs of various shapes have been reported[11]. The search for new SBUs continues and is expected to facilitate the design of new MOFs tailored to specific applications.

Reticular chemistry works best with rigid spacers but often fails with flexible ones. For example, Férey and coworkers used a flexible nitrogen-rich tricarboxylate linker to build a lanthanum MOF. By comparing its structure to that obtained with a rigid linker, they identified the limit of the isoreticular principle and illustrated the challenges facing rational design of MOFs with flexible spacers[12].

Other approaches to the design of MOFs have been inspired by the developments in supramolecular chemistry. One example utilized metal-organic polyhedra (MOPs), which can be used as building blocks with high symmetry and connectivity, to increase the topological diversity of three periodic net. Zaworotko and coworkers reported the use of MOPs with O_h symmetry, $M_2(bdc)_2L_2$ (M: Cu(II); bdc: 1,3-benzene dicarboxylate and L: solvent molecules), as highly connected nodes to construct much more complicated MOFs[13]. MOPs can be functionalized at either the vertices or the faces. The use of MOPs as building blocks extends the scale of porous MOFs in to a new level of complexity and may yield unprecedented crystal structures.

While much progress has been made toward rational design of porous MOFs, significant challenges remain, particularly with respect to using flexible linkers and designing highly thermally stable structures. We need more sophisticated understanding of the interactions between inorganic and organic building blocks across multiple length scale to overcome these challenges. Nonetheless, it is very possible that well-tailored porous MOFs with desired properties will be rationally designed in the near future and the exploration of their practical applications will be a stimulating scientific pursuit.

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