

Modular Synthesis of Porous Metal-Organic Framework

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Synthesis of new porous frameworks with specific pore size and type are of considerable interest for the appearance of zeolite-like functionalities. It is useful to take advantage of metal-organic framework (MOF) because of its designable feature.

In 1991, Robson and Hopkins resolved the structure of $\text{Zn}(\text{CN})_2$ and $\text{Cd}(\text{CN})_2$ by the single crystal X-ray diffraction.¹ The 2-fold interpenetrated diamondoid structure of both compounds represent the prototype of porous coordination frameworks (Figure 1). Soon after that, it has spawned an exponential growth in research activity devoted to the metal-organic framework (MOF).²

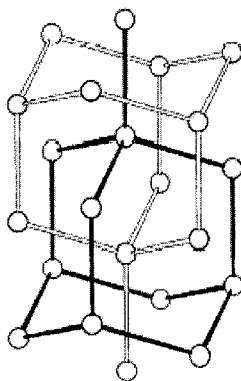


Figure 1. View of interpenetrating diamondoid unit in $\text{Zn}(\text{CN})_2$ and $\text{Cd}(\text{CN})_2$

MOF are constructed from node (transition metal or metal cluster) and bi-functional spacer (organic ligand). Based on a variety of coordination geometries of metal, different framework motifs have been discovered, such as honeycomb, octahedral network³, etc. However, these porous crystals usually suffered from interpenetration, which could significantly reduce the size of pore. Collapse is also a common phenomenon during the dehydration of crystal, since nature dislikes a vacuum. As the result, potential applications of MOFs have seldom been touched in the early years.⁴ In 1999, a non-interpenetrated cubic framework, MOF-5 (Figure 2), has been designed and synthesized by Yaghi and his coworkers.⁵ Unlike the traditional approach, in their work, (Zn_4O) core has been successfully applied as a second building unit (SBU) as shown in Figure 3, which could offer a number of advantages such as: improved control of stereochemistry of building blocks, high thermal stability etc.⁶ Based on SBU concept, a series of frameworks based on the same net as MOF-5 have been synthesized with functionalized structures and shown to have permanent porosity. Functional groups added on their spacers could dramatically change the property and size of internal channels. These crystals have also been studied as functional materials for methane and hydrogen storage and have shown promising results.^{7,8}

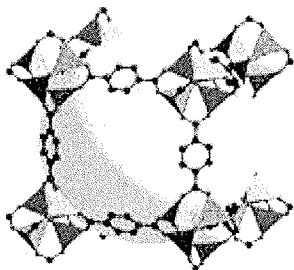


Figure 2. The MOF-5 structure

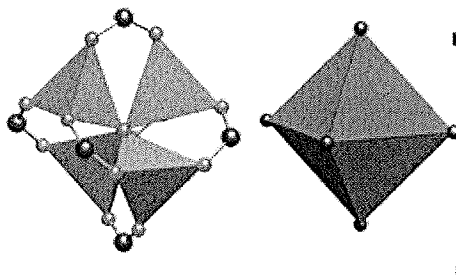


Figure 3. Zn₄O SBU

Recent theoretical calculations⁹ indicate that octupolar chromophores (with 3-fold rotational symmetry) can improve transparency/optical nonlinearity tradeoff when compared to traditional dipolar chromophores. By saliently choosing their molecular building block, Lin and his coworkers report the first NLO-active bulk materials based on MOF,¹⁰ which open the door for further investigation of other NLO-active multipolar coordination networks.

PIZA-1, a robust and very polar porous network, has been reported recently by Suslick and his co-workers.¹¹ Sorption studies of a series of molecules have been carried on this functional material. Experiments show that PIZA-1 is highly selective on the size, shape and hydrophobicity of the adsorbate. Its metalloporphyrin building blocks also indicate a potential application as oxidation catalysts, which is yet to be discovered.

The long-standing challenges of modular synthesis are just beginning to be addressed with success. It is now an open season for the functional metal-organic frameworks.¹²

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