

# Molecule Matters

## Metal Organic Frameworks (MOFs)

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Storage space is a perennial problem not only in macroscopic world but at the molecular level as well. Efficient storage of certain gases such as hydrogen, methane etc has futuristic technological applications. Therefore, race is on for the discovery of new materials with largest storage capacity per gram of the material. Metal organic framework (MOF) materials are a class of light weight hybrid materials with surface areas per gram that could cover an entire foot ball field. This article gives a glimpse of the recent advances in MOFs.

### Introduction

Porous solids are of scientific and technological interest [1]. They are classified according to their pore diameter, materials with pore size of 20 Å or less are called microporous, those with pore size in the range of 20 to 500 Å are called mesoporous and those having pore size of more than 500 Å are called macroporous. Among the well known porous materials are zeolites which may be aluminosilicates and aluminophosphates [2]. They are purely inorganic porous materials. Metal organic frameworks (MOFs) are another class of porous materials consisting of metal ions and coordinating organic spacer units. They are crystalline in nature and belong to the general family of coordination polymers. The basic building blocks for such hybrid materials are metal ions and polydentate organic ligands [3]. These open framework materials are of current interest for many technological applications such as gas storage, molecule separations and catalysis; hydrogen storage, chiral separation and heterogeneous catalysis are focus areas.



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### Key words

Porous solids, organic zeolites, coordination polymers, gas storage, MOF, SBU.

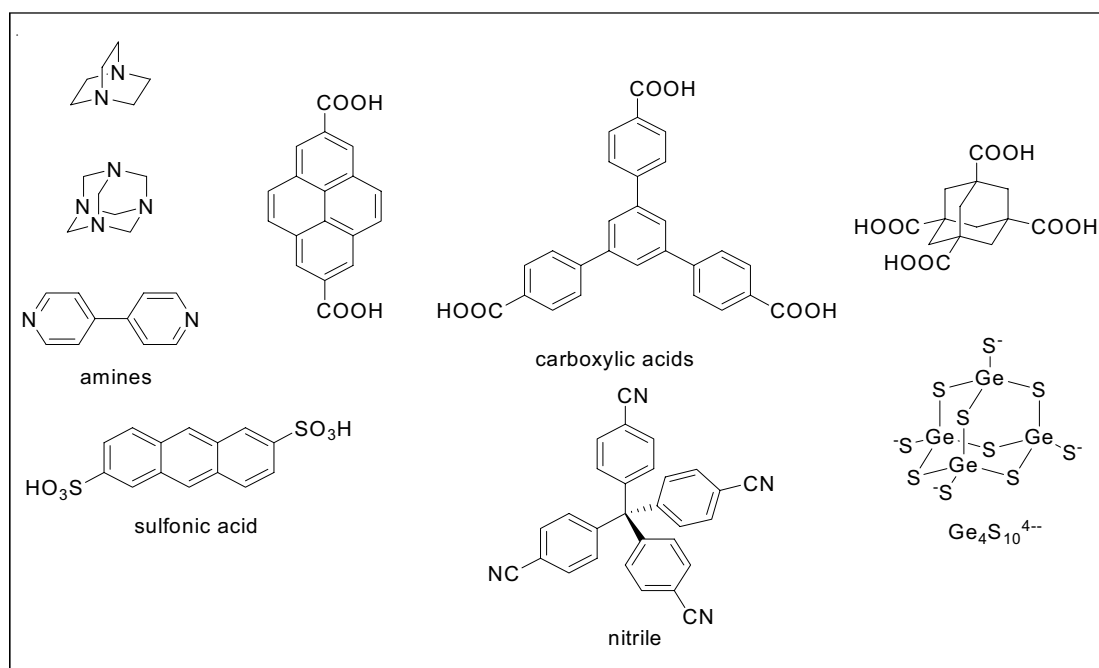


With the proper choice of the metal ion and the organic spacers, it is possible to tailor-make MOFs of specific dimension, pore size and functionalities.

### Primary Building Blocks of MOFs

The organic spacers generally contain carboxylic acid and amine functionality, although potentially any coordinating functional group such as nitrile, isonitrile and thiol can be used. The organic spacers and the metal ions form the primary building blocks in the synthesis of MOFs resulting in certain motifs which are the secondary building units (SBUs). Propagation of the SBUs into two- and three-dimensional network results in the formation of MOFs. With the proper choice of the metal ion and the organic spacers, it is possible to tailor-make MOFs of specific dimension, pore size and functionalities. According to Yaghi [3] the synthesis of MOFs is termed as reticular synthesis. Reticular synthesis is described as the process of assembling rigid molecular building blocks into predetermined ordered molecular networks. The metal ion controls the coordination geometry (square planar, tetrahedral, octahedral etc) and organic spacer controls features such as the directionality of propagation and size of the pores formed in such materials. Some of the commonly employed organic spacers and building units are shown in *Scheme 1*.

**Scheme 1. Structures of some of the spacer units used in MOFs.**

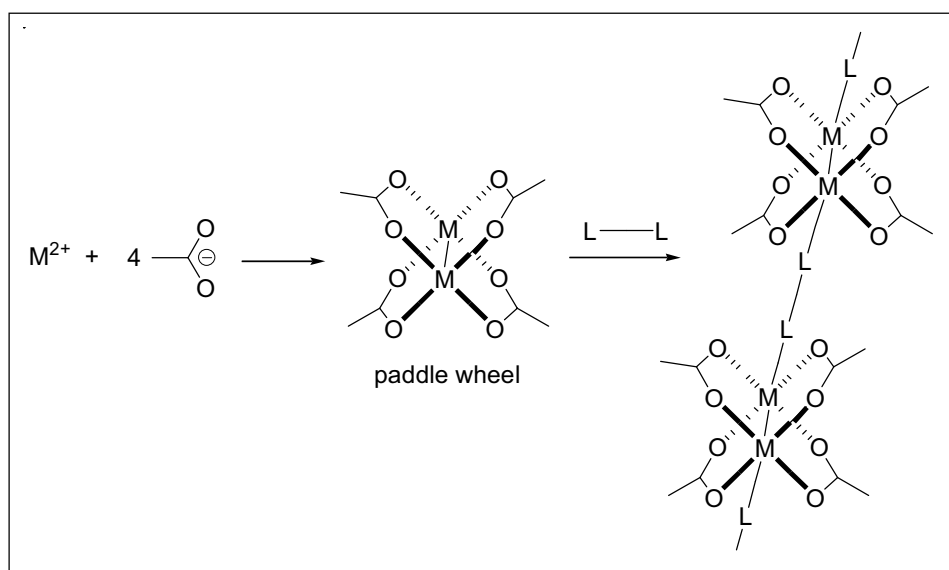


Based on the structural analysis of several MOFs, Ramanan and Whittingham [4] have suggested that the formation of the point zero charge (*pzc*) molecule at the isoelectric point is crucial for the formation of neutral MOFs with well defined structures. Formation of ionic MOFs would primarily be controlled by electrostatic interactions between the ions. The formation of *pzc* molecule occurs by the displacement of water molecules (in aqueous medium) from the aqua complex of the metal ions by the organic spacers. The initial interaction would be hydrogen bonding between the coordinated water molecules and the hetero atom of the organic spacers. Formation of well-defined geometries of *pzc* molecule is controlled by the coordination geometry of the metal ion itself.

### Secondary Building Units (SBUs)

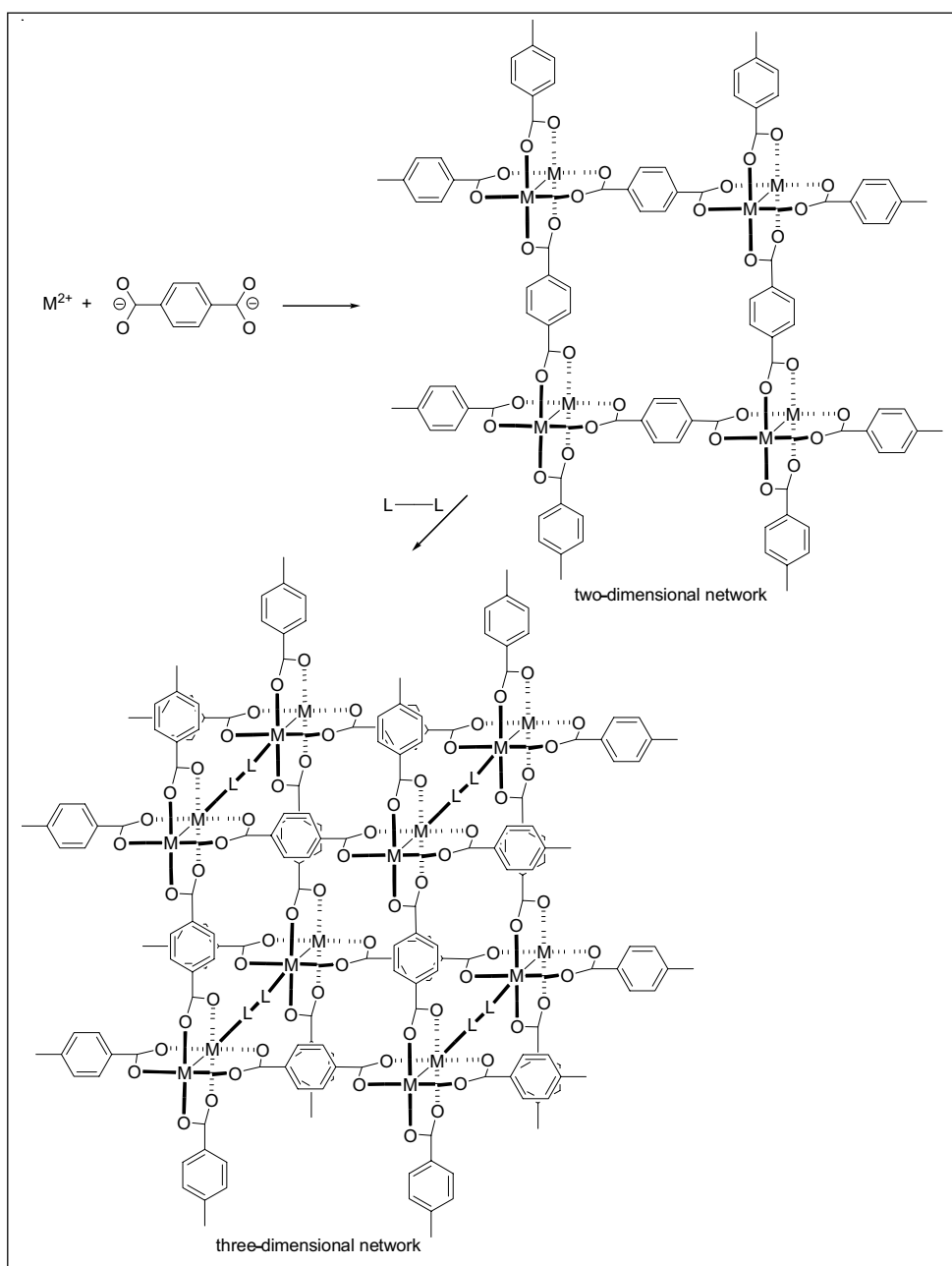
Coordination of carboxylate ion to a metal center can result in many different SBUs, of which paddle wheel and  $M_4O(CO_2)_6$  motifs will be discussed here [5]. Coordination of four carboxylate groups around two metal centers result in the formation of the paddle wheel motif with two free coordination sites on the metal centers that can propagate this SBUs into linear (one-dimensional) network (*Scheme 2*).

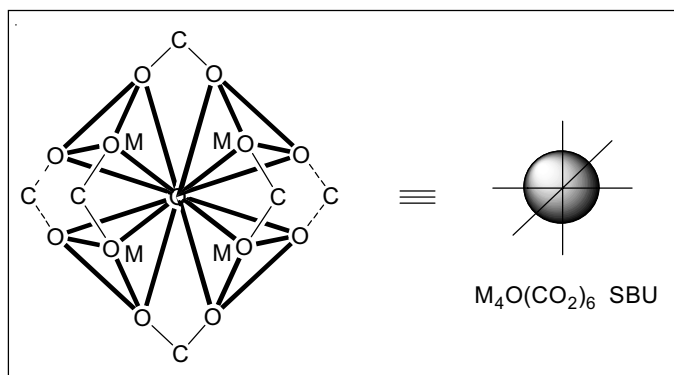
**Scheme 2. Formation of paddle wheel SBUs and one-dimensional network.**



**Scheme 3. Formation of two- and three-dimensional networks from paddle wheel SBUs made up of terephthalate and metal ions.**

If a dicarboxylic acid is used instead of a monocarboxylic acid, it could result in the formation of a two-dimensional network and with an additional ligand coordinated on the metal center (L-L), a three-dimensional network can be generated (Scheme 3).





**Scheme 4.** The  $MO_4$  tetrahedra are shown in thick lines and C and M represent the carboxylate carbons and metal ions respectively. The overall geometry is a regular octahedron in which the carbon atoms of the six carboxylate groups occupy the vertices.

Typical examples of L-L ligands are 4,4'-bipyridine and 1,4-diazabicyclo[2.2.2] octane (DABCO) (Scheme 1). Some of the organic linkers that can impart higher dimensionality to the MOFs are shown in Scheme 1. The shape and geometry of these linkers strongly influence the pore size, geometry and topology of the MOFs obtained. The octahedral geometry of the  $M_4O(CO_2)_6$  motif is defined by the four  $MO_4$  tetrahedra sharing a common vertex, and six carboxylic acid carbons occupying the vertices of the octahedron (Scheme 4) [6].

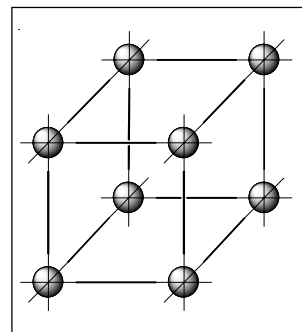
The  $M_4O(CO_2)_6$  SBUs are typically formed when the organic linker is reacted with the metal oxide rather than metal salts. The  $M_4O(CO_2)_6$  SBUs are connected by aromatic rings to yield MOFs of different structures. For example, when the SBUs are connected by *para* phenylene units (for example, terephthalic acid derivatives), the MOFs formed have a cubic structure as shown in Scheme 5.

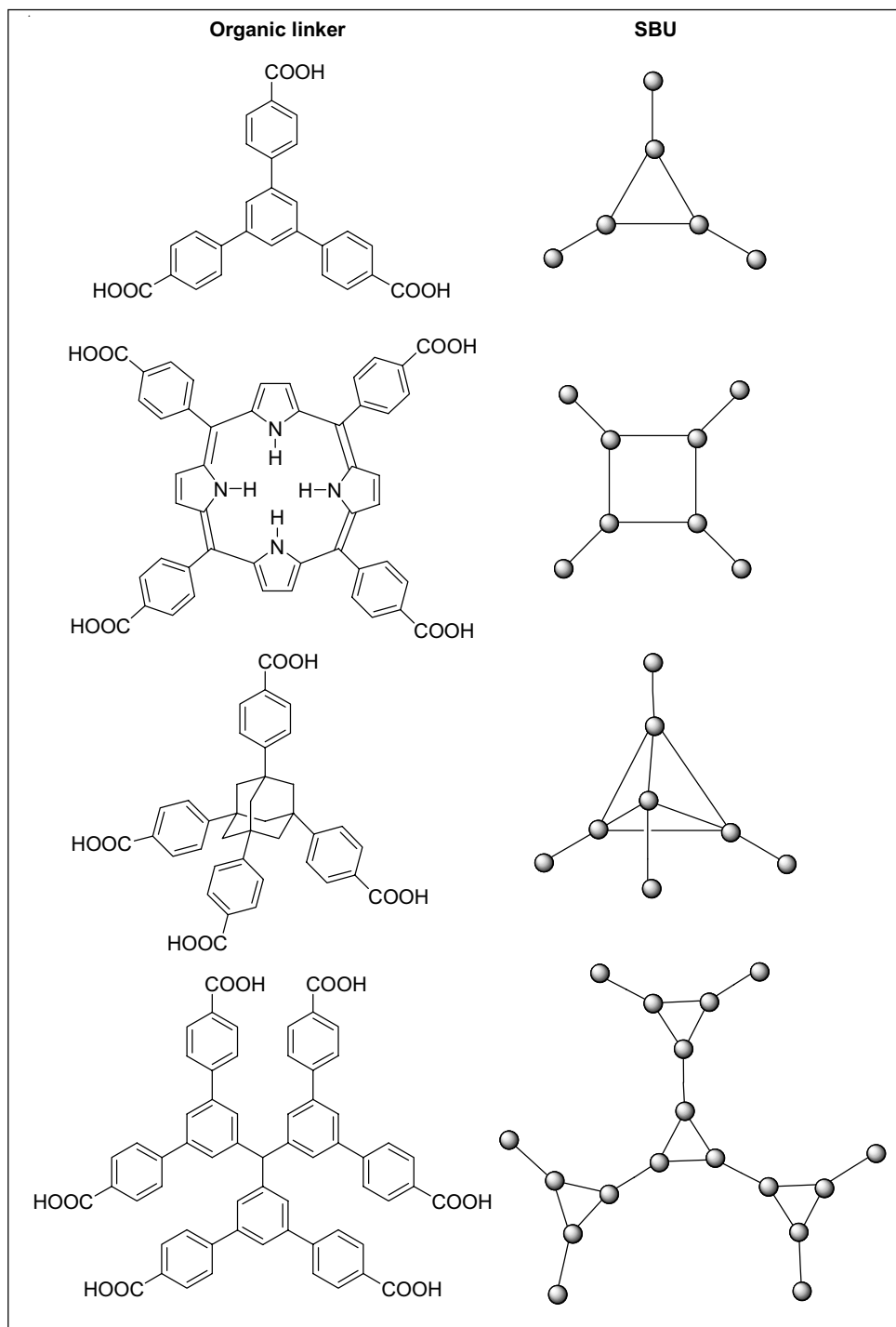
Examples of carboxylate building blocks and the topology of the SBUs that can be generated using them are shown in Scheme 6. Using the reticular approach an endless array of MOFs can be generated with varied topologies, pore dimensions and pore volumes.

### Applications of MOFs

**a) MOFs as Storage Materials:** With the fossil fuels disappearing rapidly, there is an urgent need to identify alternative energy

**Scheme 5.** Cubic unit formed by  $M_4O(CO_2)_6$  SBUs (spheres) and *para* phenylene units (thick lines).





**Scheme 6.** Representative organic linker units and the topology of the SBUs generated.



sources which are sustainable. Hydrogen is identified as the fuel of the future as it can be readily made and is the cleanest fuel one can imagine as its combustion product is just water. However, storage and transportation of hydrogen for on-board applications continue to be two major technical problems [7]. The 2010 target for hydrogen storage density is 6.0 wt% and 45 kg H<sub>2</sub> per m<sup>3</sup>. In view of their porous nature with large surface areas MOFs are considered to be promising materials for hydrogen storage. MOFs are easy to synthesize and the scale up of production is facile. MOFs with surface area greater than 1000 m<sup>2</sup> g<sup>-1</sup>, which is greater than that demonstrated for zeolites, have been reported in literature. MOF made from Zn<sup>2+</sup> and 1,3,5-(4-carboxyphenyl) benzene (Entry 1 in *Scheme 6*) has a monolayer with equivalent surface area of 4,526 m<sup>2</sup> g<sup>-1</sup>. It has a hydrogen uptake capacity of 1.2 wt% at 77 K and 1 atm [8]. Hydrogen uptake as high as 3.8 wt % has been reported for MOF synthesized from Al<sup>3+</sup> and terephthalic acid (tpa) [Al(OH)(tpa)] at 77 K and 16 bar pressure [9]. Although these results are promising, there are some issues of fundamental nature concerning the thermal and pore dimension stabilities of the MOFs. The pores of MOFs are generally filled with solvent molecules during their synthesis. Removal of these guest molecules can result in the collapse of the porous structure making them useless for any technological applications. MOFs with permanent pores are particularly useful as storage materials. From the available data there is no apparent correlation of hydrogen storage capacity to the surface area or pore volume of MOFs. Recent theoretical investigations [10] indicate that at low pressures of H<sub>2</sub>, the initial site of hydrogen adsorption is the metal clusters and with increasing pressures, uptake of more hydrogen is observed, occupying the aromatic walls of MOFs. The interaction between the MOF and hydrogen molecule is essentially weak van der Waals interaction. Based on theoretical studies it is suggested that MOFs with lighter metals (Be and Mg instead of Zn) and larger aromatic linkers are good candidates for hydrogen storage. There are nearly 5,000 MOFs with two-dimensional and three-dimensional structures reported so far, but only a fraction of these have been tested for hydrogen storage application. With the

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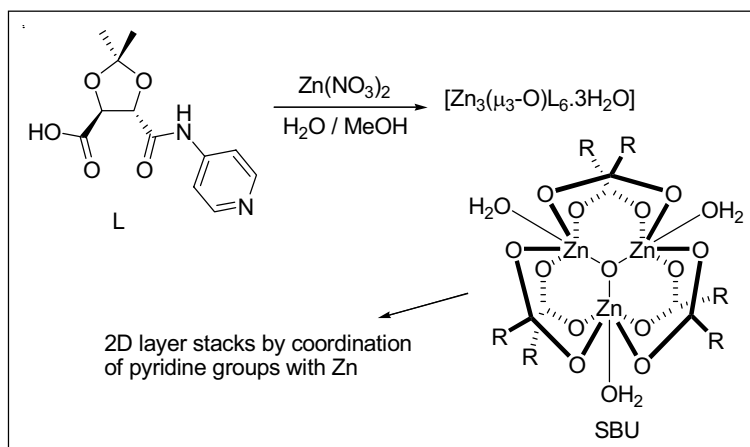


rapid advancements occurring in this area, it is hoped that some useful MOFs will emerge in the near future to meet the 2010 target set for on-board hydrogen storage. Besides hydrogen storage, efforts are underway for the storage of other gaseous and small hydrocarbon molecules (C1 to C4) in MOFs [11].

**b) Separation and Catalysis:** Zeolites are well known for shape selectivity due to their restrictive pore dimensions [12]. MOFs are also suitable materials for application in separation technology, in particular chiral separation, which has wide applications in chemical and pharmaceutical industries. MOFs bearing homochiral ligands and hence pores with chiral environment are known and have been demonstrated to be useful in chiral separation [13]. For example, MOF synthesized from the ligand shown in *Scheme 7* with  $Zn^{2+}$  is homochiral in nature in view of the chirality of the ligand. It has a layered structure with large one-dimensional chiral channels with voids accounting for 47% of the total volume. When racemic  $[Ru(2,2'-bipy)_3]Cl_2$  is treated with this MOF, it is observed that the color of the MOF changes from white to reddish yellow accompanied by the exchange of 80% of lattice protons with  $[Ru(2,2'-bipy)_3]^{2+}$ ; the exchange happens with 66% enantiomeric excess (ee) in favour of the D form of the ruthenium complex [14].

**Scheme 7. Formation of chiral MOF using enantiopure organic building unit, L. The SBU in this case is an oxo-bridged trinuclear metal carboxylate hydrate. RCOO- group in the SBU corresponds to the carboxylate derived from L wherein the two oxygen atoms correspond to the carboxylate oxygen and the amide oxygen forming a six-membered chelate. L is derived from enantiopure tartaric acid.**

The same chiral MOF is also used to demonstrate enantioselective catalytic activity. Transesterification of 2,4-dinitrophenyl acetate





with racemic alcohols ( $\pm$  1-phenylethanol) proceeded with modest enantioselectivity of 8% ee for either the *R* isomer or the *S* isomer depending upon the chirality of the MOF used. This is an example of the kinetic resolution of a racemic alcohol. Although very modest in selectivity, it is noteworthy that asymmetric induction mediated by modular porous materials has never been observed prior to this report.

### Summary and Outlook

Synthesis of MOFs is a contemporary area of research with potential in many technological applications. Creation of MOFs with predetermined architecture, pore size and permanent pores is a challenging problem. A race is on among the players in this field to synthesize a MOF with the largest surface area. Synthesis of chiral MOFs using enantiopure organic linkers and cavity functionalized MOFs to perform specific chemical reactions are currently in progress. Although porous MOFs are unlikely to compete with zeolites and metal oxide based porous materials in their thermal stabilities, these soft materials will nevertheless find use in many applications such as hydrogen storage, asymmetric transformation and separation in the future. The fact that MOFs are easy to assemble from their organic and inorganic building blocks and the ease of scale up makes them attractive candidates for investigation. The kinds of materials that can be produced in this area are limited only by the imagination of those who attempt their synthesis; as one of the leading researchers in the field, Féret put it, 'The limits are in our imagination' [3e].

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