

**Figure 9.** The three-dimensional framework of UCR-20 (left) and UCR-22 (right) families of sulfides.

consists of four 3-rings fused together. For materials reported here, the framework density defined as the number of T-atoms in  $1000\text{\AA}^3$  ranges from 4.4 to 6.5.

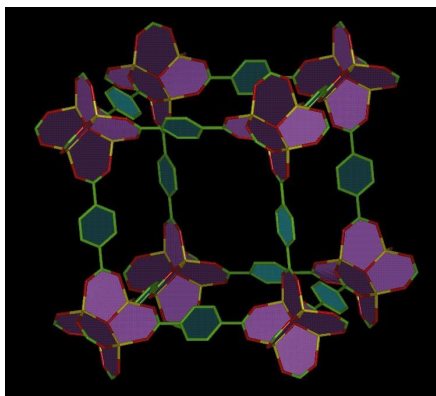
Although these chalcogenides are strictly zeolite-type tetrahedral frameworks, it is possible to view them as decoration of even simpler tetrahedral frameworks. Here, each  $M_4S_{10}$  unit can be treated as a large artificial tetrahedral atom. With this description, UCR-20 has the decorated sodalite-type structure, in which a tetrahedral site in a regular sodalite net is replaced with a  $M_4S_{10}$  unit. UCR-21 has the decorated cubic ZnS type structure. UCR-23 has the decorated  $CrB_4$  type network in which tetrahedral boron sites are replaced with  $M_4S_{10}$  units.

Upon exchange with  $Cs^+$  ions, the percentage of C, H, and N in UCR-20GaGeS-TAEA was dramatically reduced. The exchanged sample remained highly crystalline as the original sample. The  $Cs^+$  exchanged UCR-20GaGeS-TAEA displayed type I isotherm characteristic of a microporous solid. This sample has a high Langmuir surface area of  $807\text{m}^2/\text{g}$  and a micropore volume of  $0.23\text{cm}^3/\text{g}$  despite the presence of much heavier elements (Cs, Ga, Ge, and S) compared to aluminosilicate zeolites.

## 5 Microporous Metal-Organic Frameworks

Currently, the synthetic design of metal-organic frameworks (also known as coordination polymers) is a very active research area [90,91]. Many new microporous materials synthesized in the past several years belong to this family. Unlike zeolites that have an inorganic host framework, in metal-organic frameworks, the three-dimensional connectivity is established by linking metal cations or clusters with bidentate or multidentate organic ligands. The resulting frameworks are hybrid frameworks between inorganic and organic building units and should be distinguished from microporous materials in which organic amines are encapsulated in the cavities of purely inorganic frameworks.

The development of metal-organic framework materials began in the early 1990s and was apparently an extension of the earlier work on three-dimensional cyanide frameworks [14,92,93]. In  $K_2Zn_3[Fe(CN)_6]_2 \cdot xH_2O$  [94], octahedral  $Fe^{2+}$  and tetrahedral  $Zn^{2+}$  cations are joined together by linear  $CN^-$  groups to form a three-dimensional framework with cavities occupied by  $K^+$  cations and water molecules. To generate large cavities, one method is to replace short  $CN^-$  ligands with large ligands such as nitriles [93], amines, and carboxylates [95]. A large variety of structural building units are possible with this approach. However, at the early stage of their development, metal-organic frameworks were plagued by problems such as lattice interpenetration and the low stability upon guest removal.



**Figure 10.** The framework of MOP-5, one of the first microporous metal-organic frameworks [98].

During the past several years, a substantial progress has occurred in the rational synthesis of these materials and a large number of metal-organic frameworks have been made that are capable of supporting microporosity as demonstrated by their gas sorption properties [96,97,98,99]. Such success was in part because of the use of rigid di- and tri-carboxylates and judicious selections of experimental conditions. It is worth noting that despite the wide selection of organic molecules that can serve as bridges between inorganic building units, new metal-organic frameworks are often made by changes in synthesis conditions such as pH, type of solvents, and temperature, instead of using new organic linker molecules. For example,  $Zn(BDC)(DMF)(H_2O)$  (denoted as MOF-2, BDC = 1,4-benzenedicarboxylate, DMF = N, N'-dimethylformamide),  $Zn_3(BDC)_3 \cdot 6CH_3OH$  (denoted as MOF-3), and  $(Zn_4O)(BDC)_3(DMF)_8(C_6H_5Cl)$  (MOF-5) are all made from  $Zn^{2+}$  and BDC [100]. Their topological differences are caused by spacing-filling or structure-directing solvent molecules. These compounds clearly show the importance of controlling the synthesis conditions including the selection of solvent. This is somewhat similar to the synthesis in zeolites where the primary building units are the same (i.e.,  $SiO_4$  and

AlO<sub>4</sub> tetrahedra) in all structures and the difference in secondary building units and three-dimensional topologies is caused by extra-framework structure-directing agents.

Microporous metal-organic materials are complementary to oxide and chalcogenide based microporous materials such as zeolites. There are many fundamental differences between metal-organic materials and zeolites so that rather than competing with each other, they are expected to have different applications. For example, unlike zeolites and chalcogenides that usually have a negative framework, metal-organic frameworks (excluding cyanides) reported so far are usually positive or neutral. Therefore, while zeolites are cation exchangers, metal-organic frameworks can be anion exchangers.

For a given framework topology, the framework of a zeolite or a phosphate can often have a range of different charge density by varying the Si/Al ratio or doping Al<sup>3+</sup> sites with divalent cations. The difference in the framework charge density in zeolites makes it possible to tune hydrophilicity or hydrophobicity of the framework. Metal-organic structures do not seem to have such flexibility in adjusting the framework charge density, however, the hydrophilicity or hydrophobicity in metal-organic frameworks is tunable by introducing different organic groups as shown in a series of compounds denoted as IRMOF-n [101].

Metal cations in metal-organic frameworks are usually transition metals, while in oxides and chalcogenides, main group elements dominate the framework cationic sites. Therefore, metal-organic frameworks can bind to guest molecules through coordinatively unsaturated transition metal sites [102,103]. Such interaction is not common with main group elements in zeolites or microporous phosphates, even though transition-metal doped zeolites or phosphates might contain active transition metal sites.

One potential with metal-organic frameworks is the possibility to form porous materials with pore size over 10 Å by using large inorganic clusters or organic linkers. This potential is evidenced by the recent synthesis of a series of isorecticular MOFs denoted as IRMOF-n (n = 1 through 7, 8, 10, 12, 14, and 16) from different dicarboxylates [101]. These compounds have a calculated aperture size (also called free-diameter) from 3.8 to 19.1 Å. IRMOFs also demonstrate the feasibility to have different organic groups in three-dimensional frameworks without a change in the framework topology.

The idea of using chiral structure-directing agents to direct the formation of chiral inorganic frameworks has been around for some time. However, few synthetic successes have been reported. Metal-organic frameworks provide a new opportunity in the design of chiral porous frameworks because chiral organic building units can be directly used for the construction of the framework. One recent example has shown this approach to be highly promising [104].

The recent synthetic success in producing microporous metal-organic frameworks has shifted some focus from the synthetic design to the potential

applications. One promising application of metal-organic frameworks is in the area of gas storage. Several metal-organic framework materials have been found to have a high capacity for methane storage [101,105,106]. For example, at 298K and 36atm, the quantity of methane adsorbed by IRMOF-6 is as high as  $155\text{cm}^3$  (STP)/ $\text{cm}^3$ , considerably higher than other crystalline porous materials such as zeolite 5A ( $87\text{cm}^3/\text{cm}^3$ ). Such high adsorption capability is likely related to the more hydrophobic property of organic building units in these metal-organic frameworks, in addition to their high pore volumes and wide pore sizes.

In the following, we discuss in some more details metal-organic frameworks that either have a positive or neutral framework. Excluding cyanide frameworks, metal-organic frameworks with negative charges on the framework are far less common and remain to be explored in the future.

### 5.1 Cationic metal-organic frameworks

Cationic metal-organic frameworks were among the earliest to be studied. Some early examples of cationic metal-organic frameworks were formed between monovalent metal cations ( $\text{Cu}^+$  or  $\text{Ag}^+$ ) and neutral amines. Metal cations in these compounds can take different coordination geometry such as linear, trigonal or tetrahedral. Interestingly, ligands can also take different geometry. Examples of linear, trigonal, and tetrahedral ligands are 4,4'-bipyridine (4, 4'-bpy), 1,3,5-tricyanobenzene, and 4,4',4'',4'''-tetracyanotetraphenylmethane, respectively.

Examples of compounds with the cationic metal-organic frameworks include  $\text{Ag}(4,4'\text{-bpy})\text{NO}_3$  [107] and  $\text{Cu}(4,4'\text{-bpy})_2(\text{PF}_6)$  [108]. In  $\text{Ag}(4,4'\text{-bpy})\text{NO}_3$ ,  $\text{Ag}^+$  is coordinated to two 4,4'-bpy molecules in a nearly linear configuration and the three-dimensional framework is formed with the help of Ag-Ag ( $2.977\text{\AA}$ ) interactions. In  $\text{Cu}(4,4'\text{-bpy})_2(\text{PF}_6)$ ,  $\text{Cu}^+$  ions have tetrahedral coordination and 4,4'-bpy behaves very much like linear CN- groups between two tetrahedral atoms. However, much larger void space forms as a result of longer length of 4,4'-bpy and such void space is reduced by the formation of four interpenetrating diamond-like frameworks in  $\text{Cu}(4,4'\text{-bpy})_2(\text{PF}_6)$ .

Some cationic frameworks have been found to display zeolitic properties such as ion exchange with anions in the solution. However, it has been difficult to remove extra-framework species to produce microporosity. Because of this limitation, there has been an increasing interest in using carboxylates as organic linkers. The current synthetic approach for the synthesis of carboxylate-based metal-organic frameworks usually gives rise to neutral frameworks discussed below.

### 5.2 Neutral metal-organic frameworks

In oxide and chalcogenide molecular sieves, a low framework charge generally means a high thermal stability. Therefore, neutral metal-organic frameworks should

provide the best opportunity for generating microporous metal-organic frameworks. In a metal-organic compound with a neutral framework, the host-guest interaction tends to be weaker than that in a solid with a charged framework. The weak host-guest interaction makes it possible to remove guest solvent molecules at relatively mild conditions. In addition, the neutral framework also tends to be more tolerant of the loss of neutral guest molecules.

Among the first metal-organic frameworks that showed zeolite-like microporosity through reversible gas sorption are MOF-2,  $\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_x$  (denoted as HKUST-1 or Cu-BTC, BTC = 1,3,5-benzenetricarboxylate), and MOF-5 [97,98,109]. A key structural feature of Cu-BTC is the dimeric Cu-Cu (2.628 Å) unit. A detailed investigation of sorption properties showed that Cu-BTC may be useable for separation of gas mixtures such as  $\text{CO}_2$ -CO,  $\text{CO}_2$ - $\text{CH}_4$ , and  $\text{C}_2\text{H}_4$ - $\text{C}_2\text{H}_6$  mixtures [110].

The framework structure of MOF-5 is particularly simple with  $(\text{Zn}_4\text{O})^{6+}$  clusters arranged at eight corners of a cube and linear BDC linkers located on edges of the cube (Fig. 10) [98]. The  $(\text{Zn}_4\text{O})^{6+}$  cluster has a pseudo-octahedral connectivity because it connects to BDC through six edges of  $\text{Zn}_4$  tetrahedra. Even more interesting is the fact that BDC molecules can be replaced by a series of different dicarboxylates without altering the framework topology [101]. This provides an elegant means of adjusting the pore size and framework functionality.

Neutral frameworks can also be prepared from neutral organic ligands. One such example is  $\text{CuSiF}_6(4,4'\text{-bpy})_2 \cdot 8\text{H}_2\text{O}$  [106]. In this case,  $\text{Cu}^{2+}$  cations are linked into two-dimensional sheets by 4,4'-bpy ligands and these sheets are then linked into a three-dimensional framework by  $\text{SiF}_6^{2-}$  anions. This compound is microporous and has a high adsorption capacity for methane.

Metal-organic frameworks can also be created by a combined use of amines and carboxylates. For example, in  $[\text{Zn}_4(\text{OH})_2(\text{fa})_3(4,4'\text{-bpy})_2]$  (fa = fumarate), dicarboxylate and diamine molecules work together to link  $\text{Zn}_4(\text{OH})_2$  units into an interpenetrating three-dimensional framework [111]. Furthermore, carboxylate-substituted amines can simultaneously use COO- and N to bind to inorganic units to create an extended framework. One example is  $\text{Cu}(\text{INA})_2 \cdot 2\text{H}_2\text{O}$  (INA = isonicotinate or pyridine-4-carboxylate) [112].

### 5.3 Metalloporphyrin-based metal-organic frameworks

A special class of ligands are porphyrins and metalloporphyrins. Metalloporphyrins can form either cationic or neutral frameworks depending on the nature of substituent groups. Two of the earliest examples are  $\text{Cu}(\text{II})(\text{tpp})\text{Cu}(\text{I})\text{BF}_4(\text{solvent})$  and  $\text{Cu}(\text{II})(\text{tcp})\text{Cu}(\text{I})\text{BF}_4 \cdot 17(\text{C}_6\text{H}_5\text{NO}_2)$  (tpp = 5,10,15,20-tetra(4-pyridyl)-21H,23H-porphine; tcp = 5,10,15,20-tetrakis(4-cyanophenyl)-21H,23H-porphine) [113]. In both cases, the framework is constructed from equal numbers of tetrahedral (Cu)

and square planar (Cu-tpp or Cu-tcp) centers. Neither of these two compounds is stable upon solvent removal.

A stable metalloporphyrin-based metal-organic framework was recently demonstrated by Suslick *et al.* [114]. PIZA-1 with a formula of  $[\text{Co(III)T}(\text{p-CO}_2)\text{PPCo(II)}_{1.5}(\text{C}_5\text{H}_5\text{N})_3(\text{H}_2\text{O}) \cdot \text{C}_5\text{H}_5\text{N}]$  is formed from carboxylate-substituted tetraphenylporphyrins with cobalt ions. Because of the presence of carboxylate groups, the framework of PIZA-1 is neutral. It is apparent that the ability of transition metals (Cu and Co) to exist in different oxidation states helps the formation of these metalloporphyrin-based metal-organic frameworks.

No mixed valency occurs in SMTP-1 [115], a family of layered structures with a general formula of  $[\text{M}(\text{tpp})_6] \cdot \text{G}$  ( $\text{M} = \text{Co}^{2+}$ ,  $\text{G} = 12\text{CH}_3\text{COOH} \cdot 12\text{H}_2\text{O}$ ;  $\text{M} = \text{Mn}^{2+}$ ,  $\text{G} = 60\text{H}_2\text{O}$ ; or  $\text{M} = \text{Mn}^{2+}$ ,  $\text{G} = 12\text{C}_2\text{H}_5\text{OH} \cdot 24\text{H}_2\text{O}$ ). SMTP-1 differs from the above metalloporphyrin-based structures. The metal cation in the center of the porphyrin ring is also coordinated to pyridyl groups of other tpp complexes, allowing the creation of an extended layer structure without the use of separate metal cations for crosslinking tpp complexes.

#### 5.4 Metal-organic frameworks from oxide clusters

In metal-organic frameworks, the inorganic unit is often a single transition metal cation (sometimes with some coordinating solvent molecules attached). The diversity of metal-organic frameworks can be greatly increased if inorganic clusters are used as structural building units. The simplest situation is dinuclear units such as  $\text{Ag}_2$  in  $\text{Ag}(4,4'\text{-bpy})\text{NO}_3$  and  $\text{Cu}_2$  in Cu-BTC [97,107]. The  $\text{Zn}_2$  (2.940 Å) unit is found in MOF-2. Clusters containing three or four metal cations are also known. For example, a chiral metal-organic framework called D-POST-1 contains the  $\text{Zn}_3\text{O}$  unit in which the oxygen atom is located at the center of the  $\text{Zn}_3$  triangle [104]. Similarly, the  $\text{Zn}_4\text{O}$  unit containing tetrahedrally coordinated oxygen anions was recently found in MOF-5 and IRMOF series of compounds. Much larger units (e.g.,  $\text{Zn}_8\text{SiO}_4$ ) have also been reported [116,117,118]. In many cases, these inorganic clusters do not occur in the starting materials and they are formed *in situ* during the synthesis of metal-organic frameworks.

#### 5.5 Metal-organic frameworks from chalcogenide clusters

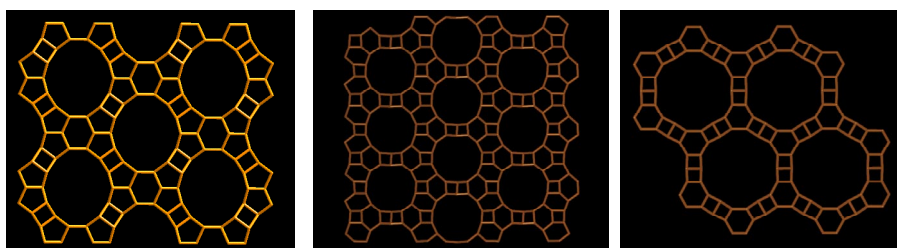
As shown above, the use of organic multidentate ligands to organize inorganic species is an effective method to prepare porous solids with tunable pore sizes. However, inorganic building units are generally limited to individual metal ions (e.g.,  $\text{Zn}^{2+}$ ) or their oxide clusters (e.g.,  $\text{Zn}_4\text{O}^{6+}$ ). To expand applications of porous materials beyond traditional areas such as adsorption and catalysis, metal-organic frameworks based on semiconducting chalcogenide nanoclusters are highly desirable. Recently, Feng *et al.* reported the organization of the cubic  $[\text{Cd}_8(\text{SPh})_{12}]^{4+}$

clusters by in-situ generated tetradentate dye molecules [119]. The structure consists of three-dimensional inorganic-organic open framework with large uni-dimensional channels. The combination of dye molecules and the inorganic cluster unit in the same material creates a synergistic effect that greatly enhances the emission of the inorganic cluster at 580nm. Such an emission can be excited by an unusually broad spectral range down to the UV, which is believed to result from the absorption of dye molecules and the subsequent energy transfer.

## 6 Extra-large Pore Crystalline Molecular Sieves

Thus far, an extra-large pore material is conveniently understood as those having a ring size of over 12 tetrahedral atoms [120]. In zeolites, the maximum pore size of a 12-ring pore is about  $8\text{\AA}$ . The recent progress in metal-organic frameworks has made it possible to obtain porous materials with pore size larger than  $8\text{\AA}$  by using larger organic linkers rather than by forming pores with more than 12 metal cations.

Among silicates, the extra-large pore has only been found in two high silica zeolites and one beryllosilicate. The first extra-large pore zeolite (UTD-1) was reported in 1996 (Fig. 11) [121,122]. UTD-1 (DON) was synthesized using bis(pentamethylcyclopentadienyl) cobalticinium cations and has a ring size of 14 tetrahedral atoms. It has a one-dimensional channel system with the approximate free diameter of  $7.5 \times 10\text{\AA}$  for the 14-ring pore. Another extra-large pore zeolite (CIT-5) was reported in 1997 [123,124]. Like UTD-1, CIT-5 (CFI) also has a ring size of 14 tetrahedral atoms with a one-dimensional channel system. The effective pore size ( $6.4\text{\AA}$  measured using the Horvath-Kawazoe method) of CIT-5 is similar to that of one-dimensional 12-ring channel in SSZ-24 (AFI) [125]. Very recently, a hydrated potassium beryllosilicate called OSB-1 (OSO) was found to have an extra-large pore size of 14 tetrahedral atoms [30].



**Figure 11.** (left) The three-dimensional framework of UTD-1 (DON) with elliptical 14-ring windows; Reprinted with permission from <http://www.iza-structures.org/> and reference [30]. (middle) the three-dimensional framework of  $\text{AlPO}_4\text{-8}$  (AET) showing 14-ring windows (right) the three-dimensional framework of VPI-5 (VFI) with 18-ring windows.