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Critical factors influencing the structures and properties of metal-organic frameworks

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Metal-organic frameworks (MOFs) have emerged as an important family of compounds that have fascinating structures and diverse applications. But until now, targeted synthesis of MOFs with desired frameworks is still a challenge. In order to appreciate the properties and to design new frameworks, it is necessary to understand how to rationalize the design and synthesis of MOFs from a fundamental perspective. This highlight review will outline the recent advances on this topic from both our and other groups and provide an overview of different factors influencing on the structures of MOFs. These examples illustrate some of present trends concerning the design of the organic ligands and SBUs, coordination assemblies, experimental conditions.

1. Introduction

In the last two decades, the design and construction of novel MOFs (metal-organic frameworks) which use a minimum amount of material to build maximum surface areas with fine control over pore size has attracted great interest, not only for their fascinating variety of architectures and topologies,1-3 but also for their potential applications in molecular adsorption and separation processes,4,5 ion exchange,6 catalysis,7,8 sensor technology,9 optoelectronics and so on.

Because of its wide breadth of application to advanced materials, controlled synthetic methods, linkers with various coordination modes, and the influences of various factors upon structures have come to prominence in this field.10-13 For the chemist, MOFs syntheses could be considered as “block-building games”: the final architecture depends on the building modules and their compatibilities. Analyses of the final geometries, of the diverse interactions and optimization of the growth processes are described as “crystal engineering”.14 MOFs are constructed mainly by coordination bonds between metal ions and ligands, together with other intermolecular interactions. The arrangement of the components in coordination polymers mostly only exist in the solid state: metal ions and organic ligands interact through coordination interactions and weaker forces in solution giving some small building blocks, and then, by self-assembly processes, MOFs grow based on the same interactions.15-18 Metal ions and organic ligands are generally called nodes and linkers.

The variety of “nodes and linkers” offers infinite possibilities for building new species with wonderful architectures and topologies. Much work has been devoted to the synthesis, structural characterization, and properties of MOFs. In this process, the accumulation of sufficient experimental data allows chemists to proceed beyond the random studies and to derive some useful laws of assembly. Towards this end, several effective synthetic strategies such as “node-and-spacer” and “secondary building units (SBUs)” have been successfully established and developed. But the control of product structure still remains a challenge in this field due to the fact the self-assembly process is effected by various external physical or chemical factors including counterion,17 template, temperature,18 pressure, solvent,19 and pH value, etc. In this contribution, we will introduce the factors including the positional isomerism, substituents and spacers of organic ligands, SBUs, solvents, metal ions and so on that make prominent influence on the formation, structure and property of MOFs.

2. Assembly strategies of organic ligands in the construction of MOFs

According to different coordinating groups, organic ligands can be divided into several categories, such as carboxylate ligands, N-containing heterocyclic ligands (pyridyl ligands, pyrryl ligands, imidazolyl ligands and so on), cyano ligands, phosphoryl ligands, sulfonyl ligands and so on. Among these various organic ligands, carboxylate ligands are often selected as multifunctional organic linkers because of their abundant coordination modes to metal ions, allowing for various structural topologies and because of their ability to act as H-bond acceptors and donors to assemble supramolecular structures.20 Compared with carboxylate ligands, the coordination pattern of N-containing heterocyclic ligands is unitary and the controllability of the structure of the target compound is higher. For attaining novel structures, mixed ligands are also a good choice for the construction of new polymeric structures. Use of a second bridging ligand to extend the metal carboxylate systems is one of the common ways to obtain higher dimensional networks. To date, a large number of mixed-ligand MOFs have been reported21-22 revealing that the combination of different ligands can result in greater tenability of structural frameworks than single ligands. The ligands containing imidazole or pyridine are regarded as important auxiliary ligands in the...
design and assembly of metal–organic coordination polymers.

2.1 Positional isomeric effect

Ligands with the same coordination groups but locating at different positions may lead to significant positional isomerism to affect the structural assemblies of MOFs.

For example, two aromatic dicarboxylic acids H$_2$IPA (isophthalic acid) (Scheme 1a) and H$_2$TPA (terephthalic acid) (Scheme 1b), possessing an angle-increased binding tendency, are active in regulating the structural assemblies of MOFs. Rigid linear ligands L (4,4′-(2,5-dimethoxy-1,4-phenylene)dipyridine) incorporating with two carboxyl-containing auxiliary ligands H$_2$IPA and H$_2$TPA have been adopted to build two complexes with Zn$^{II}$ under solvothermal conditions. In ([Zn(L)(IPA)])$_n$ (1), the H$_2$IPA ligands link the Zn$^{II}$ ions to form a 1D chain. Such 1D chains are further extended through L ligands from nearly perpendicular direction to furnish a 2D layer (Fig. 1a). When H$_2$IPA is replaced with H$_2$TPA, the resulting ([Zn(L)(TPA)]·DMF)$_n$ (2) shows a 3D supramolecular structure (Fig. 1b).

To further systematically investigate the influence of the positional isomeric ligands on the structures and properties of transition metal complexes, F. P. Huang and H. D. Bian et al. reported a series of Cd$^{II}$ coordination polymers based on the mixed-ligand system of dipyridyl ligand: 3,3′-bpt (1/1f-3,5-bis(3-pyridyl)-1,2,4-triazole) (Scheme 2) and three positional isomeric phenyl dicarboxylate anions: o-BDC (1,2-benzenedicarboxylate anion), m-BDC (1,3-benzenedicarboxylate anion) and p-BDC (1,4-benzenedicarboxylate anion) (Scheme 2, a–c), namely, [Cd$_2$(p-BDC)$_2$(3,3′-bpt)$_4$]·9H$_2$O (3), [Cd(m-BDC)(3,3′-bpt)(H$_2$O)] (4), [Cd(o-BDC)(3,3′-bpt)(H$_2$O)] (5). Complex 3 presents a two dimensional (2D) layer structures (Fig. 2a). Complex 4 presents an infinite one dimensional (1D) tubular-like chain (Fig. 2b). Complex 5 displays a 2D honeycomb structure consisting of a 1D metal–organic helical chain (Fig. 2c). Structural diversities indicate that the nature of isomeric benzene–dicarboxylates ligands plays crucial roles in modulating structures of these complexes.

2.2 Substituent effect

The substituents of organic ligands probably influence the network structures of MOFs in two aspects. On the one hand, they may possess additional interconnecting functions to extend the coordination motifs, in view of their ability to form coordination and secondary interactions such as H-bonding and aromatic stacking. On the other hand, those inert substituents may impose remarkable steric and/or electronic effects on the binding properties of organic ligands, and consequently, the network structures of the resulting MOFs.

A series of Co$^{III}$, Zn$^{II}$ MOFs have been constructed by selecting TPOM (tetrakis(4-pyridyloxymethylene)methane) incorporated with deprotonated 1,3-H$_2$bdc (isophthalic acid), 5-OH-H$_2$bdc (5-hydroxyisophthalic), 1,3,5-H$_2$btc (benzene-1,3,5-tricarboxylic) and 1,2,4,5-H$_2$btc (benzene-1,2,4,5-tetracarboxylic) (Scheme 3, a–d) as building blocks respectively. For instance, in ([Co$_2$(TPOM)(btc)$_2$(H$_2$O)]$_n$ (6), each Co atom coordinates to TPOM to form infinitely a wave-like 2D network along the b axis. There are two types of coordination environments around the Co$^{III}$ ions. The bdc$^-$ anions link two Co

![Scheme 1](image1)

![Scheme 2](image2)

![Fig. 1](image3)

![Fig. 2](image4)
Scheme 4 Illustration of the assembled system with ZnII and aromatic dicarboxylic acids including: (a) H$_2$BDC, (b) 2,6-H$_2$NDC, (c) H$_2$BPDC, (d) H$_2$TPDC.

Fig. 3 Various CoII and ZnII coordination networks of 6 (a), 7 (b), 8 (c), 9 (d) assembled from TPOM and a series of benzene-dicarboxylic acids.

28 Scheme 3 Illustration of the mixed-ligand assembled system with CoII/ZnII, TPOM, and a series of comparable R-isophthalic acids with different substituents, including: (a) 1,3-H$_2$bdc, (b) 5-OH-H$_2$bdc, (c) 1,3,5-H$_2$btc, (d) 1,2,4,5-H$_2$btc.

atoms belonging to different 2D networks to form a 3D framework. The potential voids are large enough to be filled via mutual interpenetration of an independent equivalent framework, generating a 2-fold interpenetrating 3D architecture (Fig. 3a). Complex $\{[Zn_2(TPOM)(5-OH-bdc)]_n(\text{DMF})(H_2O)]_n$ (7) possess similar 2-fold interpenetrating three-dimensional (3D) framework with bbf topology, but complex 6 crystallizes in an achiral space group (P2/c), and complex 7 crystallizes in chiral space group (P2). In comparison with complex 6, although the phenolic hydroxyl group do not engaged in metal coordination, it will significantly change the electronic density of the ligand as an electron-donating group (Fig. 3b).

Complex $\{[Co_2(TPOM)(btc)]_n(H_2O)]_n$ (8) reveals a 3D framework with biunclear Co clusters, which displays weak antiferromagnetic character. The carboxylate groups of btc$^{2-}$ adopt three different coordination modes: one is chelating in a bidentate mode, another is bridging bidentate, and the third is monodentate bridging mode (Fig. 3c). In compound $\{[Zn_2(TPOM)(btc)]_n\}$ (9), the completely deprotonated btc$^{2-}$ anions link four Zn atoms through the carboxylate coordination to form a 3D framework with larger open channels and it is the first example of TPOM as a counteraction (Fig. 3d).

2.3 Spacer effect

In principle, rigid linkers tend to construct 3D open networks with available cavities. With the increase of spacer length, interpenetration of such nets generally occurs to decrease the empty volumes of the crystal lattices. In contrast, flexible spacers may promote the generation of distorted frameworks, leading to dynamic micro porous MOFs that can shrink or expand upon external stimuli. A family of conjugated aromatics spacers can be used to design the longer rigid ligands. For example, O. M. Yaghi et al. found that diffusion of triethylamine into a solution of zinc nitrate and H$_2$BDC (Scheme 4a) in N,N‘-dimethylformamide/chlorobenzene resulted in landmark complex Zn$_5$(O(BDC)$_2$)·(DMF)$_7$·(C$_6$H$_5$Cl) (10) which has been named MOF-5. After that, they obtained a series of H$_2$BDC derivatives: 2,6-H$_2$NDC, H$_2$BPDC and H$_2$TPDC (Scheme 4b-d) by introducing the spacers between the carboxyl groups of BDC. They assembled these aromatic dicarboxylic ligands with ZnII to get an IRMOF series based on the prototype of MOF-5 which has been constructed from octahedral Zn-O SBU and BDC$^2$.

Regarding the changes of spacers with aliphatic groups, flexible carboxylic ligands such as malonic acid and glutaric acid can be obtained. Based on Zn$_5^{2+}$ and mixed-ligands of a N-centered extended tripod ligand (tris(4-(1H-imidazol-1-yl)phenyl)amine, TIPA) and two flexible aliphatic carboxylic acids (malonic acid and glutaric acid) (Scheme 5a-b), two novel zinc coordination polymers containing two unusual Zn-TIPA substructures (Zn-TIPA$^{61}$ in 11 and Zn-TIPA$^{62}$ in 12) with (10,3)-d and (10,3)-a topology have been successfully synthesized. Both complexes 11 and 12 feature (3,4)-connected non-interpenetrated 3D frameworks (Fig. 5). If the malonic and glutaric ligands are neglected from the structures, two 2-fold interpenetrated (10,3) topological networks can be observed, the incorporation of malonic and glutaric ligands further reinforce the stability of 11 and 12.

Recently, Z. Q. Shi and H. G. Zheng et al. reported a series of MOFs, namely, $\{[Zn_2(BPBP)$_$_3$(hfpipbb)]_n\}$ (13), $\{[Zn_2(BPBP)(trans-chdc)]_nH_2O)_n]$ (14), $\{[Zn_2(BPBP)(4,4'-sdb)$_$_2)_n\}$, and (10,3)-d and (10,3)-a topology have been successfully synthesized. Both complexes 11 and 12 feature (3,4)-connected non-interpenetrated 3D frameworks (Fig. 5). If the malonic and glutaric ligands are neglected from the structures, two 2-fold interpenetrated (10,3) topological networks can be observed, the incorporation of malonic and glutaric ligands further reinforce the stability of 11 and 12.

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Various ZnII coordination networks of 13 (a), 14 (b), 15 (c), 16 (d) that assembled from BPBP and a series of dicarboxylic acids.

Scheme 6 Illustration of the mixed-ligand assembled system with CoII, H4BCPBA and bipyridine ligands including: (a) bipy, (b) bpe, (c) bpp.

(15), and \{[Zn2(BPBP)(oba)]·H2O-DMA\}_{n} (16) on the basis of a bipyridine ligand BPBP and different multicarboxylate-type coligands. (BPBP = 5,5'-bis(4-pyridyl)-2,2'-bithiophene, H4hfipbb = 4,4'-hexafluoroisopropylidene)bis(benzoic acid), trans-H4chdc = trans-1,4-cyclohexane dicarboxylic acid, 4,4'-H4chdc = 4,4'-sulfonyldiacrylic acid, H2oba = 4,4'-oxybis(benzoic acid)) (Fig. 6). Complex 13 is a 3D supramolecular architecture with 3-fold interpenetration (Fig. 6a). Two crystallographically equivalent ZnII cations are bridged by four carboxylate groups adopting a bis-bidentate coordination mode to generate a dinuclear ZnII “paddle-wheel” type secondary building unit (SBU). This [Zn2(CO3)3] unit is interesting and rarely observed in other coordination compounds, the paddle-wheel is bridged by hfipbb ligands to form a 2D undulating (4, 4) network with rhomb-like windows and the SBU [Zn2(CO3)3] can be regarded as a 6-connected node. The whole framework of complex 13 can be topologically represented as a rare 6-connected mab net with the vertex symbol of \{4^4\mathbb{m} 8\}. In complex 14, the carboxylate groups of the trans-chdc ligands link the ZnII cation centers into an infinite 1D zigzag chain, such 1D zigzag chains are further linked by the BPBP ligands, leading to the formation of a 3D framework. The 3D structure of complex 14 can be clarified as a classical 4-connected diamond (dia) lattice by considering ZnII cations as the 4-connected nodes and all ligands as the 2-connected spacers. Notably, the large channel in a single framework has an approximate pore size of 18.82 Å × 26.16 Å, which allows the other five identical 3D single frameworks to penetrate and, thus, afford a 6-fold interpenetrating architecture (Fig. 6b). In complex 15, the completely deprotonated 4,4′-sdb ligand shows a bidentate coordination mode. Pairs of ZnII cations are joined by two symmetrical 4,4′-sdb ligands to generate a dinuclear ZnII “paddle-wheel” type secondary building unit (SBU). These paddle-wheel SBUs are further bridged through the second terminal carboxylate group of the symmetrical 4,4′-sdb ligands into a 1D chain. Then the BPBP ligands join all infinite 1D chains into a 2D layer (Fig. 6c). The 2D network can be simplified to a sq1 net. In complex 16, the ZnII cations are linked through the oba ligands to form 2D layers, such resulting layers are further connected by BPBP ligands, leading to the formation of a 3D framework (Fig. 6d). Complex 16 represents a \{4^{12}6^6\} α-Po peau topology by using BPBP and oba ligands as linkers.

Various base-type bridging ligands, involving paired pyridine, imidazole and triazole groups with different spacers in between, have also been applied to react with angular rigid carboxylic acids to form well-defined MOFs, which can be regulated by the spacer effect of ligands. For example, a series of flexible bipyridine ligands such as bipy, bpe, bpp (Scheme 6a-c) assemblies with H4BCPBA and CoIII afford three different MOFs

{{[Co(HBCPBA)(bipy)(H2O)]}_{n}} (17), 
{{[Co4(HBCPBA)4(bpe)_2(H2O)_3]2DMF}_{n}} (18), 
{{[Co4(HBCPBA)4(bpp)_2(H2O)_3]H2O·2DMF}_{n}} (19). In complex 17, the CoIII ions can be regarded as 4-connected nodes with all crystallographically independent bipy ligands acting as 2-connected linkers, and the HBCPBA2− ligands acting as V-shaped linkers. Therefore, the whole structure can thus be reduced as a (4, 4) sheet (Fig. 7a). To evaluate the role of ligand in the self-assembly of organic–inorganic hybrid frameworks, the reaction with bpp is carried out to afford complex 18. The structure of 18 is a pillared 2-fold interpenetrating 3D → 3D network. Two pillared 3D motifs, identical in structure interpenetrate to yield a new type of catenated network consisting of large, open, one-dimensional (1D) channels (Fig. 7b). When bpp was replaced by bpp, a structurally different complex 19 is obtained. In complex 19, the two CoIII atoms are bridged by a water molecule to form a binuclear cluster. Each binuclear CoIII is connected by three
HBCPBA$^{2-}$ anions and two bpp to form a 2D net structure (Fig. 7c).

![Diagram](image)

**Fig. 7** (a) Schematic representation of the 2D $\rightarrow$ 2D framework by two identical sheets in 17. (b) Schematic representation of the 3D $\rightarrow$ 3D framework by two identical sheets in 18. (c) View of the 2D net structure of 19.

![Diagram](image)

**Fig. 8** (a) View of the [Zn$_{6}$($\mu$-O)] cluster in 20. (b) 1D micropore along the a axis in 20.

![Diagram](image)

**Fig. 9** (a) A view of the [Zn$_{6}$($\mu$-O)CO$_{3}$]$_{3}$ cluster in 21. (b) – (c) are the coordination environment of the Zn$^{II}$ ion in 21.

![Diagram](image)

**Fig. 10** The PL intensities of 21 introduced to various pure solvents when excited at 390 nm.

3. Structures of MOFs based on different secondary building units

Most of metal-organic frameworks are produced by organic ligands as linkers to coordinate to metals or metal cluster as nodes or molecular building blocks. In order to get large pore materials, the usual way to do this is extending the organic ligands, but in practice they are often found to be highly interpenetrated and have low porosity. To solve the problem, Yaghi and co-workers developed an efficient strategy for the construction of frameworks with the use of SBU:s replace single metal ions in the MOFs, giving the structures with high stability and without a tendency to interpenetrate.

Choosing appropriate SBUs have an important significance for the construction of MOFs: First of all, predicting the topology of the target products through the configuration of SBUs as well as the coordination modes of organic ligands; Secondly, the use of multiple metal ions in a cluster bridged by multiple coordinating ligands tends to enhance the robustness of the MOFs; Thirdly, making MOFs to possess optical and electrical properties by introduction of metal centers with superior physical properties.

SBUs as the node of the construction of MOFs directly affect MOFs’ structures by their coordination geometry. According to the composition of SBUs, the types of SBUs could be divided into metal-oxygen-based cluster and W-Cu-S-based cluster. SBUs are essential to the design of directionality for the construction of MOFs and to the achievement of robust frameworks.

### 3.1 Metal-oxygen-based cluster polymers

Metal-oxygen-based SBUs have been widely researched and reported such as tetranuclear [Zn$_{6}$O(COO)$_{4}$]$_{3}$ and dinuclear [Cu$_{4}$O(COO)$_{6}$]$_{3}$, these SBUs are used as 6-connected octahedral nodes and 4-connected tetragonal nodes respectively in self-assembly reactions. Many robust MOFs have been synthesized based on transition metals carboxylate SBUs which usually comprise two, three, four or more metal centers.

J. H. Cui and H. G. Zheng et al.$^{36}$ reported a 3D non-interpenetrated framework {[Zn$_{6}$O(TCOPM)$_{3}$H$_{2}$O$_{3}$]}$_{3}$·8H$_{2}$O·3DMF (20) (TCOPM = tris-(p-carboxyphenyl)-methane) which was obtained from self-assembly of H$_{3}$TCOPM and Zn nitrate. The TCOPM anions all adopt a bidentate coordination mode to bridge two Zn centers. Zn1, Zn2, and Zn3 reside in tetrahedral environments, and each coordinates by three carboxylate oxygen atoms from different TCOPM ligands and one $\mu$-O atom at the center of the cluster. The Zn4 ion adopts an octahedral coordination geometry surrounded by the $\mu$-O atom, three carboxylate oxygen atoms, and another two oxygen atoms from two water molecules. The four Zn ions form a distorted tetrahedron around $\mu$-O (Fig. 8a).

The TCOPM ligand acts as a 3-connected node. A $\mu$-oxo bridged ZnO$_{2}$ cluster is bridged by six carboxylate groups from six TCOPM$^{2-}$ units to provide the octahedron-shaped secondary building unit (SBU), which extends infinitely to give 6-connected nets (Fig. 8b).

They also reported a MOF$^{37}$ namely, [Zn$_{6}$($\mu$-O$_{2}$)(TCOPM)$_{3}$]·3H$_{2}$O·8NO$_{3}$·5DMF (21) based on [Zn$_{6}$($\mu$-O$_{2}$)(CO$_{3}$)$_{6}$] cluster with pores for the first time. The core of the cluster consists of a single O ($\mu$-O) atom bonded to six Zn atoms, forming a regular [Zn$_{6}$($\mu$-O)] polyhedron. The two oxygen atoms of each carboxylate from TCOPM$^{2-}$ are all coordinated with three Zn atoms (Fig. 9a). [Zn$_{6}$($\mu$-O)CO$_{3}$]$_{6}$ cluster acts as six-connected SBU (Fig. 9b) and TCOPM$^{2-}$ acts as a triangular organic building block (Fig. 9c). For complex 21, it could be used as a chemical sensor for sensing of small molecules. The intensity of the PL in complex 21 depends on the identity of the guest.
molecule, with DMF > toluene > acetone > CHCl₃ > propanol > acetonitrile > ethanol > methanol > 1,4-dioxane > THF (Fig. 10), which is probably due to the majority of chromophores in complex 21 being exposed to the different solvents, and they have different interactions with solvents from each other. Another similar zinc MOF \([\text{Zn}_6(\mu_6-O)(\text{TPO})_2\text{NO}_3)_4\cdot3\text{H}_2\text{O}\) (22) (H₃TPO = tris(4-carboxyphenyl)phosphineoxide) based on the same SBU's \((\text{Zn}_6(\mu_6-O)(\text{CO}_2)_6)\) (Fig. 9a) is reported. The coordination mode of organic ligand H₃TPO is similar to the ligand H₃TCOPM which acts as a triangular building block in MOF, so they have the same topology type: the pyr form of FeS₂.

In addition to the above MOFs with symmetrical six Zn centers SBU, J. H. Cui and H. G. Zheng et al. reported another non-interpenetrating porous Zn-MOF \([\text{Zn}_6(\mu_6-OH)\text{L}_2]_7\text{H}_2\text{O}\cdot\text{DMF}\) (23) (H₃L = 3,5-bis(4-carboxyphenoxo)benzoic acid) with the decorated tfz-d topology based on Zn₃O₂ and H₃L as ligand (Fig. 11). The Zn₃O₂ clusters consist of two Zn₃O, and the cores of the clusters consist of a single O (μ-OH) atom bonded to three Zn atoms, forming a regular Zn₃O tetrahedron structure. Zn1 is bound to two carboxylate O atoms from two \(\text{L}^2\) ligands and four μ₃-hydroxy groups, and Zn2 is bound to four carboxylate O atoms from four \(\text{L}^2\) ligands and two μ₃-hydroxy groups. Both Zn1 and Zn2 give octahedral structures, while Zn3 are bridged by two carboxylate O atoms from two \(\text{L}^2\) ligands and two μ₃-hydroxy groups to give tetrahedral structures (Fig. 12).

![Fig. 11](https://via.placeholder.com/150)

**Fig. 11** View of the tetrahedron-shaped SBU in 23.

![Fig. 12](https://via.placeholder.com/150)

**Fig. 12** Coordination environment of the Zn" ion in 23.

### 3.2 W-Cu-S-based cluster polymers

In contrast to the metal-oxygen SBUs, the W-S-Cu SBUs have more variable central cores. For example, one \([\text{WS}_5\text{O}_{3n}^2\text{Cu}^3\text{O}_{3n-2}\text{O}_3]_2\) core can be varied by changing the synthesis conditions, and different combinations of \([\text{WS}_5\text{O}_{3n}]^2\) (n = 0-2) core.

![Fig. 13](https://via.placeholder.com/150)

**Fig. 13** (a) Schematic representation of the channels consisting of a left-handed helix and a right-handed helix in 24. (b) Schematic representation of a single (10,3)-b ths net along the a axis in 24, the left/right-handed helices are illustrated as pink and blue arrows, respectively.

![Fig. 14](https://via.placeholder.com/150)

**Fig. 14** (a) Coordination environment of the \([\text{WS}_4\text{Cu}_4]\) unit in 25. (b) Perspective view of the nanotubular structure of 25. (c) Hydrogen bonds between paired ligands of the interpenetrating networks (green dashed lines).

![Fig. 15](https://via.placeholder.com/150)

**Fig. 15** (a) UV-vis spectra and photograph of the inclusion complex 25 with different solvents. (b) Band gaps of the inclusion complexes versus solvent \(E_{\text{T}}\) values.

![Fig. 16](https://via.placeholder.com/150)

**Fig. 16** (a) Coordination environment of the \([\text{WS}_4\text{Cu}_5]\) unit in 26. (b)
large channels, of which some also feature chirality (i.e. the net with (10,3)-a, rrs topology). A nanotubular metal–organic framework (MOF), \([\text{WS}_3\text{Cu}_4]_3\text{(dptz)}_2\cdot\text{DMF}\) \(_n\) (25) \([\text{dptz} = 3,6\text{di-(pyridin-4-yl)-1,2,4,5-tetrazine}]\) with a pentanuclear \([\text{WS}_3\text{Cu}_4]_2^+\) unit (Fig. 14a) has been reported by Z. Z. Lu and H. G. Zheng et al.\(^{25}\) The \([\text{WS}_3\text{Cu}_4]_2^+\) units, acting as tetrahedral nodes, are linked by two paired ligands and two single ligands with four adjacent units into a diamondoid network. Six diamondoid networks associate together with the \([\text{WS}_3\text{Cu}_4]_2^+\) units of each net arranged parallel, forming square-shaped nanotubes along the c direction (Fig. 14b).

Strong C–H–N hydrogen bonds are formed between the paired dptz ligands of the interpenetrated networks with an average C–N distance of 3.291(2) Å, which stabilizes the overall nanotubular architecture (Fig. 14c). The complex 25 shows solvatochromic behavior when immersed in solvents ranging in polarity from water to chloroform (Fig. 15a). The band gaps of these solvent–included complexes are in linear correlation with the polarity of the guest solvents (Fig. 15b). The solvent molecules can be sensed by the changes in the UV–vis spectra of the corresponding inclusion compounds, showing a new way of signal transduction as a new kind of sensor.

Z. Z. Lu and H. G. Zheng et al.\(^{41}\) reported a 3D metal–organic framework, \([\text{WS}_3\text{Cu}_4]_3\text{(dpbh)}_2\cdot\text{DMF}\) \(_n\) – n-solvent (26) (dpbh = \((1E,2E)-1,2\text{-bis(pyridin-4-ylmethylene})\)hydrazine). This polymer contains one-dimensional channels (Fig. 16b) formed in four-fold interpenetrating diamondoid networks with a hexanuclear \([\text{WS}_3\text{Cu}_4]_2^+\) unit as the SBU (Fig. 16a), which has a square-pyramidal geometry and acts as a tetrahedral node. In the same paper, another polymer \([\text{WS}_3\text{Cu}_4]_2\text{(Hdpta)}_2\cdot\text{DMF}\) \(_n\) – n-solvent (27) (Hdpta = 2,5-di(pyridin-4-yl)-1H-pyrrol-1-amine) was also documented. This polymer contains a brick wall-like layer with a hexanuclear \([\text{WS}_3\text{Cu}_4]_2^+\) unit as the SBU (Fig. 17a). This \([\text{WS}_3\text{Cu}_4]_2^+\) unit is a new type of \([\text{WS}_3\text{Cu}_4]_2^+\) cluster unit in which the five Cu\(^+\) ions are in one plane with the W atom, forming a planar unit (Fig. 17b).

The above-mentioned MOFs are the same type that only one kind of SBU in MOF, also some MOFs with the coexistence of two kinds of SBUs. For example, Z. Z. Lu and H. G. Zheng et al.\(^{50}\) reported a 3D framework, \([\text{WS}_3\text{Cu}_4\text{(dpbp)}_2\text{I}_3]_x\cdot\text{DMF}\cdot\text{solvent}\) (28), based on a rod-like ligand dpbp (4,4’-di(4-pyridyl)-biphenyl), which is more than twice the length of 4,4’-bipyridine (Fig. 18a). In complex 28, the anionic net is formed by the tetranuclear \([\text{WS}_3\text{Cu}_4]_3^-\) SBU, and the cationic net is formed by the pentanuclear \([\text{WS}_3\text{Cu}_4]_2^+\) SBU, forming an unprecedented 8-fold non-equivalent interpenetrated structure (Fig. 18b). The anionic framework \([\text{WS}_3\text{Cu}_4\text{(dpbp)}_2\text{I}_3]_x\), named NET A, is constructed by the tetranuclear \([\text{WS}_3\text{Cu}_4]_3^-\) unit (Fig. 18c). The four cationic frameworks contain two independent groups of \([\text{WS}_3\text{Cu}_4\text{(dpbp)}_2\text{I}_3]_x\), named as NET B and NET C, which are built by a pentanuclear \([\text{WS}_3\text{Cu}_4]_2^+\) SBU (Fig. 18c). Large rhombus-shaped tubes with diagonal dimensions of ~20 × 10 Å are formed in spite of the high interpenetration (Fig. 18d).

4. Other factor influencing the assembly of MOFs
4.1 Solvent

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{n = 0–2} and Cu\(^+\) afford SBUs with different geometries and connectives.\(^{39}\) The nuclear numbers of cluster SBUs from 3 to 7 have been reported,\(^{36,48}\) so the W–S–Cu SBUs could be able to coordinate to more ligands compared with metal-oxygen SBUs.

In 2011, X. Q. Yao and H. G. Zheng et al.\(^{39}\) reported a (10,3)-type W–Cu–S cluster polymer, named \([\text{WOS}_3\text{CuBr(TIPA)}](\text{H}_2\text{O})(\text{DMF})]_x\) (24), based on the TIPA (tris(4-(1H-imidazol-1-yl)phenyl)amine) organic linker and the \([\text{WOS}_3\text{Cu}]^+\) SBU (Fig. 13). The (10,3)-type MOFs usually have
Two unusual solvent-controlled MOFs have been obtained from the solvothermal assemblies of H$_2$L (4,4’-dicarboxyldiphenylamine) and BIP (4,4’-bis(imidazol-1-yl)phenyl) with Co$^{II}$ nitrate in DMF/H$_2$O and CH$_3$CN/H$_2$O solvents, respectively. A 3D non-interpenetrated framework [Co$_2$(L)$_2$(BIP)$_2$·3H$_2$O]$_n$ (29) can be prepared in DMF/H$_2$O. Two L$^2$-connect two Co$^{II}$ atoms to achieve a 28-membered [Co$_2$(L)$_2$] metallocyclic ring. These rings are further connected through their corners forming 1D wave-like ladder-chain structures. BIP double lines linking the parallel [Co$_2$(L)$_2$] chains in two different directions give rise to a 3D framework net. Closer examination of the structure of complex 29 reveals that the framework adopts the CdSO$_4$ (cds) topology, a 4-connected 6$^8$ net, as shown in Fig. 19a. When using CH$_3$CN/H$_2$O instead of DMF/H$_2$O as solvent, [Co(L)(BIP)(H$_2$O)$_2$·2CH$_3$CN]$_n$ (30) possessing unusual 3-fold 2D → 2D poly catenation of (4,4) nets is obtained (Fig. 19b). The BIP ligand links neighboring Co$^{II}$ ions to form an infinitely 1D zigzag chain. The L$^2$-anions link these zigzag chains to form ladder-like 2D sheets. The 2D sheet contains a larger channel so that the large dimensions and corrugated nature of the net allow them to interpenetrate in an extensive and unusual fashion.

By a systematic variation of solvent, three unprecedented novel MOFs are obtained: [Cu$_2$(L)$_2$(H$_2$O)$_2$·3/2H$_2$O]$_n$ (31) (DMF-CH$_3$CN-H$_2$O) with three-fold interpenetrated dia topology (Fig. 20a); [Cu(L)(DMF)·5/2H$_2$O]$_n$ (32) (DMF-H$_2$O) with three-fold interpenetrated 1vt topology (Fig. 20b), and [Cu(L)(H$_2$O)·H$_2$O]$_n$ (33) (CH$_3$CN-H$_2$O) with five-fold interpenetrated 1vt topology (Fig. 21a). Views of the 2D sheets by BIDPE ligands, 5-OH-bdc$^2^-$, Cd$^{II}$ or Co$^{III}$. (b) Views of the wavelike 2D framework by 5-OH-bdc$^2^-$, BIDPE and Zn$^{II}$. (c) Views of the 1D double-stranded chain by 5-OH-bdc$^2^-$, BIDPE and Ni$^{II}$. (d) Views of the 2D framework by 5-OH-bdc$^2^-$, BIDPE and Mn$^{II}$.

Fig. 19 (a) 6$^8$ topology of CdSO$_4$-type structure of 29. (b) 3-fold 2D → 2D parallel interlock structure of 30.

Fig. 20 The topologies of 31 (a), 32 (b), 33 (c).

Fig. 21 (a) Views of the 2D sheets by BIDPE ligands, 5-OH-bdc$^2^-$, Cd$^{II}$ or Co$^{III}$. (b) Views of the wavelike 2D framework by 5-OH-bdc$^2^-$, BIDPE and Zn$^{II}$. (c) Views of the 1D double-stranded chain by 5-OH-bdc$^2^-$, BIDPE and Ni$^{II}$. (d) Views of the 2D framework by 5-OH-bdc$^2^-$, BIDPE and Mn$^{II}$.

Fig. 22 (a) Schematic representation of the (4, 4) network in 34. (b) Views of the (4, 4) sheets of 35 and 36.
(Fig. 20c) (H$_2$L = 4,4’-dicarboxyldiphenylamine). The H$_2$L ligands assemble with metal clusters to form the four-connected paddle-wheel SBUs. Comparing the synthesis system of the above MOFs, there are no other synthesis conditions change but the solvents, so the polarity of the solvent (CH$_3$CN < DMF < H$_2$O) is significantly important to determine the constructing structures. H$_2$L is a flexible V-shaped ligand, the L$^2$ anions can perform with different configurations, regulating the solvent can effectively generate the desirable architectures and topologies, and also adjust the porosity of frameworks.

### 4.2 Metal Ion

As one of the most common factors influencing the assembly of MOFs, metal ions can be viewed as a family of controllable building blocks. One particular metal element with a given valence normally defines its intrinsic coordination preference and geometry.

A series of mixed-ligand MOFs have been prepared under diffusion condition, by assembling Cd$^{	ext{II}}$, Co$^{	ext{II}}$, Zn$^{	ext{II}}$, Ni$^{	ext{II}}$, Mn$^{	ext{II}}$ nitrate with BIDPE and 5-OH-H$_2$bdc. These MOFs display various 2D and 3D structural patterns with different coordination geometries of the metal ions, clearly indicating the metal-directed assembly. In Cd$^{	ext{II}}$, Co$^{	ext{II}}$, Zn$^{	ext{II}}$ MOFs, though the metal centers take different coordination numbers (4 and 6) and geometries (octahedron, trigonal bipyramidal and tetrahedron), they are bridged by 5-OH-H$_2$bdc to afford 2D sheets (Fig. 21a-b). For the Ni$^{	ext{II}}$ MOFs, the neighboring Ni$^{	ext{II}}$ ions are linked by BIDPE ligands and 5-OH-bdc$^-$ anions to form infinitely double-stranded 1D chain (Fig. 21c). The Mn$^{	ext{II}}$ atoms were bridged by carboxylate ligands to form a binuclear cluster, each binuclear Mn was connected by four 5-OH-bdc$^-$ anions to form a 1D ladder-shaped chain, the BIDPE ligands share the binuclear Mn clusters with 5-OH-bdc$^-$ anions to further generate an infinite 2D network (Fig. 21d).

In another case, three mixed-ligand MOFs have been prepared by assembling Co$^{	ext{II}}$, Cd$^{	ext{II}}$, Zn$^{	ext{II}}$ nitrate with H$_2$L (4,4’-dicarboxyldiphenylamine) and BBP (4,4’-bis(imidazol-1-yl)di phenyl), namely, [Co(L)(BBP)].H$_2$O (34), [Cd(L)(BBP)].H$_2$O (35), [Zn(L)(BBP)].H$_2$O (36). In complex 34, the Co$^{	ext{II}}$ ions are bridged by the BBP ligands to afford 2D sheet, with the HL$^2$ decorating as arms (Fig. 22a). But for the 35 and 36, the Cd$^{	ext{II}}$ and Zn$^{	ext{II}}$ ions can be regarded as 4-connected nodes with all crystallographically independent L$^2$ and BBP ligands acting as linkers to form a (4,4) coordination sheet (Fig. 22b).

### Conclusions

This paper outlined the influence factors on the assembly of MOFs. It can be seen that the positional isomerism, substituents and spacers of organic ligands have remarkable influence on the formation and structure of MOFs including the coordination mode with metal centers, the architecture topology, dimensionality and structural transformation and so on. It is also clear that the assembly, formation and structure of MOFs can differ greatly by some other factors including SBUs, solvents and metal ions. Nevertheless, we hope that this review can provide some primary information to the design and construction of desired MOFs.

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### Notes and references

This article highlights the recent advances of different factors influencing on the structures of MOFs.