

Pore surface engineering of microporous coordination polymers

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Pore surface control of microporous coordination polymers is of great interest due to the potentially exciting functionalities it presents, such as highly selective separation, chemisorption, and novel catalysts and sensors. A discussion of our unique strategy aimed at surface engineering using metalloligands, *i.e.*, introduction of coordinatively unsaturated metal centers, is presented.

Introduction

Recently, remarkable progress has been made in the area of microporous coordination polymers (MCPs), because of their diverse topologies and fascinating properties in areas such as storage, exchange, and catalysis.¹ MCPs have unique characteristics: framework regularity, high porosity, flexibility, and a designed pore surface, which can create high-performance pores and also unprecedented porous functionalities. An investigation into the formation of highly porous and flexible frameworks has been actively engaged in over the past decade. In contrast, the surface functionalization of pores is still an unexplored research area in MCPs.

The pore walls of MCPs generally consist of organic bridging ligands, and therefore the properties of a pore's surface can be easily changed by modification using organic ligands. Fig. 1 shows an example of surface modification using dicarboxylate-type ligands. In the absence of special substituents on the ligand, a guest molecule can interact with the pore walls in the restricted space through a dispersion force

(<5 kJ mol⁻¹). The introduction of hydrogen bonding sites (*via* amido, hydroxy, carboxy, and amino substituents) can change the surface properties. Since the energy of a hydrogen bond (10–40 kJ mol⁻¹) is larger than that of a dispersion force, a highly selective uptake of selected Lewis-acid and/or Lewis-base guests can be achieved. For example, {[Co(NCS)₂(3-pia)₂·4THF}_n (where 3-pia = *N*-3-pyridylisonicotinamide) contains 3-pia ligands with an amido group, by which, guest THF molecules are entrapped in the channel through –N–H···O hydrogen bonds.² A dried sample of this MCP

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of porous coordination polymers, from which a nanochannel laboratory is being developed over the next decade.

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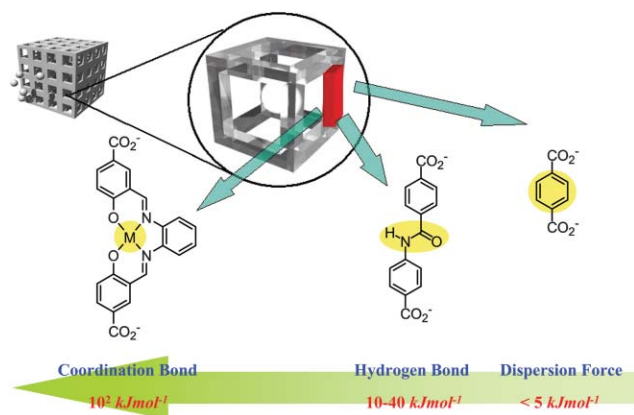


Fig. 1 Example of surface engineering by dicarboxylate-type ligands in MCP.

shows selective adsorption for guest molecules with hydrogen bonding sites, and in addition shows size/shape selectivity. For example, THF is adsorbed and cyclopentane is not.

Another strategy to modify the surface of the pores is to incorporate metal sites capable of forming coordinatively unsaturated metal centers (UMCs).³ Since UMCs can interact with Lewis-base guests through coordination bonds having an energy that is much greater than that of either the dispersion force or a hydrogen bond (*ca.* 10^2 kJ mol⁻¹), they can show highly selective incorporation for guests as well as hydrogen bonding sites. In addition, MCPs with UMCs can provide functionalities as chromic sensors and flexible frameworks, because ligation and release of the UMCs' guests often influence the coordination geometry or splitting of the d-orbitals.⁴ Moreover, it is well known that a variety of transition metal ions can act as active centers in catalyzed reactions. A combination of UMC characteristics and traditional porous properties (shape- and size-selectivity) can be used to create desired, highly efficient, and tailor-made properties. Immobilization of a UMC into a porous host has been tried using zeolites, polymeric matrices, and clays *via* ion exchange or impregnation. However, in these cases, the isolation and uniformity of the UMC was insufficient and the environment surrounding the UMC was not well understood. If a UMC can be directly incorporated onto the surface of an MCP channel, a completely isolated and uniform arrangement can be realized. Hence, it is important to establish a synthetic method for the immobilization of a UMC onto the pore surface of an MCP.

In this paper, we present a unique strategy aimed at introduction of a UMC onto an MCP's surface by metallo-ligands (MLs).

Characteristics of MLs

MLs are metal complexes that contain two or more Lewis-base sites that are able to bridge with other metal ions. MLs have several advantages in designing infinite frameworks: (1) they have multicoordination sites, (2) they have polyhedral coordination-donor building blocks whose topology controls the direction of the coordination bonds, and (3) they make a rational construction of heterometallic assembly systems

possible. Although a large number of MLs have been reported,⁵ representative MLs contain multicyanometalate anions, which have afforded a large number of magnetic and porous materials.⁶

For example, recently we reported on a novel ML, [Cu(2,4-pydc)₂]²⁻ (where 2,4-pydc = 2,4-pyridinedicarboxylate), which has a multicoordination ability in addition to the above-mentioned advantages listed in points 1–3, as shown in Fig. 2. (Hereafter, [Cu(2,4-pydc)₂]²⁻ is abbreviated as L1^{Cu}.) The L1^{Cu} group contains two types of Lewis-base binding group, 4-carboxylate (Group A) and 2-carboxylate (Group B) moieties, and is a good candidate for the construction of both hydrogen bonding and coordination frameworks. The reaction of L1^{Cu} with Lewis-acid building blocks [Fe(H₂O)₆]²⁺ and imidazole affords the hydrogen bonded assemblies, [Fe(H₂O)₆][Cu(2,4-pydc)₂] and [Cu(2,4-pydc)(imidazole)₂·2H₂O], respectively, which have ML dimer units of [Cu₂(2,4-pydc)₄]⁴⁻ and [Cu₂(2,4-pydc)₂(imidazole)₄], respectively.⁷ Each of these undergoes a supramolecular interaction (π - π and hydrogen bonds) to form one-dimensional (1-D) ML arrays, which are further linked by rich hydrogen bonding interactions *via* H₂O molecules. Selective bond formation has been accomplished in the case of combinations of first-period transition metal ions (Mn^{II}, Fe^{II}, Co^{II}, Cu^{II}, and Zn^{II}) and L1^{Cu}, as illustrated in Scheme 1.^{8,9} For Co^{II}, Cu^{II}, and Zn^{II}, L1^{Cu} forms a 4-carboxylate-bridged 1-D assembly with a repeating motif of [–M–O₂C–(py)N–Cu–N(py)–CO₂–]: [Zn(L1^{Cu})(H₂O)₃·(DMF)]·DMF]_n, [Zn(L1^{Cu})(H₂O)₂(MeOH)₂]_n and {[M(L1^{Cu})(H₂O)₄·2H₂O]_n (M = Co^{II}, Cu^{II}, and Zn^{II}). The use of a terminal 2,2'-bipyridine (2,2'-bpy) ligand, in addition to the Cu^{II} ion, gives a zigzag-shaped 1-D assembly with the similar repeating unit as the above: {[Cu(2,2'-bpy)(L1^{Cu})]·3H₂O]_n. For Mn^{II} and Fe^{II} ions, L1^{Cu} exhibits a 2-carboxylate bridging mode to form another 1-D assembly with a repeating [–M–O–C–O–Cu–O–C–O–] motif: [M(L1^{Cu})(H₂O)₄]_n (where M = Mn^{II} and Fe^{II}). This coordination selectivity is related to the strength of the Lewis-base, the electrostatic effect of the L1^{Cu} group, and the Irving–Williams order of the metal ion. A variety of magnetic properties are obtained according to the bridging mode: {[M(L1^{Cu})(H₂O)₄·2H₂O]_n (where M = Co^{II} and Cu^{II}) and {[Cu(2,2'-bpy)(L1^{Cu})]·3H₂O]_n, have a 4-carboxypyridinate bridge between magnetic centers and show a weak antiferromagnetic interaction, whereas [M(L1^{Cu})(H₂O)₄]_n (where M = Mn^{II} and Fe^{II}) have a carboxylate bridge between magnetic centers and show 1-D ferromagnetic behavior.

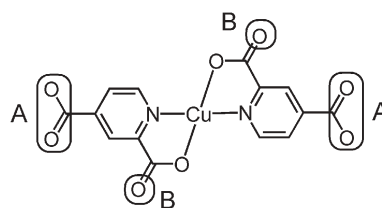
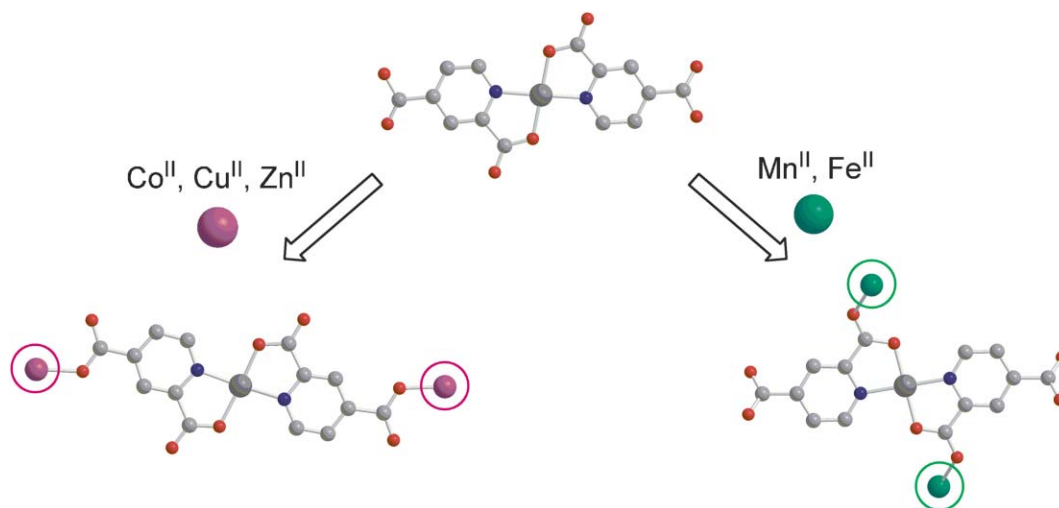


Fig. 2 Molecular structure of L1^{Cu}.



Scheme 1

MCPs with MLs as a simple linker

During the last decade, MLs other than those of the multicyanometalate type have been employed as simple linkers. The ML $[\text{Be}(\text{L})_2]$ (where $\text{L} = 3\text{-(4-pyridyl)-2,4-pentanedionate}$) reacts with CuBr_2 to form the two-dimensional (2-D) porous coordination compound, $\{[\text{CuBr}_2\text{Be}(\text{L})_2] \cdot 5.33\text{CHCl}_3\}_n$, which possesses inner cavities *ca.* $12 \times 12 \text{ \AA}^2$. The network alone occupies only $5,468 \text{ \AA}^3$ per unit cell, or 54.1% of the crystal volume and enclathrates a set of guest CHCl_3 molecules.¹⁰ The three-dimensional (3-D) porous coordination polymer $\{[\text{Ag}_2(\text{SO}_3\text{CF}_3)_2\text{RuCl}_2\text{-(pyz)}_4] \cdot \text{C}_2\text{H}_2\text{Cl}_4 \cdot 0.5(1\text{-butanol})\}_n$, which has the topology of a prototypical rutile, is constructed from the neutral ML $[\text{RuCl}_2(\text{pyz})_4]$ that contains four equatorial pyrazine molecules with free *exo*-oriented N-donor atoms in a square-planar orientation.¹¹ The channels running along the $[101]$ plane contain solvated molecules of tetrachloroethane and 1-butanol. However, the coordination sites of the metal ions within MLs are often fully occupied by organic ligands and/or counteranions: the metal ions within MLs are simple structural components of organic linkers creating the channel walls.

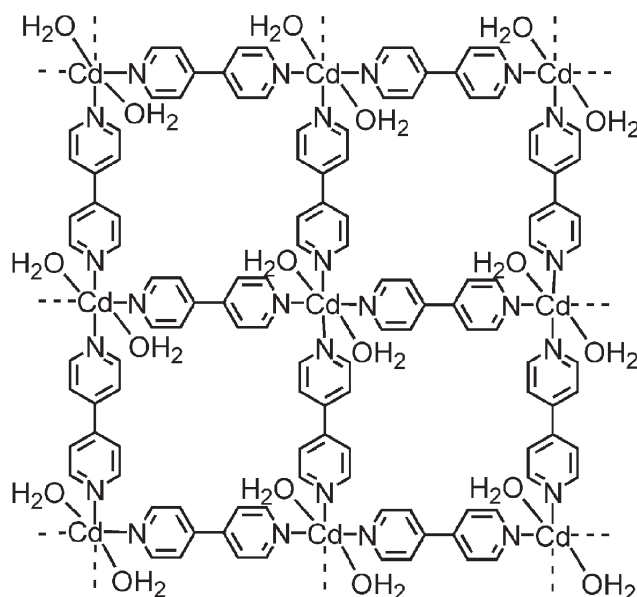
Functionalization of coordinatively UMCs

Metal ions function as nodes in a framework, and their coordination sites are generally fully occupied by coordination with linkers and, in some cases, blocking ligands and counteranions. On the other hand, some MCPs with coordination sites that contain volatile neutral molecules, such as water, alcohols, acetone, acetonitrile, and DMF have the capacity to create coordinatively UMCs within their pores after removal of any volatile molecules by heating and/or vacuum, without inducing any decomposition of their original porous framework.

It is known that there are four types of synthetic method to create coordinatively UMCs, by utilization of: (1) general transition metal ions with six coordination sites, (2) lanthanide ions, (3) multinuclear metal clusters, and (4) MLs. Fabrication of UMCs using method (4) is discussed later in this section.

There have been a large number of coordination polymers with coordinated volatile molecules located at axial sites of six-coordinate metal ions. However, examples concerned with the creation and stability of coordinatively UMCs and/or their function are scarce. A coordination network, $\{[\text{Cd}(4,4'\text{-bpy})_2(\text{H}_2\text{O})_2] \cdot 2\text{NO}_3 \cdot 4\text{H}_2\text{O}\}_n$ (where $4,4'\text{-bpy} = 4,4'\text{-bipyridine}$), has been used to catalyze the cyanosilylation of aldehydes and imines under heterogeneous conditions (Fig. 3).^{12,13} Experimental data in the case of imines leads to the conclusion that hydrophobic grid cavities bind to the substrate very efficiently to promote a rapid reaction, and that the present heterogeneous reaction should involve the selective activation of imino nitrogen by the weak Lewis-acid Cd^{II} center.¹³

A large coordination number, in the range 7–10, and the polyhedral coordination geometry of f-block (lanthanide) metal ions is useful for the discovery of new and unusual

Fig. 3 2-D grid structure of $[\text{Cd}(4,4'\text{-bpy})_2(\text{H}_2\text{O})_2]_n$.

network topologies. In addition, the existence of many coordination sites tends to facilitate the coordination of volatile molecules. Therefore, lanthanide ions are good candidates for the construction of UMCs. The 3-D structure of $[\text{Tb}_2(\text{bdc})_3(\text{H}_2\text{O})_4]_n$ (where $\text{bdc} = 1,4\text{-benzenedicarboxylate}$) contains coordinated water ligands.¹⁴ Upon thermally liberating the water ligands, a microporous compound, $[\text{Tb}_2(\text{bdc})_3]_n$, having a coordinatively UMC was fabricated, which has extended 1-D channels and the same framework structure as that of the original compound. Water adsorption isotherm data show that $[\text{Tb}_2(\text{bdc})_3]_n$ exhibits permanent microporosity, and point to the presence of accessible coordinatively UMCs within the pores, which also allows for the adsorption of ammonia.

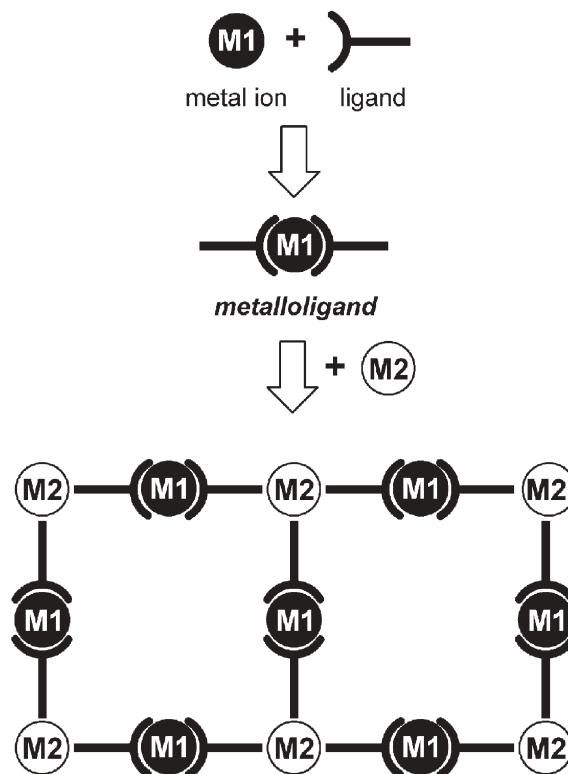
Multinuclear metal clusters can also provide an opportunity to create UMCs in extended frameworks, in that the geometric constraints placed on the metal center by virtue of extensive multidentate ligand bonding often allow a terminal volatile ligand to occupy a site on the metal ion which is not ligand-coordinated. $\{[\text{Zn}_2(\text{btc})(\text{NO}_3)(\text{EtOH})_3] \cdot \text{H}_2\text{O} \cdot 2\text{EtOH}\}_n$ (where $\text{btc} = 1,3,5\text{-benzenetricarboxylate}$) has a 3-D structure where nearly 44% of the framework is represented by an extended channel system having a 14 Å cross-section, where highly mobile ethanol and water guest molecules can reside.¹⁵ The partially and fully evacuated analogues $[\text{Zn}_2(\text{btc})(\text{NO}_3)(\text{EtOH})]_n$ and $[\text{Zn}_2(\text{btc})(\text{NO}_3)]_n$, respectively) have accessible UMCs, and show chemical adsorption of ethanol in the UMCs.

MCPs capable of creating UMCs using MLs

It is useful to take advantage of MCPs to create UMCs because of their regularity and designability. Recent success in the utilization of these advantages is found in an acetylene storage system, where multiple hydrogen bonding sites are used instead of UMCs.¹⁶ This strategy will be applicable to a wide range of MCPs having various pore sizes and functional surface properties.

A few years ago, we proposed a new synthetic method for obtaining MCPs with coordinatively UMCs using MLs, *i.e.*, a two-step self-assembly.⁹ First, an ML is synthesized that acts as a framework linker and a source of coordinatively UMCs (M1). Second, the ML is added to another metal ion (M2), which acts as a nodal unit in a framework. Consequently, two types of metal center co-exist in the framework (Scheme 2), and a larger space around the metal ion in the channel wall can be obtained, which is significant for an attack by a guest molecule. The key point of this method is a partial separation of the metal functionalities: framework node and the coordinatively UMCs.

To synthesize ML building blocks suitable for creating UMCs, suitable metals and organic ligands must be selected. Metal ions with a high coordination number, *i.e.*, six or more, are preferred, because they provide a good supply of coordination sites for both organic ligands and volatile molecules. Moreover, volatile molecules capping UMCs can be easily removed and the resulting geometry of the metal center must be stable. A Cu^{II} ion displaying a Jahn–Teller distortion is one good building block for the formation of

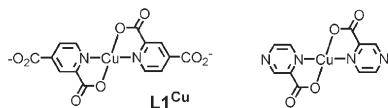


Scheme 2

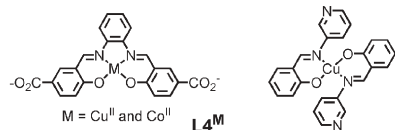
UMCs. Due to the ligand field effect, the binding of the axial ligand is sufficiently weak to allow its release. In addition, the resulting square planar geometry is stable. On the other hand, organic ligands need to have more than two coordination sites with different Lewis-basicity to avoid the formation of polymeric compounds. Chelating or macrocyclic groups are often used to form MLs, while carboxylate, pyridine, and cyanide groups are used for further assembly of MLs with other metal sources. Fig. 4 lists the MLs available as building blocks for the construction of UMCs.

Although pioneering work relating to MCPs with UMCs was carried out using porphyrin-type Cu^{II} MLs (L2^{Cu} and L3^{Cu} , see Fig. 4) in 1994,¹⁷ there are only a few other examples of such materials to date. Our group used the above-mentioned ML, L1^{Cu} , to create an MCP with UMCs. Reaction of L1^{Cu} with Zn^{II} ions in a hot DMF solution provided the MCP, $\{[\text{Zn}(\text{L1}^{\text{Cu}})(\text{H}_2\text{O})_3(\text{DMF})] \cdot \text{DMF}\}_n$.⁹ The L1^{Cu} bridges the Zn^{II} ions to form 1-D undulated chains, which are linked by H_2O molecules between the Zn^{II} and Cu^{II} ions. The bridging H_2O is also supported by a hydrogen bond with the oxygen atom of the 4-carboxylate group. In addition, their chains are connected *via* hydrogen bonds between the coordinated H_2O ligands at the Zn^{II} centers and the oxygen atoms of the 2-carboxylate group. These interactions create a 2-D network forming a large grid. Each 2-D network stacks *via* hydrogen bonds to form 1-D rhombic channels with dimensions of *ca.* $15 \times 5 \text{ \AA}^2$, as shown in Fig. 5(a). These channels are filled with DMF molecules. Half of the Cu^{II} ions on the L1^{Cu} have axial coordination sites facing the 1-D channel space, and they are coordinated with volatile DMF molecules, as illustrated in Fig. 5(b). Therefore, they are available for

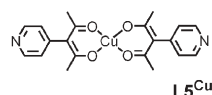
(1) pyridine-2-carboxylate type



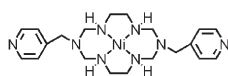
(2) schiff base type



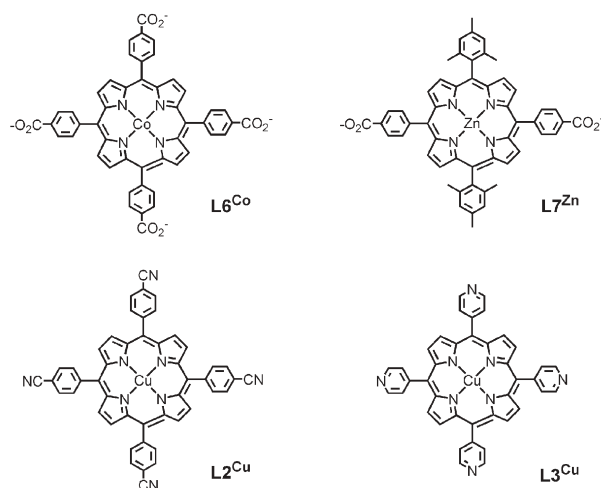
(4) acetylacetonate type



(3) azamacrocyclic type



(5) porphyrin type



(5) others

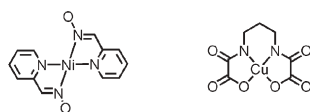
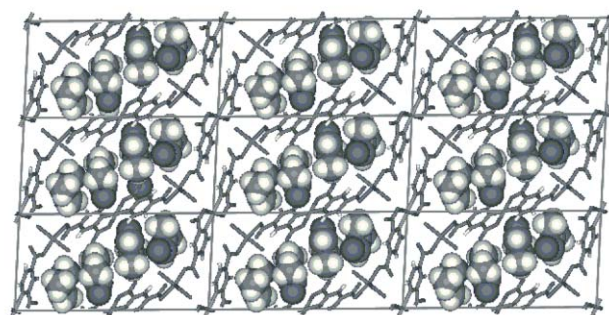


Fig. 4 MLs available as building blocks for the construction of coordinatively UMCs. The MLs with abbreviations are introduced in this article.

guest-coordination. Other MLs, $[M(H_2salphdc)]$ ($L4^M$, where $M = Co^{II}$ and Cu^{II} and $salphdc = N,N'$ -phenylenebis(salicylideneimine)dicarboxylate), with Schiff-base ligands, $H_4salphdc$, have also been synthesized (Fig. 4).¹⁸ Single crystals of $\{[Zn_3(OH)_2(L4^{Cu})_2] \cdot 2DMF\}_n$, whose topology is identical to that of the Al net in $SrAl_2$, afford 1-D large channels of approximately $14 \times 14 \text{ \AA}^2$ (Fig. 6). Interestingly, coordinatively unsaturated Cu^{II} ions line up along the c -axis at a distance of 6.1 Å. The temperature-dependence of the X-ray diffraction patterns indicates that the porous structure is maintained until $T = 573 \text{ K}$. In place of the Cu^{II} ion, the Co^{II} ion can be introduced into UMCs. The Co^{II} -incorporated porous coordination polymer, $[Zn_3(OH)_2(L4^{Co})_2]_n$, was synthesized using a similar procedure to $\{[Zn_3(OH)_2(L4^{Cu})_2] \cdot 2DMF\}_n$. The X-ray diffraction pattern is in good agreement

(a)



(b)

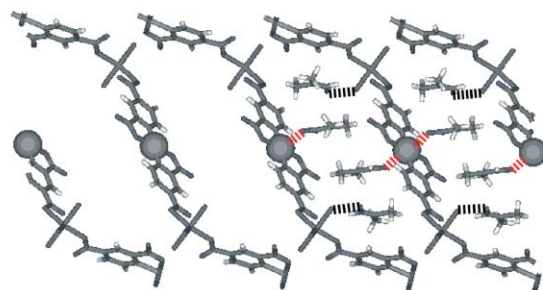


Fig. 5 Microporous framework of $\{[Zn(L1^{Cu})(H_2O)_3(DMF)] \cdot DMF\}_n$. (a) Microporous framework incorporating DMF guests represented by a space filling model along the c -axis. (b) Detailed view of host-guest interactions. The Cu^{II} ions available as coordinatively UMCs are represented by large circles. The red and black dashed lines indicate coordination and hydrogen bonds, respectively.

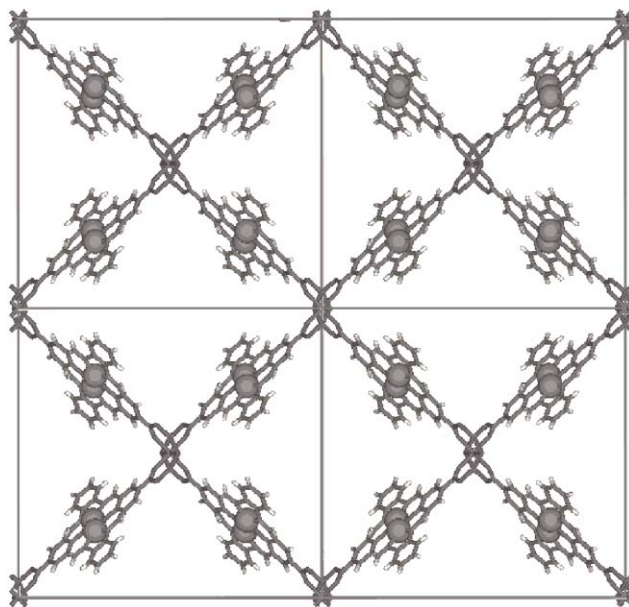


Fig. 6 Microporous framework of $[Zn_3(OH)_2(L4^{Cu})_2]_n$ along the c -axis. The guest DMF molecules are omitted for clarity. The Cu^{II} ions available as coordinatively UMCs are represented by large circles.

with that of $\{[\text{Zn}_3(\text{OH})_2(\text{L}4^{\text{Cu}})_2]\cdot 2\text{DMF}\}_n$, indicating that the same 3-D framework and coordinatively unsaturated Co^{II} ions were successfully designed. Various metal complexes with Schiff-base type ligands are known to show unique catalytic activities,¹⁹ providing a useful hint for the design of pore walls for catalytic porous compounds.

Recently, another ML, $\text{Cu}(\text{pyac})_2$ ($\text{L}5^{\text{Cu}}$, where $\text{pyac} = 3$ -(4-pyridyl)pentane-2,4-dionate), shown in Scheme 3, has been reported.²⁰ $\text{L}5^{\text{Cu}}$ contains both Lewis-base N atoms and Lewis-acid Cu^{II} sites, and is a good precursor for the construction of UMCs. Reactions of $\text{L}5^{\text{Cu}}$ with $\text{Cd}(\text{NO}_3)_2$ and CdCl_2 , acting as T-shaped and square-planar nodes, respectively, produce 1-D and 2-D porous frameworks (Scheme 3). The 1-D ladder frameworks of $\{[\text{Cd}_2(\text{NO}_3)_4(\text{L}5^{\text{Cu}})_3]\cdot 3\text{MeOH}\cdot 2\text{H}_2\text{O}\}_n$ assemble without interpenetrating to create interconnected channels along the a - and b -axes. The channels along the a -axis have dimensions of $ca. 5.7 \times 10.2 \text{ \AA}^2$, and those along the b -axis are $ca. 4.1 \times 9.8 \text{ \AA}^2$. The pores occupy about 60% of the crystal volume. The 2-D square-grid layers of $\{[\text{CdCl}_2(\text{L}5^{\text{Cu}})_2]\cdot 6\text{THF}\cdot 0.5\text{H}_2\text{O}\}_n$ are stacked, leading to a channel with dimensions of $ca. 8.0 \times 8.2 \text{ \AA}^2$. The porosity is about 63%. It is of interest to note that the Cu^{II} sites in these two porous coordination polymers are accessible for host-guest interactions. The coordination of solvent molecules to the Cu^{II} sites is evident in the crystal structures of both polymers. The guest molecules are lost at temperatures of 100°C , and the desolvated frameworks are stable up to 210 – 220°C , which indicates that the obtained coordinatively unsaturated Cu^{II} sites in the channel walls can be used for guest-binding sites.

Macrocyclic porphyrin ligands with Lewis-base sites on peripheral groups can create coordinatively UMCs at axial sites of the central metal ions. The 3-D highly porous coordination polymers, $\{[\text{Co}_{1.5}(\text{L}6^{\text{Co}})(\text{pyridine})_3(\text{H}_2\text{O})]\cdot 11\text{pyridine}\}_n$ and $\{[\text{Zn}_4\text{O}(\text{L}7^{\text{Zn}})_3]\cdot 8\text{H}_2\text{O}\}_n$, which are constructed from porphyrin-type MLs, such as those shown in Fig. 4, have been synthesized and their porous stabilities and functionalities characterized.^{21,22} Fully desolvated samples of both compounds show microporosity and different selectivity,

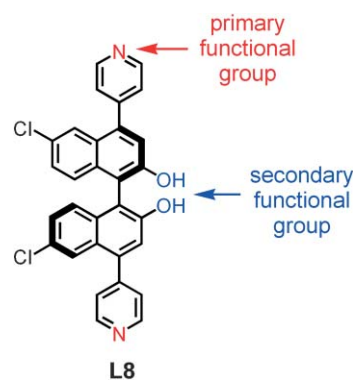


Fig. 7 Bridging ligand L8 with orthogonal functional groups.

depending on polarity of guests, which was confirmed from measurement of their adsorption of various guests. This may be caused by a difference in polarity of the central metal ion in the porphyrin MLs.

Finally, we should mention another approach where a metal ion providing a UMC is entrapped by an organic linker in a pore wall. In the bridging ligand, L8, with orthogonal functional groups, as shown in Fig. 7, the primary functional groups are linked by Cd^{II} connectors to form an extended porous network, $\{[\text{Cd}_3\text{Cl}_6\text{L}8]\cdot 4\text{DMF}\cdot 6\text{MeOH}\cdot 3\text{H}_2\text{O}\}_n$.²³ The channel wall of this porous compound has free sites acting as secondary functional groups, which further interact with other metal ions. This is in contrast with Scheme 2, although there are no guarantees that all the sites are occupied by metal ions.

Conclusions

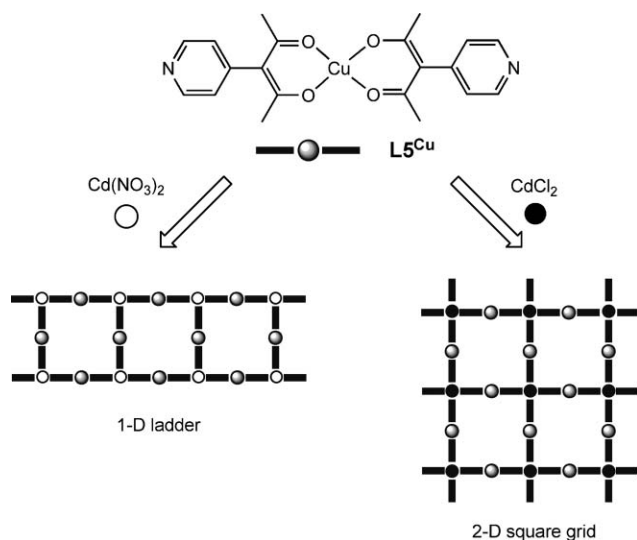
In this review, we have introduced the applicability of MLs for the construction of coordinatively UMCs in an MCP. Although a large number of MCPs have been hitherto synthesized and characterized, the coordination sites of incorporated metal ions tend to be fully occupied by nonvolatile organic and/or inorganic ligands. Even if there are metal sites with coordinating volatile guests in the micropores, their stability and reactivity have not been well researched. Our strategy of using MLs to construct UMCs can afford systematic investigation of desired porous materials with UMCs and help realize unprecedented synergistic porous functionalities.

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Scheme 3

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