Metal–organic macrocycles, metal–organic polyhedra and metal–organic frameworks

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Metal–organic macrocycles (MOMs), metal–organic polyhedra (MOPs) and metal–organic frameworks (MOFs) are metal–organic systems (MOSs) developed from appropriately designed ligands and selected metal ions. Metalladiazamacrocycles, a class of MOMs, are finite 2D MOSs formed from tricationic hexacoordinate metal ions and ditopic bridging ligands, *N*-acylsalicylhydrazide, containing diaza residues, where the size and shape of the systems have been modulated by controlling the steric repulsions between the ligands. The 2D MOM systems could be expanded to 3D MOP systems by self-assembling C_3 symmetric components and C_4 symmetric components to octahedral MOPs. By substituting some replaceable solvent sites of MOMs or MOPs, MOFs based on MOMs or MOPs as SBBs have been constructed, where the properties of the SBBs have been directly transferred to the MOF systems.

Introduction

Self-assembled metal–organic systems (MOSs) such as metal–organic macrocycles (MOMs), metal–organic polyhedra (MOPs) and metal–organic frameworks (MOFs) could have major potential applications in many areas such as molecular recognition,[1] gas storage,[2] separation,[3] drug delivery,[4] and catalysis.[5] The interactions between metal ions and ligands in the MOSs are mostly *via* coordination bonds, which are weaker than the conventional covalent bonds in organic compounds but are much stronger than the other weak interactions, such as hydrogen bonds, π–π interactions, dipole–dipole interactions and van der Waals interactions. This intermediate bond strength enables a single coordination bond to substitute multiple weak interactions for the directional self-assembly of the metal ions and the ligands in a more predictable way for the rational design of MOSs. In addition, the structures and the related properties of the MOSs can be modulated by systematic variation of the metal ions and the ligands. Depending on the nodality and/or geometry of the building components, either finite coordination supramolecules, MOMs or MOPs, which can exist in solution in equilibrium, or infinite coordination networks, MOFs, which only exist as an insoluble solid, can be generated.

Various fascinating applications have been developed in MOM and MOP systems. Some MOMs show single-molecule

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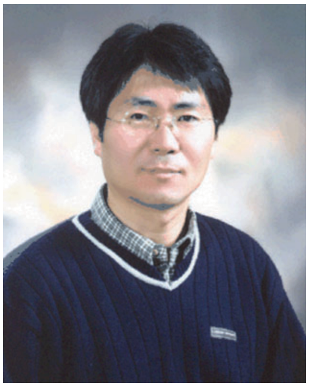

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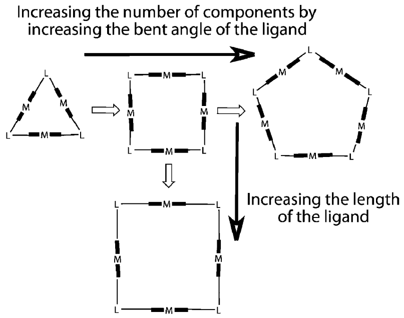
magnetic properties,[6] and selective recognition for anions such as fluoride[1d] and nitrate.[1e] Lin and co-workers developed chiral MOM systems having applications in chiral sensing and asymmetric catalysis.[5g–i] MOP systems have been developed as host systems to accommodate some reaction intermediates. Fujita and co-workers developed an unusual regioselective Diels–Alder coupling reaction between specific guests hosted inside an organo-palladium cage where the reactant-like transition state was stabilized by the MOP systems.[5a] Raymond and co-workers carried out catalytic acidic hydrolysis of orthoformates in the hydrophobic cavity of their tetrahedral MOP system with rate accelerations of up to 890-fold compared with the background hydrolysis reaction, where the protonated intermediate was stabilized by the molecular host.[5b] Kim and co-workers developed a synthetic ionic channel system based on a carefully designed MOP that showed the ability to transport small alkali-metal ions across the biomimetic lipid membrane containing ion channels made of the MOPs.[7]

MOFs have potential applications especially in gas storage, separation and catalysis. MOF-177 has been reported as a MOF with the highest amount of H_2 storage capacity at 77 K by Yaghi and co-workers,[2e] and some MOF systems showed large CH_4 storage capacities.[2f,g] Certain MOF systems showed selectivity for H_2 over N_2 through control of the pore size,[3d] and other MOF systems showed gas selectivity based on temperature dependent adjustable mesh size.[3e] Some homochiral MOF systems showed heterogeneous asymmetric catalyses.[5d–f]

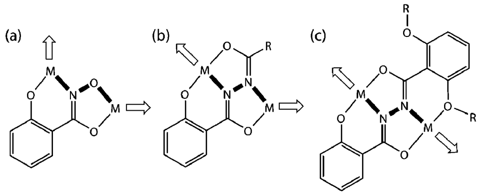
For the applications of the MOFs in these areas, not only the generation of the large void space and surface area of the framework but also the control of the shape and functionality of the framework cavity is of importance. The supramolecular building block (SBB) approach for the construction of MOFs, where the SBB is used as a node in the network, can have advantages over that of the secondary building unit (SBU) approach because of some unique features of the SBB, which could be transferred directly to those of the MOFs. In this article, we present the work done in our laboratory, covering reports of MOMs, MOPs and MOFs based on MOMs and MOPs as SBBs.

MOMs

Either infinite 1D linear chains, 1D MOFs, or finite 2D cyclic oligomers, 2D MOMs, can be obtained when both the metal ions and the ligands are ditopic components. The prerequisite for cyclic structure formation is the use of at least one building component with bent geometry. The size of the MOMs can be modulated *via* control of the length of the ditopic exo-bidentate ligands (Scheme 1). By increasing the length of the ligands, the size of the MOMs can be expanded.[8] Alternatively, the size of the MOMs can be modulated by controlling the number of the components in the cyclic ring system, where the number of components is usually controlled by control of the bending angle of the building components. The connectivity and geometry of those metal centers having a large coordination number are usually controlled by the number and stereochemistry of stable ligands ligated to the metal centers. For example, auxiliary *cis*-bidentate capping agents were used to convert tetratopic square-planar Pd(II) and Pt(II) centers to 90° bent ditopic metal centers.[9] Metal centers with a large coordination number can also be used as pseudo-ditopic metal centers when the two metal centers involved are multiply connected with bridging bidentate ligands. For example, in ferric wheels, the metal centers of coordination number six are triply connected with bridging ligands to form cyclic structures, where the metal ions topologically serve as pseudo-ditopic centers.[10]



Scheme 1 Size control of MOMs.

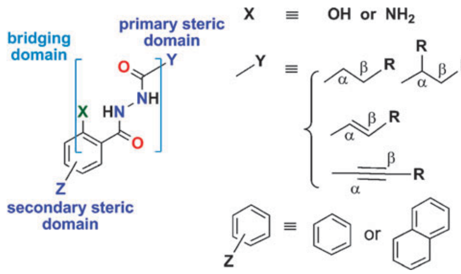


Scheme 2 Various bridging modes of multidentate ditopic ligands with increasing number of donor sites. (a) Bidentate/bidentate, (b) tridentate/bidentate and (c) tridentate/tridentate bridging modes.

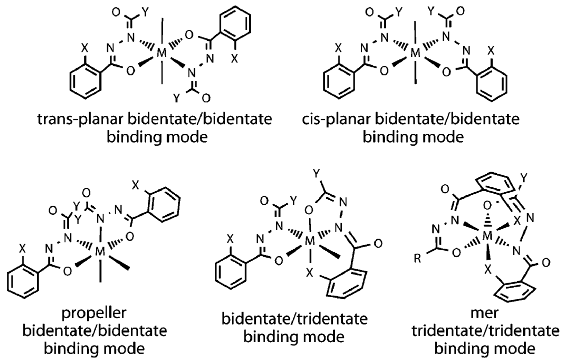
Some multidentate ligands showed ditopic bridging capability *via* simultaneous ligations to the two metal ions in two different directions (Scheme 2).[11] A potential pentadentate ligand, *N*-formylsalicylhydrazide (H_3fshz), was discovered to act as a ditopic bridging ligand *via* two different chelation modes, tridentate and bidentate binding modes, toward two metal ions.[11b] The succession of this bridging mode can lead to a cyclic structure, a MOM. The careful design and modification of some selected residues of the ligands can be utilized to control the number of the components in the MOMs and the corresponding size and stereochemistry of the MOMs.[12–28]

Metalladiazamacrocycles

Metalladiazamacrocycles are a class of MOMs with –[M–N–N]– cyclic repeating units made from metal ions and multidentate bridging ligands containing N–N diaza residues, where the ligand has three deprotonable sites with five potential donor atoms (Scheme 3).[12,13] The five donor atoms on the ligand can coordinate with two metal ions on one side in a tridentate chelation mode and on the other side in a bidentate chelation mode, and the ligand becomes a heteroditopic linker connecting the two metal ions (Scheme 2(b)). Depending on the binding mode of the second ligand to the metal center, several binding modes of the two ligands around the metal ion



Scheme 3 Pentadentate bridging ligands investigated with alterations at the three domains using various aliphatic, aromatic and other functional groups.



Scheme 4 Schematic picture of the possible binding modes of two ligands to one metal center with diverse stereochemistries.

are possible, and diverse stereochemistries of the metal centers are allowed (Scheme 4).

A prototype metalladiazamacrocycle

The reaction of *N*-acylsalicylhydrazide (H_3xshz) (where, H_3xshz = H_3fshz, *N*-formylsalicylhydrazide; H_3ashz, *N*-acetylsalicylhydrazide) with manganese(II) acetate tetrahydrate in dimethylformamide (DMF) led to a MOM called as a metalladiazamacrocycle having metal ions and diaza residues in the macrocyclic ring system (Fig. 1).[11b,14]

The cyclic repeat of the –[Mn–N–N]– linkage generates an 18-membered hexameric manganese macrocycle (Scheme 5). The bidentate binding mode and tridentate binding mode from two ligands around a metal center leads to either Λ or Δ chiral configurations and the two chiral configurations in the ring system are arranged alternatively to form a hexameric MOM of S_6 symmetry. Although the configuration around each metal center is chiral, the overall configuration of the system is achiral because of the cyclic alternation of the chiral configurations. Even though a metal ion of oxidation state +2 was used for the metal ion source, the metal ion is oxidized in air, and the final oxidation state of the metal ion in the MOM is +3 and the ligand is deprotonated to a trianionic state, which results in the overall system being neutral. An interesting feature of the MOM is that each metal ion of coordination number six is coordinated with two stable ligands in bidentate/tridentate chelation modes in five coordination sites, while the remaining Jahn–Teller distorted axial site is ligated by a replaceable monodentate solvent molecule. The hexameric metalladiazamacrocycle can serve as a potential hexatopic SBB because the six ligated solvent molecules can be replaced by other exo-bidentate bridging ligands.

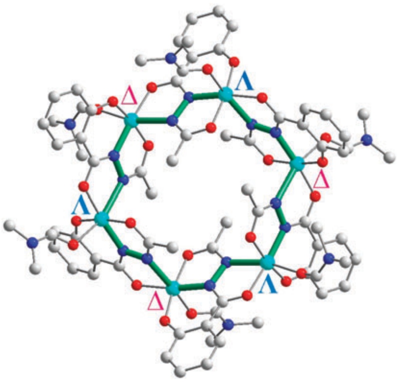
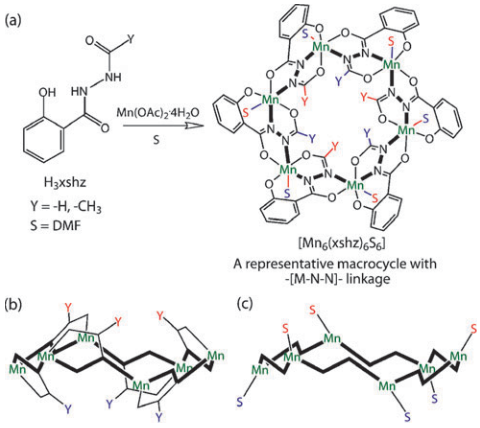


Fig. 1 Ball-and-stick representation of the hexameric metalladiazamacrocycle formed with H_3ashz ligands and Mn(III) metal ions. The M–N–N residues in the cyclic repeating system are highlighted using thick green lines; metal ions and nitrogen atoms are represented with cyan and blue balls, respectively.



Scheme 5 Schematic drawing of (a) the reaction for the preparation of metalladiazamacrocycle, (b) the side view of the MOM showing the arrangement of the primary steric domains and (c) the replaceable solvent sites in the MOM system.

Modulation of the metalladiazamacrocycles

Another interesting feature of this MOM is that all Y residues of the ligands (Scheme 5(b)) are directed toward the inner core of the macrocycle and these residues can be utilized as steric groups for the control of the nuclearity of the metalladiazamacrocycles *via* steric repulsions between these residues. However, the introduction of a saturated linear alkyl group at the –Y residue site of the ligand did not influence the nuclearity of the metalladiazamacrocycles because the steric repulsion between the residues in the primary steric domain can be released by adjusting the orientation of the flexible alkyl residues. Regardless of the length of the alkyl residues used, the same hexameric MOMs were obtained.[14] Diverse monodentate solvent molecules such as DMF, dimethylacetamide (DMA), dimethylsulfoxide (DMSO), methanol, ethanol and pyridine have been used for the preparation of the various

MOMs, but no significant effect on the structure and nuclearity of the MOMs was observed.[15] Various tricationic octahedral metal ions such as Mn^{3+}, Fe^{3+}, Co^{3+} and Ga^{3+} have been used to synthesize the MOMs.[16] However, when the VO^{2+} ion was used as the metal ion source, a linear trinuclear cluster was obtained rather than a MOM system, in which the binding mode of the ligands around the metal center is a *trans*-planar bidentate/bidentate chelation mode.[17]

To increase the steric crowding at the primary steric domain, various alkyl groups can be substituted successively at the Cα or Cβ positions of the *N*-acyl tail (Scheme 3).[18] Alkyl chain substitution at the Cβ position on the ligand produced similar hexameric MOM systems. The ligand having a dimethyl, a trimethyl, or a phenyl group at the Cβ position of the primary steric domain perturbs neither the binding mode of the ligand nor the nuclearity of the system. The introduction of the steric residue remote from the bridging domain has little effect on the system because the steric repulsions between the primary steric domains can still be released by adjusting the orientation of the flexible part of the alkyl residues, as in the case of the saturated linear alkyl residues.

Control of the steric crowding in the vicinity of the bridging domain by substituting various alkyl groups at the Cα position has led to the modulation of the nuclearities of the MOM systems.[18] Introduction of a dimethyl group at the Cα position expands the MOM system to an octameric system (Fig. 2(a)), which is not observed with dimethyl substitution at the Cβ position. Introduction of either a trimethyl group or ethyl and methyl groups at the Cα position expands the MOM system further to a decameric system (Fig. 2(b)). To increase the steric crowding of the primary steric residues further in a MOM system, a ligand with a cyclohexyl group as a primary steric residue has been introduced because this group not only is sterically bulky but also has some rigidity originating from the restrained conformation of the cyclic ring system.[19] The self-assembly of the modified ligands with Mn(III) ions expanded the MOM system to a dodecameric system (Fig. 2(c)).

Even though the macrocyclic ring system has expanded from hexameric up to dodecameric, the chiral sequence of the metal centers in the MOM system remains constant, a $\cdots(\Lambda\Delta)(\Lambda\Delta)\cdots$ alternating chiral configuration. The MOM system of S_{12} symmetry had an S_{12} symmetric pseudo-3D cavity of hydrophobic nature in the center of the macrocycle. The MOM system hosts guest molecules selectively based not only on the size but also on the symmetry of the guest molecules. Cyclohexane has been selectively hosted inside the hydrophobic cavity, but there was no evidence of hosting benzene as a guest. The small difference in the sizes of the guest molecules could be distinguished. More interestingly, cyclooctane was accommodated with a more strained conformation in S_4 symmetry rather than the more stable conformation in S_8 symmetry (Fig. 3). The flexible guest molecule has been induced-fitted into the shape and the symmetry of the host cavity. The introduction of simple and branched alkyl chains at the Cα position or of cyclic alkyl groups as primary steric residues yielded hexameric, octameric, decameric and dodecameric MOM systems depending on the bulkiness of the primary steric groups and the remoteness of the steric groups from the bridging domain.

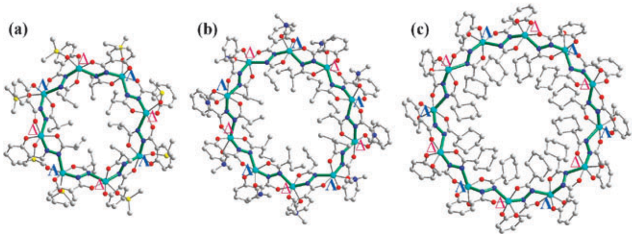


Fig. 2 Metalladiazamacrocyclic systems of (a) octameric, (b) decameric and (c) dodecameric systems formed by successively introducing dimethyl, methylethyl and cyclohexyl groups at the Cα position. Color codes are the same as in Fig. 1.

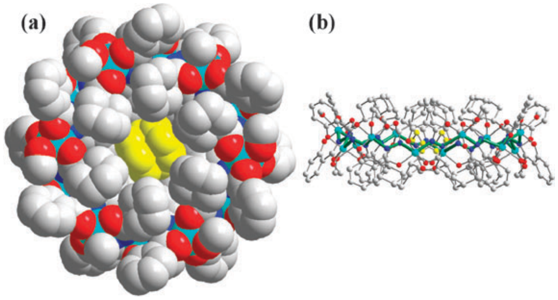


Fig. 3 A dodecameric MOM system of S_{12} symmetry accommodated cyclooctane inside the cavity with strained S_4 conformation rather than relaxed S_8 conformation. (a) Space-filling model view from the top. (b) Ball-and-stick model view from the side. The cyclooctane guest molecule is shown in yellow color. The other color codes are the same as in Fig. 1.

We have designed a ligand, *N*-3,3′-diphenylpropionylsalicylhydrazide ($H_3dppshz$), where two bulky phenyl residues have been introduced at the Cβ position of the primary steric group, which are remote from the bridging domain but sterically more demanding.[20] The self-assembly of the ligands with Mn(III) metal ions produced an icosameric MOM system (Fig. 4). Even though the steric groups have some degree of flexibility, the steric repulsions caused by these bulky groups might be too large to form a hexameric MOM. To reduce the steric repulsions in the hexameric MOM system, it has expanded its macrocyclic system to an icosameric MOM, where the macrocyclic ring consists of 20 Mn(III) metal ions and 20 ligands. Of the 20 ligands, the terminal diphenylethyl

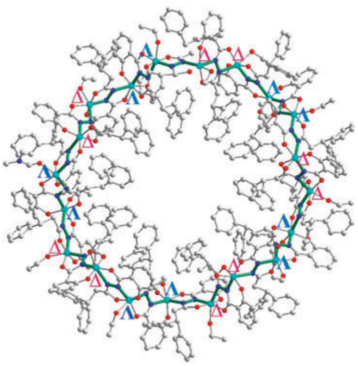


Fig. 4 Ball-and-stick representation of the icosameric metalladiazamacrocycle. Color codes are the same as in Fig. 1.

groups on the alternating 10 ligand molecules are directed toward the inner core and the remaining 10 point outward from the core, which placed the Mn(III) metal centers in a $\cdots(\Lambda\Lambda\Delta\Delta)(\Lambda\Lambda\Delta\Delta)\cdots$ chiral sequence. As a result, the symmetry of the icosameric MOM system is S_{10} rather than S_{20}. The change of the chiral sequence of the metal centers from $\cdots(\Lambda\Delta)(\Lambda\Delta)\cdots$ to $\cdots(\Lambda\Lambda\Delta\Delta)(\Lambda\Lambda\Delta\Delta)\cdots$ is the result of the different stereodispositions of the ligands around the metal centers to reduce the steric repulsions between the primary steric groups in the icosameric MOM. The successive occurrence of the same chirality in the icosameric MOM results in a slightly puckered macrocyclic ring system with a hydrophobic cavity of diameter approximately 10 Å in the core.

A rigid functional group such as a phenyl group at a primary steric domain leads to a decameric MOM, where the metal centers had the same $\cdots(\Lambda\Delta)(\Lambda\Delta)\cdots$ chiral sequence as that of the metal centers of the other decameric MOM with the ligands having flexible Cα-substituted alkyl residues.[21] The similar steric crowding in the vicinity of the bridging domain leads to the same decameric system with S_{10} symmetry. To understand the effect of the rigidity and the steric volume of the primary steric group on the formation of the oligomeric MOM system, a series of ligands with rigid primary steric residues have been investigated. Introduction of a double bond at the Cα-Cβ position of the alkyl residue with an ethyl group at Cβ in the primary steric domain led to an octameric MOM system of S_8 symmetry with the metal centers in a $\cdots(\Lambda\Delta)(\Lambda\Delta)\cdots$ chiral sequence when the reaction was performed in either methanol or ethanol solvent (Fig. 5(a)).[22] However, the same reaction in either DMF or DMA solvent yielded a dodecameric MOM of S_6 symmetry with the Mn(III) metal centers in a $\cdots(\Lambda\Lambda\Delta\Delta)(\Lambda\Lambda\Delta\Delta)\cdots$ chiral sequence (Fig. 5(b)).[13,22] While the small steric volumes of both the ligated solvent molecule and the rigid primary steric domain kept the metal centers in the alternating $\cdots(\Lambda\Delta)(\Lambda\Delta)\cdots$ chiral sequence in the octameric MOM, the combination of large steric volume of the ligated solvent molecule and small steric volume of the rigid primary domain in the vicinity of the bridging domain forced two successive metal centers to the same chiral configuration. As in the icosameric MOM system, half of the 12 primary steric domains are directed toward the core of the macrocyclic ring, while the remaining half point outward from the core to reduce steric repulsion between the primary steric groups.

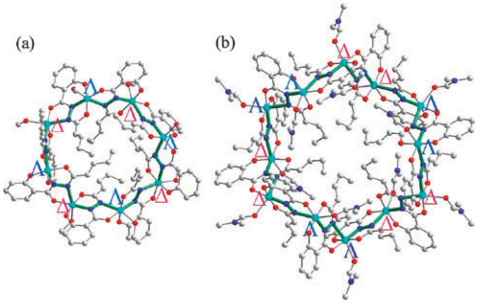


Fig. 5 Ball-and-stick representation of the MOM systems formed with ligands having a double bond at the Cα-Cβ position of the alkyl residue with an ethyl group at the Cβ position. (a) Octameric MOM system having $\cdots(\Lambda\Delta)(\Lambda\Delta)\cdots$ chiral sequence from methanol or ethanol solution. (b) Dodecameric MOM system having $\cdots(\Lambda\Lambda\Delta\Delta)(\Lambda\Lambda\Delta\Delta)\cdots$ chiral sequence from DMF or DMA solutions. Color codes are the same as in Fig. 1.

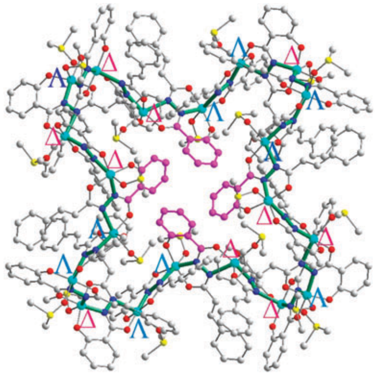


Fig. 6 Ball-and-stick representation of the icosameric metalladiazamacrocycle with puckered cradle shape formed with ligands having a double bond at the Cα-Cβ position with a rigid and bulky phenyl end. The head domains of the four ligands in *inverted* conformation are shown in pink. The other color codes are the same as in Fig. 1.

Replacement of the ethyl group with a rigid and bulky phenyl end at the vinyl Cβ position, that is, by introducing a 3-phenyl-*trans*-2-propenoyl group at the Cα position, produced another form of icosameric MOM system (Fig. 6).[23] The successive Mn(III) metal centers in this icosameric MOM were in a $\cdots(\Lambda\Lambda\Delta\Delta\Lambda\Lambda\Lambda\Delta\Delta\Delta)(\Lambda\Lambda\Delta\Delta\Lambda\Lambda\Lambda\Delta\Delta\Delta)\cdots$ chiral sequence. To reduce the steric repulsions in the core, four out of the 20 ligands in the MOM are arranged in an *inverted* orientation, where the sterically less demanding secondary steric group, a salicyl group, was directed toward the core of the MOM, while the sterically more demanding primary steric group, a 3-phenyl-*trans*-2-propenoyl group, was directed outward from the core. The *inverted* orientation of some ligands led to a cradle-shaped MOM of S_4 symmetry with no cavity in the core. The small steric volume of the rigid primary steric domain near the bridging domain again allowed two adjacent metal centers the same chiral configuration and the subsequent complicated sequence of chiral configurations in the icosameric MOM led to a cradle-shaped ring puckering.

To avoid the *inverted* orientation of the ligands in the MOM system, bulky residues have been introduced at the site of the secondary steric domains of the ligands. The phenyl group at the secondary steric domain of the ligand has been replaced with a bulky aromatic group such as a naphthoyl group. The ligand having a naphthoyl group as a secondary steric domain and a 3-phenyl-*trans*-2-propenoyl group as a rigid primary steric domain formed a hexadecameric MOM of S_8 symmetry with 16 Mn(III) metal ions and 16 ligands, where the metal centers are in a $\cdots(\Lambda\Lambda\Delta\Delta)(\Lambda\Lambda\Delta\Delta)\cdots$ chiral sequence (Fig. 7(a)).[24] In the hexadecameric MOM system, similar to the other oligomeric MOM systems with the metal centers of $\cdots(\Lambda\Lambda\Delta\Delta)(\Lambda\Lambda\Delta\Delta)\cdots$ chiral sequence, the alternating half of the primary steric domains of the ligands are directed toward the core region of the MOM system, while the remaining half are arranged up and down from the approximate macrocyclic

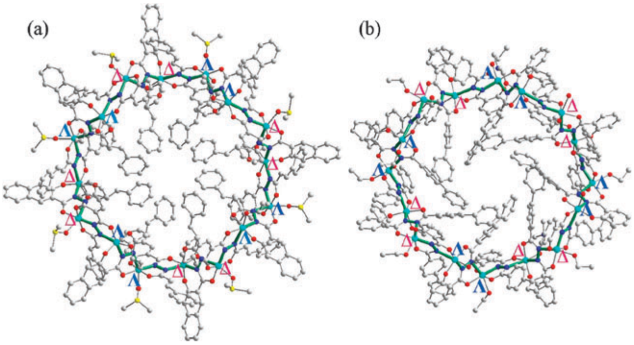


Fig. 7 Ball-and-stick representation of the hexadecameric metalladiazamacrocyclic systems. (a) A MOM formed with ligands having 3-phenyl-*trans*-2-propenoyl and bulky naphthoyl groups substituted at the primary and the secondary steric domains to avoid the *inverted* conformation of the ligands. (b) 4-Phenylbenzoyl group substituted at the primary steric domain of the ligand forms a similar kind of hexadecameric MOM system. Color codes are the same as in Fig. 1.

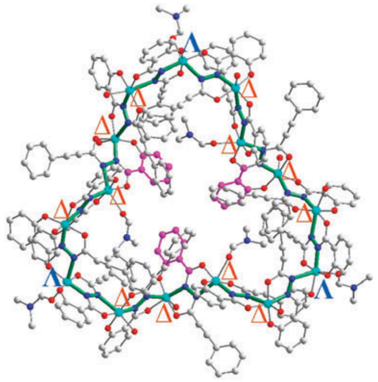


Fig. 8 A pentadecameric MOM system having an unusual ···(ΔΔΔΔΛ)(ΔΔΔΔΛ)··· chiral sequence had sextuple-twisted Möbius topology formed with the ligands with a rigid rod-like phenylpropiolyl group at the primary steric domain. The three inverted secondary steric domains of the ligands are shown in pink. The other color codes are the same as in Fig. 1.

ring plane. Even though the same residue, a 3-phenyl-*trans*-2-propenoyl group, has been used as a primary steric domain, none of the ligands was in the *inverted* orientation in the hexadecameric MOM, because the large steric volume of the secondary steric domain of the ligand, the 2-naphthoyl group, has not been allowed in the crowded core of the macrocyclic ring system. Even with the ligand of the rigid primary steric domain having a bulky phenyl group at the end and of the salicyl group as the secondary steric domain, the *inverted* orientation of the ligands in the MOM system can still be avoided when the primary steric domain has some steric volume in the vicinity of the bridging domain. The introduction of a phenyl(benzoyl) residue as a primary domain of the ligand also led to a hexadecameric MOM system of S_8 symmetry with the successive Mn(III) metal centers in a ···(ΛΛΔΔ)(ΛΛΔΔ)··· chiral sequence, where the primary steric residue is a rod-shaped steric group with a bulky phenyl group at the end, but it is a kind of Cα-substituted residue (Fig. 7(b)).[20] In this MOM, none of the ligands is in the *inverted* orientation. The extent of the ring puckering is similar to those of the other oligomeric MOMs with the same ···(ΛΛΔΔ)(ΛΛΔΔ)··· chiral sequence.

The size and shape of the steric domains and the locations and rigidities of the steric residues in the steric domains showed a combined effect on the stereochemistry of the metal centers and the consequent size, shape and nuclearity of the oligomeric MOM system. When a ligand that has a rigid rod-like primary steric domain with a bulky steric residue at the end of the domain but with small steric volume in the vicinity of the bridging domain, has been employed as a ditopic linker for the construction of a MOM system, some of the ligands in the MOM system are in the *inverted* orientation. To explore the effect of the *inverted* orientation of the ligands in the MOM system, a new ligand having a rigid primary steric domain with the least steric volume near the bridging domain but with a bulky phenyl group at the end was designed. To have a rigid steric residue with the least steric volume near the bridging domain, we have used a phenylpropiolyl group as a primary steric group because it is rigid and has a triple bond at the Cα-Cβ region and a bulky phenyl group at the end of the primary steric domain.[25] It produced a pentadecameric MOM with a 45-member macrocyclic ring with 15 Mn(III) ions and 15 ligands, where the chiral configurations of the metal ions are in a ···(ΔΔΔΔΛ)(ΔΔΔΔΛ)··· sequence (Fig. 8). The same chiral configuration of four successive metal centers results in the successive rotation of the ligand orientations up to an approximate 360° twist (double twist) along the direction of the propagation. The change of the chiral configuration of the next metal center from that of the previous four successive metal centers led to a sharp turn of the propagation direction of the system. The cyclic repeat of the chiral sequence created the sextuple-twisted pentadecameric MOM of Möbius topology. The ligands in this sextuple-twisted macrocyclic system were in various orientations, including the *inverted* orientation.

We have presented the oligomeric MOM systems synthesized using the trianionic pentadentate pseudo-ditopic ligands with octahedral tricationic metal ions. The two steric domains of the ligands have been modified with various aliphatic or aromatic systems with different steric volumes and rigidities. Depending on the different ways of arranging the steric groups around the core of the MOM system, various MOMs with different sizes, shapes, stereosequences and symmetries have been generated while keeping the same ditopic bridging mode between the two tricationic octahedral metal ions and the same tridentate/bidentate binding mode of two ligands at the metal center. In addition to studies of the steric effect of modifying the steric domains, we have studied the effect of the modification on the bridging domain in MOM formation by substituting one of the functional groups of the bridging domain or by introducing an additional donor group at the primary steric domain. We have considered a new pentadentate ligand, *N*-acetylaminobenzhydrazide (H_4aahz), which has an amine group at the site of a hydroxyl group of *N*-acetylsalicylhydrazide (H_3ashz).[26] The self-assembly of the ligand and manganese ion led to a hexameric MOM with the same bridging mode between two metal centers and the same tridentate/bidentate binding mode around a metal center. In this MOM, the ligand was triply deprotonated and served as a trianionic pentadentate ditopic bridging ligand, as with the

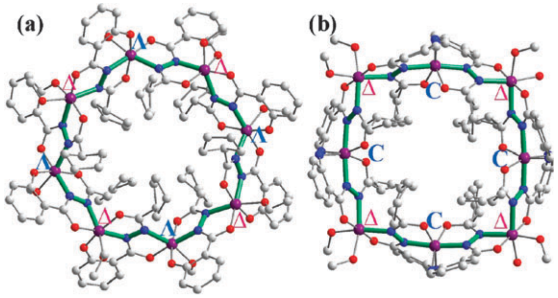


Fig. 9 Octameric MOM systems formed with ligands having a cyclopentyl group at the primary steric domain and gallium(III) metal ions. (a) The S_8 symmetric MOM with usual tridentate/bidentate binding mode around the metal ions. (b) S_4 symmetric MOM with unusual tridentate/tridentate and bidentate/bidentate binding modes around the metal ions observed with the ligand having an amine group at the bridging domain. Metal ions are represented as pink balls. The other color codes are the same as in Fig. 1.

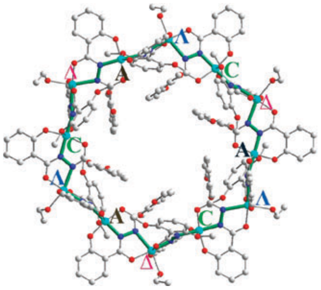


Fig. 10 A dodecameric MOM system formed with the ligand having an extra chelating methoxy group at the primary steric domain. The metal ions had an unusual $\cdots(A_A\Delta_B C_A\Lambda_B)(A_A\Delta_B C_A\Lambda_B)\cdots$ chiral sequence in the MOM system. The color codes are the same as in Fig. 1.

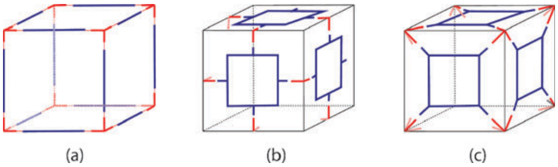
hydroxyl ligands in the other metalladiazamacrocycles. However, the reaction of the same type of an amino-substituted ligand, *N*-cyclopentylcarbonylbenzylhydrazide, with gallium ion led to another type of octameric MOM of D_4 symmetry with the same bridging mode but of different binding modes around the metal centers and consequently different stereochemistries, while the reaction of a corresponding hydroxyl analogue of the ligand, *N*-cyclopentylsalicylhydrazide, with the gallium ion resulted in the usual octameric MOM of S_8 symmetry, with the same binding mode and the same type of stereochemistry (Fig. 9).[27] In the octameric MOM system of D_4 symmetry with the amine-substituted ligand, the ligand was in a doubly deprotonated dianionic state even though it was in a pentadentate bridging mode with the metal ions; however, the metal centers are in two different binding modes: one in meridional tridentate/tridentate coordination mode around a metal center and the other in propeller bidentate/bidentate coordination mode around a metal center (Scheme 4). The meridional tridentate/tridentate coordination mode of the tridentate chelating residue having an asymmetric nature generated a different stereoconfigurations, anticlockwise (*A*) rotational configuration and clockwise (*C*) rotational configuration. The combination of this type of stereoconfiguration with the conventional Λ/Δ stereoconfiguration in this amine-functionalized MOM system led to a $\cdots(\mathrm{C_A}\Delta_\mathrm{B})(\mathrm{C_A}\Delta_\mathrm{B})\cdots$ chiral sequence. The deprotonation state of the amine group of the ligand could be controlled by the metal ions involved. Depending on the metal ion, the ligand could have different deprotonation states and consequently different charges, different stereochemistries around the metal ions and different MOM systems.

We have studied another type of modification on the bridging domain by introducing potential donor atoms at the primary steric domain of a ligand. A ligand having a 2,6-dimethoxybenzoyl group at the primary steric domain, 2,6-dimethoxybenzoylsalicylhydrazide, forms a dodecameric MOM system with Mn(III) ions (Fig. 10).[28] The ligands in this dodecameric MOM were in two different bridging modes. One ligand was in a tridentate/bidentate bridging mode between two Mn(III) metal ions through three oxygen atoms and two hydrazine nitrogen atoms as in the usual *N*-acylsalicylhydrazide in the other MOM systems, while the other ligand was in a tridentate/tridentate bridging mode through four oxygen atoms including the methoxy group on the primary domain and two nitrogen atoms on the hydrazide N–N linkage (Scheme 2(c)). The alternation of these two bridging modes generated tridentate/tridentate binding mode around the metal center with *C*/*A* chiral configuration and a tridentate/bidentate binding mode around the metal center with Λ/Δ chiral configuration. The metal centers in the MOM system were in an $\cdots(A_A\Delta_B C_A\Lambda_B)(A_A\Delta_B C_A\Lambda_B)\cdots$ chiral sequence. Out of 12 terminal 2,6-dimethoxy groups, six were arranged in an inner core, and the remaining six were arranged vertically up and down from the macrocyclic ring plane.

MOPs

Many biological systems of high symmetry are self-assembled from a large number of subunits. In the iron storage protein apoferritin, 24 protein subunits are assembled to a nearly spherical shell of octahedral symmetry *via* multiple weak interactions between the subunits.[29] The coats of many viruses have 60 facial protein subunits assembled in shells of an icosahedral symmetry.[30] Inspired by these highly symmetric biological systems, various synthetic self-assembled systems, MOPs, have been prepared by suitably designed ligands with metal ions.

When at least one of the building components of MOSs is a more than tritopic node, either 3D MOPs of finite size or infinitely extended MOFs can be generated. The appropriate combination of metal ions and ligands with different connectivity has led to finite 3D MOPs.[8,31] Two different strategies can be employed for the MOP construction: one is an edge-directed approach and the other is a face-directed approach (Scheme 6).[32–34] In the edge-directed approach, ditopic edge components are connected at the corner of the polyhedron by multitopic components. For finite structure formation, at least one component of the systems must show a bent geometry. In the face-directed approach, multitopic facial components are connected either at the edges by the ditopic components or at the corners by multitopic components. Self-assembly of metal ions and ligands that are carefully selected and designed can lead to MOP systems of predictable size and geometry. To prepare MOPs of *T* symmetry, exploitation of the building components of C_3 and C_2 symmetry with at least one



Scheme 6 Schematic drawings illustrating the construction strategies of MOP systems. (a) Linear ditopic edge components connected with C_3 symmetric corner components, (b) C_4 symmetric facial components connected with the bent ditopic edge components and (c) C_4 symmetric facial components connected with C_3 symmetric corner components.

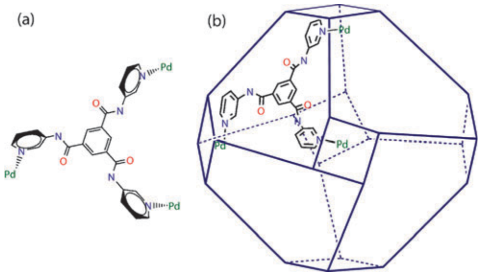
component with potential bent geometry is one of the most important factors. C_2 symmetric ditopic edge components can be connected at the corners of the tetrahedron by C_3 symmetric corner components.[32a,f] Alternatively, C_3 symmetric tritopic facial components can be linked at the edges by C_2 symmetric ditopic components.[33a–c] For MOPs of *O* symmetry, the use of building components of C_3, and C_2 and/or C_4 symmetry with at least one component with potential bent geometry is the key factor. As in the MOPs of *T* symmetry, various combinations of C_2, C_3 and C_4 symmetric components as edge, facial and corner components can lead to MOPs of *O* symmetry. C_2 symmetric ditopic edge components or C_3 symmetric tritopic facial components can be connected at the corners of the octahedron by C_4 symmetric components.[32d,34c,d] For MOPs of *I* symmetry, the use of the building components of C_3, and C_2 and/or C_5 symmetry with at least one component with potential bent geometry is essential. The self-assembly of C_3 and C_5 symmetric components led to MOPs of *I* symmetry.[35]

The size of the MOPs can usually be modulated by control of the size of the components used.[8,36] The simple expansion of the size of the components can increase the size of the system. Augmentation is the other way to control the size and/or properties of the MOPs. The augmented MOPs can be obtained when secondary building units (SBUs) are used as the building components of the MOPs instead of primary building units. For example, a paddle-wheel cluster, $[Cu_2(COO)_4]$, can serve as a square planar tetratopic SBU in the MOPs. Self-assembly of Cu(II) ions and dicarboxylic acids with appropriate bending angle could generate a Cu(II) paddle-wheel as a square-planar SBU, which is further connected in bent ditopic linkage to form an edge-directed corner-linked augmented octahedron.[32d]

Octahedral MOPs based on face-directed components

For the preparation of a cubic symmetry MOP, a C_3 symmetric building component plays a key role because all cubic groups have a C_3 symmetry element as one of their symmetry elements. When the C_3 symmetric building component is combined with a component of C_2 symmetry, a MOP with *T* symmetry can be generated; when combined with a component of C_4 symmetry, a MOP with *O* symmetry can be self-assembled, and when combined with a component of C_5 symmetry, a MOP with *I* symmetry can be self-assembled.

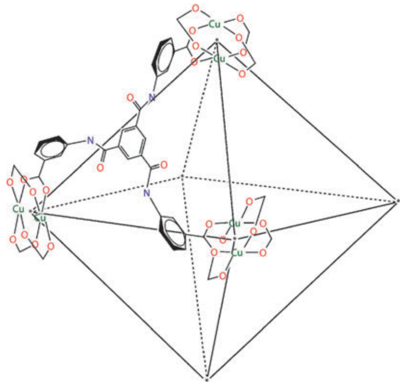
C_3 symmetric ligands have been utilized as facial components connected with C_4 symmetric square-planar metal ions at the tetranodal corners for the construction of an *O* symmetry MOP. The ligand *N*,*N*′,*N*″-tris(3-pyridinyl)-1,3,5-benzenetricarboxamide has been used as a C_3 symmetric facial component to form an octahedral cage because the 3-pyridinyl groups could be coordinated with Pd(II) ions at square-planar tetranodal corners and the positions of the three nitrogen donors of the carboxamido pyridinyl groups at ~120° out of the ligand plane direction can provide the needed curvature for the formation of a finite *O* symmetric MOP (Scheme 7).[37] The meta-positioned pyridyl nitrogen atom in the 3-pyridyl group provides the necessary curvature to form the octahedral cage. Six planar Pd(II) ions and eight facial ligands possessing curvature are self-assembled to a truncated octahedral cage. The same strategy of utilizing curved C_3 symmetric facial components for the construction of truncated octahedra has been applied using the ligand *N*,*N*′,*N*″-tris(4-pyridinylmethyl)-1,3,5-benzenetricarboxamide as another facial ligand. The 3-pyridinyl group with a nitrogen atom at the *meta*-position in the former ligand was modified to a 4-pyridinylmethyl group with a nitrogen atom at the *para*-position with an extra methylene linkage between the 4-pyridyl group and the amide linkage. The overall kink angle of 120° at the methylene group provides the necessary curvature to the ligand at the 4-pyridyl position to form the cage. From the above octahedral system, it is understood that to construct a MOP system having *O* symmetry requires a C_4 symmetric square-planar node along with a C_3 symmetric component with curvature of 120° out-of-plane bend angle. Here, 3-pyridyl as well as 4-pyridylmethyl groups fulfill the necessary requirement of 120° bend angle.



Scheme 7 Schematic picture of (a) three nitrogen donor atoms of 3-pyridyl ends of the C_3 symmetric facial ligand directed out of the ligand plane to form a finite cage system and (b) the ligand occupying the face of the octahedron coordinated with square-planar Pd(II) ions at the corner of the truncated octahedral cage.

An augmented MOP based on a $Cu_2(COO)_4$ paddle-wheel SBU

The approach of exploiting the curved C_3 symmetric facial ligands for octahedral MOP construction can be extended to an augmented system. A ligand, 3,3′,3″-[1,3,5-benzenetriyl-tris(carbonylimino)]trisbenzoate, which has a 3-carboxylate group in place of the 3-pyridinyl group of *N*,*N*′,*N*″-tris-(3-pyridinyl)-1,3,5-benzenetricarboxamide, has been used as a curved C_3 symmetric facial component connected at truncated $Cu_2(COO)_4$ paddle-wheel square-planar centers as truncated corners to form the augmented octahedral MOP (Scheme 8).[38] Here, eight ligand molecules occupy the faces of the octahedron connected with six $Cu_2(COO)_4$ paddle-wheel SBUs at the truncated corners of the octahedron. The overall charge on the MOP is zero. The 3-carboxylate group in the ligand



Scheme 8 A schematic picture of an augmented MOP system formed by connecting $Cu_2(COO)_4$ paddle-wheel SBUs at the corners of an octahedron.

provides the necessary kink angle to provide curvature to form the octahedral cage. The six Cu(II) paddle-wheel centers are coordinated with solvent molecules.

MOFs

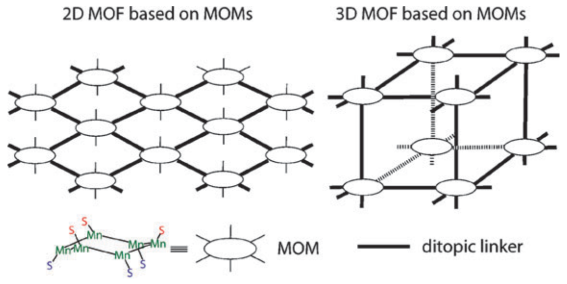
MOFs are extended solids made of metal ions and ligands as building components, where the building components are interconnected *via* coordination bonds to form infinite networks. Depending on the connectivity and geometry of the building components, 1D, 2D and 3D MOFs can be constructed. For the rational design of the MOFs, the network topology is probably one of the most important factors to be considered. When metal ions and ligands are ditopic components, either 2D MOMs or 1D MOFs can be generated. When metal ions and ligands of higher connectivity are used as building components, MOFs of higher dimensionality can be obtained. The self-assembly of the metal ions preferring a specific coordination geometry with rigid ligands increases the chance of the rational design of the MOFs. However, it is still frustrating to modulate the structures and the corresponding properties of the MOFs by systematic variation of the building components, because small modifications in the building components and subtle changes in the reaction conditions often lead to a completely unexpected result. The SBU approach was very successful for the rational design of MOFs and the systematic development of MOFs. Well-known examples of inorganic SBUs are the tetranuclear $[Zn_4O(COO)_6]$ as an octahedral hexatopic node,[39] the triangular trinuclear $[M_3O(COO)_6]$ (M = Cr(III), In(III), Al(III), Ni(II)) as a trigonal prismatic hexatopic motif,[39b,40] the linear trinuclear $[M_3(COO)_6]$ (M = Mg(II), Zn(II), Ni(II)) as a distorted octahedral hexatopic node,[41] a dinuclear paddle-wheel $[M_2(COO)_4]$ (M = Cu(II), Zn(II)) as a square-planar tetratopic node,[42] and a square tetranuclear $[M_4Cl(N_4CR)_8]$ (M = Mn(II), Cu(II)) as a cubic octatopic node.[43] Some of these rigid inorganic SBUs combined with rigid organic linkers of the same nodality can generate a series of predetermined isoreticular MOFs. The solvothermal reaction of $Zn(NO_3)_2$ with a series of linear and rigid dicarboxylic acids in amide-based solvents led to a series of isoreticular MOFs of **pcu** network topology having the tetranuclear $[Zn_4O(COO)_6]$ unit as a rigid octahedral hexatopic SBU.[39b]

Some MOMs and MOPs can have unique structural features such as high connectivity, unusual geometry and inherently large cavities. When these MOMs and MOPs are used as SBBs, their features can be transferred directly to those of the MOFs. The other advantage of the SBB approach over the SBU approach is that it is relatively easy to characterize the SBBs in solution and also in the solid state, while it is usually very difficult to understand the characteristics of the SBUs in solution. Even in the case that the SBUs in solution are well characterized, these SBUs might be only pro-SBUs, and the SBUs in the final MOFs could be different from those in solution.[44] The properties of the MOFs based on the SBB can be controlled at the level of the SBB, which has been precharacterized.

MOFs based on MOMs

We have prepared 2D and 3D MOFs using our metalladiazamacrocycles, a class of MOMs, as SBBs by connecting these MOMs with additional linker molecules (Scheme 9).

The hexameric MOMs we have presented in the previous sections consist of six hexacoordinate metal ions, where each metal ion is coordinated with two ligands in a tridentate/bidentate binding mode and the remaining sixth coordination site is occupied by a monodentate solvent molecule. Because the monodentate solvent molecule coordinated at each metal center can be replaced by other linking ligands, each metal center of the MOMs can serve as a potential tritopic node, and the hexameric MOM is a potential supramolecular hexatopic node with three replaceable sites at one side of the macrocyclic ring plane and the other three sites at the opposite side of the ring plane (Scheme 5(c)). The simple pentadentate ligand, *N*-acetylsalicylhydrazide, forms a 3D MOF system with manganese ions and 1,2-bis(4-pyridyl)ethane (bpea) bidentate ligands; here, the hexameric MOM system formed was interlinked with ditopic bpea molecules (Fig. 11).[45] Out of six solvent molecules in each hexameric MOM coordinated to six metal ions, only four of them were replaced with the bpea molecules. The ditopic bpea molecules connected the hexameric MOMs *via* $4_1/4_3$ screw symmetry to form a three-fold interpenetrating 3D network with 3-connected 4.8.16 net topology.[12,45] When the hexameric MOMs are considered as supramolecular rectangular tetratopic nodes, the individual net of the MOFs can be considered as a net of 4-connected



Scheme 9 Schematic drawings illustrating the construction of 2D and 3D MOFs based on MOMs as SBBs.

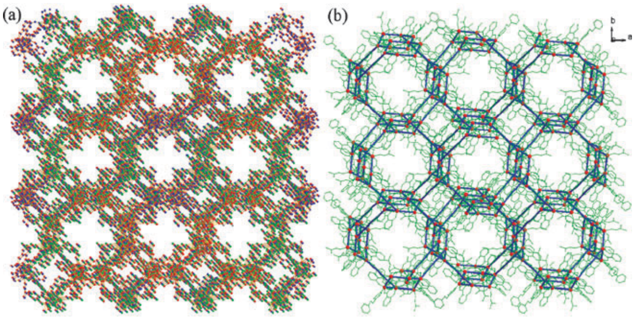


Fig. 11 A three-fold interpenetrating 3D framework formed with hexameric MOMs as a supramolecular tetratopic node interconnected with ditopic bpea bidentate ligands. (a) Three interpenetrating networks are presented in red, blue and green. (b) The schematic picture of the network connectivity overlaid on one of the single nets shown in green, where the metals are represented as red balls and the connecting lines as blue sticks. In the framework, the MOMs are interconnected with ditopic linkers *via* $4_1/4_3$ screw symmetry.

$4^2.8^4$ topology. Despite the three-fold interpenetration, the MOF system still had significant dimensions of 3D solvent channels and the methyl groups of the *N*-acetyl ends in the primary steric domains are exposed to the solvent channels. When the ligands having a series of saturated linear alkyl residues as the primary steric domains were used as primary building units, a series of isoreticular MOFs could be self-assembled based on the corresponding hexameric MOMs as SBBs.[46] Depending on the length of the alkyl chains, the size and shape of the solvent channels of the MOFs can be modulated while keeping the framework structures the same, and selective recognition based on the size and shape of the guest molecules has been demonstrated using these modulated solvent cavities.

When the *N*-acetyl end was changed with a long *N*-lauroyl alkyl chain, two different MOF systems were formed in the same reaction vial.[47] One MOF system was isoreticular to those of the previous *N*-acetyl analogues. The long *N*-lauroyl alkyl chains were packed in the solvent channels of the framework and only several scattered 0D cavities were left as solvent cavities. The second type of MOF system had the same hexameric MOM but had a two-fold interpenetrating 3D network having large 1D channels, where the unlinked hexameric MOMs were stacked along the channels (Fig. 12). As in the former MOF system, the network topology can be further simplified to a 4-connected $6^4.8^2$ net when the hexameric MOM is considered as a supramolecular rectangular tetratopic node.

When *N*-hexanoylsalicylhydrazide, which had a pentyl group as a medium length alkyl chain as the primary steric group, has been used for the construction of MOF systems with bpea linkers in the presence of diethylphthalate (def) as a templating agent and/or a potential guest molecule, two different forms of MOFs have been observed.[12] The network structure in the major form of the MOFs is the same as the MOF structure of the 3-connected 4.8.16 network topology, which was obtained under the same reaction condition but in the absence of the def. The minor form of the MOFs is a two-fold interpenetrating 3D framework of two identical nets of a 3-connected 4.12^2 topology (Fig. 13). The MOM in this MOF could be considered as a supramolecular pseudo-octahedral hexatopic node because all of the six replaceable solvent molecules were substituted with the ditopic bpea linkers and the framework can be simplified as two-fold interpenetrating networks with **pcu** net topology.

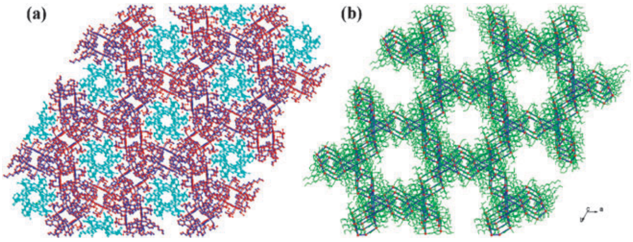


Fig. 12 A two-fold interpenetrating 3D framework formed with hexameric MOMs and bpea linkers. The MOMs are formed with ligands having lauroyl chains at the primary steric domain. (a) The two interpenetrated nets are shown in red and blue. The unlinked MOMs shown in cyan are stacked in the 1D channels. (b) The schematic picture of the network connectivity overlaid on one of the single nets shown in pale green, where the metal atoms are represented as red balls and the connecting lines as blue sticks. In the framework, the MOMs are interconnected with ditopic linkers *via* $3_1/3_2$ screw symmetry.

2D MOF systems can also be obtained with MOMs as SBBs and bpea as linking molecules under some reaction conditions. The reaction of manganese(II) acetate with *N*-propionylsalicylhydrazide (H_3pshz) and bpea in DMA solvent led to two different forms of 2D MOFs based on a hexameric MOM and an octameric MOM as SBBs, respectively,[48] while the similar reaction in DMF led to only the three-fold interpenetrating 3D MOF structure of the 3-connected 4.8.16 topology, as described earlier. The hexameric MOMs in the 2D MOF served as square tetratopic nodes and were interconnected with four ditopic bpea molecules, while the remaining two metal sites on the MOM system were coordinated with solvent molecules as the hexameric MOM in the 3D MOFs (Fig. 14). However, the ditopic bpea linkers interconnected the tetratopic SBBs to a 2D layered MOF of a 3-connected 4.8^2 net topology. The network topology can be simplified to a 2D 4-connected 4^4 net when the SBB is considered as a rectangular tetratopic node. In the 2D layered structure, weak

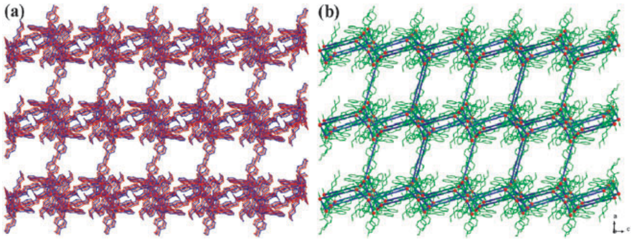


Fig. 13 A two-fold interpenetrating 3D framework formed with hexameric MOMs as a hexatopic SBB and bpea molecules as a ditopic linker. (a) The two nets in the framework shown in red and blue. (b) A schematic picture of the network connectivity overlaid on one of the single nets shown in pale green, where the metals are represented as red balls and the connecting lines as blue sticks. When the MOMs are simplified to an octahedral hexatopic node, the network is of **pcu** net topology.

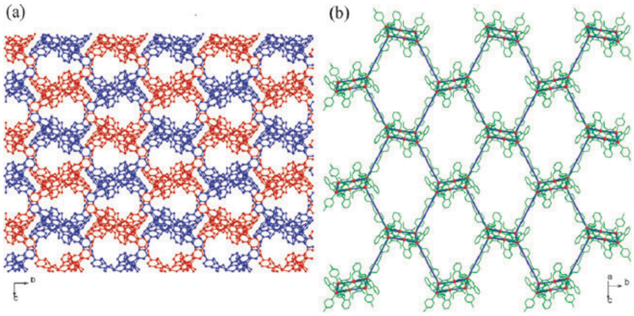


Fig. 14 A layered 2D framework formed with hexameric MOMs as an SBB and bpea linkers, where each MOM served as a rectangular-tetratopic node in the framework. (a) The 2D sheets in the framework with staggered conformation are shown in red and blue. (b) A schematic picture of the network connectivity overlaid on one of the single nets shown in pale green, where the metals are represented as red balls and the connecting lines as blue sticks. When the MOMs are simplified to a rectangular-tetratopic node, the network is of (4,4) net topology.

but extensive inter-sheet interactions have been observed, and these interactions are responsible for the staggered orientation of the neighboring sheets. Even though the sheets in this 2D layered MOF are staggered, the MOF still has significant solvent accessible space between the sheets because of the corrugated nature of the 2D sheet. In the other form of the 2D MOF, the octameric MOM served as a new type of tetratopic SBB (Fig. 15). We did not succeed in the preparation of the octameric MOM system with H_3pshz as a ditopic bridging ligand in the absence of the auxiliary ditopic linker, bpea. This octameric MOM, having a flexible saturated linear *N*-acyl residue as the primary steric domain, was only observed when the reaction was performed in DMA with bpea. Even though the octameric MOM is a potential octatopic node, it is utilized as a tetratopic node. Only the four alternating solvent molecules out of eight were replaced by the ditopic bpea linkers. All four bpea linking molecules in each MOM system are oriented toward the same facial side, which leads to the corrugated arrangement of the 2-D layers in the MOF. If the metal center linked in the layered 2D MOF is considered as a trinode, the net has a 3-connected 4.8^2 topology. Furthermore, when the octameric MOM was reduced to a square-planar tetratopic node, the topology of the net could be further simplified to a 4-connected 4^4 net. The 2D MOF based on the octameric MOM as an SBB has the same network topology as that based on the hexameric MOM as an SBB; however, the corrugated sheets in the 2D MOF based on the octameric MOM are stacked in an eclipsed orientation, which generates 3D solvent channels in the MOF. The same ligand, H_3pshz, with Mn(II) ions with bpea in DMA in the presence of def as a templating agent led to a single form of the 2D layered MOF based on the octameric MOM. The solvent DMA molecule plays an important role for the construction of the 2D layered MOF systems. The solvent is involved in the inter-sheet interactions. However, the role of the templating agent, def, is not clear because def molecules are not the constituent materials of the framework and no ordered def molecules are observed in the solvent channels, although the IR spectra indicated the presence of def molecules in the solvent channels.

As described in the earlier section, the self-assembly of manganese ions and the pentadentate ligands, H_4aahz, which have an amine residue in the site of the hydroxyl group of the bridging domain, led to a hexameric MOM, which is isostructural to that of the other hexameric MOMs having the hydroxyl group in the bridging domain.[26] However, the self-assembly of the same metal ions and the same ligands in the presence of the additional ditopic linking ligands, bpea, led to a different MOF system. While the self-assembly of the manganese ions and the ligands, H_3ashz, with bpea in DMF yielded the 3D MOF based on the hexameric MOMs as SBBs, the similar reaction with H_4aahz led to a 2D MOF (Fig. 16), though it was based on the similar hexameric MOMs.[26] Each MOM in this 2D MOF served as a tetratopic SBB connected to four ditopic bpea molecules. As in the previous 2D MOFs, the 2D layers of the framework of the same 3-connected 4.8^2 net topology are in a staggered orientation, but the MOF still has a significant solvent accessible cavity because of the corrugated nature of the 2D sheet.

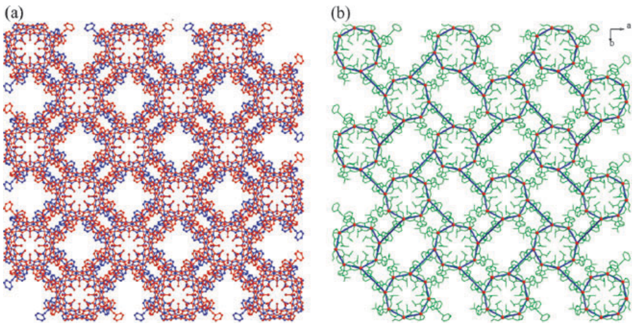


Fig. 15 A layered 2D framework formed with octameric MOMs as an SBB and bpea linkers, where each MOM served as a new type of square-tetratopic node in the framework. (a) The 2D sheets with eclipsed conformation are shown in red and blue. (b) A schematic picture of the network connectivity overlaid on one of the single nets shown in pale green, where the metals are represented as red balls and the connecting lines as blue sticks. When the MOMs are simplified to a square-tetratopic node, the network is of (4,4) net topology.

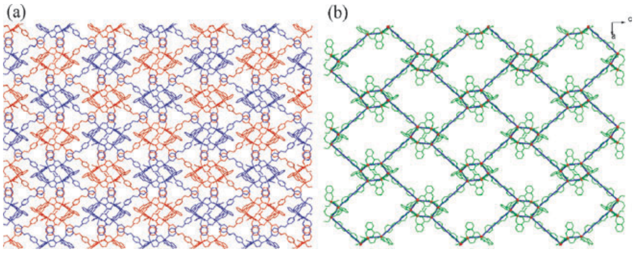
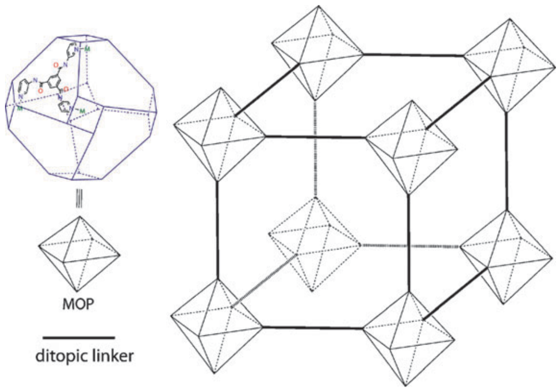


Fig. 16 A layered 2D framework formed with hexameric MOMs as an SBB and bpea linkers, where each MOM served as a rectangular-tetratopic node in the framework. (a) The 2D sheets in the framework with staggered conformation are shown with red and blue color. (b) The schematic picture of the network connectivity overlaid on one of the single nets is shown in pale green, where the metals are represented as red balls and the connecting lines as blue sticks. When the MOMs are simplified to a rectangular-tetratopic node, the network is of (4,4) net topology.

MOFs based on MOPs

While the MOMs are 2D metal–organic supramolecules, the MOPs are 3D assemblies and usually possess larger solvent cavities than the MOMs. When the MOF systems have been prepared with the MOPs as SBBs, the supramolecular properties of the MOPs can be directly transferred to the MOF systems, and it is possible to have large solvent cavities in the frameworks regardless of the arrangement of the MOPs because the MOP itself can have a large solvent cavity. As in the MOMs, when the metal centers of the MOPs have replaceable solvent sites, these sites can be utilized as additional linking sites for the construction of MOFs based on the MOPs (Scheme 10). However, the Pd(II)-based octahedral MOPs described in the earlier section do not have metal centers with replaceable solvent molecules because the square-planar environment of the Pd(II) centers is saturated by coordination with the facial component ligands. We have prepared an isostructural MOP using the Cu(II) ion as a metal center of the MOP preferring a Jahn–Teller distorted octahedral geometry because the basal coordination sites of the metal center can still be engaged in the formation of the isostructural MOP with the facial component ligands while the axial site exposed toward the outside of the MOP can be utilized as an additional linking site for the construction of the MOP-based MOF.[49] The self-assembly of Cu(II) perchlorate and *N*,*N*′,*N*″-tris(3-pyridinylmethyl)-1,3,5-benzenetricarboxamide in DMSO yielded an octahedral MOP, which is isostructural to the MOP prepared using Pd(II) metal ion, except for the ligation of the additional solvent molecules at the axial sites of the constituting Cu(II) metal centers. Even though the perchlorate counter ions could be potential anionic linkers to connect the metal centers of the MOPs, they only served as counter anions without being involved in the interconnecting the MOPs in the MOS, probably because of their weak coordination ability. A similar reaction using *N*,*N*′,*N*″-tris(3-pyridinyl)-1,3,5-benzenetricarboxamide as another C_3 symmetric facial component for the construction of the MOP while keeping other conditions the same led to isoreticular MOPs, where some metal sites of the MOPs are interconnected by the perchlorate anions to a cyclic hexameric cluster of the MOPs. To have MOF based on the extensively interconnected MOPs, a copper source having a counter anion of better donor capability was selected. The self-assembly of copper nitrate and the C_3 symmetric facial ligand, *N*,*N*′,*N*″-tris(3-pyridinyl)-1,3,5-benzenetricarboxamide, in DMSO led to a MOF based on the MOP as an SBB (Fig. 17). In this MOF, the nitrate anion served as a ditopic linker between the metal centers of the six vertices of the octahedral MOP to form two-fold interpenetrating networks of a **pcu** net topology, where the hexatopic nodes of the **pcu** net were augmented by the octahedral MOPs. In this MOF, half of the facial ligands in the MOP building block are involved in π–π stacking interactions using the central phenyl residue of the ligand with the adjacent phenyl residue from the other network, which leads to two-dimensional propagation of the π–π stacking interaction and an additional stabilization of the framework. The self-assembly of the copper nitrate and the other C_3 symmetric facial ligand, *N*,*N*′,*N*″-tris(3-pyridinylmethyl)-1,3,5-benzenetricarboxamide, led to another isoreticular MOF based on the corresponding MOP as an SBB. In this MOF, all the facial ligands in the corresponding MOP building block are involved in the π–π stacking interaction, which leads to the three-dimensional propagation of the π–π stacking interaction. While only half of the facial ligands in the former MOP building block are allowed in the concave conformation for the π–π stacking interaction, the increased ligand flexibility rendered by the introduction of an additional methylene group between the pyridyl and amide residues in the latter MOP building block allows the concave conformation of all facial ligands for the three-dimensional propagation of the π–π stacking interaction. These MOFs have large solvent cavities even though the framework was two-fold interpenetrated because the supramolecular MOP building blocks themselves have large inherent cavities. In addition, the cavity sizes of the MOFs can be controlled at the level of the SBBs. The cavity volume of the second MOF is slightly larger than that of the first MOF because the cavity volume of the second MOP is slightly larger than that of the first MOP system.



Scheme 10 A schematic drawing illustrating the construction of a 3D MOF augmented with MOPs as a hexatopic SBB.

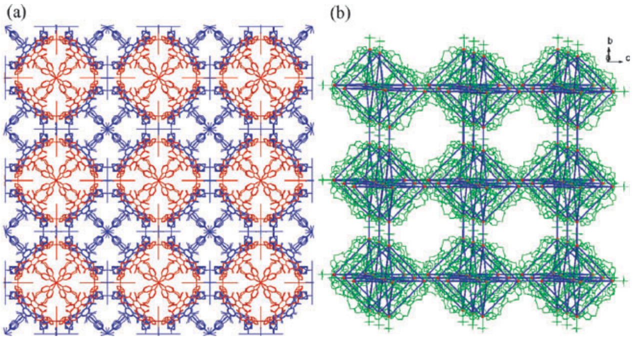


Fig. 17 A two-fold interpenetrating 3D framework made of octahedral MOPs as an SBB connected with ditopic linkers. (a) The two interpenetrating 3D networks are shown in red and blue. (b) A schematic picture of the network connectivity overlaid on one of the single nets shown in pale green, where the metals are represented as red balls and the connecting lines as blue sticks. When the MOPs are simplified to an octahedral-hexatopic node, the network is of **pcu** net topology.

It is well known that some bent dicarboxylic acids can be utilized as edge components for the construction of an edge-directed corner-linked cuboctahedral MOP with the metal ions preferring a paddle-wheel SBU. The reaction of 1,3-benzenedicarboxylic acid (H_3bdc) with either Cu(II) ion or Mo(II) ion produced an edge-directed corner-linked MOP of cuboctahedral symmetry augmented by $Cu_2(COO)_4$ paddle-wheels at the 12 vertices.[50] A 120° bending angle of the dicarboxylate at the edge provides the curvature needed for the construction of the finite MOP system. The cuboctahedral MOP can also be utilized for the self-assembly of a MOF as an SBB when the replaceable solvent molecules at the metal centers of the paddle-wheel units at the 12 cuboctahedral vertices are substituted by additional linking ligands. Chun has reported that the solvothermal reaction of 5-methyl-1,3-benzenedicarboxylic acid and 1,4-diazabicyclo-[2.2.2]octane (dabco) with zinc nitrate in DMF produced a MOF based on the cuboctahedral MOP as an SBB, where the MOPs were interconnected through their metal centers at the 12 vertices using the ditopic linker, dabco, to a cubic close packing (CCP) arrangement with a large solvent cavity.[51] Two different kinds of cavities in the tetrahedral and octahedral interstices of the MOF in the CCP arrangement of the cuboctahedral MOPs were generated in addition to the inherent cavities of the MOPs themselves.

The other strategy for constructing a MOF based on a MOP is using a ligand having the multiple functional groups covalently connected, where each functional group can be utilized as a building component of the MOP. In this MOF, the MOPs generated from the building components are covalently interconnected as SBBs regardless of their arrangements in the framework. The reaction of 1,3-bis(5-methoxy-1,3-benzenedicarboxylic acid)benzene, a ligand having two bdc units connected by a long flexible covalent linkage, with Cu(II) ion generated a two-fold interpenetrating MOF based on cuboctahedral MOPs as SBBs, where each MOP was composed of bdc units at the 24 edges and Cu(II) paddle-wheels at the 12 corners of the cuboctahedron.[52] The MOPs interconnected by quadruple covalent linkages using four adjacent edges of the cuboctahedron served as hexatopic building blocks and led to a network with a **pcu** topology augmented by the MOPs at the octahedral hexatopic nodes.

A new C_3 symmetric ligand, 5,5′,5″-[1,3,5-benzenetriyltris-(carbonylimino)]tris-1,3-benzenedicarboxylic acid, has been designed, where the three bdc units are interconnected by the covalent linkages of the 1,3,5-benzenetriyltris(carbonylimino) residue. The solvothermal reaction of the ligand with Zn(II) ion in DMF produced a MOF based on the cuboctahedral MOPs as covalently interconnected SBBs (Fig. 18).[53] As in the previous MOF, the MOPs are interconnected by the quadruple covalent linkages; however, the ligand, 5,5′,5″-[1,3,5-benzenetriyltris(carbonylimino)]tris-1,3-benzenedicarboxylic acid, serves as a tritopic node because each bdc unit is interlinked with the other two bdc units in this ligand system, while the previous ligand, 1,3-bis(5-methoxy-1,3-benzene dicarboxylic acid)benzene, served as a ditopic ligand because each bdc unit is interlinked with one other bdc unit. Each MOP that was connected with the surrounding 12 MOPs by the quadruple covalent linkages using 24 tritopic ligands led to the MOF based on the MOPs as SBBs forming a CCP arrangement. The CCP arrangement of these nano-sized MOPs generated two different kinds of interstices that could be considered as two different kinds of face-directed corner linked MOPs, tetrahedral MOP and octahedral MOP, with nano-sized cavity diameters. The combinations of three different cavities in the MOF resulted in a large solvent cavity volume. The network topology of the MOF could be simplified as a (3,24)-connected net with the Schlafli symbol $(4^3)_{24}(4^{72}.6^{132}.8^{72})_3$ when the MOP building block is considered as a 24-connected supramolecular node and the ligand is considered as a three-connected node.

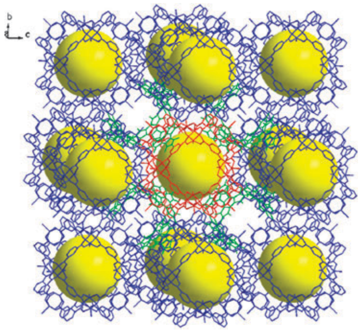


Fig. 18 A 3D framework made of cuboctahedral MOPs as an SBB, which are quadruple covalently connected with 12 neighboring MOPs by the ligand subunits. The arrangement of the MOPs in the framework can be simplified as a CCP arrangement. The solvent cavities in the individual MOP are shown with dummy big yellow balls. The central and other neighboring MOPs are shown in red and blue, respectively. The connectivity among the MOPs by the ligands is shown in light green.

The MOFs based on the MOPs can be prepared either through the metal centers having replaceable solvent sites by substituting them using additional linker ligands or using carefully designed ligands having multiple MOP-generating functional groups. These strategies might be expanded using other MOP systems with different symmetries and geometries.

Conclusions

The metalladiazamacrocycles, oligomeric MOMs, can be prepared by the carefully designed ditopic pentadentate ligand, *N*-acylsalicylhydrazide, and some octahedral tricationic metal ions that can form the –[M–N–N]– cyclic repeating unit. In the macrocyclic system, a tridentate chelation of the ligand around the metal ion and a bidentate chelation of the other ligand around the same metal ion led to either Λ or Δ chiral configurations, and the primary steric domains of the ligands are positioned toward the core of the macrocyclic system. The stereo-sequence of the metal ions and the consequent size and shape of the macrocycles could be controlled by using the steric repulsions among the primary domains of the ligands that were oriented toward the core. By increasing the steric volume of the primary steric domain of the ligand, larger oligomeric MOMs were generated to reduce the steric repulsions among the primary steric domain around the core. The constraint on the primary steric domain employing multiple bonds to reduce the rotational degree of freedom is an alternative way to increase the number of repeating units in the metalladiazamacrocycles. While the ligands having the larger steric volume near the bridging domain led to MOMs with an alternating chiral sequence, $\cdots(\Lambda\Delta)(\Lambda\Delta)\cdots$, the ligands having a rigid primary steric domain with lesser steric volume near the bridging domain allowed successive metal centers of the same chirality, such as ΛΛ or ΔΔ, as in the ···(ΛΛΔΔ)(ΛΛΔΔ)··· sequence. A ligand having a rigid primary steric domain with the least steric volume near the bridging domain but with a bulky phenyl end allowed four consecutive metal centers in the MOM system the same chirality, which led to a MOM of sextuple-twisted Möbius topology with a ···(ΔΔΔΔΛ)(ΔΔΔΔΛ)··· chiral sequence.

The strategy to make octahedral MOPs based on the face-directed corner-linkage has been demonstrated using C_3 symmetric facial ligands and C_4 symmetric metal ions as primary building units. Ligands having donor groups pointing out of the ligand plane have been designed as primary building units with necessary curvatures for the finite system. The positions of the donor atoms bent from the ligand plane facilitate the construction of the finite octahedral MOPs with the C_4 symmetric square-planar Pd(II) ion. The same strategy has been expanded for the construction of an augmented octahedral MOP, where the C_4 symmetric paddle-wheel $Cu_2(COO)_4$ unit occupied the corners of the augmented octahedral MOP as an SBU.

The MOMs and MOPs with multiple replaceable solvent sites in the systems have been utilized as SBBs for the construction of various MOFs. The sixth coordination sites at metal ions in the metalladiazamacrocycles could be replaced with ditopic linker molecules to generate MOFs, in which the metalladiazamacrocycles were utilized as SBBs. Depending on reaction conditions, such as the ligands, templating molecules and solvents used in the reaction, various 2D or 3D MOF systems could be formed while keeping the isostructural hexameric or octameric metalladiazamacrocyclic systems as SBBs. The size and shape of the cavities in the MOF systems could be controlled at the level of the SBBs. Systematic control of the alkyl chain length of the primary building units led the MOFs of isostructural hexameric MOMs as SBBs with modulated cavity sizes and shapes from 3D to 1D or 0D, where the supramolecular properties were directly transferred to the corresponding MOFs.

Like the MOMs with some replaceable solvent sites, the MOPs with multiple replaceable solvent sites have also been utilized as SBBs for the construction of MOFs. The Cu(II) analogues of the octahedral Pd(II) MOPs built using the face-directed corner-linkage strategy have been used for the hexatopic octahedral nodes. The Jahn–Teller distorted solvent site of the outer Cu(II) ion of the paddle-wheel unit in the MOP was used to connect the MOPs with ditopic anionic linkers. While perchlorate anions yielded a cyclic hexameric cluster of the MOPs, nitrate anions, which had better donor ability than the perchlorate anions, yielded a 3D MOF system in similar reaction conditions. The nitrate ion, utilized as a ditopic linker, interconnected all six vertices of the MOP to form two-fold interpenetrating networks of **pcu** net topology. The MOFs still have large solvent cavities even though the frameworks are two-fold interpenetrated because the SBBs themselves have their inherent cavities and the cavity sizes of the frameworks were controlled at the level of the SBBs.

The MOFs based on covalently interconnected MOPs have been prepared using carefully designed ligands. The ligands having multiple functional groups, which were the potential edge components for edge-directed corner-linked MOPs, have been used in an alternative strategy for the construction of MOFs based on the MOPs. The ligands with two or three bdc units connected with various covalent linking groups were used for the construction of MOFs covalently interconnected with cuboctahedral MOPs generated by an edge-directed corner-linkage strategy. With two bdc units in each ligand, the cuboctahedral MOPs as hexatopic SBBs have been interconnected *via* quadruple covalent linkages to form a two-fold interpenetrating framework of **pcu** net topology. With three bdc units in each ligand, the ligand served as a tritopic node, and each MOP served as a dodecatopic SBB connected using the quadruple covalent linkage with 12 neighboring MOPs by 24 tritopic ligands. The MOF with a CCP arrangement of the cuboctahedral MOPs produced large intrinsic tetrahedral and octahedral MOPs with face-directed edge-linkages.

MOMs and MOPs with desired size and specific properties could be prepared with careful design of ligands and the MOMs and the MOPs could be utilized as SBBs in the design of MOFs. The main advantage in the SBB approach is the direct transfer of the desired properties of the SBBs to the final MOFs and the modulation of the final MOF properties at the level of the SBBs. The MOFs built based on the MOPs having large cavities as SBBs could have large solvent cavities inherited from the SBBs themselves in addition to the cavities generated between the SBBs. The SBB approach can be further developed with other MOM or MOP systems having replaceable solvent sites for the construction of MOFs with modulated properties for gas storage, separation and catalysis.

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