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An Investigation of the Self-Assembly of Neutral, Interlaced, Triple-Stranded Molecular Braids

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Abstract: The synthesis and structures of six compounds prepared in two different systems have been explored with the purpose of isolating coordination polymers with interlaced triple-stranded molecular braid architectures. The dinuclear paddle-wheel units of $[Cu_2(maa)_4 \cdot 2H_2O]$ can be rationally tuned to form three classes of isomorphous compounds, namely $[Cu_2(maa)_4(bpp)]$ (**1**) (bpp = 1,3-bis(4-pyridyl)propane, Hmaa = 2-methylacrylic acid), $[Cu_3(maa)_6(bpp)_2]$ (**2**), and$[Cu_4(maa)_8(bpp)_4(H_2O)_2] \cdot 2H_2O$ (**3**), with a bridging bpp ligand, at controlled ligand-to-metal molar ratios, and lead to three coordination polymers having similar one-dimensional characteristics but different mono- and dinuclear nodes. Compound **1**, with a bpp:$[Cu_2(maa)_4 \cdot 2H_2O]$ stoichiometry of 1:1, contains a zigzag chain containing dinuclear nodes, whereas polymer **2**, with a bpp:$[Cu_2(maa)_4 \cdot 2H_2O]$ stoichiometry of 1.5:1, also adopts the topology of a zigzag chain but with both mono- and dinuclear nodes. Compound **3**, with a bpp:$[Cu_2(maa)_4 \cdot 2H_2O]$ stoichiometry of 2:1, contains a neutral, interlaced, triple-stranded molecular braid, which is interwoven by three single-stranded *meso*-helical chains that contain only a mononuclear node. With the three aromatic chelating terminal ligands 2,2′:6′,2′′-terpyridine (tpy), 1,10-phenanthroline (phen), and di(2-pyridyl)amine (dpa) we have also prepared three neutral complexes containing the linear, rigid bridging ligand biphenyl-4,4′-dicarboxylate (bpdc), namely $[Cd(bpdc)(tpy)] \cdot H_2O$ (**4**), $[Cu(bpdc)(phen)_2] \cdot 4.25H_2O$ (**5**), and $[Cu(bpdc)(dpa)]$ (**6**). An infinite *meso*-helix is formed initially in **4**, and then three of these chains assemble into a triple-stranded braid similar to that of **3**. Complexes **5** and **6** have a mononuclear and a looped dinuclear structure, respectively. Compounds **3** and **4** are unusual examples of triple-stranded molecular braid coordination frameworks based on different types of co--ligands.

Keywords: cobalt • copper • crystal engineering • organic–inorganic hybrid composites • self-assembly

Introduction

The design and construction of metal–organic coordination polymers is of current interest in the fields of supramolecular chemistry and crystal engineering. A major reason for this interest is the promise of being able to deliberately design new materials with useful tailor-made properties,[1] although coordination polymers are also important for the less utilitarian reason that they constitute a unique and fascinating branch of fundamental structural chemistry.[2] Interesting topological types that are unprecedented in inorganic compounds and in minerals can be observed within coordination polymer frameworks.[3] Particularly intriguing is the finding of species with novel modes of supramolecular intertwining, such as helices, rotaxanes, catenanes, and knots[4] that contribute to refining our knowledge of self-assembly processes and of the supramolecular self-organization of these species. In contrast to this variety of structures, one of the simplest possible one-dimensional architectures—the interlaced, triple-stranded molecular braid—has proven to be surprisingly rare. This structure comprises three interwoven chains in an inseparable union as removal of any one of the

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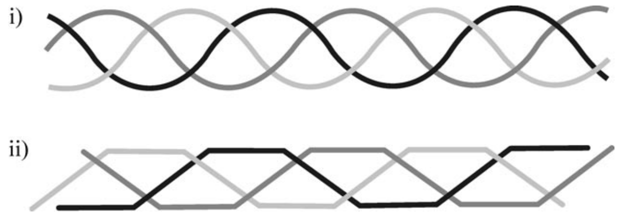
chains causes the whole assembly to unravel into three separate pieces. Discrete triple-stranded intertwining chains are generally apt to form a homochiral triple helix in crystal engineering. The first triple helix, made by Rajasekharan's group,[5] the enantiomerically pure triple-helix from Hosseini's group,[6] and the nanotube-containing triple-helix reported by Lin's group[7] serve as impressive examples of this topology. However, to the best of our knowledge, there is only one example of an interlaced, triple-stranded molecular braid, namely that reported by our group recently.[8] Therefore, the assembly of interlaced, triple-stranded molecular braids is a formidable challenge.

Conceptually, there are two extreme types of coordination-driven, triple-stranded molecular braids where i) the independent infinite chains of the braid are formed through flexible bridging ligands, and ii) the single-stranded infinite chains of the braid are fabricated from rigid bridging ligands (Scheme 1). Conformationally flexible ligands are typical building elements in the deliberate construction of unique interwoven structural motifs, such as polycatenanes, polyrotaxanes, double helices, triple helices, borromean rings, and other more unusual species,[9] while essentially rigid, rodlike organic units are usually employed to form grids, brickwalls, honeycombs, diamondoid nets, and other species of not.[10] In a recent communication, we reported one Cu^{II}–1,3-bis(4-pyridyl)propane coordination polymer with the topology of a triple-stranded molecular braid.[8] We proposed a mechanism for formation of the complex involving the reaction of a paddle-wheel Cu^{II} complex with a conformationally flexible neutral organic ligand in a 1:2 stoichiometry. Copper(II) carboxylate dihydrate adopts a classic paddle-wheel structure with a pseudo metal–metal bond bridged by four μ_2-carboxylate ligands, and tighter control over the dinuclear unit may give rise to polymer architectures if the two axial aqua ligands, which are situated 180° apart, with one on each metal, can be displaced by highly labile and readily available Lewis base ligands under mild conditions.[11] Furthermore, owing to the diversified coordination modes of carboxylate ligands, $Cu_2(O_2CR)_4$ can also be split to form $Cu(O_2CR)_2$, which may serve as a mononuclear building node.[12] Thus, this reaction can be extended to the rational design of very interesting supramolecular isomers, and three fascinating mixed-ligand complexes of Cu^{II} (**1**–**3**) have been obtained under the same controlled-crystallization conditions simply by varying the ligand:metal molar ratios. These complexes contain dinuclear nodes, dinuclear alternating with mononuclear nodes, and mononuclear nodes, respectively.



Scheme 1. Schematic representation of the types of molecular braids.

We are also studying the more difficult assembly of a molecular braid containing linear rigid ligands. It is well known that the structural geometry can be controlled and modulated by selecting the coordination geometry of the metal ions and the chemical nature of the terminal and bridging ligands. In an attempt to avoid high-dimensional molecular architectures, we chose aromatic chelating terminal ligands such as tpy, phen, and dpa for incorporation into the system of M^{II} ions with the long, linear, rigid bridging ligand bpdc. Fortunately, this work was successful and provided a triple-stranded molecular braid, a mononuclear, and a looped dinuclear structure.

As an extension of our previous work, we report herein the systematic investigation of the coordination-driven self-assembly of triple-stranded molecular braids. Two kinds of these assemblies are obtained by incorporating a highly flexible bridging ligand and a rigid, linear bridging ligand, respectively. Precise triple-stranded molecular braids have been achieved in discrete supramolecular assemblies for the first time, and this may have implications in the area of crystal engineering.

Results

Synthesis of complexes 1–3: Compound **1** was obtained with an initial molar ratio of bpp to $[Cu_2(maa)_4{\cdot}2H_2O]$ of 1:1 in CH_3OH/CH_3CN (1:1, v/v). When the bpp:maa ratio was changed to 1.5:1, **2** was obtained under otherwise identical conditions, with **1** also crystallizing out from the mother liquor. A further increase in the bpp:$[Cu_2(maa)_4{\cdot}2H_2O]$ ratio to 2:1 and beyond gave compound **3**. Complexes **1**–**3** were isolated as single phases, as confirmed by X-ray powder diffraction (XRPD). These results indicate that the formation of **1**–**3** under the same reaction conditions depends primarily on the bpp:$[Cu_2(maa)_4{\cdot}2H_2O]$ molar ratio.

The structure of complex 1: An X-ray structural analysis revealed that **1** consists of one-dimensional zigzag chains based on the paddle-wheel $Cu_2(O_2CR)_4$ node. Each copper atom in this unit has a distorted square-pyramidal environment, with four oxygen atoms from four *syn,syn*-$\eta^1{:}\eta^1{:}\mu_2$-maa groups, which form the equatorial plane, and one pyridyl nitrogen atom. However, there are some differences between the adjacent units due to the asymmetric TG (where T = *trans* and G = *gauche*) conformation of the dipyridyl ligand. One unit is connected to two T-terminal nitrogen atoms (Cu−Cu 2.642(1), Cu−N 2.153(3), Cu−O 1.960(3)–1.971(3) Å), and the adjacent one to two G-terminal nitrogen atoms (Cu−Cu 2.644(1), Cu−N 2.165(4), Cu−O 1.945(4)–1.971(3) Å) (Figure 1). This results in a highly organized, self-assembled, 1D zigzag-shaped chain with the connectivity of the two asymmetric terminal coordinated bpp ligands (N−N 8.979 Å); this 1D zigzag chain has a

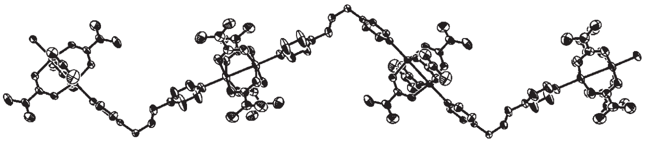


Figure 1. The one-dimensional zigzag coordination polymer with dinuclear nodes in complex **1**.

repeat period of 28.763 Å. In addition, the chains are in a parallel arrangement in the complex (Figure 2). Other studies of coordination polymers constructed by the interaction of metal cations with the flexible ligand bpp have been reported.[9k,12a,13] Among these previously known coordination polymers, sinusoidal chains similar to those in **1** have been found in [$Cu_2(O_2CCH_2C_4H_3S)_4(bpp)_2$],[12a] [Ag(bpp)]$NO_3$,[9k,13a] [Ag(bpp)]($CF_3SO_3$)·EtOH,[13b] [Ag(bpp)]X (X = ClO_4^-, PF_6^-),[13c] and [Cu(bpp)]BF_4.[13d] The former two polymers are the only ones that have the bpp ligands in a TG conformation, with an N-to-N distance of 8.894 and 8.79 Å and a repeat length of 23.64 and 23.98 Å, respectively. In all the other structures the bpp ligands display a TT conformation and have larger N-to-N separations and higher periodic wavelengths.

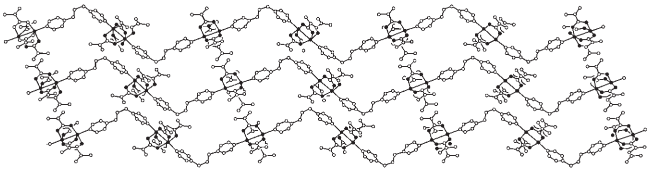


Figure 2. View along the crystallographic *b* axis of **1**.

Figure 3. The one-dimensional zigzag chain structure with alternating mono- and dinuclear nodes in complex **2**.

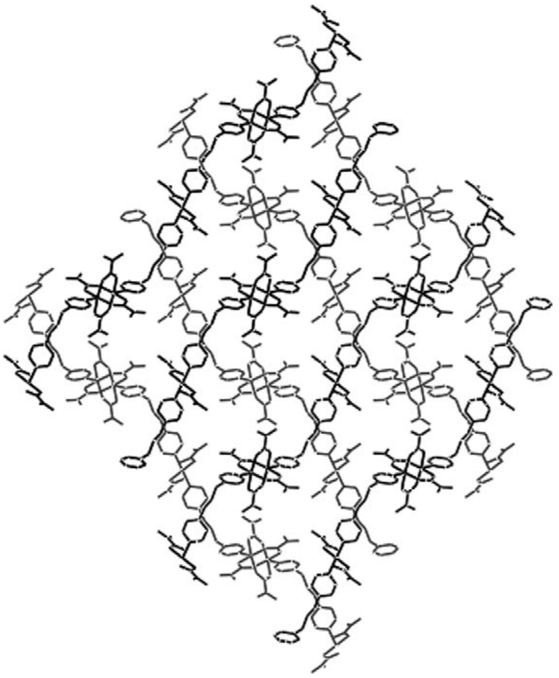


Figure 4. View along the crystallographic *c* axis of **2**.

The structure of complex 2: Complex **2** also contains a one-dimensional zigzag chain, although this time it is based on alternating paddle-wheel $Cu_2(O_2CR)_4$ and $Cu(O_2CR)_2$ nodes. Each copper atom in the dinuclear unit has the same coordination environment as in **1**, with four oxygen atoms from four *syn,syn*-η^1:η^1:μ_2-maa groups and one pyridyl nitrogen atom forming a distorted square-pyramidal environment (Cu–Cu 2.646(1), Cu–N 2.158(3), Cu–O 1.964(2)–1.978(2) Å). The Cu^{II} center in the mononuclear unit is primarily coordinated by two oxygen atoms from two monodentate maa ligands (Cu–O 1.963(3) Å) and two nitrogen atoms from two bridging bpp ligands (Cu–N 2.007(3) Å) to furnish a slightly distorted square-planar geometry. The dipyridyl ligand adopts a symmetrical TT conformation[13b–d] with an N-to-N distance of 9.040 Å, which is longer than that in **1** (Figure 3). Consequently, the spacer bpp ligands connect a mononuclear node at one terminal and a dinuclear node at the other terminal to form an infinite zigzag chain. The individual chains line up in layers, with each layer crossing the layer beneath at an angle of 53° (Figure 4). This results in the formation of infinite channels running perpendicular to each layer, which arise due to the small size of the carboxylate groups that point into the channel compared to the channel radius, as defined by the length of the bpp ligand and the Cu^{II} building blocks. The two directionally extending chains are connected by hydrogen bonds, which further generates a three-dimensional supramolecular network. To the best of our knowledge, such heternode 1D chains based on a homovalent metal and symmetric ligands are unprecedented. Other heteronuclear 1D polymers are mostly generated by heterometallic nodes or have the same metal in various valences.[14]

The structure of complex 3: The crystal structure of **3** reveals the presence of a *meso*-helix, which is generated by successive rotation and inversion operations along the growth axis (Figure 5a). This *meso*-helix has alternating helical sections (alternating right and left turns of the strand when looking down the "growth axis") and is different from the standard right-helix or left-helix as it contains centers of inversion and does not have a defined chirality. Interestingly, a neutral, interlaced, triple-stranded braid is formed with three interwoven single-stranded *meso*-helices along the *c* axis[8] (Figure 5b).

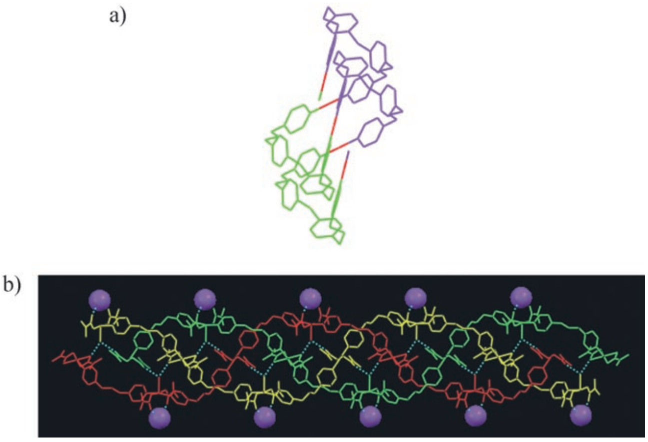


Figure 5. a) Top view of the *meso*-helix in **3**; the right-helical sections are green and the left-helical sections are purple. b) A representation of the interlaced triple-strand braid in **3**.

Comparison of the structures of coordination polymers 1–3: A comparison of the 1D architectures of **1**, **2**, and **3** demonstrates that **1** is comprised of one-dimensional zigzag chains containing a dinuclear node with a parallel arrangement, complex **2** shows an interlaced 3D supramolecular structure containing an analogous 1D zigzag polymeric chain with both mono- and dinuclear nodes, and the crystal structure of **3** reveals the presence of an interlaced, triple-stranded molecular braid, which is interwoven by three single-stranded *meso*-helices that contain only mononuclear nodes. When changing the ligand:metal molar ratio, the three compounds undergo a change from a parallel structure to an interpenetrating structure by decreasing the number of dinuclear nodes. We therefore reasoned that multimetallic fragments could reduce the degree of interpenetration observed in framework structures. Papers by Yaghi and coworkers have also shown that such multimetallic fragments in combination with long spacer ligands can increase the host channel width, reduce the degree of interpenetration, and hence bring about guest inclusion in the host.[15] Moreover, several reactivity studies of typical dinuclear paddle-wheel compounds have been performed. These reports reveal that in most cases the addition of different ligands L like pyrazine,[16] *N*,*N*′-hexamethylenetetramine,[17] and pyridyl nitronyl nitroxide[18] to dimeric tetracarboxylates allows the formation of axially connected dinuclear paddle-wheel units formulated as $[Cu_2(O_2CR)_4(L)]_n$. The literature also describes the formation of mononuclear copper(II) carboxylates from the reaction of dimeric tetracarboxylates with monofunctional nitrogen- or oxygen-donor ligands.[12]

Complex **2** exhibits an unprecedented structural feature, namely 1D zigzag chains that contain alternating dinuclear and mononuclear nodes. This breaks up the traditional coordination behavior of the $Cu_2(O_2CR)_4$ units and produces a higher level of rational design and synthesis of coordination polymers. This work shows that dinuclear paddle-wheel Cu^{II} units can be rationally controlled and can serve as both mononuclear and dinuclear nodes towards a dipyridyl ligand, and that three classes of mixed-ligand complexes can be obtained simply by manipulating the ligand-to-metal salt molar ratio. This series of compounds provides an example of isostructurality in 1D coordination polymers that exhibit different nodal characteristics and that can be selected by shifting the position of the equilibrium.

Synthesis of complexes 4–6: Coordination polymers containing metal ions and *exo*-didentate organic bridges in a 1:1 stoichiometry are usually based on either rigid-linear or zigzag chain structures.[19] In order to design 1D coordination polymers with the topology of a triple-stranded molecular braid, we carried out a case study of the M^{II}/bpdc/tpy-(phen or dpa) system, and obtained three types of complexes with different combinations.

The structure of complex 4: A single-crystal X-ray structural analysis revealed that **4** has an interlaced, triple-stranded, molecular braid topological framework. Compound **4** crystallizes in the monoclinic centrosymmetric space group *P*2/c, with one independent Cd^{II} center per asymmetric unit. This Cd^{II} center adopts a highly distorted octahedral geometry structure and is directly coordinated by three nitrogen atoms of tpy, one chelating carboxylate group, and one monodentate carboxylate group from each of two distinct bpdc ligands.

In the complex, the single chain is assembled from linear metal-connecting segments of bpdc, which exhibit two coordination fashions: bis-chelating and bis-monodentate. Bis-chelating (Cd–Cd 15.568(2) Å) and bis-monodentate (Cd–Cd 15.639(2) Å) bpdc ligands link the metal centers alternately throughout the chain, and the angle between the two adjacent ligands is 102.63(1)°. The periodicity of the chain is 45.813 Å and it contains four Cd^{II} centers per repeat unit. The two benzene rings of bpdc present a torsion angle of 44.41(2)° in the former fashion whereas they are coplanar in the latter, which result in a *meso*-helix when viewed along the *c* axis (Figure 6).

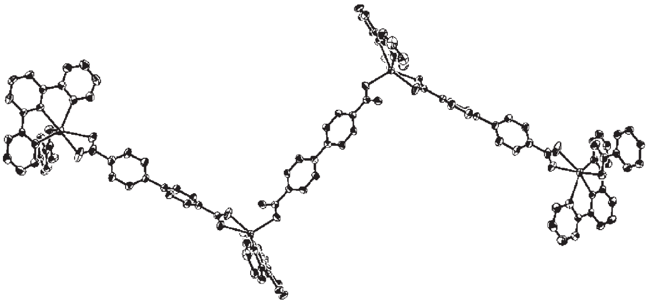


Figure 6. View of the 1D *meso*-helical structure of **4**.

The most striking structural feature of **4** is that it contains a neutral, interlaced, triple-stranded-braid architecture, which is self-assembled by the interweaving of three single-stranded *meso*-helices that extend along the *c* axis

(Figure 7). The repeat distance of the braid (15.271 Å) is one third of the repeat distance of the single chain. The tpy ligands are situated around the braid in four directions, and the Cd^{II} atoms are arranged in four parallel rows. Some intertwining motifs of double and triple helices have been synthesized previously with conformationally flexible ligands, although there is no example based on a rigid ligand. In contrast, complex **4** contains a molecular braid that is generated by a linear rigid ligand. To the best of our knowledge, this braid is the first example of such an intertwining species constructed with a linear rigid ligand.

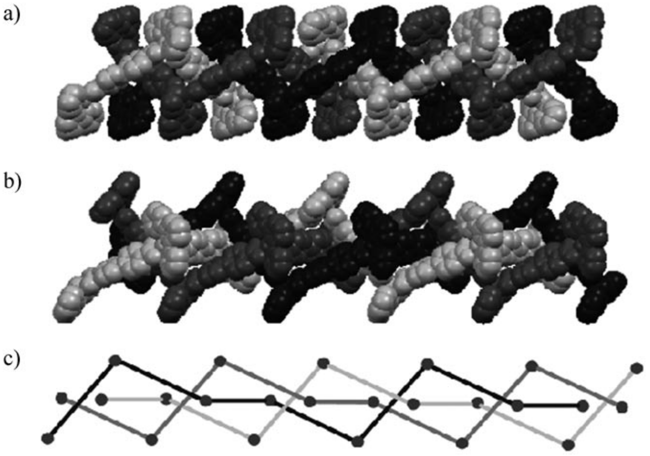


Figure 7. a) Top view of the interlaced triple-stranded molecular braid of **4**. b) Side view of the interlaced triple-stranded molecular braid of **4**. c) Definition of the interlaced, triple-stranded molecular braid topology of **4**.

There are two kinds of fascinating water molecules in current complex **4**. The first type is water dimers, which connect every two twisted single-stranded chains through strong hydrogen bonds (Figure 8) and may contribute to stabilizing the structure of the molecular braid. The second kind is single water bridges. A careful examination of the structure indicates that there are strong hydrogen-bonding interactions between the oxygen atom of water and the oxygen atoms of bpdc, with hydrogen bonds of 2.774 Å. Adjacent triple-stranded molecular braids are thus assembled into a 2D network in the *ac* plane through these hydrogen-bonding interactions. These 2D slabs stack on top of each other in a parallel fashion along the *b* axis to form a lamellar solid.

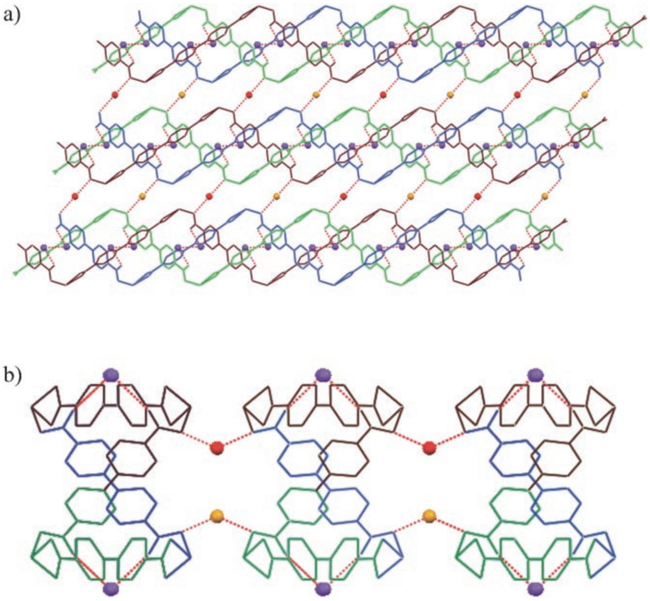


Figure 8. a) Description of the interwoven braid in detail: blue, brown, and green indicate the three strands of the triple-stranded braid, the waters connecting two strands are in purple, and the water molecules between two braids are in yellow and red. The tpy ligands have been omitted for clarity. b) Side view of the triple-stranded braid of **4**.

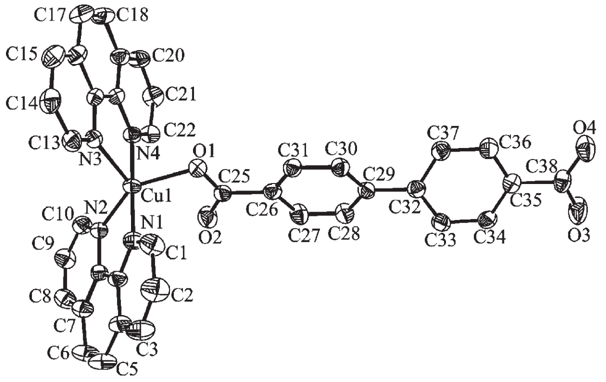


Figure 9. Perspective view of the main building block of **5**.

The structure of complex 5: There is one Cu^{II} atom, one monodentate bpdc ligand, two phen ligands, and four and a quarter lattice water molecules in each independent crystallographic unit in the crystal structure of **5**. Each Cu^{II} atom in **5** is primarily coordinated by one oxygen atom from one bpdc ligand (Cu1−O1 2.087(2) Å) and four nitrogen atoms from two chelating phen ligands (Cu1−N1 1.981(2), Cu1−N2 2.066(2), Cu1−N3 2.128(2), Cu1−N4 1.987(2) Å) to furnish a distorted trigonal-bipyramidal geometry (Figure 9). Some of the lattice water molecules are assembled into a V-shaped trimer with an O···O distance of 2.670(1) Å and an O···O···O angle of 149.2(1)°. Two additional uncoordinated carboxylate oxygen atoms are attached at two opposite ends (O4A···O6A 2.842(2), O4J···O6C 2.842(2) Å). One free lattice water molecule is located between the two uncoordinated carboxylate groups by hydrogen bonds (O3A···O8A 2.629(1), O3J···O8A 2.629(1) Å). The oxygen atom of the coordinated carboxylate group and the oxygen atom of the uncoordinated carboxylate group are joined by the free water molecules (O1I···O5A 2.917(1), O4A···O5A 2.793(1) Å). As shown in Figure 10, the bpdc ligand of **5** forms hydrogen bonds with the lattice water molecules through both its coordinated and uncoordinated oxygen atoms, which results in a two-dimensional hydrogen-bonding network.

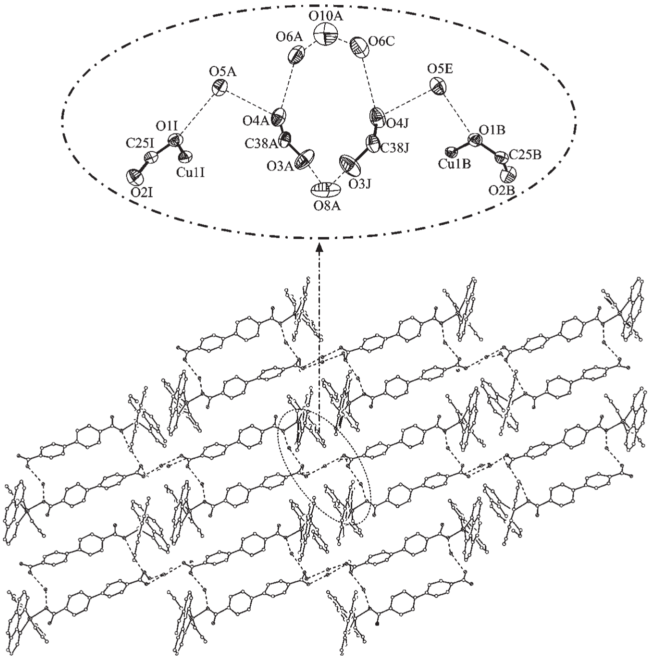


Figure 10. The two-dimensional hydrogen-bonding network of **5**.

The structure of complex 6: The X-ray structure determination revealed that complex **6** consists of molecular rings (Figure 11), with two Cu^{II} ions connected by two bpdc ligands that adopt a monodentate-chelating coordination mode. The metal centers are also coordinated by one dpa ligand to give a Jahn–Teller-distorted square-pyramidal geometry. The Cu···Cu distance in the 26-membered ring is 13.575(2) Å. The bpdc ligands have their phenyl rings in torsional positions, with a large dihedral angle of 44.443(7)°. Furthermore, the molecular rings are assembled into a one-dimensional looped chain by hydrogen-bonding interactions (N−H···O 2.738(1) Å; Figure 12).

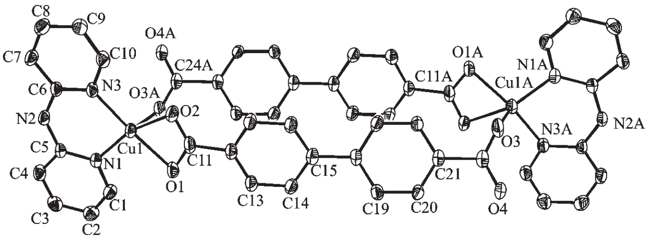


Figure 11. Perspective view of the dimer in **6**.

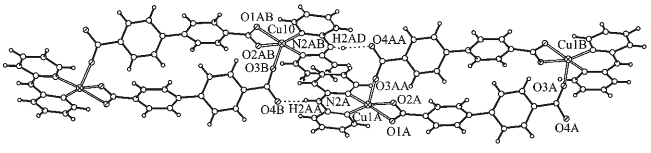


Figure 12. Self-assembly of the one-dimensional looped chain of **6** by formation of hydrogen bonds (N2AB−H2AD···O4AA 2.738(1), N2A−H2AA···O4B 2.738(1) Å).

Comparison of the structures of coordination polymers 4–6: Our investigation of the M^{II}/bpdc/tpy(phen or dpa) system has resulted in a series of compounds with different topologies, ranging from mononuclear molecular to an interlaced triple-stranded molecular braid. Complex **4** is a cadmium complex with the topology of a triple-stranded molecular braid and is prepared from the combination Cd^{II}/bpdc/tpy. The single-stranded chain of the molecular braid is a *meso*-helix, which is different from the zigzag compound $[Cd(bpdc)(phen)_2{\cdot}2H_2O]$ synthesized by Qiu's group under hydrothermal conditions.[20] Upon changing the metal center of the compound $[Cd(bpdc)(phen)_2{\cdot}2H_2O]$ for Cu^{II}, the mononuclear compound **5** is obtained at room temperature. Despite the pentacoordinate geometry of the Cu^{II} center, the structure of **5** is not extended to higher dimensionalities. In the Cu^{II}/bpdc/dpa system, a looped-ring complex crystallizes out of the mixture, and the kinetic dinuclear structure is an isomer of the proposed one-dimensional chain. The difficulty in isolating the proposed chain from this system may be due to the fast formation of the looped rings, thus indicating that the chain is disfavored from a kinetic point of view. Therefore, an appropriate combination of the metal center with the dicarboxylate and aromatic chelate ligands is critical for the formation of a neutral, interlaced, triple-stranded molecular braid.

Exclusion and inclusion of guest molecules in complexes 3–5: As described above, complexes **3**–**5** contain guest molecules. The question therefore arises as to whether the framework or the structural regularity will be maintained after removal of the guest molecules, which is vitally important for generating new microporous materials. To verify this, we used TGA and XRPD techniques to investigate the framework stability upon removal of the guest molecules from complexes **3**–**5**.

For **3**, the TGA curve reveals a weight loss of 1.88% below about 65°C; this corresponds to the loss of the free water molecules (calcd 2.00%). The polycrystalline sample is then stable up to 235°C, above which decomposition starts. A freshly ground sample of **3** was evacuated at 100°C for 5 h, which caused a weight loss that is consistent with the removal of two included water molecules per formula unit, as was also confirmed by elemental analysis. The similarity between the XRPD pattern recorded at this point and that of the original starting sample suggests the dried solid $[\{Cu_4(maa)_8(bpp)_4(H_2O)_2\}]_n$ retains the initial crystal structure of **3** (Figure S6 in the Supporting Information).

For **4**, TGA curve reveals that free water molecules are eliminated from the host on raising the temperature from room temperature to about 80°C (weight loss of 3.12%; calculated value 3.00%). The decomposition of the framework begins only above about 260°C. Upon evacuation of a freshly ground sample of **4** at 140°C for 5 h, it experiences a weight loss that is consistent with the removal of one included water molecule per formula unit, as was also confirmed by elemental analysis. The similarity between the XRPD pattern recorded at this point and that of the original starting sample suggests the dried solid $[Cd(bpdc)(tpy)]_n$ retains the initial crystal structure of **4** (Figure S7 in the Supporting Information).

For **5**, the TGA curve reveals a weight loss of 10.19% below about 70 °C, which corresponds to the loss of the free water molecules (calcd 10.32%). The polycrystalline sample is stable up to 190 °C, above which decomposition starts. A freshly ground sample of **5** was evacuated at 120 °C for 5 h, whereupon it experienced a weight loss consistent with the removal of 4.25 included water molecules per formula unit, as was also confirmed by elemental analysis. The XRPD patterns of **5** before and after water expulsion show a complete change in the pattern, which suggests breakdown of the host lattice upon exclusion of water (Figure S8 in the Supporting Information).

Discussion

As described above, we have carried out a systematic investigation of the assembly of triple-stranded molecular braids in the field of crystal engineering. This topology is an unprecedented one that is similar to the triple-helix topology in supramolecular chemistry. However, there are several crystallographic and topologic differences between the triple braid and the triple helix. For example, the single strand of the braid is a *meso*-helical chain with centers of inversion, whereas the single strand of the helix is a right-handed or left-handed helical chain that has defined chirality. Furthermore, the triple helix is a chiral structure with a screw axis, while the triple braid is a centrosymmetric structure, and finally, removal of any strand of the braid leaves the two others completely free from each other, whereas in the triple helix the remaining two strands are still twinned as a double helix. Our investigation of two different systems suggests that the formation of a triple-stranded molecular braid may occur in two steps: initial construction of an infinite *meso*-helical chain of ligated M^{II} ions, followed by interweaving of the infinite chains. In compound **3**, the *meso*-helix is constructed from the highly flexible bpp ligand first, and then three-strand helices are interwoven together by hydrogen bonds in what can be regarded as a self-recognition interaction. Similar to **3**, *meso*-helical chains can also be fabricated based on a rigid linear ligand. In the second step, three infinite chains are interwoven together with no noncovalent interactions in the triple-stranded molecular braid, while water dimers connect every two twisted single strands through hydrogen bonds on the surface of the braid. A detailed analysis of the crystal structures indicates that the main factor governing the formation of the molecular braid is not only the framework, that is, the interweaving of the *meso*-helices, but also the noncovalent interactions (hydrogen bonds) between the chains.

Conclusion

In summary, we have successfully synthesized complexes **1**–**6** from two different systems and isolated two different molecular braids constructed from a highly flexible ligand and a rigid linear ligand, respectively, in the presence of M^{II} ions with different terminal ligands. This work presents a new, facile route for the synthesis of coordination polymers with the topology of a triple-stranded molecular braid and higher-stranded molecular braids with appropriate metal ions and *exo*-didentate ligands as terminal ligands in different strands.

Experimental Section

Materials: All reagents and solvents employed were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with a Perkin–Elmer model 240C automatic instrument. IR spectra were recorded with a Nicolet 170SX FT-IR spectrophotometer as pressed KBr pellets in the range 400–4000 cm^{-1}. Thermal analysis was performed with a Netzsch STA 449C microanalyzer. The XRPD patterns were recorded with a Rigaku D/Max 3III diffractometer with a scanning rate of four degrees per minute.

Preparations

$[Cu_2(maa)_4 \cdot 2H_2O]$: $[Cu_2(maa)_4 \cdot 2H_2O]$ was prepared from the reaction of $[Cu_2(OH)_2(CO_3)]$ (2.211 g, 10 mmol) with 2-methylacrylic acid (3.442 g, 40 mmol) in methanol under reflux for 2 h. A blue-green crystalline product was obtained in approximately 87% yield. Elemental analysis calcd (%) for $C_{16}H_{24}Cu_2O_{10}$: C 38.17, H 4.80; found: C 38.28, H 4.83; IR: $\tilde{\nu}$ = 2968, 2932, 1681, 1645, 1594, 1497, 1414, 1299, 1225, 1008, 951, 856, 826, 638, 445 cm^{-1}.

$[Cu_2(maa)_4(bpp)]$ (1): A solution of 1,3-bis(4-pyridyl)propane (bpp; 0.020 g, 0.100 mmol) in acetonitrile (10 mL) was added to a methanol (10 mL) solution of $[Cu_2(maa)_4 \cdot 2H_2O]$ (0.050 g, 0.100 mmol). The clear solution was stirred for a few minutes and then allowed to evaporate at room temperature. Well-shaped green block crystals of **1** appeared after several days. The crystalline product was filtered, washed with ethanol, and dried in air. Yield: 75.3% based on copper. Elemental analysis calcd (%) for $C_{29}H_{34}Cu_2N_2O_8$: C 52.32, H 5.14, N 4.20; found: C 52.34, H 5.15, N 4.18; IR: $\tilde{\nu}$ = 2941, 1647, 1602, 1513, 1415, 1290, 1250, 1220, 968, 736, 458 cm^{-1}.

$[Cu_3(maa)_6(bpp)_2]$ (2): Compound **2** was prepared as for **1** but with 0.030 g (0.150 mmol) of bpp. Blue-green block crystals were obtained in a yield of 55.7% based on copper. Elemental analysis calcd (%) for $C_{50}H_{58}Cu_3N_4O_{12}$: C 54.71, H 5.32, N 5.10; found: C 54.74, H 5.35, N 5.13; IR: $\tilde{\nu}$ = 2947, 1648, 1610, 1594, 1420, 1355, 1274, 988, 804, 486 cm^{-1}.

$[Cu_4(maa)_8(bpp)_4(H_2O)_2] \cdot 2H_2O$ (3): See reference [8].

$[Cd(bpdc)(tpy)] \cdot H_2O$ (4): A methanol solution (5 mL) of tpy (0.1 mmol, 0.023 g) was added to a methanol solution (5 mL) of $Cd(NO_3)_2 \cdot 4H_2O$ (0.1 mmol, 0.031 g). An aqueous solution (5 mL) of Na_2bpdc (0.1 mmol, 0.029 g) was then added dropwise to give a transparent solution. After two days, pale-yellow block crystals of **4** were obtained as a single phase, as confirmed by XRPD. The yield of **4** was about 52.5% based on cadmium. Elemental analysis calcd (%) for $C_{29}H_{21}CdN_3O_5$: C 57.68, H 3.50, N 6.96; found: C 57.57, H 3.53, N 7.03; IR: $\tilde{\nu}$ = 3450, 3076, 1585, 1451, 1389, 851, 771, 707, 681 cm^{-1}.

$[Cu(bpdc)(phen)_2] \cdot 4.25H_2O$ (5): An ethanol solution (3 mL) of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.1 mmol, 0.037 g) and phen (0.2 mmol, 0.036 g) was layered on top of 3 mL of an aqueous solution of Na_2bpdc (0.1 mmol, 0.029 g). After several days, blue-green needle crystals of **5** were obtained as a single phase, as confirmed by XRPD. The yield of **5** was about 35.4% based on phen. Elemental analysis calcd (%) for $C_{38}H_{32.5}CuN_4O_{8.25}$: C 61.62, H 4.42, N 7.56; found: C 61.59, H 4.45, N

7.57; IR: $\tilde{\nu}$ = 3406, 3057, 1723, 1593, 1540, 1515, 1425, 1368, 851, 773, 723, 677 cm^{-1}.

[Cu(bpdc)(dpa)] (6): A methanol solution (5 mL) of dpa (0.1 mmol, 0.019 g) was added dropwise, with constant stirring, to an aqueous solution (5 mL) of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.1 mmol, 0.037 g). An aqueous solution (5 mL) of Na_2bpdc (0.1 mmol, 0.029 g) was then added dropwise to give a transparent solution. The reaction mixture was refluxed for 1 h and filtered; the filtrate was kept in a $CaCl_2$ desiccator. After a few days, light green crystals suitable for X-ray analysis were obtained as a single phase, as confirmed by XRPD. The yield of **6** was about 70.6% based on copper. Elemental analysis calcd (%) for $C_{24}H_{17}CuN_3O_4$: C 60.69, H 3.61, N 8.85; found: C 60.62, H 3.64, N 8.87; IR: $\tilde{\nu}$ = 3445, 3044, 1718, 1624, 1582, 1488, 1433, 1380, 824, 798, 768, 675 cm^{-1}.

X-ray crystallography

Crystal data for 1: $M_r = 665.66$; triclinic; $P\bar{1}$; $a = 9.778(2)$, $b = 9.802(2)$, $c = 17.693(3)$ Å; $\alpha = 103.344(3)°$, $\beta = 93.076(3)°$, $\gamma = 101.911(3)°$; $V = 1604.1(4)$ Å^3; $Z = 2$; $\rho_{calcd} = 1.378$ g cm^{-3}; $R_1 = 0.0518$; $wR_2 = 0.1112$; $S = 1.017$.

Crystal data for 2: $M_r = 731.75$; monoclinic; $P2_1/c$; $a = 16.194(2)$, $b = 18.476(3)$, $c = 8.930(2)$ Å; $\beta = 91.295(3)°$; $V = 2671.4(7)$ Å^3; $Z = 3$; $\rho_{calcd} = 1.365$ g cm^{-3}; $R_1 = 0.0519$; $wR_2 = 0.1420$; $S = 1.044$.

Crystal data for 3: See reference [8].

Crystal data for 4: $M_r = 603.89$; monoclinic; $P2/c$; $a = 12.452(2)$, $b = 14.546(2)$, $c = 15.271(2)$ Å; $\beta = 111.276(3)°$; $V = 2577.7(7)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.556$ g cm^{-3}; $R_1 = 0.0464$; $wR_2 = 0.1260$; $S = 1.102$.

Crystal data for 5: $M_r = 740.72$; monoclinic; $C2/c$; $a = 11.8696(14)$, $b = 32.342(4)$, $c = 17.848(2)$ Å; $\beta = 91.54(4)°$; $V = 6849.1(14)$ Å^3; $Z = 8$; $\rho_{calcd} = 1.437$ g cm^{-3}; $R_1 = 0.0511$; $wR_2 = 0.1606$; $S = 1.073$.

Crystal data for 6: $M_r = 474.95$; triclinic; $P\bar{1}$; $a = 9.066(3)$, $b = 9.266(3)$, $c = 12.700(4)$ Å; $\alpha = 99.593(7)$, $\beta = 92.832(7)$, $\gamma = 97.528(6)°$; $V = 1040.1(6)$ Å^3; $Z = 2$; $\rho_{calcd} = 1.516$ g cm^{-3}; $R_1 = 0.0603$; $wR_2 = 0.1666$; $S = 0.935$.

A suitable single crystal of each compound was carefully selected under a polarizing microscope and glued to the tip of a thin glass fiber with superglue. The data collections were performed at 293(2) K on a Bruker SMART CCD area-detector diffractometer equipped with a $Mo_{K\alpha}$ radiation source ($\lambda = 0.71073$ Å). The crystal structures were solved by direct methods with the program SHELXTL.[21] All non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using a full-matrix least-squares procedure.

CCDC-258458 (**1**), CCDC-258459 (**2**), CCDC-257085 (**3**), CCDC-262038 (**4**), CCDC-292829 (**5**), and CCDC-292830 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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