Double-Stranded Helices and Molecular Zippers Assembled from Single-Stranded Coordination Polymers Directed by Supramolecular Interactions

Xiao-Ming Chen* and Gao-Feng Liu[a]

Abstract: Using three nonlinear dicarboxylates, isophthalate (ipa), 4,4′-oxybis(benzoate) (oba), and ethylenedi(4-oxybenzoate) (eoba), we have prepared five neutral infinite copper(II) dicarboxylate coordination polymers containing lateral aromatic chelate ligands, namely $[Cu(ipa)(2,2'\text{-bpy})]_n \cdot 2nH_2O$ (**1**), $[Cu_2(ipa)_2(phen)_2H_2O]_n$ (**2**), $[Cu(oba)(phen)]_n$ (**3**), $[Cu(oba)(2,2'\text{-bpy})]_n$ (**4**), and $[Cu(eoba)(phen)]_n$ (**5**; 2,2′-bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline) by hydrothermal synthesis. X-ray single-crystal structural analyses of these complexes reveal that the nonlinear flexible or V-shaped dicarboxylates can induce the helicity or flexuousity of the polymeric chains and aromatic chelate ligands are important in providing potential supramolecular recognition sites for π–π aromatic stacking interactions. An appropriate combination of the bridging dicarboxylate and aromatic chelate can induce a pair of single-stranded helical or flexuous chains to generate a double-stranded helix or molecular zipper through supramolecular interactions, respectively.

Keywords: copper · helical structures · molecular recognition · N,O ligands · self assembly

Introduction

Over the past decade, helical structures have received much attention in coordination chemistry and materials chemistry because helicity is an essential element of life and is also important in advanced materials such as optical devices and asymmetric catalysis.[1] Consequently, many single- and double- and higher-order stranded helical complexes have been generated by self-assembly processes. However, these studies have usually been focused on the design and synthesis of polymeric helical assemblies mediated by metal–ligand coordination, in which the metal ions are helically wrapped by bridging organic ligands as documented in a large number of helical oligomers[2] and infinite coordination polymers.[3, 4] A few helical assemblies[5] of purely organic molecules organized by hydrogen bonds, as well as several inorganic helical structures[6] have been described recently. However, to our knowledge, there is only one example of intertwining of two single-stranded helicates to form infinite double helices.[7] Moreover, no neutral double- or higher-order helix assembled by single-stranded helical coordination oligomers or infinite coordination polymers directed by supramolecular interactions, such as π–π aromatic stacking and hydrogen bonding, has been reported so far, although such structures may be regarded as better biomimetic assemblies of nucleic acids than the polymeric helicates formed under direction of covalent metal coordination.

Coordination polymers formed with metal ions and *exo*-bidentate organic bridges in a 1:1 stoichiometry are usually based on either rigid linear or zigzag chain structures.[8] It has been noted that employment of flexible or V-shaped *exo*-bidentate organic bridges can improve the helicity of the polymeric chains.[4, 9] Thus, we assumed that appropriate flexible or V-shaped *exo*-bidentate organic bridges could be useful in the formation of single-stranded helical chains in the presence of aromatic chelate ligands, such as 2,2′-bipyridine (2,2′-bpy) and 1,10-phenanthroline (phen). These aromatic chelate ligands are important in maintaining the one dimensionality and may provide potential supramolecular recognition sites for π–π aromatic stacking interactions[10] to form multistranded helices. Using three V-shaped dicarboxylates, isophthalate (ipa), 4,4′-oxybis(benzoate) (oba), and ethylenedi(4-oxybenzoate) (eoba) (Scheme 1), we have hydrothermally prepared five neutral infinite copper(II) dicarboxylate coordination polymers containing aromatic chelate ligands, namely $[Cu(ipa)(2,2'\text{-bpy})]_n \cdot 2nH_2O$ (**1**), $[Cu_2(ipa)_2(phen)_2H_2O]_n$ (**2**), $[Cu(oba)(phen)]_n$ (**3**), $[Cu(oba)(2,2'\text{-bpy})]_n$ (**4**), and $[Cu(eoba)(phen)]_n$ (**5**). The bridging ligation of the simple V-shaped dicarboxylate ligands to the Cu^{II} atoms does lead to helical or flexuous chain structures. More interestingly, the helical chains may also be paired under direction of

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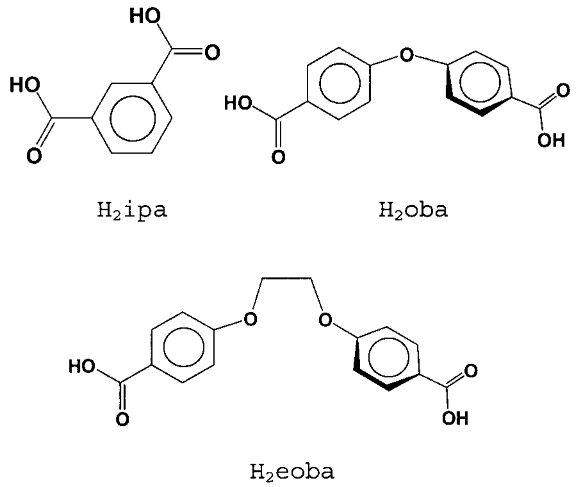

Scheme 1. Structures of the nonlinear dicarboxylates.

supramolecular recognition and attraction through both $\pi-\pi$-stacking and hydrogen-bonding interactions into double-stranded helices or molecular zippers, as revealed by single-crystal X-ray diffraction analysis.

Results and Discussion

Description of crystal structures: In the crystal structure of **1**, there is one Cu^{II} atom, one bis(monodentate) ipa ligand, one 2,2′-bpy ligand, and two lattice water molecules in each independent crystallographic unit. Each Cu^{II} atom in **1** is primarily coordinated by two oxygen atoms from two bis(monodentate) ipa ligands (Cu1−O1A 1.991(2), Cu1−O3 1.979(2) Å) and two nitrogen atoms from a chelating 2,2′-bpy ligand (Cu1−N1 2.013(3), Cu1−N2 2.014(3) Å) to furnish a distorted square-planar geometry (Figure 1 a). The pendant carboxy oxygen atoms have weak bonding interactions with the Cu^{II} atom at the axial sites (Cu1−O2 2.502(3), Cu1−O3 2.632(3) Å) due to the Jahn–Teller effect. Each pair of adjacent Cu^{II} atoms are bridged by an ipa ligand to form a chiral helical chain running along a crystallographic 2_1 axis in the *b* direction with a long pitch of 11.25 Å. These chains are decorated with 2,2′-bpy ligands alternately at two sides (Figure 1b). The ipa phenyl rings at each side of the helix are arranged in a parallel fashion with an inter-ring distance of 8.29 Å; adjacent chiral helices are racemically packed through intercalation of the lateral ipa phenyl rings in a zipperlike, offset fashion (face-to-face distances of 3.32 and 4.97 Å) into two-dimensional layers parallel to the *bc* plane. The interfacial distance of 3.32 Å indicates a strong aromatic $\pi-\pi$ stacking interaction.[10, 11] These layers are further extended into two-dimensional (2D) networks through intercalation between the lateral 2,2′-bpy ligands from adjacent layers in a zipperlike, offset fashion with the face-to-face distance of about 3.43 Å (Figure 2). Similar zipperlike intercalations have been reported previously in some three-dimensional coordination architectures constructed by two-dimensional layers.[10]

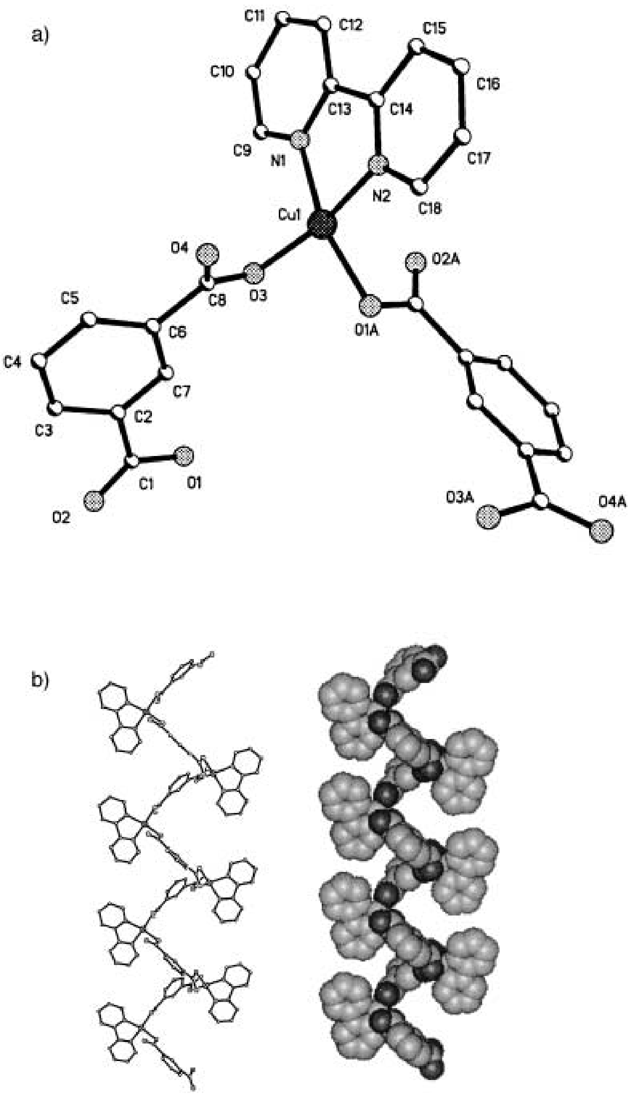

Figure 1. The metal coordination environment (a) and single-stranded helical chain (b) in **1**.

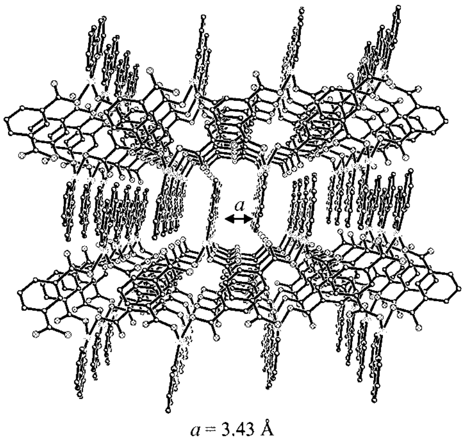

Figure 2. The three-dimensional network viewed along the *b* axis in **1**.

When phen, a chelate aromatic ligand of a larger size, was used instead of 2,2′-bpy, analogous neutral single-stranded helices are formed in **2** under similar reaction condition. As illustrated in Figure 3a, there are two different metal coordination environments in **2**; Cu1 is coordinated by two oxygen atoms from two bis(monodentate) ipa ligands (Cu1−O2

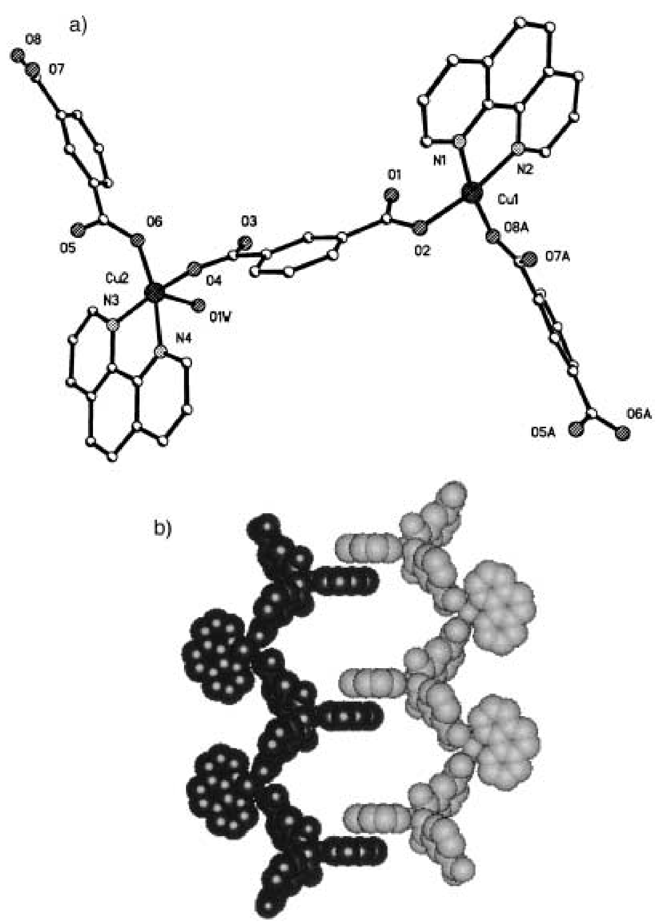

Figure 3. The metal coordination environment (a) and a pair of the helical chains (b) in **2**.

1.951(3), Cu1–O8A 1.965(3) Å) and two nitrogen atoms from a chelate phen (Cu1–N1 2.043(3), Cu1–N2 2.032(3) Å) to furnish a distorted square-planar coordination, and the remaining carboxy oxygen atoms also have weak interactions with Cu1 at the axial sites (Cu1–O1 2.716(3), and Cu1–O7A 2.652(3) Å), whereas Cu2 is ligated by two oxygen atoms from two bis(monodentate) ipa ligands (Cu2–O4 1.978(3), Cu2–O6 1.960(2) Å) and two nitrogen atoms from a chelate phen ligand (Cu2–N3 2.068(3), Cu2–N4 2.049(3) Å) at the equatorial positions, and completed by an aqua oxygen atom (Cu2–O1W 2.275(3) Å) at the apical position to furnish a square-pyramidal N_2O_2O' geometry. The ipa ligands bridge each pair of adjacent $\mathrm{Cu^{II}}$ atoms into a helical chain running along the *c* axis with a long pitch of 16.38 Å. Unlike those in **1**, the phen ligands are alternately attached to both sides of a single-stranded helical chain, and are orientated either approximately parallel or perpendiculat to the chain (Figure 3b). The approximately perpendicular orientation of half of the phen ligands allows pairing of two centrosymmetrically related single-stranded helical chains to generate a double-stranded zipperlike chain under direction of aromatic $\pi-\pi$ stacking interactions between the phen pairs. The face-to-face distance between the paired phen rings is about 3.37 Å, indicating a strong aromatic $\pi-\pi$ stacking interaction.[10, 11] To the best of our knowledge, such zipperlike double-stranded helical chains have not been documented. These double-stranded helical chains are further extended through aromatic $\pi-\pi$ stacking interactions, hydrogen bonds between the aqua ligands (and aromatic groups as well) and carboxylate oxygen atoms (O1W···O 2.746(3), C···O ca. 3.1 Å),[12] as well as van der Waals interactions into the final three-dimensional architecture in **2**.

The oba dicarboxylate in **3** is a long and flexible V-shaped ligand; the structure of the complex obtained under similar reaction conditions as for **1** comprises novel neutral double-stranded helices. As illustrated in Figure 4, the $\mathrm{Cu^{II}}$ atom in **3** is also primarily coordinated by two oxygen atoms from two bis(monodentate) oba ligands (Cu1–O2 1.948(4), Cu1–O4A 1.987(4) Å) and two nitrogen atoms from a chelate phen ligand (Cu1–N1 2.040(4), Cu1–N2 2.044(4) Å) to furnish a distorted square-planar coordination, the Cu1–O3 (2.549(3) Å) and Cu1–O1 (2.782(3) Å) distances show some weak interactions between the copper center and the carboxy oxygen atoms at the axial sites. The V-shaped oba ligands interconnect the $\mathrm{Cu^{II}}$ atoms to furnish chiral helices along the *b* axis with a pitch of 12.06 Å.

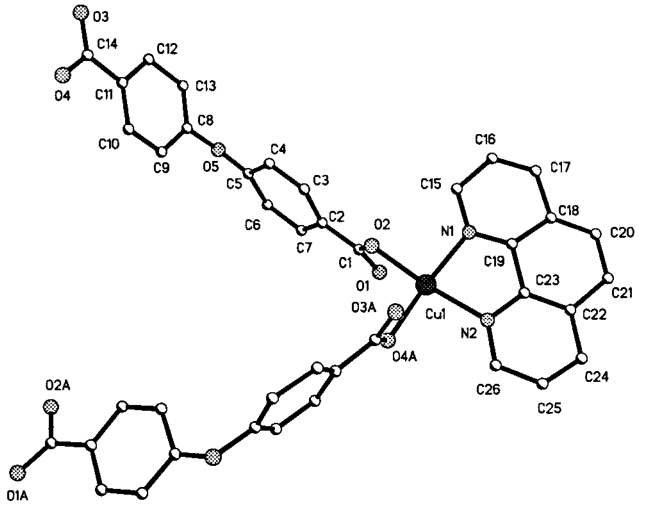

Figure 4. The metal coordination environment in **3**.

The phen ligands are extended in a parallel fashion at both sides of a single-stranded chain (Figure 5) with a face-to-face distance of 6.84 Å, resulting in a structure suitable to form aromatic intercalation. Indeed, each pair of the covalently independent and twofold axially related, homochiral polymeric chains intertwine into a unique double-stranded helix of C_2 symmetry through the $\pi-\pi$ stacking interactions between the phen ligands. The face-to-face separation between the inter-strand phen ligands in the double helix is 3.42 Å, which indicates strong aromatic $\pi-\pi$ stacking interactions.[10, 11] Significant C–H···O hydrogen bonds[12] involving the phen carbon atoms (C16 and C17) and weakly coordinated carboxy oxygen atoms (O1) (C···O 3.23–3.29 Å, C–H···O 129—161°) render additional attractions between the pair of strands. It should be mentioned that, the intertwined neutral double-stranded helices in **3** are unprecedented, and that due to the long V-shaped $\mathrm{oba^{2-}}$ ligand, the double-stranded helix is quite large with a channel with a diameter of about 5 Å[13] running along in the *b* axis. Both left- and right-handed helices

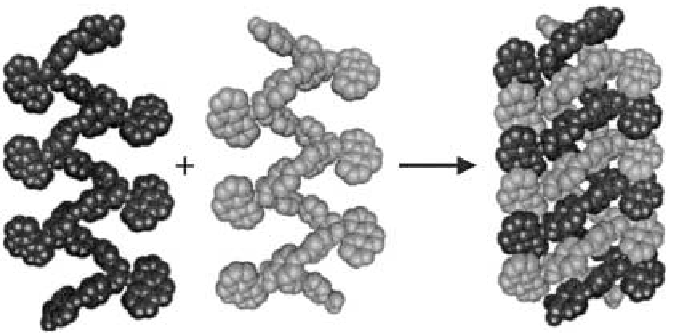

Figure 5. The double-stranded helix generated by intertwining of two single-stranded helical chains in **3**.

that coexist in the solid are further extended into a three-dimensional supramolecular network through very significant C–H···O hydrogen bonds between aromatic carbon atoms (C24 and C25) and carboxy oxygen atoms (O3) (C···O 3.09–3.14 Å; C–H···O 118–124°) and van der Waals interactions (see Figure S1 in the Supporting Information).

Unexpectedly, when 2,2′-bpy instead of phen was used, structurally different helices are formed in **4** under a similar hydrothermal reaction for the preparation of **3**. As shown in Figure 6a, the Cu^{II} atom in **4** is coordinated by four oxygen atoms from two bis(bidentate) oba ligands (Cu1–O1 2.018(4), Cu1–O4A 2.016(4), Cu1–O3A 2.415(4), Cu1–O2 2.442(4) Å) and two nitrogen atoms from a chelate phen (Cu1–N1 2.042(5), Cu1–N2 2.011(5) Å) to furnish a highly distorted octahedron coordination. Each pair of adjacent Cu^{II} atoms in **4** is interconnected to give a helical chain running along the *b* axis by the V-shaped oba bridges. The 2,2′-bpy ligands are extended at both sides of the helical chain, but the planes of every two adjacent 2,2′-bpy ligands are approximately perpendicular (dihedral angle ca. 89.3°). The lateral 2,2′-bpy ligands from adjacent chains are paired to furnish moderate $\pi-\pi$ aromatic stacking interactions in an offset fashion with a face-to-face distance of about 3.58 Å,[10, 11] which extend the helical chains into wavy two-dimensional layers parallel to the *bc* plane (Figure 6b).

To further examine the influence of the dicarboxylate geometry on the self-assembly of supramolecular entities, a more flexible eoba dicarboxylate was used instead of oba. Consequently, **5**, which features a flexuous chain structure, was obtained. As shown in Figure 7a, each Cu^{II} atom in **5** is also primarily coordinated by two oxygen atoms from two bis(monodentate) eoba ligands (Cu1–O2 1.963(4) and Cu1–O3A 1.961(4) Å) and two nitrogen atoms from a chelate phen (Cu1–N1 2.053(5), Cu1–N2 2.040(5) Å) to furnish a distorted square-planar coordination, and the pendant carboxy oxygen atoms also form weak interactions with the Cu^{II} atom at the axial sites (Cu1–O1 2.658(4), Cu1–O4A 2.593(4) Å). Unlike the other complexes reported in this work, the nonlinear flexible eoba ligands interconnect the Cu^{II} atoms to furnish flexuous chains with an adjacent Cu···Cu distance of 14.936(5) Å. The phen ligands are extended uniquely at one side of this chain (Figure 7b) in a slanted fashion. Interestingly, each pair of these flexuous chains recognize each other through offset aromatic $\pi-\pi$ stacking interactions of the phen ligands (face-to-face separation ca. 3.34 Å) to generate a zipperlike double-stranded chain, which is different from those found in **2** and **3** mainly due to the fact that all lateral phen ligands are arranged at one side of each single strand in **5**. Thus the double-stranded chain presents the first perfect molecular zipper. These double-stranded chains are further extended to form two-dimensional layers parallel to the *ab* plane.

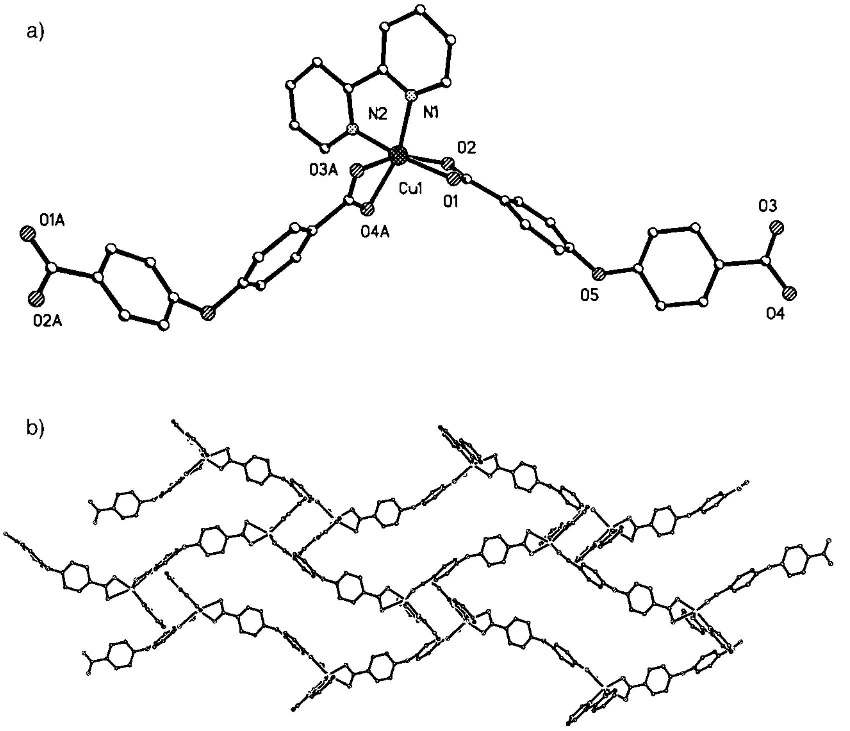

Figure 6. The metal coordination environment (a) and the two-dimensional network viewed along the *a* axis (b) in **4**.

Discussion

As shown above, V-shaped dicarboxylates and metal–ligand coordination can furnish one-dimensional helical chains in **1**–**4**, and the nonlinear flexible dicarboxylate (eoba) generates a flexuous chain such as in **5**. The most critical factor for the helicity of the polyermic chain is presumed to be the geometry and flexibility of the dicarboxylate ligand. Interestingly, the long V-shaped dicarboxylate ligand in **3** is twisted in such a way that the two phenyl rings form a dihedral angle of 74°; this in turn leads to the slanted orientation of the phen ligand to the helical axis (ca. 60°). With this optimized helicity,

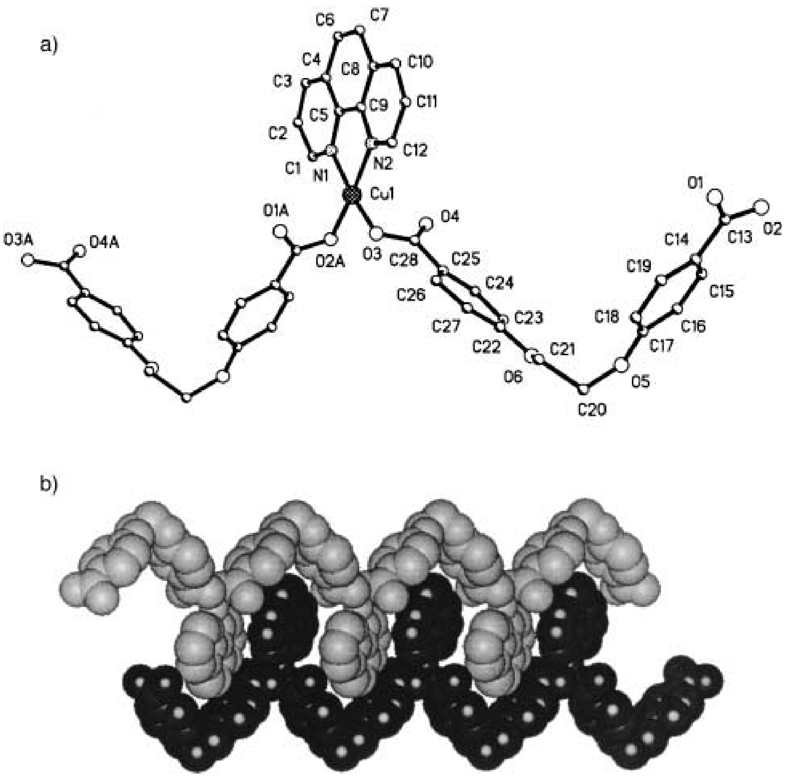

Figure 7. The metal coordination environment (a) and the zipperlike double-stranded chain (b) in **5**.

two single-stranded helical chains can recognize each other and intertwine under the direction of supramolecular interactions to give the structure **3**. Similarly, the long and flexible eoba bridges furnish the intercalation of two strands to generate the molecular zipper structure for **5**. These observations strongly suggest the length and flexibility of the *exo*-bidentate ligand is essential for the intertwining or zipping of two strands. In contrast, the dicarboxylate in **1** and **2** is very rigid and not twisted, hence the 2,2′-bpy ligands in **1** are oriented parallel to the helical axis, and thus in a way unfavorable for the formation of a double-stranded helix. On the other hand, in the presence of aqua ligands, both the coordination geometry and hence the helicity of the single-stranded chain are then optimized. The presence of the larger aromatic phen ligands further enhances the π–π aromatic stacking interactions, and thus results in the formation of the double-stranded helix in **2**. In contrast, although the bridging dicarboxylate ligands are the same as those in **3**, due to the change in the coordination geometry around the metal atom in **4**, adjacent 2,2′-bpy ligands are orientated in an approximately perpendicular fashion, which is disadvantageous for generating an intertwined double-stranded helix. This suggests that supramolecular interactions are also very important in the formation of double-stranded helices and zipperlike chains. In fact, in the presence of the larger lateral aromatic ligand phen, the chains can be directed by stronger π–π stacking interactions into double-stranded helices or zipperlike chains (**2**, **3**, and **5**). In contrast, when the lateral chelate ligands are the smaller aromatic 2,2′-bpy ligands, no double-stranded helix is formed (**1** and **4**). Therefore, an appropriate combination of the dicarboxylate and aromatic chelate ligands is critical to the formation of double-stranded helices or molecular zippers.

Conclusion

This work demonstrates that V-shaped *exo*-bidentate ligands can be employed in ternary Cu^{II}/dicarboxylate/aromatic chelate systems to generate both one-dimensional helical and zipperlike polymers. Moreover, the length and geometry of the bridging ligand and the coordination environment, as well as the size of the lateral aromatic chelate ligand influence the helicity and the possibility of intertwining or zipping, and thus, in turn, the generation of double-stranded helices or molecular zippers. An appropriate combination of long dicarboxylate and aromatic chelate ligands may lead to the formation of double-stranded helices or molecular zippers that are self-organized uniquely by supramolecualar recognition and attractions.

Experimental Section

Materials: The nonlinear dicarboxylic acid H_2eoba was synthesized according to the literature method.[14] All other reagents and solvents employed were commercially available and used as received without further purification. The C, H, N microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Nicolet 5DX spectrometer.

Preparations

[Cu(ipa)(2,2′-bpy)]$_n$·2nH$_2$O (1): A mixture of $Cu(NO_3)_2\cdot 4H_2O$ (0.2 mmol), H_2ipa (0.2 mmol), 2,2′-bpy (0.2 mmol), Et_3N (0.4 mmol), and water (10 mL) was stirred for 20 min in air, then transferred and sealed in a 23 mL Teflon reactor, which was heated at 150 °C for six days and then cooled to room temperature at a rate of 5 K h^{-1}. Blue block crystals were obtained in 87% yield after washing with water and drying in air. Elemental analysis (%) calcd for $C_{18}H_{16}CuN_2O_6$: C 51.49, H 3.84, N 6.67; found: C 51.47, H 3.82, N 6.70; IR (KBr): $\tilde{\nu}$ = 3484s, 3122m, 2103w, 1796w, 1675m, 1643s, 1604s, 1566s, 1478m, 1448s, 1396s, 1164w, 782m, 751m, 731w, 593w cm^{-1}.

[Cu$_2$(ipa)$_2$(phen)$_2$(H$_2$O)]$_n$ (2): A mixture of $Cu(NO_3)_2\cdot 4H_2O$ (0.2 mmol), H_2ipa (0.2 mmol), phen (0.2 mmol), Et_3N (0.4 mmol), and water (10 mL) was stirred for 20 min in air, then transferred and sealed in a 23-mL Teflon reactor, which was heated at 140 °C for five days and then cooled to room temperature at a rate of 5 K h^{-1}. Blue block crystals were obtained in 74% yield after washing with water and drying in air. Elemental analysis (%) calcd for $C_{40}H_{26}Cu_2N_4O_9$: C 57.62, H 3.14, N 6.72; found: C 57.57, H 3.12, N 6.76; IR (KBr): $\tilde{\nu}$ = 3391s, 3162m, 2143w, 1778s, 1697m, 1635s, 1611s, 1568s, 1468m, 1452s, 1394s, 1159m, 779m, 757m, 734w, 584w cm^{-1}.

[Cu(oba)(phen)]$_n$ (3): Compound **3** was prepared as for **1** by using H_2oba instead of H_2ipa. Blue platelike crystals were obtained in 49% yield. Elemental analysis (%) calcd for $C_{26}H_{16}CuN_2O_5$: C 62.46, H 3.23, N 5.60;

found: C 62.44, H 3.21, N 5.62; IR (KBr): $\tilde{\nu} = 3052$m, 1923w, 1601s, 1561s, 1499s, 1383s, 1303w, 1237m, 1160m, 1100w, 1010w, 876m, 853m, 781m, 721w, 665m cm^{-1}.

[Cu(oba)(2,2′-bpy)]$_n$ (4): Compound **4** was prepared as for **3** by using 2,2′-bpy instead of phen. Blue platelike single crystals were obtained in 42 % yield. Elemental analysis (%) calcd for $C_{24}H_{16}CuN_2O_5$: C 60.57, H 3.39, N 5.89; found: C 60.54, H 3.21, N 5.92; IR (KBr): $\tilde{\nu} = 3107$m, 1923w, 1606s, 1558s, 1504s, 1388s, 1311m, 1253s, 1152m, 1092w, 1006w, 874m, 856m, 780m, 718w, 667m cm^{-1}.

[Cu(eoba)(2,2′-bpy)]$_n$ (5): A mixture of $Cu(NO_3)_2 \cdot 4H_2O$ (0.2 mmol), H_2eoba (0.2 mmol), 2,2′-bpy (0.2 mmol), Et_3N (0.4 mmol), and water (10 mL) was stirred for 20 min in air, then transferred and sealed in a 23-mL Teflon reactor, which was heated at 150 °C for six days and then cooled to room temperature at a rate of 5 K h^{-1}. Blue block crystals were obtained in 37 % yield after washing with water and drying in air. Elemental analysis (%) calcd for $C_{18}H_{16}CuN_2O_6$: C 51.49, H 3.84, N 6.67; found: C 51.47, H 3.82, N 6.70; IR (KBr): $\tilde{\nu} = 3381.7$m, 3229w, 3081w, 3043w, 2947m, 2878w, 2551w, 1913w, 1656m, 1611s, 1507s, 1421s, 1246s, 1173s, 1108m, 938m, 855m, 781s, 687m, 666m, 535w cm^{-1}.

Crystal structure determination: Diffraction intensities for the five complexes were collected at 273 K on a Siemens R3m diffractometer by using the ω-scan technique. Lorentz polarization and absorption corrections were applied.[15] The structures were solved by direct methods and refined with the full-matrix least-squares technique using the SHELXS-97 and SHELXL-97 programs.[16, 17] Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically (C–H 0.96 Å); the hydrogen atoms of the water molecules were located from difference maps and refined with isotropic temperature factors. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[18] The crystallographic data and selected bond lengths and angles for **1**–**5** are listed in Table 1 and Table 2, respectively.

CCDC-175789 (**1**), CCDC-175790 (**2**), CCDC-183436 (**3**), CCDC-183437 (**4**), CCDC-183438 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.can.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44) 1223-336033; or deposit@ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the NSFC (No. 20131020 & 29971033) and Foundation for University Key Teachers by the Ministry of Education of China. We thank the Chemistry Department of The Chinese University of Hong Kong for the donation of the diffractometer.

Table 2. Selected bond lengths [Å] and bond angles [°] for **1**–**5**.

	1		
Cu(1)–O(3)	1.979(2)	Cu(1)–N(2)	2.013(3)
Cu(1)–O(1A)	1.991(2)	Cu(1)–N(1)	2.014(3)
O(3)-Cu(1)-O(1A)	92.31(11)	O(3)-Cu(1)-N(1)	96.85(11)
O(3)-Cu(1)-N(2)	165.71(10)	O(1A)-Cu(1)-N(1)	163.38(10)
O(1A)-Cu(1)-N(2)	93.06(11)	N(2)-Cu(1)-N(1)	81.36(11)
	2		
Cu(1)–O(2)	1.951(3)	Cu(2)–O(4)	1.978(3)
Cu(1)–O(8A)	1.965(3)	Cu(2)–N(4)	2.049(3)
Cu(1)–N(2)	2.032(3)	Cu(2)–N(3)	2.068(3)
Cu(1)–N(1)	2.043(3)	Cu(2)–O(1W)	2.275(3)
Cu(2)–O(6)	1.960(2)		
O(2)-Cu(1)-O(8A)	95.78(12)	O(6)-Cu(2)-O(4)	97.91(12)
O(2)-Cu(1)-N(2)	170.41(11)	O(6)-Cu(2)-N(4)	168.54(11)
O(8A)-Cu(1)-N(2)	91.83(13)	O(4)-Cu(2)-N(4)	88.22(12)
O(2)-Cu(1)-N(1)	91.04(12)	O(6)-Cu(2)-N(3)	92.39(12)
O(8A)-Cu(1)-N(1)	171.60(11)	O(4)-Cu(2)-N(3)	167.84(11)
N(2)-Cu(1)-N(1)	81.91(13)	N(4)-Cu(2)-N(3)	80.56(12)
O(2)-Cu(1)-N(1)	92.3(2)	O(4A)-Cu(1)-N(2)	93.9(2)
O(4A)-Cu(1)-N(1)	174.2(2)	N(1)-Cu(1)-N(2)	81.4(2)
	3		
Cu(1)–O(2)	1.948(4)	Cu(1)–N(1)	2.040(4)
Cu(1)–O(4A)	1.987(2)	Cu(1)–N(2)	2.044(4)
O(2)-Cu(1)-O(4A)	92.92(17)	O(2)-Cu(1)-N(2)	173.25(16)
O(2)-Cu(1)-N(1)	92.27(17)	O(4A)-Cu(1)-N(2)	93.88(17)
O(4A)-Cu(1)-N(1)	174.20(15)	N(1)-Cu(1)-N(2)	81.41(17)
	4		
Cu(1)–N(2)	2.009(4)	Cu(1)–N(1)	2.043(5)
Cu(1)–O(4A)	2.018(4)	Cu(1)–O(3A)	2.414(4)
Cu(1)–O(1)	2.017(3)	Cu(1)–C(14A)	2.530(5)
N(2)-Cu(1)-O(4A)	91.5(2)	O(1)-Cu(1)-N(1)	96.9(2)
N(2)-Cu(1)-O(1)	163.1(2)	N(2)-Cu(1)-O(3A)	92.7(2)
O(4A)-Cu(1)-O(1)	96.7(2)	O(4A)-Cu(1)-O(3A)	59.91(14)
N(2)-Cu(1)-N(1)	81.3(2)	O(1)-Cu(1)-O(3A)	104.18(14)
O(4A)-Cu(1)-N(1)	154.95(14)	N(1)-Cu(1)-O(3A)	96.3(2)
	5		
Cu(1)–O(2)	1.963(4)	Cu(1)–N(2)	2.040(5)
Cu(1)–O(3A)	1.961(4)	Cu(1)–N(1)	2.053(5)
O(2)-Cu(1)-O(3A)	94.4(2)	O(2)-Cu(1)-N(1)	174.7(2)
O(2)-Cu(1)-N(2)	93.3(2)	O(3A)-Cu(1)-N(1)	90.6(2)
O(3A)-Cu(1)-N(2)	172.3(2)	N(2)-Cu(1)-N(1)	81.8(2)

[a] Symmetry codes: A) $-x+1, y-1/2$ for **1**; A) $x, y, z-1$ for **2**; A) $-x+1, y+1, -z+3/2$ for **3**; A) $x+1, -y+1/2, z+1/2$ for **4**; A) $x-1, y-1, z$ for **5**.

Table 1. Crystal data and structure refinement for **1**–**5**.

	1	**2**	**3**	**4**	**5**
empirical formula	$C_{18}H_{16}N_2O_6Cu$	$C_{40}H_{26}N_4O_9Cu_2$	$C_{26}H_{16}N_2O_5Cu$	$C_{24}H_{16}N_2O_5Cu$	$C_{28}H_{20}N_2O_6Cu$
formula weight	419.87	833.73	499.95	475.93	544.00
temperature [K]	293(2)	293(2)	293(2)	293(2)	293(2)
wavelength [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$C2/c$	$P2_1/c$	$P2_1/n$
a [Å]	11.57(1)	10.20(1)	36.17(3)	12.38(1)	12.56(1)
b [Å]	11.25(1)	11.81(1)	6.03(1)	15.20(1)	8.09(1)
c [Å]	13.74(1)	16.38(1)	23.88(1)	11.48(1)	24.48(2)
α [°]		87.01(1)			
β [°]	91.62(1)	89.72(1)	113.65(1)	92.32(1)	98.07(1)
γ [°]		65.94(1)			
V [Å^3]	1787.8(2)	1799(2)	4772(6)	2158(3)	2461(3)
Z	4	2	8	4	4
$F(000)$	860	848	2040	972	1116
ρ [Mg m^{-3}]	1.560	1.539	1.392	1.465	1.468
μ [mm^{-1}]	1.260	1.246	0.954	1.051	0.934
data/restrains/parameters	3907/0/245	7841/0/497	4924/0/308	4244/0/290	5302/0/335
GooF	1.047	1.055	1.032	1.042	1.113
R_1 ($I = 2\sigma(I)$)	0.0516	0.0505	0.0655	0.0687	0.0712
wR_2 (all data)	0.1467	0.1443	0.1910	0.2078	0.2084

[a] $R_1 = \Sigma||F_o| - |F_c||/|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

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Received: April 10, 2002 [F4024]