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Different interpenetrated coordination polymers based on flexible dicarboxylate ligands: topological diversity and magnetism

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Through tuning the nature of secondary ligands, ligand-to-metal molar ratio and metal ions, a family of entangled metal-organic frameworks have been prepared. This work evidently indicates that the effect of secondary ligands is critical in construction of these networks arrangement, which are also well regulated by the ligand-to-metal molar ratios and geometric preferences of metal centers. In addition, the stabilities of these compounds are discussed.
Different interpenetrated coordination polymers based on flexible
dicarboxylate ligands: topological diversity and magnetism

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Abstract

Through tuning the nature of secondary ligands, ligand-to-metal molar ratio and metal ions, three coordination polymers, namely \{[Ni_2(bcp)_2(4,4’-bipy)(H_2O)_4]·3.5H_2O\}_n (1), \{[Co_2(bcp)(bpt)]_2·2.29H_2O·bpt\}_n (2), [Co_2(bcp)_2(bib)]_n (3) and \{[Co(bcp)(2,2’-bipy)(H_2O)]·H_2O\}_n (4), have been synthesized and characterized. The structural feature of 1 shows 3D three-fold parallel interpenetrating framework with CdSO_4 topology. In 2, it exhibits a 2D→3D interpenetrating motif with pseudorotaxane. Compound 3 shows two identical 2D layers with 2^2·4^8·6^5 topology that are interpenetrated in a parallel fashion, resulting in a twofold interpenetrating motif containing polyrotaxane and polycatenane character. However, a 1D zipper-like double-stranded chain is observed in polymer 4. This work evidently indicates that the effect of secondary ligands and geometric preferences of metal centers are critical in construction of the resulting networks. In addition, the magnetic property was also discussed in compounds 2 and 3.

Keywords: Carboxylate; Entangled structure; Magnetism
Introduction

The flourishing realm of crystal engineering has provided a sound junction between aesthetics of crystalline architectures and their potential functions.\textsuperscript{1-5} Metal-organic frameworks with entangled motifs have attracted extreme concern for their intrinsic aesthetic appeal and properties. More specific types of entangled structures, such as polycatenation (\textit{e.g.} Borromean), polythreading (\textit{e.g.} polyrotaxane), and polyknotting (\textit{e.g.} self-interpenetration), are of particular interest.\textsuperscript{6} Many topologically interesting entangled structures have been discussed in comprehensive reviews.\textsuperscript{1c,6a,6g,6h,6k} So at this point, much effort have mainly focused on the discovery of new entanglement patterns and understanding their formation mechanisms.\textsuperscript{7-9}

Usually, entangled coordination polymers are formed by flexible and long organic ligands. For example, the V-shaped and flexible organic linkers (\textit{e.g.} 4,4'-oxybis(benzoic acid)) take as a excellent building block and constructs different entangled motifs due to its flexuous geometry and various binding modes.\textsuperscript{8} Thus, one effective way to modulate the type of entangled motif is to extend the flexibility and length of the ligand.\textsuperscript{10} Recently, we have been interested in the syntheses and characterization of entangled MOFs containing the organic dicarboxylates of 4,4'-oxybis(benzoic acid) (H\textsubscript{2}oba), 1,2-bis(4-carboxy-phenoxy)ethane (H\textsubscript{2}bce) and 1,3-bis(4-carboxy-phenoxy)propane (H\textsubscript{2}bcp).\textsuperscript{10d,11} Among the three type of flexible dicarboxylate ligands, the segment of –O-X-O- chains are different with respect with the relative orientation of CH\textsubscript{2} groups. More interestingly, the employment of H\textsubscript{2}bcp, Co(II) and bpp leads an unexceptional sextuple-stranded molecular braid.\textsuperscript{10d} However, systematic investigation the coordination chemistry of H\textsubscript{2}bcp has been rarely documented.\textsuperscript{10d} On the other hand, the control of product architectures still remains a major challenge in this field, because the self-assembly process is frequently influenced by the type and spatial disposition of the ligand binding site, metal-to-ligand ratio, stereoelectronic preferences of the metal ion, and other factors.\textsuperscript{12-14}

With this background in mind, we continued to our investigation and chose H\textsubscript{2}bcp as a bridging ligand to react with the d-block metal ions in the presence of different
N-donor ligands. Three new coordination polymers, namely 

\[ \{[\text{Ni}_2(\text{bcp})_2(4,4'{-}\text{bipy})(\text{H}_2\text{O})_4] \cdot 3.5\text{H}_2\text{O}\}_n (\text{1}), \quad \{[\text{Co}_2(\text{bcp})_2(\text{bpt})_2] \cdot 2.29\text{H}_2\text{O} \cdot \text{bpt}\}_n (\text{2}), \]

\[ \{[\text{Co}_2(\text{bcp})_2(\text{bib})]_n \quad (\text{3}) \quad \text{and} \quad \{[\text{Co}(\text{bcp})(2,2'{-}\text{bipy})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}\}_n \quad (\text{4}) \]

(H_2bcp=1,3-bis(4-carboxy-phenoxy)propane, bpt=2,5-bis(4-pyridyl)-1,3,4-thiadiazole, 
4, 4'-bipy =4,4'-bipyridine, bib=2,3-bis(4-pyridyl)butane and 2, 
2'-bipy=2,2'-bipyridine), were designed and synthesized. Compound 1 exhibits 3D 
threefold \(\text{CdSO}_4\) topological net, polymer 2 has 2D polythreading architecture, 
Compound 3 shows two identical 2D layers with \(2^2.4^4.6^5\) topology with polyrotaxane 
and polycatenane feature, and compound 4 shows a zipper-like double-stranded chain. 
The crystal structures and topological analyses of these compounds, along with a 
systematic investigation on the coordination modes of bcp ligand, metal ions and 
nearligand on the ultimate frameworks, will be represented and discussed in detail. 
Furthermore, the magnetic property was also discussed in compounds 2 and 3.

**Experimental**

**Materials and Method**

All reagents were purchased from commercial sources and used as received. IR 
spectra were recorded with a Perkin–Elmer Spectrum One spectrometer in the region 
4000–400 cm\(^{-1}\) using KBr pellets. TGA were carried out with a Metter–Toledo TA 50 
in dry dinitrogen (60mL.min\(^{-1}\)) at a heating rate of 5°C min\(^{-1}\). X-ray powder 
diffraction (XRPD) data were recorded on a Rigaku RU200 diffractometer at 60KV, 
300mA for \(\text{Cu} \text{K}_\alpha\) radiation (\(\lambda = 1.5406\) Å), with a scan speed of 2 °C/min and a step 
size of 0.02° in 20. Magnetic susceptibility data of powdered samples restrained in 
parafilm were measured on Oxford Maglab 2000 magnetic measurement system in the 
temperature range 300–1.8 K and at field of 1KOe.

**X-ray Crystallography:** Single crystal X-ray diffraction analyses of the four 
compounds were carried out on a Bruker SMART APEX II CCD diffractometer 
equipped with a graphite monochromated MoK\(\alpha\) radiation (\(\lambda = 0.71073\) Å) by using 
\(\phi\omega\) scan technique at room temperature. The intensities were corrected for Lorentz 
and polarization effects as well as for empirical absorption based on multi-scan 
techniques; all structures were solved by direct methods and refined by full-matrix
least-squares fitting on $F^2$ by SHELX-97.\textsuperscript{15} Absorption corrections were applied by using multi-scan program SADAB\textsuperscript{s}.\textsuperscript{16} Non-hydrogen atoms were refined anisotropically. It was assigned to some non-hydrogen atoms an isotropic temperature factor of 1.3 times the isotropic temperature factor of the atom to which they were attached. The hydrogen atoms of organic ligands were placed in calculated positions and refined using a riding on attached atoms with isotropic thermal parameters 1.2 times those of their carrier atoms. The water hydrogen atoms were located from difference maps and refined with isotropic thermal parameters 1.5 times those of their carrier atoms. The hydrogen atoms of lattice water molecules in compound 1 and 2 were not located using the different Fourier method. The entire disordered water molecule O3W, O4W, O5W, O6W, and O7W have the occupancies of 0.25 in compound 1. The disordered water molecule O13 has the occupancy of 0.77 and 0.23, and O14 has the occupancy of 0.52 and 0.48 in compound 2, respectively. The disordered water molecule O2W has the occupancy of 0.50 and 0.50 in compound 4. The available crystals of the compound 2 diffracted very weakly, especially at higher diffraction angles. This is most likely related to the disorder in the solvent molecule. Namely, the crystal quality and data in 2 was not good enough so a sufficient fraction of the unique data is above the 2 sigma level. The crystal quality was not good. After several attempt of data collection, the reported one is found to be the best one. Thus, more restraints were applied during refinement of the structures including distance restraints and thermal restraints which have been used in some unreasonable atoms in order to permit acceptable refinement of these parameters in compounds. Table 1 shows crystallographic data of 1–4. Selected bond distances and bond angles, parameters are listed in Table 2. Selected bond distances and angles of hydrogen bonds are given in Table S1. CCDC: 913913-913915 for 1,2,4, and 971937 for 3.

**Synthesis of these complexes**

\([\text{Ni}_2(\text{bcp})_2(4,4’\text{-bipy})_2(\text{H}_2\text{O})_4]·3.5\text{H}_2\text{O})_n\) (1)

A mixture of NiSO$_4$·7H$_2$O (0.026g, 0.1mmol), H$_2$bcp (0.032g, 0.1mmol), 4,4’-bipy (0.012g, 0.1mmol), CH$_3$OH (2mL) and deionised water (10mL) was stirred for 30min in air. The pH of the resulting solution was adjusted to 7 using dilute NaOH (0.1mol/L)
and kept at 150 °C for 72h at oven, and then cooled down to 25 °C. The resulting crystals formed were filtered off, washed with water and dried in air.

\[ C_{54}H_{59}N_{4}Ni_{2}O_{19.5} \] (1193.48). Calcd: C, 54.34; H, 4.98; N, 4.69. Found C, 54.01; H, 4.77; N, 4.50. IR (KBr, cm\(^{-1}\)): 3389(s), 2982(m), 2768(w), 2035(w), 1599(m), 1408(vs), 1266(m), 1138(w), 1011(m), 988(w), 866(w), 759(m), 658(s).

\([\{Co_2(bcp)_2(bpt)_2\} \cdot 2.29H_2O \cdot bpt]_n \) (2)

The synthesis procedure of 2 is similar to that for 1, except that bipy and NiSO\(_4\)-7H\(_2\)O were replaced by bpt (0.1mmol) and CoSO\(_4\)-7H\(_2\)O (0.1mmol), respectively. C\(_{70}\)H\(_{56.58}\)Co\(_2\)N\(_{12}\)O\(_{14.29}\)S\(_{3}\) (1508.55) Calcd: C, 55.73; H, 3.78; N, 11.14. Found C, 55.26; H, 4.12; N, 11.22. IR (KBr, cm\(^{-1}\)): 3320(s), 2997(m), 2332(w), 1988(w), 1612(vs), 1452(vs), 1208(m), 997(w), 822(s), 721(m), 659(w), 577(w).

\([Co_2(bcp)_2(bib)]_n \) (3)

The synthesis procedure of 3 is similar to that for 2, except that bipy was replaced by bib (0.11mmol). C\(_{48}\)H\(_{44}\)Co\(_2\)N\(_2\)O\(_{12}\) (958.71). Calcd: C, 60.13; N, 2.92; H, 4.63. Found: C, 55.81; N, 2.69; H, 4.51. IR (KBr, cm\(^{-1}\)): 3072(m); 1605(vs); 1542(vs); 1419(vs); 1248(vs); 1162(s); 1046(m); 789(vs); 650(m).

\([\{Co(bcp)(4,4'-bipy)(H_2O)\} \cdot H_2O]_n \) (4)

The synthesis procedure of 4 is similar to that for 2 except that bpt is replaced by 2,2'-bipy (0.1mmol). C\(_{27}\)H\(_{26}\)CoN\(_2\)O\(_8\) (565.43). Calcd: C, 57.35; H, 4.63; N, 4.95. Found C, 57.33; H, 4.68; N, 5.01. IR (KBr, cm\(^{-1}\)): 3350(m), 2997(w), 2128(w), 1899(w), 1672(vs), 1432(vs), 1245(m), 898(w), 778(m), 648(w), 558(w).

Results and Discussion

\([\{Ni_2(bcp)_2(4,4'-bipy)_2(H_2O)_4\} \cdot 3.5H_2O]_n \) (I)

The asymmetric unit of 1 contains two independent Ni atoms (in special position), one bcp ligand (in general position), two 4,4'-bipy ligands and two independent coordinative water molecules (in general position), and some lattice water molecules. The bcp adopts bis(monodentate)[(k\(^1\)-(k\(^1\))-µ\(_2\)] mode (Schem.1c). Each Ni(II) is coordinated by two trans 4,4'-bipy ligands, two trans bcp ligands, and two trans water molecules, to give an octahedral geometry (Fig.1a). Furthermore, the water molecules bond to the uncoordinated oxygen atoms of the carboxylate ligands. The Ni-O/N bond
lengths are within the normal range. Both the 4,4'-bipy and bcp ligands simultaneously bridge adjacent two metal ions in two direction, thus, a 3D coordination polymer is produced (Fig. 2a). The metal atoms essentially act as 4-connecting nodes, and the network has CdSO$_4$\{(6\times 8) vs [6.6.6.6.6(2).*]\}$^1$ topology (Fig. 2b). The spaciousness of the net leads to the interpenetration of three identical nets (Fig. 2c). The nets are crosslinked by extensive hydrogen bonding between water molecules and the uncoordinated carboxylate oxygen atoms.

/Insert Fig. 1 and Fig. 2/

\{[Co$_2$(bcp)$_2$(bpt)$_2$]·2.29H$_2$O·bpt\}_n (2)

The structural unit contains two unique Co(II) atoms, two bcp ligands, two coordinative bpt ligands, one free bpt ligand and 2.29 lattice water molecules (Fig. 1b). The bcp adopts a (k$^1$·k$^1$)·(k$^1$·k$^1$)·µ$_4$ fashion and connects neighboring Co(II) ions(Scheme. 1b), forming a Co$_2$(RCO$_2$)$_4$ paddle-wheel units. However, the Co atoms don’t lie opposite each other across the dimer, as they would in e.g. a Cu$_2$(RCO$_2$)$_4$ dimer, but rather are offset, with weaker interactions to oxygen atoms on the opposite side of the dimer. The cobalt atoms are bridged into dimers by the carboxylate groups of four different bcp ligands; these ligands adopt a V-shaped conformation and thus the dimers are bridged into 1D chains containing large ‘loops’ between the dimers (Fig. 2b). The square pyramidal geometries of the metal atoms are completed by monodentate bpt ligands which lie in the axial site and project above and below the chains; the different sides of the chains contain crystallographically different bpt ligands.

The chains are arranged in sheets (Fig. 3a), and these sheets are arranged such that the monodentate bpt ligands project into the loops of chains in the adjacent sheets on either side of it. Each sheet has one close neighbor through which its bpt ligands project such that the coordinated pyridyl groups are roughly level with the loops in the adjoining sheet (Fig. 3b). The sheet on the other side is further away, and here the interdigitation occurs such that the uncoordinated pyridyl sets are level with the adjoining sheet loops. This larger separation creates square channels in which lie the uncoordinated water molecules and intercalated bpt molecules (Fig. 3b). Each loop of
each chain is thus penetrated by two bpt ligands from adjoining chains, in which results in new twofold 2D→3D polythreaded architecture (Fig. 3c). Recently, we have reported a new compound of \([\text{Cu}_4(\text{oba})_4(\text{bpt})_2(\text{H}_2\text{O})_3] \cdot 6\text{H}_2\text{O}\)\(^{10h}\). The structure of the Cu(II) compound exhibits a fascinating 2D→3D polythreaded architecture, which contains a side arm of bpt in one layer involving nine polymeric units at a time. Interestingly, if hydrogen bonds are taken into account, the resulting structure displays a 5-fold interpenetrated 3D motif topological framework. The difference between the and \([\text{Cu}_4(\text{oba})_4(\text{bpt})_2(\text{H}_2\text{O})_3] \cdot 6\text{H}_2\text{O}\)\(^n\) suggests that the coordinative mode of bpt may play an important role in modulating the interpenetrated character.

\[\text{[Co}_2(\text{bcp})_2(\text{bib})]_n\ (3)\]

The structure of 3 contains one unique Co atom, half unique bib and one unique bcp ligand. The Co(II) atom is coordinated by four oxygen atoms from two adjacent bcp ligands and one nitrogen atom to provide the square-pyramidal geometry. However, Co1 could be considered to have octahedral coordination if the second Co1-O6 bond of 2.293 Å was taken into account (Fig. 1c). The Co-O/N bond lengths are within the normal range. The bcp adopts a \((k^1-k^1)-(k^1-k^1)-\mu_4\) fashion. Two crystallographically equivalent Co(II) atoms are linked by four carboxylate groups of bcp using bis(bidentate) mode to give a paddle-wheel unit of \([\text{Co}_2(\text{CO}_2)_4]\) fragment in which the Co···Co distance is 2.878(4) Å. These dimers are connected via the backbones of the bcp ligands such that each pair of adjoining dimers is connected by two bcp ligands, in which result in the ‘loops’ motif. These chains are then crosslinked by 4,4’-bipy ligands, which bond to the axial positions of the dimers and create the (4,4) sheet (Fig. 4a).

Pairs of sheets interpenetrate in a 2D→2D parallel fashion, as shown in Fig. 4b. The interpenetration is such that each metal-bcp loop has a flexible bib ligand from the other net passing through it. The sheets individually can be described as having (4,4) topology, however, this description simplifies the loops into a single linkage and thus becomes inadequate for describing the interpenetration (Fig. 4c). Thus, the net could be better described as 6-connected 2\(^2\),4\(^8\),6\(^5\) topology containing polyrotaxane and polycatenane feature (Fig. 4d-4e).\(^{11e}\)
It has been noted that aromatic chelating ligands (such as 2,2'-bipy and 1,10-phen) often lead to low dimensional polymers and may provide potential supramolecular recognition sites for π–π aromatic stacking interactions to form multi-stranded helices.\(^{22}\) In the structure of 4, there is one Co\(^{II}\) atom, one bcp ligand, and one 2,2'-bipy ligand, one coordinated water molecule and one lattice water molecule in each unit (Fig. 1d). Each Co\(^{II}\) atom in 4 is primarily coordinated by three oxygen atoms from two carboxylate groups of adjacent bcp ligands and one coordinated water molecule, and two nitrogen atoms from a chelating 2,2'-bipy to furnish a distorted octahedral geometry. Each pair of adjacent Co\(^{II}\) atoms is bridged by bcp ligands to form a chain running along the \(b\)-direction with a long pitch of 16.3 Å (Fig. 5a). These chains are further extended into two-dimensional (2D) networks through interdigitation of the lateral 2,2'-bipy ligands from adjacent chains (Fig. 5b). The offset fashion with a face-to-face distance is 3.76(8) Å, indicating aromatic π–π stacking interactions (Fig. 5c).\(^{22}\) To the best of our knowledge, such zipper-like double-stranded helical chains have been documented in some examples.\(^{23}\) The double-stranded helical chain is stabilized by hydrogen bond interactions between the uncoordinated oxygen atoms of carboxylate groups and the water molecules.

/Fig. 3, Fig. 4 and Fig. 5/

**Comparison of the structures of coordination polymers**

The simultaneous use of the N-donors and aromatic V-shaped dicarboxylate ligands affords diverse entangled networks. Herein, we systematic explored the coordination chemistry of bcp ligand, and constructed some new entangled motifs in our group, as concluded in Scheme. 2. Although we are unable to propose definitive reasons as to why the compounds exhibit different topologies with our present state of knowledge, some of the general trends observed are discussed below.

**Effect of secondary ligand:**

The polymers are strongly related to the secondary ligand. The following discussion provides a qualitative explanation for this conclusion. Although the 4,4'-bipy, 2,2'-bipy, bpt and bib ligands are all neutral N-containing linkages, they are quite
different. For example, the bpt has an angular disposition of its terminal pyridyl spacers due to its central thiaiazole ring and two more potential N-donor atoms, which may favor to construct the unexpected and unpredictable motifs.\textsuperscript{13,24} Recently, we have reported one new entangled compound of \{[Co\textsubscript{2}(bcp)\textsubscript{2}(bpt)\textsubscript{2}·2H\textsubscript{2}O]\}_n, which shows 3D 6-connected net with \(2^3\cdot4^8\cdot6^5\) topology containing polyrotaxane character and unusual self-penetrating topology.\textsuperscript{10b} For instance, the bpt taking a monodentate mode binds to metal center in 2, whereas for 1, the 4,4'-bipy adopts bridging mode to extend the full network. The free bpt ligand in compound 2 may be one of the important factors for the construction of the structure as it might function as templates and occupy the pores, thus preventing higher dimensional network. Furthermore, the existence of coordinated water molecules in complex 1 is also one important factor in inducing the coordinative mode of bcp. The different feature of neutral ligand in 1 and 2 may explain the different coordination of bcp ligand. These feature leads to the formation of completely different coordination architectures in 1 and 2. While in 2 and 3, although bcp and metal center have the similar coordinative modes, the resulting network are different. The difference may be caused by the different intrinsic skeletons between bpt and bib. In compounds 1 and 3, the N-donor ligands of 4,4'-bipy and bib shows bis(monodentate) fashion, the sizes of backbones are different. Thus, only a molecular ring of [Co(bcp)]\textsubscript{n} is observed in 3. To further examine the influence of the secondary ligand on the self-assembly entities, an aromatic chelating ligand 2,2'-bipy was introduced into Co-bcp system. Consequently, compound 4, featuring zipper-like chain structure, was obtained. The neighboring chains make double-stranded chains through supramolecular recognition. This could be related to the fact that chelating ligands such as 2,2'-bipy serve as a “passive” role in occupying coordinative sites on metal centers and produce steric constrains.\textsuperscript{8a} Comparing the neutral ligands in 1 and 3, the difference is the position of the pyridyl ring. The 2,2'-bipy ligand has a comparatively large steric hindrance, which may decrease the ability of coordination to metal ion and result in the low dimensional network. The V-shaped and flexible carboxylate ligand bcp is also fundamental for the construction of chains in the presence of terminal ligands such as phen and
2,2'-bpy, while the linear ligands bpt and 4,4'-bipy contribute to higher
dimensionalities in complexes 1 and 2, thus showing that the shape of the ligands
plays an important role in the architecture of complexes. Thus, the ancillary ligand has
a significant effect on the formation and structure of the coordination polymers. In
order to construct peculiar topological polymers, an effective method can be to
introduce different ancillary ligands.

**Effect of metal nature:**

It is interesting that, although 1 and \([\text{Co(bcp)}(4,4'-\text{bipy})_{0.5}]_n\) bind to the same
organic ligands, the Co\(^{\text{II}}\) and Ni\(^{\text{II}}\) complexes give completely different products.\(^{11e}\)

From the above description, the compound dimeric Co(II) unit exhibits 6-connected
nets with \(2^2.4^8.6^5\) topology containing polyrotaxane character, while the compound 1
only has one metallic unit and shows three-fold interpenetrating \(\text{CdSO}_4\) topological
motif. Furthermore, the Co(II) and Ni(II) ions have the similar distorted octahedral
geometries, but their coordination environments are different. In compound of
\([\text{Co(bcp)}(4,4'-\text{bipy})_{0.5}]_n\), there are two bis(bidentate) bcp and two 4,4'-bipy ligands
around the metal ions, whereas in complex 1, which contains two bis(monodentate)
bcp ligands, two 4,4'-bipy ligands and two terminal water molecules around the metal
ions. More ligands surround each Co(II) ion than that of the Ni(II) ion. We also
reported a polymer of \([\text{Mn}_2(\text{bcp})_2(\text{bpe})(\text{DMF})]\)_n, which contains tetranuclear
subunit and shows 2D→3D inclined interpenetration motif with polyrotaxane
character.\(^{25}\) The results indicate that the metal radius may promote interpenetration
and higher dimensionality. Similar results are found for the other complexes with
related dicarboxylate ligands.\(^{26}\) A rational assembly of metal ions is critical for the
formation of novel and higher dimensional networks.

**Ligand-to-metal molar ratio:**

Two distinct structures of two compounds \([\text{Co}_2(\text{bcp})_2(\text{bpp})_2(\text{H}_2\text{O})_2]]_n\) and
\([\text{Co}_2(\text{bcp})_2(\text{bpp})_2\text{CH}_3\text{OH}]_n\) were reported in our recent communication.\(^{13}\) The
former compound shows an unique interlaced sextuple-stranded molecular braid,
which is interwoven by three double-stranded \textit{meso}-helices. When the ligand: metal
molar ratio is 2:1, the structure of the latter set undergoes a 2D sheet, which reveals a
three-fold 2D→3D parallel interpenetrating motif. A compound of
\([\text{Co}_2(\text{bcp})_2(\text{bpt})_2 \cdot 2\text{H}_2\text{O}]_n\), with metal-ligand stoichiometry of 1:1, exhibits Pcu
motif containing unusual self-penetrating topology\textsuperscript{19d} whereas polymer 2, with a
Co(II): bpt stoichiometry of 1:0.5, adopts 2D→3D polythreaded architecture. Not
surprisingly, the multimodal ligand, with an enhanced number of donor atoms, was
particularly sensitive to the metal-to-ligand ratio.\textsuperscript{11a}

Condition of the syntheses

The pH values of the reaction solutions play a role in determining the final
products. The pH values of the reaction solutions will be significantly decreased after
crystallization of complexes 1-4, whereas for \([\text{Co}_2(\text{bcp})_2(\text{bpp})_2(\text{H}_2\text{O})_2]_n\), it is
slightly higher pH value (ca. 7.5).\textsuperscript{13} A possible explanation for this observation is that
the isolation of complexes 1-3 incorporation of rigid N-donor component will affect
relevant the solution concentration of basicity. Moreover, with regard to other metal
ions (Co(II) and Mn(II)), such a pH effect on the assembly is not valid, indicating its
specific selectivity to Ni(II).\textsuperscript{11,13,25,19d}

As discussed above, a variety of framework structures can be achieved on the basis
of the choice of secondary ligands, ligand-to-metal molar ratio and metal ions.
However, all the variable factors cannot be accurately forecasted at this stage.

/Scheme 1 and Scheme 2/

Thermogravimetric Analyses and XRPD

To study the stabilities of the polymers, thermogravimetric analyses (TGA) of
complexes 1-4 were performed (Fig. S1). The compound 1 shows two of weight loss
steps. The first weight loss began at 20°C and completed at 208°C. The observed
weight loss of 8.8% is corresponding to the loss of the water molecules (calcd 7.37%).
The second weight loss occurs in the range 230–539°C, which can be attributed to the
elimination of bipy and bcp ligands. The compound 2 also has two observed weight
loss, first weight loss of 19.2% is corresponding to the loss of the crystallization water
and free bpt (calcd 18.6%). A gradual weight loss from 251 °C dictates that the
complex was decomposing continuously when the temperature was rising up. The
20.4% mass remnant at 336 °C is consistent with CoO (22.1 % predicted). The
compound 3 shows one of weight loss step. The mass of 3 remains largely unchanged until the decomposition onset temperature of ca. 360 °C. All removal of organics was completely by 770 °C, indicated by a further weight loss, roughly consistent with expulsion of the bcp and bib ligands. The compound 4 also has two observed weight loss, first weight loss of 6.4% is corresponding to the loss of the crystallization water and coordinated water molecule (calcd 7.1 %). A precipitous weight loss of 79.5 % was completed by 805 °C, corresponding to fracture of the net with the expulsion of all organic ligands.

Additionally, to confirm the phase purity of compounds, the original samples were characterized by X-ray powder diffraction (XRPD) at room temperature. The patterns that were simulated from the single-crystal X-ray data of compounds were in agreement with those that were observed (Fig. S2).

**Magnetism**

The $\chi_A T$ value for 2 was 3.31 cm$^3$ K mol$^{-1}$ at 300 K, and this is much larger than the spin only value (1.88 cm$^3$ K mol$^{-1}$) for the $S = 3/2$ state, but close to the value (3.38 cm$^3$ K mol$^{-1}$) when the spin and orbital moment exist independently. When decreasing the temperature, the $\chi_M T$ decreases gradually and reaches a local minimum (0.24 cm$^3$ K mol$^{-1}$) at ~20 K. In the $\chi_M$ versus $T$ plot, the local maximum was observed at ~210-220 K, and this indicates the antiferromagnetic interaction between Co ions in the paddle-wheel dimer (Fig. 6a). When the data above 150 K were analyzed using a dimer model, the $J$ value was estimated as ~76 cm$^{-1}$. However, the behavior below 50 K cannot be explained by the dimer model. In the $\chi_M$ versus $T$ plot, the local minimum was observed at ~50 K, and $\chi_M$ increased significantly below ~20 K; in the $\chi_M T$ versus $T$ plot, a local maximum (0.46 cm$^3$ K mol$^{-1}$) is observed at ~10 K. If the 1-dimensional alternating chain model is used, the parameters were obtained as follows; $J = -77.5$ cm$^{-1}$, $\lambda = -173$ cm$^{-1}$, $\kappa = 0.90$, $\nu = -0.13$ cm$^{-1}$, TIP = 0.0018 cm$^3$ mol$^{-1}$, angle = 24°, $J' = -2.0$ cm$^{-1}$, $\alpha = 0.80$ and the agreement factor $R = 8.6 \times 10^{-4}$. That means that it is an alternating chain with $J_1 = -140$ cm$^{-1}$ and $J_2 = -16$ cm$^{-1}$, and the increase in $\chi_M$ below 50 K may be due to the dimensionality (Fig. 6a). In this simulation, antiferromagnetic interaction between
chains were considered, and the interaction per one Co was estimated as $J' = -2.0$ \text{cm}^{-1}; although the fitting quality below 20 K was not satisfactory, the decrease in $\chi_A T$ below 10 K may be due to the antiferromagnetic interaction between the chains. The angle (24°) corresponds to the crystal structure (22.1°) well. The obtained TIP value seems to be large, but this may be due to the higher states with orbital angular momentum. The $-2J$ value of 2 is in the normal range for the dinuclear cobalt-carboxylate complexes.\(^{28}\)

The $\chi_M T$ value per dinuclear cobalt(II) unit in 3 was 6.24 cm\(^3\) K mol\(^{-1}\) at 300 K, and this is much larger than the spin only value (3.75 cm\(^3\) K mol\(^{-1}\)) for the $S = 3/2$ state, but close to the value (6.75 cm\(^3\) K mol\(^{-1}\)) when the spin and orbital momenta exist independently. When decreasing the temperature, the $\chi_A T$ decreases gradually and reaches a minimum (0.22 cm\(^3\) K mol\(^{-1}\)) at 2.0 K. In the $\chi_M$ versus $T$ plot, the local maximum was observed at ~10 K, and this indicates the antiferromagnetic interaction between Co ions in the dinuclear unit. When the data was analyzed using a dimer model [28], the parameters were obtained as follows: $J = -5.9$ cm\(^{-1}\), $\lambda = -107$ cm\(^{-1}\), $\kappa = 0.66$, $\nu = 4.29$ cm\(^{-1}\), $\theta = -0.66$ K, TIP = 0.0018 cm\(^3\) mol\(^{-1}\) and the agreement factor $R = 6.1 \times 10^{-4}$. As shown in Fig. 6b.

It is well-know that for exchange interaction in these molecules, a superexchange mechanism governs a main metal-metal interaction, in which the electronic structure of the bridging of the O-C-O moiety determines the magnitude of the antiferromagnetic interaction. The parameter $\Phi_{\text{bend}}$ of the Co-O-C-Co is very important. It is well-know that the larger $\Phi_{\text{bend}}$ could generate a larger decrease in $-2J$ because of reduced overlap of the Co $d_{x2-y2}$ orbital with the 2px carboxylate oxygen orbital in the symmetric HOMO.\(^{29}\) In the case of 2, the $\Phi_{\text{bend}}$ is 11.5(3)°, which is slightly smaller than that of [Co\(_2\)(oba)\(_2\)(bib)·H\(_2\)O], and larger than that observed for [Co\(_3\)(oba)\(_3\)(bpmp)\(_2\)].\(^{29c}\) According to the structure of compound 2, it could be presumed that the main magnetic interactions between the paddle-wheel unit metal centers, while the superexchange interactions between Co ions through the bcp bridge can be ignored due to the length of the bcp ligands.

/Insert Fig. 6/
Conclusion

In conclusion, we have presented a rational synthetic strategy that successfully achieved a family of interesting polymeric entangled compounds by a combination of flexible dicarboxylate ligand and different N-donor ligands. Although the resulting structural motifs are impossible to predict with our present state of knowledge, the strategy reveals a potential approach for rational design of entangled systems with long flexible ligands. Accordingly, this present findings herein will further enrich the crystal engineering strategy and offer the possibility of modulating the formation of desired solid-state materials.

Acknowledgments

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References:


(13) (a) J. J. M. Amoore, C. A. Black, L. R. Hanton and M. D. Spicer, *Cryst. Growth Des.*, 2005, 5, 1255; (b) F. Y. Cui, K. L. Huang, Y. Q. Xu, Z. G. Han, X. Liu, Y. N. Chi and C. W. Hu,


(16) G. M. Sheldrick, SADABS 2.05; University of Göttingen: Germany, 2002.


Fig 1. The structures of compounds: (a) the coordination geometry of the metal centre and the ligand geometry in 1 (symmetric code: (i) \(-x+3/2, -y+1, z\); (ii) \(-x, y, -z+1/2\); (b) the coordination geometry of the metal centre and the ligand geometry in 2; (c) the coordination geometry of the metal centre and the ligand geometry in 3 (symmetric code: (i) \(-x-1, -y+2, z\); (ii) \(-x+1, y+1, z\); (c) the coordination geometry of the metal centre and the ligand geometry in 4.

Fig. 2 (a) The 3D coordination polymer of 1. Hydrogen atoms and water molecules are omitted for clarity; (b) a schematic representation of the CdSO$_4$ (cds) network topology; only the metal atoms are shown; links represent the bridging ligands; and (c) the three interpenetrating networks.

Fig 3. The structure of compound 2: (a) A single layer of 1D chains in the structure of 2; (b) Interdigitation of adjacent layers of chains, and the formation of channels contains intercalated
water and bpt molecules; (c) The penetration of one chain loop by two bcp ligands from adjoining chains; the metal atom coordinated to the bcp ligand is included in this view to indicate the coordinated and uncoordinated pyridyl groups.

Fig. 4 (a) a perspective view of the sheet-like structure; (b) schematic view of two-interpenetrated network; (c) a representation of interlocked nets; (d) the polyrotaxane motif; (e) the polycatenane motif in 3.

Figure 5: The structure of compound 4: (a) viewing of the 1D helical chain; (b) the 2D supramolecular sheets formed by aromatic stacking interactions; and (c) optional view of zipperlike double-stranded chains.

Fig. 6 (a) Plots $X_M T$ versus $T$ for 2, and (b) plots $X_M T$ versus $T$ for 3, solid lines represent fits to the data.
Scheme 1. The kinds of coordinative modes for bcp ligand.

Scheme 2. Conclusion of the coordination chemistry of bcp ligand. [11a,11e,19d, 25]
Table 1 the crystallographic data of 1–4.

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<td>Pī</td>
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Table 2. Selected bond distances (Å) and angles (°)

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