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Topological Diversification in Metal-Organic Frameworks: Secondary Ligand and Metal Effects

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A series of interesting coordination polymers have been prepared by the combination of a V-shaped 4,4'-oxybis(benzoic acid) (H₂oba) and neutral organonitrogen ligands with different metal ions, namely, {[M(oba)(bpe)]·H₂O}_n [M = Mn (1), Co (2)], [M(oba)(N3)]_n [N3 = dipyridin-2-ylamine; M = Cd (3), Cu (4)] and {[Zn(oba)(N5)]·2H₂O}_n (5) [bpe = 1,2-bis(4-pyridyl)ethene, N5 = bis(pyridin-2-yl)pyridine-2,6-diamine]. The framework structures of these neutral polymeric complexes have been determined by single-crystal X-ray diffraction studies. Compound 1 has a threefold pcu-type network structure. Although 2 has the same ligands and coordination modes as 1, it consists of corrugated 2D layers formed of a series of squares, which allows the sheets to interpenetrate in an unusual 2D \rightarrow 3D parallel fashion. Polymers 3 and 4 ex-

Introduction

The crystal engineering of metal-organic frameworks (MOFs) is of great current interest not only because of their significant potential functions in gas storage, chemical separations, microelectronics, nonlinear optics, and heterogeneous catalysis, but also because of their intriguing architectures and intricate entangled motifs.^[1-3] The mutual entanglement of structural motifs is a commonly encountered feature in coordination polymer chemistry.^[1a-1d,2a,3-5] However, the formation of extended coordination framework solids with desired structural features and/or physicochemical properties greatly depends on the sophisticated selection and utilization of multitopic building blocks as well as tectonic interactions.^[1a,6] Conformationally nonrigid ligands are usually building elements for the assembly of interesting entangled networks, thanks to their varied geometries.^[7,8] 4,4'-Oxybis(benzoic acid) (H₂oba) is a typical example of a long, V-shaped, flexible ligand which has been used to promote the formation of polycatenated and self-penetrating

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hibit double-helical chains formed by π - π stacking interactions from the phenyl rings of the N3 ligands. Compound **5** forms a 2D supramolecular architecture directed by hydrogen bonding between the NH groups of the N5 ligand, the uncoordinated carboxylate oxygens, and the intercalated water molecules. This work markedly indicates that the effect of auxiliary ligands is significant in the construction of these network structures, which are also well regulated by the metal centers. Thermogravimetric analysis (TGA) and XRPD results for compound **1** as well as luminescent properties for compounds **3** and **5** are discussed.

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coordination polymers. For instance, $\{[Cu(oba)(H_2O)]_2, 0.5H_2O\}$ exhibited a unique fivefold 4-connected 4^28^4 (lvt)^[9a,9b] interpenetrating structure with nine interwoven helices.^[9c,9d]

On the other hand, in the two-ligand MOF assembly systems, both organic and inorganic secondary ligands can manipulate the structural topologies through coordination in either terminal or bridging fashions.^[10] For example, Cao and his coworkers used the secondary ligands as terminal and bridging ligands to tune the formation of helical structures.^[11] As for the dipyridyl ligands, some analogous linkers derived from the proper modification of the classic 4,4'bipyridine molecule have been employed,^[10] which present unrivaled backbone flexibility and thus impose profound steric effects on the direction of the unexpected coordination frameworks. Recently, we have reported a 4-crossing [2]-catenane motif based on oba and 1,3-bis(4-pyridyl)propane (bpp).^[12] However, the systematic investigation of the role of auxiliary ligands in the construction of coordination nets is not well documented to date. Therefore, the development of a comprehensive research program is required, and the rational design of new frameworks would be a longrange challenge.

With this background in mind, we continued our investigation and chose H_2 oba as a bridging ligand to react with d-block metal ions. The neutral bpe, N3, and N5 ligands were introduced into the M^{II} /oba system, and a series of



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polymers with unusual topologies were obtained, namely, $\{[M(oba)(bpe)]\cdot H_2O\}_n [M = Mn (1), Co (2)], [M(oba)-(N3)]_n [M = Cd (3), Cu (4)] and <math>\{[Zn(oba)(N5)]\cdot 2H_2O\}_n$ (5). To the best of our knowledge, compound 2 represents the first example in the M/oba system that possesses an interpenetrating $2D \rightarrow 3D$ structural feature. The crystal structures and topological analysis of these compounds, along with a systematic investigation of the effect of the coordination modes of the oba anions, metal ions, and neutral ligands on their ultimate frameworks, will be discussed.

Results and Discussion

${[Mn(oba)(bpe)] \cdot H_2O}_n$ (1)

The structure of 1 contains one unique Mn atom, one oba ligand, one bpe ligand, and intercalated water molecules (all of which are related by symmetry). The $\{MnO_4N_2\}$ coordination spheres are each defined by two oxygen atoms from one chelating oba carboxylate, two oxygen atoms from two different bidentate-bridging carboxylate groups, and two cis-oriented bpe nitrogen donors. Bond lengths and angles about the metal centers in 1 are consistent with a distorted octahedral geometry caused by the presence of chelating/bidentate-bridging ligands and are given in Table 1. The Mn-O bond lengths span a range of 2.091(4) to 2.300(4) Å. The Mn atoms are bridged into pairs by carboxylate groups, and the Mn-Mn distance is 4.276 Å (Figure 1). These Mn dimers are then connected to other dimers by the oba ligand bridges. Each oba bridge bonds to two Mn atoms through one carboxylate group to form a dimer, and then to a third Mn atom, which is part of another dimer, through the other chelating carboxylate group. The bridging mode of the oba ligand is very similar to that in the $[Co(oba)(bpa)]_n$ [bpa = 1,2-bis(4-pyridyl)ethane] complex,^[13] which may be responsible for their analo-



Figure 1. The coordination environment of the Mn^{II} atom in 1.

Table 1. Selected bond lengths [Å] and angles [°].

Complex 1			
$\begin{array}{c} \text{Complex I} \\ \hline Mn(1)-O(1) \\ Mn(1)-N(1) \\ Mn(1)-O(4)\#2 \\ O(1)-Mn(1)-O(2) \\ O(1)-Mn(1)-N(2)\#1 \\ O(2)-Mn(1)-N(2)\#1 \\ O(2)-Mn(1)-O(5)\#3 \\ \text{Symmetry codes: #1: 1} \\ \text{Symmetry codes: #1: 1} \\ \hline x = 1/2 - x = 1/2 + z \end{array}$	$\begin{array}{c} 2.304(4)\\ 2.254(4)\\ 2.097(4)\\ 57.76(14)\\ 81.11(14)\\ 90.39(14)\\ 146.64(14)\\ + x, y, 1 + z; \#2\end{array}$	$\begin{array}{l} Mn(1)-O(2) \\ Mn(1)-N(2)\#1 \\ Mn(1)-O(5)\#3 \\ O(1)-Mn(1)-N(2) \\ O(1)-Mn(1)-O(4)\#2 \\ O(2)-Mn(1)-O(4)\#2 \\ N(1)-Mn(1)-N(2)\#1 \\ \vdots \ 2 - x, -1/2 + y, 1/2 - 0 \end{array}$	2.262(4) 2.281(4) 2.099(4) 101.16(14) 151.86(14) 97.20(14) 174.50(15) z; #3: 1 +
$\frac{x, 112 - y, -112 + 2}{\text{Complex } 2}$			
$\begin{array}{c} \hline Co(1)-O(1) \\ Co(1)-N(1) \\ Co(1)-O(3)\#1 \\ O(1)-Co(1)-O(3)\#1 \\ O(2)-Co(1)-N(1) \\ O(2)-Co(1)-N(1) \\ O(2)-Co(1)-O(4)\#1 \\ O(3)\#1-Co(1)-N(2) \\ Symmetry codes: $$\#1:$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$	$\begin{array}{c} 2.011(3) \\ 2.052(4) \\ 2.166(3) \\ 97.34(10) \\ 156.00(12) \\ 105.66(9) \\ 150.68(12) \\ c, -1 + y, 1 + z. \end{array}$	$\begin{array}{c} Co(1)-O(2)\\ Co(1)-N(2)\\ Co(1)-O(4)\#1\\ O(1)-Co(1)-O(4)\#1\\ O(2)-Co(1)-O(3)\#1\\ N(1)-Co(1)-N(2)\\ O(4)\#1-Co(1)-N(2) \end{array}$	2.277(3) 2.054(3) 2.083(3) 157.87(11) 87.02(9) 96.89(13) 89.92(13)
Complex 3			
$\begin{tabular}{ c c c c c } \hline Cd(1)=O(1) \\ Cd(1)=N(1) \\ Cd(1)=O(4)\#1 \\ O(1)=Cd(1)=N(3) \\ O(1)=Cd(1)=O(5)\#1 \\ O(2)=Cd(1)=O(5)\#1 \\ O(2)=Cd(1)=O(5)\#1 \\ O(4)\#1=Cd(1)=N(1) \\ Symmetry codes: \#1: 1 \end{tabular}$	$\begin{array}{c} 2.380(13) \\ 2.302(13) \\ 2.404(11) \\ 162.9(4) \\ 96.9(4) \\ 107.6(5) \\ 105.0(4) \\ 94.9(4) \\ + x,1/2 - y, 1/2 \end{array}$	Cd(1)-O(2) Cd(1)-N(3) Cd(1)-O(5)#1 O(1)-Cd(1)-O(4)#1 O(2)-Cd(1)-N(1) O(2)-Cd(1)-N(4)#1 N(1)-Cd(1)-N(3) O(5)#1-Cd(1)-N(1) + z.	2.348(12) 2.288(13) 2.342(11) 104.7(4) 103.7(4) 153.7(4) 84.4(4) 150.7(4)
Complex 4			
$\begin{array}{c} Cu(1)-O(1)\\ Cu(1)-N(1)\\ Cu(1)-O(3)\#1\\ O(1)-Cu(1)-O(2)\\ O(1)-Cu(1)-N(3)\\ O(1)-Cu(1)-N(3)\\ O(2)-Cu(1)-N(3)\\ O(3)\#1-Cu(1)-N(3)\\ Symmetry codes: \#1: 1\end{array}$	$\begin{array}{r} 2.414(2)\\ 1.970(2)\\ 2.4524(19)\\ 57.96(8)\\ 104.09(8)\\ 102.35(7)\\ 95.04(9)\\ 93.96(8)\\ +x,1/2-y,1/2+\end{array}$	Cu(1)-O(2) Cu(1)-N(3) Cu(1)-O(4)#1 O(1)-Cu(1)-N(1) O(1)-Cu(1)-O(3)#1 O(2)-Cu(1)-N(1) O(2)-Cu(1)-O(3)#1 O(4)#1-Cu(1)-N(3) z.	1.984(2) 1.988(2) 2.0137(18) 100.71(8) 155.62(7) 158.51(9) 104.82(7) 152.01(9)
Complex 5			
$\begin{array}{c} Zn(1)-O(1)\\ Zn(1)-N(3)\\ Zn(1)-O(4)\#1\\ O(1)-Zn(1)-N(1)\\ N(1)-Zn(1)-N(3)\\ O(4)\#1-Zn(1)-N(3)\\ O(4)\#1-Zn($	2.093(3) 2.107(4) 2.063(3) 89.15(15) 91.73(16) 125.47(16)	Zn(1)-N(1) Zn(1)-N(5) O(1)-Zn(1)-N(3) N(1)-Zn(1)-N(5) O(4)#1-Zn(1)-N(5)	2.065(4) 2.088(4) 134.46(15) 176.37(16) 84.22(16)
Symmetry codes: #1: -	-1 + x, y, z.		



Figure 2. A view of a layer of squares in the structure of 1.



gous structures. The dimers are thus bonded to four oba ligands, two of which bridge the Mn atoms to form the dimer, and two others which each chelate to a different Mn atom in the dimer. The dimers thus act as a 4-connecting node to generate a layer formed of a series of squares (Figure 2). These sheets are then bridged by the bpe ligands to generate a 3D network. Each Mn dimer is bridged to a dimer in the sheet above and below by pairs of bpe ligands (Figure 3). If each pair is treated as a single link, the dimers become 6-connecting nodes, and the overall topology is that



Figure 3. A single box-like cavity in 1 formed by the bridging of the layers in Figure 2 by the oba ligands.



Figure 4. The three interpenetrating pcu networks in 1. Nodes represent the centers of the Mn dimer nodes, and the links represent either oba ligand bridges or pairs of oba ligand bridges.

of a pcu-related net. Figure 4 shows a single box-like cavity of the net; the openness of the single net leads to three interpenetrating networks.

$\{[Co(oba)(bpe)] \cdot H_2O\}_n$ (2)

The asymmetric units of **2** crystallize in the triclinic $P\bar{1}$ space group (Table 2). Both contain one divalent metal atom, one oba ligand, one bpe ligand, and one lattice water molecule. The structure consists of a corrugated 2D layer formed of a series of squares in which the metal ions are bridged in one direction by the oba ligand and in the other by the bpe ligand. The open, corrugated nature of the sheets allows them to interpenetrate in an unusual 2D \rightarrow 3D parallel fashion,^[14] as shown in Figure 5. Each sheet is penetrated by two others (one above and one below), which have parallel but not coincident mean planes. This leads to an overall 3D entanglement, which is a very uncommon motif. This structure is isomorphous with the {[Cu(oba)(bpe)]·H₂O}_n compound, which was investigated in detail in our previous communication.^[14]



Figure 5.The unusual $2D \rightarrow 3D$ parallel interpenetration of the sheets in **2**.

$[M(oba)(N3)]_n [M = Cd (3), Cu (4)]$

It has been noted that aromatic chelate ligands (such as 2,2'-bipyridine and 1,10-phenanthroline) often lead to 1D polymers and may provide potential supramolecular recognition sites for π - π aromatic stacking interactions to

Table 2. Crystal data and structure refinement information for compounds 1-5.

Compounds	1	2	3	4	5
Formula	C ₂₆ H ₂₀ MnN ₂ O ₆	C ₂₆ H ₂₀ CoN ₂ O ₆	C ₂₄ H ₁₇ CdN ₃ O ₅	C ₂₄ H ₁₇ CuN ₃ O ₅	$C_{29}H_{25}ZnN_5O_7$
FW	511.38	515.37	539.82	490.96	620.93
Temp. / K	298(2)	298(2)	298(2)	298(2)	298(2)
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	ΡĪ	$P2_1/c$	$P2_1/c$	$P2_1/c$
a / Å	10.697(3)	9.314(5)	12.732(10)	12.327(2)	14.8933(11)
<i>b</i> / Å	18.619(5)	11.334(7)	15.832(13)	15.540(3)	8.1547(6)
c / Å	12.600(3)	12.472(7)	11.304(9)	11.252(2)	23.1093(17)
a / °	90	69.658(9)	90	90	90
β/°	107.418(5)	80.316(9)	94.529(10)	96.093(3)	90.1890(10)
γ/°	90	87.866(9)	90	90	90
$V / Å^3$	2394.4(11)	1216.6(12)	2272(3)	2143.3(7)	2806.6(4)
Z	4	2	4	4	4
F (000)	1052	530	1080	1004	1280
$D_{\rm c}$ / g cm ⁻³	1.419	1.407	1.578	1.521	1.469
GOF	0.784	0.638	1.033	0.513	1.085
$R_1^{[a]} [I > 2\sigma(I)]$	0.0562	0.0379	0.1205	0.0294	0.0574
$_{W}R_{2}^{[a]}$ (all data)	0.1831	0.0616	0.3499	0.0382	0.1910

[a] $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|$, $wR_2 = \{\sum [w(F_0^2 - F_c^2)^2] / \sum (F_0^2)^2\}^{1/2}$.



Figure 6. The coordination environment of the Cd center in 3.

form multistranded helices.^[7g] Therefore, the heterocyclic aromatic chelate ligands, N3 (dipyridin-2-ylamine) and N5 [bis(pyridin-2-yl)pyridine-2,6-diamine], were introduced with the aim of synthesizing noninterpenetrating 1D nets. In contrast to other aromatic chelate ligands (2,2'-bipyridine), the tailored diimine contains an active amine (–NH) hydrogen, and the aromatic rings in N3 and N5 may induce intermolecular hydrogen bonding and π - π stacking interactions to lead to stable supramolecular networks.

Compounds 3 and 4 are isostructural, and thus only 3 is described here in detail. In the crystal structure of 3, there is one Cd^{II} atom, one bis(bidentate) oba ligand, and one N3 ligand in each independent crystallographic unit (Figure 6). Each Cd^{II} atom in **3** is primarily coordinated by four oxygen atoms from two bis(bidentate) oba ligands and two nitrogen atoms from a chelating N3 to establish a distorted octahedral geometry. The average Cd-O bond length is 2.36 Å, and the largest O-Cd-O angle is 153.7(4)°, which indicates a distorted octahedral coordination sphere. Each pair of adjacent Cd^{II} atoms is bridged together by an oba ligand to form a chiral chain running along a crystallographic 2_1 axis in the *b* direction with a long pitch of 15.1 Å. These chains are decorated with N3 ligands alternating on two sides and are further extended into 2D networks through interdigitation of the lateral N3 ligands from adjacent chains in a zipper-like, offset fashion with a faceto-face distance of ca. 3.72 Å, which indicates aromatic π -



Figure 7. View of a zipper-like double-chain in the structure of 3.

 π stacking interactions (Figure 7).^[7g] To the best of our knowledge, such zipper-like double-stranded helical chains have been documented for only one previous example.^[15] The double-stranded helical chains are stabilized by hydrogen bonds between the carboxylate oxygen atom (O4) and the nitrogen atom of the –NH group of the N3 ligand.

${[Zn(oba)(N5)] \cdot 2H_2O}_n$ (5)

When N5, a chelating aromatic ligand of a larger size, was used instead of N3 under similar reaction condition, an analogous neutral single-stranded chain is formed (5). As illustrated in Figure 8, the oba ligand adopts a bis(monodentate) mode and links neighboring Zn1 atoms to form a single-stranded chain. Zn1 is coordinated by two oxygen atoms from two different oba ligands [Zn1-O4 2.062(3), Zn1–O1 2.095(3) Å] and three nitrogen atoms from a tridentate N5 ligand [Zn-N1 2.063(4), Zn1-N5 2.087(4), Zn1-N3 2.106(4) Å]. The two oxygen atoms of the carboxylate are located in two apical positions and establish a trigonal bipyramidal N₃O₂ geometry for the Zn atom. Unlike those in 3, the N5 ligands are attached to only one side of the single-stranded helical chain, and are oriented perpendicularly to the chain. The approximately perpendicular orientation of the N5 ligands allows for pairing of two centrosymmetrically related single-stranded helical chains directed by hydrogen bonds between an uncoordinated oxygen atom of a carboxylate group and the nitrogen atom of one of the -NH groups. These pairs are then further interconnected into 2D layers by hydrogen bonding between the other -NH groups, the intercalated water molecules, and the other uncoordinated carboxylate groups. Notably, the lateral N5 ligands from adjacent chains are not paired to



Figure 8. The coordination environment of the Zn^{II} ion in compound 5. All hydrogen atoms have been omitted for clarity.



afford π - π stacking interactions, which may be attributed to the improper orientation between N5 molecules. The lattice water molecules intercalate into the spaces between the chains and form small water clusters, as shown in Figure 9. The lattice water molecules further bind to the uncoordinated oxygen atom (O5) to generate a chair-like formation.



Figure 9. View of a pair of hydrogen-bonded chains in 5.

Comparison of the Structures of Coordination Polymers

The simultaneous use of the flexible, rigid, and aromatic chelating ligands and the aromatic V-shaped dicarboxylate ligands affords diverse entangled networks, as shown in Scheme 1. 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 the Secondary Ligand

The connectivities of the polymers are strongly related to the secondary ligand. The following discussion provides a qualitative explanation for this conclusion. Although the bpp and bpe ligands are both neutral N-containing linkers, they are quite different. For example, the bpp ligand can assume different conformations (TT, TG, GG, and GG') that display quite different N-to-N distances,^[16] and it is more flexible than bpe. When the bpp ligand was introduced into the Cu^{II}/Co^{II}/Ni^{II}/H₂oba system, we obtained three 2D isostructural polymers displaying 4-crossing [2]catenane motifs (Figure S1).^[12] Another two isostructural polymers (2 and { $[Cu(oba)(bpe)] \cdot H_2O_n^{[14]}$) with 2D layers made up of a series of squares were prepared by the combination of bpe, oba, and Cu^{II}/Co^{II}. In these structures, however, each sheet is penetrated by two others (one above and one below), which have parallel but not coincident mean planes, to lead to an unusual 3D entanglement. Jin and his coworkers obtained a 3D threefold architecture for the [Co $(oba)(bpa)]_n$ complex.^[13] The presence of flexible bpa ligands may play an important role in the generation of further interpenetration in the $[Co(oba)(bpa)]_n$ complex. Furthermore, the coordination modes of the oba ligands in the $[Co(oba)(bpa)]_n$ and $[Co(oba)(bpe)]_n$ complexes are different. To further examine the influence of the secondary ligand on the self-assembly of supramolecular entities, two aromatic chelate ligands were used instead of bpp and bpe. Consequently, 3 and 4, featuring helical chain structures, were obtained. The neighboring chains make zipper-like double-stranded chains through supramolecular recognition. In contrast, the presence of the larger aromatic N5 ligands weakens the π - π stacking interactions in 5 and results in the formation of 2D grid-like nets in the presence of hydrogen bonds. Thus the ancillary ligand has a significant effect on the formation and structure of the coordination polymers. In order to construct polymers of peculiar topologies, an effective method can be to introduce ancillary ligands.

Effect of the Metal Nature

It is interesting that, although 1 and 2 bind to the same ligands and have similar molecular compositions, the Co^{II} (2) and Mn^{II} (1) complexes give completely different products. From the structural descriptions above, the Mn^{II} compound 1 contains three interpenetrating 3D pcu-type nets. while the Cu^{II}/Co^{II} complexes **2** have 2D undulated layers formed of a series of squares. Furthermore, the Co^{II} and Mn^{II} ions are all hexacoordinate and have distorted octahedral geometries, but their coordination environments are different. In compound 2 there are two chelating oba and two bpe ligands around the metal ions, whereas in complex 1, which contains dimeric Mn units, there is one terminal chelating and two terminal bridging oba ligands and two bpe ligands around each metal ion. More ligands surround each Mn^{II} ion than the Cu^{II}/Co^{II} ions. Moreover, the oba ligand adopts chelating-bidentate and bridging-bidentate coordination modes in 1, which promotes interpenetration and higher dimensionality. Similar results are found for the other complexes with oba ligands in the presence of flexible ligands.^[13] A rational assembly of metal ions is critical for the formation of novel and higher dimensional networks.

As discussed above, a variety of framework structures can be achieved on the basis of the choice of the different



Scheme 1. Reactions of the oba ligand.

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secondary ligands. Their network arrays vary from 2D open layers (4-crossing [2]-catenane motifs^[12] and unusual $2D \rightarrow 3D$ parallel interpenetration) and 3D porous structures (3D threefold interpenetration) to zipper-like doublestranded helical chains. On the other hand, the choice of metal center may also tune the resultant extended networks of the MOFs. However, all the variable factors cannot be accurately forecasted at this stage.

Thermogravimetric Analyses

To study the stability of the polymers, thermogravimetric analysis (TGA) of complex 1 was performed. The TGA diagram of 1 indicates two weight loss steps. The first weight loss began at 20 °C and was complete at 125 °C. The observed weight loss of 4.3% corresponds to the loss of the lattice water molecule (calcd. 3.6%). The second weight loss occurs in the 330-541 °C range, which can be attributed to the elimination of bpe and oba ligands (Figure S2). Additionally, to confirm the phase purity and stability of compound 1, the original sample and the dehydrated sample were both characterized by X-ray powder diffraction (XRPD) at room temperature. The pattern that was simulated from the single-crystal X-ray data of compound 1 was in good agreement with those that were observed (Figure 10), which indicates that compound 1 was obtained as a single phase. After heating of compound 1 at 150 °C for 4 h, the guest water molecule was removed (the evacuated framework is defined as 1'). The XRPD pattern of 1' is similar to that of compound 1, although minor differences can be seen in the positions, intensities, and widths of some peaks, which indicates that the framework of compound 1 is retained after the removal of the guest molecule. Immersion of the desolvated phase in H₂O regenerated a sharper XRPD pattern. Therefore the dehydration and rehydration process is reversible for the material, and it belongs to



Figure 10. Comparison of XRPD patterns of the simulated pattern from the single-crystal structure determination, the as-synthesized product, and the desolvated and resolvated phases in compound 1.

Kitagawa's third generation of MOFs, showing a dynamic nature.^[17]

Photoluminescent Properties

The emission spectra of complexes **3** and **5** in the solid state at room temperature were investigated. It was observed that an emission occurs at 386 nm (Figure S3, $\lambda_{ex} = 260$ nm) for **3**, which is larger than that of the free N3 ligand and is probably due to the H bonding, π – π stacking, and the enhanced rigidity of **3**.^[18] It was also observed that an intense emission occurred at 400 nm (Figure S3, $\lambda_{ex} = 260$ nm) for **5**. Interestingly, a clear blueshift of the emission occurs in **5**. By comparison to the spectrum of the free N5 ligand,^[18] the emission spectrum of **5** is tentatively assigned to the intraligand (π – π *) fluorescence. The blue fluorescent emission occurring in **3** and **5** suggests that they may be used as new blue-light-emitting materials.

Conclusions

In conclusion, the simultaneous reaction of secondary ligands and V-shaped dicarboxylate ligands with d-block metals affords a new type of interesting polymeric entangled compounds. Notably, the first example of the $2D \rightarrow 3D$ interpenetrating structural feature observed in **2** illustrates again the aesthetic diversity of coordinative network chemistry. Topological analysis of a series of related complexes indicates that longer and flexible secondary ligands are liable to form previously unobserved topologies. Also, the metal ion plays an important role in modulating the resulting dimensionality and topology of the frameworks. It is believed that more metal complexes containing N-donor ligands and aromatic V-shaped polycarboxylate with interesting structures as well as physical properties will be synthesized.

Experimental Section

Abbreviations: bpa = 1,2-bis(4-pyridyl)ethane, bpe: 1,2-bis(4-pyridyl)ethene, bpp: 1,3-bis(4-pyridyl)propane, dde = H_2 oba: 4,4'-oxy-bis(benzoic acid), pcu: α -polonium.

Materials and Instruments: All reagents were purchased from commercial sources and used as received. IR spectra were recorded with a Perkin–Elmer Spectrum One spectrometer in the 4000–400 cm⁻¹ range using KBr pellets. The luminescent spectra of the solid samples were acquired at ambient temperature with a JOBIN YVON/ HORIBA SPEX Fluorolog t3 system (slit: 0.2 nm). TGA was carried out with a Mettler–Toledo TA 50 in dry dinitrogen (60 mLmin⁻¹) at a heating rate of 5 °C min⁻¹. XRPD data were recorded with a Rigaku RU200 diffractometer at 60 KV, 300 mA for Cu- K_{α} radiation ($\lambda = 1.5406$ Å), a scan speed of 2 °C min⁻¹, and a step size of 0.02° in 2 θ .

Synthesis of the Complexes

 $\{[M(oba)(bpe)] \cdot H_2O\}_n$ [M = Mn (1); Co (2)]: A mixture of MnSO₄·6H₂O (0.021 g, 0.11 mmol), dde (0.029 g, 0.1 mmol), bpe (0.025 g, 0.1 mmol), NaOH (0.5 M, 0.4 mL), and deionized 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 48 h. The solution was then cooled to room temperature at a rate of 5 °Ch⁻¹ to yield a very fine pale yellow crystalline product (1) in 50% yield based on Mn. C₂₆H₂₀MnN₂O₆ (511.38): calcd. C 61.29, H 3.56, N 5.50; found C 61.52, H 3.28, N 5.62. IR (KBr): $\tilde{v} = 3469$ (m), 3063 (w), 2298 (w), 1618 (m), 1597 (s), 1405 (vs), 1273 (m), 1064 (m), 882 (vs), 608 (m), 517 (w) cm⁻¹. The synthesis of **2** was performed using the same procedure as for complex **1** except that MnSO₄·6H₂O was replaced by CoSO₄·7H₂O (0.027 g,0.1 mmol). Yield: 58% based on Co. C₂₆H₂₀CoN₂O₆ (515.37): calcd. C 60.59, H 3.91, N 5.44; found C 59.88, H 4.11, N 5.23. IR (KBr): $\tilde{v} = 3461$ (m), 3058 (w), 2297 (w), 1607 (m), 1589 (s), 1410 (vs), 1275 (m), 1058 (m), 881 (vs), 605 (m), 508 (w) cm⁻¹.

[M(oba)(N3)]_n **[M = Cd (3), Cu (4)]:** Synthetic procedures similar to that for **1** were used. Yield: 52% based on Cd. C₂₄H₁₇CdN₃O₅ (539.81): calcd. C 53.39, H 3.17, N 7.78; found C 53.88, H 3.41, N 7.70. IR (KBr): $\tilde{v} = 1608$ (vs), 1552 (s), 1443 (s), 1224 (m), 858 (s) cm⁻¹. C₂₄H₁₇CuN₃O₅ (490.95): calcd. C 58.83, H 3.29, N 8.58; found C 53.88, H 3.34, N 7.75. Yield: ca. 55% based on Cu. IR (KBr): $\tilde{v} = 1605$ (vs), 1558 (s), 1446 (s), 1218 (m), 879 (s) cm⁻¹.

{[**Zn(oba)(N5)]·2H₂O**}_{*n*} (5): A synthetic procedure similar to that for **1** was used. Yield: 49% based on Zn. $C_{29}H_{25}N_5O_7Zn$ (620.91): calcd. C 56.10, H 4.06, N 11.28; found C 56.87, H 3.68, N 11.40. IR (KBr): $\tilde{v} = 13443$ (v), 3303 (s), 1621 (vs), 1558 (s), 1448 (s), 1217 (m), 871 (s) cm⁻¹.

X-ray Crystallography: Single-crystal X-ray diffraction studies of 1-5 were performed with a Bruker SMART APEX II CCD diffractometer equipped with graphite-monochromated Mo- K_{α} radiation ($\lambda = 0.71073$ Å) by using an ω -2 θ scan technique at room temperature. The structures were solved by direct methods and successive Fourier difference synthesis (SHELXS-97),^[19] and refined using the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97).^[20] The positions of the H atoms for pyridyl rings, benzene rings and -NH groups were generated by a riding model on idealized geometries, while the H atoms of water molecules were located in difference Fourier maps. In the case of 2, the final value is not ideal, which may be attributed to the quality of the crystal. Notably, the goodness-of-fit for compound 4 was only 0.513, which was also attributed to the quality of the crystal. The crystallographic data and other pertinent information for 1–5 are summarized in Table 2. Selected bond lengths and bond angles are listed in Table 1.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre: CCDC-692071 (for 1), -692072 (for 2), -692072 (for 3), and -692074 (for 4) -692075 (for 5). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Description of the 4-crossing [2]-catenane motif, TG curve for **1**, and luminescence spectra for **3** and **5**.

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