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Three-Dimensional Homochiral Transition-Metal Camphorate Architectures Directed by a Flexible Auxiliary Ligand

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Reported here are four homochiral and one racemic chiral compounds assembled from transition metals (Fe^{2+}, Co^{2+}, and Ni^{2+}), rigid enantiopure camphoric acid, and flexible 4,4′-trimethylenedipyridine; they feature an unusual homochiral three-dimensional supramolecular assembly (resulting from catenation of 4-connected bilayers) as well as a homochiral 3-fold interpenetrating diamond net and a noninterpenetrating primitive cubic net.

Crystalline open-framework materials with chiral frameworks are of great interest because of their potential applications in enantioselective processes such as catalysis and separation.[1,2] However, few traditional zeolite-type inorganic frameworks can be made homochiral in the bulk form.[3–5] Recent progresses in crystal engineering of coordination polymer frameworks have opened up new routes toward the synthesis of homochiral solids.[2,3] One successful method for the synthesis of homochiral materials is to use organic enantiopure chiral building blocks for the construction of extended frameworks.[1,6]

While it is possible to create three-dimensional (3D) homochiral frameworks using only enantiopure ligands as cross-linkers,[6e] it is often advantageous to apply a multiligand synthetic strategy because the use of two functionally different complementary ligands provides an additional level of control in the framework structure and charge density distribution. One widely used dual-ligand synthetic strategy in crystal engineering is to combine a bi- or polydentate carboxylate ligand with a diimine ligand.[7] In our earlier work on chiral D-camphorates, we observed that a predominant structural mode resulting from the use of such a dual-ligand method is the formation of neutral homochiral metal carboxylate substructures (e.g., chains or sheets) that are subsequently linked or pillared by auxiliary neutral bipyridine ligands into 3D homochiral frameworks.[6a,d] With this strategy, the topology of the homochiral framework can be controlled by using different bipyridine ligands such as 4,4′-bipyridine or *trans*-1,2-bis(4-pyridyl)ethylene. In this work, we show that different homochiral framework topologies can also result from the conformational flexibility of a single type of ligand, 4,4′-trimethylenedipyridine (TMDPy) in this case. We also show a rare and unusual example of catenation of two-dimensional (2D) bilayers into a 3D interlocked supramolecular assembly. While catenation is common in metal−organic framework materials, it is rarely observed in the homochiral framework.

Furthermore, the previous research on crystalline homochiral frameworks was often based on metal centers such as Zn^{2+} and Cd^{2+} that are generally non-redox-active. The creation of homochiral open-framework architectures containing redox-active metal centers has the potential of providing multifunctional materials that integrate enantioselective catalysis with redox catalysis. The work reported here is an early step toward this important goal.

Here we report four new homochiral and one racemic chiral 3D materials synthesized from D- or DL-camphoric acid (D- or DL-H_2Cam) and TMDPy (Table 1).[8] These materials

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Table 1. Summary of Crystal Data and Refinement Results[a]

	formula	space group	a (Å)	b (Å)	c (Å)	β (deg)	$R(F)$	Flack	topology
1	Ni(D-cam)(TMDPy)	$C222$	11.1411(2)	21.1153(5)	9.7008(2)	90.00	0.0540	0.00(3)	4^26^38
2	Co(D-cam)(TMDPy)·$2H_2O$	$P2_12_12_1$	9.6171(2)	14.5971(5)	16.3977(4)	90.00	0.0413	0.02(3)	dia (3-fold)
3	Fe_2(D-cam)$_2$(TMDPy)	$C2$	18.9760(3)	12.3214(2)	14.0540(3)	105.619(1)	0.0505	0.06(3)	pcu
4	Co_2(D-cam)$_2$(TMDPy)	$C2$	19.0446(6)	12.2585(4)	14.0227(4)	106.480(2)	0.0491	0.04(3)	pcu
4a	Co_2(DL-cam)$_2$(TMDPy)	$C2/c$	19.0677(5)	12.3768(3)	14.1151(4)	107.527(2)	0.0522		pcu

[a] H_2Cam = camphoric acid; TMDPy = 4,4′-trimethylenedipyridine.

feature an unusual homochiral 3D supramolecular assembly resulting from catenation of 4-connected bilayers (compound **1**) as well as a homochiral 3-fold interpenetrating diamond net (compound **2**) and a noninterpenetrating primitive cubic (pcu) net (crystals **3**, **4**, and **4a**). Such a topological diversity is closely associated with the conformational flexibility of the auxiliary TMDPy ligand.

Compounds **1**−**4** were prepared from enantiopure D-cam and all of them crystallized in the chiral space groups, whereas **4a** was prepared from racemic DL-cam and crystallized in achiral space group *C*2/*c*. Compound **4a** has essentially the same crystal structure as **4** (nearly identical cell constants too), with the only difference being the opposite handedness in 50% of the chiral ligands. This is also quite unusual because the packings of chiral molecules generally differ for pure enantiomers and for racemates as a consequence of differing symmetry requirements. The flexible TMDPy ligand was incorporated in all structures and plays an important role in the construction of various metal camphorate architectures (metal = Ni^{2+}, Co^{2+}, and Fe^{2+}) observed here.

The topological feature of compound **1** is most unusual because it features a previously unobserved 4-connected bilayer motif that is catenated with adjacent ones to form a 3D supramolecular structure. As shown in Figure 1a, the Ni^{2+} site is 4-connected despite its octahedral coordination. This is because each Ni^{2+} ion is bonded with two separate TMDPy ligands with the *TT* conformation[9] (Scheme 1) and two separate D-cam ligands. The central part (excluding two end carboxylic groups) of the D-cam ligand has two statistical orientations related through a 2-fold rotation axis (Figure S1 in the Supporting Information). Two carboxylate groups of the D-cam ligand chelate two Ni^{2+} ions into a homochiral zigzag chain along the *a* axis. The resulting parallel chains are doubly bridged by the TMDPy ligands, generating a bilayer parallel to the *bc* plane (Figure 1b). By reduction of the bridging D-cam and TMDPy ligands as linear linkers,

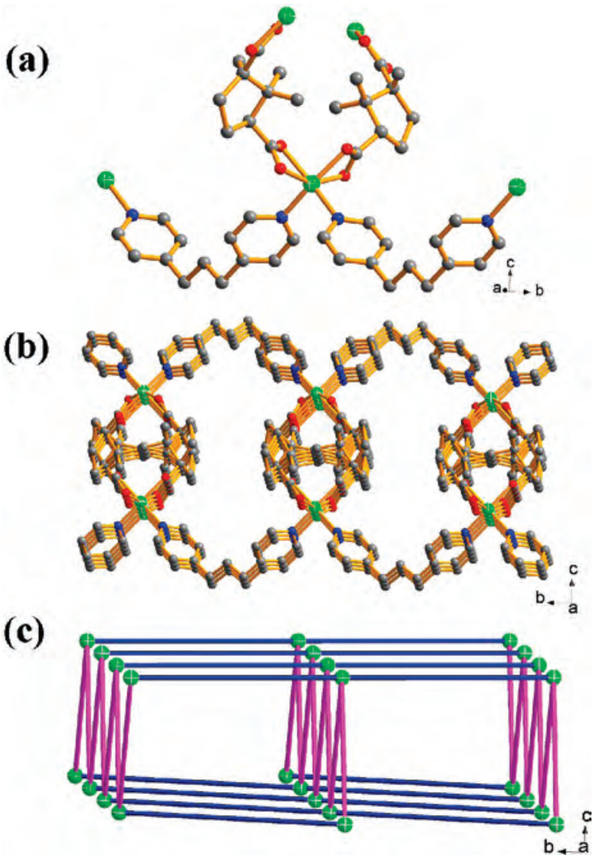
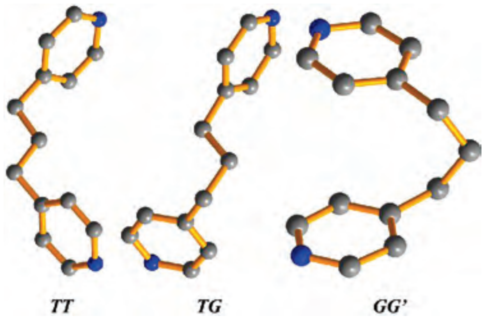


Figure 1. (a) 4-connected coordination for Ni^{2+} in **1**. The camphorate ligand has two statistical orientations, only one of which is shown here. (b) Bilayer structure in **1**. (c) Topological representation of the 2D 4-connected 4^26^38 bilayer.

Scheme 1. Conformational Isomers of the TMDPy Ligand (*TT* in **1**; *TG* in **2**, and *GG′* in **3**, **4**, and **4a**)



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(8) **Synthesis of Ni(D-cam)(TMDPy) (1).** A hydrothermal reaction of D-H_2Cam (0.1009 g), TMDPy (0.0832 g), $Ni(NO_3)_2\cdot6H_2O$ (0.1452 g), and $NaCO_3$ (0.0523 g) in H_2O (5 mL) was performed at 180 °C for 6 days, and the mixture was then cooled to room temperature. The green rectangular-prismatic crystals of **1** were obtained in 74% yield. **Synthesis of Co(D-cam)(TMDPy)·2H₂O (2).** A hydrothermal reaction of D-H_2Cam (0.1005 g), TMDPy (0.1135 g), $Co(NO_3)_2\cdot6H_2O$ (0.1508 g), and Na_2CO_3 (0.0999 g) in H_2O (4 mL) was performed at 160 °C for 8 days, and the mixture was then cooled to room temperature. The red crystals of **2** were obtained in 80% yield. **Synthesis of** $\mathbf{Fe^{II}_2}$**(D-cam)₂(TMDPy) (3).** A hydrothermal reaction of D-H_2Cam (0.100 g), TMDPy (0.0994 g), $FeSO_4\cdot6H_2O$ (0.1477 g), and Na_2CO_3 (0.050 g) in H_2O (5 mL) was performed at 160 °C for 3 days, and the mixture was then cooled to room temperature. The yellow crystals of **3** were obtained in 71% yield. **Synthesis of** $\mathbf{Co_2}$**(D-cam)₂(TMDPy) (4).** A hydrothermal reaction of D-H_2Cam (0.1018 g), TMDPy (0.1000 g), $Co(CH_3COO)_2\cdot4H_2O$ (0.1253 g), and K_2CO_3 (0.0573 g) in H_2O (4.2607 g) was performed at 160 °C for 6 days, and the mixture was then cooled to room temperature. The red crystals of **4** were obtained in 81% yield. **Synthesis of** $\mathbf{Co_2}$**(DL-cam)₂(TMDPy) (4a).** A hydrothermal reaction of DL-H_2Cam (0.1023 g), TMDPy (0.0934 g), $Co(CH_3COO)_2\cdot4H_2O$ (0.1423 g), and K_2CO_3 (0.0612 g) in H_2O (4.4512 g) was performed at 160 °C for 6 days, and the mixture was then cooled to room temperature. The red crystals of **5** were obtained in 87% yield.

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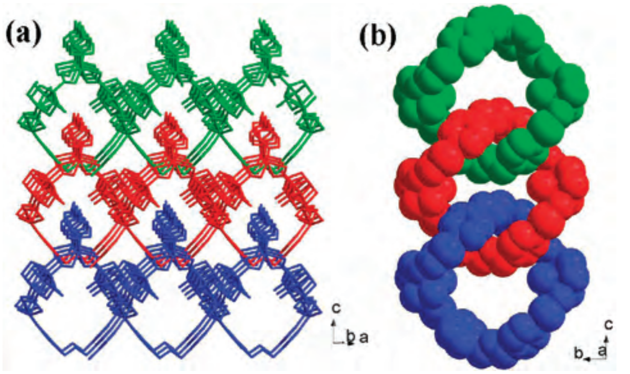

Figure 2. (a) Parallel polycatenation of the bilayers in compound **1** to form a 3D interlocked supramolecular assembly. (b) Space-filling model that shows the catenation of the four-membered rings in compound **1**.

such an unusual bilayer can be topologically represented as a 4-connected net containing zigzag and linear chains (Figure 1c). The Schläfli symbol of this uninodal net is 4^26^38.[10] The 2D gridlike (4,4) single layer is very common in metal–organic structures; however, the 4-connected bilayer structure reported here is, to our knowledge, unprecedented.

The open space within each bilayer leads to the formation of catenation between adjacent bilayers that are parallel to one another and crystallographically equivalent (Figure 2a). The catenation occurs between the four-membered rings from adjacent bilayers. Each four-membered ring is formed by four Ni^{2+} ions, two D-cam, and two TMDPy ligands (Figure 2b). The bilayers are perpendicular to the *c* axis and stacked in the AA sequence. This results in a 3D supramolecular assembly that is made of an infinite parallel polycatenation of the 4-connected bilayer (2D + 2D → 3D).[11]

In compound **2**, the Co^{2+} ion has an octahedral coordination geometry similar to that of the Ni^{2+} ion in **1** (Figure 3a). It is 4-connected to four symmetry-related Co^{2+} ions via two D-cam and two TMDPy ligands with the *TG* conformation[9] (Scheme 1). Compared to **1**, compound **2** exhibits a fully covalent 3D framework with diamond topology. Even though **2** has a 3-fold interpenetrating diamond net, it still possesses some free space to accommodate guest water molecules (Figure 3b).

Interestingly, by replacement of $Co(NO_3)_2 \cdot 6H_2O$ with $Co(CH_3COO)_2$ in the synthesis of **2**, a new homochiral compound **4** with a totally different framework topology is obtained. Unlike the 4-connected topology in **1** and **2**, compound **4** is based on the 6-connected paddlewheel $[Co_2(COO)_4N_2]$ building blocks, in which cobalt dimers are bridged by four bidentate carboxylate groups from four D-cam ligands with a metal–metal separation of 2.948 Å (Figure 3c). The cross-linking of adjacent dimers by D-cam ligands leads to a homochiral gridlike (4,4)-layered substructure. The auxiliary TMDPy ligands with the *GG′* conformation[9] (Scheme 1) serve as pillars and link the $[Co(\text{D-cam})]_n$ layer into a neutral 6-connected 3D network (Figure 3d). This noninterpenetrating framework can be simplified into the pcu net.

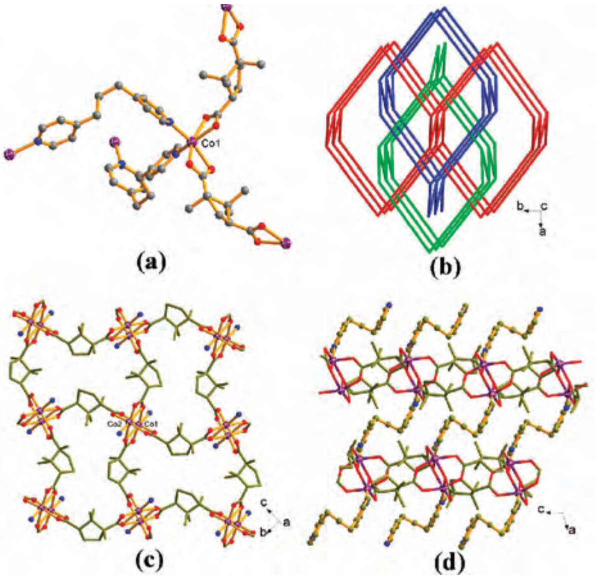

Figure 3. (a) 4-connected coordination of cobalt observed in **2**. (b) Schematic representation of the 3-fold interpenetrating diamond net of **2**. (c) Homochiral 2D (4,4) layer in **4**, showing the 6-connected paddlewheel units. (d) 3D pillared framework in **4**.

Compound **3** is isostructural to **4**. The replacement of Co^{2+} in **4** by Fe^{2+} in **3** results in a slightly larger unit cell. The Fe···Fe separation in the paddlewheel $[Fe_2(COO)_4]$ unit is 2.846 Å. Although the paddlewheel $[Fe_2(COO)_4]$ unit is well-known in some discrete structural types,[12] multidimensional structures based on these paddlewheel $[Fe_2(COO)_4]$ building blocks are really rare.

The thermal stabilities of **2** and **4** were analyzed on crystalline samples from 30 to 1000 °C at a rate of 15 °C min^{-1}, under a nitrogen atmosphere with a flowing rate of 100 mL min^{-1} (Figures S8 and S9 in the Supporting Information). The framework of **2** is retained up to 270 °C after loss of the guest water molecules. The residue of 16.2% is likely that of CoO (calcd 15.3%). The thermogravimetric analysis (TGA) curve of anhydrous phase **4** is largely unchanged up to 300 °C. The residue of 21.5% is likely that of CoO (calcd 21.1%).

In conclusion, we present here four homochiral and one racemic chiral metal camphorate architectures prepared through the integration of transition metals with a dual-ligand assembly approach. The various conformations of the TMDPy ligand help to control the homochiral metal camphorate connectivity into three distinct structural architectures that contain unusual structural motifs. The work represents an early step toward the synthesis of multifunctional materials that have the potential to integrate enantioselectivity with catalytic redox activity.

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Supporting Information Available: Additional structural figures, TGA diagrams, and X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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