



Homochiral coordination polymers from a chiral dicarboxylic acid and dipyridyl ligands: Structural diversity, photoluminescence and magnetic properties



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ABSTRACT

Utilizing the mixed-ligand strategy, six new homochiral coordination polymers based on enantiopure (1*R*,2*R*)-1,2-cyclohexanedicarboxylic acid and varied auxiliary bipyridyl ligands, $[Zn_3(L)_2(OH)_2]$ (**1**), $[Cu_3(HL)_2(L)_2(bpy)_3] \cdot 4H_2O$ (**2**), $[M(L)(bpe)_2(H_2O)_2] \cdot H_2O$ ($M = Co$, **3**; Ni , **4**; Cd , **5**), $[Ni(L)(bpa)(H_2O)_3] \cdot 2H_2O$ (**6**), [$H_2L = (1R,2R)$ -1,2-cyclohexanedicarboxylic acid, $bpy = 4,4'$ -bipyridine, $bpe = 1,2$ -bis(4-pyridyl)-ethylene, $bpa = 1,2$ -bis(4-pyridyl)ethane] have been hydrothermally synthesized. Compound **1** shows a 2D 6³-hcb network in the absence of any bipyridyl ligand. Compound **2** is a 2D (4,4)-connected grid network in the presence of bpy . Compounds **3–5** are isomorphous and feature 1D staggered-sculls chains by using bpe instead of bpy . Compound **6** possesses a 1D left-handed helical chain sustained by flexible bpa ligand. Each type of these coordination structures is further extended into 3D supramolecular frameworks through different intermolecular interactions. Solid-state circular dichroism (CD) spectra of compounds **1–6** exhibit strong CD signals. Magnetic susceptibility measurement indicates weak antiferromagnetic interactions between the Cu(II) ions in compound **2**. Compound **5** displays a strong fluorescent emission at 413 nm in solid state at room temperature.

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1. Introduction

Chirality, as “an artistic signature of nature”, plays a vital role in many areas of society and science [1,2]. In recent years, rational design and fabrication of chiral coordination polymers (CPs) has received remarkable attention not only because of their intriguing variety of structures [3,4], but also because of their potential applications such as asymmetric catalysis, enantioselective sorption and separation, and so on [5–7]. Up to now, many strategies have been developed to prepare homochiral CPs, in which the most effective one is the usage of chiral building blocks or chiral auxiliary ligand. The judicious selection of chiral linkers can give rise to the desired structural homochiral CPs. Some natural chiral carboxylate ligands with flexible conformations, such as *L*-lactic acid [8,9], *L*-tartaric acid [10], *L*-aspartic acid [11], *L*-glutamic acid [12], and *D*-camphoric acid [13,14], have been widely investigated for chiral compounds. Recently, the mixed-ligand strategy, cooperation of chiral multicarboxylate and various N-donor ligand may be considered as an attractive methodology to construct homochiral CPs [15–19].

Compared to rigid multicarboxylate ligands, the flexible ligands may adopt more versatile conformations according to the geometric requirements of different metal ions, which may lead to unpredictable, yet interesting architectures and properties. A series of flexible multicarboxylate ligands, such as 1,3-cyclohexanedicarboxylate [20], 1,4-cyclohexanedicarboxylate [21], 1,3,5-cyclohexanetricarboxylate [22], 1,2,4,5-cyclohexanetetracarboxylate [23,24] and 1,2,3,4,5,6-cyclohexanehexacarboxylate [25–27] have been employed to prepare CPs due to their various conformations. Recently, few coordination polymers with the 1,2-cyclohexanedicarboxylate have been reported in literature [28–32]. The enantiopure (1*R*,2*R*)-1,2-cyclohexanedicarboxylic acid as a flexible chiral ligand has two adjacent carboxylic groups, which provide diverse coordination modes (chelating, bridging, chelating/bridging and monodentate etc) and meanwhile act as hydrogen-bond acceptors and donors to generate new features. Moreover, the enantiopure ligand as chiral starting source translates its inherent chirality to the final complexes. The bipyridyl ligands with different spacer lengths are powerful for preparation of coordination polymers. The varied bipyridyl ligands should have important influence on coordination geometry. However, the cooperation of chiral multicarboxylates with varying bipyridyl ligands to create homochiral CPs has been less explored [13].

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In this article, we reacted enantiopure (1*R*,2*R*)-1,2-cyclohexanedicarboxylic acid (H_2L) with different metal(II) ions in the absence/presence of linear bipyridyl ligands under hydrothermal conditions, which resulted in six new homochiral coordination polymers, $[Zn_3(L)_2(OH)_2]$ (**1**), $[Cu_3(HL)_2(L)_2(bpy)_3] \cdot 4H_2O$ (**2**), $[M(L)(bpe)_2(H_2O)_2] \cdot H_2O$ ($M = Co$, **3**; Ni , **4**; Cd , **5**), and $[Ni(L)(bpa)(H_2O)_3] \cdot 2H_2O$ (**6**). The homochiral structures of these compounds were determined by single-crystal X-ray diffraction and solid-state CD spectra. The magnetic properties of **2** and the photoluminescent properties of **5** were also reported.

2. Experimental

2.1. Materials and physical measurements

All chemicals and reagents of analytical grade were commercial origin without further purification. The IR spectra were recorded on a Bruker NicoletIS50 spectrometer in the 400–4000 cm^{-1} range. Powder X-ray diffraction (PXRD) data were recorded using a Bruker D8 ADVANCE. Solid-state photoluminescent spectra were measured on a F-4500 fluorescence spectrometer. The solid-state circular dichroism (CD) spectra were recorded on a JASCO J-815 spectrometer following the standard procedure, using discs prepared from well-ground crystals. Temperature-dependent and field-dependent magnetic measurements were carried out on a Quantum Design SQUID MPMS-XL5 magnetometer. Diamagnetic corrections were made with Pascal's constants.

2.2. X-ray crystallography

Single-crystal X-ray diffraction analyses of **1–6** were carried out on a Bruker APEX II-CCD diffractometer equipped with a graphite-monochromated $Mo\ K\alpha$ ($\lambda = 0.71073\ \text{\AA}$) radiation source at 298 K. All structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 using SHELXTL-97 program. All the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms attached to carbon were located in calculated positions and refined using the riding model. The hydrogen atoms of coordinated water molecules were placed from difference Fourier maps. The hydrogen atoms of the lattice water molecules could not be located. The crystallographic data are listed in Table 1. The selected bond lengths and angles for **1–6** are listed in Table S1–6. The weak intermolecular hydrogen bonds for **2–6** are shown in Table S7.

2.3. Synthesis

2.3.1. Synthesis of $[Zn_3(L)_2(OH)_2]$ (**1**)

A mixture of H_2L (0.0086 g, 0.05 mmol), $Zn(OAc)_2 \cdot 2H_2O$ (0.011 g, 0.05 mmol), NaOH (0.004 g, 0.1 mmol) and $H_2O/EtOH$ (2 mL/2 mL) was stirred for 30 min and heated to 110 °C for 3 day in a 23 ml Teflon-lined stainless steel container. After cooling to room temperature, colorless block crystals of **1** were obtained in 32.3% yield (based on H_2L). *Anal. Calc.* For $Zn_3O_{10}H_{22}C_{16}$: C, 33.56; H, 4.23. *Found:* C, 33.30; H, 4.67%. IR (KBr pellet, cm^{-1}): 3496s, 2938vs, 2857s, 1643m, 1598s, 1421s, 1382vs, 1283m, 1112s, 1085w, 851s, 806m, 780m, 582 w, 465w.

2.3.2. Synthesis of $[Cu_3(HL)_2(L)_2(bpy)_3] \cdot 4H_2O$ (**2**)

A mixture of H_2L (0.0086 g, 0.05 mmol), $Cu(ClO_4)_2 \cdot 6H_2O$ (0.0185 g, 0.05 mmol), 4,4'-dipyridine (0.0078 g, 0.05 mmol) and 3 ml water was sealed in a 23 ml Teflon-lined stainless steel container and heated to 110 °C for 3 days, which was slowly cooled to room temperature. Blue-green rod crystals of **2** were collected with a yield of 49% (based on H_2L). *Anal. Calc.* For $Cu_3O_{20}N_6H_{74}C_{62}$:

C, 52.67; H, 5.28; N, 5.94. *Found:* C, 52.32; H, 5.33; N, 5.77%. IR (KBr pellet, cm^{-1}): 3442m, 2938vs, 2857s, 1678m, 1607s, 1562m, 1490m, 1418w, 1292m, 1220s, 1148m, 896w, 815m, 645m.

2.3.3. Synthesis of $[Co(L)(bpe)_2(H_2O)_2] \cdot H_2O$ (**3**)

A mixture of H_2L (0.0086 g, 0.05 mmol), $CoCl_2 \cdot 6H_2O$ (0.0120 g, 0.05 mmol), 1,2-Di(4-pyridyl)ethylene (0.0180 g, 0.10 mmol) and 5 ml H_2O was sealed in a 23 ml Teflon lined stainless steel container and heated to 140 °C for 3 days. The reaction mixture was slowly cooled to room temperature. Red rod crystals of **3** were collected with a yield of 65% (based on H_2L). *Anal. Calc.* For $CoO_7N_4H_{36}C_{32}$: C, 59.30; H, 5.56; N, 8.65. *Found:* C, 60.12; H, 5.66; N, 8.62%. IR (KBr pellet, cm^{-1}): 3213b, 2927m, 2857w, 2514w, 2143w, 1794s, 1616w, 1545m, 1410m, 1339w, 1289w, 1224w, 1075w, 1011m, 968w, 882s, 712m, 547m, 427m.

2.3.4. Synthesis of $[Ni(L)(bpe)_2(H_2O)_2] \cdot H_2O$ (**4**)

Compound **4** was prepared by the similar procedure to that described for **3**, except that $CoCl_2 \cdot 6H_2O$ was replaced by $NiCl_2 \cdot 6H_2O$ (0.0125 g, 0.05 mmol). Green rod crystals of **4** were collected with a yield of 73.2% (based on H_2L). *Anal. Calc.* For $NiO_7N_4H_{36}C_{32}$: C, 59.32; H, 5.57; N, 8.68. *Found:* C, 60.30; H, 5.66; N, 8.66%. IR (KBr pellet, cm^{-1}): 3526w, 3227br, 2942s, 2856m, 1596m, 1545s, 1417m, 1339w, 1289m, 1217m, 1111w, 1068m, 1018s, 975s, 826s, 769w, 719m, 547s, 470w.

2.3.5. Synthesis of $[Cd(L)(bpe)_2(H_2O)_2] \cdot H_2O$ (**5**)

Compound **5** was prepared by the similar procedure to that described for **3**, except that $CoCl_2 \cdot 6H_2O$ was replaced by $Cd(NO_3)_2 \cdot 4H_2O$ (0.0120 g, 0.05 mmol). Pale yellow rod crystals of **5** were collected with a yield of 83% (based on H_2L). *Anal. Calc.* For $CdO_7N_4H_{36}C_{32}$: C, 54.77; H, 5.14; N, 7.98. *Found:* C, 54.30; H, 5.18; N, 7.66%. IR (KBr pellet, cm^{-1}): 3397b, 3041w, 2835s, 2849w, 1602s, 1566s, 1424s, 1327m, 1303m, 1220w, 1075m, 979m, 829s, 783w, 719w, 547s.

2.3.6. Synthesis of $[Ni(L)(bpa)(H_2O)_3] \cdot 2H_2O$ (**6**)

A mixture of H_2L (0.0086 g, 0.05 mmol), $NiCl_2 \cdot 6H_2O$ (0.0125 g, 0.05 mmol), 1,2-Di(4-pyridyl)ethane (0.0090 g, 0.05 mmol), NaOH (0.004 g, 0.1 mmol), and 6 ml H_2O was sealed in a 23 ml Teflon lined stainless steel container and heated to 110 °C for 2 days, which was slowly cooled to room temperature. Blue block crystals of **6** were collected. Yield of 52% (based on H_2L). *Anal. Calc.* For $NiO_9N_2H_{32}C_{20}$: C, 47.70; H, 6.36; N, 5.56. *Found:* C, 47.87; H, 6.48; N, 5.35%. IR (KBr pellet, cm^{-1}): 3541w, 2938m, 2857w, 1625m, 1553m, 1409s, 1346m, 1292m, 1229s, 1112m, 1067m, 1023s, 806m, 707s, 600s, 527s.

3. Results and discussion

3.1. Descriptions of crystal structure

3.1.1. $[Zn_3(L)_2(OH)_2]$ (**1**)

Single-crystal X-ray diffraction analysis reveals that **1** crystallizes in the orthorhombic chiral space group $P2_12_12_1$, showing a homochiral 2D network. The asymmetric unit of **1** is composed of three Zn(II) ions, two L^{2-} ligands, two μ_3 -OH oxygen atoms. As shown in Fig. 1a, Zn1 is four-coordinated in a distorted tetrahedral geometry by two carboxyl oxygen atoms (O1 and O5) from two different L^{2-} ligands and two μ_3 -OH oxygen atoms (O9 and O10). Zn2 is surrounded by the four carboxyl oxygen atoms (O2A, O4C, O5 and O7D) from four different L^{2-} ligands and two μ_3 -OH oxygen atoms (O9 and O10A), exhibiting a distorted octahedral geometry. Zn3 adopts a distorted trigonal bipyramidal geometry, in which three carboxyl oxygen atoms O3B, O7 and O8E from

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