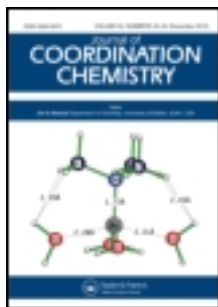


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Syntheses and properties of two chiral multidentate carboxylate copper coordination compounds

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Syntheses and properties of two chiral multidentate carboxylate copper coordination compounds

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A chiral ligand, (R)-2-(4-(carboxymethoxy)phenoxy)propanoic acid, is employed as building block to construct two chiral coordination compounds, [Cu(L)(bipy)(H₂O)] (**1**) and [Cu₂(L)₂(phen)₄(H₂O)₁₃] (**2**), by the solvent-thermal method and the volatilization method, respectively. The compounds are characterized by single-crystal X-ray diffraction (XRD), IR spectra, XRD, TGA, and circular dichroism spectra. Compound **1** is comprised of right-handed helical chains and **2** shows a separated structure, both of which extend to 3-D supramolecular framework by hydrogen bonds and $\pi \cdots \pi$ interactions. CD indicates both compounds retain original stereo character with strong fluorescence at room temperature.

Keywords: X-ray; Coordination; Chiral; Helical

1. Introduction

Inorganic–organic hybrid compounds with broad applications have received significant attention [1]. The design and synthesis of chiral metal–organic coordination compounds have especially evoked interest owing to unique properties [2]. Building logical non-centrosymmetric or chiral coordination compounds is still a challenge for materials and synthetic chemists. Chiral coordination compounds can be obtained by two routes. The first is spontaneous resolution upon crystallization without any chiral sources, which is reported to be used in construction of some chiral coordination compounds [3]. However, spontaneous resolution is still a relatively scarce phenomenon and cannot be predicted *a priori* because the mechanisms of the processes are not fully understood. Moreover, spontaneous resolution will result in a racemic mixture which cannot be easily separated. The second is stereoselective synthesis using enantiopure chiral species. Compared to the first way, this route is more feasible and effective. Recently, ligands containing single or multiple asymmetric centers are used to synthesize chiral coordination compounds, most of which have helical chains or channel structures with good predictability of space configuration [4].

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Coordination polymers based on chiral carboxylic acid ligands showed advantageous properties as magnetic materials, porous materials, nonlinear optical materials, and in asymmetric synthesis [5]. Carboxylates are efficient for generation of helical coordination polymers [6]. Inspired by the aforementioned considerations, we select chiral carboxylates as building blocks [7]. We synthesized a chiral ligand with phenoxy propanoic acid structure to construct new coordination compounds and introduce auxiliary ligands to extend delocalization of π electrons and enhance molecular rigidity. Auxiliary ligands can enhance performance considering 2,2-bipy and phen exhibit fluorescence enhancement.

In this article, we report two chiral coordination compounds, $[\text{Cu}(\text{L})(\text{bipy})(\text{H}_2\text{O})]$ (**1**) and $[\text{Cu}_2(\text{L})_2(\text{phen})_4(\text{H}_2\text{O})_{13}]$ (**2**). Compound **1** is comprised of right-handed helical chains and **2** shows a separated structure, both of which extend to 3-D supramolecular framework by hydrogen bonds and $\pi \cdots \pi$ interactions. The optical activities and the luminescence properties are investigated.

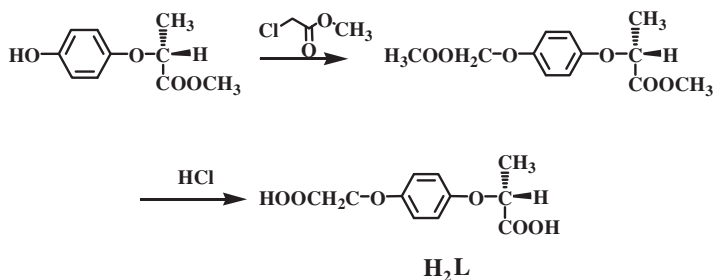
2. Experimental

2.1. Materials and methods

All reagents and solvents were purchased from commercial sources and used without purification. IR spectra were recorded from 4000 to 400 cm^{-1} using KBr pellets on a Spectrum One FT-IR spectrometer. ^1H NMR spectra were performed on a Bruker AV 300 MHz spectrometer. X-ray powder diffraction (XRPD) data were collected on a Bruker D8 AVANCE diffractometer. Elemental analyses were performed on a CARLO ERBA 1106 analyzer. Circular dichroism (CD) spectra were recorded on a JASCO J-810. Thermogravimetric measurements were carried out on a Perkin-Elmer TGA-7 analyzer. Luminescence spectra for solid samples were measured at room temperature on a Perkin-Elmer LS 55 luminance meter.

2.2. Preparation of the ligand

H_2L (scheme 1) was synthesized by a two-step procedure. In the first step, methyl chloroacetate (18 g, 163 mmol) was dropped into a mixture of methyl R-(+)-2-(4-hydroxyphenoxy)propanoate (21.6 g, 110 mmol), anhydrous K_2CO_3 (64 g, 463 mmol),



Scheme 1. Synthesis route of the ligand.

sodium iodide (16 g, 107 mmol), and disodium hydrogen phosphate (5 g, 35.4 mmol) in anhydrous acetone (350 mL). After refluxing for 10 h, the mixture was filtered to remove unreacted K_2CO_3 . Acetone was then distilled off and product was obtained [8]. In the second step, hydrochloric acid (2 g, 56 mmol) was added to a solution of methyl R-(+)-2-(4-hydroxy phenoxy)propionate (12.8 g, 50 mmol) in ethanol and water (1 : 1). The mixture was stirred for 5–6 h at 60°C. The ethanol was then distilled off and PEG-400 (1 g) was added. After heating for 7–8 h the mixture was cooled to room temperature to get light yellow powder. The powder was recrystallized with water to get white crystals (94% ee). Elemental Anal. Calcd for $\text{C}_{11}\text{H}_{12}\text{O}_6$ (%): C, 55.00; H, 5.04. Found (%): C, 55.02; H, 5.01. IR data (KBr, cm^{-1}): 3047 (m), 2584 (w), 1717 (s), 1507 (s), 1428 (m), 1208 (s), 1138 (s), 1078 (m), 821 (s) (figure S1). ^1H NMR (DMSO- d_6 , 400 MHz): δ 6.88 (m, 4H), 4.71 (q, $J = 6.8$ Hz, 1H), 4.58 (s, 2H), 1.47 (d, $J = 6.8$ Hz, 3H) (figure S2).

2.3. Syntheses of **1** and **2**

2.3.1. Synthesis of $[\text{Cu}(\text{L})(\text{bipy})(\text{H}_2\text{O})]$ (1**).** A mixture of $\text{Cu}(\text{AcO})_2 \cdot \text{H}_2\text{O}$ (0.399 g, 0.2 mmol), H_2L (0.048 g, 0.2 mmol), and 2,2-bipy (0.0396 g, 0.2 mmol) was dissolved in 2 mL of distilled water and 4 mL of DMF. The resulting mixture was then transferred and sealed in a 20 mL Teflon-lined stainless steel vessel and heated at 90°C for 2 days. After the reactor was slowly cooled to room temperature, purple blue block crystals were filtered off, washed with distilled water, and dried in air. Yield: 78%. IR data (KBr, cm^{-1}): 3423 (m), 3060 (w), 2898 (w), 1676 (m), 1630 (s), 1506 (s), 1419 (m), 1316 (m), 1216 (s), 950 (w), 822 (m), and 776 (m). Elemental Anal. Calcd for $\text{C}_{21}\text{H}_{20}\text{CuN}_2\text{O}_7$ (%): C, 53.00; H, 4.24; N, 5.89. Found (%): C, 53.06; H, 4.21; N, 5.90.

2.3.2. Synthesis of $\text{Cu}_2(\text{L})_2(\text{phen})_4(\text{H}_2\text{O})_{13}$ (2**).** Compound **2** was synthesized by the reaction of H_2L (0.048, 0.2 mmol) and $\text{Cu}(\text{AcO})_2 \cdot \text{H}_2\text{O}$ (0.399 g, 0.2 mmol) in CH_3OH (15 mL) which was stirred for 0.5 h. The precipitate collected by filtration was redissolved in a solution of 1,10-phenanthroline (0.0396 g, 0.2 mmol) in 20 mL of water and stirred for 1 h. After filtration, green stick crystals suitable for X-ray diffraction (XRD) were obtained by slow diffusion for several days [9]. Yield: 53%. IR data (KBr, cm^{-1}): 3368 (w), 3050 (w), 1598 (s), 1505 (m), 1427 (m), 1391 (m), 1207 (m), 1091 (w), 848 (m), 723 (s), 569 (w). Elemental Anal. Calcd for $\text{C}_{70}\text{H}_{78}\text{Cu}_2\text{N}_8\text{O}_{24}$ (%): C, 54.61; H, 4.91; N, 7.28. Found (%): C, 54.58; H, 4.89; N, 7.30.

3. Results and discussion

XRD measurements for **1** and **2** were carried out on a Rigaku R-AXIS RAPID imaging plate diffractometer with graphite-monochromated Mo- $\text{K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation at 293 K. Empirical absorption corrections based on equivalent reflections were applied. The structures of **1** and **2** were solved by direct methods using SHELXS 97 [10]. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 . Hydrogen atoms bound to C were placed in calculated positions and treated as riding.

Table 1. Crystallographic data for **1** and **2**.

| | 1 | 2 |
|--|--|--|
| Chemical formula | C ₂₁ H ₂₀ Cu N ₂ O ₇ | C ₇₀ H ₇₈ Cu ₂ N ₈ O ₂₄ |
| Formula weight | 475.93 | 1558.48 |
| Crystal system | Orthorhombic | Triclinic |
| Space group | <i>P</i> 2 ₁ | <i>P</i> 1 |
| Unit cell dimensions (Å, °) | | |
| <i>a</i> | 6.9652(14) | 10.306 |
| <i>b</i> | 15.046(3) | 12.007 |
| <i>c</i> | 19.065(4) | 16.177 |
| α | 90 | 71.060 |
| β | 90 | 72.800 (19) |
| γ | 90 | 87.217 (18) |
| Volume (Å ³), <i>Z</i> | 1998.1(7), 4 | 1806.3(16), 1 |
| Calculated density (g cm ⁻³) | 1.582 | 1.433 |
| <i>F</i> (000) | 980 | 812 |
| Reflection collection | 19,449 | 12,004 |
| Unique reflections | 4557 [<i>R</i> (int)=0.0235] | 9449 [<i>R</i> (int)=0.0636] |
| Number of parameters | 281 | 939 |
| Goodness-of-fit on <i>F</i> ² | 1.028 | 0.996 |
| <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] | <i>R</i> ₁ =0.0216 <i>wR</i> ₂ =0.0540 | <i>R</i> ₁ =0.0715 <i>wR</i> ₂ =0.1831 |
| <i>R</i> indices (all data) | <i>R</i> ₁ =0.0234 <i>wR</i> ₂ =0.0545 | <i>R</i> ₁ =0.1236 <i>wR</i> ₂ =0.2206 |

The crystal parameters, data collection, and refinement results are summarized in table 1, selected bond lengths and angles are listed in table 2, and hydrogen-bond parameters are provided in table S1. CCDC reference numbers for **1** and **2** are 872,686 and 872,687, respectively.

3.1. Descriptions of structures

3.1.1. [Cu(L)(bipy)(H₂O)] (1). X-ray analysis reveals that **1** crystallized in the chiral orthorhombic space group *P*2₁. The asymmetric unit contains one crystallographically unique Cu(II), two L, a 2,2-bipy, and a water molecule. The Cu(II) possesses a coordination number of five, coordinating with two oxygen atoms from two different L and two nitrogen atoms from one 2,2-bipy, as shown in figure 1, in a distorted rectangular pyramid. All L exhibit monodentate coordination; uncoordinated carboxylic oxygen atoms in L have weak interactions with Cu(II) at 2.87 Å. Compound **1** is chiral consistent with L, angle O1–C2–O3 is 112.0°, and angle C2–C1–O3 is 120.3°, which forms a right-handed helical chain along the *b*-axis, as shown in figure 2(a). The pitch of the helix is 19.065 Å. The helical character in **1** is probably due to the space angles produced by the chiral center of L. The prominent feature of **1** is the helical channels along the *c*-axis with a width of 10.868 Å × 5.227 Å, with potential as asymmetric catalysts. An analogous achiral ligand, namely 2,2'-(1,4-phenylenebis(oxy))diacetic acid, reacting with 2,2-bipy and Cu(OAc)₂ could produce a coordination compound with a zigzag chain [11]. O–H...O interactions bridge adjacent helical chiral chains into 2-D network which is further connected to 3-D supramolecular framework by π – π interactions of 2,2-bipy.

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

| | | | |
|-------------------|-----------|-------------------|-----------|
| Compound 1 | | | |
| Cu(1)–O(6)#1 | 1.957(1) | Cu(1)–O(2) | 1.966(1) |
| Cu(1)–N(1) | 2.003(1) | Cu(1)–N(2) | 2.035(1) |
| Cu(1)–O(7) | 2.264(1) | O(6)#1–Cu(1)–O(2) | 91.63(5) |
| O(6)#1–Cu(1)–N(1) | 169.23(6) | O(2)–Cu(1)–N(1) | 94.82(5) |
| O(6)#1–Cu(1)–N(2) | 92.26(6) | O(2)–Cu(1)–N(2) | 170.41(5) |
| N(1)–Cu(1)–N(2) | 80.09(6) | O(6)#1–Cu(1)–O(7) | 91.49(5) |
| O(2)–Cu(1)–O(7) | 90.62(5) | N(1)–Cu(1)–O(7) | 97.05(6) |
| N(2)–Cu(1)–O(7) | 98.04(6) | | |
| Compound 2 | | | |
| Cu(1)–N(1) | 1.993(14) | Cu(1)–N(4) | 2.025(10) |
| Cu(1)–O(1) | 2.049(10) | Cu(1)–N(2) | 2.108(14) |
| Cu(1)–N(3) | 2.143(14) | Cu(2)–N(5) | 1.980(14) |
| Cu(2)–O(7) | 1.981(11) | Cu(2)–N(8) | 1.999(10) |
| Cu(2)–N(7) | 2.026(11) | Cu(2)–N(6) | 2.213(13) |
| N(1)–Cu(1)–N(4) | 176.2(6) | N(1)–Cu(1)–O(1) | 88.0(5) |
| N(4)–Cu(1)–O(1) | 95.6(4) | N(1)–Cu(1)–N(2) | 81.5(5) |
| N(4)–Cu(1)–N(2) | 94.7(5) | O(1)–Cu(1)–N(2) | 151.2(4) |
| N(1)–Cu(1)–N(3) | 101.7(5) | N(4)–Cu(1)–N(3) | 79.3(5) |
| O(1)–Cu(1)–N(3) | 95.5(5) | N(2)–Cu(1)–N(3) | 112.9(4) |
| N(5)–Cu(2)–O(7) | 94.8(5) | N(5)–Cu(2)–N(8) | 175.3(6) |
| O(7)–Cu(2)–N(8) | 89.4(5) | N(5)–Cu(2)–N(7) | 95.2(5) |
| O(7)–Cu(2)–N(7) | 150.7(5) | N(8)–Cu(2)–N(7) | 82.1(5) |
| N(5)–Cu(2)–N(6) | 81.6(5) | O(7)–Cu(2)–N(6) | 95.7(5) |
| N(8)–Cu(2)–N(6) | 95.9(5) | N(7)–Cu(2)–N(6) | 113.0(5) |

Symmetry transformations used to generate equivalent atoms for **1**: #1 $-x+1/2, -y+1, z+1/2$.

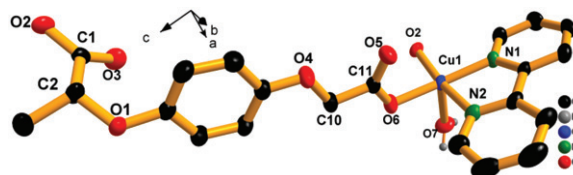


Figure 1. Molecular structure of **1** displaying the crystallographic-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

3.1.2. $\text{Cu}_2(\text{L})_2(\text{phen})_4(\text{H}_2\text{O})_{13}$ (2**).** X-ray analysis reveals that **2** crystallized in the chiral triclinic space group $P1$. The asymmetrical unit consists of two Cu(II), two L, and four phen. Both Cu(II) possess a coordination number of five with four nitrogen atoms from two different phen and one oxygen atom from L, as shown in figure 3. Cu(II) exhibits a distorted rectangular pyramid. Both L exhibit monodentate coordination and the configuration of chiral carbon is consistent with that in L; π - π interaction plays an important role in **2**. Two independent chiral molecules connect with each other to form an asymmetric unit of **2**, many of which are further packed together into a chain by π - π interactions. These π - π interactions occur in different positions of the ligand. Interaction between complex molecules are on the middle phenyl rings of phen with a bond length of 3.558 Å; interaction in chain construction are on the middle phenyl rings in right and on the side phenyl rings in left, with a bond length of 3.574 Å. Two other kinds of π - π interactions with distance of 3.582 Å and 3.751 Å bridge adjacent 1-D chains into a 2-D network with numerous complicated H-bonds between water

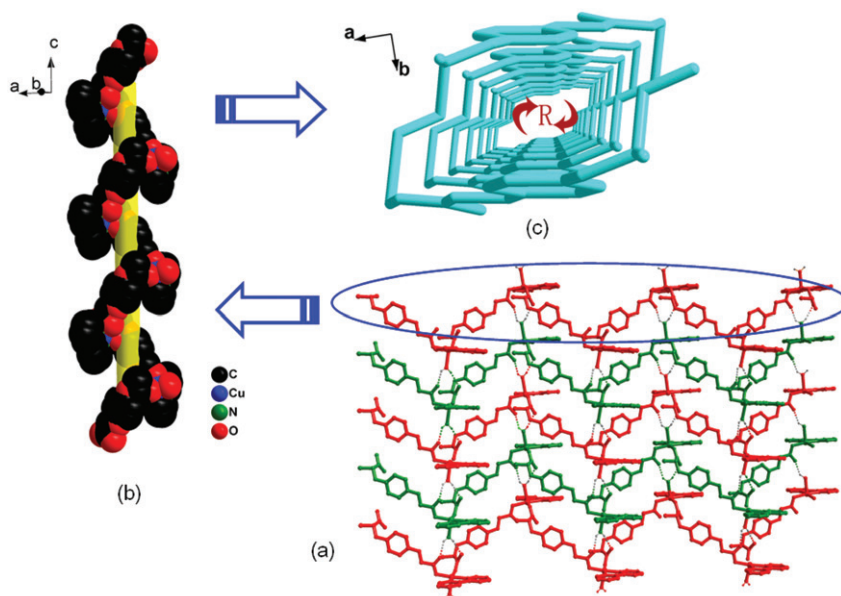


Figure 2. (a) The 2-D supramolecular network connected by H-bonds between adjacent helical chiral chains; (b) the right-handed chiral helical along the *c*-axis; and (c) the right-handed helical channel.

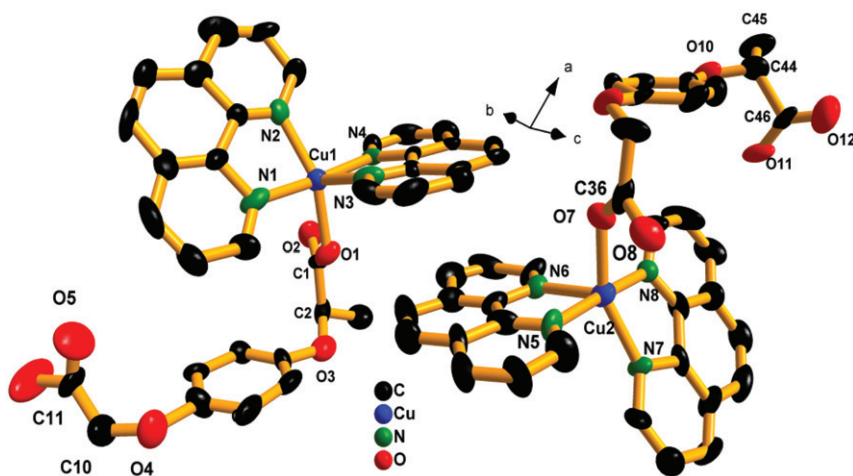


Figure 3. Molecular structure of **2** displaying the crystallographic-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. All hydrogen atoms and water molecules are omitted for clarity.

molecules and carboxylates bridging the 2-D network into a 3-D supramolecular framework. Figure 4 exhibits four different π - π interactions.

3.2. XRPD and thermal analyses

XRPD was used to determine the purity of **1** and **2**. As shown in “Supplementary material”, the peaks of **1** closely match those in simulated patterns generated from

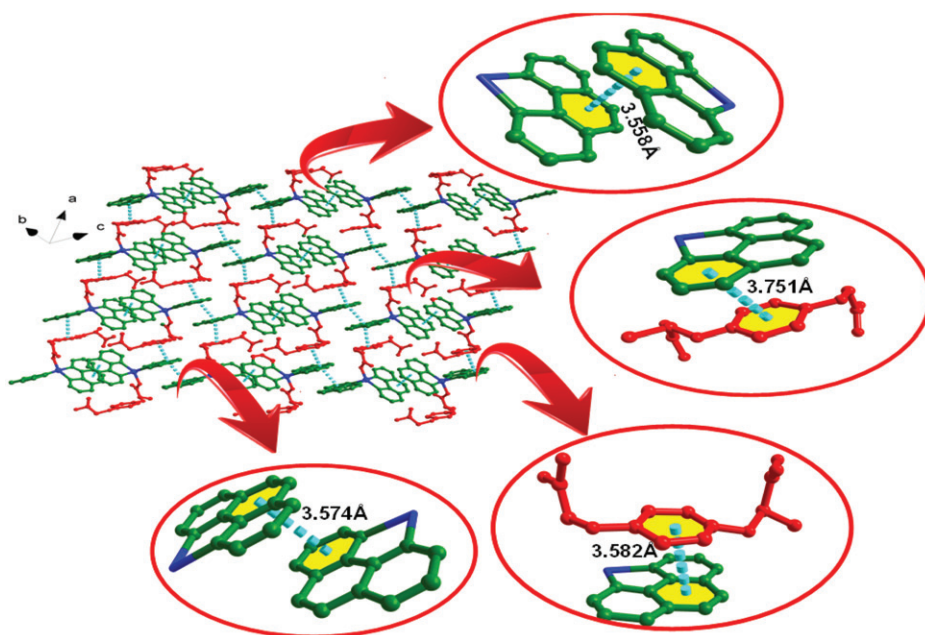


Figure 4. The 2-D supramolecular network of **2** connected by four kinds of $\pi \cdots \pi$ interactions; water molecules are omitted for clarity.

single-crystal diffraction data, indicating high phase purity of the product. The peaks of **2** displayed in measured pattern seem not to be accord with those in the simulated patterns completely. The intensity of some peaks changed and a few peaks disappeared. The phenomenon is probably due to loss of crystallized water molecules in **2** during the process of heating in XRPD analysis.

To study the stability of these compounds, TGA of **1** and **2** are performed (Supplementary material). Compound **1** lost a coordination water molecule from 163°C (Calcd: 3.78%, Found: 6.47%), while **2** immediately collapsed at the beginning of heating, owing to loss of crystallized water (Calcd: 15.01%, Found: 13.11%). The loss of L in **1** appears from 229°C to 311°C (Calcd: 46.59%, Found: 49.61%). The curve of **2** has a rapid weight loss at 243°C, which indicates loss of L (Calcd: 33.46%, Found: 32.38%). The third weight loss is from auxiliary ligand (Calcd: 32.82%, Found: 32.66% for **1**; Calcd: 46.26%, Found: 43.25% for **2**). Compound **1** decomposed completely at 500°C and the residue is presumed to be CuO (Calcd: 16.81%, Found: 16.19%). Compound **2** is more stable and continued to decompose up to 565°C (Calcd: 10.27%, Found: 11.26%).

3.3. CD spectra and photoluminescent properties

CD spectrum is a powerful technique to obtain conformational information of chiral molecules. As shown in figure 5, the CD spectra of **1**, **2**, and the ligand measured in DMF show strong signals corresponding to the absorptions of the UV spectra. The UV spectra are shown in inset. The maximum peaks of coordination compounds have

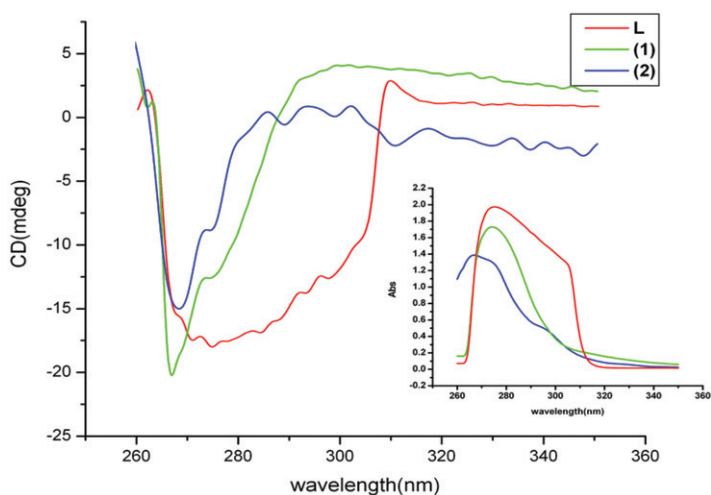


Figure 5. CD spectra of ligand, **1**, and **2** in DMF (inset: UV absorption spectra in DMF).

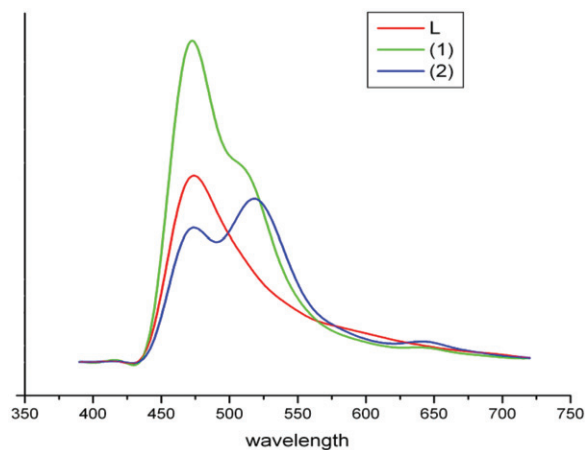


Figure 6. Solid-state fluorescence emission spectra of ligand, **1**, and **2** at room temperature.

a slightly blue shift relative to ligand from 265 nm to 273 nm, which arises from the presence of a large conjugated π -system of the molecule. The negative maximum peaks in accord with the X-ray results indicate that **1** and **2** maintained the right-handed configuration during coordination.

We also investigated the luminescence properties of **1** and **2** for potential applications as light-emitting diodes. The solid-state fluorescence emission spectra at room temperature are shown in figure 6. Compared with ligand, in which a fluorescence emission is observed at $\lambda_{\max} = 465$ nm upon excitation at 350 nm, **1** exhibits a strong blue emission band at 468 nm and a green band at 513 nm upon excitation at 350 nm. Compound **2** shows a blue emission band at 469 nm and a broad strong green band at 510 nm with excitation at 335 nm. We speculate that the intensity of blue bands

are probably due to strong luminescence of ligand, the auxiliary ligands can obviously affect the luminescence and produce co-fluorescence effect which manifest as the green bands. These observations indicate that **1** and **2** may be candidates for photoactive materials in asymmetric reactions.

4. Conclusion

Chiral coordination polymers can be achieved from achiral or racemic ligands by spontaneous resolution upon crystallization, which is difficult to predict [12]. Therefore, we used enantiopure chiral carboxylic acid as the source of chirality to construct coordination polymers.

In particular, we prepared two chiral metal–organic frameworks from a chiral ligand, $\text{Cu}(\text{OAc})_2$, and two auxiliary ligands (phen and 2,2-bipy). Compound **1** is comprised of right-handed chains assembled by the solvent-thermal method and **2** shows separated structure containing four different kinds of π -bonds. Compounds **1** and **2** are extended to 3-D supramolecular sheets by hydrogen bonds and $\pi \cdots \pi$ interactions. Both compounds exhibit significant CD and can be excited directly and emit strong fluorescence at room temperature. Our study provides insight into the synthesis of chiral coordination polymers from chiral ligands.

Acknowledgments

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