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Syntheses, structures and catalytic properties of chiral Co(II) coordination polymers based on (*R*)-4-(4-(1-carboxyethoxy)phenoxy) benzoic acid

Xin Xu [a], Ying-Hui Yu [a], Guang-Feng Hou [a,b,*], Xue-Wei Li [a], Chang-Yue Ren [a], Dong-Sheng Ma [a,*]

[a] School of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, China
[b] Engineering Research Centre of Pesticide of Heilongjiang University, Heilongjiang University, Harbin 150080, China

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ABSTRACT

To investigate the construction of novel chiral coordination polymers and the effect of different substituents on the ligands, three complexes, namely [Co(L)(bimb)]·EtOH·H_2O [bimb = 4,4′-bis((1*H*-imidazol-1-yl)methyl)-biphenyl, L = (*R*)-4-(4-(1-carboxyethoxy)phenoxy)-3-fluorobenzoic acid (**1**); L = (*R*)-4-(4-(1-carboxyethoxy)phenoxy)-3-chlorobenzoic acid (**2**); L = (*R*)-4-(4-(1-carboxyethoxy) phenoxy)-3-nitroaniline acid (**3**)], have been hydrothermally synthesized and characterized by IR, elemental analyses, thermogravimetric analysis, solid state circular dichroism (CD), powder and single-crystal X-ray diffractions. Structure analysis indicates that complexes **1**–**3** are isomorphic, featuring two-dimensional (2D) 2-fold interpenetrated sq1 structures. In addition, their second harmonic generation efficiency and catalytic activity for the aldol reaction were investigated.

1. Introduction

It is well known that enantiopure solids are quite important materials because of their potential applications in non-linear optics, chiral separation, asymmetric catalysis and so on [1–6]. Therefore, their preparation and analysis are important in many fields of science. However, enantiopure solids are not readily available, especially porous enantiopure solids. The inorganic zeolite β (polymorph A) represents a kind of rare porous chiral inorganic solids, but its pure enantiomer has not yet been obtained due to a stacking disorder [7,8]. Although organic enantiopure compounds can be simply synthesized or separated from natural products, their stabilities are relative low and their porosities are not easy to retain. Recently, the construction of metal-organic coordination polymers (CPs) afforded an effective way toward the preparation of enantiopure solids – chiral coordination polymers (CCPs) [9–18]. To date, three strategies have been adopted to achieve CCPs: (a) spontaneous resolution upon crystallization without chiral sources, (b) chiral induction by utilizing chiral molecules as templates and (c) adoption of enantiopure ligands. However, strategies (a) and (b) have high unpredictability and uncertainty, limiting their use in the rational synthesis of CCPs [19,20]. Adopting chiral ligands has been proven to be the most feasible and effective way for CCP construction [21,22]. Amino acids, tartaric acids, camphorsulfonic acid and their derivatives have been reported a lot as chiral sources in CCP syntheses [23–29]. As basic chemicals, lactic acid is inexpensive and environmentally friendly, and this could be used as an ideal chiral source for constructing CCPs [30–33]. However, lactic acid based CCPs are still limited due to its structural flexibility. Therefore, modification with rigid aromatic groups to lactic acid provides valuable insight for the rational design of CCPs [32]. An ongoing study in our group is the design and synthesis of new chiral carboxylate ligands [30,31]. Compared with other ligands, carboxylates with various coordination modes could give rise to coordination polymers with diverse structures. As a derivative of lactic acid, chiral 2-(4-hydroxyphenoxy)propanoic acid is readily available, and this molecule could be further decorated by the reaction of the hydroxy group to form new chiral multicarboxylate ligands.

In the present work, three 2-(4-hydroxyphenoxy)propanoic acid based chiral ligands have been synthesized, namely (*R*)-4-(4-(1-carboxyethoxy)phenoxy)-3-fluorobenzoic acid (H_2cpfa), (*R*)-4-(4-(1-carboxyethoxy)phenoxy)-3-chlorobenzoic acid (H_2cpca) and (*R*)-4-(4-(1-carboxyethoxy)phenoxy)-3-nitrobenzoic acid (H_2cpna). These three ligands have different substituents, but exhibit similar V-shaped configurations, and are expected to form novel helical architectures [34–38]. The Co(II) ion was selected to react with these three ligands, incorporating 4,4′-bis(1*H*-imidazol-1-yl-methyl)biphenyl (bimb) as a second N-donor ligand, to

* Corresponding authors at: School of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, China (G.-F. Hou).
E-mail addresses: hougf@hlju.edu.cn (G.-F. Hou), rwws8828@sina.com (D.-S. Ma).

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obtain three CCPs, [Co(L)(bimb)]·EtOH·H_2O {L = $[cpfa]^{2-}$ (**1**); L = $[cpca]^{2-}$ (**2**); L = $[cpna]^{2-}$ (**3**)}. Complexes **1**–**3** are isomorphic with two-dimensional 2-fold interpenetration structures, and their thermal stabilities, circular dichroism spectra, non-linear optical and catalytic properties have been investigated.

2. Experimental

2.1. Materials and general methods

All commercially available chemicals were reagent grade and used as received. The ligand bimb was prepared according to literature methods [39–41]. The IR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer equipped with a DGTS detector (32 scans) using KBr disks in the range 4000–500 cm^{-1}. Elemental analyses of C, H and N were performed on a Perkin-Elmer 2400 elemental analyzer. Thermal analyses were conducted on a Perkin-Elmer STA 6000 with a heating rate of 10 °C min^{-1} in a temperature range from 30 to 800 °C under air atmosphere. ^1H NMR spectra were recorded on a Bruker Avance (400 MHz) spectrometer in DMSO/CD_3Cl with TMS as the standard. UV–Vis diffuse reflectance spectra were recorded for the complexes in the solid state, using a Cary 5000 UV–Vis–NIR analyzer. X-ray powder diffraction (PXRD) measurements, with a 2θ range from 5° to 50°, were performed on a Rigaku D/Max–IIIB X-ray diffractometer with Cu Kα (λ = 1.5406 Å) radiation (40 kV and 200 mA) and a Ni filter. The circular dichroism spectra (CD) of **1**–**3** were recorded at room temperature with a Jasco J-810(S) spectropolarimeter (KCl pellets). The second-order non-linear optical intensities were estimated by measuring microcrystalline samples relative to urea with a Spectra Physics Quanta Ray Prolab 170 Nd:YAG laser using a first-harmonics output of 1064 nm, with a pulse width of 10 ns and a repetition rate of 10 Hz [42].

2.2. Synthesis of (R)-4-(4-(1-carboxyethoxy)phenoxy)-3-chlorobenzoic acid (H_2cpca)

Step 1: Anhydrous potassium carbonate (6.93 g, 50 mmol) was added to a DMF solution (100 mL) of (*R*)-(+)-2-(4-hydroxyphenoxy)propionic acid (3.65 g, 20 mmol) and stirred for 3 h at 80 °C, to which 3,4-dichlorobenzonitrile (3.44 g, 20 mmol) was then added and stirred at 100–105 °C for 10 h. The solvent was then removed from the mixture by evaporation and 100 ml water was added. The pH value was adjusted to 1–2 by adding cool hydrochloric acid (1.0 mol/L) to get 2-(4-(4-cyano-2-chlorophenoxy)phenoxy)propanoic acid as a white solid. Yield: 5.40 g, 85%. *Step 2:* A mixture of 2-(4-(4-cyano-2-chlorophenoxy)phenoxy)propanoic acid (15.89 g, 50 mmol) and NaOH (10 g, 25 mmol) in water (50 mL) was stirred at 100 °C for 10 h. After cooling to room temperature, the pH of the mixture was adjusted to 4–5 with cool hydrochloric acid (1.0 mol/L) to obtain a white solid of H_2cpca, which was dried in air. Yield: 15.66 g, 93%. (see Scheme 1) Elemental *Anal.* Calc. for $C_{16}H_{13}ClO_6$ (336.72): C, 57.21; H, 4.06. Found: C, 57.27; H, 4.13%. IR (KBr, cm^{-1}): 3424 (m), 2989 (w), 1721 (m), 1691 (w), 1586 (w), 1503 (m), 1199 (s), 896 (w), 834 (w), 696 (w). ^1H NMR (DMSO) δ, ppm: 1.51 (3H, d), 4.83 (1H, d), 6.86 (1H, d), 6.94 (2H, d), 7.00 (2H, d), 7.83 (1H, d), 8.01 (1H, d), 13.08 (2H, s).

2.3. Synthesis of (R)-4-(4-(1-carboxyethoxy)phenoxy)-3-nitrobenzoic acid (H_2cpna)

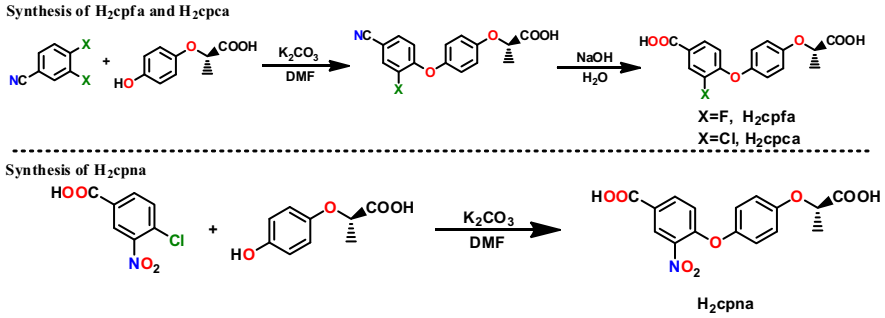
A mixture of (*R*)-(+)-2-(4-hydroxyphenoxy)propionic acid (4.52 g, 24.81 mmol) and anhydrous potassium carbonate (12.00 g, 86.82 mmol) in DMF (125 mL) was added into a 250 mL three-necked flask, then the whole equipment was purged three times with N_2. The resultant solution was heated to 80 °C and allowed to stir for 3 h. 4-Chloro-3-nitrobenzoic acid (5.00 g, 24.81 mmol) was added, the solution was heated to 135 °C and kept for 16 h. After TLC detection (P/E/AcOH = 2:1:0.05) indicated the completion of the reaction, the DMF was removed by rotary evaporation and water (75 mL) was added. The pH value was adjusted to 3-4 with cool hydrochloric acid (1.0 mol/L) to get H_2cpna as a yellow solid. Elemental *Anal.* Calc. for $C_{16}H_{13}NO_8$ (347.28): C, 55.34; H, 3.77, N, 4.03; found: C, 55.13; H, 3.87, N, 4.11%. IR (KBr, cm^{-1}): 3424 (m), 2997 (w), 1730 (m), 1619 (s), 1535 (s), 1502 (s), 1241 (s), 1105 (m), 841 (m), 769 (w). ^1H NMR (DMSO) δ, ppm: 1.51 (3H, d), 4.83 (1H, d), 6.86 (1H, d), 6.94 (2H, d), 7.00 (2H, d), 7.83 (1H, d), 8.01 (1H, d), 13.08 (2H, s).

2.4. Synthesis of [Co(cpfa)(bimb)]·EtOH·H_2O (**1**)

A mixture of H_2cpfa (64.0 mg, 0.2 mmol), $CoCl_2$ (28.0 mg, 0.2 mmol), bimb (63.0 mg, 0.2 mmol), ethanol (5 mL) and H_2O (5 mL) was stirred for 2 h in air and then transferred and sealed in a Teflon reactor (15 mL). The reaction mixture was heated at 120 °C for 3 days and then cooled to room temperature at a rate of 10 °C h^{-1}. Red crystals of complex **1** were obtained in 53% yield (based on Co). Elemental *Anal.* Calc. for $C_{38}H_{37}CoFN_4O_8$ (755.65): C, 60.40; H, 4.94; N, 7.4. Found: C, 60.73, H, 4.61; N, 7.73%. IR (KBr, cm^{-1}): 3117 (w), 2975 (w), 1657 (m), 1500 (s), 1437 (m), 1205 (s), 1089 (m), 943 (w), 846 (w).

2.5. Synthesis of [Co(cpca)(bimb)]·EtOH·H_2O (**2**)

The preparation of **2** was similar to that of **1** except that H_2cpca (67 mg, 0.2 mmol) was used instead of H_2cpfa. Red crystals of **2** were obtained in 55% yield (based on Co). Elemental *Anal.* Calc. for $C_{38}H_{37}CoClN_4O_8$ (772.10): C, 59.11; H, 4.83; N, 7.26. Found: C, 59.47, H, 4.49; N, 7.63%. IR (KBr, cm^{-1}): 3138 (w), 2348 (w), 1609 (m), 1521 (s), 1385 (s), 1250 (m), 1095 (m), 826 (w).



Scheme 1. Synthesis routes to H_2cpfa, H_2cpca and H_2cpna.