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Syntheses, structures, magnetic properties and luminescence of four coordination polymers based on an asymmetric semirigid tricarboxylate ligand

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ABSTRACT

In this work, four new complexes, $[Mn(\mu_3\text{-Hcpoia})(phen)(H_2O)]_n$ **1**, $[Mn_2(\mu_4\text{-Hcpoia})_2(\mu_2\text{-bib})(H_2O)_2]_n$ **2**, $[Zn(\mu_2\text{-Hcpoia})(phen)(H_2O)]_n$ **3**, and $[Zn_2(\mu_2\text{-Hcpoia})_2(\mu_2\text{–}4,4'\text{-bpy})(H_2O)_2]_n \cdot 2nH_2O$ **4** (H_3cpoia = 4-(4-carboxyphenoxy)isophthalic acid, phen = phenanthroline, bib = 1,4-di(1H-imidazol-1-yl)benzene, 4,4′-bpy = 4,4′-bipyridine) have been synthesized by solvothermal reactions. Complexes **1**–**4** were fully characterized by IR spectroscopy, elemental analyses, thermogravimetric analyses, powder and single-crystal X-ray diffraction. Complexes **1** and **2** present two-dimensional (2D) structures based on the dinuclear Mn(II) secondary building units with the vertex symbols of (4.8^2) and $(3^2.4^4)(3^4.4^6.6^4.7)$, respectively. Complex **3** possesses one-dimensional (1D) structure and reveals a uninodal 2-connected chain with the **2C1** topology. Complex **4** exhibits a 1D ladder-like double chain, containing a 1D metal–organic chain interconnected by the 4,4′-bpy ligand with the vertex symbol of $(4^2.6)$. Such a rich structural diversity of **1**–**4** is driven by various factors, including the type of the metal(II) ions and the ancillary ligands, as well as the coordination mode of ligand. Complexes **1** and **2** show antiferromagnetic interactions ($J = -0.719\ \text{cm}^{-1}$ for **1**, and $\boldsymbol{J} = -6.981\ \text{cm}^{-1}$ for **2**) in dimeric units with the Mn-Mn distances of 4.451(1) and 3.151(5) Å, respectively, that are related to double *syn–anti* carboxylate bridges and four bis-bidentate carboxylate groups with *syn–syn* and *μ–oxo* modes. The solid-state luminescent behaviors of **3**, **4** were also investigated systematically.

1. Introduction

Metal-organic coordination polymers (CPs) have currently attracted considerable attention not only for their intriguing structural architectures and topologies but also for their potential applications, such as gas storage/separation [1–3], luminescence [4–6], magnetism [7–9], catalysis [10,11] and chemical sensing [12,13] and so on. Among the various types of CPs, the manganese-based coordination polymers with half-filled d-electron spherical distribution of Mn(II) ions that are immune to the crystal field effect [14], have received considerable interests in the fields of supramolecular chemistry and crystal engineering not only for their remarkable magnetochemical properties [15,16] but also for their rich biochemistry [17]. Similarly, the CPs with d^{10} configuration of Zn(II) ions that are also not influenced by the crystal field effect of the ligands, show intriguing fluorescent behavior relevant to potential applications in light-emitting diodes (LEDs) [18] and anions, cations or small molecules sense [19–21].

It is well-known that by the judicious choice of the organic spacer and the central metal, it is possible to elaborate a specific architecture and even to create expected properties related to the architecture [22,23]. Since long, mixed multicarboxylate and nitrogen donor linkers have been widely utilized to construct CPs. The mixed-ligands strategy incorporating N-donor co-linkers with different lengths and rigidness/flexibility has been proved successfully to create various CPs [24,25].

Recently, we have focused our attention on asymmetric semirigid tricarboxylate ligands with bent backbones based on the following considerations: (1) two benzene rings can appropriately rotate around the centric atom (C, O, *S*, and N atoms), which may lead to the appearance of a new crystalline material with new structures [26,27]. (2) The carboxylate groups can be completely or partially deprotonated which can result in diverse coordination patterns and high dimension-

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alities, especially when acting as a multiply bridging space, and it has been proven usefully in accessing great structural diversity.

Hence, in the present work, one asymmetric semirigid tricarboxylate ligand with three carboxylic groups attached at 2-, 4-, and 4′-positions, 4-(4-carboxyphenoxy)isophthalic acid (H_3cpoia), was employed to assemble Mn(II) and Zn(II) ions into coordination polymers with the help of terminal ligand phenanthroline (phen), linear ligands 1,4-di(1H-imidazol-1-yl)benzene (bib) and 4,4′-bipyridine (4,4′-bpy) as the secondary ligands. As far as we know, H_3cpoia is poorly used for the generation of CPs. Fortunately, four novel CPs with diverse molecular structures $[Mn(\mu_3\text{-Hcpoia})(phen)(H_2O)]_n$ **1**, $[Mn_2(\mu_4\text{-Hcpoia})_2(\mu_2\text{-bib})(H_2O)_2]_n$ **2**, $[Zn(\mu_2\text{-Hcpoia})(phen)(H_2O)]_n$ **3**, and $[Zn_2(\mu_2\text{-Hcpoia})_2(\mu_2\text{–}4,4'\text{-bpy})(H_2O)_2]_n\cdot 2nH_2O$ **4** have been obtained. They were characterized by IR spectroscopy, elemental analyses (EAs), X-ray crystallography, thermogravimetric analyses (TGAs) and powder X-ray diffraction (PXRD). The magnetic properties **1** and **2** have been studied in detail. Solid-state luminescent properties of complexes **3** and **4** were also examined at ambient temperature.

2. Experimental section

2.1. Material and general methods

H_3cpoia was received from Jinan Trading Company, China. All other reagents and solvents were purchased from commercial sources and used without further purification. The IR spectra were recorded from a KBr pellet in the range of 4000–400 cm^{-1} on a BRUKER TENSOR27 Spectrometer and given in Fig. S1. EAs were carried out using a CHNO-Rapid instrument. PXRD data were recorded on a Riguka Smartlab X-ray diffractometer with Cu–Kα radiation ($\lambda = 1.5406$ Å) in the range of 5–50° with 2θ at a rate of 5 °/min^{-1}. TGAs were carried out on a Dupont thermal analyzer with temperature range of 25–800 °C under N_2 flow with a heating rate of 10 °C min^{-1}. Magnetic susceptibility data were obtained by SQUID magnetometer (Quantum MPMS) in the range of 2.0–300 K by using an applied field of 1000 *Oe*. The alternating current (AC) magnetic susceptibility was recorded with oscillating frequencies (10, 32, 100, 320 and 1000 Hz) in an AC field of 1000 *Oe*. Fluorescent spectra were characterized at room temperature using a Fluoromax-4 Spectrofluorometer with a xenon arc lamp as the light source. The quantum yields were measured on an Edinburgh instrument FLS920.

2.1.1. Synthesis of $[Mn(\mu_3\text{-Hcpoia})(phen)(H_2O)]_n$ (1)

A mixture of H_3cpoia (0.0302 g, 0.1 mmol), $MnCl_2\cdot 4H_2O$ (0.0396 g, 0.2 mmol), phen (0.0396 g, 0.2 mmol), 1 mL KOH (0.2 mol/L) and 6 mL water was added to a 13 mL Teflon-lined stainless steel and heated under autogenous pressure at 413 K for 72 h and then cooled to room temperature naturally. Yellow block-shaped crystals of **1** were collected by filtration, washed with H_2O, and dried in air (yield ~ 81%, based on Mn). Analysis calculated for $C_{27}H_{18}MnN_2O_8$ C 58.55, H 3.25, N 5.06%; found: C 58.43, H 3.39, N 5.26%. IR (KBr, *υ*, cm^{-1}): 3370w, 3209m, 1695s, 1625s, 1595s, 1557m, 1382s, 1232s, 1163m, 850m, 802m, 787m, 774m, 729m (Fig. S1).

2.1.2. Synthesis of $[Mn_2(\mu_4\text{-Hcpoia})_2(\mu_2\text{-bib})(H_2O)_2]_n$ (2)

The synthesis of **2** was similar to that of **1** except that phen was replaced by bib (0.0420 g, 0.2 mmol). Colorless block crystals were obtained (yield 63% based on Mn). Analysis calculated for $C_{21}H_{15}MnN_2O_8$: C 52.69, H 3.14, N 5.85%; found: C 53.43, H 3.23, N 6.02%. IR (KBr, *υ*, cm^{-1}): 3421w, 3334w, 3149w, 1669m, 1603m, 1509s, 1432s, 1324m, 1243m, 1127s, 1125m, 1092m, 1013m, 935m, 856m, 793m, 789m, 762m, 624m (Fig. S1).

2.1.3. Synthesis of $[Zn(\mu_2\text{-Hcpoia})(phen)(H_2O)]_n$ (3)

A mixture of 4-(4-carboxyphenoxy)isophthalic acid (0.0302 g, 0.1 mmol), $Zn(NO_3)_2\cdot 6H_2O$ (0.0595 g, 0.2 mmol), phen (0.0198 g, 0.1 mmol), 1 mL DMF and 1 mL KOH (0.2 mol/L) was added to water (6 mL) in a 13 mL of Teflon-lined stainless steel and heated under autogenous pressure at 393 K for 72 h and then cooled to room temperature naturally. Colorless block-shaped crystals were collected by filtration, washed with H_2O, and dried in air (yield ~ 61%, based on Zn). Analysis calculated for $C_{27}H_{18}N_2O_8Zn$ C 57.47, H 3.19, N 4.97%; found: C 57.32, H3.53, N 5.12%. IR (KBr, *υ*, cm^{-1}): 3385m, 1664m, 1625m, 1605m, 1552s, 1420s, 1387m, 1356s, 1242s, 1163m, 773m, 700m, 632w (Fig. S1).

2.1.4. Synthesis of $[Zn_2(\mu_2\text{-Hcpoia})_2(\mu_2\text{–}4,4'\text{-bpy})(H_2O)_2]_n\cdot 2nH_2O$ (4)

A mixture of 4-(4-carboxyphenoxy)isophthalic acid (0.0302 g, 0.1 mmol), $Zn(NO_3)_2\cdot 6H_2O$ (59.5 mg, 0.2 mmol), 4,4′-bpy (31.2 mg, 0.2 mmol) and 0.25 mL KOH (0.2 mol/L) was added to water (6 mL) in a 13 mL of Teflon-lined stainless steel and heated under autogenous pressure at 393 K for 72 h and then cooled to room temperature naturally. Colorless block-shaped crystals were collected by filtration, washed with H_2O, and dried in air (yield ~ 61%, based on Mn). Analysis calculated for $C_{20}H_{16}NO_9Zn$ C 50.07, H 3.33, N 2.92%; found: C 49.82, H 3.27, N 3.23%. IR (KBr, *υ*, cm^{-1}): 3429m, 1626s, 1603s, 1658m, 1462m, 1354s, 1255m, 824m, 789m, 725m (Fig. S1).

2.2. X-ray crystallographic data collection and structural determination

Crystallographic diffraction data for complex **1** were collected in the Beijing Synchrotron Radiation Facility (BSRF) beamline 3W1A, which was mounted with a MARCCD-345 detector ($\lambda = 0.7200$ Å) with the storage ring working at 2.5 GeV at 100(2) K. Data were collected by the MARCCD program and processed using *HKL*2000 [28]. The data for complexes **2**–**4** were collected on a Bruker D8-Quest diffractometer equipped with a photon 100 detector by using a graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 200(2) K for **2**, 298(2) K for **3** and **4**. Data integrations were performed using SAINT program [29] and the absorption corrections were determined using the SADABS [30].

Structures of **1**–**4** were solved *via* direct methods employed in the *SHELXS-97* [31] program and refined by full-matrix least-squares methods against F^2 with *SHELXL*-2016 [32]. After all non-H atoms were refined anisotropically, hydrogen atoms attached to C atoms were placed geometrically and refined using a riding model approximation, with C–H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. H atoms attached to O atoms were located from difference Fourier maps, and their bond lengths were restrained in the range from 0.82 to 0.84 Å, and they were refined using a riding model, with $U_{iso}(H) = 1.5U_{eq}(O)$. For complex **4**, a disordered water molecule in the unit cell was subtracted by the SQUEEZE (PLATON) procedure [33]. The formula unit was deduced through a combination of EA and TGA characterizations. The topological analyses were performed on the TOPOS program [34]. The more detailed information were listed in the CIF files (Supporting information). Crystal data and structure refinement details of complexes **1**–**4** were summarized in Table 1. Crystallographic data for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC numbers of 1849536–1849539 for **1**–**4**.

3. Results and discussion

3.1. Preparation

In our initial recipes, we were going to employ one terminal ligand (phen) and two bridge ligands (4,4′-bpy and bib) to coordinate with Mn(II) and Zn(II) ions, in order to get the structures of their complexes. The experiment was designed as shown in Scheme 1. In the first route, complexes **1** and **3** were successfully achieved by a mixture of Mn(II) or Zn(II) ions, H_3cpoia and phen in aqueous solution, respectively. In the second route, we failed to obtain suitable