



Two double and triple interpenetrated Cd(II) and Zn(II) coordination polymers based on mixed O- and N-donor ligands: Syntheses, crystal structures and luminescent properties

Li Zhang^a, Xiaohui Li^b, Yan Zhang^{a,*}

^a Department of Applied Chemistry, Hengshui University, Hebei Province, Hengshui, 053000, China

^b College of Sciences, Agricultural University of Hebei, Hebei Province, Baoding, 071001, China

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ABSTRACT

Two interpenetrated 3D coordination polymers, namely $[\text{Cd}_2(\text{tdc})_2(\text{bpp}) (\text{DMA})]_n$ (**1**) and $[\text{Zn}_2(\text{tdc})_2(\text{bib})_2]_n \cdot 2n(\text{DMA})$ (**2**) (H_2tdc = 2,5-thiophenedicarboxylic acid, bpp = 1,3-di(4-pyridyl)propane, bib = 1, 4-bis(imidazolyl)butane, DMA = N,N-dimethylacetamide), have been solvothermally synthesized by the self-assembly of flexible N-donor and dicarboxylate ligands. Single crystal X-ray diffraction analyses revealed that compound **1** features a 2-fold interpenetrated 3D framework based on dinuclear $[\text{Cd}_2(\text{COO})_3]$ subunits and can be simplified into a 6-connected pcu topology, and compound **2** features a 3-fold interpenetrated 3D framework with 4-connected dia topology. Moreover, the thermal stabilities and luminescent properties of these two compounds were also investigated.

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1. Introduction

As a new class of hybrid materials, coordination polymers (CPs) have attracted tremendous interests from scientists not only owing to their diverse topological frameworks but also owing to their promising applications in luminescence, catalysis, magnetism, gas storage and so on [1–5]. Under this background, much effort has been devoted to this field with the aim of rational design and construction of CPs, and simultaneously, many effective synthetic strategies also have been successfully established and developed by chemists such as pillar-layer strategy, mixed-ligand self-assembly strategy, post-synthetic modification, second building block method, and template synthesis [6–10]. Among these strategies to construct CPs, the mixed-ligand self-assembly strategy is one of the most effective and the most commonly used methods to synthesize new functional CPs [11–14]. Therefore, selection of appropriate mixed ligands may play a crucial role in directing the synthesis of target products. According to previously reported mixed-ligand-based CPs, we know that N-donor and O-donor mixed-ligand is one of the most commonly used combinations [15–17]. The O-donor carboxylate ligands can assume many kinds of bridging or

chelating modes to connect metal ions, and the linear N-donors ligands (such as dipyridyl- or diimidazol-based ligands) can act as bridges to construct high-dimensional CPs. Moreover, the linear N-donor and O-donor mixed-ligand can benefit to construct novel interpenetrated CPs. Based on the above considerations, in this work, we selected linear O-donor ligand (2,5-thiophenedicarboxylic acid) and N-donor ligand (bpp or bib) as the mixed-ligand to assemble with Cd(II) ions or Zn(II) ions (Scheme 1), successfully obtained two novel interpenetrated CPs, namely $[\text{Cd}_2(\text{tdc})_2(\text{bpp}) (\text{DMA})]_n$ (**1**) and $[\text{Zn}_2(\text{tdc})_2(\text{bib})_2]_n \cdot 2n(\text{DMA})$ (**2**) (H_2tdc = 2,5-thiophenedicarboxylic acid, bpp = 1,3-di(4-pyridyl)propane, bib = 1, 4-bis(imidazolyl)butane, DMA = N,N-dimethylacetamide). In this study, we reported the syntheses, crystal structures and luminescent properties of these two compounds.

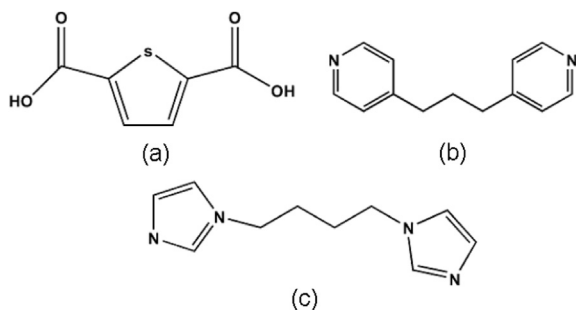
2. Experimental

2.1. Materials and methods

All the chemicals used in this work were commercially purchased and used without further purification. Elemental analysis of C, H and N were performed on an EA1110 CHNS-O CE elemental analyzer. Thermogravimetric experiments were performed using a

* Corresponding author.

E-mail address: yan_zhang3157@163.com (Y. Zhang).



Scheme 1. (a) The H_2tdc ligand. (b) The bpp ligand. (c) The bib ligand.

TGA/NETZSCH STA449C instrument heated from 30 to 800 °C (heating rate of 10 °C/min, nitrogen stream). Powder X-ray diffraction data were collected using PANalytical X'Pert Pro powder diffractometer with $Cu-K\alpha$ radiation and $5^\circ \leq 2\theta \leq 50^\circ$. Fluorescence spectra of the solid samples were performed on an Edinburgh Analytical instrument FLS920.

2.2. Syntheses

2.2.1. Synthesis of $[Cd_2(tdc)_2(bpp)(DMA)]_n$ (**1**)

A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (0.06 g, 0.2 mmol), H_2tdc (0.034 g, 0.2 mmol), bpp (0.038 g, 0.2 mmol) and DMA (3 mL) was sealed in a Teflon-lined stainless steel reactor under autogenous pressure at 120 °C for 72 h and then cooled to room temperature slowly. Colorless prism crystals of **1** were obtained in 43% yield based on $Cd(NO_3)_2 \cdot 4H_2O$. Elemental analyses for $C_{29}H_{27}N_3O_9S_2Cd_2$ (850.48): Calcd. (%) C, 40.92; H, 3.17; N, 4.94. Found (%): C, 40.95; H, 3.23; N, 4.99%.

2.2.2. Synthesis of $[Zn_2(tdc)_2(bib)_2]_n \cdot 2n(DMA)$ (**2**)

A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.152 g, 0.5 mmol), H_2tdc (0.085 g, 0.5 mmol), bib (0.095 g, 0.5 mmol) and DMA (3 mL) was sealed in a 23 mL Teflon-lined stainless steel reactor under autogenous pressure at 120 °C for 72 h and then cooled to room temperature slowly. Colorless block crystals of **2** were obtained in 54% yield based on $Zn(NO_3)_2 \cdot 6H_2O$. Elemental analyses for $C_{40}H_{50}N_{10}O_{10}S_2Zn_2$ (1025.80): Calcd. (%) C, 46.79; H, 4.87; N, 13.65. Found (%): C, 46.82; H, 4.85; N, 13.70.

2.2.3. X-ray crystallography

Single crystal X-ray diffraction data of compounds **1** and **2** were collected on Oxford Xcalibur E diffractometer (Mo- $K\alpha$ radiation, $\lambda = 0.71073$ Å, graphite monochromator) at 293(2) K. Empirical absorption corrections were applied to the data using the SADABS program [18]. The structure was solved by the direct method and refined by the full-matrix least-squares on F^2 using the SHELXL-97 program [19]. All of the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms attached to carbon atoms were located at their ideal positions. Experimental details for the structure determination are presented in Table 1. Selected bond lengths and angles for compounds **1** and **2** are listed in Table 2.

3. Result and discussion

3.1. Crystal structure of compound **1**

Single crystal X-ray structural analysis reveals that compound **1** crystallizes in the monoclinic $P2_1/c$ space group and features a 2-fold interpenetrated pcu topological network. The asymmetric

unit of **1** contains two $Cd(II)$ ions, two tdc^{2-} ligands, one bpp ligand and one coordinated DMA molecule. As shown in Fig. 1a, both $Cd1$ and $Cd2$ are six-coordinated with distorted octahedral coordination geometries. For $Cd1$, it coordinated by four carboxylate oxygen atoms, one nitrogen atom and one coordinated DMA molecule. For $Cd2$, it coordinated by five carboxylate oxygen atoms and one nitrogen atom. The $Cd-O$ distances and the $Cd-N$ distances are in the range of 2.198(2)–2.479(3) Å, 2.320(3)–2.326(3) Å, respectively. The tdc^{2-} ligand can be divided into two kinds according to the coordination mode: (i) one linking three $Cd(II)$ ions with its one carboxylate group in chelating mode and the other carboxylate group in syn, syn-(O,O') mode; (ii) the second linking three $Cd(II)$ ions with its one carboxylate group in chelating-bridging mode and the other in syn, syn-(O,O') mode. Two adjacent $Cd(II)$ ions are bridged by three carboxylate groups, generating a dinuclear $[Cd_2(COO)_3]$ subunit with the $Cd \cdots Cd$ separation of 3.625 Å (Fig. S1). These dinuclear $[Cd_2(COO)_3]$ subunits are further extended into a 2D layer via the connection of the tdc^{2-} ligands (Fig. 1b). The bpp ligands as bridges further connected the adjacent 2D layers into a 3D pillar-layer framework (Fig. 1c). Topologically speaking, each dinuclear $[Cd_2(COO)_3]$ subunit is bounded to six adjacent ones via the connection of tdc^{2-} and bpp ligands, so it can be reduced into a 6-connected node, and the tdc^{2-} and bpp ligands can be looked as linear linkers, thus, the single framework of **1** can be simplified into a 6-connected pcu topological network with the point symbol of $\{4^{12}, 6^3\}$ (Fig. S2). Notably, there are 1D channels in the single framework viewing along crystallographical c axis. The 1D channels are so large that another equivalent one can be accommodated in that channels, resulting in a 2-fold interpenetrated 3D framework of **1** (Fig. 1d).

3.2. Crystal structure of compound **2**

Single crystal X-ray diffraction analysis revealed that compound **2** crystallizes in the triclinic $P-1$ space group with the asymmetric unit containing two $Zn(II)$ ions, two tdc^{2-} ligands, one and two halves bib ligands. As shown in Fig. 2a, both $Zn1$ and $Zn2$ are tetrahedrally coordinated by two carboxylate oxygen atoms and two nitrogen atoms. The $Zn-O$ and $Zn-N$ distances range from 1.881(3)–1.999(3) Å, 1.971(3)–2.011(4) Å, respectively. The tdc^{2-} ligand and bib ligand act as bis(monodentate) bridging ligands in the crystal structure. Under the synergetic effect of tdc^{2-} and bib , all $Zn(II)$ ions are connected together, giving rise to a 3D framework (Fig. 2b). Topologically speaking, if each $Zn(II)$ ions can be reduced into 4-connected nodes, and the tdc^{2-} and bib can be regarded as linear linkers, this 3D framework can be simplified into a 4-connected dia topological network with the point symbol of $\{6^6\}$ (Fig. S3). Viewing along crystallographical b axis, there exist large 1D quadrilateral channels, which are so large that can accommodate another two equivalent ones. Thus, the whole framework of **2** is 3-fold interpenetrated (Fig. 2c). After interpenetration, compound **2** still has solvent accessible void space of 29.6% of the total crystal volume calculated by PLATON program. The solvent accessible void space is occupied by the lattice DMA molecules.

3.3. PXRD patterns and thermal analysis

To prove the phase purities of the as-synthesized samples of compounds **1** and **2**, powder X-ray diffraction analyses were performed. As shown in Fig. S4a, the experimental patterns of compound **1** corresponds well to the simulated ones based on the single crystal diffraction data, indicating that the bulk samples of compounds **1** is in pure phase. As shown in Fig. S4b, the main peak positions of the experimental pattern are in agreement with that of the simulated pattern, but there are also some small differences

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