

A novel three-dimensional chiral (3,8,9)-connected framework: Synthesis, structure, optical band gap and photoluminescence



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ABSTRACT

A novel coordination polymer, namely, $[\text{Cd}_7(4,4'\text{-tmbpt})_3(\text{D-cam})_6(\text{OH})_2] \cdot 8.25\text{H}_2\text{O}$ (**1**), where 4,4'-tmbpt = 1-((1*H*-1,2,4-triazol-1-yl)methyl)-3,5-bis(4-pyridyl)-1,2,4-triazole, and D-H₂cam = D-camphoric acid, has been synthesized under hydrothermal condition. Compound **1** exhibits a three-dimensional homochiral (3,8,9)-connected framework, which is a rare example of coordination polymer with homochiral highly connected structure based on the chiral source of D-H₂cam. The structure of the compound was determined by single-crystal X-ray diffraction analysis and further characterized by infrared spectrum (IR), elemental analysis and UV–Vis spectrum. Moreover, the optical band gap and photoluminescent property of the compound have been investigated.

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Currently, chiral coordination polymers (CPs) are of special interest because of their potential applications in the fields of asymmetric heterogeneous catalyses [1], enantioselective fluorescence sensing [2], nonlinear optics [3], ferroelectrics [3,4], and so on. So far, three strategies for constructing chiral CPs have been developed. In the first method, chiral CPs can be constructed by totally achiral components. However, this method cannot guarantee all the bulk samples of CPs to be chiral, because the achiral nature of organic ligand tends to generate enantiomorphs [5,6]. This method is relatively rare and cannot be predicted beforehand [7]. More importantly, it must rely on luck by chance. In the second approach, chiral CPs can be prepared by the introduction of chiral template or enantiopure co-ligand which can direct the homochiral crystallization of an intrinsically chiral CP [5,6,8]. In the third approach, chiral CPs can be synthesized by the combination of metal ions or metal clusters as nodes and chiral ligands as linkers. The third method is the simplest and most effective strategy to obtain homochiral CPs, which does not need to separate the racemic mixture like the first method [5,6]. This method can impart the chirality to the resultant structures, and also adjust the properties of the chiral CPs via the modification of the chiral organic ligands [9]. Among the various chiral ligands, D-camphoric acid (D-H₂cam, Scheme S1) is particularly appealing because it has two carboxylic acid groups located in a suitable geometry to act as a bent, divergent linker between two metal cations [10]. Moreover, it is commercially available and relatively inexpensive [5].

On the other hand, highly connected structures (the number of connections ≥ 8) with robust framework stabilities and remarkable surface areas are of current interest [11–14]. However, the preparation of CPs with highly connected structures is still a challenge due to the limited coordination numbers of single metal centers and steric hindrances of the organic ligands [15–17]. In our previous work, the 1-((1*H*-1,2,4-triazol-1-yl)methyl)-3,5-bis(4-pyridyl)-1,2,4-triazole (4,4'-tmbpt) ligand has been proven to be an effective ligand for the preparation of CPs with highly connected structures [18–20]. In order to continue and improve our study, in this work, D-H₂cam was selected as a chiral source to construct a homochiral highly connected CP. By using the multidentate N-heterocyclic co-ligand 4,4'-tmbpt (Scheme S1), we successfully synthesized a homochiral highly connected CP $[\text{Cd}_7(4,4'\text{-tmbpt})_3(\text{D-cam})_6(\text{OH})_2] \cdot 8.25\text{H}_2\text{O}$ (**1**) under hydrothermal condition (Experimental in the Supporting information). The structure of compound **1** was determined by single-crystal X-ray diffraction analysis and further characterized by infrared spectrum (IR), elemental analysis and UV–Vis spectrum. In addition, the optical band gap and photoluminescent property of the compound have been investigated.

Single-crystal X-ray diffraction analysis reveals that compound **1** crystallizes in the monoclinic chiral space group *C*2 (*X*-ray crystallography in the Supporting information). The asymmetric unit of **1** consists of seven Cd(II) ions (the occupancy of Cd3 and Cd4 is 0.5), three 4,4'-tmbpt ligands, six D-cam²⁻ anions, two hydroxyl groups, and eight and a quarter water molecules. As illustrated in Fig. 1, Cd1 is seven-coordinated in a pentagonal bipyramid coordination geometry, defined by one nitrogen atom from one 4,4'-tmbpt ligand and six oxygen atoms from three

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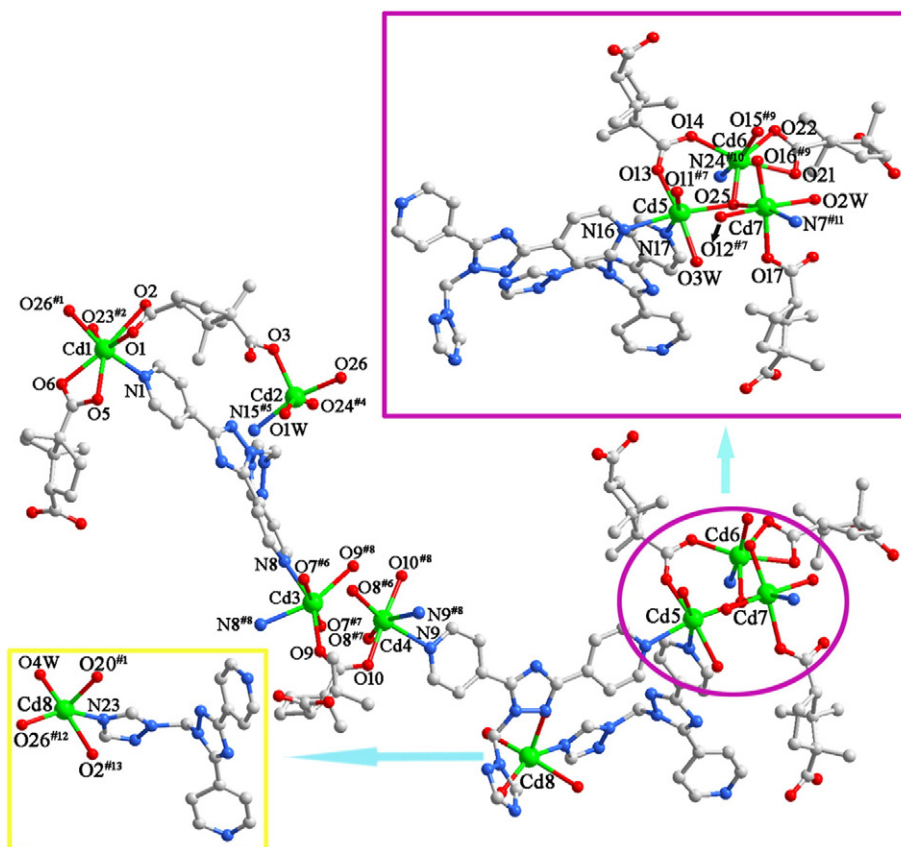


Fig. 1. View of the coordination environments of Cd(II) ions. Symmetry codes: ^{#1} $x, y - 1, z$; ^{#2} $-x + 1/2, y - 5/2, -z - 1$; ^{#4} $-x + 1/2, y - 3/2, -z - 1$; ^{#5} $-x + 1, y - 1, -z$; ^{#6} $-x + 1, y + 1, -z$; ^{#7} $x, y + 1, z$; ^{#8} $-x + 1, y, -z$; ^{#9} $-x + 1/2, y + 1/2, -z - 1$; ^{#10} $-x + 1, y, -z - 1$; ^{#11} $x, y + 2, z$; ^{#12} $x + 1/2, y + 1/2, z$; ^{#13} $x + 1/2, y + 3/2, z$.

different $D\text{-cam}^{2-}$ anions and one hydroxyl group. Cd2 and Cd8 are five-coordinated in trigonal bipyramid coordination geometries, furnished by one nitrogen atom from one 4,4'-tmbpt ligand and four oxygen atoms from one hydroxyl group, one water molecule and two individual $D\text{-cam}^{2-}$ anions. Cd3 to Cd7 atoms are six-coordinated in octahedral coordination spheres, but their coordination environments are different. Cd3 and Cd4 are coordinated by two nitrogen atoms from two individual 4,4'-tmbpt ligands and four oxygen atoms from four different $D\text{-cam}^{2-}$ anions. Cd5 is coordinated by two nitrogen atoms from two different 4,4'-tmbpt ligands and four oxygen atoms from one hydroxyl group, one water molecule and two individual $D\text{-cam}^{2-}$ anions. Cd6 is surrounded by one nitrogen atom from one 4,4'-tmbpt ligand and five oxygen atoms from three different $D\text{-cam}^{2-}$ anions and one hydroxyl group. Cd7 is coordinated by one nitrogen atom from one 4,4'-tmbpt ligand and five oxygen atoms from three different $D\text{-cam}^{2-}$ anions, one water molecule and one hydroxyl group. The Cd–N bond lengths are in the range of 2.295 (9)–2.450 (7) Å, and the Cd–O bond distances are in the range of 2.170 (13)–2.560 (8) Å (Table S1). Cd1, Cd2 and Cd8, as well as Cd5, Cd6 and Cd7 are connected by one hydroxyl group to form two trinuclear units $[\text{Cd}_3(\mu_3\text{-OH})]^{5+}$, while Cd3 and Cd4 are connected by four carboxylate groups to generate a binuclear unit $[\text{Cd}_2(\text{COO})_4]$ (Fig. 2). The carboxylate groups of the $D\text{-cam}^{2-}$ anions in compound **1** adopt four kinds of coordination modes: $\mu_2\text{-}\eta^2\text{:}\eta^1$, $\mu_2\text{-}\eta^1\text{:}\eta^1$, $\mu_1\text{-}\eta^1\text{:}\eta^1$ and $\mu_1\text{-}\eta^1\text{:}\eta^0$. In this way, the $D\text{-cam}^{2-}$ anions link the binuclear and trinuclear units to form a three-dimensional (3D) framework (Fig. S1). Each 4,4'-tmbpt ligand acts as a tridentate ligand, further coordinates to the metal ions and consolidates the complicated 3D framework.

From the topological point of view, the 4,4'-tmbpt ligands can be regarded as 3-connected nodes, the binuclear units and the trinuclear clusters formed by the Cd1, Cd2 and Cd8 atoms can be considered as two kinds of 8-connected nodes (Fig. 3), the trinuclear units formed by the Cd5, Cd6 and Cd7 atoms can be viewed as 9-connected nodes

(Fig. 4a), and the $D\text{-cam}^{2-}$ anions can be reduced to linkers. Thus, the complicated 3D framework of **1** can be simplified as a (3,8,9)-connected framework with a $(4^2 \cdot 5)_2(4^3)(4^7 \cdot 5^7 \cdot 6^{11} \cdot 7 \cdot 8^2)(4^{12} \cdot 5^7 \cdot 6^7 \cdot 7^2)(4^{11} \cdot 5^9 \cdot 6^{13} \cdot 7^3)$ topology (Fig. 4b).

The UV–Vis absorption spectrum data of compound **1** were collected in the crystalline state at room temperature. As shown in Fig. S2a, compound **1** shows an absorption band from about 210 to 230 nm, which may be attributed to the metal perturbed $\pi\text{-}\pi^*$ intra-ligand electron transition [21,22].

Some CPs have been reported to be promising semiconductors in the literature [21,23]. Sparked by this, we investigated the conductivity potential of compound **1** in this work. The diffuse reflectivity spectrum data for powder samples of **1** were collected to obtain the band gap (E_g). The absorption (α/S) data were converted from the reflectivity according to the Kubelka–Munk function: $\alpha/S = (1 - R)^2 / 2R$ (R is the

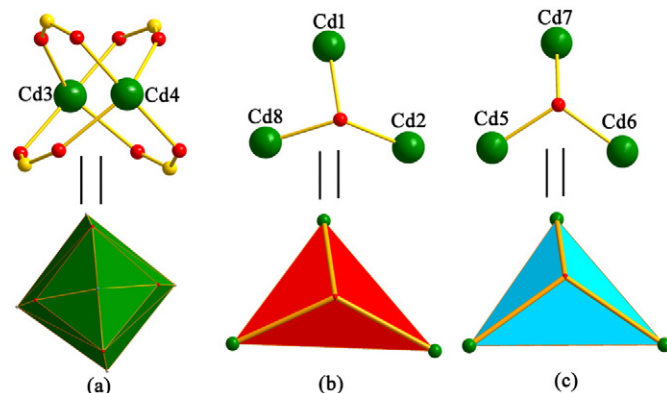


Fig. 2. View of the binuclear and trinuclear units in compound **1**.

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