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A novel 3D self-catenated coordination polymer with multiform helical chains

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ABSTRACT

A novel noncentrosymmetric coordination polymer, namely, $[Cd_2L(H_2O)_2]\cdot$solvent (**1**) (H_4L = tetrakis[4-(carboxyphenyl)oxamethyl]methane acid), has been successfully solvothermally synthesized and characterized by signal-crystal X-ray diffraction, IR spectra, element analysis, powder X-ray diffraction and thermogravimetric analysis. The structure study shows that **1** exhibits a 3D framework based on 1D carboxylate-metal chains. Furthermore, **1** contains three types of helical chains along the *c* axis. From a topological perspective, **1** can be reduced to a new self-catenated binodal (4,6)-connected $(6^6)(6^{15})$ topology. In addition, the second-order nonlinear optical and fluorescent properties of **1** have also been investigated.

Coordination polymers (CPs) or metal–organic frameworks are attracting more and more interests in recent years because of their fascinating structures and potential applications in gas sorption, magnetism and catalysis [1]. The helices have attracted a great interest in coordination chemistry and materials chemistry for their ubiquitous in nature and artificial structures and practical implications in biology, optical devices and asymmetric catalysis [2]. Up to now, many chemists have made contributions to the field, and the design and synthesis of helical structures has shown remarkable progress [3–6]. CPs with single-, double-, triple- and even multiple-stranded helices have been comprehensively studied [4]. Wang and his co-workers have reported pioneering works in the field of isolating multiform helical CPs [5]. In addition, another noticeable structure, reported by Zheng group, is the first 3D self-interpenetrating chiral framework with six kinds of helices [6]. However, it is still a great challenge for generating new 3D CPs with multiform helices [5–7].

On the other hand, nonlinear second harmonic generation (SHG) behavior has been widely concerned for their applications in many fields such as optoelectronic devices and photonics technologies [8]. CPs with advantages in synthesis and structures bring out a new category of potential nonlinear-optical (NLO) materials. The design and synthesis of NLO active CPs has been considered as an effective way for preparing new functional materials [8a]. An interesting work is that Cao and his partners have introduced second-order NLO and ferroelectric properties into the porous framework to prepare multifunctional material [9a,b]. Otherwise, Du et al. have also reported NLO active CPs with strong SHG response, with approximately 1.1 times that of urea [9c]. However, although a lot of works have been paid to this field, the synthesis of NLO active CPs remains challenges because such compounds require the absence of a center of symmetry [10]. Specifically, it is still difficult to construct the NLO active CPs with achiral ligands, while the reported NLO active CPs is mostly synthesized by chiral ligands [9,10].

On the basis of the above considerations, it is meaningful but still difficult to synthesis new noncentrosymmetric CPs with multifarious helices by using achiral ligands. To achieve this aim, we choose tetrakis[4-(carboxyphenyl)oxamethyl]methane acid (H_4L) [11] to prepare the complex. The ligand can form many coordination modes as a result of the carboxylate parts rotating around the central carbon atom [12]. Fortunately, we have successfully synthesized and characterized a new self-catenated noncentrosymmetric coordination polymer, namely, $[Cd_2L(H_2O)_2]\cdot$ solvent (**1**). The structural studies reveal that the self-catenated framework of **1** contains three types of helical chains. In addition, the second-order nonlinear optical and fluorescent properties of **1** have also been investigated.

The solvent reaction of $CdCl_2\cdot2.5H_2O$ and H_4L (1:1 molar ratio) in a mixture of *N*,*N*-dimethylacetamide (DMA) and H_2O (7: 2 volume ratio) resulted in the formation of colorless block-shaped crystals of **1**. The purity of **1** was confirmed by powder X-ray diffraction (PXRD). It should be noted that solvents play very important roles in the formation of **1**. The best quality block-shaped crystals of **1** can only be isolated when the volume ratio of DMA/H_2O is about 7:2. In addition, when we replaced the solvent DMA with *N*,*N*-dimethylformamide, a significantly different framework could be isolated [12f].

A single crystal X-ray diffraction analysis [13] reveals that **1** crystallizes in the orthorhombic space group *Fdd*2. In the asymmetric unit, there are two crystallographically independent Cd ions with two

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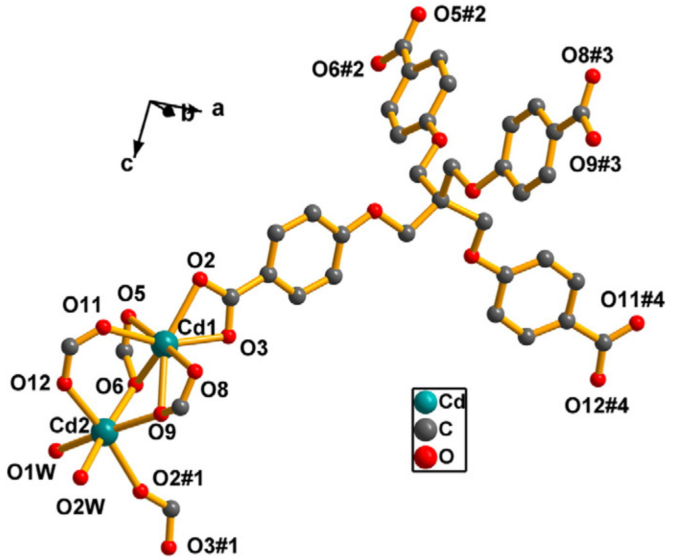

Fig. 1. Coordination environments of Cd1 and Cd2 ions. Symmetry transformations used to generate equivalent atoms: #1: $x, y, -1 + z$; #2: $1/2 - x, -y, 3/2 + z$; #3: $-1/4 + x, 1/4 - y, 7/4 + z$; #4: $-1/2 + x, y, 1/2 + z$.

different coordination environments. As shown in Fig. 1, Cd1 ion is coordinated by seven carboxylate oxygen atoms (O2, O3, O5, O6, O8, O9 and O11) from four carboxylate groups to form a distorted pentagonal bipyramidal geometry (Cd–O 2.254(14)–2.568(14) Å). Cd2 ion is coordinated by four carboxylate oxygen atoms (O2#1, O6, O9 and O12) with the Cd–O distance between the range of 2.218(19)–2.326(11) Å and two coordinated water molecules with the Cd–O distance of Cd2–O1W 2.233(16) Å and Cd2–O2W 2.284(17) Å, respectively. All of the carboxylate groups of the L^{4-} ligand in **1** are deprotonated and display two types of bridging modes: μ^2-η^2:η^1 and *syn-syn*-μ^2-η^1:η^1-bridging fashions (Fig. S2). Viewed along the *c* axis, the two types of carboxylate groups are alternately connected by Cd ions to generate a 1D Cd–O–Cd chain with Cd · · · Cd distance of 3.436 and 3.998 Å, respectively (Figs. 2a and S1a). We have estimated the charge distribution in 1D Cd–O–Cd chain according to the reference reported by Bu group [14]. The result suggests that the charge distribution throughout the chains of **1** follows the sequence (0, 0, 0, 0…) (Fig. S1c), which means each cationic center of chain carry no charge. In compound **1**, thanks to the tetrahedral ligands, 1D Cd–O–Cd chains are connected into a 3D framework (Fig. S1b). Notably, although each carboxylate groups of the X^{4-} anions connect the two kinds of Cd ions in only two types of coordination models, they connect four binuclear Cd units through different complexation modes to form chiral tetrahedral SBUs (Fig. S3), leading to the formation of noncentrosymmetric **1**. All of the open channels in the structure are filled with solvent molecules, and total solvent volume is 8429.7 $Å^3$, which is calculated to be 43.0% of total volume by PLATON program [15]. In addition, net topology of **1** is also been examined. In **1**, if Cd2 ion is regarded as a rod-like linker, Cd1 ion is considered as a six-connected node and L^{4-} ligand can be considered as a four-connected node, then the network of **1** can be reduced to a novel (4,6)-connected $(6^6)(6^{15})$ topology (Fig. 2b) with long symbol $(6_3.6_3.6_3.6_4.6_3.6_5)(6.6.6.6.6.6.6_2.6_3.6_3.6_3.6_3.6_3.6_3.6_5.6_5)$ [16]. Further study on the topological structure reveals that the six-membered ring, which is shown in black, interlocked with another two red six-membered rings to form the self-catenated framework (Fig. 2b).

Interestingly, a further study on the structure indicates that the framework of **1** contains three types of helical chains corresponding to three types of channels along the *c* axis (Fig. 3). The characters of the first type of channels are that there are two rows of coordination water along the two opposite corners. Inspecting the first type of channels, left-handed (1-L) and right-handed (1-R) double-stranded helical chains constructed by ligands bridging Cd1 atoms with a pitch of 14.2 Å (Fig. 3a) can be found. The second type of channels, in which three-fold helical chains (2-L and 2-R) formed by Cd1 atoms and ligands with a pitch of 21.3 Å (Fig. 3b) can be found, contains only one row of coordination water. In the third type of channels, there is no coordination water molecular appearance. In addition, three-fold helical chains (3-L and 3-R) with a pitch of 21.3 Å (Fig. 3c), which are similar to that of the second channels, can also be found. The number of left- and right-

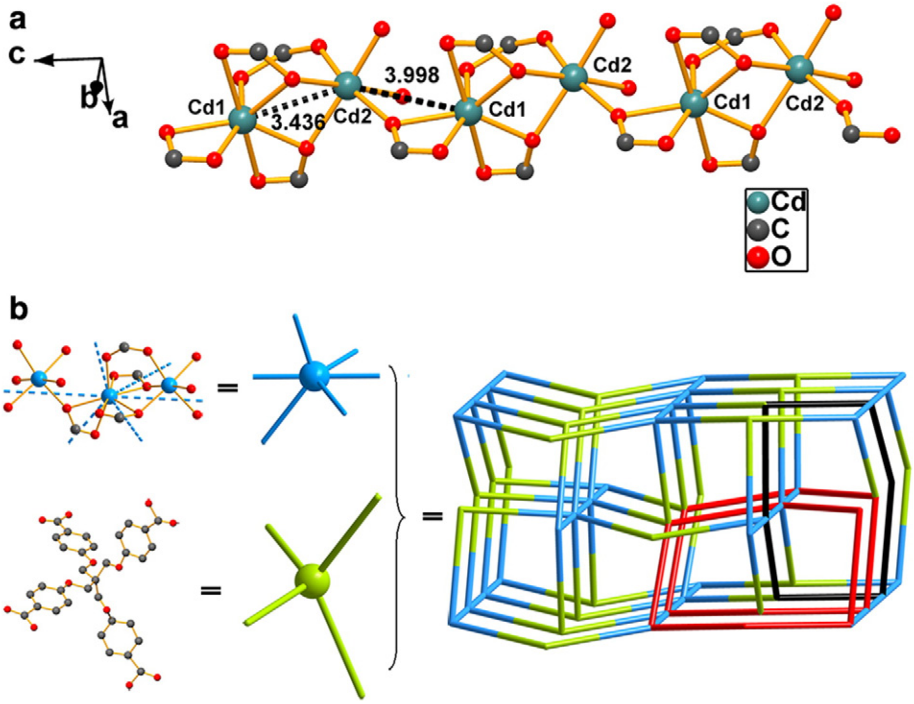

Fig. 2. (a) View of 1D Cd–O–Cd chain of **1**. The adjacent Cd · · · Cd distances in the chain are 3.436 and 3.998 Å, respectively. (b) View of the $(6^6)(6^{15})$ topology of **1**. Some of the interlocked six-membered rings are highlighted in red and black, respectively.