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Two stacked $2D_{chiral}/2D_{chiral} \rightarrow 2D_{achiral}$ sheets based on V-shaped imidazolyl ligand and flexible aliphatic acids

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ABSTRACT

Two new stacked $2D_{chiral}/2D_{chiral} \rightarrow 2D_{achiral}$ coordination polymers $\{[Cd(BIDPE)(pim)]\cdot(H_2O)\}_n$ (**1**) and $\{[Cd(BIDPE)(glu)]\cdot(H_2O)\}_n$ (**2**) were prepared under hydrothermal conditions based on V-shaped ligand 4,4′-bis(imidazol-1-yl)diphenyl ether (BIDPE) and flexible polycarboxylic acids. In addition, the solid-state photoluminescent spectra were measured at room temperature.

Coordination polymers have attracted great attention not only for their structural diversity [1], but also for their potential applications in the fields of photochemistry [2,3], gas adsorption and separation [4], molecular magnetism [5], and heterogeneous catalysis [6,7]. However, it's still a challenge to exactly predict the structure of MOFs. Flexible carboxylic ligands can be considered to be excellent candidates for the preparation of functional coordination polymers. It may adopt various coordination modes and produce various structures and topologies; it also can act as a hydrogen bond acceptor.

Interpenetration is an approach of the nature to avoid the voids or open space in a single network. The interpenetrating structure is not only dependent upon the metal coordination geometry, but also upon the shapes and lengths of the bridging linkers [8]. The design of metal–organic frameworks is still challenging and the occurrence of interpenetration sometimes requires that the different bridging ligands match each other in shape and length [9,10]. Going further with our previous work with V-shaped imidazolyl ligand 4,4′-bis(imidazol-1-yl)diphenyl ether(BIDPE) [11], we tried to explore the assembly with mixed BIDPE and other ligands. In this paper, two fascinating stacked $2D_{chiral}/2D_{chiral} \rightarrow 2D_{achiral}$ coordination polymers were reported based on BIDPE and flexible aliphatic acids: pimelic acid (H_2pim) and glutaric acid (H_2glu). These complexes were characterized by IR spectra, X-ray powder diffraction and X-ray crystallography [12,13]. The selected bond lengths and angles are given in the Supporting Information (Table S1). Further, the luminescent properties of BIDPE ligand and complexes **1**–**2** were studied.

X-ray crystallography analysis reveals that the asymmetric unit of **1** contains one independent Cd(II) cation, one BIDPE ligand, one pim^{2-} anion and one latticed water. As shown in Fig. 1, Cd(II) is an octahedral coordination environment with two N atoms from two BIDPE and four O atoms from two pim^{2-} anions. The neighboring Cd(II) ions linked V-shaped BIDPE into an infinitely 1D helical chain, the adjacent distance of Cd···Cd is 16.621 Å, and the angle of N1–O5–N3 is 124.666(59)°. Pim^{2-} anion, adopting trans-configuration, also linked Cd1(II) ions to form infinitely helical chain, and the adjacent distance of Cd···Cd is 10.274 Å. These two kinds of helical chains further linked to form a wavelike 2D layer containing irregular window by sharing the Cd(II) ions. The window is a 52-membered large loop composed of four metal ions, two BIDPE and two pim^{2-} anions. In this sheet the helical directions of $(BIDPE\text{-}Cd\text{-}BIDPE)_n$ and $(pim\text{-}Cd\text{-}pim)_n$ are the same, and it can be regarded as $2D_{chiral}$ layer (Fig. 2).

In complex **1**, a pair of identical $2D_{chiral}$ layers interlocked each other to generate $2D_{chiral} + 2D_{chiral} \rightarrow 2D_{chiral}$ sheet. The helical chains of $(BIDPE\text{-}Cd\text{-}BIDPE)_n$ and $(pim\text{-}Cd\text{-}pim)_n$ from different sheets are coincided to form a double helical chain in interlocked 2D sheet. The adjacent $2D_{chiral}$ sheets are stacked in offset ABAB manner, and the helical directions of A and B are reversed, so complex **1** is achiral (Fig. 3). The interpenetration mode and the formation of the double helical chain in **1** benefit not only from the shape of the two bridging ligands but also from the match of the two ligands in length.

Similarly, the asymmetric unit of **2** contains one independent Cd(II) cation, one BIDPE, one glu^{2-} anion and one latticed water. As shown in Fig. 4, Cd(II) displays a distorted CdN_2O_3 coordination sphere that can be best described as trigonal bipyramidal coordination environment with two N atoms from two BIDPE and three O atoms from two glu^{2-} anions. Each glu^{2-} anion has an oxygen atom (O1) hanging over a trigonal

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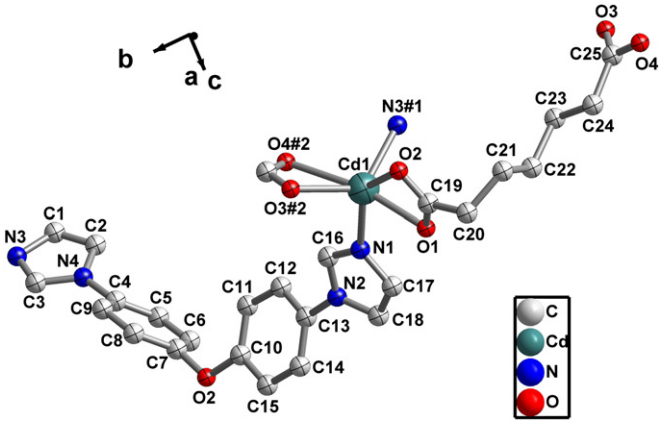

Fig. 1. Coordination environment of **1**. The hydrogen atoms are omitted for clarity. Symmetry codes: #1 = −0.5 − x, −0.5 + y, −1.5 − z; #2 = 1.5 − x, 0.5 − y, 1.5 + z.

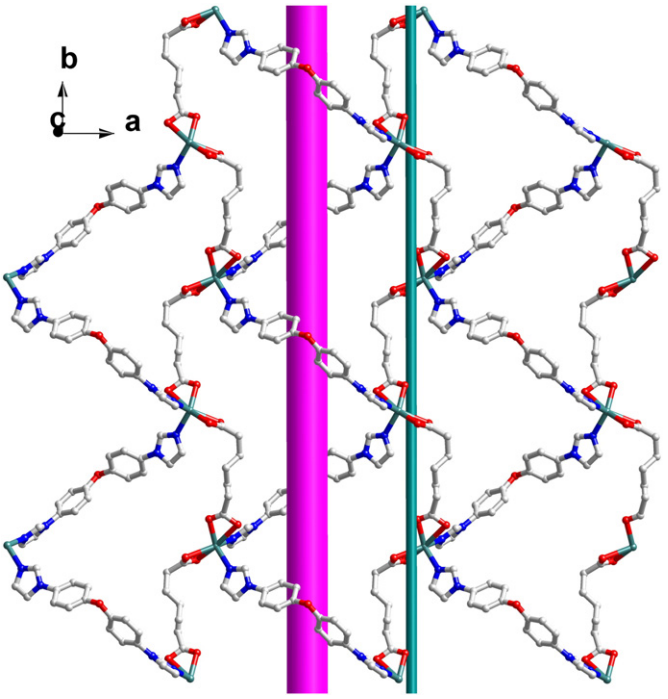

Fig. 2. The neighboring Cd1(II) ions linked BIDPE or pim^{2-} anions into infinitely 1D helical chain; the helical directions of $(BIDPE\text{-}Cd\text{-}BIDPE)_n$ and $(pim\text{-}Cd\text{-}pim)_n$ are the same in one sheet.

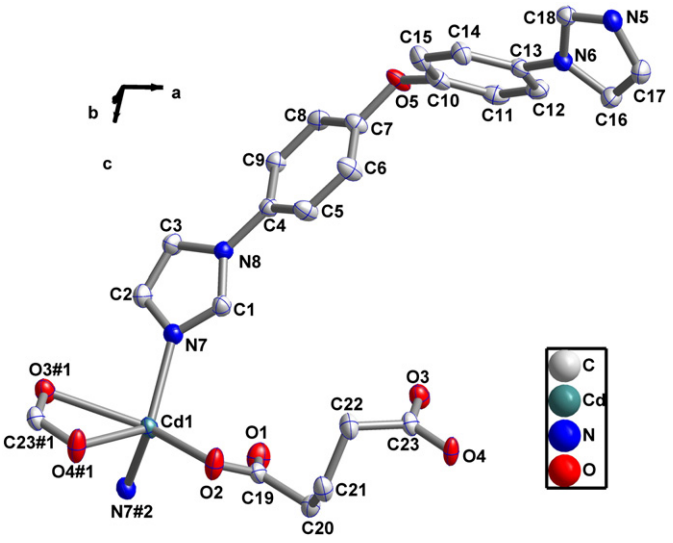

Fig. 4. Coordination environment of **2**. The hydrogen atoms are omitted for clarity. Symmetry codes: #1 = −1 + x, y, z; #2 = −1 + x, y, 1 + z.

bipyramidal face with the length of Cd–O at 2.536 Å, taking into account the weak coordination. The neighboring Cd(II) ions linked V-shaped BIDPE into an infinitely 1D chain, the adjacent distance of Cd···Cd is 16.938 Å, and the angle of N7–O5–N5 is 126.591(48)°. Glu^{2-} anion, adopting trans-configuration, linked Cd(II) ions to form infinitely helical chain, and the adjacent distance of Cd···Cd is 8.568 Å. These two kinds of chains further form a wavelike 2D sheet containing irregular window by sharing the Cd(II) ions. The window is a 48-membered loop composed of four metal ions, two BIDPE, and two glu^{2-} anions. In 2D sheet, the helical directions of $(glu\text{-}Cd\text{-}glu)_n$ are the same, which can also be regarded as $2D_{chiral}$ sheet. Further inspection shows that the lattice water and carboxyl groups actually contacted each other by strong H-bonding (O···O distances are 1.885 and 2.319 Å). These two H-bonds linked the ends of glu^{2-}, which caused the bend of glu^{2-} anion (Fig. 5). The helical directions of adjacent $2D_{chiral}$ sheets are reversed, and adjacent $2D_{chiral}$ sheets are stacked in an offset ABAB manner, so complex **2** is achiral too (Fig. 6). Complex **2** was not interpenetrated mainly attribute to the length glu^{2-} shorter than pim^{2-}, which caused the window to be shrunken.

The PXRD experimental and computer-simulated patterns of the corresponding complexes **1** and **2** are shown in the Supporting Information (Figs. S2 and S3). The results demonstrate that the experimental PXRD patterns perfectly match the simulated one based on the single-crystal X-ray data. To characterize compounds **1** and **2** in terms of thermal stability, its thermal behaviors were studied by

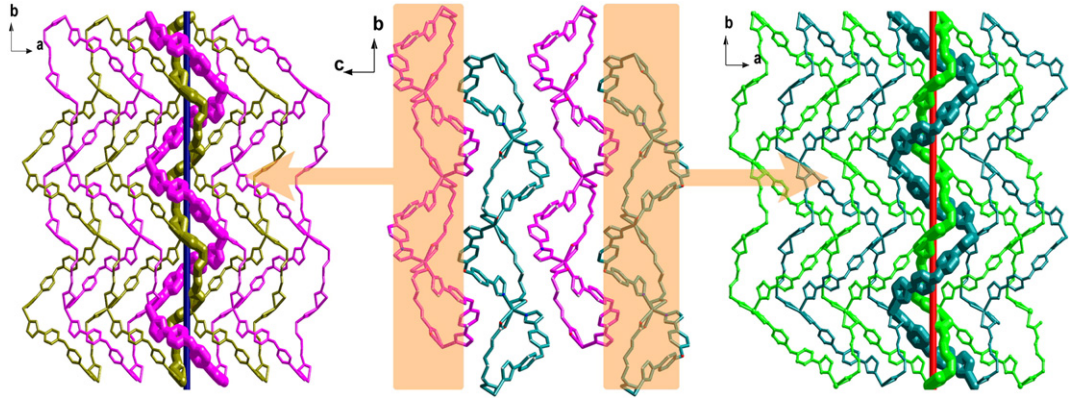

Fig. 3. View of $2D_{chiral} + 2D_{chiral} \rightarrow 2D_{chiral}$ interlocked sheet constructed by two identical 2D layers, and the adjacent $2D_{chiral}$ sheets are stacked in offset ABAB manners to form $2D_{achiral}$ network.