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Syntheses, structures and luminescent properties of two new two-fold interpenetrating 2D coordination polymers based on 4′-(4-carboxyphenyl)-4,2′:6′,4″-terpyridine

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ABSTRACT

Two new coordination polymers, $[Zn_2(cptpy)_2Cl_2]_n \cdot 0.5nH_2O$ (**1**) and $[Cd_2(cptpy)_4]_n \cdot 3.5nH_2O$ (**2**) (Hcptpy = 4′-(4-carboxyphenyl)-4,2′:6′,4″-terpyridine), were synthesized under hydrothermal conditions and characterized by elemental analysis, IR and single crystal X-ray diffraction. Compound **1** shows a new two-fold interpenetrating 3-connected 2D framework with the *hcb* topological net and the Schläfli symbol of 6^3. Compound **2** displays a two-fold interpenetrating (4,4)-connected 2D framework with the *sql* topological net and the Schläfli symbol of $\{4^4 \cdot 6^2\}$. Interestingly, compounds **1** and **2** were obtained in the similar reaction conditions. The structural diversity of compounds **1** and **2** may illustrate the marked effect of the metal ion of the reaction solution. Additionally, photoluminescence properties of compounds **1**–**2** have been investigated.

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Rational design and syntheses of metal organic frameworks (MOFs) have attracted great interest for researchers in the field of coordination chemistry and crystal engineering due to their fascinating architectures and topological frameworks and promising applications as guest exchange, molecular adsorption, magnetism, catalysis, fluorescence, electronics and so on [1–7]. Generally, the diversity in the framework architectures of such coordination polymers depends on many factors, such as the coordination geometry of metal centers, the coordination ability of organic ligand and the reaction conditions [8–12]. Among these factors, the selection of organic ligand with suitable binding groups is especially crucial. Compared with chelating 2,2′:6′,2″-terpyridine derivative ligands, the 4,2′:6′,4″-terpyridine derivatives are widely used as bridging ligand for the building MOFs which has been described as higher dimensional structures of coordination polymers and may lead to the formation of nanosized cages, honeycomb porous frameworks, Kagomé structure and so on [13–16].

Taking above factors into consideration, the bis-functional trigonal ligand, 4′-(4-carboxyphenyl)-4,2′:6′,4″-terpyridine (Hcptpy, Scheme 1) is applied in the field of coordination chemistry [13,17–19] according to the following consideration: (a) Hcptpy, as a semi-rigid bridging ligand, can link metal atoms via coordination bond to construct high dimensional and honeycomb porous coordination polymer and (b) It has a large π-conjugated nonlinear structure with N, O donors that can offer additional hydrogen bonding and π–π interactions to consolidate the whole framework structures. Herein, we present hydrothermal synthesis and crystal structures of two new two-fold interpenetrating 2D Zn/Cd polymeric frameworks, namely $[Zn_2(cptpy)_2Cl_2]_n \cdot 0.5nH_2O$ (**1**) and $[Cd_2(cptpy)_4]_n \cdot 3.5nH_2O$ (**2**), as well as their luminescent property and thermal stability.

Hcptpy ligand was prepared according to literature method [20]. Compounds **1** and **2** were synthesized by the reactions of $ZnCl_2$ or $CdCl_2$ with Hcptpy under hydrothermal conditions (Supporting information). X-ray single crystal structural analysis reveals that compound **1** displays a two-fold interpenetrating 3-connected 2D framework structure. The asymmetric unit of **1** contains two crystallographically independent Zn(II) ions, two $(cptpy)^-$ and two Cl^- anions and half lattice water molecule. As shown in Fig. 1a, Zn1 center is penta-coordinated to two oxygen atoms (O1, O2) from one $(cptpy)^-$ anion, two nitrogen atoms (N1A, N3B) from two different $(cptpy)^-$ anions and one chlorine anion, respectively. The coordination geometry of Zn1 center can be described as a distorted ZnN_2O_2Cl trigonal bipyramid geometry, the O1, N1 and Cl1 atoms comprise the equatorial plane, and the N3B, O2 atoms occupy the axial positions [N3B–Zn1–O2 = 157.3(3)°]. At the same time, the coordination environment of Zn2 is similar to that of Zn1, the Zn–N bond lengths lie in 2.049(7)–2.106(7) Å and the Zn–O bond lengths are in the range of 2.004(3) to 2.361(3)Å, which are consistent with the corresponding values reported [17a].

In **1**, Hcptpy ligand is deprotonated to form $(cptpy)^-$ anion. Three $(cptpy)^-$ anions adopting μ_3-η^2:η^1:η^1 coordination mode (Fig. S1) connected Zn(II) ions to form a 40-membered ($Zn_3O_2N_5C_{30}$) ring with a

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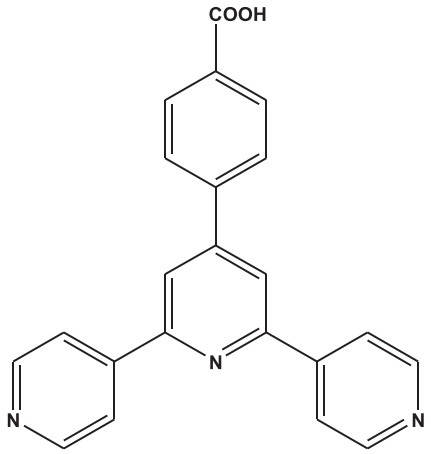

Scheme 1. Molecular structure of Hcptpy ligand.

grid pore 13.099 × 15.274 × 15.379 Å. The adjacent $Zn_3O_2N_5C_{30}$ rings shared one Zn(II) ion and one $(cptpy)^-$ anion generating two similar 2D wave layers constructed by Zn1 and Zn2 motifs (Fig. 1b). In these two similar structures, each individual 2D layer is parallel-interpenetration with another giving rise to a 2D + 2D → 2D interpenetration bi-layer array (Fig. S2). If each five-coordinated Zn(II) ion and $(cptpy)^-$ anion act as 3-connected nodes, the complicated architecture of **1** is simplified to a 3-connected 2D *hcb* topological network with the Schläfli symbol of 6^3 [17b] (Fig. S3). The bi-layer structures further formed a 3D supramolecular architecture by hydrogen bonding interaction to steady the whole framework (Fig. S4).

Compound **2** crystallizes in triclinic system with P-1 space group and shows a two-fold interpenetrating 2D framework. The asymmetric unit

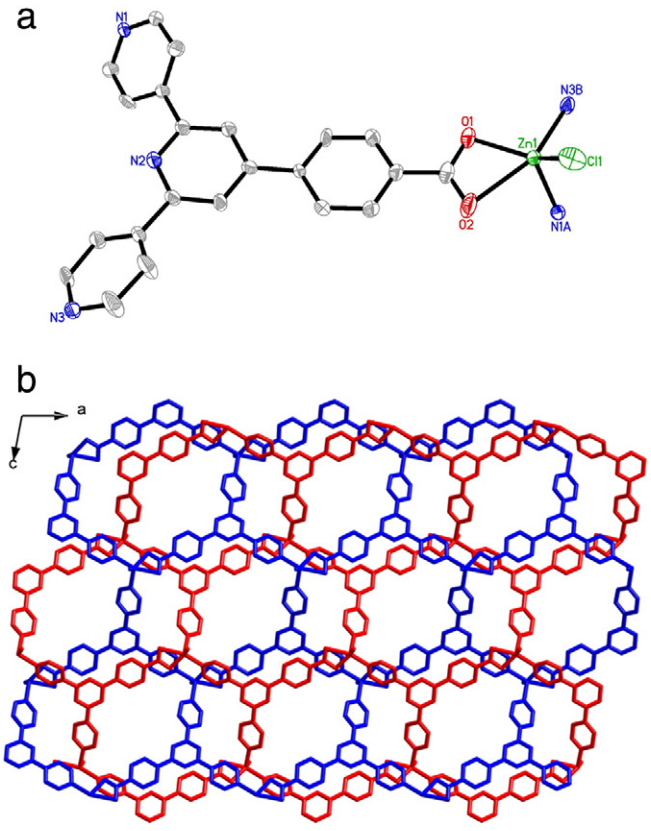

Fig. 1. (a) The coordination environment of Zn1 ion in **1** with 30% thermal ellipsoids (all hydrogen atoms and solvent molecules are omitted for clarity). (b) Perspective view of the parallel penetration of the layers constructed by the Zn1 and Zn2 motifs in **1**.

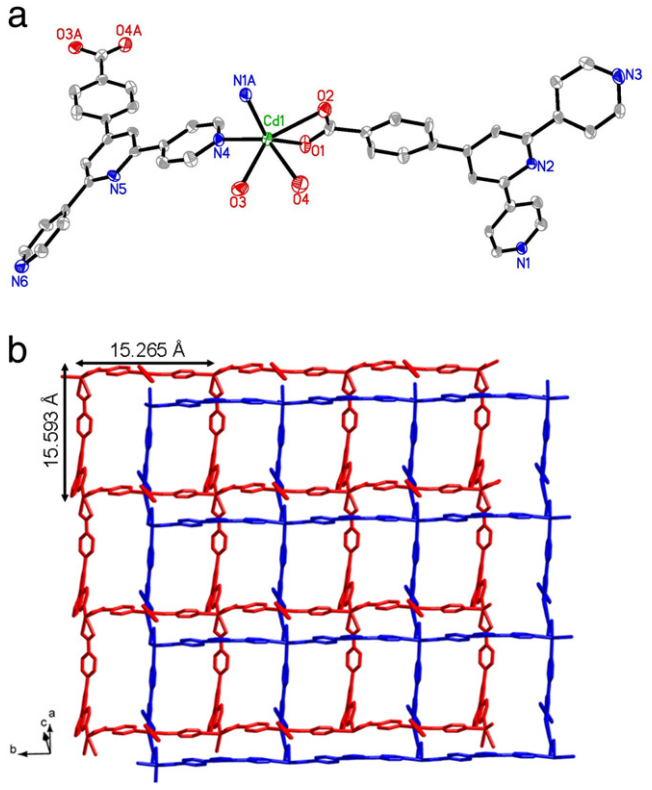

Fig. 2. (a) The coordination environment of Cd1 ion in **2** with 30% thermal ellipsoids (all hydrogen atoms and solvent molecules are omitted for clarity). (b) Perspective view of the parallel penetration of the layers constructed by the Cd1 and Cd2 motifs in **2**.

of **2** contains two crystallographically independent Cd(II) ions, four $(cptpy)^-$ anions and three lattice water molecules. As shown in Fig. 2a, the Cd1 center is hexa-coordinated to four oxygen atoms (O1, O2, O3, O4) from different $(cptpy)^-$ anions and two nitrogen atoms (N1A, N4) from two different $(cptpy)^-$ anions, respectively. The coordination geometry of Cd1 center can be described as a distorted octahedron, the N4, O3, O4 and O2 atoms comprise the equatorial plane, and the N1A, O1 atoms occupy the axial positions [N1A–Cd1–O1 = 139.9 (2)°]. The coordination environment of Cd2 center is similar to that of Cd1, the Cd–N distances fall in the range of 2.280(7) Å to 2.300(7) Å, and the Cd–O bond lengths vary from 2.290(5) to 2.429(6) Å, which are consistent with the corresponding values reported for Cd-pyridyl and Cd-carboxylic complexes [18a].

Notably, the Cd(II) ions are connected by one pyridyl nitrogen atom and one carboxylate oxygen atom of the different $(cptpy)^-$ ligands with a μ_2-η^1:η^2 bridging mode to form two similar 2D layers. The through-space apertures within a single layer motif measure 15.265 × 15.593 Å (Fig. 2b). The large rectangular windows within the layers allow interpenetration of parallel sets of layers with each other. As a result, each individual 2D layer is parallel-interpenetration with another giving rise to a 2D + 2D → 2D interpenetration bi-layer array (Fig. S5). From the topological perspective, if each six-coordinated Cd(II) ion acts as 4-connected node and $(cptpy)^-$ anion is also severed as 4-connected node, the architecture of **2** is simplified to a (4,4)-connected 2D *sql* [18b–d] topological network with the Schläfli symbol of $\{4^4 \cdot 6^2\}$ as shown in Fig. S6. The π…π stacking interaction between the pyridyl rings and phenyl rings (centroid-to-centroid distance of 3.864 Å and 3.868 Å) in neighboring layers sustains the system of interpenetrated bi-layers (Fig. S7). Interestingly, the uncoordination pyridyl rings in ligands $(cptpy)^-$ serve as side arms hanging on the opposite side of the layer. Thus, the bi-layer networks generate a 2D + 2D → 2D tetra-layer structure through π…π stacking interaction between phenyl rings and pyridine rings (centroid-to-centroid distance of 3.647 Å and 3.624 Å), and then the tetra-layer structures are further superimposed

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