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Preparation, crystal structure and properties of two novel metal-organic frameworks assembled from pyridine-3,5-dicarboxylic acid *N*-oxide

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ABSTRACT

Two novel coordination polymers, $[Cu(PDCO)\cdot(H_2O)]_n$ **(1)** and $[Cd(PDCO)(bipy)\cdot(H_2O)\cdot 5H_2O]_n$ **(2)**, (H_2PDCO = pyridine-3,5-dicarboxylic acid *N*-oxide, bipy = 4,4′-bipyridine), have been synthesized under hydrothermal conditions, and their structures were determined by single-crystal X-ray diffraction studies. Polymer **1** features a three-dimensional (3D) network with nonequivalent nodes of $(6^3)_2(6^9\cdot 8^5\cdot 10)$ topology. Polymer **2** exhibits one-dimensional (1D) double-stranded chains. The magnetic character of **1** as well as the gas adsorption and luminescent properties of **2** have been investigated.

Over the past few years, research in the area of metal–organic frameworks (MOFs) continues to be interesting not only for their potential and interesting properties such as host–guest chemistry, catalysis and magnetic behavior but also for their fascinating architectures and topological networks [1,2]. It is well known that the MOFs are essentially assembled by very strong and highly directional coordinative interactions between metal centers and multitopic organic ligands. In some MOFs, weak interactions, such as hydrogen bonding and π–π stacking interactions, greatly affect the structures of coordination compounds. In many cases, they may link low-dimensional entities into high-dimensional supramolecular networks [3].

An interesting class of the MOF is compounds from multifunctional nitrogen and oxygen-donor connectors, pyridine polycarboxylic acids, which has been extensively utilized to generate zero-, one-, two-, and three-dimensional MOFs [4]. However, compounds containing the pyridine-3,5-dicarboxylic acid *N*-oxide ligand have not been reported before. This ligand possesses several discrete metal-binding sites and limited steric hindrance and can offer possibilities to form the unexpected, unpredictable and interesting structures. With the aim of preparing novel materials with beautiful architecture and excellent physical properties, we start to elaborate new high-dimensional coordination compounds based on H_2PDCO and bipy ligands. In this paper, we report two interesting coordination polymers $[Cu(PDCO)\cdot(H_2O)]_n$ **(1)** and $[Cd(PDCO)(bipy)\cdot(H_2O)\cdot 5H_2O]_n$ **(2)**. Besides, the magnetic character, as well as the gas adsorption and luminescent properties have been investigated.

Compound **1** was synthesized hydrothermally in the presence of H_2PDCO and 4,4-bipy [5]. Single-crystal X-ray diffraction analysis [6] revealed that **1** crystallizes in the *Pbca* space group and features a 3D network built from PDCO and Cu(II) atoms. As shown in Fig. 1a (Bottom), treating the 8-number ring (Cu1–O3#2–C7#2–O4#2–Cu1#4–O3#3–C7#3–O4#3) (Symmetry codes are listed in the supplementary material) as a building unit, each unit is surrounded by four PDCO ligands and two carboxylate groups of one PDCO ligand coordinate to three Cu1 atoms (Cu1, Cu1#4 and Cu1#5) via bidentate and monodentate modes respectively, thus obtain a 2D honeycomb-like layer in the *ac* plane. The *N*-oxide groups of PDCOs protrude from the *ac* plane (see the rose color arrow in Fig. 1a) and link Cu1 atoms in the neighbouring layer to form a dense 3D framework, which has no solvent accessible void found by calculation using PLATON [9] (top of Fig. 1b).

To analyze and understand more clearly the complicated structure of the Cu1–PDCO framework, we take advantage of the "topological approach" [10]. As shown in Fig. 1a (top), the PDCO ligand can be abstracted as a V-shaped connector with an additional side arm. This connector has two kinds of nodes, D and E, which are denoted to the PDCO ligand and dinuclear Cu1 unit, respectively. The V-shaped part of the connector forms a 2D honeycomb-like layer in the *ac* plane by coordinating to Cu1 atoms, leaving the side arm pointing up or down alternately from the layer. The whole three-dimensional Cu1–PDCO host framework can then be achieved by letting the side arms in one layer coordinate to the Cu1 atoms in adjacent layers, giving an ABAB packing style (bottom of Fig. 1b).

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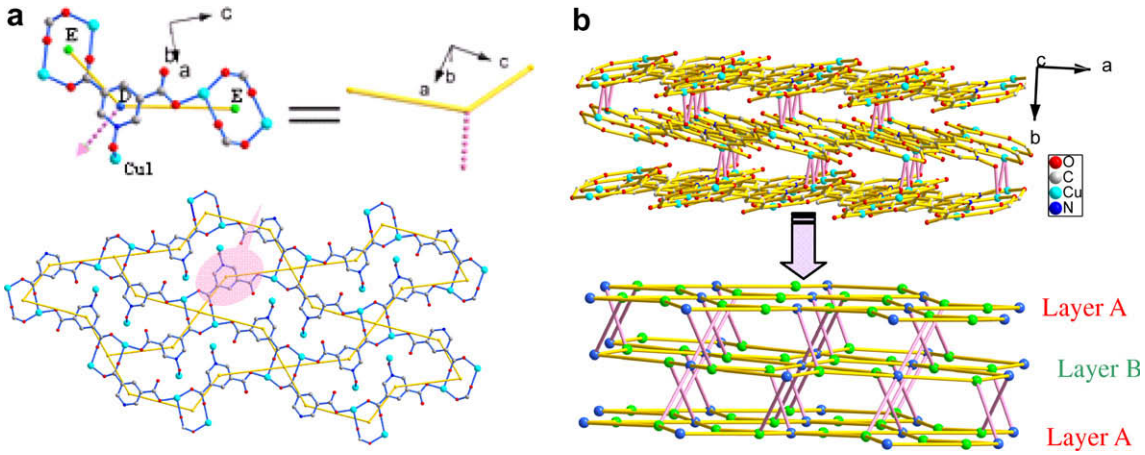

Fig. 1. (a) Bottom: 2D honeycomb-like layer formed by carboxylate groups of PDCO ligands coordinating to Cu1 atoms. Top: the PDCO ligand can be abstracted as a V-shaped connector with an additional side arm; (b) top: perspective view of the 3D framework of **1**. Bottom: Schematic illustration of the *ABAB* packing style of the Cu1-PDCO host framework.

Fortunately, we can easily identify that node D is 6-connected while nodes E is 3-connected, which is relatively rare. The overall topology of the 3D framework is best described as a $(6^3)_2(6^9 \cdot 8^5 \cdot 10)$ network.

When the H_2PDCO and 4,4′-bipy ligands were used to react with Cd $(NO_3)_2 \cdot 6H_2O$, instead of Cu $(NO_3)_2 \cdot 6H_2O$, compound **2** was isolated. As depicted in Fig. S2, the Cd1 atoms are interlinked by the PDCO ligands to form 1D double-stranded chains with the Cd···Cd separation of 7.7456 Å. Intra-chain hydrogen bonds (O6–H6B···O2) and π–π interactions between the bipy ligands (centroid-centroid distance 3.804 Å) are found to further stabilize these chains (Fig. 2a). Thus these 1D double-stranded chains in **2** constitute a 3D microporous supramolecular network. Within the 3D microporous supramolecular network, there are nanosized cavities with 10.35 × 10.89 Å along *a*-axis (Fig. 2b and Fig. S3). A calculation using PLATON led to the solvent-accessible volume of **2** as being 23.3% of the total crystal volume (233.6 $Å^3$ out of the 1002.2 $Å^3$ unit cell volume). The free water molecules, which are further stabilized by hydrogen bonds (see in Table S2), fill in the cavities of host framework.

To verify whether the framework of **2** can be sustained after the removal of the guest molecules, the as-synthesized products were calcinated at 250 °C and 1022 Torr for 3 h to fully dispose of water molecules and were used to make powder X-ray diffraction (PXRD) and thermal gravimetric analysis (TGA) (Figs. S4 and S5). The permanent porosity of **2** is confirmed by its N_2 adsorption/desorption isotherm with the typical Type-III gas sorption behavior (Fig. 3) and a dinitrogen uptake of approximately 65 cm^3(STP)/g at P/P_0 = 1.0, which reveals a Langmuir surface area of 23.35 $m^2\ g^{-1}$ (BET surface area, 16.43 $m^2\ g^{-1}$) as well as pore volume of 0.054 $cm^3\ g^{-1}$. Therefore, this MOF may be suitable as a candidate of porous materials. Meanwhile, the desorption hysteresis of **2** implies that possible weak guest–host hydrogen-bonding interactions might exist under relatively higher pressure.

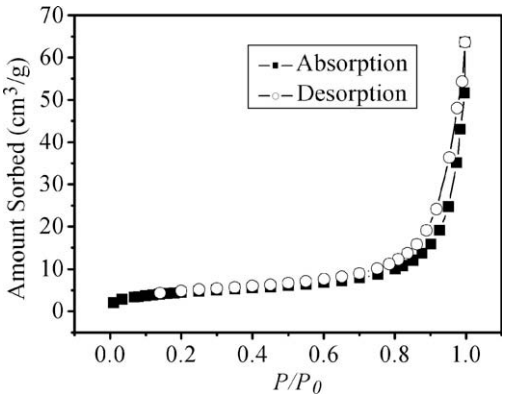

Fig. 3. Adsorption/desorption isotherm of nitrogen gas (77 K) for **2**.

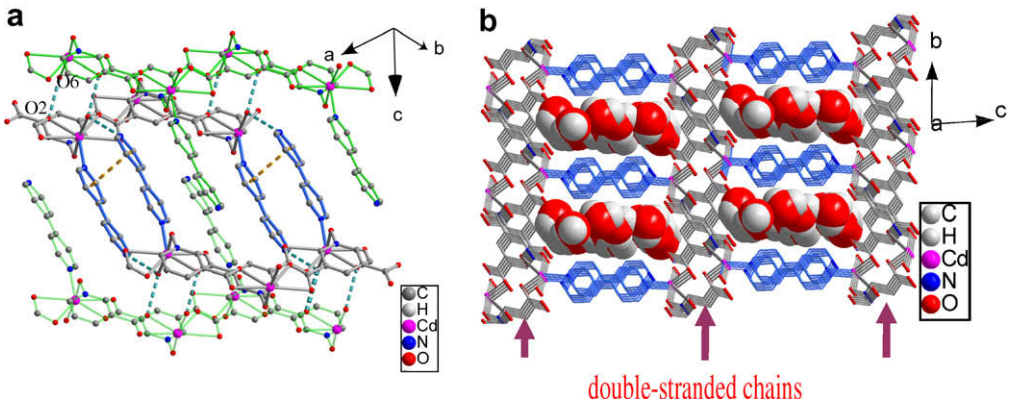

Fig. 2. (a) The 3D supramolecular network of **2**. Intra-chain hydrogen bonds (dark cyan) and π–π interactions (orange) are represented by dashed lines. (b) Perspective view of the 3D supramolecular network with solvated water molecules located at the cavities of the interlayers (the double-stranded chains have been indicated by arrows).