

Two different porous coordination polymers regulated by the conformations of flexible ligands



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ABSTRACT

Two porous coordination polymers, $\{[\text{Cu}(2,3\text{-pydc})(\text{bpp}) \cdot 2.5\text{H}_2\text{O}]_n\}$ (**1**) and $\{[\text{Cu}(2,3\text{-pydc})(\text{bpp}) \cdot 3.5\text{H}_2\text{O}]_n\}$ (**2**) (2,3-H₂pydc = pyridine-2,3-dicarboxylic acid, bpp = 1,3-bis(4-pyridyl)propane), have been synthesized with the same reactant ratio in different solvents. Two complexes have the same components, coordination environment of Cu(II), as well as the coordination mode of ligands, but represent two quite different porous architectures. **1** is a homochiral 2D → 3D porous polymer with polycatenated layers of achiral ligands. **2** is a 2D centrosymmetric pillared-bilayer porous polymer with water-filled channels. They have been characterized by infrared spectroscopy, elemental analysis, thermogravimetric analysis and X-ray crystallography.

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The design and synthesis of novel coordination polymers have been paid much attention because of their intriguing variety of structures and fascinating properties [1,2]. Of particular interest is to construct chiral or porous coordination polymers [3,4]. Up to date, many interesting porous coordination polymers have been constructed by the flexible ligands [5,6]. The construction of porous coordination polymers is influenced by many factors, such as metal ions, organic ligands, counteranions, experimental temperature, solvent molecules and pH [7]. It could be potential dynamic materials as they may sustain the changes caused by external stimuli. We have recently investigated a series of flexible coordination polymers based on flexible dipyrindyl ligands, such as the Cu/Ag-RCO₂-bpp (R = phenyl or pyridyl, bpp = 1,3-bis(4-pyridyl)propane) systems [8]. In order to study the influence of experimental conditions on the structural and properties of these polymers, herein we report two different porous coordination polymers of the same components, regulated by the conformations of the flexible ligands under different solvents, $\{[\text{Cu}(2,3\text{-pydc})(\text{bpp}) \cdot 2.5\text{H}_2\text{O}]_n\}$ (**1**) and $\{[\text{Cu}(2,3\text{-pydc})(\text{bpp}) \cdot 3.5\text{H}_2\text{O}]_n\}$ (**2**) (2,3-H₂pydc = pyridine-2,3-dicarboxylic acid, bpp = 1,3-bis(4-pyridyl)propane). **1** is a 3D homochiral porous polymer with 2D polycatenated layers. **2** is a 2D pillared-bilayer porous polymer with water-filled channels.

The room-temperature solution reactions of Cu(OH)₂ with H₂pydc and bpp in mixed solvents of H₂O and MeOH, generate complex **1**, while the same reactants in mixed solvents of H₂O and triethylamine (TEA) give complex **2** [9].

1 crystallizes in the P4₁2₁2 chiral space group [10,15], while its enantiomer in the P4₃2₁2 chiral space group can be synthesized under

another experimental conditions [11]. There are one Cu(II) atom, one 2,3-pydc²⁻ ligand, one bpp ligand and 2.5 water molecules in the asymmetric unit. The Cu(II) atom is five-coordinate in a distorted square-pyramidal coordination environment, which is coordinated by two O atoms and one N atom from two 2,3-pydc²⁻ ligands, one N atom of bpp ligand, and one N atom from another bpp (Fig. 1a). The 1D chains are linked by the bpp ligands of *TT* conformation [12] with a N–N distance of 9.3221(1) Å and a dihedral angle of 71.374° between the two pyridyl rings (Fig. 3), thus leading to a 2D layer (Fig. 1b). The 1D nanosized elliptical-shaped tubes occur in the dimension of 10.02 × 10.30 Å (Fig. 1c). Moreover, the 2D layers with 1D nanosized elliptical-shaped tubes polycatenate with two near identical motifs on the *bc* plane (Fig. 1d). The interpenetration layers give an interesting 2D → 3D polymer (Fig. 1e). **1** retains a void of 636.6 Å³, 15.3% of the unit cell volume, calculated by PLATON [13], which is larger than its enantiomer [11].

The X-ray crystal structure of complex **2** is a 2D pillared-bilayer polymer with water-filled channels, crystallized in *Pbcn* space group. The asymmetric unit contains one Cu(II) atom, one 2,3-pydc²⁻ ligand, one bpp ligand and 3.5 water molecules. The Cu(II) atom is also five-coordinate with a square-pyramidal coordination environment (Fig. 2a). The coordination mode adopted by the 2,3-pydc²⁻ ligand in **2** is the same as in complex **1** (Fig. 2b), that is, the pyridyl N atom and 2-position carboxylate O atom of the 2,3-pydc²⁻ ligand chelate one Cu(II) atom and a 3-position carboxylate O atom coordinates to another Cu(II) atom, resulting in a zigzag chain. The zigzag chains are linked by the bpp ligands, which adopt a different *TG* conformation [12], with an N–N distance of 8.5313(1) Å and a dihedral angle of 67.904° between the two pyridyl rings (Fig. 3), resulting in a 2D layer.

It should be noted that the framework of **2** is similar to the literature [14], but is different in the number of guest water molecules, solvent-accessible void volume, as well as crystallographic parameters. Similar

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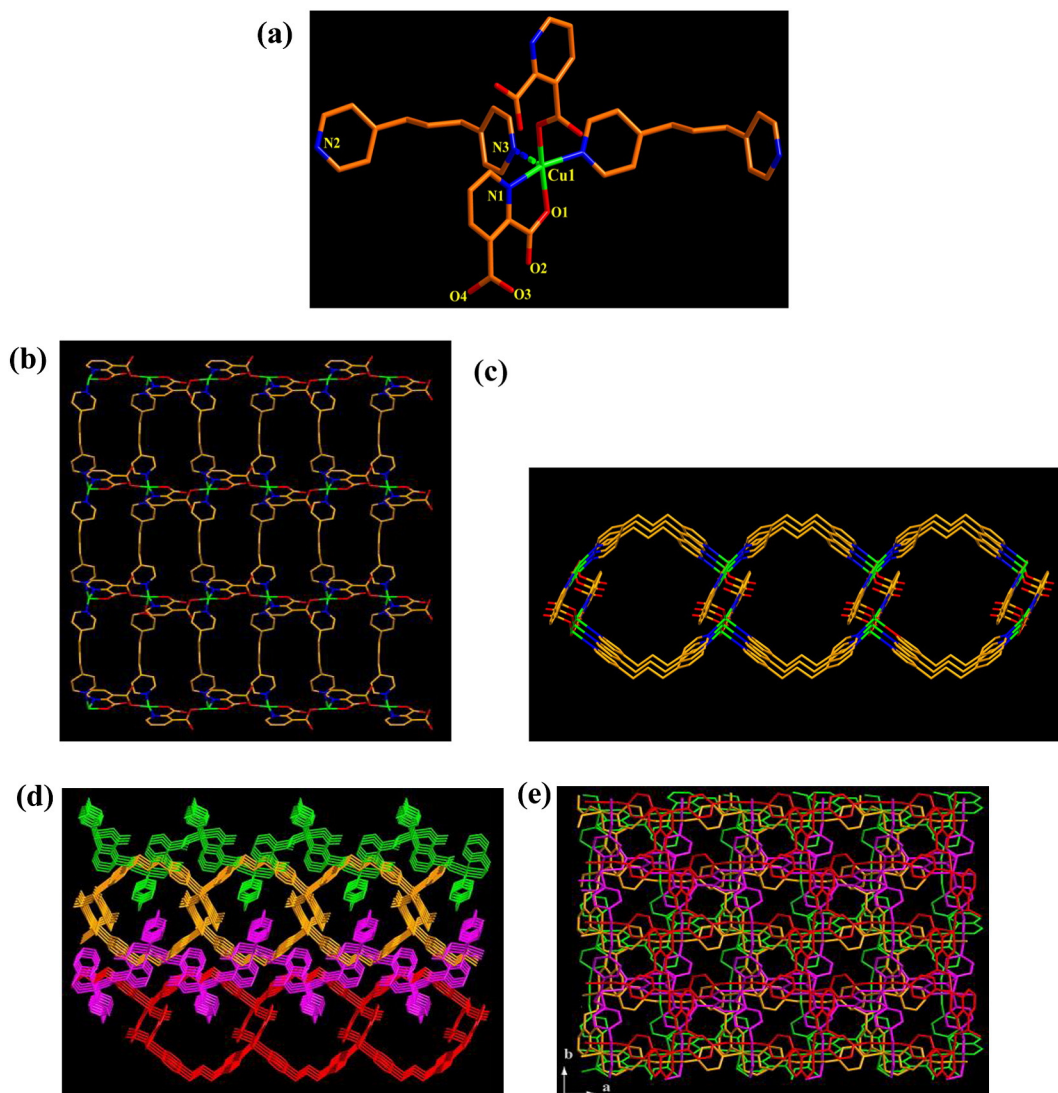


Fig. 1. Coordination environment of the Cu(II): (a) the undulating 2D layer with a (4,4) topology along the crystallographic *c*-axis, (b) elliptical-shaped tubes along *a*-axis in the dimension of $10.02 \times 10.30 \text{ \AA}$ (c), the polycatenated elliptical tube on the *bc* plane (d), and the 2D \rightarrow 3D interpenetration polymer (e) in **1**.

to literature, the 2D layer is composed of the $[\text{Cu}(2,3\text{-pydc})(\text{pyridine-CH}_2\text{CH}_2\text{CH}_2\text{-})]$ on the *ab* plane (Fig. 2c, d), which is connected via a “pillar” composed of the pyridine part of the same bpp ligand to another layer along the crystallographic *c*-axis, forming the 2D pillared-bilayer porous architecture. The 1D water-filled channels were found along the *a*-axis inside of the pillared-bilayer (Fig. 2e). The estimated solvent-accessible void volume is 973.3 \AA^3 per unit cell, which is 22.4% of the unit cell volume, calculated by PLATON [13].

To estimate the thermal stability of the title complexes, thermal analysis experiments were carried out on single-phase polycrystalline samples under nitrogen atmosphere (Fig. S1). In the TG curve of **1**, the first weight loss of 9.3% at 35–90 °C corresponds to the removal of two and a half guest water molecules per formula unit (calcd. 9.5%), and then, a major weight loss occurred at 175–370 °C, which may correspond to the loss of organic ligands. For **2**, the first weight loss of 12.3% below 100 °C is attributed to the loss of the three and a half guest water molecules (calcd, 12.9%).

In summary, we have assembled two porous Cu(II) coordination polymers with different conformations of the flexible linker under different solvents. Both complexes have the same components, coordination environment of Cu(II) atoms, as well as the same coordination mode of the 2,3-pydc²⁻ ligand. The crucial difference is the conformations of flexibly bridging bpp ligands. The bpp ligand with *TT* conformation leads to a

2D \rightarrow 3D porous homochiral polymer, while the *TG* conformation results in a 2D pillared-bilayer porous centrosymmetric polymer. The results may provide a feasible strategy toward the regulated assembly of dynamic porous coordination polymers via the solvents and the conformations of flexible linkers.

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Appendix A. Supplementary data

CCDC 1017626 and 1017627 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found in the section of Supporting Information at <http://dx.doi.org/10.1016/j.inoche.2014.09.034>. These data include MOL files and InChiKeys of the most important compounds described in this article.

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