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Syntheses, structures and photocatalytic properties of two coordination polymers based on bis(1,2,4-triazol-4-ylmethyl)benzene and multicarboxylates

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ABSTRACT

Two coordination polymers $\{[Cu_4(OH)_2(btrb)_2(btc)_2]\cdot 4H_2O\}_n$ (**1**) and $\{[Cd_2(btrb)(adc)_2(H_2O)]\cdot H_2O\}_n$ (**2**) were synthesized with hydrothermal method and characterized (btrb = 1,4-bis(1,2,4-triazol-4-ylmethyl)benzene, btc = 1,3,5-benzenetricarboxylate, adc = 1,3-adamantanedicarboxylate). **1** shows an unusual (3,10)-connected two-dimensional metal–organic framework based on the tetranuclear copper(II) cluster $[Cu_4(\mu_3\text{-}OH)_2]$. **2** is an interesting three-dimensional network based on the one-dimensional metal–organic nanotube. **1** shows good photocatalytic activity for the degradation of methyl blue (MB). The luminescence of **2** was investigated.

The coordination polymers have attracted great interest due to their fascinating structures, topological novelty and potential applications as functional materials such as gas absorption, luminescence and catalysis [1–6]. The metal ions and organic ligands are the key factors for assembling the coordination polymers with structural diversity. 1,2,4-Triazole and its derivatives are very interesting ligands because they combine the coordination geometry of both pyrazole and imidazole with regard to the arrangement of their three heteroatoms. The 1-substituted 1,2,4-triazole ligands have been widely synthesized and characterized [7–12]. However the 4-substituted 1,2,4-triazole ligands have been less synthesized and characterized [13–16]. At the same time, rigid organic aromatic multicarboxylate ligands present versatile coordination modes and are very effective building blocks for the construction of coordination polymers [17–19]. The coordination polymers based on flexible bis(triazole) N-donor ligands and aromatic multicarboxylate ligands can result in novel topologies and intriguing properties.

In previous work, we synthesized a lot of coordination polymers using flexible 1-substituted and 4-substituted bis(triazole) building blocks [20–25]. For example, $[Cd_3(bbtz)_6(H_2O)_6](BF_4)_6\cdot 1.75H_2O$ shows 2D (4,4) networks and 1D ribbons of rings polycatenated in a 3D array (bbtz = 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene) [20]. $\{[Cd(btre)Cl]\cdot OH\}_n$ forms a 3D microporous cationic network (btre = 1,2-bis(1,2,4-triazol-4-yl)ethane). Whereas $\{[Cd(btre)Cl][CdCl(dca)_2]\cdot 0.5H_2O\}_n$ exhibits a polythreading coordination array formed from a 3D microporous cationic network and 1D anion ladders [24].

With this background information, we sought to synthesize of novel coordination polymers with intriguing properties based on bis(triazole) and multicarboxylate ligands. The 4-substituted 1,2,4-triazole ligand 1,4-bis(1,2,4-triazol-4-ylmethyl)benzene (btrb), an isomer of 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene (bbtz), should be a good building block to construct coordination polymers with novel topologies. In the present work, we synthesized two coordination polymers $\{[Cu_4(OH)_2(btrb)_2(btc)_2]\cdot 4H_2O\}_n$ (**1**) and $\{[Cd_2(btrb)(adc)_2(H_2O)]\cdot H_2O\}_n$ (**2**) using hydrothermal method (btc = 1,3,5-benzenetricarboxylate, adc = 1,3-adamantanedicarboxylate). **1** shows an unusual (3,10)-connected two-dimensional metal–organic framework based on the tetranuclear copper(II) cluster $[Cu_4(\mu_3\text{-}OH)_2]$. **2** is an interesting three-dimensional network based on the one-dimensional metal–organic nanotube.

The crystals of **1** and **2** were prepared by the reaction of btrb, $Cu(NO_3)_2$ and btc or $Cd(NO_3)_2$ and adc using hydrothermal method [26]. Single-crystal X-ray analysis [27] revealed that **1** consists of a (3,10)-connected two-dimensional metal–organic framework based on the tetranuclear copper(II) cluster $[Cu_4(\mu_3\text{-}OH)_2]$. In the $[Cu_4(\mu_3\text{-}OH)_2]$ moiety, Cu1 ion has a square-pyramidal geometry with a CuO_4N chromophore and is coordinated by three carboxylate oxygen atoms (O1, O3A, O6C) from three btc, one μ_3-OH (O7) and one triazole nitrogen atom (N5B) from one btrb ligand (Fig. 1). The square-pyramidal coordination geometry of the Cu2 ion is coordinated by one carboxylate

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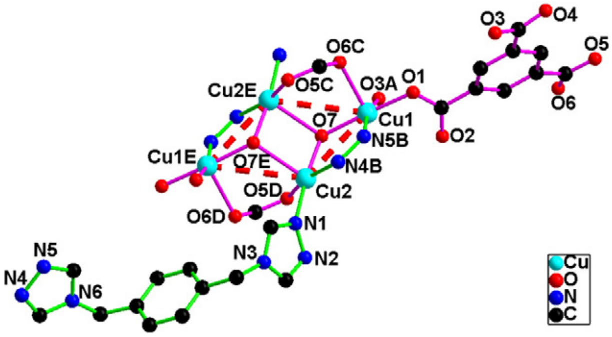

Fig. 1. The coordination environment of the Cu(II) atoms in **1**.

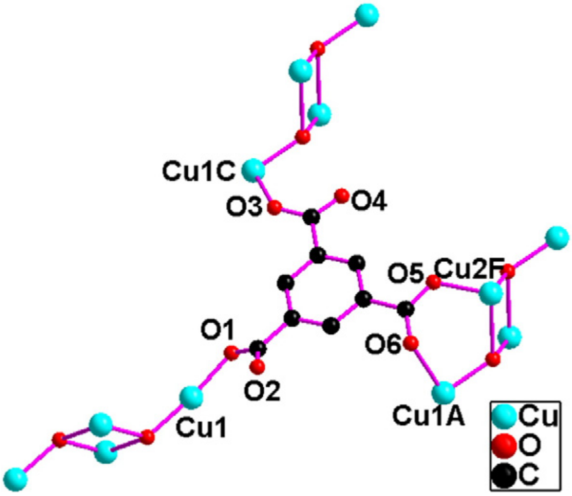

Fig. 2. The coordination mode of the btc ligand in **1**.

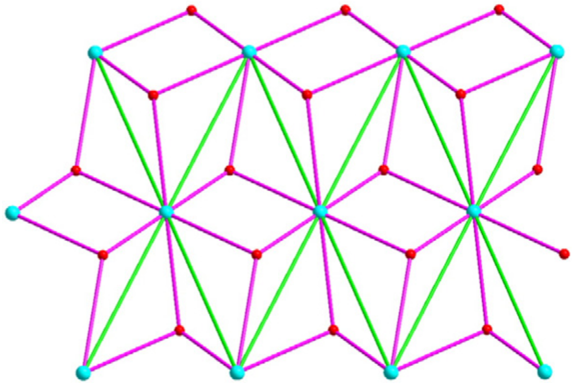

Fig. 4. Schematic depiction of the (3,10)-connected 2D network in **1**. The turquoise and red balls show the 10-connected [$Cu_4(\mu_3\text{-}OH)_2$] tetranuclear copper(II) clusters and the 3-connected btc ligands, respectively. The bright green sticks represent the 2-connected btrb ligands.

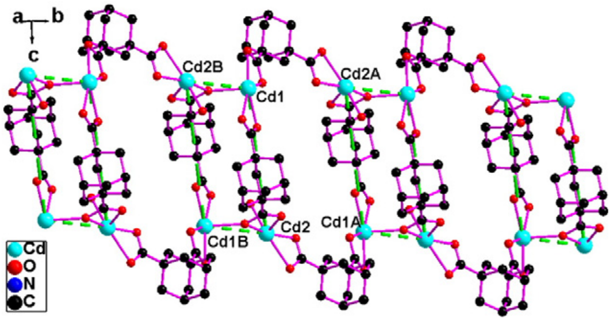

Fig. 5. The one-dimensional metal–organic nanotube [$Cd_2(adc)_2(H_2O)$]$_n$ in **2**.

oxygen atom (O5D) from one btc, two μ_3-OH (O7, O7E) and two triazole nitrogen atoms from two btrb ligands (N1, N4B).

One μ_3-OH group (O7) connects three Cu(II) ions (Cu1, Cu2, Cu2E) and deviates from the Cu atoms plane over 0.630(2) Å (Fig. 1). The Cu2–O7–Cu1, Cu2–O7–Cu2E and Cu1–O7–Cu2E bond angles are 121.09(12), 95.77(9) and 115.46(11)°, respectively. Two μ_3-OH groups (O7, O7E) separate the Cu ions and generate a tetranuclear [$Cu_4(\mu_3\text{-}OH)_2$] moiety with a chair arrangement with the Cu···Cu separations in the range of 3.2448(2)–3.6904(1) Å (Cu1···Cu2, 3.3837(1) Å; Cu1···Cu2E, 3.6904(1) Å; and Cu2···Cu2E, 3.2448(2) Å). There is one kind of btc ligand in **1**. Two carboxylate groups (O1O2, O3O4) of one btc ligand have a monodentate coordination mode bonding one Cu(II) ion (Cu1 or Cu1C) of two tetranuclear Cu(II) clusters. One carboxylate (O5O6) shows a bisdentate coordination mode bridging two Cu(II) ions (Cu1A, Cu2F) of the third tetranuclear Cu(II) cluster (Fig. 2).

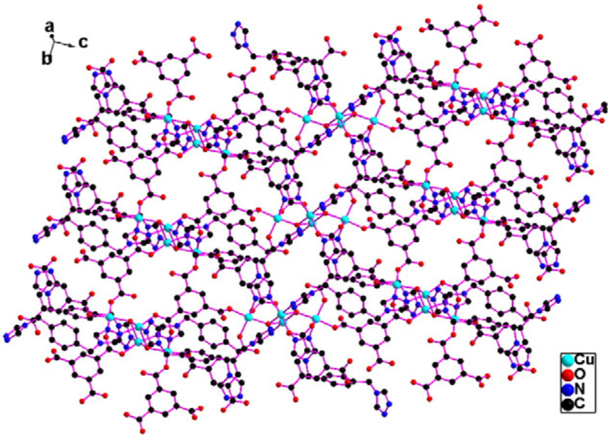

Fig. 3. The 2D network in **1**.

All the btc ligands are 3-connected and connect three [$Cu_4(\mu_3\text{-}OH)_2$] tetranuclear copper(II) clusters. All btrb ligands exhibit the anti-conformation and bridge two [$Cu_4(\mu_3\text{-}OH)_2$] tetranuclear copper(II) clusters. Each [$Cu_4(\mu_3\text{-}OH)_2$] tetranuclear copper(II) cluster connects six btc and four btrb ligands (Fig. S1). The tetranuclear copper(II) clusters are bridged by the btc and btrb ligands to construct an unusual two-dimensional metal–organic framework (Fig. 3).

Topologically, the [$Cu_4(\mu_3\text{-}OH)_2$] tetranuclear copper(II) cluster is simplified as one node which is 10-connected. The btc is a 3-connected node. The btrb ligand shows as 2-connected node. The 2D network can be described as a (3,10)-connected 2D network based on

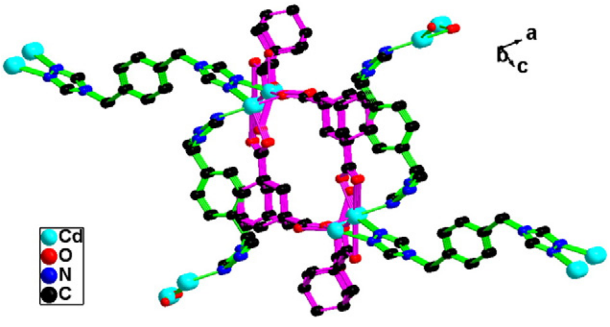

Fig. 6. Each one-dimensional metal–organic nanotube [$Cd_2(adc)_2(H_2O)$]$_n$ connects four identical metal–organic nanotubes in **2**.