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Short communication

Two new Zn(II)/Cu(II) complexes based on bi- and tritopic 1,2,4-triazole derivatives with glutaric acid: Syntheses, structures, luminescent and magnetic properties

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ABSTRACT

Two new Zn(II)/Cu(II) coordination polymers, $[Zn(OPBT)(GA)]_n$ (**1**) and $\{[Cu_2TTPA(GA)_2]\cdot 1.5H_2O\}_n$ (**2**), have been successfully synthesized from flexible glutaric acid (H_2GA) with different bi- and tritopic 1,2,4-triazole derivatives (OPBT = 1.1′-(oxybis(1,4-phenylene))bis(1*H*-1,2,4-triazole), TTPA = tris(4-(1*H*-1,2,4-triazol-1-yl)phenyl)amine) and Zn(II)/Cu(II) nitrate salts. Their structures have been characterized by infrared spectra, elemental analyses, single crystal and powder X-ray diffraction analyses and thermogravimetric analyses. Both complexes **1** and **2** feature different 2D layers with **sql** topologies, which can be further arranged ABAB-type, leading to different 3D supramolecular frameworks by C-H···O hydrogen bonding or O-H···O/N hydrogen bonding/π···π stacking interactions. Moreover, the photoluminescence spectra of complex **1** are examined and variable-temperature magnetic susceptibility measurements of complex **2** reveal antiferromagnetic interactions between binuclear Cu(II) ions of paddle-wheel second building units (SBUs).

The design and construction of metal-organic frameworks (MOFs) based on metal ions or clusters and multitopic organic ligands have attracted widespread attention in recent years, due to their intriguing structural topologies [1] and their potential applications such as magnetism [2], luminescence [3–6], gas storage and separation [7,8], catalysis [9], sensing materials [10,11]. Much effort has been devoted to their practical applications for the construction of novel MOFs in combination with various carboxylates and N-donor ligands [12–17]. However, selection/design of suitable organic ligands still plays a crucial role in the construction of MOFs with desired structures and properties. According to the previous literatures, compared with benzene- and triazine-centered triangular ligands, the O- or N-centered ligands more easily meet the geometric requirements of metal ions [18–22]. For example, the coordination polymers based on diphenyl ether or triphenylamine derivatives have received intense interest due to their fascinating framework topologies and properties [23–26].

As a continuation of our previous study, herein we introduced two and three triazoles into the above backbones, and synthesized two bi- and tritopic ligands: 1,1′-(oxybis(1,4-phenylene))bis(1*H*-1,2,4-triazole) (OPBT) and tris(4-(1*H*-1,2,4-triazol-1-yl)phenyl)amine (TTPA) as shown in Scheme S1 (Electronic Supplementary Information (ESI)). At the same time, combined with the flexible glutaric acid (H_2GA), two new complexes $[Zn(OPBT)(GA)]_n$ (**1**) and $\{[Cu_2TTPA(GA)_2]\cdot 1.5H_2O\}_n$ (**2**) were synthesized under hydrothermal reaction conditions [27].

Single X-ray crystal structure analysis of complex **1** was solved in the monoclinic crystal system of *C*2/*c* [28], the detailed information for complex **1** is summarized in Table S1 (ESI). The asymmetric unit of complex **1** contains a Zn(II) ion, an OPBT ligand and a deprotonated H_2GA ligand. Each Zn ion is four-coordinated by two nitrogen atoms from two different OPBT ligands and two oxygen atoms from two different GA^{2-} ligands to form a distorted $\{ZnN_2O_2\}$ tetrahedral geometry (Fig. 1a). The Zn—N bond lengths are 2.0144(14) and 2.0311(14) Å, and the Zn—O bond lengths are 1.9303(13) and 1.9439(13) Å, respectively (Table S2).

The OPBT ligands adopting μ_2-bridge coordination modes (Fig. S1a, ESI) link Zn ions to form a 1D chain, and GA^{2-} ligands adopting μ_1-η^1:η^0 coordination modes (Fig. S2a) also connect Zn ions to generate a 1D chain (Fig. 1b, left). In this way, these 1D chains are further extended into a single 2D layer (Fig. 1b, middle). The topological analysis of crystal structure in **1** is performed by software TOPOS 4.0 [29]. Thus, the single 2D layer can be described as a 4-connected $(4^2\cdot 6^2)$-**sql** topology (Fig. 1b, right). In complex **1**, there are intralayer hydrogen bonding interactions (Table S3). Furthermore, adjacent layers are further arranged in ABAB-type, leading to a 3D supramolecular structure by hydrogen bonding (C7-H7···O4#7 = 2.55 Å, #7: x, $-y$, $z-1/2$) interactions with the **sql** topologies (Fig. 1c and d).

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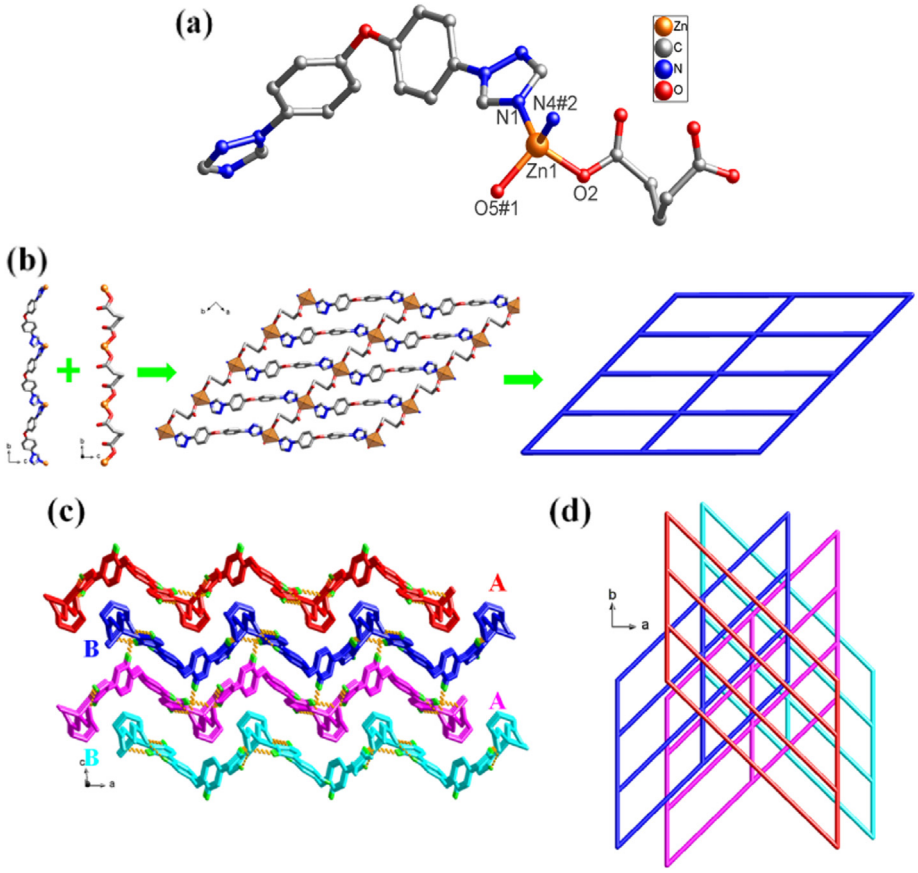

Fig. 1. (a) Coordination environment of Zn(II) ions in complex **1**. The hydrogen atoms are omitted for clarity. Symmetry codes: #1 = $x, y + 1, z$; #2 = $x + 1/2, y - 3/2, z$. (b) Two 1D chains constructed by Zn(II) ions and OPBT or GA^{2-} ligands along the different direction respectively (left); the single 2D layer (middle); the **sql** topology (right). (c) The ABAB-type stacking 3D supramolecular framework by hydrogen bonding interactions (orange dashed lines). (d) The **sql** topologies of layers A and B.

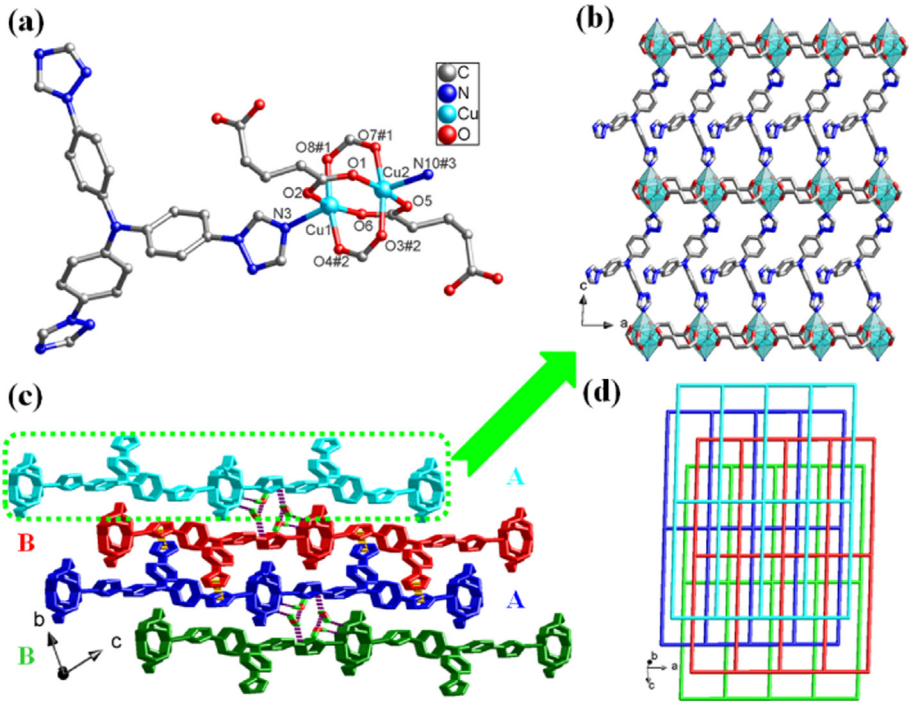

Fig. 2. (a) Coordination environment of Cu(II) ions in complex **2**. The lattice water molecules and hydrogen atoms are omitted for clarity. Symmetry codes: #1 = $x - 1, y, z$; #2 = $x + 1, y, z$; #3 = $x, y + 1, z - 1$. (b) The 2D layer constructed by Cu(II) ions, TTPA and GA^{2-} ligands. (c) The 3D supramolecular structure by π···π stacking (orange dashed lines) and hydrogen bonding interactions (violet dashed lines). (d) The **sql** topologies of layers A and B.