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A fluorescence chemosensor for benzonitrile derived from *in-situ* synthesis of azolate–carboxylic acid and zinc(II) ions

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ABSTRACT

A new zinc(II) homometallic coordination polymer (CP), $\{[Zn(TAA\text{-}OH)_2]\cdot 1.5H_2O\}_n$ (1) (HTAA-OH = 2-(5-hydroxy-1H-1,2,4-triazole-1-yl) acetic acid) has been synthesized *via* an *in-situ* synthetic approach and structurally characterized in detail. In 1, the HTAA-OH ligand is generated *in-situ* by the nucleophilic addition of 2-(1H-1,2,4-triazole-1-yl) acetic acid. CP 1 features a 2D structure with *sql* topology, where the neighboring Zn(II) ions are bridged through two oxygen atoms of carboxyl group and two nitrogen atoms of triazole from the HTAA-OH ligands. Luminescence study shows that 1 dispersed in acetonitrile performs a distinct luminescence enhancing effect upon addition of benzonitrile, indicating that 1 is a promising fluorescence chemosensor for benzonitrile.

The development of crystalline coordination polymers (CPs) has attracted considerable attention in recent years because of their impressive molecular topologies and significant properties [1]. Such crystalline materials can be synthesized by self-assembly of metal ions and small organic molecules, resulting in tailored multidimensional networks and exhibiting remarkable properties, such as high thermal stability and adjustable chemical functionality. Due to their tailored topologies and tunable properties, they are promising candidates for gas storages and separation [2], molecular nanomagnets [3], and luminescence sensors [4]. These potentials should largely rely on the nature of the target materials such as the ability of the pore specific size and surface, open metal sites and the host-guest interaction [5]. As a result, much work has been devoted to preparing multi-functionalized CPs *via* various synthetic strategies. One of the most challenging but promising synthetic strategies to achieve such CPs is the simultaneous assembly of metal ions and small organic ligands under hydro(solvo)thermal condition, resulting in unpredictable final products, which could also be known as an *in-situ* synthetic approach [6]. Through this synthetic strategy, new CPs that are inaccessible or not easily formed under conventional conditions may be easily obtained in high yield. Various multi-functionalized CPs have been successfully realized *via* cycloaddition of organic nitriles with azide or ammonia, carbon–carbon bond formation, decarboxylation of aromatic carboxylates, and other *in-situ* synthetic approach [7–10]. However, an *in-situ* reaction of CPs is still difficult to achieve, partly because of the difficulties of the cleavage and/or formation of bonds during the crystallization process.

Significantly, the predesigned organic ligands play an important role in the formation of the desirable CPs. Among these employed organic ligands, azolate-carboxylic acid ligands have been widely employed as versatile multi-chelating ligands in the construction of such functionalized CPs [3b,3c,11]. These bridging ligands usually consist of various coordination sites, resulting in a variety of bridging modes that can generate beautiful structures and appealing properties. For example, in previous study, 1H-1,2,3-triazole-4,5-dicarboxylic acid (H_3TDA) is confirmed to be a good candidate to synthesize such crystalline materials with interesting properties [3b,3c,11d,12]. As a continuous exploitation on the study of azolate-carboxylic acid as ligand, 2-(1H-1,2,4-triazole-1-yl) acetic acid (HTAA) is also expected as a multi-chelating flexible ligand to construct multi-functionalized CPs [13]. In this contribution, HTAA is employed as a bridging linker, which can lead to a new linker, 2-(5-hydroxy-1H-1,2,4-triazole-1-yl) acetic acid (HTAA-OH) through an *in-situ* reaction by the nucleophilic addition. And consequently, a new 2D *sql* topological zinc(II) homometallic CP, $\{[Zn(TAA\text{-}OH)_2]\cdot 1.5H_2O\}_n$ (1) has been obtained and structurally characterized in detail. Luminescence performance reveals 1 is a promising fluorescence chemosensor for benzonitrile.

Hydrothermal reaction of $Zn(NO_3)_2\cdot 6H_2O$ and HTAA in the presence of NaOH in water at 160 °C gives the crystals of 1 in *ca.* 10% yield, where HTAA can result in HTAA-OH through an *in-situ* reaction by the nucleophilic addition (Scheme 1). Such phenomenon can be frequently observed in hydro(solvo)thermal reactions, resulting in unpredictable final products with fascinating topological structures and appealing properties [6–10,14]. It should be mentioned that the synergistic effect of the solvents and temperature plays an important role in the crystallization of 1. We also tried to employ other common solvents and mixed

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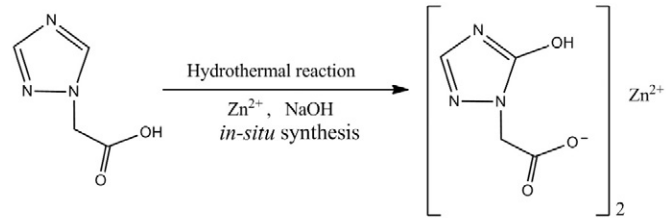

Scheme 1. *In-situ* synthesis of 1.

solvents of water, methanol, ethanol, acetonitrile and DMF at different temperature and other conditions to synthesis the crystals of 1. Unfortunately, no crystals of 1 can be obtained. Single-crystal X-ray diffraction analysis reveals that 1 crystallizes in the triclinic space group *P*-1. Each unit cell contains crystallographically independent one Zn(II) ion, two HTAA-OH ligands, one and a half uncoordinated water molecules (Fig. 1a). Each Zn(II) ion adopts a distorted tetrahedral $\{ZnO_2N_2\}$ coordination geometry (Fig. 1b) with two oxygen atoms (O1A and O4B, respectively) and two nitrogen atoms (N3 and N6, respectively) from two HTAA-OH ligands. The bond lengths of Zn–N are in the range of 1.991(5)–2.034(6) Å and those of Zn–O are 1.936(5)–1.958(6) Å, respectively. The neighboring Zn(II) ions are bridged through two oxygen atoms of carboxyl group and two nitrogen atoms of triazole from the HTAA-OH ligands, generating a two-dimensional sheets with the edge length of 7.37 Å and 8.61 Å, respectively (Fig. 1c). Obviously, such similar 2D structures can also be observed in the CPs assembled by the original HTAA ligand such as $\{[Ni(TAA)_2] \cdot 2H_2O\}_n$ [13a], $\{[Cu(TAA)_2] \cdot 3H_2O\}_n$ [13c], $\{[M(TAA)_2(H_2O)_2]\}_n$ (M = Co, Ni and Zn) [13c] and $\{[Cu(TAA)_2]\}_n$ [13e]. A further investigation on the synthetic condition indicated that most of

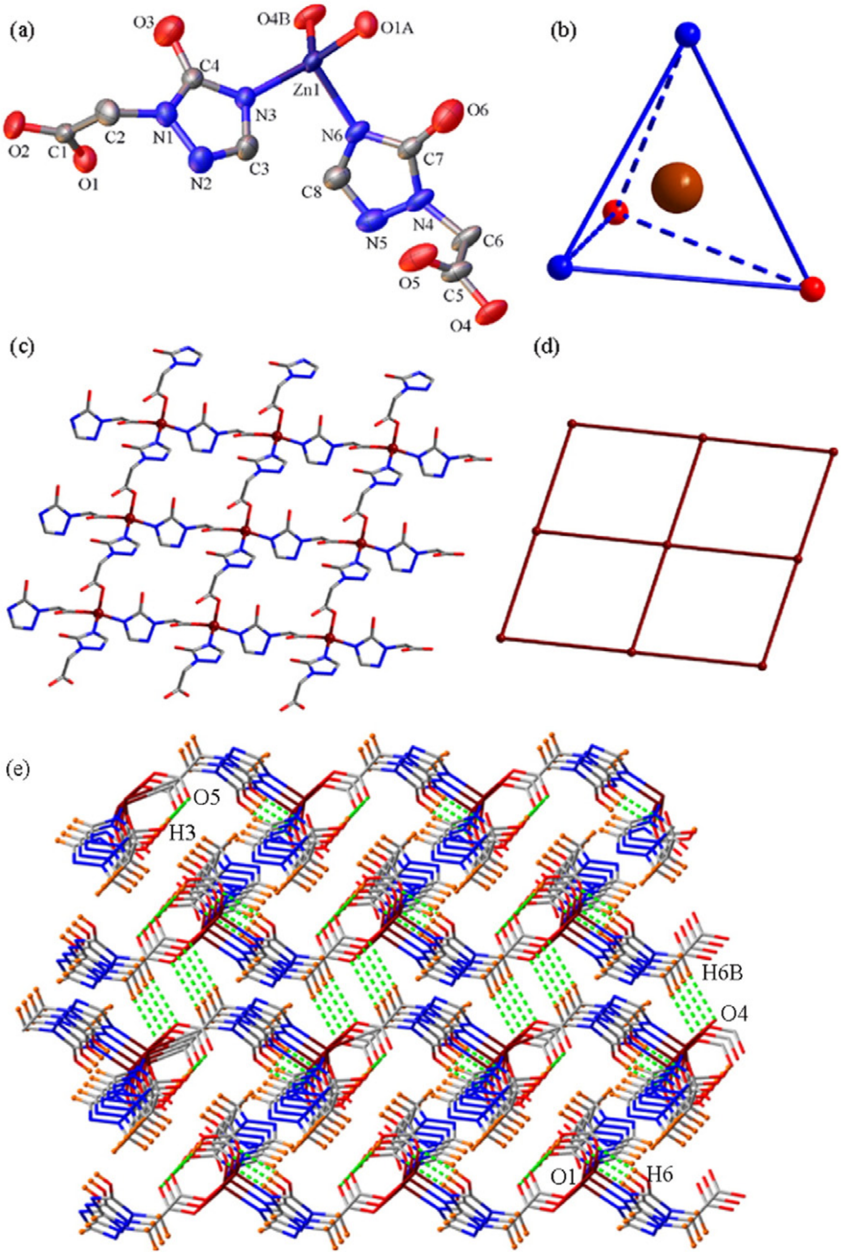

Fig. 1. (a) The coordination environments of Zn(II) ions in 1 (thermal ellipsoids are drawn at the 30% probability level). All hydrogen atoms and uncoordinated water molecules were omitted for clarity; (b) the distorted tetrahedron $\{ZnO_2N_2\}$ coordination geometry in 1; (c) the two-dimensional net of 1; (d) a schematic representation of tetragonal plane net of *sql* topology. Purple: Zn; red: O; blue: N; black: C. [Symmetry code: (A) −1 + x, y, z; (B) x, −1 + y, z]; (e) the stacking form of adjacent layers *via* the hydrogen bonds of 1. The green dashed lines stand for the hydrogen bonds. [Symmetry code: (B) x, −1 + y, z].