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Synthesis and characterization of a novel one-dimensional Zn(II) coordination polymer based on in situ generated 1-methyl-2-(3H-[1,2,3]triazol-4-yl)-1H-benzoimidazole

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ABSTRACT

One novel 1D chain of $\{[Zn_2(\mathbf{L})_3(H_2O)(NO_3)]\cdot 2.5H_2O\}_n$ (**HL** = 1-methyl-2-(3H-[1, 2, 3]triazol-4-yl)-1H-benzoimidazole) has been hydrothermally constructed from in situ generated 1-methyl-2-(3H-[1, 2, 3]triazol-4-yl)-1H-benzoimidazole ligand at 160 °C. Compound **1** exhibits a 1D butterfly-like chain architecture, which is further assembled into a 3D supermolecular network by interchain hydrogen bonds. TGA studies show that compound **1** is highly thermally stable. The fluorescent property in the solid state is also explored, and the emission spectrum shows a blue shift of 62 nm compared with that of **HL**, which may be assigned to ligand-to-metal charge transfer.

Hydro(solvo)thermal in situ metal–ligand reactions, as a new bridge between coordination chemistry and organic synthetic chemistry, have many advantages over conventional synthetic routes and have attracted intensive interest in recent years [1]. This “one-pot” approach precludes the necessity of synthesizing the linkers, thus simplifying tedious synthesis and purification steps. The slow release of the in situ generated linkers in presence of metal ions can lead to the growth of high-quality crystalline products or even larger single crystals. Moreover, the approach provides alternative pathways to MOFs with in situ synthesized linkers, which are inaccessible or not easily obtained by conventional synthetic methods. It should be mentioned that the discovery of in situ synthesized linkers is serendipitous. In the past decade, several interesting hydro(solvo)thermal in situ metal–ligand reactions were found, including decarboxylation [2,1d], hydrolysis, hydroxylation, cycloaddition, substitution, alkylation, acylation, amination and so on [1b]. As we know, great interest has also been focused on the design and synthesis of benzimidazole derivatives and their metal complexes in recent years because of their intriguing architectures and potential applications in the field of materials [3]. In particular, high-nuclearity and poly-nuclearity transition metal clusters have been intensively pursued in order to develop their physical properties for use to transport, storage, catalysis, optics and magnetism [4]. Zeng's group has reported several compounds with luminescent properties [5]. In this context, we synthesized a novel 1D chain zinc (II) complex of $\{[Zn_2(\mathbf{L})_3(H_2O)(NO_3)]\cdot 2.5H_2O\}_n$ with **L** ligand (**HL** = 1-methyl-2-(3H-[1, 2, 3]triazol-4-yl)-1H-benzoimidazole) by the way of in situ reaction. Significantly, 1D chain is assembled into a 3D supramolecular framework through interchain hydrogen bonding interactions.

The light-yellow clubbed crystals of compound **1** [6] were obtained by the in situ ligand formation in a hydrothermal approach with $Zn(NO_3)_2\cdot 6H_2O$ and **Hmtca** [7] at 160 °C. In addition, further experiments have shown that a higher reaction temperature favors decarboxylation of **Hmtca**. There was no crystal under the hydrothermal synthesis when the temperature is lower than 140 °C. **HL** has been synthesized, which was confirmed by 1H-NMR (Fig. S1) and ESI-MS (Fig. S2) in the supplementary information. However, the experimental results show that carboxyl group of **Hmtca** is very important to the formation of compound **1**, because compound **1** could not been obtained, when directly employing **HL** in hydrothermal reaction.

X-ray single crystal structure analysis revealed that **1** crystallizes in the space group *C2/c* [8]. Selected bond lengths and angles for **1** are listed in Table S1. The asymmetric unit (Fig. 1a) of **1** contains two crystallographically unique Zn(II) ions, three **L** ligands, one disordered nitrate ion and one coordinated water molecular and 2.5 lattice water molecules. Each Zn(II) atom in **1** is coordinated by one oxygen atom from water molecular or nitrate ion (Zn1–O1 = 2.245(5) Å and Zn2–O2 = 2.288(4) Å), and five nitrogen atoms from different deprotonated chelate ligands (Zn–N = 2.085(4)–2.229(4) Å) to finish distorted octahedral geometries. All Zn–N distances lie within the range of corresponding bond distances according to the literature [9].

The benzimidazole rings and triazole rings in **L** ligands are approximately coplanar. Otherwise, there are two kinds of coordination

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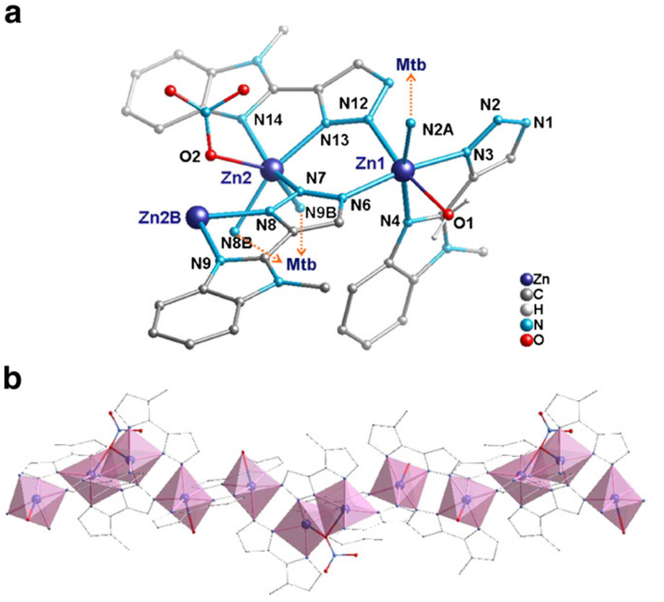

Fig. 1. (a) Coordination environments of Zn(II) in **1**. Hydrogen atoms have been removed for clarity. Symmetry codes: (A) 0.5-x, 0.5-y, -z; (B) -x, y, 0.5-z. (b) Perspective view of the 1D chain in which Zn was shown in polyhedral model.

modes of **L** ligands in the asymmetry unit, as illustrated in Fig. S3. The **L** ligand bridges Zn atoms alternately by two coordination modes, further forming a 1D chain structure (Fig. 1b).

An interesting structural feature of compound **1** is that the butterfly-like chain is further connected into a three-dimensional supramolecular structure (Fig. 2) through three types of hydrogen bonds between (a) carbon atoms on benzene rings and the coordinated water molecules ($d_{\mathrm{C28\cdots O1}}=3.438(7)$ Å), (b) the coordinated water and lattice water molecules ($d_{\mathrm{O1\cdots O3W}}=2.853(7)$ Å), and (c) the interactions between lattice water molecules ($d_{\mathrm{O3W\cdots O1W}}=3.149(1)$ Å, $d_{\mathrm{O2W\cdots O2Wi}}=1.900(3)$ Å).

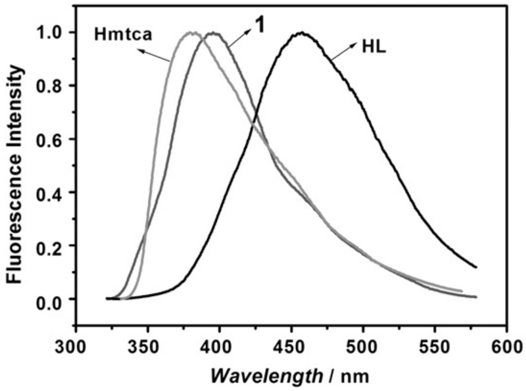

Fig. 3. The emission spectra of **1**, free **HL** and **Hmtca** at room temperature.

On the other hand, the disordered nitrate ions that located in the interspace of chains also have abundant hydrogen bonding interactions with the ligands, further stabilizing the structure, which remains to play a critical role in packing into a higher network. The hydrogen bonding information is listed in Table S2.

The thermogravimetric (TG) test for **1** was performed on a Netzsch STA 449 C instrument under a nitrogen atmosphere in the temperature range from 30 to 1000 °C. As shown in Fig. S4, the TG curve of **1** shows a weight loss of 5.32% from room temperature to 329 °C, corresponding to the removal of the 2.5 guest H_2O molecules (5.30%). Upon further heating, the desolvated framework decomposed through another two steps of weight loss. The as-synthesized sample of **1** was also characterized by powder X-ray diffraction (PXRD) obtained on Bruker D8 ADVANCE Diffractometer (Cu Kα radiation, 40 kV, 40 mA) in the 2θ range of 5–60°, with 0.1° 2θ step size and 1 s/step scan speed. As

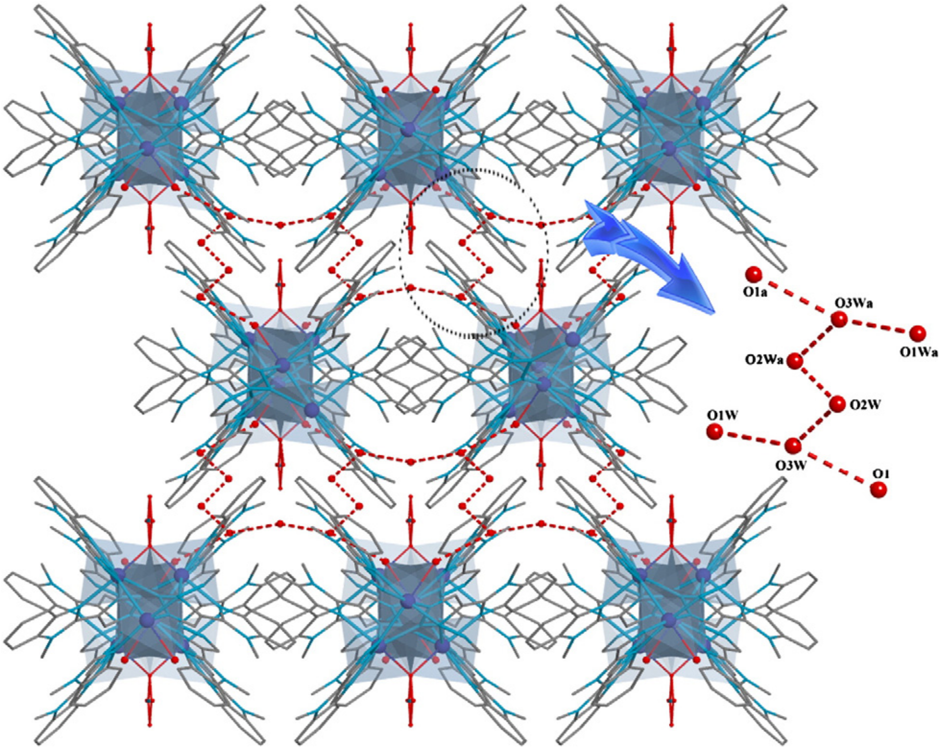

Fig. 2. Three dimensional structure for **1** connected by water molecular (red dotted lines).