



An interpenetrated framework based on pentanuclear tetrahedral cluster with four-connected mdf network



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ARTICLE INFO

Article history:

Received 13 April 2015

Received in revised form 22 May 2015

Accepted 5 June 2015

Available online 6 June 2015

Keywords:

Metal–organic frameworks

Pentanuclear tetrahedral cluster

Topology

Photoluminescent

ABSTRACT

A new three-dimensional metal–organic framework constructed from pentanuclear tetrahedral cluster and linear dicarboxylic acid ligand, $[Zn_5(btz)_6(ndc)_2(H_2O)] \cdot 3DMA$ (**1**) (btz = benzotriazole, H_2ndc = 1,4-naphthalenedicarboxylic acid) has been synthesized by the modular building blocks (MBBs) strategy under the solvothermal condition. Single X-ray diffraction reveals that **1** is a two-fold interpenetrated framework with mdf topology, in which pentanuclear $\{Zn_5(btz)_6\}$ cluster acts as a 4-connected node. Moreover, the luminescent properties of **1** dispersed in different metal ions and solvents have been investigated systematically.

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In recent years, much effort has been devoted to the synthesis of metal–organic frameworks (MOFs) through the reasonable selection of metal ions or metal clusters as connectors and organic ligands as linkers, which has been prompted by their potential applications in gas storage [1–3], catalysis [4,5], separation [6,7], small-molecule sensing [8–11] and so on. Despite large numbers of MOFs have been reported, there remain challenges to explore effective synthetic strategies for the preparation of novel MOFs. Some synthetic strategies undoubtedly help to shed light on the prediction, design, and synthesis of the resulting, but they are not easy to identify metal ions with which the intended framework geometry can be generated, or to establish the exact chemical conditions for the in situ formation of specific SBUs. Bottom-up synthesis can overcome these difficulties. Very recently, Zheng and our group have used this strategy to synthesize a series of MOFs. Zheng and co-workers have utilized two pentanuclear metal clusters $[M_5(btz)_6(NO_3)_4(H_2O)_4]$ (btz = benzotriazole; M = Co (1), Ni (2)), as the secondary building units and the radical anion as the organic linker to realize the step-by-step synthesis of two twofold interpenetrated three dimensional diamond networks [12]. Our group have also obtained three microporous interpenetrated frameworks based on the same pre-designed tetrahedral metal cluster and linear carboxylic ligands [13]. Inspired by that, we chose the metal cluster $[Zn_5(btz)_6(NO_3)_4(H_2O)]$ as an initial reaction precursor, aromatic

dicarboxylic as ligand. The selected ligand based on the following considerations: (i) hindrance: benzene is equal to the sterically bulky substituent, which can influence interesting topology and framework interpenetration; (ii) organic linkers themselves are solid-state luminescent materials, which can act as rigid organic ligands to construct luminescence MOFs [14]. Inspired by the above consideration, here we report a novel MOF based on pentanuclear metal cluster and 1,4-naphthalenedicarboxylic acid (ndc) as linkers for the first time. In addition, **1** is a two-fold interpenetrated framework with mdf topology. The mdf net is a four-connected uninodal net with point symbol 8^6 and the long vertex symbol $(8_1 \cdot 8_3 \cdot 8_4 \cdot 8_4 \cdot 8_4 \cdot 8_4)$. To the best of our knowledge, only one example of coordination polymer with mdf topology has been obtained so far [15].

The precursor was prepared from $Zn(NO_3)_2 \cdot 6 H_2O$ and 1H-benzotriazole (Hbtz) in methanol solution. The solvothermal reaction of ndc ligand with the precursor in DMA solution afforded compound **1** [16]. Then the structure and properties of **1** were characterized carefully with various techniques, including X-ray diffraction analysis [17], elemental analyses, luminescent properties, PXRD (Fig. S1), TG (Fig. S2) and IR (Fig. S3). Moreover, the chemical stabilities of **1** have been also investigated in the air, water, acid and base solutions.

Single-crystal X-ray diffraction analysis reveals that compound **1** crystallizes in the tetragonal space group $I4_1/a$, as expected, all the nitrate groups that were bonded to the apical sites of the precursor were replaced by ndc linkers. The asymmetric unit of **1** consists of five Zn ions, six benzotriazole ligands, two ndc ligands and one coordinated

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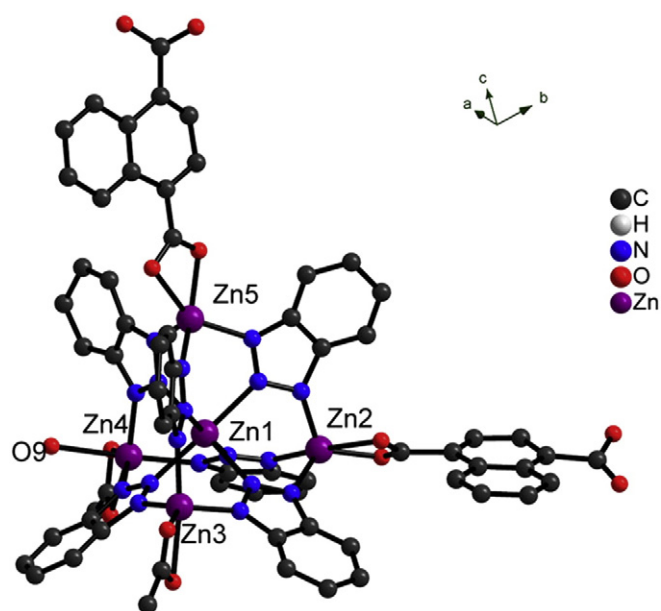


Fig. 1. Ellipsoids of the coordination environment of Zn^{2+} ion in compound **1**. Hydrogen atoms have been omitted for clarity. Color codes: Zn, violet; C, gray; N, blue; O, red.

water molecule (Fig. 1). As anticipated, five Zn atoms are assembled together with six benzotriazole ligands exhibiting a pentanuclear cluster. The pentanuclear cluster is composed of a tetrahedral arrangement of four six-coordinate Zn^{2+} ions centered on the fifth one. Each of the six μ_3 -btz ligands straddled an edge of the tetrahedron and is bound to the central metal through the nitrogen atom in the 2-position. Six nitrogen atoms from six btz ligands therefore complete the coordination sphere of the central Zn^{2+} ion, while each Zn^{2+} ion at the vertex of the pentanuclear cluster is chelated by three nitrogen atoms from three btz ligands and two oxygen atoms from a chelating a carboxylic group from ndc ligand. Notably, the octahedral coordination geometry of Zn4 is satisfied by an additional aqua molecule. As shown in Fig. 2a, the most striking features are the connections between different Zn^{2+} ions by ndc ligands to form an unprecedented 3D framework with two kinds of 1D channels and two types of helical tubes constructed from interweaving triple helical chains and double-helical chains, respectively. Three left-handed helical chains enlace together to form a helical tube with square channel along the *c*-axis (Fig. 2b). The diagonal length of the square channel is 17.62 Å. In addition the left-handed large square channel is surrounded by left helical chain, with diagonal length of about 25.53 Å (Fig. 2c). Furthermore, two right-handed helical chains interweaved to produce a rectangular channel, in which the diagonal lengths are 19.79 Å (Fig. 2d). Owing to the large voids in a single net, double equivalent networks interpenetrated to maintain the stability of the whole structure. The topological analysis approach can be employed to understand the intricate structure better. As illustrated in Fig. 3a, each pentanuclear cluster acts as a four-connected node and further links to the nearest neighbors through ndc ligands, and the overall 3D framework can be rationalized as a four connected mdf net with the long vertex symbol $8_1.8_3.8_4.8_4.8_4.8_4$. Intriguingly, the mdf topology differs from dia framework our group has produced. The dia framework is synthesized by using a pre-designed tetrahedral metal cluster and an amine-substituted dicarboxylic acid amino-1,4-benzenedicarboxylate. The dicarboxylic acid ndc was employed as the linking component with the aim of producing additional structures that have the same skeleton as 1,4-benzenedicarboxylate but contain benzene group. Results indicated that the

steric hindrance of the organic ligand is of key importance for the topology of metal–organic frameworks. Fig. 3b shows the interpenetration between two mdf nets.

The phase purity and stability of compound **1** were confirmed by X-ray powder diffraction. The simulated and experimental PXRD patterns of **1** are shown in Fig. S1. The stabilities of **1** were investigated in the air, water, acid and base (Fig. S1) because of the poor stabilities of solvothermally synthetic compounds in general [18]. The peak positions are in good agreement with each other, indicating the phase purity of the products. The differences in intensity may be due to the preferred orientation of the powder samples.

As we know, much attention has been paid to d^{10} transition metals, as a result of their outstanding photoluminescence. So we studied solid-state luminescent spectra of the compound **1**, which displays intense purple luminescence at 387 nm with excitation at 361 nm (Fig. 4a). In order to explain the nature of the emission, we analyzed the photoluminescent property of ndc and benzotriazole. The results revealed that the free ndc ligand exhibits an emission peak at 481 nm upon excitation at 365 nm (Fig. S4), while solid benzotriazole ligand displays weak luminescent at room temperature. In comparison with the emission peaks of the ligand, the luminescent emission wavelength of **1** is blue shift. This is probably attributed to the coordination effects of the ligand to Zn(II) cations, which increases the ligand conformational rigidity and reduces the non-radiative decay of the intraligand [19].

Compound **1** also exhibited solvent-dependent photoluminescence. As shown in Fig. 4b, the luminescence properties of **1** in different solvents are investigated. The solvents used are dichloromethane (CH_2Cl_2), chloroform (CHCl_3), acetonitrile, ethanol, methanol, *N,N*-dimethylformamide (DMF), ethyl acetate, tetrahydrofuran (THF) and acetone. Luminescence intensity is significantly enhanced in dichloromethane (CH_2Cl_2) and chloroform (CHCl_3), while quenching effects are observed in acetone. The quenching behavior can be rationalized by considering that acetone may interact with the framework, and thus quench the emission through coupling with the vibrational states of the CO and OH oscillators [20,21]. The experimental PXRD patterns of solvent-**1** (Fig. S5) were carried out, proving that the 3D framework of **1** still remained its original structure. Thus, compound **1** may be a potential luminescent probe for the detection of CH_2Cl_2 , CHCl_3 and acetone. Interestingly, the fluorescence intensity of the standard emulsion gradually decreased with the addition of CH_2Cl_2 (Fig. S6a) and CHCl_3 solvents (Fig. S6b).

Metal–organic frameworks constructed from d^{10} metal ions and conjugated organic linkers are promising candidates for potential photoactive materials. Considering **1** is closely related structures with high conjugated frameworks, which allow comparative investigation of luminescence properties relative to structural features. To examine the potential of **1** for the sensing of metal ions, the activated sample **1** is immersed in aqueous solutions containing $\text{M}(\text{NO}_3)_x$ ($\text{M} = \text{Cd}^{2+}$, Fe^{3+} , Co^{2+} , Zn^{2+} , Ni^{2+} , or Cu^{2+}). As shown in Fig. 5a, the PL intensity of compound **1** is dependent on the metal ion-aqueous solutions, particularly in the cases of $\text{Zn}(\text{NO}_3)_2$ and $\text{Fe}(\text{NO}_3)_3$. The Fe^{3+} and Zn^{2+} ions have effect on the luminescence intensity.

Meanwhile, compound **1** was immersed in DMA solutions containing different concentrations of $\text{Zn}(\text{NO}_3)_2$ for further luminescence studies (Fig. S7). Interestingly, the luminescence intensity of the Zn^{2+} -incorporated **1** is heavily dependent on the concentration of the metal ion. The luminescence intensity decreases quickly with the concentration of Zn^{2+} increased.

Detecting anions in aqueous solutions especially for some pollutant anions in waste water has become an important issue due to their harmfulness to human health and environment [22]. The luminescence properties of **1** in different anions aqueous solutions were investigated. The anions used are Br^- , Cl^- , I^- , CH_3COO^- , SCN^- , SO_4^{2-} , SO_3^{2-} , CO_3^{2-} , and N_3^- . As seen in Fig. 5b, the PL intensity of **1** is dependent on the anion-aqueous solutions, these results imply **1** can serve as luminescence probes to recognize SO_3^{2-} and Br^- in aqueous solutions.

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