

A 3D-diamond-like metal–organic framework: Crystal structure, nonlinear optical effect and high thermal stability



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ABSTRACT

A new metal–organic framework $[Zn(cpt)(ATZ)]_n$ (**1**, HATZ = 5-amino-1H-tetrazol, Hcpt = 4-(4H-1,2,4-Triazol-4-yl)benzoic acid), has been solvothermally synthesized and structurally characterized by single crystal X-ray diffraction. Structural analysis shows that compound **1** is a three-dimensional (3D) framework with 3-fold interpenetrated diamond topology where the Zn(II) centers are all 4-coordinated. Compound **1** exhibits high thermal stability up to 370 °C, and weak second-order nonlinear optical coefficient as ca. 0.13 times as that of potassium dihydrogen phosphate (KDP), and also displays blue photoluminescence at room temperature.

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Using multidentate and multifunction organic ligands in constructing metal–organic frameworks (MOFs) or porous coordination polymers (PCPs) has received much attention not only because of their intriguing topological networks [1–3], but also due to their ubiquitous potential applications in various areas, such as gas storage and selective separation [4,5], chemical sensing [6], proton conductors [7], nonlinear optics [8] and heterogeneous catalysis [9,10]. However, rational design of MOFs with predicted structures and properties is still a challenge for chemists and material scientists [1–3]. An effective method to synthesize the desired MOFs is choosing suitable inorganic metal or metal clusters nodes and organic bridging ligands [11]. 5-Substituted tetrazoles have been proven to be good organic linkers in construction of versatile MOFs (Scheme S1, ESI) [12], and show interesting nonlinear optical, magnetic and gas storage properties [13–15]. Amino has been introduced in 5-substituted tetrazoles (HATZ = 5-amino-1H-tetrazol), which exhibited more abundant and complicated coordination modes. Furthermore, carboxylate and triazole groups are widely used in construction of versatile MOFs [16]. In this work, the multidentate (HATZ) and multifunction (Hcpt = 4-(4H-1,2,4-Triazol-4-yl) benzoic acid) organic ligands were used to synthesize a 3D 3-fold interpenetrated diamond topology MOFs, $[Zn(cpt)(ATZ)]_n$ (**1**). To the best of our knowledge,

this new compound is the first example, with second-order nonlinear optical effects, which was constructed from the Hcpt and/or ATZ ligands. In addition, the thermal stability and photoluminescent property of compound **1** have also been investigated.

In this work, Hcpt (4-(4H-1,2,4-triazol-4-yl)benzoic acid) was prepared by the reaction of 4-aminobenzoic acid with N,N'-dimethylformamide azine dihydrochloride (DMAZ) in a one-pot reaction [17]. Compound **1** was solvothermally synthesized by employing $Zn(NO_3)_2 \cdot 6H_2O$, Hcpt and HATZ in mixed N,N'-dimethylformamide (DMF) and H_2O solvents [18]. Compound **1** was formulated as $[Zn(cpt)(ATZ)]_n$ based on single crystal X-ray diffraction, elemental analysis and thermal gravimetric analysis (TGA). Single crystal X-ray crystallography reveals that compound **1** crystallizes in the orthorhombic $P2_12_12_1$ space group and possesses an extended 3D framework constituted by the Zn(II) cations and organic ligands cpt and ATZ anions. The asymmetric unit consists of one crystallographically independent Zn(II) ion, one cpt and one ATZ anion. The coordination geometry of Zn(II) cation can be viewed as a distorted tetrahedral: one carboxylate oxygen atom from the cpt ligand, one N atom from 1,2,4-triazol groups of another cpt ligand, and the remaining two N atoms from two isolate ATZ ligands, respectively (Fig. 1a). Each ATZ ligand acts as a bidentate bridging linker and binds two Zn atoms through 1,4-nitrogen atoms of the tetrazole group, which has been observed in the reported literature [19]. The Zn–N bond distance of 1.971(4) Å and 2.037(3) Å is similar to those found in tetrazole-based tetrahedral Zn coordination polymers with the same coordination mode of 5-substituted tetrazole as that in compound **1** [20]. The $ZnON_3$ distorted tetrahedron is connected by the ATZ ligands

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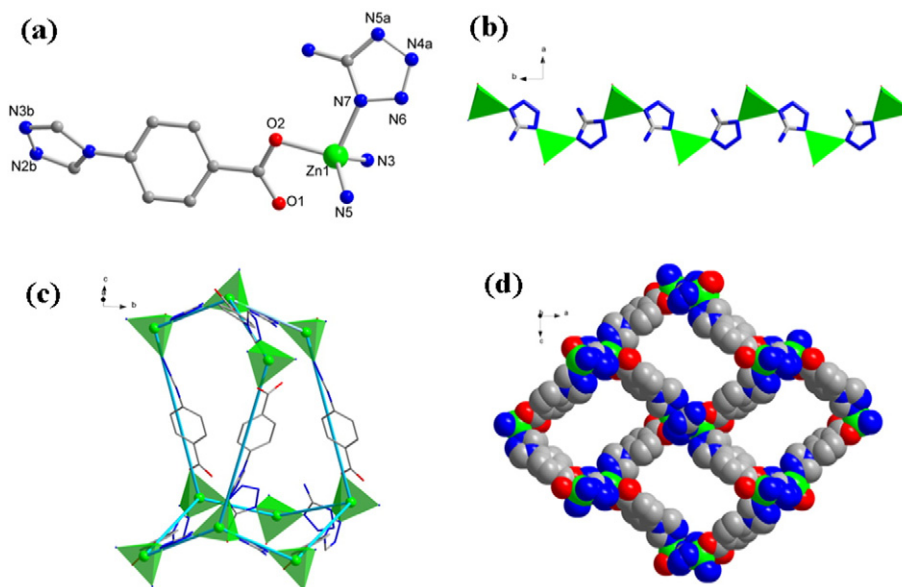


Fig. 1. (a) Local coordination environment of Zn^{II} atoms in [Zn(cpt)(ATZ)]_n (H atoms omitted for clarity. Symmetry codes: $a = 2 - x, 0.5 + y, 0.5 - z$; $b = 0.5 - x, 1 - y, 0.5 + z$); (b) the ZnON₃ distorted tetrahedron is connected by the ATZ ligands to form extended 1D zigzag single chains along the *b* axis; (c) perspective view of a single dia unit cage; (d) space-filling model of a 3D single dia framework showing the 1D channels along the *b* axis. Bright green, blue, red and gray spheres represent Zn, N, O and C atoms, respectively.

to form an extended 1D zigzag single chain along the *b* axis (Fig. 1b). The Zn(II) ions act as 4-connected nodes which are connected with each other in three dimensions by the cpt and ATZ linkers to generate a 3D diamonded (dia) framework (Fig. 1c, d).

As can be seen in Fig. 1d, the 3D framework possesses large channels which are large enough to allow further nucleation in the void space to generate a complex 3-fold interpenetrated 3D framework (Fig. 2a). Topological analysis by TOPOS 4.0 [21] revealed the presence of 4-c Zn(II) nodes and the overall structure has a dia net topology with the Schläfli point symbol {6⁶} [22]. Interpenetration analysis by TOPOS 4.0 confirmed the presence of 3-fold interpenetration (Fig. 2b) with the Schläfli extended point symbol [6(2) · 6(2) · 6(2) · 6(2) · 6(2) · 6(2)] and thus reducing the void volume completely. As far as we know, this new compound is the first used cpt ligands for constructing mixture ligand MOFs, and with a three-fold interpenetrated diamond topological net.

IR absorption peak centered at 3380 cm⁻¹ (Fig. S1) can be assigned to the characteristic vibration of N–H, suggesting the presence of amino groups of ATZ ligand. Compared with the free Hcpt ligand, the absence of a strong absorption at around 1700 cm⁻¹ in compound **1** indicated that the carboxylate group was completely deprotonated. Two strong sharp peaks at 1623 and 1367 cm⁻¹ for compound **1** could be attributed to the asymmetric and symmetric of the –COO vibrations (ν_{as} and ν_s),

respectively. The bands at 1562 cm⁻¹ for compound **1** could be associated with $\nu(\text{C}=\text{N})/\text{ring}$ stretching vibrations plus $\delta(\text{N}-\text{H})_{\text{NH}_2}$ of the ATZ ligand [23].

The as-synthesized sample of compound **1** has been characterized by powder X-ray diffraction (PXRD) (Fig. S2). The experimental PXRD pattern corresponds well with the resulted simulated pattern of the single crystal data, indicating the pure phase of compound **1**. The thermal stability of compound **1** was examined by the thermal gravimetric analysis (TGA) technique (Fig. S3). The result indicated that compound **1** showed high thermal stability up to 370 °C. The weight loss of 25.5% from 370 to 397 °C was attributed to the decomposition of the ATZ ligand (calcd 24.9%) and then the whole framework began to collapse.

Since compound **1** crystallized in the acentric space group *P2₁2₁2₁*, which belonged to the crystal class 222, its second-order nonlinear optical effect was examined. The measurement of second harmonic generation (SHG) response was obtained by placing a sieved (80–100 mesh) powder sample by the method of Kurtz and Perry. The fundamental wavelength is 1064 nm generated by a Q-switched Nd:YAG laser. The output ($\lambda = 532$ nm) was filtered first to remove the multiplier and was then displayed on an oscilloscope. This procedure was then repeated using standard NLO material (microcrystalline KH₂PO₄), and the ratio of the second harmonic intensity outputs was calculated. Second

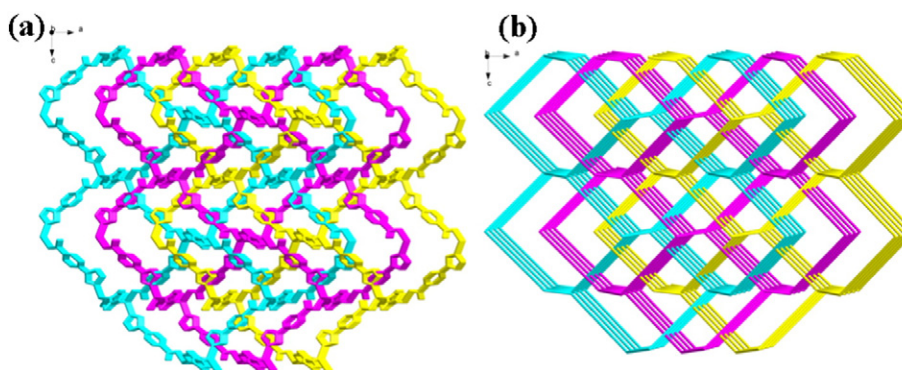


Fig. 2. (a) View of the 3-fold interpenetrated 3D framework of compound **1** and (b) topological representation of the 3-fold interpenetrating nets in compound **1** (three different 3D nets are shown in three different colors).

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