

Luminescence, adsorption and topological analysis of a new two-fold interpenetrating 3D Cd(II) coordination polymer based on a tetracarboxylate ligand

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ABSTRACT

A new 3D microporous coordination polymer $[\text{Cd}(\text{H}_2\text{BTTB})]_n \cdot 0.5n\text{H}_2\text{O}$ (**1**), (H_4BTTB = 4,4',4'',4'''-benzene-1,2,4,5-tetrayltetrabenzoic acid), was constructed under solvothermal condition and structurally characterized by elemental analysis, FT-IR spectroscopy, powder X-ray diffraction (PXPD) and thermogravimetric analyses (TGA). Single crystal X-ray diffraction indicates that compound **1** displays a two-fold interpenetrating dinodal (4,4)-connected three-dimensional coordination network with the **pts** topological net and the point symbol of $\{4^2 \cdot 8^4\}$. Furthermore, photoluminescence and adsorption of **1** were investigated.

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1. Introduction

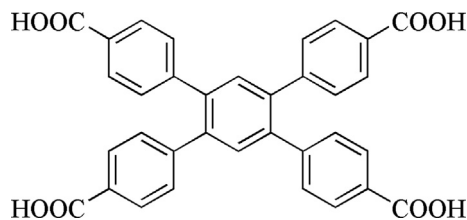
Over the last decades, the rational design and synthesis of new porous coordination polymers (CPs) with unique structure and function has attracted great interest for researchers in the field of coordination chemistry owing to their intriguing variety of architectures and topological frameworks [1], as well as their wide potential application as gas storage or gas separation, catalysis, sensor properties and so on [2–4]. According to previous reported work, the diversity in the self-assembly process of such coordination polymers influenced by many factors, such as the coordination geometry of metal centers, the coordination ability of organic ligand, number of coordination donors provided by ligands and the reaction conditions (medium, pH value, temperature) [5–11]. Among these factors, the selection of organic ligand with suitable binding groups has a large impact on the building of coordination polymers with novel structures. Therefore, tetracarboxylate-based ligands have successfully been used for the construction of metal-organic frameworks (MOFs) [12]. For example, Hupp and co-workers have synthesized catenated and noncatenated high porous MOFs utilizing 4,4',4'',4'''-benzene-1,2,4,5-tetrayltetrabenzoic acid

linkers and showing selective gas storage capacities [13]. Recently, Walton et al. [14] have shown that the structural diversities can be modulated by using d^{10} metal ions with H_4BTTB and all show a higher adsorption preference for CO_2 over N_2 and CH_4 .

On the basis of the above considerations, a semi-rigid tetracarboxylate ligand, 4,4',4'',4'''-benzene-1,2,4,5-tetrayltetrabenzoic (H_4BTTB , Scheme 1) is employed in the realm of crystal engineering [15] according to the following consideration: (i) Much work is required to establish rational synthetic strategies to the desired architectures using semi-rigid or rigid building blocks. While, the H_4BTTB ligand can be very advantageous when designing interesting multidimensional architectures because it contains four carboxylate groups and can adopt various coordination modes to metal ions resulting from completely or partially deprotonated sites to allow for the large diversity in the topologies. (ii) Most importantly, if there are protonated or un-coordinated carboxylic groups in H_4BTTB based on self-assembly process of MOFs, and these possible active sites may allow the interaction between guest molecules/ions and the framework, which means it may have promising luminescence sensor [16]. Herein, in this work, we describe our recent research on the synthesis, crystal structure, and topological analysis of a new 3D two-fold interpenetration coordination polymer $[\text{Cd}(\text{H}_2\text{BTTB})]_n \cdot 0.5n\text{H}_2\text{O}$ (**1**), as well as its gas adsorption and luminescent properties were also investigated.

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Scheme 1. Molecular structure of H_4BTTB ligand.

Table 1
Crystallographic data and structural refinement parameters for **1**.^a

Complex	1
Empirical formula	$C_{68}H_{42}Cd_2O_{17}$
Formula weight	1355.76
Crystal system	orthorhombic
Space group	<i>Pban</i>
<i>a</i> (Å)	15.788(3)
<i>b</i> (Å)	28.744(5)
<i>c</i> (Å)	10.8783(17)
α (°)	90
β (°)	90
γ (°)	90
<i>V</i> (Å ³)	4936.7(15)
<i>Z</i>	2
ρ_{calc} (g·cm ⁻³)	0.908
<i>F</i> (000)	1352
Reflections collected	23192
<i>S</i> on <i>F</i> ²	1.072
<i>R</i> _{int}	0.0981
<i>R</i> ₁ , <i>wR</i> ₂ ^a [<i>I</i> > 2σ(<i>I</i>)]	0.0769, 0.2239
<i>R</i> ₁ , <i>wR</i> ₂ ^a (all data)	0.1315, 0.2570

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}.$$

2. Experimental

2.1. Materials and physical measurements

1,2,4,5-Tetrakis(4-carboxyphenyl)-benzene (H_4BTTB) was prepared via Suzuki coupling of 1,2,4,5-tetrabromobenzene and 4-ethoxycarbonylphenylboronic acid as reported previously [17]. Other chemicals were of reagent grade and used without further purification. Infrared spectra were obtained from KBr pellets on a Bruker EQUINOX 55 Fourier transform infrared spectrometer in the 400–4000 cm^{-1} region. Elemental analyses (C, H, N) were performed on an elemental Vario EL III elemental analyzer. Thermal gravimetry analyses (TGA) were carried out with a Universal V2.6 DTA system at a rate of 10 °C/min in a nitrogen atmosphere. Photoluminescent spectra were measured using a Hitachi F-4500 Fluorescence Spectrometer for the solid powder samples at room temperature. The gas sorption isotherm of **1** was measured with ASAP 2020 M adsorption equipment.

2.2. Preparation of $[Cd(H_2BTTB)]_n \cdot 0.5nH_2O$ (**1**)

Compound **1** was prepared by solvothermal reaction of $CdCl_2 \cdot 2.5H_2O$ (0.0229 g, 0.1 mmol) and H_4BTTB (0.0279 g, 0.05 mmol) in distilled water (4 mL) and *N,N*-dimethylacetamide (DMA) (1 mL) and using 0.5 mol·L⁻¹ NaOH aqueous solution to adjust the pH to 5.0 that was placed in a Teflon-lined stainless steel vessel (25 mL), heated to 180 °C for 72 h and then cooled to room temperature at a rate of 5 °C/h. The colorless crystalline product was obtained, washed with distilled water (5 mL), and dried in air to give 0.0250 g, yield 37.0% based on H_4BTTB . Elemental Anal. calc. for: $C_{68}H_{42}Cd_2O_{17}$: C, 60.23; H, 3.12. Found: C, 61.95; H, 3.44%. IR

(KBr, cm^{-1}): 3424 (s), 1588 (s), 1541 (m), 1467 (w), 1392 (vs), 1178 (w), 1119 (w), 1017 (m), 854 (w), 786 (m), 745 (w), 722 (w), 5542 (w).

2.3. Single crystal X-ray diffraction

Suitable single crystal of compound **1** was carefully selected under an optical microscope and glued to thin glass fibers. Intensity data were collected on a Bruker Smart APEX II CCD diffractometer with graphite-monochromated Mo- K_{α} radiation ($\lambda = 0.71073$ Å) at room temperature. Empirical absorption corrections were applied using the SADABS program. The structure was solved by direct method and refined by the full-matrix least-square based on F^2 using the SHELXTL-97 program. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms of organic ligands were generated geometrically. Crystal data and structural refinement parameters for **1** are summarized in Table 1. Selected bond distances and bond angles are listed in Table S1.

3. Results and discussion

3.1. Structural discussion

A luminescent three-dimensional Cd-MOF, $[Cd(H_2BTTB)]_n \cdot 0.5nH_2O$, was synthesized solvothermally in mixture solvent. X-ray single crystal structural analysis reveals compound **1** crystallizes in the orthorhombic system with *Pban* space group. The asymmetric unit of **1** contains one Cd(II) ion, one deprotonated (H_2BTTB)²⁻ ligand and half lattice water molecule.

As shown in Fig. 1, Cd1 center is octa-coordinated to eight oxygen atoms (O1, O2, O1A, O2A, O3, O4, O3A, O4A) from four different (H_2BTTB)²⁻ anions. The coordination geometry of Cd1 center can be described as a distorted CdO₈ dodecahedral geometry. The Cd–O bond lengths lie in 2.302(6) to 2.678(14) Å, which is comparable to other cadmium (II) complexes reported [18]. In compound **1**, the five phenyl rings of (H_2BTTB)²⁻ ligand are non-planar, four outer phenyl groups are twisted with respect to the central one, the dihedral angles between the central and outer phenyl rings are the same of 57°, which result from the freely rotating phenyl rings combined by intervening C–C groups. As a result, four carboxylate groups of one (H_2BTTB)²⁻ ligand show bidentate-chelating coordination modes to link four Cd(II) ions generating a two-fold interpenetrating 3D framework in the self-assembly process of coordination polymer, as shown in Fig. 6.

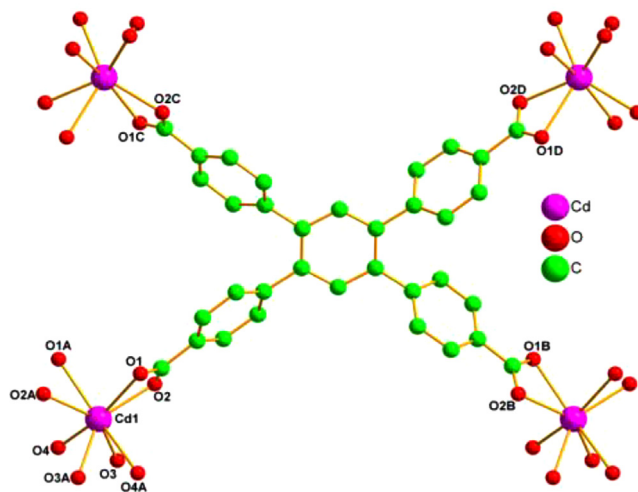


Fig. 1. The coordination environment of Cd^{2+} ion in compound **1**.

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