



Microporous Cd(II) metal-organic framework as fluorescent sensor for nitroaromatic explosives at the sub-ppm level



Xing-Po Wang, Lu-Lu Han, Zhi Wang, Ling-Yu Guo, Di Sun*

Key Lab of Colloid and Interface Chemistry, Ministry of Education, School of Chemistry and Chemical Engineering, Shandong University, Jinan, Shandong, 250100, China

ARTICLE INFO

Article history:

Received 16 August 2015
Received in revised form
4 November 2015
Accepted 11 November 2015
Available online 17 November 2015

Keywords:

Biphenyltetracarboxylic acid
Pts net
Fluorescence probe

ABSTRACT

A novel Cd(II) metal-organic framework (MOF) based on a rigid biphenyltetracarboxylic acid, $[\text{Cd}_4(\text{bptc})_2(\text{DMA})_4(\text{H}_2\text{O})_2 \cdot 4\text{DMA}]$ (**1**) was successfully synthesized under the solvothermal condition and characterized by single-crystal X-ray diffraction and further consolidated by elemental analyses, powder X-ray diffraction (PXRD), infrared spectra (IR) and luminescent measurements. Single crystal X-ray diffraction analysis reveals that compound **1** is 4-connected **Pts** (Point symbol: $\{4^2 \cdot 8^4\}$) network based on $[\text{Cd}_2(\text{COO})_4]$ secondary building units (SBUs). Its inherent porous and emissive characteristics make them to be a suitable fluorescent probe to sense small solvents and nitroaromatic explosives. Compound **1** shows obviously solvent-dependent emissive behaviors, especially for acetone with very high fluorescence quenching effect. Moreover, compound **1** displays excellent sensing of nitroaromatic explosives at sub-ppm level, giving a detection limit of 0.43 ppm and 0.37 ppm for nitrobenzene (NB) and *p*-nitrotoluene (PNT), respectively. This shows this Cd(II) MOF can be used as fluorescence probe for the detection of nitroaromatic explosives.

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1. Introduction

Nitroaromatics, such as nitrobenzene (NB), *p*-nitrotoluene (PNT), *m*-nitrotoluene (MNT), *o*-nitrotoluene (ONT), 2,4-dinitrotoluene (2,4-DNT) and so on, are a kind of highly explosive compounds and are very difficult to be detectable, so detection of these nitroaromatic explosives are becoming more and more necessary and urgent [1]. Generally, different methods are used to detect nitroaromatic explosives, such as Gas chromatography-mass spectrometry [2], Raman spectroscopy [3], Ion mobility spectrometry [4] and Fluorescence spectroscopy [5]. Among these methods, Fluorescence spectroscopy is mostly used because of its good selectivity, high sensitivity and easy accessibility [6], however, the spectrometers-based detections are lack of portability, thus seriously impeding the practical application. Recently, fluorescent materials for explosives detection including small organic molecules, nanomaterials as well as macromolecular polymer have developed quickly [7,8]. But the potentials of MOFs in this field have been less evaluated yet, because it is a great challenge for researchers to obtain appropriate luminescent MOFs to detect

nitrobenzene compounds at a very low concentration and highly selectivity.

Luminescent MOFs as one kind of fluorescent materials attracted much attention due to their special advantages such as crystalline nature, tunable structure, permanent porosity, and a wide range of physicochemical properties [9]. Usually, the fluorescent behavior of MOFs is influenced by the organic ligands and metal ions, so to obtain luminescent MOFs, organic ligands with chromophores or metal ions such as Pd^{II} , Pt^{II} , Zn^{II} , Cd^{II} , Ln^{III} , or utilizing the combination of these two parts often were under the scope of consideration [10–12]. Until now, the studies on luminescent MOFs are still very routine, extended applications of the luminescent properties are very little. In 2009, the first microporous crystalline metal-organic material for detection of trace explosives in the vapor phase was reported by Li et al. [13] From then, many fluorescent MOFs containing Cd^{2+} and Zn^{2+} were developed as sensors for detecting nitroaromatic explosives, but it still very difficult to design MOFs to detect specific nitroaromatic explosives at a low concentration and high selectivity, so study on this field is in its infancy and much more work are still needed.

Herein, we choose biphenyl-3,3',5,5'-tetracarboxylic acid (H_4bptc) as a linker to construct MOFs. The H_4bptc ligand has four carboxyl groups which can completely or partially deprotonated, so

* Corresponding author.

E-mail address: dsun@sdu.edu.cn (D. Sun).

it displays diverse coordination modes with metal ions. Moreover, two sets of carboxylates separated can form different dihedral angles through the rotation of C–C single bonds; thus, it may ligate metal centers in different orientations or conformations. As indicated by a CSD (Cambridge Structure Database) survey with the help of ConQuest, version 1.8, [14] totally 39 coordination compounds based on H_4bptc ligands were found, but only three were Cd(II)/ H_4bptc MOFs [15]. In this work, we solvothermally assembled $Cd(NO_3)_2 \cdot 4H_2O$ and H_4bptc to isolate a novel Cd(II)/ H_4bptc compound, namely, $[Cd_4(bptc)_2(DMA)_4(H_2O)_2 \cdot 4DMA]$ (**1**), which shows a 3D 4-connected **PtS** network based on two kinds of dinuclear $[Cd_2(COO)_4]$ SBUs. The solid-state emission spectrum for **1** exhibits maximum emission peak at 360 nm at room temperature, but it shows obvious quenching effect when dispersing in acetone. Moreover, this compound shows sensitive response to nitrobenzene compounds at sub-ppm level through a fluorescence quenching mechanism.

2. Experimental

2.1. Materials and physical measurements

All metal salts, organic ligands and solvents used in this work were bought commercially and used as received. Elemental analyses of C, H, and N were conducted on an EA1110 CHNS-O CE elemental analyzer. Photoluminescence spectra were measured on a Hitachi F7000 Fluorescence Spectrophotometer. FT-IR (Fourier transform infrared) spectra were recorded on a Nicolet Magna 750FT-IR spectrometer. Powder-XRD measurements were measured on a D/Max-2500 X-ray diffractometer using Cu $K\alpha$ radiation. Thermogravimetric analyses (TGA) were performed on a Netzsch STA 449C thermal analyzer from room temperature to 800 °C under nitrogen atmosphere at a heating rate of 10 °C/min.

2.2. Synthesis of $[Cd_4(bptc)_2(DMA)_4(H_2O)_2 \cdot 4DMA]$ (**1**)

A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (30.8 mg, 0.1 mmol), H_4bta (33.0 mg, 0.1 mmol) and 5 mL DMA-EtOH (v:v = 1:1) was sealed in a 25 mL Teflon-lined reaction vessel, then heated to 120 °C in 10 h and kept at 120 °C for 50 h, then slowly cooled to 30 °C in 13 h. Colorless block crystals of **1** was isolated by filtration, washed with H_2O , and dried in air. Elemental analysis calcd (%) for **1** ($C_{52}H_{61}Cd_4N_5O_{23}$): C 39.68, H 3.90, N 4.45; found: C 39.98, H 4.65, N 4.42. Selected IR peaks (cm^{-1}): 1578(s), 1403(s), 1343(s), 1017(w), 782(s), 653(s), 584(w).

3. X-ray crystallography

Single crystal of the compound **1** with appropriate dimensions was picked out under an optical microscope and mounted on a Nylon loop for data collection. Data for them were collected on a Bruker Apex II CCD diffractometer with graphite-monochromated Cu $K\alpha$ radiation source ($\lambda = 1.54184 \text{ \AA}$). For **1**, data were collected using omega scans of $0.5^\circ/\text{frame}$ until a complete hemisphere had been collected. Cell parameters were indexed by SMART software and refined with SAINT on all observed reflections [16]. Absorption corrections were applied with the program SADABS [17]. The data were integrated and scaled using the Bruker SAINT software package, and the structure was solved and refined using SHELXTL V6.12 [18]. Atoms were located from iterative examination of difference F-maps following least squares refinements of the earlier models. H atoms were placed in calculated positions and included as riding atoms with isotropic displacement parameters 1.2–1.5 times U_{eq} of the attached C atoms. SQUEEZE/PLATON was used to treat disordered solvents in the voids in the structural refinement

of **1** in X-ray experiment. Pertinent crystallographic data collection and refinement parameters are collated in Table S1, ESI†. Selected bond lengths and angles are collated in Table S2, ESI†. Topological analysis of the coordination networks was performed with the program package TOPOS [19].

4. Results and discussion

4.1. Crystal structure

4.1.1. $[Cd_4(bptc)_2(DMA)_4(H_2O)_2 \cdot 4DMA]$ (**1**)

Single-crystal X-ray diffraction analysis reveals that compound **1** crystallizes in orthorhombic crystal system with space group of *Pbcn*, and there are four crystallographically independent Cd(II) ions, two $bptc^{4-}$ anions, four DMA molecules, as well as two coordinated water molecules. All the Cd(II) ions in **1** are six-coordinated. As shown in Fig 1a, Both Cd1 and Cd4 are coordinated with six carboxylate oxygen atoms belonging to four different $bptc^{4-}$ anions and locate in a distorted CdO_6 octahedral geometry. Cd2 also shows CdO_6 octahedral geometry, but three of six O atoms are from three different $bptc^{4-}$ anions, one from DMA molecule and the rest are from aqua ligands. Cd3 is coordinated by three $bptc^{4-}$ anions and three DMA molecules, giving a distorted CdO_6 octahedron. The Cd–O bond lengths are in the range of 2.185(3)–2.522(3) Å, which are in normal ranges as observed in related compounds [15,20]. And inter-benzene dihedral angles of two unique $bptc^{4-}$ ligands are 14.6(2) and 28.0(2)°, respectively. The $bptc^{4-}$ in **1** is fully deprotonated to become an anionic ligand with $(\kappa^1-\kappa^1)-(\kappa^1-\kappa^1)-(\kappa^1-\kappa^1)-(\kappa^1-\kappa^2)-\mu_8$ and $(\kappa^1-\kappa^1)-(\kappa^1-\kappa^2)-(\kappa^1-\kappa^1)-(\kappa^1-\kappa^1)-\mu_6$ coordination modes. As shown in Fig. 1b and c, four carboxyl groups coordinated with two pairs of Cd(II) ions to form two kinds of dinuclear $[Cd_2(COO)_4]$ SBUs (Cd1 and Cd2, Cd3 and Cd4, respectively), which are extended by $bptc^{4-}$ ligands to form the resultant 3D framework. In this 3D framework, $bptc^{4-}$ ligands act as the approximate plane quadrilateral 4-connected linkers (Fig. 1d and e), and two kinds of dinuclear SBUs located in a distorted tetrahedral geometry linked by $bptc^{4-}$ ligands to form the 3D framework.

From a topological point of view, there are two kinds of 4-connected nodes (4-c square and 4-c tetrahedron) in this MOF with the ratio of 1:1. So the 3D framework can be simplified as a **PtS** net with Point symbol of $\{4^2 \cdot 8^4\}$, as shown in Fig. 1f and g. The solvent-accessible void of **1** is about 35.9% (5398.6 \AA^3) of the crystal unit cell volume (15057.1 \AA^3) by PLATON calculation. The void space of the **1** consists of infinite 2D intercross channels and discrete irregular cavities, with the largest and smallest internal free diameter of about 6.18 Å and 2.05 Å (taking into account the van der Waals radii), respectively.

4.2. Luminescence and sensing properties

The solid-state emission spectrum of compound **1** was measured at room temperature. The free ligand H_4bptc displays photoluminescence with emission maxima at 405 nm ($\lambda_{ex} = 350 \text{ nm}$), which was assigned to intraligand $\pi \rightarrow \pi^*$ transition [21]. As shown in Fig. 2, compound **1** shows photoluminescence with emission maximum at 360 nm ($\lambda_{ex} = 300 \text{ nm}$). Compared with free ligand H_4bta , the maximum emission peak has a blue shift of 45 nm. Cd(II) ion is very difficult to oxidize or reduce due to its d^{10} configuration, so the emissions are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal transfer (LMCT) in nature [22]. So this emission should be assigned to intraligand ($\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$) emission [23]. What's more, the chelation of ligand to metal centre may effectively increases the rigidity of the ligand and reduces the loss of energy by radiationless decay [24],

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