



A luminescent cadmium metal-organic framework with potential detection of nitroaromatic compounds



Jian-Long Du^{a,*}, Xuan Lu^a, Tian-Li Shen^a, Chao-Ping Li^a, Ya-Juan Mu^b, Li-Jun Li^{a,*}

^a College of Chemistry & Environmental Science, and Chemical Biology Key Laboratory of Hebei Province, Hebei University, Baoding 071002, PR China

^b College of Traditional Chinese Medicine, Hebei University, Baoding 071000, PR China

ARTICLE INFO

Article history:

Received 13 April 2015

Received in revised form

14 May 2015

Accepted 20 May 2015

Available online 11 June 2015

Keywords:

Metal-organic frameworks

Crystal structure

Luminescence

Nitroaromatic compounds

Selective sensing

ABSTRACT

A novel metal-organic framework (MOF) $[\text{Cd}_3(\text{L})_2(\mu_2\text{-H}_2\text{O})_2] \cdot (\text{H}_2\text{O})_3$ (**1**) ($\text{H}_3\text{L} = 5$ -(4-carboxy-benzylamino)-isophthalic acid), has been successfully synthesized under hydrothermal condition. Single crystal structure analysis reveals that **1** displays a three-dimensional (3D) framework, which represents a rarely obtained (4, 8)-connected topology. The compound exhibits strong fluorescent emission in the solid state at room temperature. Interestingly, the fluorescence of **1** dispersed in *N,N*-dimethylformamide (DMF) can be selectively and sensitively quenched by nitroaromatic compounds (NACs), which shows that the complex could be a potential fluorescent sensor for detection of these compounds.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Rapid detection of explosives or explosive like substances has drawn much attention in order to better combat terrorism and control environmental pollution [1]. Nitroaromatic compounds (NACs) have been well known for their widespread use as significant industrial materials in chemical synthesis and the manufacture of explosives. In addition to their explosive nature, they are also considered as environmental contaminants because of their high toxicity [2]. Hence, how to detect NACs quickly and quantitatively has become a hot topic for researchers.

Though various complicated technologies, such as X-ray dispersion, gas chromatography–mass spectrometer (GC–MS), ion mobility spectroscopy (IMS), have been developed for the purpose of detection, fluorescence quenching based detection is highly promising due to its simplicity and high sensitivity. Numerous explosives, such as nitroaromatics, nitramines and nitrates, are good electron acceptors with electron-withdrawing groups. Electron rich coordination networks are excellent candidates for chemical sensing applications, since the efficient electron transfer from conjugated polymers to the guest molecules results in fluorescence quenching. Metal-organic frameworks (MOFs) have attracted much attention in recent years due to their fascinating structures and their potential applications, such as gas storage and

separation [3], heterogeneous catalysis [4], and drug delivery [5]. The high surface areas, tailored pore size and functionality makes them suitable candidates as chemical sensors [6–8]. Up to now, several MOFs have been developed for sensing of nitroaromatic explosives [9–11]. For example, Li et al. reported, for the first time, a luminescent MOF for the high sensitivity sensing of nitroaromatic explosives [12]. Su and co-workers demonstrated a d-f heterometallic MOF, which could detect nitrobenzene with high selectivity [13].

Based on the above considerations, we select H_3L as a π -conjugated ligand ($\text{H}_3\text{L} = 5$ -(4-carboxy-benzylamino)-isophthalic acid), to react with Cd(II) ion, and successfully obtain a new 3D MOF $[\text{Cd}_3(\text{L})_2(\mu_2\text{-H}_2\text{O})_2] \cdot (\text{H}_2\text{O})_3$ (**1**). The luminescent property of **1** has been studied in the solid state at room temperature. In addition, the dispersed solution of **1** in *N,N*-dimethylformamide (DMF) exhibits strong fluorescence emission which could be quenched by NACs. The high selectivity and sensitivity of fluorescence quenching by these compounds suggest the potential application of **1** as an efficient chemical sensor.

2. Experimental section

$[\text{Cd}_3(\text{L})_2(\mu_2\text{-H}_2\text{O})_2] \cdot (\text{H}_2\text{O})_3$ (**1**): A mixture of CdSO_4 (50 mg, 0.14 mmol), H_3L (22 mg, 0.07 mmol), KOH (2 drops, 1 mol/L), and 10 mL distilled water was sealed in a 25 mL Teflon-lined stainless vessel and heated to 140 °C for 48 h. After being cooled to room

* Corresponding authors.

E-mail addresses: dujl@hbu.edu.cn (J.-L. Du), llj@hbu.edu.cn (L.-J. Li).

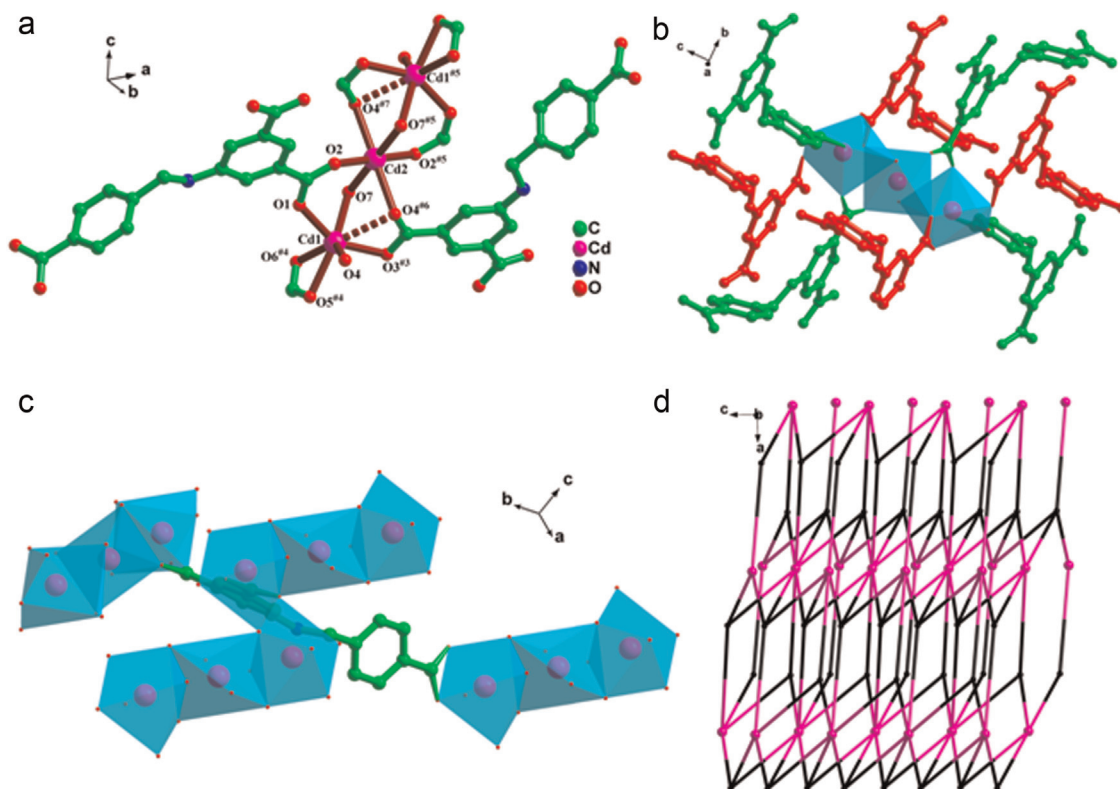


Fig. 1. (a) Coordination environment of trinuclear Cd(II) cluster in **1**. (Symmetry codes: #3: $-x, y+1/2, -z+1/2$; #4: $-x+1; y+1/2, -z+3/2$; #5: $-x, -y+2, -z$; #6: $x, y, z-1$; #7: $-x, -y+2, -z+1$.) (b) The 8-connected node of each trinuclear unit. (c) The 4-connected node of each L ligand. (d) Topological representation of (4, 8)-connected net of **1**.

temperature, pale yellow crystals were obtained. Yield: 30% based on H_3L . (CCDC reference number 1049487.) IR (KBr pellet, cm^{-1}): 3442br, 2360m, 2341w, 1698w, 1631s, 1559m, 1508m, 1404m, 1384s, 1319w, 1101w, 860m, 772s, 723m, 670w, 457w, 428w. Anal. calcd (%) for $C_{32}H_{30}N_2O_{17}Cd_3$: C, 36.54; H, 2.87; N, 2.66; found: C, 36.63; H, 2.81; N, 2.73.

3. Results and discussion

Single crystal X-ray diffraction analysis reveals that **1** crystallizes in the monoclinic space group $P2_1/c$ (Table S1). As depicted in Fig. 1a, each asymmetric unit consists of two crystallographically independent Cd(II) ions, Cd(1) ion is coordinated by six carboxylate oxygen atoms (O1, O3#3, O4, O4#6, O5#4, O6#4) of four L ligands and one μ_2 -oxygen atom (O7) of one water molecule. Cd

(2) ion displays an octahedral geometry with four carboxylate oxygen atoms (O2, O2#5, O4#6, O4#7) occupying the equatorial plane, and two μ_2 -oxygen atoms (O7, O7#5) occupying the axial position. And Cd–O distances lie in range of 2.1572(19)–2.603(2) Å, the angles around Cd(II) ions are between 55.39(8)° and 180.0° (Table S2). Further investigation on the structure of **1** indicates that three Cd(II) ions (Cd(1), Cd(2), Cd(1)#5) form a novel trinuclear unit, and each trinuclear unit bridges eight L ligands (Fig. 1b). With the linkage of L ligands, the trinuclear units extend into a three-dimensional (3D) framework (Figs. S1 and S2). Topologically, each trinuclear unit can be regarded as a 8-connected node, while each L ligand can be considered as a 4-connected node, respectively (Fig. 1b and c). The whole framework exhibits a **alb**-4,8-Cmce topology with a Schläfli symbol of $(4^5 \cdot 6)_2 (4^{10} \cdot 6^{14} \cdot 8^4)$ (Fig. 1d).

To confirm the phase purity of bulk materials, powder X-ray

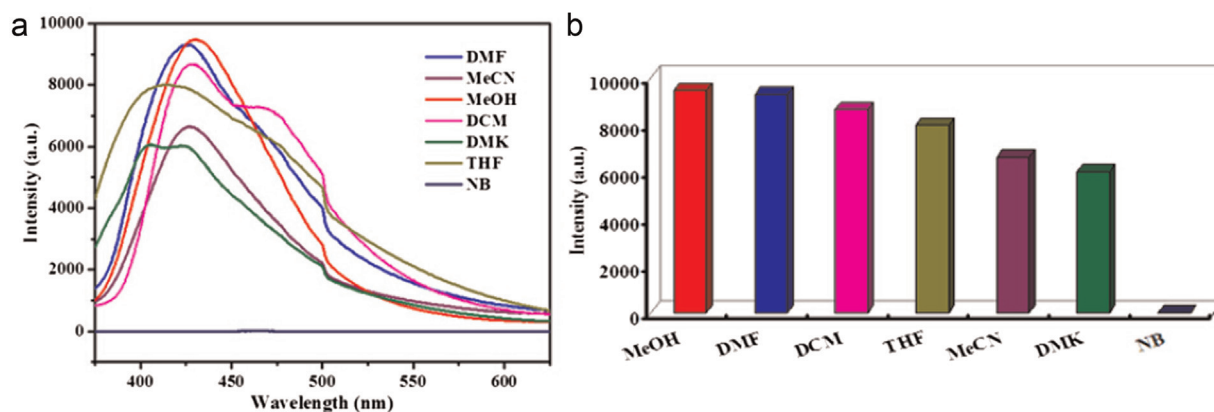


Fig. 2. (a) Emission spectra of **1** in different organic solvents ($\lambda_{ex}=355$ nm). (b) Emission intensity in different organic solvents.

Download English Version:

<https://daneshyari.com/en/article/1642392>

Download Persian Version:

<https://daneshyari.com/article/1642392>

[Daneshyari.com](https://daneshyari.com)