

Short communication

Luminescent sensing of a new 8-connected topological metal-organic framework



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ARTICLE INFO

Article history:

Received 15 May 2016

Received in revised form 4 June 2016

Accepted 11 June 2016

Available online 11 June 2016

Keywords:

Luminescent sensing

Topology, DFT

ABSTRACT

A new metal-organic framework having formula $\{[\text{Cd}_3(\text{H}_2\text{O})(\text{L})_2][\text{Cd}(\text{im})_3(\text{H}_2\text{O})_2] \cdot 3 \text{H}_2\text{O}\}$ ($\text{H}_4\text{L} = 5$ -bis(4-carboxylbenzyl)aminoisophthalic acid and im = imidazole) (**1**) has been synthesized. X-ray investigation reveals that **1** is rare 4,4,8-connected $(4^6)(4^5 \cdot 6)(4^{11} \cdot 6^{15} \cdot 8^2)$ topology. The present work indicates that **1** could be a prospective candidate for developing novel luminescence sensors for the selective sensing of nitrobenzene which can be used as a precursor for explosives. Furthermore, the luminescent property of **1** in different solvents analytes as well as nitrobenzene have been investigated and the observed quenching in fluorescence have been corroborated by theoretical calculations.

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As an active research area of porous materials, metal-organic frameworks (MOFs) obtained by self-assembly from organic linkers and metal ions or clusters provides prevailing platform for developing functional materials [1–3]. Moreover, microporous MOFs with appreciable surface areas and recognition capability have drawn particular attention because they can act as excellent candidate for the rapid recognition and sensing of cations, anions, small molecules [4–6]. The first work for detecting of MOF-based fluorescence sensor was reported in 2009 [7]. After that, luminescent MOFs (LMOFs) as explosive detectors represents a brand new sub-field of MOF research and some MOFs are used for recognition and detection of electron-deficient nitroaromatic molecules [8–10]. However, this area of research is still in its early stage when compared with the other established applications of MOFs [8–10].

The MOFs possess tunable structures which are stable and crystalline in nature and it is possible to integrate functional groups within one single MOF through careful design [11]. The ligand-based strategy for developing new luminescent MOFs is most commonly used technique. In our effort to develop MOFs with luminescence sensing, a new ligand, 5-bis(4-carboxylbenzyl)aminoisophthalic acid (H_4L) (Fig. S5), having two isophthalate and one benzoate groups connected through triethylamine moiety was selected as an organic framework. The choice was based on the consideration that the flexible organic

moiety facilitates the generation of MOFs having a microporous structure and enhanced fluorescence properties which may be used for the efficient and selective detection of nitroaromatics and cations [12–13]. In this contribution, solvothermal reaction of H_4L and Cd(II) center in the presence of ancillary ligand imidazole (im) has yielded a compound having formula $\{[\text{Cd}_3(\text{H}_2\text{O})(\text{L})_2][\text{Cd}(\text{im})_3(\text{H}_2\text{O})_2] \cdot 3 \text{H}_2\text{O}\}$ (**1**) [14], which has been characterized by elemental analyses, IR and single crystal X-ray diffraction (Fig. S1–S3). X-ray investigation reveals that **1** is rare 4,4,8-connected $(4^6)(4^5 \cdot 6)(4^{11} \cdot 6^{15} \cdot 8^2)$ topology.

The structure of **1** is a complicated 3D network comprising of trinuclear $\text{Cd}_3(\text{COO})_8(\text{H}_2\text{O})$ clusters (Fig. 1a and Fig. S4) bridged by L ligands. Each carboxylate group of the Cd_3 cluster belongs to a different L ligand (Fig. 1b), and each L ligand (of which there are two crystallographically different types) bridges four clusters. The L ligand displays two kinds of coordination modes to connect seven Cd(II) centers with four carboxylate groups, adopting μ_3 - η^2 : η^1 -bridging, μ_2 - η^1 : η^1 -bridging, μ_2 - η^2 : η^1 -bridging, and μ_1 - η^1 : η^1 -bridging coordination modes (Fig. S5) [15]. The overall network has $(4^6)(4^5 \cdot 6)(4^{11} \cdot 6^{15} \cdot 8^2)$ topology (Fig. 1c) [16–19], where the clusters act as 8-connecting nodes, and the two crystallographically different L ligands are also topologically distinct 4-connecting nodes. The negative charge on the $[\text{Cd}_3(\text{L})_2]^{2-}$ framework is counter-balanced by $[\text{Cd}(\text{imidazole})_3(\text{H}_2\text{O})_2]^{2+}$ counter-cations intercalated in the structure. The structure also contains three crystallographically distinct intercalated water molecules. Pairs of counterions and two of each type of intercalated water molecule lie in

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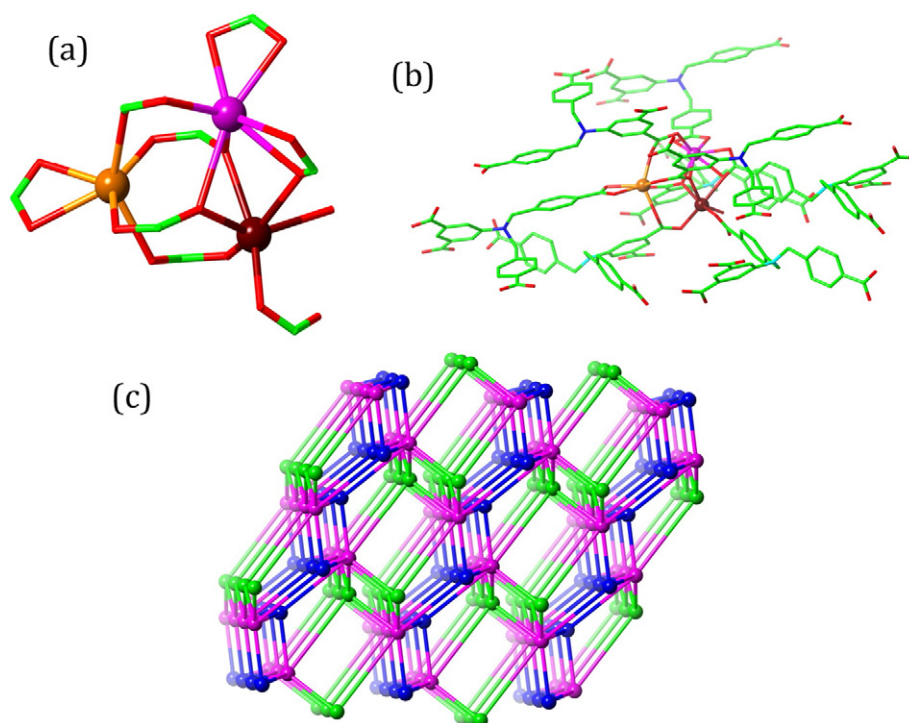


Fig. 1. (a) Local structure of the $\text{Cd}_3(\text{O}_2\text{C})_8(\text{H}_2\text{O})$ cluster in the structure of **1**; (b) Extended view of the cluster and the complete attached ligands; (c) The trinodal 4,4,8-connected net of **1**.

distinct cavities in the framework, with extensive hydrogen bonding between the framework, counterions and water molecules indicative of templation of the 3D framework structure by the counter-cations and solvent.

The photoluminescence (PL) spectra of **1** in the solid state were recorded at room temperature (Fig. S6). On excitation at 300 nm, **1** exhibited an emission peak at 410 nm. This emission band can be assigned to ligand-centered emission, because the emission was observed at 360 nm ($\lambda_{\text{ex}} = 275$ nm) for free ligand H₄L. In addition, the fluorescence properties of **1** in different solvent emulsions were investigated (Fig. 2a). The predominant feature is that the photoluminescent intensities are largely dependent on the solvent molecules, particularly in the case of nitrobenzene (NB), which exhibits significant quenching behavior [19–20]. The physical interaction of the solute and solvent plays a vital role in such fluorescence behavior [21]. To examine sensing ability of **1** towards NB in more detail, a batch of suspensions of **1** with gradually increasing NB contents in DMF was prepared to monitor the emissive response (Fig. 2b). The luminescence intensity decreased up to 50% at 100 ppm, and almost complete quenching was observed at

300 ppm. Therefore, these results indicate that electron transfer from the electron-donating framework to the highly electron-deficient NB molecule can take place upon excitation with concomitant quenching in fluorescence [22–25]. The absorption spectrum for NB exhibits significant overlap with the emission of **1** (Fig. S7), which clearly indicates that both electron- and energy-transfer mechanisms are present for the fluorescence quenching by NB, while only electron transfer mechanism exists for other nitro analytes [25].

To gain more insight into the quenching mechanism associated with the analytes mentioned in the present investigation, the HOMO–LUMO energies of the nitrobenzene along with the other analytes were calculated by density functional theory at the B3LYP/6-31G* level (Fig. 3, Table S1). The possible reason associated with the quenching of luminescence in **1** may be the charge transfer from framework of **1** to the LUMO of the analytes. This charge transfer will occur when the energy associated with the LUMO of the donor lie at the higher scale than the LUMO of the acceptor in the analyte. From the results it can be anticipated that the observed maximum fluorescence intensity quenching in the case of nitrobenzene when used as analyte is due to the easy electron

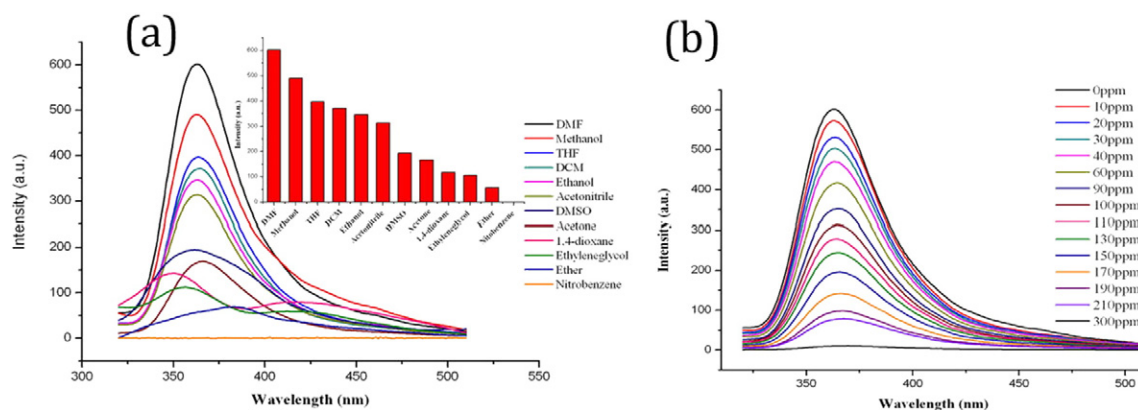


Fig. 2. (a) Comparison of the luminescence intensity of **1** in different solvents; (b) Emission spectra of **1** dispersed in DMF with the titration of NB, and the quenching of the original emission.

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