



Fluorescent sensing of nitroaromatics by two coordination polymers having potential active sites

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ABSTRACT

Two new d^{10} based coordination polymers having formula $[Cd(HL1)(L2)]$ (**1**) and $[Zn(HL1)(L2)]$ (**2**) ($H_3L1 = 5-(4\text{-carboxyphenoxy})isophthalic\ acid$ and $L2 = 3-(4\text{-methyl-6-(pyridine-3-yl)pyridine-2-yl)pyridine}$) have been synthesized and characterized using IR, thermogravimetric analyses (TGA), photoluminescence and single-crystal X-ray diffraction techniques. The single-crystal X-ray investigation reveals that both of **1** and **2** show 2D layer architectures with square lattice topology. The photoluminescence investigation indicates that both **1** and **2** could be a prospective candidate for developing luminescence sensors for the highly sensing of nitroaromatic analytes. Furthermore, the luminescent property of **1** and **2** in different solvents analytes as well as nitrobenzene derivative have been investigated and the observed quenching in fluorescence have been corroborated by theoretical calculations.

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1. Introduction

As an active research area of porous materials, metal–organic frameworks (MOFs) are the potential candidates for chemosensors [1–5]. The first work for detection of different analytes using MOF-based fluorescence sensor was reported in 2009 [6]. 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 nitroaromatic molecules [7,8]. The advantages and challenges of LMOF based sensors are well summarized [9,10].

At present, three strategies can be used to explore the LMOF [4d,5,11,12]: 1) introduction of functional sites (Lewis acidic/basic sites) in the micropores, 2) generation of unsaturated open metal sites; 3) pre-design of tunable micropore shape and size of MOFs. Thus, the selection of the ligand plays a crucial role in the design and construction of the LMOFs fluorescence detection of analytes.

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Herein, we have selected the mixed ligands of 5-(4-carboxyphenoxy)isophthalic acid (H_3L1) and 3-(4-methyl-6-(pyridine-3-yl)pyridine-2-yl)pyridine ($L2$) to synthesize LMOFs complexes with d^{10} metal centers viz. $Cd(II)/Zn(II)$ for the detection of nitroaromatic compounds. This choice is based on the following reasons: 1) numerous explosives are good electron acceptors with electron withdrawing $-NO_2$ groups [13], including the hazardous explosives nitrobenzene (NB), 4-nitrotoluene (4-NT), 2-nitrotoluene (2-NT), 1,3-dinitrobenzene (1,3-DNB), 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), which are common chemical constituents of commercial explosives; 2) H_3L1 is a flexible tripodal ligand with aromatic rings and $L2$ has nitrogen atoms with lone-pair electrons, which may be conducive to promote luminescent character; 3) d^{10} metal ions, such as $Zn(II)$ and $Cd(II)$, usually show high complexation affinity to carboxylate and do not interfere with fluorescence, because they can display varied coordination numbers and geometries, and exhibit outstanding luminescent properties [14].

In this contribution, solvothermal reaction of $H_3L1/L2$ and $Cd(II)/Zn(II)$ centers has yielded two coordination polymers having formula $[Cd(HL1)(L2)]$ (**1**) and $[Zn(HL1)(L2)]$ (**2**), which have been characterized by IR, TGA and single crystal X-ray diffraction. The photoluminescent results indicated that the two LMOFs **1** and **2**

can distinguish between nitroaromatic analytes with different numbers of $-\text{NO}_2$ groups, which is a proven approach for a highly selective detection of nitroaromatic molecules.

2. Materials and Method

All chemicals were purchased from Jinan Henghua Sci. & Tec. Co. Ltd. without further purification. Powder X-ray diffraction (PXRD) was collected on a Bruker D8 ADVANCE X-ray diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at 50 kV, 20 mA with a scanning rate of $6^\circ/\text{min}$ and a step size of 0.02° . The simulated powder patterns were calculated using Mercury 2.0. The purity and homogeneity of the bulk products were determined by comparison of the simulated and experimental X-ray powder diffraction patterns. Fourier transform infrared (FT-IR) spectra as KBr pellet were measured in the range of $400\text{--}4000 \text{ cm}^{-1}$. Thermogravimetric analysis was performed under N_2 atmosphere from room temperature to 800°C at a heating rate of $10^\circ\text{C min}^{-1}$.

2.1. Photoluminescence measurements

The photoluminescence properties of **1** and **2** were investigated in the solid state and/or in N,N -dimethylformamide (DMF) emulsions at room temperature using a RF-5301PC spectrofluorophotometer. The **1**/**2**-DMF emulsions were prepared by adding 3 mg of **1**/**2** powder into 3.00 mL of DMF and then ultrasonic agitation the mixture for 30 min before testing.

2.2. X-ray crystallography

Room-temperature single crystal X-ray diffraction data collection were carried out on a Bruker SMART APEX diffractometer that was equipped with a graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) by using an ω -scan technique. The intensities were corrected absorption effects by using SADABS. The structures were solved by direct methods (SHLEXS-97) [15] and refined by a full-matrix least-squares procedure based on F^2 (SHELXL-97) [16]. All the hydrogen atoms were generated geometrically and refined isotropically using the riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystallographic details and selected

bond dimensions for **1** and **2** are listed in Tables S1 and S2. CCDC no.: 1485988–1485989.

2.3. Synthesis of $[\text{Cd}(\text{HL1})(\text{L2})]$ (**1**)

A mixture of $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.01 mmol), $\text{H}_3\text{L1}$ (0.01 mmol), L2 (0.01 mmol) and H_2O (10 mL) was heated in a 25 mL capacity stainless-steel reactor lined with Teflon. The pH of the resulting solution was adjusted to 5 and kept at 160°C for 72 h. The solution was then cooled to room temperature at rate of 2°C h^{-1} , colorless crystalline product **1** was produced. The resulting colorless single crystals obtained were washed with absolute ethanol three times to get **1** (yield 30% based on Cd). IR (KBr, cm^{-1}): 3064 (m); 2913 (m); 1702(v); 1609 (vs); 1552 (v); 1510(m); 1484 (v); 1343(vs), 1249(v); 1092 (m); 962(m); 848 (v); 696(v).

2.4. Synthesis of $[\text{Zn}(\text{HL1})(\text{L2})]$ (**2**)

The same synthetic method as that of **1** was used except that $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ was chosen instead of $\text{Zn}(\text{OAc})_2 \cdot 6\text{H}_2\text{O}$ (0.01 mmol). (yield 55% based on Zn). IR (KBr, cm^{-1}): 3070 (v); 2923 (m); 1713(vs); 1625 (vs); 1562 (v); 1457 (v); 1337(v); 1238 (vs); 1103 (m); 972(v); 857(m); 771 (v); 769(v); 686(v); 644 (m).

2.5. Computational details

In order to ascertain the nature of highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbital (LUMO) of different nitro analytes and the ligands density functional theory (DFT) calculations were performed. Optimized molecular geometries were calculated using the B3LYP exchange-correlation functional [17]. The 6-31G** basis set for other atoms were used for geometry optimization. All the calculations were performed using Gaussian 09 programme [18].

3. Results and discussion

3.1. Molecular structure

X-ray crystallographic analysis reveals that **1** crystallizes in a

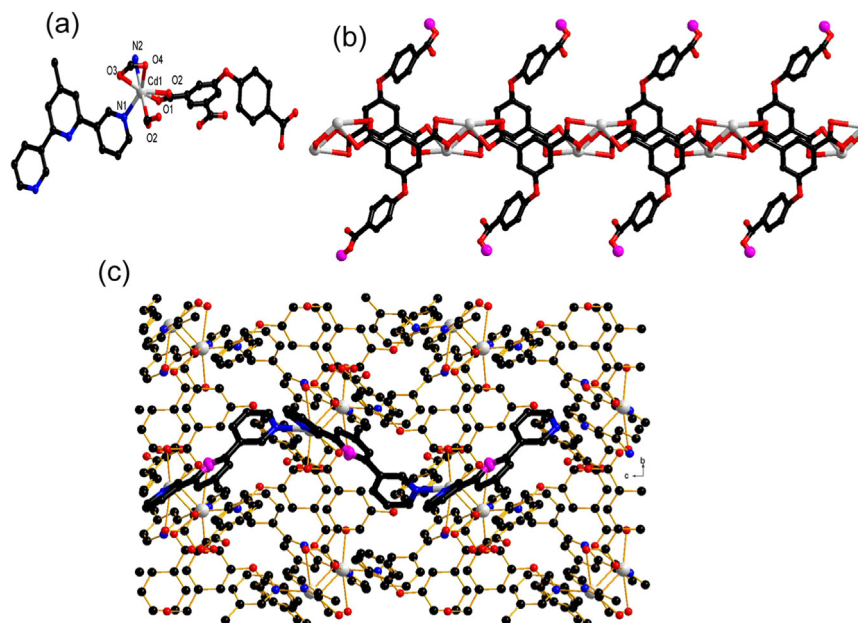


Fig. 1. (a) Local coordination geometry of Cd(II) the in the structure of **1**; (b) Extended view of 1D chain and the complete attached HL1 ligands; (c) The 2D layer net of **1**.

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