



An unusual (3,10)-coordinated 3D network coordination polymer as a potential luminescent sensor for detection of nitroaromatics and ferric ion



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ABSTRACT

A cadmium coordination polymer $\{[\text{Cd}_3(\text{itp})_2(\text{btc})_2] \cdot 4\text{H}_2\text{O}\}_n$ (**1**) (itp = 1-imidazol-1-yl-3-(1,2,4-triazol-4-yl)propane, btc = 1,3,5-benzenetricarboxylate) was synthesized and characterized. **1** shows an unusual (3,10)-coordinated 3D network based on the $[\text{Cd}_3(\text{COO})_4]$ trimeric clusters. **1** is a good luminescence sensor for detection of nitrophenol nitroaromatics TNP, 2,4-DNP, 4-NP, ANP and 2-NP, especially for TNP. **1** also exhibits high sensitive and selective luminescence sensor for detection of Fe^{3+} even in the presence of the competing ions. These selective luminescence quenching phenomena are mainly attributed to the energy-transfer quenching mechanism. **1** is a good luminescence sensor for detection of nitrophenol nitroaromatics and Fe^{3+} . The detection limits of TNP, ANP and Fe^{3+} are 0.12 μM , 0.71 μM and 0.12 μM , respectively.

1. Introduction

Coordination polymers (CPs) or metal-organic frameworks (MOFs) have been given great attention in inorganic chemistry and materials science, because of their fascinating topologies and their significant potential applications as functional materials in catalysts, luminescent sensors, magnetism, adsorption, chiral materials [1–8]. Ferric ion (Fe^{3+}), is a ample trivalent metal ion for all organisms and play important role in biological systems [9]. Deficiency or excess of iron will result in various serious functional disorders in biological systems [10]. Although some detective methods such as inductively coupled plasma (ICP), ion mobility spectroscopy (IMS), atomic adsorption spectroscopy and voltammetry. They usually need expensive equipment and are not portable for manipulation. Therefore, the development of new, cheap and rapid detection method is essential. The luminescent probes have been obtained great development recently because of their selective, sensitive and cost-efficient real-time monitoring. The luminescent sensors based on MOFs or CPs have been developed for the detection of metal ions such as K^+ , Mg^{2+} , Co^{2+} , Cu^{2+} and Al^{3+} [11–15]. However relative fewer probes for Fe^{3+} were reported [16–20].

Nitroaromatics (NACs) such as nitrobenzene (NBZ), 2-nitrophenol (2-NP), 4-nitrophenol (4-NP), 2,4-dinitrophenol (2,4-DNP), 2-amino-4-nitrophenol (ANP) and 2,4,6-trinitrophenol (TNP) are serious pollution

sources, environmentally deleterious and explosive [21]. For the first time, Li and co-workers reported a highly luminescent microporous Zn-MOF sensor for detection of NACs [22]. In recent years, a lot of the luminescent MOFs displayed good sensing for detection NACs [23–26]. But no luminescent sensor is reported for detection of 2-amino-4-nitrophenol (ANP) until now.

In our effort to synthesize unusual coordination polymers and functional materials, we synthesized many coordination polymers using flexible bis(1,2,4-triazole) N-donor ligands and multicarboxylate ligands [27–33]. For example, an unusual (4,4)-connected 3D porous Cd-MOF can act as a luminescent sensor for detection of nitrobenzene [30]. $\{[\text{Cd}_2(\text{obt})_2(\text{Meip})_2] \cdot \text{H}_2\text{O}\}_n$ and $\{[\text{Cd}(\text{obt})(\text{ndc})] \cdot 0.5\text{H}_2\text{O}\}_n$ display high sensitivity in the detection of nitroaromatics, especially for p-nitrophenol and p-nitroaniline [31]. In the present work, a cadmium coordination polymer $\{[\text{Cd}_3(\text{itp})_2(\text{btc})_2] \cdot 4\text{H}_2\text{O}\}_n$ (**1**) was synthesized and characterized using a ligand itp containing both imidazole and triazole rings (itp = 1-imidazol-1-yl-3-(1,2,4-triazol-4-yl)propane, btc = 1,3,5-benzenetricarboxylate). **1** shows an unusual (3,10)-coordinated 3D network based on the $[\text{Cd}_3(\text{COO})_4]$ trimeric clusters. **1** is a good luminescence sensor for detection of nitrophenol nitroaromatics and Fe^{3+} .

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2. Experimental section

2.1. Materials and physical measurements

All reagents were of analytical grade and used without further purification. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240 C analyser. IR spectra were obtained for KBr pellets on a Nicolet 170SX FT-IR spectrophotometer in the 4000–400 cm^{-1} region. X-ray powder diffractions were performed on a D/MAX-3C diffractometer with the Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) at room temperature. The luminescence measurements were carried out at room temperature and the spectra were collected with a PerkinElmer LS50B spectrofluorometer.

2.2. Synthesis of $\{[\text{Cd}_3(\text{itp})_2(\text{btc})_2] \cdot 4\text{H}_2\text{O}\}_n$ (**1**)

$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.20 mmol) in H_2O (5 mL) was added into a solution of itp (.10 mmol) and H_3btc (0.10 mmol) in H_2O (10 mL) which was adjusted to pH 6.5 with a dilute NaOH solution. The mixture was sealed in a Teflon-lined stainless steel vessel (25 mL) and heated to 130 °C for 24 h. It was allowed to cool to room temperature at the rate of 5 °C per hour. Colorless crystals **1** were collected. Anal. calcd. for $\text{C}_{34}\text{H}_{36}\text{Cd}_3\text{N}_{10}\text{O}_{16}$: C, 34.67; H, 3.08; N, 11.89%. Found: C, 34.38; H, 3.12; N, 11.73%. IR data (cm^{-1}): 3447w, 3117m, 1613s, 1569s, 1546s, 1519w, 1433m, 1353s, 1231w, 1106m, 1088m, 1036m, 929m, 891m, 845m, 768m, 727s, 715s, 655m.

2.3. X-Ray data collection and structure determination

The measurement of **1** was made by using a Rigaku Saturn diffractometer with an enhanced X-ray source Mo $K\alpha$ ($\lambda = 0.71073 \text{ \AA}$). The single crystal was mounted on a glass fiber at 293 K. The structures were solved by direct methods and refined with full-matrix least-squares technique (SHELXTL-97) [34]. The positions of the hydrogen atoms of itp and btc ligands were determined with theoretical calculations. The parameters of the crystal data collection and refinement of **1** are given in Table 1. Selected bond lengths and angles are listed in Table S1 in ESI†. Hydrogen bonds are listed in Table S2 in ESI†.

Table 1
Crystallographic data for **1**.

Formula	$\text{C}_{34}\text{H}_{36}\text{Cd}_3\text{N}_{10}\text{O}_{16}$
Fw	1177.93
T/K	293(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
$a/\text{\AA}$	9.384(2)
$b/\text{\AA}$	12.990(3)
$c/\text{\AA}$	16.997(4)
α (°)	90
β (°)	90.338(5)
γ (°)	90
$V/\text{\AA}^3$	2071.9(9)
$F(000)$	1164
Z	2
ρ (g cm^{-3})	1.888
μ (mm^{-1})	1.609
Reflections collected	9771
Unique reflections	3795 $R_{\text{int}} = 0.0986$
Parameter	298
Goodness of fit	1.057
R_1 [$I > 2\sigma(I)$]	0.0807
wR_2 (all data)	0.1463

3. Results and discussion

3.1. Crystal structure of $\{[\text{Cd}_3(\text{itp})_2(\text{btc})_2] \cdot 4\text{H}_2\text{O}\}_n$ (**1**)

1 shows an unusual (3,10)-coordinated 3D network based on the $[\text{Cd}_3(\text{COO})_4]$ trimeric clusters. The asymmetric unit of **1** consists of one and a half Cd(II) atoms, one btc, one itp ligand and disordered lattice water. Cd1 is in a distorted pentagonal-bipyramidal geometry and coordinates five carboxylate oxygen atoms (O2B/O3D/O4D/O5C/O6C) from three btc ligands and two nitrogen atoms (N3/N2A) from two itp ligands (Fig. S1 in ESI†). Cd2 is in a distorted octahedral geometry and coordinates four carboxylate oxygen atoms (O1/O1B/O4D/O4E) from four btc ligands and two nitrogen atoms (N4/N4B) from two itp ligands (Fig. S1 in ESI†).

Three Cd(II) atoms are bridged by btc ligands and form the $[\text{Cd}_3(\text{COO})_4]$ trimeric clusters. Each btc ligand connects three $[\text{Cd}_3(\text{COO})_4]$ trimeric clusters (Fig. 1a). Each itp ligand bridges two $[\text{Cd}_3(\text{COO})_4]$ trimeric clusters (Fig. 1b). Each $[\text{Cd}_3(\text{COO})_4]$ trimeric cluster joins six btc and four itp ligands and extend to construct the 3D network (Fig. 1c).

When simplifying the topology, the $[\text{Cd}_3(\text{COO})_4]$ trimeric cluster is treated as a 10-coordinated node (Fig. S2 in ESI†), and the btc ligands exhibit 3-coordinated nodes. As a result, the 3D structure of **1** can be simplified as a (3,10)-coordinated network (Fig. 1d) with a point symbol of $\{3.4.5\}_2\{3^4.0.4^6.0.5^{18}.0.6^{14}.0.7^2.0.8\}$, which belongs to the 3,10T4 topological type [35].

According to ToposPro TTO Collection, the 3,10T4 topology exists in two coordination polymers, which contain homonuclear trimeric complex groups. In the Co-containing structure $\{[\text{Co}_3(\text{HL})_2(\text{trz})_2(\text{H}_2\text{O})_2]\} \{ \text{H}_3\text{L} = 5\text{-(benzoic-4-ylmethoxy)isophthalic acid}; \text{Htrz} = 1,2,4\text{-triazole} \}$ [36], the Co atoms correspond to the Cd atoms of **1**, the HL ligands have the same structural function as the btc ligands, and the trz ligands play the same role of the itp ligands in **1**, while water molecules bridge the Co atoms in the trimers. The crystal structure of another analog, $\{[\text{Ni}_3(\text{btc})_2(\text{btre})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}\}$ (btre = 1,2-bis(1,2,4-triazol-4-yl)ethane) [37], contains the btc ligands with the same structural function as in **1**, while the btre ligands are structurally similar to the itp ligands in **1**, and the bridging water molecules play the same role as in the Co-containing analog.

3.2. Luminescent properties and sensing of solvent molecules

The luminescence of **1** and free ligand itp in the solid state was investigated at room temperature (Fig. 2). **1** exhibits strong blue emission band maxima at 432 nm, upon the excitation at 314 nm. The free itp ligand shows the emission maxima 442 nm upon excitation at 360 nm. Compared with the free itp ligand, the luminescence of **1** has 10 nm slightly blue-shifted and stronger intensity. These emissions of **1** can probably be attributed to the intra-ligand (π - π^*) charge transition [38,39].

In order to study the potential luminescence sensing application of **1** for detection of nitroaromatics, the luminescent properties of **1** dispersed in various kinds of solvents were investigated. The finely ground sample of **1** (3 mg) was dispersed in different solvents (3 mL) tetrahydrofuran (THF), toluene, benzene (BZ), ethanol (EtOH), methanol (MeOH), acetonitrile, N,N-dimethylformamide (DMF) and nitrobenzene (NBZ), then treated by ultrasonication for 30 min and aged for 1 day to form a stable solid layer and solution, respectively. **1** remained the usage weight and crystal framework unchanged after recycled from different solvents. As shown in Fig. 3, the intensities of the emissions greatly depend on the solvent molecules. The emission is completely quenched in NBZ solution.

To explore the ability of **1** to detect nitrobenzene (NBZ), the luminescence-quenching experiment was performed with incremental addition of nitrobenzene (NBZ) to **1** dispersed in EtOH. **1** responds quickly to the nitrobenzene in EtOH solution. High luminescence quenching

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