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Multifunctional luminescent Cd (II)-based metal-organic framework material for highly selective and sensitive sensing 2,4,6-trinitrophenol (TNP) and Fe^{3+} cation

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ABSTRACT

Two multifunctional luminescent Cd(II)-MOFs materials, namely $\{[Cd_3(BPDPE)(BDC)_3\cdot(DMF)_2]_2\cdot DMF\cdot 2H_2O\}_n$ (**1**) and $\{[Cd(BPDPE)(NDC)\cdot(H_2O)]\cdot(H_2O)\}_n$ (**2**) (BPDPE = 4,4′-bis(pyridy)diphenyl ether, H_2BDC = 1,4-benzenedicarboxylate, H_2NDC = 2,6-naphthalenedicarboxylic acid), were synthesized and systematically characterized. Complex **1** possesses a 3D structure constructed by BPDPE and BDC^{2-} linking nonlinear trinuclear secondary building units $[Cd_3(COO)_6]$, while complex **2** reveals a 2D wave-like sheet assembled by BPDPE linking $[Cd(NDC)]_n$ chain, the adjacent sheets interact each other by various H-bondings. Photoluminescence measurement revealed that complex **1** exhibits stronger emission peak by comparison of organic ligands, thereby serving as a promising candidate for fluorescent sensing materials. It is surprising find that complex **1** can highly sensitive fluorescent sense 2, 4, 6-trinitrophenol (TNP) through luminescence quenching effect. In addition, complex **1** shows highly sensitive fluorescent sensing for Fe^{3+} cation than for other metal ions. Furthermore, the quenching mechanisms of complex **1** as multifunctional sensors have been studied.

1. Introduction

Recent years, the novel materials with high selectivity, sensitivity and low detection limits for detection of environmental hazardous substances have received great attention [1]. Metal-organic frameworks (MOFs), as a part of ordered hybrid materials, have attracted significant attention on account of their intriguing architectures [2,3] and broad applications in molecular magnetism [4], heterogeneous catalysis [5,6], gas storage and separate [7], chemical sensing [8–10], *etc*. Among these applications, luminescence metal-organic frameworks (LMOFs), as an organic/inorganic hybrid luminescence ordered materials, have attracted significant attentions for they can be used for rapid and selective detection of analyses such as metal ions and small organic molecules. Compared to traditional detection methods such as Raman spectrum, gas chromatography, ion mobility spectrum, and so on [11], LMOFs detection method shows great advantages because of its quick response, high sensitivity, and reversibility, which can make it promising for sensing applications.

Nowadays, great attention is focused on rapid-detecting hazardous organic substances applied in different industrial productions [12]. These highly toxic substances include nitro aromatic compounds such as nitrobenzene (NB), 2,4,6-trinitrophenol (TNP) and 2,4,6-trinitroluene (TNT) are important materials of industrial explosives, especially TNP, it can lead to the pollution of soil and aquatic systems when be released into the environment [13]. There are many LMOFs had been developed for the detection of TNP [14–17]. However, multifunctional sensors based on LMOFs are very rare [18–20]. Therefore, it is very necessary to develop new luminescent MOFs as the candidates of multifunctional sensors.

Among various metal ions, Fe^{3+} ion is an important metal ion in living organisms, which plays a critical role in delivering and exchanging oxygen in the blood. It is also an important component of hemoglobin and many enzymes and an activator of the redox enzyme. Both deficiency and excess of Fe^{3+} ions can induce various disorders such as liver disease, heart disease, cancer and Parkinson's disease [12]. Thus, it is very important to detect Fe^{3+} for assessing human health.

Combination of the environmental protection and our research work [22], a rich electronic ligand 4,4′-bis(pyridy)diphenyl ether (BPDPE) with pyridine groups and central oxygen atoms was selected to construct multifunctional luminescent sensors, here two new Cd(II)-

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LMOF materials **1** and **2** were reported based on BPDPE with diverse carboxylic acids, structural analyses show that the carboxylic acids display two different coordination modes thus result in diverse MOFs. Luminescent sensing properties were studied carefully under irradiation at ambient temperature, the results show that complex **1** has higher selectivity and sensitivity for TNP ($k_{sv} = 8.955 \times 10^4\,M^{-1}$) than other nitro-aromatic compounds, and for Fe^{3+} ions ($k_{sv} = 8567\,M^{-1}$) than other metal ions by quenching effect, which therefore could be used as potential bifunctional sensor material.

2. Experimental section

2.1. Synthesis of $\{[Cd_3(BPDPE)(BDC)_3\cdot(DMF)_2]_2\cdot DMF\cdot 2H_2O\}_n$ (1)

Complex **1** was synthesized by $Cd(NO_3)_2\cdot 6H_2O$ (0.1 mmol, 30.8 mg), BPDPE (0.05 mmol, 16.2 mg), H_2BDC (0.05 mmol, 8.3 mg) and DMF:H_2O (2ml/2 ml) in a 25 ml Teflon-lined stainless steel vessel that was heated at 100 °C for 48 h. After cooled to room temperature at a cooling rate of 0.5 °C·min^{-1}, a large quantity of colorless bulk crystals were obtained, washed with DMF-H_2O (1:1) and dried under ambient conditions. (Yield 70% based on BPDPE). Anal. Calcd for $C_{107}H_{95}N_9O_{33}Cd_6$: C, 47.43; H, 3.53; N, 4.65; found C, 47.25; H, 3.76; N, 4.89. IR(KBr, cm^{-1}): 3441(s), 3055(m), 2928(m), 1655(s), 1566(s), 1490(s), 1383(s), 1287(m), 1237(s), 1174(m), 1110(m), 1015(m), 882(w), 819(m), 749(s) 764(w), 597(w), 528(m).

2.2. Synthesis of $\{[Cd(BPDPE)(NDC)\cdot(H_2O)]\cdot(H_2O)\}_n$ (2)

Complex **2** was synthesized similar to complex **1**, except H_2BDC was replaced by H_2NDC. A large quantity of colorless rod-likes crystals were obtained and washed with DMF, and then dried under ambient conditions. (Yield: 64% based on BPDPE). Anal. Calcd for $C_{34}H_{26}O_7N_2Cd$: C, 59.39; H, 3.78; N, 4.10; found C, 59.58; H, 3.66; N, 4.19. IR (KBr, cm^{-1}): 3445(s), 1609(s), 1556(s), 1483(s), 1404(s), 1358(s), 1226(s), 1099(w), 1005(m), 924(w), 868(m), 790(s), 549(w).

3. Results and discussion

3.1. Structure description of complex 1 and 2

Complex **1** was constructed by 2D $\{Cd_3(bdc)_6\}_n$ sheets and BPDPE ligands, exhibiting a 3D 2-fold interpenetrated framework. The asymmetrical unit consists of three Cd(II) ions (Cd1, Cd2 and Cd3), one BPDPE, three BDC^{2-} and two coordinated DMF molecules. As shown in Fig. 1, Cd1 is surrounded by six oxygen (O1, O9, O12a, O5, O3c, O8b) atoms derived from six different BDC^{2-} ligands and the bond lengths of Cd1-O are in the range of 2.190(5)-2.389(5) Å. Cd2 is coordinated with five oxygen (O1, O9, O10, O11a, O15) atoms and one N (N1) atom, of which four oxygen (O1, O9, O10, O11a) atoms come from three different BDC^{2-} ligands, one oxygen (O15) atom is assigned to the DMF molecule, and one N1 atom derives from BPDPE. Moreover, the Cd2-O and Cd2-N bond lengths are calculated to be 2.298(5)-2.546(4) Å and 2.304 Å, respectively. The coordination environment of Cd3 is similar with Cd2. The Cd3-O bond lengths are in the range of 2.298(7)-2.546(5) Å and the Cd3-N bond length is 2.305 Å. Surprisingly, the Cd2-Cd1-Cd3 is not a linear cluster, and the bond angle of Cd2-Cd1-Cd3 is 143.562°.

In complex **1**, Cd(II) ions were linked by BDC^{2-} to form an infinite 2D sheet with trinuclear $[Cd_3(COO)_6]$ SBU, parts of space was occupied the coordinated DMF (Fig. 1b and c). Simultaneously, these neighboring sheets are further connected by the BPDPE to form a 3D framework (Fig. 1d). From *c* axis, the rectangular area of the channel is up to ~11.5 × 9.2 Å^2, so the adjacent 3D frameworks were further penetrated, leading to a 2-fold penetrated 3D framework.

As illustrated in Fig. 2a, the asymmetric unit of complex **2** is comprised of one Cd^{2+} ions, one BPDPE, one NDC^{2-}, one coordinated water molecule and one free water molecule. The Cd(II) center is octahedral coordinated environment with four oxygen (O1, O2, O4, O5) atoms and two nitrogen (N5, N8) atoms. Among those coordinated atoms, three oxygen (O2, O4, O5) atoms are come from two NDC^{2-}, one oxygen from coordinated H_2O, and two nitrogen atoms come from two different BPDPE ligands. In this compound, all Cd-N [2.357(7)-2.401(8) Å] and Cd-O bond lengths [2.248(7)-2.521(7) Å] are in the normal range of reported Cd(II)-based complexes [23].

In complex **2**, each NDC^{2-} links two different Cd(II) ions alternately to form an infinite 1D zigzag-like chain. At same times, $[Cd_2BPDPE_2]$ loop structure was formed by two BPDPE linking two Cd(II) ions. Then, the adjacent 1D chains were linked by the rings, thus forming a 2D infinite layer framework (Fig. 2b). Meanwhile, the abundant amount of hydrogen bonds in **2** can be attributed to the existence of uncoordinated oxygen and water molecules. Finally, these 2D layers further form a 3D supramolecular framework with the help of hydrogen bonds (Fig. 2c).

3.2. PXRD and thermogravimetric analyses (TGA)

Complexes **1** and **2** were characterized to confirm the phase purity by powder X-ray diffraction (PXRD). The two PXRD patterns of the samples are completely consistent with the stimulated patterns, proving its high purities (Figs. S2 and S3). The thermal stability of **1** and **2** were evaluated by TGA. The curve of **1** shows the primary mass loss of 8.1% from 45 °C to 260 °C, which can be attributable to the loss of guest slovents and coordinated DMF molecules (calcd. 8.27%). The framework begins to collapse at 390 °C. The TGA plot of **2** illustrates that the compound have a mass loss of 5.65% from 40 °C to 240 °C, which can be caused by the departure of guest and coordinated H_2O molecules (calcd. 5.24%), and the framework begins to decompose from 375 °C (Fig. S4).

3.3. Luminescence behaviors and sensing properties

As well-known, MOFs constructed with d^{10} Cd(II) ions and conjugated ligands are potential photoactive materials [24,25]. To prove whether the two compounds can be served as photoactive materials, the solid-state luminescent properties of **1** and **2** were studied at room temperature. As shown in Fig. 3, the maximum emission peak of **1** was observed at ~376 nm (λ_{ex} = 330 nm), displaying a small blue shift compare with BPDPE ($\Delta\lambda$ = 15 nm), the emission behavior is similar with H_2BDC. Complex **2** exhibits medium emissions at ~422 and ~444 nm, similar with H_2NDC, but exhibits a bit red shifts by comparison of with BPDPE ($\Delta\lambda$ = 22 and 40 nm), so the emissions of **1** and **2** are mainly attributed to the ligand to ligand charge transfer of carboxylic acids [26].

Firstly, the fluorescent intensities were investigated in different organic solvents, 3 mg powder of **1** was dispersed in 3 ml different solvents, including acetonitrile (CH_3CN), benzene, dichloromethane (CH_2Cl_2), dichloromethane ($CHCl_3$), dimethylacetamide (DMA), N,N′-dimethylformamide (DMF), ethanol, H_2O, methylbenzene, methanol, tetrahydrofuran (THF), 2-propanol, 1-propanol, and NB. As shown in Fig. 4, the luminescence intensities of **1** are obviously rely on those organic solvents, the strongest emission intensity is in CH_3CN, while the weaker is in THF, interestingly, the luminescence intensities of **1** in NB solution show a completely quench. Such solvent-dominated luminescence features prompted us to further explore the possibility of sensing other nitro aromatic compounds.

The nitro aromatic compounds are important chemical reactant and are extensively applied in chemical industry, which can cause explosions and environmental damage. Therefore, it is crucial that fast and effective detection of NACs. Preliminary studies show TNP has maximal quenching compare with other NACs (Fig. 5). In order to study the sensing ability towards NACs more detailly, fluorescence titration experiments were carried out. The suspend solutions were prepared with **1** dispersed in DMF (1mg/1 ml) and then gradual addition of 1 mM stock solutions of nitro aromatics, such as 2,6-DNT, NB, 2,4-DNT, TNT,