

Research paper

A fluorescent anthracene-based metal–organic framework for highly selective detection of nitroanilines

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ABSTRACT

Aiming to develop an effective fluorescence probe for detecting nitroanilines compounds, a new 3D “pillar-layered” metal–organic framework [Cd(dpa)(pta)]·nDMF (**1**) was constructed through solvothermal reaction of Cd²⁺ with 9,10-di(pyridine-4-yl)anthracene (dpa) and terephthalic acid (pta). As expected, **1** displays selective fluorescence quenching response toward nitroanilines, including 2-nitroaniline, 4-nitroaniline and 2,4-dinitroaniline, attributable to the cooperation of absorption competition and energy transfer mechanism, which can effectively distinguish nitroanilines from other nitrobenzene and anilines compounds. Furthermore, the quenching efficiency exhibits different varying trends for these three nitroanilines along with the change of exciting wavelength, which can be used to effectively distinguish them from each other.

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1. Introduction

Metal–organic frameworks (MOFs) attract increasing attention in recent years, owing to their structural diversity and potential applications in many fields such as gas storage and separation, catalysis, sensing, drug delivery, and so on [1,2]. Particularly, the utilization of luminescent MOFs in spectral detection [3,4] is of growing interest because of their easy operability, rapid response, high sensitivity and selectivity, which depends closely on the intrinsic properties of MOFs used [5]. Notably, the permanent porosity and large internal surface area of MOFs benefit the concentration of guest molecules on their outer or inner surface, and thus enable them to be promising sensitive candidates for detecting trace amount of chemicals [6].

Since the first report in 2009 [7], more and more fluorescent MOFs based on aromatic ligands have been developed for the identification and detection of nitroaromatic compounds [8,9], due to their potential threat to human health and global security [10,11]. As one important kind of nitroaromatic compound, nitroanilines are widely used in the synthesis of engineering plastics, medicine, agrochemicals, various organic dyes, anti-aging agents, and so on [12]. Notably, nitroanilines are of high chemical stability as other nitroaromatic compounds owing to the strong

electron-withdrawing effect of nitro groups [13], but with stronger toxicity than aniline, trinitrotoluene (TNT) and trinitrophenol (TNP). What's worse is that nitroanilines can infiltrate into biological ecosystem through direct discharge of industrial castoffs or from the decomposition of herbicides and pesticides [14], and furthermore apt to accumulate in biological ecosystem. Currently, nitroanilines have been regarded as one of the priority pollutants that may result in very serious environment and human health issues [14]. Contrasting to the wide investigation of the fluorescence detection of nitrobenzene compounds, the MOFs-based fluorescence detection of nitroanilines was less explored, let alone distinguishing nitroanilines from other anilines and nitrobenzenes [15].

Herein, we design a new three dimensional (3D) MOFs [Cd(dpa)(pta)]·nDMF (**1**) based on luminescent 9,10-di(pyridine-4-yl)anthracene (dpa) [16] and terephthalic acid (pta) ligand. As expected, **1** exhibits strong dpa-centered fluorescence emission, and gratifyingly displays quick and selective fluorescence quenching response toward trace amount of nitroanilines, which provides a promising method to selectively detect nitroanilines.

2. Materials and methods

dpa was synthesized according to previous reports [17,18], while all the other reagents and solvents for the synthesis were purchased from commercial sources and used as received.

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Thermogravimetric analysis (TGA) was carried out on a Rigaku standard TG-DTA analyzer at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$, with an empty Al_2O_3 crucible used as reference. Powder X-ray diffraction (PXRD) was recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA with a Cu-target tube and a graphite monochromator. Simulation of the PXRD pattern was performed based on single-crystal data using diffraction-crystal module of the Mercury program. Fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer equipped with a plotter unit. UV-Visible absorption spectra were measured on a U-3010 Spectrophotometer.

3. Experimental

Synthesis of **1** (CCDC:1,534,561): A mixture of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (31 mg, 0.1 mmol), dpa (16.6 mg, 0.05 mmol), and pta (16.6 mg, 0.1 mmol) in 3 mL DMF was stirred in air for 30 min and sealed in a 10 mL Teflon lined stainless steel container. Then the reaction system was heated at $85\text{ }^{\circ}\text{C}$ for 3 d. After cooling down to room temperature, yellow block crystals were obtained (yield: ca. 59% based on dpa). EA (%) Calcd for $\text{C}_{32}\text{H}_{20}\text{CdN}_2\text{O}_4$: C 63.11, H 3.32, N 4.60; found C 63.09, H 3.35, N, 4.57. FT-IR (cm^{-1} , KBr): 3064 s, 2922 s, 2855 s, 1953 m, 1825 m, 1676vs, 1604 s, 1565vs, 1380 s, 1294 m, 1220vs, 951 s, 885 m, 828vs, 749vs, 677 s, 613vs.

4. Results and discussion

4.1. Single-crystal X-ray diffraction analysis

Single-crystal structural analysis reveals that **1** crystallizes in the $P\bar{1}(2)$ space group of triclinic system. The asymmetric unit of **1** contains one Cd(II) ions, one dpa ligand, one pta ligand, and some uncoordinated solvent molecules. As shown in Fig. 1a, Cd (II) adopts an 6-coordinated mode accomplished by two N atoms from two dpa ligands, four O atoms from three carboxylate groups of three pta ligands (one carboxylate groups in chelating mode and the other two in monodentate mode), to form an distorted octahedral coordination geometry with the Cd–O distances ranging from 2.24 to 2.44 Å and the Cd–N distance of 2.33–2.39 Å (Table S2). Two neighboring Cd(II) ions are bridged by two carboxylate groups both in $\mu_2\text{-O:O'}$ mode, giving a binuclear Cd_2 cluster with a distance of Cd...Cd of 4.71 Å (Fig. 1b1 and b2). Each binuclear cluster is connected with other four cluster via pta ligand (Fig. 1c), forming a two dimensional (2D) layer (Fig. 1d and Fig. S1). The 2D layers are further pillared by dpa ligand to give a three dimensional (3D) “pillar-layered” structure (Fig. 1e and f). Removing solvent molecules from the pore space will give an accessible volume of 36.7% for **1** as estimated by using the SOLV function of PLATON program. Meanwhile, a channel with a sectional area of about $6.3 \times 6.2\text{ \AA}^2$ was observed extending along *c* axis. However, the BET measurement is failed due probably to the decomposition of framework caused by activation treatment.

In topological point of view, the binuclear Cd cluster can be considered as six-connected node, while dpa and pta ligands as two-connected linker, which gives an uninodal 6-connected pcu topology for **1** with the a Schläfli symbol of $\{4^6\}$ (Fig. 1f).

4.2. Powder X-ray diffraction (PXRD) and thermogravimetric analyses (TGA)

The phase purity and stability of the samples **1** were clarified before further investigation by powder X-ray diffraction (PXRD) measurement and thermogravimetric analyses (TGA). As shown in Fig. S2, the PXRD pattern of **1** matches well with the simulated one based on single-crystal data, implying high phase purity of the

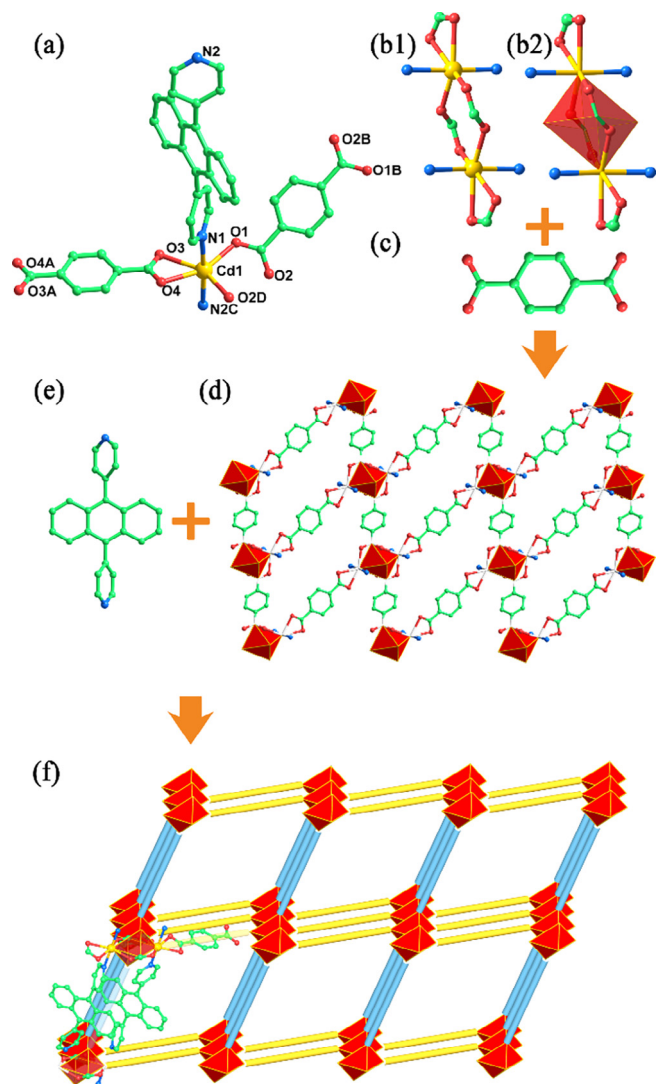


Fig. 1. The crystal structure of **1**: a) the coordination environment of Cd(II) ion; b1) Cd binuclear cluster; b2) the simplified octahedron of Cd binuclear cluster; c) pta ligand; d) 2D layer; e) dpa ligand; f) Schematic representation of the 3D topologic network.

as-prepared sample. For the TGA curve, the first weight loss of about 20% occurs in the temperature range from 84 to $228\text{ }^{\circ}\text{C}$, corresponding to the escape of free DMF molecules, while the second one occurring above $360\text{ }^{\circ}\text{C}$ may be ascribed to the decomposition of the framework (Fig. S3), which manifests the high thermal stability of **1**.

4.3. Fluorescence property and detection behaviors

1 exhibits strong fluorescence emission in solid states as designed (Fig. S4), and the fluorescence detection of organics by **1** was carried out in DMF system. Before recording, **1** sample was finely ground and then dispersed in DMF by ultrasonication for 30 min to form a stable suspension. The strongest emission of **1** suspension (1 mg/mL) with excitation of 348 nm (Fig. S5) locates at 432 nm that is much close to the 430 nm of dpa solution (1 mg/mL) under the similar condition (Fig. S6), unveiling the dpa-centered emission nature of **1**.

The detection behaviors of **1** suspension was recorded toward various organics, including alcohols (methanol and ethanol), ketones (acetone, N-methylpyrrolidone), ethers (THF), amides (N,

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