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A new three-dimensional bis(benzimidazole)-based cadmium(II) coordination polymer

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ABSTRACT

A new coordination polymer (CP), formulated as $[Cd(L)(DCTP)]_n$ (**1**) (L = 1,1′-(1,4-butanediyl)bis(2-methylbenzimidazole), H_2DCTP = 2,5-dichloroterephthalic acid), was synthesized under hydrothermal conditions and the performance as luminescent probe was also investigated. Single-crystal X-ray diffraction reveals CP **1** is a 3D 3-fold interpenetrated **dia** network with large well-defined pores. It is found that CP **1** revealed highly sensitive luminescence sensing for Fe^{3+} ions in acetonitrile solution with a high quenching efficiency of K_{SV} = 2541.238 $L \cdot mol^{-1}$ and a low detection limit of 3.2 μM (S/N = 3). Moreover, the photocatalytic efficiency of **1** for degradation of methylene blue could reach 82.8% after 135 min. Therefore, this coordination polymer could be viewed as multifunctional material for selectively sensing Fe^{3+} ions and effectively degrading dyes.

1. Introduction

In the recent years, the metal organic frameworks (MOFs) or coordination polymers (CPs) as advanced functional materials with diverse structural characteristics and tunable pore size have been extensively applied in the fields of luminescence sensing, gas storage and separation, catalysis, and magnetism [1–6]. One of the most fascinating features is sensing and detection of metal ions, which play a crucial role in medicinal science, environmental science, biological science and the industrial manufacture [7,8]. Among these ions, iron ions are one of the most important and essential elements in our living biological systems, especially in the process of synthesizing hemoglobin [9,10]. However, ingestion of excess iron ions can cause seriously heart and liver disease, diabetes and certain tumors symptoms [11]. The moderate amount of iron ions into the diet can help transport and store oxygen; help prevent hemoglobin disease; promote growth and quick thinking; reduce cholesterol accumulation; contribute to the treatment of mental disorders [12]. On the other hand, many techniques including spectrophotometry [13], voltammetry [14], atomic absorption spectroscopy [15], and inductively coupled plasma mass spectrometry [16] have been developed to detect Fe^{3+} ions. However, the drawbacks such as complicated pretreatment procedures, relatively high cost, and low anti-inference ability have limited their application in chemical sensing. Recently, luminescence detection technique has become one of the most powerful tools for imaging and sensing trace amounts of Fe^{3+} ions due to their sensitivity, simplicity, and real-time monitoring in short response time [17]. More significantly, a variety of luminescent Ln-based CPs has been applied for sensing metal ions for unique luminescent property, magnetic property, and their versatile coordination geometry with a high sensitivity and anti-interference ability [18,19]. However, the chemical sensors for sensing Fe^{3+} ions based on d^{10} CPs are still limited. Therefore, it is very significant and essential to develop CPs with high stability, better recyclability and less pollution to be employed as luminescent sensors for detection of Fe^{3+} ions.

CPs with open coordination sites, powerful luminophore and stable network might offer a useful pathway to develop luminescence sensing. To be well known, incorporation of chlorine atoms to the linkers of carboxylate groups is an effective way to construct CPs with open coordination sites [20]. Considering that, the linear 2,5-dichloroterephthalic acid (H_2DCTP) ligand is one of the most suitable ligands for its negative charge, which affords them with the capacity to bind strongly to metal atoms [21]. At the same time, the two carboxylic groups can adopt various coordination modes which can fit into most of metal environments [22]. Moreover, the linear carboxylate could improve the energy density and thermal stability of the CPs. On the other hand, the flexible bis(benzimidazole) derivatives can freely twist around two —CH_2— groups with disparate angles to generate different conformations, which also can exhibit strong coordination capacity and enhance the whole conjugation degree.

Based on the above consideration, by introducing a linear carboxylate 2,5-dichloroterephthalic acid (H_2DCTP) and a flexible 1,1-(1,4-butanediyl)bis(2-methylbenzimidazole (L) with the Cd(II) salts, we generated a 3D 3-fold interpenetrated coordination polymer, formulated as $[Cd(L)(DCTP)]_n$ (**1**), under hydrothermal conditions. More significantly, this coordination polymer exhibited a high sensitivity (Stern–

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Volmer constant $K_{SV} = 2541.238\ L \cdot mol^{-1}$) and a low detection limit (3.2 μM) for sensing Fe^{3+} ions in acetonitrile solution. The high anti-interference ability of the coordination polymer for sensing Fe^{3+} ions may extend its application in chemical sensing. Furthermore, the photocatalytic performance of Cd(II) CP for degradation of methylene blue (MB) was investigated in detail.

2. Experimental Section

2.1. Materials and Measurements

The ligand L was synthesized according to the previous literatures reported [23,24]. $Cd(OAc)_2 \cdot 2H_2O$ (98% wt) and 2,5-dichloroterephthalic acid (H_2DCTP, 98% wt) were supplied from Aladin Ltd. (Shanghai, China). The other reagents and organic solvents were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used as received without further purification. Elemental analyses of C, N and H were collected with a Perkin-Elmer 240C (America) elemental analyzer. A Varian FT-IR 640 spectrometer (Nicolet, America) was employed to collect the date (4000-400 cm^{-1}) of FT-IR spectra (KBr pellets). The X-ray powder diffraction (XRPD) patterns were carried out on a D/Max-2500 diffractometer (Rigaku, Japan) at 40 kV, 100 mA for a Cu-target tube and a graphite monochromator. Thermogravimetric analyses (TGA) were performed by heating the crystalline sample from 20 to 800 °C at a rate of 10 °C·min^{-1} under nitrogen gas flow on TG 209 (NETZSCH, Germany) equipment. An F-7000 fluorescence spectrophotometer (Hitachi, Japan) was used to collect the spectra for the powdered solid samples and liquid samples which were measured at room temperature. Solid UV–vis diffuse reflectance spectra were measured with a 1901 UV–vis Spectrometer (Puxi, China), and a $BaSO_4$ plate was employed as the reflectance standard.

2.2. Synthesis of $[Cd(L)(DCTP)]_n$ (**1**)

A mixture of $Cd(OAc)_2 \cdot 2H_2O$ (26.6 mg, 0.1 mmol), the free ligand L (32.4 mg, 0.1 mmol), H_2DCTP (23.5 mg, 0.1 mmol), and water (10 mL) was sealed into a 25 mL Teflon-lined stainless container and heated to 140 °C for 72 h, and then cooling to room temperature at a rate of 5 °C h^{-1}. Colorless blocky crystals were collected by filtration, washing with distilled water and drying in air. Yield: 46.3% based on $Cd(OAc)_2 \cdot 2H_2O$. Anal. Calcd $C_{28}H_{24}CdCl_2N_4O_4$ (Mr = 663.81): C, 50.66; H, 3.64; N, 8.44%; Found: C, 50.70; H, 3.62; N, 8.42%. IR (KBr, cm^{-1}): 3115 w 3077 w, 2941 w, 1612 s, 1576 s, 1561 m, 1449 m 1388 s, 1217 m, 1078 s, 921 w, 845 m, 741 w, 624 m, 524 w.

2.3. X-ray Crystallography

X-ray single-crystal diffraction data for CP **1** were collected at 296(2) K on a Bruker Smart 1000 CCD area detector equipped with graphite monochromated Mo–K_α radiation (λ = 0.71073 Å) by applying the ω-scan method. Absorption corrections were applied by using the multicar program SADABS [25]. Structural solutions and refinements for the title CP **1** were solved by direct method of applying SHELXS-2016 program, and refined through full-matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms employing SHELXTL program package [26]. Anisotropic thermal parameters were applied to all non-hydrogen atoms. All the hydrogen atoms were generated geometrically. The central Cd^{2+} ions of CP **1** were located at the E-maps. The selected crystal parameters, data collection, and refinements are summarized in Table S1, the selected bond distances and angles for the CP **1** are given in Table S2.

2.4. Luminescence Experiments

A series of stable emulsions were prepared as below: a finely ground powder sample of CP **1** (4.0 mg) was immersed in an organic solvent (4.0 mL), treated by ultrasonication for 30 min, and then aged for 1 day. The selected organic solvents include dimethyl sulfoxide (DMSO), acetonitrile, *N*-methyl pyrrolidone (NMP), dimethylacetamide (DMAC), methanol, ethanol, butyl alcohol, ethylene glycol, dichloromethane (CH_2Cl_2), *N*,*N*-Dimethylformamide (DMF). The as-synthesized samples were suspended into acetonitrile solution containing 0.01 M selected nitrate: $M(NO_3)_n$ ($M^{n+} = Cd^{2+}$, Ag^+, Cu^{2+}, Zn^{2+}, Na^+, Ni^{2+}, Pb^{2+}, or Fe^{3+} respectively) for 24.0 h to form metal-CP **1** (M^{n+}-CP **1**).

2.5. Photocatalytic Experiments

The photocatalytic performance of CP **1** was investigated with photodegradation of the MB under UV irradiation through a typical process: 0.01 mol of CP **1** was mixed with 10.0 mg/L MB solution of 100.0 mL, magnetically stirred in the dark environment for 30.0 min to gain a balance between desorption and adsorption. After 30.0 min, the mixture was exposed to UV irradiation from a 400 W high pressure halogen lamp and kept magnetically stirring. Then, 5.0 mL of the sample was taken out every 15.0 min and centrifuged to remove the residual catalyst, which was analyzed employing a UV–vis spectrophotometer at an absorption wavelength of 664.0 nm. This process was also done instead of CP **1** by taking equal amounts of $Cd(OAc)_2 \cdot 2H_2O$ as a blank experiment under the same condition. The degradation efficiency (D) of dye is defined as follow:

$$D = [(A_0 - A_t)/A_0] \times 100\% \quad (1)$$

where A_0 represents the initial absorbance of dyes solution and A_t represents the absorbance of the dye at time t.

3. Results and Discussion

3.1. Crystal Structure of $[Cd(L)(DCTP)]_n$

X-ray single-crystal diffraction analysis reveals that CP **1** crystallizes in the monoclinic *C*2/*c* group, and its asymmetric unit is comprised of half of a Cd^{2+} ion, half of an L ligand, and half of a $DCTP^{2-}$ ligand. Each central Cd^{2+} ion exhibits a distorted octahedral coordination geometry with two nitrogen atoms (Cd(1)–N(1) = 2.273(2) Å) from two different L ligands and four oxygen atoms (Cd(1)–O(1) = 2.492(2) Å, Cd(1)–O(2) = 2.266(2) Å) from two types of $DCTP^{2-}$ ligands (Fig. 1a). The mean bond distances of Cd—N and Cd—O are 2.273 Å and 2.379 Å, respectively, which are well consistent with that found in the other Cd-based CPs reported [27].

For CP **1**, the N-donor L ligands acting as μ_2 *trans*-conformation ligands connect with the adjacent Cd^{2+} centers to form a 1D "V"-like chain with Cd···Cd distance of 12.680(6) Å and Cd···Cd···Cd angle of 64.507(1)° (Fig. S1). At the same time, two arms of benzimidazole in each entire L ligand are parallel. On the other hand, the completely deprotonated carboxylic groups of $DCTP^{2-}$ ligands in **1** adopt a bidentate bridging (κ^1-κ^1)-(κ^1-κ^1)-μ_2 fashion mode to construct a 1D "wave"-like chain with Cd···Cd distance of 11.169(5) Å and Cd···Cd···Cd angle of 119.202(0)° (Fig. S2). Then, the 1D "V"-like chains and "wave"-like chains interplay with each other to form a complicated 3D framework with large cavities (Fig. 1b). Both the L and $DCTP^{2-}$ ligands in **1** can be viewed as linkers, the central Cd^{2+} ions as 4-connected nodes from the topological point of view. Thus, a single 3D network can be formed into a 4-connected **dia** topological network with the point symbol {6^6} (Fig. 1c). The representative 3D open network with hexagon-shaped channels reveals large cavities about of 12.680 Å × 11.169 Å × 12.680 Å. With the purpose of minimizing the presence of cavities and stabilizing the network during the assembly process, the two different identical networks are filled in the big cavities, generating a threefold-interpenetrating 3D framework (Fig. 1c). The longest distance of 12.680 Å is applied 2 times to a single net to construct the entire framework that can be classified as type Class Ia, Z = 3 × 1 = 3