A multifunctional three-fold interpenetrated coordination polymer showing excellent luminescent sensing for Cr(VI)/ Fe(III) and photocatalytic properties

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ABSTRACT

A three-fold interpenetrated coordination polymer $[Cd_2(L)(bibp)_3]_n$ (**1**) (H_4L = 5,5′-(1,4-phenylenebis(-methoxy))diisophthalic acid, bibp = 4,4′-bis(imidazolyl)biphenyl) has been rationally constructed, successfully solvothermally synthesized and fully characterized. Complex **1** shows a 3D three-fold interpenetrated novel topological framework with the point symbol $(4. 6^9)_2(4^2. 6^2. 7. 8)$, and represents a variety of potential applications. Luminescence studies demonstrate that **1** has high selectivity and sensitivity for pollutant Cr(VI) (CrO_4^{2-} and $Cr_2O_7^{2-}$) anion and Fe(III) cation; Photocatalytic studies show that **1** exhibits great degradation activity of three organic dyes (methylene blue (MB), Rhodamine B (RhB) and MalachiteGreen oxalate (MGO)). Furthermore, the possible mechanisms of the luminescent quench and photocatalytic properties have been deduced.

1. Introduction

Water, the source of our life, has being polluted following the development of our industrialization. The polluted water not only harms to our environment but also threaten our lives. Hence, it is of great importance to identify, monitor and remove the heavy metal cations, anions, and small organic dye molecules in waste water directly [1,2]. Scientists have been developed various spectroscopic and analytical methods for the detection of these species [3]. But most of these methods have their own limitations, such as high costs, low sensitivity, and easy interference, and so on, which restricted their applications [4]. Coordination polymers have attracted tremendous interest as a kind of omnifarious functional crystalline porous materials, which have wide application in luminescence, catalysis, gas storage, separation, medical science, and so forth [5–7]. All of these functions are dependent on their unique structures and topological diversities [8]. In recent years, luminescent materials, especially the luminescent CPs as a kind of chemical sensor have been attracting much attention for their selectivity, sensitivity, portability and short response time, and a number of guest-

dependent luminescent CPs had been successfully synthesized and reported [9,10]. Compared with the prosperous reports of the synthesis of luminescent CPs, the systematically studies of the dynamic behaviors and the sensing mechanisms are very limited. Most reports simply deduced that as the fluorescence quenching is normally caused by the transfer of the excited electrons or the energy from CPs to electron-deficient analytics [11]. However, it is important to conduct further research on the corresponding mechanisms. In another aspect, how to remove the contaminant form waste water is a severe problem and should be solved. Generally, using materials to absorb the contaminant from the water or degrade the contaminant into harmless small molecules are two main methods to meet this problem, and recently researches indicated that CPs are great potential materials in this field [12,13].

As mentioned above, the capabilities of CPs largely depend on their structure. So, preselecting organic ligands and metal-salt clearly and rationally is the first step to meet the final desirable structure. Carboxylic acids, especially flexible or semi-rigid multidentate aromatic carboxylic acids have two obviously characteristics. One is the coordination centers that can flexibly twist around to meet

Table 1
Summary of crystal data and structure refinement parameters for complex **1**.

Complex	**1**
Formula	$C_{39}H_{28}CdN_6O_5$
Formula weight	773.07
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	10.4600 (9)
b (Å)	37.964 (3)
c (Å)	9.4331 (8)
α (°)	90
β (°)	101.177(2)
γ (°)	90
V (Å^3)	3674.9 (5)
Z	4
D_{calcd} (Mg m^{-3})	1.397
μ (mm^{-1})	0.65
Reflections collected	6478
Data/parameters	3275/460
$F(000)$	1568
T (K)	298
R_{int}	0.147
Final R indices[$I > 2\sigma(I)$]	$R_1 = 0.0853$ $wR_2 = 0.1508$
R indices (all data)	$R_1 = 0.1601$ $wR_2 = 0.1680$
S	1.050

different coordination environment. The other is the carboxylic groups that can partially or fully deprotonated and adopt various coordination modes when they coordinate with metal ions. In another aspect, N-donor ligands, are often been carefully chosen as the secondary ligands. This is because the rigidly ones can be used for their stability to reduce the uncertainly structure in the end, while the flexible ones can meet different coordinate modes, which further enrich the complexity of the structure [14]. In addition, d^{10} metal ions are considered have good ability for the transfer of the excited electrons. Herein, concerned above and motivated by our interest in multifunctional CPs, we adopted a dual-ligand strategy with one semi-rigid tetracarboxylic acid 5,5′-(1,4-phenylenebis(-methoxy))diisophthalic acid (H$_4$L) and one rigidly N-donor 4,4'-bis(imidazolyl)biphenyl (bibp) as auxiliary ligand to react with Cd(NO$_3$)$_2$·6H$_2$O, and successfully synthesized a 3D three-fold CP [Cd$_2$(L)(bibp)$_3$]$_n$ (**1**) under solvothermal condition. Complex **1** shows excellent luminescent sensing for Cr$_2$O$_7$$^{2-}$/ CrO$_4$$^{2-}$ anions and Fe(III) cation based on the quenching mechanism. The effects on photocatalytic activity of some organic dye of **1** have also been investigated.

2. Experimental section

2.1. Materials and physical measurements

All reagents and solvents were purchased from Jinan Henghua Sci. Tec. Co. Ltd., and used without further purification. Infrared spectra were recorded on the Nicolet 170SX spectrometer in the 4000-400 cm^{-1} region by using KBr pellets. Elemental analysis of C, H, N were performed in a model 2400 PerkinElmer analyzer. Thermogravimetric (TG) analyses were measured on a Perkin-Elmer TGA-7 thermogravimetric analyzer under air conditions from room temperature to 800 °C with a heating rate of 10 °C min^{-1}. The X-ray powder diffractions (PXRD) were collected on an Enraf-Nonius CAD-4 X-ray single crystal diffractometer with Cu-Kα radiation. Topological analysis were performed and confirmed by the Topos program and the Systre software [15,16].

2.2. Synthesis of [Cd$_2$(L)(bibp)$_3$]$_n$ (1)

A mixture of Cd(NO$_3$)$_2$·6H$_2$O (0.069 g, 0.2 mmol), bibp (0.029 g, 0.1 mmol), H$_4$L (0.047 g, 0.1 mmol), DMF (4.5 mL) and H$_2$O (4.5 mL) were stirred for 0.5 h in air. And then the solution was transformed into the Teflon-lined stainless steel vessel (15 mL), sealed, and heated to 130 °C for 3 days. Subsequently, the vessel was cooled to the room temperature at the degree of 5 °C h^{-1}. Colorless block crystals were collected with the yield of 62.35% (based on H$_4$L). Anal. Calcd for C$_{39}$H$_{28}$CdN$_6$O$_5$: C, 60.59; H, 3.65; N, 10.87%. Found: C, 60.01; H, 3.77, N, 10.36%. IR (KBr disk, cm^{-1}): 3423 (w), 1610 (m), 1571 (s), 1517 (s), 1449 (m), 1407 (m), 1371 (s), 1307 (m), 1262 (m), 1127 (w), 1066 (m), 962 (w), 824 (m), 782 (w), 729 (w), 646 (w), 520 (w).

3. X-ray crystal structure determination

The suitable crystal of complex **1** was collected for single crystal X-ray diffraction. The data were collected on a Bruker Apex Smart CCDC diffractometer, using graphite-monochromated Mo-kα radiation (λ = 0.71073 Å) by using the $\omega-2\theta$ scan mode at room temperature (298 K). The structure was solved by direct methods using SHELXS-97 [17]. The non-hydrogen atoms were defined by the Fourier synthesis method. Positional and thermal parameters were refined by the full matrix least-squares method (on F^2) to convergence [18]. Crystallographic data for complex **1** is given in Table 1. Selected bond lengths and angles for **1** are listed in Table S1†. CCDC number for complex **1** is 1446052.

4. Results and discussion

4.1. Crystal structure of [Cd$_2$(L)(bibp)$_3$]$_n$ (1)

Singal-crystal X-ray structural analysis reveals that **1** crystallizes in the monoclinic space group $P2(1)/c$, featuring a new topological framework. In its asymmetric unit (Fig. 1a), the central Cd(II) ion is in a hexa-coordinated environment which was constructed with O1, O2 and O4a from two L^{4-} ligands, and N2, N4, N6 from three bibp ligands. The surroundings built a slightly distorted octahedron with O1, O2, O4a and N4 in the plane position and N2, N6 in the axial position (N2-Cd1-N6 = 177.9°). The bond angles surrounding Cd(II) are in the range from 86.9(2)° to 177.9(3)°. The distances of Cd-O bonds vary from 2.291(5) to 2.702(6) Å, while the Cd-N bond lengths range from 2.294(7) to 2.343(7) Å, which are in normal range. Interestingly, the Cd-Os plane and the Cd-Ns plane are almost vertical with the dihedral angle of 88.0(2)°. As shown in Fig. 1b, the L^{4-} ligands connect Cd(II) ions to build a 1D [Cd-L] chain in (0, 1, 1) and (0, −1, 1) directions, the bibp ligands connect Cd(II) ions to build a 2D [Cd-bibp] wavy plane in *bc* plane. The neighboring [Cd-bibp] wavy planes are then propped up by [Cd-L] chains. A 3D framework is formed. The void in the framework is filled *via* mutual interpenetration of two more independent frameworks, generating a three-fold interpenetrating 3D architecture. From the view of topological point, the L^{4-} ligand and the Cd(II) ions could be simplified as 4- and 5-connected nodes. Thus, the overall of the frameworks could be simplified as (4, 5)-connected 2-nodal net with the point symbol for net is (4. 6^9)$_2$(4^2. 6^2. 7. 8) (Fig. 1c).

5. Luminescent properties

The luminescent spectrum of the as-synthesized complex **1** was measured at room temperature. The free H$_4$L exhibits an emission band at 364 nm (λ_{ex} = 275 nm), which is derived from the $\pi^* \to \pi$ or $\pi^* \to n$ transitions. The emission peak of **1** was found at 375 nm (λ_{ex}

Fig. 1. a) Coordination environment of Cd in complex **1** (hydrogen atoms are omitted for clarity), Symmetry codes: (i) $x - 1$, $-y + 1/2$, $z - 3/2$; (ii) $x + 1$, y, z; (iii) $x - 1$, y, z; (iv) $-x$, $-y$, $-z + 2$; (v) $x + 1$, $-y + 1/2$, $z + 3/2$; (vi) $-x + 1$, $-y$, $-z - 1$; **b)** The [Cd-L] liner in (0, −1, 1)(left upper) and (0, 1, 1)(left under) directions, the 2D [Cd-bibp] wavy plane in *bc* plane(right upper), and a unit of 3D framework in bc plane of complex **1**(right under); and **c)** The three-fold interpenetrating topological framework of complex **1** with the point symbol for net (4. $6^9)_2(4^2$. 6^2. 7. 8).

= 270 nm) with a slightly concomitant blueshift 11 nm (Figure S2†) compared with that of free H$_4$L. The similarity of the luminescent spectrum of the free H$_4$L and **1** indicated that the emission band of **1** should be mainly attributed to ligand-to-ligand change transfer (LLCT) from the H$_4$L ligand. While, as previously reported [19], depended on the molecular calculation, the photoemission of Cd(II) coordination polymer is mainly to be the ligand-to-metal change transfer (LMCT). Therefore, the emission band of **1** may be assigned to LLCT and admixing with LMCT transition [20].

5.1. Sensing of $Cr_2O_7^{2-}$ and CrO_4^{2-} ions

As the prevalent toxic ions in wastewater, $Cr_2O_7^{2-}$ and CrO_4^{2-} ions can accumulate in living organisms, leading to cancer, deformity, and gene mutation, and also cause a significant threat to the environment. In light of the excellent luminescence and good water stability of complex **1**, the selective sensing abilities of **1** for $Cr_2O_7^{2-}$ and CrO_4^{2-} ions were evaluated. The as-synthesized **1** (3 mg) was suspended in the aqueous solution (4 mL, 0.01 mol L^{-1}) containing

Fig. 2. The photoluminescent spectra (**a**) and intensities (**b**) for complex **1** in aqueous solution with various inorganic anions.

a variety of different potassium salts with different kinds of anions: I^-, Cl^-, OH^-, IO_3^-, NO_3^-, ClO_3^-, OH^-, SCN^-, $H_2PO_4^-$, CO_3^{2-}, $S_2O_8^{2-}$, $Cr_2O_4^{2-}$, SO_4^{2-}, $Cr_2O_7^{2-}$, and CrO_4^{2-}. The photoluminescent spectra were recorded after the complex-ion suspensions were sonicated for 30 min in the dark (Fig. 2). The $Cr_2O_7^{2-}$ and CrO_4^{2-} ions afford the most striking turnoff quenching effect by naked-eye observation, while other ions show much weaker or negligible effect on the luminescence intensity for complex **1**. To further determine the sensitivity of complex **1** toward the $Cr_2O_7^{2-}$ and CrO_4^{2-} ions, a series of concentration-dependent (Fig. 3) and time-dependent (Figure S3†) luminescence experiments were carried out. The luminescence intensity of complex **1** could be remarkably influenced by the concentration of $Cr_2O_7^{2-}$ and CrO_4^{2-} ions (Fig. 3a, c), which gradually decreased with the concentration increase of $Cr_2O_7^{2-}$ and CrO_4^{2-} ions. The luminescence was completely quenched at the concentration of 10^{-3} mol L^{-1}. Quantitatively, these quenching effects can be rationalized by the Stern-Volmer Equation $I_0/I- 1 = K_{sv}[M]$, in which the values I_0 and I are the luminescent intensities of **1** without and with addition of $Cr_2O_7^{2-}$ and CrO_4^{2-} ions, respectively, K_{sv} is the quenching constant, and [M] is the concentration of $Cr_2O_7^{2-}$ and CrO_4^{2-} ions. Depending on the quenching experiment data, the liner correlation coefficient in the K_{sv} curve of **1** with the exits of $Cr_2O_7^{2-}$ and CrO_4^{2-} ions is 0.99823 and 0.99966, (Fig. 3b, d) respectively, suggesting that the quenching effect of $Cr_2O_7^{2-}$ and CrO_4^{2-} ions on the fluorescence of **1** matches well with the Ster-Volmer model, and the quenching belongs to static quenching. Furthermore, the K_{sv} values are calculated to be 6.6900 × 10^3 M^{-1} and 6.4065 × 10^4 M^{-1} respectively, suggesting that the

strong quenching effect on the luminescence of **1** for $Cr_2O_7^{2-}$ and CrO_4^{2-} ions.

To further understand the mechanism of luminescent reduction induced by anions, the time-dependent adsorption intensity measurement was taken. We immersed **1** into the solution of $Cr_2O_7^{2-}$ and CrO_4^{2-} ions respectively, took samples at various time intervals and analyzed by liquid UV/Vis spectroscopic analysis. The spectra indicate that the adsorption intensity of the $Cr_2O_7^{2-}$ and CrO_4^{2-} ions does not change with time (Figure S3†). All of these results indicate that the amount of adsorbed anions in **1** is not the main factor in fluorescence quenching. But, the UV/Vis spectra of $Cr_2O_7^{2-}$ and CrO_4^{2-} ions exhibit two wide adsorption bands from 230 to 420 nm (Figure S4a- b†), which almost overlapped the whole range of adsorption bands of complex **1**, while other anions have no absorb in this wavelength range (Figure S5a†). This is probably the reason for the observed luminescent quenching phenomenon. [21] All these results reveal that complex **1** could be the potential luminescent probes for detecting the toxic $Cr_2O_7^{2-}$ and CrO_4^{2-} ions. As confirmed by the powder X-ray diffraction patterns (Figure S6a†), the crystal structure of **1** could does not be destroyed after being immersed in anion solutions.

5.2. Sensing of Fe(III) cation

The potential application for detecting metal cations in water was also examined. We simply immersed the as-synthesized **1** (3 mg) was simply immerged into the aqueous solution (4 mL, 0.01 mol L^{-1}) of $AgNO_3$ or MCl_x (M = Na^+, K^+, Ca^{2+}, Mn^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, Cu^{2+}, and Fe^{3+}). Fig. 4 clearly clarifies that the metal ions with saturated electron configuration cannot cause a significant the reduction of luminescent intensity, except for Fe(III) which can lead to complete quenching to the solution. The PXRD patterns (Figure S6a†) confirmed that the crystal structure of **1** is very stable in metal ion solutions. In addition, the Fe(III) shows a strong absorption from 250 to 400 nm [22] while other anions show no obvious absorption in this range (Figure S5b†). This wide range band overlaps the emission spectra of **1**, indicating the Fe(III) ions could effectively suppress the transfer of the excitation energy to metal ions, further leading to a sharp decrease in the luminescent intensity and even quenching. This could be the reason for the observed luminescent quenching [23].

Interestingly, the concentration-depend quenching coefficient does not match well with Stern-Volmer equation, and the I_0/I versus [M] plot deviates from the straight line (Fig. 5). This phenomenon suggests that, unlike static quenching in $Cr_2O_7^{2-}$ and CrO_4^{2-} ion solutions, the luminescent quenching of **1** in Fe(III) solution could belong to dynamic quenching or both. In dynamic quenching, the electron or energy transfers directly between the excited-state of the analyte and quencher by collisions, whereas in static quenching, the non-emissive intermediate is formed, which is responsible for the quenching [24]. If the quenching progress is both incorporated with static and dynamic quenching, the change of fluorescence quenching could be described as

$$I_0/I = (1 + K_c[M])(1 + K_s[M]) \tag{1}$$

where K_c and K_s represent Stern-Volmer collisional and static constants, respectively. As dynamic quenching can cause a decrease of luminescent lifetime, K_c can be calculated by the Stern-Volmer equation

$$\tau_0/\tau = 1 + K_c[M] \tag{2}$$

where τ_0 is the original photoluminescence lifetime of CP, fitting the plot which obtained from the concentration-dependent lifetime experiment (Fig. 6), leads to the value $K_c = 253.19$ M^{-1}. If the

Fig. 3. Emission spectra and liner relationships for complex **1** in aqueous solutions of different $Cr_2O_7^{2-}$(**a** and **b**) and CrO_4^{2-} (**c** and **d**) concentrations.

concentration [M] in Eq. (1) is very low, the item $K_cK_s[M]^2$ could be neglected, yielding to a linear equation

$$I_0/I = 1 + (K_c + K_s)[M] \qquad (3)$$

The static constant K_s = 4888.34 M^{-1} could be obtained at low concentration from Eq. (3) with K_c = 253.19 M^{-1} (Fig. 6). Therefore, the overall Stern-Volmer constant K_{sv} could be calculated from the sum of corresponding K_c and K_s, that is 5141.53 M^{-1}.

The time-dependent adsorption intensity measurement in Figure S4c† shows that the adsorption intensity of **1** in Fe(III) solution decreased with time and stayed at a lower level. This indicates that the concentration of Fe(III) in solution continuously decreases at first, and then remains steady; which proves that complex **1** has certain ability for adsorbing the Fe^{3+} cation. As reported previously [25], the extent of excited-state energy transfer largely depends on the distance of fluorophore and analyte, and this efficiency can be prominent if the two are close enough. Because the distance between complex **1** and Fe(III) is shorter than that of complex **1** and $Cr_2O_7^{2-}$/CrO_4^{2-}, the energy transfer from complex **1** to Fe(III) is more easily than that from complex **1** to $Cr_2O_7^{2-}$/CrO_4^{2-}. Perhaps this is the reason for the distinction of the two quenching mechanism of complex **1** for $Cr_2O_7^{2-}$/CrO_4^{2-} and Fe^{3+}.

5.3. Photocatalysis capability for organic dyes

A large number of commercial organic dyes we use in our daily life are also toxic and even carcinogenic. It could cause many unpredictable environmental problems if we discharge the dyed wastewater directly without any purifying. Some reported d^{10} CPs [26] show good photocatalytic capability in the degradation of

Fig. 4. The photoluminescent spectra (**a**) and intensities (**b**) for complex **1** in aqueous solution with various inorganic caions.

Fig. 5. Emission spectra and liner relationship for complex **1** in aqueous solution of different Fe^{3+} concentrations.

Fig. 6. The dynamic quenching constant K_c and static quenching constant K_s for complex **1** in Fe^{3+} solution.

organic dyes under UV irradiation. To investigate the catalytic capability of complex **1** for degradation of dye, three common organic dyes (methylene blue (MB), Rhodamine B (RhB) and MalachiteGreen oxalate (MGO)) were selected for the experiments. 20 mg complex **1** was dispersed in aqueous solutions of three dyes (6 mol L^{-1}, 100 mL), respectively. The mixture was stirred in the dark for 30 min for the adsorption-desorption equilibrium, then the mixture was transferred and placed under the lighting of Hg lamp (125 W) with continuous stirring. Aliquots of the mixture samples were taken out with 15 min intervals, centrifuged. Then, the sample was analyzed by UV-Vis measurement. [27] Blank comparison experiments were taken in the absence of **1**.

The photocatalytic activity of **1** in three different dye solutions is shown in Fig. 7. The entire three absorbance peaks decrease obviously. Moreover, the variation trend of the concentration ratios of the three dyes (c/c_0) against time (min) with **1** in solutions were plotted, with c_0 representing the initial concentration of three dyes after stirred in the dark for 30 min. As depicted in Fig. 7, complex **1** shows remarkable photocatalytic capacity for the three organic dyes, and could be nearly completely degraded (98.7% for MB, 100% for RhB, and 99.9% for MGO) in 120 min. The results indicate that complex **1** also could be a candidate for photocatalytic activity in the degration of some organic dyes.

The coordination environment, the kinds of the central metal ions, and the coordinated mode of the ligand could have tremendous influence on the photocatalytic activities. It's proposed that under the irradiation of the UV-vis light, the organic ligands could be induced to generate O or N-metal charge transfer, promoting the electron form the highest occupied orbital (HOMO) to the lowest

unoccupied molecular orbital (LUMO). Meanwhile, the HOMO strongly needs the electron to return to its stable state. Simultaneously, the electron is captured from water molecule, oxygenating hydroxyl radical (•OH), which could decompose certain dyes effectively to complete the photocatalytic process [28]. The PXRD patterns (Figure S6b†) confirmed that the crystal structure of **1** is also very stable in dye solutions.

6. Conclusion

A novel 3D three-fold CP ($[Cd_2(L)(bibp)_3]_n$ (**1**)) has been successfully solvothermal synthesized depending on a semi-rigid tetracarboxylic acid. As a good candidate for chemical sensor, complex **1** can rapidly and selectively detect $Cr_2O_7^{2-}$/ CrO_4^{2-} anions and Fe(III) cation, based on the luminescence quenching mechanism. Photocatalytic degradation experiments show that **1** also possess a good capacity for the degradation of three kinds of organic dyes (MB, RhB, and MGO). This study confirms that the luminescent CPs can be rationally synthesized and could be used as multifunctional material not only for chemical sensor but also photocatalyst for degradation. The related studies are still under way.

Fig. 7. The absorption spectra and the plots of concentration ratios (c/c_0) against irradiation time (min) of MB (**a**), MGO (**b**), and RhB (**c**).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2017.09.005.

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