



A fluorescent coordination polymer for selective sensing of hazardous nitrobenzene and dichromate anion



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ARTICLE INFO

Article history:

Received 18 August 2016

Received in revised form

12 December 2016

Accepted 17 December 2016

Available online 19 December 2016

Keywords:

Coordination polymer

Crystal structure

Dual functional sensor

Nitrobenzene

Dichromate anion

ABSTRACT

A one-dimensional coordination polymer, namely $[\text{Cd}(\text{bipy})][\text{HL}]_n$ (**1**) ($\text{H}_3\text{L} = 2'$ -carboxybiphenyl-4-ylmethylphosphonic acid, and $\text{bipy} = 2,2'$ -bipyridine) has been synthesized under the hydrothermal condition. The structure of the compound has been determined by single crystal X-ray diffraction analysis, and further characterized by elemental analysis, infrared spectrum, thermogravimetric analysis, and UV–vis absorption spectrum. This compound can be used as an excellent dual functional fluorescent sensor for the selective and sensitive detection of the hazardous environmental contaminants nitrobenzene and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) anion. Compound **1** represents a rare example of dual functional fluorescent sensor, which can detect nitrobenzene and $\text{Cr}_2\text{O}_7^{2-}$ simultaneously. The sensing mechanism of the compound has been confirmed theoretically and experimentally. Moreover, the optical band gap and temperature variable photoluminescence of the compound have been investigated.

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1. Introduction

During the past few years, with the development of modern industry, water pollution is becoming more serious. Some industrial waste water contains hazardous materials such as nitrobenzene (NB) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) anion. NB is a well-known explosive and toxic pollutant, which is widely used in industrial manufacturing and military operations [1–3]. It can enter environment in many ways and can irritate skin, eyes, cardiovascular and central nervous systems [4]. As a possible carcinogenic or mutagenic agent, NB has been categorized as one of the hazardous pollutants by the Agency for Toxic Substances and Disease Registry, U.S. Public Health Service [5,6]. However, because of the strong electron withdrawing nature of the nitro group on the aromatic ring, NB is generally stable in water [7]. $\text{Cr}_2\text{O}_7^{2-}$ is known as the human carcinogen, which is widely used in the fields of leather-tanning, pigment manufacturing, detergent and wood preservation [8,9]. A small quantity of $\text{Cr}_2\text{O}_7^{2-}$ can lead to serious health issues, including the damage of mucous membrane, skin and so on [10]. $\text{Cr}_2\text{O}_7^{2-}$ in the waste water can be absorbed on the surfaces

of solid matter and sediments, which can exist stably in the water for a long time [9]. In order to decrease the damage of NB and $\text{Cr}_2\text{O}_7^{2-}$ on the environment and human beings, the development of efficient sensors for multiple analytes is highly demanding.

Up to now, many analytical and spectroscopic techniques, such as cyclic voltammetry, Raman spectroscopy and gas chromatography, have been used for the detection of hazardous chemicals, but many of them are expensive, time-consuming and inconvenient [3,11–13]. Recently, a simple, convenient, economic and rapid fluorescence quenching based detection method using luminescent coordination polymers (LCPs) has attracted increasing interest [1,14–17]. CPs are crystalline solids constructed by metal ions or metal clusters and organic ligands via coordination bonds or weak interactions. They have one, two or three dimensional networks [14,18] and display applications in many fields such as catalysis, adsorption, drug delivery, magnetism and luminescence [14–16,19–21]. Owing to the nearly limitless combinations of metal ions and organic ligands, CPs have designable architectures and tunable chemical and physical properties, which make them good candidates for fluorescence sensing [14,22]. Results from documents indicate that CPs constructed by electron-rich π -conjugated aromatic ligands may be efficient luminescent sensing materials [19,23].

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In this work, we report a dual functional fluorescence sensor [Cd(bipy)][HL] (**1**), which was constructed by the π -conjugated aromatic ligands 2'-carboxybiphenyl-4-ylmethylphosphonic acid (H_3L , Scheme 1) and 2,2'-bipyridine (bipy, Scheme 1) with the Cd(II) ion. In our previous work, H_3L has been used for the construction of CPs with Cu(II), Zn(II) and Cd(II) ions by employing the N-donor ligands 1-((1*H*-1,2,4-triazol-1-yl)methyl)-3,5-bis(4-pyridyl)-1,2,4-triazole and 1,10-phenanthroline as the auxiliary ligands. These CPs exhibit various structures from 1D to 3D and display different properties such as photoluminescence and photocatalysis [24,25]. To improve our work, we have investigated the luminescent sensing behavior of compound **1** in this work. The structure of the compound has been determined by single crystal X-ray diffraction analysis, and further characterized by elemental analysis, infrared spectrum (IR), thermogravimetric analysis and UV–vis absorption spectrum. This compound can act as an efficient dual functional fluorescent sensor for the selective detection of NB and $Cr_2O_7^{2-}$. The sensing mechanism of the compound has been confirmed theoretically and experimentally. Moreover, the optical band gap and temperature variable photoluminescence of the compound have been investigated.

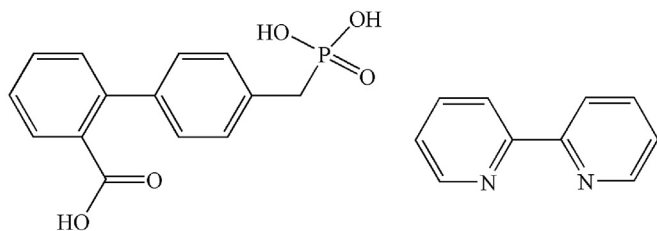
2. Experimental section

2.1. Materials and methods

H_3L was prepared according to the method reported previously [24,26]. Other commercially available chemicals and solvents are of analytical grade and were used as received without further purification. The C, H and N elemental analyses data were collected on a Perkin-Elmer 240 elemental analyzer. The IR spectrum measurement was carried out on a Mattson Alpha-Centauri spectrometer in the range of 4000–400 cm^{-1} . Thermogravimetric analysis measurement was performed on a Perkin-Elmer TG-7 analyzer heated from room temperature to 800 °C under nitrogen. The UV–vis absorption spectrum and diffuse reflection spectrum of the compound were measured on a Cary 500 spectrophotometer. The photoluminescent spectra of the compound were recorded on a Perkin-Elmer FLS920 spectrometer.

2.2. Synthesis of [Cd(bipy)][HL]_n (**1**)

A mixture of Cd(CH₃COO)₂·2H₂O (0.04 g, 0.15 mmol), H_3L (0.029 g, 0.1 mmol), bipy (0.023 g, 0.15 mmol), NaOH (0.012 g, 0.3 mmol) and 8 mL H₂O was sealed in a 15 mL Teflon reactor and heated at 140 °C for 3 days. After the mixture had been cooled to room temperature at a rate of 10 °C/h, colorless crystals of **1** were collected in a 37% yield. Anal. Calcd for C₂₄H₁₉CdN₂O₅P ($M_r = 558.80$): C, 51.58; H, 3.43; N, 5.01%. Found: C, 51.65; H, 3.49; N, 4.90%. IR (cm^{-1}): 3371 (m), 3052 (m), 1550 (s), 1476 (s), 1440 (m), 1392 (s), 1312 (w), 1243 (w), 1199 (w), 1156 (s), 1069 (s), 945 (s), 850 (w), 763 (s), 653 (w), 523 (s).



Scheme 1. Structures of the π -conjugated ligands H_3L (left) and bipy (right).

Table 1
Crystal data and structure refinements for compound **1**.

Formula	C ₂₄ H ₁₉ CdN ₂ O ₅ P
M_r	558.80
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	10.7014(4)
b (Å)	9.6085(3)
c (Å)	21.4859(8)
α (°)	90
β (°)	92.048(3)
γ (°)	90
V (Å ³)	2207.86(14)
Z	4
D_{calc} (g cm ⁻³)	1.681
$F(0\ 0\ 0)$	1120
R_{int}	0.0442
GOF on F^2	1.054
R_1 [$I > 2\sigma(I)$]	0.0473
wR_2 (all data)	0.0903

Table 2
Selected bond distances (Å) and angles (°) for compound **1**.

Cd(1)–O(3) ^{#1}	2.234(2)	Cd(1)–O(4)	2.293(3)
Cd(1)–O(3) ^{#2}	2.314(2)	Cd(1)–N(2)	2.321(3)
Cd(1)–N(1)	2.333(3)	Cd(1)–O(5)	2.442(3)
O(3) ^{#1} –Cd(1)–O(4)	94.53(10)	O(3) ^{#1} –Cd(1)–O(3) ^{#2}	80.38(9)
O(4)–Cd(1)–O(3) ^{#2}	104.68(10)	O(3) ^{#1} –Cd(1)–N(2)	100.93(11)
O(4)–Cd(1)–N(2)	160.09(11)	O(3) ^{#2} –Cd(1)–N(2)	90.32(10)
O(3) ^{#1} –Cd(1)–N(1)	112.66(10)	O(4)–Cd(1)–N(1)	92.48(11)
O(3) ^{#2} –Cd(1)–N(1)	157.81(11)	N(2)–Cd(1)–N(1)	70.06(12)
O(3) ^{#1} –Cd(1)–O(5)	147.34(10)	O(4)–Cd(1)–O(5)	55.01(9)
O(3) ^{#2} –Cd(1)–O(5)	95.18(9)	N(2)–Cd(1)–O(5)	111.49(11)
N(1)–Cd(1)–O(5)	83.08(11)		

Symmetry codes: ^{#1} $-x + 1, -y + 1, -z + 2$; ^{#2} $x, y + 1, z$.

2.3. X-ray crystallography

The X-ray intensity data of compound **1** were collected on an Oxford Diffraction Gemini R Ultra diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) at 293 K. The structure of compound **1** was solved by direct method of SHELXS-97 [27] and refined by full-matrix least-squares techniques using the SHELXL-97 program [28]. Anisotropic displacement parameters were applied to all the non-H atoms. Hydrogen atoms on C atoms and the phosphonate O atom (O2) in compound **1** were generated geometrically and refined using a riding model with $d(C-H) = 0.93-0.97$ Å, $U_{iso} = 1.2U_{eq}(C)$ and $d(O-H) = 0.85$ Å, $U_{iso} = 1.5U_{eq}(O)$. The crystallographic data and structure refinement parameters are summarized in Table 1, and selected bond distances and angles are listed in Table 2.

3. Results and discussion

3.1. Structural analysis of [Cd(bipy)][HL]_n (**1**)

Single-crystal X-ray diffraction analysis indicates that compound **1** crystallizes in the monoclinic space group $P2_1/c$. As shown in Fig. 1a, the asymmetric unit of **1** consists of one Cd(II) ion, one bipy ligand and one HL anion. Cd1 is six-coordinated in an octahedral coordination geometry, furnished by two nitrogen atoms from one bipy ligand and four oxygen atoms from three different HL anions. The Cd–N bond lengths are 2.321(3) and 2.333(3) Å, respectively. The Cd–O bond lengths are in the range of 2.234(2)–2.442(3) Å. All the bond lengths are in the normal ranges as other Cd(II)-containing coordination polymers [13,29]. The coordination mode of the HL anion can be described as $\mu_3-\eta^2:\eta^0:\eta^0:\eta^1:\eta^1$ (μ_3

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