



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



Zheng Zhu^{a,1}, Mei Wang^{a,1}, Cun-gang Xu^a, Zi-ao Zong^a, Dong-mei Zhang^a, Shuang-yu Bi^{b,*}, Yu-hua Fan^{a,*}

^a Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao, Shandong 266100, PR China

^b Max Planck Institute for Terrestrial Microbiology LOEWE Center for Synthetic Microbiology (SYNMIKRO), Marburg 35043, Germany

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ABSTRACT

A three-fold interpenetrated coordination polymer $[\text{Cd}_2(\text{L})(\text{bibp})_3]_n$ (**1**) ($\text{H}_4\text{L} = 5,5'-(1,4\text{-phenylenebis(methoxy)})\text{diisophthalic acid}$, $\text{bibp} = 4,4'\text{-bis(imidazolyl)biphenyl}$) 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 $\text{Cr}_2\text{O}_7^{2-}$) 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 been polluted following the development of our industrialization. The polluted water not only harms to our environment but also threatens 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 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 systematic 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 analytes [11]. However, it is important to conduct further research on the corresponding mechanisms. In another aspect, how to remove the contaminant from 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 multi-dentate aromatic carboxylic acids have two obviously characteristics.

* Corresponding authors.

E-mail addresses: yuxiao_009@163.com (S.-y. Bi), fanyuhua301@163.com (Y.-h. Fan).

¹ These authors contributed equally.

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

Complex	1
Formula	C ₃₉ H ₂₈ CdN ₆ O ₅
Formula weight	773.07
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	10.4600 (9)
<i>b</i> (Å)	37.964 (3)
<i>c</i> (Å)	9.4331 (8)
α (°)	90
β (°)	101.177(2)
γ (°)	90
<i>V</i> (Å ³)	3674.9 (5)
<i>Z</i>	4
<i>D</i> _{calcd} (Mg m ⁻³)	1.397
μ (mm ⁻¹)	0.65
Reflections collected	6478
Data/parameters	3275/460
<i>F</i> (000)	1568
<i>T</i> (K)	298
<i>R</i> _{int}	0.147
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0853 <i>wR</i> ₂ = 0.1508
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1601 <i>wR</i> ₂ = 0.1680
<i>S</i>	1.050

One is the coordination centers that can flexibly twist around to meet 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, d¹⁰ 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 (H₄L) and one rigidly N-donor 4,4'-bis(imidazolyl)biphenyl (bibp) as auxiliary ligand to react with Cd(NO₃)₂·6H₂O, and successfully synthesized a 3D three-fold CP [Cd₂(L)(bibp)₃]_n (**1**) under solvothermal condition. Complex **1** shows excellent luminescent sensing for Cr₂O₇²⁻/CrO₄²⁻ 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-K α radiation. Topological analysis were performed and confirmed by the Topos program and the Systre software [15,16].

2.2. Synthesis of [Cd₂(L)(bibp)₃]_n (**1**)

A mixture of Cd(NO₃)₂·6H₂O (0.069 g, 0.2 mmol), bibp (0.029 g, 0.1 mmol), H₄L (0.047 g, 0.1 mmol), DMF (4.5 mL) and H₂O (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 H₄L). Anal. Calcd for C₃₉H₂₈CdN₆O₅: 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 CCD diffractometer, using graphite-monochromated Mo- α radiation ($\lambda = 0.71073$ Å) by using the ω -2 θ 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 [Cd₂(L)(bibp)₃]_n (**1**)

Singal-crystal X-ray structural analysis reveals that **1** crystallizes in the monoclinic space group *P*2₁(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 L⁴⁻ 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 L⁴⁻ 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 L⁴⁻ 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 (4.6⁹)₂(4². 6². 7. 8) (Fig. 1c).

5. Luminescent properties

The luminescent spectrum of the as-synthesized complex **1** was measured at room temperature. The free H₄L exhibits an emission

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