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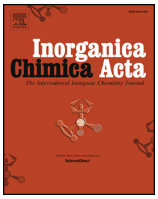

A multifunctional four-fold interpenetrated coordination polymer: Quantifiable evaluation of luminescent sensing for Cr(VI)/Cu(II) and photocatalytic properties

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ABSTRACT

A four-fold interpenetrated coordination polymer $\{[Zn_2(L)(bibp)_3]\cdot DMF\cdot H_2O\}_n$ (**1**) (H_4L = 5,5′-(biphenyl-4,4′-diylbis(methylene)) bis(oxy) diisophthalicacid, bibp = 4,4′-bis(imidazolyl)biphenyl) has been rationally constructed, successfully solvothermally synthesized. Complex **1** was characterized by single-crystal X-ray diffraction, elemental analysis, IR spectra, powder X-ray diffraction (PXRD), and thermogravimetric (TG) analysis, and it shows a 3D four-fold interpenetrated **bbf**-topological framework. Luminescence studies demonstrate that **1** has high selectivity and sensitivity for pollutant Cr(VI) (CrO_4^{2-} and $Cr_2O_7^{2-}$) anion and Cu(II) cation; Photocatalytic studies show that **1** exhibits great degradation activity of four organic dyes (methylene blue (MB), Rhodamine B (RhB), Methyl orange (MO) and Orange IV (OIV)). Meanwhile, the possible mechanism of the photocatalytic property has been deduced.

1. Introduction

Following the development of our industrialization, the water pollution is increasingly severe. The polluted water not only harms to our environmental but also threatens the livings. How to identify, monitor and remove the heavy metal cations, anions, and small organic dye molecules in waste water directly become a great challenge for us to overcome this target [1]. As a new class porous materials and the structure could be predict ability in a certain degree, coordination polymers (CP) offer a unique platform for the development of solid state luminescent materials [2]. The fluorescence sensing based on luminescent CP has gained great interests due to its selectivity, sensitivity, portability and short response time [3]. Numerous guest-dependent luminescent CPs had been successfully synthesized and reported for the sensing of cations [4], anions [5], small molecules [6], vapors [7], and even nitroaromatic explosives [8]. The relevant reports indicated that CPs is a great potential material in this field.

The capabilities of CPs are largely depending on their structure, and to obtain an effective CP sensor, a binding site and a powerful luminophore is required [9]. 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 seem to be the ideal candidates. This is because, on the one hand, the coordination centers that can flexibly twist around to meet different coordination environment; on the other hand, when coordinate with metal ions, the carboxylic groups that can partially or fully deprotonated to adopt various coordination modes. In another aspect, as auxiliary ligand, the *N*-donor ligands also could take considerably effect on the final structure. The rigidly ones can reduce the uncertainly structure in the end for their stability, while the flexible ones could further enrich the complexity of the structure as they can meet different coordinate modes [10]. In addition, d^{10} metal ions are considered have good ability for the transfer of the excited electrons. Herein, concerned above, we chose one semi-rigid tetracarboxylic acid 5,5′-(biphenyl-4,4′-diylbis(methylene))bis(oxy)diisophthalic acid (H_4L) and one rigidly *N*-donor 4,4′-bis(imidazolyl)biphenyl (bibp) as auxiliary ligand to react with $Zn(NO_3)_2\cdot 6H_2O$, and successfully synthesized a 3D Four-fold CP $\{[Zn_2(L)(bibp)_3]\cdot DMF\cdot H_2O\}_n$ (**1**) under solvothermal condition. Complex **1** shows excellent luminescent sensing for $Cr_2O_7^{2-}/CrO_4^{2-}$ anions and Cu(II) cation based on the quenching mechanism. The effects on photocatalytic activity of **1** for certain organic dyes have also been investigated.

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

Empirical formula	$C_{69.15}H_{56.31}Zn_2N_9O_{13}$
Formula weight	1352.14
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	7.87240(10)
b (Å)	24.0870(4)
c (Å)	17.1977(3)
α (°)	90
β (°)	92.5360(10)
γ(°)	90
V (Å^3)	3257.88(9)
Z	2
D_{calcd}(Mg m^{-3})	1.378
μ (mm^{-1})	0.81
Reflections collected	8601
Data/parameters	5837/534
F(0 0 0)	1396
T (K)	170
R_{int}	0.0726
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0875$ w$R_2 = 0.2583$
R indices (all data)	$R_1 = 0.1240$ w$R_2 = 0.2832$
Gof	1.03

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, w$R_2 = [\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]^{1/2}$.

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 with the Varian 640FT-IR by using KBr pellets. Elemental analysis of C, H, N were performed in the 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 powder X-ray diffractions (PXRD) of **1** was collected on an Enraf-Nonius CAD-4 X-ray single-crystal diffractometer with Cu-Kα radiation. Topological analysis was performed and confirmed by the Topos program and the Systre software.[11,12] UV-vis absorption spectra were recorded on a SP-1901 UV–vis spectrophotometer.

2.2. Synthesis of $\{[Zn_2(L)(bibp)_3]\cdot DMF\cdot H_2O\}_n$(**1**)

A mixture of $Zn(NO_3)_2\cdot 6H_2O$ (0.059 g, 0.2 mmol), bibp (0.029 g, 0.1 mmol), H_4L (0.054 g, 0.1 mmol), H_2O (3.0 mL), DMF (6.0 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 flake crystals were collected in 84.23% yield (based on H_4L). Anal.Calcd for $C_{69.15}H_{56.31}Zn_2N_9O_{13}$: C, 61.43; H, 4.20; N, 9.32%. Found: C, 60.94; H, 4.21; N, 9.33%. IR (KBr disk, cm^{-1}): 3407 (m), 3121 (w), 1651 (w), 1620 (m), 1561 (s), 1519 (s), 1452 (m), 1396 (s), 1366 (s), 1308 (m), 1256 (m), 1056 (m), 820 (m), 777 (m), 730 (m), 654 (w).

2.3. X-ray crystal structure determination

Single-crystal X-ray diffraction for the suitable crystal of complex **1** was obtained on a Bruker Apex Smart CCDC diffractometer, using graphite-monochromated Mo-kα radiation (λ = 0.71073 Å) at 170 K. The structure was solved by direct methods using SHELXS-97 [13]. 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 [14]. 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 1535069.

3. Results and discussion

3.1. Structure of complex $\{[Zn_2(L)(bibp)_3]\cdot DMF\cdot H_2O\}_n$ (**1**)

Single-crystal X-ray structural analysis reveals that **1** crystallizes in the monoclinic space group $P2(1)/n$ featuring a **bbf**-topological framework. Its asymmetric unit (Fig. 1a) consists of two Zn(II) cations, one L^{4-} ligand, three bibp ligands, one lattice DMF and one lattice water molecule. The Zn(II) center exhibits tetrahedral coordination sphere which is arranged by two O atoms from two different L^{4-} ligands and two N atoms from two different bibp ligands. The distances of Zn-O_1/O_2 and Zn-N_1/N_4 are 1.9510(17)/1.9573(16)Å and 2.018(2)-2.005(2) Å, respectively. The L^{4-} ligands are connected by two Zn(II) cations to form a 2D zigzag fold ($[Zn\text{-}L]_n$) in bc plane (Fig. 1b). And the bibp ligands are joined by two Zn(II) cations to construct a 1D zigzag line ($[Zn\text{-}bibp]_n$) alone b axis(Fig. 1c). The adjacent $[Zn\text{-}L]_n$ folds are further sewed up with two identical $[Zn\text{-}bibp]_n$ lines to constructing a 3D framework (Fig. 1d). The empty space of such frameworks is filled by other three identical frameworks, leading to a four-fold interpenetrated network, and resulting in a 3D framework (Fig. 1e). And because of the exists of interpenetrated network, the framework of **1** contains no residual solvent accessible void, based on PLATON calculation.

From the view of topological point, the Zn(II) center and the L^{4-} ligand could be simplified as two kinds of 4-connected nodes. Thus, the overall 3D framework of **1** is a 2-nodal 4, 4-c network, and the point symbol of it is $(6^4.8^2)(6^6)_2$, determined by TOPOS program.

3.2. Luminescent properties

The solid-state emission and excitation spectra of free H_4L and bibp ligand and complex **1** were measured at room temperature (Fig. S2†). The free H_4L and bibp ligand exhibit emission band at 405 nm (λ_{ex} = 275 nm) and 377 nm (λ_{ex} = 275 nm) respectively, which is derived from the $\pi^* \rightarrow \pi$ or $\pi^* \rightarrow n$ transitions. The emission peak of **1** was found at 382 nm (λ_{ex} = 330 nm) which gives luminescence spectra more similar to that of the bibp ligand than the H_4L. Furthermore, there is a slightly concomitant blueshift 5 nm compared with that of free bibp ligand. The similarity of the luminescent spectrum of the free bibp and **1** indicated that the emission band of **1** should be mainly attributed to ligand-to-ligand charge transfer (LLCT) from the bibp ligand. While, as previously report[15], depending on the molecular calculation, the photoemission of Zn(II) coordination polymer is mainly to be the ligand-to-metal charge transfer (LMCT). Therefore, the emission band of **1** may be assigned to LLCT and admixing with LMCT transition [16].

3.3. Pollutant-ion sensing

The metal ions, such as Cu(II) and Cr(VI) ions, are prevalent toxic in wastewater, which can accumulate in living organisms. These contaminants not only cause a significant threat to the environment but also do harmful to the livings' health. To evaluate the selective sensing ability of complex **1** toward $Cr_2O_7^{2-}$ and CrO_4^{2-} ions, the luminescence spectra of as-synthesized **1** (3 mg) dispersed in the aqueous solution (4 mL, 0.01 mol L^{-1}) 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-}) were recorded after the complex-anion suspensions were sonicated for