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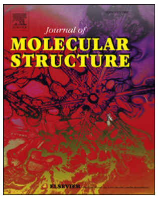

Two zinc(II) coordination polymers for selective luminescence sensing of iron(III) ions and photocatalytic degradation of methylene blue

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ABSTRACT

Two Zn(II) coordination polymers (CPs), $[\mathrm{Zn(L1)(DCTP)}]_n$ (**1**) and $[\mathrm{Zn(L2)(DCTP)}]_n$ (**2**) [L1 = 1,3-bis(5,6-dimethylbenzimidazol-1-ylmethyl)benzene, H_2DCTP = 2,5-dichloroterephthalic acid, L2 = 1,4-bis(benzimidazol-1-ylmethyl)benzene] were hydrothermally synthesized and characterized by elemental analyses, IR spectra, thermogravimetric analyses, fluorescence spectra and single-crystal X-ray diffraction. CP **1** forms a 2D (4,4) layered structure, which is finally extended to a 3D supramolecular framework by the π-π stacking interactions. CP **2** possesses a 3D 3-fold interpenetrating **dia** network. Both CPs can be as highly selective probes for detection of Fe^{3+} in aqueous solutions based on luminescence quenching. Further, two compounds exhibit photocatalytic activities for degradation of the methylene blue under UV irradiation.

1. Introduction

The Fe^{3+} cations take part in electron transferring and oxygen transportation in biochemical process for all living system [1,2]. Excessive or insufficient Fe^{3+} can interfere with cellular homeostasis and metabolism lead to anemia and methemoglobinemia [3]. However, most traditional analytical techniques for detecting Fe^{3+} such as chromatography, inductively coupled plasma mass spectrometry, and atomic absorption spectroscopy suffer from sophisticated operation and high cost [4]. Thus, it is very essential to develop a high-efficiency, convenient, quick-response and low-cost sensing approach to probe Fe^{3+}. Hence, chemical sensors based on luminescent d^{10} CPs have received considerable attention because of their low cost, high selectivity, quick response, and good reversibility [5–7].

Up to now, the great progress has been made in the synthesis CPs with promising properties [8–17], however, there are many challenges to construct new CPs as luminescent functional materials. Many factors (including pH, temperature, solvent systems, organic ligands, central metal ions) affect the final structures and properties of CPs [18,19]. It is an effective strategy to construct new metal CPs via the self-assembly of dicarboxylate and N-donor mixed ligands. Especially, aromatic dicarboxylates can bridge metal ions to generate charge neutral networks, then, the N-containing neutral ligands may further extend the metal carboxylate frameworks into high dimensional architectures [20,21]. 2,5-dichloroterephthalic acid (H_2DCTP) shows versatile coordination modes and two carboxylates in it are predisposed to 180° at the central phenyl ring, providing constrained and proper binding directions to metal centers. Semi-rigid bis(benzimidazole) ligands are widely employed as typical N-donor ligands in the synthesis of CPs, since they can satisfy the coordination needs of transition metal centers by freely rotating and bending their $-(CH_2-Ph-CH_2)-$ space [22–28]. Our group have reported a few interesting CPs exhibiting photocatalytic activities based on H_2DCTP and bis(benzimidazole) mixed-ligands [29,30]. As part of our ongoing work, two new CPs with the formulae of $[\mathrm{Zn(DCTP)(L1)}]_n$ (**1**) and $[\mathrm{Zn(DCTP)(L2)}]_n$ (**2**) were synthesized and characterized (L = 1,3-bis(5,6-dimethylbenzimidazol-1-ylmethyl)benzene, L2 = 1,4-bis(benzimidazol-1-ylmethyl)benzene), and the influence of different semi-rigid bis(benzimidazole) ligands on the final structures and properties of ternary Zn(II) CPs were investigated. The photocatalytic properties of two CPs were also discussed. Additionally, CPs **1**–**2** are chosen as luminescent probe for highly selective sensing of Fe^{3+} ions.

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2. Experimental

2.1. Materials and measurements

The proligand L1 and L2 were prepared by a literature method [31]. All other reagents and solvents were purchased from commercial sources and used without further purification. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a PerkinElmer 240C analyzer. Thermogravimetric (TG) analysis experiments were carried out on a Netzsch STA449 F1 thermal analyzer from 25 to 800 °C under N_2 atmosphere at a heating rate of 10 °C min^{-1}. The solid-state UV–vis diffuse-reflectance spectra were recorded on a UV–vis spectrophotometer (Puxi, T9) at room temperature, and a $BaSO_4$ plate was used as the reflectance standard. X-ray diffraction patterns were collected by using a Rigaku D/Max-2500 PC X-ray diffractometer at 40 kV, 100 mA for a Cu-target tube ($\lambda = 1.5418$ Å), with a scan speed of 2°/min and a step size of 0.02°. FT-IR spectra were obtained for KBr pellets on an Avatar 360 (Nicolet) spectrophotometer at the range of 4000-400 cm^{-1}. The luminescence excitation and emission spectra for powdered solid samples were recorded with an Edinburgh Instruments FS5 fluorescence spectrophotometer.

2.2. Preparation of the complexes

2.2.1. Synthesis of [Zn(DCTP)(L1)]$_n$ (**1**)

L1 (39.4 mg, 0.1 mmol), $Zn(OAc)_2 \cdot H_2O$ (43.9 mg, 0.2 mmol), H_2DCTP (23.5 mg, 0.1 mmol) were added to H_2O (10 mL). Then the mixture was sealed in a Teflon-lined stainless steel vessel (25 mL) and heated to 140 °C for 3 days under autogenous pressure, followed by cooling to room temperature at a rate of 5 °C h^{-1}. Colorless block crystals of CP **1** were obtained. Yield 57.4% based on Zn. Anal. Calc. for $C_{34}H_{28}ZnN_4O_4Cl_2$ (Mr = 692.91): C, 58.94; H, 4.07; N, 8.09%. Found: C, 58.76; H, 4.18; N, 7.87%. IR (KBr, cm^{-1}): 1637 (s), 1508 (w), 1474 (m), 1438 (m), 1379 (s), 1352 (s), 1330 (s), 1075 (m), 838 (s), 797 (s), 717 (m).

2.2.2. Synthesis of [Zn(DCTP)(L2)]$_n$ (**2**)

CP **2** was prepared in the same way as that for CP **1**, except using L2 (33.8 mg, 0.1 mmol) instead of L1. Colorless crystals of CP **2** were collected. Yield 38.7% based on Zn. Anal. Calc. for $C_{30}H_{20}ZnN_4O_4Cl_2$ (Mr = 636.80): C, 56.58; H, 3.17; N, 8.80%. Found: C, 56.41; H, 3.28; N, 9.01%. IR (KBr, cm^{-1}): 1618 (s), 1591 (s), 1560 (s), 1508 (s), 1466 (m), 1369 (s), 1302 (m), 1190 (s), 1078 (s), 919 (m), 828 (s), 751 (s).

2.3. X-ray crystallography

Crystallographic data for CP **1** and CP **2** were collected at 293 K on a Bruker Smart 1000 CCD diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) by ω-scan mode. The SADABS program was used to collect, index, scale and apply analytical absorption correction based on faces of the crystal with multi-scan mode [32]. Both structures were solved by direct methods and refined through full-matrix least-squares on F^2 using SHELXL-2014 program [33]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms of the organic ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. The crystallographic data of CP **1** and CP **2** are listed in Table 1, and selected bond length and bond angle values are supplied in Table S1.

3. Results and discussion

3.1. Crystal structures

3.1.1. Crystal structure of [Zn(L1)(DCTP)]$_n$ (**1**)

Single crystal X-ray diffraction analysis indicates that CP **1** crystallizes in triclinic crystal system and $P\overline{1}$ space group. The asymmetric unit of CP **1** contains one crystallographically independent Zn(II) ion, two halves of L1 ligands and two halves of $DCTP^{2-}$ ligands. The coordination environment of CP **1** is shown in Fig. 1a. The Zn1 ion is four-coordinated by two oxygen atoms (O1, O3) from different $DCTP^{2-}$ ligands and two nitrogen atoms (N1, N4A, Symmetry code: A: $x, y+1, z$) from two distinct L1 ligands, and exhibits a distorted tetrahedron environment with τ_4 parameter of 0.9, which is calculated to describe the geometry of a four-coordinated metal system [34]. The bond lengths of Zn–N are 2.017 (2) and 2.024 (2) Å, while the Zn–O bond lengths are 1.969 (2) and 1.947 (2) Å.The bond angles around Zn(II) center are in range of 97.4(9)-116.9(9)°. Meanwhile, the bond lengths of Zn–O and Zn–N are in the normal range compared with the previously reported Zn (II)-based CPs.

In CP **1**, The $DCTP^{2-}$ ligands adopt a (κ^1-κ^0)-(κ^1-κ^0)-μ_2 coordinating mode, linking the neighboring Zn(II) centers to form a 1D [Zn-DCTP-Zn]$_n$ chain, with a Zn⋯Zn separation of 11.055 (6) and 11.180 (6) Å, respectively (Fig. S1). Meanwhile, Zn(II) center are further linked by L1 ligand to construct another 1D linear chain, [Zn–L1–Zn]$_n$, with a Zn⋯Zn distance of 11.681 (8) Å (Fig. S2). The L1 ligands adopt *trans*-conformations with a $N_{donor}\cdots N\text{-}C_{sp3}\cdots C_{sp3}$ torsion angle of 133.4 (3)° and the dihedral angle between two benzimidazole rings is 65.1 (6)°. The 1D linear [Zn-DCTP-Zn]$_n$ chains are further extended by L1 ligands into a 2D layered structure (Fig. 1b). CP **1** exists a tetranuclear unit which consists of two $DCTP^{2-}$, two L1 ligands and four Zn(II) centers. The 2D layer could be simplified to a 4,4-**sql** network with point symbol $\{4^4.6^2\}$ (Fig. 1c). The neighboring 2D layers are finally extended into a 3D supramolecular framework by the π-π stacking interactions among the imidazole (Cg1: N1–C9–N2–C15–C10) and benzene rings (Cg2: C10–C11–C12–C13–C14–C15, symmetry related by the transformation of $1-x, 1-y, 1-z$) from different L1 ligands with a centroid-centroid distance of 3.574 (2) Å, an inter-planar angle $\alpha = 1.43°$ and slipping angles β or γ of 11.0 or 10.0°, and an averaged $d_{\pi\text{-}\pi}$ distance of 3.520 (1) Å. (Fig. 1d).

3.1.2. Crystal structure of [Zn(L2)(DCTP)]$_n$ (**2**)

The asymmetric unit of CP **2** consists of crystallographically independent one Zn(II) ion, two halves of L2 and $DCTP^{2-}$ ligands. The coordination environment of CP **2** is shown in Fig. 2a. The Zn(II) ion displays a four-coordinated mode, completed by two carboxylate oxygen atoms from two $DCTP^{2-}$ ligands (O1, O1A) and two N (N1, N1A, Symmetry code: A: $1-x, y, 1/2-z$) atoms from two L2 ligands, and also exhibits a distorted tetrahedron coordination environment with τ_4 parameter of 0.9. The bond lengths of Zn–N is 2.011 (1) Å, while the Zn–O bond lengths is 1.962 (1) Å. The bond angles around Zn(II) center are in range of 98.3(9)-116.7(6)°.

In CP **2**, the completed deprotonated $DCTP^{2-}$ ligands adopt a (κ^1-κ^0)-(κ^1-κ^0)-μ_2 coordinating mode, joining the Zn(II) centers to form a 1D [Zn-DCTP-Zn]$_n$ chain, with a Zn⋯Zn separation of 11.307 (9) Å (Fig. S3). Further, adjacent Zn(II) center is linked by L2 ligand to construct another 1D linear chain, [Zn–L2–Zn]$_n$, with a Zn⋯Zn distance of 13.296 (9) Å (Fig. S4). Two types 1D linear chains are cross-linked into complicated 3D network. The adjacent ten zinc(II) ions are connected by L2 and $DCTP^{2-}$ ligands to form a 3D single cage unit which delimited by four cyclohexane-like frames in a chair conformation (Fig. 2b). CP **2** can be considered as a 4-connected **dia** topology (Fig. 2d). Further, the CP **2** displays a