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Coordination Assemblies of Zn(II) Coordination Polymers: Positional Isomeric Effect and Optical Properties

Chang-Jie Liu, Tong-Tong Zhang, Wei-Dong Li, Yuan-Yuan Wang and Shui-Sheng Chen *

School of Chemistry and Chemical Engineering, Fuyang Normal University, Fuyang 236041, China; liuchangjie0519@163.com (C.-J.L.); ztt18130221327@163.com (T.-T.Z.); weidongli2018@163.com (W.-D.L.); yyyw19856834636@163.com (Y.-Y.W.)

* Correspondence: fyuniv@163.com

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Abstract: Two Zn(II) coordination polymers (CPs) [Zn(L)(pphda)] (1) and [Zn(L)(ophda)]·H$_2$O (2) were prepared by reactions of ZnSO$_4$·7H$_2$O based on the N-donor 1,4-di(1H-imidazol-4-yl)benzene (L) ligand and two flexible carboxylic acids isomers of 1,4-phenylenediacetic acid (H$_2$pphda) and 1,2-phenylenediacetic acid (H$_2$ophda) as mixed ligands, respectively. Structures of CPs 1 and 2 were characterized by elemental analysis, Infrared spectroscopy (IR), thermogravimetric analysis and single-crystal X-ray diffraction. The CP 1 is a fourfold interpenetrating 6$^6$-diamond (dia) architecture, while 2 is a 2D (4, 4) square lattice (sql) layer based on the Zn$_2$(cis-1,2-ophda$^{2-}$)$_2$ binuclear Zn(II) subunits. The luminescent property, including luminescence lifetime and quantum yield (QY), have been investigated for CPs 1 and 2.

Keywords: assembly; coordination polymers; optical properties

1. Introduction

The deliberate design of coordination polymers (CPs) have recently prevailed due to their intriguing structure and potential applications [1–6]. Recently, the luminescent CPs are widely employed to detect guest molecules with high sensitivity and selectivity. For example, Liu et al. has built a microporous luminescent CP {[Zn$_5$(L)$_2$(DMF)$_2$(µ$_3$-H$_2$O)]·2DMF} (H$_5$L = 3,5-di(3′,5′-dicarboxylphenyl)benzoic acid, DMF = N,N-Dimethylformamide), which is stable in air as well as in acidic/basic aqueous media at room temperature. Moreover, the luminescent CP behaves as a luminescent sensor for the highly selective and sensitive detection of Fe$^{3+}$, Fe$^{2+}$, Cu$^{2+}$ and Ag$^+$ ions and o-nitrophenol (MNP), p-nitrophenol (PNP), 2,4-dinitrophenol (DNP), 2,4,6-trinitrophenol (TNP) and 4-nitrotoluene (4-NT) [7]. However, the successful assembly of CPs have faced great challenges in crystal engineering, because many factors have affected the resulting structures, such as rational choice of the bridging ligand and metal centers, temperature, solvent, pH value and the nature of anions [8–12]. Above all, the reasonable design of ligands is the most key factor. Generally speaking, the length, rigidity, functional groups, coordination modes, or substituent groups of organic molecules have great effects on the resulting frameworks of CPs [13,14]. According to the previous studies, the N-donor and O-donor organic compounds are two kinds of the most important ligands, which have been widely used to construct various CPs because of their rich coordination modes, and modifiable backbones [15,16]. Noticeably, rigid rod-type ligands such as bipyridine (bpy), terephthalic acid or their analogues, often employ as linear pillars to construct entangled CPs [17,18]. Besides the rigid ligands, the flexible ligands including flexible N-donor (4-pyridyl)ethane (bpe), (4-pyridyl)propane (bpp), 1,2-bis(4-pyridyl)ethylene (bpec), and O-donor 1,4-phenylenediacetic acid (H$_2$pphda) and 1,2-phenylenediacetic acid (H$_2$ophda) have different shapes associated with the trans
or gauche conformation, favoring the formation of interesting topologies [19–22]. In our previous study, we have synthesized a rigid multi-N-donor 1,4-di(1H-imidazol-4-yl)benzene (L) ligand and employed to build porous coordination polymer with favorable gas adsorption properties [23]. Moreover, the N-donor ligand exhibit good compatibility with O-donor carboxylic acids, as a result, a number of diverse CPs have successfully been built based on the system of imidazole and polycarboxylates [24,25]. As our continual work, we have chosen the N-donor ligand together with two auxiliary carboxylic acid isomers (H$_2$pphda and H$_2$ophda) to build two Zn(II) coordination polymers. Obviously, we expect to investigate the effect for auxiliary carboxylic acid isomers with position isomerism of functional groups. In this contribution, we report two Zn(II) CPs of [Zn(L)(pphda)] (1) and [Zn(L)(ophda)]·H$_2$O (2), based on the reactions of ZnSO$_4$·7H$_2$O with mixed ligands of L and H$_2$pphda, H$_2$ophda, respectively.

2. Materials and Methods

2.1. Materials and Physical Techniques

All the reagents were purchased from Jinan Henhua company (Jinan, China), and the N-donor L organic ligand was prepared on the basis of the reported literature [23]. Infrared spectrum (IR) was investigated a Bruker Vector 22 fourier transform infrared spectrophotometer (Instrument Inc., Karlsruhe, Germany). Perkin-Elmer 2400 elemental analyzer was used to complete elemental analyses (PerkinElmer, Waltham, MA, USA). The UV/vis spectra were recorded using a computer-controlled PE Lambda 900 UV/vis spectrometer (PerkinElmer, Massachusetts, MA, USA). Thermogravimetric analyses (TGA) were analyzed by a simultaneous 2960 thermal analyzer (Thermal Analysis Instrument Inc., New Castle, DE, USA) under nitrogen atmosphere with a heating rate of 5 °C min$^{-1}$. The photoluminescence spectra, decay lifetimes and quantum yield in solid state were carried out using HORIBA FluoroMax-4 fluorescence spectrophotometer (Horiba, Kyoto, Japan).

2.2. Synthesis of [Zn(L)(pphda)] (1)

A mixture of ZnSO$_4$·7H$_2$O (28.7 mg, 0.1 mmol), L (21.4 mg, 0.1 mmol), H$_2$pphda (19.4 mg, 0.1 mmol) and H$_2$O (15 mL) was added in the mixed solution of water and N,N-dimethylformamide (DMF) (10 mL, v:v = 9:1), adjusted to neutral solution with NaOH solution (0.025 mol L$^{-1}$). The mixture was then placed in a 25 mL glass tube and reacted at 100 °C for 48 hours, and was cooled to ambient temperature by reducing 10 °C/h, colorless block crystals of 1 were obtained (yield: 66%). Analytically calculated (Anal. Calcd) for C$_{22}$H$_{18}$N$_4$O$_4$Zn(%): C, 56.49; H, 3.88; N, 11.98. Found: C, 56.32; H, 3.99; N, 11.82. IR (KBr pellet, cm$^{-1}$): 3385(m), 3410(m), 3124(m), 2725(m), 1636(m), 1610(vs), 1539(s), 1481(s), 1422(m), 1361(m), 1262(m), 1145(m), 1078(s), 968(m), 951(s), 838(m), 781(m), 692(w), 650(m), 485(s).

2.3. Synthesis of [Zn(L)(ophda)]·H$_2$O (2)

A similar synthesis procedure as 1 was employed to obtain 2, except that the isomer of H$_2$opyda (19.4 mg, 0.1 mmol) replaced H$_2$ppyda. A new compound of 2 were collected in a 62% yield. Anal. calcd for C$_{22}$H$_{20}$N$_4$O$_5$Zn (%): C, 54.39; H, 3.99; N, 11.82. IR (KBr pellet, cm$^{-1}$): 3435(vs), 1648(m), 1577(s), 1395(m), 1378(m), 1283(w), 1176(w), 1138(w), 1078(w), 969(m), 859(w), 844(m), 720(w), 647(w), 628(w), 585(w), 531(w), 489(w), 422(w).

2.4. Crystallographic Data Collection and Refinements

The data collections for CPs 1 and 2 were measured on a Bruker SMART APEX II (Bruker, Karlsruhe, German) with Mo Kα radiation (λ = 0.71073 Å) at 296(2) K. The diffraction data were integrated by using the SAINT program [26]. Absorption corrections were performed by multiscan absorption corrections using the SADABS program [27]. The structure were solved and refined using the OLEX2 program suite, equipped with ShelXT and ShelXL programs [28]. All non-hydrogen atoms were located from Fourier map directly by ShelXT and refined anisotropically. Hydrogen atoms on all non-hydrogen atoms were placed in calculated positions, and their coordinates and displacement...
parameters were constrained to ride on the carrier atoms. Hydrogen atoms of the water molecule were located from electron density maps. The crystal parameters and relevant bond lengths and angles are summarized in Table 1 and Table S1. Cambridge Crystallographic Data Centre (CCDC) numbers of 1959066 for 1 and 1959068 for 2. (See Supplementary Materials)

Table 1. Crystallographic data for coordination polymers 1 and 2.

| Crystal Parameter | 1                  | 2                  |
|-------------------|--------------------|--------------------|
| Empirical formula | C$_{22}$H$_{18}$N$_4$O$_4$Zn | C$_{22}$H$_{20}$N$_4$O$_5$Zn |
| Formula weight    | 467.77             | 485.81             |
| Temperature / K   | 296(2)             | 296(2)             |
| Crystal system    | Orthorhombic       | Triclinic          |
| Space group       | P nna              | P-1                |
| a / Å             | 12.3264(11)        | 10.6434(11)        |
| b / Å             | 21.1865(17)        | 10.7143(11)        |
| c / Å             | 7.7490(6)          | 11.7601(12)        |
| α / °             | 109.8560(10)       |                    |
| β / °             | 102.1290(10)       |                    |
| γ / °             | 110.4050(10)       |                    |
| Mu (mm$^{-1}$)    | 1.252              | 1.161              |
| V (Å$^3$)         | 2023.7(3)          | 1097.0(2)          |
| Z, Dcalc / (Mg/m$^3$) | 4.1.535          | 2.1.471            |
| F(000)            | 960                | 500                |
| θ range / °       | 1.92–27.54         | 1.98–26.00         |
| Reflections collected | 113,01            | 8830               |
| Independent reflections | 2324             | 4685               |
| Goodness-of-fit on F$^2$ | 1.100           | 1.056              |
| R$_{int}$         | 0.0145             | 0.0147             |
| R$_1$ [I > 2σ (I)]$^a$ | 0.0324        | 0.0260             |
| wR$_2$ [I > 2σ (I)]$^b$ | 0.0907        | 0.0752             |

$^a$ R$_1 = \Sigma||F_o|| - |F_c||/\Sigma|F_o|$. $^b$ wR$_2 = \Sigma w(|F_o|^2 - |F_c|^2)/\Sigma w(F_o)^2$,$^{1/2} \Sigma$, where $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$. P = (F$_o^2 + 2F_c^2)/3$.

3. Results

3.1. Structural Descriptions

3.1.1. Structure of [Zn(L)(pphda)] (1)

The Zn(II) atom lies on a glide and shows a distorted tetrahedral configuration from two O atoms (O1, O1A) from two pphda$^{2-}$ anions, as well as two N atoms (N1, N1A) from two separate L ligands (Figure 1a). The Zn–N bond length is 2.009(2) Å and Zn–O bond length is 2.0067(18) Å, and the coordination angles around Zn1 ranges from 89.98(11) to 121.23(8)°. The carboxyl groups from pphda$^{2-}$ anions adopt trans conformation to coordinate with two Zn(II) atoms with the angle of –CH$_2$– of 111.82°, and this coordination mode is consistent with the reported literature [29]. In 1, each pphda$^{2-}$ anion acts as a linear ligand to bridge two Zn(II) ions in a bi-µ$_1$-η$^1$-η$^0$-monodentate mode to give rise to a one-dimensional (1D) chain (Zn(II)/pphda$^{2-}$ chain) with the Zn···Zn distance of 12.12 Å (Figure 1b). The L ligands also link Zn(II) atoms to form 1D zigzag Zn(II)/L chain with a Zn···Zn distance of 13.772(8) Å. The combination of the 1D chains of Zn(II)/pphda$^{2-}$ and Zn(II)/L produce three-dimensional (3D) structure for 1. Notably, each Zn(II) atom is linked by two L ligands and two pphda$^{2-}$ anions into an adamantanoid cage (Figure 1c). This single large adamantane gives a huge chamber, which allows another three independent equivalent networks to interpenetrate mutually, forming a fourfold interpenetrating 3D 6$^6$-dia architecture (Figure 1d,e) [30,31].
3.1.2. Structure of \([\text{Zn(L)(ophda)}]\)·\(\text{H}_2\text{O}\) (2)

When auxiliary 1,4-phenylenediacetic acid was replaced by its isomer of 1,2-phenylenediacetic acid in the reaction of \(\text{pphda}^2\)·\(\text{H}_2\text{O}\), compound 2 was produced. The geometric midpoints of the aromatic L-rings lie on inversion centres. The asymmetric unit contains one Zn(II) atom, two halves of L ligands, one ophda\(^2\)\(^{-}\) ligand, and one lattice water molecule. As shown in Figure 2a, the central Zn(II) atom coordinates with two N atoms (N1, N3) from two distinct L ligands and two O atoms (O1, O3A) from cis-ophda\(^2\)\(^{-}\) ligands, with Zn–N bond lengths of 2.0197(16) and 2.0205(16) Å and Zn–O ones of 1.9652(14) and 1.9673(13) Å (Table S1). Different from the pphda\(^2\)·\(\text{H}_2\text{O}\) ligand, the ophda\(^2\)\(^{-}\) is a flexible ligand and uses its two carboxylate groups in \(\mu_1\)-η\(^1\)::η\(^0\)-monodentate cis-conformation to link two Zn(II) atoms. Two different cis-1,2-ophda\(^2\)\(^{-}\) ligands utilize four carboxylate groups to link two Zn(II) atoms, forming a binuclear \(\text{Zn}_2\text{(cis-1,2-ophda}^2\text{)}_2\) unit with Zn–Zn distance of 5.608(5) Å. In 2, each \(\text{Zn}_2\text{(cis-1,2-ophda}^2\text{)}_2\) binuclear unit connects other four same ones by linear L molecules via Zn–N coordination, forming a 2D (4, 4) layer by taking \(\text{Zn}_2\text{(cis-1,2-ophda}^2\text{)}_2\) as 4-connectors and the linear L ligands as two-connectors (Figure 2b,c). The rich intermolecular hydrogen bond pattern includes O–H···O, N–H···O and C–H···O (N(4)–H(4) 0.8600 Å, H(4)···O(2) 1.9000 Å, N(4)–O(2) 2.753(2) Å, N(4)–H(4)···O(2) 170°; C(8)–H(8) 0.9300 Å, H(8)···O(4) 2.5000 Å, C(8)–O(4) 3.366(3) Å, C(8)–H(8)···O(4) 155°; C(5)–H(5) 0.9300 Å, H(5)···O(4) 2.5800 Å, C(5)–O(4) 3.468(2) Å, C(5)–H(5)···O(4) 159°; C(12)–H(12) 0.9300 Å, H(12)···O(2) 2.3900 Å, C(12)–O(2) 3.162(2) Å, C(12)–H(12)···O(2) 140°) (Figure 2d, Table S2).

![Figure 1](image-url)

**Figure 1.** (a) Zn(II) coordination environment of 1 with the ellipsoids drawn at the 50% probability level. Symmetry codes: A x, 0.5 − y, 0.5 − z; B 2 − x, 1 − y, −z. (b) The 1D zigzag \([\text{Zn(L)}]_n\) and \([\text{Zn(ophda)}]_n\) chain. (c) View of perspective and simplified single diamond motif in 1 (green line: L; yellow line: pphda\(^2\)\(^{-}\)). (d) 3D framework structure of 1. (e) Fourfold interpenetrating dia net of 1.
The UV–vis absorption spectra were recorded for the two crystalline materials (Figure 3a). The UV–vis show absorption bands ranging from 250 to 300 nm in the UV region, which belongs to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ intraligand transitions arising from the ligand [32]. The weak absorption of CP 1 are observed around 550 nm, which is probably a result of the d–d spin-allowed transition of the $d^{10}$ (Zn$^{2+}$) ion [33]. The description and literature have been supplemented in the revised manuscript. Furthermore, the values of band gaps ($E_g$), which was determined as the intersection point between the energy axis ($h\nu$) and the line derived from the linear portion of the absorption edge in a plot of the K-M (Kubelka–Munk) theory $F$ vs the incident photon energy $h\nu$ [34], are estimated as 3.56 eV.
for 1 and 3.55 eV for 2 (Figure 3b), indicating that the as-synthesized crystalline materials are optical semiconductors [35,36].

\[ t = A \exp\left(-\frac{t}{\tau}\right) \]

**Figure 3.** The UV-Vis spectra (a) and the corresponding Eg values (b) for the CPs 1 and 2.

### 3.4. Photoluminescent Property

Coordination polymers comprising of d<sup>10</sup> metal centers and π-conjugated organic ligands have potential photoluminescent property [37–39]. The fluorescence properties of CPs 1 and 2, together with the L ligand have been tested (Figure 4). As illustrated in Figure 4, organic L molecules exhibit emission band at 445 nm (\( \lambda_{ex} = 370 \text{ nm} \)), belonging to \( \pi^* \rightarrow \pi \) intraligands transition [40,41]. CPs 1 and 2 show emission maxima at 427, and 439 nm upon excitation at 368, and 367 nm. In comparison with the free L ligand, the emission bands of CPs 1 and 2 are 18, 6-nm blue-shifted. The emissions of these CPs 1 and 2 may belong to the intraligand fluorescence because of their similarity between their emission of CPs and the free L ligand [42,43]. Furthermore, the study of decay lifetimes and quantum yield (QY) will be further investigated (Figure 5). The luminescence lifetimes based on exponential function as \( I(t) = A \exp(-t/\tau) \) for 1 and 2 are 14.09, and 15.11 ns (Figure 5b,d) [44], and the shorter luminescence lifetimes are attributable to the characteristic of a singlet state, rather than a triplet state (>10<sup>−3</sup> s) [45]. Moreover, the corresponding QY values of CPs 1 and 2 are 2.42% and 3.23% (Figure 5a,c), respectively.

**Figure 4.** Fluorescence spectra of CPs 1, 2 and L.
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The authors declare no conflicts of interest.

Supplementary Materials:

The following are available online at http://www.mdpi.com/xxx/s1, Table S1: The crystal parameters of 1 and 2, Table S2: hydrogen bonds, Figure S1: Thermal Analyses, Figure S2: X-Ray Powder Diffraction Analyses.

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