Synthesis, Structure and Photoelectric Property of a 3D Supramolecular Zinc Coordination Polymer Postprint

Authors: LUO Ya-Nan, LIU Zhi-Chen, Jiang Hui-Ying, YU Li-Ying, Xiao-Yang Yu

Date: 2017-11-05T00:00:00+00:00

Abstract

Using a rigid azo ligand 4-[(8-hydroxy-5-quinolinyl)azo]-benzoic acid (H2L), a new supramolecular compound [Zn(L)(H2O)2]n (1) has been solvothermally synthesized and structurally characterized by X-ray single-crystal diffraction, infrared spectrum, elemental analysis, power X-ray diffraction and thermal analysis. Compound 1 crystallizes in monoclinic, space group C2/c with a = 30.372(8), b = 11.415(3), c = 9.248(3) Å, = 106.94(3)°, V = 3067.20(15) Å3, C16H13N3O5Zn, Mr = 392.66, Z = 8, Dc = 1.701 Mg/m3; F(000) = 1600, = 1.636 mm−1, reflections collected: 7290, reflections unique: 2735, Rint = 0.0282, R = 0.0351, wR (all data) = 0.0919, GOOF on F2 = 1.036. Compound 1 exhibits a one-dimensional (1D) zig-zag chain structure connected into a three-dimensional (3D) supramolecular network through hydrogen bonding interactions. Fluorescent property and electrochemical property were detected on compound 1.

Full Text

Preamble

Synthesis, Structure and Photoelectric Property of a 3D Supramolecular Zinc Coordination Polymer

Authors: LUO Ya-Nan, LIU Zhi-Chen, JIANG Hui-Ying, YU Li-Ying, YU Xiao-Yang

Affiliation: College of Chemical and Pharmaceutical Engineering, Jilin Institute of Chemical Technology, Jilin 132022, China

ABSTRACT

Using the rigid azo ligand 4-[(8-hydroxy-5-quinolinyl)azo]-benzoic acid (H L), a new supramolecular compound [Zn(L)(H O)] (1) has been solvothermally synthesized and structurally characterized by single-crystal X-ray diffraction, infrared spectroscopy, elemental analysis, powder X-ray diffraction, and thermal analysis. Compound 1 crystallizes in the monoclinic space group C2/c with a = 30.372(8), b = 11.415(3), c = 9.248(3) Å, = 106.94(3)°, V = 3067.20(15) Å³, C H N O Zn, M = 392.66, Z = 8, Dc = 1.701 Mg/m³, F(000) = 1600, = 1.636 mm ¹. A total of 7290 reflections were collected, yielding 2735 unique reflections with R = 0.0282, R = 0.0351, wR(all data) = 0.0919, and GOOF on F² = 1.036. Compound 1 exhibits a one-dimensional (1D) zig-zag chain structure that extends into a three-dimensional (3D) supramolecular network through hydrogen bonding interactions. The fluorescent and electrochemical properties of the compound were also investigated.

Keywords: coordination polymer; co-sensitization; solar cell; fluorescent property; electrochemical property

1. INTRODUCTION

Over the past decade, supramolecular coordination polymer materials constructed from organic bridging ligands and transition metal ions have attracted considerable attention due to their diverse architectures and potential applications in molecular recognition, sensing, photology, and electrochemistry [1-5]. In the construction of these materials, the rational selection and design of multifunctional organic ligands is crucial for achieving desired functions [6-9]. The azo ligand 4-[(8-hydroxy-5-quinolinyl)azo]-benzoic acid represents a promising candidate for several reasons [10-14]: (i) it possesses multiple coordination sites, enabling versatile coordination modes; (ii) the presence of both oxygen and nitrogen atoms allows it to serve as hydrogen bond donors or acceptors, facilitating the assembly of various supramolecular structures; and (iii) the quinoline ring exhibits strong chelating ability toward metal ions due to the ortho arrangement of the hydroxyl group and nitrogen atom.

In recent years, metal-organic coordination polymers with optical properties have been explored as spectral sensitizers in dye-sensitized solar cells (DSSCs) [15]. Notably, the Grätzel group successfully co-sensitized nanocrystalline TiO films with squarylium cyanine and bisthiophene dyes, achieving a photoelectric conversion efficiency of 7.43%—the highest value reported thus far for DSSCs co-sensitized with metal-organic coordination polymers [16]. Based on these considerations, H L appears to be an excellent ligand for constructing supramolecular coordination polymer materials with diverse structures, excellent fluorescent performance, and favorable electrochemical properties.

2. EXPERIMENTAL

2.1 Materials and Instruments

Infrared spectra (KBr pellets) were recorded on a Nicolet Impact 410 FT-IR spectrometer in the 4000–400 cm ^{1} range. Elemental analyses for C, H, and N were performed on a Perkin-Elmer 2400 Elemental Analyzer. Powder X-ray diffraction (PXRD) patterns were obtained on a Siemens D5005 diffractometer using Cu-K radiation (= 0.15418 nm) with a graphite monochromator. Thermogravimetric analyses (TGA) were carried out on a Perkin-Elmer TGA 7 thermogravimetric analyzer at a heating rate of 10 °C min ^{1} under N atmosphere. Fluorescence properties were measured using an LS55 luminescence spectrometer. Electrochemical impedance measurements were performed on a CHI660D electrochemical workstation with a three-electrode system in the dark, with a frequency range of 0.05–10 Hz and applied potential between 0–0.700 V. Photocurrent-photovoltage (J-V) curves of sealed cells were measured under AM 1.5 illumination (100 mW cm ^{2}) using a solar simulator.

The fill factor (FF) and photoelectric conversion efficiency ( ) are defined as: - FF = (J × V)/(J × V) - = (FF × J × V)/P

where J and V are the photocurrent density and photovoltage at maximum power output, J and V are the short-circuit photocurrent density and open-circuit photovoltage, respectively, and P is the incident light power.

2.2 Synthesis of [Zn(L)(H O)]

A mixture of ZnCl (30 mg, 0.22 mmol), H L (5 mg, 0.015 mmol), ethanol (10 mL), H O (2 mL), and dimethylformamide (DMF, 2 mL) was stirred at 25 °C until a clear red solution formed. After 2 hours, the pH was adjusted to 5.0 using 2 mol/L NaOH. The mixture was sealed in a 25 mL Teflon-lined stainless-steel vessel and heated at 100 °C for 3 days, followed by cooling to 25 °C over 18 hours using a programmed cooling ramp. Red block crystals were filtered, washed with deionized water, and dried in air. Yield: 50% based on Zn.

Elemental analysis calculated (%) for C H N O Zn (392.66): C, 48.89; H, 3.31; N, 10.69. Found: C, 47.54; H, 3.03; N, 10.12%. IR (KBr pellet, /cm ^{1}, Fig. S1): 3448 (s), 1602 (w), 1540 (m), 1502 (s), 1516 (s), 1466 (s), 1409 (s), 1398 (s), 1386 (s), 1253 (m), 1189 (s), 1131 (s), 1035 (m), 852 (w).

2.3 Structure Determination

A red single crystal of dimensions 0.30 mm × 0.10 mm × 0.10 mm was mounted on a Bruker Apex II CCD area-detector diffractometer (MoK , = 0.71070 Å) at 293 K. A total of 7290 reflections were collected using - scans at room temperature, yielding 2735 independent reflections (R = 0.0282), of which 2319 were observed with I > 2 (I). Empirical absorption corrections were applied using the SADABS program. The structure was solved by direct methods (SHELXS-97) [17] and refined by full-matrix least-squares techniques on F^{2}. All non-hydrogen

atoms were refined anisotropically. Hydrogen atoms were placed geometrically using the OLEX2 program [18]. Final refinement parameters: R = 0.0351, wR = 0.0919 (w = 1/[²(F ²) + (0.0447P)² + 3.2819P], where P = (F ²)/3), (Δ/) = 0.002, S = 1.036, (Δ) = 0.581 and (Δ) = -0.443 e/Å³. Selected bond lengths and angles are given in Table 1 , and hydrogen bond parameters in Table 2 .

2.4 Fabrication of DSSCs

TiO film area: 0.25 cm². Film electrodes were immersed in a compound 1 solution (5 × 10 M in absolute ethanol) for 3 h at room temperature, then in N719 solution (5 × 10 M in 1:1 acetonitrile/absolute ethanol) for 20 h at room temperature. The co-sensitized films were dried in air. Counter electrodes were prepared by thermal platinization (5 mM H PtCl in dry isopropanol, heated at 400 °C for 10 min). The electrolyte consisted of 0.5 M LiI, 0.05 M I , and 0.1 M 4-tert-butylpyridine in 1:1 acetonitrile-propylene carbonate (volume ratio).

---

3. RESULTS AND DISCUSSION

3.1 Crystal Structure

Compound 1 was synthesized from ZnCl and H L under solvothermal conditions. Single-crystal X-ray diffraction analysis reveals that 1 crystallizes in the monoclinic space group C2/c and exhibits an infinite 1D zig-zag chain structure. As shown in Fig. 1 [Figure 1: see original paper], the asymmetric unit contains one Zn(II) atom, one L² ligand, and two coordinated water molecules. The Zn1 atom is five-coordinated by four oxygen atoms (O(1) , O(3), O(4), O(5)) and one nitrogen atom (N(3)), forming a slightly distorted square pyramidal geometry. The atoms O(1) , O(3), O(4), and N(3) define the basal plane, while O(5) occupies the apical position (Fig. S2). The Zn–O/N bond distances (1.988(2)–2.096(2) Å) are comparable to those in related Zn(II) complexes [19].

Each L² ligand provides three donor atoms for coordination. The carboxylate group adopts a monodentate coordination mode (Scheme S1). The ligand exhibits a -terdentate binding mode in which the 8-hydroxyquinoline group chelates one Zn(II) cation while the carboxylate group coordinates to a second Zn(II) cation in a monodentate fashion. As shown in Fig. 2 [Figure 2: see original paper], Zn(II) cations are linked by L² ligands into infinite zig-zag chains along the a axis with a Zn ··· Zn separation of approximately 29.06 Å.

In the crystal packing, adjacent zig-zag chains interact through hydrogen bonds to form a 3D supramolecular network. The 1D chains are connected via O–H ··· O interactions (d(O(4) ··· O(1)) = 2.751(3) Å, O(4)–H(4A) ··· O(1) = 153°; d(O(5) · · · O(2)) = 2.767(3) Å, O(5)–H(5A) · · · O(2) = 159°) to generate a 2D layered structure (Fig. 3(a) [Figure 3: see original paper]). Additionally, O(5) acts as a hydrogen bond donor to O(2) from neighboring layers, forming

a 3D supramolecular network (d(O(5) ··· O(2)) = 2.581(3) Å, O(5)-H(5B) ··· O(2) = 164°) (Fig. 3(b) [Figure 3: see original paper]).

Phase purity of the bulk material was confirmed by comparing its PXRD pattern with the simulated pattern from single-crystal data (Fig. S3). The TGA curve for compound 1 is provided in the Supporting Information (Fig. S4). The material loses its two coordinated water molecules between 110–210 °C (experimental: 8.56%, calculated: 9.19%). A total mass loss of 52.96% from 370–990 °C corresponds to decomposition of the L² ligand (calculated: 53.60%).

3.4 Fluorescent Property

The solid-state fluorescent properties of compound 1 and the H L ligand were measured at room temperature under identical conditions. As shown in Fig. 4 [Figure 4: see original paper], the free ligand exhibits an emission maximum at 381 nm upon excitation at 220 nm, attributable to - * or n- * intraligand electronic transitions, including the -N=N-based - * transition [20]. Compound 1 displays an emission maximum at 384 nm when excited at 222 nm, with similar emission characteristics that can be primarily assigned to intraligand electronic transfer.

3.5 Electrochemical Property

Photoelectric conversion efficiency measurements were performed for compound 1. Fig. 5 [Figure 5: see original paper] shows the photocurrent-photovoltage curves of DSSCs based on compound 1/N719/TiO and N719/TiO photoanodes. The photovoltaic performance of the DSSC with the compound 1/N719/TiO photoanode shows significant improvement compared to the N719/TiO device. The short-circuit photocurrent density (J), open-circuit photovoltage (V), fill factor (FF), and photoelectric conversion efficiency ( ) increase from 10.58 mA · cm ², 648 mV, 0.49, and 3.45% to 11.71 mA · cm ², 678 mV, 0.57, and 4.5%, respectively.

The H L ligand is a rigid molecule containing both benzene and quinoline rings. In compound 1, each 1D zig-zag chain is connected to adjacent chains through hydrogen bonds to form a 3D supramolecular network. These structural features endow compound 1 with an extended -conjugated system and a highly rigid framework exhibiting excellent aggregation-induced emission (AIE) properties. The enhanced photovoltaic performance indicates that co-sensitization with compound 1 and N719 facilitates electron transfer and collection. The increased J arises from improved light harvesting in the DSSC. While N719 absorbs primarily at 550 nm in the visible region, the combination with compound 1 enhances absorption intensity in the 300–400 nm range, leading to higher light harvesting efficiency. The improved FF suggests lower electron transfer resistance at the compound 1/N719/TiO interface compared to N719/TiO . These results indicate that the HOMO and LUMO levels of compound 1 are well-matched with the TiO conduction band energy level. Overall, co-sensitization

with compound 1 and N719 enhances DSSC efficiency by extending absorption into the 300–400 nm region.

4. CONCLUSION

In summary, a novel supramolecular zinc coordination polymer has been successfully synthesized under solvothermal conditions. Photoelectric conversion efficiency measurements demonstrate a definite improvement for the compound 1/N719/TiO photoanode compared to N719/TiO alone. Modification of the TiO electrode with both compound 1 and N719 not only extends the photoresponse of the DSSC into the UV region of the solar spectrum but also enhances optical absorption intensity. The fluorescent and electrochemical properties of compound 1 suggest its potential applications in photology and electrochemistry.

REFERENCES

1. Long, J. R.; Bloch, E. D.; Britt, D.; Lee, C.; Donna, C. J.; Uribe-Romo, F. J.; Furukawa, H.; Yaghi, O. M. Metal insertion in a microporous metal-organic framework lined with 2,2 -bipyridine. *J. Am. Chem. Soc.* 2010, 132, 14382–14384.

2. Zhang, D. D.; Zhou, X. B.; Jian, L. J.; Lin, M. J.; Li, H. P.; Chen, J. X.; Zhang, Z. C. Synthesis, structure and norbornene polymerization catalyzed by bis{(2-benzhydryl-4,6-dimethyl-phenyl)-(3,5-di-tert-butyl-2-methyl-benzylidene)-amine-N,O}nickel(II). *Chin. J. Struct. Chem.* 2017, 36, (page numbers not provided in original).

3. Tan, X. W.; Li, C. H.; Li, H. F.; Yang, Y. Q. Synthesis, electrochemical and fluorescent properties of a new zinc(II) complex through self-assembly reaction of 2,2 -bipyridine-3,3 -dicarboxylic acid. *Chin. J. Struct. Chem.* 2017, 36, 310-315.

4. Wu, L.; Guo, X. L.; Wang, Z. J.; Chen, J. X. Syntheses, crystal structure, and fluorescent property of a new (4,10)-connected 3D Cd(II) coordination polymer. *Chem. Lett.* 2015, 44, 451–453.

5. Zhang, C. L.; Zheng, H. G. Synthesis, crystal structure and fluorescent property of one Zn(II) complex with 1,3-bis(imidazol-1-yl)benzene and 1,3-benzenedicarboxylate. *Chin. J. Struct. Chem.* 2016, 35, 1070-1076.

6. Luo, Y. N.; Xu, X. Z.; Sun, F. X.; Yu, X. Y.; Zhang, X.; Zhang, T.; Yu, L. Y. Synthesis, structure and properties of two new coordination polymers based on 4-[(8-hydroxy-5-quinolinyl)azo]-benzenesulfonic acid. *Chem. Res. Chin. Univ.* 2014, 30, 27–31.

7. Zhu, X. F.; Zhang, H.; Zhou, Y. H.; Guan, L. Hydrothermal synthesis, crystal structure, and magnetic properties of two new coordination polymers [Ni(IHQS)(4,4 -bipy) . ·(H O)] and [Cu(IHQS)(4,4 -bipy) . ·H O] . *Z. Anorg. Allg. Chem.* 2010, 636, 457–461.

8. Wu, T.; Xu, H. Y.; Kong, F. Z.; Yu, Z. Y.; Wang, R. H. Synthesis and structure of a Mn(II)-triazolyl coordination polymer consisting of dinuclear units. *Chin. J. Struct. Chem.* 2012, 31, 1557–1562.

9. Wang, J. J.; Gou, L.; Hu, H. M.; Han, Z. X.; Li, D. S.; Xue, G. L.; Yang, M. L.; Shi, Q. Z. Ligand and pH-controlled Zn(II) bilayer coordination polymers based on biphenyl-3,3 ,4,4 -tetracarboxylate. *Cryst. Growth Des.* 2007, 7, 1514–1521.

10. Feng, X.; Wang, L. Y.; Wang, J. G.; Xie, C. Z.; Zhao, J. S.; Sun, Q. A unique example of a 3D framework based on the binuclear dysprosium(III) azobenzene-3,5,4 -tricarboxylate with 3,6-connected topology showing ferromagnetic properties. *CrystEngComm.* 2010, 12, 3476–3482.

11. Gu, X. J.; Lu, Z. H.; Xu, Q. High-connected malodorous metal-organic framework. *Chem. Commun.* 2010, 46, 7400–7402.

12. Li, L.; Yang, Y. L.; Fan, R. Q.; Wang, X.; Zhang, Q. M.; Zhang, L. Y.; Yang, B.; Cao, W. W.; Zhang, W. Z.; Wang, Y. Z.; Ma, L. Q. Photocurrent enhanced dye-sensitized solar cells based on TiO loaded K SiW O Co(II)(H O)·xH O photoanode materials. *Dalton Trans.* 2014, 43, (page numbers not provided).

13. Zhang, L. L.; Lu, C. Y.; Chen, S. P.; Yu, F. S.; Li, X.; Tan, J. T.; Yang, X. W. Synthesis, structure and properties of novel 3-D porous lanthanide-3,4 ,5-azobenzenetricarboxylate frameworks. *Inorg. Chem. Commun.* 2011, 14, 143–145.

14. Yu, X. Y.; Cui, X. B.; Zhang, X.; Jin, L.; Luo, Y. N.; Yang, J. J.; Zhang, H.; Zhao, X. A novel 3D cadmium coordination polymer constructed from hydrazine and benzene-1,2,4,5-tetracarboxylic acid: synthesis, structure and fluorescent property. *Inorg. Chem. Commun.* 2011, 14, 848–851.

15. Zhang, L. Y.; Yang, Y. L.; Fan, R. Q.; Wang, P.; Li, L. Enhance the performances of dye-sensitized solar cell by a new type of sensitizer to co-sensitize zinc oxide photoelectrode with ruthenium complex. *Dyes Pigm.* 2012, 92, 1314–1319.

16. Yum, J. H.; Jang, S. R.; Walter, P.; Geiger, T.; Nüesch, F.; Kim, S.; Ko, J.; Grätzel, M.; Nazeeruddin, M. K. Efficient co-sensitization of nanocrystalline TiO films by organic sensitizers. *Chem. Commun.* 2007, 44, 4680–4682.

17. Sheldrick, G. M. *SHELXTL V. 5.10. Structure Determination Software Suite*. Bruker AXS: Madison, 1998.

18. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* 2009, 42, 339-341.

19. Qi, Y.; Che, Y. X.; Zheng, J. M. A zinc(II) coordination polymer constructed from mixed-ligand 1,2-bis(2-(1H-imidazol-1-yl)ethoxy)ethane and 1,4-benzenedicarboxylic acid. *CrystEngComm.* 2008, 10, 1137-1139.

20. Yu, X. Y.; Ye, L.; Zhang, X.; Cui, X. B.; Zhang, J. P.; Xu, J. Q.; Hou, Q.; Wang, T. G. Fluorescent metal-organic polymers of zinc and cadmium from hydrothermal in situ acylation reaction. *Dalton Trans.* 2010, 39, 10617-10625.

Table 1. Selected Bond Lengths (Å) and Bond Angles (°)

Parameter	Value
Zn(1)-O(1)	2.074(2)
Zn(1)-O(4)	2.083(2)
Zn(1)-O(5)	2.024(2)
Zn(1)-O(3)	1.988(2)
Zn(1)-N(3)	2.096(2)
N(1)-N(2)	1.258(3)
O(3)-Zn(1)-O(1)	92.13(8)
O(3)-Zn(1)-O(5)	99.86(9)
O(5)-Zn(1)-O(1)	101.61(8)
O(1) -Zn(1)-O(4)	160.58(8)
O(3)-Zn(1)-O(4)	93.12(9)
O(5)-Zn(1)-N(3)	161.24(10)
O(3)-Zn(1)-N(3)	79.91(8)
O(4)-Zn(1)-N(3)	98.38(8)
O(1) -Zn(1)-N(3)	89.32(8)
O(5)-Zn(1)-O(4)	95.89(9)

Symmetry transformation: i: 0.5+x, 0.5-y, 0.5+z

Table 2. Hydrogen Bond Lengths (Å) and Bond Angles (°)

D-H ··· A	d(D-H)	d(H ··· A)	d(D ··· A)	D-H ··· A
O(4)-H(4A) ··· O(1)	-	-	2.751(3)	153°
O(5)-H(5A) ··· O(2)	-	-	2.767(3)	159°
O(5)-H(5B) ··· O(2)	-	-	2.581(3)	164°

Symmetry codes: iii: 1-x, -y, 1-z; iv: 1.5-x, -0.5+y, 1.5-z; v: x, -y, 0.5+z

Note: Figure translations are in progress. See original paper for figures.