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Photoluminescences and 3D supramolecular structure with unique dimeric Zn (II) units featuring 2-substituted 8-hydroxyquinoline

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ARTICLE INFO

Article history: Received 1 May 2012 Accepted 12 June 2012 Available online 17 June 2012

Keywords: 8-hydroxyquinoline Dimeric zinc(II) Crystal structure Photoluminescent property

ABSTRACT

A 2-substituted-8-hydroxyquinoline ligand (*E*)-2-[2-(4-nitrophenyl)ethenyl]-8-hydroxyquinoline (HL) was synthesized and characterized by ESI-MS, NMR spectroscopy and elemental analysis. Using solvothermal method, a dimeric complex $[Zn_2Cl_2L_2]$ ·2DMF (1) was fabricated by self-assembly of Zn(II) ions with ligand HL, and characterized with single-crystal X-ray diffractions, powder X-ray diffractions (PXRD), thermal analyses (TGA) and elemental analyses (EA). Complex 1 features a lamellar solid constructed by aromatic stacking interactions and nonclassical C-H^{...}O hydrogen bonds. To further investigate the property of the above complex, the photoluminescent properties of 1 are also discussed.

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Since the reports by C. W. Tang and Vanslyke [1], organic lightemitting diodes (OLEDs) have received considerable attention due to their potential application in various displays [2-4]. The organic devices offer clear advantages over inorganic counterparts, such as low cost and high luminous efficiency. These devices are able to produce all emission colors in accordance with a wide selection of organic emitting materials. Over the years, extensive efforts have been devoted to the development of highly efficient OLEDs, especially the white OLEDs. To obtain white emission, various strategies for small-molecule OLEDs have been developed, mainly concerning fabricating multiplayer devices by consecutive evaporation involving three primary colors (blue, green, and red) or two special colors (blue and vellow). However, multiplayer construction of devices will increase the cost of fabrication processes. In order to reduce the cost and obtain white OLEDs with minimal process of fabrication, it would be necessary to discover multifunction and highly efficient yellow light-emitting materials.

Motivated by the success of tris(8-hydroxyquinolinato)aluminum (Alq3) in vacuum-deposited LEDs, organic chelate metal complexes based on 8-hydroxyquinoline derivatives have in particular attracted a lot of attention [5]. Recent reports have suggested that the zinc analog of Alq₃, bis(8-hydroxyquinoline) zinc (II) (Znq₂) complexes may be potential candidates to enhance the electron-transporting properties for OLEDs [6]. Additionally, Sapochak et al. revealed that improvements of EL performance might be achieved by control of the oligomerization of 8-hydroxyquinoline chelates of Zn(II) and/or by improving the PL efficiency by judicious substitution of the ligand [6b]. In contrast, many

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solid EL metal complex materials have only been identified by their chemical compositions rather than their structures. So some of their molecular structures may be much more complicated than their empirical formulae. These Zn(II) complexes may actually be characterized to be dimeric or multinuclear structures in the solid [7]. This fact shows that in the absence of X-ray structures, some conclusions about their luminescence properties may be controversial [8]. Therefore, it is important to obtain the single crystal because X-ray diffraction on single crystals is the best method for providing their molecular structure and packing. On the other hand, in order to retain the excellent photoelectron properties of 8-hydroxyquinoline itself and achieve yellow-light emission, a feasible approach is to modify the 2-, 5- or 7-position of the 8-hydroxyquinoline rings with different functional groups [9]. Inspired by these results, we have focused on the synthesis of multinuclear zinc(II) complexes based on novel substituted 8-hydroxyquinoline [10], which indicated that the trimeric zinc(II) complexes emit yellow luminescence in solution and solid state.

In our continuing efforts to design and synthesize yellow emitting materials, we have obtained some novel substituted 8-hydroxyquinoline ligands successfully, and report herein the syntheses, crystal structure, and luminescence property of one neutral, dimeric Zn(II) complexes, namely $[Zn_2Cl_2L_2]$ ·2DMF (1) [HL = (E)-2-[2-(4-nitrophenyl)]ethenyl]-8-hydroxyquinoline]. The supramolecular structure of 1 features a lamellar solid constructed by aromatic stacking interactions and nonclassical C-H^{...}O hydrogen bonds. We also investigated its thermal stability, fluorescence property, which indicated that 1 emits yellow luminescence at 579 nm in the solid state.

As outlined in Scheme 1, bidentate ligand HL (**2**) [11] was synthesized by Deacetylation of (E)-2-[2-(4-nitrophenyl)ethenyl]-8-acetoxyquinoline [12], which was obtained by the condensation of 8-hydroxyquinaldine

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^{1387-7003/\$ –} see front matter 0 2012 Elsevier B.V. All rights reserved. doi:10.1016/j.inoche.2012.06.015



Scheme 1. Synthesis of ligand HL and complex 1.

with 4-Nitrobenzaldehyde in acetic anhydride. Heating $ZnCl_2$ and HL in a mixture of DMF and MeOH afforded red, block crystals [13]. It was formulated as $Zn_2Cl_2L_2 \cdot 2DMF$ on the basis of X-ray crystallography, elemental analysis and IR spectroscopy.

Single-crystal structure analysis reveals that **1** crystallizes in the triclinic space group P-1 with Z=2 [14]. The asymmetric unit contains one half of a formula unit, that is, one unique Zn(II) atom, ligand L, a chlorine atom and one coordinated DMF molecule (Fig. 1). The structure of **1** is built around a dimeric Zn (II) structure. The zinc atoms (Zn1 and Zn1A) found in the dimeric unit are pentacoordinate, and adopt a trigonal–bipyramidal geometry with the equatorial plane occupied by the NO2 donors of two L ligands and the apical position by one chlorine atom and one oxygen atom of DMF molecule. The bond lengths around Zn(II) are 1.999(2)–2.151(2) for Zn1–0, 2.206(2) for Zn1–N and 2.267(8) for Zn1–Cl, respectively. The two Zn(II) ions are bridged by phenolato oxygen atoms of two L ligands, with the Zn...Zn distance of 3.346(3) Å and the Zn–O–Zn angle of 107.406(5)°. However, complex **1** appears to be neutral, since its hydroxyl groups of coordinated L ligands are deprotoned.

There are significant hydrogen bonds in **1**. Weak nonclassical C–H^{...}Cl intramolecular hydrogen bonds between chlorine atom and the C–H group of DMF (C^{...}Cl=3.376 Å; C–H^{...}Cl=126.0°) as well as intermolecular nonclassical C–H^{...}O hydrogen bonds involving the aromatic C–H groups and oxygen atoms of adjacent 4-nitrophenyl units of ligands L (C^{...}O=3.322 Å; C–H^{...}O=148.0°) play a vital role in the consolidation of the solid structure (Fig. 2). Moreover, it is notable that each cluster of **1** involves abundant intermolecular π ··· π stacking interactions. As shown in Fig. 3, each ligand is parallel to the one in the side of the neighboring unit along the *a* axis, and π ··· π interaction exists between quinoline and 4-nitrophenyl rings with a face-to-face distance of 3.594 Å. By the coactions of the two kinds of noncovalent interactions, the structure extends to a 3D network.

To prove that the crystal structure of dimeric **1** is truly representative of their bulk materials, X-ray powder diffraction (XRPD) experiment was carried out on the as-synthesized samples. As we can see in Fig. 4, the XRPD experimental patterns of 1 are in good agreement with the simulated pattern. The thermal stability of 1 was investigated through thermogravimetric analysis (TGA) experiments (Fig. 5) in the temperature range of 40–800 °C under a flow of nitrogen with heating rate of 10 °C ⋅ min⁻¹. There is no obvious weight loss until 200 °C. On further heating, the complexes decompose rapidly until about 225 °C (weight loss for 1: 15.70%), which well corresponds to the loss of two coordinated DMF molecules (calcd: 15.73%). The weight loss of 7.68% from 422 to 455 °C was due to the release of two coordinated chlorine atoms (calcd 7.65%). The organic groups start to decompose gradually after the temperature increases to 460 °C. From TGA results, the dimeric complex is found to have formed stable five-membered chelate rings, which may be attributed to the fact that the M-N and M-O bonds are highly polarized. [15] Together with the results of the elemental analyses, we can conclude that the synthesized bulk materials of 1 have high purity.

Luminescent properties of compounds HL and 1 were investigated in the solid state at room temperature (Fig. 6). The fluorescent spectra of HL and 1 display maximum emission wavelengths at 536 and 579 nm upon excitation at 370 nm, respectively. The results indicate that the complex 1 has yellow emission, which predominantly originates from metal-to-ligand charge transfer (MLCT) transition in the solid state. However, the corresponding complex 1 exhibits a red shift in the solid state compared with free ligand HL. The results may be attributed to the following two reasons: the coordination of metal ions enhances the mobility of the electron transition in backbone due to back-coupling π -bond between the metal and the ligand, and decreases the electron transition energy of intraligand charge transfer. On the other hand, the ligand is coordinated with metal ions to form additional five-membered rings, which increases the π - π ^{*} conjugation length and the conformational coplanarity, accordingly reduces the energy gap between the π and π^* molecular orbital of the ligand [10]. Finally, the emission peak of compound 1 was red shifted by \approx 37 nm compared to that of Znq2 (542 nm). [16] This red shift is connected to the 2-substituted 2-(4-nitrophenyl)ethenyl



Fig. 1. Perspective views of the coordination geometries of Zn(II) atoms with 50% probability ellipsoids in 1 (H atoms were omitted for clarity).



Fig. 2. The supramolecular structure of 1 mediated by C-H^{...}O hydrogen bonding (yellow dashed lines).

group of ligand HL and the supramolecular interactions in **1**. However, this efficient yellow light-emitting material has potential significance for its employment in the white OLEDs.

In conclusion, a unique dimeric complex was fabricated by selfassembly of Zn(II) ions with a 2-substituted-8-hydroxyquinoline ligand. The supramolecular structure of **1** features a lamellar solid constructed by aromatic stacking interactions and nonclassical $C-H^{...}O$ hydrogen bonds. Additionally, the luminescence properties of compound **1** show that it emits yellow luminescence in solid state. With a precise knowledge of their single-crystal structures, the present research holds great promise in the development of novel multinuclear zinc(II) optical materials, and may contribute to the understanding of structure–property relationships.



Fig. 3. $\pi^{...}\pi$ stacking interactions between quinoline and 4-nitrophenyl rings in **1**.



Fig. 4. XRD patterns of complexes 1.



Fig. 5. TGA curves of complex 1.



Fig. 6. Fluorescent emission spectra of 1 and HL in the solid state at room temperature.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (20802010 and 21172047) and 211 project of Guangdong Province.

Appendix A. Supplementary material

CCDC 878062 contains the supplementary crystallographic data for **1**. The data can be obtained free of charge via <<u>http://www.ccdc.cam.</u> ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax:(+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche. 2012.06.015.

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- [11] Synthesis of (*E*)-2-[2-(4-nitrophenyl)ethenyl]-8-hydroxyquinoline (HL, **2**). A solution of acetoxyquinoline **3** (2.0 g, 6.0 mmol) in pyridine (30 mL) was refluxed for 24 n. After the mixture was cooled and precipitated in distilled water (300 mL). The yellow solid obtained was filtered and washed with water, and dried in vacuo to give compound of **2** (1.63 g, 93%). ¹H NMR (d₆-DMSO, 400 MHz) δ : 9.71 (s, 1H), 8.36–8.28 (m, 4H), 7.96 (d, *J*=8.4 Hz, 2H), 7.82 (d, *J*=8.4 Hz, 1H), 7.72(d, *J*=16.4 Hz, 1H), 7.45–7.37 (m, 2H), 7.11 (dd, *J*=1.6, 7.2 Hz, 1H); ¹³C NMR (d₆-DMSO, 400 MHz) δ : 152.27, 152.11, 147.40, 142.73, 138.04, 136.78, 132.26, 131.54, 128.03, 127.82, 127.65, 124.21, 120.68, 117.77, 110.47. ESI-MS m/z: 293.1 ([M + H]⁺). Anal. calcd for C₁₇H₁₂N₂O₃: C 69.86, H 4.14, N 9.58; found C 69.68, H 4.42, N 9.52.
- [12] Synthesis of (*E*)-2-[2-(4-nitrophenyl]ethenyl]-8-acetoxyquinoline (**3**). To a solution of 8-hydroxyquinaldine (1.35 g, 8.5 mmol) in acetic anhydride (10 mL) was added 4-nitrobenzaldehyde (1.28 g, 8.5 mmol). The mixture was heated under reflux for 16 h. After cooled, it was subsequently poured into ice water (300 mL) and stirred overnight. The yellow solid obtained was filtered and washed with water. The solid residue was recrystallized from CH₂Cl₂ to afford **3** (2.27 g, 80%); ¹H NMR (CDCl₃, 400 MHz) & 8.29-8.24 (m, 2H), 8.19 (d, *J* = 8.4 Hz, 1H), 7.79-7.73 (m, 3H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.53 (d, *J* = 15.6 Hz, 1H), 7.46 (d, *J* = 7.2 Hz, 1H), 2.58 (s, 3H); EI-MS m/z; 335.41 [(M + 1)⁺], 256.48 (M-79)⁺, Ana1. calcd for C₁₉H₁₄N₂O₄: C 68.26, H 4.22, N 8.38; found C 68.15, H 4.52, N 8.63.
- [13] Synthesis of $Zn_2Cl_2L_2 \cdot 2DMF$ (1). A mixture of $ZnCl_2$ (2.7 mg, 0.02 mmol), HL (2.9 mg, 0.01 mmol), H₂O (0.2 mL), DMF (0.5 mL), and MeOH (2 mL) in a capped vial was heated at 65 °C for one day. Yellow blocklike crystals of 1 were filtered, washed with MeOH, and dried at room temperature. Yield: 3.4 mg (75%), elemental analysis: found C: 51.75, H: 3.69, N: 9.05 calculated for ($C_{20}H_{17}ClN_{3}O_4Zn$) C: 51.20, H: 4.02, N:8.86 (%); IR (KBr, ν/cm^{-1}): 3440.76, 1655.76, 1593.98, 1553.42, 1514.08, 1450.79, 1435.46, 1414.72, 1375.01, 1340.10, 1299.56, 1277.43, 1103.11, 1058.51, 964.74, 949.77, 869.25, 838.41, 754.41, 736.05, 699.35, 680.69, 614.40, 579.90, 541.12, 515.36, 476.20.
- 541.12, 515.36, 470.20. [14] Crystal data for compound 1: C₂₀H₁₇ClN₃O₄Zn: FW = 464.19, Triclinic, space group P-1, a = 8.2389(9) Å, b = 10.5174(10) Å, c = 11.6342(13) Å, α = 82.213(4)°, β = 84.905(4)°, γ = 76.176(4)°, V = 968.23(18) Å³, Z = 2, Dcalc = 1.592 mg/m³, λ = 0.71073 Å, T = 293(2) K, R1 (wR2) = 0.0393 (0.0999) [1>2sigma(1)], and 0.0575 (0.1135) [all data], Bruker Smart 1000 CCD are a detector, MoKα radiation. The structure was solved by direct methods and refined on F2 by full-matrix least squares methods using SHELXTL 97. CCDC reference number 878062.
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