Structure and photophysical properties of a dimeric Zn(II) complex based on 8-hydroxyquinoline group containing 2,6-dichlorobenzene unit

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A B S T R A C T

A novel 2-substituted-8-hydroxyquinoline ligand (E)-2-[2-(2,6-dichlorophenyl)ethenyl]-8-hydroxyquinoline (HL) was synthesized and characterized by ESI-MS, NMR spectroscopy, and elemental analysis. Using solvothermal method, a dimeric complex (ZnL2)2 (1) was fabricated by self-assembly of Zn(II) ions with ligand HL. X-ray structural analysis shows that 1 exhibits a binuclear core, which is bridged by two 8-hydroxyquinoline rings. The supramolecular structure of 1 features a lamellar solid constructed by aromatic stacking interactions, Cl···Cl interactions and nonclassical C···H···Cl hydrogen bonds derived from 2,6-dichlorophenyl group of the ligand HL. The aggregation behavior of zinc salts and HL in solutions was investigated with a variety of techniques, including 1H NMR, UV–vis, and photoluminescence (PL). In addition, we also studied the photophysical properties of compound 1 by UV–vis and PL. The experimental results show that the complex 1 emits yellow luminescence in the solid state.

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1. Introduction

Initially the 8-hydroxyquinoline ligand has been mainly applied for analytical purposes and separation techniques. Due to the extraordinary coordinating abilities, this ligand is an excellent reagent for spectrophotometric analysis and it can be used for the extraction of metal ions as well as metal ion sensing.1–4 More recently, tris(8-hydroxyquinoline) (Alq3) has attracted significant attention due to their excellent solid-state properties including good electron mobility and high luminescence.5–12 Although Alq3 is often referred to as the ‘archetypal’ electroluminescent material, its structural diversity limits our ability to understand structure–property relationships in detail as organic light-emitting devices (OLEDs). Alq3 has two geometric isomers,13 the meridional (mer-Alq3) and facial (fac-Alq3) forms having C1 and C3 symmetry, respectively. Geometric isomerization and several polymorphic phases identified14,15 suggesting that thin films deposited under different conditions may have structural variations that contribute to device property variations. So 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.

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. In the luminescent complexes reported thus far, the Zn(II) ion is often four-coordinated by two monoanionic bidentate ligands, such as salicylideneamine18 dipyrrin,19 quinolinolate,17 and benzothiazolate,20 although the latter two ligands induce recoordination in the vapor phase to give rise to luminescent multinuclear five- or six-coordinated complexes.17,20,21 However, multinuclear five or six-coordinated zinc(II) complexes with excellent luminescent properties have been little known until now. Recently, Sapochak shows that the symmetry of the tetramer ([Znq2]4) leads to a molecular and electronic structure with significantly different electroluminescence (EL) properties.17 So they propose that improvements of EL performance might be achieved by control of oligomerization of 8-hydroxyquinoline chelates of Zn(II) and/or by improving the PL efficiency by judicious substitution of the ligand. 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.22–27 Inspired by these results, we have focused on the synthesis of multinuclear zinc(II) complexes based on novel substituted-8-hydroxyquinoline, which led to successful fabrication of a trimeric zinc(II) complex emitting yellow luminescence in solution and solid state.

We report here the assembly of a novel lamellar solid based on novel dimeric zinc(II) complex by combination of coordination, π···π stacking interactions, Cl···Cl interactions, and hydrogen bonds. The aggregation behavior of zinc salts and HL in solutions
was investigated by a variety of techniques, including $^1$H NMR, UV–vis, and PL. We also studied the fluorescence property in solution and solid state. The results showed that complex 1 exhibits a red shift compared with free ligand HL and emits yellow luminescence.

2. Results and discussion

2.1. Synthesis considerations and spectroscopic characterization

As outlined in Scheme 1, bidentate ligand HL was synthesized by sebacelation of (E)-2-[[2-(2,6-dichlorophenyl)ethenyl]-8-acetoxyquinoline, which was obtained by the condensation of $8\text{-Cl}$-quinoline moiety. While a less intense and broader band lies at 7.45 ppm of trans configuration in the vinylene units. Upon mixing 2:1 molar ratio of HL and zinc salt in DMSO-$d_6$, the resonance at 9.71 ppm corresponding to H–O proton of the quinoline. One doublet at 7.87 ppm with a coupling constant $\Delta$ 16.4 Hz, indicates the presence of trans configuration in the vinylene units. Upon mixing 2:1 molar ratio of HL and zinc salt in DMSO-$d_6$, the resonance at 9.71 ppm corresponding to H–O proton of the quinoline gradually disappeared after 1 h. With the passage of time, the resonances in the pyridyl ring of quinoline shifted downfield while the resonances in the phenoxide ring shifted upfield with respect to that of the free ligand. These results indicate the occurrence of the coordination between the ligand HL and Zn(OAc)$_2$ (Fig. 1).

The UV–vis absorption spectra of HL and complex 1 in methanol solution are shown in Fig. 2. The absorption spectrum of HL contains four bands at 205, 240, 283, and 329 nm, whereas the absorption spectrum of 1 contains three bands at 209, 300, and 415 nm. In the absorption spectrum of the ligand HL, the absorption band at 238 nm originates from intraligand $\pi-\pi^*$ transition of quinoline moiety. While a less intense and broader band lies at lower energy (329 nm). As previously reported, this band is associated with a transition in which substantial charge density is transferred from the oxygen atom to the quinoline moiety of the chromophore. The absorption bands of the complex 1 exhibit a red shift comparing to that of HL, which can be attributed to the increasing conjugated degree of the complex 1.

In order to further investigate the interaction mode of ligand HL with Zn$^{2+}$ ion, the coordination reaction of HL with Zn$^{2+}$ ion was monitored through a UV–vis and fluorescence spectroscopic titration. The absorption bands of HL in MeOH dramatically changed upon addition of Zn$^{2+}$ ions. As depicted in Fig. 2, the band of HL showed significant bathochromic shift from 283 to 300 nm. The peak at 329 nm was found to become weak and disappeared in the end in the presence of increasing amounts of Zn$^{2+}$ ion. A new band at 415 nm is attributed to the charge transfer from metal to ligand band. No differences were observed in the absorption spectra after the 1:2 ratio of Zn$^{2+}$/HL, so this experiment clearly indicates the formation of [ZnL$_2$]$.^+_*$ Results from the spectrophotometric titrations were corroborated by titrations followed by emission spectra. As shown in Fig. 3, Addition of Zn$^{2+}$ produced a new emission band centered at 610 nm with increasing intensity, while emission band of ligand at 508 nm decreased simultaneously. This experiment clearly showed that the coordination reached the end point at 1:2

![Scheme 1. Synthesis of ligand HL and complex 1.](image)

![Fig. 1. $^1$H NMR spectra showing the coordination processes of complex 1 (The initial concentration of HL in DMSO-$d_6$ is 0.06 M.](image)

ratio of Zn$^{2+}$/L. Fluorescence photograph was obtained under irradiation of UV light (365 nm). Obvious color change from blue to yellow could be seen by naked eyes. The fluorescence intensity of complex 1 is less than HL. This decrease in intensity may be attributed to the $\pi-\pi^*$ stacking of 1 in DMF solvent, which causes an intersystem crossing to a nonradiative triplet state.
2.3. Structure description

Single-crystal structure analysis reveals that 1 crystallizes in the monoclinic space group $P\overline{2}_1/n$ with $Z=4$. The asymmetric unit contains one half of a formula unit, that is, one unique Zn(II) atom and two ligands L. The structure of 1 is built around a dimeric Zn(II) structure. The zinc atoms (Zn1 and Zn1A) found in the dimeric unit is pentacoordinate, resulting in distorted trigonal bipyramidal geometry. Two of the ligands are involved in bridging through the phenolato oxygens, while the remaining two other ligands are bound to Zn(1) atom only. In detail, the Zn1 atom adopts a trigonal bipyramidal geometry with the equatorial plane occupied by the N2O donors of three ligands around the Zn1 and the apical position by two phenol oxygen atoms (Fig. 4). The bond lengths and angels around Zn(II) are 2.132(3) and 2.222(3) Å for Zn–N, 1.959(3) and 2.206(3) Å for Zn–O, 74.95° and 169.89° for O–Zn–O, 78.58°–135.08° for O–Zn–N, and 105.07° for N–Zn–N, respectively.

There are significant hydrogen bonds in 1. Weak nonclassical C–H–O intramolecular hydrogen bonds between the phenolato oxygen and the C–H group of dichlorophenyl ring or ethenyl (C⋯O=3.170–3.282 Å; C–H⋯O=134.0–151.0°) as well as intermolecular nonclassical C–H⋯Cl hydrogen bonds involving the aromatic C–H groups and Cl– atoms of adjacent 2,6-dichlorophenyl units of ligands HL (C⋯Cl=3.571 Å; C–H⋯Cl=143.0°) play a vital role in the consolidation of the solid structure (Fig. 5b). Moreover, it is notable that each cluster of 1 involves abundant intermolecular π–π stacking interactions. As shown in Fig. 5a, almost all aromatic rings of 1 possess significant face-to-face π–π stacking interactions between the ligands to form 1D chain along b-axis. The chains further extend to a 3D network as a result of intermolecular C–H⋯Cl hydrogen bonds. It is of interest to note that there are two types of Cl⋯Cl interactions in 1 (intramolecular cis Cl⋯Cl geometry, 3.4908(14) Å with $\theta_1=\theta_2=129.66°$; intermolecular trans Cl⋯Cl geometry, 3.6075(14) Å with $\theta_1=\theta_2=117.27°$), which also play an important role in the assembly of the complex 1 in the solid state.
2.4. Photophysical properties

The synthesized product of 1 was characterized by X-ray powder diffraction (XRD). As shown in Fig. 6a, the XRD patterns are very consistent with the results simulated from single-crystal data, illuminating the high purity of the as synthesized sample. Luminescent properties of compounds HL and 1 were investigated in the solid state at room temperature. The fluorescent spectra of HL and 1 display maximum emission wavelengths at 465 and 571 nm upon excitation at 350 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 blue-shift in the solid state compared with free ligand HL. The results may be attributed to the following two reasons: (1) 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; (2) 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 orbitals of the ligand. Additionally, complex 1 shows an obvious blue-shift compared with its solution state. The blue-shift phenomenon may result from the decrease of the excited-state
energy when the solvent molecules get close to photactive metal centers.\textsuperscript{30} In order to further study the photophysical properties of HL and 1, the fluorescence lifetimes of HL and 1 were determined in the solid state. As shown in Fig. 7, the \( \tau \) values are 62, 67 \( \mu \)s, respectively. In addition, the fluorescence quantum yields (FPL) of ligand HL and complex 1 were calculated by comparing the integrated photoluminescence intensities and the absorbancy values of HL (or 1) with the reference quinine sulfate. Quinine sulfate (literature \( \Phi_\text{PL}=0.55 \)) was dissolved in 0.5 M \( \text{H}_2\text{SO}_4 \) (refractive index \( n = 1.33 \)). The samples (HL or 1) were dissolved in DMF (\( n = 1.43 \)). The absorbency was controlled <0.05 for the samples and quinine sulfate. The quantum yield was calculated using the equation below:

\[
\Phi = \frac{\Phi_\text{PL}(0.55) / \text{ST} / \text{ST} / \text{ST})}{\Phi_\text{PL} / \text{ST} / \text{ST} / \text{ST})},
\]

where \( \Phi \) is the quantum yield, \( A \) is the absorbency, \( F \) is the integrated photoluminescence intensity, \( n \) is the refractive index of the solvent, \( S \) is sample, \( ST \) is standard of quinine sulfate (\( \Phi_\text{PL}=0.55 \)). Based on the equation, the quantum yields are calculated as 0.025 and 0.013 for HL and complex 1 in DMF, respectively. This difference in quantum yield is in accordance with the decrease in fluorescence intensity and due to the same reason as discussed above. The quantum yields of HL and 1 less than 0.1 are due to the heavy atom effect of Cl substitution.\textsuperscript{31}

4. Experimental section

4.1. Chemicals and instruments

All of the chemicals are commercial available, and used without further purification. Elemental analyses were performed with an EA1110 CHNS-O CE elemental analyzer. The IR (KBr pellet) spectrum was recorded (400–4000 cm\textsuperscript{-1} region) on a Nicolet Magna 750 FT-IR spectrometer. Powder X-ray diffraction (PXRD) data were collected on a DMAX2500 diffractometer using Cu K\( \alpha \) radiation. The calculated PXRD patterns were produced using the SHELXTL-XPOW program and single-crystal reflection data. All fluorescence measurements were carried out on an LS 50B Luminescence Spectrometer (Perkin Elmer, Inc., USA). All UV–vis absorption spectra were recorded on a Lambda 20 UV/Vis Spectrometer (Perkin Elmer, Inc., USA). \( ^1 \text{H} \) and \( ^{13} \text{C} \) NMR experiments were carried out on a MERCURYplus 400 spectrometer operating at resonance frequencies of 100.63 MHz. Electrospray ionization mass spectra (ES-MS) were recorded on a Finnigan LCQ mass spectrometer using dichloromethane/methanol as mobile phase.

4.2. Synthesis of ligand HL and complex 1

4.2.1. Synthesis of (E)-2-(2,6-dichlorophenyl)ethylidencyclo-oxyquinoline To a solution of 8-hydroxyquinoline (1.36 g, 8.5 mmol) in pyridine (30 mL) was added (E)-2-(2,6-dichlorophenylethenyl)-8-acetoxyquinoline (2.0 g, 5.6 mmol) in acetic anhydride (10 mL) was added 2,6-dichlorobenzaldehyde (1.48 g, 8.5 mmol). The mixture was heated under reflux for 10 h. After the mixture was cooled, it was subsequently poured into ice water (200 mL) and stirred overnight. The yellow solid obtained was filtered and washed with water. The solid residue was recrystallized from \( \text{CH}_2\text{Cl}_2 \) to afford (E)-2-(2,6-dichlorophenylethenyl)-8-acetoxyquinoline (2.49 g, 82\%): \( ^1 \text{H} \) NMR (\( \text{CDCl}_3, 400 \text{MHz} \)) \& 8.17 (d, \( J=8.4 \text{ Hz}, 1 \text{H} \)), 7.91 (d, \( J=16.4 \text{ Hz}, 1 \text{H} \)), 7.70 (dd, \( J=1.6, 8.0 \text{ Hz}, 1 \text{H} \)), 7.61 (d, \( J=8.4 \text{ Hz}, 1 \text{H} \)), 7.51–7.43 (m, 3 \text{H} \), 7.38 (d, \( J=8.0 \text{ Hz}, 2 \text{H} \)), 2.54 (s, 3 \text{H} \), ESI-MS \( m/z \): 358.0 [\text{M}+\text{H}]\textsuperscript{+}). Elemental analysis: found C: 63.5, H: 3.28, N: 3.72; calculated for (\( \text{C}_{19}\text{H}_{13}\text{Cl}_2\text{NO}_2 \)) C: 63.71, H: 3.88, N: 3.72.%.

4.2.2. Synthesis of (ZnL\textsubscript{2})\textsubscript{2} (HL) A solution of (E)-2-(2,6-dichlorophenylethenyl)-8-acetoxyquinoline (2.0 g, 5.6 mmol) in pyridine (30 mL) was refluxed for 30 min, then water (15 mL) was added. The reaction mixture was refluxed for 12 h. After the mixture was cooled, water (200 mL) was added to the mixture. The yellow solid obtained was filtered and washed with water, and dried in vacuo to give compound of HL (1.69 g, 96\%). \( ^1 \text{H} \) NMR (\( \text{DMSO-d}_6, 400 \text{MHz} \)) \& 8.71 (s, 1 \text{H} \), 8.34 (d, \( J=8.8 \text{ Hz}, 1 \text{H} \)), 8.00 (d, \( J=16.4 \text{ Hz}, 1 \text{H} \)), 7.85 (d, \( J=8.4 \text{ Hz}, 1 \text{H} \)), 7.59 (d, \( J=8.0 \text{ Hz}, 2 \text{H} \)), 7.45–7.31 (m, 4 \text{H} \), 7.11 (dd, \( J=1.6, 7.2 \text{ Hz}, 1 \text{H} \), \( ^{13} \text{C} \) NMR (\( \text{DMSO-d}_6, 400 \text{MHz} \)) \& 152.8, 152.2, 138.0, 136.2, 134.8, 133.6, 128.7, 128.0, 127.7, 120.4, 117.7, 110.3. ESI-MS \( m/z \): 316.0 [\text{M}+\text{H}]\textsuperscript{+}). Elemental analysis: found C: 63.5, H: 3.28, N: 3.72; calculated for (\( \text{C}_{19}\text{H}_{13}\text{Cl}_2\text{NO}_2 \)) C: 63.71, H: 3.66, N: 3.91 (%).

3. Conclusion

In the present work, a novel dimeric complex (\text{ZnL}_2)_2 (1) was fabricated by self-assembly of Zn(II) ions with a novel 2-substituted-8-hydroxyquinoline ligand (HL). The supramolecular structure of 1 features a lamellar solid constructed by aromatic stacking interactions, Cl–Cl interactions and nonclassical C–H–Cl hydrogen bonds derived from 2,6-dichlorophenyl group of the ligand HL. The aggregation behavior of zinc salts and HL in solutions was investigated with a variety of techniques, including \( ^1 \text{H} \) NMR, UV–vis, and PL. The luminescence properties of compound 1 show that it emits yellow luminescence at 561 nm (\( \lambda_{\text{em}}, \text{max} \)) 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) materials, and may contribute to the understanding of structure–property relationships.

Fig. 7. Fluorescence decay curves of HL (Ex, 350 nm; Em, 470 nm) and 1 (Ex, 380 nm; Em, 594 nm).

4.3. X-ray crystallography

Single-crystal XRD data for the compound was collected using a Bruker Smart 1000 CCD diffractometer with Mo Kα radiation (λ=0.71073 Å) at room temperature. The empirical absorption correction was applied by using the SADABS program. All other atoms were refined anisotropically in all compound 1. Crystal data and details of the data collection are given in Table 1, whereas the selected bond distances and angles are presented in Table 2. The CCDC number is 873149.

**Table 1**

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**Table 2**

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Symmetry transformations used to generate equivalent atoms: #1 –x+3/2, y, -z+3/2.

Acknowledgements

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2012.06.103. These data include MOL files and InChIKeys of the most important compounds described in this article.

References and notes

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