

A schiff base zinc complex and its electroluminescent properties

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Abstract

A zinc complex with a schiff base, ZnL, was synthesized and characterized by elemental analyses, infrared spectra, differential thermal analysis and thermogravimetry, in which the ligand compound is *N, N'*-bis(2-hydroxy-1-naphthylidene)-3, 6-dioxo-1, 8-diaminooctane (H₂L). The blue fluorescence of the complex in both solution and solid states was observed. The electroluminescence devices with the ZnL complex as the emitting layer were constructed, which exhibited blue emission with a peak at 455 nm and the maximum brightness of 650 cd m⁻².
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1. Introduction

Since the report of efficient electroluminescence (EL) from a bilayer organic light-emitting diode (OLED) by C.W. Tang and S.A. VanSlyke [1], OLEDs based on organic materials have attracted considerable interest and constitute a rapidly developing field due to their potential application in the development of energy-efficient, low-cost, full-color, flat-panel displays and other emissive products [2–10].

It is well known that blue-, green-, and red-light-emitting materials are used for the three primary colors of full-color displays. Among these, the blue-emitting materials are one of the key color with red (R), green (G) and blue (B) components since a blue EL emitter is essential for the development of a full-color display based either on the “color changing medium” technology or the R. G. B filtered white emission [11]. However, it is much more difficult to obtain highly efficient blue-light emission due to its intrinsic characteristic of the large band gap of the emitting material. Although many blue fluorescent dyes exhibiting excellent performance, such as distyrylarylene derivatives, have been

explored so far, the common way to improve efficiency and stability of OLEDs is to use the fluorescent dye doping technique [12–16]. In practical application, however, the doping method is rather sophisticated and inconvenient for device fabrication because it is difficult to control the deposition rate in co-evaporation process and the doping ratio. Organic metal-chelate complexes generally offer many attractive properties, such as displaying a double role of electron transport and light emission, high thermal stability, and ease of sublimation. So organic metal-chelate complexes in particular have attracted a lot of attentions. The major disadvantages of metal-chelate complexes, however, are their low electron transport ability and the lack of suitable blue-emitting complexes.

Aluminum complexes with 8-hydroxy-quinoline and its derivatives are excellent metal-chelate complexes widely used in OLEDs [1,11,17,18], and are the best electron transport material. Salicylaldehyde schiff bases are similar to 8-hydroxy-quinoline in structure in which they have at least one hydroxyl group, a coordination nitrogen atom, and a delocalised π -conjugated system [19]. Therefore, organic metal-chelate complexes of salicylaldehyde schiff base ligands usually also should exhibit good luminescent properties [20–22]. Kim et. al. [21] have reported the photoluminescence (PL) and EL of the aromatic bridged azomethine metal complexes, the results indicated that some of these complexes have complicated structures which exist as dimer or dinuclear complexes due to its

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rigid conformation of the aromatic bridged structures. Though the type of complexes exhibits strong blue or blue-green emission, they were insoluble in common organic solvents except for dimethylsulfoxide which has higher boiling point (b. p. 189 °C), and most of them were difficultly sublimated in vacuum. So most of the complexes were difficultly used for fabricating EL devices by vacuum deposition or spin-coating method. To improve the properties of solubility, stability and electron transporting capability of schiff base zinc complexes, we designed a type of schiff base complexes in which the ligands were condensated from conjugated aromatic aldehydes and oxa-alkyldiamines (diglycolamine or triglycolamine). The complexes containing heteroatoms in flexible alkyl chain not only provide coordination atoms for metal ions, but also increase the polarity of the molecules. So the ligand backbone may play an important role in improving stability of the complexes compared with longer alkyl chain schiff base ligands. 2-Hydroxy-1-naphthaldehyde instead of salicylaldehyde was used to increase the conjugated system of the complexes which can improve their electron transport ability. In the previous paper [23], the properties of Zn²⁺, Ni²⁺, Co²⁺ and Cu²⁺ complexes with *N, N'*-bis(2-hydroxy-1-naphthylidene)-3-oxa-1, 5-diaminopentane were studied. It was shown that the Zn (II)-complex has intense emission at ca. 455 nm in solid state and in methanol solution. In this paper, a ligand, *N, N'*-bis(2-hydroxy-1-naphthylidene)-3, 6-dioxa-1, 8-diaminooctane (H₂L), and its Zn (II)-complex were synthesized. The Zn (II)-complex, which could be soluble in common organic solvents and sublimated easily in vacuum, was characterized by elemental analyses, infrared (IR) spectra and differential thermal analysis and thermogravimetry (DTA–TG). The UV–vis absorption and luminescent characteristics were investigated particularly. The OLEDs based on the complex were fabricated and their EL properties were studied.

2. Experimental details

2.1. Materials and methods

2-Hydroxy-1-naphthaldehyde was purchased from Fluka Co. and recrystallized from ethanol. 3, 6-dioxa-1, 8-diaminooctane was an Acros chemical. Zinc acetate dihydrate was analytical grade reagent. The other solvents were all commercially available. *N, N'*-diphenyl-*N, N'*-bis(3-methylphenyl)-(1, 1'-biphenyl)-4, 4'-diamine (TPD) and tris(8-hydroxyquinoline) aluminum (Alq₃) were obtained from Aldrich, and purified with train sublimation prior to devices processing.

The IR spectra in KBr (400–4000 cm⁻¹) were measured on a Nicolet Magna fourier transform infrared (FT-IR) spectrophotometer. C, H, and N analyses were obtained using an Elemental Vario-EL automatic elemental analysis instrument. UV–vis absorption spectra were recorded on a Hitachi UV-3010PC spectrometer. The PL and EL spectra were measured on a Hitachi MPF-4 spectrometer. TG and DTA measurements were recorded on a DT-30 thermal analysis instrument made in China in flowing dry nitrogen at the heating rate of 10 °C/min on approximately 10 mg sample.

2.2. Synthesis and characterization of the ligand (H₂L) and the zinc-complex (ZnL)

The ligand (H₂L) was prepared by adding drop-wise solution of 3, 6-dioxa-1, 8-diaminooctane (2.22 g, 15 mmol) in absolute methanol (20 mL) to a methanolic solution (100 mL) of 2-hydroxy-1-naphthaldehyde (5.16 g, 30 mmol) with magnetic stirring at room temperature. After 2 h, a yellow precipitate was formed, and stirring was continued for 2 h at 60 °C. The precipitate was filtered and recrystallized from methanol to yield 5.56 g (81%) of product; m.p. 163–164 °C. Anal. Calc. for C₂₈H₂₈N₂O₄ (%): C, 73.68; H, 6.14; N, 6.14. Found: C, 73.53; H, 6.21; N, 6.09. FT-IR (KBr) (cm⁻¹): 3051 (ν_{ArO-H}), 1633 (ν_{-CH=N-}), 1123 (ν_{-C-O-C-}).

The complex ZnL was prepared by adding an aqueous solution (5 mL) containing zinc acetate dihydrate (0.2634 g, 1.2 mmol) to a methanolic solution (10 mL) of the ligand (0.456 g, 1 mmol). The mixture was heated to 60 °C with stirring for 2 h, a yellow precipitate was formed. Continuing stirring for 5 h at room temperature. The precipitate was filtered, and washed successively with distilled water, diluted aqueous solution of NaHCO₃, and methanol. The product was dried under reduced pressure, and purified with re-crystallization from chloroform/hexane. Anal. Calc. for C₂₈H₂₆N₂O₄Zn (%): C, 64.69; H, 5.04; N, 5.39. Found: C, 64.57; H, 5.12; N, 5.31. FT-IR (KBr) (cm⁻¹): 1615 (ν_{-CH=N-}), 1120 (ν_{-C-O-C-}), 647 and 553 (ν_{Zn-O}), 448 (ν_{Zn-N}).

2.3. Preparation of EL devices with the Zn (II)-complex

The multiplayer OLED was fabricated by means of a vacuum-deposition method. A cleaned ITO (indium tin oxide)-coated glass with a sheet resistance $R_{\square} \sim 100 \Omega/\square$ was placed in a vacuum chamber (2×10^{-4} Pa) and organic layers were sequentially deposited at a rate of 0.1–0.4 nm/s by thermal evaporation. The emitting area of the EL devices was $3 \times 4 \text{ mm}^2$. A quartz crystal oscillator placed near the substrate was used to measure the thickness of the thin film. The PL spectra of the Zn (II)-complex film on a quartz substrates were studied. The EL spectra, the Commission Internationale de L'Eclairage coordinates (CIE) were measured with a Hitachi MPF-4 Fluorescence spectrophotometer. The luminance–current–voltage characteristics were measured simultaneously by the EL test system made in Beijing Normal University, PR China. All the performance measurements were carried out under ambient atmosphere without encapsulation.

3. Results and discussion

3.1. Thermal property

The thermogravimetry (TG) and differential thermal analysis (DTA) were carried out using a DT-30 thermal analysis instrument in flowing dry nitrogen at the heating rate of 10 °C/min on approximately 10 mg sample. The result of TG and DTA measurements of the Zn-complex is shown in Fig. 1.

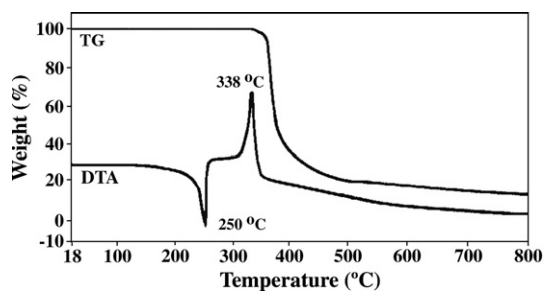


Fig. 1. TG–DTA of Zn (II)-complex.

The thermogram of the complex ZnL indicates that the complex is thermally stable up to nearly 338 °C. It can be seen from Fig. 1 that the DTA curve shows an endothermic peak at 250 °C, but without mass loss in the TG curve. It indicates that the temperature is the melting point of the ligand, which is in agreement with the result obtained by a capillary tube method. At 338 °C an exothermic peak is observed in the DTA curve, corresponding to a sharp weight loss in the TG curve, it shows that the complex undergoes decomposition. From Fig. 1, it is shown that there is no endothermic behavior in the DTA curve and no mass loss in the TG curve up to 250 °C. The result suggests that there is neither lattice nor coordination water in the complex.

3.2. IR spectra

An important feature of the IR spectrum of the zinc-complex is the absence of the band at 3051 cm^{-1} due to the $\nu(\text{ArO-H})$ stretching mode. This observation indicates that the complex formation takes place by deprotonation of the hydroxyl group of Ar–OH moiety.

A very strong band at 1633 cm^{-1} assigned to $\text{C}=\text{N}$ stretching vibration of the IR spectrum of the schiff base ligand is shifted to lower wave number by about 18 cm^{-1} because of the complex formation in which the vibration is at 1615 cm^{-1} , suggesting that coordination of the schiff base groups through nitrogen atoms with the metal ion occurred.

The stretching vibration of the aliphatic $\nu(-\text{C}-\text{O}-\text{C}-)$ frequency of 1123 cm^{-1} of the ligand is nearly unchanged upon forming the complex where it is at 1120 cm^{-1} . It was indicated that the oxygen from oxa-alkyl chain didn't coordinate to zinc ion. In addition, some new bands in the IR spectrum of the complex were found to be weak band respectively at 647, 553 and 448 cm^{-1} , which are absent in the spectrum of the free ligand, may be ascribed to the Zn–O and Zn–N vibrations, respectively [24,25].

It is noted that a broad band of the asymmetric and symmetric O–H stretching modes around the region 3400 cm^{-1} and around 1575 cm^{-1} presumably due to H–O–H bending

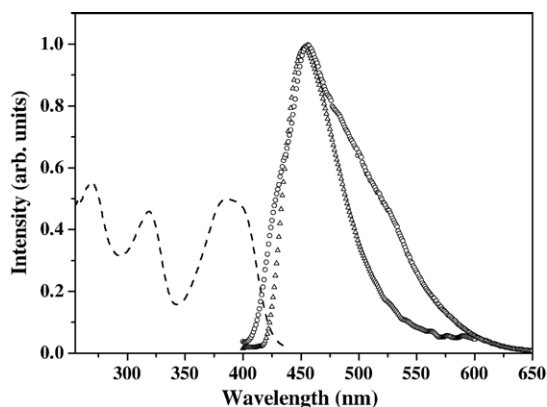


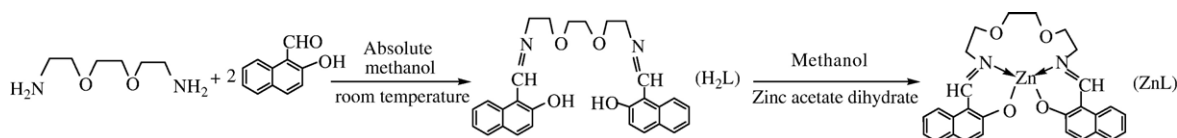
Fig. 2. The absorption (– – –) and PL spectra of Zn-complex in dichloromethane solution ($\Delta \Delta \Delta \Delta$), and in thin film ($\circ \circ \circ \circ$).

vibrations are not observed in the spectrum of the complex, which are indicative of the absence of the water molecule. The result corroborates the assumptions made on the basis of TG, DTA and elemental analyses studies. The structure proposed for the complex is shown in Scheme 1.

3.3. Photophysical and electrochemical properties

The photophysical properties of the ZnL were examined by UV–vis and fluorescence spectrometers in dichloromethane solution. The electronic absorption and the PL emission spectra of the complex are shown in Fig. 2. We can see that the absorption spectrum of the Zn (II)-complex shows absorptions at $\lambda_{\text{max}} = 385, 319$ and 270 nm , respectively. Among them, the absorption band at 385 nm corresponds to the lowest unoccupied molecular orbital level of the ZnL complex, and it has a significant influence on the characteristic emission spectrum, so the PL spectra of the ZnL was selected at 385 nm as the excitation wavelength. Because the optical absorption edge is at ca. 420 nm, the optical bandgap energy was demonstrated to be 2.97 eV.

The UV–vis absorption bands of the complex ZnL closely match that of the protonated ligand precursor. Thus, the electronic spectra of the Zn-complex can be characterized by the metal-perturbed $\pi-\pi^*$ transition of the ligand-centered. The complex exhibits bright blue emission with peak at 455 nm in solution as well as in the thin film. It was found that the PL spectrum of the ZnL in pure thin film is much broader than that in dichloromethane solution, suggesting that the complex in the solid state has more intermolecular interaction than that in solution situation, and thus may lead to change of the emission band. Meanwhile it was found that slight self-quenching of the solid state has brought about the compact piling of the solids.



Scheme 1. Synthetic route of the ligand (H_2L) and Zn-complex (ZnL).

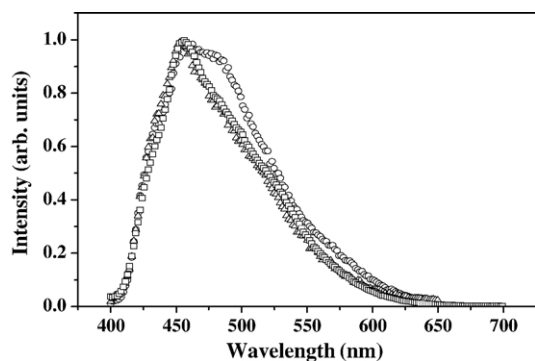


Fig. 3. The PL spectrum of the Zn-complex thin film ($\square\square\square\square$) and the EL spectra of the device I ($\Delta\Delta\Delta\Delta$) and II ($\circ\circ\circ\circ$).

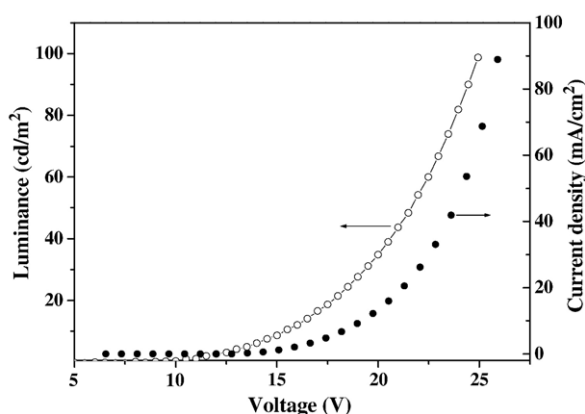


Fig. 4. The current density–voltage–luminance characteristics of the device I.

3.4. EL properties

The Zn (II)-complex can be easily sublimed and made uniform thin films in vacuum vapor deposition, thus employed the complex as an emitting layer in OLED. According to the optical bandgap energy of the Zn-complex, *N*, *N'*-diphenyl-*N*, *N'*-bis(3-methylphenyl)-(1, 1'-biphenyl)-4, 4'-diamine (TPD) and tris(8-hydroxyquinoline)aluminum (Alq₃) were chosen as hole and electron transporting materials, respectively. The double-layer devices were fabricated with the structure of ITO/TPD/Zn-complex/LiF/Al (device I). Though no electron

transporting layer designedly employed in the device, a blue EL emission was also observed. It indicates that the ZnL complex has definite electron transporting ability. Fig. 3 shows the PL spectrum of the ZnL complex thin film and the EL spectra of the devices. The EL spectral pattern resembles the PL spectrum of the Zn-complex thin film.

Fig. 4 shows the current density–voltage and brightness–voltage characteristics of the device I. The turn-on voltage of the device I was observed at 8.0 V, the maximum luminance and EL efficiency were measured to be 98 cd/m² and 0.12 cd/A, respectively.

To improve the diode performance, the device of ITO/TPD/ZnL/Alq₃/LiF/Al (device II) was fabricated. The EL spectrum obtained from the device II is shown in Fig. 3. It is seen that the spectrum displays a broad band centered at 455 nm with a small shoulder of 485 nm, but the EL spectral pattern was found to be similar to that of the PL of the complex thin film. Because the PL spectrum of the complex was measured with a single layer vacuum deposited film while the EL spectrum was obtained from multiple layer structures, and the small difference between the EL and PL spectra could be occurred. The current density–voltage–luminance characteristic curves of the device II are shown in Fig. 5. The turn-on voltage of the device B is observed at 5 V, the maximum brightness is about 650 cd m⁻² and the device exhibits maximum efficiency of 0.63 cd/A at about 9.5 V. The EL color of the device II is blue with CIE coordinates *x*: 0.195, *y*: 0.234.

4. Conclusions

A zinc complex containing oxa-alkyl chain and naphthols was synthesized and investigated for OLEDs. The ZnL complex exhibits strong blue fluorescence, good thermal stability and was easily made uniform thin films in vacuum vapor deposition. OLEDs based on the complex showed a strong blue emission at 455 nm. The results turn out that the flexible chain-having schiff base complexes are advantageous over the aromatic bridged ones in solubility as well as processability for OLEDs. A proper design of the metal ions and the ligands condensed from a heteroatom alkyldiamine and a conjugated aromatic aldehyde is crucial to achieve high stability and excellent EL characteristics.

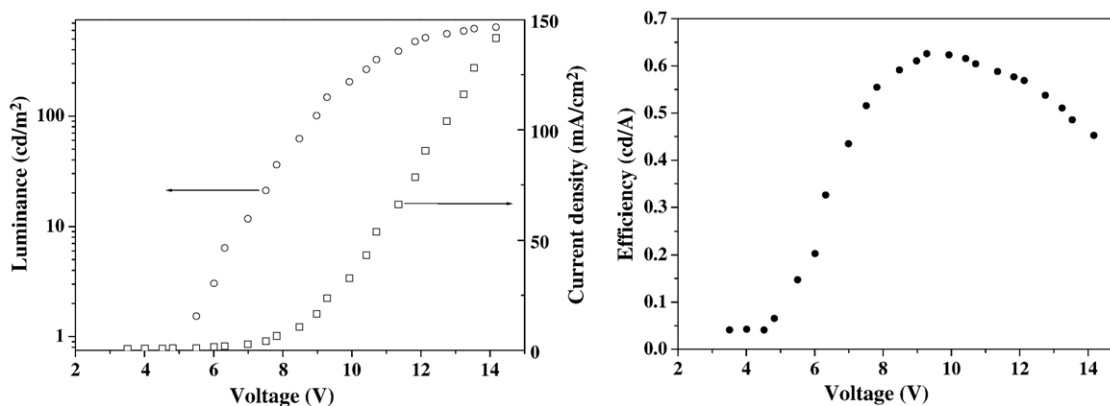


Fig. 5. The current density–voltage–luminance characteristics (left) and the efficiency curve (right) of the device II.

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