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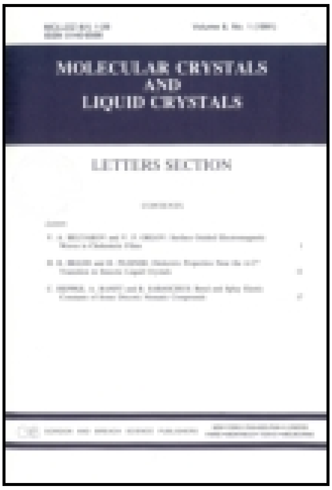

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Synthesis and OLED Properties of Zinc Complexes Based on Quinaldic Acid

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Synthesis and OLED Properties of Zinc Complexes Based on Quinaldic Acid

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Metal-chelate materials based on polycyclic aromatic ligands are attractive for tuning emission colors of organic light-emitting diodes (OLED). In this work, quinaldic acid (QA) and 8-hydroxyquinoline (HQ) were employed as organic ligands and the corresponding zinc complexes (Zn(HQA), Zn(QA), Zn(HQ)) were synthesized. The structures of Zn(HQA), Zn(QA), and Zn(HQ) were determined by ^{1}*H-NMR,* ^{13}*C-NMR, FT-IR, UV-Vis and XPS. Zinc complexes showed thermal stability up to 350°C under nitrogen flow by TGA. The photoluminescence (PL) was measured from DMSO solution. The Zn(HQA) emitted a yellow light around 550 nm, while Zn(HQ) emitted a green light around 500 nm. Electroluminescence (EL) device having the structure of ITO/NPB/Zn(HQA)/Liq/Al was fabricated. The device emitted a yellow light around 550 nm. The maximum luminance of 190 cd/m*^{2} *and current of 50 mA/cm*^{2} *were observed at 15 V in the Zn(HQA)-containing device.*

Keywords Organic light-emitting diodes; photoluminescence; zinc complex; quinaldic acid

Introduction

Organic light-emitting diodes (OLEDs) consisting of luminescent chelate complexes have become highly attractive, in particular, due to their relative high stability and volatility. Alq3 is the most well known example of such chelate compounds where q is the 8-hydroxyquinolinato ligand, which is both good emitter and a highly efficient electron-transporting material [1,2].

Since the first OLEDs with Zn complexes were reported in 1993 [3], synthesis of novel zinc complexes as active materials for OLEDs have focused on improving electron mobility or producing blue shift emission compared to Znq2 [4,5]. The electroluminescent performance of zinc complexes as the emitter is just comparable with that of Alq3 [6]. However, in many instances, the electron-transporting mobility of zinc complexes goes beyond that of Alq3 [7]. So zinc complexes have good advantages to enhance the electron-transporting properties for OLEDs [8, 9].

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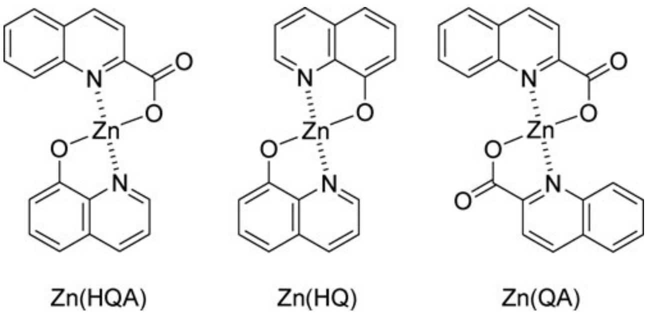

Figure 1. Structures of synthesized Zn-complexes.

In this work, quinaldic acid (QA) and 8-hydroxyquinoline (HQ) were employed as organic ligands and the corresponding zinc complexes (Zn(HQA), Zn(QA), and Zn(HQ)) were synthesized. The structures of Zn(HQA), Zn(QA), and Zn(HQ) were determined by ^{1}H-NMR, ^{13}C-NMR, FT-IR, UV-Vis and XPS. The PL and EL properties of the zinc complexes were investigated.

Experimental

1. *Materials*

Quinaldic acid and 8-hydroxyquinoline were purchased from Aldrich and used without further purification. Zinc acetate dihydrate was purchased from Fluka. Both of ethanol and acetone were purchased from ACROS chemical Co. The Figure 1 shows structures of synthesized Zn-complexes.

2. *Synthesis*

2.1. *Synthesis of Zn(HQA)*

The synthetic scheme of Zn(HQA) is shown in Figure 2. First, quinaldic acid (0.173 g, 1.0 mmol) was entirely dissolved in ethanol (20 mL) along with heating to 75°C. Then, the ethanol solution of quinaldic acid stirred under N_2. After 30 min, 8-hydroxyquinline

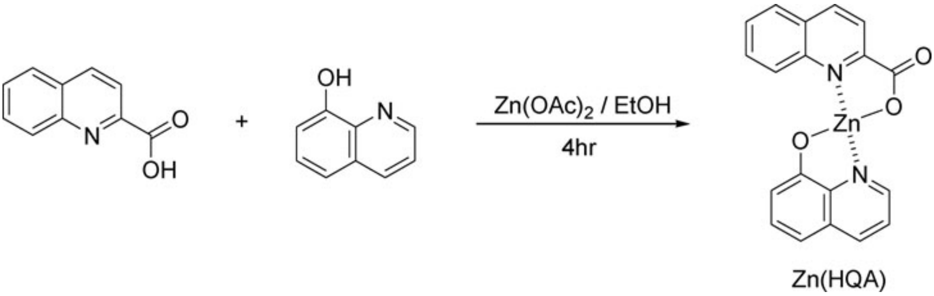

Figure 2. Representative synthetic scheme of Zn(HQA).

(0.145 g, 1.0 mmol) dissolved in ethanol (10 mL) and zinc acetate dihydrate (0.219 g, 1.0 mmol) dissolved in distilled water (3 mL) were slowly added into the ethanol solution of quinaldic acid using dropping funnel with stirring. After 24 h at 75°C, a yellow precipitate was produced. The yellow precipitate was collected by filtration and washed with distilled water, ethanol, and acetone, then dried overnight. IR (KBr pellet, cm^{-1}) 1626 (COO^{-}), 3215, 3063 (aromatic C—H), 1576 (aromatic C=C), 1242, 1108 (C—O); Calcd.(%) C 59.78, N 7.34, O 12.57, H 3.17, Zn 17.54; Found (%) C 59.01, N 6.90, O 13.20, H 3.20, Zn 17.65; ^{1}H-NMR (500 MHz, [D$_6$]DMSO, ppm) δ 8.78(2H), 8.68(1H), 8.40(2H), 8.17(1H), 8.01(1H), 7.81(1H), 7.60(1H), 7.40(1H), 6.95(1H), 6.84(1H); ^{13}C-NMR (125 MHz, [D$_6$] DMSO, ppm) δ 165.62, 161.90, 151.87, 151.80, 145.19, 143.91, 140.84, 139.77, 138.76, 131.35, 129.97, 129.42, 129.22, 128.46, 128.18, 121.63, 120.32, 112.14, 109.83; UV-Vis (λ_{max}, nm, in DMF) 270.

2.2. *Synthesis of Zn(HQ)*

In order to compare the properties of Zn(HQA) with Zn(HQ), the synthesis of Zn(HQ) was performed similarly to the scheme in Figure 2 [8, 9]. In this case, 8-hydroxyquinoline (0.29 g, 2.0 mmol) only was used to react with zinc acetate dihydrate (0,219g, 1.0 mmol), and Zn(HQ) was obtained as a yellow precipitate. IR (KBr pellet, cm^{-1}) 1576 (aromatic C=C), 3225 (aromatic C—H), 1241, 1108 (C—O); Calcd.(%) C 61.12, N 7.92, O 9.05, H 3.42, Zn 18.49; Found (%) C 60.40, N 7.50, O 10.10, H 4.00, Zn 17.96; ^{1}H-NMR (500 MHz, [D$_6$]DMSO, ppm) δ 8.69(1H), 8.41(1H), 7.50(1H), 7.38(1H), 6.92(1H), 6.80(1H); ^{13}C-NMR (125 MHz, [D$_6$] DMSO, ppm) δ 145.19, 139.79, 138.78, 129.94, 129.48, 126.25, 121.51, 112.14, 109.34; UV-Vis (λ_{max}, nm, in DMF) 274.

2.3. *Synthesis of Zn(QA)*

Zn(QA) was also prepared to compare the properties with other Zn complexes according to the similar procedure to Zn(HQ). IR (KBr pellet, cm^{-1}) 1628 (COO^{-}) 3060, 3031 (aromatic C—H) 1565, (aromatic C=C), 1185 (C—O); Calcd.(%) C 58.63, N 6.84, O 15.62, H 2.95, Zn 15.96; Found (%) C 57.9 N 6.40, O 16.1, H 3.10, Zn 16.49; ^{1}H-NMR (500 MHz, [D$_6$]DMSO, ppm) δ 8.80(2H), 8.40(1H), 8.21(1H), 8.00(1H), 7.82(1H); ^{13}C-NMR (125 MHz, [D$_6$] DMSO, ppm) δ 165.5, 151.40, 143.83, 140.92, 131.47, 129.28, 128.50, 128.20, 128.10, 120.20; UV-Vis (λ_{max}, nm, in DMF) 314.

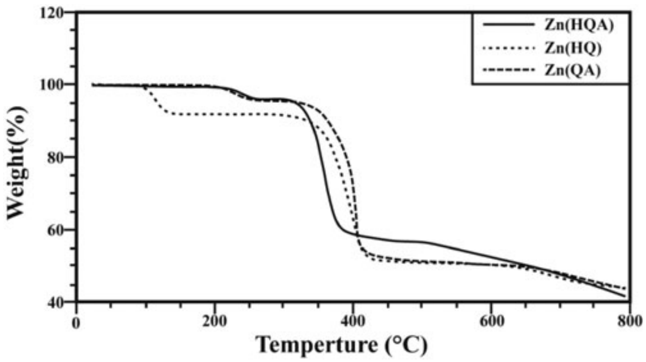

Figure 3. TGA thermograms of Zn(HQA), Zn(HQ) and Zn(QA).

2.3.1. Instrumentation. Infrared spectra were recorded on a Scimitar 1000 (Varian). ^{1}H-NMR and ^{13}C-NMR spectra were obtained with a VNMRS500 NMR spectrometer. X-ray photoelectron spectroscopy (XPS) was carried out at Busan branch of Korea Basic Science Institute. UV-Vis absorption spectra were measured by a UV-VIS Spectrometer (Shimadzu UV-3100S). The PL spectrum was measured using a Perkin-Elmer LS45 luminescence spectrometer. The characteristics of the current density-voltage-luminance (I-V-L) were measured by IVL 300 series (JBS Inc.).

2.3.2. Device fabrication. The devices were fabricated on indium tin oxide (ITO) glass substrates. The organic layers were vacuum-deposited using thermal evaporation at a vacuum pressure of 2×10^{-7} torr. 1,4-Bis(1-naphthylphenylamino)biphenyl (NPB) as a hole transport layer, Zn(HQA) as an emitting layer, 8-hydroxyquinolate lithium (Liq) as an electron injection layer, and Al as a cathode were respectively employed. The OLED device has a following structure: ITO/NPB[50 nm]/ Zn(HQA) [50 nm]/Liq[5 nm]/Al[120 nm].

Results and Discussion

1. Structure Characterization

The chemical structures of the zinc complexes, Zn(HQA), Zn(HQ) and Zn(QA), were determined by ^{1}H-NMR, ^{13}C-NMR, FT-IR, and XPS. From the IR spectra of Zn(HQA)

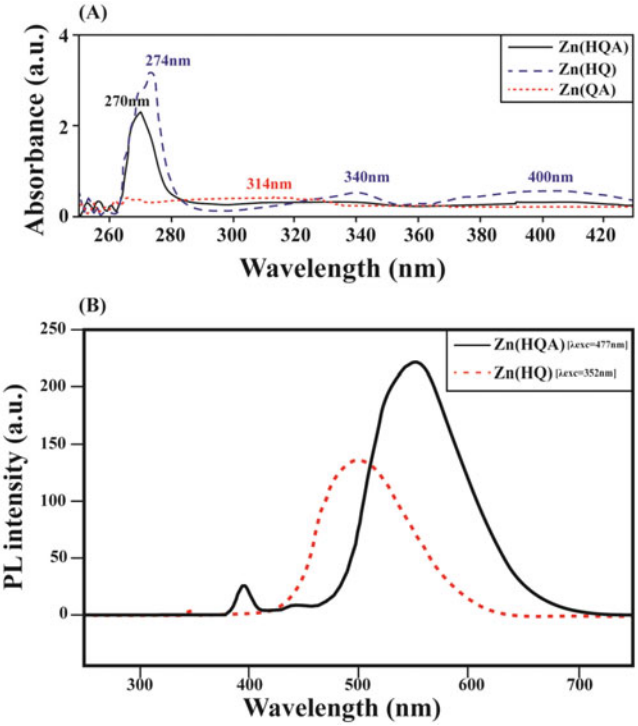

Figure 4. (A) UV-Vis and (B) PL spectra of Zn(HQA), Zn(HQ) and Zn(QA). PL was not observed from Zn(QA).

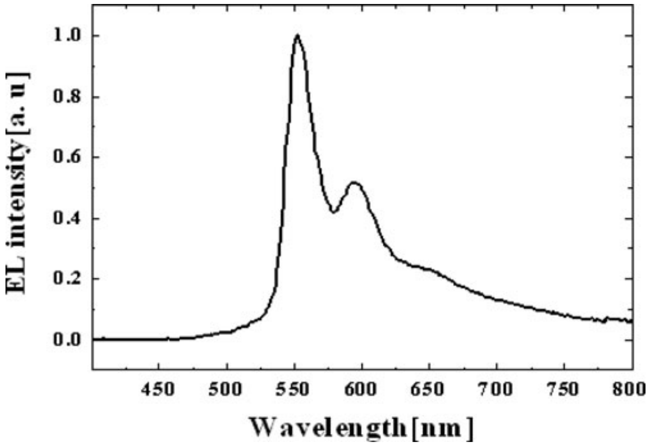

Figure 5. EL spectrum of Zn(HQA).

and Zn(QA), we observed the band at 1626 cm^{-1}, confirming the presence of carboxylate group. The band by carboxylate ligand was not observed in the IR spectrum of Zn(HQ). The bands at 1576 and 1565 cm^{-1} exhibited the bending vibration by aromatic C=C. The bands at 1108 and 1185 cm^{-1} are assigned to the C−O bonds. The ^{1}H-NMR spectra show the aromatic protons from the peaks of around 7 and 9 ppm. The peaks are matched with the protons of Zn(HQA), Zn(HQ) and Zn(QA). The ^{13}C-NMR spectrum of Zn(HQA) also supports the chemical structure from fourteen proton-decoupled ^{13}C-peaks due to the aromatic rings together with carboxylate peak at 165 ppm. All the carbons of Zn(HQ) and Zn(QA) could be respectively assigned to the each peak of their ^{13}C-NMR spectra. The XPS spectra show the presence of zinc atoms in Zn(HQA), Zn(HQ) and Zn(QA). The analysis from XPS spectra also agrees with the elemental composition of the Zn-complexes.

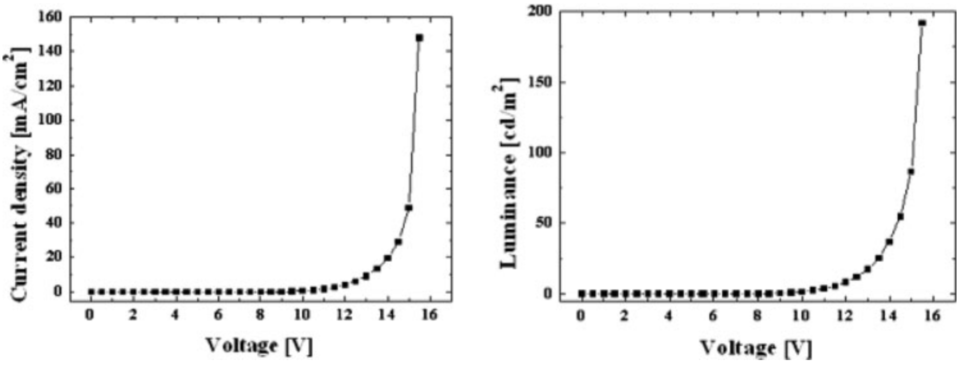

Figure 6. Current density-voltage-luminance (I-V-L) characteristics of the Zn(HQA) device.

2. Thermal Stability

We have measured the thermal stability of the zinc complexes by TGA. The thermal stability of OLED materials is very important, because the durability of multilayer devices significantly depends on the thermal stability of materials.

Zn(HQA) and Zn(QA) exhibited thermal stability up to 200°C as shown in Figure 3. The initial weight loss has started over the 200°C, and rapid decomposition happens over 300°C. In case of Zn(HQ), the initial weight loss occurred around 100°C, which seems dehydration of hydrated waters. Zn(HQ) also showed rapid decomposition over 300°C. It means that the zinc complexes have enough thermal stability for the process of vacuum deposition.

3. UV-Vis Absorption and Photoluminescence (PL) Properties

The light absorption and PL properties of the zinc complexes were measured by UV-Vis absorption and PL spectra in DMF solution as shown in Figure 4. The UV-Vis absorption spectra of Zn(HQA) and Zn(HQ) exhibited the maximum absorption at 270 nm and 274 nm, respectively, which are attributed to $\pi \rightarrow \pi *$ transitions. And Zn(HQ) shows other weak absorptions at longer wavelengths of 340 nm and 400 nm. Although the absorption by Zn(QA) was observed around 314 nm, the intensity was very low. It seems that the carboxylate ligands to Zn have not conjugated with aromatic rings enough to show UV-Vis absorption. The PL spectra of Zn(HQA) and Zn(HQ) exhibited maximum emissions at 551 nm and 500 nm under excitation at 477 nm and 352 nm, respectively. However, Zn(QA) did not emit the visible light.

4. Electroluminescence (EL) Properties

A OLED device of Zn(HQA) was fabricated with the configuration of ITO/NPB/Zn(HQA)/Liq/Al. In the cases of Zn(HQ) and Zn(QA), stable OLED devices were not fabricated at this point, because they showed black decompositions during the deposition process even though the zinc complexes showed enough thermal stability for OLED by TGA. The EL spectrum of Zn(HQA) is shown in Figure 5. The EL spectrum of the Zn(HQA) device shows a yellow maximum emission from 550 nm and 600 nm, the former of which is very close to PL wavelength of 551 nm .

The current density-voltage-luminance (I-V-L) characteristics of the device are shown in Figure 6. The device showed a maximum current density 150 mA/m^2 and the turn-on voltage of around 10 V. The maximum luminance exhibited about 190 cd/m^2 at voltage of around 15 V.

Conclusion

We synthesized zinc complexes from quinaldic acid (QA) and 8-hydroxyquinoline (HQ), which is respectively Zn(HQA), Zn(HQ), and Zn(QA). The chemical structures of the zinc complexes were determined by ^{1}H-NMR, ^{13}C-NMR, FT-IR, UV-Vis and XPS. Zn(HQA) and Zn(HQ) exhibited PL emission at 551 nm and 500 nm, respectively, but Zn(QA) did not emit visible rays. We could fabricate the OLED device with only Zn(HQA) among the zinc complexes. The current density-voltage-luminance (I-V-L) characteristics of the Zn(HQA) device showed a maximum current density of 150 mA/m^2 at 10 V, and maximum luminance of 190 cd/m^2 at 15 V.

Funding

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