Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 19 Apr 2010

Mol. Cryst. Liq. Cryst., Vol. 520: pp. 90/[366]–96/[372], 2010

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400903582840

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We have synthesized (8-hydroxy-7-propylquinoline) zinc(II) ($Zn(HPQ)_2$) to use in OLED. Photoluminescence (PL) peak of $Zn(HPQ)_2$ was observed at 555 nm which showed yellow emission. In the cyclic voltammetry (CV) experiment, the HOMO and the LUMO of the $Zn(HPQ)_2$ measured to be 6.7 eV and 3.3 eV. So we expected that $Zn(HPQ)_2$ could be used as emitting layer (EML) and electron transporting layer (ETL). In this study, we investigated the efficiency properties of OLED based on $Zn(HPQ)_2$ as ETL. The device structures were ITO/NPB/Alq_3/$Zn(HPQ)_2$/LiF/Al. Prior to film deposition, ITO substrate performed surface treatment by UV-ozone for 1 minute. We fabricated devices by thickness change of $Zn(HPQ)_2$, so we founded optimal condition about thickness. Improvement of the OLED performance can be attributed to the reduction of the electron injection barrier of the $Zn(HPQ)_2$ layer.

Keywords Cyclic voltammetry; EML; ETL; ITO; OLED; $Zn(HPQ)_2$

1. Introduction

Electroluminescent (EL) devices based on organic thin films are similar to semiconductor base light-emitting diodes in that they were also considered to be one of the next generation flat-panel displays [1]. They are attractive for the in low-driving voltage, low power consumption, high contrast, easy fabrication and low cost. Since the report of the light-emitting diodes based on tris-(8-hydroxyquinoline) aluminum (Alq_3), a number of organic materials have been synthesized, and many researchers have attempted to obtain high performance organic light-emitting diode (OLED) [2]. Recently, organic metal complexes have attracted much attention because of their potential applications in OLED [3,4]. Organic metal complexes have been shown to be particularly useful in OLED because of their relatively high stability and volatility. Alq_3 is the most well known example and it has been used as a green

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emitter or an electron transporting material in OLED [5]. In particular, research on Zn complexes as an emitting, as well as electron transport, material has advanced [6–8]. Zn complexes with containing new ligands synthesized and used electroluminescence materials [9]. A hole transporting layer (HTL) and an electron transporting layer (ETL) were used to accelerate carrier transport. The ETL plays an important role in transporting electrons and blocking holes, thus preventing holes from moving into the electrode without recombining with electrons [10]. A hole-blocking layer (HBL) and an electron-blocking layer (EBL) were also inserted between the HTL and the emission layer (EML) or between the ETL and the EML to increase exciton recombination. Among the several layers comprising OLED, the luminescence efficiencies of OLED are significantly affected by the existence of ETL and HBL [11].

In this study, we synthesized a new material, (8-hydroxy-7-propylquinoline) zinc(II) ($Zn(HPQ)_2$). The purpose of the synthesis was the development of highly efficient electron transporting material. The ionization potential (IP) and the electron affinity (EA) of $Zn(HPQ)_2$ was measured using cyclic voltammetry (CV). We fabricated OLED based on $Zn(HPQ)_2$ as ETL. We confirmed electrical and optical properties to depend on each processing condition by fabricating OLED. Our results showed that performance of $Zn(HPQ)_2$ was good to use it as ETL.

2. Experimental

2.1. *Synthesis of the $Zn(HPQ)_2$*

In a round bottomed flask, 8-hydroxy-7-propylquinoline (HPQ) (0.9362 g) was dissolved in 25 mL of methanol at room temperature under a nitrogen atmosphere. The solution was stirred for 1 h and then zinc acetate dihydrate (0.5488 g) in methanol (15 mL) was added dropwise during stirring. The yellow precipitates was collected by filtration and washed with methanol, and dried under vacuum overnight at room temperature. Figure 1 shows the chemical structure of $Zn(HPQ)_2$ used in this study. Calcd. (%) C: 78.44, N:5.08, O: 12.68, Zn: 3.79, Found (%) C: 82.76, N: 6.89, O:6.89, Zn: 3.45, ^{1}H-NMR (DMSO-d_6, ppm, 300 MHz): 8.62 (d,1H), 8.32 (d, 1H), 7.56 (m, 1H), 7.35 (d, 1H), 6.87 (d, 1H), 2.81 (t, 2H), 1.71 (m, 2H), 0.98 (t, 3H). ^{13}C-NMR (DMSO-d_6, ppm, 300 MHz): 159.78, 144.98, 139.01, 138.53, 131.21, 128.02, 124.90, 120.47, 107.95, 32.56, 22.75, 14.30.

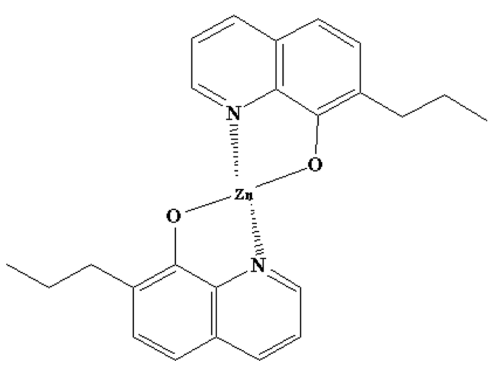

Figure 1. Chemical structure of $Zn(HPQ)_2$.

Table 1. The device structures

Device	Structure
Device 1	ITO/NPB(40 nm)/Alq_3(60 nm)/LiF(0.5 nm)/Al(100 nm)
Device 2	ITO/NPB(40 nm)/Alq_3(60 nm)/Zn$(HPQ)_2$(5 nm)/ LiF(0.5 nm)/Al(100 nm)
Device 3	ITO/NPB(40 nm)/Alq_3(60 nm)/Zn$(HPQ)_2$(10 nm)/ LiF(0.5 nm)/Al(100 nm)
Device 4	ITO/NPB(40 nm)/Alq_3(60 nm)/Zn$(HPQ)_2$(20 nm)/ LiF(0.5 nm)/Al(100 nm)

The redox potentials of the Zn$(HPQ)_2$ were determined by CV using Potentiostat 263A (PerkinElmer, U.S.A). Electrochemical measurement was performed with three electrodes systems, an Ag/AgCl (0.1 M $AgNO_3$) as reference electrode, a Pt wire as a counter electrode and an ITO or Al as a working electrode. On the ITO and Al electrodes used as working electrodes, Zn$(HPQ)_2$ was coated at a thickness of 120 nm by thermal evaporation. The constant scan rate was 400 mV/s in 0.1 M tetrabutylammoniumperchlorate (Bu_4NClO_4) with acetonitrile [12]. CV was performed to measure the energy gap of Zn$(HPQ)_2$. It was found that the films of Zn$(HPQ)_2$ can be irreversibly oxidized and reduced. The oxidation and reduction onset potentials of Zn$(HPQ)_2$ were measured to be +1.9 V and −1.5 V. So the EA and IP of Zn$(HPQ)_2$ were determined to be 3.3 eV and 6.7 eV.

2.2. *Experimental Processes*

The OLED was fabricated on indium-tin-oxide (ITO) coated glass substrates with a sheet resistance of 15 Ω/sq, and the thickness of the ITO was 120 nm. Prior to film deposition, ITO substrate performed surface treatment by UV-ozone for 1 min. We fabricated the OLED with a use of NPB, Alq_3 and Zn$(HPQ)_2$ as a HTL, EML and ETL, respectively. The structure of devices was ITO/NPB/Alq_3/Zn$(HPQ)_2$/LiF/Al. Table 1 showed the device structures. All the conditions of experiments were same but we only changed thickness of Zn$(HPQ)_2$, 0 nm, 5 nm, 10 nm, 20 nm.

The organic layer and cathode were evaporated under 2×10^{-6} torr. Deposition rate of the organic layers and cathode were 1 Å/s, 10 Å/s, respectively. The emission area of each OLED was 3 mm × 3 mm.

The photoluminescence (PL) spectrum was measured using LS45 (PerkinElmer, U.S.A) luminescence spectrometer. UV-ozone surface treatments used UV/O3-CLEANNER (Jeligh Company Inc.). The characteristics of the current density-voltage-luminance were measured with an IVL 300 series (JBS Inc.). All measurements were performed at room temperature in air.

3. Results and Discussion

3.1. *Optical Properties*

We investigated PL spectrum for the optical properties of Zn$(HPQ)_2$. The PL spectrum of Zn$(HPQ)_2$ is shown in Figure 2. The PL spectrum of Zn$(HPQ)_2$ was measured using films deposited on quartz substrates. The PL peak of Zn$(HPQ)_2$ was observed at 555 nm. The Zn$(HPQ)_2$ produced a yellow emission.

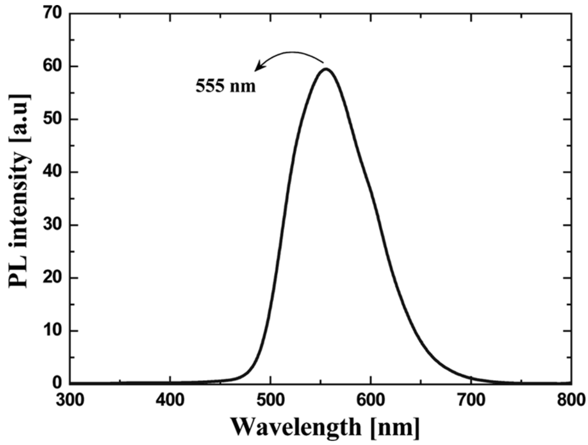

Figure 2. PL spectrum of Zn(HPQ)$_2$.

3.2. *Electrochemical Properties*

The cyclic voltammogram of Zn(HPQ)$_2$ is shown in Figure 3. The oxidation onset potential and the reduction onset potential of Zn(HPQ)$_2$ were measured to be +1.9 V and −1.5 V. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels values were calculated by estimating the energy level of ferrocence (FOC). The energy level of FOC was assumed to be 4.8 eV below the vacuum level [13,14]. The HOMO and the LUMO energy levels of Zn(HPQ)$_2$ were calculated to be 6.7 eV and 3.3 eV. The expectation is that

$$\text{HOMO (IP)} = (E^{\text{oxidation onset}} + 4.8)\,\text{eV},$$
$$\text{LUMO (EA)} = (E^{\text{reduction onset}} + 4.8)\,\text{eV}.$$

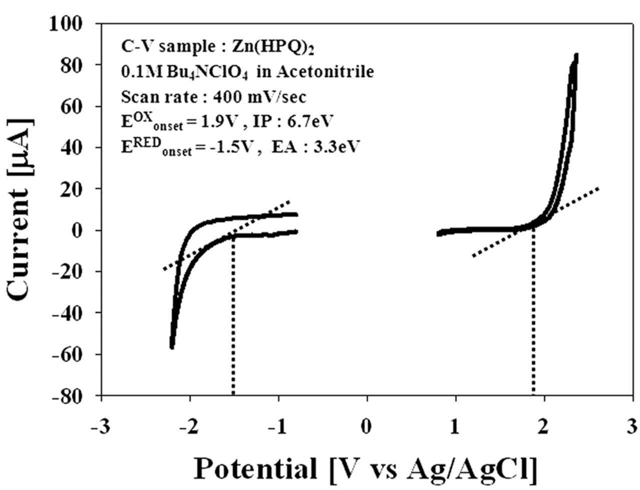

Figure 3. Cyclic voltammogram of Zn(HPQ)$_2$.

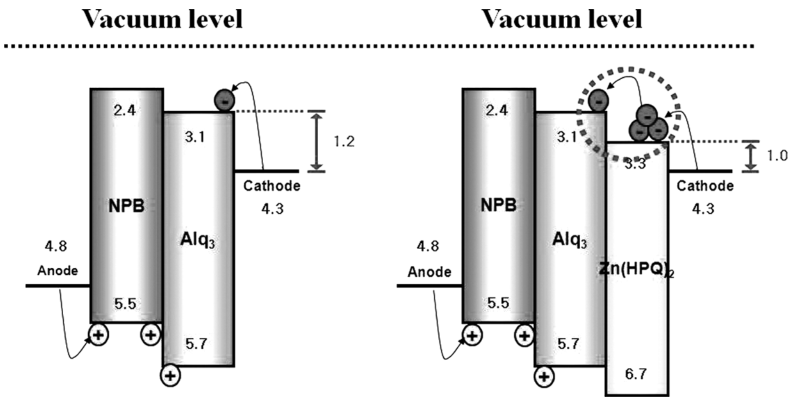

Figure 4. Schematic energy band diagram of the devices using $Zn(HPQ)_2$ as the electron transporting layer.

Figure 4 shows a schematic energy level diagram using $Zn(HPQ)_2$ as ETL. Figure 4 is helpful to understand the mechanisms of OLED. As showed in this figure, $Zn(HPQ)_2$ reduced the barrier between cathode and EML and electron can be easily injected.

3.3. *Electrical Properties*

Figure 5 shows the current density-voltage characteristics of device 1, 2, 3, and 4. The device with $Zn(HPQ)_2$ as electron transporting material exhibited an increase in current density. Also Figure 6 shows the luminance-voltage characteristics of the devices. As showed in the figure, device 2 has low driving voltage of about 7.2 V. The maximum luminance is 2256 cd/m^2. The $Zn(HPQ)_2$ showed a good electron transporting property and enhanced the device performance.

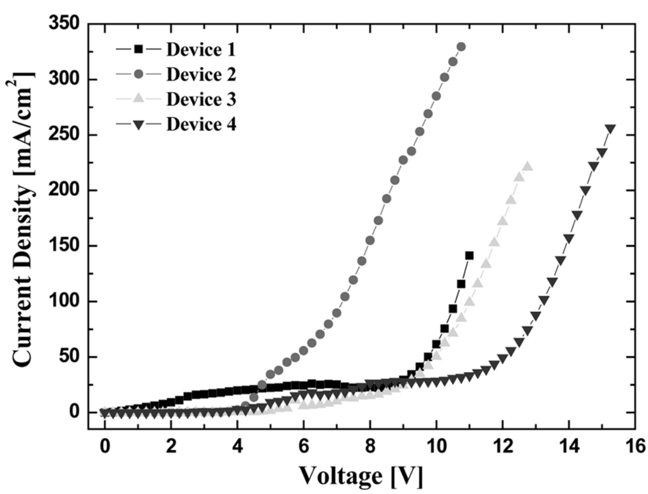

Figure 5. Current density-voltage characteristics.

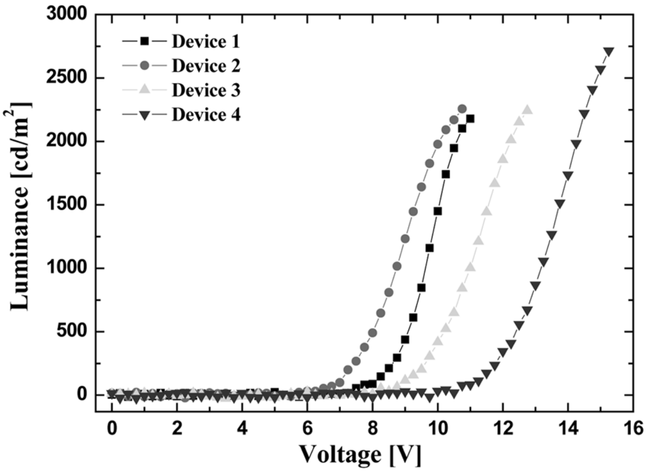

Figure 6. Luminance-voltage characteristics.

4. Conclusions

In this study, we synthesized Zn(HPQ)$_2$ as the new electron transporting material. It was determined to exhibit yellow emission with wavelength of 555 nm. We investigated the EA and IP of Zn(HPQ)$_2$ by cyclic-voltammetry. The HOMO level and the LUMO level of Zn(HPQ)$_2$ were measured to be 6.7 eV and 3.3 eV, respectively. In this study we used Zn(HPQ)$_2$ as ETL in order to improve the electron injection behavior, it was inserted between cathode and EML. The LUMO level of Alq_3 was 3.1 eV and the work function of Al was 4.3 eV, therefore the energy gap was 1.2 eV between Alq_3 and Al. But the energy gap was 1.0 eV between Zn(HPQ)$_2$ and Al. So Zn(HPQ)$_2$ could reduce the electron injection barrier between cathode and EML. From the results, we have obtained the OLED with high luminance and low driving voltage. In particular, the property when thickness of Zn(HPQ)$_2$ was 5 nm was highest. Zn(HPQ)$_2$ as ETL can be applied in improving the OLED performance. We think that Zn(HPQ)$_2$ made it possible for the electron mobility and the hole mobility to balance.

Acknowledgement

This study was supported by research funds from Dong-A University.

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