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: 17 Oct 2011

To cite this article: Yoon Ki Jang, Dong Eun Kim, Oh-Kwan Kwon, Young Soo Kwon, Won Sam Kim & Burm Jong Lee (2006): Study on Luminescent and Electron Transporting Properties of OLEDs Using Zn(phen)q and Zn(HPB)q, Molecular Crystals and Liquid Crystals, 462:1, 127-134

To link to this article: http://dx.doi.org/10.1080/07370650601013047

Mol. Cryst. Liq. Cryst., Vol. 462, pp. 127–134, 2007

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/07370650601013047

Study on Luminescent and Electron Transporting Properties of OLEDs Using Zn(phen)q and Zn(HPB)q

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Recently, high luminance and efficiency were realized in organic light-emitting diodes (OLEDs) with multilayer structure. Alq_3 is the most well known material and it has been used as electron transporting material in the OLEDs. We synthesized a novel materials, [(1,10-phenanthroline)(8-hydroxyquinoline)] (Zn(phen)q) and [(2-(2-hydroxyphenyl) benzoxazole)(8-hydoxyquinoline)] (Zn(HPB)q). We measured luminescent properties of Zn(phen)q and Zn(HPB)q using as emitting materials. We investigated that electron transporting properties of Zn(phen)q and Zn(HPB)q compared with those of Alq_3 which is used as electron transporting materials. The LUMO level Zn(phen)q and Zn(HPB)q were measured 3.2 eV and 3.5 eV, respectively. As a result, electron transporting properties of Zn(phen)q and Zn(HPB)q were better than that of Alq_3. Therefore, Zn(phen)q and Zn(HPB)q are useful as an electron transporting materials to enhance the performance of OLEDs.

Keywords: electron transporting property; OLEDs; Zn(HPB)q; Zn(phen)q

This work was supported by the MOCIE through the CIIPMS at Dong-A University.
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1. INTRODUCTION

Organic light-emitting diodes based on a low molecular compound, are attractive as a next generation flat panel display, due to low driving voltage, high contrast, easy of fabrication, low cost, and wide viewing angle [1,2].

Since the first 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 OLEDs [3]. Recently, high luminance and efficiency were realized in OLEDs with multilayer structure including emitting materials such as metal-chelate complex [4]. By varying the central metal atom (Al, Ga, In, Be, Mg, Zn, Cu, etc.), a variety of other metal complex with 8-hydroxyquinoline have been designed and synthesized for use in the OLEDs [5]. Since, the 8-hydroxyquinolinline ligand has currently been used by many researchers because of its thermal stability, carrier mobility, and its improved performance [6,7].

In this study, we synthesized novel materials such as [(1,10-phenanthroline)(8-hydroxyquinoline)] Zn(phen)q and [(2-(2-hydroxyphenyl)benzoxazole)(8-hydoxyquinoline)] (Zn(HPB)q). The ionization potential (IP) and electron affinity(EA) of Zn(phen)q and Zn(HPB)q were measured by cyclic-voltammetry(CV). We have investigated luminescent properties of Zn(phen)q and Zn(HPB)q. We also investigated electron transporting properties of Zn(phen)q, Zn(HPB)q and Alq_3. Alq_3 is one of the most widely used materials for electron transport and green emission for OLEDs, due to its excellent stability and luminescent properties [8]. We fabricated blue OLEDs using lithium tetra-(8-hydroxyquinolinato) boron ($LiBq_4$) as emitting material measure electron transporting properties.

2. EXPERIMENTAL

2.1. Synthesis of Zn(phen)q

In a round bottomed flask, 1,10-phenanthroline (0.18 g) was dissolved in 20 ml of absolute ethanol at room temperature under a nitrogen atmosphere. The solution was stirred for 1 h, after which a zinc acetate dihydrate (0.219 g) in water (3 ml) was added dropwise while stirring continued. After the addition was completed, the reaction solution was further stirred for 3 h, at which time an absolute ethanol solution of 8-hydroxyquinoline (0.145 g) was slowly added dropwise during stirring. The yellow precipitate was collected by filtration, purified by recrystallization from acetone and ethanol, and dried under overnight.

Calcd. (%) C:67.28, O:4.52, N:11.07, Zn:17.12, Found (%) C:68.11, O:4.32, N:11.35, Zn:17.57 IR (KBr, cm^{-1}): 3327, 1604, 1577, 1500, 1469, 1391, 1329, 1110, 743. UV-Vis (nm, in THF): 260, 289, 342, 390. (Reference: 8-hydroxyquinoline; 243, 287, 320, 1,10-phenanthroline; 237, 261, 325.)

2.2. Synthesis of Zn(HPB)q

In a round bottomed flask, 2-(2-hydroxyphenyl)benzoxaxazole (HPB) (0.211 g) was dissolved in 20 ml of absolute ethanol at 70°C under a nitrogen atmosphere. The solution was stirred for 1 h, after which zinc acetate dihydrate (0.219 g) in water (3 ml) and 8-hydroxyquinoline (q) (0.145 g) in absolute ethanol (10 ml) were added dropwise while stirring continued. After the addition was completed, the reaction was further carried out for 3 h. The yellow precipitates were collected by filtration, purified by recrystallization from acetone and ethanol, and dried under overnight. Calcd. (%) C:65.34, O:11.88, N:6.90, Zn:16.08, Found (%) C:64.82, O:12.20, N:7.01, Zn:15.96, ^{1}H NMR (300 MHz, DMSO, ppm) δ 8.61(m, 1H), 8.32 (m, 2H), 8.13 (m, 1H), 7.86 (m, 1H), 7.64 (m, 1H), 7.47 (m, 2H), 7.32 (m, 4H), 6.91 (m, 4H), 6.57 (m, 1H). ^{13}C NMR (75 MHz, DMSO, ppm) δ 170.01, 164.93, 161.22, 147.44, 145.34, 139.67, 138.73, 134.11, 134.54, 129.86, 129.39, 128.60, 125.11, 124.81, 123.31, 121.53, 119.13, 113.48, 112.39, 109.38. FT-IR (KBr, cm^{-1}): 3327, 1604, 1577, 1500, 1469, 1391, 1329, 1110, 743. UV-vis (nm, in DMF): 260, 294, 322, 335, 382. (Reference: 8-hydroxyquinoline (q):243, 287, 320. 2-(2-hydroxyphenyl)benzoxazole (HPB): 237, 283, 286, 293, 322, 335.)

2.3. Fabrication Process of OLEDs

Figure 1 shows the molecular structures of Zn(phen)q and Zn(HPB)q used in this study.

The OLEDs were fabricated on indium-tin-oxide (ITO) coated glass substrates with a sheet resistance of 10 $\Omega/\square$ and a thickness of 120 nm. Prior to film deposition, the ITO substrate surface was treated with UV-ozone for 1 minute. UV-ozone treatment enhanced the performance of OLEDs [9].

The IP and EA of Zn(phen)q and Zn(HPB)q were measured using CV (potentionstat 263 A, Seiko EG&G Instrument). We obtained the IP from ITO electrode and the EA from Al electrode. For all CV, an electrolyte solution of 0.1 M Bu_4NClO_4 in acetonitrile was used. A three-electrode compartment electrochemical cell consisted of an ITO or Al glass electrode as the working electrode in the prepared sample,

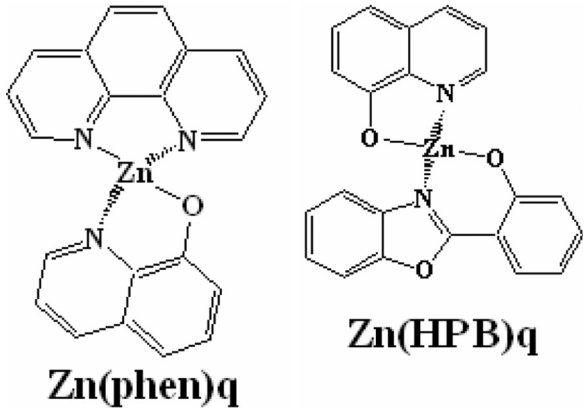

FIGURE 1 The molecular structures of Zn(phen)q and Zn(HPB)q.

a platinum wire (0.8 mm) as the counter electrode, and Ag/AgCl as the reference electrode. The cyclic voltammograms were obtained at a scan rate of 400 mV/sec.

The structure of the devices were ITO/NPB/Zn(phen)q or Zn(HPB)q/Alq_3/LiF/Al. Zn(phen)q and Zn(HPB)q were used as emitting layer. Also, the structure of the devices were ITO/NPB/$LiBq_4$/Zn(phen)q, Zn(HPB)q or Alq_3/LiF/Al. Zn(phen)q, Zn(HPB)q and Alq_3 were used as electron transporting layer. We are fixed the thickness of hole transporting layer, emitting layer and electron transporting layer with 40 nm, 60 nm and 10 nm, respectively.

The organic materials were successively evaporated on top of the ITO substrate under 5×10^{-6} torr with deposition rate of about 1.0 Å/s. A metal cathode was deposited under 5×10^{-6} torr with deposition rate of about 10 Å/s(Al) and 0.1 Å/s(LiF), respectively. The emission area of each device was $3 \times 3\,mm^2$. 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.).

3. RESULTS AND DISCUSSION

We investigated luminescent properties of Zn(phen)q and Zn(HPB)q. The structure of the devices were ITO/NPB(40 nm)/Zn(phen)q or Zn(HPB)q(60 nm)/Alq_3 (10 nm)/LiF(0.5 nm)/Al(100 nm). The current density-luminance characteristic of the device using Zn(phen)q and Zn(HPB)q as emitting materials show in Figure 2. As shown in this

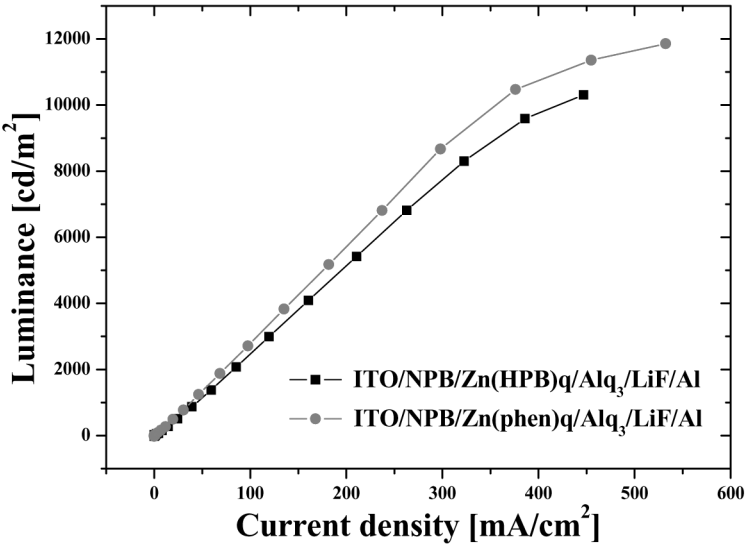

FIGURE 2 Current density-luminance characteristic of Zn(phen)q and Zn(HPB)q used as emitting materials.

figure, a maximum luminance of Zn(phen)q and Zn(HPB)q were 11856 cd/m^2 and 10309 cd/m^2, respectively. Luminescent properties of Zn(phen)q was better than Zn(HPB)q. The EL spectra measured Zn(phen)q and Zn(HPB)q using as emitting materials. The EL peaks of Zn(phen)q and Zn(HPB)q were observed to be 549 nm and 540 nm, respetively. Zn(phen)q and Zn(HPB)q are produced a yellowish green emission.

We compared the electron transporting properties of Zn(phen)q and Zn(HPB)q with that of Alq_3. The electron transporting layer plays an important role in transporting electrons and blocking holes, thus preventing holes from moving into the electrode without recombining with electrons.

We fabricated blue OLEDs using $LiBq_4$ as an emitting material. $LiBq_4$ has boron compounds in general much more stable than the corresponding aluminum compounds [10,11]. The structure of the devices were ITO/NPB(40 nm)/$LiBq_4$(60 nm)/Zn(phen)q, Zn(HPB)q or Alq_3(10 nm)/LiF(0.5 nm)/Al(100 nm). The current density-voltage-luminance characteristics using Zn(phen)q, Zn(HPB)q and Alq_3 as electron transporting materials shows in Figure 3. We found that the properties of devices were low turn-on voltage, increase luminance, and decrease driving voltage using electron transporting layer.

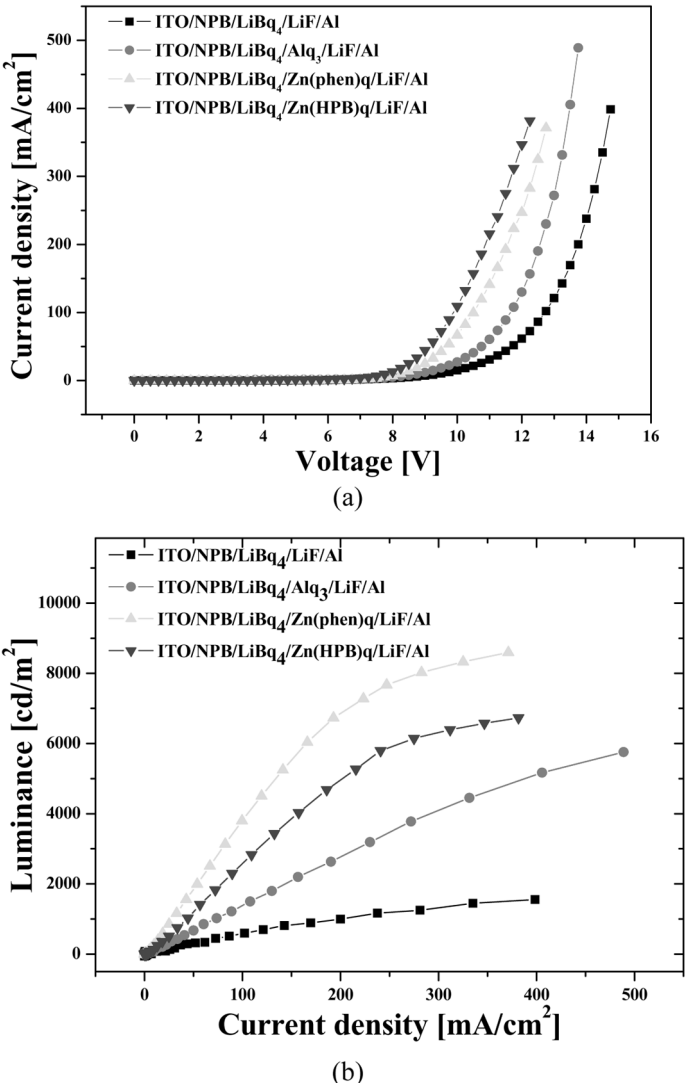

FIGURE 3 (a) Current density-voltage and (b) current density-luminance characteristics used Zn(phen)q, Zn(HPB)q and Alq_3 as electron transporting materials.

Zn(phen)q and Zn(HPB)q using as electron transporting materials improved of the performance of OLEDs. Thus, the electron transporting properties of Zn(phen)q and Zn(HPB)q were better than Alq_3.

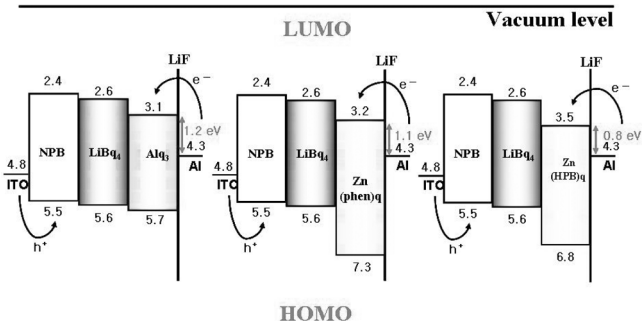

FIGURE 4 Schematic energy level diagrams used Zn(phen)q, Zn(HPB)q and Alq_3 as electron transporting materials.

Zn(phen)q and Zn(HPB)q were measured by cyclic-voltammetry (CV). The oxidation onset potential and the reduction onset potential of Zn(phen)q and Zn(HPB)q were measured +2.5 V, −1.6 V and +2.0 V, −1.3 V, respectively. The HOMO (highest occupied molecular orbital) and LUMO(lowest unoccupied molecular orbital) 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 [12,13]. The HOMO and LUMO energy levels of Zn(phen)q and Zn(HPB)q were calculated as 7.3 eV, 3.2 eV and 6.8 eV, 3.5 eV, respectively.

Figure 4 is schematic energy level diagrams used Zn(phen)q, Zn(HPB)q and Alq_3 as electron transporting materrial. Figure 4 is helpful in understanding the mechanisms of OLEDs. As shown in Figure 4, the LUMO level of Zn(phen)q and Zn(HPB)q lower than that of Alq_3. Thus, devices performance increased using Zn(phen)q and Zn(HPB)q as electron transporting material because electrons can be easily injection from metal until emitting material. At the same time, the HOMO level of Zn(phen)q and Zn(HPB)q are far greater than the HOMO level of Alq_3, and hence the Zn(phen)q and Zn(HPB)q layer will block the hole transport from ITO.

4. CONCLUSION

In this study, we synthesized Zn(phen)q and Zn(HPB)q as the novel electroluminescence materials. We have investigated luminescent properties of Zn(phen)q and Zn(HPB)q. The EL spectra of Zn(phen)q and Zn(HPB)q observed yellowish green emission. The HOMO and LUMO levels of the Zn(phen)q were measured 7.3 eV and 3.2 eV. Also, Zn(HPB)q were measured 6.8 eV and 3.5 eV. We used $LiBq_4$ as

emitting layer and then, we measured electron transporting properties of Zn(phen)q, Zn(HPB)q and Alq_3. As a results, the performance of the devices using Zn(phen)q and Zn(HPB)q as an electron transporting materials were better than that of Alq_3. The Zn(phen)q and Zn(HPB)q as electron transporting material can be applied in improving the OLEDs performance.

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