

Improvement of Mixed Electron Transport Structure Red Phosphorescent Organic Light-Emitting Diodes

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In this paper, we demonstrate development of red phosphorescent Organic Light-Emitting Diodes (OLEDs) as the doping concentrations are varied with lithium-quinolate (Liq) doped electron transport layer (ETL). The experimental device has both mixed electron transport layer and electron injection layer. The device configuration was ITO/NPB (50 nm)/4,4'-N'-N'-dicarbazole-biphenyl (CBP) doped with 8% bis(2-phenylquinoline)iridium(III) (acetylacetonate) [Ir(pq)₂(acac)] (30 nm)/Bphen doped with X% Liq (30 nm)/Liq (2 nm)/Al (100 nm), where the doping concentration of Liq in ETL was varied as 5%~65%. When the Liq was mixed in the ETL, the efficiency and operating voltage of the experimental devices were improved in comparison with the reference device due to greater electron transport efficiency and an improved hole-electron balance.

Keywords Electron transport layer; organic light-emitting diodes; phosphorescent

Introduction

Since 1987, with Tang and VanSlyke's discovery of efficient organic light-emitting diodes (OLEDs), there have been many studies to enhance the high efficiency of OLEDs. Recently, OLEDs have attracted increasing attention for use in various potential applications, including as a solid state source and flat panel display (FPDs), as a backlight unit for liquid crystal display (LCDs), because of the many advantages such as a wide viewing angle, compactness, flexibility, high resolution, fast response time, and an easy manufacturing process. Therefore, one of the promising next generation display technologies is the use of OLEDs [1–3]. However,

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OLEDs have various defects, in particular, devices stability and high power consumption are major issues in the used of OLEDs in applications such as for solid light source and as a FPDs.

Many researchers have investigated the high efficiency and low operation voltage device performance in OLEDs. In general, OLEDs consist of an anode for hole injection, a cathode for electron injection and an emitting layer with charge recombination in which excitons are formed. The mobility of a hole is higher than that of an electron by about a centuple, an as a result, non-emissive cationic species form in the emission layer [4]. Accordingly, there is an obstruction of hole-electron recombination, followed by the formation of a dark spot, luminance decay and subsequent low efficiency of the device. Many methods have been reported to obtain higher efficiencies and improve the electronic characteristics by balancing the hole-electron pairings in the emitting layer.

Many researchers have researched the injection of balanced carriers into the emitting layer. A typical method is that the electron transport layer (ETL) is doped with n-type dopant such as Ca, Mg, and Li with a low work function. They lead to an efficient electron injection from the cathode into the emission layer [5–7]. However, the fabrication of OLEDs treated with a n-type metal dopant is very difficult and complex because the n-type metal dopant materials are very reactive and sensitive in the open atmosphere. In this study, to obtain a high efficiency and improve the device’s electronic characteristics, we studied OLEDs using the organic material, lithium-quinolate (Liq) as a dopant for the ETL.

Device Fabrication

We fabricated three types phosphorescent OLEDs as shown in Figure 1. All devices used in this study are mental devices which have a structure of indium tin oxide (ITO) (150 nm, anode)/4,4’-bis[N-(naphthyl)-N-phenyl-amino]biphenyl (NPB) (50 nm, hole transporting layer)/4,4’-N-N’-dicarbazole-biphenyl (CBP) doped with 8% bis(2-phenyl-quinoline)iridium(III) (acetylacetonate) [Ir(pq)₂(acac)] (30 nm,

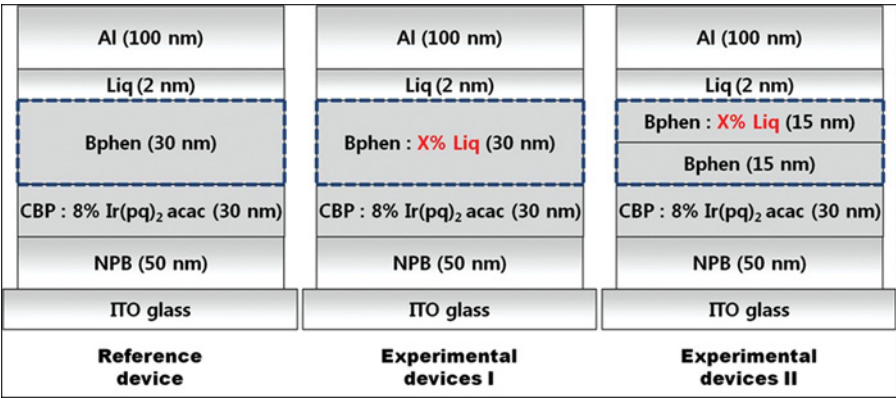


Figure 1. The device structure of the reference device and the experimental devices.

emission layer)/ETL (30 nm, hole blocking and electron transporting layer)/lithium quinolate (Liq) (2 nm, electron injection layer)/Al (100 nm, cathode), where Ir (pq)₂(acac) was used as red emitting dopant. The reference device has the pure 4,7-diphenyl-1,10-phenanthroline (Bphen) as the ETL over the whole ETL region. On the other hand, for the experimental devices I, we have the mixed ETL consisting of Bphen doped with X% Liq over the whole ETL region, and for the experimental devices II with a double ETL, one layer with pure Bphen (15 nm) and one layer with X% Liq doped Bphen (15 nm). The doping ratio of Liq was varied in the range of 5%~65% in the experimental devices.

The ITO on glass substrates with a sheet resistance of 30 Ω /sq (emitting region was $3 \times 3 \text{ mm}^2$) was used as a transparent anode. The ITO glass was chemically cleaned in an ultrasonic bath by following sequence: acetone, methanol, de-ionized water and isopropyl alcohol. Afterwards, the cleaned ITO substrates had been dried by using N₂ gas. Then, pre-cleaned ITO was treated by Oxygen plasma with the power conditions of 125 W for 2 min. under low vacuum of 2×10^{-2} torr. All organic layers were deposited in succession by high vacuum (5×10^{-7} torr) thermal evaporation at a rate of 1.0 $\text{\AA}$ /sec and 0.1 $\text{\AA}$ /sec for Liq, respectively. The deposition of the organic layers without a vacuum break, the Al cathode was vacuum deposited to a thickness of 100 nm at a rate of 10 $\text{\AA}$ /sec.

Measurements

The current density–voltage (J–V) characteristics of the OLEDs were measured with a source measure unit (Keithley 236) with the DC voltage bias, the optical and electrical properties of the devices such as the luminance, luminous efficiency, Commission International de L'Eclairage (CIE) coordinates and electroluminescence (EL) spectra characteristics were analyzed by CHROMA METER CS-1000 instruments. All measurements were carried out under ambient conditions at room temperature.

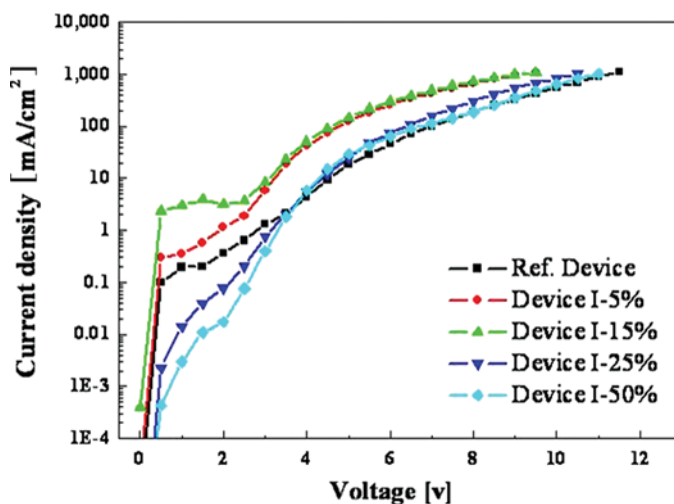


Figure 2. The current density versus voltage characteristics of electron only devices.

Results and Discussion

In general, alkali metal based organo-metallic compounds are known to have good electron injection efficiency because the electron injection barrier between the ETL and Al is low. Liq reduces carrier transportation because it is an insulator which has a high dielectric constant. However, when the Liq layer exists as a thin film at the organic layer and cathode metal interface, it is possible for tunneling of the carrier to occur. It is known that Bphen has been used as ETL material due to its higher electron mobility and Liq has good electron injection efficiency. Therefore, we expected that a little Liq doped in ETL would easily lead to the efficient injection of electrons from the cathode to the ETL as shown in Figure 2. In addition, the Figure 3 shows a comparison between the energy level diagrams of experimental devices I and II. When the Liq doped in Bphen, electrons can be directly injected from the cathode into the lowest unoccupied molecular orbital (LUMO) of the Liq doped in Bphen rather into that of Bphen alone, it leads to more efficient

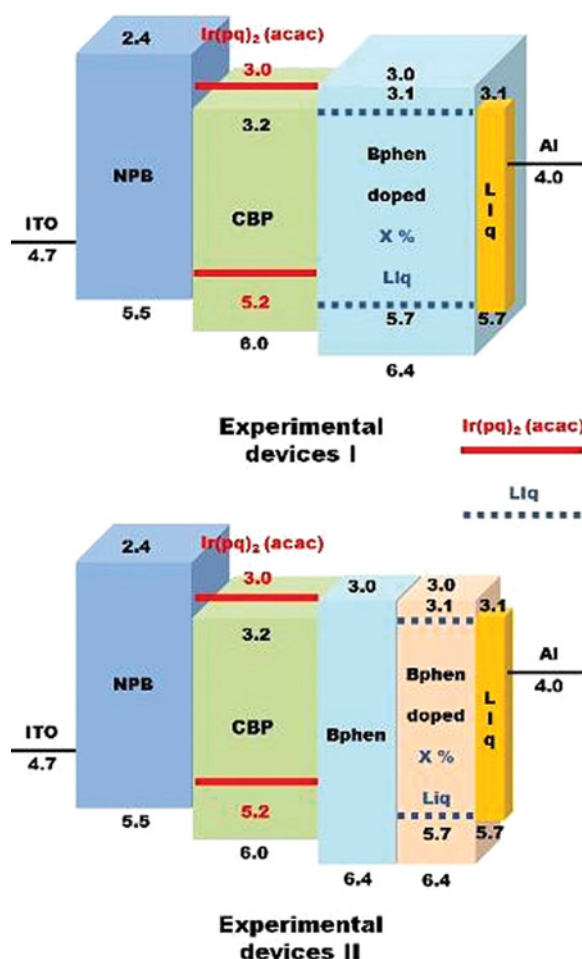


Figure 3. The electronic energy level diagrams for experimental devices I and II.

electron injection. This is because the electron injection barrier between the cathode and the ETL is lowered by about 0.1 eV in the case of a device with Liq doped Bphen as the ETL.

Figure 4(a) shows the current density versus voltage curves of the reference device and experimental devices I. The doping ratio of the Liq was controlled to range from 5%~0% in experimental devices I. The current density was increased according to the increase of the doping ratio of Liq, but it was decreased by more than 15% because of the poor electron transportation properties of the Liq. However, the current density of all experimental devices I is higher than that of the reference device. It proves that the Liq doped in the ETL improves the driving

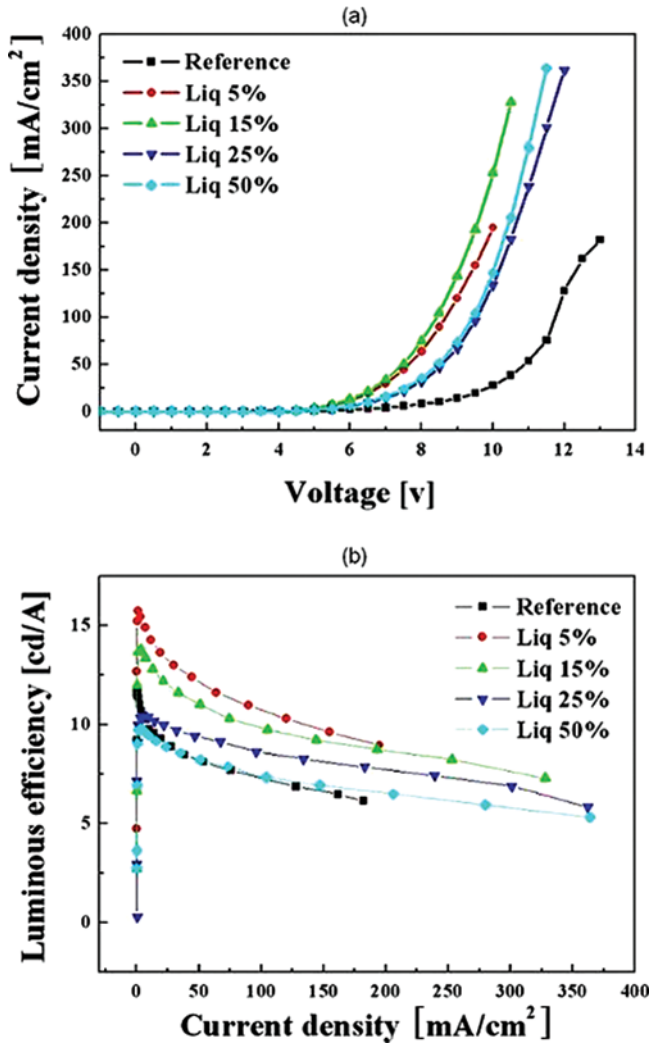


Figure 4. (a) Current density versus voltage and (b) luminous efficiency versus current density characteristics of the reference device and experimental devices I.

voltage of device. It is assumed to be due to good interfacial contact between the cathode and the ETL when the Liq was doped in the ETL.

The luminous efficiency characteristics show a dissimilar tendency in the current density curves, as shown in Figure 4(b). Although the electron injection into the device is the most efficient in the device with the 15% Liq, the maximum efficiency value was obtained in the device with a doping ratio 5% Liq because the recombination of holes and electrons is well balanced in the 5% Liq doped device. Moreover, heavy doping of Liq (15%~50%) causes unbalanced holes and electrons in EML due to excess or insufficient electrons and decreases the device efficiency compare with 5% Liq doped device. Nevertheless, the Liq doped ETL structure devices have

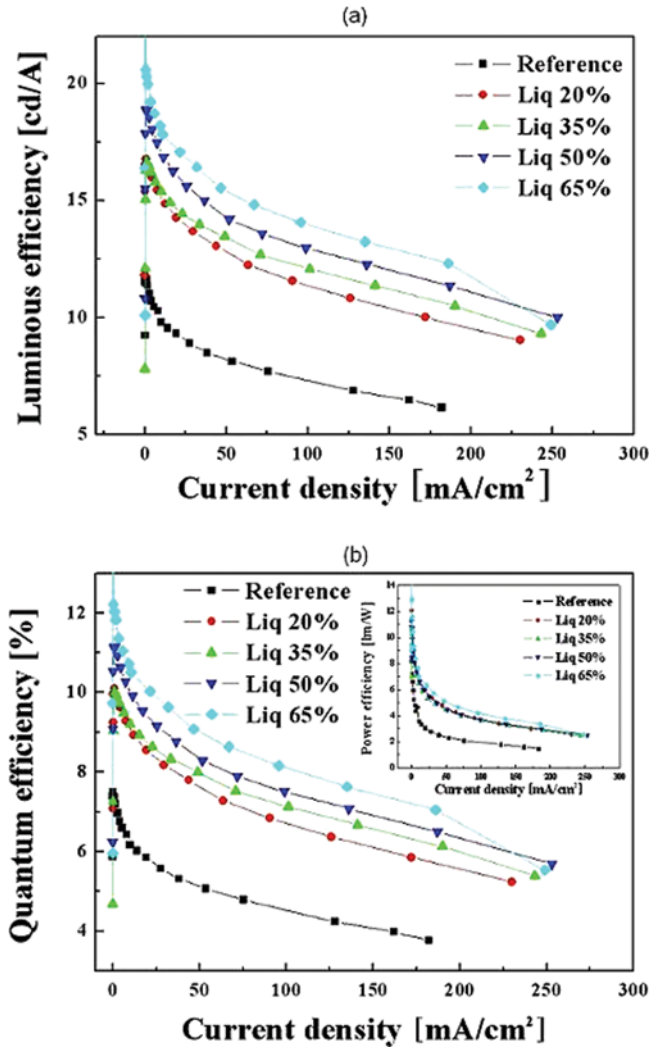


Figure 5. (a) Luminous efficiency and (b) quantum efficiency versus current density (inset: power efficiency versus current density) of the reference device and experimental devices II.

improved electrical characteristics compared with the reference device in efficiency and driving voltage characteristics.

In addition, we fabricated the experimental devices II for greater improvement of device efficiency. The experimental devices II with a double ETL consist of first layer with pure Bphen (15nm) and second layer with a mixture of Bphen and Liq. The doping ratio of the Liq was controlled to range from 20%~65% in Bphen (15nm). Figure 5 shows the efficiency characteristics of experimental devices II. Although experimental devices I have the highest efficiency in the device with 5% Liq doped ETL, the highest max. luminous efficiency of experimental device II is observed in the device with 65% Liq doped ETL. The reason for this is because that when the Liq was doped over the extensive region of Bphen (30nm), the Liq due to its insulator property reduced the electron transport ability of Bphen. On the other hands, the narrow Liq doped region (15nm) helps to migrate the electrons from the cathode into the pure Bphen layer. In the case of the experimental devices II, the device with the 65% Liq doped ETL has the Max. luminous efficiency, quantum efficiency and power efficiency of 20.6 cd/A, 12.2% and 12.9 lm/W, respectively. These results are superior to the efficiency values of experimental devices I optimized with 5% Liq doped Bphen, which have a luminous efficiency, quantum efficiency and power efficiency of 15.7 cd/A, 9.5% and 11.9 lm/W, respectively. Therefore, the double layered ETL structure of experimental devices II enhanced the device efficiency by about 30% when compared with experimental devices I and by about 45% in comparison with the reference device.

All devices fabricated in this study showed similar electroluminescence (EL) spectra at 10 V as shown in Figure 6. They have a maximum emission peak at about 601 nm due to $\text{Ir}(\text{pq})_2(\text{acac})$. It indicates that there was no charge leakage out of the emitting layer and only emissions from the dopant materials were obtained.

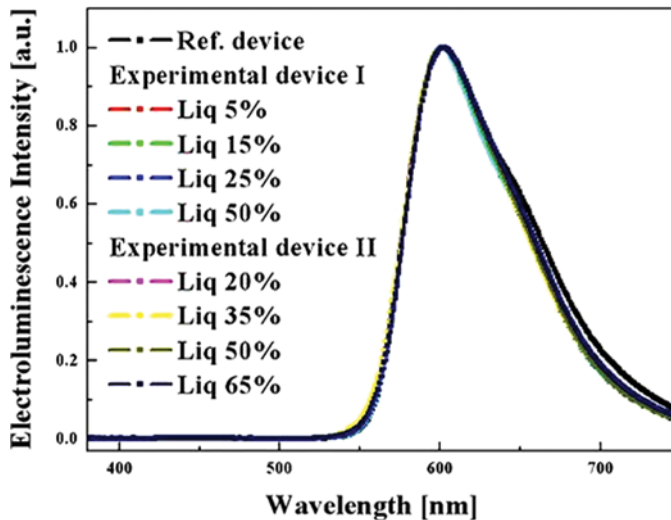


Figure 6. Electroluminescence (EL) spectra of all devices fabricated in this study.

Conclusions

In this study, we have demonstrated that the device performance of OLEDs can be improved by using a mixed electron transport structure. When the Liq was doped in Bphen, the electrical properties such as the driving voltage and efficiency were enhanced by about 30%~45% because of the lowered electron injection barrier and good interfacial contact between the cathode and the ETL. Therefore, it can be concluded that improved electron injection leads to the balanced charge recombination of holes and electrons and enhanced the electrical properties of the device.

Acknowledgment

This work was supported by Energy Resources Technology Development program (2007-E-CM11-P-07) of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Knowledge Economy and Strategy Technology Development program (No. 10030834) from Ministry of Knowledge Economy (MKE). Moreover, this research was also supported by the ERC program of the Korea Science and Engineering Foundation (KOSEF) grant funded by the Korea Ministry of Education, Science and Technology (MEST) (No. R11-2007-045-03001-0).

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