

Highly Efficient Red Phosphorescent OLEDs Fabricated Using Extremely Low Doping Technology

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Highly efficient red phosphorescent organic light-emitting devices (PHOLEDs) were fabricated using extremely low doping technology in a simple device configuration. They were developed by making use of the narrow-bandgap fluorescent host material bis(10-hydroxybenzo[h] quinolino)beryllium complex (Bebq₂) and red dopant tris(1-phenylisoquinoline)iridium (Ir(piq)₃). Maximum current and power efficiencies of 11.60 cd/A and 13.02 lm/W, respectively, are demonstrated with an extremely low doping level of 1 wt%. These results reveal a practical way to make highly efficient PHOLEDs by reducing dopant self quenching.

Keywords Energy transfer; light-emitting diode; low doping; phosphorescent OLED

Introduction

Organic light emitting diodes (OLEDs) have attracted considerable attention because of their potential applications in flat-panel displays [1–3] and in next generation lighting [4,5]. High-efficiency phosphorescent OLEDs (PHOLEDs) have generated intense research interest until now as they have the potential to produce 100% internal quantum efficiency. The doping concentration in PHOLEDs is usually very high, as much as 6–10 wt%, compared with less than 1 wt% in fluorescent devices. Energy transfer between the host and guest molecules can occur through either coulombic interactions (long-range interactions) or electron exchange (short-range interactions). The former is called dipole-dipole or Förster-type energy transfer. Fluorescent devices are mainly reported to utilize this energy transfer mechanism between the host singlet to the dopant singlet. Therefore, 0.1~0.5 wt% doping condition for the energy transfer is sufficient for fluorescent devices.

The energy transfer from the host triplet to the dopant triplet follows the electron exchange mechanism called the “Dexter mechanism.” Therefore, high doping

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concentrations are required in the triplet emitter systems. In our previous studies, we reported that the required doping concentration for ideal Dexter energy transfer in PHOLEDs was about 1~2 wt% [6]. However, real PHOLEDs generally use more than 3 wt% doping concentrations due to the other reason. Usually, the host materials in PHOLEDs have wide band-gap characteristics due to the large exchange energy between the singlet and triplet states. Therefore, dopant molecules work as deep trapping sites in such host guest systems. High doping concentrations over 3 wt% are essential to achieve good carrier transport in such PHOLEDs.

When we reduce the doping concentration in a device without charge trapping in the triplet host guest system, self-quenching of singlet and triplet excitons occurring through processes such as recombination loss of two singlet excitons and/or triplet-triplet annihilation can be minimized. Earlier, Kawamura *et al.* reported that the phosphorescence photoluminescence quantum efficiency of tris(2-phenylpyridine)iridium ($\text{Ir}(\text{ppy})_3$) is decreased by ~5% with an increase in doping concentration from 2 to 6 wt% [7]. Consequently, the selection of suitable host candidates is a critical issue in fabricating high efficiency PHOLEDs. In our previous studies, a narrow band-gap fluorescent host material, bis(10-hydroxybenzo[h]quinolinato)beryllium complex (Bebq_2) doped with a 4 wt% concentration of tris(1-phenylisoquinoline) iridium ($\text{Ir}(\text{piq})_3$) as the minimum doping value was reported for red PHOLEDs [8]. By contrast, in this study, we report the use of an extremely low doping (~1 wt%) technology in conjunction with a simple device configuration to produce highly efficient red PHOLEDs, even in devices which are subject to significant levels of charge trapping. This low doping technology was developed by reducing the emissive layer thickness from 50 nm to 30 nm.

Experimental

In this work, we have fabricated several red PHOLEDs using the following two device structures (Fig. 1):

Device A: ITO/DNTPD (40 nm)/ Bebq_2 : $\text{Ir}(\text{piq})_3$ (50 nm)/LiF/Al.

Devices B, C, D: ITO/DNTPD (40 nm)/ Bebq_2 : $\text{Ir}(\text{piq})_3$ (30 nm)/ Bebq_2 (20 nm)/LiF/Al.

The dopant concentration for the control device A was 4%; this was already reported to be the minimum doping concentration to produce the most efficient organic bi-layered structure [8]. In order to reduce the emitting layer thickness, an organic triple-layered structure was designed. To investigate the device characteristics, we used different doping concentrations for devices B (3%), C (2%), and D (1%). The materials for fabricating the devices by sublimation, Bebq_2 and $\text{Ir}(\text{piq})_3$ were purchased from Gracel Corporation and N,N'-di(4-(N,N'-diphenyl-amino)phenyl)-N,N'-diphenylbenzidine (DNTPD) was purchased from Chemipro Corporation. The material structures and energy band diagram are shown in Figure 1. Glass substrates of dimensions $2.5 \times 2.5 \text{ cm}^2$ were coated with 150 nm of indium-tin oxide (ITO), whose sheet resistance was 12 Ohm/sq, to make the PHOLEDs. The ITO glass was cleaned via sonification in isopropylalcohol (IPA) and acetone, then rinsed in deionized water. Finally, it was irradiated in a UV-ozone chamber. All the organic materials were deposited using the vacuum evaporation technique, at a pressure of $\sim 3.0 \times 10^{-7}$ torr. Doping was carried out by co-evaporation from independent sources, and the effusion rates were monitored using a quartz-crystal microbalance.

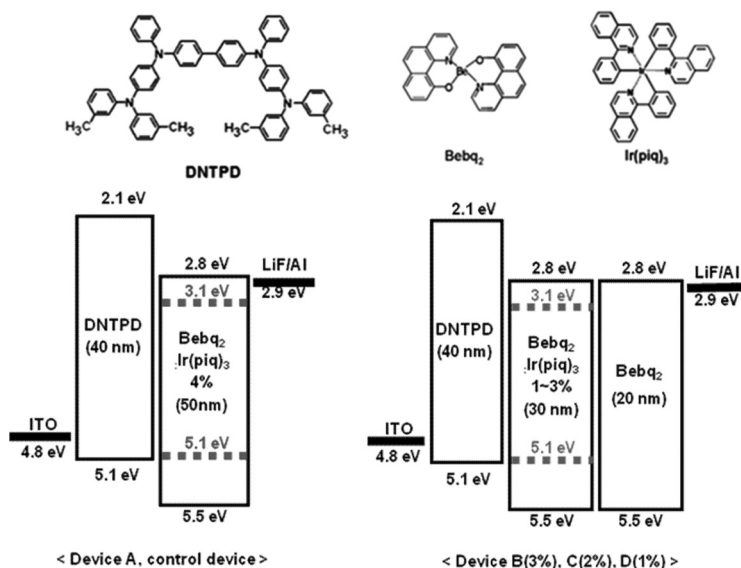


Figure 1. Device and molecular structures used in the present studies.

Subsequently, Al was deposited *in situ* at a deposition rate of $\sim 5 \text{ \AA/s}$ and was used as a cathode. The current density-voltage (J-V) and luminance-voltage (L-V) data of the PHOLEDs were measured using a Keithley SMU 238 and Minolta CS-100A, respectively. Also, the electroluminescence (EL) spectra and CIE color coordinates were obtained using a Minolta CS-1000A spectroradiometer.

Results and Discussion

The HOMO (highest occupied molecular orbital) energy levels are 5.1, 5.5, and 5.1 eV for DNTPD, Beq₂, and Ir(piq)₃, respectively. DNTPD has almost no injection barrier since its Fermi energy level is similar to UV-ozone treated ITO. Figure 1 shows all the energy levels of used materials. In our devices, the injection barrier is existed about 0.4 eV at the DNTPD/Beq₂ interface. The LUMO (lowest unoccupied molecular orbital) level of the Beq₂ material (2.8 eV), which is very close to the Fermi energy level of the LiF cathode (2.9 eV), offers almost no barrier to the electron injection between the emitting layer and the LiF cathode. Furthermore, the LUMO energy levels of the host and the dopant are almost the same. Therefore, the electron movement in our devices must be very good. However, there is a big HOMO energy gap of 0.4 eV between Beq₂ and Ir(piq)₃. Hole carrier trapping by Ir(piq)₃ molecules can be observed in such high energy gap host guest systems. The hole trapping emission mechanism in this host guest system was already reported in our previous studies [9]. In order to achieve good carrier transport in the light emitting layer, the guest concentration should be higher than the generally required doping concentration for energy transfer alone. Previously, we reported that our Beq₂ and Ir(piq)₃ host guest system required a minimum doping concentration of about 4% [8] with an emissive layer thickness of 50 nm. When this was reduced, it was also possible to reduce the minimum doping concentration since the emission zone and carrier transport area were both made smaller. This was

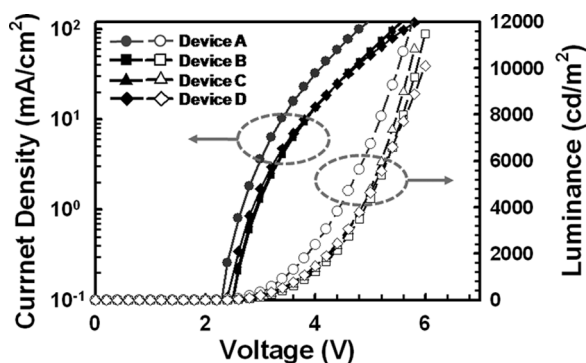


Figure 2. J-V-L characteristics of fabricated device A~D.

expected since a reduction in doping concentration leads to a reduction in exciton-exciton self-quenching, thereby, increasing the device efficiency. Therefore, the thickness of the emissive layer was reduced from 50 nm to 30 nm and a 20 nm thick Beq₂ was used as an electron transporting layer to compensate the total thickness reduction and to eliminate other hetero-interface issues.

Figure 2 shows the J-V characteristics of fabricated red PHOLEDs. At a given constant voltage of 4.0 V, current densities of 31.84, 13.24, 13.31 and 13.73 mA/cm² were observed in the fabricated devices A, B, C, and D, respectively. The driving voltage to reach 1000 cd/m² is 3.5 V for device A and 3.9 V, 3.9 V, and 3.8 V for devices B to D, respectively. All three devices (B to D) have a smaller emissive layer thickness and show similar J-V and L-V characteristics because of similar charge trapping in the emissive layer. Low turn-on voltages of between 2.2 and 2.3 V were also observed in devices B, C, and D. Usually, in multi layered OLEDs, such low turn-on voltages are very difficult to achieve. However, our organic triple-layered structure does not have any serious current injection barriers at each hetero-interface. In addition, charge carrier transport in the emitting layer is not bad due to the narrow band-gap host material.

The current and power efficiency characteristics of the fabricated devices are shown in Figure 3. The maximum current and power efficiencies were 10.93 cd/A and 14.10 lm/W for device B, 11.65 cd/A and 14.99 lm/W for device C, 11.60 cd/A and 13.02 lm/W for device D, respectively. At a given constant luminance of 1000 cd/m², the current and power efficiencies were 9.41 cd/A and 7.58 lm/W for device B, 10.35 cd/A and 8.55 lm/W for device C, and 10.88 cd/A and 9.00 lm/W for device D, respectively. These current efficiency data correspond to 11.2%, 12.3%, and 12.9% external quantum efficiencies (EQE) for devices B, C, and D, respectively. By contrast, the control device A had a current and power efficiency of 8.83 cd/A (10.5% EQE) and 8.16 lm/W. Hence, very high current and good power efficiencies were obtained using this organic triple-layered structure with low doping technology. The efficiency enhancement by reducing self quenching is about 25% at 1000 cd/m².

Figure 4 shows EL spectra at a brightness of 1000 cd/m² for devices A to D. A clean red light was observed at 624 nm in all four phosphorescent devices, indicating almost complete energy transfer from the narrow band gap Beq₂ host material to the Ir(piq)₃ dopant. The color coordinates at 1,000 cd/m² are (0.67, 0.32) in devices

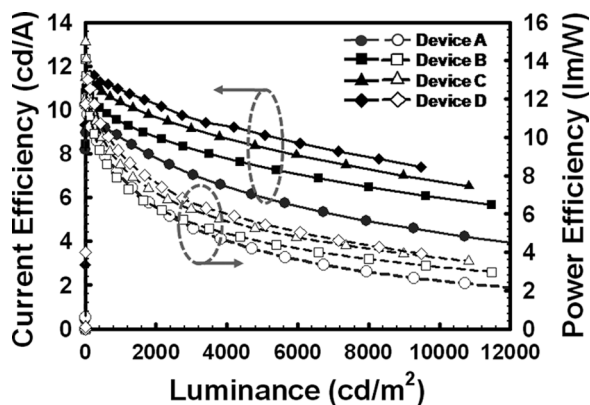


Figure 3. Current efficiency-luminance and power efficiency-luminance characteristics of fabricated device A~D.

A and B and (0.66, 0.32) in device C and D, respectively. All four devices show very good deep red color coordinates. However, device D which has 1.0% doping concentration shows a very weak host emission at about 504 nm, indicating that a 1.0% doping concentration is the minimum possible doping concentration.

Interesting and intriguing results regarding the performance of red PHOLEDs with an organic triple-layered structure and 1% doping condition were obtained in this study. In our previous studies, we reported that the ideal host guest system (a system with almost no charge trapping) requires 1% doping technology regardless of emitting layer thickness [6]. Highly efficient organic bi-layered PHOLEDs with a 50 nm emitting layer were demonstrated in such an ideal host-dopant system. When the $\text{Ir}(\text{piq})_3$ dopant was used in a Bebq_2 host system with the same organic bi-layered structure, the doping concentration was high because the hole carrier mobility can be reduced by hole-carrier trapings of the dopant molecules. To overcome hole trapping, an organic triple-layered structure was designed to have smaller emissive layer thickness (30 nm). The charge balance in this organic triple-layered structure is very good and hole carrier transport in the emitting layer is also not

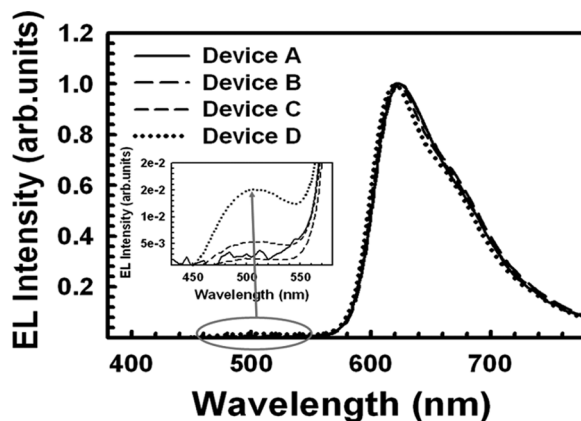


Figure 4. EL spectra of fabricated device A~D.

bad. As a result, extremely low doping technology such as ideal Dexter energy transfer is realized. High-efficiency characteristics were obtained by reducing exciton self-quenching and minimizing the hole-trapping zone.

Conclusions

Highly efficient red PHOLEDs with an organic triple-layered structure and a low (1%) doping condition were demonstrated herein. Efficient energy transfer from the host to Ir complex with a minimized emissive layer thickness was realized in phosphorescent devices. This simple structure with a low doping technology in charge trapped devices is very useful for designing an efficient host-dopant system and for the fabrication of highly efficient PHOLEDs. In addition, this technology is very useful for saving manufacturing costs through a simple structure with reduction of expensive Ir dopants.

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