

Green to white to blue OLEDs by using PBD as a chromaticity-tuning layer

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Available online 18 October 2004

Abstract

Blue to white to green light-emitting diodes with structure ITO/PVK:DPPhP(5%)/PBD(x nm)/Alq₃(5 nm)/LiF(0.3 nm)/Al have been obtained. DPPhP (1,3-diphenyl-5-(9-phenanthryl)-4,5-dihydro-1-H-pyrazole), which performs good blue-emitting and hole-transporting properties, is synthesized and used as dopant. When the thickness of PBD layer varies from 0 to 5 to 10 nm, green to white to blue emission is achieved. Based on the energy band theory and carrier tunneling theory, we consider that PBD layer plays a chromaticity-tuning role and the color-variable EL is ascribed to its modulation function on carrier recombination zone.

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Keywords: OLEDs; Green to white to blue; PBD as chromaticity-tuning layer

1. Introduction

Since Tang and Vanslyke [1] first reported the usage of multi-layer organic thin films for light-emitting devices, organic light-emitting diodes (OLEDs) have been widely studied because of their potential applications in flat-panel displays [2–6]. Recently, color variable OLEDs attract considerable attention because one of the challenges in real display is color tuning [7–9]. The common approaches to color variable displays are voltage controlled and polarity controlled devices. For voltage controlled method, a blend of emissive materials is usually used and the emitting color changes with the applied voltage. For polarity controlled approach, a blend of two active emissive materials is sandwiched between two different redox layers. The function of the redox layers is to modify the carrier injection and transportation. Therefore the modified device can emit different colors under forward bias or reverse bias [8]. In this paper, we report a method to obtain color variable OLEDs by inserting a hole-blocking layer between

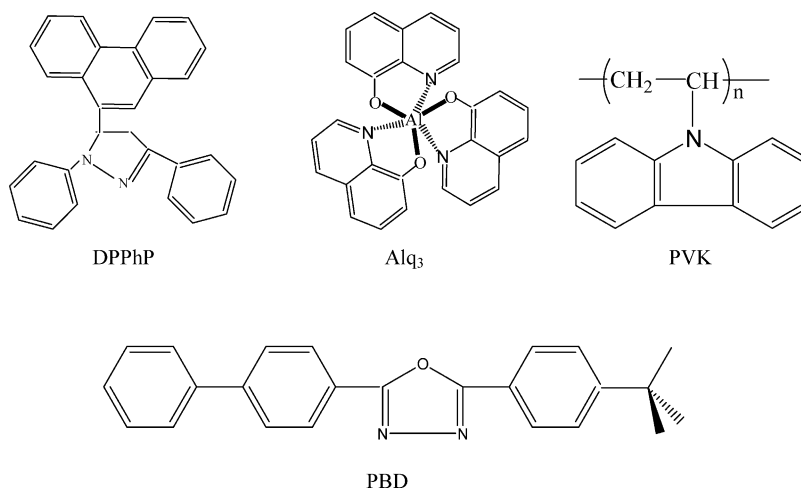
two emissive layers. The mechanism is to tune the charge recombination zone by adjusting the thickness of the inserted hole-blocking layer. People can obtain their expected colors by adjusting the two emitting layers and the thickness of the inserted layer.

In our previous work [10], a good blue emissive material, 1,3-diphenyl-5-(9-phenanthryl)-4,5-dihydro-1H-pyrazole (DPPhP) has been synthesized. Here, we use PVK:DPPhP(5%) and Alq₃ as emissive layer and PBD as hole-blocking layer to fabricate four OLEDs with structure ITO/PVK:DPPhP(5%)/PBD(x nm)/Alq₃(5 nm)/LiF(0.3 nm)/Al, $x=0$ (device A), 5 (device B), 10 (device C), 15 (device D). Green to white to blue light-emitting diodes have been achieved.

2. Experiments

All the chemical structure of the materials are shown in Fig. 1. ITO-coated glass substrates with a sheet resistive of 60 Ω /cm were cleaned consecutively in ultrasonic baths containing DI-water, ethanol and acetone and then dried in an oven. The PVK: DPPhP film was fabricated by

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Fig. 1. Molecular structure of DPPhP, Alq₃, PVK and PBD.

spin-coating method. Other organic materials and LiF were vapor-deposited under a pressure of 2×10^{-6} Torr at rate of about 0.02 nm/s. The luminance and CIE coordinates are measured by PR-650 spectrosan spectrometer. The active area of the device is $(\pi \times 2^2)$ mm². The photoluminescence and electroluminescence spectra were measured using a HITACHI-4010 fluorescence-spectrophotometer. All the measurements were carried out at room temperature in air under DC condition.

3. Results and discussion

Fig. 2 shows the normalized EL spectra of device A, B, C and D. We can see the maximum emitting wavelength of device A is 514 nm. This peak is the characteristic emission from Alq₃ and we found that the peak did not move with the applied voltage increase. The device exhibits bright green emission. This can be explained that when no PBD is inserted, PVK:DPPhP layer only used as hole-transporting layer because they are all good hole-transporting materials [10]. When holes are injected from anode, they can quickly move toward cathode and recombine with electrons in bulk Alq₃ layer. However, when a 5 nm PBD layer is inserted, white emission can be obtained in device B. The CIE coordinates vary from (0.23, 0.37) to (0.32, 0.39) when the voltage changes from 10 to 27 V. From Fig. 2 we can see there are two peaks in the spectra for device B. Obviously, excitons have generated in both PVK:DPPhP and Alq₃ layer. Because the HOMO of PBD is 6.52 eV (as shown in Fig. 4), it is 1.02 eV high than that of PVK (5.5 eV). Then PBD can block the holes in PVK:DPPhP layer. However, the thickness of PBD is only 5 nm. Based on the energy level (as shown in Fig. 4) and field-assisted tunneling at the surface, we consider this is the result of the field-assisted charge crossing through the energy barrier under high field. The chance of the charge crossing is direct ratio to

the electric field [11].

$$\text{Rate}_T \propto E \exp \left\{ -\frac{\pi^2}{h} (2mE_g)^{1/2} \left[\frac{E_g}{qE} \right] \right\}$$

where E is electric field. Therefore some holes will tunnel the interface barrier under relative high field and leak into the Alq₃ layer. However, when the thickness of PBD layer increases to 10 nm, only blue emission (peaked at 430 nm) can be obtained and the peak does not move with the variation of the applied voltage. The same phenomenon has also occurred in device D (PBD layer is 15 nm). This indicates that all the excitons have been confined in the PVK:DPPhP layer when the thickness of PBD is equal to or above 10 nm (Fig. 3).

In addition, the maximum absorption wavelength for DPPhP is 355 nm, but the emission of PVK peaks at 400 nm. It is not a good overlap for their absorption and emission spectra. So we suggest the pure blue emission from devices C or D originates from a trap mechanism, other than Förster or Dexter energy transfer. This also can be deduced

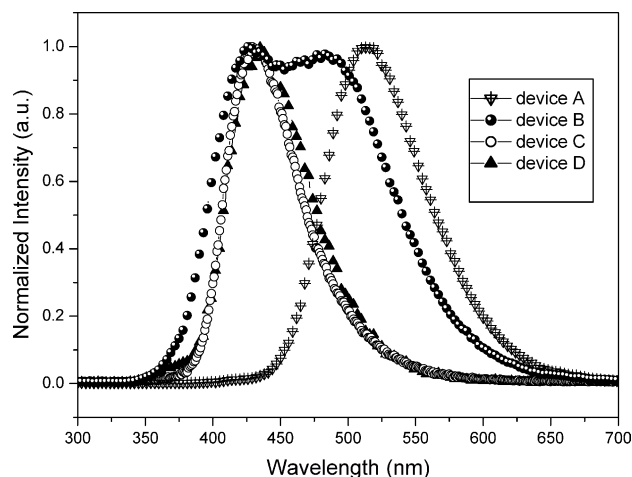


Fig. 2. The EL spectra of device A, B, C and D.

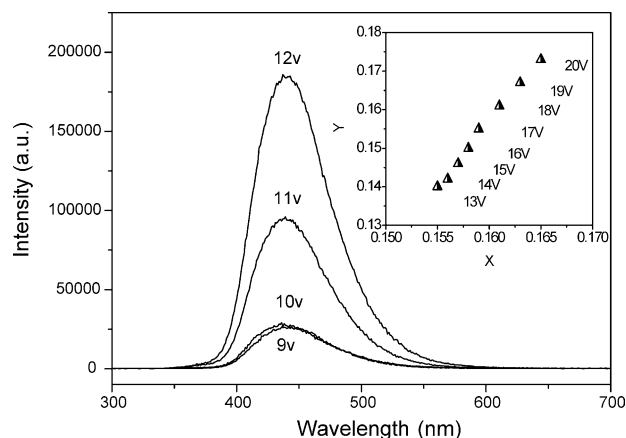


Fig. 3. The EL spectra and CIE coordinates of device D.

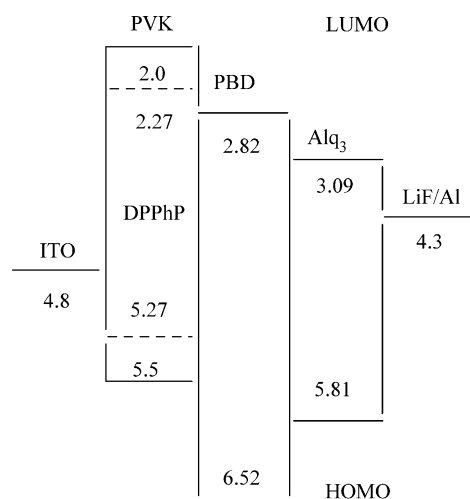


Fig. 4. Energy level scheme of the devices.

from the energy level scheme as shown in Fig. 4. The LUMO and HOMO for PVK and DPPhP are (2.0, 5.5 eV) and (2.27, 5.27 eV), respectively. When holes inject from anode, because there is an additional energy barrier (ΔE) about 0.23 eV for the holes to reach the HOMO of PVK, they will be trapped by DPPhP molecules. Actually, it is same for electrons that there is an additional energy barrier (ΔE) about 0.27 eV for them to reach the LUMO of PVK. Therefore carriers will be trapped and recombine directly in DPPhP molecules when electric field is operated. Characteristic emission from DPPhP will be observed. Fig. 3 shows the EL and CIE coordinates of device D. It can be seen no emission from PVK is observed even at low voltage.

4. Conclusion

Green to white to blue light-emitting diodes with structure ITO/PVK:DPPhP(5%)/PBD(x nm)/Alq₃ (5 nm)/LiF(0.3 nm)/Al have been obtained. When the thickness of PBD varies from 0 to 5 to 10 nm, green to white to blue emission is achieved. Pure blue emitting devices can be obtained when the thickness of PBD is equal or above 10 nm. The blue emission is suggested to originate from trap mechanism. The method to obtain pure blue emitting devices is to confine the excitons in the emitting layer. Based on the energy band theory and carries tunneling theory, we consider that PBD plays a chromaticity-tuning role in the OLEDs and the color-variable EL is ascribe to its modulation function on carrier recombination zone. This work is meaningful for full-color displays.

Acknowledgements

This work is supported by the '973' National Key Basic Research Special Foundation of China (No. 2003CB314707), National Natural Science Foundation of China (No. 90301004 and 10374001), and National Natural Science Foundation of Beijing city (No. 2032015), and RFDP (No. 20020004004).

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