

Efficient white organic light emitting devices with dual emitting layers

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Abstract

In this paper, a new white organic light-emitting device (OLED) with the structure of indium tin oxide/CF_x/1,4-bis[N-(1-naphthyl)-N'-phenylamino]-biphenyl (NPB) (30 nm)/NPB: 2,8-di(*t*-butyl)-5,11-di[4-(*t*-butyl)phenyl]-6,12-diphenylnaphthacene (20 nm; 1.6 %)/2-methyl-9,10-di(2-naphthyl) anthracene: *p*-bis(*p*-*N,N*-di-phenyl-aminostyryl)benzene (40 nm, 3%)/aluminum tris(8-hydroxyquinoline) (20 nm)/LiF (1 nm)/Al (200 nm) has been investigated. The device showed white emission with a high-luminous yield of 9.75 cd/A at 20 mA/cm², but its Commission Internationale de l'Eclairage chromaticity coordinates appeared to change from (0.34, 0.42) at 6 mA/cm² to (0.27, 0.37) at 20 mA/cm² due to the shift of recombination zone. The change of color with drive current was suppressed by introduction of an electron-blocking layer of NPB along with a hole-blocking layer of aluminum (III) bis(2-methyl-8-quinolinato)4-phenylphenolato to the white OLED which successfully confined the recombination site and achieved a luminous yield of 9.9 cd/A at 20 mA/cm².

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1. Introduction

Recently, white organic electroluminescent devices (WOLEDs) have attracted a lot of research and commercialization interests due to their demonstrated applications in the fabrication of a full color display with a color filter [1], or as backlight for liquid crystal displays and paper-like illuminating sources. For large area lighting applications, these thin and potentially flexible WOLEDs are particularly desirable owing to their promise of adapting to future roll-to-roll coating technology in manufacturing high-quality and low cost, diffusible lighting as compared to inorganic LED or fluorescent lamp. White-light emission can be constructed by mixing two complementary colors (e.g. cyan+red) or three primary colors (red, green, and blue) colors in OLEDs.

There are commonly two ways of achieving white OLED, one of which is the single-emitting layer white OLEDs [2–5], whose CIE_{x,y} coordinates are independent to current density. This is because there is only one exciton-recombination zone, but its EL efficiency is usually low. The other type is the multi-emitting layer white OLEDs [6–9], the major advantage of which is that it has much higher efficiency than that of the single emitting layer device. The drawback of multi-layered white OLEDs is that the variation of CIE_{x,y} coordinates are often dependent upon drive current density which is due to the shift of exciton-recombination zone. Careful control of the location of exciton-recombination zone [10] and the energy transfer between the host and dopant molecules have been shown to be critical in obtaining a balanced white emission of high efficiency and color with CIE_{x,y} coordinates near (0.33, 0.33).

In this paper, we report a new white OLED structure incorporating a dual-layered emitting layer (EML) of blue and yellow to synthesize the white emission with high efficiency. The blue and yellow dopants reported herewith

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are *p*-bis(*p*-*N,N*-di-phenyl-aminostyryl)benzene (DSA-Ph) [11] and 2,8-di(*t*-butyl)-5,11-di[4-(*t*-butyl)phenyl]-6,12-diphenylnaphthacene (TBRb) [12], respectively. The strategy of inserting both electron and hole blocking layers to control the recombination zone in the dual-emitting-layered white OLEDs is shown to be effective in suppressing the color-shift at different drive current density. In terms of operational stability, we found that the white OLED is more stable than the blue component device. It seems that adding TBRb in NPB can improve the balance of carrier injection into emitting layer to reach longer operational durability.

2. Experimental details

Devices were fabricated by vapor phase deposition method, where indium tin oxide (ITO) was used as a transparent anode electrode, CF_x as a hole injecting material [13], NPB as a hole transporting material and yellow light host material, TBRb as a yellow light dopant material, 2-methyl-9,10-di(2-naphthyl) anthracene (MADN) as a blue light host material [14], DSA-Ph as a blue light dopant material, aluminum tris(8-hydroxyquinoline) (Alq_3) as an electron transporting material, LiF as an electron injecting material, and Al as a cathode electrode material. MADN, and TBRb were purchased from e-Ray Optoelectronics Corp. (Taipei, Taiwan). The organic films were formed by vapor phase deposition on the patterned ITO-coated glass substrates with a sheet resistance of approximately $20 \Omega/\square$ (emitting area is $3 \text{ mm} \times 3 \text{ mm}$), which had been cleaned by successive ultrasonic treatments in acetone, detergent, de-

ionized water ($18.2 \text{ M}\Omega\text{-cm}$), and methanol. As shown in Fig. 1, the structures of WOLEDs fabricated were: [ITO (75 nm)/ CF_x /NPB (30 nm)/NPB:TBRb (20 nm; 1.6%)/MADN:DSA-Ph (40 nm; 3%)/ Alq_3 (20 nm)/LiF (1 nm)/Al (200 nm)] (Device A) and [ITO (75 nm)/ CF_x /NPB (30 nm)/NPB:TBRb (20 nm; 1.6%)/BAIq (3 nm)/MADN:DSA-Ph (15 nm; 3%)/NPB (10 nm)/MADN:DSA-Ph (25 nm; 3%)/ Alq_3 (20 nm)/LiF (1 nm)/Al (200 nm)] (Device B). Organic powders of NPB, MADN, DSA-ph, TBRb, and Alq_3 in graphite cells were heated to obtain the growth rate of 0.01–0.4 nm/s (which are dependent on organic materials) under the operating pressure of $<1 \times 10^{-5}$ Torr. The current density–voltage (J – V) characteristics were measured with a Keithley 2400 programmable current source unit. The intensities of the electroluminescence (EL) emission from the devices were measured by Photo Research PR-650 and lifetime measurements were performed in a glove box at a constant current density of 20 mA/cm^2 .

3. Results and discussions

The device structures and dopant materials, i.e. DSA-Ph and TBRb, are depicted in Fig. 1. Fig. 2 shows the voltage–current density and voltage–luminescence characteristics of devices A and B. The device A shows the maximum luminance of $41,280 \text{ cd/m}^2$ at current density of 450 mA/cm^2 comparing to the device B which shows the maximum luminance of $35,538 \text{ cd/m}^2$ at current density of 400 mA/cm^2 . Fig. 3 also shows a maximum power efficiency of 4.13 lm/W at 0.5 mA/cm^2 for device A and a maximum power efficiency of 2.96 lm/W at 0.5 mA/cm^2 for device B. Device A reveals the maximal external quantum efficiency (E.Q.E.) of approximately 4.36% at 200 mA/cm^2 , but device B shows the maximum E.Q.E. of approximately 3.93% at 40 mA/cm^2 .

In the WOLED of device A the sky-blue light emission was generated by doping the highly fluorescent DSA-Ph dopant into the stable blue host molecule of MADN in which the optimal doping concentration has been determined in separate experiments to be about 3%. The yellow emission was derived from the doping TBRb in NPB in which the optimal concentration to obtain a white emission was 1.6%. By controlling the thickness of the blue (40 nm) and yellow (20 nm) emitting layers, it is possible to partition excitons electro-generated in both of these blue and yellow emitting layers from which white emission can thus be obtained from this device with high efficiency. Further increasing the thickness of yellow EML or decreasing the thickness of blue EML will cause the x and y value of CIE coordinates raise. Fig. 4 shows the variation of EL spectra of device at different driving current density at 6, 20, 100 and 200 mA/cm^2 of devices A and B in which DSA-Ph and TBRb reveals the emission peaks at approximately 468 and 560 nm, respectively. At low current densities, the blue

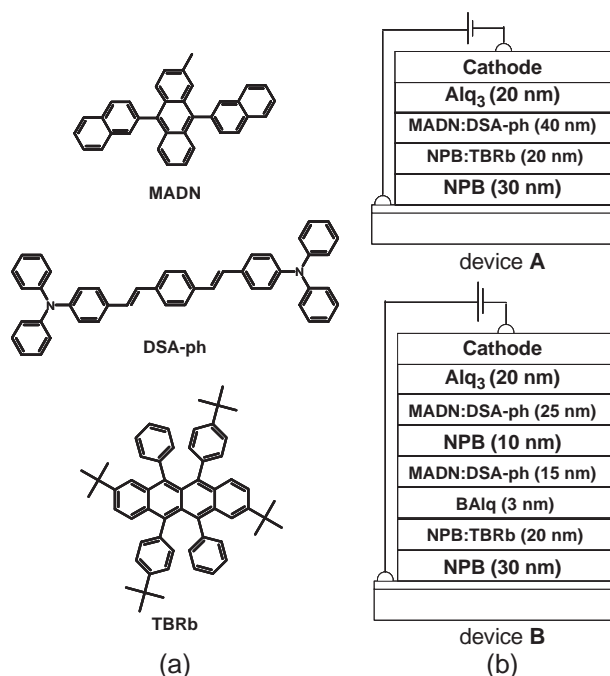


Fig. 1. (a) Molecular structure of MADN, DSA-ph, and TBRb. (b) The configuration of device A and device B.

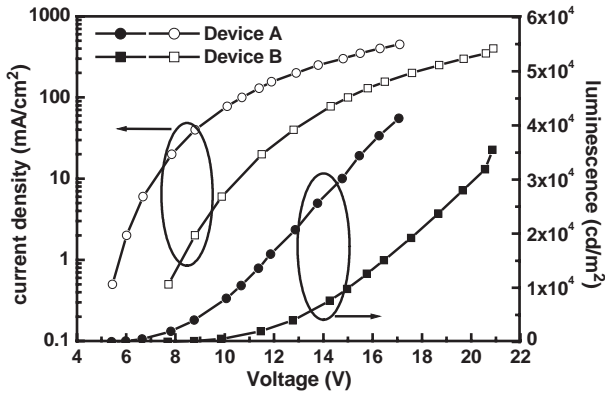


Fig. 2. The voltage–current density and voltage–luminescence characteristics of device A and device B. (□) is $J-V$ curve of device B. (○) is $J-V$ curve of device A. (■) is $B-V$ curve of device B. (●) is $B-V$ curve of device A.

luminescence was found to contribute much less to the white EL of device A, but the luminescence of blue emission significantly increased at high current densities. We attribute this large change in yellow emission in device A to the hole-trapping nature of TBRb, which would lead to leave a few holes recombined with electron in the blue emitting layer at low current density. At high current drive conditions, more holes will be available for recombination in the blue emitting layer as the doping concentration of TBRb is limited. Although adjusting the thickness of the

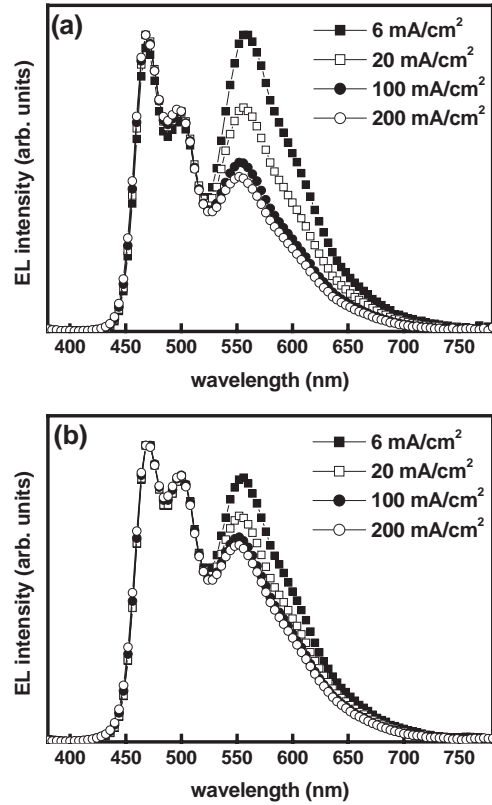


Fig. 4. Variation of EL spectra with current density for device A (a) and device B (b).

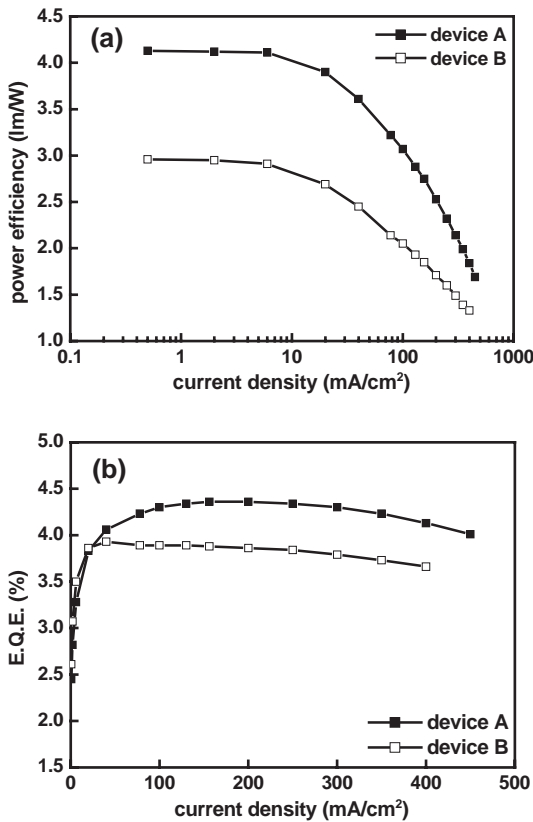


Fig. 3. Variation of power efficiency and E.Q.E. with drive current density for device A and device B.

blue and yellow emitting layers slightly alleviated the shift of CIE coordinates with current density, the desired white emission could not be obtained. Furthermore, the mobility of organic material is not constant, but electric field dependent according to Poole–Frenkel law. The move of recombination zone due to the different mobility at various electric fields (i.e. current density) would occur no matter how we arrange the thickness of blue and yellow emission layers.

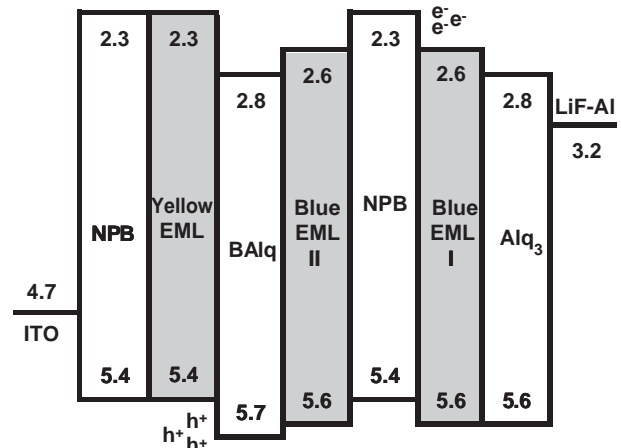


Fig. 5. The energy diagram of device B. It was suggested that gray areas are main emitting light areas.

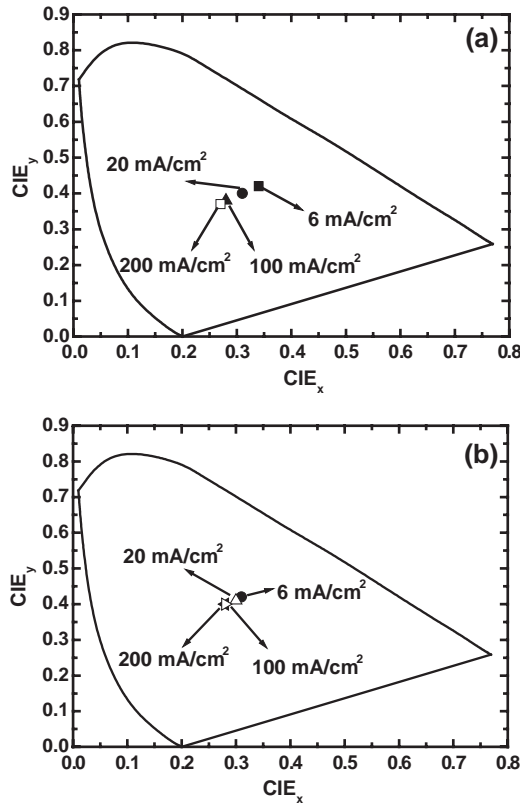


Fig. 6. The change of CIE chromaticity diagram at different current density for device A (a) and device B (b).

The change in white EL spectra with drive current density can be greatly suppressed if appropriate electron and hole blocking layers are inserted as in device B to confine the exciton in their respective blue and yellow emitting layers. Fig. 5 shows the energy diagram of device B. Here, BAQ was used as the hole blocker to confine more holes in yellow EML to avoid hole leakage to blue EML via increasing current density. NPB, which was used as electron blocker, divide whole blue EML (40 nm) into the major (EML I) and minor (EML II) emissive region (Fig. 2) to maintain certain ratio of blue light as drive current density change. When the thickness of the blue EML I and II were 15 and 25 nm, respectively, the device reached higher efficiency and less CIE coordinates shift via current density increase. Fig. 6 shows that the change of CIE chromaticity at different drive current density (6–200 mA/cm²) for devices A and B. As the current density increases from 6 to 200 mA/cm², large CIE_{x,y} coordinates change from (0.34, 0.42) to (0.27, 0.37) for device A comparing to only a small change in CIE_{x,y} coordinates

Table 1
EL performances of device A and device B driven at 20 mA/cm²

Device	Voltage (V)	Lum. yield (cd/A)	Power eff. (lm/W)	E.Q.E. (%)	CIE		<i>t</i> ₈₀ (h)
					<i>x</i>	<i>y</i>	
A	7.85	9.75	3.90	3.83	0.31	0.40	800
B	11.53	9.9	2.69	3.86	0.30	0.41	17

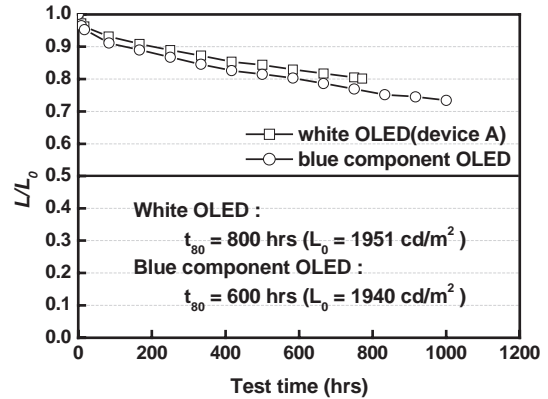


Fig. 7. The 80% lifetime diagram of white device and blue device. (*t*₈₀ means the time of decay to 80% of initial luminescence).

from (0.31, 0.42) to (0.28, 0.40) for device B was observed. It is concluded that the insertion of NPB as electron blocking layer for the DSA-Ph doped blue emitting layer and BAQ as hole blocking layer for the TBRb doped yellow emitting layer are effective in suppressing the color change of white emission due to different drive conditions. However, the lifetime of device B (*t*₈₀~17 h) is much shorter than device A. It is believed that device B having blocking layers could cause large joule heat at the interface [15] which may gradually cause the local aggregation of molecules such as dimerization and crystallization, resulting in accelerated degradation of device. Furthermore, higher drive voltage of device B may be caused not only by blocker insertion but also by the increase of thickness. Table 1 compares the overall EL performances of devices A and B at a drive current of 20 mA/cm².

Fig. 7 shows the aging test of white device and blue component device. White OLED has 80% life-time of about 800 h at 1951 cd/m² while blue OLED has 80% life-time of about 600 h at 1940 cd/m². It could be explain that adding TBRb in NPB can better balance carrier injection causing the enhancement in operational durability [16].

4. Conclusions

White light-emitting diodes with dual blue and yellow emitting layers using the new blue dopant DSA-Ph in MADN, and the yellow dopant TBRb in NPB were successfully fabricated as in device A. We found the device lifetime of the dual-emitting layered white OLED is longer than the blue device but the white EL color tends to shift significantly with drive current conditions. The change in

white EL spectra with drive current density can be greatly suppressed if appropriate electron (NPB) and hole (BALq) blocking layers are inserted as in device B to confine the exciton in their respective blue and yellow emitting layers.

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