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White Organic Light-Emitting Diodes with Color Stability

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Abstract : The authors have demonstrated white oraganic light-emitting diodes (WOLED) using 1,4-bis[2-(4′-diphenylaminobiphenyl-4-yl)vinyl]benzene as fluorescent blue emitter and iridium(III) bis(5-acetyl-2-phenylpyridinato-N,C2′) acetylacetonate as phosphorescent red emitter. The optimized WOLED using red host material as bis(2-methyl-8-quinolinato) -4-phenylphenolate exhibited proper color stability in comparison with the control device using 4,4′-N,N′-dicarbazole-biphenyl as red host. The white device showed a maximum luminance of 21100 cd/m^2 at 14 V, luminous efficiency of 9.7 cd/A at 20 mA/cm^2, and Commission Internationale de I'Eclairage ($CIE_{x,y}$)coordinates of (0.32, 0.34) at 1000 cd/m^2. The devices also exhibited the color shift with $\triangle CIE_{x,y}$ coordinates of ± (0.01,0.01) from 100 to 20000 cd/m^2.

Keywords : white organic light-emitting diodes, 1,4-bis[2-(4′-diphenylaminobiphenyl-4-yl) vinyl]benzene, iridium(III) bis(5-acetyl-2-phenylpyridinato-N,C2′) acetylacetonate, bis(2-methyl-8-quinolinato)-4-phenylphenolate, color stability

1. Introduction

Organic light-emitting diodes (OLEDs) and organic thin-film transistor have attracted increasing attention in recent years[1-5]. Today, OLEDs are considered to be one of the flat-panel displays of the next generation due to low-voltage operation, wide-viewing angle, a high contrast and mechanical flexibility[6].

White OLEDs (WOLEDs) have drawn increasing attention as a solid-state light source and backlights in liquid-crystal displays (LCDs) and full-color OLEDs due to their light weight, low operating voltage and high contrast[7-13]. WOLEDs have demonstrated by two colors (light blue and yellow), three colors (blue, green, and red), excimer/exciplex emission and microcavity [14-16]. Many researchers consider small molecule for WOLEDs because of lower efficiency, a difficult stack of organic molecules, and absence of emission materials in polymer WOLEDs. For full-color OLEDs and LCDs, WOLEDs should have color stability at the whole operating voltage. In

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this study, we demonstrated WOLEDs using a phosphorescent red emitter doped in two different hosts, 4,4′-N,N′-dicarbazole-biphenyl (CBP) and bis(2-methyl-8-quinolinato)-4-phenylphenolate (BAlq) and fluorescent blue emitter doped in 2-methyl-9,10-di(2-naphthyl)anthracene (MADN). The white device with red host of BAlq showed a minimal change of Δ Commission Internationale de I'Eclairage ($CIE_{x,y}$) coordinates of (0.01, 0.01) for the brightness change from 100 to 20000 cd/m^2.

2. Experimental

The CBP, BAlq, 4,4',4''-tris[2-naphthyl (phenyl)amino] triphenylamine (2-TNATA), N,N′-bis-(1-naphyl)-N,N′-diphenyl-1,1′-biphenyl-4,4′-diamine (NPB), tris(8-hydroxy-quinolinato)aluminium (Alq_3), and lithium quinolate (Liq) are purchase by Rohm and Haas company. The 2,9-dimethyl-4,7-diphenyl-1,10-phenanhroline (BPhen) are purchase by Sigma-Aldrich company. The MADN, 1,4-Bis[2-(4′-diphenylaminobiphenyl-4-yl)vinyl]benzene (DABPV-ph), and iridium(III) bis(5-acetyl-2-phenylpyridinato-N,C2′) acetylacetonate ($(acppy)_2Ir(acac)$) are synthesize by co-work Lab. of Sungkyunkwan University. The grade of organic materials has more than 99%. Indium tin oxide (ITO)-coated glass was cleaned in an ultrasonic bath by the following sequence in acetone, methanol, distilled water and isopropyl alcohol. Thereafter, pre-cleaned ITO was treated by O_2 plasma with the conditions of 2×10^{-2} Torr, 125 W for 2 min. WOLEDs were fabricated using the high vacuum (5×10^{-7}Torr) thermal evaporation of organic materials onto the surface of the ITO-coated glass substrate (10 Ω/sq, emitting area was 3 mmx3 mm). The deposition rates were 1.0~1.1 Å/sec for all organic materials and 0.1 Å/sec for Liq, respectively. Without a vacuum break after the deposition of organic layers, the Al cathode was deposited at a rate of 10 Å/sec. The ultra violet (UV)/visible. and PL were measured with LS 50B. With the DC voltage bias, the optical and electrical properties of WOLEDs such as the current density, luminance, luminous efficiency, and electroluminescence (EL) spectra of the emission characteristics were measured with Keithley 2400 and CHROMA METER CS-100A instruments. The $CIE_{x,y}$ coordinates were also calculated with Keithley 2400 and CHROMAMETERCS-100A instruments. All measurements were carried out under ambient conditions at room temperature.

3. Results and Discussion

As shown in Fig. 1, the device structure was as follows ITO/2-TNATA/NPB/DABPV-ph:MADN/$(acppy)_2Ir(acac)$:CBP (deviceA) or $(acppy)_2Ir(acac)$:BAlq (device B)/BPhen (device A) or BAlq (device B)/Alq_3/Liq/Al. The doping concentrations of DABPV-ph in MADN and $(acppy)_2Ir(acac)$ in CBP or BAlq were optimized to 7 and 8%, respectively.

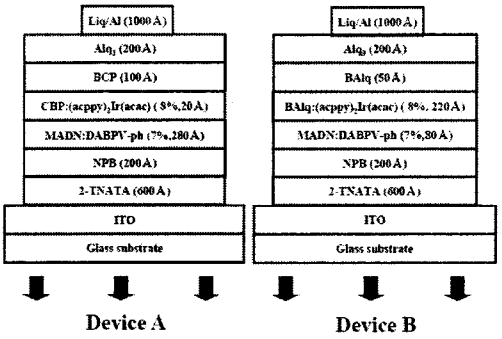

Fig. 1. The structures of white device A and B.

Fig. 2 shows the UV/visible absorption and PL spectra of DABPV-ph as a blue emitter and $(acppy)_2Ir(acac)$ as a red emitter. The maximum UV/visible absorption peaks of

blue and red emitters were 399 and 317nm, respectively. In case of UV/visible spectrum of $(acppy)_2Ir(acac)$, the bands below 370 nm were assigned to the spin-allowed $^1\pi$-π^* transition of cyclometalated ligand, and the band around 430 nm can be assigned to spin-allowed metal-ligand charge transfer band (^{1}MLCT). Also, the band around 513 nm can be assigned to the spin-forbidden ^{3}MLCT band. The maximum PL peaks of blue and red emitters were 452.5 and 590 nm, respectively. The sub PL peaks of blue emitter also were 476.5 nm. The PL spectrum of blue dopant have both blue and green emission.

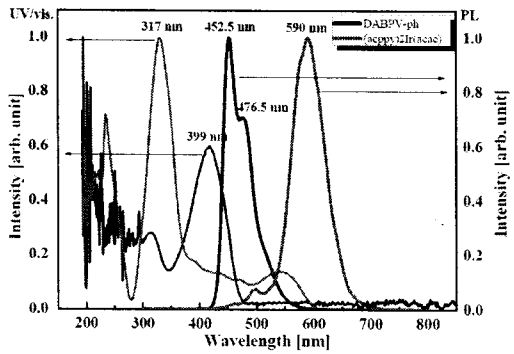

Fig. 2. UV/vis. absorption and PL spectrum of DABPV-ph and $(acppy)_2Ir(acac)$.

Fig. 3 (a) and (b) show the energy level diagram of the device A and B. The effectiveness of charge confinement is dependent on emitting layer (EML). Device A confined exciton between the EML and BCP as a hole blocking layer, but device B had a exciton formation zone between blue and red EML because BAlq played also as a hole blocking layer[17].

The current density versus voltage characteristics of the two devices are shown in Fig. 4. At a voltage of 14 V, a maximum current density of 304 and 276 mA/cm^2 were achieved by device A and B, respectively. Device B showed lower current density at operating voltages on the whole range of applied voltages.

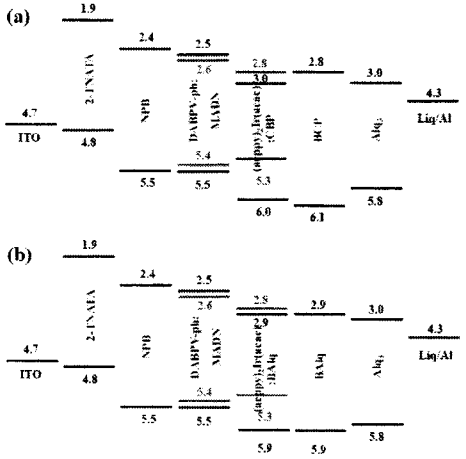

Fig. 3. The energy-level diagram of the device A and B. Numbers showed the HOMO and LUMO of various materials used in this study.

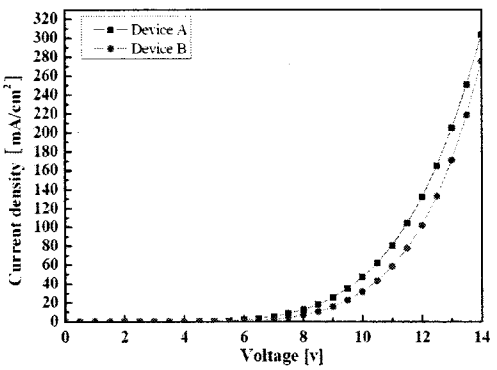

Fig. 4. The characteristics of current density versus voltage characteristics of device A and B.

Fig. 5 shows the luminance versus the applied voltages characteristics of device A and B, which showed a maximum luminance of 26100 and 21100 cd/m^2 at 14 V, respectively. The turn-on voltage at the luminance of 1 cd/m^2 was about 4 and 5 V. At 20 mA/cm^2, the device A and B showed luminance of 2233 and 1938 cd/m^2,

respectively. The inset Fig. 5 shows the current density versus luminous efficiency characteristics, where a maximum luminous efficiency of device A and B were 11.3 and 9.7 cd/A at 15.9 and 12.8 mA/cm^2 and a luminous efficiency of 11.2 and 9.68 cd/A at 20mA/cm^2, respectively.

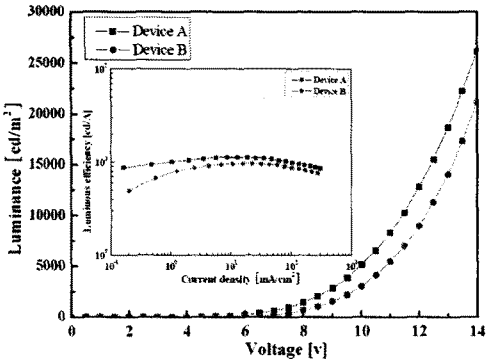

Fig. 5. Characteristics of luminance versus voltage characteristics of the device A and B. Inset: Luminous efficiency versus current density characteristics.

Fig. 6 shows the CIE$_{x,y}$ coordinates from 100 to 20000 cd/m^2. Device A and B showed a color change from (0.36, 0.38) and (0.32, 0.34) at 100 cd/m^2 to (0.25, 0.33) and (0.31, 0.33) at 20000 cd/m^2. The devices exhibited the color shift with ΔCIE$_{x,y}$ coordinates of ±(0.11,0.05) and (0.01,0.01) from 100 to 20000 cd/m^2, respectively. It was assumed that excitons formed between EML and BCP in device A and white emission occured by diffusing excitons in red EML and the more voltages increased, the more CIE$_{x,y}$ coordinates shifted to blue region because of tripet-triplet (T-T) annihilation of thin red EML (20Å). In case of device B, excitons formed between blue and red EML. When high voltages was applied, excitons diffused in two ways, blue and red EML at the same time. So device B showed the color chromaticity close to the exact white emission (x=0.33, y=0.33) at whole range of operating voltages.

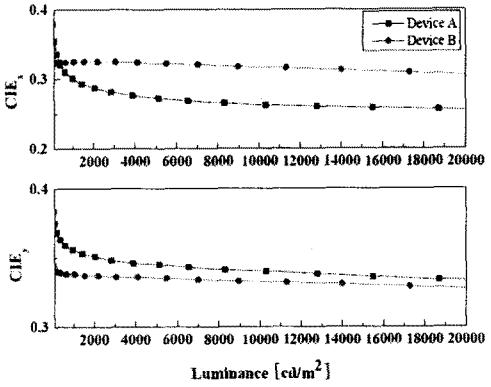

Fig. 6. CIE$_{x,y}$ coordinates of device A and B from 100 to 20000 cd/m^2 .

4. Conclusions

It was demonstrated in this study that the WOLEDs using fluorescent blue- and phosphorescent red-emitter were fabricated. The optimized white device with red host of BAlq formed exicitons formation zone between blue and red EML and reduced T-T annihilation. The white device showed a minimal change of ΔCIE$_{x,y}$ coordinates of (0.01, 0.01) from 100 to 20000 cd/m^2.

Acknowledgment

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