Optical Materials 37 (2014) 376–381

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Electroluminescence of fluorescent–phosphorescent organic light-emitting diodes with regular, inverted, and symmetrical structures

Su-Hua Yang *, Po-Jen Shih, Wen-Jie Wu

Department of Electronic Engineering, National Kaohsiung University of Applied Sciences, Kaohsiung, Taiwan, ROC

ARTICLE INFO

Article history:
Received 16 April 2014
Received in revised form 18 June 2014
Accepted 21 June 2014
Available online 12 July 2014

Keywords:
Fluorescence
Phosphorescence
Electroluminescence
Emission layer

ABSTRACT

The influence of the device structure on the electroluminescence (EL) properties of fluorescent–phosphorescent organic light emitting diodes (OLEDs) was demonstrated. Four devices with regular-, inverted-, compensated- and symmetrical-emission layers (EMLs) were prepared. In regular-EML device, DCJTB emission increased when the phosphorescent sensitized EML was thickened. In inverted-EML device, low electron energy barrier at the Bphen/BCzVB interface resulted in weakened blue emission. The compensated-EML device, prepared with a red color-compensated layer, showed a color-tunable broadband white emission. Conversely, device with a quantum-like symmetrical-EML showed a narrow color-temperature range. Stable EL efficiency was obtained from regular, compensated, and symmetrical-EML devices. In contrast, EL efficiency of inverted-EML device rolled off significantly, though it had the highest EL efficiency of 11.4 cd/A.

1. Introduction

Organic light emitting diodes (OLEDs), which feature in their thin and flat configuration and are light and flexible, have caused a great revolution on displays and lighting technologies [1]. Nowadays, scientists are not only interested in the unique configuration of OLEDs but also on their outstanding performance, such as low driving-voltage, low power consumption, fast response time, wide operation temperature range, high product yield, and high potential for applications in flexible and large-area screens [2–4].

For the fabrication of a highly efficient OLED, several approaches have been investigated, that include the synthesis of new organic substances [5,6], modification on device structures [7,8], improvement on electrode property [9–11], and enhancement on light extraction [12,13]. For the device structure modification to improve the efficiency of OLEDs, molybdenum oxide MoO_3 [14] and aluminum phthalocyanine chloride (AlPcCl) [15] have been used as the hole injection-enhanced buffer layer, and the ZrO_2 film is used as the electron injection layer [16]. Liao fabricated an OLED using a mixed host structure [17]; this OLED showed a high current efficiency of 36.0 cd/A and power efficiency of 27.5 lm/W. Additionally, by incorporating a layer embedded with Au nanoparticles, Sung achieved an efficiency increment of more than 38% [18]. And, Knauer prepared a stacked inverted structure, which realized a maximum current efficiency of 205 cd/A at 103 cd/m^2 and maintained a high current efficiency of 200 cd/A at 1011 cd/m^2 [8].

Moreover, a phosphorescent OLED, prepared by Gao with double exciton blocking layers, showed an enhanced electroluminescence (EL) efficiency and yielded a maximum current efficiency of 58.5 cd/A at 117 cd/m^2 with a power efficiency of 50.9 lm/W [19]. In addition, the technology of phosphorescent OLEDs which employs a fluorescent–phosphorescent (FP) hybrid emission layer (EML) and utilizes singlet and triplet excitons to obtain a quantum efficiency of nearly 100% [20,21]. This technique has been used to generate primary colors for displays and to fabricate efficient broadband emission required for white lightings [17,20,21].

It is not only the EL efficiency but also the color tunability of OLED being attracted a great deal of attention. An OLED, fabricated by Jou with three EMLs and a nano-scale hole modulating layer, showed a temperature span ranging from 1580 to 2600 K and a color rendering index varying from 68 to 91 [22]. An OLED with a broad range of color temperatures from 1500 to 10,000 K was prepared by stacking upper orange transparent and lower blue bottom OLEDs and introduced a ZnSe dielectric capping layer [23].

The EL efficiency, color tunability, and stability are greatly related to the composition of EML and layer-layout of the device. Hence, In this study, four different EMLs with regular-, inverted-, compensated- and symmetrical-structures were prepared. The influence of structural alteration on the EL properties of the FP hybrid OLEDs were analyzed and discussed in detail.

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* Corresponding author. Tel.: +886 7 3814526x5631; fax: +886 7 3811182.
E-mail address: shya@cc.kuas.edu.tw (S.-H. Yang).

http://dx.doi.org/10.1016/j.optmat.2014.06.029
0925-3467/

2. Experimental process

The FP-hybrid devices with four different EML structures were prepared as follows. For the substrate, an indium tin oxide (ITO) coated glass with a resistivity of 15 Ω per square was used. N,N′-bis(naphthalen-1-yl)-N,N′-bis(phenyl)-benzidine (NPB) and 4,7-diphenyl-1,10-phenanthroline (Bphen) were used as the hole- and electron-transporting layer materials, respectively. 4,4′-bis(carbazol-9-yl)biphenyl (CBP) was used as the host material. In addition, blue 1,4-bis[2-(3-N-ethylcarbazoryl)vinyl]benzene (BCzVB), green tris-(phenylpyridine)-iridine [Ir(ppy)$_3$], and red 4-(dicyanomethylene)-2-tert-butyl-6-(1,1,7,7-tetramethyljulolidin-4-yl-vinyl)-4H-pyran (DCJTB) were used as the dye dopants. LiF and Al were used as the electron injection layer and cathode materials, respectively.

The device with a regular-EML (noted as regular-Dev) had a structure of ITO/NPB/CBP:BCzVB (20 nm)/CBP (1 nm)/CBP:Ir(ppy)$_3$ (x nm)/CBP:Ir(ppy)$_3$:DCJTB [$(20-x)$ nm]/Bphen/LiF/Al, in which the value of the thickness parameter x was varied from 0 to 6. The CBP:BCzVB and CBP:Ir(ppy)$_3$ layers were blue EML (B-EML) and green EML (G-EML), respectively. The orange CBP:Ir(ppy)$_3$:DCJTB layer was an phosphorescent sensitized EML (PS-EML) [24].

When the structural position of the B-EML and PS-EML in regular-Dev was interchanged, the structure of inverted-EML device (noted as inverted-Dev) was formed, which was ITO/NPB/PS-EML (16 nm)/G-EML (4 nm)/CBP (1 nm)/B-EML (20 nm)/Bphen/LiF/Al. Furthermore, compensated-EML device (noted as compensated-Dev) had a color-compensated EML structure of ITO/NPB/B-EML (20 nm)/CBP (1 nm)/G-EML (4 nm)/PS-EML [$(16-y)$ nm]/CBP:DCJTB (y nm)/Bphen/LiF/Al, which was based on the structure of regular-Dev and had a color-compensation film composed of a red CBP:DCJTB layer (R-EML) inserted between the PS-EML and Bphen layer. The value of the thickness parameter y was varied in the range of 10–16. Additionally, the structure of symmetrical-EML device (noted as symmetrical-Dev) was ITO/NPB/B-EML$_{up}$ [$(20-z)$ nm]/CBP (1 nm)/G-EML (2 nm)/PS-EML (2 nm)/R-EML (12 nm)/PS-EML (2 nm)/G-EML (2 nm)/CBP (1 nm)/B-EML$_{dn}$ (z nm)/Bphen/LiF/Al, in which the multiple EMLs had a symmetrical and quantum-like structure. Herein, the value of the thickness parameter z was varied from 0 to 15. The structure of symmetrical-Dev was a combination of the structures of inverted-Dev and compensated-Dev and was quantized.

For the preparation of the devices, the ITO surface was cleaned with an organic solvent, dried with high-purity nitrogen gas, and then subjected to oxygen plasma treatment. The organic materials, LiF, and Al were deposited layer by layer on ITO glass at deposition rates of 0.5–0.8 Å/s by a thermal vacuum evaporation system at 5×10^{-6} Torr. The deposition rate of the materials was controlled by adjusting the heating current provided to the crucible. The thicknesses of the films were monitored in situ using a 5 MHz quartz crystal thickness monitor. In this study, the doping concentrations of BCzVB, Ir(ppy)$_3$, and DCJTB in each device were maintained at 7, 6, and 0.75 wt%, respectively. In addition, the thicknesses of the NPB, Bphen, LiF, and Al layers were fixed at 30, 50, 1, and 200 nm, respectively. The total thickness of the EMLs of each device was 41 nm and the emission area was 0.24 cm^2. The detailed structural information of the devices is listed in Table 1.

To measure the EL properties of the devices, a Keithley 2410 programmable voltage–current source was used. The luminance intensity and the Commission Internationale del'Eclairage (CIE) chromaticity of the devices were measured by a Minolta Chroma Meter model CS-100A. A Newport OSM-400 spectrophotometer was used to measure the EL spectra of the devices at the maximum luminance intensity. All the measurements were carried out in air at room temperature, and the devices were not encapsulated.

3. Results and discussion

The structure schemes of the devices are shown in Fig. 1(a–d), and the energy level diagram of the compensated-Dev is shown in Fig. 1(e). A PS-layer was deposited. In this layer, spectra overlapped entirely between the emission of Ir(ppy)$_3$ and the absorption of DCJTB; hence, energy was able to transfer from Ir(ppy)$_3$ to the DCJTB [24], and the luminance intensity of the devices was improved. In addition, to manipulate exciton diffusion in the EMLs the triplet energy states (T_1) of CBP (T_1 = 2.56 eV), Ir(ppy)$_3$ (T_1 = 2.4 eV), and BCzVB (T_1 = 1.92 eV) were considered [25–27]. Accordingly, a 1 nm-thick undoped CBP interlayer was inserted between the B-EML and G-EML to block the diffusion of excitons into the adjacent layers. The excitons were confined in the B-EML and the energy could efficiently transfer from CBP host to the BCzVB guest. In the meantime, the exciton diffusion from G-EML to the B-EML was prohibited. Energy loss was thus minimized.

From the measurements of energy absorptions and emissions of the CBP host and dye guests, good spectral overlaps were observed between the CBP emission and BCzVB absorption as well as between the Ir(ppy)$_3$ emission and DCJTB absorption [24]. Therefore, effective Förster energy transfer is possible in the CBP–BCzVB and Ir(ppy)$_3$–DCJTB systems [28]. In contrast, the Förster energy transfer is ineffective in the CBP–DCJTB and CBP–Ir(ppy)$_3$ systems. However, Dexter energy transfer is possible if molecules are close enough to each other [21,29].

Fig. 2(a) shows the current density properties of devices with different EML structures, in which the EML structure of A-device (noted as A-Dev) was B-EML (20 nm)/CBP (20 nm) and that of B-device (noted as B-Dev) was B-EML (20 nm)/G-EML (20 nm). The current density of A-Dev was higher than that of B-Dev. This reveals that the transport of carriers was hindered owing to a number of trap levels that were formed when the Ir(ppy)$_3$ was doped in the CBP. It is also found that the addition of DCJTB electron trap centers in the PS-EML resulted in the current density of regular-Dev decreasing significantly as compared to that of B-Dev. An increase in the current density of regular-Dev was observed when the PS-EML thickness was decreased (increasing the G-EML thickness).

Fig. 2(b) shows the EL spectra of regular-Dev measured at 12 V when the thickness parameter x of the G-EML varied from 0 to 6. The emission peaks of BCzVB were at 452, 479, and 515 nm; those of Ir(ppy)$_3$ were at 536 and 551 nm; and those of DCJTB were at 580, 596, and 614 nm. In the PS-EML, the electron trapping ability of DCJTB was stronger than that of Ir(ppy)$_3$. The injected electrons were trapped to form excitons on the DCJTB, hence, red emission was observed. When the PS-EML thickness was decreased and the G-EML thickness was increased, a decreased red emission was measured; a decreased blue emission was also observed, particularly at 452 and 479 nm for the short emission wavelengths of BCzVB. When the G-EML thickness was further increased to 6 nm (x = 6), the amount of electrons trapped in the DCJTB decreased; consequently, the current density was increased (Fig. 2(a)) and the blue emission was enhanced.

For the inverted-Dev, the orange PS-EML was adjacent to NPB and the B-EML was next to Bphen. The highest occupied molecular orbital (HOMO) level of NPB was close to that of Ir(ppy)$_3$ and DCJTB, and the lowest unoccupied molecular orbital (LUMO) level of Bphen was approximately the same as that of BCzVB. Accordingly, a higher current density was obtained, as shown in Fig. 2(a). The maximum EL efficiency and luminance intensity of the inverted-Device were 11.4 cd/A at 12.5 mA/cm^2 and 14,900 cd/m^2 at 196 mA/cm^2, respectively, which were higher than