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Exciton Confinement and Triplet Harvesting for Efficient White Organic Light Emitting Diodes

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A blue light emitting diode based on wide band gap host for a blue fluorescence light emitting layer has been developed to fabricate hybrid white organic light emitting diode comprising of a fluorescence blue and a phosphorescence red light emitting layers. We have tested various wide band gap host materials including CBP, BALq, and TcTa, and among them the device with TcTa host has shown good performance which could be attributed to tight exciton confinement. A phosphorescence red dopant (RD) has been introduced into BALq layer to harvest triplet states of the fluorescence blue emission layer and we have succeeded in obtaining the balanced emission of the blue and the red emissions with high efficiency. The device showed the maximum external quantum efficiency of 16% at 0.1 mA/cm^2 and 13% of external quantum efficiency with (0.29, 0.23) of CIE coordinates at 10 mA/cm^2 .

Keywords: fluorescence; hybrid; OLED; phosphorescence; white

INTRODUCTION

In recent years, optimization of organic light emitting diode (OLED) as well as synthesis of electroluminescent materials has been attracting great attention. Especially, white light emitting diode (WOLED) is getting more important for their potential applications in high quality and large area flat panel displays with color filters and an alternative lighting source [1–4]. The combination of white OLED and a color

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filter has an advantage of not requiring so much accurate alignment as separately depositing red, green and blue pixels.

There have been several approaches to achieve white light from OLED including multilayer structure of several emitting layers, single emission layer including several different color emitting dopants, exciplex/excimer emission structure, down-conversion phosphor system using blue OLED and phosphors, and white light emitting single molecule structure. Careful control of doping concentration or the thickness of each emitting layer is important to prevent a cascade complete energy transfer from blue to green or red.

Fluorescence materials have been widely used for WOLED, however, WOLED from fluorescence materials has limitation of efficiency. To improve efficiency of WOLED, phosphorescence materials have been also used, however, lack of stable and deep blue phosphorescent material make it difficult to apply phosphorescence WOLED for practical uses. Recently, hybrid WOLED has been reported by Sun *et al.* [5] The hybrid WOLED containing fluorescence blue material and phosphorescence green and red materials and the harvesting of the triplet states of the blue fluorescence emission layer by energy transfer into phosphorescence materials provided improved external quantum efficiency of about 11% at 10 mA/cm².

Here, we report a new hybrid WOLED containing a fluorescence emission layer and a phosphorescence emission layer. In hybrid WOLED, it was crucial to find a host material for blue fluorescence host because conventional fluorescence blue hosts have low triplet energy band gap which leads to triplet quenching. We have tested various wide band gap materials for a new blue host material and found that the device with 4,4,4-tris(N-carbazolyl)triphenylamine (TcTa) host has shown good performance. In our blue device structure of N,N'-Bis(naphthalen-1-yl)-N,N'-bis(phenyl)benzidine(a-NPB)/TcTa:blue dopant/Aluminum(III) bis(2-methyl-8-quinolate)4-phenylphenolate (Balq), a phosphorescence red dopant was introduced into the Balq layer to harvest triplet states in the fluorescence blue emission layer. The optimized hybrid WOLED showed about 16% of the maximum external quantum efficiency at 0.1 mA/cm² and 13% of external quantum efficiency at 10 mA/cm².

EXPERIMENTAL

The OLED grade materials of 4,4,4-tris[2-naphthyl(phenyl)amino]-triphenylamine (2-TNATA), a-NPB, 4,4'-bis(2,2'-diphenylvinyl)-1,1'-biphenil (DPVBi), tris(8-hydroxyquinoline)aluminum (III) (Alq3), Balq, TcTa, and 4,4'-Bis(carbazol-9-yl)biphenyl (CBP) were purchased

and used without further purification. Proprietary materials of a fluorescence blue dopant and a phosphorescence red dopant were also used and the structures will be disclosed later. Thin films of the organic materials were fabricated in a high vacuum chamber below 5×10^{-7} torr and thin films of LiF and Al were deposited as a cathode electrode. The electroluminescence spectrum was measured using a Minolta CS-1000. The current-voltage and luminescence-voltage characteristics were measured with a current/voltage source/measure unit (Keithley 238) and a Minolta CS-100.

RESULTS AND DISCUSSION

Figure 1 shows the results with a blue fluorescence device, a red phosphorescence device, and an initial hybrid OLED. With the device structure of ITO/2-TNATA/a-NPB/blue EML/Alq3/LiF/Al, the blue

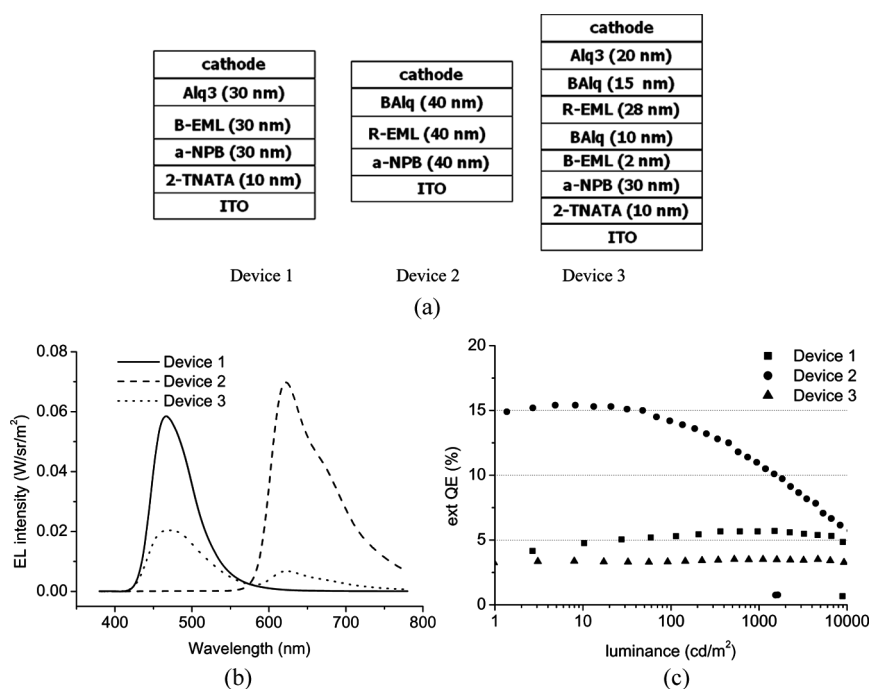


FIGURE 1 The device structures (a), the electroluminescence spectra (b) and the external quantum efficiency profile with luminance (c) of the blue fluorescence (device 1), the red phosphorescence (device 2) and the blue and red hybrid (device 3) devices.

device with fairly good performance was obtained and about 6% of external quantum efficiency was observed at 1000 cd/m^2 . In the emission layer (EML), DPVBi as a host and a proprietary blue dopant were used and the doping concentration is about 1%. The red phosphorescence device with the structure of ITO/a-NPB/red EML/BAlq/LiF/Al also showed good device performance with about 11% of external quantum efficiency at 1000 cd/m^2 . BAlq as a host and a proprietary red phosphorescence dopant were used in the EML and the doping concentration was about 6%. We have put two EML's together in one device to demonstrate hybrid WOLED. We have tried to optimize emission layers to obtain balanced emissions from the blue fluorescence and the red phosphorescence. One example of our optimized device shows that very low efficiency and even lower than the efficiency of the blue fluorescence device, although the blue and the red emissions were observed as shown in Figure 1 (b). We believe that the triplet exciton of the red phosphorescence layer could be transferred to the triplet state of the blue host which decays non-radiatively. Therefore, it is hard to obtain red phosphorescence in this kind of hybrid OLED and a wide band gap blue host is needed crucially to demonstrate high efficiency hybrid WOLED.

To find a proper blue host for hybrid WOLED, we have tested various wide band gap materials including CBP, BAlq and TcTa. They have wider triplet band gap than usual phosphorescence dopants and have been widely used as a host for phosphorescence devices. The testing device structure is shown in Figure 2 (a). We have used the same blue dopant as used in the above fluorescence device and the doping concentration was about 5%. Among the tested host materials, the device with TcTa showed the best results and about 6% of external quantum efficiency was obtained at 1000 cd/m^2 . The device with TcTa shows similar efficiency to the above device with DPVBi host and about two times higher efficiency than the devices with CBP and BAlq.

We have investigated the origin of the high efficiency in our blue emitting device by analyzing recombination zone. Three devices were fabricated as shown in Figure 3 (a). The blue dopant was doped in the EML close to the hole transporting material of a-NPB (Device 1), close to the electron transporting material of BAlq (Device 3), and center of the EML (Device 2). As shown in Figure 3 (c), the device 3 showed similar device characteristics to the whole EML doped device while the other two devices exhibited much lower efficiencies. The spectrum of the device 3 was somewhat different from those of the device 1 and the device 2. The main emission of the device 1 and the device 2 might be originated from TcTa host. These results indicate that the recombination zone in the EML is very close to BAlq and the

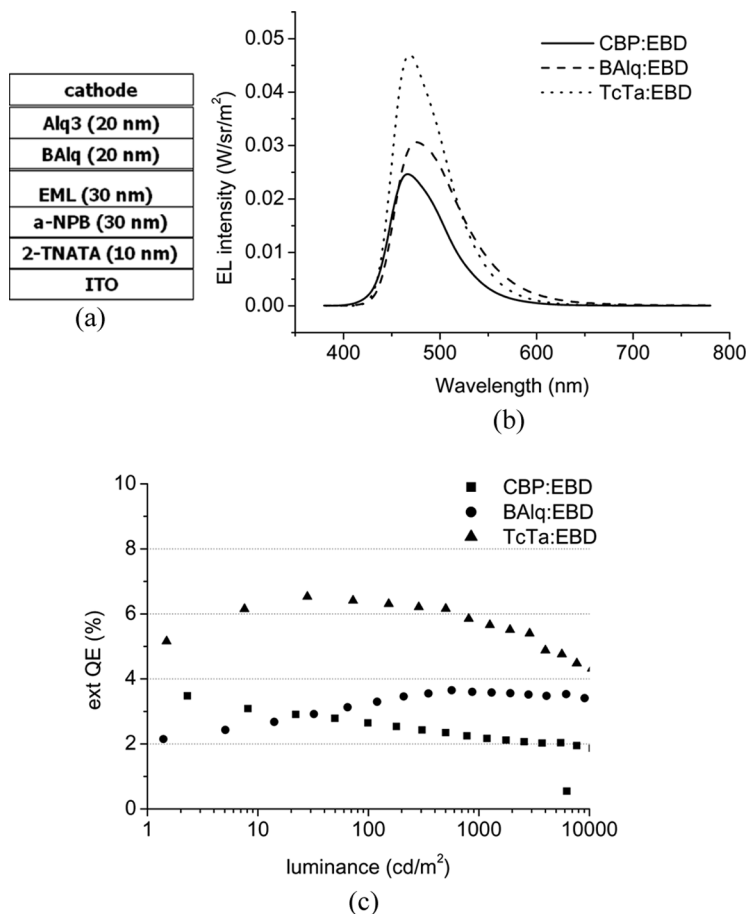


FIGURE 2 The device structures (a), the electroluminescence spectra (b) and the external quantum efficiency profile with luminance (c) of the devices with various blue hosts.

recombination zone is tightly confined in this region. The schematic band diagram of the device explains the high efficiency of our blue device. As shown in Figure 4, there is high hole injection barrier between TcTa and BAIq compared with other barriers, therefore, hole confinement is expected in the EML close to BAIq and most recombination occurs in this region. We believe that this tight exciton confinement is attributed to the high efficiency of our blue device with TcTa host.

We have put the red phosphorescence dopant into the BAIq layer to harvest triplet states in the blue fluorescence EML as shown in

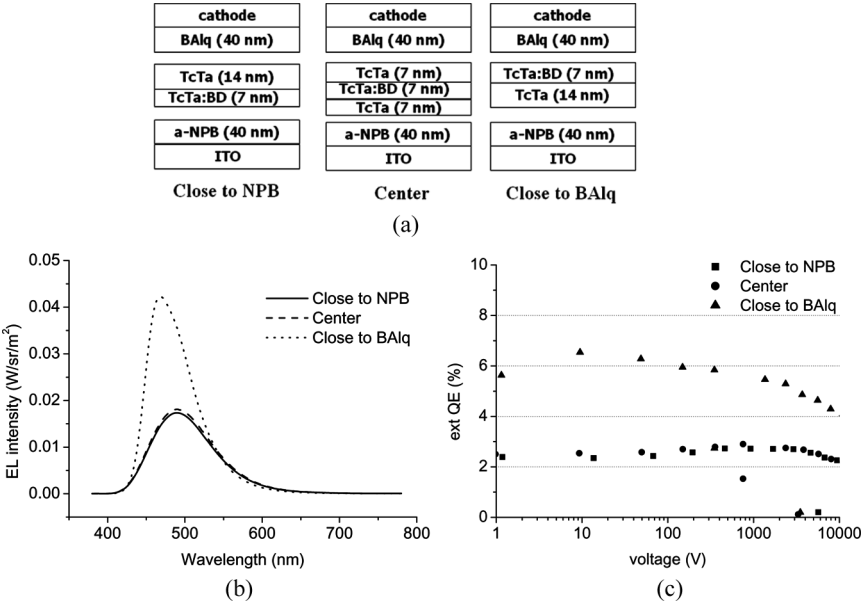


FIGURE 3 The device structures (a), the electroluminescence spectra (b) and the external quantum efficiency profile with luminance (c) of the blue devices with various doping positions.

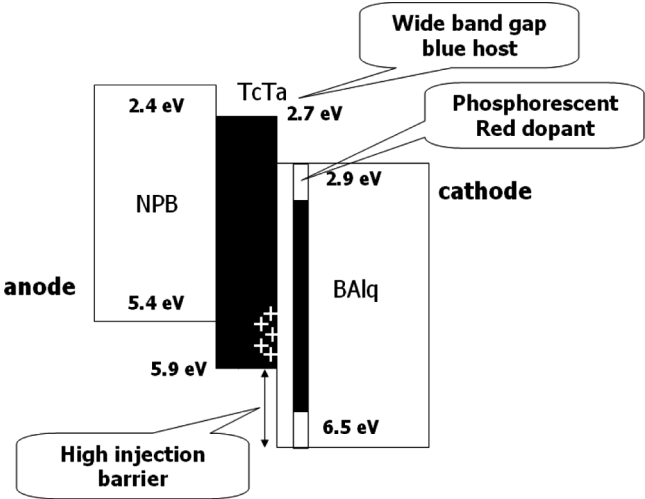


FIGURE 4 The schematic band diagram of the hybrid OLED.

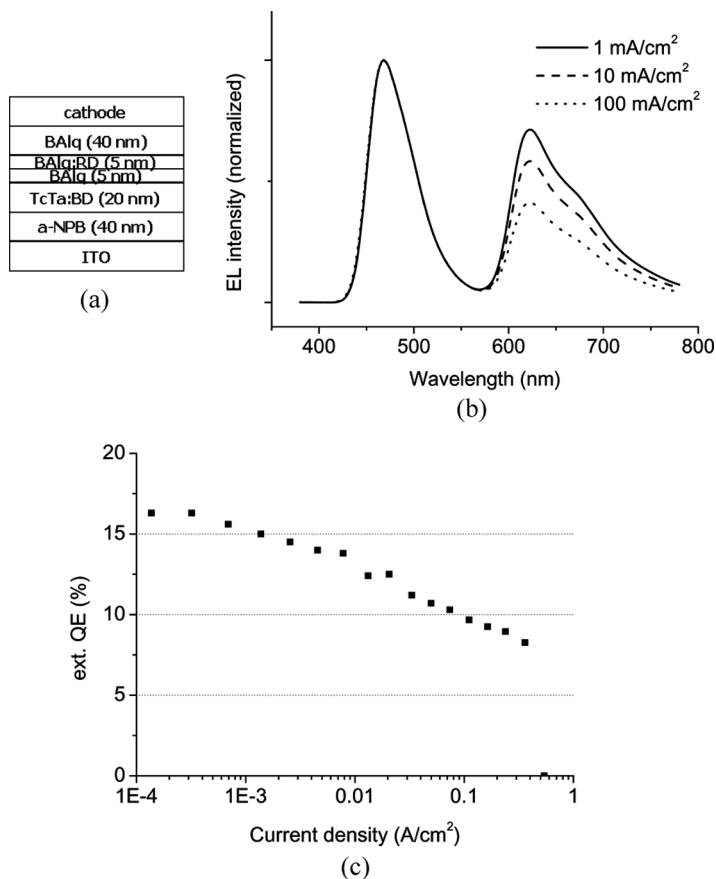


FIGURE 5 The electroluminescence spectra (a) and the external quantum efficiency profile with current density (b) of the hybrid OLED.

Figure 4 and Figure 5 (a). By optimizing the distance between the blue EML and the red triplet harvesting layer (THL), we have succeeded in obtaining the balanced emission of the blue and the red emissions with high efficiency from the device structure of NPB/TcTa:BD/BAIq/BAIq:RD/BAIq/LiF/Al. The distance between the EML and the THL affects emission color and efficiency. It has been found that the optimum distance from the blue EML to the red THL was 5 nm. The harvest of triplet states of blue EML resulted in substantial efficiency improvement. This device showed maximum external quantum efficiency of 16% at 0.1 mA/cm² and 13% of external quantum efficiency, (0.29, 0.23) of CIE coordinates at 10 mA/cm² and as shown

in Figure 5 (b) and (c), which is higher value than the previous results by Sun *et al.* [5]. Further optimizations of the device to improve device performance and to obtain three color white OLED are under investigation, and will be reported later.

CONCLUSION

A new blue fluorescence device with a wide band host and high efficiency has been developed. The tight exciton confinement might be attributed to the high efficiency of our blue device. We have successfully fabricated hybrid WOLED by introducing the red phosphorescence dopant into the region close to the EML in our blue device. The harvest of triplet states of blue EML resulted in substantial efficiency improvement. This device showed maximum external quantum efficiency of 16% at 0.1 mA/cm^2 and 13% of external quantum efficiency with (0.29, 0.23) of CIE coordinates at 10 mA/cm^2 . We believe that our results provide in-depth understanding of hybrid WOLED and show a challenge to obtain WOLED with 100% internal efficiency.

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