Dependence of Light-Emitting Characteristics of Blue Phosphorescent Organic Light-Emitting Diodes on Electron Injection and Transport Materials

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We investigate the light-emitting performances of blue phosphorescent organic light-emitting diodes (PHOLEDs) with three different electron injection and transport materials, that is, bathocuproine(2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) (Bphen), 1,3,5-tri(m-pyrid-3-yl-phenyl)benzene (Tm3PyPB), and 2,6-bis(3-(carbazol-9-yl)phenyl)pyridine (26DCzPPy), which are partially doped with cesium metal. We find that the device characteristics are very dependent on the nature of the introduced electron injection layer (EIL) and electron transporting layer (ETL). When the appropriate EIL and ETL are combined, the peak external quantum efficiency and peak power efficiency improve up to 20.7% and 45.6 lm/W, respectively. Moreover, this blue PHOLED even maintains high external quantum efficiency of 19.6% and 16.9% at a luminance of 1,000 cd/m² and 10,000 cd/m², respectively.

Keywords: Organic light-emitting diodes (OLED), blue, phosphorescent, electron transporting material, cesium, doping.

I. Introduction

Phosphorescent organic light-emitting diodes (PHOLEDs) are promising and tunable solid-state lighting sources for both lighting and display applications owing to their high light-emitting performances [1]-[5]. In particular, white organic light-emitting diodes (OLEDs) have been attractive candidates for future solid-state lighting sources since their power efficiencies have surpassed those of incandescent bulbs [1]-[3]. However, the light-emitting efficiency of blue PHOLEDs is much lower than their longer wavelength counterparts (such as green, orange, and red), thus restricting the performance of white PHOLEDs [6], [7]. In pursuing highly efficient blue PHOLEDs, various results have been demonstrated through the development of host materials and device structures [8]-[20]. Many types of device engineering, such as a mixed host, stepwise doping, or double emissive layer structure, have been reported to be applicable to blue PHOLEDs [8]-[14].

Enhanced blue PHOLED performances achieved through the development of carbazole-, trizine-, pridine-, or phenylsilane-type wide band-gap materials have also been reported [15]-[20]. Triplet exciton confinement in the emissive layer (EML) of PHOLEDs has been known as one of the key factors affecting the device characteristics [14], [18], [21], [22]. Since the blue electro-phosphorescent dopants have high triplet energy ($T_1$) levels, wideband gap hole transporting materials and electron transporting materials with high $T_1$ levels are required [12]-[14], [23]-[26]. Recently, Zheng and others found that the use of a hole transporting layer (HTL) with $T_1$ levels...
improved the light-emitting performances of an iridium(III) bis(2,4-difluorophenyl)pyridinato)tetrakis(1-pyrazolyl)borate (FIr6) doped blue PHOLED with 1,4-Bis(triphenylsilyl)benzene (UGH2) as the host [23]. Their study resulted in 1,1-bis[(di-4-tolylamino)phenyl]cyclohexane (TAPC) ($T_1 = 2.87$ eV) giving a better exciton confinement compared to that of devices made with bis(N-(1-naphthyl)-N-phenylamino)biphenyl (NPB) ($T_1 = 2.29$ eV). However, there have been few systematic studies of the effect of the electron transporting layer (ETL) on the device characteristics.

In this work, we fabricate five blue PHOLEDs based on iridium(III)bis(4,6-difluorophenyl)-pyridinato-$N,C_2'$ picolinate (FIrpic) with different combinations of electron injection materials and transport materials. We demonstrate that light-emitting characteristics such as current density, turn-on voltage, and performance are correlated with the energy level as well as the triplet energy of the introduced electron injection layer (EIL) and ETL.

II. Experiment

Five blue PHOLEDs (Devices A through E) are fabricated using a configuration of indium tin oxide (ITO)/TAPC (50 nm) /4,4',4''-tris(N-carbazolyl)trisphenylamine (TcTa):FIrpic (7%, 10 nm)/2,6-bis(3-(carbazol-9-yl)phenyl)pyridine (26DCzPPy):FIrpic (20%, 10 nm)/ETL ($x$ nm)/EIL (50–$x$ nm)/LiF (1 nm)/Al (120 nm), as shown in Fig 1. TAPC with a wider triplet energy level ($T_1$) of 2.9 eV, which is higher than that of FIrpic ($T_1 = 2.62$ eV), and with a high-lying of the lowest unoccupied molecular orbital (LUMO) energy level, is used as the HTL/electron blocking layer [24]-[26]. As a standard device, a cesium (Cs) non-doped device with Bphen material (Device A) is prepared. A non-doped Bphen, Tm3PyPB, or 26DCzPPy layer is used as an ETL/hole blocking layer, the thickness of which is $x$ nm with $x$ varying from 20 to 50. Cesium doped into the ETL material is used as the n-type EIL, the thickness of which is (50–$x$) nm (Devices B through E). As the EML, we employ a double EML (D-EML) structure using TcTa and 26DCzPPy for the host materials of FIrpic in the two adjacent EMLs [8], [9]. The chemical structures of the materials and energy level diagrams used in this study are shown in Fig. 2 (the energy levels are taken from the literature).

ITO is cleaned using a standard oxygen plasma treatment. The OLED grade materials are purchased and used without further purification. All organic layers are deposited in a high-vacuum chamber below $5 \times 10^{-7}$ torr, and thin LiF and Al films are deposited as a cathode electrode. The OLEDs are transferred directly from a vacuum into an inert environment glove-box, where they are encapsulated using a UV-curable epoxy and a glass cap with a moisture getter. The electroluminescence (EL) spectrum is measured using a Minolta CS-1000. The current density-voltage (J-V) and luminescence-voltage (L-V) characteristics are measured using a current/voltage source/measure unit (Keithley 238) and a Minolta CS-100, respectively.

III. Results and Discussion

The EL spectra of the blue PHOLEDs (Devices A through E) are shown in Fig. 3 according to the EIL and ETL materials. All devices exhibit a similar maximum luminescence wavelength at a driving current of 10 mA/cm$^2$, near 470 nm,
which originates from the triplet emission of FIrpic dopant and the second vibration peaks with a wavelength of approximately 500 nm. The slight differences in the relative intensities of the second vibration peaks can be understood by the slight shift of the recombination zone as well as the different optical properties of the ETL/EIL combination [25]-[27].

Figure 4 shows the current density-voltage-luminance (J-V-L) curves of the blue PHOLEDs (Devices A through E) according to the EIL and ETL materials. We can easily see that the different combinations of ETL and EIL greatly influence the J-V-L characteristics of the blue PHOLEDs. Compared to standard Device A with only Bphen as the ETL/EIL, Device B with Cs doped Bphen as the EIL shows an increased current density as well as luminance at the same voltage. For example, the current density and luminance at a driving voltage of 4.5 V shows 8.5 mA/cm² (Device A) and 25.8 mA/cm² (Device B) and 1544 cd/m² (Device A) and 5699 cd/m² (Device B), respectively. This could be attributed to the difference in the electrical conductivity of the Cs doped Bphen as the EIL, which results in a reduction of the total resistance of the organic layers and an enhancement of the charge injection from the electrode [11], [25], [28].

In terms of the external quantum efficiency (EQE) characteristics, Device B shows a slight increase compared to standard Device A; however, this increase is not impressive due to the lower $T_1$ of Bphen (2.5 eV) compared to that of FIrpic (2.65 eV) [25]. In Fig. 5, the EQE characteristics of blue PHOLEDs are plotted against the current density. To overcome the low efficiency of Device B, we fabricate Devices C and D, which have wider $T_1$ materials (Tm3PyPB and 26DCzPPy) as ETL/EIL, along with Cs doping. To achieve efficient blue PHOLEDs, an effective confinement of the triplet exciton is necessary [10], [14], [17]. Since the triplet energy level of both Tm3PyPB and 26DCzPPy ($T_1 = 2.78$ eV and 2.71 eV, respectively) is higher than that of FIrpic, the triplet exciton of FIrpic can be confined within the EML. Accordingly, we find highly enhanced EQEs in Devices C and D, as shown in Fig. 5. The peak EQEs of Devices C and D are 20.7% and 21.5%, respectively, while those of Devices A and B are only 10.1% and 12.1%.

Moreover, these enhanced EQEs that are a 1.9-fold enhancement compared with that of Device B with Bphen (18.7 lm/W) of around 100 cd/m², along with reduced driving voltages, result in a significantly increased maximum luminance efficiency (LE) of 36.7 lm/W (Device C with Tm3PyPB) and 35.8 lm/W (Device D with 26DCzPPy) without an out-coupling enhancement technique. In Fig. 6, the LE characteristics of the blue PHOLEDs are plotted against brightness.

To obtain higher LE, especially for lighting applications with OLED technology, a low driving voltage is necessary. Note that the turn-on voltage of Device D is 0.5 V lower than that of Device C, which can be explained by a lower electron injection.
barrier from the ETL to the EML. The LUMO levels of 26DCzPPy and Tm3PyPB are 2.56 eV and 2.78 eV, respectively. Thus, Device C with Tm3PyPB encounters an additional electron injection barrier (0.22 eV), which causes an increased driving voltage compared with that of Device D. However, there is another aspect to consider in terms of the current density slope at the light-emitting region. Even though the driving voltage of Device D is lower than that of Device C, the current density slope of Device C is much steeper than that of Device D, as Tm3PyPB has a much higher electron mobility and an adequate HOMO level for hole blocking than does 26DCzPPy. For instance, the current density of Device C at a driving voltage of 6.0 V shows 69.6 mA/cm$^2$, while that of Device D is only 29.2 mA/cm$^2$. By combining the advantages of Device C (steep current density slope) and Device D (low driving voltage), we fabricate Device E, which is constituted by 26DCzPPy ETL and Cs doped Tm3PyPB EIL. As a result, we develop a highly efficient blue PHOLED, which shows a low driving voltage as well as a steep increase of the current density. Consequently, the maximum LE of Device E reaches up to 45.6 lm/W and can be expected to be over 100 lm/W, considering the potential of the improved out-coupling technique to achieve a 2.3-fold enhancement [1], [3], [25].

IV. Conclusion

Investigating the nature of a Cs-doped ETL, we successfully developed highly efficient blue PHOLEDs along with a reduced driving voltage and an enhanced quantum efficiency, in which a peak power efficiency of 45.6 lm/W without an out-coupling enhancement was shown.

References

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