Electroluminescence characteristics of *n*-type matrix materials doped with iridium-based green and red phosphorescent emitters

Heume-Il Baek¹ and Changhee Lee^{1,a)}

¹*School of Electrical Engineering and Computer Science and Inter-University Semiconductor Research Center, Seoul National University, Seoul 151-744, Republic of Korea*

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The electroluminescence characteristics of various *n*-type matrix materials with various orders of electron mobility doped with the phosphorescent green emitter fac-tris(2-phenylpyridine) iridium(III) [Ir(ppy)₃] and the phosphorescent red emitter bis(2-(2'-benzo [4,5-a] thienyl)pyridinato-*N*, *C*^{3'})iridium(acetyl-acetonate) [btp₂Ir(acac)] were evaluated and compared to those of the *p*-type 4,4''-*N*,*N*'-dicarbazole-biphenyl (CBP) reference matrix. For Ir(ppy)₃, the device with the *n*-type matrix 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene was found to have the highest efficiency and operational lifetime, whereas for btp₂Ir(acac) the device with the *p*-type matrix CBP was found to have the highest efficiency. Our study of hole- and electron-dominant devices and analyses of electroluminescence spectra show that the main recombination zone position and the electron-hole balance change as the matrix material changes, resulting in changes in the characteristics of the organic light emitting diodes. © 2008 American Institute of Physics. [DOI: 10.1063/1.2890399]

I. INTRODUCTION

It is known that the addition of an extra hole blocking layer (HBL) or electron transport layer (ETL) with hole blocking properties enables the production of highly efficient phosphorescent organic light emitting diodes (OLEDs) because triplet excitons are then confined in the light emitting layer (EML).^{1,2} 4,4'-*N*,*N*'-dicarbazole-biphenyl (CBP) has been widely used as a matrix material for phosphorescent OLEDs because it exhibits ambipolar conduction when doped with a phosphorescent emitter³ and its triplet level is of sufficient energy to offer exothermic energy transfer conditions for red and green phosphorescent emitters.^{4,5} However, CBP is inherently a *p*-type material from the viewpoint of carrier mobility (its hole mobility is at least one order of magnitude higher than its electron mobility)⁶ and thus a HBL is essential to prevent exciton leakage toward the ETL.

High band gap *n*-type materials such as 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP),¹ 4,7-diphenyl-1,10-phenanthroline,⁷ 4-biphenyl-oxolatoaluminum(III)bis(2-methyl-8-quinolinato)4-phenylphenolate (BALq), 3-phenyl-4-(18-naphthyl)-5-phenyl-1,2,4-triazole (TAZ),⁸ and 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBi) (Ref. 9) are usually used as ETLs in phosphorescent OLEDs because of their suitable lowest unoccupied molecular orbital (LUMO) levels and hole blocking properties. These *n*-type materials can also be used as matrix materials for phosphorescent emitters, and some of them exhibit reasonable performance even without an extra HBL.¹⁰⁻¹⁴

For green phosphorescent OLEDs with iridium-based emitters, maximum external quantum efficiencies (EQEs) of 19% (Ref. 10) and 19.3% (Ref. 15) were obtained from the *n*-type matrix TAZ [doped with 12% bis(2-phenylpyridine)

iridium(III) acetylacetonate] and the combination of the *p*-type matrix 4,4',4''-tris(*N*-carbazolyl)-triphenylamine and *n*-type matrix TAZ (doped with fac-tris(2-phenylpyridine) iridium(III) [8%Ir(ppy)₃]), respectively, whereas about 13% EQE was obtained from the *p*-type matrix CBP.^{2,3,16,17}

For red phosphorescent OLEDs with iridium-based emitters, there were several reports that evaluate both *p*-type and *n*-type matrices.¹²⁻¹⁴ The devices with *p*-type matrix such as CBP (when doped with 7% bis(2-(2'-benzo[4 5-a] thienyl)pyridinato-*N*, *C*^{3'})iridium (acetyl-acetonate) [btp₂Ir(acac)]) and 4,4'-bis[*N*-(1-naphthyl)-*N*-phenyl-amino]biphenyl [α -NPD, when doped with 20% tris(1-phenyliso-quinoline)iridium(III)] were found to exhibit a bit higher performance than those with *n*-type matrix such as TPBi and BALq. Therefore, the device efficiencies of the red phosphorescent OLEDs exhibited different tendencies on the type of the matrix materials with those of the green phosphorescent OLEDs. In addition, the type of the matrix material, thereby the charge carrier conduction properties, decides the necessity of the HBL. The selection of the proper matrix material is very important task to optimize the performance of the OLEDs; thus further understanding about these tendencies on the type of the matrix materials in both green and red phosphorescent devices is required.

In this study, the device characteristics of both red and green phosphorescent OLEDs with various *n*-type matrix materials with various orders of electron mobility were compared with those of the reference *p*-type matrix of CBP. In addition, we examined the electrical properties of both hole- and electron-dominant devices and their electroluminescence spectra to investigate the underlying mechanism and thus explain the differences in the characteristics of the OLEDs with different matrix and emitter combinations.

^{a)}Author to whom correspondence should be addressed. Electronic mail: chlee7@snu.ac.kr.

FIG. 1. (Color online) The HOMO and LUMO energy levels of the phosphorescent emitters and matrix materials used in the fabrication of the phosphorescent OLEDs and the hole- and electron-dominant devices. The dotted and dashed lines indicate the energy levels of btp₂Ir(acac) and Ir(ppy)₃, respectively.

II. EXPERIMENTAL METHODS

We prepared two types of devices: devices with multilayer OLED structures and hole- and electron-dominant devices. The OLED devices consist of an indium tin oxide (ITO) anode, a 40 nm poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) hole injection layer, a 50 nm α -NPD hole transport layer (HTL), a 30 nm EML, a 10 nm BCP HBL (optional), a 40 nm tris(8-hydroxyquinoline)aluminum (Alq₃) ETL, and a LiF (0.5 nm)/Al (100 nm) cathode. Ir(ppy)₃ and btp₂Ir(acac) were used as phosphorescent green and red emitters, respectively. BCP, TPBi, and TAZ were used as *n*-type matrix materials and CBP was used as a *p*-type matrix material. Thus we tested eight EML combinations with a fixed doping concentration of the phosphorescent emitter of 8%. Figure 1 shows the highest occupied molecular orbital (HOMO) and LUMO levels of the matrix and emitter materials used in this study; these energy levels were obtained from the literature.^{3,6,10,18,19}

The configuration of the electron-dominant devices was ITO/PEDOT:PSS (40 nm)/TPBi (10 nm)/EML (100 nm)/Alq₃ (10 nm)/LiF (0.5 nm)/Al (100 nm), where nondoped TPBi was used as the HBL and PEDOT:PSS was used to reduce the leakage current of the devices. The configuration for the hole-dominant devices was ITO/PEDOT:PSS (40 nm)/ α -NPD (10 nm)/EML (100 nm)/Al (100 nm). The same interfacial materials were used in the two cases to enable direct comparisons of their current-voltage characteristics.

All the layers in these devices were prepared by thermal evaporation onto ITO substrates except for their PEDOT:PSS layers, which were spin coated at 4000 rpm for 30 s. The substrates were ultrasonically cleaned by dipping them into various solvents. Organic and metal evaporations were conducted under a base pressure of 5×10^{-6} Torr without breaking the vacuum and the evaporation speed was 1–1.5 Å/s for the organic materials and 3–5 Å/s for the metals. The doping concentration was adjusted by varying the relative evaporation speeds of the host and dopant materials, and the evaporation speeds were monitored with a quartz-oscillator thickness monitor. The current-voltage (*I*-*V*) characteristics were measured by using a Keithley 236 source measurement

unit, and the luminance and EQE were calculated from photocurrent measurement data obtained with a calibrated Si photodiode (Hamamatsu). The electroluminescence spectra were obtained with a photomultiplier tube combined with a monochromator (Acton Spectropro-275). In the lifetime tests, every device was capped with a glass lid by using an UV-curable epoxy in an Ar-filled glovebox; the water concentration was maintained under 1 ppm.

III. RESULTS AND DISCUSSION

A. Characteristics of the OLEDs with various matrix materials

The matrix materials used in this study are considered to have sufficiently high triplet (*T*₁) energies for Ir(ppy)₃ (*T*₁ = 2.42 eV) and btp₂Ir(acac) (*T*₁ = 2.02 eV) to prevent back energy transfer from dopant to host.^{10,11,20,21} However, the efficiencies of the phosphorescent OLEDs with different matrix materials varied significantly, as shown in Fig. 2. All devices were found to exhibit their maximum efficiency at a low current density, except the CBP matrix devices without a HBL which were found to exhibit their maximum efficiency at a high current density. Interestingly, the difference between the efficiencies of devices with and without a HBL when a *n*-type matrix is used is not very large, whereas for devices with a CBP matrix (*p*-type) this difference is large. In addition, better performance was obtained in devices without a separate HBL when a *n*-type matrix was used, whereas a separate HBL was found to be essential to achieve a reasonable efficiency with a CBP matrix. Of the green devices [Fig. 2(a)], most of the *n*-type matrix (TPBi, TAZ) devices have a maximum efficiency that is similar to that of the CBP devices (with a HBL), and the TPBi devices without a HBL were found to exhibit the best overall EQE. For the red devices, the performance of the CBP device with a HBL is much better [Fig. 2(b)] than that of any other *n*-type matrix device. The performance of the BCP devices was too poor for a meaningful comparison.

n-type matrix materials typically exhibit hole blocking properties so an extra HBL is unnecessary. These hole blocking properties are due to the carrier mobilities and HOMO levels of these matrix materials. The electron mobilities of CBP,¹⁸ BCP,²¹ TPBi,⁹ and TAZ (Ref. 8) are of the orders of magnitude of 10⁻⁴, 10⁻³, 10⁻⁵, and 10⁻⁷ cm²/V s, respectively, and the hole mobility of CBP is of the order of 10⁻³ cm²/V s. The hole mobilities of *n*-type matrix materials are typically at least one order of magnitude lower than their electron mobilities. Therefore, the differences between the efficiencies of the phosphorescent OLEDs shown in Fig. 2 originate from differences between the charge carrier conduction properties of the EMLs, which vary from combination to combination of the emitter and matrix materials.

Figure 3 shows the results of the accelerated operational lifetime tests of the phosphorescent green OLEDs with various matrix materials. The half-lifetimes of the devices (the time for the luminance to fall to 50% of its initial value) seem to be correlated with their efficiencies. In particular, the variations of the lifetimes from the devices with HBL to those without HBL (for the same matrix material) are very

(a)

(b)

FIG. 2. (Color online) External quantum efficiencies of OLEDs with various matrix materials as functions of current density: devices doped with (a) 8% Ir(ppy)₃ and (b) 8% btp₂Ir(acac). The filled and open symbols are for OLEDs with a 10 nm BCP HBL and those without any HBL, respectively.

closely correlated with their efficiencies. Therefore, phosphorescent OLEDs with significantly improved lifetimes can be obtained by selecting an appropriate *n*-type matrix for the EML and omitting an extra HBL, which is known to be a limiting factor for operational lifetimes.²²

B. Characteristics of the hole- and electron-dominant devices

A high doping concentration (6–10%) is usually used for phosphorescent emitters to achieve high efficiencies; such high dopant concentrations are expected to have a substantial influence on the carrier conduction properties of matrix materials. The carrier conduction properties of CBP hosts doped with Ir(ppy)₃ and btp₂Ir(acac) have been relatively well reported;^{6,18} the electron mobility of a btp₂Ir(acac)-doped CBP matrix can vary by up to three orders of magnitude depending on the dopant concentration. No information about the carrier conduction properties of *n*-type matrix ma-

FIG. 3. (Color online) Operational lifetime test results for OLEDs with various matrix materials doped with 8% Ir(ppy)₃. The dashed and continuous lines indicate devices with a 10 nm BCP HBL and those without a HBL, respectively. Only devices with a HBL were tested for the CBP matrix. All devices were driven under a constant current bias to achieve an initial luminance of 2000 cd/m². (An initial luminance of 1000 cd/m² was used for the BCP matrix devices due to their lower efficiencies.)

terials doped with Ir(ppy)₃ or btp₂Ir(acac) is available. Thus we prepared hole- and electron-dominant devices with various combinations of phosphorescent emitters and matrix materials to compare their charge carrier conduction properties. We use the terms “hole dominant” and “electron dominant” instead of “hole only” and “electron only” because additional layers such as α -NPD and Alq₃ were used to assist hole and electron injection. In addition, the blocking of the opposite carrier is not perfect, even though TPBi was used to block hole injection and Al (4.3 eV) cathodes were used instead of LiF/Al (2.9 eV) to block electron injection.

Figure 4 shows the current density versus voltage (*J*-*V*) curves of the hole- and electron-dominant devices. A qualitative comparison of these *J*-*V* characteristics is possible, although they are not directly proportional to the carrier mobilities of the corresponding organic layers because different injection efficiencies are expected at different interfaces. In the Ir(ppy)₃-doped devices [Fig. 4(a)], the electron-dominant devices with a *n*-type matrix were found to exhibit much higher current conduction than the hole-dominant devices, with the opposite results obtained for devices with a CBP matrix. Similar results were obtained in btp₂Ir(acac)-doped devices [Fig. 4(b)], but the gap between the hole- and electron-dominant devices is much narrower for the *n*-type matrix devices and almost the same curve was obtained for the CBP matrix devices. In addition, a higher current conduction is expected in electron-dominant devices (with a *n*-type matrix) doped with Ir(ppy)₃ than devices doped with btp₂Ir(acac) because deeper electron traps are formed for btp₂Ir(acac) than for Ir(ppy)₃, as indicated by their energy levels (see Fig. 1). Therefore, the electron-hole recombination zone is expected to be more biased toward the HBL (or ETL) side of the phosphorescent red OLEDs than in the green OLEDs,²³ which is why the performance of red OLEDs with a *n*-type matrix is worse than that of red OLEDs with a CBP matrix; the lower hole mobility of *n*-type matrix materials retards the hole supply toward the position of highest electron concentration. In contrast, due to the formation of relatively shallow electron traps by Ir(ppy)₃ molecules, the electron supply toward the position of highest hole concentration might be sufficient even when the matrix is changed to *n*-type due to its lower hole mobility, so the

FIG. 4. (Color online) Current density vs voltage characteristics of the hole- and electron-dominant devices with various matrix materials: devices doped with (a) 8% Ir(ppy)₃ and (b) 8% btp₂Ir(acac). The open and filled symbols are for the hole- and electron-dominant devices, respectively.

main recombination zone would be shifted toward the HTL side (see Fig. 5). Hole-dominant devices with a TAZ host were found to exhibit the smallest current conduction for all emitters due to its low mobility, and also to reach their break down conditions at a lower current density than the other devices. The above J - V characteristics enable the explanation of the performance and properties of phosphorescent green and red OLEDs with p -type and n -type matrix materials.

C. Electroluminescence spectra analysis

There are very subtle differences between the electroluminescence spectra of the OLEDs with different matrix ma-

FIG. 5. (Color online) The conceptual diagram for the relative hole and electron flux and recombination zone position in the p -type and n -type matrix materials doped with Ir(ppy)₃ and btp₂Ir(acac).

terials, as shown in the inset in Fig. 6, although somewhat broadened spectra were found for the Ir(ppy)₃-doped devices, and the intensities of the vibronic peaks (675 nm) of the btp₂Ir(acac)-doped devices were found to be somewhat higher for the devices with a n -type matrix. As mentioned above, the electron blocking in the hole-dominant devices is not perfect, so they also produce weak electroluminescence. However, the shapes of their electroluminescence spectra are significantly different, as shown in Fig. 6, because the differences in the positions of their recombination zones are amplified by the high EML thickness of 100 nm. In the Ir(ppy)₃-doped devices, the spectrum was found to broaden as the matrix was changed from p -type (CBP) to n -type (TPBi and TAZ). Similarly, the intensities of the vibronic peaks (675 nm) of the btp₂Ir(acac)-doped devices were found to increase as the matrix was changed from p -type to n -type. More substantial changes were observed in the n -type matrix devices with lower electron mobility (TAZ).

From the J - V characteristics of the hole- and electron-dominant devices, a shift of the recombination zone toward the HTL side is anticipated for a n -type matrix with lower electron mobility (see Fig. 5). We were able to reproduce the electroluminescence spectra of the devices with a n -type matrix from those of the CBP matrix devices by applying Eq. (1) for the planar microcavity effect:²⁴

FIG. 6. (Color online) Normalized electroluminescence spectra of the hole-dominant devices with various matrix materials: devices doped with (a) 8% Ir(ppy)₃ and (b) 8% btp₂Ir(acac). The insets show the normalized spectra of the OLEDs with the corresponding EML structures. The continuous lines were calculated from the spectra of the CBP matrix devices by taking into account the shift in the position of the main recombination zone toward the HTL side.

$$I_{\text{ext}}(\Delta x, \lambda) \approx \left[1 + R_1 + 2\sqrt{R_1} \cos\left(\frac{4\pi n(\Delta x)}{\lambda}\right) \right] I_{\text{int}}(\lambda), \quad (1)$$

where I_{ext} , I_{int} , R_1 , n , Δx , and λ are the output light intensity from the cavity, the light intensity inside the cavity, the reflectance of the metal electrode (a value of 0.95 was used for the Al cathode), the refractive index of the organic material (a value of 1.75 was used), the position of the recombination zone relative to that of the CBP matrix device, and the wavelength, respectively. I_{int} was assumed to be the normalized light intensity of the CBP matrix devices, and the results with

$\Delta x = 45$ and 60 nm were found to provide a satisfactory fit of the spectrum of the Ir(ppy)₃-doped TPBi and TAZ devices, respectively. Similarly, results calculated with $\Delta x = 40$ and 60 nm were used to fit the spectra of the btp₂Ir(acac)-doped TPBi and TAZ devices, respectively, and are shown as continuous lines in Fig. 6. Thus shifts toward the HTL side of the recombination zone of 40–45 and 60 nm are expected for the TPBi and TAZ matrix devices with respect to the CBP matrix devices. Therefore, the use of *n*-type matrix materials results in a shift of the recombination zone toward the HTL side and this shift increases when a *n*-type host with a lower electron mobility is used.

IV. CONCLUSIONS

The properties of phosphorescent green and red OLEDs with various *n*-type matrix materials with various orders of electron mobility were compared with those of devices in which CBP was used as a *p*-type reference matrix. Devices with a *n*-type matrix were typically found to exhibit better performance when an extra HBL was not used, while a HBL was found to be essential to achieve reasonable efficiency in devices with the *p*-type host. Of the Ir(ppy)₃-doped green phosphorescent devices, those with the *n*-type matrix material TPBi were found to exhibit the best performance, including the longest operational lifetime, whereas the *p*-type matrix material CBP was found to exhibit the best performance when the phosphorescent red emitter btp₂Ir(acac) was used. The variation in the performance of the green and red phosphorescent OLEDs with the change in the matrix from *p*-type to *n*-type can be explained by the results of our hole- and electron-dominant device study, which found that electron-hole recombination is less efficient in red OLEDs with a *n*-type matrix. In addition, our investigation of the electroluminescence spectra showed that the use of *n*-type hosts results in a shift of the recombination zone toward the HTL side that is inversely proportional to the hole mobility of the matrix material. Furthermore, phosphorescent green OLEDs with significantly improved lifetimes can be obtained by selecting an appropriate *n*-type matrix for the emissive layer and omitting an extra HBL.

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