Triplet host engineering for triplet exciton management in phosphorescent organic light-emitting diodes

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(Received 5 September 2007; accepted 4 December 2007; published online 4 March 2008)

The device performances of green phosphorescent organic light-emitting diodes with a triplet mixed host emitting layer were correlated with the energy levels and composition of the host materials. Two hole-transport-type host materials, (4,4′-*N*,*N*′-dicarbazole)biphenyl (CBP) and 4,4′,4″-tris(*N*-carbazolyl)triphenylamine (TCTA), were combined with two electron-transport-type host materials, 1,3,5-tris(*N*-phenylbenzimidazole-2-yl)benzene (TPBI) and PH1. The maximum quantum efficiency was obtained in the 5:5 mixed host in the case of TCTA:TPBI and TCTA:PH1, while CBP:PH1 showed the best performances in the 9:1 mixed host. The quantum efficiency of the green mixed host devices was improved by more than 50% compared with that of the corresponding single host devices. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2841058]

I. INTRODUCTION

Organic light-emitting diodes (OLEDs) are attractive as a next generation display due to their merits of good picture quality, thickness, and flexibility. OLEDs have a wide color gamut with wide viewing angle and a total panel thickness that is thinner than that of liquid crystal displays. However, the power consumption and lifetime characteristics of OLEDs still need to be improved further to expand the application of OLEDs from small size display to large size display.

One efficient way to reduce the power consumption of OLEDs is to use phosphorescent OLEDs (PHOLEDs) because they can give better quantum efficiency than fluorescent OLEDs.[1,2] Many studies have attempted to improve the light-emitting efficiency of PHOLEDs through the development of materials and device structures. High efficiency was achieved by using a triazine-type host material[3] and many iridium- or platinum-based triplet dopant materials have been synthesized.[4–7] Hole blocking layers were also important to gain high efficiency[8–10] and exciton blocking materials were effective to enhance the recombination efficiency of holes and electrons inside the emitting layer.[10,11] Many studies have also attempted to devise a device structure for high efficiency.[12–15] A charge confining structure was reported by our group and the quantum efficiency could be greatly enhanced due to the confinement of holes and electrons inside the emitting layer.[13] It was also effective to extend the lifetime of green PHOLEDs.[14] The triplet exciton blocking structure near the hole transport layer side was also studied and was found to be capable of increasing the efficiency of green PHOLEDs by more than threefold.[11] In these studies, the mechanism for efficiency improvement was charge confinement. Holes and electrons could be confined inside the emitting layer with little leakage out of the emitting layer. In addition, triplet quenching was prohibited by using an exciton blocking layer.[11]

In this work, a triplet mixed host structure was developed as an approach to confine excitons inside the emitting layer and to manage triplet excitons by controlling the charge injection. Two hole-transport-type host materials, (4,4′-*N*,*N*′-dicarbazole)biphenyl (CBP) and 4,4′,4″-tris(*N*-carbazolyl)triphenylamine (TCTA), were combined with two electron-transport-type host materials, 1,3,5-tris(*N*-phenylbenzimidazole-2-yl)benzene (TPBI) and PH1. Device performances were correlated with the energy levels of the host materials and the relative composition of the two host materials in the emitting layer.

II. EXPERIMENTAL

The device configuration used in this experiment was indium tin oxide (150 nm)/*N*,*N*′-diphenyl-*N*,*N*′-bis-[4-(phenyl-*m*-tolyl-amino)-phenyl]-biphenyl-4,4′-diamine (60 nm)/*N*,*N*′-di(1-naphthyl)-*N*,*N*′-diphenylbenzidine (30 nm)/mixed host light-emitting layer (30 nm)/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) (5 nm)/tris(8-hydroxyquinoline) aluminum (20 nm)/LiF (1 nm)/Al (200 nm). Four different kinds of mixed host device were fabricated to investigate the effect of host energy levels and host composition on the device performances of mixed host devices. Four reference devices with single host material were also prepared for comparison. Host materials for the

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TABLE I. HOMO and LUMO levels of host materials.

Materials	HOMO	LUMO
CBP	5.9	2.6
TCTA	5.7	2.4
PH1	5.9	2.8
TPBI	6.2	2.9

emitting layer were CBP, TCTA, PH1, and TPBI. We previously reported on PH1, which has a spirobifluorene backbone structure.[13] PH1 was a commercialized product of Merck with triplet energy of 2.4 eV. Hole-transport-type CBP and TCTA hosts were mixed with electron-transport-type PH1 and TPBI hosts. The relative compositions of the two host materials in the light-emitting layer were varied as 100:0, 95:5, 90:10, 75:25, and 50:50. Tris(2-phenylpyridine) iridium was used a phosphorescent dopant at a doping concentration of 5%. The current density–voltage–luminance characteristics of the devices were measured with a Keithley 2400 source measurement unit and CS 1000 spectrophotometer.

III. RESULTS AND DISCUSSION

A mixed host structure in fluorescent OLEDs is known to be effective in maximizing efficiency through management of holes and electrons in the light-emitting layer.[16–21] However, few studies have investigated triplet mixed host systems for high performances in PHOLEDs.[22] The requirement for host materials in triplet devices is different from that of singlet devices in that two host materials in the mixed host structure should have a wide triplet bandgap as well as the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) suitable for charge injection. Therefore, TCTA, TPBI, and CBP, with a triplet bandgap of 2.6 eV, and PH1, with triplet bandgap of 2.4 eV, were chosen as the triplet matrix materials for green PHOLEDs. The HOMO and LUMO levels of the four host materials are summarized in Table I. CBP and TCTA have appropriate HOMO levels for hole injection, while TPBI and PH1 have LUMO levels for efficient electron injection. PH1 was not good enough for efficient hole injection because of its poor hole transporting character and relatively deep HOMO level of 5.9 eV compared with 5.7 eV of TCTA. Therefore, the combination of hole and electron-transport-type host materials can be beneficial to control holes and electrons in the light-emitting layer. To correlate the recombination of holes and electrons in the light-emitting layer with host energy levels and host composition, the device performances of the following four mixed host devices were investigated according to the relative content of host materials: CBP:PH1, CBP:TPBI, TCTA:PH1, and TCTA:TPBI.

Figure 1 shows the representative current density–voltage and current density–luminance curves of the TCTA:PH1 mixed host devices. All the results of the four mixed host devices are summarized in Fig. 2, according to the relative content of host materials. The current density and luminance of the mixed host devices were measured at 6 V. The four mixed host devices showed different current density

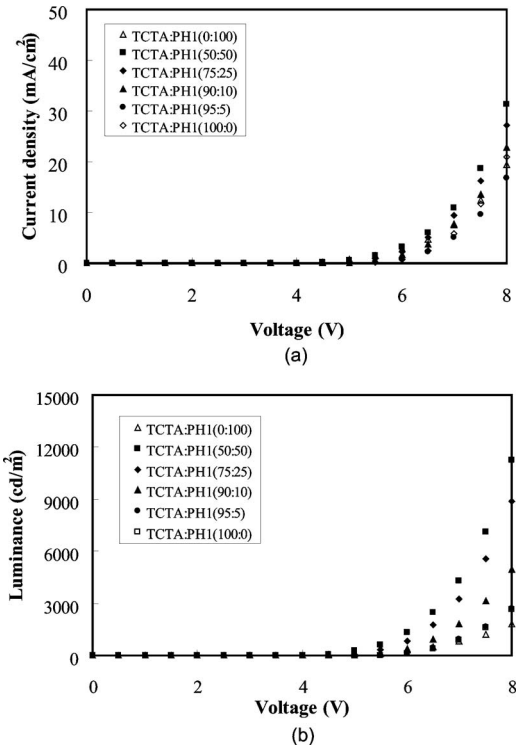

FIG. 1. Current density–voltage–luminance curves of TCTA:PH1 mixed host devices according to host composition: (a) current density–voltage and (b) luminance-voltage.

dependency on the composition of the mixed hosts. The current density of CBP:PH1 was gradually increased with increasing PH1 content in the mixed host device. The addition

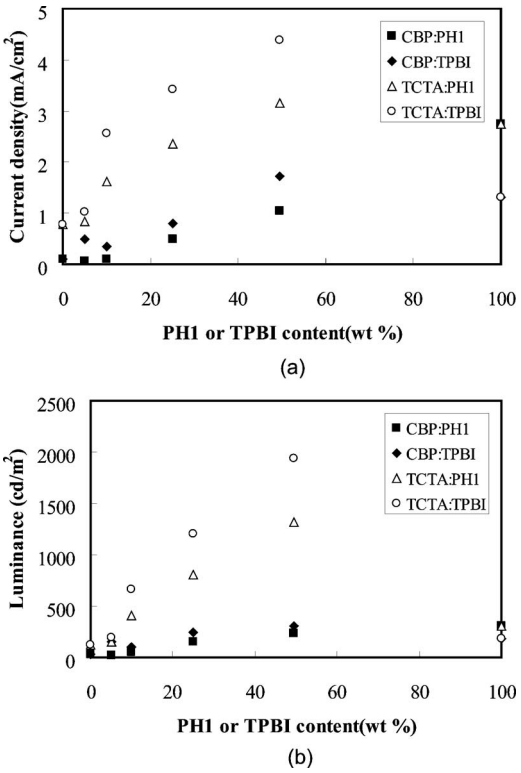

FIG. 2. Current density and luminance of mixed host devices according to TPBI or PH1 content in mixed host devices: (a) current density and (b) luminance.

of PH1 to CBP increased the current density as the electron injection from BCP to PH1 was facilitated due to the low energy barrier for electron injection, even though the hole injection was not improved. Compared with CBP:PH1, the CBP:TPBI devices showed a maximum current density at 50% loading of TPBI. The current density of CBP:TPBI (50:50) was higher than that of the standard devices. The high current density in CBP:TPBI (50:50) can be explained by the efficient electron injection from the cathode to TPBI. Hole injection from NPB to TPBI was restricted because of the HOMO level difference of 0.6 eV between NPB and TPBI. The hole injection of TPBI was enhanced by CBP addition. In the case of CBP, electron injection from BCP to CBP was limited due to the LUMO level gap of 0.3 eV between BCP and CBP. Therefore, the addition of TPBI to CBP was helpful to increase the electron injection from BCP to the emitting layer. Therefore, the hole and electron injection in the CBP:TPBI device was facilitated and a high current density could be obtained.

TCTA:PH1 and TCTA:TPBI devices also showed similar results, even though the current density values of TCTA:PH1 and TCTA:TPBI were much higher than those of CBP:PH1 or CBP:TPBI. The maximum current density was obtained in the device with 50% of PH1 or TPBI in TCTA. The combination of the good hole injection properties of TCTA with the low energy barrier for hole injection and good electron injection properties of TPBI with low electron injection barrier enhanced the current density of the mixed host devices. The high current density of TCTA-based mixed host devices was due to the superior hole injection properties of TCTA compared to CBP. The luminance of the mixed host devices also exhibited a similar behavior to the current density.

The quantum efficiency and power efficiency of the mixed host devices were measured and plotted against PH1 or TPBI content in the light-emitting layer (Fig. 3). The maximum quantum efficiency in TCTA-based devices was obtained in the devices with 50% PH1 or TPBI, while the maximum quantum efficiency in CBP:PH1 devices was observed in the device with 10% PH1. The quantum efficiency of the CBP:TPBI device was not improved at all. The quantum efficiency dependence on the host composition in mixed host devices can be explained by the charge balance in the light-emitting layer. In TCTA mixed host devices, hole injection from NPB to TCTA is efficient due to the low energy barrier for hole injection (0.2 eV). Therefore, more electrons have to be injected from the electron transport layer side and the charge balance was optimized in the TCTA:PH1 (50:50) and TCTA:TPBI (50:50) devices. Compared with the TCTA-based devices, the hole injection of CBP device was not as efficient as that of TCTA. Therefore, the charge balance was optimized in the CBP:PH1 (90:10) device. At high PH1 content, the electrons are in excess, thereby decreasing the quantum efficiency. In contrast to CBP:PH1, which showed a high quantum efficiency of 13.2%, no improvement of quantum efficiency was detected in the CBP:TPBI mixed host devices. The hole and electron balance could not be improved in the CBP:TPBI devices even though the quantum efficiency of the mixed host device was better than that of

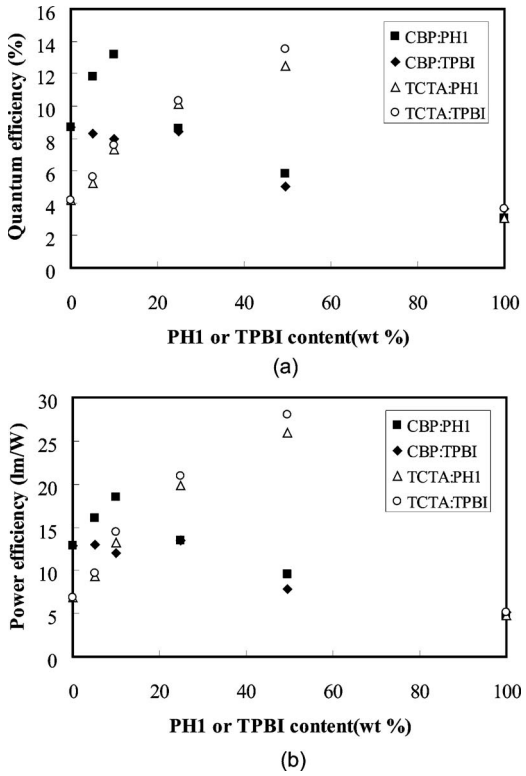

FIG. 3. Quantum efficiency and power efficiency of mixed host devices according to TPBI or PH1 content in mixed host devices: (a) quantum efficiency and (b) power efficiency.

TPBI. The quantum efficiency of the TPBI devices could be improved by adding CBP because the hole injection of CBP is better than that of TPBI. However, the quantum efficiency of the CBP device could not be improved by TPBI in spite of the good electron injection properties of TPBI. The strong hole blocking properties of TPBI limit the hole injection from NPB to the CBP:TPBI mixed host layer, resulting in poor charge balance in the light-emitting layer. The evidence for the hole blocking function of TPBI was presented by the electroluminescence (EL) spectra of the TPBI mixed host devices. Figure 4 shows the EL spectra of the CBP:TPBI and TCTA:TPBI mixed host devices according to the composition of the mixed hosts. Similar EL spectra were observed in the green emission region around 511 nm, but there was a big difference in the blue emission region around 450 nm. There was no blue emission by NPB in the TCTA:TPBI devices except for the standard devices, while NPB emission was clearly observed in the CBP:TPBI devices. The NPB emission originated from the recombination of holes accumulated at the interface between NPB and the emitting layer due to poor hole injection and electrons overflowed from the emitting layer due to good electron injection.[13] In the TCTA:TPBI devices, hole transport was dominated by TCTA, even in the presence of TPBI, leading to no emission of NPB. However, in the CBP:TPBI devices, holes were accumulated at the interface between NPB and the emitting layer due to poor hole injection, resulting in NPB emission. NPB emission was observed in all compositions in the CBP:TPBI devices.

In all the mixed host devices studied in this work except

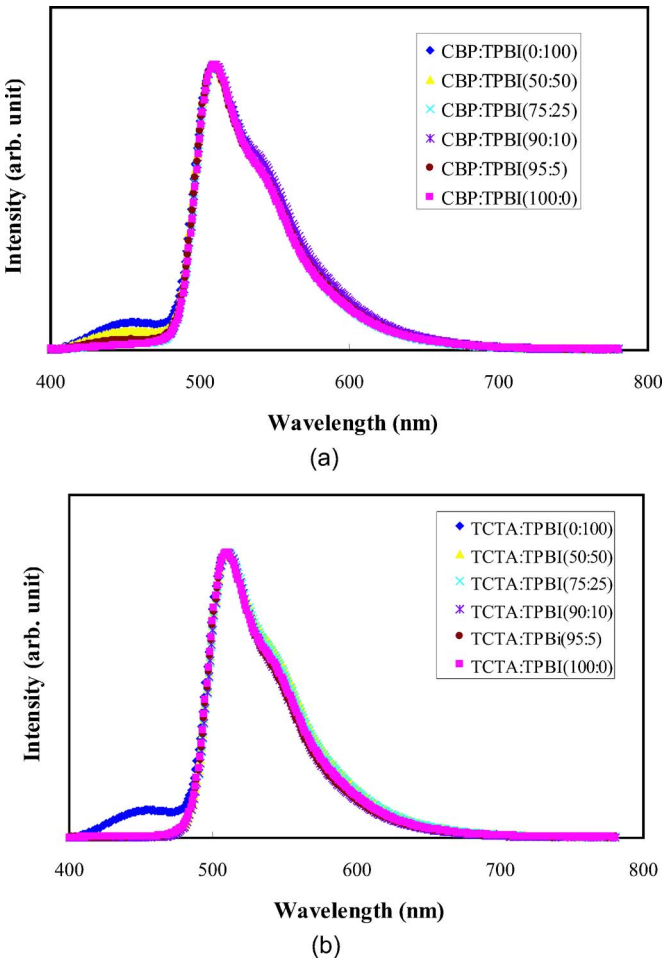

FIG. 4. (Color online) Electroluminescence spectra of CBP:TPBI and TCTA:TPBI mixed host devices according to host composition: (a) CBP:TPBI and (b) TCTA:TPBI.

CBP:TPBI, the maximum quantum efficiency was quite similar, despite the variation in the host composition to get maximum quantum efficiency. This indicates that the charge balance in the mixed host devices was the main reason for the high efficiency. From these results, it can be concluded that the combination of hole-transport-type host, with its good hole injection properties, and electron-transport-type host, with its good electron injection properties, can improve the light-emitting efficiency of triplet devices.

IV. CONCLUSIONS

The light-emitting efficiency of green PHOLEDs was improved by using triplet mixed host structures in the light-emitting layer. The optimum host composition to maximize the efficiency differed depending on the hole injection and electron injection properties of the host materials. The optimum content of the electron-transport-type host in the mixed hosts was high in the device with good hole injecting hosts, while it was rather low in the device with moderate hole injecting hosts. Even though the optimum composition of the two host materials differed depending on the host materials, the maximum quantum efficiency was similar due to the similar charge balance in the mixed host structures.

ACKNOWLEDGMENTS

This work was supported by Grant No. RTI04-01-02 from the Regional Technology Innovation Program of the Ministry of Commerce, Industry and Energy (MOCIE).

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