Relationship between host energy levels and device performances of phosphorescent organic light-emitting diodes with triplet mixed host emitting structure

Sung Hyun Kim and Jyongsik Jang
School of Chemical and Biological Engineering, Seoul National University, Shinlim-dong, Kwanak-gu, Seoul 151-742, Korea

Jun Yeob Lee[a)]
Department of Polymer Science and Engineering, Dankook University, Hannam-dong, Yongsan-gu, Seoul 140-714, Korea

(Received 17 May 2007; accepted 30 July 2007; published online 23 August 2007)

Green phosphorescent organic light-emitting diodes (PHOLEDs) with a triplet mixed host emitting layer were developed and device performances were studied by changing host materials in light-emitting layer. Power efficiency of green PHOLEDs could be improved from 12.7 to 29.1 lm/W by using triplet mixed host emitting layer. Combination of hole-transport-type host with good hole injection properties and electron-transport-type host with good electron injection properties was effective to get high efficiency in triplet mixed host devices. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2773941]

Organic light-emitting diodes (OLEDs) have been developed for more than 20 years and there have been many studies to get high performances in OLEDs. In particular, many studies were focused on improving lifetime and luminance efficiency of OLEDs.[1–6]

One efficient approach to get long lifetime and high efficiency in OLEDs is to use mixed host system instead of using a single host material.[1–6] Aziz *et al.* reported mixed host system of tris(8-hydroxyquinoline) aluminium (Alq_3) and N,N'-di(1-naphthyl)-N,N'-diphenylbenzidine (NPB) and lifetime of mixed host device could be improved.[1] They explained that the long lifetime in mixed host system was due to less cationic Alq_3 formation in mixed host system which is known to degrade long-term device performances of OLEDs. Since the report of Aziz *et al.*, other mixed host systems have been developed.[2–6] Alq_3:rubrene mixed host systems were effective to get long lifetime and high efficiency in red fluorescent devices[2,3] and 2-methyl-9,10-di(2-napthyl) anthracene:Alq_3 improved efficiency and long-term stability of red OLEDs.[4] Other than these studies, (4,4′-N,N'-dicarbazole)biphenyl (CBP):Alq_3 also showed high efficiency compared with Alq_3 devices[5] and light-emitting mechanism of mixed host system was also reported.[6]

Even though there was a previous patent about triplet mixed host using NPB:Alq_3,[7] device performances were not good enough and there has been no paper about improved device performances in phosphorescent OLEDs (PHOLEDs) using triplet mixed host structure. In this work, various triplet mixed host systems with hole-transport-type host and electron-transport-type host materials were studied to study the relationship between host energy levels and device performances of green PHOLEDs. Two hole-transport-type host materials, 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 spirobifluorene based phosphorescent host (PH1).

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)/NPB(30 nm)/mixed host light-emitting layer (30 nm)/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (5 nm)/Alq_3(20 nm)/LiF(1 nm)/Al(200 nm). Four different mixed host devices were fabricated to investigate the effect of host energy levels on device performances of mixed host devices. Four standard devices with single host material were also prepared as references for comparison. Host materials for emitting layer were CBP, TCTA, PH1, and TPBI. PH1 was commercially available and supplied from Merck Co. It has a spirobifluorene-type backbone structure with electron transport properties because of spirobifluorene units. The triplet band gap of PH1 was 2.4 eV and the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) level of PH1 were 5.9 and 2.8 eV, as reported earlier.[8] HOMO and LUMO levels of four host materials are summarized in Table I. The relative composition of two host materials in light-emitting layer was fixed with 1:1. tris(2-phenylpyridine) iridium ($Ir(ppy)_3$), a phosphorescent dopant, and doping concentration was fixed at 5%. Current density–voltage–luminance characteristics of the devices were measured with Keithley 2400 source measurement unit and PR 650 spectrophotometer.

CBP and TCTA were used as hole-transport-type host materials because comparison of CBP and TCTA can give

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	6.1	2.8

[a)]Author to whom correspondence should be addreseed; electronic mail: leej17@dankook.ac.kr

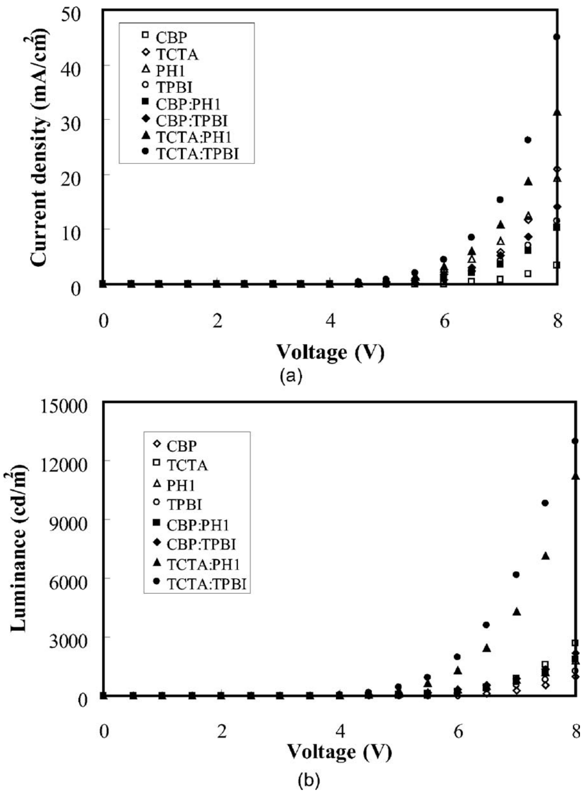

FIG. 1. Current density–voltage–luminance curves of phosphorescent mixed host devices. (a) Current density-voltage and (b) luminance-voltage.

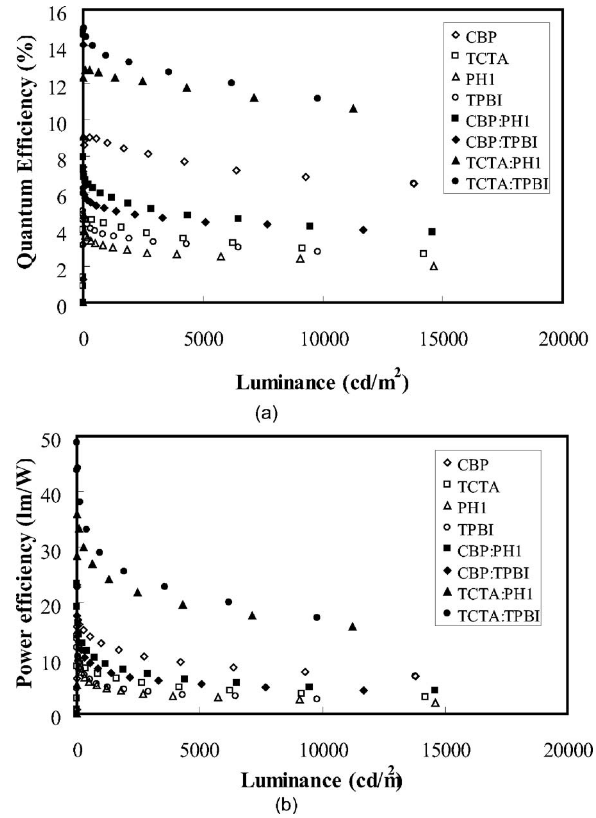

FIG. 2. Quantum efficiency and power efficiency curves of phosphorescent mixed host devices. (a) Quantum efficiency–luminance and (b) power efficiency-luminance.

information about the effect of HOMO and LUMO levels of hole-transport-type host materials on luminance efficiency of triplet mixed host devices. TCTA is better than CBP in terms of hole injection and electron blocking due to 0.2 eV upward shift of HOMO and LUMO levels. TPBI and PH1 were chosen as electron transport host materials as hole blocking properties of TPBI and PH1 are different due to 0.2 eV difference of HOMO levels between the two host materials. LUMO levels of two materials were similar to each other. Therefore, four different devices with different combinations of hole-transport-type and electron-transport-type materials were prepared to study the effect of host energy levels on light-emitting efficiency of triplet mixed host devices.

Figure 1 shows current density–voltage and luminance-voltage curves of four mixed host devices. The highest current density could be obtained in TCTA:TPBI mixed host device, while CBP:PH1 mixed host device showed the lowest current density. The high current density in TCTA:TPBI mixed host device can be explained by efficient hole injection through TCTA and electron injection from TPBI. The HOMO level of TCTA is 5.7 eV, facilitating hole injection from NPB to light-emitting layer, and the LUMO level of TPBI is 2.8 eV, resulting in effective electron injection from electron transport layer. Compared with TCTA, CBP has 0.4 eV energy barrier for hole injection from NPB to CBP, which leads to low current density in CBP mixed host devices. Hole mobility of hosts and charge trapping in TCTA and CBP layers should also be considered, and it is speculated that less hole trapping in TCTA devices had positive effect on current density. Low current density of PH1 mixed host devices compared with that of TPBI might be due to low electron mobility of PH1 (1.6×10^{-6} cm^2/V s), considering similar LUMO levels in TPBI and PH1. Electron trapping effect may be similar in PH1 and TPBI devices due to similar LUMO level, and electron mobility is thought to be responsible for the difference of current density. Even though CBP mixed host devices did not show better current density than standard devices, TCTA mixed host devices exhibited much higher current density than standard devices. Hole transport host material determined hole injection from hole transport layer and electron-transport-type host material contributed to electron injection. Therefore, it can be concluded that proper combination of hole-transport-type host and electron-transport-type host can improve both hole and electron densities in light-emitting layer. Luminance of mixed host devices was also high in TCTA mixed host devices, while it was rather low in CBP mixed host devices due to low current density.

Quantum efficiency of mixed host devices was plotted against luminance in Fig. 2. High quantum efficiency over 12% could be achieved in TCTA mixed host devices, while low quantum efficiency about 5% was obtained in CBP mixed host devices. Best quantum efficiency was observed in TCTA:TPBI mixed host device and quantum efficiency at 1000 cd/m^2 was 13.5%. There was more than 50% enhancement of quantum efficiency in TCTA:TPBI mixed host devices compared with CBP standard device which show the best performances among four standard devices. The improvement of quantum efficiency in TCTA devices is closely related with hole and electron balance in light-emitting layer. Holes are injected efficiently in TCTA standard device due to low energy barrier of 0.2 eV for hole injection, while electron injection is quite limited due to high energy barrier of 0.4 eV for electron injection. Hole is a majority carrier in TCTA device and quantum efficiency of TCTA device, is

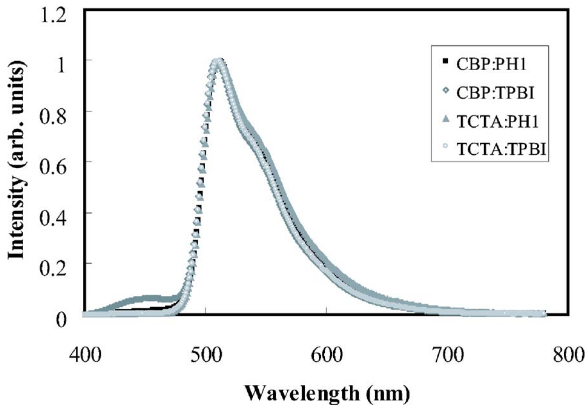

FIG. 3. (Color online) Electroluminescence spectra of phosphorescent mixed host devices.

quite low due to charge unbalance. Similar behavior is observed in TPBI and PH1 devices. Therefore, addition of TPBI or PH1 in TCTA host is beneficial to get high recombination efficiency of holes and electrons. The addition of TPBI or PH1 which aids electron injection in mixed host structure can increase electron density in light-emitting layer, resulting in hole and electron balance in TCTA devices. However, the charge balance is not improved in CBP devices by TPBI or PH1 as hole density in CBP devices is not so high as that of TCTA device. CBP device has a charge injection barrier for both holes and electrons, leading to relatively high quantum efficiency compared with other standard devices in spite of low current density. Even though electron injection through TPBI or PH1 is also efficient in CBP mixed host devices, rather low hole density in CBP devices decreases quantum efficiency of CBP mixed host devices. It is expected that quantum efficiency of CBP mixed host devices can be improved by managing host composition in light-emitting layer considering charge balance.

Power efficiency of mixed host devices was also plotted in Fig. 2. As can be expected from current density and quantum efficiency, TCTA:TPBI mixed host device showed power efficiency of 29 lm/W at 1000 cd/m^2. Efficient charge injection through each host material and high quantum efficiency by charge balance greatly enhanced power efficiency of TCTA based mixed host devices.

The difference of device performances between TCTA mixed host devices and CBP mixed host devices can be understood by electroluminescence spectra (Fig. 3). TCTA mixed host devices exhibit only one emission peak from $Ir(ppy)_3$ at 514 nm without any blue emission from NPB, while CBP mixed host devices show an additional NPB emission at 458 nm in addition to $Ir(ppy)_3$ emission. The NPB emission is originated from hole accumulation at the interface between NPB and emitting layer and electron overflow from emitting layer due to excess electrons. CBP:TPBI device shows clear NPB emission, which is attributed to high current density in TPBI containing devices. Current density of PH1 devices was lower than that of TPBI devices, and weak NPB emission was observed in CBP:PH1 device. Therefore, the NPB emission in CBP mixed host devices indirectly indicates that hole injection is limited by CBP.

In summary, quantum efficiency of green PHOLEDs could be improved by using a triplet mixed host emitting structure. TCTA:TPBI and TCTA:PH1 mixed host devices with low energy barrier for hole and electron injection were effective to improve recombination efficiency and driving voltage of triplet devices.

[1] H. Aziz, Z. D. Popovic, N.-X. Hu, A.-M. Hor, and G. Xu, Science **283**, 1900 (1999).
[2] C. Brown and D. Kondakov, SID J. **12**, 323 (2004).
[3] W. Wen and T. H. Liu, SID Int. Symp. Digest Tech. Papers **35**, 784 (2004).
[4] Y. G. Lee, H. Lee, S. K. Kang, T. S. Oh, S. Lee, and K. H. Koh, Appl. Phys. Lett. **89**, 183515 (2006).
[5] B. J. Chen, X. W. Sun, and K. R. Sarma, Appl. Phys. Lett. **88**, 243505 (2006).
[6] C. Hsiao, Y. Chen, T. Lin, C. Hsiao, and J. Lee, Appl. Phys. Lett. **89**, 163511 (2006).
[7] R. C. Kwong, M. G. Hack, T. Zhou, J. J. Brown, and T. D. Ngo, U.S. Patent No. 6803720 (12 October 2004).
[8] S. H. Kim, J. Jang, and J. Y. Lee, Appl. Phys. Lett. **90**, 173501 (2007).