High Efficiency in Phosphorescent Organic Light-Emitting Doides Using Carbazole Type Exciton Blocking layer

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Abstract

High efficiency in Phosphorescent Organic light-emitting diodes using carbazole type exciton blocking layer were investigated and detailed mechanism for light emission process was studied. Efficiency of green PHOLEDs was enhanced by a factor 3.7.

1. Introduction

There have been many researchers to get high efficiency in PHOLED by optimizing material and device structures.[1-3] Theoretically, phosphorescent devices can give four times higher light emitting efficiency than fluorescent devices and 100 % internal efficiency in PHOLEDs was already reported by Adachi et al.[4] There have been many models to improve light-emitting efficiency of PHOLEDs. The effect of a hole blocking layer could improve the efficiency of PHOLEDs as a result of blocking hole injection from light-emitting layer (EML) to electron transport layer (ETL). Electron blocking layer was also used in blue PHOLEDs to block electron injection from EML to hole transport layer (HTL). In addition, double EML structure was studied and it gave also high efficiency.[5,7]

In this work, we investigated the use of (4, 4' –dicarbazole)biphenyl (CBP) and N'N-dicarbazolyl-3,5-benzene (mCP) as an exciton blocking layer to get high efficiency in PHOLEDs. The device structure of the PHOLEDs was correlated with exciton blocking mechanism and device performance.

2. Experimental

The PHOLEDs were prepared by thermal evaporation of organic layers at a base pressure of 5 × 10-7 Torr at a rate of 1Å/s. Glass substrates were cleaned with acetone and isopropyl alcohol in an ultrasonic bath for 15 min respectively and were dried at 120 ℃ for 2 hr before use. The ITO glass was exposed to UV-ozone for 10 min for surface treatment and the glass substrate was transferred to evaporation chamber. The standard OLED configuration used in this experiment was ITO (150 nm)/ NPB (30 nm)/PH1: $Ir(ppy)_3$, 30 nm, 5 % doping)/Balq (5 nm)/ Alq_3 (20 nm)/LiF (1 nm)/Al (200 nm). Three devices with different HTL structure were fabricated to investigate the effect of CBP and mCP exciton blocking layers (EBL) on devices performances. Devices I had NPB (30 nm) as a HTL and device II had both NPB (20 nm) and CBP (10 nm) as a double layer, while device III had NPB (20 nm) and mCP (10 nm) as a double layer HTL. PH1 was supplied from Merck Co. and it has a spirobifluorene units. Triplet bandgap of PH1 was 2.4 eV and highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were 5.9 eV and 2.8 eV, respectively. Electron mobility of PH1 was 1.2×10^{-6} $cm^2/V.s$ from time of flight measurement and hole mobility could not be determined. Energy level of organic materials was obtained by cyclovoltametric measurement and surface analyzer. Current-voltage-luminance characteristics of the devices were measured with Keithley 2400 source measurement unit and CS-1000 spectrophotometer.

3. Results and discussion

I-V-L characteristics of the three devices with different device configurations were measured to study the charge confine effect of EML in PHOLEDs. Figure 1 shows current density-voltage characteristics of green devices with carbazole type EBL compared

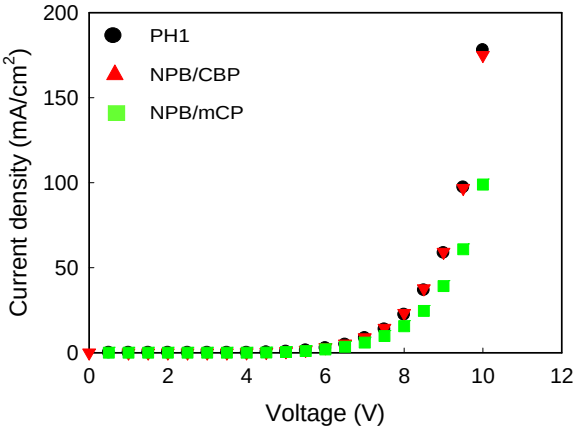

Fig. 1. Current density-voltage curves of green Phosphorescent devices with different HTL structures

with standard devices. Current density of device III with NPB and mCP double layer as a HTL was rather low compared with that of device I and device II. The similar current density in device I and device II is due to similar energy barrier between organic layers.

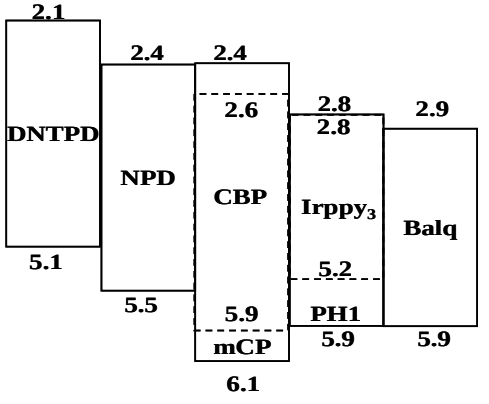

Fig. 2. energy level diagram of green phosphorescent devices with different HTL structures

Figure 2 indicates each energy level of used materials of this work. Device I has 0.4 eV HOMO difference between HTL and EML, which is the same as that of the device II. Therefore, hole injection in device I and device II can be similar, leading to similar current density in the device. Compared with device II, device III has large energy barrier of 0.6 eV between NPB and mCP, resulting in low current density even though there is no energy barrier between mCP and PH1.

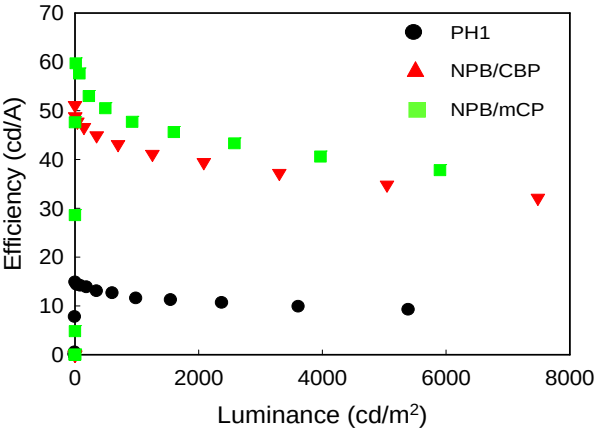

Fig. 3. Current efficiency-luminance curves of green phosphorescent devices with different HTL structures

Current efficiency-luminance of three devices was plotted in Figure 3 based on current density and luminance of devices. Device II shows current efficiency value of 41cd/A compared with 13 cd/A of device I at 1000 cd/cm^2, while devices III with mCP as an EBL showed the best current efficiency value of 48 cd/A. mCP can play a role of barrier as electron blocking layer and reduce exciton quenching as exciton blocking layer in terms of energy level diagram, resulting in efficient recombination of holes and elections inside emitting layer. Even though NPB is efficient as an electron blocking layer due to high LUMO energy barrier of 0.4 eV between NPB and PH1, triplet energy level of NPB is only 2.3 eV[6], which is not high enough for exciton blocking from EML because triplet energy level of host and dopant materials is 2.4 eV. Compared with NPB, mCP has triplet energy level of 2.9 eV[6] and it can block triplet exciton diffusion and quenching. CBP can also act as an EBL due to wide triplet bandgap of 2.6 eV even though it is not efficient as an electron blocking layer as mCP. However, it can reduce hole accumulation at the interface between HTL and EML because holes can be injected from CBP to PH1 layer without any energy barrier. This is also applied for mCP devices. Holes are transported through host material rather than dopant materials and hole accumulation can be reduced in the device with CBP and mCP as an EBL, resulting in efficient recombination of holes and electrons inside EML. To confirm above explanation, electroluminescence spectra of PH1 devices were investigated. Green emission with peak position of 515 nm was observed in all devices which is originated

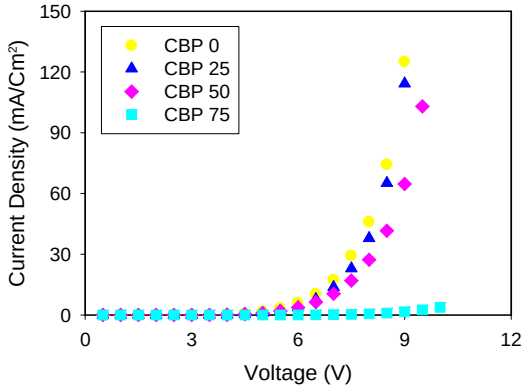

Fig. 4. Current density-luminance curves of green phosphorescent devices with mixed HTL structures

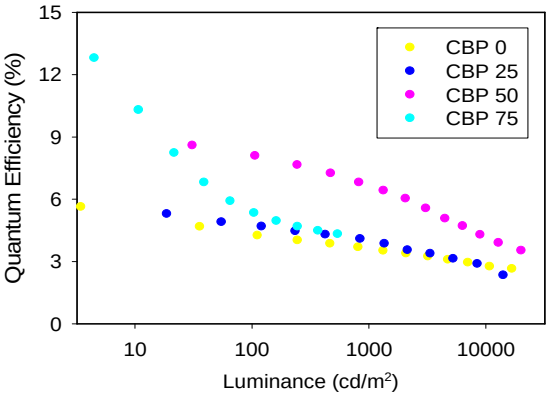

Fig. 5. Quantum efficiency-luminance curves of green phosphorescent devices with mixed HTL structures

Green emission with peak position of 515 nm was observed in all devices which is originated from $Ir(ppy)_3$ triplet emission. In addition to green emission, device I also showed another broad peak at 458 nm which assigned to NPB emission[9], while device II and III exhibited no emission in blue wavelength range. The NPB emission in device I may be due to hole accumulation at the interface between NPB and PH1 and electron overflow from PH1 to NPB. In general, holes are strongly trapped by dopant materials in $Ir(ppy)_3$ doped devices[5] and holes can be accumulated between NPB and PH1 because hole transport through $Ir(ppy)_3$ is limited. The accumulated holes can recombine with some electrons injected from EML inside NPB, giving rise to NPB emission[8]. Compared with device I with blue emission, no blue emission in device II and III is due to reduced hole accumulation at the interface between HTL and EML. Holes are injected from CBP or mCP layer and can be transported through PH1 host materials. Therefore, hole accumulation can be greatly reduced and host of holes can recombine with electrons in EML, leading to efficient green emission. NO blue emission in PH1 device with CBP EBL supports this explanation. LUMO level of CBP is only 2.6 eV and electrons can be efficiently injected from PH1 to CBP and NPB layer, which will induce NPB blue emission through recombination with accumulated holes at the interface. However, NPB emission was not observed and this supports that efficient hole transport dominate light emission in PH1 device with CBP or mCP EBL. It can be inferred from electroluminescence spectra that recombination zone of holes and electrons was shifted from HTL side to EML by EBL considering the disappearance of blue emission in device II and III.

The exciton blocking function of mCP was confirmed from photoluminescence (PL) spectra. PL intensity was high in the device with CBP and mCP EBL, indirectly proving that CBP and mCP reduce triplet exciton quenching by NPB. Even though mCP has a wider triplet bandgap than CBP, PL intensity was quite similar to each other. This result indicates that mCP and CBP show similar performances as a triplet EBL. Considering similar exciton blocking effect but different efficiency in CBP and mCP devices, the high efficiency in mCP device might be due to good hole-electron balance n emitting layer which originated from less hole flow in mCP device.

Figure 4 shows current density-voltage curves of composite HTL devices with different CBP content. Current density of CBP25 was similar to that of standard device with NPB HTL, while it was decreased at high CBP content above 50 %. Current flow in the device was dominated by NPB at low CBP content, while it was determined by CBP at high CBP content, indicating that continuous phase contribute greatly to current density in the composite HTL devices. Holes are injected into NPB in CBP0 and CBP25 devices and current density typically follows NPB device characteristics. However, holes are injected into CBP in CBP75 and current flow is dominated by CBP because CBP is a continuous phase. There is a large hole injection energy barrier of 0.8 eV between DNTPD(5.1 eV) and CBP(5.9 eV), limiting hole injection from DNTPD to CBP. In addition, HOMO level of NPB(5.5 eV) is lower than that of CBP by 0.4 eV, acting as a deep hole trap in HTL. Therefore, hole injection and transport are very difficult in CBP75 device. Compared with CBP 75,

CBP50 shows current density-voltage characteristics of both NPB and CBP because both materials are present equally.

Quantum efficiency-luminance plots of composite HTL devices are shown in Figure 5. Quantum efficiency was greatly improved in CBP50, while other devices showed similar quantum efficiency value. The high quantum efficiency in CBP50 devices can be explained by efficient hole transport and exciton blocking effect of composite HTL. CBP50 composite HTL transports holes efficiently through NPB and CBP even though it is not as efficient as NPB. In addition, holes in CBP material can be injected easily to PH1 layer because there is no energy barrier between CBP and PH1. Therefore, hole accumulation at the interface between HTL and PH1 layer can be reduced due to effective hole injection from HTL to PH1 by CBP. In addition, triplet exciton quenching by NPB in green PHOLEDs can also be depressed as CBP can block exciton quenching of Ir(ppy)3. Triplet bandgap of CBP is 2.6 eV compared with 2.3 eV of NPB and it can block exciton quenching of Ir(ppy)3 with triplet bandgap of 2.4 eV. As recombination zone of typical green PHOLEDs is placed near HTL, it can be expected that triplet exciton blocking by CBP contribute to high efficiency.

4. Summary

CBP and mCP as an exciton blocking layer in green PHOLEDs was effective to get high luminance efficiency and current efficiency was enhanced from 13 cd/A to 41 cd/A and 48 cd/A by CBP and mCP respectively. mCP was more efficient than CBP because of electron blocking properties and wide triplet bandgap. There was no emission from NPB in the device with CBP and mCP exciton blocking layer and it is required to use exciton blocking in green PHOLED with electron transport type host materials. It was also effective to get high efficiency of PHOLEDs with composite hole transfer layer.

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