

# Improvement of device performance by co-doping of an emitting dopant with hole- and electron-transport materials

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## ABSTRACT

We demonstrated that the efficiency of green organic light-emitting diodes (OLEDs) was improved by co-doping with hole transport material, N'-bis-(1-naphyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB) and electron transport material, bis(2-methyl-8-quinolinato)-4-phenylphenolate aluminum (BALq), into emitting layer. Co-doping with NPB and BALq can improve charge balance which makes it possible to enhance device efficiency. The maximum luminous and quantum efficiency of BDAT-P doped device was measured to be 5.56 cd/A and 1.99 %, respectively. Device co-doped with NPB, BALq and BDAT-P resulted in the most efficient device, in which maximum luminous and quantum efficiency were 8.36 cd/A and 3.19 %, respectively.

**Keywords:** BDAT-P, co-doping, organic light-emitting diodes, green emission

## 1 INTRODUCTION

Organic light-emitting diodes (OLEDs) have attracted broad attention due to their potential application with self emission, fast response time, low-power consumption, low operation voltage, high contrast, high brightness, high efficiency ultrathin structure and light weight for full color display since Kodak reports green device based on small molecule [1-4]. There have been many studies to improve OLEDs performance. A technology for development of OLEDs is the guest-host doped emitter system [5-6]. It is hard to balance the holes and electrons in the emitting layer because of difference in mobility between a hole and an electron in organic material. In order to solve this problem, multilayered OLEDs, consisting of several layers such as hole transport layer (HTL), electron transport layer (ETL), and emitting layer (EML) have been studied [7]. The charge balance is an important factor in OLED performance. However, carrier transport in most OLED devices is highly imbalanced, which can cause the movement of recombination zone from the EML into the ETL interface. Co-doping system is a good method to improve charge balance which can lead to high device performance.

In this study, a green fluorescent material, (2Z)-3-[4,4''-bis(dimethylamino)-1,1':4',1''-terphenyl-2'-yl]-2-phenylacrylonitrile (BDAT-P), was synthesized as a

emitting material and doped devices using BDAT-P as the dopant with various device structures were fabricated in order to investigate the effect of co-doping with hole transport and electron transport materials on device efficiency.

## 2 EXPERIMENTAL

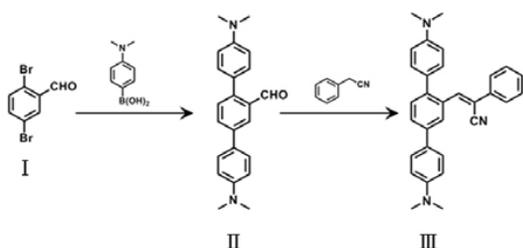
### 2.1 Synthesis

Synthesis of BDAT-P was shown in scheme 1. All solvents involved in the experiments were reagent grade and were purified by the usual methods before use. 2,5-Dibromobenzaldehyde (I) was commercially available (Aldrich). The molecular structure of BDAT-P was confirmed by <sup>1</sup>H and <sup>13</sup>C-NMR spectroscopy, MS (FAB) spectrum and elemental analysis.

**4,4''-bis(dimethylamino)-1,1':4',1''-terphenyl-2'-carbaldehyde (II)** was obtained from the reaction of 2,5-dibromobenzaldehyde (I) with 4-(dimethylamino)phenylboronic acid by Suzuki coupling. The mixture of 2,5-dibromobenzaldehyde (I) (800 mg, 3.03 mmol), 4-(dimethylamino)phenylboronic acid (1.10 g, 6.66 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (140 mg), Na<sub>2</sub>CO<sub>3</sub> (963 mg) and Aliquat336 (0.433 ml) in mixed solvent of toluene (64 ml)-H<sub>2</sub>O (40 ml)-THF (16 ml) was mildly refluxed under N<sub>2</sub> atmosphere with stirring for 3 hr. The reaction mixture was cooled, filtered and washed with mixture of ethyl acetate and n-hexane (1 : 5). Removal of the solvents and drying under high vacuum afforded 785 mg (2.28 mmole) of the product (II) as a green solid and further purification was not required. Yield: 75 %; <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm) 10.069 (s, 1H), 8.189 (s, 1H), 7.804 (d, 1H), 7.475 (d, 1H), 7.290 (d, 2H), 7.588 (d, 2H), 6.810 (d, 4H), 3.013 (s, 12H); <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>) δ (ppm) 193.40, 150.16, 143.83, 139.50, 133.71, 131.04, 131.01, 128.99, 128.18, 127.56, 127.39, 125.10, 124.64, 112.67, 112.06, 40.46, 40.39.

**2Z)-3-[4,4''-bis(dimethylamino)-1,1':4',1''-terphenyl-2'-yl]-2-phenylacrylonitrile (BDAT-P) (III)** was prepared from the Knoevenagel reaction of 4,4''-bis(dimethylamino)-1,1':4',1''-terphenyl-2'-carbaldehyde (II) with benzyl cyanide. The mixture of 4,4''-bis(dimethylamino)-1,1':4',1''-terphenyl-2'-carbaldehyde (400 mg, 1.16 mmol), benzyl cyanide (0.536 ml, 4.64 mmol) and sodium ethoxide (prepared by the reaction of 64 mg of Na with 10 ml of absolute EtOH) in 150 ml of EtOH was stirred at room temperature for 4 days. The yellow solid formed in reaction

mixture was filtered and washed with EtOH and MeOH. Removal of the solvents and drying under vacuum afforded 343 mg (0.73 mmole) of the product (III) as a yellow solid. Mp 243.3 °C (DSC); Yield: 66.6 %; <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ (ppm) 8.338 (*d*, 1H, aromatic), 7.668 (*dd*, 1H, aromatic), 7.640 (*d*, 2H aromatic), 7.624 (*s*, 1H, vinyl), 7.615 (*d*, 2H, aromatic), 7.471 (*d*, 1H, aromatic), 7.396 (*t*, 2H, aromatic), 7.344 (*t*, 1H, aromatic), 7.275 (*d*, 2H, aromatic), 6.842 (*d*, 2H, aromatic), 6.776 (*d*, 2H, aromatic), 3.002 (*s*, 12H, methyl); <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>) δ (ppm) 150.07, 149.86, 143.37, 140.46, 139.50, 134.48, 131.81, 130.79, 130.21, 128.94, 128.76, 128.19, 127.86, 127.79, 127.33, 126.39, 125.94, 118.41, 112.84, 112.03, 111.75, 40.53, 40.40; Anal. calcd. for C<sub>31</sub>H<sub>29</sub>N<sub>3</sub>: C: 83.92, H: 6.59, N: 9.47. Found: C: 83.77, H: 6.55, N: 9.25. MS (FAB) calcd for C<sub>31</sub>H<sub>29</sub>N<sub>3</sub> (M<sup>+</sup>) m/z 443, found 443.



Scheme 1. Synthesis of BDAT-P.

## 2.2 Measurement

<sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded on a Varian Unity INOVA 500 spectrometer operating at 499.761 MHz and 125.701 MHz, respectively. Elemental analysis was performed on a CE instrument EA1112 analyzer. Mass spectrum (FAB-MS) was measured on JEOL, JMS-AX505WA, HP 5890 Series II Hewlett-Packard 5890A (capillary column) using standard conditions. The melting point was measured to be 366.2 °C by differential scanning calorimetry (DSC) using a Seiko Exstar 7000 (DSC7020) with a scan rate of 10 °C/min at the temperature range of 40 ~ 400 °C. UV-visible absorption and photoluminescence (PL) spectra were measured by HP model 8453 and Perkin Elmer LS55, respectively.

The HOMO energy level of 5.23 eV for BDAT-P was measured by cyclic voltammetric method using a EpslianEC-2000 at a scan rate of 100 mV/s and LUMO energy level of 2.54 eV was calculated from measured HOMO energy level. The value of optical band gap was observed as 2.69 eV which was obtained from UV-visible absorption spectrum. Electroluminescence (EL) spectra and brightness-current-voltage characteristics of the device were measured by using Keithley 2400, CHROMA METER CS-1000A. All the measurements were carried out at room temperature.

## 2.3 Fabrication of OLED

The OLED was fabricated by the high vacuum thermal deposition ( $8 \times 10^{-7}$  torr) of organic materials onto the surface of indium tin oxide (ITO) coated in glass substrate. An ITO coated glass was cleaned in an ultrasonic bath by regular sequences: in acetone, methanol, distilled water and isopropyl alcohol. The cleaned substrate was immediately loaded into the deposition chamber in order to prevent air contamination. The devices have the structure of ITO (100 nm)/NPB (50 nm)/MADN:BDAT-P (8 %) (30 nm)/Balq (30 nm)/Liq (2 nm)/Al (100 nm) (device A), ITO/NPB/MADN:BDAT-P (8 %) NPB (4 %)/Balq/Liq/Al (device B), ITO/NPB/MADN:BDAT-P (8 %):Balq (4 %)/Balq/Liq/Al (device C)/ ITO/NPB/MADN:BDAT-P (8 %):NPB (4 %):Balq (4 %)/Liq/Al (device D), in which NPB, BDAT-P, Balq and Liq were used as a hole transporting layer (HTL), an emitter layer (EML), electron transporting layer (ETL) and an electron injection layer (EIL), respectively.

## 3 RESULTS AND DISCUSSION

Figure 1 showed the HOMO and LUMO energy levels of materials used in fabricating the device in this study, where the device structures were Indium tin oxide (1000 Å)/NPB (500 Å)/MADN:BDAT-P (8 %)(device A) or BDAT-P (8 %):NPB (4 %)(device B) or BDAT-P (8 %):Balq (4 %)(device C) or BDAT-P (8 %):NPB(4 %):BALq (4 %)(device D) (300 Å)/BALq (300 Å)/Liq (20 Å)/Al (1000 Å), respectively. The doping concentrations of BDAT-P, NPB and BALq were optimized to 8, 4 and 4%, respectively.

Voltage vs. current density and voltage vs. luminance characteristics of all devices were given in Figure 2. Luminance maxima of device A, B, C and D were 7594 (at 242 mA/m<sup>2</sup>), 20620 (at 377 mA/m<sup>2</sup>), 23300 (at 403 mA/m<sup>2</sup>) and 21640 (at 382 mA/m<sup>2</sup>) (device D) cd/m<sup>2</sup>, respectively.

Figure 3 well represented the effect of co-doping of NPB and/or BALq with BDAT-P on device efficiency. The maximum luminous and quantum efficiency of device A, B, C and D were observed to be 5.56, 8.93, 8.40 and 8.36 cd/A and 1.99, 3.28, 3.08 and 3.19 %, respectively. The efficiency of co-doped devices B, C and D was much more enhanced than that of device A doped with only BDAT-P.

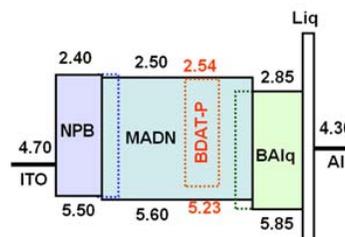


Figure 1. The HOMO and LUMO energy levels of materials used in fabrication of device.

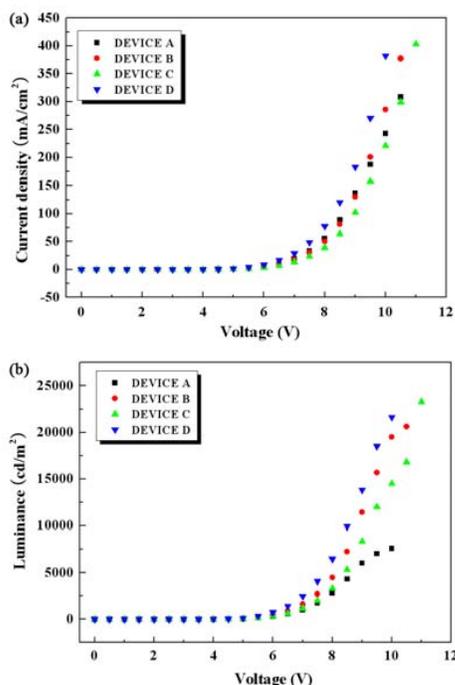


Figure 2. (a) Voltage vs. current density and (b) voltage vs. luminance characteristics with various EML.

As shown in Figure 2 and 3, the effect of co-doping with hole transport material (Device B) on device efficiency was larger than that of electron transport material (Device D). Figure 3 represented that co-doping of both of NPB and Balq with BDAT-P gave more stable device property than that with only NPB although device efficiency of the former was slightly lower than that of the latter. At this point, based on the data of this research, the enhancement of device efficiency by co-doping with NPB and/or BALq can't be explained obviously but it can be assumed that co-doping with NPB and/or BALq can offer improved charge balance which makes it possible to create more excitons in the region of EML.

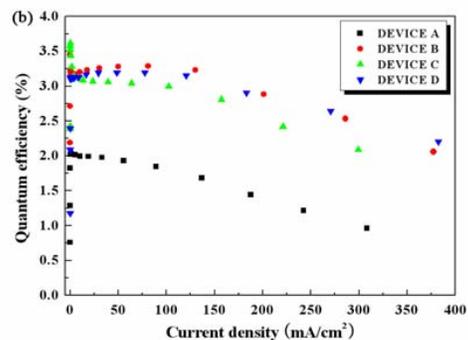
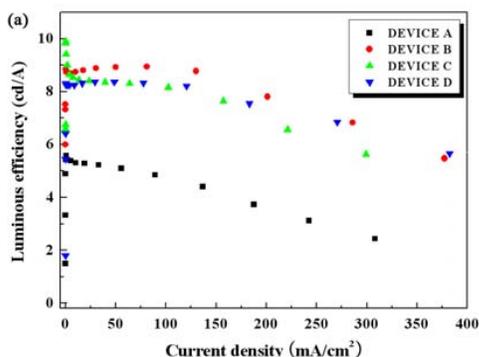


Figure 3. (a) Current density vs. luminous efficiency and (b) quantum efficiency vs. current density characteristics with variation of EML.

Figure 4 (a) showed EL spectra of devices A, B, C and D. EL emission peaks of these devices were ranged from 498 to 503 nm corresponding to green emission, in which peak wavelengths of EL spectra of device A, B, C and D were measured to be 500, 502, 503 and 498 nm, respectively.

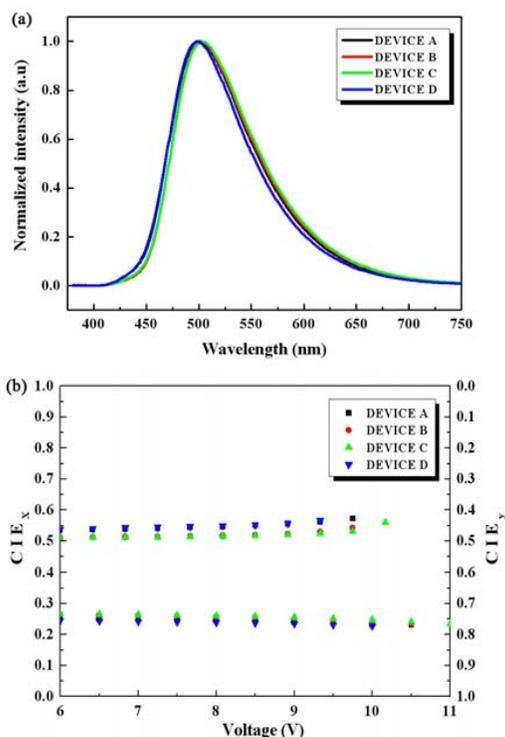


Figure 4. (a) Normalized EL spectra and (b) CIE<sub>xy</sub> coordinates of devices A, B, C and D.

As shown in Figure 5 (b), CIE<sub>xy</sub> coordinates of devices A, B, C and D also represented that the devices emitted green light. Commission Internationale de l'Éclairage

(CIE<sub>xy</sub>) coordinates of devices A, B, C and D were measured to be (0.234, 0.438), (0.241, 0.470), (0.247, 0.476) and (0.227, 0.434) at 10 V, respectively.

#### 4 CONCLUSION

A green fluorescent material, (2Z)-3-[4,4"-bis(dimethylamino)-1,1':4',1"-terphenyl-2'-yl]-2-phenylacrylonitrile (BDAT-P), was synthesized for use in OLED application. The maximum luminous and quantum efficiency of BDAT-P doped device was measured to be 5.56 cd/A and 1.99 %, respectively. The efficiency was highly enhanced by co-doping of NPB and/or BAq with BDAT-P. Based on both of device efficiency and stability of the efficiency, device D which was co-doped with NPB, BAq and BDAT-P resulted in the most efficient device, in which maximum luminous and quantum efficiency were 8.36 cd/A and 3.19 %, respectively. Therefore, it can be concluded that the co-doping of hole and/or electron-transport material into EML in doped device can improve the device efficiency much more.

#### ACKNOWLEDGEMENT

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