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A New Yellow Emissive Fluorescent Material for Highly Efficient Organic Light-Emitting Diodes

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A new yellow fluorescent material, (2Z)-3-[4,4″-bis(dimethylamino)-1,1′:4′,1″-terphenyl-2′-yl]-2-phenylacrylonitrile (BDAT-P), was synthesized for organic light-emitting diodes. This compound has an electron donor-acceptor group which leads to intramolecular charge transfer property.

Optoelectronic properties of a device with the structure of ITO/NPB/MADN:BDAT-P (x %)/BPhen/Liq/Al were measured and the measurement demonstrated that the device using BDAT-P as a dopant revealed highly efficient device performance with greenish yellow electroluminescent emission. Maximum luminance of the device was measured to be 18300 ($x = 8\%$), 10880 ($x = 12\%$) and 11810 ($x = 16\%$) cd/m^2, respectively. The maximum luminous and quantum efficiency values were observed to be 12.5 ($x = 8\%$), 9.17 ($x = 12\%$) and 12.79 ($x = 16\%$) cd/A, and 3.83 ($x = 8\%$), 2.8 ($x = 12\%$) and 3.81 ($x = 16\%$) %, respectively. The device emitted greenish yellow light corresponding to Commission Internationale de I'Eclairage (CIE$_{xy}$) coordinates of (0.319, 0.569) ($x = 8\%$) and (0.321, 0.569) ($x = 12\%$) and (0.356, 0.578) ($x = 16\%$) at 10 V.

Keywords BDAT-P; organic light-emitting diode; yellow dopant; yellow emissive

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 including guest-host system to improve OLEDs performance [5]. White organic light-emitting diodes (WOLEDs) have application to backlights of liquid-crystal display (LCD), large area solid-state lighting and full color flat-panel display [6–8]. In order to achieve white color, triple emission layers from red, green and blue emitter were developed. Another method to achieve WOLEDs is the two complementary colors way like as blue mixed with

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yellow or orange color. This method has advantages such as low material cost and simple fabrication process [9–12]. There have been some researches using yellow and sky blue or yellow and blue emitter for fabrication of WOLEDs [9,13]. According to a recent survey, WOLED using the combination with blue emission material and its complimentary color, yellow is preferred by most of the customers. Furthermore, one of the sensitive color for human eyes is yellow [14,15]. Thus, yellow emissive material is important for WOLEDs.

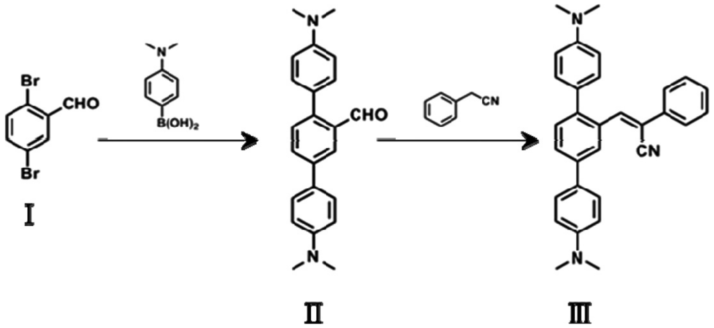
In this study, we designed and synthesized a new yellow fluorescent material, BDAT-P, that has intramolecular charge transfer (ICT) property for use in yellow OLEDs. In order to achieve yellow light emission with high device performance, device using BDAT-P as a dopant was fabricated and its device performance was measured.

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 ^{1}H and ^{13}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-dibromobenzalaldehyde (I) with 4-(dimethylamino)phenylboronic acid by Suzuki coupling. The mixture of 2,5-dibromobenzalaldehyde (I) (800 mg, 3.03 mmol), 4-(dimethylamino)phenylboronic acid (1.10 g, 6.66 mmol), $Pd(PPh_3)_4$ (140 mg), Na_2CO_3 (963 mg) and Aliquat336 (0.433 ml) in mixed solvent of toluene (64 ml)-H_2O (40 ml)-THF (16 ml) was mildly refluxed under N_2 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%; ^{1}H-NMR (500 MHz, $CDCl_3$) 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); ^{13}C-NMR (125 MHz, $CDCl_3$)



Scheme 1. Synthesis of BDAT-P.

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%; ^{1}H-NMR (500 MHz, $CDCl_3$) 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); ^{13}C-NMR (125 MHz, $CDCl_3$) 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 $C_{31}H_{29}N_3$: C: 83.92, H: 6.59, N: 9.47. Found: C: 83.77, H: 6.55, N: 9.25. MS (FAB) calcd for $C_{31}H_{29}N_3$ (M^+) m/z 443, found 443.

2.2. *Measurement*

^{1}H-NMR and ^{13}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 (8×10^{-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 device has the structure of ITO (100 nm)/NPB (50 nm)/ MADN:BDAT-P (x %) (30 nm)/BPhen (30 nm)/Liq (2 nm)/Al (100 nm), in which NPB, BDAT-P, BPhen and Liq were used as a hole transporting layer (HTL), an emitter layer (EML), a hole blocking and electron transporting layer (HBL, ETL) and an electron injection layer (EIL), respectively.

3. Results and Discussion

Figure 2(a) showed UV absorption and PL spectra of BDAT-P in chloroform solution and PL spectrum of MADN in film, in which they were used as the dopant and the host material, respectively. The UV absorption and PL peaks of BDAT-P measured to be at 325 nm with shoulder at 400 nm and 551.5 nm, respectively. The PL spectrum of BDAT-P showed yellow light emission and large Stokes shift which hardly caused an overlap between absorption and emission bands of BDAT-P. This leads to little self-absorption of the emitted light so that the BDAT-P is very advantageous for OLED application. Although it was not fully overlapped, MADN was used as the host material for OLEDs using BDAT-P as the dopant because the overlap between UV-visible absorption band of BDAT-P and the PL band of MADN was favorable to Förster energy transfer from MADN to BDAT-P. Figure 2(b) represented the HOMO and LUMO energy levels of the materials used in device with the structure of ITO/NPB/MADN:BDAT-P/BPhen/Liq/Al. It showed that the correlation of energy band gap of MADN with that of BDAT-P was suitable to Förster energy transfer from MADN to BDAT-P.

Figure 3(a) and (b) showed the current density vs. voltage and current density vs. luminance of BDAT-P doped OLEDs at various doping concentration of 8, 12 and 16%, in which the luminance maxima were 18300 (at 219 mA/cm^2), 10880 (at 176 mA/cm^2,) and 11810 (at 169 mA/cm^2,) cd/m^2, respectively. As doping

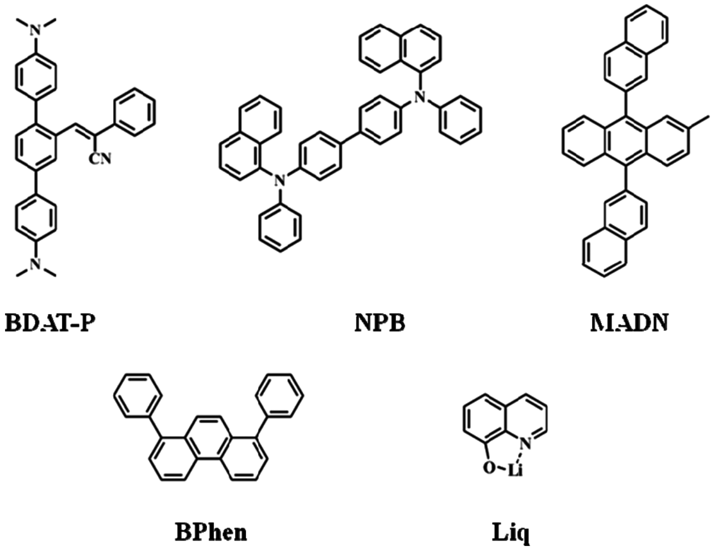
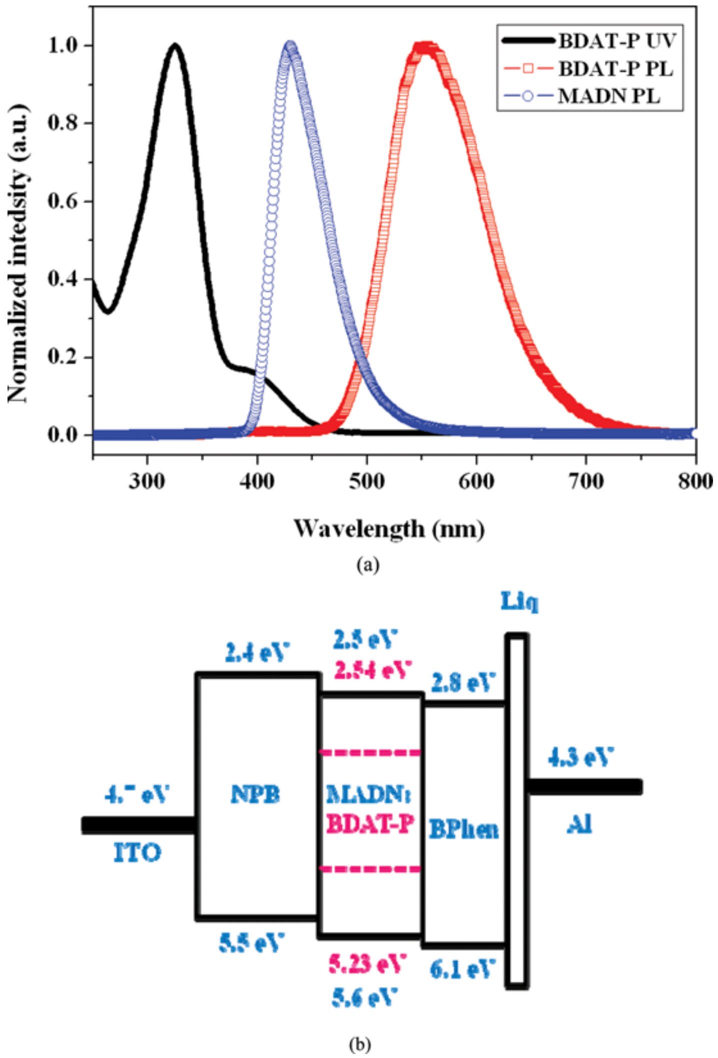


Figure 1. The molecular structure of BDAT-P., NPB, MADN, BPhen and Liq.



(a)

(b)

Figure 2. (a) Normalized UV-Visible absorption and PL spectra of BDAT-P and PL spectrum of MADN and (b) the schematic energy band diagram of the device structure of ITO/NPB/MADN:BDAT-P/BPhen/Liq/Al.

concentration increased from 8% to 16%, luminance was decreased, which was ascribed to the increase of concentration quenching of dopant molecules.

As shown in Figure 4(a) and (b), device doped with the new yellow fluorescent BDAT-P into MADN represented high luminous efficiency and quantum efficiency. The maximum luminous and quantum efficiency values were observed to be 12.5 (x = 8%), 9.17 (x = 12%) and 12.79 (x = 16%) cd/A, and 3.83 (x = 8%), 2.8 (x = 12%) and 3.81 (x = 16%) %, respectively. Based on Figures (3) and (4), although EL emission peak was much more shifted to short wavelength compared to that of PL, device with doping concentration of 8% was observed to be the most stable and efficient.

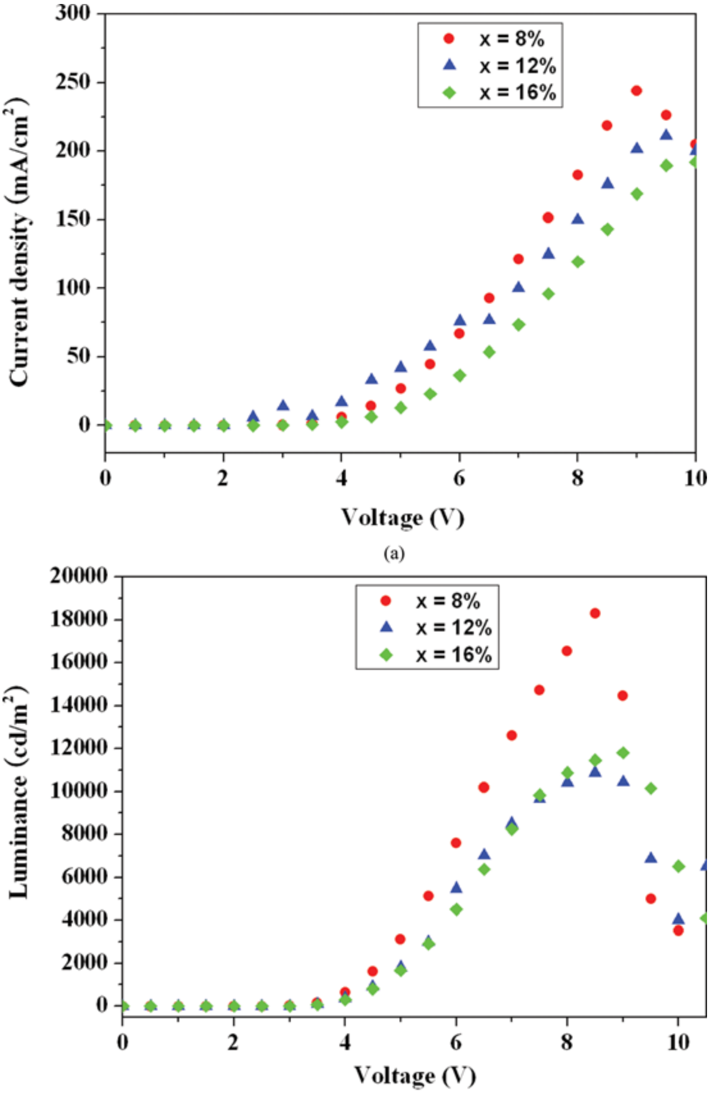
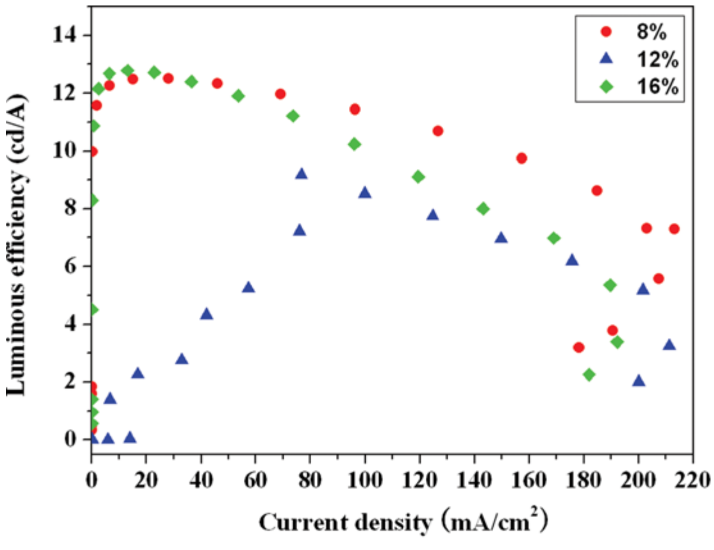
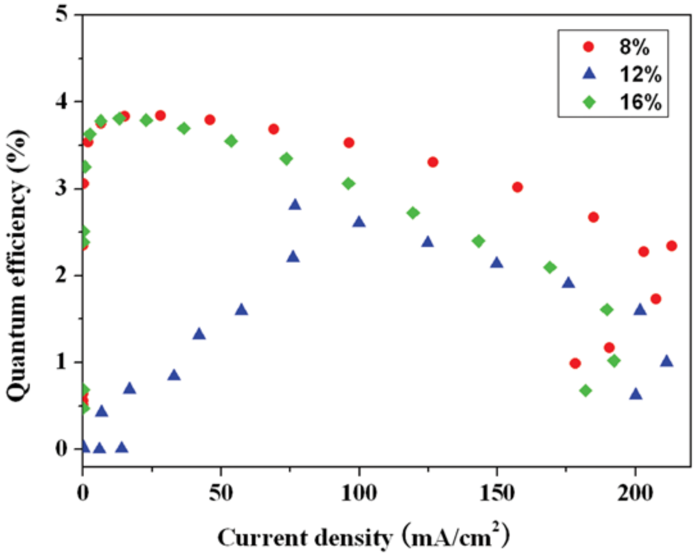


Figure 3. (a) Current density vs. voltage and (b) current density vs. luminance characteristics with variation of doping concentration.

Figure 5(a) showed the EL spectra of BDAT-P with variation of doping concentration (x = 8, 12 and 16%). EL emission peaks were shifted to longer wavelength as doping concentration was increased and they were measured to be 526 (x = 8%), 529 (x = 12%) and 534 (x = 16%) nm, respectively. Although yellow light emission was improved with the increase of doping concentration, except for EL emission color, most of EL properties of device with doping concentration of 8% were superior to those of device with doping concentration 12 and 16%. Yellow light emission is not for full color display but for WOLEDs so it is assumed that



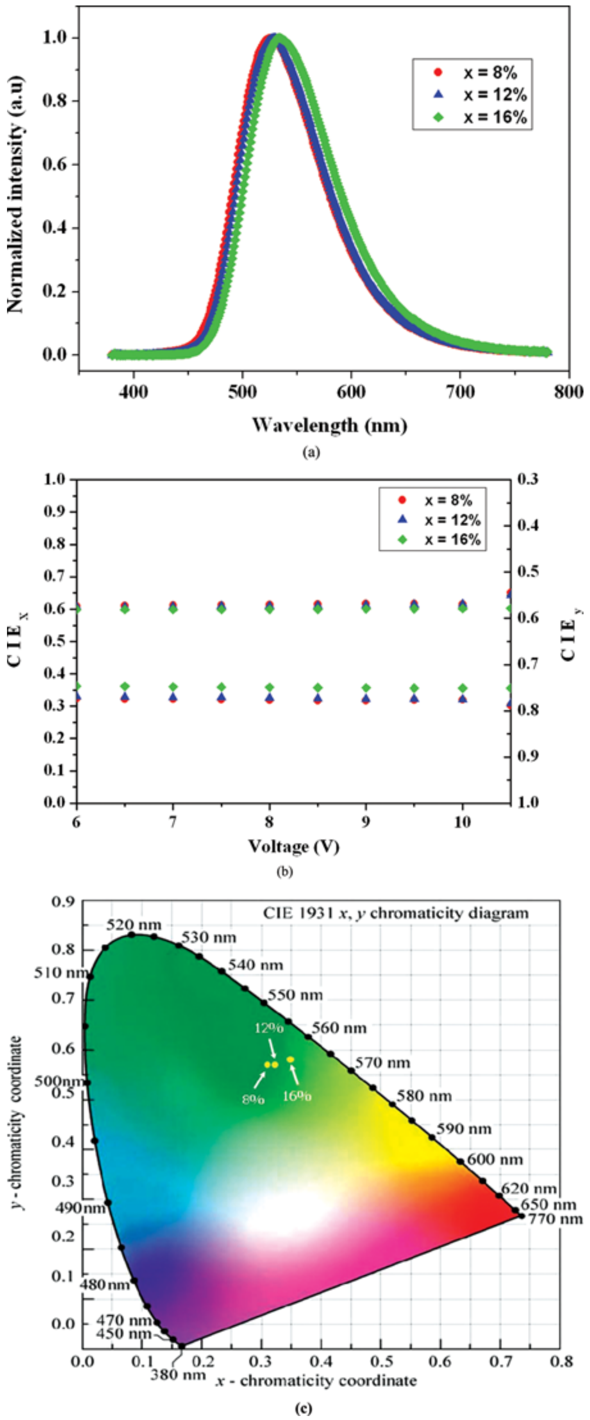
(a)



(b)

Figure 4. (a) current density vs. luminous efficiency and (b) quantum efficiency vs. current density characteristics with variation of doping concentration.

doping concentration of 8% is more favorable than that of 12 and 16%. As shown in Figure 5(b), Commission Internationale de I'Eclairage (CIE_{xy}) coordinates of device were measured to be (0.319, 0.569) (x = 8%), (0.321, 0.569) (x = 12%) and (0.356, 0.578) (x = 16%) at 10 V, respectively. Observed CIE_{xy} coordinates represented that the device with doping concentration from 8 to 16% emitted yellowish green EL emission, which was shown in Figure 5(c).



(a)

(b)

(c)

Figure 5. (a) Normalized EL spectra, (b) measured CIExy coordinates and (c) chromaticity diagram measured with variation of doping concentration.

4. Conclusions

We have synthesized a new yellow fluorescent material, BDAT-P, in two steps and demonstrated that device doped with BDAT-P into MADN resulted in highly efficient greenish yellow OLEDs.

EL peaks of BDAT-P doped device were observed to be 526 ($x = 8\%$), 529 ($x = 12\%$) and 534 ($x = 16\%$) nm. The devices showed maximum luminance of 18300 ($x = 8\%$), 10880 ($x = 12\%$) and 11810 ($x = 16\%$) cd/m^2. The maximum luminous efficiency and quantum efficiency of the device were achieved to be 12.5 ($x = 8\%$), 9.17 ($x = 12\%$) and 12.79 ($x = 16\%$) cd/A and 3.83 ($x = 8\%$), 2.8 ($x = 12\%$) and 3.81 ($x = 16\%$) %, respectively. Therefore, it can be concluded that a newly synthesized fluorescent BDAT-P may be a good candidate for use in fabrication of WOLEDs with high efficiency.

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