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The Effect of the Molecular Structure on the Optoelectronic Properties of a Fluorophore for Use in Organic Light-Emitting Diodes

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A novel yellow light-emitting material, (2Z)-3-[4,4″-bis(dimethylamino)-1,1′:4′,1″-terphenyl-2′-yl]-2-phenylacrylonitrile (BDAT-P), having the modified molecular structure from red fluorescent compound, (2Z,2′Z)-3,3′-[4,4″-bis(dimethylamino)-1,1′:4′,1″-terphenyl-2′,5′-diyl]bis(2-phenylacrylonitrile) (ABCV-P), was synthesized in order to study the effect of the molecular structure on the optoelectronic properties of a light-emitting material. UV-visible absorption and photoluminescence (PL) emission peaks measured in various solvent systems were summarized in Table I. In the respective solvent system, the bathochromic shift of PL emission peak relative to the peak of UV-visible absorption was much larger for ABCV-P with two electron donor–acceptor pairs than for BDAT-P with one electron donor–acceptor pair. EL emission peaks of devices using BDAT-P and ABCV-P as the host emitters measured to be 573 and 613 nm, respectively. Commission Internationale de l'Eclairage (CIExy) coordinate of device using BDAT-P was measured to be (0.4855, 0.5021) at 7 V, which was correspond to the yellow color.

Keywords: BDAT-P, Charge Transfer, ABCV-P, Yellow Light-Emitting, Molecular Structure.

1. INTRODUCTION

The advantages of organic light-emitting diodes (OLEDs) are low operating voltage, low power consumption, self-emission, high contrast, fast response time, wide-viewing angle, ultrathin structure and light weight.[1] There have been many research efforts in order to develop OLEDs for full color display since report by Tang and VanSlyke on high-performance double-layer OLED.[2] Recently, white organic light-emitting diodes (WOLEDs) have attracted major attention as a full color display with a color filter, flexible display, solid-state light source and backlights in liquid-crystal display (LCD) due to their advantages. Warm white color is required for lighting applications whereas the pure white one should be used for display applications.[3–4] There have been many studies on WOLEDs including the methods of additive mixture of three primary colors or two complementary colors in order to improve the efficiency of device.[5–6] Although a yellow light-emitting material is not one of three primary colors for full color display, it can be used for fabrication of WOLEDs[7] and, thus, the synthesis of yellow emissive material can also play an important role for development of WOLEDs.

In this work we report the effect of the molecular structure on the optoelectronic properties of fluorescent material for use in OLED application and the synthesis of novel yellow fluorescent compound, BDAT-P.

2. EXPERIMENTAL DETAILS

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 measurement 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

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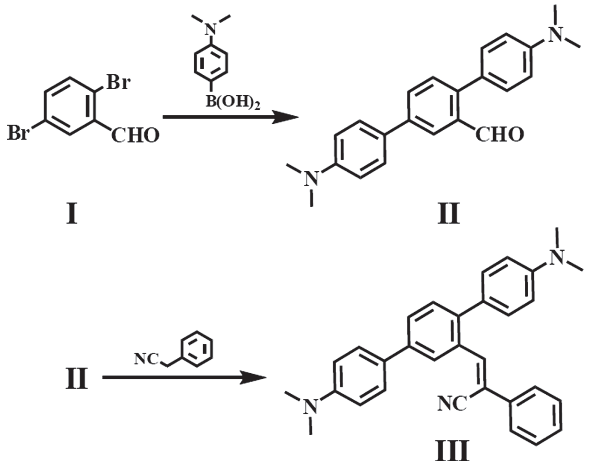

Scheme 1. Synthetic procedure of BDAT-P.

atmosphere with stirring for 3 hr. The reaction mixture was cooled, filtered and washed with ethyl acetate and *n*-hexane. 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, 1 H), 8.189 (s, 1 H), 7.804 (d, 1 H), 7.475 (d, 1 H), 7.290 (d, 2 H), 7.588 (d, 2 H), 6.810 (d, 4 H), 3.013 (s, 12 H); ^{13}C-NMR (125 MHz, $CDCl_3$) 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, MeOH and chloroform. 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, 1 H, aromatic), 7.668 (dd, 1 H, aromatic), 7.640 (d, 2 H, aromatic), 7.624 (s, 1 H, vinyl), 7.615 (d, 2 H, aromatic), 7.471 (d, 1 H, aromatic), 7.396 (t, 2 H, aromatic), 7.344 (t, 1 H, aromatic), 7.275 (d, 2 H, aromatic), 6.842 (d, 2 H, aromatic), 6.776 (d, 2 H, aromatic), 3.002 (s, 12 H, 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.

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. 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 PL spectra were measured by HP model 8453 and Perkin Elmer LS55, respectively.

Electroluminescence spectra and brightness-current–voltage characteristics of the device were measured using keithley 2400, CHROMA METER CS-1000A. All the measurement was carried out at room temperature.

2.3. Fabrication of OLED

The device with the structure of ITO (100 nm)/NPB (50 nm)/BDAT-P (40 nm)/BCP (10 nm)/Alq_3 (20 nm)/Liq (2 nm)/Al (100 nm) was fabricated by the high-vacuum thermal deposition (8×10^{-7} Torr) of organic materials onto the surface of indium tin oxide (ITO)-coated glass substrate. The deposition rates were 1.0~1.1 Å/sec for organic materials, 0.1 Å/sec for lithium quinolate (Liq) and 10 Å/sec for aluminum (Al) cathode. The EL emission spectra were recorded on Perkin Elmer LS-55 and device performance was measured using Keithley 236 and CHROMA METER CS-100A instruments.

3. RESULTS AND DISCUSSION

Optoelectronic properties such as the PL and EL emission colors, the charge-transporting property and the luminescent performance of a fluorescent compound used in OLED application depend on the molecular structure such as conjugation length, molecular planarity and rigidity of the molecule. One type of red emissive material that may be most commonly used in OLEDs is electron donor–acceptor molecules with strong intramolecular charge transfer (ICT).[8]

In our previous work, we have reported study on some optoelectronic properties of ABCV-P which have electron donor–acceptor groups within the molecule.[9] Presently, we have synthesized BDAT-P having the

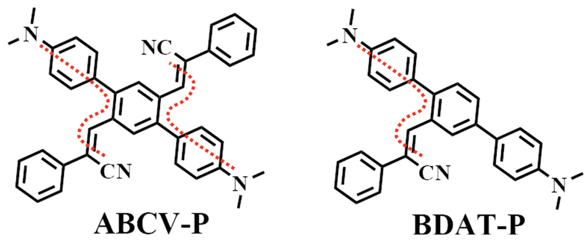

Fig. 1. The molecular structures of BDAT-P and ABCV-P.

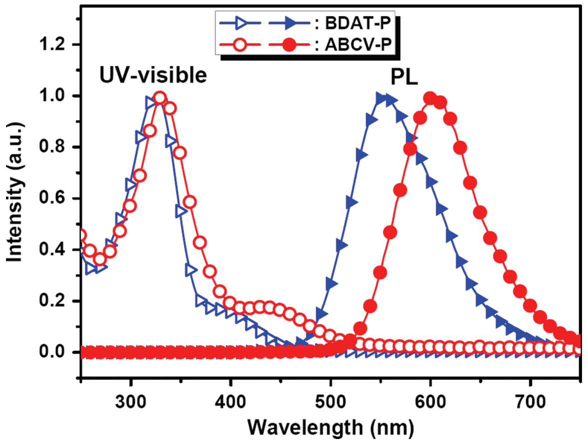

Fig. 2. Normalized UV-visible absorption and PL emission spectra of BDAT-P and ABCV-P measured in chloroform solution.

modified molecular structure from that of ABCV-P in order to modify some optoelectronic properties and their molecular structures were shown in Figure 1. As shown in Figure 1 with dotted line, BDAT-P has one pair of interacting dimethylamino (an electron donor) and cyano (an electron acceptor) groups whereas ABCV-P does two pairs of them and, thus, it is expected that the degree of ICT induced by those donor–acceptor groups in BDAT-P is different from that in ABCV-P, which may lead to the considerable difference in their optoelectronic properties.

Figure 2 showed UV-visible absorption and PL emission spectra of BDAT-P and ABCV-P in chloroform solution. Both of PL emission spectra of BDAT-P and ABCV-P exhibited large Stokes shifts due to considerable bathochromic shifts in emission wavelengths, which were caused by the presence of photo-induced ICT excited states,[10–11] in the molecules.

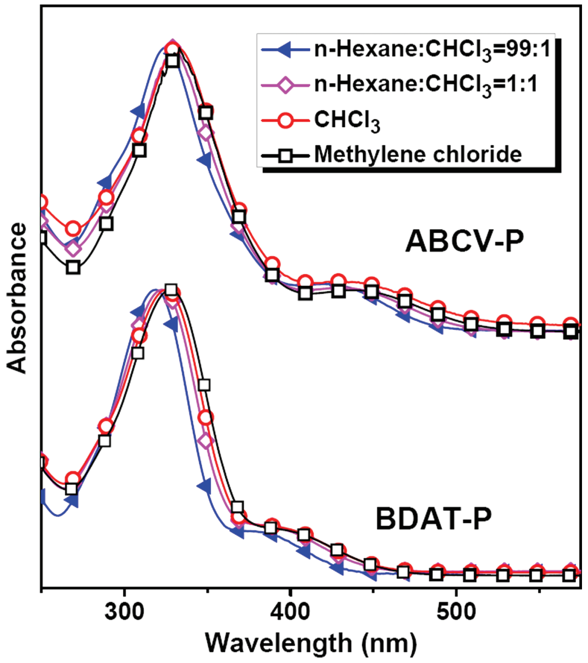

Fig. 3. Normalized UV-visible absorption spectra of BDAT-P and ABCV-P measured in solution (1.0×10^{-5} M) with variation of solvent polarity.

Table I. The peak wavelengths, measured by nanometer (nm), of UV-visible absorption and PL emission spectra of BDAT-P and ABCV-P obtained in various solvents (1.0×10^{-5} M).

	BDAT-P		ABCV-P	
Solvent	λ^{UV}_{max}	λ^{PL}_{max}	λ^{UV}_{max}	λ^{PL}_{max}
99:1[a]	319.0	490.5	325.0	540.5
1:1[b]	323.0	541.0	329.0	585.0
$CHCl_3$	325.0	551.5	332.0	604.5
MC[c]	328.0	582.5	333.0	623.5

Note: [a]*n*-Hexane: $CHCl_3 = 99{:}1$; [b]*n*-Hexane: $CHCl_3 = 1{:}1$; [c]methylene chloride.

Figure 3 showed UV-visible absorption spectra of BDAT-P and ABCV-P with variation of solvent polarity. The peak wavelengths of UV-visible absorption and PL emission spectra of BDAT-P and ABCV-P measured in each solvent system were summarized in Table I. The difference of peak wavelengths of UV-visible spectra measured in the respective solvent system between BDAT-P and ABCV-P was very small and represented similar values from 5 to 7 nm. Furthermore, the shape of UV-visible spectra of BDAT-P was similar to that of ABCV-P. The results of UV-visible measurement could be interpreted as the molecular structure of BDAT-P such as conjugation length and co-planarity of molecule except for molecular rigidity and the number of electron donor–acceptor pairs was similar to that of ABCV-P.

Unlike the UV-visible absorption spectra of BDAT-P and ABCV-P, PL emission spectra of them were highly affected by the solvent polarity. Figure 4 showed that PL emission spectra of BDTA-P and ABCV-P with variation of solvent polarity. Based on the results of UV-visible measurement, the effect of solvent polarity on PL emission spectra could be assumed to be caused by

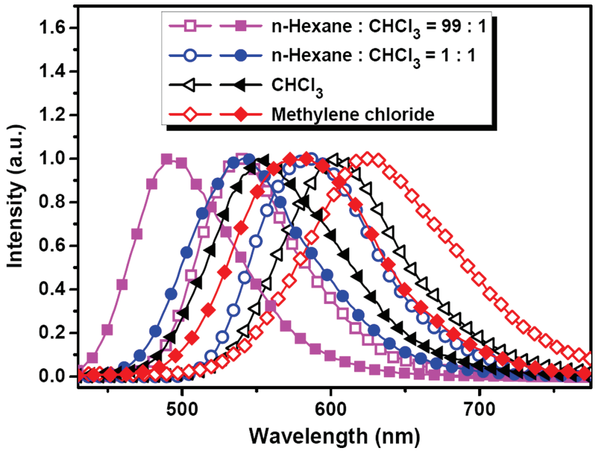

Fig. 4. Normalized PL emission spectra of BDTA-P and ABCV-P with variation of solvent polarity, in which the filled and open symbols represent the PL emission spectra of BDTA-P and those of ABCV-P, respectively.

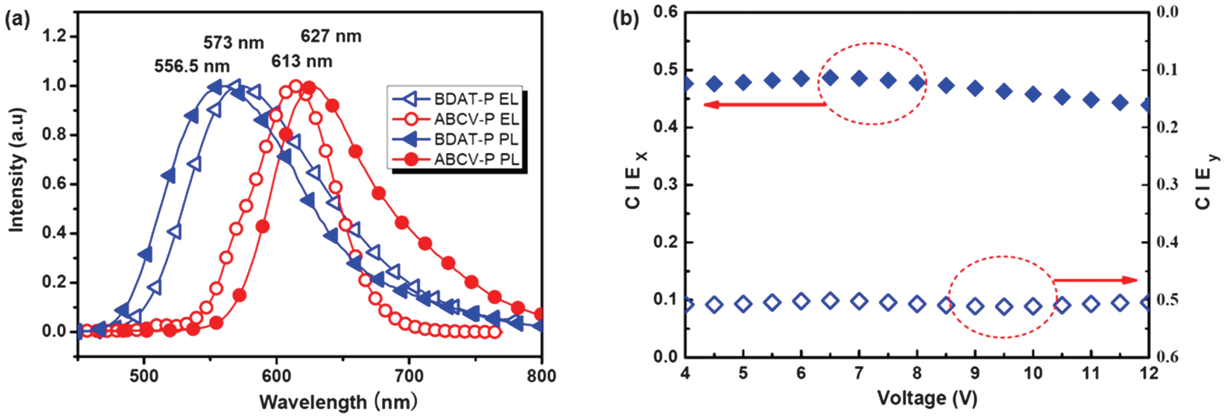

Fig. 5. (a) PL spectra of BDAT-P and ABCV-P in film states and EL spectra of BDAT-P and ABCV-P (b) CIE_{xy} versus applied voltage (V) characteristics of BDAT-P.

the stabilization of excited state with solvent polarity. As shown in Figure 4, fluorescence emission spectra of BDAT-P and ABCV-P were dramatically shifted to red wavelength relative to the UV-visible absorption spectra as increasing the solvent polarity. This suggests that photo induced excited state with a large molecular dipole moment is involved in fluorescence emission. As shown in Figure 1, both of BDAT-P and ABCV-P have electron donor–acceptor pairs in the molecule and they lead to a charge separation by ICT in the photo-induced excited state, which correspond to the ICT excited state. The molecular dipole moment in the ICT excited state will be increased with the increase of charge separation in the molecule. Therefore, the PL peak wavelength of a fluorescent compound with a stronger ICT character is more shifted to red region compared to that with a weaker ICT one relative to the peak wavelength of each UV-visible absorption spectrum, in which all spectra are obtained in solution.

Table I summarized the peak wavelengths of UV-visible absorption and PL emission spectra of BDAT-P and ABCV-P obtained in various solvents and it well represented the effect of the molecular structure on the PL property of a fluorophore using in OLEDs. The degree of red shifts of PL emission peaks relative to the peaks of UV-visible absorption in the respective solvent system was measured to be 175.0 (n-Hexane/$\mathrm{CHCl_3}$ = 99/1), 218.0 (n-Hexane/$\mathrm{CHCl_3}$ = 1/1), 226.5 ($\mathrm{CHCl_3}$) and 254.5 nm (MC) for BDAT-P and 215.5 (n-Hexane/$\mathrm{CHCl_3}$ = 99/1), 256.0 (n-Hexane/$\mathrm{CHCl_3}$ = 1/1), 272.5 ($\mathrm{CHCl_3}$) and 290.5 nm (MC) for ABCV-P, respectively. The additional bathochromic shift of PL emission of ABCV-P compared to that of BDAT-P in each solvent system was evidently observed. Based on the result of UV-visible measurement, the difference of conjugation length between BDAT-P and ABCV-P is not sufficient to explain the degree of that additional red shift of ABCV-P. As shown in Figure 1, the major difference between the molecular structures of BDAT-P and ABCV-P is the number of electron donor–acceptor pairs in the molecule, in which BDAT-P has one electron donor–acceptor pair whereas ABCV-P does two pairs of them. Therefore, it can be suggested that the additional bathochromic shift of PL emission of ABCV-P compared to that of BDAT-P is originated from the difference of the degree of ICT caused by the difference of the number of electron donor–acceptor pairs in the molecule. Figures 5(a) and (b) showed EL spectra of devices using BDAT-P and ABCV-P as the host emitters along with their PL spectra in film states and CIE_{xy} coordinate of device using BDAT-P, respectively. The peak wavelengths of EL emission were observed to be 573 nm for BDAT-P and 613 nm for ABCV-P, respectively and the PL emission peaks of BDAT-P and ABCV-P in film states were measured to be 556.3 and 627 nm, respectively. The EL emission peak of BDAT-P were observed at shorter wavelength by 40 nm compared to that of ABCV-P and this result was well correlated with the effect of the ICT on the PL properties of them. CIE_{xy} coordinate of EL emission of BDAT-P was measured to be (0.4855, 0.5021) at 7 V, which corresponded to the yellow color. The maximum luminance of the devices using ABCV-P and BDAT-P as the host emitters was measured to be 0.704 cd/A at 4.5 V and 0.629 cd/A at 4 V, respectively, and the maximum luminous efficiency of them was 3320 cd at 14 V and 21.6 cd at 6 V, respectively.

4. CONCLUSION

We demonstrated that the some modification of the molecular structure made it possible to tune emission color and this was helpful in designing a novel light-emitting material. In order to study the effect of the molecular structure on the optoelectronic properties of a light-emitting compound, a novel yellow light-emitting material, BDAT-P, was synthesized. The molecular structure of BDAT-P was modified from that of ABCV-P which was red light-emitting fluorophore. The major difference between the molecular structures of BDAT-P and ABCV-P was the number of electron donor–acceptor pairs inducing ICT. ABCV-P with two electron donor–acceptor pairs in the molecule exhibited more red-shifted PL emission peak in the respective solvent system and EL emission peak compared to BDAT-P with one donor–acceptor pair in the molecule. Finally, the number of electron donor–acceptor pairs in the molecule inducing ICT affected optoelectronic properties like emission region.

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