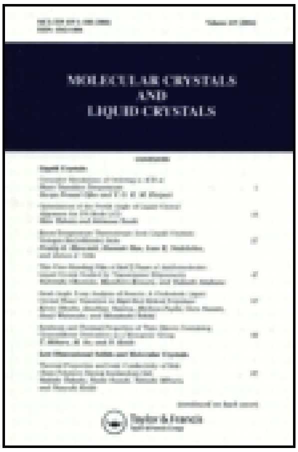

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The Effects of Molecular Structure on Surface Morphology of Thin Film and Optoelectronic Property of a Fluorophore

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A yellow fluorescent material, (2Z)-3-[4,4″-bis(dimethylamino)-1,1′:4′,1″-terphenyl-2′-yl]-2-phenylacrylonitrile was synthesized in order to investigate the effect of molecular structure on surface morphology of its thin film and its optoelectronic property. Atomic force microscopy measurment for thin films of 4-(dicyanomethylene)-2-methyl-6-(julolidin-4-yl-vinyl)-4H-pyran, (2Z)-3-[4,4″-bis(dimethylamino)-1,1′:4′,1″-terphenyl-2′-yl]-2-phenylacrylonitrile and (2Z,2′Z)-3,3′-[4,4″-bis(dimethylamino)-1,1′:4′,1″-terphenyl-2′,5′-diyl]bis(2-phenylacrylonitrile) represented that surface morphology of thin film of a fluorophore was dependent on its molecular structure such as coplanarity and molecular polarity. Surface morphology of thin film of BDAT-P showed much less amorphous than that of ABCV-P. Atomic force microscopy measurment for BDAT-P and ABCV-P was well corresponding to observed optoelectronic properties of them. The luminance of non-doped devices for BDAT-P and ABCV-P was measured to be 31.6 cd/m^2 at 6 V and 249 cd/m^2 at 6 V, respectively.

Keywords: BDAT-P; an yellow fluorophore; surface morphology; amorphous

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 report green device based on small molecule [1–4]. For full color display three primary colors red, green and blue were developed and studied. And yellow and orange colors were studied for white OLEDs [5–7]. Most of fluorescent materials affiliated red color including yellow and orange colors are tend to molecular aggregation and concentration quenching in solid state, due to attractive dipole-dipole interactions of effective intermolecular π-stacking and which lead to low device performance [8]. To solve those problems many method were suggested and effective method is using emitting materials as dopant into host materials. However doped OLEDs are hard to adapt for mass

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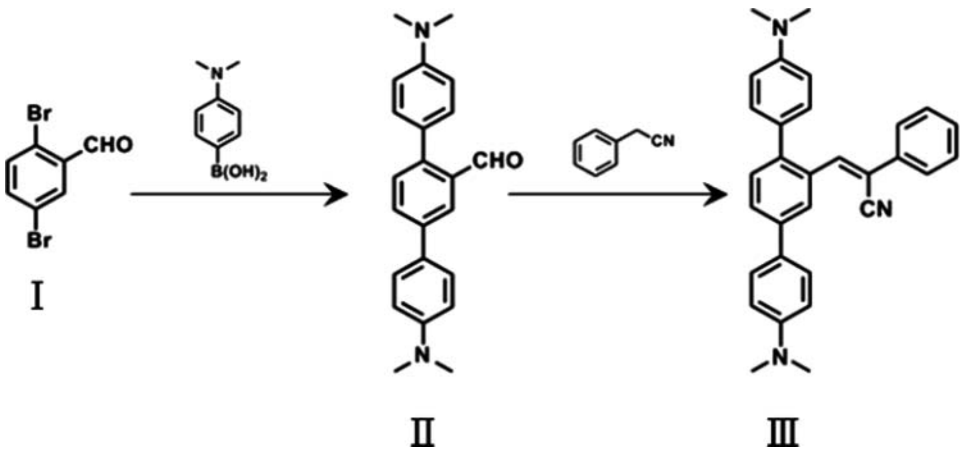
production processes which required high consistency in product quality than non-doped OLEDs with amorphous emissive materials considering the reproducibility of the optimum of doping levels and the unstable emission color with driving voltage [9].

In this work, an yellow fluorescent material, (2Z)-3-[4,4′′-bis(dimethylamino)-1,1′:4′,1′′-terphenyl-2′-yl]-2-phenylacrylonitrile (BDAT-P) was synthesized and its opto-electronic properties based on surface morphology of its thin film were studied.

2. Experimental

2.1. Synthesis

BDAT-P was synthesized as shown in Scheme 1. All solvents involved in the experiments were reagent grade and were purified by the usual methods before use. The molecular structure of BDAT-P was confirmed by 1H and 13C-NMR spectroscopy, MS (FAB) spectrum and elemental analysis.



Scheme 1. Synthesis of BDAT-P.

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, $CDCl_3$) 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 $\sim$ 400°C. UV-visible absorption and photoluminescence (PL) spectra were measured by HP model 8453 and Perkin Elmer LS55, respectively.

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. AFM measurement and fabrication of OLED

The sample 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. ITO-coated glass was cleaned in an ultrasonic bath by the following sequence: in acetone, methanol, diluted water and O_2 plasma under the conditions of 2×10^{-2} torr, 125W and 2 min. The cleaned substrate was immediately loaded into the deposition chamber in order to avoid air contamination. Atomic force microscopy (AFM) measurement was performed using NS4A in the tapping mode, on a 1 μm x 1 μm scale.

The devices with the structure of ITO/NPB (50 nm)/emitters (BDAT-P, ABCV-P) (30 nm)/BCP (10 nm)/Alq_3 (20 nm)/Liq (2 nm)/Al (100 nm) were fabricated by the same procedure as used in the preparation of sample for AFM measurements, in which NPB, emitters, BCP, Alq_3 and Liq were used as a hole transporting layer (HTL), emitting layer (EML), a hole blocking layer (HBL), electron transporting layer (ETL) and an electron injection layer (EIL), respectively. Electroluminescence (EL) spectra and device performance

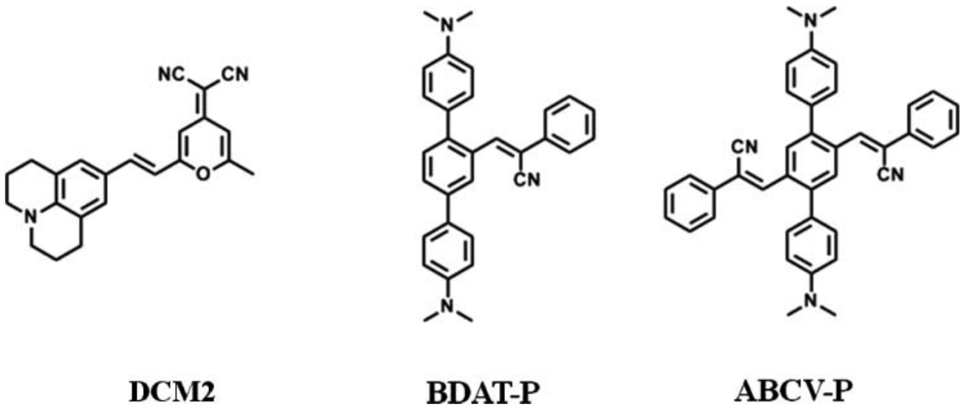


Figure 1. Molecular structure of DCM2, BDAT-P and ABCV-P.

were measured using Perkin Elmer LS-55 and keithley 238, CHROMA METER CS-100A. All the measurements were carried out at room temperature.

3. Results and Discussion

Most of OLEDs based on small molecules are fabricated by successive layer-by-layer deposition of an organic compound onto a previously deposited organic layer. Accordingly, OLED device performance depends on the characteristics of thin layers. Surface morphology and interfacial characteristics of those layers determine the long term stability and efficiency of OLEDs. Surface morphology of an organic thin film in OLEDs highly depends on the molecular structure of corresponding organic material. Figure 1 showed molecular structure of BDAT-P, (2Z,2′Z)-3,3′-[4,4″-bis(dimethylamino)-1,1′:4′,1″-terphenyl-2′,5′-diyl]bis(2-phenylacrylonitrile) (ABCV-P) and 4-(dicyanomethylene)-2-methyl-6-(julolidin-4-yl-vinyl)-4H-pyran (DCM2). They all have intramolecular charge-transfer (ICT) character. Coplanar and highly polar molecular structure of DCM2 makes aggregation among the DCM2 molecules in solid-state, which leads to significant fluorescence concentration quenching of DCM2. However, the molecular structure of ABCV-P is not coplanar and this prevents the ABCV-P molecules from aggregating among them. This was well supported by the previous study on ABCV-P and DCM2 based on surface morphology and optoelectronic properties of them [10].

As shown in Figure 1, the molecular structure of BDAT-P is similar to that of ABCV-P. However, BDAT-P molecule is lacking in one of two 2-phenylacrylonitrile moieties at the middle benzene ring of bis(dimethylamino)-terphenyl moiety compared to ABCV-P molecule. Because of this deficiency of one substituent at that benzene ring in BDAT-P, crowding of middle benzene ring of terphenyl moiety decreased compared to that of ABCV-P and this lessens the distortion of coplanarity of BDAT-P molecule compared to that of ABCV-P molecule. In order to investigate the effect of molecular structure on surface morphology of thin layer, AFM measurement for the thin solid films of DCM2, BDAT-P and ABCV-P was performed. Figure 2 showed the AFM images (1 μm × 1 μm) obtained for thin solid film sample of (a) ITO/NPB (40 nm)/DCM2 (80 nm), (b) ITO/NPB (40 nm)/BDAT-P (80 nm) and (c) ITO/NPB (40 nm)/ABCV-P (80 nm), respectively. The AFM image of DCM2 thin film certainly showed stacking of small particles due to the planer and polar molecular structure of DCM2 which lead to the strong intermolecular

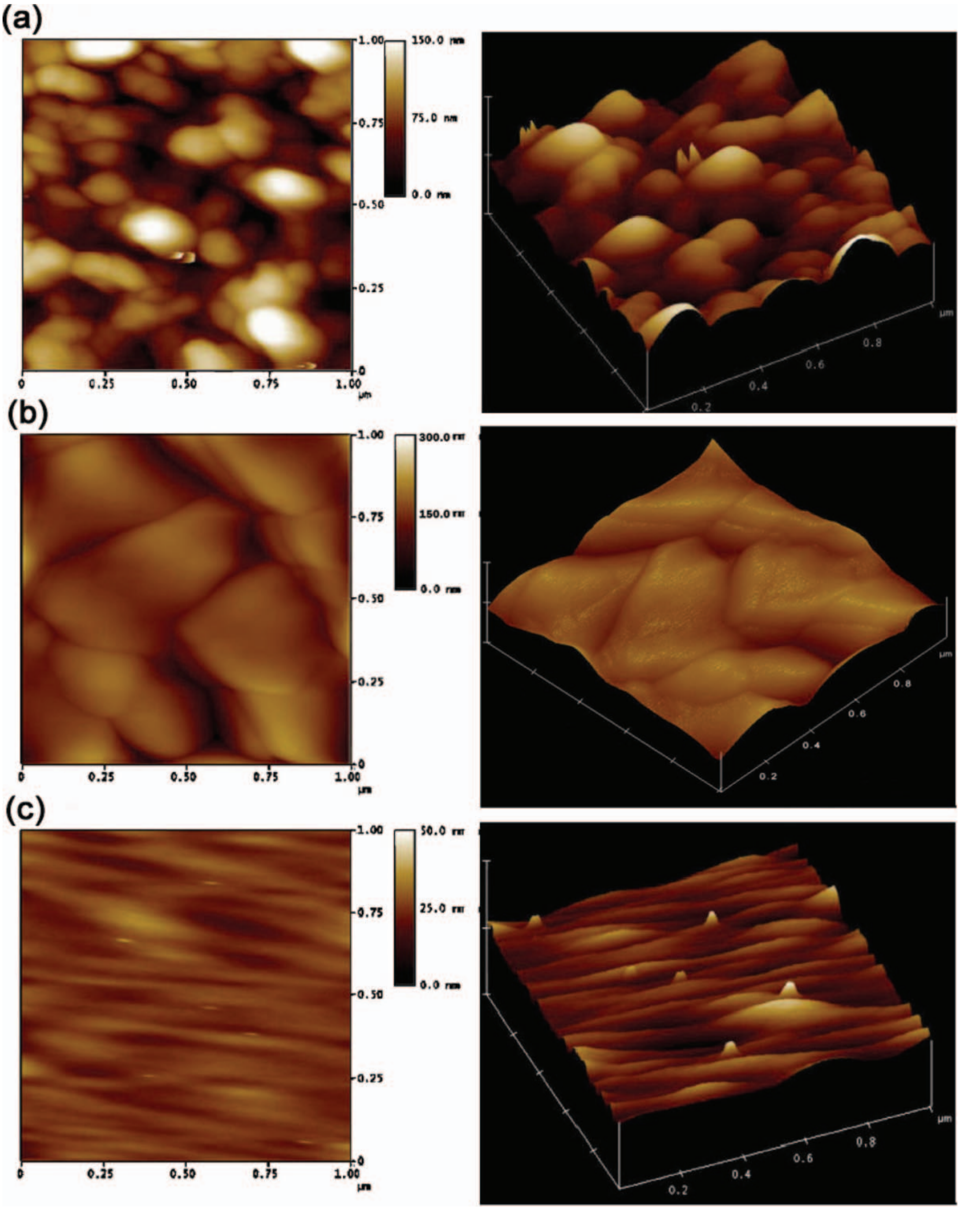


Figure 2. Tapping-mode AFM topographic images of BDAT-P, ABCV-P and DCM2 thin films in (a) ITO/NPB/ (40 nm)/DCM2 (80 nm), (b) ITO/NPB (40 nm)/BDAT-P (80 nm) and (c) ITO/NPB (40 nm)/ABCV-P (80 nm).

dipole-dipole interaction, whereas ABCV-P which had noncoplanar and bulky molecular structure represented amorphous AFM image of its thin solid film. Although the AFM image of BDAT-P thin solid film showed a stacking structure, the surface morphology of BDAT-P thin solid film also represented some amorphous property. However, the degree of amorphous property in BDAT-P thin solid film dramatically decreased compared to that in ABCV-P thin solid film. The decrease of amorphous property in BDAT-P thin solid

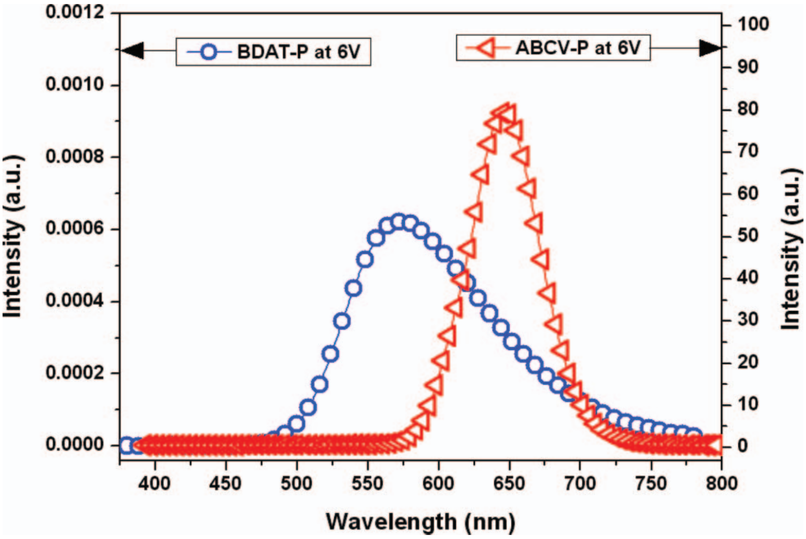


Figure 3. EL spectra of devices ITO/NPB (50 nm)/BDAT-P (30 nm)/BCP (10 nm)/Alq_3 (20 nm)/Liq (2 nm)/Al (100 nm) and ITO/NPB (50 nm)/ABCV-P (30 nm)/BCP (10 nm)/Alq_3 (20 nm)/Liq (2 nm)/Al (100 nm).

film compared to that in ABCV-P thin solid film is ascribed to the difference in molecular structure between BDAT-P and ABCV-P.

The result of AFM measurement for DCM2, BDAT-P and ABCV-P was well corresponding to that of EL measurement for them. Figure 3 and 4 showed EL spectra and luminance-voltage characteristics obtained for non-doped OLEDs using BDAT-P and ABCV-P as the host-emitters, respectively. EL spectrum of DCM2 for non-doped device

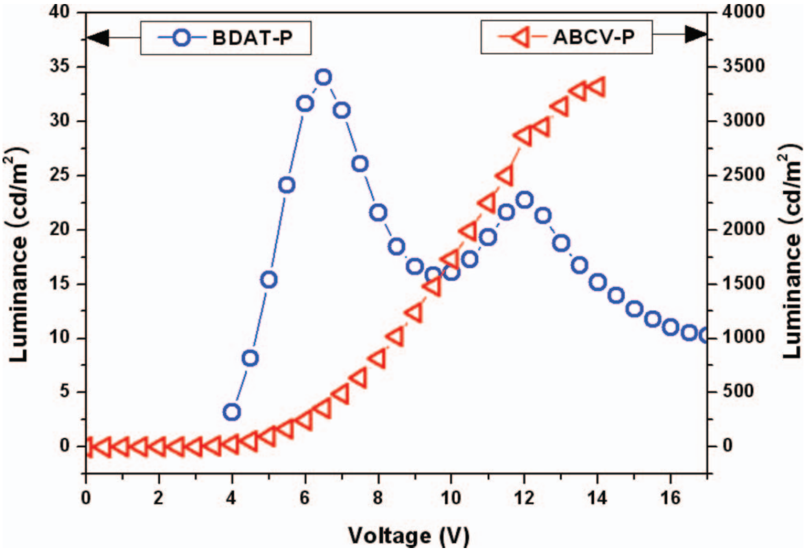


Figure 4. Luminance-voltage characteristic of non-doped devices, ITO/NPB (50 nm)/BDAT-P (30 nm)/BCP (10 nm)/Alq_3 (20 nm)/Liq (2 nm)/Al (100 nm) and ITO/NPB (50 nm)/ABCV-P (30 nm)/BCP (10 nm)/Alq_3 (20 nm)/Liq (2 nm)/Al (100 nm).

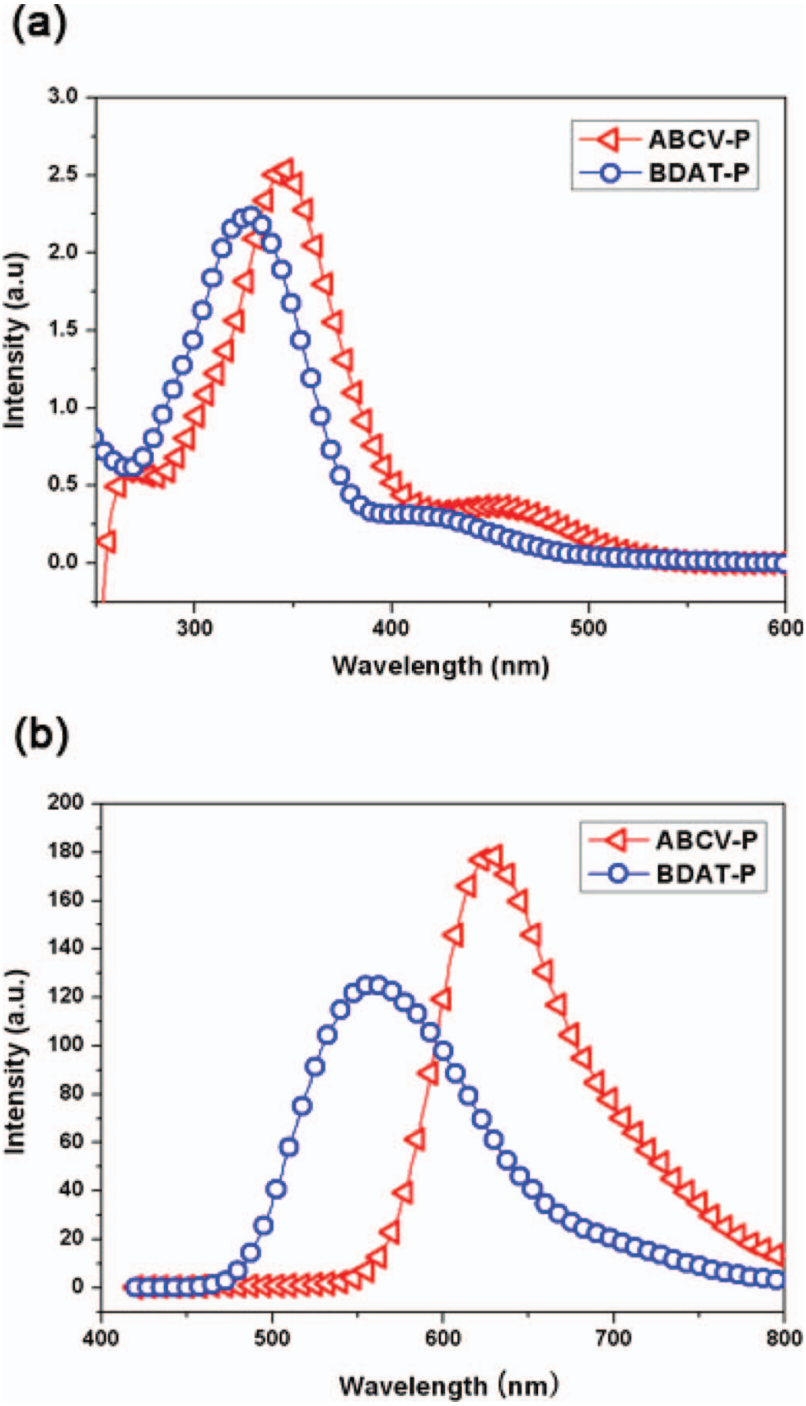


Figure 5. (a) UV-visible and (b) PL spectra of BDAT-P and ABCV-P, in which PL of BDAT-P and ABCV-P were peaked at 543 and 616 nm, respectively.

could not be observed because it did not emit light. As shown in Figure 3 and 4, EL emission of BDAT-P was ignorable compared to that of ABCV-P, in which EL emission peaks of BDAT-P and ABCV-P were observed at 573 and 619.5 nm, respectively, and luminance of non-doped devices for BDAT-P and ABCV-P was measured to be 31.6 cd/m^2 at 6 V and 249 cd/m^2 at 6 V, respectively. Moreover, luminance-voltage characteristics exhibited that the stability of device for BDAT-P was very poor. The electroluminescence properties of BDAT-P and ABCV-P were well correlated with the difference in surface morphology between their thin sold films, in which the surface morphology was obtained by AFM measurement.

The UV-visible absorption and photoluminescence (PL) spectra of BDAT-P and ABCV-P thin solid films were shown in figure 5. Although PL emission of BDAT-P thin solid film was not comparable to that of ABCV-P thin solid film, the PL spectrum of BDAT-P represented its PL emission was considerable in contrast to no PL emission from DCM2 solid film. PL emission peaks of BDAT-P and ABCV-P thin solid films were observed at 543 and 616 nm, respectively.

4. Conclusions

In order to investigate the effect of molecular structure on surface morphology of thin layer and optoelectronic properties, BDAT-P, an yellow fluorophore, with similar molecular structure to that of ABCV-P but lacking in one of two 2-phenylacrylonitrile moieties at the middle benzene ring of bis(dimethylamino)-terphenyl moiety compared to ABCV-P molecule was synthesized. Based on AFM measurement, surface morphology of BDAT-P thin film became much less amorphous than that of ABCV-P thin film and this resulted in poor EL emission of non-doped device for BDAT-P compared to that for ABCV-P. Therefore, it could be concluded that surface morphology of thin layer of a fluorophore was dependent upon its molecular structure such as coplanarity and molecular polarity.

Acknowledgment

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