Difluorobenzothiadiazole based two-dimensional conjugated polymers with triphenylamine substituted moieties as pendants for bulk heterojunction solar cells

W. H. Lee¹, B. T. Liu², R. H. Lee^{1*}

¹Department of Chemical Engineering, National Chung Hsing University, 402 Taichung, Taiwan

²Department of Chemical and Materials Engineering, National Yunlin University of Science & Technology, 640 Yunlin, Taiwan, R.O.C.

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Abstract. Three donor/acceptor (D/A)-type two-dimensional polythiophenes (PTs; PBTF13, PBTF12, PBTF11) featuring difluorobenzothiadiazole (DFBT) derivatives as the conjugated (acceptor) units in the polymer backbone and *tert*-butyl-substituted triphenylamine (tTPA)-containing moieties as (donor) pendants have been synthesized and characterized. These PTs exhibited good thermal stabilities, broad absorption spectra, and narrow optical band gaps. The cutoff wavelength of the UV–Vis absorption band was red-shifted upon increasing the content of the DFBT units in the PTs. Bulk heterojunction solar cells having an active layer comprising blends of the PTs and fullerene derivatives [6,6] phenyl-C₆₁/71-butyric acid methyl ester (PC₆₁BM/PC₇₁BM) were fabricated; their photovoltaic performance was strongly dependent on the content of the DFBT derivative in the PT. Incorporating a suitable content of the DFBT derivative in the polymer backbone enhanced the solar absorption ability and conjugation length of the PTs. The photovoltaic properties of the PBTF13-based solar cells were superior to those of the PBTF11- and PBTF12-based solar cells.

Keywords: polymer synthesis, difluorobenzothiadiazole, polythiophene derivative, and bulk heterojunction solar cells

1. Introduction

Conjugated polymers with electron donor/acceptor (D/A) units in the polymer backbone have attracted much attention for their applications in optoelectronic devices, including polymer solar cells (PSCs), organic thin film transistors (OTFTs), and polymer light emitting displays (PLEDs) [1–7]. Major advances in the solar energy conversion efficiencies of PSCs have been accomplished by replacing the double-layer cell with a bulk-heterojunction (BHJ) based on a conjugated polymer/fullerene derivative blend as the photoactive layer [8–10]. The bipolar characteristics of D/A-type conjugated polymers, containing both electron- and hole-transporting moieties, can result in lower-energy band gaps and higher

charge mobilities for the photoactive layers, thereby enhancing the PV efficiencies of PSCs [11–15]. Polythiophene (PT) derivatives bearing electron-donating and -withdrawing pendant groups, so-called two-dimensional (2-D) low band gap conjugated polymers, have been proposed by several groups for PSC applications [16–25]. The introduction of conjugated moieties as pendant units that absorb broadly in the UV and visible regions can, therefore, lead to the greater harvesting of solar light. Moreover, the conjugated pendant moieties can enhance the charge mobilities of the polymers.

The incorporation of electron-deficient moieties within the polymer backbone and the appending of electron-donating units would, ideally, promote charge

*Corresponding author, e-mail: rhl@dragon.nchu.edu.tw
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balance and efficient conjugation within the extended conjugated framework of the polymer [26–28]. Triphenylamine (TPA) derivatives are among the most popular electron-donor groups because of their good electron-donating and hole-transporting performance, and good solubility in organic solvents [29, 30]. Fan *et al.* [30] reported two benzodithiophene-based 2-D polymers featuring extended conjugated thienyltriphenylamine substituents; polymers presenting these extended TPA-based conjugated pendants exhibited good thermal, photophysical, and photovoltaic performance. In addition, benzothiadiazole (BT) derivatives are widely used as acceptor units because of their strong electron-withdrawing properties, intense light absorption, and good photochemical stability [31, 32]. Many BT-based conjugated polymers providing good PV performance have been synthesized through the copolymerization of BT units with various electron-donating groups (e.g., benzodithiophene, dithienosilole, 4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene) [33–35]. Furthermore, incorporating fluorine atoms at the 5- and 6-positions of the BT unit can lower the energy levels of the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) of the resulting conjugated polymers, resulting in PSCs displaying higher open-circuit voltages; higher hole mobility is also obtained because of stronger intermolecular interactions among the polymer chains [30, 36–38]. The PV performance of difluorobenzothiadiazole (DFBT)-based polymers is usually superior to that of BT-based polymers [39–41]. Nevertheless, the introduction of DFBT units into polymer backbones usually results in conjugated polymers having poor solubility [38, 42].

Recently, we synthesized a series of PTs presenting conjugated TPA-containing moieties as side chains [22]. The incorporation of bulky pendant units in a PT twists the main chain out of planar π -conjugation, thereby decreasing the effective conjugation length of the polymer backbone [43–47]. As a result, these PTs have higher band gap energies and are less capable of harvesting solar light [17]. Therefore, precise control over the molar ratio of the electron-donating and -withdrawing units in the polymer chain is necessary to optimize the solubility, film quality, and optical and PV performance of resulting devices. To test this concept, in this study we synthesized three 2-D PTs (PBTFA13, PBTFA12, PBTFA11) featuring DFBT derivatives as the conjugated units

in the polymer backbone with *tert*-butyl-substituted triphenylamine (*t*TPA)-containing moieties as pendant units. UV–Vis absorption spectroscopy and cyclic voltammetry (CV) revealed the effect of the DFBT content on the photophysical and electrochemical properties of the polymers. We also employed atomic force microscopy (AFM) and transmission electron microscopy (TEM) to study the morphologies of thin films prepared from the PT/PC₆₁BM blends. We then fabricated PSCs having a conventional structure [indium tin oxide (ITO)-coated glass/hole-transporting medium (HTM)/photoactive layer/Ca (20 nm)/Al (100 nm)], spin-coating a blend of each PT with PC₆₁BM or PC₇₁BM to form a composite film-type photoactive layer on the HTM layer deposited on ITO-coated glass. From studies of the PV performance of these PSCs, herein we discuss the influence of the DFBT content of our PTs on the PSC performance.

2. Experimental details

2.1. Chemicals

Tris(dibenzylideneacetone)dipalladium(0) [Pd₂(dba)₃], tri(*o*-tolyl)phosphine [P(*o*-tolyl)₃], and other reagents and chemicals were purchased from Aldrich (St Louis, MO, USA), Alfa (New Jersey, USA), Acros (Geel, Belgium), and TCI Chemical (Tokyo, Japan), and used as received. *o*-Dichlorobenzene (*o*-DCB) was freshly distilled over appropriate drying agents prior to use as a solvent, and was purged with N₂. 2,5-Bis(trimethylstannyl)thiophene (**1**) and (*E*)-4-{5-[2-(2,5-dibromothiophen-3-yl)vinyl]thien-2-yl}-*N,N*-(4,4'-di-*tert*-butyl)diphenyl]aniline (**2**) were synthesized according to procedures reported in the literature [29, 48, 49]. 4,7-Bis(5-bromothiophen-2-yl)-5,6-difluorobenzo[*c*][1,2,5]thiadiazole (**3**) was purchased from SunaTech and used as received. The synthesis of the PTs PBTFA11, PBTFA12, and PBTFA13, featuring 4,7-bis(thien-2-yl)-5,6-difluorobenzo[*c*][1,2,5]thiadiazole moieties as conjugated units in the polymer backbone with conjugated *t*TPA-containing moieties as side chains, is illustrated in Figure 1.

PBTFA11

A solution of **1** (0.41 g, 1.0 mmol), **2** (0.35 g, 0.50 mmol), and **3** (0.25 g, 0.50 mmol) in dry *o*-DCB (30 mL) was stirred at room temperature under N₂ for 10 min and then a solution of Pd₂(dba)₃ (55 mg, 0.040 mmol) and P(*o*-tolyl)₃ (73 mg, 0.16 mmol) in

Figure 1. Synthesis of PBTF11, PBTF12, and PBTF13

dry *o*-DCB (10 mL) was added dropwise. The solution was heated at 120 °C for 48 h with stirring. After cooling to room temperature, the solution was poured into MeOH (100 mL). The precipitate was filtered into a Soxhlet thimble and extracted with MeOH, hexane, acetone, and *o*-DCB. The polymer PBTF11 was recovered through concentration of the *o*-DCB fraction under vacuum. Drying under vacuum for 24 h provided a black solid (0.05 g, 5.0%). ¹H NMR (δ [ppm], 600 MHz, CD₂Cl₂): 0.76–1.42 (m, 18H), 6.40–7.62 (m, 23H). Anal. Calcd for [(C₁₈H₆N₂S₄F₂)(C₄₀H₃₇NS₃)1.7]: C, 69.64; H, 4.65; N, 3.50; S, 19.65. Found: C, 69.74; H, 4.59; N, 3.52; S, 19.69.

PBTF12

Using the same procedure as that described for the synthesis of PBTF11, the reaction of **1** (0.41 g, 1.0 mmol), **2** (0.47 g, 0.67 mmol), and **3** (0.16 g, 0.33 mmol), provided a black solid (0.2 g, 19.0%). ¹H NMR (δ [ppm], 600 MHz, CD₂Cl₂): 0.78–1.40 (m, 18H), 6.30–7.42 (m, 29H). Anal. Calcd for [(C₁₈H₆N₂S₄F₂)(C₄₀H₃₇NS₃)2.6]: C, 71.55; H, 4.99; N, 3.15; S, 18.46. Found: C, 71.51; H, 5.02; N, 3.13; S, 18.49.

PBTF13

Using the same procedure as that described for the synthesis of PBTF11, the reaction of **1** (0.41 g, 1.0 mmol), **2** (0.53 g, 0.75 mmol), and **3** (0.12 g, 0.25 mmol), provided a black solid (0.16 g, 15.0%). ¹H NMR (δ [ppm], 600 MHz, CD₂Cl₂): 0.82–1.37

(m, 18H), 6.50–7.41 (m, 33H). Anal. Calcd for [(C₁₈H₆N₂S₄F₂)(C₄₀H₃₇NS₃)3.8]: C, 72.88; H, 5.23; N, 2.90; S, 17.61. Found: C, 72.90; H, 5.21; N, 2.94; S, 17.58.

2.2. Characterization of copolymers

¹H NMR (600 MHz) spectra were recorded using a Varian Unity Inova spectrometer (Agilent, California, USA). The average molecular weights of the polymers were measured through gel permeation chromatography (GPC) on a Waters chromatography system (Waters 717 Plus Autosampler, Waters Co., Milford, MA, USA) equipped with two Waters Styragel linear columns; polystyrene standards were used, with THF as the eluent. The glass transition temperatures (*T*_g) and thermal decomposition temperatures (*T*_d; temperature at which weight loss reached 5%) of the copolymers were measured using differential scanning calorimetry (DSC-2010; TA Instruments, New Castle, DE, USA) and thermogravimetric analysis (TGA-2050; TA Instruments, New Castle, DE, USA), respectively. Both analyses were performed under N₂ atmospheres at scanning (both heating and cooling) rates of 10 °C·min^{−1}. The temperatures at the intercepts of the curves in the thermograms (endothermic, exothermic, or weight loss) with the leading baseline were taken as estimates of the values of *T*_g and *T*_d. Absorption spectra were measured using a Hitachi U3010 UV–Vis spectrometer (Hitachi High-Tech Co., Tokyo, Japan); dilute *o*-DCB solutions of the PTs were filtered through a 0.45 μm filter to remove insoluble materials prior to spectral measurement. The redox potentials of the polymers were determined in anhydrous N₂-saturated 0.1 M Bu₄NClO₄ in MeCN using a CHI 611D electrochemical analyzer (Ch Instruments, Texas, USA; scanning rate: 50 mV·s^{−1}) equipped with Pt electrodes and an Ag/Ag⁺ (0.10 M AgNO₃ in MeCN) reference electrode. Bu₄NClO₄ (98%, TCI) was recrystallized three times from MeOH and water (1:1) and then dried at 100 °C under reduced pressure. A Pt plate coated with a thin polymer film was used as the working electrode; a Pt wire and an Ag/Ag⁺ electrode were used as the counter and reference electrodes, respectively. The electrochemical potential was calibrated against ferrocene/ferrocenium. The morphologies of the films prepared from PT/PC₆₁BM (or PC₇₁BM) blends were studied using atomic force microscopy (AFM, SII SPA400; Seiko Instruments, Inc., Chiba, Japan; operated in tapping mode) and transmission

electron microscopy (TEM, JEM-1400; JEOL Taiwan semiconductors Ltd., Hsinchu, Taiwan).

2.3. Fabrication and characterization of PSCs

The PSCs fabricated in this study had structures of ITO-coated glass/HTM/photoactive layer/Ca (20 nm)/Al (100 nm), where the photoactive layer comprised an interpenetrating network of PT and a fullerene derivative (PC₆₁BM or PC₇₁BM; Nano Carbon LLC, Warsaw, Poland). ITO-coated glass (sheet resistance: 20 Ω^{-2}) was purchased from Applied Film (AF Co., Alzenau, Germany). PC₆₁BM and PC₇₁BM were purchased from Nanocarbon and used as received. The PSCs were fabricated as follows: glass substrates with patterned ITO electrodes were washed well and then cleaned through O₂ plasma treatment. A thin film of the HTM, poly(3,4-ethylenedioxythiophene) doped with polystyrenesulfonate (PEDOT:PSS, AI4083; Heraeus Clevios Co., Hanau, Germany), was deposited on the ITO layer through spin-casting. The sample was dried at 150 °C for 30 min in a glove box. A solution of PT and PC₆₁BM (or PC₇₁BM) (30 mg·mL⁻¹) in *o*-DCB was stirred overnight, then filtered through a 0.2 μ m polytetrafluoroethylene (PTFE) filter and spin-coated (1500 rpm, 30 s) onto the HTM layer to prepare the PT/PC₆₁BM (or PC₇₁BM) composite film-based photoactive layer. The sample was dried at 110 °C for 10 min in a glove box. In a high-vacuum chamber, the Ca/Al-based cathode was thermally deposited onto the PT/PC₆₁BM (or PC₇₁BM) composite layer. The active area of the PSC was 0.04 cm². After electrode deposition, the PSC was encapsulated. The cathode deposition rate was determined using a quartz thickness monitor (STM-100/MF; Sycon Instruments, East Syracuse, NY, USA). The thickness of thin films was measured using a surface texture analysis system (Dektak 3030ST; Veeco Instruments, Inc., Hsinchu, Taiwan). The PV properties of the PSCs were measured, using a programmable electrometer equipped with current and voltage sources (Keithley 2400; Keithley Instruments, Inc., Cleveland, OH, USA), under illumination with solar-simulating light (100 mW·cm⁻²) from an AM1.5 solar simulator (NewPort Oriel 96000; Newport Corporation Taiwan, Taipei, Taiwan).

3. Results and discussion

3.1. Characterization of PTs

The conjugated PTs were synthesized through Stille coupling of the distannane **1** with the dibromides **2**

and **3**. The chemical structures of the monomers were confirmed using ¹H NMR spectroscopy and elemental analysis. The repeat unit ratios (*m/n*; see Figure 1) of the PTs PBTFA11, PBTFA12, and PTBFA13 were modulated by controlling the feed ratio of the DFBT derivative (**3**) and the conjugated pendant *t*TPA-containing thiophene derivative (**2**). For PBTFA11, PBTFA12, and PTBFA13, the actual values of *m/n* were determined from the relative integral areas of the peaks at 6.30–7.60 ppm (representing protons of the vinylene, phenyl, and thiophene groups) and 0.9–1.3 (representing protons of the *tert*-butyl groups) in the ¹H NMR spectra of the copolymers; they were approximately 1:1.7, 1:2.6, and 1:3.8, respectively. For the PTs, the content of DFBT moieties in the polymer backbone was lower than the feed content of **3** in the reaction mixture during polymerization, presumably because of the relatively poor solubility of DFBT in the reaction solution. In addition, through GPC using THF as the eluent and polystyrene internal standards, we determined the number-average molecular weights (*M_n*) and weight-average molecular weights (*M_w*) of the conjugated PTs. Table 1 reveals that the values of *M_n* and *M_w* of the conjugated polymers were in the ranges 6.5–8.2 and 14.5–30.2 kg·mol⁻¹, respectively. The introduction of the DFBT unit into the polymer backbone usually brings about the PTs with poor solubility [36, 42]. Moreover, the poor solubility of the polymers might be possibly due to the absence of the long alkyl side chain on the polymer backbone [38]. The early termination of the propagation of the polymer chains resulted from poor solubility of the polymers in the reaction solution [29, 50]. As a result, the PTs exhibited low average molecular weights. Apart from that, the reaction product of PTs was purified by Soxhlet extraction with different organic solvents. The oligomers of PT were therefore removed. As a result, low yields of reaction products were obtained for these PTs.

Table 1. molecular weights and thermal properties of the PTs

PT	<i>M_n</i> [kg·mol ⁻¹]	<i>M_w</i> [kg·mol ⁻¹]	<i>T_g</i> [*] [°C]	<i>T_d</i> ^{**} [°C]
PBTFA13	8.2	30.2	118.5	245.5
PBTFA12	7.3	20.2	124.2	268.6
PBTFA11	6.5	14.5	— ^{***}	278.1

^{*}*T_g*: Measured at a heating rate of 10 °C·min⁻¹.

^{**}*T_d*: Temperature at which weight loss reached 5%.

^{***}Not detectable.

Figure 2. TGA (a) and DSC (b) thermograms of PBTFAs 11, PBTFAs 12, and PBTFAs 13

The operational stability of a PSC is closely related to the thermal stability of its conjugated polymer. Thus, high values of T_g and T_d are desirable. We used DSC and TGA to determine the thermal properties of the PTs. TGA and DSC thermograms of PTs are shown in Figure 2. The values of T_d for PBTFAs 13, PBTFAs 12, and PBTFAs 11 were 245.5, 268.6, and 278.1 °C, respectively. The thermal stability of the DFBT derivative **3** (T_d = 325 °C) was higher than that of the conjugated pendant compound **2** (T_d = 275 °C). As a result, the thermal stability of the PTs increased upon increasing the content of the DFBT derivative. We determined the glass transition temperatures from the second round of DSC heating scans. No glass transition was evident for PBTFAs 11. The values of T_g for PBTFAs 13 and PBTFAs 12 were 118.5 and 124.2 °C, respectively. High T_g (>100 °C) of PTs make them suitable for PSC applications.

3.2. Optical properties of PTs

Figure 3 displays the normalized UV–Vis absorption spectra of the DFBT-based PTs in *o*-DCB solution and as solid films; Table 2 summarizes the corresponding absorption data. The absorption bands of the DFBT-based PTs in *o*-DCB ranged from 325 to 800 nm, with each polymer providing two broad

Figure 3. Normalized UV–Vis absorption spectra of the PTs (a) in *o*-DCB solution and (b) as thin films

absorption bands. We attribute the first absorption band in the range 325–500 nm to the $n\text{--}\pi^*$ transitions of the conjugated side chains and the $\pi\text{--}\pi^*$ transitions of the conjugated main chain [29]. The second absorption band in the range 500–800 nm originated from intramolecular charge transfer (ICT) between the thiophene derivative-based donor units and the DFBT-based acceptor units [30]. Moreover, the absorption intensity of the second absorption band increased upon increasing the content of DFBT units in the copolymer, both in solution and in the thin film state. In addition, the red-shifts and full widths at half-maximum of the absorption bands of the copolymers in the films were greater than those in solution, presumably because of strong noncovalent interactions (e.g., π -stacking) between the polymer backbones and conjugated pendant units [30, 51]. Notably, the spectra of PBTFAs 11 in solution and as a thin film exhibited an additional shoulder peak in the range from 680 to 780 nm. The incorporation of a higher content of the DFBT derivative decreased the steric bulk of the conjugated pendant units and could, therefore, planarize the polymer main chain to some extent [36]. As a result, the absorption wavelengths of the polymers containing higher DFBT contents exhibited longer absorption onsets. Accordingly, PBTFAs 11 displayed the absorption shoulder peak. On the other hand, the intensity of the second absorption band was lower than that of the first absorption band for the PTs, presumably because of the low content of DFBT units in the polymer backbone. In addition, we used the onset wavelengths of the absorption bands to determine the band gap energies (E_g) of the conjugated polymers in the thin film state. The values of E_g for PBTFAs 13, PBTFAs 12, and PBTFAs 11 were 1.69, 1.59, and 1.57 eV, respectively. Lower values of E_g were observed for the copolymers containing higher contents

of DFBT units. Broader absorption and a lower band gap energy typically improve the solar light absorption efficiency of the photo-energy conversion layer in PSCs, resulting in the generation of larger photocurrents.

Figure 4 presents normalized UV–Vis absorption spectra of the PT/PC₆₁BM composite films. The absorption band of the DFBT-based conjugated copolymer ranged from 375 to 800 nm, while the absorption band of PC₆₁BM ranged from 300 to 375 nm. The maximal absorption intensities of the conjugated copolymer and PC₆₁BM were near 420 and 325 nm, respectively. Moreover, the absorption intensity of the conjugated polymer decreased upon increasing the

PC₆₁BM content for the DFBT-based PT/PC₆₁BM composite films.

3.3. Electrochemical properties of PTs

We employed CV to investigate the electrochemical behavior of our PTs and to estimate the energy levels of their HOMOs. Figure 5 displays the oxidation behavior in the CV curves of the PTs. Table 2 summarizes the electrochemical properties of the copolymers. The oxidation potentials ($E_{\text{on}}^{\text{ox}}$) of PBTF A13, PBTF A12, and PBTF A11 were 0.52, 0.54, and 0.59 V, respectively. From those values, we calculated the HOMO energy levels of the copolymers according to the Equation (1):

$$\text{HOMO} = -e(E_{\text{on}}^{\text{ox}} - E_{\text{on}}^{\text{ox, ferrocene}} + 4.71) [\text{eV}] \quad (1)$$

where 4.71 eV is the energy level of ferrocene below the vacuum level and the value of $E_{\text{on}}^{\text{ox}}$ of ferrocene/ferrocene⁺ is 0.09 V in 0.1 M Bu₄NClO₄/MeCN. The HOMO energy levels obtained for PBTF A13, PBTF A12, and PBTF A11 were –5.23, –5.25, and –5.30 eV, respectively. Higher HOMO energy levels were observed for the PTs containing higher contents of the TPA-containing conjugated pendant units; these values generally correlate with the electron-donating ability of the polymers [29]. In addition, because we observed no reversible n-doping process in the CV spectra, we estimated the LUMO energy levels from the HOMO energy levels and the values of E_g from the UV–Vis absorption spectra, using the Equation (2):

$$\text{LUMO} = \text{HOMO} + E_g [\text{eV}] \quad (2)$$

The LUMO levels obtained were –3.54 eV for PBTF A13, –3.66 eV for PBTF A12, and –3.73 eV for

Figure 4. Normalized UV–Vis absorption spectra of (a) PBTF A11/PC₆₁BM, (b) PBTF A12/PC₆₁BM, and (c) PBTF A13/PC₆₁BM blend films

Figure 5. Cyclic voltammograms of PBTF A11, PBTF A12, and PBTF A13

Table 2. Optical properties, electrochemical onset potentials, and electronic energy levels of the PTs

PTs	$\lambda_{\text{max}}^{\text{abs}}$ * [nm]	$\lambda_{\text{max}}^{\text{abs}}$ ** [nm]	$E_{\text{g}}^{\text{opt***}}$ [eV]	$E_{\text{on}}^{\text{ox}}$ [V]	HOMO [eV]	LUMO [eV]
PBTFA13	427, 550	413, 578	1.69	0.52	−5.23	−3.54
PBTFA12	425, 550	414, 585	1.59	0.54	−5.25	−3.66
PBTFA11	422, 540, 590	422, 550, 710	1.57	0.59	−5.30	−3.73

*Maximal absorption wavelength of the polymer in solution.

**Maximal absorption wavelength of the polymer as a thin film.

***Calculated from the onset absorption ($\lambda_{\text{max}}^{\text{abs}}$) of the polymer thin film: $E_{\text{g}} = 1240/\lambda_{\text{onset}}$.

PBTFA11. Thus, lower LUMO energy levels were obtained for the PTs containing higher contents of the electron-deficient DFBT units. Accordingly, the electrochemical properties of these PTs could be tuned by varying the content of the electron-accepting DFBT unit in the polymer backbone. In general, the HOMO energy level of the conjugated polymer is a parameter that affects the performance of BHJ-type cells. High open-circuit voltages (V_{OC}) are typically obtained for PSCs fabricated from conjugated polymers with low HOMO energy levels [29].

3.4. Morphologies of thin films of PT/PC₆₁BM blends

The performance of a PSC is strongly dependent on the morphology of its conjugated polymer/fullerene

derivative composite film [52–54]. To avoid recombination of excitons, the morphology of the P/N heterojunction phase must be controlled at the nano-scale level [29]. We used AFM to investigate the compatibility and morphologies of our conjugated polymer/PC₆₁BM composite films. Figure 6 displays topographic and phase-contrast images of PBTFA₁₃/PC₆₁BM composite films (1:1, 1:2, and 1:3, w/w) after annealing at 110 °C for 10 min; Figures 7 and 8 present the corresponding images of the PBTFA12/PC₆₁BM and PBTFA11/PC₆₁BM composite films (1:1, 1:2, and 1:3, w/w), respectively. The phase-contrast images reveal that the distribution of the PC₆₁BM units in the polymers was uniform for the DFBT-based PT/PC₆₁BM composite films. In each case, we observed a phase-separated interpenetrating network

Figure 6. Tapping-mode AFM (a–c) topographic and (d–f) phase images of PBTFA13 blend films [(a, d) w/w = 1:1; (b, e) w/w = 1:2; (c, f) w/w = 1:3] that had been subjected to annealing at 110 °C for 10 min

with sizable PC₆₁BM domains. Some degree of phase separation is critical for efficient formation of free

carriers to provide PSCs displaying optimal PV properties.

Figure 7. Tapping-mode AFM (a–c) topographic and (d–f) phase images of PBTF A12 blend films [(a, d) w/w = 1:1; (b, e) w/w = 1:2; (c, f) w/w = 1:3] that had been subjected to annealing at 110 °C for 10 min

Figure 8. Tapping-mode AFM (a–c) topographic and (d–f) phase images of PBTF A11 blend films [(a, d) w/w = 1:1; (b, e) w/w = 1:2; (c, f) w/w = 1:3] that had been subjected to annealing at 110 °C for 10 min

3.5. PV properties of PSCs incorporating PT/PC₆₁BM Films

We fabricated PSCs incorporating PT/PC₆₁BM and PT/PC₇₁BM blends as photoactive layers, prepared through spin-coating. Figure 9a presents the best PV performance of these PSCs; the statistic values of PCE, along with open-circuit voltages (V_{OC}), short-circuit current densities (J_{SC}), fill factors (FFs), and PCEs, are summarized in Table 3. Three runs of PV evaluation test were performed for each PSC sample. In general, high values of V_{OC} are typically obtained for PSCs fabricated from conjugated polymers having low HOMO energy levels. We found, however, that the values of V_{OC} for the PBTF13/PC₆₁BM-based PSCs were higher than those of the PBTF12/PC₆₁BM- and PBTF11/PC₆₁BM-based PSCs, even though the HOMO energy level of PBTF13 was higher than those of PBTF12 and PBTF11. This phenomenon was a result of PBTF13 having a

LUMO energy level higher than those of PBTF12 and PBTF11. Thus, there must have been a relatively strong driving force for dissociation of excitons at the BHJ interface of the PBTF13/PC₆₁BM blend. Consequently, the lower degree of charge recombination loss resulted in the relatively higher values of V_{OC} for the PSCs based on the PBTF13/PC₆₁BM blend films [55, 56]. Moreover, the values of J_{SC} of the PSCs incorporating PBTF13/PC₆₁BM blends were higher than those of the PSCs based on PBTF12/PC₆₁BM and PBTF11/PC₆₁BM. Therefore, the PV properties of the PBTF13/PC₆₁BM-based PSCs (PSC I-1–PSC I-3) were superior to those of the PBTF12/PC₆₁BM- (PSC II-1–PSC II-3) and PBTF11/PC₆₁BM-based (PSC III-1–PSC III-3) PSCs. On the other hand, the optimal compositions of PT to PC₆₁BM for the PBTF13/PC₆₁BM, PBTF12/PC₆₁BM, and PBTF11/PC₆₁BM based PSCs were approximately 1:3, 1:2, and 1:1 (w/w),

Figure 9. Current density–potential characteristics of illuminated (AM 1.5G, 100 mW/cm²) PT/PC₆₁BM- and PT/PC₇₁BM-based solar cells under the best conditions, a) PT/PC₆₁BM-based cells and b) PT/PC₇₁BM-based cells

Table 3. Photovoltaic performance of PSCs of conventional structure prepared with PT/PC₆₁BM and PT/PC₇₁BM photoactive layers

PSC*	Photoactive layer	PT/PC ₆₁ BM (or PC ₇₁ BM) [w/w]	V_{OC} [V]	J_{SC} [mA·cm ⁻²]	FF	PCE [%]	Best PCE [%]
PSC I-1	PBTF13/PC ₆₁ BM	1:1	0.52±0.02	4.25±0.03	0.38±0.02	0.84±0.02	0.86
PSC I-2	PBTF13/PC ₆₁ BM	1:2	0.56±0.03	4.21±0.02	0.40±0.02	0.94±0.03	0.97
PSC I-3	PBTF13/PC ₆₁ BM	1:3	0.58±0.03	4.72±0.03	0.46±0.01	1.27±0.05	1.32
PSC II-1	PBTF12/PC ₆₁ BM	1:1	0.49±0.02	3.74±0.03	0.34±0.01	0.62±0.04	0.66
PSC II-2	PBTF12/PC ₆₁ BM	1:2	0.54±0.02	4.30±0.01	0.35±0.02	0.81±0.06	0.87
PSC II-3	PBTF12/PC ₆₁ BM	1:3	0.51±0.01	3.20±0.02	0.35±0.02	0.57±0.02	0.59
PSC III-1	PBTF11/PC ₆₁ BM	1:1	0.56±0.02	3.77±0.03	0.36±0.03	0.76±0.03	0.79
PSC III-2	PBTF11/PC ₆₁ BM	1:2	0.49±0.02	2.80±0.02	0.35±0.02	0.48±0.02	0.49
PSC III-3	PBTF11/PC ₆₁ BM	1:3	0.48±0.03	2.68±0.01	0.31±0.03	0.40±0.03	0.41
PSC IV	PBTF13/PC ₇₁ BM	1:3	0.64±0.03	8.65±0.02	0.39±0.02	2.17±0.03	2.20
PSC V	PBTF12/PC ₇₁ BM	1:2	0.61±0.02	7.25±0.03	0.40±0.01	1.77±0.02	1.79
PSC VI	PBTF11/PC ₇₁ BM	1:1	0.59±0.02	6.23±0.02	0.38±0.02	1.40±0.03	1.43

*PV properties of illuminated (AM1.5 solar simulator, 100 mW·cm⁻²) PT/PC₆₁BM and PT/PC₇₁BM-based PSCs.

respectively. The optimal content of PC₆₁BM seemed to be related to the content of electron-deficient DFBT units in the PT backbone. PBTF A11, which had a relatively high DFBT content, required a lower PC₆₁BM content to achieve the best PV performance.

In an attempt to further improve the PV performance of the PT-based PSCs, we introduced PC₇₁BM as the electron acceptor in the photoactive layer of the PSCs. Figure 9b presents the photocurrent density–

voltage plots of the PSCs incorporating PBTF A13/PC₇₁BM (w/w = 1:3), PBTF A12/PC₇₁BM (w/w = 1:2), and PBTF A11/PC₇₁BM (w/w = 1:1) blends (PSC IV–PSC VI, respectively). Table 3 summarizes the PV properties of these PSCs. PV properties of the PSCs based on the PT/PC₇₁BM blend films were superior to those of the PSCs based on the PT/PC₆₁BM blend films, because of the stronger and broader absorption of PC₇₁BM in the visible region

Figure 10. Tapping-mode AFM (a–c) topographic and (d–f) phase images of PT blend films [(a, d) PBTF A11/PC₇₁BM (w/w = 1:1); (b, e) PBTF A12/PC₇₁BM (w/w = 1:2); (c, f) PBTF A13/PC₇₁BM (w/w = 1:3)] that had been subjected to annealing at 110 °C for 10 min

[29]. Moreover, the values of J_{SC} and PCE of the PBTF A13/PC₇₁BM- and PBTF A12/PC₇₁BM-based PSCs were higher than those of the PBTF A11/PC₇₁BM-blend PSCs. The AFM images in Figure 10 indicate that phase-separated interpenetrating networks with sizable domains were formed in the photoactive layers for the PT/PC₇₁BM blend films. Moreover, the phase separation for the PBTF A13/PC₇₁BM blend film was more obvious than that for the PBTF A12/PC₇₁BM and PBTF A11/PC₇₁BM blend

Figure 11. TEM images of (a) PBTF A11/PC₇₁BM (w/w = 1:1), (b) PBTF A12/PC₇₁BM (w/w = 1:2), and (c) PBTF A13/PC₇₁BM (w/w = 1:3) blend films that had been subjected to annealing at 110 °C for 10 min

films. We recorded TEM images (Figure 11) to further characterize the distribution of PC₇₁BM in the PT/PC₇₁BM films. The dark areas in the images represent PC₇₁BM domains, because the electron-scattering density of PC₇₁BM was greater than that of the conjugated polymers. The presence of phase-separated interpenetrating networks with sizable domains in the photoactive layer was confirmed for the PBTF A13/PC₇₁BM and PBTF A12/PC₇₁BM blend films. In contrast, the phase separation on the nano-scale was insignificant for the PBTF A11/PC₇₁BM blend film, presumably because of the low content of PC₇₁BM. Apart from that, the external quantum efficiency (EQE) spectra of these PT/PC₇₁BM based PSCs recorded under monochromatic irradiation are shown in Figure 12. The partial photo-response at a wavelength near 350 nm was contributed by the absorption of PC₇₁BM [22]. The maximal EQE value of PBTF A13 based PSC was higher than those of PBTF A11 and PBTF A12 based PSCs. As a result, the PV properties of the PSC featuring the PBTF A13/PC₇₁BM blend film were superior to those of the PSCs based on the PBTF A11/PC₇₁BM and PBTF A12/PC₇₁BM blend films.

4. Conclusions

We have synthesized three 2-D PTs (PBTF A13, PBTF A12, PBTF A11) featuring an electron-deficient DFBT derivative as the conjugated units in the polymer backbone and *t*TPA-containing moieties as pendant units. The incorporation of these moieties enhanced the conjugation effect within the extended conjugated frameworks of the polymers. The light absorption ability of the PTs was dependent upon the molar ratio of the electron-donating *t*TPA-based pendant units and the electron-withdrawing DFBT units

Figure 12. EQE spectra of PT/PC₇₁BM-based solar cells under the best conditions

in the polymer chains. The PV performance of the PBTF13-based PSCs was superior to that of the PBTF12- and PBTF11-based PSCs.

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