

Novel 4,7-Dithien-2-yl-2,1,3-benzothiadiazole-based Conjugated Copolymers with Cyano Group in Vinylene Unit for Photovoltaic Applications

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Two novel conjugated copolymers utilizing 4,7-dithien-2-yl-2,1,3-benzothiadiazole (DTBT) coupled with cyano (-CN) substituted vinylene, as the electron deficient moiety, have been synthesized and evaluated in bulk heterojunction solar cell. The electron deficient moiety was coupled with carbazole and fluorene unit by Knoevenagel condition to provide poly(bis-2,7-((Z)-1-cyano-2-(5-(7-(2-thienyl)-2,1,3-benzothiadiazol-4-yl)-2-thienyl)ethenyl)-*alt*-9-(1-octylonyl)-9*H*-carbazol-2-yl-2-butenenitrile) (PCVCNDTBT) and poly(bis-2,7-((Z)-1-cyano-2-(5-(7-(2-thienyl)-2,1,3-benzothiadiazol-4-yl)-2-thienyl)ethenyl)-*alt*-9,9-dihexyl-9*H*-fluoren-2-yl) (PFVCNDTBT). The optical band gaps of PCVCNDTBT (1.74 eV) and PFVCNDTBT (1.80 eV) are lower than those of PCDTBT (1.88 eV) and PFVDTBT (2.13 eV), which is advantageous to provide better coverage of the solar spectrum in the longer wavelength region. The high V_{oc} value of the PSC of PCVCNDTBT (~ 0.91 V) is attributed to its lower HOMO energy level (-5.6 eV) as compared to PCDTBT (-5.5 eV). Bulk heterojunction solar cells based on the blends of the polymers with [6,6]phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) gave power conversion efficiencies of 0.76% for PCVCNDTBT under AM 1.5, 100 mW/cm².

Key Words : Carbazole, Benzothiadiazole, Alternating copolymer

Introduction

Polymer solar cells (PSCs) have raised much interest for the development of desirable future energy source, as they have properties of low-cost, lightweight, solution-processability and flexibility. The most common type of polymer solar cell is employing bulk heterojunction (BHJ) active layer which is composed of a blend of electron-donating conjugated polymer, and electron-accepting material such as (6,6)-phenyl C₆₁-butyric acid methyl ester (PC₆₁BM). Many new conjugated polymers with low band gaps are being researched for PSCs to cover the long wave-length region for the improvement of total photovoltaic current.¹⁻⁶

For the generation of efficient intra-molecular charge transfer (ICT),⁷ 4,7-dithien-2-yl-2,1,3-benzothiadiazole (DTBT) unit has been used extensively as the electron deficient moiety, and copolymerized with many kinds of electron rich segments, such as fluorene,^{8,9} silafluorene,^{10,11} carbazole,¹² dithienosilole,¹³ and cyclopenta[2,1-*b*:3,4-*b'*]dithiophene.¹⁴ Especially, 2,7-carbazole derivatives have been successfully used in polymer solar cells to provide high power conversion efficiency (PCE) up to 6.0% power conversion efficiency, one of the highest certified value by National Renewable Energy Laboratory (NREL) reported to date.¹⁵

It is reported that the bandgaps of the polymers were reduced by increasing the ratio of the vinylene groups to

thiophene unit and incorporation of cyano group in the vinylene units.^{16,17} The utilization of the cyano substituted vinylene unit coupled with DTBT moiety can provide effective electron deficient unit for the ICT.

In this paper, we report the synthesis and photovoltaic properties of poly(bis-2,7-((Z)-1-cyano-2-(5-(7-(2-thienyl)-2,1,3-benzothiadiazol-4-yl)-2-thienyl)ethenyl)-*alt*-9-(1-octylonyl)-9*H*-carbazol-2-yl-2-butenenitrile) (PCVCNDTBT), which has cyano substituted vinylene units between the DTBT and carbazole unit of PCDTBT. By utilization of the effective ICT of the cyano substituted vinylene unit, this new polymer, PCVCNDTBT, can provide lower optical bandgap as compared to PCDTBT. In addition to this, the effective electron withdrawing ability of the cyano group can lower the HOMO energy level of PCVCNDTBT as compared to PCDTBT, which will increase the V_{oc} value of the device. Poly(bis-2,7-((Z)-1-cyano-2-(5-(7-(2-thienyl)-2,1,3-benzothiadiazol-4-yl)-2-thienyl)ethenyl)-*alt*-9,9-dihexyl-9*H*-fluoren-2-yl) (PFVCNDTBT) was also synthesized to reduce the band gap of PFVDTBT.

Experimental

Materials and Instruments. ¹H and ¹³C NMR spectra were recorded with a Varian Gemini-300 (300 MHz) spectrometer and chemical shifts were recorded in ppm units with

TMS as the internal standard. Flash column chromatography was performed with Merck silica gel 60 (particle size 230-400 mesh ASTM) and ethyl acetate/hexane or methanol/methylene chloride gradients unless otherwise indicated. Analytical thin layer chromatography (TLC) was conducted using Merck 0.25 mm silica gel 60F pre-coated aluminum plates with fluorescent indicator UV254. UV spectra were recorded with a Varian CARY-5E UV/vis spectrophotometer. Cyclic voltammetric waves were produced by using a EG&G Parc model 273 potentiostat/galvanostat. The differential scanning calorimetry analysis was performed under a nitrogen atmosphere (50 mL/min) on a DSC 822 at heating rates of 10 °C/min. Thermo gravimetric analysis was performed with a Dupont 951 TGA instrument in a nitrogen atmosphere at a heating rate of 10 °C/min to 700 °C. High resolution mass spectra (HRMS) were recorded on a JEOL JMS-700 mass spectrometer under fast atom bombardment (FAB) conditions in the Korea Basic Science Institute Daegu Branch. Solar cells with the configurations of indium tin oxide (ITO)/poly(3,4-ethylenedioxyethyniophene):polystyrene sulfonic acid (PEDOT:PSS)/polymer:PC₆₁BM/Al were fabricated. Before the fabrications of the devices, the ITO-coated glass substrate was cleaned by ultrasonic treatment using detergent, deionized water, acetone, and isopropyl alcohol in sequence and dried in an oven for 24 h. The PEDOT:PSS (Clevios PH) was spin-cast at 4000 rpm for 40 s, and then dried at 140 °C for 10 min in air. On top of PEDOT:PSS layer, solution of 1 wt % polymer:PC₆₁BM (1:2 w/w) in 1,2-dichlorobenzene was spin-coated at 1000 rpm in a N₂-filled glove box. Top electrode (Al) was deposited on the active layer in a vacuum (< 10⁻⁷ Torr) thermal evaporator. A titanium oxide (TiO_x) precursor solution was prepared using the sol-gel method.¹⁸ The TiO_x precursor solution was spin-cast on cleaned FTO substrates after a UV-ozone treatment for 10 min and heated at 80 °C for 10 min in air for conversion to TiO_x by hydrolysis. Current density-voltage (*J-V*) characteristics of the devices were measured using a Keithley 2635A Source Measure Unit. Solar cell performance was measured with an Air Mass 1.5 Global (AM 1.5 G) solar simulator with an irradiation intensity of 100 mW cm⁻². The hole mobility can be calculated from the space-charge-limited current (SCLC) by Eqn. (1).

$$J_{\text{SCLC}} = 9/8 \epsilon_r \epsilon_0 \mu (V^2/L^3) \quad (1)$$

where ϵ_r is the dielectric constant of the material, ϵ_0 is the permittivity of free space, μ is the carrier mobility constant of the material, L is the distance between the cathode and anode, which is equivalent to the film thickness, and V is the applied voltage. Atom force microscopy (AFM) measurements were obtained with a Veeco NanoScope IIIa AFM at room temperature. Commercial silicon cantilevers (Veeco) with typical spring constants of 21-78 N m⁻¹ was used to operate the AFM in tapping mode. Images were taken continuously with the scan rate 2.0 Hz.

All reagents were purchased from Aldrich or TCI, and used without further purification. Solvents were purified by normal procedure and handled under moisture-free atmosphere.

2,7-Dibromo-9-(1-octylonyl)-9*H*-carbazole (**1**),¹¹ 5,5'-(2,1,3-benzothiadiazole-4,7-diyl)bis-2-thiophenecarboxaldehyde (**6**),¹⁹ and 9,9-dihexyl-9*H*-fluorene-2,7-diacetonitrile (**8**)²⁰ were synthesized using similar methods reported.

Synthesis of 9-(1-Octylonyl)-9*H*-carbazole-2,7-dicarbaldehyde (2). 2,7-Dibromo-9-(1-octylonyl)-9*H*-carbazole (**1**) (20 g, 36 mmol) in THF (200 mL) was treated with 1.6 M *n*-BuLi in hexane at -78 °C under argon. After 1 h at -78 °C, the temperature was warmed to room temperature and the reaction mixture was stirred for 30 min. Then the reaction mixture was cooled to -78 °C again and 10 mL (130 mmol) of *N,N'*-dimethylformamide (DMF) was added. The reaction mixture was gradually warmed to room temperature and stirred overnight. The reaction mixture was diluted with 200 mL of ether and washed with 3 × 150 mL of water. The organic phase was dried (MgSO₄), and after removal of the solvent under reduced pressure, flash column chromatography provided 7.0 g (43%) of compound **2**, a yellow solid: *R*_f 0.35 (33% ethyl acetate/*n*-hexane). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 10.18 (s, 2 H), 8.31 (m, 2 H), 8.15 (s, 1 H), 8.02 (s, 1 H), 7.82 (d, 2 H, *J* = 7.5 Hz), 4.76-4.68 (m, 1 H), 2.36-2.26 (m, 2 H), 2.07-1.97 (m, 2 H), 1.22-1.11 (m, 24 H), 0.83 (t, 6 H, *J* = 6.9 Hz). ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 192.73, 143.43, 140.00, 135.44, 134.96, 128.04, 126.66, 122.18, 121.37, 113.43, 110.78, 57.64, 33.97, 31.92, 29.63, 29.48, 29.31, 27.03, 25.14, 22.80, 14.30. IR (KBr) ν 2951.5, 2925.2, 2852.3, 2723.1, 1687.5, 1566.2, 1230.9, 812.4 cm⁻¹. HRMS (*m/z*, FAB⁺) Calcd for C₃₁H₄₃NO₂ 461.3294, Found 461.3286.

Synthesis of 2,7-Bis(hydroxymethyl)-9-(1-octylonyl)-9*H*-carbazole (3). 9-(1-Octylonyl)-9*H*-carbazole-2,7-dicarbaldehyde (**2**) (6 g, 13 mmol) and NaBH₄ (3 g, 79 mmol) were dissolved in methanol (200 mL) at 0 °C under argon. After being stirred for 1 h at 0 °C, the temperature was warmed to room temperature and the reaction mixture was stirred for 5 h. Then the solvent was removed and the organic residue was diluted with 200 mL of ethyl acetate and washed with 3 × 100 mL of water. The organic phase was dried (MgSO₄), and after removal of the solvent under reduced pressure, flash column chromatography provided 4.4 g (73%) of compound **3**, a yellow solid: *R*_f 0.23 (100% ethyl acetate). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 8.10 (t, 2 H, *J* = 9.6 Hz), 7.59 (s, 1 H), 7.44 (s, 1 H), 7.25 (t, 2 H, *J* = 9.3 Hz), 4.90 (d, 4 H, *J* = 4.8 Hz), 4.62-4.54 (m, 1 H), 2.29-2.24 (m, 2 H), 1.98-1.90 (m, 2 H), 1.29-1.02 (m, 24 H), 0.85 (t, 6 H, *J* = 5.7 Hz). ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 142.73, 139.32, 138.82, 138.31, 123.45, 122.00, 120.69, 120.41, 118.19, 118.08, 110.42, 107.67, 66.53, 56.78, 33.90, 32.02, 29.69, 29.59, 29.45, 27.14, 22.86, 14.35. IR (KBr) ν 3289.0, 2949.0, 2924.0, 2853.8, 1604.6, 1456.7, 1437.4, 1241.2, 1032.3, 708.5 cm⁻¹. HRMS (*m/z*, FAB⁺) Calcd for C₃₁H₄₇NO₂ 465.3607, Found 465.3609.

Synthesis of 2,7-Bis(bromomethyl)-9-(1-octylonyl)-9*H*-carbazole (4). 2,7-Bis(hydroxymethyl)-9-(1-octylonyl)-9*H*-carbazole (**3**) (4.3 g, 9.2 mmol) in benzene (50 mL) was treated with PBr₃ (2.6 mL, 28 mmol) at 0 °C under argon. After stirring for 6 h at 45 °C, the reaction mixture was cooled to room temperature and diluted with 30 mL of

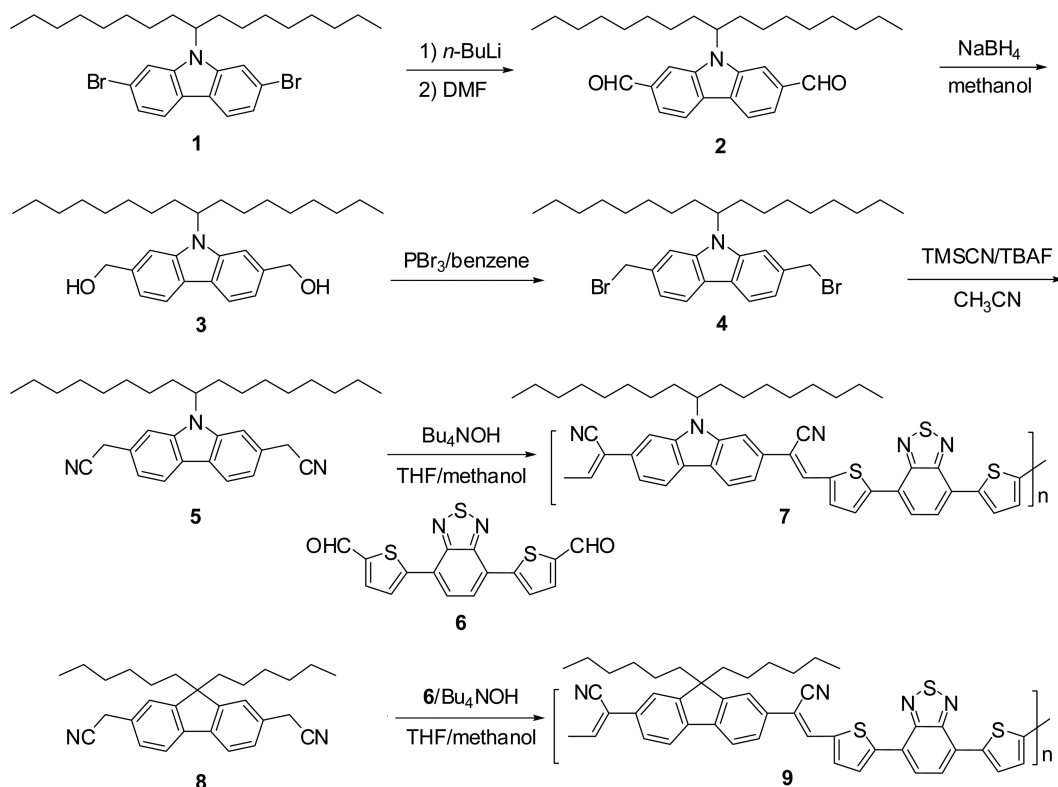
water. The aqueous layer was separated and extracted with 3 × 50 mL of CHCl₃. The combined organic layer was dried (MgSO₄) and concentrated. The oily residue, 2,7-bis(bromomethyl)-9-(1-octylnonyl)-9*H*-carbazole (**4**), was used in next step without purification, since the compound was very unstable in ambient condition.

Synthesis of 2,7-Bis(cyanomethyl)-9-(1-octylnonyl)-9*H*-carbazole (5**).** Crude 2,7-bis(bromomethyl)-9-(1-octylnonyl)-9*H*-carbazole (**4**), trimethylsilyl cyanide (5 mL, 37 mmol) and tetrabutylammonium fluoride (TBAF) (37 mL, 37 mmol) were dissolved in acetonitrile (50 mL). After being stirred for 5 h, the reaction mixture was diluted with 200 mL of ethyl acetate and washed with 3 × 100 mL of water. The organic phase was dried (MgSO₄), and after removal of the solvent under reduced pressure, flash column chromatography provided 1.4 g (37%) of compound **5**, a yellow solid (17% ethyl acetate/*n*-hexane). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 8.10 (t, 2 H, *J* = 9.1 Hz), 7.57 (s, 1 H), 7.41 (s, 1 H), 7.20 (t, 2 H, *J* = 9.1 Hz), 4.59-4.56 (m, 1 H), 3.99 (s, 4 H), 2.30-2.27 (m, 2 H), 2.01-1.93 (m, 2 H), 1.21-0.96 (m, 24 H), 0.86 (t, 6 H, *J* = 6.8 Hz). ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 142.84, 139.42, 127.90, 127.44, 123.31, 121.90, 121.39, 121.11, 119.11, 118.63, 111.23, 108.61, 57.03, 33.90, 32.02, 29.63, 29.57, 29.42, 27.05, 24.60, 22.58, 14.38. IR (KBr) ν 2950.1, 2923.9, 2852.7, 2248.7, 1602.4, 1465.9, 795.2 cm⁻¹. HRMS (*m/z*, FAB⁺) Calcd for C₃₃H₄₅N₃ 483.3613, Found 483.3618.

Synthesis of Poly(bis-2,7-((*Z*)-1-cyano-2-(5-(7-(2-thienyl)-2,1,3-benzothiadiazol-4-yl)-2-thienyl)ethenyl)-*alt*-9,9-(1-

octylnonyl)-9*H*-carbazol-2-yl-2-butenedinitrile) (7**).** The compound **5** (0.35 g, 0.72 mmol) and 5,5'-(2,1,3-benzothiadiazole-4,7-diyl)bis-2-thiophenecarboxaldehyde (**6**) (0.26 g, 0.72 mmol) in THF (20 mL) and MeOH (10 mL) were treated with 1 M Bu₄NOH (0.36 mL, 0.36 mmol) at 65-66 °C under argon. The reaction mixture was further heated at 70 °C for 2 days. After cooling to room temperature, the reaction mixture was poured into the solution of 100 mL of acetone and 300 mL of methanol. The precipitate was dissolved with minimum amount of chloroform, and poured into the 300 mL of methanol. After filtration, the precipitate was purified by Soxhlet extraction with methanol and dried in vacuum for 24 h to generate 68 mg of polymer PCVCNDTBT (**7**).

Synthesis of Poly(bis-2,7-((*Z*)-1-cyano-2-(5-(7-(2-thienyl)-2,1,3-benzothiadiazol-4-yl)-2-thienyl)ethenyl)-*alt*-9,9-dihexyl-9*H*-fluoren-2-yl) (9**).** The compound **6** (0.18 g, 0.52 mmol) and 9,9-dihexyl-9*H*-fluorene-2,7-diacetonitrile (**8**) (0.21 g, 0.52 mmol) in THF (20 mL) and MeOH (10 mL) were treated with 1 M Bu₄NOH (0.26 mL, 0.26 mmol) at 65-66 °C under argon. The reaction mixture was further heated at 70 °C for 2 days. After cooling to room temperature, the reaction mixture was poured into the solution of 100 mL of acetone and 300 mL of methanol. The precipitate was dissolved with minimum amount of chloroform, and poured into the 300 mL of methanol. After filtration, the precipitate was purified by Soxhlet extraction with methanol and dried in vacuum for 24 h to generate 50 mg of polymer (PFVCNDTBT) (**9**).



Scheme 1. Synthetic routes for the monomers and the polymers.

Results and Discussion

Synthesis and Characterization. The general synthetic routes toward the monomers and polymers are outlined in Scheme 1. 2,7-Dibromo-9-(1-octylonyl)-9*H*-carbazole (**1**) was formylated in THF using *n*-BuLi and DMF to afford 9-(1-octylonyl)-9*H*-carbazole-2,7-dicarbaldehyde (**2**), which was treated with NaBH₄ to generate 2,7-bis(hydroxymethyl)-9-(1-octylonyl)-9*H*-carbazole (**3**). The diol **3** was brominated with PBr₃ in benzene to generate 2,7-bis(bromomethyl)-9-(1-octylonyl)-9*H*-carbazole (**4**). The resulting dibromide **4** was cyanized with trimethylsilyl cyanide by the nucleophilic substitution reaction to give 2,7-bis(cyanomethyl)-9-(1-octylonyl)-9*H*-carbazole (**5**). Alternating copolymers, PCVCNDTBT (**7**) and PFVCNDTBT (**9**), were obtained under Knoevenagel condensation, using 5,5'-(2,1,3-benzothiadiazole-4,7-diyl)bis-2-thiophenecarboxaldehyde (**6**) and tetrabutylammonium hydroxide as catalyst at 65 °C.

As shown in Table 1, the number-average molecular weight (M_n) and the weight-average molecular weight (M_w) of the PCVCNDTBT were 4,000 and 5,400, respectively, with polydispersity index of 1.4. M_n and M_w of PFVCNDTBT were 8,400 and 13,000 with polydispersity index of 1.5. The thermal properties of the polymer were evaluated by differential scanning calorimetry (DSC) and thermo gravimetric analysis (TGA) in nitrogen. High thermal stability is required to prevent the degradation of polymers in photovoltaic devices upon annealing. PCVCNDTBT shows lose less than 5% of its weight on heating to 367 °C. Glass transition temperature measured by DSC under N₂ was 78 °C. PFVCNDTBT shows lose less than 5% of its weight on heating up to 428 °C. Glass transition temperature measured by DSC under N₂ was 72 °C. The high thermal stability of the resulting polymers prevents the deformation of the polymer morphology and is important for organic photovoltaics application. PCVCNDTBT was soluble in organic solvents such as chloroform, tetrahydrofuran, dichloromethane and chlorobenzene, but PFVCNDTBT was insoluble in common organic solvents. Because DTBT with CN group in vinylene unit, very rigid and flat structure, provides low solubility, PFVCNDTBT with dihexyl unit, shorter alkyl chain as compared octadecane in PCVCNDTBT, wasn't soluble in common organic environment.

Optical Properties. All spectroscopic properties were measured both in THF solutions and as thin films on glass slides. The UV-vis absorption spectra of the polymers in THF solution and in thin film are presented in Figure 1. As

Table 1. Characterization of the polymers

Copolymers	M_n^a	M_w^a	M_w/M_n^a	T_g^b (°C)	T_d^c (°C)
PCVCNDTBT	4,000	5,400	1.4	78	367
PFVCNDTBT	8,400	13,000	1.5	72	428

^aThe number-average molecular weight (M_n) and the weight-average molecular weight (M_w) were determined by GPC in THF using a calibration curve of polystyrene as the standard. ^bGlass transition temperature determined by DSC. ^cDecomposition temperature corresponding to 5% weight loss in N₂ determined by TGA.

shown in Figure 1(a), PCVCNDTBT shows absorption maxima at 404 and 535 nm and PFVCNDTBT shows similar absorption maxima at 408 and 534 nm, in THF solution. As shown Figure 1(b), PCVCNDTBT shows the maximum absorption peaks at 425 and 561 nm and PFVCNDTBT exhibits the maximum absorption peaks at 431 and 570 nm, in solid state. The second absorption maxima of the solid thin films exhibit red shifts (26–36 nm) as compared to the corresponding peaks in dilute solutions. The maximum absorption peak of PFVCNDTBT is 120 nm red-shifted as compare to the known poly(flourenevinylene-alt-4,7-dithien-2-yl-2,1,3-benzothiadiazole) (PFVDTBT),²¹ which lacks only the cyano group as compared to our PFVCNDTBT. This big red shift can be attributed to the efficient ICT by the introduction of the cyano group in PFVCNDTBT.

Electrochemical Properties. The LUMO energy levels of the polymers were determined from the band gaps which were estimated from the absorption edges, and the HOMO energy levels which were estimated from the cyclic voltammetry.²² The CVs were performed with a solution of tetrabutylammonium tetrafluoroborate (Bu₄NBF₄) (0.10 M) in acetonitrile at a scan rate of 80 mV/s at room temperature. Polymer films were prepared by dipping platinum working electrodes into the polymer solution, which was prepared with minimum amount of THF, and then air-drying. A

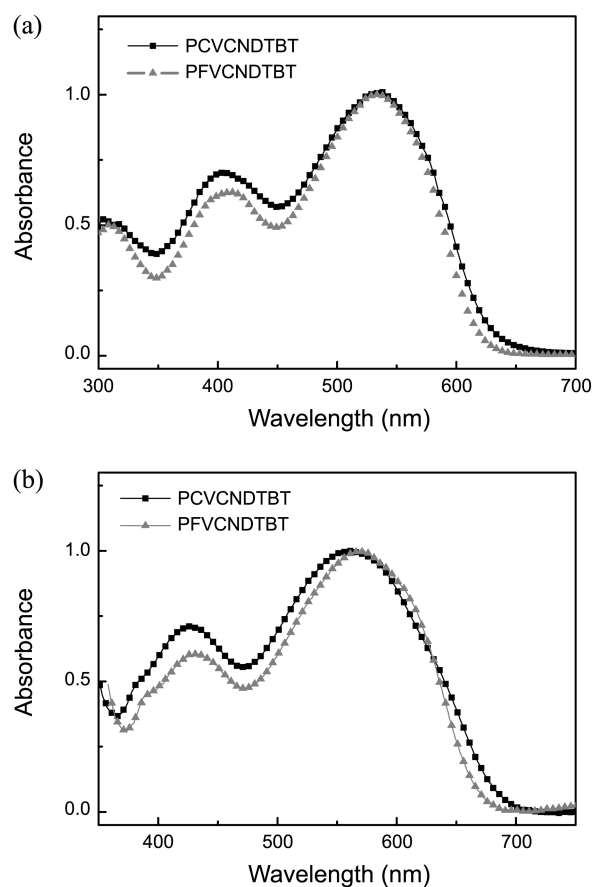


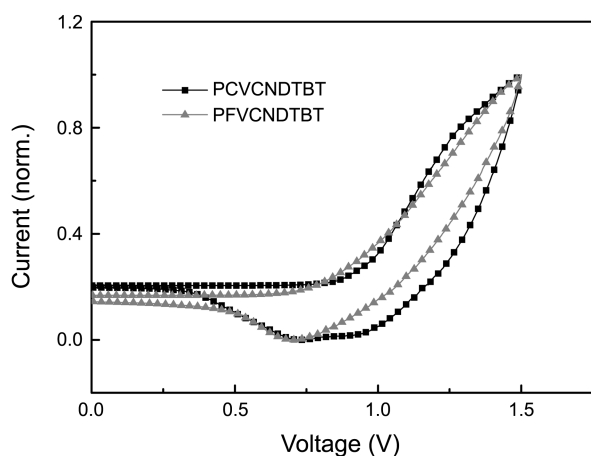
Figure 1. The normalized UV-visible absorption spectra of PCVCNDTBT and PFVCNDTBT (a) in THF solution and (b) in thin film.

Table 2. Electrochemical potentials and energy levels of the polymers

Polymers	E_{onset}^a (V)	HOMO ^b (eV)	LUMO ^c (eV)	E_g^d (eV)
PCVCNDTBT	0.81	-5.57	-3.83	1.74
PFVCNDTBT	0.59	-5.35	-3.55	1.80

^aOnset oxidation potentials measured by cyclic voltammetry. ^bCalculated from the oxidation potentials. ^cCalculated from the HOMO energy levels and E_g . ^dEnergy band gaps were estimated from the onset wavelengths of the optical absorption.

platinum wire and an Ag/AgNO₃ electrode were used as the counter electrode and reference electrode, respectively. The energy level of the Ag/AgNO₃ reference electrode (calibrated by the FC/FC⁺ redox system) was 4.76 eV below the vacuum level. The oxidation potentials derived from the onset of electrochemical p-doping are summarized in Table 2. HOMO levels were calculated according to the empirical formula $E_{\text{HOMO}} = -([E_{\text{onset}}]^{\text{ox}} + 4.76)$ (eV).^{22,23} During the anodic scan, the oxidation onset potential of PCVCNDTBT was 0.81 V and exhibited irreversible p-doping process, which provides the HOMO energy level of the polymer to be -5.57 eV. The absorption onset wavelength is 712 nm, which corresponds to band gap of 1.74 eV. The LUMO energy level, calculated from the value of the band gap and HOMO energy level, was -3.83 eV. The oxidation onset potential of PFVCNDTBT was 0.59 V and exhibited irreversible p-doping process, which provides the HOMO energy level to be -5.35 eV. The absorption onset wavelength was 689 nm, which correspond to band gap of 1.80 eV. The LUMO energy level, calculated from the value of the band gap and HOMO energy level, was -3.55 eV. The HOMO energy level of PCVCNDTBT is lower than of PCDTBT, which may enhance the V_{oc} value of the PSCs. The optical band gaps of PCVCNDTBT (1.74 eV) and PFVCNDTBT (1.80 eV) are lower than those of PCDTBT (1.88 eV) and PFVDTBT (2.13 eV), which is advantageous to provide

**Figure 2.** Cyclic voltammograms of the polymers recorded from thin films coated onto platinum wire electrodes in an electrolyte solution of Bu₄NBF₄ (0.10 M) in acetonitrile with a reference electrode of Ag/AgNO₃ (0.10 M) at room temperature. Scan rate = 80 mV/s.

better coverage of the solar spectrum in the longer wavelength region.

Photovoltaic Cell Characteristics. The current-voltage characteristics of the solar cells, under simulated 100 mW/cm² AM 1.5 G white light illumination, based on the blend of PCVCNDTBT/PC₆₁BM are shown in Figure 3. Table 3 lists the photovoltaic properties obtained from the J - V curves

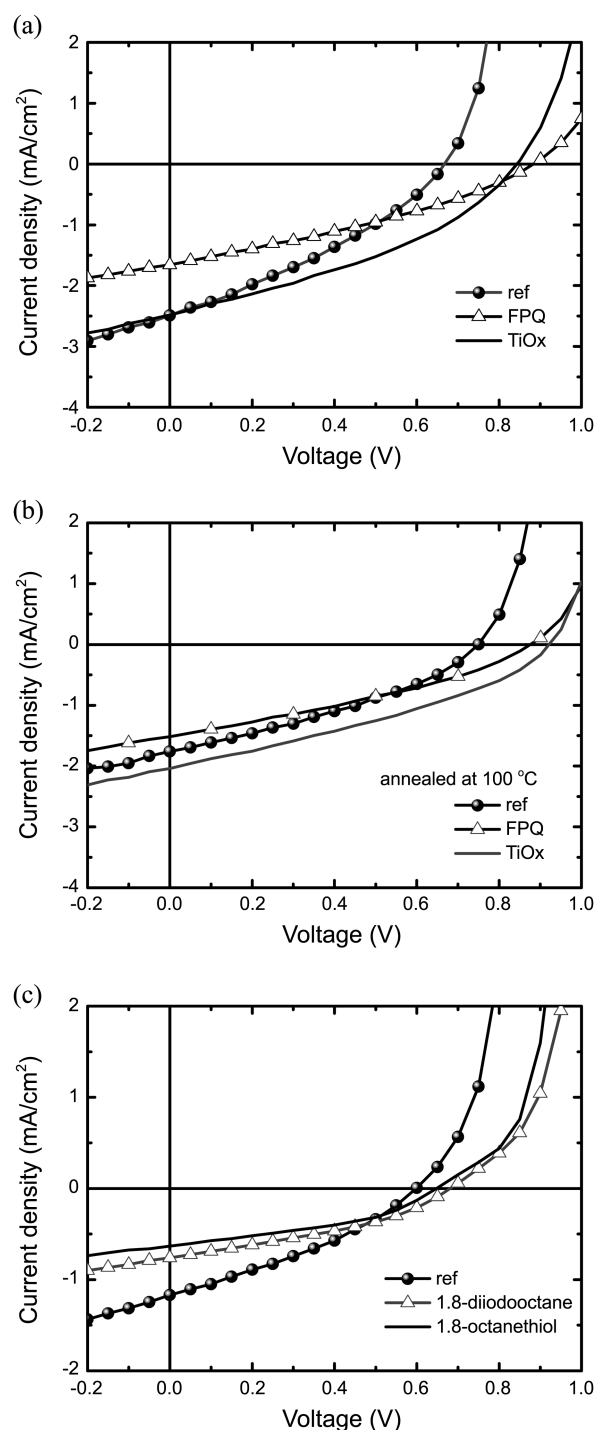
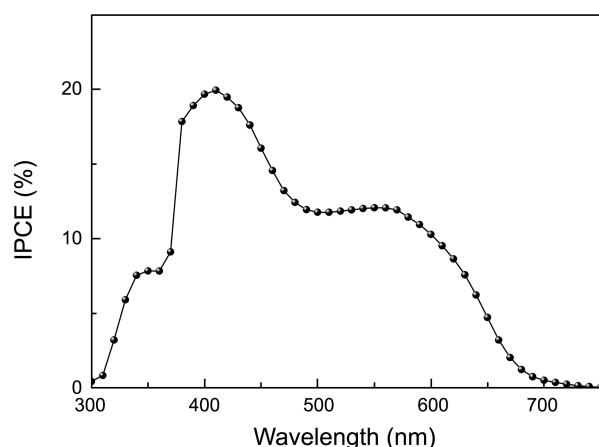
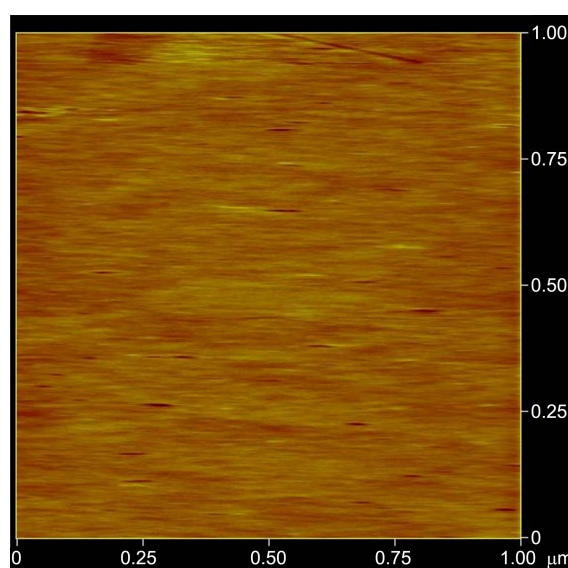
**Figure 3.** Current-voltage characteristics of polymer:PC₆₁BM (1:2 w/w) bulk-heterojunction solar cells under white light illumination (AM 1.5 conditions). J - V curves of the devices (a) fabricated with TiOx and FPQ, (b) annealed at 100 °C and (c) treated with additives.

Table 3. Photovoltaic performances of the device with the configuration of ITO/PEDOT:PSS/PCVCNDTBT:PC₆₁BM /TiO_x(FPQ)/Al

Polymer:PC ₆₁ BM (1:2 w/w)	Annealing temp. (°C)	Additives	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	Eff. (%)
-	-	-	2.49	0.67	0.33	0.55
with TiO _x	-	-	2.48	0.84	0.36	0.76
with FPQ	-	-	1.66	0.88	0.33	0.48
-	100	-	1.73	0.75	0.35	0.46
with TiO _x	100	-	2.19	0.91	0.34	0.67
with FPQ	100	-	1.52	0.88	0.33	0.43
-	-	1,8-diiodooctane	0.76	0.68	0.36	0.19
-	100	1,8-diiodooctane	0.69	0.68	0.37	0.18
-	-	1,8-octanedithiol	0.69	0.68	0.37	0.18
-	100	1,8-octanedithiol	0.60	0.70	0.38	0.16

for the devices with the configuration of ITO/PEDOT:PSS/copolymer:PC₆₁BM (1:2, w/w)/TiO_x/Al. The device without TiO_x layer showed an open-circuit voltage (V_{oc}) of 0.67 V, a short-circuit current density (J_{sc}) of 2.5 mA/cm², and a fill factor (FF) of 0.33, giving a power conversion efficiency of 0.55%. The device with poly(9,9'-bis(6"-N,N,N-trimethylammoniumhexyl)fluorene-*alt*-phenylene) (FPQ) layer showed a V_{oc} of 0.88 V, a J_{sc} of 1.66 mA/cm², and a FF of 0.33, giving a power conversion efficiency of 0.48%, diminished property as compare to basic device. The device with TiO_x layer demonstrated a V_{oc} value of 0.84 V, a J_{sc} value of 2.5 mA/cm², and a FF of 0.36, leading to the power conversion efficiency of 0.76%, a slightly improved performance as compare to the case without TiO_x layer. The V_{oc} value of the device with TiO_x layer is higher than that of the device without TiO_x layer, which is attributed to electron-transporting ability of the TiO_x layer.¹⁸ PFVCNDTBT showed very low solubility to provide much difficulty to have spin-coating and no meaningful photovoltaic characteristics were obtained.

As illustrated in Figure 4, the incident photon to current efficiency (IPCE) of the PSCs, for the best device as a function of wavelength, shows the maximum of 20% at 410 nm. The significant absorbance of the conjugated polymers up to 700 nm contributed to the total photovoltaic current because the solar photon flux is significant in this wavelength range.^{24,25} The AFM topographies of the polymer

**Figure 4.** The IPCE spectra of photovoltaic devices with the configuration of ITO/PEDOT:PSS/polymer:PC₆₁BM(1:2)/Al.**Figure 5.** Tapping mode AFM topographic image at 0-10 nm height scale for polymer/PC₆₁BM (1:4) blend film.

blend (PCVCNDTBT:PC₆₁BM=1:2 w/w) was presented in Figure 5, where the images were obtained in a surface area of $1 \times 1 \mu\text{m}^2$ by the tapping mode. The root mean square surface roughness (rms) of the polymer films is 0.32 nm.

Since it is believed that the charge carrier mobility is very important to J_{sc} , we measured the hole mobility of the PCVCNDTBT:PC₆₁BM blend films by space charge limited current (SCLC) method.²⁶ The device with the configuration of ITO/PEDOT/PCVCNDTBT:PC₆₁BM/Al was fabricated. The hole mobility of PCVCNDTBT was measured to be $5.86 \times 10^{-7} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is quite lower than the optimum value, by around $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.²⁷

Conclusion

In conclusion, two alternating copolymers, PCVCNDTBT and PFVCNDTBT, with electron rich unit and electron deficient moiety for the efficient ICT were synthesized by Knoevenagel coupling polymerization and characterized. The high V_{oc} value of the PSC of PCVCNDTBT (~ 0.91 V) is attributed to its lower HOMO energy level (-5.6 eV) as compared to PCDTBT (-5.5 eV). The optical band gaps of

PCVCNDTBT (1.74 eV) and PFVCNDTBT (1.80 eV) are lower than those of PCDTBT (1.88 eV) and PFVDTBT (2.32 eV), which is advantageous to provide better coverage of the solar spectrum in the longer wavelength region. Bulk heterojunction solar cells based on blends of the polymer with PC₆₁BM gave power conversion efficiency of 0.76% for PCVCNDTBT under AM 1.5, 100 mW/cm².

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