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-octylnonyl))-9H-carbazol-2-yl-2-butenenitrile) (PCVNDTBT) 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-diheptyl-9H-fluoren-2-yl) (PFVCDTBTT). The optical band gaps of PCVNDTBT (1.74 eV) and PFVCDTBT (1.80 eV) are lower than those of PCDTBT (1.88 eV) and PFVDTBTT (2.13 eV), which is advantageous to provide better coverage of the solar spectrum in the longer wavelength region. The high *F* value of the PSC of PCVNDTBT (~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-C₆BM) gave power conversion efficiencies of 0.76% for PCVNDTBT 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 (BJH) active layer which is composed of a blend of electron-donating conjugated polymer, and electron-accepting material such as carbazole, dithienosilole, and cyclopenta[2,1-b:3,4-b]dithiophene. 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.

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. 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-octylnonyl))-9H-carbazol-2-yl-2-butenenitrile) (PCVNDTBT), which has cyano substituted vinylene units between the DTBT and carbazole unit of PCDTBT. By utilizing of the effective ICT of the cyano substituted vinylene unit, this new polymer, PCVNDTBT, 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 PCVNDTBT as compared to PCDTBT, which will increase the *F* 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-diheptyl-9H-fluoren-2-yl) (PFVCDTBT) was also synthesized to reduce the band gap of PFVDTBTT.

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
Keithley 2635A Source Measure Unit. Solar cell permittivity of free space, with typical spring constants of 21-78 N m
room temperature. Commercial silicon cantilevers (Veeco) were obtained with a Veeco NanoScope IIIa AFM at
applied voltage. Atom force microscopy (AFM) measurements were taken with a Keithley 2635A Source Measure
unit, which is equivalent to the film thickness, and \( V \) is the applied voltage. Atom force microscopy (AFM) measure-
ments were taken with a Veeco NanoScope IIIa AFM at room temperature. Commercial silicon cantilevers (Veeco)
with typical spring constants of 21-78 N m
were used to operate the AFM in tapping mode. Images were taken con-
tinuously 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-octynyl)-9H-carbazole (1).11 5,5'-2,1,3-
benzothiadiazole-4,7-diylbis-2-thiophenecarboxaldehyde (6),19 and 9,9-diethyl-9H-fluorene-2,7-diacetonitrile (8)20
were synthesized using similar methods reported.

Synthesis of 9-(1-Octynyl)-9H-carbazole-2,7-dicarb-
aldehyde (2). 2,7-Dibromo-9-(1-octynyl)-9H-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: \( R_t \) 0.35 (33% ethyl acetate/n-hexane).13 H NMR (300 MHz, CDCl3) \( \delta \) (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).13 C NMR (75 MHz, CDCl3) \( \delta \) (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) \( \nu \) 2951.5, 2925.2, 2852.3, 2723.1, 1678.5, 1566.2, 1230.9, 812.4 cm
.13 HRRMS (m/z, FAB)’ Cald for C31H31NO2: 461.3289, Found 461.3286.

Synthesis of 2,7-Bis(hydroxymethyl)-9-(1-octynyl)-
9H-carbazole (3). 9-(1-Octynyl)-9H-carbazole-2,7-dicarb-
aldehyde (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: \( R_t \) 0.23 (100% ethyl acetate).13 H NMR (300 MHz, CDCl3) \( \delta \) (ppm): 8.10 (t, \( J = 9.6 \) 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).13 C NMR (75 MHz, CDCl3) \( \delta \) (ppm): 142.73, 139.32, 132.82, 138.31, 132.45, 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) \( \nu \) 3289.0, 2949.0, 2924.0, 2853.8, 1604.6, 1566.2, 1437.4, 1347.4, 1214.2, 1032.3, 708.5 cm
.13 HRRMS (m/z, FAB)’ Cald for C31H31NO2: 465.3607, Found 465.3609.

Synthesis of 2,7-Bis(bromomethyl)-9-(1-octynyl)-
9H-carbazole (4). 2,7-Bis(hydroxymethyl)-9-(1-octynyl)-9H-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

\[ J_{SC, LC} = \frac{9}{8\epsilon_0\epsilon_r\mu(V^2/L^3)} \] 

where \( \epsilon_r \) is the dielectric constant of the material, \( \epsilon_0 \) is the permittivity of free space, \( \mu \) 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
were 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.
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(bromo-methyl)-9-(1-octynyl)-9H-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-octynyl)-9H-carbazole (5). Crude 2,7-bis(bromomethyl)-9-(1-octynyl)-9H-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)-2,7-bis(9H-carbazole-9-yl)-2,7-bis(5,5′-(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-di-hexyl-9H-fluoren-2-yl) (9). The compound 6 (0.18 g, 0.52 mmol) and 9,9-dihexyl-9H-fluorene-2,7-diacetonitrile (8) (0.21 g, 0.52 mmol) 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-octylnonyl)-9H-carbazole (1) was formylated in THF using n-BuLi and DMF to afford 9-(1-octylnonyl)-9H-carbazole-2,7-dicarbalddehyde (2), which was treated with NaBH₄ to generate 2,7-bis(hydroxymethyl)-9-(1-octylnonyl)-9H-carbazole (3). The diol 3 was brominated with PBr₃ in benzene to generate 2,7-bis(bromomethyl)-9-(1-octylnonyl)-9H-carbazole (4). The resulting dibromide 4 was cyanized with trimethylsilyl cyanide by the nucleophilic substitution reaction to give 2,7-bis(cyanomethyl)-9-(1-octylnonyl)-9H-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-thiophene carboxaldehyde (6) and tetrabutylammonium hydride at catalyst at 65 °C.

As shown in Table 1, the number-average molecular weight (Mₙ) and the weight-average molecular weight (M_w) of the PCVCNDTBT were 4,000 and 5,400, respectively, with polydispersity index of 1.4. Mₙ 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 application and is important for organic photovoltaics introduction of the cyano group in PFVCNDTBT. Because DTBT with CN group in vinylene 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 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(fluorene vinylene-alt-4,7-dithien-2-yl-2,1,3-benzothiadiazole) (PFVDTBT), 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. The CVs were performed with a solution of tetrabutylammonium tetrafluoroborate (Bu₄NBF₄) (0.10 M) in acetonitril 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](image-url)
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

\[ E_{\text{HOMO}} = -(E_{\text{onset}}^{\text{ox}} + 4.76) \text{ (eV)} \].

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 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.

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**Table 2.** Electrochemical potentials and energy levels of the polymers

<table>
<thead>
<tr>
<th>Polymers</th>
<th>( E_{\text{onset}}^{\text{a}} ) (V)</th>
<th>HOMO(^b) (eV)</th>
<th>LUMO(^c) (eV)</th>
<th>( E_g^{d} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCVCNDTBT</td>
<td>0.81</td>
<td>-5.57</td>
<td>-3.83</td>
<td>1.74</td>
</tr>
<tr>
<td>PFVCNDTBT</td>
<td>0.59</td>
<td>-5.35</td>
<td>-3.55</td>
<td>1.80</td>
</tr>
</tbody>
</table>

\(^a\) Onset oxidation potentials measured by cyclic voltammetry. \(^b\) Calculated from the oxidation potentials. \(^c\) Calculated from the HOMO energy levels and \( E_g \). \(^d\) Energy band gaps were estimated from the onset wavelengths of the optical absorption.

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**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.

**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.
for the devices with the configuration of ITO/PEDOT:PSS/ copolymer:PC$_{61}$BM (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/cm$^2$, 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/cm$^2$, and a FF of 0.33, giving an 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/cm$^2$, 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. 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. The AFM topographies of the polymer blend (PCVCNDTBT:PC$_{61}$BM=1:2 w/w) was presented in Figure 5, where the images were obtained in a surface area of 1 $\times$ 1 $\mu$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:PC$_{61}$BM blend films by space charge limited current (SCLC) method. The device with the configuration of ITO/PEDOT/PCVCNDTBT:PC$_{61}$BM/Al was fabricated. The hole mobility of PCVCNDTBT was measured to be 5.86 $\times$ 10$^{-7}$ cm$^2$ V$^{-1}$ s$^{-1}$, which is quite lower than the optimum value, by around 10$^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$. The AFM topographies of the polymer

### Table 3. Photovoltaic performances of the device with the configuration of ITO/PEDOT:PSS/PCVCNDTBT:PC$_{61}$BM/TiO$_x$(FPQ)/Al

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

### Figure 4. The IPCE spectra of photovoltaic devices with the configuration of ITO/PEDOT:PSS/polymer:PC$_{61}$BM(1:2)/Al.

### Figure 5. Tapping mode AFM topographic image at 0-10 nm height scale for polymer/PC$_{61}$BM (1:4) blend film.

### 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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