# Synthesis and Characterization of Highly Conjugated Side-Group-Substituted Benzo[1,2-*b*:4,5-*b*']dithiophene-Based Copolymer for Use in Organic Solar Cells

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ABSTRACT: A new donor-acceptor (D-A) conjugated copolymer based on benzo[1,2-*b*:4,5-*b*']dithiophene (BDT) and thieno[3,4*c*]pyrrole-4,6-dione (TPD) was synthesized via a Stille crosscoupling reaction. A highly conjugated thiophene-based side group, tris(thienylenevinylene) (TTV), was incorporated into each BDT unit to generate the two-dimensional D-A copolymer (PBDT-TTV). An alkoxy-substituted BDT-based TPD copolymer (PBDT-OR) was synthesized using the same polymerization method for comparison. PBDT-TTV thin films produced two distinct absorption peaks. The shorter wavelength absorption (458 nm) was attributed to the BDT units containing the TTV group, and the longer wavelength band (567–616 nm) was attributed to intramolecular charge transfer between the BDT donor and the TPD acceptor. The highest occupied molecular orbital energy levels of PBDT-OR and PBDT-TTV were

**INTRODUCTION** Polymer solar cells (PSCs) that use solutionprocessable organic molecules as donors have attracted intense attention as promising next-generation renewable energy sources.<sup>1-3</sup> Bulk-heterojunctions (BHJs) consisting of blends of a conjugated donor polymer and a fullerenederivative electron acceptor have potential as components of inexpensive, lightweight, solution-processable, large-area flexible devices for use in energy-generating applications. Donor-acceptor (D-A) molecular architectures, in which a wide variety of electron-withdrawing groups can be combined with electron-donating groups, constitute the central strategy for this approach.<sup>4-6</sup> Benzo[1,2-*b*:4,5-*b*']dithiophene (BDT) is a large planar molecule obtained by fusing benzene with two flanking thiophene rings and is of particular interest as a new building block for donor polymers. Some BDTcontaining copolymers exhibit high power conversion efficiencies (PCEs) in organic photovoltaics (OPVs).<sup>7-11</sup> The use

calculated to be -5.53 and -5.61 eV, respectively. PBDT-TTV thin films harvested a broad solar spectrum covering the range 300–700 nm. A comparison with the PBDT-OR films revealed stronger interchain  $\pi$ - $\pi$  interactions in the PBDT-TTV films and, thus, a higher hole mobility. A polymer solar cell device prepared using PBDT-TTV as the active layer was found to exhibit a higher power conversion efficiency than a device prepared using PBDT-OR under AM 1.5 G (100 mW/cm<sup>2</sup>) conditions. © 2017 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2017**, *00*, 000–000

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of donor polymers containing conjugated side chains, known as two-dimensional (2D) conjugated polymers, is expected to improve the performances of OPVs because their extended conjugated side groups broaden the absorption spectra range in the visible region and increase the molar extinction coefficient, which can enhance the  $J_{SC}$  values of PSCs. BDT-based polymers that incorporate various conjugated side chains have been widely studied and have contributed to highly efficient OPV applications.<sup>12-16</sup> Recently, Tajima and coworkers reported the synthesis and characterization of a conjugated tris(thienylenevinylene) (TTV) group that incorporated BDTbased conjugated terpolymers.<sup>17-19</sup> The TTV units were introduced into the main chain between the BDT donors and various acceptor units. The highly conjugated TTV side chains increased the hole mobility by improving interchain charge transport to form better connections between the polymer chains.<sup>19</sup> Among potential electron acceptors,

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SCHEME 1 Synthetic route to the PBDT-TTV monomer.

thieno[3,4-*c*]pyrrole-4,6-dione (TPD) is an important building blocks due to good electron delocalization in the solid state as a result of a relatively compact and planar structure.<sup>20-22</sup>

In this article, we report the synthesis and characterization of a new 2D conjugated copolymer (PBDT-TTV) based on the combination of a highly conjugated TTV substituted BDT donor and a TPD acceptor (Scheme 1). The TTV groups were attached directly to the BDT structure to broaden the absorption band and increase the hole mobility of the resulting D–A copolymer, thereby improving the short circuit current ( $J_{SC}$ ) of the associated device. The optical, electrochemical, and photovoltaic properties of this copolymer were determined. An alkoxy-substituted BDT-based TPD copolymer (PBDT-OR) was synthesized using the same polymerization method to compare its optoelectronic and photovoltaic properties with those of

PBDT-TTV. The synthetic routes to the monomers and polymers are outlined in Schemes 1 and 2.

# EXPERIMENTAL

# Instrumentations

The optical absorption spectra were measured by a Shimadzu UV-3100 UV-VIS-NIR spectrometer. The number- and weight-average molecular weights of polymers were determined by gel permeation chromatography (GPC) on Viscotek T60A instrument, using chloroform as eluent and polystyrene as standard. The thermogravimetric analysis (TGA) was measured by using a TA Q100 instrument and operated under nitrogen atmosphere. Cyclic voltammetry (CV) was performed on an AUTOLAB/PG-STAT12 model system with a three-electrode cell in a solution of  $Bu_4NBF_4$  (0.10 M) in



SCHEME 2 Synthetic routes to PBDT-OR and PBDT-TTV.

acetonitrile at a scan rate of 50 mV/s. Polymer film coatings on ITO anode electrode were formed by spin-coating method.

# Fabrication of Organic Solar Cells

The current density-voltage (J-V) characteristics of the polymer photovoltaic cells were determined by illuminating the cells with simulated solar light (AM 1.5G) at an intensity of 100 mW/cm<sup>2</sup> using an Oriel 1000W solar simulator. Electronic data were recorded using a Keithley 236 sourcemeasure unit. All measurements were carried out under ambient conditions. The illumination intensity was calibrated using a standard Si photodiode detector from PV Measurements Inc., which was calibrated at the National Renewable Energy Laboratory (NREL). The external quantum efficiency (EQE) was measured as a function of wavelength (from 300 to 1100 nm) using a Xenon Short Arc Lamp as the light source (McScience K3100 EQX). The light source was calibrated using a Si reference photodiode. The measurements were carried out after masking all but the active cell area of the fabricated device, and the measurements were conducted under ambient conditions.

# **Fabrication of Hole-Only Devices**

The hole mobility of the polymer film was determined by employing the space-charge limited current (SCLC) model to the *J–V* measurement of the device. The hole-only devices were fabricated with the structure ITO/PEDOT:PSS/polymers/Au. The hole mobilities of the fabricated devices were calculated from the SCLC by the following equation:

$$J_{\rm SCLC} = (9/8)e_{\rm r}e_0\mu(V^2/L^3)$$

where  $e_r$  is the dielectric constant of the polymer layer,  $e_0$  is permittivity of free space,  $\mu$  is the SCLC mobility, *L* is the distance between the cathode and anode, which is equivalent to the film thickness, and *V* is the applied voltage.

## **Materials**

Compound  $\mathbf{1}$ ,<sup>23</sup>  $\mathbf{4}$ ,<sup>24</sup>,  $\mathbf{8}$ ,<sup>20</sup> and  $\mathbf{9}$ <sup>25</sup> were synthesized according to previously published procedures.

# Syntheses of Monomer

#### Synthesis of Compound 2

In a 250 mL flask, compound **1** (10.0 g, 32.4 mmol), paraformaldehyde (1.46 g, 48.6 mmol), 8.1 mL of HCl (35%, 97 mmol), and 50 mL of 1,4-dioxane were mixed and stirred at 0 °C for 10 min. The mixture was stirred at 60 °C for 24h, and then poured into water, neutralized with sodium bicarbonate, extracted with ethyl acetate. After drying over anhydrous MgSO<sub>4</sub>, the solvent evaporated. The product was used without further purification. Yield: 9.26 g (80%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, ppm):  $\delta$  6.88 (d, *J* = 3.6 Hz, 1H), 6.58 (d, *J* = 3.6 Hz, 1H), 4.76 (s, 2H), 2.71 (d, *J* = 6.6 Hz, 2H), 1.60 (m, 1H), 1.26 (s, 24H), 0.90–0.86 (m, 6H).

# Synthesis of Compound 3

In a 100 mL flask, compound **2** (9.0 g, 25.2 mmol) and triethyl phosphite (12.6 g, 75.6 mmol) were mixed and stirred at 160 °C for 6 h. Excess triethyl phosphite was removed by vacuum distillation, then the residue was purified with column chromatography on silica gel with hexane and ethyl acetate [1:1 (v/v)] as eluent to give a pale yellow-ish liquid. Yield: 8.67 g (75%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, ppm): δ 6.77 (t, J = 3.6 Hz, 1H), 6.57 (d, J = 3.3 Hz, 1H), 4.06 (m, 4H), 3.30 (d, J = 20.7 Hz, 2H), 2.68 (d, J = 6.6 Hz, 2H), 1.58 (m, 1H), 1.27 (m, 24H), 0.90–0.86 (m, 6H). 13C NMR (CDCl<sub>3</sub>, 75 MHz, ppm): δ 143.86, 143.81, 129.68, 129.54, 126.90, 126.78, 124.96, 124.92, 62.35, 62.26, 39.85, 39.83, 34.34, 33.08, 31.85, 31.83, 29.93, 29.60, 29.57, 29.28, 29.06, 27.15, 26.53, 26.50, 22.62, 16.37, 16.29, 14.07, 14.05. Fab-Mass; (m/z): 458 (M<sup>+</sup>). Anal. Calcd. for C<sub>25</sub>H<sub>47</sub>O<sub>3</sub>PS: C, 65.46; H, 10.33; O, 10.46; P, 6.75; S, 6.99. Found: C, 63.21; H, 10.50; O, 9.36; S, 7.21.

# Synthesis of Compound 5

A 20.9 mL (20.9 mmol) of potassium *tert*-butoxide (1.0 M in THF) was added dropwise to the solution of compound **3** (8.0 g, 17.4 mmol) and compound **4** (3.84 g, 17.4 mmol) in THF (30 mL) at 0 °C. The mixture was stirred at room temperature for 2 h. The mixture was poured into water, extracted with CHCl<sub>3</sub>, dried with anhydrous MgSO<sub>4</sub>. The solvent was removed via rotary evaporation, and the residue was purified with column chromatography on silica gel with hexane as eluent to give a pale yellow solid. Yield: 7.78 g, 85%.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, ppm):  $\delta$  7.17 (d, J = 4.8 Hz, 1H), 7.03 (dd, J = 0.9, 3.6 Hz, 1H), 6.98 (m, 3H), 6.92–6.83 (m, 5H), 6.63 (d, J = 3.6 Hz, 1H), 2.71 (d, J = 6.9 Hz, 2H), 1.62 (m, 1H), 1.26 (s, 24H), 0.88 (t, J = 6.3, 6.6Hz, 6H). 13C NMR (CDCl<sub>3</sub>, 75 MHz, ppm):  $\delta$  144.44, 142.47, 141.75, 140.84, 140.16, 127.69, 127.62, 127.11, 126.53, 126.32, 126.04, 125.97, 125.83, 124.36, 122.19, 121.53, 121.43, 121.34, 120.13, 39.93, 34.80, 33.19, 33.16, 31.90, 31.88, 29.93, 29.61, 29.32, 26.57, 22.68, 22.67, 14.12. Fab-Mass; (m/z): 524 (M<sup>+</sup>). Anal. Calcd. for C<sub>32</sub>H<sub>44</sub>S<sub>3</sub>: C, 73.23; H, 8.45; S, 18.32. Found: C, 74.13; H, 8.21; S, 17.32.

# Synthesis of Compound 6

Into a solution of compound **5** (3.0 g, 5.7 mmol) in THF (20 mL) at -78 °C was added, by syringe, 4.6 mL (7.43 mmol) of *n*-butyl lithium (1.6 M in *n*-hexane). The mixture was stirred at -78 °C for 20 min, and allowed to warm to 0 °C, then benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione (0.5 g, 2.29 mmol) was added. After the addition, the reaction mixture was heated at 50 °C for 2 h. The reaction mixture was cooled to room temperature, and tin chloride dihydrate (5.2 g) dissolved in 10 mL of HCl was added. The mixture was stirred at room temperature for 2 h, and then quenched with water. The mixture was extracted with CHCl<sub>3</sub> and dried with anhydrous MgSO<sub>4</sub>. The solvent was removed via rotary evaporation, and the residue was purified with column chromatography on silica gel with



hexane and  $CHCl_3$  [4:1 (v/v)] as eluent to give a reddish solid. Yield: 3.67 g, 52%.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, ppm):  $\delta$  7.70 (d, *J* = 5.7 Hz, 2H), 7.51 (d, *J* = 5.7 Hz, 2H), 7.40 (d, *J* = 3.6 Hz, 2H), 7.17 (d, *J* = 3.9 Hz, 2H), 7.07 (s, 4H), 7.01–6.85 (m, 10H), 6.64 (d, *J* = 3.6 Hz, 2H), 2.72 (d, *J* = 6.6Hz, 4H), 1.63 (m, 2H), 1.27 (s, 48H), 0.91–0.87 (m, 12H). 13C NMR (CDCl<sub>3</sub>, 75 MHz, ppm):  $\delta$  144.55, 143.54, 142.11, 140.75, 140.15, 138.99, 138.34, 136.50, 128.96, 127.88, 127.52, 126.64, 126.58, 126.43, 125.87, 123.76, 123.28, 122.36, 122.14, 121.05, 120.09, 39.94, 34.81, 33.15, 31.91, 31.88, 29.93, 29.61, 29.32, 26.58, 22.68, 14.13. Mass (MALDI-TOF); (*m*/*z*): 1236 (M<sup>+</sup>). Anal. Calcd. for C<sub>74</sub>H<sub>90</sub>S<sub>8</sub>: C, 71.91; H, 7.34; S, 20.75. Found: C, 71.52; H, 7.21; S, 20.20.

# Synthesis of Compound 7

Compound **6** (3.0 g, 2.42 mmol) was dissolved in 50 mL of dry THF at -40 °C for 1 h under a nitrogen atmosphere, then 6.0 mL of LDA (6.06 mmol, 1.0 M in THF) was added dropwise. The reaction was stirred at -40 °C for 1 h, then 7.3 mL of trimethyltin chloride (7.28 mmol, 1.0 M in THF) was added to the reaction mixture. The reaction was stirred at -40 °C for 15 min and was allowed to warm to room temperature. The mixture was poured into water, extracted with CHCl<sub>3</sub>, dried with anhydrous MgSO<sub>4</sub>. The solvent was removed via rotary evaporation, and the residue was precipitated with CHCl<sub>3</sub> and methanol to reddish solid. Yield: 3.1 g, 82%.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, ppm):  $\delta$  7.71 (s, 2H), 7.41 (d, J = 3.6 Hz, 2H), 7.19 (d, J = 3.9 Hz, 2H), 7.08 (s, 4H), 7.01– 6.85 (m, 10H), 6.64 (d, J = 3.3 Hz, 2H), 2.72 (d, J = 6.6 Hz, 4H), 1.63 (m, 2H), 1.27 (s, 48H), 0.89 (t, J = 6.6 Hz, 12H), 0.42 (s, 18H). 13C NMR (CDCl<sub>3</sub>, 75 MHz, ppm):  $\delta$  144.51, 143.31, 143.21, 143.03, 141.98, 140.89, 140.17, 139.26, 137.33, 130.84, 128.88, 127.39, 126.64, 126.38, 125.86, 122.29, 122.09, 121.92, 121.24, 120.13, 39.94, 34.82, 33.16, 31.91, 31.88, 29.93, 29.61, 29.32, 26.58, 22.69, 22.68, 14.13, -8.25. Mass (MALDI-TOF); (m/z): 1561 (M<sup>+</sup>). Anal. Calcd. for C<sub>80</sub>H<sub>106</sub>S<sub>8</sub>Sn<sub>2</sub>: C, 61.53; H, 6.84; S, 16.42; Sn, 15.20. Found: C, 61.89; H, 6.75; S, 15.82.

# Synthesis of PBDT-OR

Compound **8** (0.300 g, 0.39 mmol), compound **9** (0.294 g, 0.39 mmol), and tetrakis(triphenylphosphene)palladium(0) (22 mg,  $1.94 \times 10^{-2}$  mmol) were dissolved in toluene (10.0 mL) and DMF (2.5 mL) under a nitrogen atmosphere. The reaction mixture was heated at 80 °C for 15 h. When the reaction had finished, the mixture was precipitated from the 10 mL of HCl and 150 mL of methanol. The polymer was dissolved in small amount of CHCl<sub>3</sub> and precipitated in methanol. The resulting polymer was further purified by Soxhlet extraction using methanol, acetone, and hexane then dried in vacuum to give dark solid. Yield: 0.25 g, 62%. Anal. Calcd. for (C<sub>60</sub>H<sub>81</sub>NO<sub>4</sub>S<sub>5</sub>)<sub>n</sub>: C, 69.26; H, 7.85; N, 1.34; O, 6.15; S, 15.40. Found: C, 68.79 H, 7.96 N, 1.30; S, 15.32.



**FIGURE 1** TGA plots for PBDT-OR and PBDT-TTV obtained with a heating rate of 10  $^{\circ}$ C min<sup>-1</sup> under an inert atmosphere. [Color figure can be viewed at wileyonlinelibrary.com]

#### Synthesis of PBDT-TTV

Compound 7 (0.350 g, 0.224 mmol), compound 9 (0.17 g, 0.224 mmol), and tetrakis(triphenylphosphene)palladium(0) (13 mg,  $1.12 \times 10^{-2}$  mmol) were dissolved in toluene (10.0 mL) and DMF (2.5 mL) under a nitrogen atmosphere. The reaction mixture was heated at 80 °C for 12 h. When the reaction had finished, the mixture was precipitated from the 10 mL of HCl and 150 mL of methanol.

The polymer was dissolved in small amount of  $CHCl_3$  and precipitated in methanol. The resulting polymer was further purified by Soxhlet extraction using methanol, acetone, and hexane then dried in vacuum to give dark solid. Yield: 0.27 g, 66%. Anal. Calcd. for  $(C_{108}H_{133}NO_2S_{11})_n$ : C, 70.89; H, 7.33; N, 0.76; O, 1.75; S, 19.27. Found: C, 69.68; H, 7.26; N, 0.74; S, 19.19.

#### **RESULTS AND DISCUSSION**

#### Syntheses and Characterizations of the Polymers

PBDT-OR and PBDT-TTV were obtained via the Stille coupling reactions of compounds 8 and 9 and compounds 7 and 9, respectively. The branched alkyl groups 2-ethylhexyl and 2hexyldecyl were introduced onto the BDT and TPD units to enhance the solubility of the polymers. The number-average molecular weights  $(M_n)$  of PBDT-OR and PBDT-TTV were determined by performing GPC with a polystyrene standard in chloroform eluent and found to be 25,100 g/mol (D = 1.9) and 31,200 g/mol (D = 2.0), respectively. The synthesized polymers readily dissolve in chlorinated organic solvents such as chloroform and chlorobenzene and form good uniform thin films. The introduction of the branched alkyl groups was found to impart the required solubility to the polymers in these solvents. The thermal stabilities of the polymers were investigated by performing TGA. The TGA curves show that PBDT-OR and PBDT-TTV exhibit excellent thermal stability (Fig. 1). The decomposition temperatures  $(T_d)$  for 5% weight loss of PBDT-OR and PBDT-TTV are 330 and 353

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**FIGURE 2** (a) Normalized UV-visible absorption spectra of PBDT-OR and PBDT-TTV in CHCl<sub>3</sub> solution and in the thin film state and (b) UV-visible molar absorption coefficients and PL intensities of the polymers in a  $1 \times 10^{-5}$  M chloroform solution. [Color figure can be viewed at wileyonlinelibrary.com]

°C, respectively, which indicates that the conjugated side groups provide more stability than the alkoxy groups.

## **Optical and Electrochemical Properties**

The UV-visible absorption spectra of PBDT-OR and PBDT-TTV in chloroform solution and in the thin film state are shown in Figure 2. The absorption maxima ( $\lambda_{max}$ ) of PBDT-OR in solution and in the thin film state occurred at 530 nm with a weak shoulder peak (approx. 580 nm). No significant differences were observed between the absorption peaks of PBDT-OR in the solution and thin film states, indicating the absence of significant  $\pi$ - $\pi$  stacking or overlapping among the polymer chains in the PBDT-OR film. The UV-visible spectra of PBDT-TTV in the solution and film states contained two  $\lambda_{\rm max}$  values at 450 and 570 nm and a shoulder peak at 610 nm. The absorption maximum of PBDT-TTV at shorter wavelengths (approx. 450 nm) was attributed to the conjugated TTV side group in the BDT unit because this peak agreed well with the absorption peak of compound 6 [Fig. 2(a)].<sup>19</sup> The absorption band of PBDT-TTV was slightly broader (approx. 20 nm) than that of PBDT-OR, and the intensity of the shoulder peak of PBDT-TTV was higher than that of PBDT-OR. The TTV terpolymer synthesized by Tajima et al. contained a TTV content of 20 mol %; therefore, the the intensity at longer wavelengths (approx. 600 nm); however, the absorption intensity of PBDT-TTV at 450 nm was significantly higher than the absorption at 600 nm due to the high TTV unit content in PBDT-TTV. The absorption cross section of PBDT-TTV is much stronger than that of PBDT-OR over the range 300-700 nm [Fig. 2(b)]. The increase in absorption improved the probability of exciton formation in PBDT-TTV. These differences were attributed to strong intermolecular interactions among the TTV side groups of PBDT-TTV. The UV-visible absorption coefficients ( $\alpha$ ) and photoluminescence (PL) spectra of the polymers are shown in Figure 2(b). The absorption coefficients and PL results were obtained from a single solution sample (chloroform solvent, 1  $\times$  10  $^{-5}$  M), and the PBDT-OR and PBDT-TTV solutions were excited at 533 and 555 nm, respectively. The absorption coefficients of PBDT-OR and PBDT-TTV were  $4.7 \times 10^4$ and 9.7  $\times$   $10^4~M^{-1}~cm^{-1}.$  Note that the value of  $\alpha$  for PBDT-TTV (9.7  $\times$  10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>) was two times the value obtained for PBDT-OR (4.7  $\times$  10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>) at 460 nm due to the introduction of highly conjugated TTV side groups into the BDT units. The broad and strong absorption spectrum of PBDT-TTV suggested that it was an excellent light absorber for PSCs and that the use of PBDT-TTV in PSCs could provide a higher  $J_{\rm SC}$  value than the value obtained using PBDT-OR. PL emission peaks in the PBDT-OR and PBDT-TTV solutions were observed at 680 and 675 nm, respectively, as expected from their UV-visible spectra. Note that the PL intensity of PBDT-TTV was slightly lower than that of PBDT-OR, even though its absorption coefficients were higher than those of PBDT-OR. Strong intermolecular interactions resulting from the introduction of the conjugated TTV side groups may have increased PL quenching.<sup>26,27</sup>

absorption intensity at shorter wavelengths was lower than

The highest occupied molecular orbital (HOMO) levels of the polymer films were calculated from CV measurement using the equation  $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.8)$  eV, where  $E_{\text{ox}}$  is the onset oxidation potential relative to the ferrocene external standard (Supporting Information Fig. S1).<sup>28</sup> The HOMO levels of the polymer films were relatively low lying: -5.53 eV for PBDT-OR and -5.61 eV for PBDT-TTV. These results could not be readily explained, although the TTV groups appeared to play an important role in decreasing the HOMO level. The optical band gaps of PBDT-OR and PBDT-TTV were determined from the absorption onsets and found to be 1.90 and 1.87 eV, respectively. The calculated lowest unoccupied molecular orbital (LUMO) levels of the PBDT-OR and PBDT-TTV thin films were found to be -3.63 and -3.74 eV, respectively, which are higher (by approx. 0.6 eV) than that (-4.30 eV) of the acceptor, PC<sub>70</sub>BM ([6,6]-phenyl C<sub>71</sub>-butyric acid methyl ester),<sup>29</sup> and thus charge transfer from the polymers to PC70BM will be favorable. The optical and electrochemical properties of the polymers are summarized in Table 1.

# **Theoretical Calculations**

Molecular structure optimizations for PBDT-OR and PBDT-TTV were performed with density functional theory (DFT). The electronic structures were modeled with DFT as



Polymer	Solution ( $\lambda_{max}$ , nm) <sup>a</sup>	Film (λ <sub>max</sub> , nm)	$E_{\rm g}~({\rm eV})^{\rm b}$	Е <sub>НОМО</sub> (eV)	E <sub>LUMO</sub> (eV) <sup>c</sup>
PBDT-OR	533	534	1.90	-5.53	-3.63
PBDT-TTV	442, 565, 616	458, 567, 616	1.87	-5.61	-3.74

**TABLE 1** UV–Visible Maximum Absorption Wavelengths ( $\lambda_{max}$ ), Band-Gap Energies ( $E_g$ ), and Ionization Potentials ( $E_{HOMO}$ ) of PBDT-OR and PBDT-TTV

<sup>a</sup> Measurements performed in chloroform.

 $^{\rm b}$  Estimated from the onset of the absorption of the thin solid film  $(E_{\rm g}=1240/\lambda_{\rm onset}).$ 

implemented in the Gaussian 09 program at the B3LYP/6-31(G) level of theory.<sup>30</sup> To simplify these calculations, the branched alkyl groups were replaced with methyl groups, and results were obtained for only one repeating unit of the polymer. Supporting Information Figure S2 shows the electron density distributions of the HOMOs and the LUMOs of the model polymers, which were estimated from the results for one repeat unit. In Supporting Information Figure S2, the electron densities of the HOMOs for PBDT-OR and PBDT-TTV are delocalized along the polymer backbones, and the electron densities of the LUMOs are mainly located in the electron-accepting TPD units; these results indicate that <sup>c</sup> Calculated from the optical band-gap energy.

strong ICT states are possible in these D–A copolymers. Moreover, the electron density of the HOMO of PBDT-TTV is delocalized onto the conjugated side groups in the BDT unit. Thus, the electrons are better delocalized in PBDT-TTV, which may be due to the longer conjugation length of the TTV side groups.

# **Space-Charge Limited Current Characteristics**

We measured the hole mobilities of the polymer thin films and the polymer: $PC_{70}BM$  blend films by using the SCLC method in order to characterize the vertical carrier transport properties of the OPV devices. To obtain the SCLC curves,





**FIGURE 3** Field-dependent hole mobilities of (a) polymer only and (b) polymer:PC<sub>70</sub>BM blend films, determined by fitting the J-V curves in the SCLC regime of the hole-only devices. [Color figure can be viewed at wileyonlinelibrary.com]

**FIGURE 4** (a) J-V characteristics and (b) external quantum efficiencies of the polymer/PC<sub>70</sub>BM devices. [Color figure can be viewed at wileyonlinelibrary.com]

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**TABLE 2** Photovoltaic Properties of the Polymer/PC70BMDevices

Polymer	Blend Ratio	V <sub>oc</sub> (V)	J <sub>SC</sub> (mA/cm²)	FF	PCE (%)
PBDT-OR	1:1	0.84	6.35	0.60	3.21 (3.17) <sup>a</sup>
	1:2	0.84	4.51	0.64	2.44 (2.35) <sup>a</sup>
PBDT-TTV	1:1	0.83	8.58	0.52	3.70 (3.64) <sup>a</sup>
	1:2	0.85	10.0	0.56	4.76 (4.72) <sup>a</sup>

<sup>a</sup> Average PCE value for four devices.

hole-only devices were fabricated with the structure ITO/ PEDOT:PSS/polymer or blend film/MoO<sub>3</sub>/Ag, and the mobilities were calculated with the Mott–Gurney equation.<sup>29</sup> The calculated hole mobilities of the pure PBDT-OR and PBDT-TTV films were  $3.8 \times 10^{-5}$  and  $1.6 \times 10^{-4}$  cm<sup>2</sup>/V s respectively, as shown in Figure 3. The hole mobilities of the PBDT-OR:PC<sub>70</sub>BM (1:1) and PBDT-TTV:PC<sub>70</sub>BM (1:2) blend films were  $2.2 \times 10^{-5}$  and  $1.0 \times 10^{-4}$  cm<sup>2</sup>/V s, respectively, that is, the trend is similar to that in the mobilities of the pure polymer films. The mobility in the PBDT-TTV film is higher than that in the PBDT-OR film, which is probably due to the strong interchain interactions among the conjugated TTV side groups.<sup>18,19</sup>

## **Organic Photovoltaic Characteristics**

PSCs were fabricated with the layered structure ITO/ PEDOT:PSS (60 nm)/polymer:PC<sub>70</sub>BM (80 nm)/Ca/Al (100 nm). Figure 4 shows the *J*–*V* curves of the PSCs, and their photovoltaic parameters are summarized in Table 2. The PCEs of the PBDT-OR and PBDT-TTV devices were found to be 3.21% and 4.76%, respectively. Regardless of the blend ratio, the PCEs and *J*<sub>SC</sub> values of the PBDT-TTV devices were always higher than those of the PBDT-OR devices. The *J*<sub>SC</sub> values of PSCs are affected by many factors, including the light absorption of the active layer, the band gap, the carrier mobility, and the film formation properties of the active layer. The light absorption bandwidth of PBDT-TTV (1.87 eV) were slightly smaller than that of PBDT-OR (1.90 eV), and the optical absorption coefficient of PBDT-TTV was higher than that of PBDT-OR; these differences significantly enhance the  $J_{SC}$  values of the PBDT-TTV devices. Given the hole mobilities of the polymers, the PBDT-TTV devices are expected to exhibit higher  $J_{SC}$  values than the PBDT-OR devices. Note that the incorporation of the conjugated TTV side groups into the BDT units, which increases the strength of the intermolecular interactions,<sup>19</sup> significantly increases the absorption intensity and hole mobility, and thereby enhances the  $J_{SC}$  and PCE values of the PBDT-TTV solar cell devices.

To investigate the differences between the photovoltaic performances of the PSCs, atomic force microscopy (AFM) images of the surface morphologies of the solar cell devices were obtained (Fig. 5). In general, nanoscale phase separation is required to overcome the short exciton diffusion lengths (approx. 10 nm) of donor polymers and provide efficient charge separation.<sup>31</sup>

The root-mean-square (RMS) roughnesses of the PBDT-OR:PC70BM (1:1) and PBDT-TTV: PC70BM (1:2) films were found to be 5.8 and 1.3 nm, respectively. Moreover, the phase separation in the PBDT-TTV:PC<sub>70</sub>BM film is less than that in the PBDT-OR blend film (Fig. 5). This reduced phase separation increases the total area for charge separation between the donor polymer and the PCBM acceptor and leads to a higher photocurrent and a higher efficiency. Relatively high levels of phase separation are evident in the PBDT-OR:PC70BM blend film, which is likely to decrease the photocurrent density. The EQE values of the PBDT-OR and PBDT-TTV solar cell devices were measured to evaluate their photoresponses as a function of wavelength and are shown in Figure 4(b). The PBDT-OR and PBDT-TTV devices yield EQE plots that are similar to their UV-visible absorption spectra, which indicate that their excitons are mainly generated in the polymer phase. The  $J_{SC}$  values calculated by integrating the EQE curves were found to be within 10% of the corresponding  $J_{SC}$  values obtained from the J-V curves. The



**FIGURE 5** AFM tapping-mode height images of (a) PBDT-OR/PC<sub>70</sub>BM (1:1) and (b) PBDT-TTV/PC<sub>70</sub>BM (1:2). Scan size is 2  $\mu$ m × 2  $\mu$ m. [Color figure can be viewed at wileyonlinelibrary.com]



spectral response of the PBDT-OR:PC<sub>70</sub>BM (1:1) device shows that photons with wavelengths in the range 350–700 nm contribute significantly to the EQE, with a maximum EQE of 45% at 410 nm. The PBDT-TTV:PC<sub>70</sub>BM (1:2) device exhibits a similar spectral response in the range 350–700 nm; however, a maximum EQE of 57% was obtained at 480 nm, which results in a much higher  $J_{SC}$ .

## CONCLUSIONS

In conclusion, we have performed the synthesis and characterization of a 2D conjugated polymer, PBDT-TTV, comprising a TPD acceptor and a BDT donor containing highly conjugated TTV side groups. We found that the TTV groups in PBDT-TTV play a crucial role in its absorption spectra, charge transfer, and blend film morphological properties. This study has demonstrated the usefulness of the incorporation of 2D conjugated side groups into D–A polymers, which was found to result in a high OPV performance.

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