Thieno[3,2-b]thiophene-Substituted Benzodithiophene in Donor–Acceptor Type Semiconducting Copolymers: A Feasible Approach to Improve Performances of Organic Photovoltaic Cells

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ABSTRACT: Thieno[3,2-b]thiophene-substituted benzo[1,2-b:4,5-b'] dithiophene donor units (TTBDT) serve as novel promising building blocks for donor-acceptor (D-A) copolymers in organic photovoltaic cells. In this study, a new D-A type copolymer (PTTBDT-TPD) consisting of TTBDT and thieno[3,4-c]pyrrole-4,6-dione (TPD) is synthesized by Stille coupling polymerization. A PTTBDT-TPD analog consisting of TTBDT and alkylthienyl-substituted BDT (PTBDT-TPD) is also synthesized to compare the optical, electrochemical, morphological, and photovoltaic properties of the polymers. Bulk heterojunction photovoltaic devices are fabricated using the polymers as p-type donors and [6,6]-phenyl C₇₁-butyric acid methyl ester (PC₇₁BM) as the n-type acceptor. The power conversion efficiencies of the devices fabricated using PTTBDT-

INTRODUCTION Organic photovoltaic cells (OPVs) have drawn widespread attention owing to their potential low cost, large area fabrication, light weights, and flexibility.¹ Bulk heterojunction (BHJ) OPVs with sandwiched structures and bicontinuous interpenetrating networks of electron donor and acceptor materials have the most successful device structure and are most widely used.² Recently, significant progress has been achieved in regard to OPV performance, with the highest power conversion efficiency (PCE) of more than 9%.³ Conjugated polymers with alternating donor and acceptor units have low band gap energies due to intramolecular charge transfer (ICT).⁴ Among the numerous reported donor units, benzo[1,2-b:4,5-b']dithiophene (BDT) is one of the most promising building blocks in D-A type copolymers for highperformance OPVs.⁵ Its large planar π -conjugated structure promotes facile π - π stacking, improves the charge carrier mobility, and facilitates the introduction of alkoxy or aryl side chains, which can improve the solubility of the polymers. Moreover, the highest occupied molecular orbital (HOMO) energy level and UV-visible absorption of the polymer can be **KEYWORDS**: benzodithiophene; conjugated polymers; copolymerization; organic photovoltaic cells; semiconducting polymer; step-growth polymerization; structure-property relations; thienothiophene

controlled by modification of the BDT unit.⁵ Recently, several research groups have reported the synthesis of low band gap polymers containing alkylthienyl-substituted BDT with PCEs of up to 7%.⁵

Thieno[3,2-b]thiophene-substituted benzo[1,2-b:4,5-b']dithiophene (TTBDT) was demonstrated as a good electron donor unit for high-performance D-A type low band-gap polymers.⁶ A D-A copolymer (PTTBDT-FTT) consisting of TTBDT and 2-ethylhexyl 3-fluorothieno[3,4-b]thiophene-2-carboxylate (FTT) units showed a maximum PCE of 7.7%. This result inspired us to investigate the detailed effects of TTBDT on the optical, electrochemical, and morphological properties of D-A type conjugated polymers.

In this article, we report the synthesis of a new D-A type copolymer (PTTBDT-TPD) composed of TTBDT and a thieno[3,4-c]pyrrole-4,6-dione (TPD) derivative. A PTTBDT-TPD analog, PTBDT-TPD, composed of an alkylthienyl-substituted BDT derivative (TBDT) and TPD, was also synthesized in order to compare the optoelectronic and

TPD and PTBDT-TPD are 6.03 and 5.44%, respectively. The difference in efficiency is attributed to the broad UV–visible absorption and high crystallinity of PTTBDT-TPD. The replacement of the alkylthienyl moiety with thieno[3,2-b]thiophene on BDT can yield broad UV–visible absorption due to extended π -conjugation, and enhanced molecular ordering and orientation for organic photovoltaic cells. © 2014 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 3608–3616

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SCHEME 1 Reagents and conditions: (i) *n*-BuLi, 2-ethylhexylbromide, THF, -78 °C, 12 h; (ii) *n*-BuLi, 4,8-dehydrobenzo[1,2-b:4,5-b'] dithiophene-4,8-dione, SnCl₂·H₂O/HCl, 0 °C, then 50 °C, THF; (iii) TMEDA, *n*-BuLi, Sn(Me)₃Cl, -78 °C, THF.

photovoltaic properties of the polymers. By introducing the alkylthienothiophene (TT) moiety on the BDT building block, we expected that the absorption band would broaden as compared to that of the analog containing alkylthiophene, due to the extended π -conjugation of the side chain. We also expected enhanced intermolecular interactions, which would improve the charge carrier mobility and short circuit current ($J_{\rm SC}$) in OPV devices. The detailed synthetic routes for the monomers and the novel BDT-based D2A polymers are outlined in Scheme 1, and the molecular structures of the polymers are shown in Scheme 2.

EXPERIMENTAL

Materials

All starting organic compounds were purchased from Aldrich, Alfa Aesar, or TCI Korea, and were used without further purification. Tetrakis(triphenylphosphine)palladium(0)-were purchased from Strem. [6,6]-Phenyl C₇₁-butyric acid methyl ester (PC₇₁BM) was purchased from EM-index. Solvents were dried and purified by fractional distillation over sodium/benzophenone and handled in a moisture-free atmosphere. Column chromatography was performed using silica gel (Merck, Kieselgel 60 63–200 MYM SC). 1,3-Dibromo-5-heptyl-thieno[3,4-c]pyrrole-4,6(5H)-dione (TPD)⁷ and 2,6-bis(trimethyltin)–4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (TBDT)⁸ were synthesized in a similar manner according to the methods described in previous reports.

Measurements

¹H- and ¹³C NMR spectra were recorded using a Varian Mercury Plus 300 MHz spectrometer, and the chemical shifts were recorded in units of ppm with chloroform as the internal standard. Elemental analysis was carried out using the Vario Micro Cube in the Korea Basic Science Institute (Busan, Korea). Absorption spectra were measured using a JASCO JP/ V-570 model. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) analysis relative to a polystyrene standard using a Waters highpressure GPC assembly (model M590). Thermal analyses were carried out on a Mettler Toledo TGA/SDTA 851e under a N₂ atmosphere with a heating and cooling rate of 10 °C/min. Cyclic voltammetry (CV) was performed on a CH Instruments Electrochemical Analyzer. The CV measurements were carried



SCHEME 2 Synthetic routes and molecular structures of PTTBDT-TPD and PTBDT-TPD.

out in acetonitrile containing 0.1 M tetrabutylammonium tetra-fluoroborate (TBABF₄) as the supporting electrolyte, Ag/AgNO₃ as the reference electrode, a platinum wire as the counter electrode, and a platinum working electrode.

Two-Dimensional Grazing-Incidence X-Ray Diffraction Experiments

Two-dimensional (2D) grazing-incidence X-ray diffraction (GIXD) measurements were performed under vacuum at the 3C beamline in the Pohang Light Source, Korea. To obtain results comparable to those of the OPV devices, the samples were prepared on PEDOT:PSS-modified Si substrates under the same conditions as those used for the fabrication of the solar cells. The wavelength of the X-ray was 0.1651 nm, and the incidence angle (the angle between the critical angle of the sample and that of Si) was 0.13°. The 2D-GIXD patterns were recorded using a 2D CCD detector (Rayonix SX165), and the X-ray irradiation time was set to 0.5–10 s depending on the saturation level of the detector. The 2D-GIXD images from the films were analyzed according to the relationship between the scattering vector *q* and the d spacing, $q = 2\pi/d$.

Fabrication of Organic Thin-Film Transistor Devices

Organic thin film transistors were fabricated using a bottom-contact geometry device [channel length (*L*) of 12 μ m and width (*W*) of 120 μ m]. The source and drain contacts consisted of Au (100 nm) and the dielectric was silicon oxide (SiO₂) with a thickness of 300 nm. The SiO₂ surface was cleaned, dried, and pretreated with a solution of 10.0 mM octyltrichlorosilane (OTS-8) in toluene at room temperature for 2 h under a nitrogen atmosphere to produce smooth, nonpolar surfaces, on to which the polymers could be spin-coated. The polymers were dissolved at a concentration of 0.5 wt % in chlorobenzene. Organic semiconductors films were spin-coated at 1000 rpm for 50 s to achieve a thickness of 60 nm. Device fabrication procedures and measurements were carried out in air at room temperature.



Fabrication of Photovoltaic Devices

The devices were fabricated with the structure ITO/ PEDOT:PSS/polymer:PC71BM/Ca/Al. The procedure for cleaning the ITO surface included sonication and rinsing in distilled H₂O, methanol, and acetone. The hole-transporting PEDOT:PSS layer (45 nm) was spin-coated on to the ITO anodes from a solution purchased from Heraeus (CleviosTM P VP AI4083). Each polymer:PC₇₁BM solution was then spincoated onto the PEDOT:PSS layer. The polymer solution for spin-coating was prepared by dissolving the polymer (8 mg mL^{-1}) in chloroform/1,8-diiodooctane (DIO) (97:3). Ca and Al contacts were formed sequentially by vacuum deposition at a pressure of $<3 \times 10^{-6}$ Torr, providing an active area of 0.09 cm². The thickness of the active layer was measured using a KLA Tencor Alpha-step IQ surface profilometer with an accuracy of ± 1 nm. The current density-voltage (*I-V*) characteristics of all polymer photovoltaic cells were determined by illuminating the cells with simulated solar light (AM 1.5 G) with an intensity of 100 mW cm⁻² using an Oriel 1000 W solar simulator. Electronic data were recorded using a Keithley 236 source-measure unit, and all characterizations were carried out in an ambient environment. The illumination intensity was calibrated by employing a standard Si photodiode detector (PV Measurements), which was calibrated at the National Renewable Energy Laboratory. The external quantum efficiency (EQE) was measured as a function of wavelength in the range of 360-800 nm using a halogen lamp as the light source. The calibration was performed using a Si reference photodiode. All the characterization steps were carried out in an ambient laboratory atmosphere.

Synthesis of Monomers and Polymers

Synthesis of 2-(2-Ethylhexyl)thieno[3,2-b]thiophene (1)

Thieno[3,2-b]thiophene (10 g, 7.13 mmol) was dissolved in dry THF (100 mL) under an N2 atmosphere; the solution was cooled to -78 °C and *n*-butyllithium (35 mL, 10.69 mmol, 2.0 M in hexane) was added dropwise. The reaction mixture was stirred at -78 °C for 1 h and then brought to room temperature. Stirring was continued for 20 min, and then the reaction mixture was re-cooled to -78 °C. A solution of 2-ethylhexylbromide (12.7 mL, 10.69 mmol) was added dropwise. The mixture was slowly brought to room temperature and stirred overnight. Water was added to the reaction mixture, and the aqueous phase was extracted three times with ethyl acetate. The organic layer was separated and dried with anhydrous MgSO₄, and the resulting solution was concentrated by evaporation. The crude product was purified using silica column chromatography to give 1 as a colorless oil (13.8 g, 80% yield).

¹H NMR (300 MHz, CDCl₃, ppm): δ 7.40 (d, 1H), 7.28 (d, 1H), 6.94 (s, 1H), 2.82 (d, 2H), 1.70 (m, 1H), 1.39 (m, 8H), 0.94 (m, 6H). ¹³C NMR (75 MHz, CDCl₃, ppm): δ 141.8, 128.9, 125.4, 119.1, 118.5, 117.2, 48.3, 36.1, 33.8, 30.8, 27.5, 24.4, 15.4, 12.1.

Synthesis of 4,8-Bis((2-ethylhexyl)thieno[3,2-b]thiophene)benzo[1,2-b:4,5-b']dithiophene (2)

Compound 1 (4.5 g, 1.80 mmol) and THF (100 mL) were added to a flask under an inert atmosphere. The solution

was cooled using an ice-water bath, and 9.2 mL of *n*-butyllithium (2.67 mmol, 2.0 M in pentane) were added dropwise. The mixture was warmed to 50 °C and stirred for 2 h. 4,8-Dehydrobenzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione (1.00 g, 0.45 mmol) in THF (20 mL) was added, and the mixture was stirred for 1 h at 50 °C. After cooling to ambient temperature, $SnCl_2 2H_2O$ (8.00 g, 14.4 mmol) in 10% HCl (16 mL) was added, and the mixture was stirred for 2 h. The resulting solution was poured into 200 mL of methanol and extracted three times with ethyl acetate. The organic layer was separated and dried with anhydrous MgSO₄. The obtained crude product was purified using silica-gel column chromatography, with methylene chloride/hexane as the eluent. A yellow solid was obtained after the solvents were removed (3.0 g, 75% yield).

¹H NMR (300 MHz, CDCl₃, ppm): δ 7.68 (d, 2H), 7.57 (s, 2H), 7.50 (d, 2H), 7.02 (s, 2H), 2.89 (d, 4H), 1.88 (m, 2H), 1.59–1.28 (m, 16H), 0.94–0.88 (m, 12H). ¹³C NMR (75 MHz, CDCl₃, ppm): δ 145.5, 139.1, 134.1, 133.9, 132.1, 128.7, 126.1, 125.0, 124.2, 122.5, 120.1, 49.1, 42.5, 39.3, 35.8, 28.4, 27.1, 16.4, 12.7. Anal. Calcd. for C₃₈H₄₂S₆: C, 66.04; H, 6.13; S, 27.84. Found: C, 65.98; H, 6.10; S, 27.70.

Synthesis of 2,6-Bis(trimethyltin)-4,8-bis((2ethylhexyl)thieno[3,2-b]thiophene)-benzo[1,2-b:4,5b']dithiophene)

Compound 2 (1.2 g, 0.17 mmol), N,N,N',N'-tetramethylethylenediamine (0.7 mL, 0.43 mmol), and THF (100 mL) were added to a flask under an inert atmosphere. The solution was cooled to -78 °C, and 1.8 mL of *n*-butyllithium (3.00 mL, 0.43 mmol, 2.0 M in pentane) was added. The solution was stirred at -78 °C for 1 h and then 4.3 mL of trimethyltin chloride (0.43 mmol, 1.0 M in THF) was added in one portion. The reaction mixture was stirred for 2 h, and the cooling bath was then removed. The reaction mixture was heated to room temperature and stirred for 12 h. The resulting solution was poured into 200 mL of cold water and extracted three times with ethyl acetate. The organic layer was separated and dried with anhydrous MgSO₄. The solvent was removed under vacuum and the resulting residue was crystallized in methanol. A yellow solid was obtained (1.1 g, 75% yield).

¹H NMR (300 MHz, CDCl₃, ppm): δ 7.78 (s, 2H), 7.60 (s, 2H), 7.02 (s, 2H), 2.95 (d, 4H), 1.88 (m, 2H), 1.59–1.28 (m, 16H), 0.94–0.88 (m, 12H), 0.38 (s, 18H). ¹³C NMR (75 MHz, CDCl₃, ppm): δ 144.1, 140.9, 138.2, 135.7, 134.2, 130.5, 128.0, 125.4, 123.1, 119.6, 119.1, 48.7, 45.1, 40.3, 32.1, 30.7, 26.4, 22.9, 14.4, -144. Anal. Calcd. for C₄₄H₅₈S₆Sn₂: C, 51.98; H, 5.75; S, 18.92. Found: C, 51.80; H, 5.71; S, 18.88.

Poly{4,8-bis((2-ethylhexyl)thieno[3,2-b]thiophene)benzo[1,2-b:4,5-b']dithiophene-alt-5-heptyl-4H-thieno[3,4c]pyrrole-4,6(5H)-dione}

Stille cross-coupling was used to synthesize the copolymers. TTBDT (400 mg, 0.40 mmol) was mixed with TPD (355 mg, 0.40 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (15.2 mg, 2.6 µmol), toluene (5 mL), and DMF (1 mL) for the polymerization. The



FIGURE 1 TGA curves of the polymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

reaction mixture was stirred at 110 $\,^\circ\text{C}$ for 2 day, and then excess 2-bromothiophene and tripropyl(thiophen-2-yl)stannane (the end-capper) dissolved in 1 mL of anhydrous toluene was added, and stirring was continued for 12 h. For polymer purification, the reaction mixture was cooled to approximately 50 °C and 200 mL of methanol was added slowly with vigorous stirring. The polymer fibers were collected by filtration and re-precipitation from methanol and acetone. Oligomers and catalyst residues were removed by washing for 2 d in a Soxhlet apparatus with acetone. Column chromatography using chloroform as the eluent was then performed on the polymer. Re-precipitation in chloroform/ methanol was repeated several times. The polymer yield was 35%. The resulting polymer was soluble in common organic solvents. Anal. Calcd. for C51H55NO2S7: C, 65.27; H, 5.91; S, 23.92. Found: C, 64.98; H, 6.01; S, 23.02.

Poly{4,8-bis((2-ethylhexyl)thiophene)-benzo[1,2-b:4,5b']dithiophene-alt-5-heptyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione}

Stille cross-coupling was used to synthesize the copolymers. TBDT (400 mg, 0.40 mmol) was mixed with TPD (181 mg, 0.40 mmol, 1.0 equiv), Pd(PPh₃)₄ (15.2 mg, 2.6 µmol), toluene (5 mL), and DMF (1 mL) for the polymerization. The reaction mixture was stirred at 110 °C for 2 days, and then excess 2-bromothiophene and tripropyl(thiophen-2-yl)stannane (the end-capper) dissolved in 1 mL of anhydrous toluene was added, and stirring was continued for 12 h. For polymer purification, the reaction mixture was cooled to approximately 50 °C and 200 mL of methanol was added slowly with vigorous stirring of the reaction mixture. The polymer fibers were collected by filtration and reprecipitation from methanol and acetone. Oligomers and catalyst residues were removed by washing for 2 days in a Soxhlet apparatus with acetone. Column chromatography using chloroform as the eluent was then performed on the polymer. Re-precipitation in chloroform/methanol was repeated several times. The polymer yield was 48%. The resulting polymer was soluble in common organic solvents.

Anal. Calcd. for $C_{47}H_{55}NO_2S_5$: C, 68.32; H, 6.71; S, 19.40. Found: C, 67.52; H, 6.53; S, 18.77.

RESULTS AND DISCUSSION

Synthesis and Characterization of Monomers and Polymers

1,3-Dibromo-5-(heptyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)dione (TPD) was synthesized according to reported procedures. PTBDT-TPD and PTTBDT-TPD were prepared by Stillecoupling polymerization with TPD and TBDT or TTBDT using Pd(PPh₃)₄ as the catalyst. The initially obtained crude polymers were purified by successive washing with hot methanol, hexane, and acetone via a Soxhlet extractor. The average molecular weights and polydispersity indices (PDIs) of the polymers were determined using GPC calibrated with polystyrene standards. The number average molecular weights (Mn) of PTBDT-TPD and PTTBDT-TPD were 23,000 and 20,000 g/mol, respectively, with PDIs of 3.1 and 2.8, respectively. As shown in Figure 1, the decomposition temperatures (5% weight loss) of PTBDT-TPD and PTTBDT-TPD were 396 and 427 °C, respectively, indicating that the TTBDTcontaining polymer was more thermally stable than the corresponding TBDT containing polymer. The molecular weights and PDIs of the polymers are summarized in Table 1.

Optical and Electrochemical Properties

The UV-visible absorption spectra of PTBDT-TPD and PTTBDT-TPD in chloroform and in the thin film state are shown in Figure 2(a,b), respectively. The absorption maxima (λ_{max}) of PTBDT-TPD and PTTBDT-TPD in solution appeared at 609 and 626 nm, whereas the absorption peaks in the thin films were observed at 616 and 625 nm, respectively. The λ_{max} of PTTBDT-TPD was red-shifted by approximately 10 nm with respect to PTBDT-TPD in solution and in the film state, because the TT side groups in the TTBDT unit increased the effective conjugation length of PTTBDT-TPD. The absorption bands of PTTBDT-TPD were red-shifted and broader as compared to those of PTBDT-TPD. Notably, the absorption intensity of PTTBDT-TPD at 350-550 nm was much higher than that of PTBDT-TPD. The measured absorption coefficient (ε) of the PTTBDT-TPD thin film was 1.6 times higher (1.3 imes 10⁵ cm⁻¹) than that of PTBDT-TPD (9.8 \times 10⁴ cm⁻¹) at 550 nm [Fig. 2(b)]. The enhanced absorption intensity of PTTBDT-TPD at short wavelengths (350-550 nm) could be attributed to the introduction of the TT group on the BDT unit. The optical band gaps (E_{g}^{opt}) of the polymer thin films were determined

TABLE 1 Average Molecular Weights and Thermal Properties

 of the Synthesized Polymers

Polymer	M _n (g∕mol)ª	<i>M</i> _w (g/mol) ^a	PDI ^a	<i>T</i> _d ^b (°C)
PTBDT-TPD	23,000	71,000	3.1	396
PTTBDT-TPD	21,000	58,000	2.8	427

 $^{\rm a}$ $M_{\rm n},$ $M_{\rm w},$ and PDI of the polymers were determined by gel permeation chromatography using polystyrene standards in CHCl_3.

 $^{\rm b}$ Temperature at 5% weight loss with a heating rate of 10 $^\circ\text{C/min}$ under nitrogen.





FIGURE 2 Normalized absorption spectra of PTBDT-TPD and PTTBDT-TPD in (a) chloroform and (b) thin film state on quartz. (c) CV curve and (d) HOMO and LUMO energy levels of polymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to be 1.86 eV for PTBDT-TPD and 1.85 eV for PTTBDT-TPD by their UV-visible absorption edges.

The energy levels of the frontier orbitals (HOMO and LUMO) of the donor polymer are one of crucial parameters that govern the overall performance of the BHJ OPVs. The CV measurements were performed under an Ar atmosphere in a solution of tetra-*n*-butylammonium tetrafluoroborate (TBABF₄; 0.10 M) in acetonitrile at a scan rate of 50 mV/s at room temperature. A platinum plate, platinum wire, and Ag/AgNO₃ electrode were used as the working, counter, and reference electrodes, respectively. The HOMO energy level was determined by measuring the oxidation onsets (E_{ox}) of the polymer films. To obtain the oxidation potentials of the polymer films, the reference electrode was calibrated with the ferrocene/ferrocenium (Fc/Fc⁺) couple, which has a redox potential with an absolute energy level of -4.80 eV in vacuum; the potential of this external standard under the same experimental condi-

tions was 0.098 eV. The oxidation onsets of the PTBDT-TPD and PTTBDT-TPD films were measured by CV to be 0.93 and 0.82 V, respectively. The obtained CV curves of the polymer films are shown in Figure 2(c). According to eq 1,⁹ the $E_{\rm HOMO}$ levels were calculated to be -5.63 and -5.52 eV for PTBDT-TPD and PTTBDT-TPD, respectively.

$$E_{\rm HOMO} = -e(E_{\rm ox}^{\rm onset} + 4.70) \, \text{eV} \tag{1}$$

The lowest unoccupied molecular orbital (LUMO) energy (E_{LUMO}) levels of PTBDT-TPD and PTTBDT-TPD, calculated using eq 2, were -3.77 and -3.67 eV, respectively.

$$E_{\rm LUMO} = E_{\rm HOMO} + E_{\rm g,opt} \tag{2}$$

The CV data are summarized in Table 2. The relatively low HOMO energy levels of PTBDT-TPD and PTTBDT-TPD are beneficial for high V_{OC} values of photovoltaic devices, since the V_{OC} value is proportional to the energy difference between the

TABLE 2 Optical and Electrochemical Properties of Synthesized Polymers

Polymers	$\lambda_{\max, abs}$ (nm)	λ_{\max} (nm)	ε (cm ⁻¹)	$\lambda_{ ext{edge}}$ (nm)	Optical E_{g}^{opt} (eV) ^b	HOMO (eV)	LUMO (eV)
Solution	Film ^a	Film ^a	Film ^a				
PTBDT-TPD	544,609	557,616	$9.8 imes10^4$	666	1.86	-5.63	-3.77
PTTBDT-TPD	544,626	544,625	$1.3 imes10^5$	668	1.85	-5.52	-3.67

^a Polymer film on a quartz plate by spin-casting from solution in chloroform at 1500 rpm for 30 s. $^{\rm b}$ Calculated from the absorption band edge of the copolymer films, $E_{\rm g}=1240/\lambda_{\rm edge}.$



FIGURE 3 Transfer characteristics of OTFTs fabricated using the copolymers as the active layers at a constant source-drain voltage of -60 V: (a) PTBDT-TPD and (b) PTTBDT-TPD. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE 3 Photovoltaic Performance of Polymer:PC₇₁BM-Based Polymer Solar Cells Under an Illumination of AM 1.5G, 100 mW cm⁻²

Polymers	Ratio (w/w)	DIO (3 vol %)	V _{OC} ^a (V)	J _{SC} ^a (mA/cm ²)	<i>FF</i> ^a (%)	PCE ^a (%)	Mobility (cm²/Vs) ^b
PTBDT-TPD	1:1	No	1.01	4.74	32	1.54	$2.0 imes10^{-4}$
	1:1	Yes	0.94	9.27	63	5.44	
PTTBDT-TPD	1:1	No	0.94	7.20	32	2.15	$1.2 imes10^{-3}$
	1:1	Yes	0.91	10.69	62	6.03	

^a Photovoltaic properties of polymer:PC₇₁BM-based devices spin-coated from chloroform solution with a device configuration of ITO/ PEDOT:PSS/polymer:PC₇₁BM (1:1)/Ca/AI.

^b The field-effect carrier mobilities of the polymers were measured by fabricating thin film transistors with a bottom contact geometry using Au electrodes.



FIGURE 4 J-V curves of (a) PTBDT-TPD and (b) PTTBDT-TPD. EQE spectra of optimized OPVs incorporating polymers.



FIGURE 5 (a) Two-dimensional grazing-incidence X-ray diffraction (GIXD) image of pure PTBDT-TPD and PTTBDT-TPD (top), and PTBDT-TPD and PTTBDT-TPD and PTTBDT-TPD:PC₇₁BM (1:1, w/w, with DIO) blend films (bottom), (b) out-of-plane linecuts of pure polymer films, and (c) polymer:PC₇₁BM (1:1) blend films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

 $E_{\rm HOMO}$ of the donor and the $E_{\rm LUMO}$ of the acceptor. The HOMO and LUMO energy levels of the polymers are illustrated in Figure 2(d). The UV-vis absorption properties, optical band-gap energies, and HOMO/LUMO energy levels of the polymers are summarized in Table 2.

Hole Mobility Measurement of the Polymer Films

The charge carrier mobilities of the polymers were measured by fabricating bottom contacted organic thin film transistors (OTFTs) using the polymers as the active layers.¹⁰ Figure 3 shows the drain current versus drain-source voltage curves and the transfer characteristics of the OTFTs fabricated using PTBDT-TPD and PTTBDT-TPD as the p-type channel materials. The OTFTs exhibited typical *p*-channel transistor characteristics. The field-effect mobility was calculated in the saturated regime using eq 3:

$$I_{\rm DS} = (W/2L)\mu C_{\rm i} (V_{\rm gs} - V_{\rm th})^2$$
 (3)

where I_{DS} is the drain-source current in the saturated region, μ is the field-effect mobility, C_i is the capacitance per unit

area of the insulating layer, and $V_{\rm gs}$ and $V_{\rm th}$ are the gate and threshold voltages, respectively.¹¹ As summarized in Table 3, the OTFTs fabricated using PTTBDT-TPD showed a hole mobility of 1.2×10^{-3} cm² V⁻¹ s⁻¹, which was higher than that of the device fabricated using PTBDT-TPD (2.0×10^{-4} cm² V⁻¹ s⁻¹). Notably, these values were comparable to (or exceed) the value that was proposed to be necessary to reduce photocurrent loss and obtain high-performance OPV devices (specifically, 10^{-3} cm² V⁻¹ s⁻¹).¹² The higher hole mobility of PTTBDT-TPD than PTBDT-TPD could be attributed to the stronger interpolymer chain interactions in PTTBDT-TPD induced by the TT units.

Performances and Film Morphologies of BHJ OPVs

To test the photovoltaic performances of PTBDT-TPD and PTTBDT-TPD, we fabricated OPV devices using the polymers as the p-type donors and $PC_{71}BM$ as the electron acceptor with the device configuration of indium tin oxide/ PEDOT:PSS/polymer:PC₇₁BM/Ca/Al. The active layers were spin-coated from a solution of the donor polymer and acceptor in chloroform. The donor to acceptor composition ratio of the active layers was adjusted from 2:1 to 1:2 (w/w) for optimization. The fabricated devices showed the highest short-circuit currents (J_{sc}) at the donor to acceptor composition ratio of 1:1. 1,8-Diiodooctane (DIO, 3 vol %) was used as a processing additive to optimize the morphology of the *p-n* heterojunction in the active layer. The photovoltaic parameters of the optimized devices are summarized in Table 3.

Figure 4(a,b) shows the current *J*–*V* curves of the OPVs based on the polymer:PC₇₁BM (1:1, w/w) with and without the DIO processing additive. In the absence of the additive, the devices exhibited relatively low PCEs of 1.54 and 2.15% for PTBDT-TPD and PTTBDT-TPD, with $V_{\rm OC}$ values of 1.01 and 0.94 V, respectively, which was consistent with the measured HOMO energy levels of the polymers.

The performances of the photovoltaic cells based on PTBDT-TPD:PC₇₁BM and PTTBDT-TPD:PC₇₁BM (1:1) films were greatly enhanced by the use of the DIO additive. The PCEs increased dramatically from 1.54 to 5.44% for the PTBDT-TPD:PC₇₁BM-based device and from 2.15 to 6.03% for the PTTBDT-TPD:PC₇₁BM-based device. However, the $V_{\rm OC}$ values of the DIO-containing devices decreased slightly as compared to those of the devices without DIO. This prominent PCE improvement could be attributed to the significant increase of *Jsc.* The *Jscs* were increased from 4.74 to 9.27 mA/cm² for the PTBDT-TPD:PC₇₁BM device and from 7.20 to 10.69 mA/ cm² for the PTTBDT-TPD:PC₇₁BM device. Moreover, the fill factors (*FF*) were also improved in the DIO-processed devices.

The enhanced *Jsc* value of the PTTBDT-TPD:PC₇₁BM device could be attributed to the enhanced polymer crystallinity and well-organized *p-n* heterojunction morphology of the PTTBDT-TPD:PC₇₁BM active layer. 2D-GIXD was performed to gain insight into the characteristics of the polymer nanostructures in the pure and blend films, such as crystallite





FIGURE 6 TEM images of polymer:PC₇₁BM blends (1:1 w/w) cast from chloroform: (top) PTBDT-TPD:PC₇₁BM (1:1) without DIO; PTTBDT-TPD:PC₇₁BM (1:1) without DIO; (bottom) PTBDT-TPD:PC₇₁BM (1:1) with DIO; PTTBDT-TPD:PC₇₁BM (1:1) with DIO.

orientation, crystal coherence length, and intermolecular distance.¹³ Figure 5 shows the 2D-GIXD images of the pure polymers and polymer:PC71BM (1:1, w/w) blends. Both polymer films showed a reflection peak at $Q_{xy} = 0.36$ Å⁻¹ $[(d_{100}) = 17.5 \text{ Å}]$ in the in-plane direction. In addition, a weak reflection peak at $Q_z = \sim 1.73 \text{ Å}^{-1} [(d_{010}) = 3.63 \text{ Å}]$ in the out-of-plane direction corresponded to π - π stacking between the polymer chains. These two observations suggested that PTBDT-TPD was weakly crystalline with a primarily face-on orientation with respect to the substrate. PTTBDT-TPD exhibited the same face-on orientation, but the d_{010} crystalline peaks were more pronounced, indicating that the TT groups induced a more crystalline lamellar structure by promoting interchain stacking within the polymer. Figure 5 (bottom) shows the GIXD image of the polymer:PC₇₁BM blend films.

Interestingly, the PTTBDT-TPD:PC₇₁BM (1:1, w/w) blend film showed pronounced (100) and (010) reflection peaks, indicating that the polymer stacks in the blend film were highly ordered. In contrast, the PTBDT-TPD:PC₇₁BM film showed relatively weak (100) and (010) reflection peaks.

The morphologies of the polymer:PC₇₁BM active layers were investigated using transmission electron microscopy (TEM). The active layer films without DIO showed severe phase-segregation in the TEM images (Fig. 6). The dark regions in the TEM images correspond to large $PC_{71}BM$ domains (~100 nm), which are far bigger than typical exciton diffusion lengths (~10 nm). This would cause poor exciton dissociation and thus a low current density in OPV devices. In contrast, homogeneous morphologies were observed for the

DIO processed active layer films, as shown in Figure 6 (bottom). The well-organized nanoscale p-n junction would result in a more efficient charge separation, leading to a much higher J_{sc} . Interestingly, the formation of nanoscale networks was markedly enhanced in the PTTBDT-TPD:PC₇₁BM film as compared to the PTBDT-TPD:PC₇₁BM.

Figure 4(c,d) shows the EQE curves of OPVs fabricated under the optimized device fabrication conditions. The EQEs of the devices with DIO were much higher than those without DIO, and the device fabricated using PTTBDT-TPD exhibited higher EQEs than those using PTBDT-TPD. In addition, the spectral responses of the OPV devices suggested that photons within 350–700 nm contributed to the EQE with a maximum EQE of 55% (at 412 nm) and 65% (at 450 and 550 nm) for PTBDT-TPD and PTTBDT-TPD devices, respectively.

CONCLUSIONS

In conclusion, to investigate the effect of alkylthieno[3,2b]thiophene on BDT units for D-A type copolymers, we synthesized two polymers composed of TBDT or TTBDT as the donor units and TPD as the acceptor unit. TTBDT yielded a broad UV-visible absorption, enhanced hole mobility, and higher crystallinity of the copolymer. The organic photovoltaic device fabricated using PTTBDT-TPD as the p-type donor and PC₇₁BM as the acceptor showed a PCE of 6.03%.

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