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Syntheses and solar cell applications of conjugated copolymers containing tetrafluorophenylene units



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ABSTRACT

Novel conjugated copolymers containing tetrafluorophenylene unit have been synthesized and evaluated in bulk heterojunction solar cell. The tetrafluorophenylene unit, as the strong electron deficient moeity, has been applied for the syntheses of donor-acceptor type copolymers with a narrow-band-gap for bulk heterojunction solar cells. **DTBT**, tetrafluorophenylene and four types of **BDT** derivatives as the electron rich units were incorporated using Stille polymerization to generate **PE-BDTF**, **PO-BDTF**, **PE-BDTF** and **PO-BDTTF**. The introduction of even 1% of tetrafluorophenylene unit substituting DTBT of BDTDTBT type of polymers results in significant decrease of the band gap of the polymers. The device with **PO-BDTF**:PC₇₁BM (1:1) showed an open-circuit voltage (V_{OC}) of 0.75 V, a short circuit current (J_{SC}) of 11.80 mA/cm², and a fill factor (*FF*) of 0.59, which yields PCE of 5.22%.

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1. Introduction

Caused by the rapid progress of the development of new conjugated polymers as the electron donors, the power conversion efficiency (PCE) of bulk heterojunction (BHJ) solar cells with fullenrene derivatives, as the electron acceptors, has now reached around 10% [1]. The most common type of polymer solar cell is employing BHJ active layer which is composed of a blend of electron-donating conjugated polymer, and fullerene-derived acceptor such as (6,6)-phenyl C₆₁-butyric acid methyl ester (PC₆₁BM) or (6,6)-phenyl C₇₁-butyric acid methyl ester (PC₆₁BM) or (6,6)-phenyl C₇₁-butyric acid methyl ester (PC₇₁BM) [2–7]. Narrow-band-gaps (1.2 < Eg < 2.0 eV), to cover the long wave-length region for the improvement of total photovoltaic current, have been provided by many donor–acceptor (D–A) types of electron deficient unit [8–11]. Many types of electron rich and

* Corresponding authors. E-mail address: hssuh@pusan.ac.kr (H. Suh). deficient units have been reported including benzo[1,2-b:4,5-b'] dithiophene (BDT) and 2,1,3-benzothiadiazole (BT) unit, respectively [12–20].

Fluorinated conjugated polymers for BHJ solar cells have raised much interest, originated from the high electronegativity and small size of the fluorine atom. The mono and difluorinated conjugated moiety has been incorporated extensively to provide strong electron deficiency, planar structure, good solubility, and improved morphology [21–24].

Here, we report conjugated polymers with tetrafluorophenylene moiety [25] to provide lower band gaps and deeper HOMO energy levels for the improvement of the coverage of the solar spectrum and higher open-circuit voltage, respectively. The copolymers of two units, BDT-DTBT and BDT-tetrafluorophenylene, are synthesized and utilized for the OPVs [26]. Dialkoxy or dithiphene substituted **BDTs** are chosen here as the electron rich co-unit to make use of its solubilizing characteristics and effective tuning of the band gap. The ratios of two units, BDT-DTBT and BDTtetrafluorophenylene, should be optimized to provide the proper processability, hole-mobility and band gaps. The properties of the



series could be compared with the reported BDT-DTBT, with PCE value of 3.93%, which has exactly same structure as compared to our **PO-BDTF** except BDT-tetrafluorophenylene unit [19].

For the evaluation in bulk heterojunction solar cell, new conjugated copolymers in relation to contents of BDT-DTBT and BDTtetrafluorophenylene have been synthesized using Stille polymerization to generate poly[2.1,3-benzothiadiazole-4,7-div]-2,5-thiophenedivl[4.8-bis[2-ethyhexyloxy]benzo[1.2-b:4.5-b']dithiophene-2,6-diyl]-2,5-thiophenediyl-co-2,6-ditetrafluorophenyl[4,8bis[2-ethyhexyloxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl] (PE-BDTF). poly[2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl [4,8-bis[2-octyldodecyloxy]benzo[1,2-b:4,5-b']dithiophene-2,6diyl]-2,5-thiophenediyl-co-2,6-ditetrafluorophenyl[4,8-bis[2octyldodecyloxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl] (PO-BDTF). poly[2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl [4,8-bis[5-(2-ethylhexyl)-2-thienyl]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl]-2,5-thiophenediyl-co-2,6-ditetrafluorophenyl[4,8bis[5-(2-ethylhexyl)-2-thienyl]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl] (PE-BDTTF) and poly[2,1,3-benzothiadiazole-4,7-diyl-2,5thiophenediyl[4,8-bis[5-(2-octyldodecyloxy)-2-thienyl]benzo[1,2b:4,5-b' |dithiophene-2,6-diyl]-2,5-thiophenediyl-co-2,6-ditetrafluorophenyl[4,8-bis[5-(2-octyldodecyloxy)-2-thienyl]benzo[1,2b:4,5-b' dithiophene-2,6-diyl (PO-BDTTF).

2. Experimental section

2.1. 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) with 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. High resolution mass spectra (HRMS) were recorded on a JEOL JMS-700 mass spectrometer under electron impact (EI) or fast atom bombardment (FAB) conditions in the Korea Basic Science Institute (Daegu). Molecular weights and polydispersities of the polymers were determined by gel permeation chromatography (GPC) analysis with a polystyrene standard calibration. The UV-vis absorption spectra were recorded by a Varian 5E UV/VIS/NIR spectrophotometer, while the Oriel InstaSpec IV CCD detection system with xenon lamp was used for the photoluminescence and electroluminescence spectra measurements.

Solar cells were fabricated on an indium tin oxide (ITO)-coated glass substrate with the following structure; ITO-coated glass substrate/poly(3,4-ethylenedioxythiophene):poly(stylenesulfonate) (PEDOT:PSS) (4 nm)/polymer:PCxBM (~100 nm)/Al (100 nm). The ITO-coated glass substrate was first cleaned with detergent, ultrasonicated in acetone and isopropyl alcohol, and subsequently dried overnight in an oven. PEDOT:PSS (Baytron PH) was spin-casted from aqueous solution to form a film of 40 nm thickness. The substrate was dried for 10 min at 140 °C in air and then transferred into a glove box to spin-cast the charge separation layer. A solution containing a mixture of polymer:PC_xBM in ODCB solvent with concentration of 7wt/ml % was then spin-casted on top of the PEDOT/PSS layer. The film was dried for 60 min at 70 °C in the glove box. The sample was heated at 80 °C for 10 min in air. Then, an aluminum (Al, 100 nm) electrode was deposited by thermal evaporation in a vacuum of about 5×10^{-7} Torr. Current density–voltage (J-V) characteristics of the devices were measured using a Keithley 236 Source Measure Unit. Solar cell performance was measured by using an Air Mass 1.5 Global (AM 1.5 G) solar simulator with an irradiation intensity of 1000 W/m^{-2} . An aperture (12.7 mm²) was used on top of the cell to eliminate extrinsic effects such as cross-talk, waveguiding, shadow effects, etc. The spectral mismatch factor was calculated by comparison of solar simulator spectrum with AM 1.5 spectrum at room temperature.

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. 4,7-Bis(5-bromo-2-thienyl)-2,1,3-benzothiadiazole (**2**) [12], 2,6-bis(trimethyltin)-4,8-bis(2-ethyhexyloxy)benzo[1,2-b:3,4-b'] dithiophene (**4**) [27], and 2,6-bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (**8**) [28] were synthesized using similar methods reported.

2.1.1. Synthesis of 4,8-bis(2-octyldodecyloxy)benzo[1,2-b:3,4-b'] dithiophene (**3**)

To the solution of benzo[1,2-b:4,5-b']dithiophene-4,8-dion (1) (4.0 g, 18.0 mmol), zinc powder (2.6 g, 40.0 mmol) in EtOH (16 ml) and DMF (16 ml) was added 5 N NaOH aqueous solution (25 ml) and the mixture was stirred under reflux for 3 h. After adding 1-iode-2octyldodecane (22.3 g, 54.0 mmol) and tetrabutylammoniumbromide (0.9 g, 3.6 mmol), the reaction mixture was further refluxed for 12 h. The reaction mixture was then extracted with ethyl acetate, and the combined organic layer was washed with water and dried over anhydrous MgSO₄. After removing the solvent under reduced pressure, the residue was purified by flash chromatography to give 4.9 g (35%) of compound **3** as a colorless oil: 1 H NMR (300 MHz, CDCl₃) δ (ppm) 7.48 (d, 2H, J = 5.5 Hz), 7.36 (d, 2H, I = 5.5 Hz, 4.17 (d. 4H, I = 4.7 Hz), 1.92–1.80 (m. 2H), 1.72–1.60 (m. 4H), 1.53–1.20 (m, 60H), 0.90–0.87 (t, 12H, I = 6.9 Hz); ¹³C NMR (75 MHz, CDCl₃) δ (ppm) 144.9, 131.7, 130.2, 126.1, 120.5, 39.4, 32.2, 31.6, 30.3, 30.1, 30.0, 29.9, 29.6, 27.2, 22.9, 14.4; HRMS (FAB+, m/z) calcd for C₅₀H₈₆O₂S₂ 783.6148, found 783.6158.

2.1.2. Synthesis of 2,6-bis(trimethyltin)-4,8-bis(2-octyldodecyloxy) benzo[1,2-b:3,4-b']dithiophene (**5**)

To a solution of compound 3 (4.0 g, 5.1 mmol) in anhydrous THF (35 ml) was added dropwise n-butyllithium (2.5 M in hexane) (8.2 ml, 20.4 mmol) via syringe at -78 °C under argon atmosphere. The mixture was stirred at -78 °C for 30 min and then at room temperature for 30 min. After the mixture was cooled to -78 °C again, trimethyltin chloride (1 M in THF) (25.5 g, 25.5 mmol) was added. The mixture was warmed to room temperature and stirred for 12 h. After quenching the reaction with water, the volatile species were evaporated under reduced pressure. The residue was extracted with diethyl ether, and the combined organic layer was washed with water, dried over anhydrous MgSO₄, and concentrated under reduced pressure. Recrystallization affords 5.0 g (88%) of compound 5 as a colorless crystals; mp 38.5 °C; ¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.51 (s, 2H), 4.17 (d, 4H, J = 4.9 Hz), 1.91–1.80 (m, 2H), 1.70–1.60 (m, 4H), 1.52-1.26 (m, 60H), 0.94-0.54 (t, 12H, J = 7.1 Hz), 0.45 (s, 18H); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 143.5, 140.6, 134.1, 133.1, 128.2, 39.4, 32.2, 31.6, 30.4, 30.1, 30.0, 29.9, 29.7, 29.6, 27.3, 22.9, 14.4, -8.1; HRMS (FAB+, m/z) calcd for C₅₆H₁₀₂O₂S₂Sn₂ 1110.5374, found 1110.5370.

2.1.3. Synthesis of 4,8-bis(5-octyldodecylthiophen-2-yl)benzo[1,2b; 4,5-b']dithiophene (7)

In a dried three-neck 250 ml argon purged flask, n-butyllithium (2.5 M in hexane) (10.9 ml, 27.2 mmol) was added dropwise (30 min) to a solution of 2-octyldodecylthiophene (6.0 g, 18.2 mmol) in 40 ml THF at 0 °C. After warming to 50 °C and stirring for 2 h, the reaction mixture was treated with 4,8-dehydrobenzo [l,2-b:4,5-b']dithiophene-4,8-dione (1) (2.0 g, 9.1 mmol) and

stirred for 1.5 h at 50 °C. After cooling the reaction mixture to ambient temperature, SnCl₂·2H₂O (15.4 g, 68.1 mmol) in 30 ml HCl (10%) was added and the mixture was stirred for additional 2 h, after which it was subsequently poured into ice water and extracted with diethyl ether. The combined extracts were dried with anhydrous MgSO₄ and then concentrated under reduced pressure. The residue was purified by flash chromatography to give 5.0 g (30%) of compound **7** as a yellow oil; ¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.65 (d, 2H, J = 5.9 Hz), 7.45 (d, 2H, J = 5.9 Hz), 7.29 (d, 2H, J = 3.6 Hz), 6.89 (d, 2H, J = 3.6 Hz), 2.86 (d, 4H, J = 6.5 Hz), 1.78–1.72 (m, 2H), 1.36–1.22 (m, 64H), 0.89 (t, 12H, J = 7.0 Hz); ¹³C NMR (75 MHz, CDCl₃) δ (ppm) 146.0, 139.3, 137.5, 136.8, 127.9, 127.6, 125.6, 124.3, 123.7, 40.3, 34.9, 33.6, 32.2, 30.2, 29.9, 29.6, 26.9, 22.9, 14.3; HRMS (FAB+, m/z) calcd for C₅₈H₉₁S₄ 915.6004, found 915.6007.

2.1.4. Synthesis of 2,6-bis(trimethyltin)-4,8-bis(5octyldodecylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (**9**)

In a dry two-neck 50 ml argon purged flask, compound 7 (1.5 g, 1.4 mmol) was dissolved in 20 ml anhydrous THF. After cooling to 0 °C, the reaction mixture was treated with a solution n-butyllithium (2.50 M in hexane) (1.5 ml, 3.8 mmol). The reaction mixture was then stirred for 2 h at room temperature. After cooling to 0 °C, the reaction mixture was treated with SnMe₃Cl solution (1 M in THF) (5.5 ml, 5.5 mmol) in one portion. The reaction mixture was stirred at 0 °C for 30 min and then warmed to room temperature and stirred for 2 h. Subsequently, the reaction mixture was quenched by the addition of 10 ml distilled water, and extracted by diethyl ether. Finally, the combined organic phase was dried with anhydrous MgSO₄ and concentrated to obtain yellow viscous crude product. Recrystallization afforded 1.0 g (74%) of compound 9 as light-yellow oil; ¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.69 (s, 2H), 7.32 (d, 2H, J = 3.5 Hz), 6.90 (d, 2H, J = 3.6 Hz), 2.87 (d, 4H, J = 6.5 Hz), 1.80-1.70 (m, 2H), 1.40-1.22 (m, 64H), 0.88 (t, 12H, J = 7.0 Hz), 0.40(s, 18H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm) 145.6, 143.5, 142.4, 138.2, 138.0, 131.4, 127.8, 125.6, 122.7, 40.3, 34.9, 33.7, 32.2, 30.3, 30.0, 29.6, 27.0, 23.0, 14.4, -8.1; HRMS (FAB+, m/z) calcd for C₆₄H₁₀₆S₄Sn₂ 1242.5221, found 1242.5226.

Synthesis of Poly[2,1,3-benzothiadiazole-4,7-diyl-2,5-thio-phenediyl[4,8-bis[2-ethyhexyloxy]benzo[1,2-b:4,5-b']dithio-phene-2,6-diyl]-2,5-thiophenediyl-*co*-2,6-ditetrafluorophenyl[4,8-bis[2-ethyhexyloxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl] (**PE-BDTF**) and **PE-BDTF5.**

The copolymers were synthesized by using BDT-DTBT and BDTtetrafluorophenylene units with ratio of 99:1. To a stirred solution of 2,6-bis(trimethyltin)-4,8-bis(2-ethyhexyloxy)benzo[1,2-b:3,4b']dithiophene (**4**) in 30 mL of chlorobenzene, were added 4,7bis(5-bromo-2-thienyl)-2,1,3-benzothiadiazole (10)tetrafluorodibromobenzene (11), 40 mol% of P(o-tolyl)₃, and 5 mol% of Pd₂(dba)₃. After being stirred at 80 °C for 2 days, the reaction mixture was added 1 ml (2.99 mmol) of phenyltributylstannane, and further heated at 80 °C for 3 h. Then the reaction mixture was treated with 1 ml (9.55 mmol) of bromobenzene, and refluxed for 6 h. After cooling to room temperature, the reaction mixture was poured into 100 mL of methanol. The precipitated solid was filtered and dissolved with minimum amount of chloroform, and poured into the 200 mL of acetone. After filtration by glass filter, the precipitate was purified by Soxhlet extraction with methanol and dried in vacuum for 48 h to generate PE-BDTF. For the synthesis of PE-BDTF5, BDT-DTBT and BDT-tetrafluorophenylene units were used with a ratio of 95:5 following exactly same procedure.

Synthesis of Poly[2,1,3-benzothiadiazole-4,7-diyl-2,5-thio-phenediyl[4,8-bis[2-octyldodecyloxy]benzo[1,2-b:4,5-b']dithio-phene-2,6-diyl]-2,5-thiophenediyl-*co*-2,6-ditetrafluorophenyl[4,8-

bis[2-octyldodecyloxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl] (**PO-BDTF**) and **PO-BDTF5**.

This dark purple copolymer was prepared by a procedure similar to that for **PE-BDTF**, using 2,6-bis(trimethyltin)-4,8-bis(2octyldodecyloxy)benzo[1,2-b:3,4-b']dithiophene (**5**), 7-bis(5bromo-2-thienyl)-2,1,3-benzothiadiazole (**10**) and tetrafluorodibromobenzene (**11**) as the monomers. For the synthesis of **PO-BDTF5**, BDT-DTBT and BDT-tetrafluorophenylene units were used with a ratio of 95:5 following exactly same procedure.

Synthesis of Poly[2,1,3-benzothiadiazole-4,7-diyl-2,5-thio-phenediyl[4,8-bis[5-(2-ethylhexyl)-2-thienyl]benzo[1,2-b:4,5-b'] dithiophene-2,6-diyl]-2,5-thiophenediyl-*co*-2,6-ditetra-fluorophenyl[4,8-bis[5-(2-ethylhexyl)-2-thienyl]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl] (**PE-BDTTF**) and **PE-BDTTF5.**

This dark purple copolymer was prepared by a procedure similar to that for **PE-BDTF**, using 2,6-bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene (**8**), 7-bis(5-bromo-2-thienyl)-2,1,3-benzothiadiazole (**10**) and tetra-fluorodibromobenzene (**11**) as the monomers. For the synthesis of **PE-BDTTF5**, BDT-DTBT and BDT-tetrafluorophenylene units were used with a ratio of 95:5 following exactly same procedure.

Synthesis of Poly[2,1,3-benzothiadiazole-4,7-diyl-2,5-thio-phenediyl[4,8-bis[5-(2-octyldodecyloxy)-2-thienyl]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl]-2,5-thiophenediyl-*co*-2,6-ditetra-fluorophenyl[4,8-bis[5-(2-octyldodecyloxy)-2-thienyl]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl] (**PO-BDTTF**), **PO-BDTTF5**.

This dark purple copolymer was prepared by a procedure similar to that for **PE-BDTF**, using 2,6-bis(trimethyltin)-4,8-bis(5-(2-octyldodecyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (**9**), 7-bis(5-bromo-2-thienyl)-2,1,3-benzothiadiazole (**10**) and tetra-fluorodibromobenzene (**11**) as the monomers. For the synthesis of **PO-BDTTF5**, BDT-DTBT and BDT-tetrafluorophenylene units were used with a ratio of 95:5 following exactly same procedure.

3. Results and discussion

3.1. Synthesis and characterization of the polymers

The general synthetic routes toward polymers are outlined in Scheme 1. 2,6-Bis(trimethyltin)-4,8-bis(2-ethyhexyloxy)benzo[1,2b:3,4-b' dithiophene dithiophene (4), 4,7-bis(5-bromo-2-thienyl)-2,1,3-benzothiadiazole (10) and tetrafluorodibromobenzene (11) were copolymerized through Stille coupling reaction with Pd(0)catalyst to yield **PE-BDTF** and **PE-BDTF5**. 2,6-Bis(trimethyltin)-4,8-bis(2-octyldodecyloxy)benzo[1,2-*b*:3,4-*b*']dithiophene (5), 4,7bis(5-bromo-2-thienyl)-2,1,3-benzothiadiazole (10) and tetrafluorodibromobenzene (11) were copolymerized through Stille coupling reaction with Pd(0)-catalyst to yield PO-BDTF and PO-BDTF5. 2,6-Bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2vl)benzo[1.2-b:4.5-b'] dithiophene (8). 4.7-bis(5-bromo-2thienyl)-2,1,3-benzothiadiazole (10)and tetrafluorodibromobenzene (11) were copolymerized through Stille coupling reaction with Pd(0)-catalyst to yield PE-BDTTF and PE-BDTTF5. 2,6-Bis(trimethyltin)-4,8-bis(5-(2-octyldodecyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (9), 4,7-bis(5-bromo-2thienyl)-2,1,3-benzothiadiazole (10)and tetrafluorodibromobenzene (11) were copolymerized through Stille coupling reaction with Pd(0)-catalyst to yield **PO-BDTTF** and **PO-**BDTTF5.

The molar feed ratios of monomer 4,7-bis(5-bromo-2-thienyl)-2,1,3-benzothiadiazole (**10**) to tetrafluorodibromobenzene (**11**) were 99:1 for **PE-BDTF, PO-BDTF, PE-BDTTF** and **PO-BDTTF** and 95:5 for **PE-BDTF5, PO-BDTF5, PE-BDTTF5** and **PO-BDTTF5**. The structures and purities of the monomers were confirmed by ¹H NMR, ¹³C NMR, and HRMS.



Scheme 1. Synthetic route for the synthesis of the polymers.

Table 1
Polymerization results and thermal properties of polymers.

Polymer	$M_{\rm n}^{\rm a}({\rm g/mol})$	Mw ^a (g/mol)	PDI ^a	TGA $(T_d)^b$	DSC (Tg)
PE-BDTF	5000	5700	1.1	337	101
PO-BDTF	37,000	49,000	1.3	315	109
PE-BDTTF	10,000	14,000	1.3	348	103
PO-BDTTF	34,000	39,000	1.1	391	111
PE-BDTF5	35,000	45,000	1.3	310	97
PO-BDTF5	1000	1100	1.1	315	98
PE-BDTTF5	5600	8400	1.5	350	98
PO-BDTTF5	2200	3500	1.6	362	89

 $^{\rm a}$ Molecular weight ($M_{\rm w}$) and polydispersity (PDI) of the polymers were determined by gel permeation chromatography (GPC) in THF using polystyrene standards.

^b Onset decomposition temperature (5% weight loss) measured by TGA under N₂.

Table 1 summarizes the polymerization results including molecular weight, polydispersity index (PDI) and thermal stability of the polymers. As shown in Table 1, the number-average molecular weight (M_n) and the weight-average molecular weight (M_w) of the copolymers were in the range of 1000–37,000 (M_n) and 1100–49,000 (M_w), respectively, with PDI (polydispersity indices, M_w/M_n) values in the range of 1.1–1.6.

The thermal properties of the polymers were characterized by both differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). The DSC and TGA of the polymers are summarized in Table 1. The DSC analysis was performed under a nitrogen atmosphere (50 mL/min) on a annealing. The copolymers showed good thermal stability with a glass transition temperature (T_g) of the range of 89–111 °C measured by DSC 2920 at heating rates of 10 °C/min over the temperature range of 30–250 °C. The



Fig. 1. The normalized UV–visible absorption spectra of the polymer: **PE-BDTF**, **PO-BDTF**, **PE-BDTTF** and **PO-BDTTF** in chloroform solution (a) and in thin solid state (b), **PE-BDTF5**, **PO-BDTF5**, **PE-BDTF5** and **PO-BDTF5** in chloroform solution (c) and in thin solid state (d).

TGA was performed with TGA 2950 in a nitrogen atmosphere at a heating rate of 10 °C/min to 600 °C. TGA showed that copolymers are thermally stable with only about 5% weight loss in nitrogen at temperatures (T_d) of the range of 315–391 °C. The copolymers have high decomposition temperatures. The high thermal stability of the resulting copolymers prevents the deformation of the polymer morphology and is important for organic photovoltaics application [29].

3.2. Optical properties

The solution was prepared using ODCB as a solvent and the thin film by spin-coating on quartz plates from the solution in ODCB at room temperature. The UV–vis absorption spectra of the copolymers in solution and as thin films are shown in Fig. 1 and summarized in Table 2.

The chloroform solutions of **PE-BDTF**, **PO-BDTF**, **PE-BDTTF** and **PO-BDTTF** showed absorption bands with maximum peaks at around 346–426 and 546–598 nm. (Fig. 1a) The solid films of **PE-BDTF**, **PO-BDTF**, **PE-BDTTF** and **PO-BDTTF** showed absorption bands with maximum peaks at around 368–461 and 602–644 nm.

Table 2	
Characteristics of the UV-vis absorption spectra.	

Copolymers	Solution λ_{max}^{a} (nm)	Film λ_{max} (nm)
PE-BDTF	415, 567	423, 622
PO-BDTF	426, 598	433, 630
PE-BDTTF	346, 546	461, 644
PO-BDTTF	359, 582	368, 602
PE-BDTF5	440, 681	434, 664
PO-BDTF5	425, 634	423, 635
PE-BDTTF5	435, 675	442, 623
PO-BDTTF5	424, 590	441, 610

^a Solution absorption in chloroform.

(Fig. 1b) The chloroform solutions of PE-BDTF5, PO-BDTF5, PE-BDTTF5 and PO-BDTTF5 showed absorption bands with maximum peaks at around 424–440 and 634–681 nm. (Fig. 1c) The solid films of PE-BDTF5, PO-BDTF5, PE-BDTTF5 and PO-BDTTF5 showed absorption bands with maximum peaks at around 423-442 and 610–664 nm. (Fig. 1d) The polymer solutions with 5% ratio of tetrafluorophenylene unit showed red shift as compared to the case of 1%. The polymer solutions of high molecular weight (**PO-BDTF**, **PO-BDTTF** and **PE-BDTF5**) with the longer effective conjugation length exhibited red-shifted absorption as compared to the corresponding polymers only with different alkyl group (PE-BDTF, PE-BDTTF and PO-BDTF5) which has lower molecular weights. The shoulder peaks of all the copolymers at about 400 nm have been ascribed to a delocalized excitonic π - π * transition in the conjugated chains and the long-wavelength absorption peaks attributed to the intramolecular charge transfer (ICT) between the electron rich and electron deficient units [30]. The absorption onsets of the polymers in solution were found to be 727-805 nm, corresponding to optical band gaps of 1.54-1.71 eV.

3.3. Electrochemical properties

The HOMO and LUMO energy levels were estimated from the oxidation and reduction onset values of the cyclic voltammetry (CV). The CV was performed with a solution of tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) (0.10 M) in acetonitrile at a scan rate of 100 mV/s at room temperature under argon atmosphere. A platinum electrode (~0.05 cm²) coated with a thin polymer film was used as the working electrode. Pt wire and 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 4.8 eV below the vacuum level. The CV spectra are shown in Fig. 2, and the oxidation potentials derived from the onsets of electrochemical p-doping are



Fig. 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 (a) PE-BDTF, PO-BDTF, PE-BDTFF, and PO-BDTFF, (b) PE-BDTF5, PO-BDTF5, PE-BDTF5 and PO-BDTTE5

summarized in Table 3. HOMO and LUMO levels were calculated according to the empirical formula $(E_{HOMO} = -([E_{onset}]^{ox} + 4.8) \text{ eV})$ and $(E_{LUMO} = -([E_{onset}]^{red} + 4.8) \text{ eV})$, respectively. The polymers exhibit irreversible processes in an oxidation scan. The oxidation and reduction onsets of PE-BDTF, PO-BDTF, PE-BDTTF and PO-**BDTTF** were exhibited at (0.89, -0.56), (0.95, -0.51), (0.87, -0.48) and (0.95, -0.42), respectively. The HOMO levels of the polymers estimated from the oxidation onsets were -5.75 to -5.67 eV. The LUMO energy levels of the polymers were determined to be -4.32to -4.24 eV. The PE-BDTF, PO-BDTF, PE-BDTTF and PO-BDTTF exhibited electrochemical band gaps of 1.35-1.47 eV, which are about 0.4 eV lower than those of the corresponding polymers [9,10] without tetrafluorophenylene unit.

The oxidation and reduction onsets of PE-BDTF5, PO-BDTF5, **PE-BDTTF5** and **PO-BDTTF5** were exhibited at (0.8, -0.43), (0.93, -0.7), (0.83, -0.4) and (0.76, -0.42), respectively. The HOMO levels of the polymers estimated from the oxidation onsets were -5.73 to -5.56 eV. The LUMO energy levels of the polymers were determined to be -4.40 to -4.10 eV. The PE-BDTF5, PO-BDTF5, PE-BDTTF5 and PO-BDTTF5 exhibited electrochemical band gaps of 1.18-1.63 eV, which are lower than those of the corresponding polymers with 1% tetrafluorophenylene unit, except the case of PO-BDTF.

3.4. Photovoltaic properties

The OPVs were fabricated by spin-casting of chlorobenzene (CB) solutions of PC₆₁BM/polymers or PC₇₁BM/polymers. All polymers were applied as donors into a conventional BHJ type OPV device with PC₆₁BM or PC₇₁BM as acceptor, which has been widely used

for this purpose. Typical J-V characteristics of devices with the configuration of ITO/PEDOT:PSS (40 nm)/polymer:PCxBM (1:1, 1:2 or 1:3) (100 nm)/Al (100 nm) under AM 1.5G irradiation (100 mW/ cm²) are depicted in Fig. 3 and summarized in Table 4. The photovoltaic parameters of all the polymers, including open circuit voltage (V_{OC}), short circuit current (J_{SC}), fill factor (*FF*), and power conversion efficiency (PCE) are summarized in Table 4. The devices with **PE-BDTF**:PC₆₁BM (1:3), **PO-BDTF**:PC₆₁BM (1:1), **PE-**BDTTF:PC₆₁BM (1:3) and PO-BDTTF:PC₆₁BM (1:1) layers showed open-circuit voltages (V_{OC}) of 0.60, 0.77, 0.51 and 0.73 V, short circuit currents (I_{SC}) of 2.58, 6.79, 1.01 and 2.38 mA/cm², and fill factors (FF) of 0.43, 0.52, 0.36 and 0.38, giving power conversion efficiencies of 0.66, 2.47, 0.18 and 0.66%, respectively. The device with **PO-BDTF**:PC₇₁BM (1:1) layers, using dichlorobenzene as the solvent, showed an open-circuit voltage (V_{OC}) of 0.75 V, a short circuit current (I_{SC}) of 11.80 mA/cm², and a fill factor (FF) of 0.59, giving a power conversion efficiency of 5.22%, higher value as compared to the cases with chloroform and chlorobenzene as the solvents for the spin coating. The effect of annealing and adding various kind additives was investigated without much success as shown in the supplement part (Table S1-S4 and Fig. S1). The series with 5% ratio of tetrafluorophenylene unit, PE-BDTF5, PO-BDTF5, PE-BDTTF5 and PO-BDTTF5, showed too low solubility to fabricate meaningful devices.

The field-effect carrier mobilities of the polymers were measured by fabricating thin film field-effect transistors (FETs) using the top-contact geometry. Fig. S2-S5 show the FET transfer characteristics of the polymer devices of the OTS-modified SiO₂. Hole mobilities of the polymers were calculated from the transfer characteristics of the OFETs. The field-effect hole mobilities of PE-

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	actrochemical potentials and energy levels of the copolymers.							
Copolymers	Optical band gap ^a (eV)	HOMO ^b (eV)	LUMO ^c (eV)	$E_{\rm ox}^{\rm d}$ (V)	$E_{\rm red}^{\rm d}({\rm V})$	Electrochemical band gap ^e (eV)		
PE-BDTF	1.56	-5.69	-4.24	0.89	-0.56	1.45		
PO-BDTF	1.71	-5.75	-4.29	0.95	-0.51	1.46		
PE-BDTTF	1.54	-5.67	-4.32	0.87	-0.48	1.35		
PO-BDTTF	1.69	-5.75	-4.28	0.95	-0.52	1.47		
PE-BDTF5	1.48	-5.60	-4.37	0.8	-0.43	1.23		
PO-BDTF5	1.62	-5.73	-4.10	0.93	-0.7	1.63		
PE-BDTTF5	1.57	-5.63	-4.40	0.83	-0.4	1.23		
PO-BDTTF5	1.62	-5.56	-4.38	0.76	-0.42	1.18		

Optical energy band gap was estimated from the onset wavelength of the optical absorption. $E_{\rm g} = 1240 / \lambda_{\rm onset}$.

Determined by UPS.

 $LUMO = HOMO + \Delta E_{opt}$ film.

Onset oxidation and reduction potential measured by cyclic voltammetry.

Calculated from the E_{ox} and E_{red} .



Fig. 3. Current density-potential characteristics of the polymers solar cells under the illumination of AM 1.5, 100 mW/cm² (a) **PE-BDTF**:PC₆₁BM, (b) **PO-BDTF**:PC₆₁BM, (c) **PE-BDTF**:PC₆₁BM, (d) **PO-BDTF**:PC₆₁BM, (e) **PO-BDTF**:PC₆₁BM, (c) **PE-BDTF**:PC₆₁BM, (d) **PO-BDTF**:PC₆₁BM, (e) **PO-BDTF**:PC₆₁BM, (c) **PE-BDTF**:PC₆₁BM, (c) **PE-BDTF**:PC₆₁BM,

Table 4				
Photovoltaic properties	of the	copolymer	solar	cells.

Copolymers	Ratio copolymer:PC _x BM	$V_{\rm OC}$ (V)	J _{SC} (mA/cm ²)	FF	PCE (%)
PE-BDTF (PC ₆₁ BM)	1:2	0.56	2.41	0.40	0.61
	1:3	0.60	2.58	0.43	0.66
PO-BDTF (PC ₆₁ BM)	1:1	0.72	6.79	0.45	2.47
	1:2	0.73	7.26	0.39	2.08
	1:3	0.71	7.83	0.35	1.98
PO-BDTF (PC71BM)	1:1 (DCB)	0.75	11.80	0.59	5.22
	1:1 (CB)	0.75	8.15	0.54	3.29
	1:1 (CF)	0.77	5.87	0.54	2.41
PE-BDTTF (PC ₆₁ BM)	1:1	0.32	0.61	0.32	0.06
	1:3	0.51	1.01	0.36	0.18
PO-BDTTF (PC ₆₁ BM)	1:1	0.73	2.38	0.38	0.66
	1:3	0.67	1.81	0.40	0.49



Fig. 4. IPCE curves of the polymer solar cells after annealing at 100 °C under the illumination of AM 1.5, 100 mW/cm². IPCE curves of (a) **PE-BDTF**:PC₆₁BM (1:3), (b) **PO-BDTF**:PC₆₁BM (1:1), (c) **PE-BDTTF**:PC₆₁BM (1:3), (d) **PO-BDTTF**:PC₆₁BM (1:1), (e) **PO-BDTF**:PC₇₁BM (1:1) blend films cast from chlorobenzene (a–d) and three types of solutions (e).



Fig. 5. Atomic force microscopy images of (a) **PE-BDTF**:PC₆₁BM (1:3), (b) **PO-BDTF**:PC₆₁BM (1:1), (c) **PE-BDTTF**:PC₆₁BM (1:3), (d) **PO-BDTF**:PC₆₁BM (1:1), (e) **PO-BDTF**:PC₇₁BM (1:1), (f) **PO-BDTF**:PC₇₁BM (1:1), and (g) **PO-BDTF**:PC₇₁BM (1:1) blend films cast from chlorobenzene (a–d and f), dichlorobenzene (e), and chloroform (g).

BDTF, PO-BDTF, PE-BDTTF and **PO-BDTTF** are 1.39×10^{-6} , 2.4×10^{-4} , 1.07×10^{-6} , and 9.67×10^{-7} cm²/V, respectively.

The incident photon to current efficiency (IPCE) spectra of the photovoltaic devices from **PE-BDTF**:PC₆₁BM (1:3), **PO-BDTF**:PC₆₁BM (1:1), **PE-BDTTF**:PC₆₁BM (1:3), and **PO-BDTTF**:PC₆₁BM (1:1) blend films cast with chlorobenzene solution and **PO-BDTF**:PC₇₁BM (1:1) blend films cast from three types of solutions are presented in Fig. 4. The IPCE peak of **PO-BDTF**:PC₆₁BM (1:1) film shows about 40% IPCE value from 300 nm to 750 nm with maximum value at about 341 nm, higher value as compared to the other polymers of the series.

Especially, the IPCE value of **PO-BDTF**:PC₇₁BM (1:1) blend films by spin-casting using dichlorobenzene solution showed higher value at the broad range as compared to films using the other solutions as shown in Fig. 4e.

The morphology of the copolymers/PC₆₁BM or copolymers/PC₇₁BM films cast from their solution in chlorobenzene, dichlorobenzene, or chloroform were studied by atomic force microscopy (AFM) as shown in Fig. 5, where the images were obtained in a surface area of $2.5 \times 2.5 \ \mu\text{m}^2$ by the tapping mode.

The morphologies of **PE-BDTF**:PC₆₁BM (1:3), **PO-BDTF**:PC₆₁BM (1:1), **PE-BDTTF**:PC₆₁BM (1:3), **PO-BDTTF**:PC₆₁BM (1:1) blend films from chlorobenzene solutuion are 9.25, 3.16, 9.77, and 8.47 nm, respectively. The morphologies of **PO-BDTF**:PC₇₁BM (1:1) blend films from chlorobenzene, dichlorobenzene, and chloroform solutions are 2.48, 2.65 and 7.92 nm, respectively. The surface of the active layer of **PO-BDTF**:PC₇₁BM (1:1) with dichlorobenzene is quite smooth, with a root-mean-square (rms) value of 2.65 nm, which results in the highest PCE value out of the series.

4. Conclusion

Novel conjugated copolymers in relation to contents of BDT-DTBT and BDT-tetrafluorophenylene have been synthesized via Stille coupling reaction with Pd catalyst to generate **PE-BDTF**, **PO-BDTF**, **PE-BDTTF**, **PO-BDTTF5**, **PO-BDTF5**, **PE-BDTTF5** and **PO-BDTTF5** for OPV devices. The introduction of tetrafluorophenylene unit should be optimized to afford the appropriate processability, hole-mobility and band gaps. The best device with **PO-BDTF**:PC₇₁BM (1:1) showed an open-circuit voltage (V_{OC}) of 0.75 V, a short circuit current (J_{SC}) of 11.80 mA/cm², and a fill factor (FF) of 0.59, which yield PCE of 5.22%. Further optimization of the ratio of BDT-tetrafluorophenylene unit may improve the morphology, hole-mobility and band gap leading to the better performance of the device. As compared to the band gap of BDT-DTBT (2.18 eV) [19], the introduction of small amount of tetrafluorophenylene unit substituting DTBT decreased the band gap (1.23–1.63 eV) significantly. In case of PTBDTDTBT also, by applying same modification, the band gap of PTBDTDTBT (1.62 eV) [20] was decreased to 1.18-1.47 eV. Since the introduction of even 1% of tetrafluorophenylene unit substituting DTBT of BDTDTBT type of polymers results in significant decrease of the band gap of the polymers, similar type of tactics could be applied for the generation of lower band gap polymers especially for the tandem solar cell structure, similar type of tactics could be applied for the generation of lower band gap polymers especially for the tandem solar cell structure.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2015.06.052.

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