



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 moiety, 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-BDTTF** 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 fullerene 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 (PC₇₁BM) [2–7]. Narrow-band-gaps (1.2 < E_g < 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 donating conjugated polymers, using electron rich unit and electron deficient unit [8–11]. Many types of electron rich and

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 dithiophene 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 BDT-tetrafluorophenylene, should be optimized to provide the proper processability, hole-mobility and band gaps. The properties of the

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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 BDT-tetrafluorophenylene have been synthesized using Stille polymerization to generate poly[2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl[4,8-bis[2-ethoxyhexyloxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl]-2,5-thiophenediyl-co-2,6-ditetrafluorophenyl[4,8-bis[2-ethoxyhexyloxy]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-2,6-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**), 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[4,8-bis[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-2,5-thiophenediyl[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-ditetrafluorophenyl[4,8-bis[5-(2-octyldodecyloxy)-2-thienyl]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl] (**PO-BDTTF**).

2. Experimental section

2.1. Materials and instruments

^1H and ^{13}C 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 Oriol 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:PC_xBM (~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/m². 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-ethoxyhexyloxy)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-dione (**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-iodo-2-octyldodecane (22.3 g, 54.0 mmol) and tetrabutylammonium-bromide (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; ^1H NMR (300 MHz, CDCl₃) δ (ppm) 7.48 (d, 2H, $J = 5.5$ Hz), 7.36 (d, 2H, $J = 5.5$ Hz), 4.17 (d, 4H, $J = 4.7$ 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, $J = 6.9$ Hz); ^{13}C 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, CDCl₃) 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[1,2-b: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[1,2-b:4,5-b']dithiophene-4,8-dione (**1**) (2.0 g, 9.1 mmol) and

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