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New Alkylthio-Thieno[3,2-b]thiophene-Substituted Benzodithiophene-Based High Efficient Photovoltaic Polymer

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♦EXPERIMENTAL

♦ Materials

Reagents were purchased from Aldrich, Alfa Aesar, or TCI Korea, and used without further purification. [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). 4,8-Dehydrobenzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione, 2-ethylhexyl-4,6-dibromo-3-fluorothieno[3,4-*b*]thiophene-2-carboxylate (FTT)^[1], and 2,6-bis(trimethyltin)-4,8-bis((2-ethylhexyl)thieno[3,2-b]thiophene)-benzo[1,2-b:4,5-b']dithiophene) (TTBDT)^[2] was synthesized similarly to methods described in previous reports.

♦ Measurements

¹H and ¹³C NMR spectra were recorded using a Varian Mercury Plus 300MHz spectrometer and the chemical shifts were recorded in units of ppm with chloroform as the internal standard. Elemental analysis was carried out using a 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) relative to a polystyrene standard using a Waters high-pressure GPC assembly (model M590). Thermal analyses were carried out on a Mettler Toledo TGA/SDTA 851^e 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 out in acetonitrile containing 0.1 M tetrabutylammoniumtetrafluoroborate (TBABF₄) as the supporting electrolyte using Ag/AgNO₃ as the reference electrode, a platinum wire as the counter electrode, and a platinum working electrode.

♦ Fabrication of Inverted Photovoltaic Devices

Inverted BHJ OPV devices with ITO/ZnO/polymer:PC₇₁BM(1:1.5, w/w)/MoO₃/Ag structures were fabricated. The precursor solution (concentration of solution; 0.75 M), was prepared by dissolving zinc acetate [Zn(CH₃COO)₂·2H₂O] in 2-methoxyethanol solution containing ethanolamine as stabilizer. The solution stirred at 60 °C for 30 min to become homogeneous solution. The precleaned ITO substrates were treated with UV–ozone. The fabrication of sol-gel ZnO was made from spin coating the precursor solution at 2000 rpm for 40 s. the substrate was immediately annealed onto hot plate at 380 °C with a heating rate of 20 °C min⁻¹. Then, substrates were transferred to a N₂-filled globe box. The active layer of polymer:PC₇₁BM (97% chlorobenzene/3% DIO mixture) was prepared by spin coating at a speed of 1000 rpm for 30 s. The device was solvent annealed for 1 h at ambient temperature in the glove box. The device fabrication was completed by thermal evaporation of 10 nm MoO₃ and 100 nm Ag as the anode under vacuum at a base pressure of 3×10^{-6} torr. The measured effective area of the device was 0.09 cm².

Measurements of OPV Devices

The thickness of the active layer was measured using a KLA Tencor Alpha-step IQ surface profilometer. 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/cm² using an Oriel 1000 W solar simulator. Electronic data were recorded using a Keithley 236 source-measure unit. All characterizations 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 EQE was measured as a function of wavelength in the range between 300~1100 nm using a Xenon Short Arc Lamp as the light source (McScience K3100 EQX); calibration was performed using a Si reference photodiode. The measurements were carried out after masking all but the active cell area of the fabricated device. Characterization was performed under ambient conditions.

Fabrication of Hole- only Devices

The hole mobilities of the active layer were determined by applying the space charge limited current (SCLC) model to the J-V measurements of the devices. The hole-only devices of the polymers were fabricated on top of a prepatterned ITO substrate. After cleaning the ITO with aqueous detergent, deionized water, acetone, and 2-propanol, UV-ozone treatment was applied for 15 min. PEDOT: PSS (Clevios P VP AI4083) was spin-coated from an aqueous dispersion phase to a layer 30 nm thick. The coated substrate was then baked at 120 °C for 60 min. After baking, a solution of the copolymer in chlorobenzene was spin-cast on top of the PEDOT:PSS layer to a thickness of ~ 100 nm, and the samples were dried for 6 h at room temperature under vacuum conditions. The device fabrication was completed by thermal evaporation of 10 nm MoO₃ and 100 nm Ag as the anode in vacuo at a base pressure of 3×10^{-6} Torr. A similar way was employed to measure the hole only mobility of the polymer:PC71BM blend through the charge-limited current (SCLC) method with device of space а structure ITO/PEDOT:PSS/polymer:PC71BM/MoO₃/Ag. The hole mobilities were calculated from the space charge limited current (SCLC) using the following equation:

$$J_{SCLC} = (9/8)\varepsilon_r \varepsilon_0 \mu (V^2/L^3)$$

where J is the current density, εr is the dielectric constant of the polymers, εo is the permittivity of the vacuum, μ is the hole mobility, L is the film thickness of the blend films, $V = V_{appl} - V_{bi}$, V_{appl} is the applied potential, and V_{bi} is the built-in voltage which results from the difference in the work function of the anode and the cathode.

Synthesis of Monomers and Polymers

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

24 mL of *n*-butyllithium (54 mmol, 1.6 M in hexane) was added dropwise into thiophene (5.0 g, 36 mmol) and 100 mL of dry THF at 0 °C under argon protection. After the mixture was

stirred at 0 °C for 1.5 h, sulfur powder (1.4 g, 54 mmol) was added in one portion, and then the resulting suspension was stirred at 0 °C for 2 h. Subsequently, 2-ethylhexylbromide (7.0 mL, 54 mmol) was added dropwise. The reaction mixture was stirred overnight at room temperature. Then, ice-water containing NH₄Cl was added to the reaction, and the mixture was extracted with EtOAc, washed with water, and dried over MgSO₄. After the removal of solvent, purification was carried out by silica gel column chromatography using hexane as eluent and compound **3** (10.5 g, yield 92%) was obtained as a colorless oil. ¹H NMR(300 MHz, CDCl₃, ppm): δ 7.38 (d, 1H), 7.29 (s, 1H), 7.19 (d, 7.19), 2.87 (d, 2H), 1.60-1.56 (q, 1H), 1.56-1.28 (q, 8H), 0.88(m, 6H). ¹³C NMR (75 MHz, CDCl₃, ppm): δ 138.1, 135.4, 133.3, 125.7, 124.2, 121.7, 38.9, 37.8, 35.1, 29.4, 28.2, 25.0, 15.4, 12.3.

Synthesis of 4,8-bis((2-ethylhexylthio)thieno[3,2-b]thiophene)-benzo[1,2-b:4,5b' dithiophene (2) Compound 1 (10.3 g, 36.2 mmol) and THF (100 mL) were added to a flask under an inert atmosphere. The solution was cooled using an ice-water bath, and 27.2 mL of nbutyllithium (43.4 mmol, 1.6 M in hexane) were added dropwise to the flask. 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 (2.0 g, 9.1 mmol) in THF (20 mL) was added, and the mixture was stirred for 1 h at 50 °C. After cooling to ambient temperature, SnCl₂·2H₂O (8.0 g, 22.7 mmol) in 10% HCl (16 mL) was added, and the mixture was stirred for an additional 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 removing the solvents (4.0 g, 75% yield). ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.66 (d, 2H), 7.56 (s, 2H), 7.51 (d, 2H), 7.37 (s, 2H), 2.94 (d, 4H), 1.65-1.63 (m, 2H), 1.53–1.39 (m, 16H), 0.94–0.88 (m, 12H). ¹³C NMR (75 MHz, CDCl₃, ppm): δ 139.8, 137.1, 135.4, 131.3, 130.0, 129.7, 128.1, 126.8, 125.7, 122.9, 120.0, 40.1, 38.4, 32.2, 30.3, 26.3, 24.9, 16.1, 11.8. Anal. Calcd for C₃₈H₄₂S₈: C, 60.43; H, 5.61; S, 33.96. Found: C, 60.31; H, 5.48; S,

34.1.

2,6-bis(trimethyltin)-4,8-bis((2-ethylhexylthio)thieno[3,2-b]thiophene)-**Synthesis** of benzo[1,2-b:4,5-b']dithiophene (STTBDT). Compound 2 (2.0 g, 2.7 mmol), N,N,N',N'tetramethylethylenediamine (0.8g, 6.8 mmol), and THF (100 mL) were added to a flask under an inert atmosphere. The solution was cooled to -78 °C, and 4.2 mL of *n*-butyllithium (6.8 mmol, 1.6 M in hexane) were added. The solution was stirred at -78 °C for 1 h and then 8.0 mL of trimethyltin chloride (8.1 mmol, 1.0 M in THF) were 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 then the residue was crystallized in isopropyl alcohol (IPA). A greenish yellow solid was obtained (2.2 g, 71% yield). ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.71 (s, 2H), 7.62 (s, 2H), 7.07 (s, 2H), 2.93 (d, 4H), 1.82-1.63 (m, 2H), 1.53–1.39 (m, 16H), 0.99–0.95 (m, 12H), 0.43 (s, 18H). ¹³C NMR (75 MHz, CDCl₃, ppm): δ 142.1, 140.2, 138.1, 134.9, 132.5, 130.7, 129.3, 127.2, 124.9, 121.2, 118.3, 45.3, 42.4, 36.6, 35.1, 28.2, 26.5, 17.3, 14.1, -144 Anal. Calcd for C₄₄H₅₈S₈: C, 48.89; H, 5.41; S, 23.73. Found: C, 48.80; H, 5.37; S, 23.69.

General Polymerization Procedure

Two copolymers were synthesized by Stille coupling polymerization as shown in Scheme 2. 2,6-Bis(trimethyltin)-4,8-bis((2-ethylhexyl)thieno[3,2-b]thiophene)-benzo[1,2-b:4,5-

b']dithiophene (TTBDT), 2,6-bis(trimethyltin)-4,8-bis((2-ethylhexylthio)thieno[3,2b]thiophene)-benzo[1,2-b:4,5-b']dithiophene (STTBDT), and 2-ethylhexyl-4,6-dibromo-3fluorothieno[3,4-*b*]thiophene-2-carboxylate (FTT) monomers were synthesized as previously reported. Tetrakis-(triphenylphosphine)palladium in 5 mL anhydrous toluene and 1 mL DMF was stirred at 110 °C overnight, and then an excess of 2-bromothiophene and tripropyl(thiophen-2-yl)stannane, the end-capper, dissolved in 1 mL of anhydrous toluene was added and stirred for 12 h. 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 were re-precipitated from methanol and acetone. The polymers were then purified further by washing for 1 d in a Soxhlet apparatus with acetone to remove oligomers and catalyst residues. Column chromatography with chloroform was then performed. Re-precipitation in chloroform/methanol was repeated several times. The resulting polymers were soluble in common organic solvents.

Poly{4,8-bis((2-ethylhexyl)thieno[3,2-b]thiophene)-benzo[1,2-b:4,5-b']dithiophene-alt-2ethylhexyl-4,6-dibromo-3-fluorothieno[3,4-b]thiophene-2-carboxylate} (PTTBDT-FTT). 2,6-Bis(trimethyltin)-4,8-bis((2-ethylhexyl)thieno[3,2-b]thiophene)-benzo[1,2-b:4,5b']dithiophene (TTBDT) (400 mg, 0.4 mmol) was mixed with 2-ethylhexyl-4,6-dibromo-3fluorothieno[3,4-*b*]thiophene-2-carboxylate (FTT) (195 mg, 1.0 equiv), tetrakis(triphenylphosphine)palladium (15.2 mg, 2.6 μ mol), toluene (5 mL), and DMF (1mL). The polymer yield was 48%. Anal. Calcd for C₅₃H₅₇S₈: C, 63.56; H, 5.74; S, 25.61. Found: C, 63.18; H, 5.55; S, 23.28. M_n = 25 000, PDI = 2.5. T_d = 425 °C.

Poly{4,8-bis((2-ethylhexylthio)thieno[3,2-b]thiophene)-benzo[1,2-b:4,5-b']dithiophene*alt*-2-ethylhexyl-4,6-dibromo-3-fluorothieno[3,4-b]thiophene-2-carboxylate} (PSTTBDT-

FTT). 2,6-Bis(trimethyltin)-4,8-bis((2-ethylhexylthio)thieno[3,2-b]thiophene)-benzo[1,2-b:4,5-b']dithiophene (STTBDT) (400 mg, 0.4 mmol) was mixed with 2-ethylhexyl-4,6-dibromo-3-fluorothieno[3,4-*b*]thiophene-2-carboxylate (FTT) (175 mg, 1.0 equiv), tetrakis(triphenylphosphine)palladium (15.2 mg, 2.6 μ mol), toluene (5 mL), and DMF (1mL). The polymer yield was 35%. Anal. Calcd for C₅₃H₅₇S₁₀: C, 59.73; H, 5.39; S, 30.09. Found: C, 59.65; H, 5.58; S, 28.98. M_n = 21,000, PDI = 2.3. T_d = 386 °C.



Fig. S1. TGA plots of PTTBDT-FTT and PSTTBDT-FTT.



Fig. S2. (a) Cyclic voltammetric curve and (b) the HOMO and LUMO energy levels of polymers.



Fig. S3. Field-dependent hole mobilities of pure polymer and polymer: $PC_{71}BM$ blend films calculated from the hole-only devices by fitting *J-V* curves in the SCLC regime.

Table S1. Molecular, optical and electrochemical properties of conjugated polymers

Polymer	M_n	PDI	$T_d^{[b]}$	$\lambda_{max, abs}$	λ_{max}	λ_{edge}	Optical		
	(g/mol) ^[a]		$(^{\circ}C)$	(nm)	(nm)	(nm)	$E_{\rm g}^{\rm opt}$	НОМО	LUMO
				Solution	Film ^[c]	Film ^[c]	(eV) ^[d]	(eV)	(eV)
PTTBDT-FTT	25,000	2.5	425	691	707	780	1.59	-5.31	-3.72
PSTTBDT-FTT	21,000	2.3	386	703	717	795	1.56	-5.35	-3.79

 $\overline{[a]}M_n$, M_w , and *PDI* of the polymers were determined by gel permeation chromatography using polystyrene standards in CHCl₃. ^[b] Temperature at 5 % weight loss by a heating rate of 10 °C/min under nitrogen. ^[c]Polymer film on a quartz plate by spin-casting from chloroform solution at 1500 rpm for 30 s. ^[d] Calculated from the absorption band edge of the copolymer films, $E_g = 1240/\lambda_{edge}$.

Table S2. Calculated hole mobilities of the pure polymer or polymer/ $PC_{71}BM$ (1:1.5 w/w) system at optimized conditions using the SCLC method

Active layer	Solvent	Thickness	$\mu_{h}^{[a]}$
		(nm)	$(cm^2 V^{-1} s^{-1})$
PTTBDT-FTT	CB	100	1.22 x 10 ⁻³
PTTBDT-FTT : PC71BM	CB+DIO	100	9.50 x 10 ⁻⁵
PSTTBDT-FTT	CB	100	6.45 x 10 ⁻³
PSTTBDT-FTT : PC ₇₁ BM	CB+DIO	100	1.26 x 10 ⁻⁴

^[a]The hole-only devices with structure of ITO/PEDOT:PSS/polymer or polymer:PC₇₁BM (1:1.5 w/w)/MoO₃/Ag.

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