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Supporting Information

Synergistic Effects of an Alkylthieno[3, 2-b]thiophene π-Bridging Backbone Extension on the Photovoltaic Performances of Donor–acceptor Copolymers

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Experimental section

1. Materials and Methods

Materials

All starting materials and reagents were purchased form Sigma-aldrich, TCI Korea, Acros organics, and Frontier Scientific Inc., and were used as received. 3-octylthiophene, trimethyltin chloride in tetrahydrofuran (THF), n-butyllithium in n-hexane, nonanoyl chloride, potassium carbonate (K_2CO_3) potassium hydroxide (KOH), ethyl thioglycolate, 18-Crown-ether-6, lithium hydroxide (LiOH), sulfuric acid, tetrabutylammonium iodide, tetrakis(triphenylphosphine)palladium(0), 2-brotmothiophene, 2-(tributylstannyl)thiophene, copper powder, bis(triphenylphosphine)palladium(II) dichloride [$Pd(PPh_3)_4$], diisopropyl azodicarboxylate, phthalimide, 2-butyloctan-1-ol, 2-ethylhexyl bromide, hydrazine monohydrate, quinoline, glacial acetic acid, anhydrous acetic anhydride, chloroform, dichloromethane (DCM), N,N-dimethylformamide (DMF), methanol, THF, toluene, chlorobenzene (CB), and trichlorobenzene (TCB) were purchased from Sigma-aldrich. 3-Bromothiophene, selenophene, aluminum chloride ($AlCl_3$), N-bromosuccinimide (NBS), and triphenylphosphine were purchased from TCI Korea. Tris(dibenzylideneacetone)dipalladium(0) [Pd_2dba_3], tri-*o*-tolylphosphine [P(*o*-Tolyl)$_3$], and thionyl chloride were purchased from Acros organics. Thiophene-3,4-dicarboxylic acid was purchased from Frontier Scientific Inc.. [6,6]-Phenyl C_{71}-butyric acid methyl ester ($PC_{71}BM$) was purchased from Solenne, Inc.. Column chromatography was performed using silica gel (Merck, Kieselgel 60 63-200 MYMSC). The monomer, 4,8-dihydrobenzo[1,2-b:4,5-b']dithiophene-4,8-dione was synthesized according to the literature procedure.[1] Moisture sensitive reactions were conducted in the presence of N_2 atmosphere.

Characterization

All monomers were characterized by ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) on a Bruker AVANCE III 600 spectrometer in chloroform-d solutions at room temperature. The ^{1}H NMR chemical shift are presented in the unit of d (ppm) relative to tetramethylsilane (TMS, d = 0) and referenced to the peaks signals corresponding to the residual non-deuterated solvent. The absorption spectra of the polymers were measured by a UV-visible spectrophotometer (Mecasys, UV-3220). Number-average (M_n) and weight-average (M_w) molecular weights of the polymers were determined with gel permeation chromatography (GPC, Agilent) in TCB at 220 °C, using PLgel Olexis column, and calibrated against narrow polydispersity polystyrene standards. AFM measurements were performed using a MultiMode 8 Scanning Probe Microscope (VEECO Instruments Inc.) in tapping mode. TEM images were obtained using a Hitachi-7600 system with an accelerating voltage of 100 kV. TEM samples were prepared from actual devices that were transferred to an aqueous hydrogen fluoride solution, and the floated films were transferred to Cu grids (Ted Pella). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed by using a DSC 2910 (TA Instruments) and a TGA 2050 (TA Instruments) under a N_2 atmosphere at a heating and cooling rate of 10 °C min^{-1}, respectively.

Cyclic voltammetry analysis

The cyclic voltammetry (CV) was conducted on a PowerLab/AD instrument model system with glassy carbon disk, Pt wire, and Ag/Ag+ electrode as the working electrode, counter electrode, and reference electrode, respectively in a 0.1 M tetrabutylammonium hexafluorophosphate ($n\text{-Bu}_4\text{NPF}_6$)-anhydrous acetonitrile solution at a potential scan rate of 50 $\text{mV}\cdot\text{s}^{-1}$. Polymer film was drop cast onto the glassy carbon working electrode from a 5.0 mg mL^{-1} hot CB solution and dried under house nitrogen stream prior to measurements. The electrochemical onsets were determined at the position where the current starts to differ from the baseline. The potential of Ag/AgCl reference electrode was internally calibrated by using the ferrocene/ferrocenium redox couple (Fc/Fc^+). The energy levels were estimated using the equations: HOMO = – (4.80 + E_{onset}, ox), and LUMO = – (4.80 + E_{onset}, red).

Computational studies

Density functional theory (DFT) calculations were performed to facilitate an in-depth understanding of the electronic structure of the polymer by Gaussian 09 software package.

Hybrid three-parameter B3LYP functional combined with 6-31G(d) basis set was used to obtain the optimized structures at the singlet ground state.[2] For simplicity, the 2-butyloctyl, 2-ethylhexyl, and n-octyl chains appended to the conjugated backbone were trimmed with methyl chains at branched position. The highest occupied molecular orbital (HOMO) as well as lowest unoccupied molecular orbital (LUMO) energy levels were analyzed using minimized singlet geometries to approximate the ground state.

Time-correlated single photon counting (TCSPC) measurements

The TCSPC method was used to record photoluminescence lifetime profiles of the PBT, PBT-OT and PBT-OTT neat polymers and their blends on the glass substrate. Details of the apparatus have been described previously.[3, 4] Output of a home-built optical parametric oscillator (OPO) running at near infrared region was doubled to generate the excitation pulses at 550 nm. The repetition rate was 500 kHz. A singlet lens was used to focus the excitation pulse onto the sample and the fluorescence was collected by a parabolic mirror. Fluorescence was dispersed by a monochromator (Spectra Pro 3000i, Acton), and detected with a single photon detection module (id 100–50, id Quantique). The full width at half maximum (FWHM) of the instrument response function (IRF) was 70 ps. Magic angle detection was used to avoid the effect of polarization. All measurements were performed at ambient temperature.

Transient absorption measurements

Pump probe differential transmission measurements were performed on the solar cell with at ambient temperature. The light source for excitation was the home-built OPO laser same as T CSPC. Group velocity dispersion (GVD) of the fundamental output of the OPO was compens ated by a pair of SF 10 prisms to provide transform-limited 100 fs pulses at 1150 nm. The rep etition rate and pulse energy were adjusted to 500 kHz and 30 nJ, respectively, to prevent pho to damage. Pump pulses at 550 nm were generated by the second harmonic generation in a 3 mm thick lithium triborate (LBO) crystal. The pump pulse energy at 550 nm was about 1 nJ. GVD of the optics along the pump beam path was compensated by a pair of fused silica pris ms. The probe beam at 1150 nm was spectrally resolved by a bandpass filters with a bandwid th of 5 nm, prior to the photodetector. IRF estimated by the cross correlation between the scat tered pump and the gate pulses was 120 fs (FWHM).

2. Synthesis of procedures

2.1 Synthesis of thiophene-based π-bridges

Trimethyl(4-octylthiophen-2-yl)stannane (2)

To a solution of 1 (5.00 g, 0.0255 mol) in 100 mL THF, 2.5 M solution of n-BuLi in n-hexane (10.2 mL, 0.0255 mol) was added dropwise at –78 °C. The solution was stirred at –78 °C for 2 hr and 1.0 M solution of trimethyltin chloride (25.5 mL, 0.0255 mol) in THF was added in one portion. The solution was allowed to warm to room temperature and was stirred for 1 hr and 50 ml of water and 50 ml of ethyl acetate were added. The organic layer was washed twice with 50 mL of water and dried over anhydrous $MgSO_4$ .The organic layer was evaporated and dried over vacuum to afford a pale liquid (7.32 g, 80% yield). ^1H NMR (600 MHz, $CDCl_3$, δ): 7.15 (s, 1H), 6.97 (s, 1H), 2.60-2.59 (t, 2H), 1.58 (m, 2H), 1.29-1.22 (m, 10H), 0.85-0.83 (t, 3H), 0.35 (m, 9H). ^{13}C NMR (150 MHz, $CDCl_3$, δ): 144.62, 137.24, 136.65, 125.65, 31.90, 30.76, 29.99, 29.51, 29.45, 29.27, 22.68, 14.11, -8.29.

1-(3-Bromothiophen-2-yl)decan-2-one (4)

To a mixture of 3-bromothiophene (30.00 g, 0.184 mol), $AlCl_3$ (49.00 g, 0.368 mol) and CH_2Cl_2 (200 mL), nonanoyl chloride (32.51g, 0.184 mol) was added dropwise at room temperature. The final mixture was stirred for 2 hr when GC/MS indicated that starting material had been completely converted to target. The reaction mixture was poured into cold HCl (6M, 200 mL) and organics were extracted with n-hexane (3 x 100 mL). The combined organic extracts were washed with brine (2 x 100 mL) and water (100 mL). After drying over anhydrous $MgSO_4$, the target was purified by silica column chromatography, eluting with n-hexane and then EtOAc/n-Hexane, 2:8 (53.12 g, 91%). ^1H NMR (600 MHz, $CDCl_3$, δ): 7.53 (d, 1H), 7.13 (d, 1H), 3.05 (t, 2H), 1.78 (m, 2H), 1.35(m, 10H), 0.92 (t, 3H). ^{13}C NMR (150 MHz, $CDCl_3$, δ): 192.81, 138.66, 133.63, 131.66, 113.69,41.56, 31.83, 29.41, 29.24, 29.15, 24.20, 22.65, 14.09.

3-Octylthieno[3,2-b]thiophen-2-ethyl-carboxylate (5)

Compound 4 (19.98 g, 0.063 mol) and K_2CO_3 (13.41 g, 0.097 mol) were mixed with DMF (70 mL). To this mixture, ethyl thioglycolate (6.91 mL, 0.063 mol) was added dropwise at 60 °C. A catalytic amount of 18-Crown-ether-6 was added. The mixture was stirred overnight and poured into water (500 mL). The organic materials was extracted by ethyl acetate the times. The organic layers were combined, washed by brine two times, and then water dried over anhydrous $MgSO_4$. After evaporating solvent, the crude compound 5 was obtained and purified by silica column chromatography, eluting with 5% ethyl acetate giving a yellow oil (17.32 g, 85%). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.48 (d, 1H), 7.24 (d, 1H), 4.29 (q, 2H), 3.10 (t, 2H), 1.71 (m, 2H), 1.32 (m, 10H), 0.81 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$, δ): 163.2, 144.56, 141.7, 141.1, 131.2, 128.6, 120.0, 60.9, 31.83, 29.3 (overlap), 24.6, 22.65, 14.09.

3-Octylthieno[3,2-b]thiophene-2-carboxylic acid (6)

Compound 5 (16.49 g, 0.051 mol) was mixed with LiOH (30 mL,10% water solution), THF (50 mL), MeOH (20 mL) and a catalytic amount of tetrabutylammonium iodide in a 500 mL flask. This mixture was refluxed overnight. After cooling to room temperature, the liquid was acidified with concentrated HCl. A yellow solid was collected by filtration and washed several times with water. The solid was heated with n-hexane (100 mL) and cooled to room temperature. After filtration, the solid was collected and dried under vacuum to get a light yellow powder (14.66 g, 97%). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.54 (d, 1H), 7.20 (d, 1H), 3.12 (t, 2H), 1.71 (m, 2H), 1.35 (m, 10H), 0.81 (t, 3H). ^{13}C NMR (150 MHz, $CDCl_3$, δ): 145.20, 142,03, 141.67, 131.68, 126.74, 120.10, 31.88, 29.64, 29.54, 29.35, 29.29, 29.19, 27.12, 22.66, 14.11.

3-Octylthieno[3,2-b]thiophene (7)

A solution of compound 6 (14.22 g, 0.048 mol), copper powder (1.98 g) and quinoline (80 mL) was heated at 240 - 260 °C in a Woods metal bath. When no further bubbles of carbon dioxide gas could be detected (about 2 hr), the mixture was cooled to room temperature and n-hexane (200 mL) was added to the quinoline mixture. This mixture was washed repeatedly with HCl (1-2 M solution). The organic layer was dried over anhydrous $MgSO_4$ and evaporated by vacuum to remove the solvent. The compound 7 was obtained by chromatography on silica gel, eluting with n-hexane (8.11 g, 67%). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.39 (m, 1H), 7.27 (m, 1H), 7.02 (s, 1H), 2.77 (t, 2H), 1.81 (m, 2H), 1.36 (m, 10H), 0.93 (t, 3H). ^{13}C NMR (150 MHz, $CDCl_3$, δ): 139.97, 138.70, 134.91, 126.55, 121.70, 119.91, 31.88, 29.97, 29.38, 29.37, 29.24, 28.62, 22.67, 14.10.

Trimethyl(6-octylthieno[3,2-b]thiophen-2-yl)stannane (8)

To a solution of 7 (4.00 g, 0.016 mol) in 80 mL THF, 2.5 M solution of n-BuLi in n-hexane (6.66 mL, 0.017 mol) was added dropwise at –78 °C. The solution was stirred at –78 °C for 2 hr and 1.0 M solution of trimethyltin chloride (23.8 ml, 0.024 mol) in THF was added in one portion. The solution was allowed to warm to room temperature and was stirred for 1 hr and 50 ml of water and 70 ml of ethyl acetated were added. The organic layer was washed twice with 70 mL of water and dried over anhydrous $MgSO_4$ .The organic layer was evaporated and dried over vacuum to afford a pale liquid (5.91 g, 89 % yield). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.29 (s, 1H), 6.98 (s, 1H), 2.74 (t, 2H), 1.78 (m, 2H), 1.32 (m, 10H), 0.92 (t, 3H), 0.44 (t, 9H). ^{13}C NMR (150 MHz, $CDCl_3$, δ): 145.64, 140.84, 140.33, 134.55, 127.04, 121.75, 31.88, 30.14, 29.40, 29.36, 29.25, 28.69, 22.68, 14.11, -8.32.

2.2 Synthesis of electron-donor monomers

2-(2-Ethylhexyl)selenophene (10) were synthesized according to previously reported methods.[1, 5]

4,8-Bis(5-ethylhexylselenophen-2-yl)benzo[1,2-b;4,5-b']dithiophene (12)

Under N_2 atmosphere, n-BuLi (11.2 ml, 2.5 M, 0.028 mol) was added dropwise to a solution of 2-ethylhexylselenophene (6.49 g, 0.027 mol) in THF (100 mL) at 0 °C. After being warmed to 50 °C and stirred for 1.5 hr. 4,8-Dihydrobenzo[1,2-b:4,5-b'] dithiophene-4,8-dione (1.47 g, 0.0067 mol) was added directly to the reaction mixture at 50 °C, which was then stirred for another 2 hr at 50 °C. Subsequently, the reaction mixture was cooled to room temperature and tin (II) chloride dehydrate (4.74 g, 0.021 mol) in 15% HCl (30 mL) was added and further stirred for 2 hr, which was poured into ice water. The reaction mixture was extracted with diethyl ether. The organic layers were combined, washed with brine, dried over anhydrous $MgSO_4$ and concentrated under vacuum to afford yellow oil. The crude was purified by column chromatography on silica gel using n-hexane as an eluent to obtain sticky yellow viscous oil (3.12 g, 69 %). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.58 (d, 2H), 7.37(d, 2H), 7.33 (d, 2H), 6.96 (d, 2H), 2.85 (d, 4H), 1.57 (m, 2H), 1.47-1.25 (m, 16H), 0.88-0.83 (m, 12H). ^{13}C NMR (150 MHz, $CDCl_3$, δ): 153.90, 142.76, 138.80, 136.24, 130.02, 127.52, 127.40, 126.27, 123.52, 42.2, 37.01, 32.48, 28.94, 25.72, 23.02, 14.15, 10.90.

2,6-Bis(trimethyltin)-4,8-bis(5-ethylhexylselenophen-2-yl)benzo[1,2-b;4,5-b']dithiophene (13, Donor)

A solution of compound 12 (1.68 g, 0.0025 mol) was dissolved in THF (100 mL). Under N_2 atmosphere, the solution was cooled to –78 °C using dry ice/acetone before n-BuLi (3.99 ml, 2.5 M, 0.01 mol) was added slowly and stirred at –78 °C for 1 hr and trimethyltin chloride (1

M in THF, 9.99 g, 0.01 mol) was added in one portion (the mixture became clear). The solution was slowly warmed to room temperature and allowed to stir overnight. The mixture was then poured into 200 ml of ice water and extracted with DCM. The organic layers were combined, washed with brine, dried over anhydrous $MgSO_4$ and evaporated the solvent to get yellow residue. The residue was recrystallized from ethanol to yield yellow solid (1.75 g, 70 %). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.63 (d, 2H), 7.35 (d, 2H), 6.98 (d, 2H), 2.85 (m, 4H), 1.65 (m, 2H), 1.47-1.26 (m, 16H), 0.90 (t, 6H), 0.88 (t, 6H), 0.32 (m, 18H). ^{13}C NMR (150 MHz, $CDCl_3$, δ): 153.56, 143.61, 143.02, 142.24, 137.04, 131.30, 129.81, 127.47, 124.60, 42.25, 37.09, 32.51, 28.97, 25.83, 23.02, 14.16, 10.96, -8.35. Elemental analysis: $C_{40}H_{58}S_2Se_2Se_2$: calcd: C, 48.12; H, 5.86; S, 6.42. found: C, 48.11 ; H, 5.64; S, 6.53.

2.3 Synthesis of electron-acceptor monomers

2-Butyloctylamine (16)

Triphenylphosphine (36.46 g, 0.139 mol) and phthalimide (20.45 g, 0.139 mol) were dissolved in DCM (180 ml) and then cooled to 0 °C. After then 2-butyloctan-1-ol (23.48 g, 0.126 mol) was added and stirred for 30 min, the dropwise addition of diisopropyl azodicarboxylate (28.11 g, 0.139 mol) under 10 °C. Subsequently, the mixture was stirred for another 1 hr at room temperature and then it was concentrated in a vacuum. After redissolving in n-hexanes and filtration the resulting oil was subjected to a short silica column and concentrated. Then hydrazine monohydrate (12.3 ml, 0.253 mol) and THF (12.3 ml) were added and the mixture was refluxed overnight. After cooling 2 M KOH was added and the product was extracted with ethyl acetate, washed with brine and dried over $MgSO_4$. The product was distilled to give colorless oil (12.84 g, 55%). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 2.53 (d, 2H), 1.27-1.19 (m, 17H), 1.08 (s, 2H), 0.84 (6H). ^{13}C NMR (150 MHz, $CDCl_3$, δ): 45.24, 40.89, 31.90, 31.57, 31.25, 29.77, 29.03, 26.77, 23.13, 22.68, 14.11, 14.09.

5-(2-Butyloctyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (17)

In a 250 ml round bottom flask, a solution of thiophene-3, 4-dicarboxylic acid (5.98 g, 0.035 mol) in acetic anhydride (150 mL) was refluxed overnight. After cooling to room temperature, the solvent was removed and the crude product was used for the next step without any purification. The brown solid was dissolved in toluene (320 mL) then 2-butyloctylamine (9.67 g, 0.052 mol) was added and the mixture was refluxed for 24 hr. The reaction mixture was cooled down and the solvent was removed under reduced pressure. The crude solid was dissolved in thionyl chloride (280 mL) and the mixture was refluxed for 4 hr. After the removal of the volatiles, the crude product was purified by column chromatography using DCM/n-hexanes (1:1) as the eluent and then was recrystallized from ethanol to yield light orange solid (6.63 g, 59%). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.83 (s, 2H), 3.54 (d, 2H), 1.88-1.87 (m, 1H), 1.28-1.38 (m, 14H), 0.88-0.93 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$, δ): 162.95, 136.64, 125.41, 77.22, 77.01, 76.80, 42.73, 36.88, 32.81, 31.45, 31.13, 29.64, 28.45, 26.23, 23.02, 22.64, 14.08, 14.05

1,3-Dibromo-5-(2-butyloctyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (18, Acceptor 1)

Compounds **17** (4.00 g, 0.012 mol) was dissolved in a mixture of sulfuric acid (19 mL) and trifluoroacetic acid (63 mL). While stirring, NBS (6.64 g, 0.037 mol) was added in six portions to the solution and the reaction mixture was stirred in dark at room temperature overnight. The brown-red solution was diluted with water (200 mL). The mixture was extracted with DCM. The organic phase was dried over anhydrous $MgSO_4$ and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography using DCM:n-hexane (1:1) to afford the title product as light orange solid (3.56 g, 62%). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 3.51 (d, 2H), 1.84 (m, 1H), 1.38-1.25 (m, 14H), 0.92-0.0.89 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$, δ): 160.67, 134.74, 112.91, 77.22, 77.01, 76.80, 43.08, 36.86, 32.82, 32.47, 32.15, 29.59, 28.48, 26.27, 22.96, 22.64, 14.09, 14.07. Elemental analysis: $C_{16}H_{21}Br_2NO_2S$: calcd: C, 42.59; H, 4.69; N, 3.10; S, 7.11. found: C, 45.33; H, 5.12; N, 3.61; S, 6.88.

5-(2-Butyloctyl)-1-(4-octylthiophen-2-yl)-3-(4-octylthiophen-3-yl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (19)

Compound 18 (0.36 g, 0.756 mmol) was dissolved into toluene (80 mL) and DMF (16 ml). trimethyl(4-octylthiophen-2-yl)stannane (0.81 g, 2.27 mmol), and $Pd(PPh_3)_4$ (87.5 mg, 10 mol %) were added to the reaction mixture. The solution was refluxed overnight then cooled and poured into water. The mixture was extracted twice with DCM. The organic phases were combined, washed with brine, and dried over anhydrous $MgSO_4$. The solvent was removed under reduce pressure and the crude product was purified by column chromatography using DCM:n-hexane as the eluent (2:8) and was then recrystallized from ethanol to afford a yellow solid (0.38 g, 70 %). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.79 (s, 2H), 6.95 (s, 2H), 3.48 (d, 2H), 2.57-2.54 (t, 4H), 1.83-1.81 (m, 1H), 1.57-1.56 (m, 4H), 1.28-1.27 (m, 20H), 1.26-1.18 (m, 14H), 0.83-0.78 (m, 12H). ^{13}C NMR (150 MHz, $CDCl_3$, δ): 162.97, 144.95, 136.75, 132.17, 131.08, 128.05, 123.52, 36.91, 31.87, 31.82, 30.46, 30.41, 29.69, 29.39, 29.29, 29.26, 28.54, 23.07, 22.67, 22.64, 14.10, 14.08.

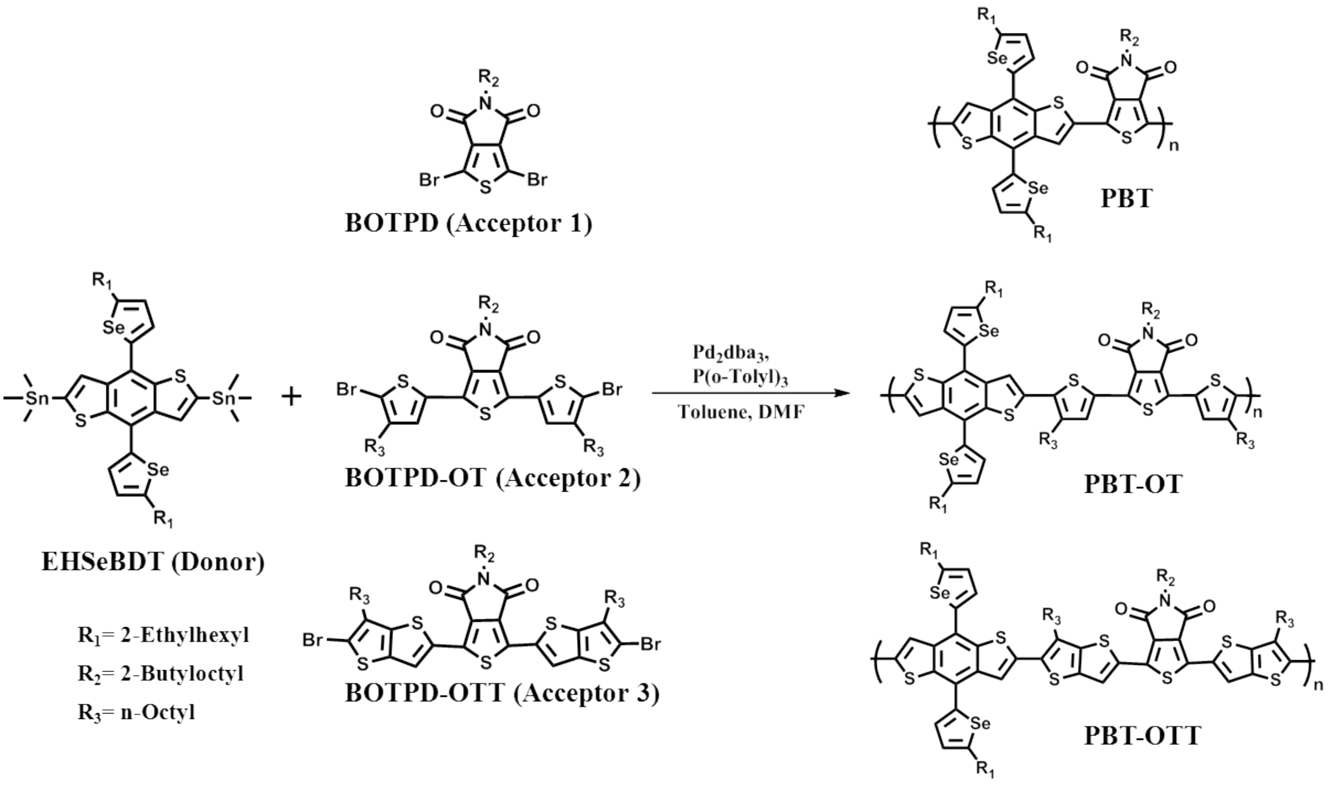
1-(5-Bromo-4-octylthiophen-2-yl)-3-(5-bromo-4-octylthiophen-3-yl)-5-(2-butyloctyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (20, Acceptor 2)

Compound 19 (0.479 g, 0.669 mmol) was dissolved in acetic acid (50 ml) and chloroform (50 ml). While stirring, NBS (0.298 g, 1.67 mmol) was added to the solution and the reaction mixture was stirred in dark at room temperature overnight. The mixture was extracted with DCM. The organic phases were combined, washed with brine, and dried over anhydrous $MgSO_4$. The solvent was removed under reduce pressure and the crude product was purified by column chromatography using then DCM:n-hexane as the eluent (1:1) to afford a yellow solid (0.47 g, 81%). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.54 (s, 2H), 3.47 (d, 2H), 2.51-2.49 (t, 4H), 1.83-1.81 (m, 1H), 1.55-1.53 (m, 4H), 1.28- 1.27 (m, 20H), 1.26-1.18 (m, 14H), 0.82-0.77 (m, 12H). ^{13}C NMR (150 MHz, $CDCl_3$, δ): 162.75, 143.72, 135.48, 131.89, 130.25, 128.32, 113.56, 77.22, 77.01, 76.80, 43.02, 36.92, 31.87, 31.82, 31.49, 3.18, 29.68, 29.66, 29.51, 29.34, 29.23, 28.52, 26.27, 23.06, 22.67, 22.64, 14.11, 14.08. Elemental analysis: $C_{42}H_{61}Br_2NO_2S_3$: calcd: C, 58.12; H, 7.08; N, 1.61; S, 11.08. found: C, 58.40; H, 6.84; N, 1.86; S, 10.46.

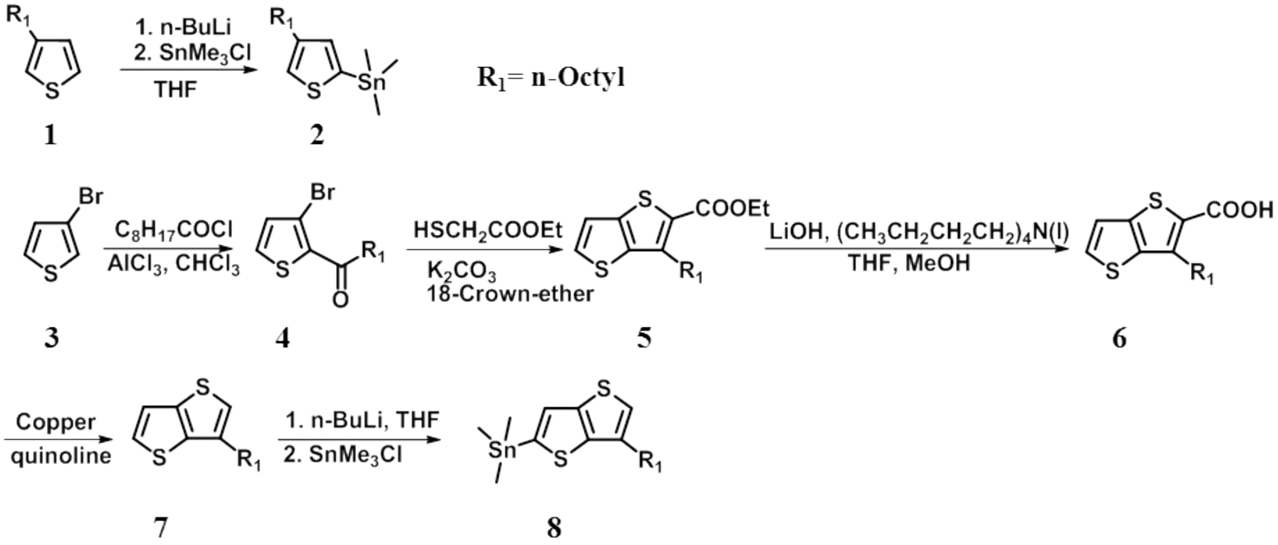
5-(2-Butyloctyl)-1-(6-octylthieno[3,2-b]thiophen-2-yl)-3-(6-octylthieno[3,2-b]thiophen-3-yl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (21)

Compound 18 (1.00 g, 2.09 mmol) was dissolved into toluene (100 mL) and DMF (20 ml). Trimethyl(4-octylthiophen-2-yl)stannane (2.34 g, 5.63 mmol), and $Pd(PPh_3)_4$ (0.241 g, 10 mol %) were added to the reaction mixture. The solution was refluxed overnight then cooled and poured into water. The mixture was extracted twice with chloroform. The organic phases were combined, washed with brine, and dried over anhydrous $MgSO_4$. The solvent was removed under reduce pressure and the crude product was purified by column chromatography using then DCM:n-hexane as the eluent (2:8) and was then recrystallized from n-hexane to afford an orange solid (0.89 g, 51 %). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.40 (s, 2H), 7.29 (s, 2H), 3.61 (d, 2H), 2.77-2.74 (t, 4H), 1.95-1.91 (m, 1H), 1.80-1.77 (t, 4H), 1.41-1.37 (m, 20H), 1.34-1.3 (m, 14H), 0.93-0.88 (m, 12H). ^{13}C NMR (150 MHz, $CDCl_3$, δ): 163.01, 141.63, 139.68, 137.07, 135.12, 133.13, 128.54, 124.86, 122.91, 77.22, 77.00, 76.79, 43.05, 37.07, 31.87, 31.83, 31.60, 31.28, 29.83, 29.70, 29.35, 29.24, 28.60, 26.36, 23.07, 22.67, 22.65, 14.10.

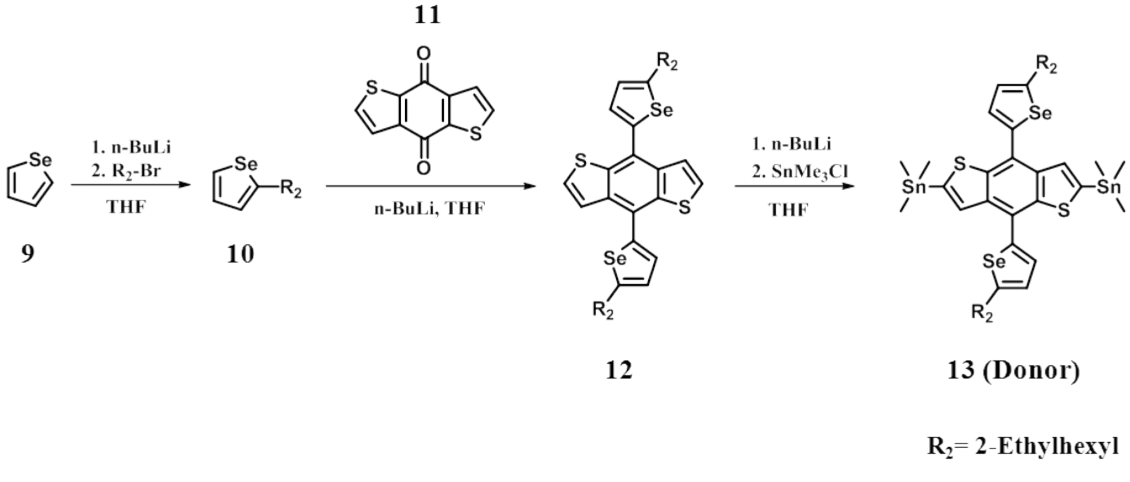
1-(5-Bromo-6-octylthieno[3,2-b]thiophen-2-yl)-3-(5-bromo-6-octylthieno[3,2-b]thiophen-3-yl)-5-(2-butyloctyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (22, Acceptor 3) Compound 21 (1.10 g, 1.34 mmol) was dissolved in acetic acid (50 ml) and chloroform (50 ml). While stirring, NBS (0.714 g, 4.01 mmol) was added to the solution and the reaction mixture was stirred in dark at room temperature overnight. The mixture was extracted with chloroform. The organic phases were combined, washed with brine, and dried over anhydrous $MgSO_4$. The solvent was removed under reduce pressure and the solid was then redissolved in chloroform. Subsequently, the solution added dropwise into methanol (250 ml). The precipitation was filtered and dried in vacuum to afford a red solid (1.07 g, 82 %). ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.32 (s, 2H), 3.6 (d, 2H), 2.77-2.75 (t, 4H), 1.74 (m, 1H), 1.58 (m, 4H), 1.40-1.39 (m, 20H), 1.36-1.29 (m, 14H), 0.93-0.87 (m, 12H). ^{13}C NMR (150 MHz, $CDCl_3$, δ): 162.92, 140.13,138.07, 136.56, 134.36, 132.47, 128.78, 122.32, 113.73, 77.22, 77.01, 76.79, 43.08, 37.07, 31.86, 31.82, 31.59, 31.27, 29.69, 29.31, 29.21, 29.10, 28.60, 27.99, 26.35, 23.07, 22.66, 14.11, 14.09. Elemental analysis: $C_{46}H_{61}Br_2NO_2S_5$: calcd: C, 56.37; H, 6.27; N, 1.43; S, 16.36. found: C, 56.33; H, 6.13; N, 1.64; S, 16.36.



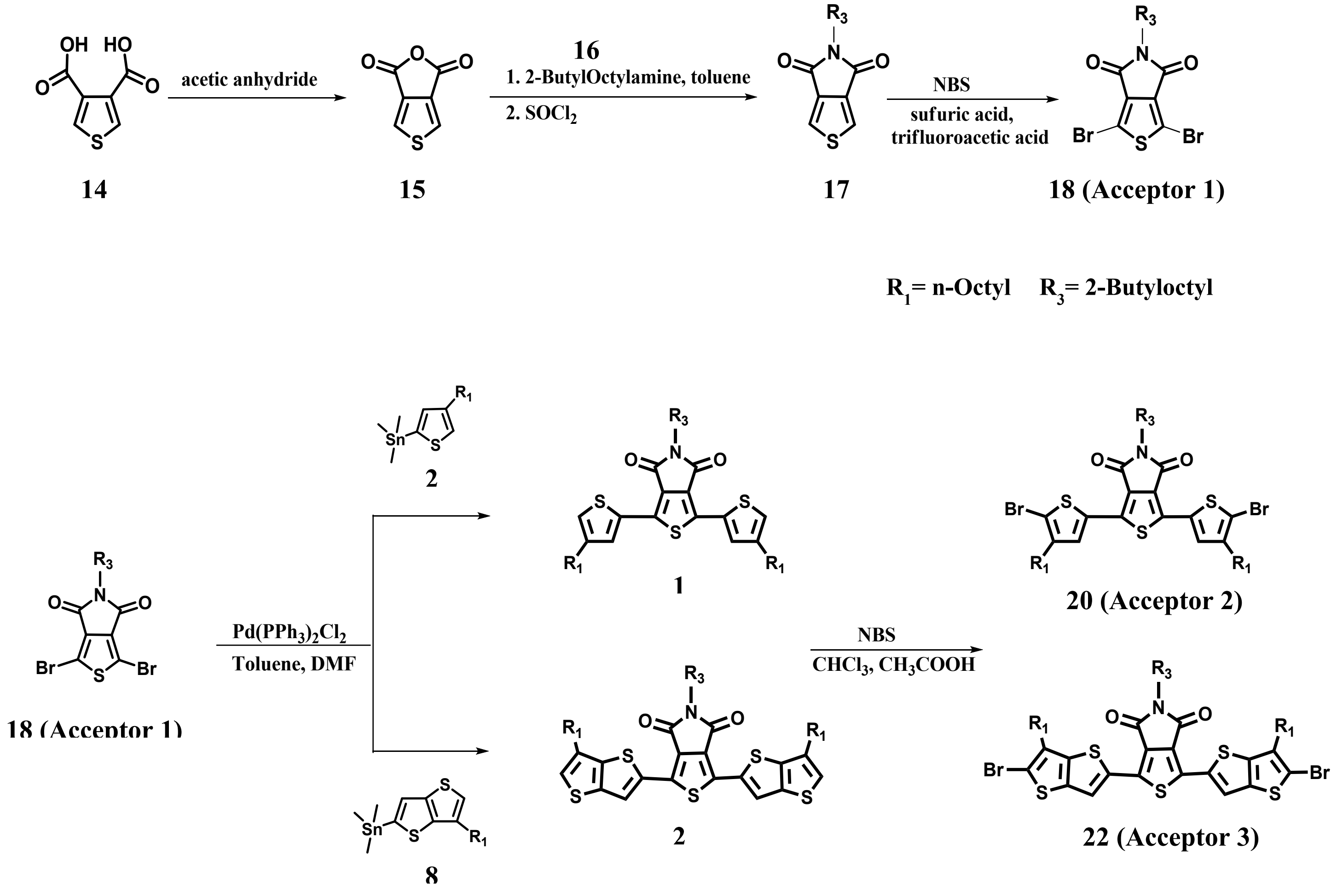
Scheme S1. Synthetic strategy of PBT, PBT-OT, and PBT-OTT.



Scheme S2. Synthesis of thiophene-based π-bridges.



Scheme S3. Synthesis of an electron-donor monomer.



Scheme S4. Synthesis of electron-acceptor monomers.

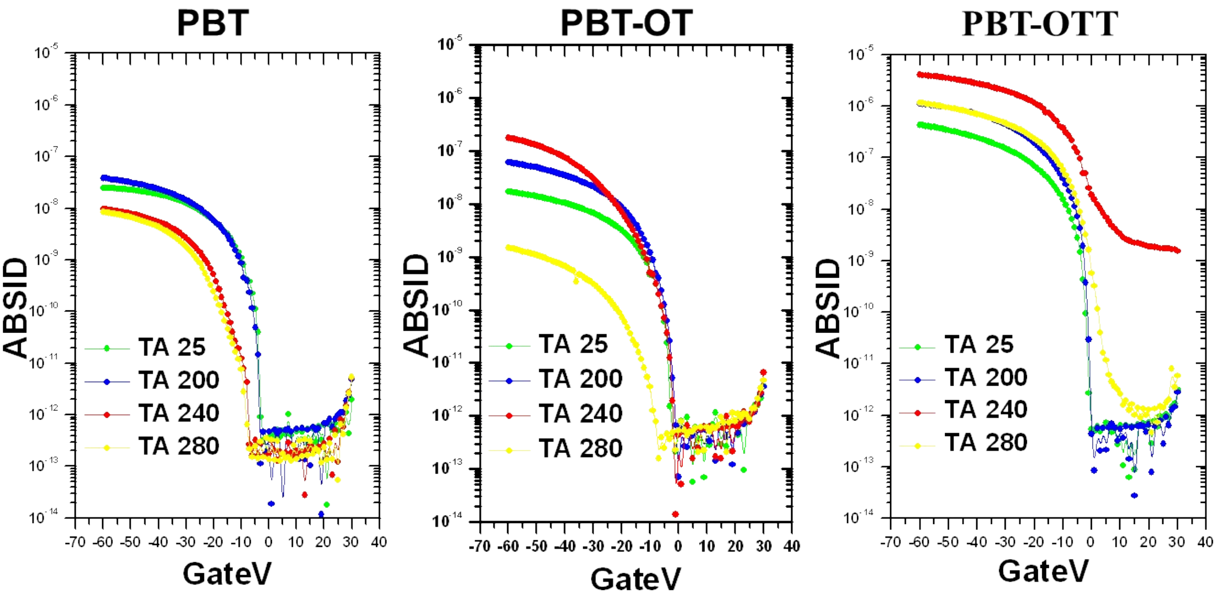


Figure S1. Typical curves of PBT, PBT-OT, and PBT-OTT-based hole-only devices.

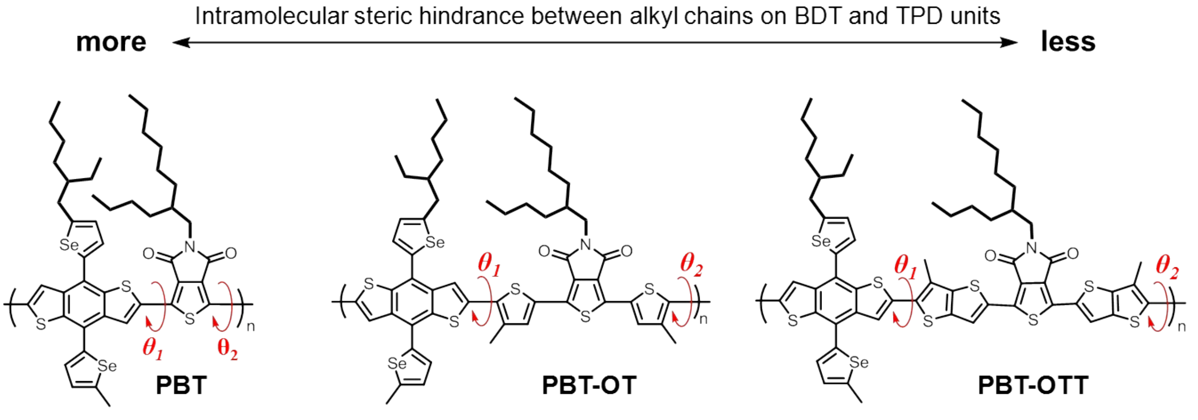


Figure S2. Molecular geometry used for computational data and intramolecular steric hindrance between alkyl chains on BDT and TPD units for PBT, PBT-OT, and PBT-OTT.

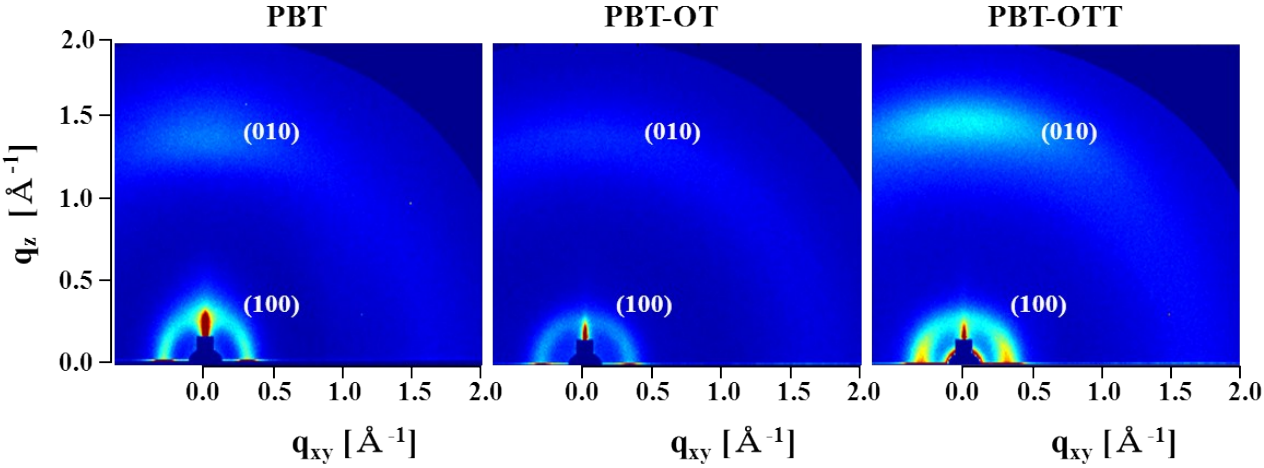


Figure S3. GIWAXS patterns of films of as-cast PBT, PBT-OT, and PBT-OTT.

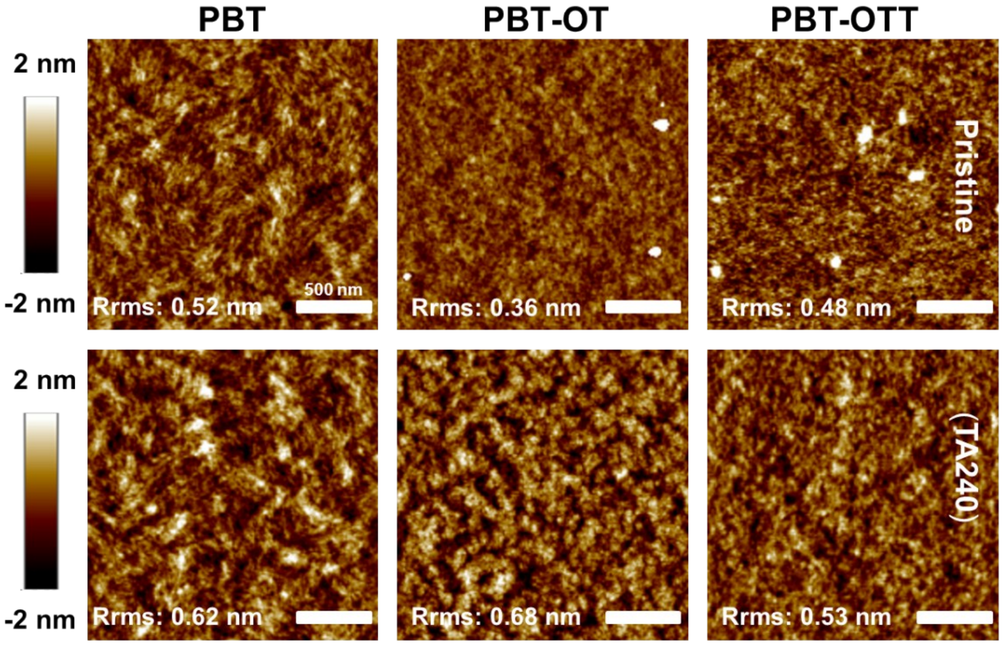


Figure S4. AFM height images of the polymer films at conditions without and with thermal annealing at 240 °C.

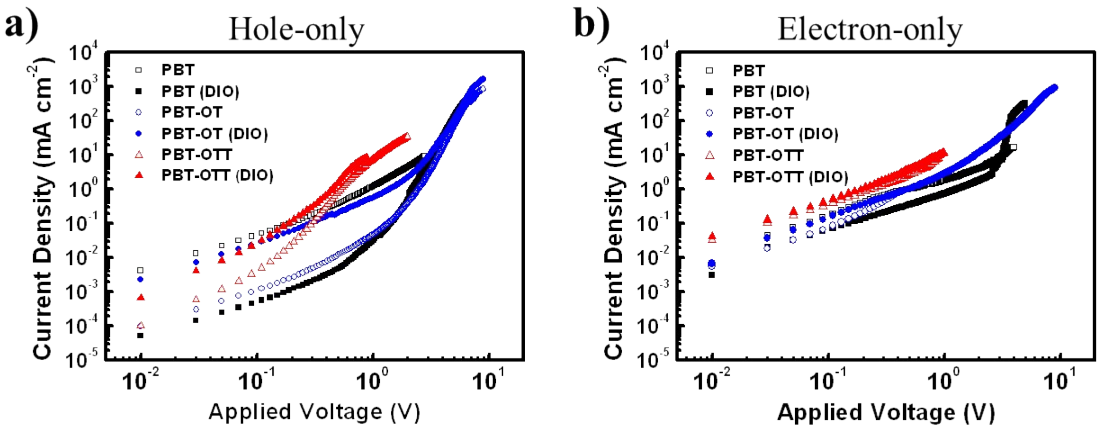


Figure S5. Dark current density versus effective voltage characteristics of a) hole-only devices and b) electron only devices, with photoactive layers of polymers: $PC_{71}BM$ (1:1.5, w/w) blends without DIO and with DIO additive. In the case of electron-only devices the V_{bi} =1.5 V is used.

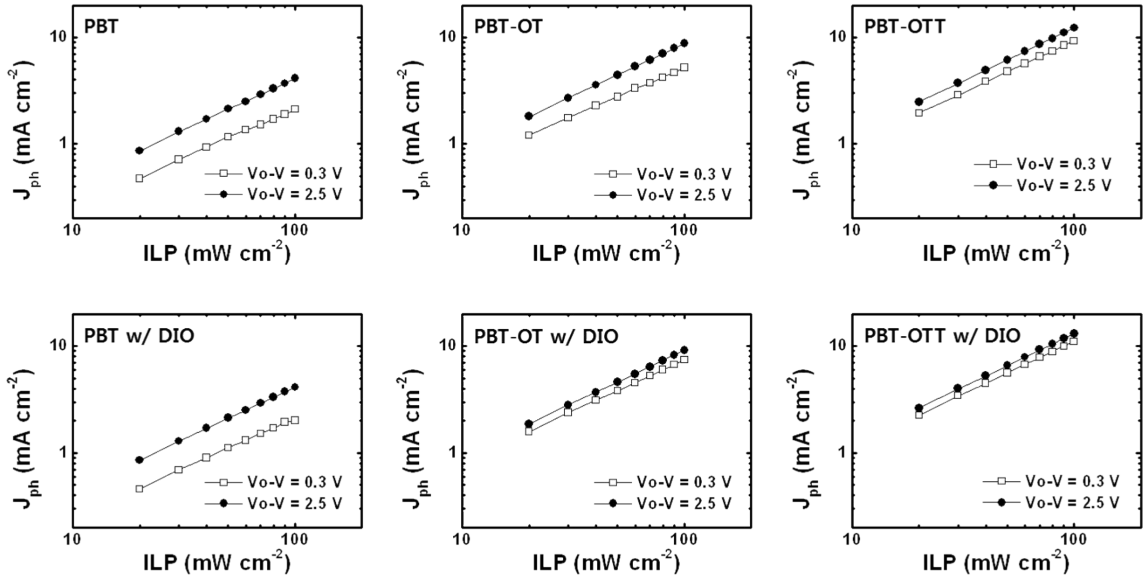


Figure S6. Incident light power-dependent photocurrent plots of OPVs for calculating S factors.

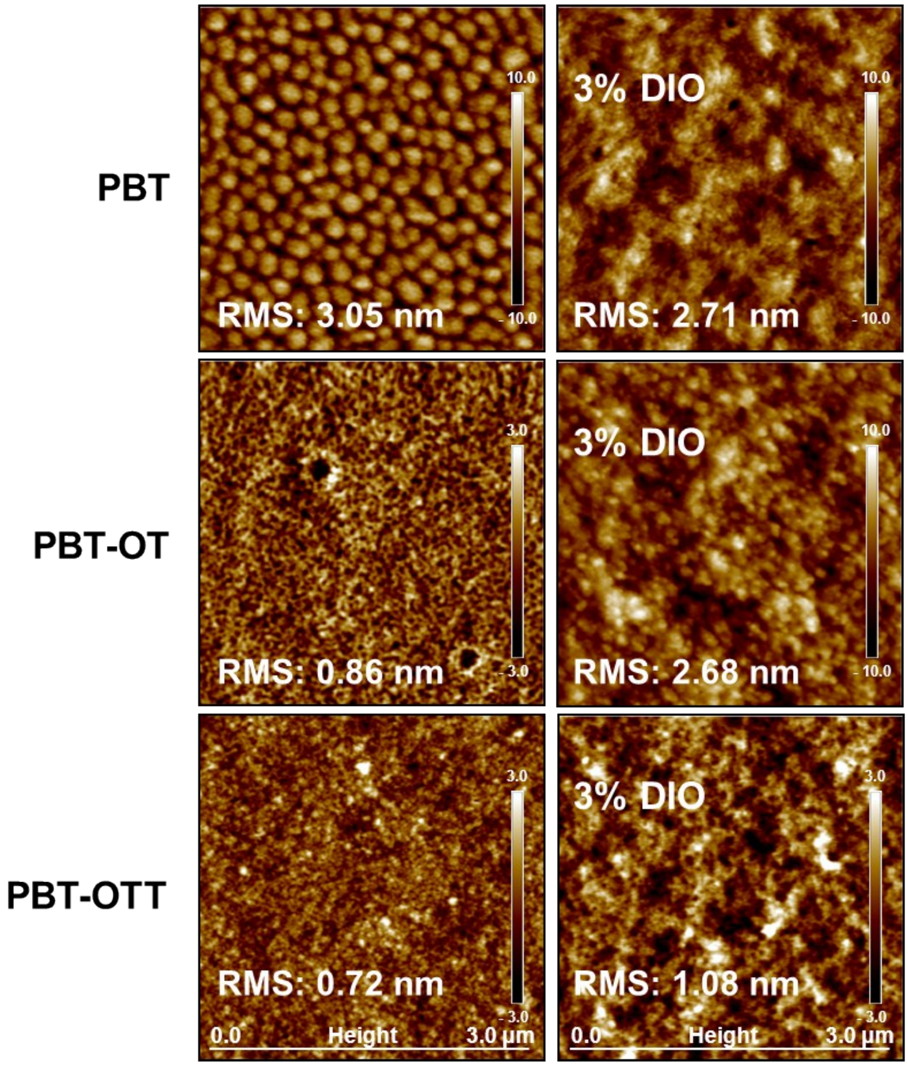


Figure S7. AFM height images of the polymer:$PC_{71}BM$ films at conditions without and with DIO.

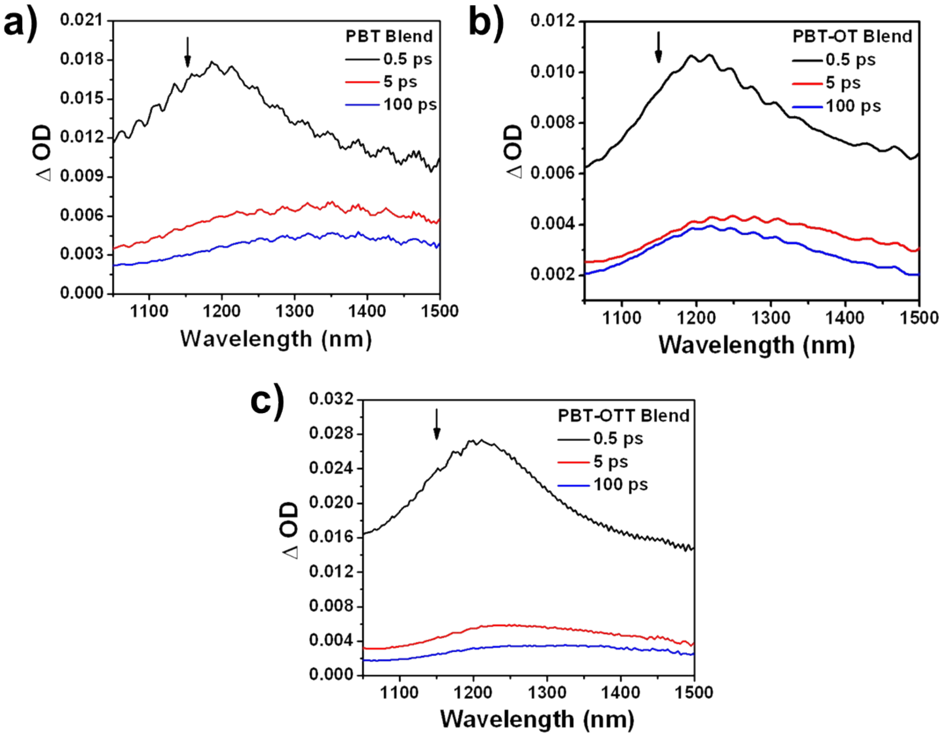


Figure S8. Transient absorption spectra of (a) PBT, (b) PBT-OT, and (c) PBT-OTT blends recorded at 0.5, 5, and 100 ps.

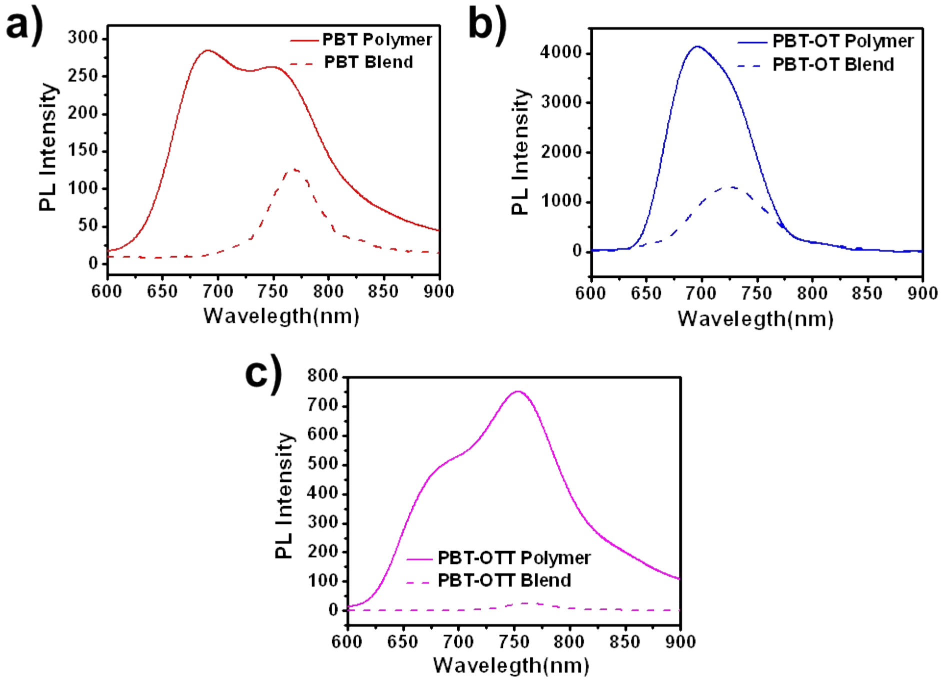


Figure S9. Steady-state fluorescence spectra of (a) PBT, (b) PBT-OT, and (c) PBT-OTT polymers and their blends with $PC_{71}BM$.

Table S1. Molecular weights, thermal properties, and surface energy of the polymers.

Polymer	$\overline{Mn}$ [g/mol][a)]	PDI[a)]	T_d [°C][b)]	Surface E [mN m^{-1}]
PBT	17,000	2.8	404	14.0
PBT-OT	28,000	4.1	400	18.6
PBT-OTT	22,000	2.8	407	19.6

a) Measured by GPC using polystyrene standards and trichlorobenzene as eluent.

b) Percentage weight loss temperature measured by TGA under nitrogen atmosphere

Table S2. *d*-Spacing and π-π distance values of pure polymers without and with thermal annealing (TA) at 240 °C.

Polymer	TA	(100) *d*-spacing	π-π distance
	(°C)	[Å]	[Å]
PBT	w/o	23.26	4.11
	240	23.41	4.13
PBT-OT	w/o	22.54	4.08
	240	22.64	4.07
PBT-OTT	w/o	22.54	3.84
	240	22.14	3.78

Table S3. Calculated dihedral angles of the polymer.

Polymer	π-bridge	θ_1	θ_2
PBT	none	1.45	2.08
PBT-OT	3-methylthiophene	21.08	21.13
PBT-OTT	3-methylthieno[3, 2-b]thiophene	27.35	24.85

Table S4. OFET properties of PBT derivatives at different thermal annealing temperatures.

Polymer	$TA_{temp.}$	I_{on}/I_{off}	threshold voltage (V)	mobility (cm^2/Vs)
PBT	RT	7.4×10^4	-1.9	6.38×10^{-5}
	200	3.3×10^5	-3.4	3.57×10^{-4}
	240	3.6×10^4	-1.2	1.73×10^{-4}
	280	4.1×10^4	-1.5	1.39×10^{-4}
PBT-OT	RT	8.1×10^4	-1.0	1.91×10^{-4}
	200	8.6×10^5	-1.3	6.25×10^{-4}
	240	3.0×10^6	-3.1	1.55×10^{-3}
	280	6.4×10^3	-1.9	4.38×10^{-6}
PBT-OTT	RT	8.1×10^5	-5.4	3.77×10^{-3}
	200	7.1×10^6	2.4	8.97×10^{-3}
	240	2.6×10^3	-1.9	1.48×10^{-2}
	280	1.1×10^6	-8.8	3.69×10^{-3}

Table S5. Photovoltaic properties of OSCs based on PBT-OTT/$PC_{71}BM$, under the illumination of AM1.5G, 100 mW cm^{-2}.[a)]

additive	blend ratio[b)]	spin speed (rpm)	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF [%]	PCE [%]
-	1:1.0	2000	9.47	0.84	48.8	3.88
-	1:1.5	1500	10.98	0.84	58.0	5.35
-	1:2.0	2000	7.99	0.84	37.0	2.48
CN, 5%	1:1.5	1500	8.80	0.86	58.0	4.39
DPE, 3%	1:1.5	1500	11.34	0.86	62.6	6.10
DIO, 1%	1:1.5	1500	11.51	0.88	61.7	6.25
DIO, 2%	1:1.5	1500	11.32	0.88	65.3	6.50
DIO, 3%	1:1.2	2000	11.78	0.86	64.0	6.48
DIO, 3%	1:2.0	2000	11.60	0.86	64.5	6.43
DIO, 3%	1:1.5	1000	11.12	0.84	62.0	5.80
DIO, 3%	1:1.5	1100	11.55	0.82	62.8	5.95
DIO, 3%	1:1.5	1200	11.49	0.84	62.1	5.99
DIO, 3%	1:1.5	1300	12.00	0.84	62.9	6.33
DIO, 3%	1:1.5	1400	12.47	0.84	67.0	7.02
DIO, 3%	1:1.5	1600	11.81	0.84	67.5	6.70
DIO, 3%	1:1.5	2000	11.45	0.84	62.6	6.02
DIO, 3%	1:1.5	1200	9.90	0.84	53.1	4.42[c)]
DIO, 3%	1:1.5	1300	11.93	0.86	64.4	6.61[d)]

a) CB as solvent and PEDOT as interfacial layer were used.

b) Blend ratios are PBT-OTT:$PC_{71}BM$ weight ratios (w:w).

c) MoO3 was used as interfacial layer.

d) The efficiency was yielded using inverted device structure.[6]

Table S6. Mobility results of space charge limited current (SCLC) devices based on polymers: $PC_{71}BM$ (1:1.5, w/w) blends without DIO and with DIO additive.

Polymer	μ_h [cm^2/V·s]	μ_e [cm^2/V·s]	μ_e/μ_h
PBT	4.45×10^{-6}	3.28×10^{-6}	0.74
PBT (DIO 3%)	3.86×10^{-5}	3.46×10^{-5}	0.90
PBT-OT	3.63×10^{-5}	1.59×10^{-5}	0.44
PBT-OT (DIO 3%)	4.98×10^{-5}	3.75×10^{-5}	0.75
PBT-OTT	5.10×10^{-5}	6.53×10^{-5}	1.28
PBT-OTT (DIO 3%)	7.24×10^{-5}	8.09×10^{-5}	1.12

Table S7. *d*-Spacing and π-π distance values of polymer/$PC_{71}BM$ (1:1.5, w/w) blends.

Polymer	DIO (%)	(100) *d*-spacing [Å]	FWHM [Å^{-1}]	correlation length [Å]
PBT	-	23.4	0.088	128.0
	3	23.5	0.045	243.9
PBT-OT	-	23.2	0.184	61.6
	3	22.7	0.181	62.4
PBT-OTT	-	22.3	0.204	55.3
	3	22.2	0.147	76.7

Table S8. Contact angle values of PBT, PBT-OT, PBT-OTT, and $PC_{71}BM$ films and the corresponding surface energy calculated using the geometric mean equation, $(1+\cos\theta)\gamma_{pl}=2(\gamma_s{}^{d}\gamma_{pl}{}^{d})^{1/2}+2(\gamma_s{}^{p}\gamma_{pl}{}^{p})^{1/2}$, where γ_{pl} and γ_s are the sample and probe liquid respectively.[7] The polymers and $PC_{71}BM$ were dissolved in CB and spin-coated on the ITO glass at the condition of 1 wt% concentration, 1300 rpm for 90 s. Subsequently, the contact angle of each film was measured by using water and glycerol. From contact angle data, the surface tension of the polymers can be determined using the geometric mean equation which is commonly used to obtain the surface energy with two kinds of liquid where θ_i is the droplet contact angle of water or glycerol on the polymers and $PC_{71}BM$ films; γ^{total} is the total surface tension; γ^{d} and γ^{p} are the dispersive and polar components of γ^{total}; γ^{i} is the total surface tension of the i material (i = water or glycerol); $\gamma_i{}^{d}$ and $\gamma_i{}^{p}$ are the dispersive and polar components of $\gamma_{i.}$

	θ^{water} [deg]	$\theta^{glycerol}$ [deg]	γ^{d} [mN m^{-1}]	γ^{p} [mN m^{-1}]	γ^{total} [mN m^{-1}]
PBT	99.5	93.5	5.34	8.62	14.0
PBT-OT	97.1	86.3	3.62	14.99	18.6
PBT-OTT	89.3	83.9	9.05	10.58	19.6
$PC_{71}BM$	80.6	69.4	8.60	20.52	29.1

Table S9. TA kinetics with time constants obtained from three exponential fits for bulk heterojunction PBT/$PC_{71}BM$, PBT-OT/$PC_{71}BM$, and PBT-OTT/$PC_{71}BM$ devices measured at 1150 nm probe. Results also include for same blends with DIO additive. Fitting function was $\Delta T/T(\tau) = A_1\exp(-\tau/\tau_1) + A_2\exp(-\tau/\tau_2) + A_3\exp(-\tau/\tau_3)$, and A is normalized amplitude in percentage where $A = A_i/(A_1+A_2+A_3)\times 100$.

	τ_1 (ps)	A_1/A (%)	τ_2 (ps)	A_2/A (%)	τ_3 (ps)	A_3/A (%)
PBT blend	1.42	62	20	21	400	17
PBT-OT blend	0.80	57	25	20	550	23
PBT-OTT blend	0.60	75	27	10	550	15
PBT blend (DIO)	0.94	81	30	6	600	13
PBT-OT blend (DIO)	0.80	69	16	14	650	17
PBT-OTT blend (DIO)	0.62	74	16	14	700	12

Table S10. Time correlated single photon counting photoluminescence decay with two exponential fits obtained for PBT, PBT-OT, and PBT-OTT blends with $PC_{71}BM$.

	τ_1 (ns)	τ_2 (ns)
PBT blend	0.293	2.34
PBT-OT blend	0.285	1.89
PBT-OTT blend	0.248	1.89

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