Electronic Supplementary Material (ESI) for Energy & Environmental Science.

# Electronic Supplementary Information (ESI)

## Well-Controlled Thieno[3,4-c]pyrrole-4,6-(5H)-dione Based Conjugated Polymers for High Performance Organic Photovoltaic Cells with a Power Conversion Efficiency Exceeding 9%

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## Experimental Section

### Materials

All starting organic compounds were purchased from Aldrich, Alfa Aesar, or TCI Korea, and were used as received without further purification. Tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$) was purchased from Strem. $PC_{71}BM$ was purchased from EM-index. The solvents were dried and purified by fractional distillation over sodium/benzophenone and were handled under a moisture-free atmosphere. Column chromatography was performed using silica gel (Merck, Kieselgel 60 63-200 MYM SC). (6-Octylthieno[3,2-b]thiophen-2-yl)trimethylstannane[1], 2,5-bis(trimethylstannyl)thiophene[2], 5,5'-bis(trimethylstannyl)-2,2'-bithiophene[3], thieno[3,4-c]furan-1,3-dione[4], and 7-(4-bromobutyl)pentadecane[5] were synthesized according to previously reported procedures.

### Measurements

$^1H$ and $^{13}C$ NMR spectra were recorded using a Varian Mercury Plus 300MHz spectrometer and chemical shifts were recorded in ppm units, using chloroform as the internal standard. Elemental analysis was carried out using a Vario Micro Cube at the Korea Basic Science Institute (Busan, Korea). Absorption spectra were measured using a JASCO JP/V-570. The molecular weights of the polymers were determined using gel permeation chromatography (GPC), which was calibrated with 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 an $N_2$ atmosphere with a heating and cooling rate of 10 $°C \cdot min^{-1}$. Cyclic voltammetry (CV) was performed on a CH Instruments Electrochemical Analyzer. The CV measurements were carried out using acetonitrile containing 0.1 M $TBABF_4$ as the supporting electrolyte, and $Ag/AgNO_3$, a platinum wire, and platinum as the reference electrode, counter electrode, and working electrode, respectively.

## Two-dimensional grazing-incidence X-ray diffraction (2D-GIXD)

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

## Fabrication of inverted photovoltaic devices

Inverted bulk hetero-junction (BHJ) OPV devices were fabricated with an indium tin oxide (ITO)/ZnO /polymer:$PC_{71}BM/MoO_3/Ag$ structure. The precursor solution (0.75 M) was prepared by dissolving zinc acetate $[Zn(CH_3COO)_2 \cdot 2H_2O]$ in a solution of 2-methoxyethanol containing ethanolamine as a stabilizer. The solution was stirred at 60 °C for 30 min, in order to achieve homogeneity. The pre-cleaned ITO substrates were treated with UV–ozone. The sol-gel ZnO structure was fabricated by spin-coating the precursor solution at 2000 rpm for 40 s. The substrate was immediately annealed on a hot plate at 380 °C at a heating rate of 20 $°C \cdot min^{-1}$, and was subsequently transferred to a $N_2$-filled glove box. The polymer/$PC_{71}BM$ (97% chlorobenzene/3% DIO mixture) active layer was prepared. The device was solvent-annealed for 1 h at ambient temperature in a glove box; device fabrication was completed by thermally evaporating 10 nm of $MoO_3$ and 100 nm of Ag as the anode under vacuum at a base pressure of $3 \times 10^{-6}$ Torr. The measured effective area of the device was 0.10 $cm^2$.

## OPV devices

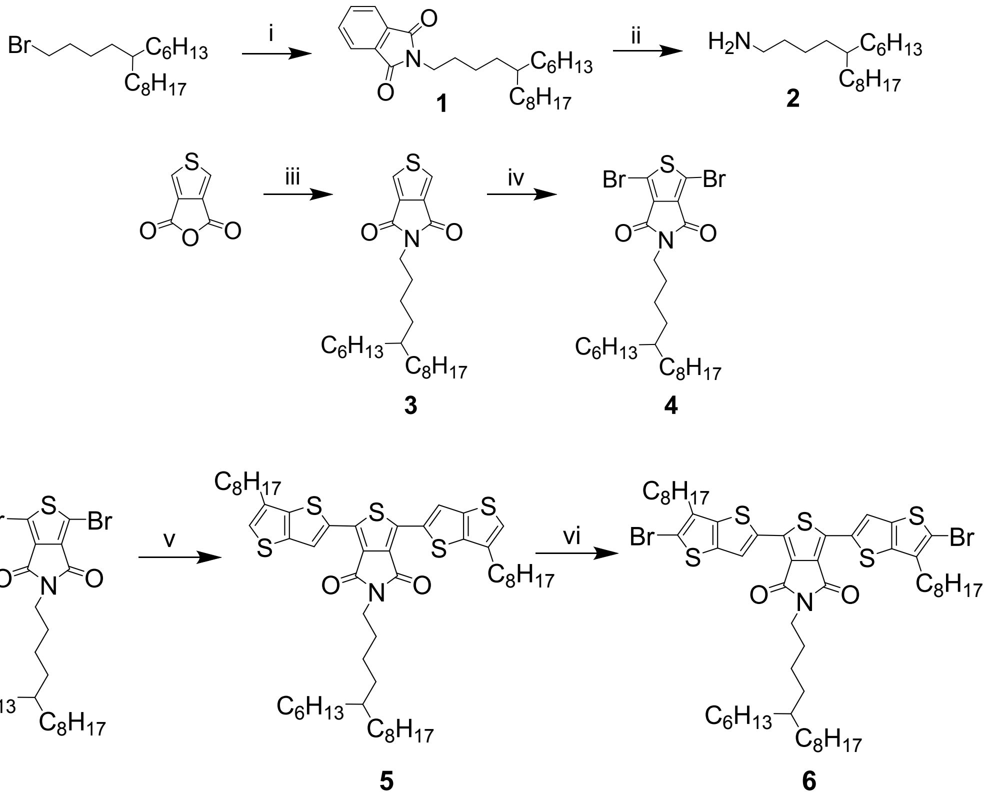
The thickness of the active layer was measured using a KLA Tencor Alpha-step IQ surface profilometer. The current density–voltage (*J–V*) characteristics of the polymer photovoltaic cells were determined by illuminating the cells with simulated solar light (AM 1.5G) at an intensity of 100 $mW/cm^2$ using an Oriel 1000 W solar simulator. Electronic data were recorded using a Keithley 236 source-measure unit. All characterization measurements 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 external quantum efficiency (EQE) was measured as a function of wavelength (from 300~1100 nm) using a Xenon Short Arc Lamp as the light source (McScience K3100 EQX). The light source was calibrated using a Si reference photodiode. The measurements were carried out after masking all but the active cell area of the fabricated device, and the measurements were conducted under ambient conditions.

## Fabrication of hole-only devices

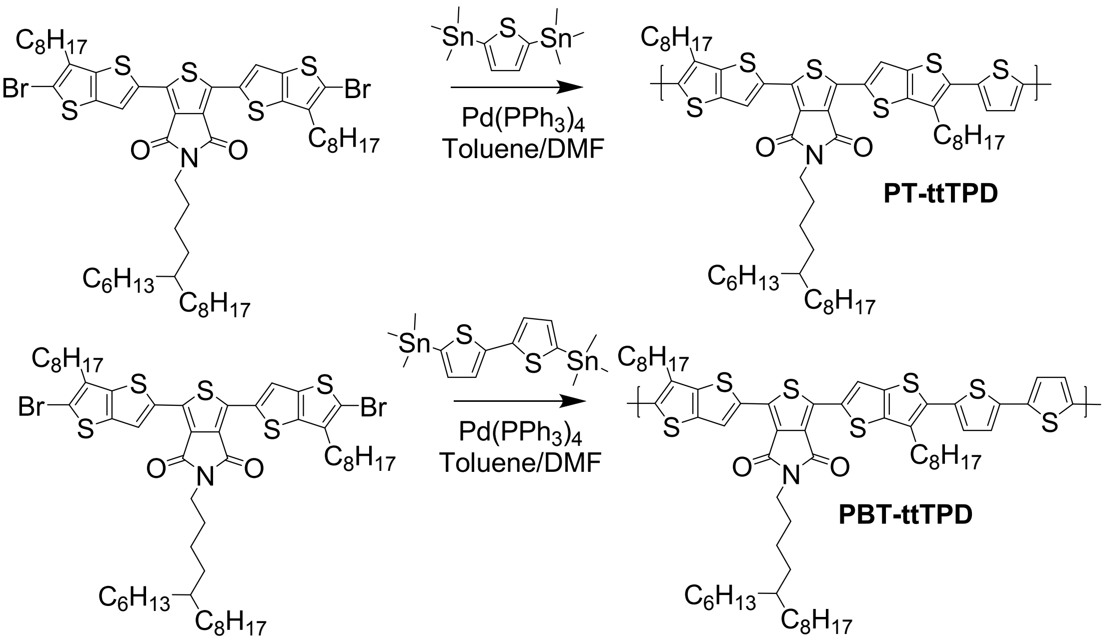
The hole mobility of the active layer was determined by applying the space charge limited current (SCLC) model to the $J-V$ measurement data. Hole-only devices were fabricated on pre-patterned ITO substrates. After cleaning the ITO with an aqueous detergent, deionized water, acetone, and 2-propanol, the ITO was treated with UV-ozone for 15 min. A 30 nm thick PEDOT/PSS (Clevios P VP AI4083) layer was spin-coated on the substrate from an aqueous dispersion. The coated substrate was then baked at 120 °C for 60 min. Subsequently, a solution of the copolymer in chlorobenzene was spin-cast on the PEDOT/PSS layer to form a layer with a thickness of ~100 nm, and the samples were dried for 6 h at room temperature under vacuum. Finally, 10 nm of $MoO_3$ and 100 nm of Ag were thermally evaporated as the anode in vacuo at a base pressure of $3 \times 10^{-6}$ Torr. The SCLC method was employed to measure the hole-only mobility of the polymer/$PC_{71}BM$ blend using a device with the following structure: ITO/PEDOT:PSS/polymer:$PC_{71}BM$/$MoO_3$/Ag. The hole mobilities were calculated using the following equation:

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

where $J$ is the current density, $\varepsilon_r$ is the dielectric constant of the polymers, $\varepsilon_o$ is the permittivity of vacuum, $\mu$ is the hole mobility, $L$ is the thickness of the blend films, and $V = V_{appl} - V_{bi}$, where $V_{appl}$ and $V_{bi}$ are the applied potential and built-in voltage resulting from the difference in the work functions of the anode and cathode, respectively.



**Scheme S1.** Reagents and conditions: (i) Phthalimide potassium salt, DMF, 90 °C, 16 h; (ii) hydrazine, MeOH, 80 °C, 12 h; (iii) 5-hexyltridecyl-1-amine, toluene, 100 °C, overnight; (iv) NBS, $H_2SO_4$, trifluoroacetic acid, 12 h; (v) trimethyl(6-octylthieno[3,2-b]thiophen-2-yl)stannane, $Pd(pph_3)_2Cl_2$, DMF, 150 °C, 12 h; (vi) NBS, DMF, 8 h.



**Scheme S2.** Synthesis and chemical structures of polymers.

## Synthesis of monomers and polymers

**Synthesis of 2-(5-hexyltridecyl)isoindoline-1,3-dione (1)** In a 250-mL flask, 7-(4-bromobutyl)pentadecane (15.0 g, 0.043mol), phthalimide potassium salt (9.6 g, 0.051 mol), and 200 mL of DMF were mixed and stirred at 90 °C for 16 h. The reaction was terminated by adding 100 mL of water. The crude product was obtained following extraction using hexane. Yield: 13.8 g (75%). $^1$H NMR (300 MHz, $CDCl_3$) δ: 7.83–7.81 (m, 2H), 7.69–7.67 (d, 2H), 3.65 (t, 2H), 1.67–1.57 (m, 1H), 1.34–1.28 (m, 30H), 0.85 (m, 6H).

**Synthesis of 5-hexyltridecan-1-amine (2)** A mixture of 2-(5-hexyltridecyl)isoindoline-1,3-dione (10.0 g, 0.024 mol), hydrazine (3.09 g, 0.096 mol), and 100 mL of MeOH was refluxed for 12 h. To the mixture, 100 mL of 10% KOH was added and the mixture was extracted with 200 mL of methylene dichloride. The product was obtained after the solvent was evaporated. Yield: 6.67 g (82%).$^1$H NMR (300 MHz, $CDCl_3$) δ: 2.68 (t, 2H), 1.52 (m, 1H), 1.30–1.01 (m, 30H), 0.85 (m, 6H).

**Synthesis of 5-(5-hexyltridecyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (3)** Thieno[3,4-c]furan-1,3-dione (3.0 g, 0.0194 mol) and 5-hexyltridecan-1-amine (6.6 g, 0.0232 mol) were mixed in 300 mL of toluene. After the mixture was stirred for 24 h at 100 °C, the solvent was completely removed. The crude product was purified by column chromatography using hexane/dichloromethane (1:1) as the eluent; subsequently, the product was recrystallized from hexane. Yield: 7.5 g (73%). $^1$H NMR (300 MHz, $CDCl_3$) δ: 7.79 (s, 2H), 3.59 (t, 2H), 1.59 (m, 1H), 1.23–1.18(m, 30H), 0.86 (m, 6H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ: 165.1, 145.2, 138.5, 40.2, 39.8, 38.5, 37.1, 36.2, 35.1, 33.3, 32.3, 30.5, 29.8, 29.6, 28.3, 27.0, 26.8, 26.3, 25.9, 25.1. 22.7, 14.1. Anal. Calc. for $C_{25}H_{41}N$: C, 71.55; H, 9.85; N, 3.34. Found: C, 71.48; H, 9.92; N, 3.28.

**Synthesis of 1,3-dibromo-5-(5-hexyltridecyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (4)**

N-bromosuccinimide (5.30 g, 0.030 mol) was added to a mixture of **3** (5.0 g, 0.012 mol), sulfuric acid (30 mL), and trifluoroacetic acid (100 mL); the mixture was stirred for 12 h. The crude product was purified by column chromatography using hexane/dichloromethane (1:1) as the eluent; the product was subsequently recrystallized from ethanol. Yield: 4.9 g (76%).$^1$H NMR (300 MHz, $CDCl_3$) δ: 3.58 (t, 2H), 1.59 (m, 1H), 1.23-1.19 (m, 30H), 0.87 (m, 6H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ: 170.3, 155.1, 142.5, 41.3, 40.2, 39.3, 38.2, 37.1, 36.4, 34.8, 33.3, 31.7, 30.2, 29.1, 28.6, 27.9, 27.3, 27.0, 26.3, 25.2. 23.1, 16.3. Anal. Calc. for $C_{25}H_{39}N$: C, 52.00; H, 6.81; N, 2.43. Found: C, 51.84; H, 6.93; N, 2.54.

**Synthesis of 5-(5-hexyltridecyl)-1,3-bis(6-octylthieno[3,2-b]thiophen-2-yl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (5)** Trimethyl(6-octylthieno[3,2-b]thiophen-2-yl)stannane (5.39 g, 0.012 mol) was added to a stirred solution of **4** (3.00 g, 0.005 mol) and bis(triphenylphosphine)palladium(II) dichloride (95 mg, 0.06 mmol) in DMF (50 mL). The mixture was refluxed overnight. The resulting mixture was extracted with ethyl acetate and brine. The organic layer was washed with sodium bicarbonate and brine, and then dried over anhydrous $MgSO_4$. The solvent was removed and the crude product was purified via column chromatography with hexane as the eluent to yield **5** (2.5 g, 58%) as a light orange solid. $^1$H NMR (300 MHz, $CDCl_3$) δ: 8.30 (s, 2H), 7.08 (s, 2H), 3.66 (t, 2H), 2.69 (t, 4H), 1.73-1.70 (m, 5H), 1.41-1.23 (m, 50H), 0.97-0.86 (m, 12H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ: 169.1, 160.3, 140.2, 137.5, 127.3, 123.1, 122.8, 122.0, 121.3, 40.2, 39.8, 39.2, 38.9, 38.4, 38.0, 37.8, 37.4, 35.2, 34.7, 34.1, 33.3, 32.9, 31.5, 30.5, 30.1, 29.9, 29.3, 29.2, 28.5, 28.1, 27.4, 25.6, 24.9, 24.5, 22.7, 12.5. Anal. Calc. for $C_{53}H_{77}N$: C, 69.15; H, 8.43; N, 1.52. Found: C, 68.98; H, 8.51; N, 1.61.

**Synthesis of 1,3-bis(5-bromo-6-octylthieno[3,2-b]thiophen-2-yl)-5-(5-hexyltridecyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (6)** Bromosuccinimide (0.97 g, 0.005 mol) was added to a stirred solution of **5** (2.00 g, 0.002 mol) in DMF (150 mL) in the dark. The mixture was stirred at room temperature overnight. A bright orange precipitate formed and the mixture was filtered and the precipitate was thoroughly washed with methanol. The solid was then washed once with cold diethyl ether and purified via flash chromatography to give 2.30 g (80%) of **6**. $^1$H NMR (300 MHz, $CDCl_3$) δ: 8.20 (s, 2H), 3.64 (t, 2H), 2.68 (t, 4H), 1.70-1.65 (m, 5H), 1.32-1.22 (m, 50H), 0.88-0.83 (m, 12H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ: 170.1, 165.2, 145.1, 140.8, 130.2, 128.2, 125.3, 124.6, 122.2, 41.3, 40.9, 39.9, 39.1, 38.8, 38.0, 37.6, 37.2, 36.3, 35.1, 34.9, 34.2, 33.3, 32.1, 31.6, 30.4, 30.1, 29.3, 29.0, 28.2, 27.9, 27.2, 26.7, 25.3, 24.2, 23.1, 13.1. Anal. Calc. for $C_{53}H_{75}N$: C, 59.03; H, 7.01; N, 1.30. Found: C, 58.78; H, 7.21; N, 1.28.

**General polymerization procedure**

The two copolymers were synthesized by Stille coupling polymerization, as shown in Scheme 2. 2,5-Bis(trimethylstannyl)thiophene, 5,5'-bis(trimethylstannyl)-2,2'-bithiophene, and **6** were synthesized using procedures previously reported. Tetrakis-(triphenylphosphine)palladium in 4 mL anhydrous toluene and 1 mL DMF was stirred at 110 °C overnight, following which 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 day with acetone in a Soxhlet apparatus, to remove oligomers and catalyst residues. The polymers were then subjected to column chromatography using chloroform as the eluent; subsequently, the polymers were re-precipitated from chloroform/methanol several times. The resulting polymers were soluble in common organic solvents.

**Poly{2,5-bis-thiophene-*alt*-1,3-bis(6-octylthieno[3,2-b]thiophen-2-yl)-5-(5-hexyltridecyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione} (PT-ttTPD)** 2,5-Bis(trimethylstannyl)thiophene (200 mg, 0.49 mmol) was mixed with **6** (526 mg, 1.0 equiv), tetrakis(triphenylphosphine)palladium (16 mg, 2.6 μmol), toluene (4 mL), and DMF (1 mL). The polymer yield was 48%. Anal. Calc. for $C_{57}H_{77}N$: C, 68.42; H, 7.76; N, 1.40. Found: C, 68.38; H, 7.92; N, 1.35. $M_n$ = 85 000, PDI = 2.4. $T_d$ = 323 °C.

**Poly{5,5'-bis-2,2'-bithiophene-*alt*-1,3-bis(6-octylthieno[3,2-b]thiophen-2-yl)-5-(5-hexyltridecyl)-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione} (PBT-ttTPD)** 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (200 mg, 0.40 mmol) was mixed with **6** (438 mg, 1.0 equiv), tetrakis(triphenylphosphine)palladium (14 mg, 2.6 μmol), toluene (4 mL), and DMF (1mL). The polymer yield was 35%. $C_{61}H_{79}N$: C, 67.67; H, 7.35; N, 1.29. Found: C, 67.52; H, 7.52; N, 1.20. $M_n$ = 70 000, PDI = 2.8. $T_d$ = 325 °C.

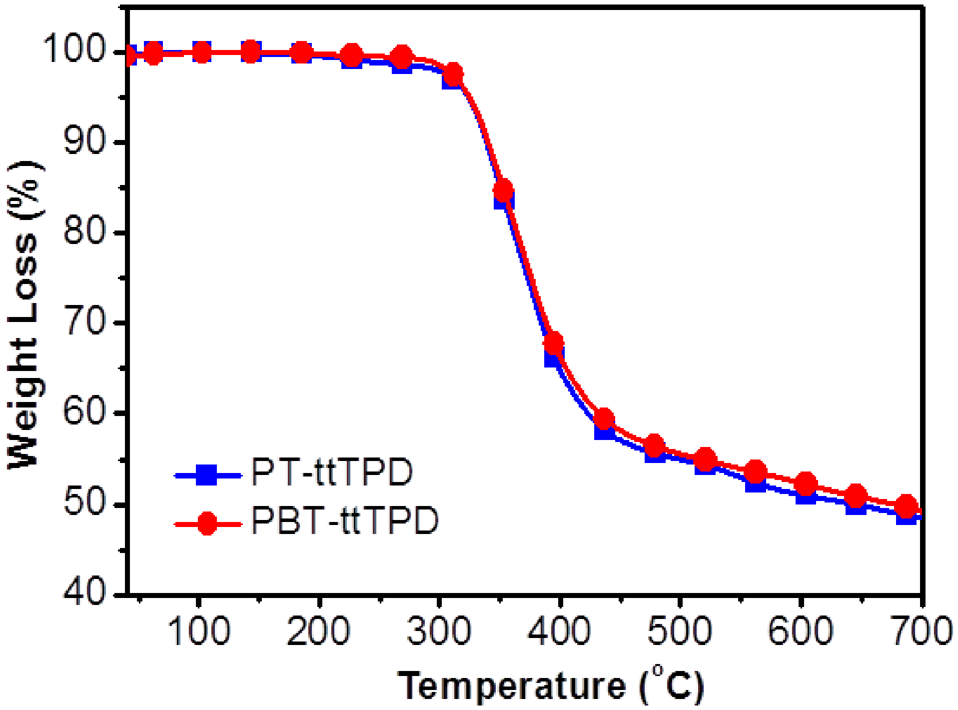


**Figure S1.** Thermogravimetric analysis of the copolymers.

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

| Polymer | $M_n$ (g/mol)[a] | PDI | $T_d$ (°C)[b] | $\lambda_{max, abs}$ (nm) | $\lambda_{max}$ (nm) | $\lambda_{edge}$ (nm) | Optical $E_g^{opt}$ (eV)[d] | HOMO (eV)[e] | LUMO (eV)[f] |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Solution | Film[c] | Film[c] | | | |
| PT-ttTPD | 85,000 | 2.4 | 323 | 518 | 567 | 708 | 1.75 | -5.65 | -3.90 |
| PBT-ttTPD | 70,000 | 2.8 | 325 | 522 | 572 | 720 | 1.72 | -5.54 | -3.82 |

[a] $M_n$ and PDI of the polymers were determined by gel permeation chromatography using a polystyrene standard in $CHCl_3$.

[b] Temperature at 5% weight loss at a heating rate of 10 °C $min^{-1}$ under nitrogen.

[c] Polymer film on a quartz plate by spin-casting from chloroform at 1500 rpm for 30 s.

[d] Calculated from the absorption band edge of the copolymer films, $E_g=1240/\lambda_{edge}$.

[e] HOMO energy levels were determined from the $E_{ox/onset}$ of the first oxidation potential of ferrocene, -4.7eV.

[f] LUMO = $E_g^{opt}$ + HOMO (eV).

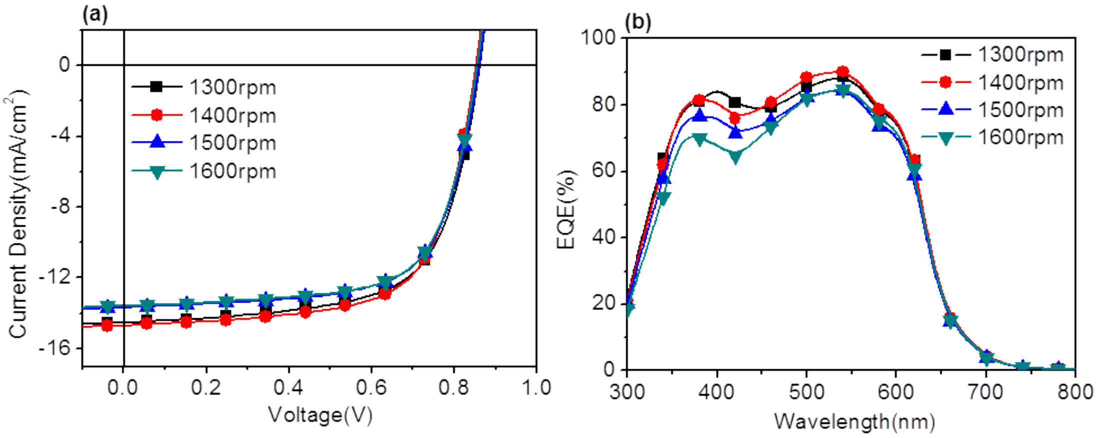


**Figure S2.** *J–V* curves for ITO/ZnO/PT-ttTPD:$PC_{71}BM$ (1.0:1.3) (CB solvent processed with 3 vol% DIO)/$MoO_3$/Ag configuration with different active layer spin rate. (b) EQE spectra of the OPVs based on PT-ttTPD:$PC_{71}BM$ (1.0:1.3) with different active layer spin rates.

**Table S2.** Comparison of the photovoltaic properties of the OPVs based on PT-ttTPD:$PC_{71}BM$ (1.0:1.3) with different active layer thicknesses under an illumination of AM 1.5 G, 100 mW cm$^{-2}$.

| Polymer | Spin rate [rpm] | $V_{OC}$ [V] | $J_{SC}$ [mA/cm$^2$] | *FF* [%] | PCE [%] |
|---|---|---|---|---|---|
| PT-ttTPD : $PC_{71}BM$<br>(CB/3vol%DIO)<br>(1.0 : 1.3 w/w ratio) | 1300 | 0.86 | 14.50[13.35][a] | 66 | 8.23 |
| | 1400 | 0.85 | 14.67[13.48][a] | 67 | 8.30 |
| | 1500 | 0.86 | 13.66[12.59][a] | 68 | 7.93 |
| | 1600 | 0.85 | 13.56[12.48][a] | 68 | 7.91 |

[a] Calculated from the EQE spectra.

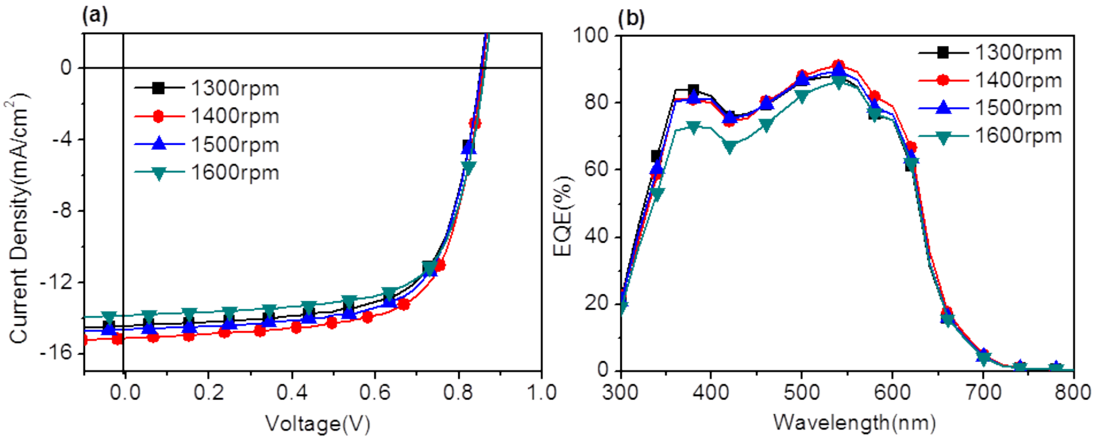


**Figure S3.** *J*–*V* curves for ITO/ZnO/PT-ttTPD:PC$_{71}$BM (1.0:1.5) (CB solvent processed with 3 vol% DIO)/MoO$_3$/Ag configuration with different active layer spin rate. (b) EQE spectra of the OPVs based on PT-ttTPD:PC$_{71}$BM (1.0:1.5) with different active layer spin rates.

**Table S3.** Comparison of the photovoltaic properties of the OPVs based on PT-ttTPD:PC$_{71}$BM (1.0:1.5) with different active layer spin rates under an illumination of AM 1.5 G, 100 mW cm$^{-2}$.

| Polymer | Spin rate [rpm] | $V_{OC}$ [V] | $J_{SC}$ [mA/cm$^2$] | *FF* [%] | PCE [%] |
|---|---|---|---|---|---|
| PT-ttTPD : PC$_{71}$BM<br>(CB/3vol%DIO)<br>(1.0:1.5 w/w ratio) | 1300 | 0.85 | 14.42[13.27][a] | 68 | 8.32 |
| | 1400 | 0.86 | 15.30[13.65][a] | 70 | 9.21 |
| | 1500 | 0.85 | 14.64[13.40][a] | 69 | 8.54 |
| | 1600 | 0.86 | 13.84[12.73][a] | 69 | 8.22 |

[a] Calculated from the EQE spectra.

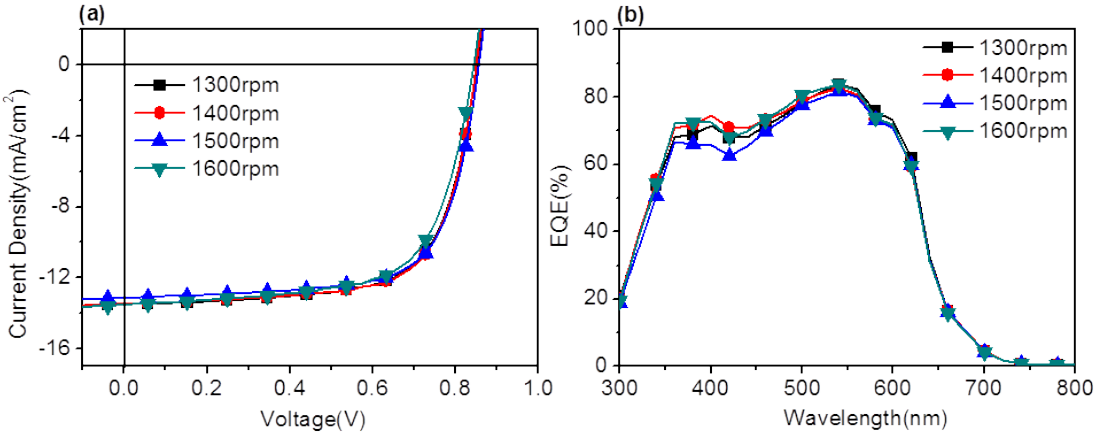


**Figure S4.** *J–V* curves for ITO/ZnO/PT-ttTPD:$PC_{71}BM$ (1.0:1.7) (CB solvent processed with 3 vol% DIO)/$MoO_3$/Ag configuration with different active layer spin rates. (b) EQE spectra of the OPVs based on PT-ttTPD:$PC_{71}BM$ (1.0:1.7) with different active layer spin rates.

**Table S4.** Comparison of the photovoltaic properties of the OPVs based on PT-ttTPD:$PC_{71}BM$ (1.0:1.7) with different active layer spin rates under an illumination of AM 1.5 G, 100 mW cm$^{-2}$.

| Polymer | Spin rate [rpm] | $V_{OC}$ [V] | $J_{SC}$ [mA/cm$^2$] | *FF* [%] | PCE [%] |
|---|---|---|---|---|---|
| PT-ttTPD : $PC_{71}BM$ (CB/3vol%DIO) (1.0:1.7 w/w ratio) | 1300 | 0.85 | 13.52[12.43][a] | 69 | 7.89 |
| | 1400 | 0.85 | 13.47[12.41][a] | 70 | 7.96 |
| | 1500 | 0.86 | 13.13[12.04][a] | 70 | 7.83 |
| | 1600 | 0.84 | 13.51[12.44][a] | 67 | 7.60 |

[a] Calculated from the EQE spectra.

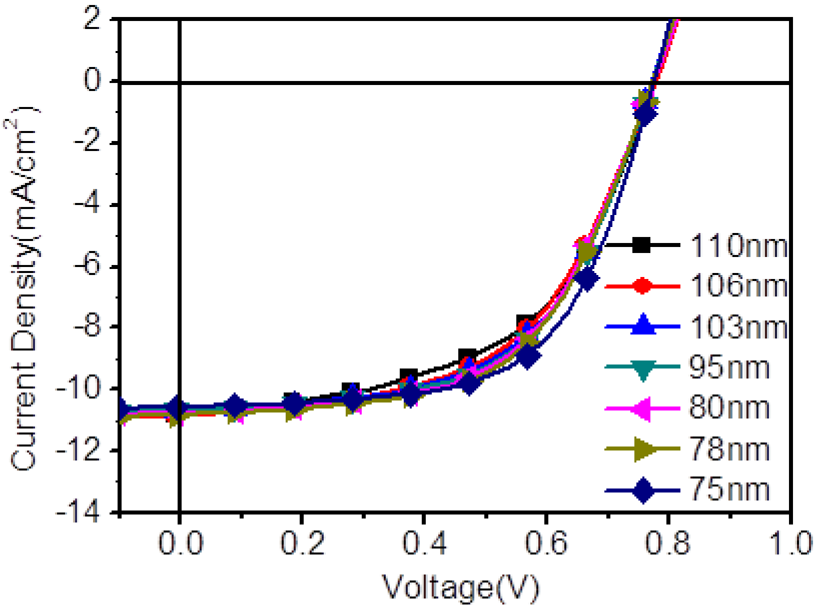


**Figure S5.** *J–V* curves for ITO/ZnO/PBT-ttTPD:PC$_{71}$BM (1.0:1.5) (CB solvent processed with 3 vol% DIO)/MoO$_3$/Ag configuration with different active layer thicknesses.

**Table S5.** Comparison of the photovoltaic properties of the OPVs based on PBT-ttTPD:PC$_{71}$BM (1.0:1.5) with different active layer thicknesses under an illumination of AM 1.5 G, 100 mW cm$^{-2}$.

| Polymer | Thickness [nm] | $V_{OC}$ [V] | $J_{SC}$ [mA/cm$^2$] | *FF* [%] | PCE [%] |
|---|---|---|---|---|---|
| PBT-ttTPD : PC$_{71}$BM (CB/3vol%DIO) (1.0:1.5 w/w ratio) | 110 | 0.78 | 10.76 | 53 | 4.44 |
| | 106 | 0.78 | 10.84 | 54 | 4.57 |
| | 103 | 0.77 | 10.67 | 57 | 4.69 |
| | 95 | 0.77 | 10.67 | 58 | 4.75 |
| | 80 | 0.77 | 10.75 | 57 | 4.77 |
| | 78 | 0.77 | 10.81 | 58 | 4.84 |
| | 75 | 0.78 | 10.56 | 62 | 5.05 |

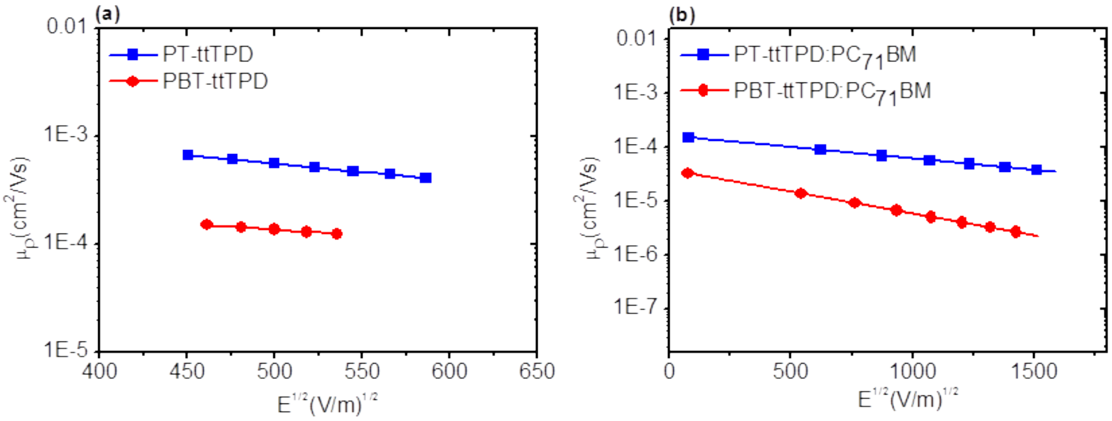


**Figure S6.** (a-b) Field-dependent hole mobilities of neat polymer and polymer:PC$_{71}$BM blend films calculated from the hole-only devices by fitting *J-V* curves in the SCLC regime.

**Table S6.** Calculated hole mobilities of the pure polymer or polymer/PC$_{71}$BM (1:1.5 w/w, processed with 3 vol% DIO) system under the optimized conditions using the SCLC method.

| Active layer | Solvent | Thickness | $\mu_h$[a] |
|---|---|---|---|
| | | (nm) | (cm$^2$ V$^{-1}$ s$^{-1}$) |
| PT-ttTPD Neat State | CB | 121 | 3.31 x 10$^{-3}$ |
| PT-ttTPD Blend State | CB/3vol%DIO | 163 | 1.78 x 10$^{-3}$ |
| PBT-ttTPD Neat State | CB | 128 | 4.98 x 10$^{-4}$ |
| PBT-ttTPD Blend State | CB/3vol%DIO | 164 | 3.78 x 10$^{-5}$ |

[a]Hole-only devices with the following structure: ITO/PEDOT:PSS/polymer or polymer:PC$_{71}$BM (1:1.5 w/w)/MoO$_3$/Ag.

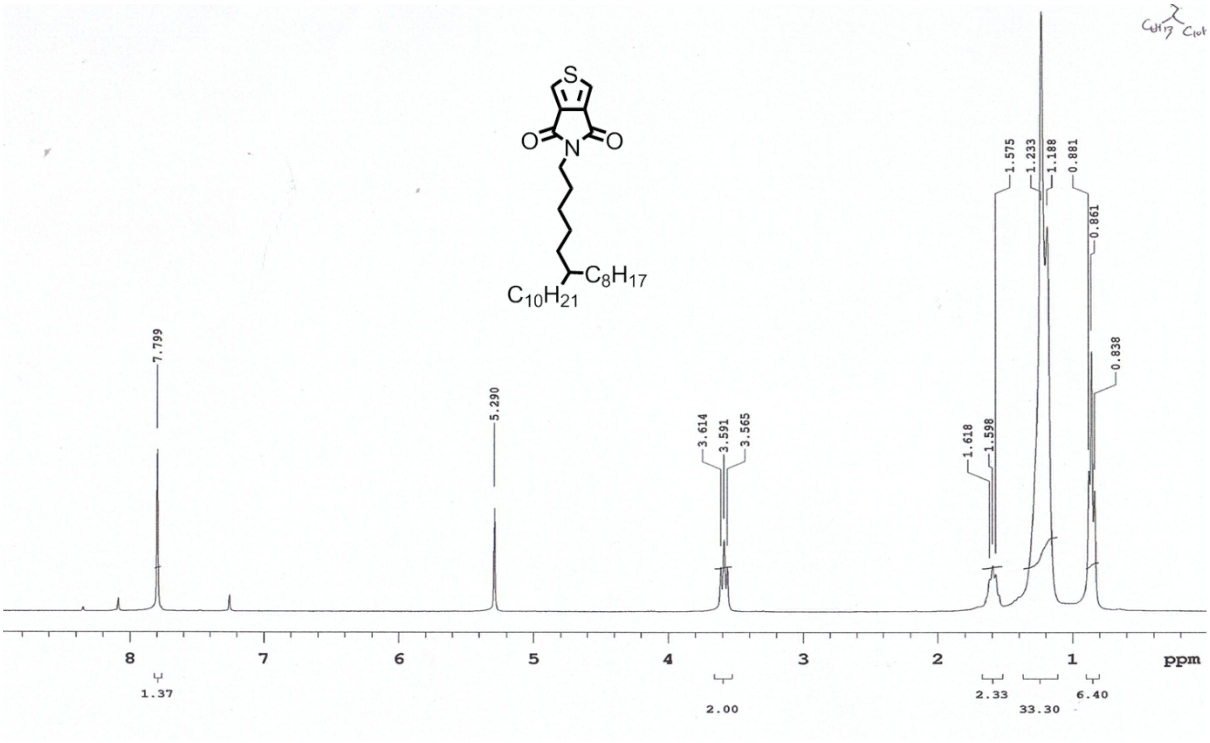


**Figure S7.** $^1$H NMR spectrum of **3**.

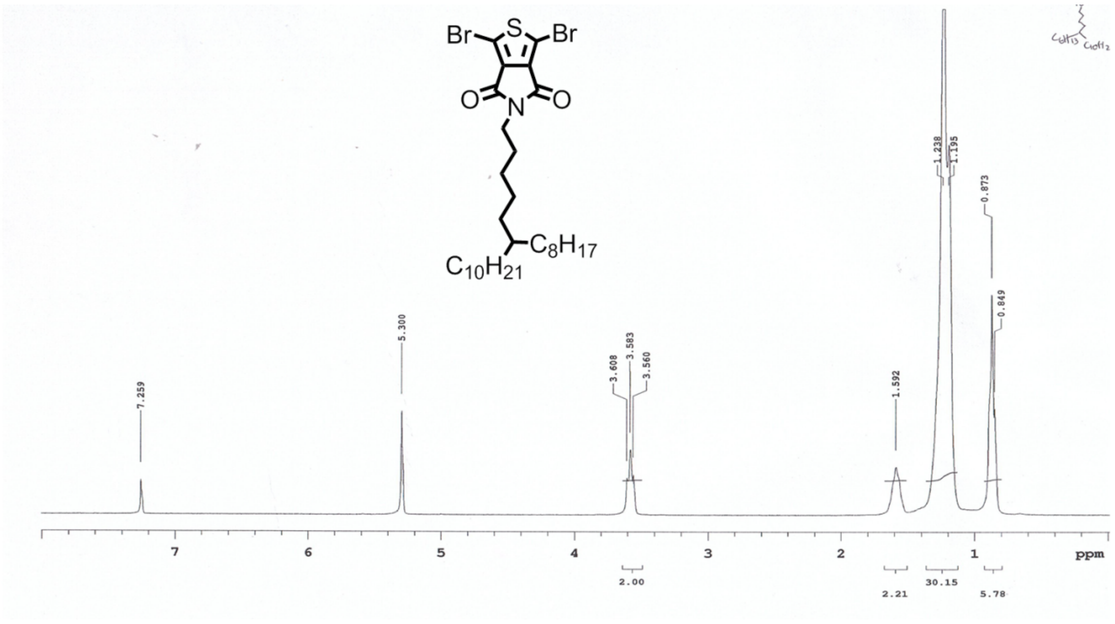


**Figure S8.** $^1$H NMR spectrum of **4**.

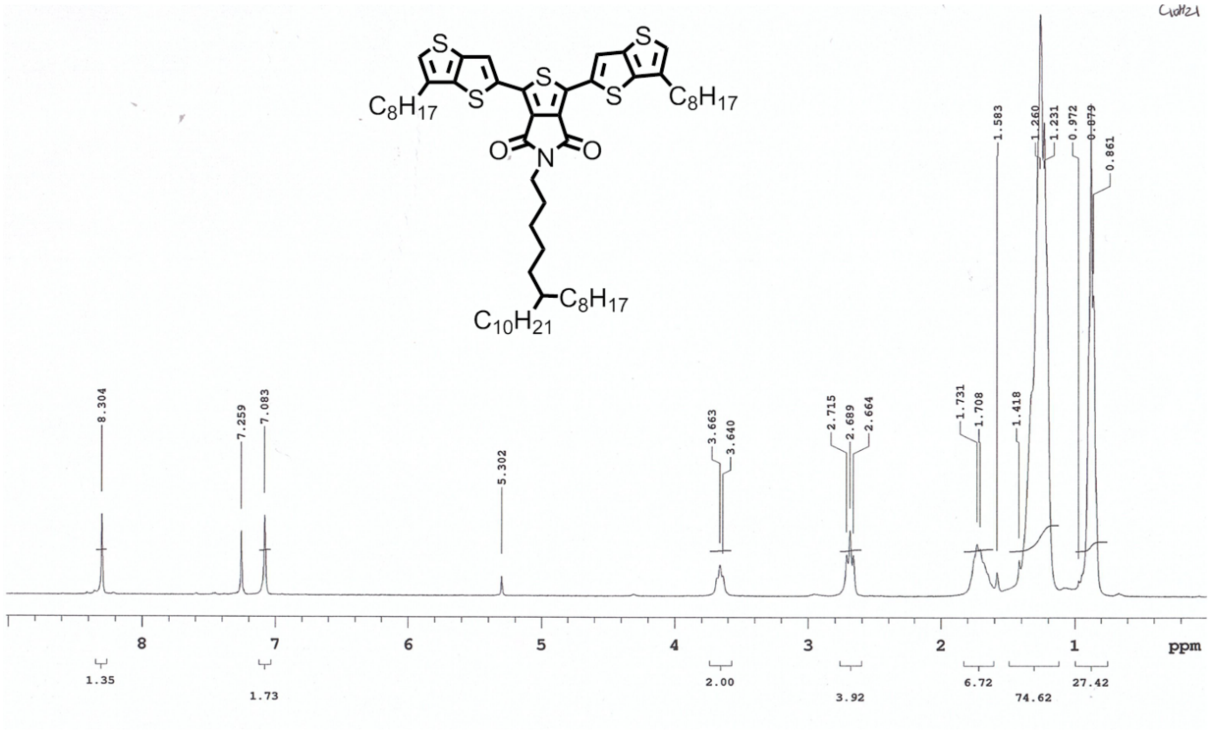


**Figure S9.** ${}^1$H NMR spectrum of **5**.

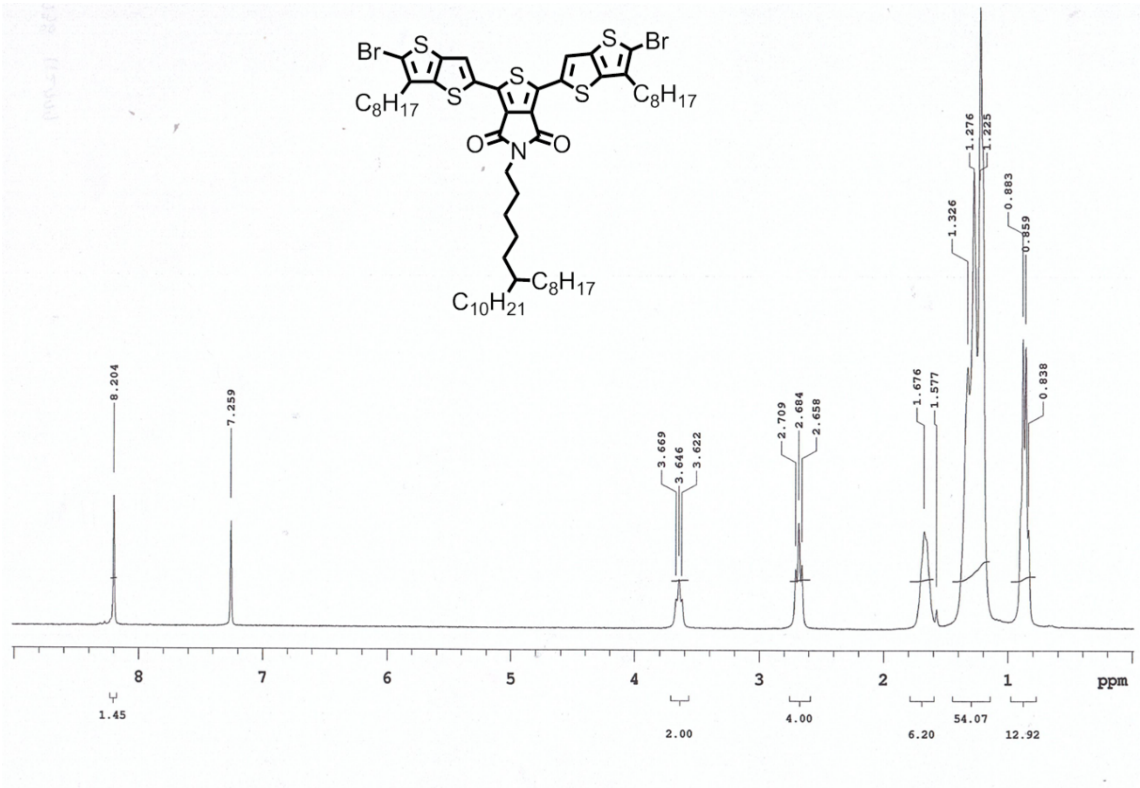


**Figure S10.** ${}^1$H NMR spectrum of **6**.

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