Supplementary Information for

Introduction of a Conjugated Side Chain as an Effective Approach to Improving Donor-Acceptor Photovoltaic Polymers

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Experimental methods

Characterization

^{1}H NMR (400 MHz) spectra were measured using an NMR spectrometer (JEOL, Alpha 400) equipped with an Oxford superconducting magnet system. Gel permeation chromatography (GPC) was performed on a Shimadzu Prominence system using a UV detector and $CHCl_3$ as the eluent at 40 °C. The $CHCl_3$solution was filtered with a PTFE filter (pore size: 1.0 μm) before sample injection. UV-vis spectra were recorded using a

UV-vis spectrometer (Jacso, V-650). Cyclic voltammograms (CVs) were recorded on a potentiostat (Hokuto Denkou, HSV-100). A Pt plate coated with a thin polymer film was used as the working electrode. A Pt wire and an Ag/Ag^+ (0.01 M $AgNO_3$ in acetonitrile) electrode were used as the counter and reference electrodes (calibrated against Fc/Fc^+), respectively. The AFM measurements were carried out using an atomic force microscope (Digital Instruments, Nanoscope 31) operated in tapping mode.

Fabrication and characterization of the field-effect transistor

The transistors were built on highly doped n-type (100) Si substrates (< 0.02 Ω cm) with 300-nm-thick thermally grown silicon dioxide. Octadecyltrichlorosilane (OTS) modified SiO_2 was formed by soaking the substrates in a toluene solution of OTS (5 mmol/L) for 12 h in a dry N_2-filled glove box. The capacitance of the gate dielectric was $C_i = 10.7 \pm 0.7$ nF cm^{-2}, which was measured by using the charging time. A $CHCl_3$ solution of the polymer (5 mg mL^{-1}) was directly spin-coated onto the dielectric substrates (1000 rpm, 40 s). Gold electrodes (L = 50 μm, W = 8 mm) were evaporated onto the surface through a metal mask. The electrical characteristics of the transistors were measured using an I-V measurement system (Keithley, 2400 and 6430) at room temperature. All the transistors were measured under ambient conditions.

Synthesis

All chemicals were purchased from Alfa, Aldrich, or Wako and used without further purification. The following compounds were synthesized according to literature procedures:

2,6-di(trimethyltin)-4,8-di(2-ethylhexyloxy)benzo[1,2-b:4,5-b'] dithiophene (monomer **1**) [S1],

(*E*,*E*,*E*)-2,5-dibromo-3-{2-[5-(2-{5-[2-(5-hexyl-thiophen-2-yl)-vinyl]-thiophen-2-yl}-vinyl)-thiophen-2-yl]-vinyl}-thiophene (monomer **2**) [S2],

1,3-Dibromo-5-octylthieno[3,4-c]pyrrole-4,6-dione (monomer **3**) [S1],

2,6-di(trimethyltin)-N-[1-(2'-ethylhexyl)-3-ethylheptanyl]-dithieno[3,2-b:2',3'-d]pyrrole (monomer **4**) [S3], and

3,6-dithien-2-yl-2,5-dibutyl-pyrrolo[3,4-c]pyrrole-1,4-dione (monomer **5**) [S4]

Synthesis of P1

Monomer **1** (308.9 mg, 0.4 mmol), monomer **3** (169.2 mg, 0.4 mmol), and dry toluene (15 mL) were added to a 50 mL double-neck round bottom flask. The reaction container was purged with N_2 for 30 min to remove O_2. $Pd(PPh_3)_4$ (3%, 14 mg) was added, and the reaction mixture was heated to 110 °C. The solution was stirred at 110 °C for 48 h. The resulting sticky solution was cooled to room temperature and poured into methanol (200 mL), and the precipitate was collected by filtration, and then washed with methanol. The solid was dissolved in $CHCl_3$ (150 mL) and passed through a column packed with alumina, celite, and silica gel. The column was eluted with $CHCl_3$. The combined polymer solution was concentrated and poured into methanol, and the precipitate was collected and dried.

Yield: 200 mg (71%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.5-8.0 (br, 2H), 4.5-3.5 (br, 6H), 2.1-0.6 (br, 45H). M_n = 18.2 kg/mol; polydispersity = 1.74.

Synthesis of TTV1

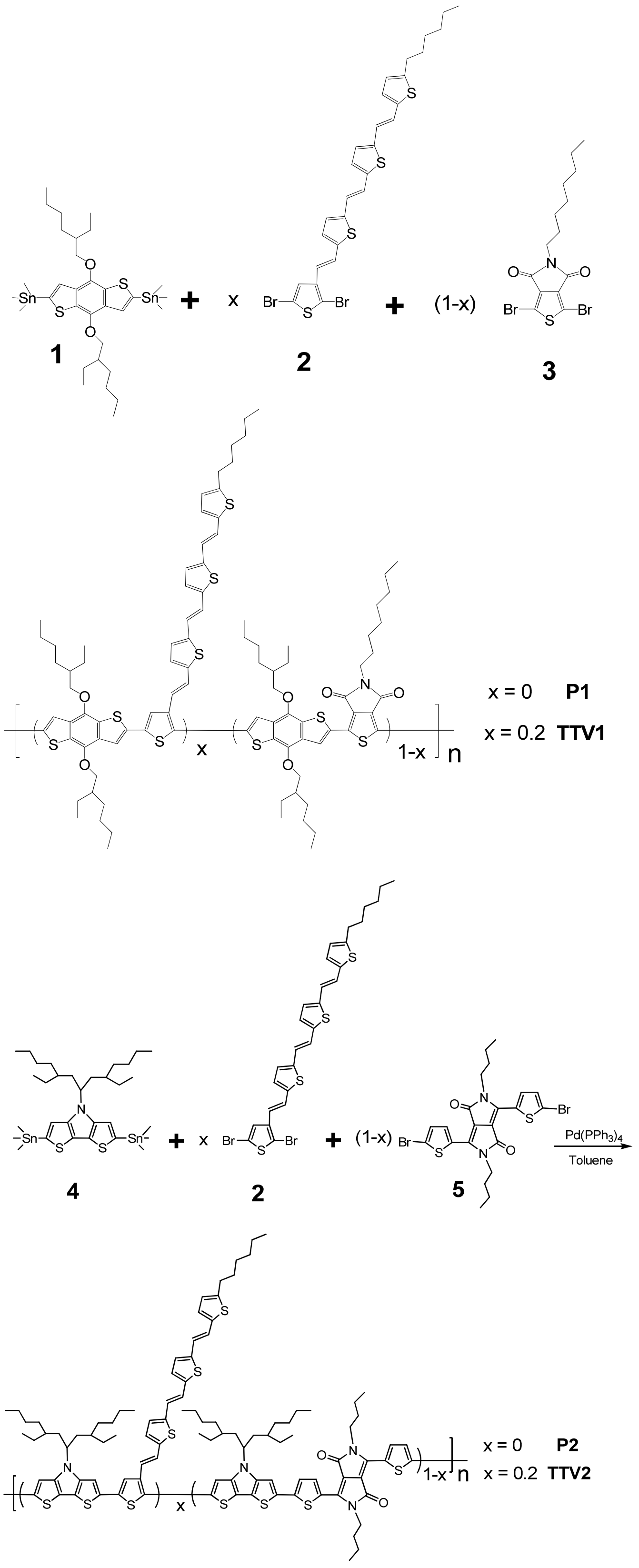
The same procedure as for **PBDT-TPD** was used with monomer **1** (308.9 mg, 0.4 mmol), monomer **2** (52.0 mg, 0.08 mmol), and monomer **3** (136.4 mg, 0.32 mmol) were used as starting materials. Yield: 180 mg (60%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.5-8.0 (br), 7.1-6.6 (br), 4.5-3.5 (br), 2.7 (br), 2.1-0.6 (br). M_n = 28.3 kg/mol; polydispersity = 1.54.

Synthesis of P2

The same procedure as for **PBDT-TPD** was used but with monomer **4** (201.4 mg, 0.353 mmol), and monomer **5** (262.5 mg, 0.353 mmol) as starting materials. Yield: 250 mg (86%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 9.00 (br, 2H), 7.5-6.8 (m, 4H), 4.50 (br, 1H), 4.10 (br, 4H), 2.1-0.6 (m, 48H). M_n = 18.9 kg/mol; polydispersity = 2.04.

Synthesis of TTV2

The same procedure as for **PBDT-TPD** was used but with monomer **4** (174.7 mg, 0.235 mmol), monomer **2** (30.6 mg, 0.047 mmol), and monomer **5** (107.4 mg, 0.188 mmol) as starting materials. Yield: 170 mg (86%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 9.00 (br), 7.5-6.5 (m), 4.5-3.8 (br), 2.7 (br), 2.1-0.6 (m). M_n = 21.1 kg/mol; polydispersity = 1.95.



Scheme S1. Synthetic routes for P1, P2, TTV1, and TTV2.

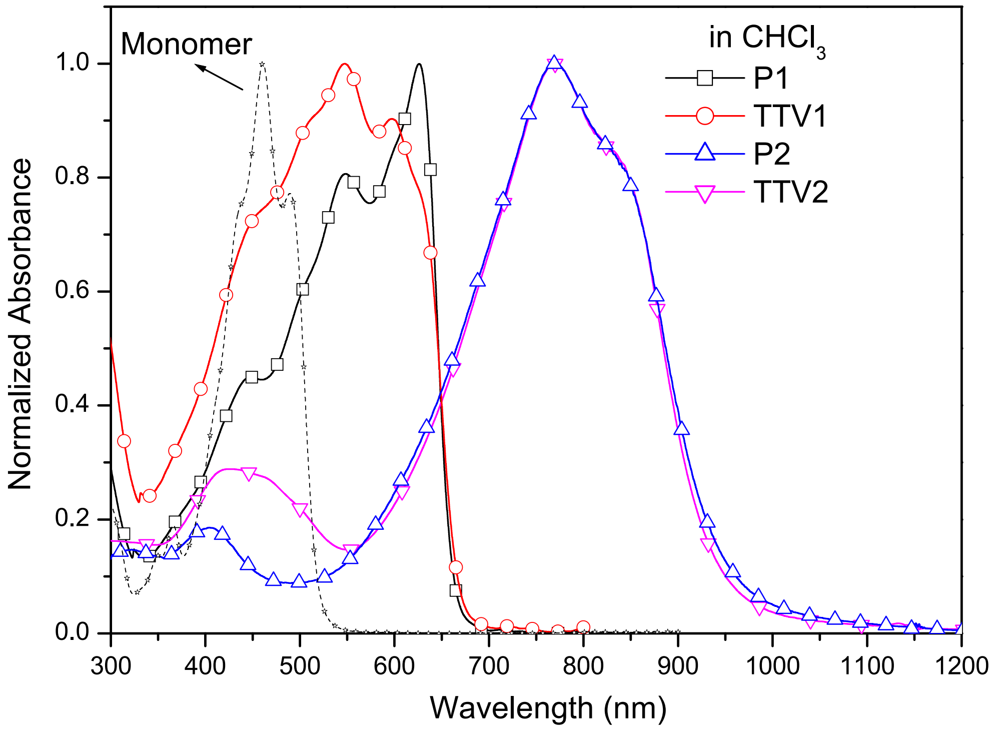


Figure S1. Normalized absorption spectra of four polymers in $CHCl_3$ solutions.

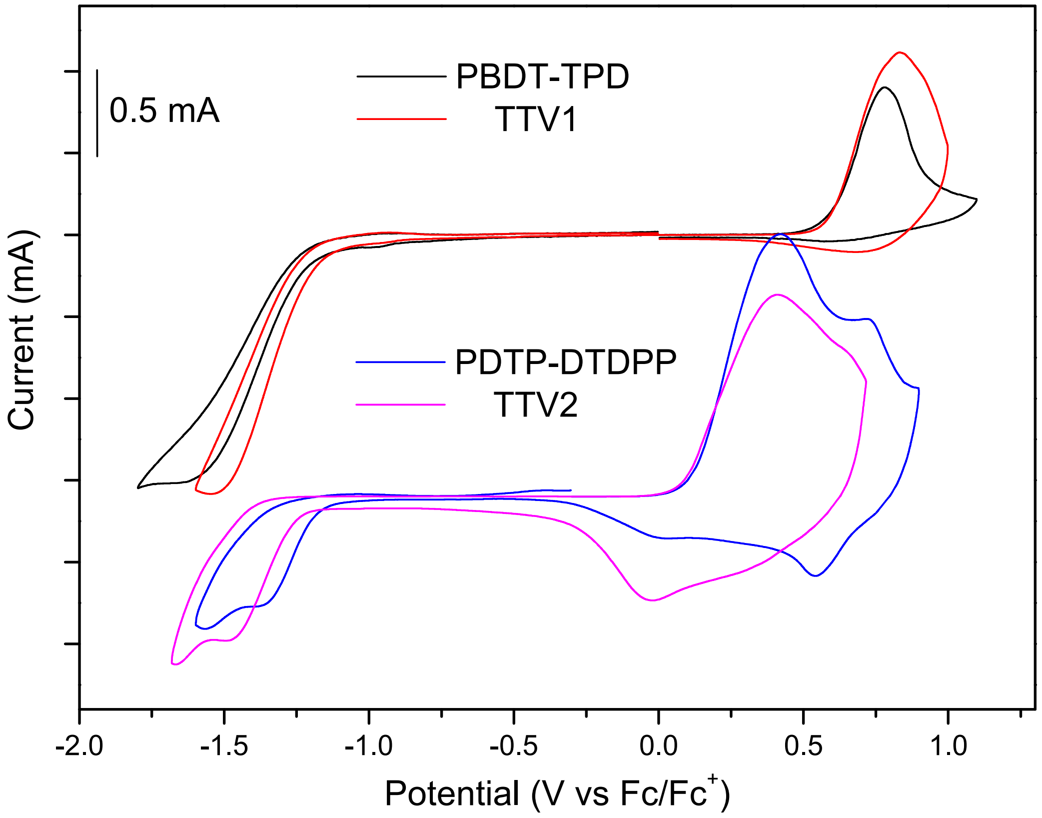


Figure S2. Cyclic voltammogram of the polymer films on a platinum plate in 0.1 mol/L acetonitrile solution of $[Bu_4N]PF_6$ (Bu = butyl) at a scan rate of 50 mV/s.

Table S1. Photovoltaic performance of PSCs based on the four copolymers in combination with $PC_{70}BM$, cast from pristine $CHCl_3$.

Polymer:$PC_{71}BM$(1:1.5, w/w)	V_{OC} (V)	J_{SC} (mA/cm^2)	FF	PCE (%)
P1	0.80	4.33	0.58	1.99%
TTV1	0.80	3.51	0.59	1.67%
P2	0.42	7.63	0.53	1.69%
TTV2	0.46	8.07	0.52	1.93%

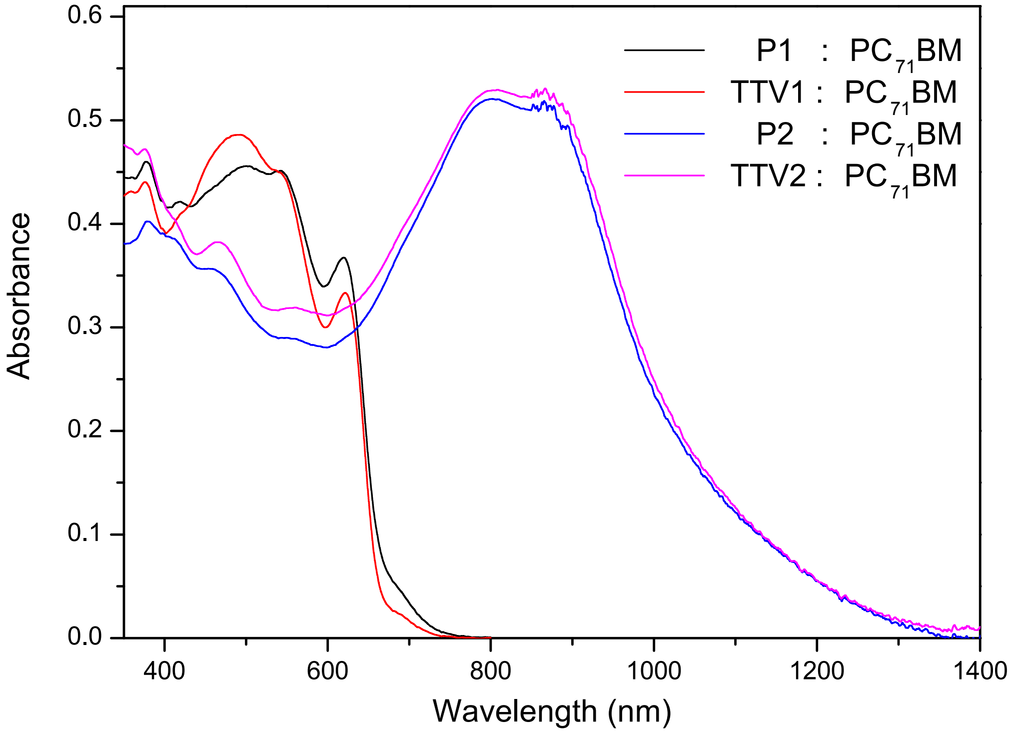


Figure S3 Absorption spectra of the photovoltaic devices based on the four polymers.

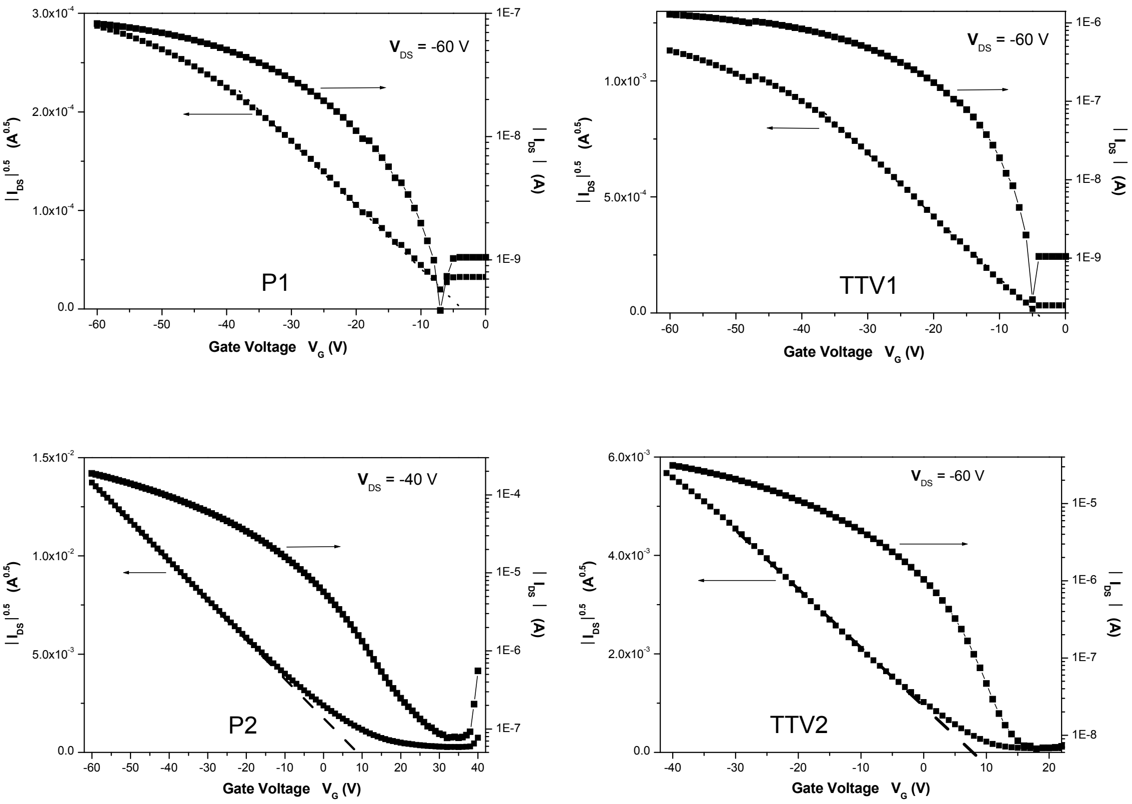


Figure S4 Transfer curves of field-effect transistors based on the four polymers.

Table S2: Field-effect transistor properties of the four polymers.

Polymer	Mobility (cm^2 V^{-1} s^{-1})	On/off ratio	Threshold voltage (V)
P1	4.5×10^{-5}	1×10^2	−4
TTV1	8.3×10^{-4}	1×10^3	−4
P2	4.6×10^{-2}	2×10^3	9
TTV2	1.7×10^{-2}	2×10^3	8

References

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