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Supporting Information

A D-A copolymer donor containing an alkylthio-substituted thieno[3,2-b]thiophene unit

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1. General characterization

^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance-400 spectrometer. Absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Gel permeation chromatography (GPC) was performed on a Waters 1515-2410 series GPC coupled with differential refractive index detector using THF as eluent and polystyrenes as standards. Thermogravimetric analysis was done by using a Perkin Elmer Diamond TG/DTA thermal analyzer under nitrogen. Cyclic voltammetry was done by using a Shanghai Chenhua CHI620D voltammetric analyzer under argon in an anhydrous acetonitrile solution of tetra-n-butylammonium hexafluorophosphate (0.1 M). A glassy-carbon electrode was used as the working electrode, a platinum-wire was used as the counter electrode, and a Ag/Ag^{+} electrode was used as the reference electrode. The polymer was coated onto glassy-carbon electrode and all potentials were corrected against Fc/Fc^{+}. AFM was performed on a Multimode microscope (Veeco) using tapping mode. X-ray diffraction (XRD) of thin films was performed on a Rigaku D/max-2500 X-ray diffractometer in reflection mode by using Cu Kα radiation (40 kV, 200 mA).

2. Synthesis

All reagents were purchased from J&K Co., Aladdin Co., Innochem Co. and other commercial suppliers. All reactions dealing with air- or moisture-sensitive compounds were carried out using standard Schlenk techniques. 3,6-Dimethoxythieno[3,2-b]thiophene[1] and (3,3'-difluoro-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylstannane)[2] were prepared according to literature.

2-Hexyldecane-1-thiol. To a solution of 7-(bromomethyl)pentadecane (1.43 g, 4.68 mmol) in THF (10 mL) were added hexamethyldisilathiane (1 g, 5.6 mmol) and tetrabutylammonium fluoride (44.0 mL, 44.0 mmol, 1.0 M in THF with 5% water) at -10 °C. The reaction mixture was warmed to room temperature and stirred overnight.

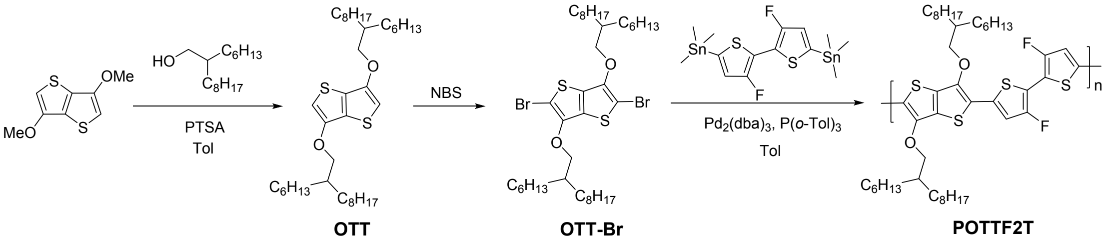
The reaction mixture was diluted with dichloromethane and washed with saturated NH_4Cl. The organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent, the crude product was purified via column chromatography (silica gel) using petroleum ether as eluent to give 2-hexyldecane-1-thiol as a colorless oil (1.05 g, 88%). ^1H NMR ($CDCl_3$, 400 MHz, δ/ppm): 2.53 (d, J = 5.7 Hz, 2H), 1.15-1.48 (m, 26H), 0.88 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 40.10, 32.34, 32.33, 31.92, 31.88, 29.95, 29.61, 29.34, 28.58, 26.62, 26.59, 22.69, 22.68, 14.12, 14.11.

3,6-Bis((2-hexyldecyl)thio)thieno[3,2-b]thiophene (STT). To a solution of 3,6-dimethoxythieno[3,2-b]thiophene (200 mg, 1 mmol) and **2-hexyldecane-1-thiol** (1.3 g, 5.03 mmol) in toluene (20 mL) was added *p*-toluenesulfonic acid (40 mg, 0.20 mmol). The reaction mixture was heated to reflux for 12 h. After removal of the solvent, the crude product was purified via column chromatography (silica gel) using petroleum ether as eluent to give **STT** as a colorless oil (458 mg, 70%). ^1H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.23 (s, 2H), 2.91 (d, J = 5.8 Hz, 4H), 1.58 (m, 2H), 1.24-1.43 (m, 48H), 0.88 (s, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 140.97, 126.26, 125.66, 39.38, 37.84, 32.97, 31.92, 31.85, 29.90, 29.59, 29.57, 29.34, 26.50, 26.47, 22.71, 22.68, 14.15, 14.13. MALDI-TOF MS (m/z): 652.4 (M^+).

2,5-Dibromo-3,6-bis((2-hexyldecyl)thio)thieno[3,2-b]thiophene (STT-Br). To a solution of **STT** (400 mg, 0.61 mmol) in chloroform (5 mL) was added NBS (240 mg, 1.35 mmol) at room temperature. The mixture was stirred for 3h. After removal of the solvent, the crude product was purified via column chromatography (silica gel) using petroleum ether as eluent to give **STT-Br** as a colorless oil (450 mg, 90%). ^1H NMR ($CDCl_3$, 400 MHz, δ/ppm): 2.86 (d, J = 3.8 Hz, 4H), 1.22-1.53 (m, 50H), 0.88 (s, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 139.15, 126.16, 118.71, 39.18, 38.18, 32.81, 31.93, 31.85, 29.88, 29.59, 29.54, 29.34, 26.49, 26.46, 22.72, 22.68, 14.16, 14.14. MALDI-TOF MS (m/z): 810.3 (M^+).

PSTTF2T. To a mixture of **STT-Br** (101.5 mg, 0.125 mmol), (3,3'-difluoro-[2,2'-

bithiophene]-5,5'-diyl)bis(trimethylstannane) (66.1 mg, 0.125 mmol), $Pd_2(dba)_3$ (5.7 mg, 0.006 mmol) and P(*o*-Tol)$_3$ (15.2 mg, 0.049 mmol) in a Schlenk flask was added toluene (3 mL) under argon. The mixture was heated to reflux for 28 h. Then the solution was cooled to room temperature and added into 150 mL methanol dropwise. The precipitate was collected and further purified via Soxhlet extraction using methanol, hexane, chloroform and chlorobenzene in sequence. The chlorobenzene fraction was concentrated and added into methanol dropwise. The precipitate was collected and dried under vacuum overnight to give **PSTTF2T** as a black solid (45 mg, 41%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 7.13 (br, aromatic protons), 2.90 (br, aliphatic protons), 1.68-0.86 (br, aliphatic protons). Elemental analysis (%) calcd for $C_{46}H_{68}F_2S_6$: C, 64.89; H, 8.05. Found: C, 64.43; H, 7.77.



Scheme S1 Synthetic route for **POTTF2T**.

3,6-Bis((2-hexyldecyl)oxy)thieno[3,2-b]thiophene (OTT). To a solution of 3,6-dimethoxythieno[3,2-b]thiophene (200 mg, 1 mmol) and 2-hexyl-1-decanol (1.21 g, 5 mmol) in toluene (20 mL) was added *p*-toluenesulfonic acid (40 mg, 0.20 mmol). The reaction mixture was heated to reflux for 12 h. After removal of the solvent, the crude product was purified via column chromatography (silica gel) using petroleum ether as eluent to give **OTT** as a colorless oil (380 mg, 67%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 6.23 (s, 2H), 3.94 (d, J = 5.7 Hz, 4H), 1.81 (m, 2H), 1.28-1.43 (m, 48H), 0.86-0.89 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 150.41, 128.61, 97.61, 73.53, 37.84, 31.94, 31.88, 31.41, 30.03, 29.70, 29.61, 29.37, 26.88, 26.85, 22.71, 14.14. MALDI-TOF MS (m/z): 619.5 (M - H^+).

2,5-Dibromo-3,6-bis((2-hexyldecyl)oxy)thieno[3,2-b]thiophene (OTT-Br). To a solution of **OTT** (380 mg, 0.67 mmol) in chloroform (5 mL) was added NBS (265 mg, 1.48 mmol) at room temperature. The mixture was stirred for 3h. After removal of the solvent, the crude product was purified via column chromatography (silica gel) using petroleum ether as eluent to give **OTT-Br** as a colorless oil (470 mg, 90%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 4.09 (d, J = 5.5 Hz, 4H), 1.71 (m, 2H), 1.29-1.53 (m, 48H), 0.87-0.90 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ/ppm): 147.79, 126.52, 95.30, 75.41, 38.54, 31.92, 31.85, 31.02, 31.01, 30.00, 29.67, 29.59, 29.35, 26.77, 26.75, 22.71, 22.69, 14.14. MALDI-TOF MS (m/z): 778.4 (M^+).

POTTF2T. To a mixture of **OTT-Br** (102 mg, 0.13 mmol), (3,3'-difluoro-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylstannane) (69.1 mg, 0.13 mmol), $Pd_2(dba)_3$ (6.0 mg, 0.0065 mmol) and P(*o*-Tol)$_3$ (15.9 mg, 0.052 mmol) in a Schlenk flask was added toluene (3 mL) under argon. The mixture was heated to reflux for 28 h. Then the solution was cooled to room temperature and added into 150 mL methanol dropwise. The precipitate was collected and further purified via Soxhlet extraction using methanol, hexane, and chloroform in sequence. The chloroform fraction was concentrated and added into methanol dropwise. The precipitate was collected and dried under vacuum overnight to give **POTTF2T** as a black solid (85 mg, 77%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm): 6.66 (br, aromatic protons), 4.30 (br, aliphatic protons), 1.68-0.88 (br, aliphatic protons). Elemental analysis (%) calcd for $C_{46}H_{68}F_2O_2S_4$: C, 67.44; H, 8.37. Found: C, 66.94; H, 8.32.

3. NMR

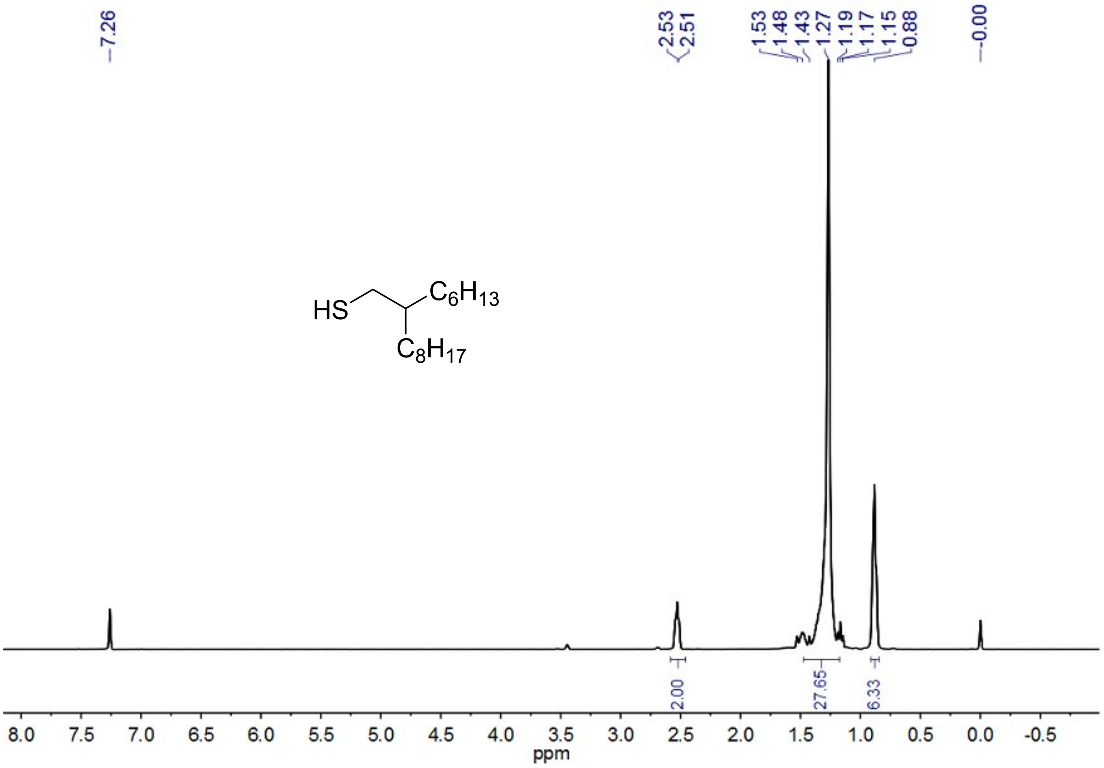


Fig. S1 ^{1}H NMR spectrum of **2-hexyldecane-1-thiol** ($CDCl_3$, 298 K).

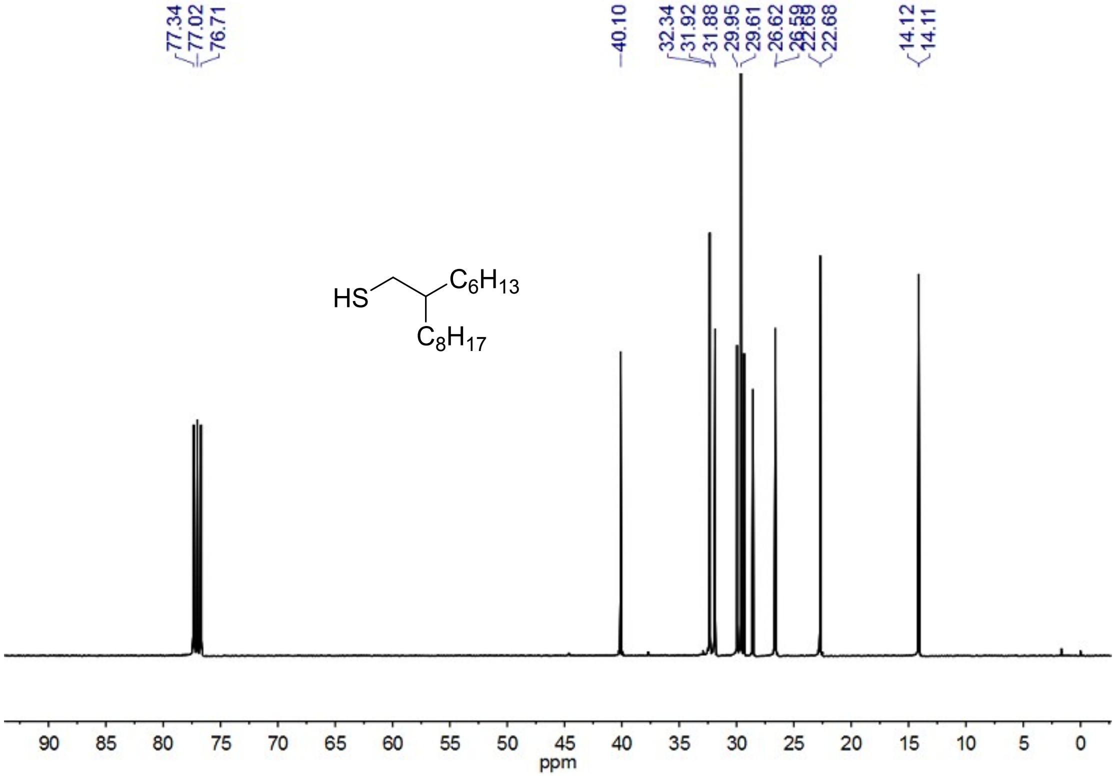


Fig. S2 ^{13}C NMR spectrum of **2-hexyldecane-1-thiol** ($CDCl_3$, 298 K).

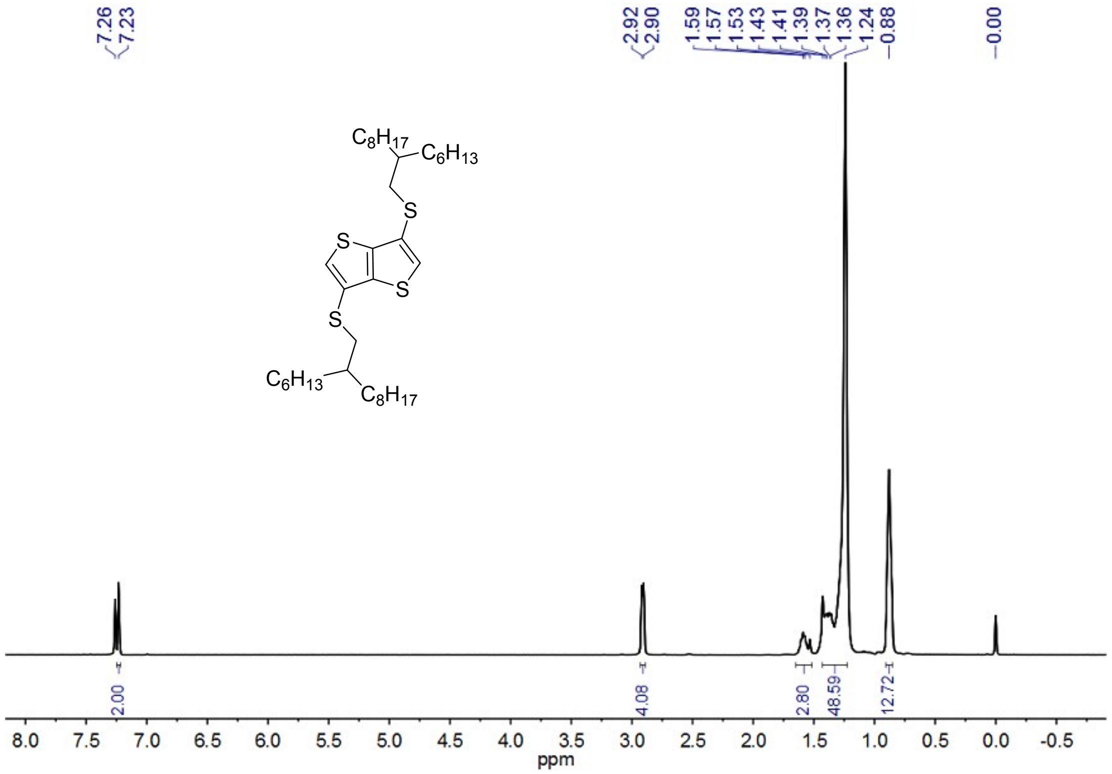


Fig. S3 ^{1}H NMR spectrum of **STT** ($CDCl_3$, 298 K).

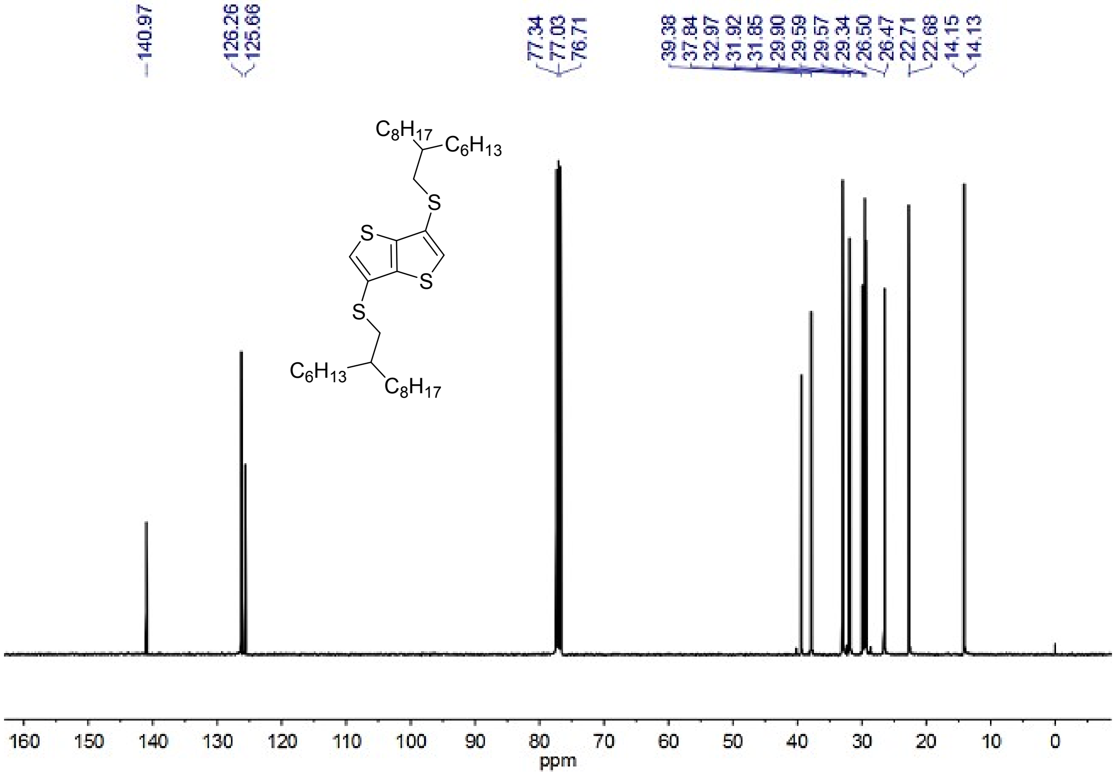


Fig. S4 ^{13}C NMR spectrum of **STT** ($CDCl_3$, 298 K).

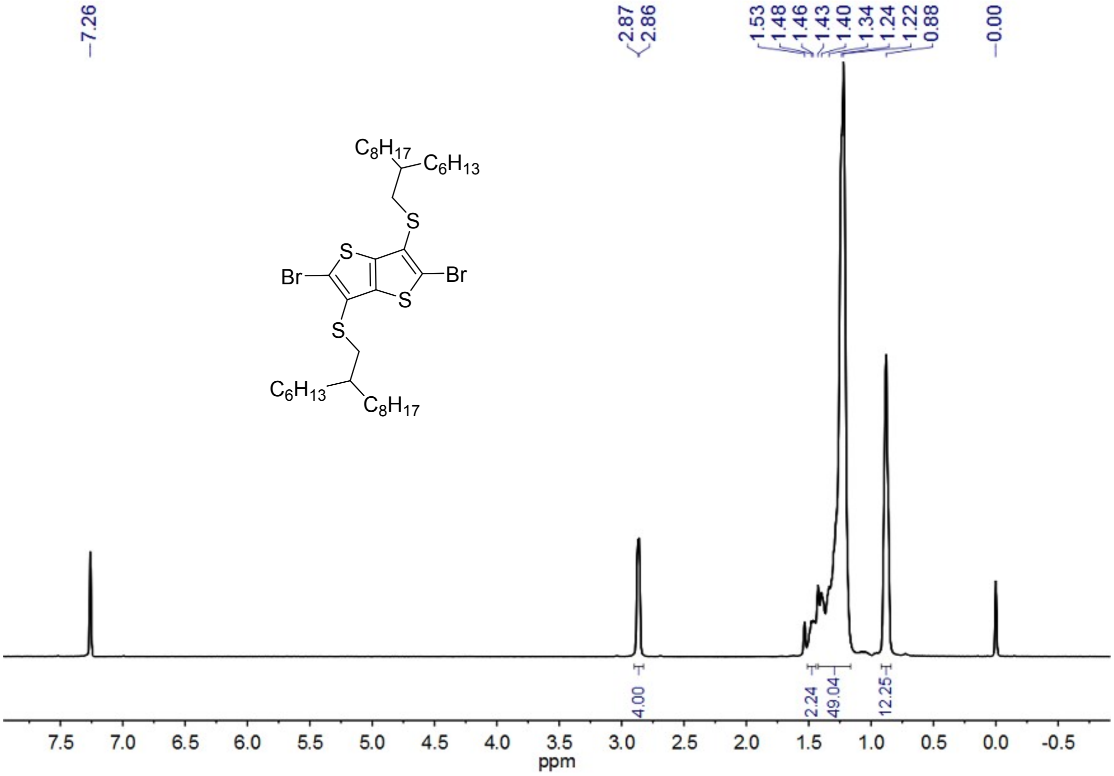


Fig. S5 ^{1}H NMR spectrum of **STT-Br** ($CDCl_3$, 298 K).

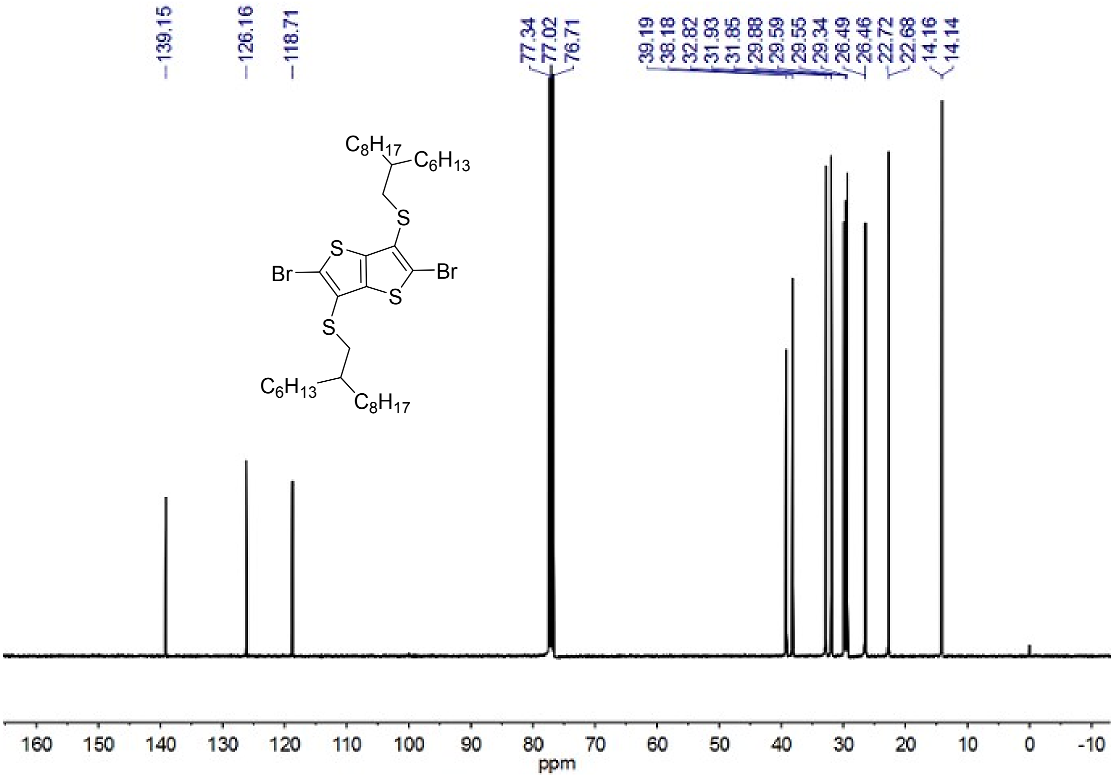


Fig. S6 ^{13}C NMR spectrum of **STT-Br** ($CDCl_3$, 298 K).

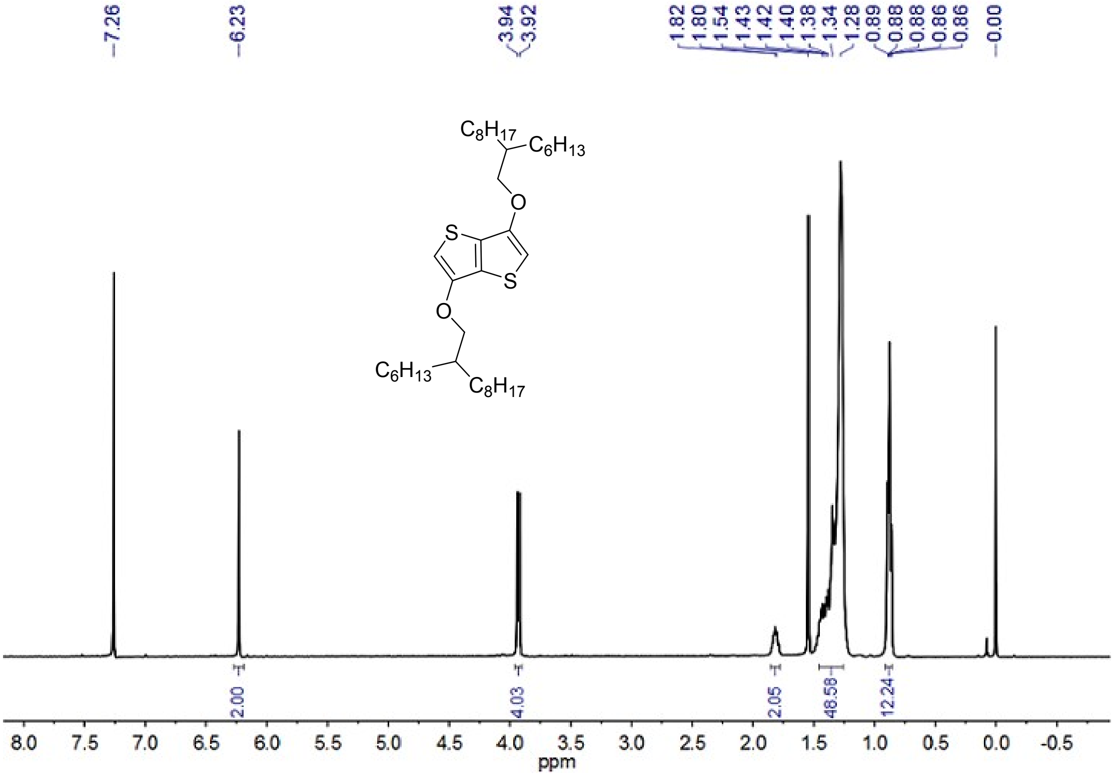


Fig. S7 ^{1}H NMR spectrum of **OTT** ($CDCl_3$, 298 K).

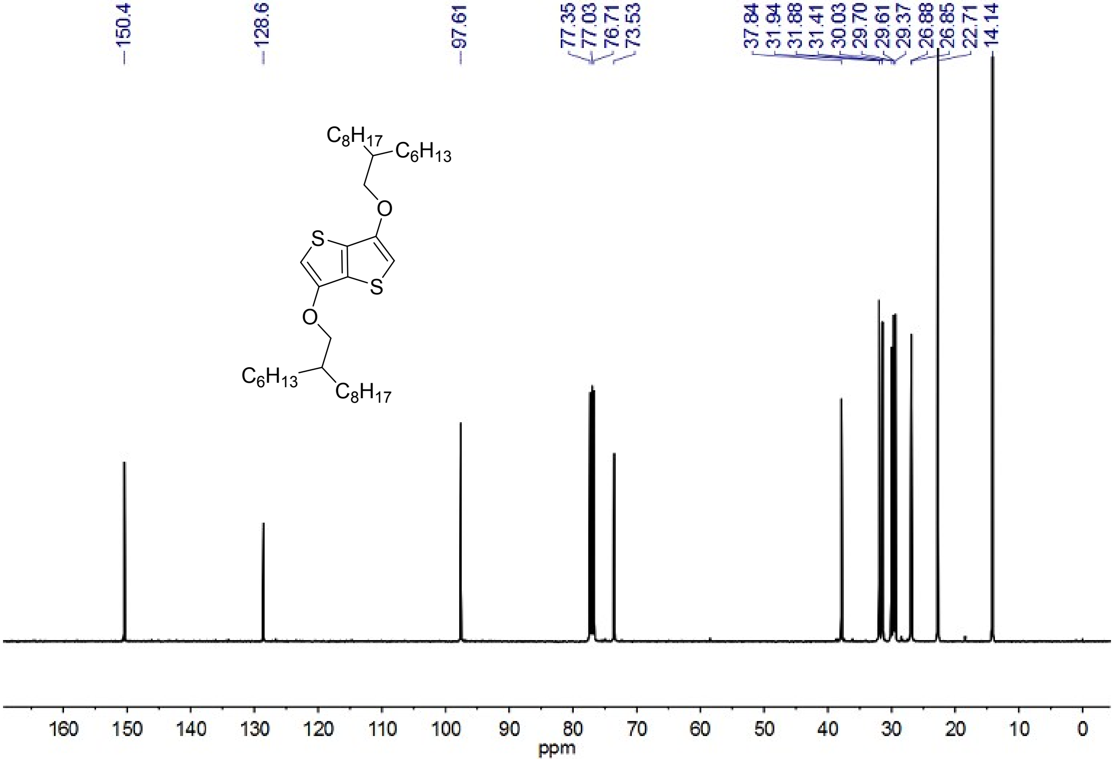


Fig. S8 ^{13}C NMR spectrum of **OTT** ($CDCl_3$, 298 K).

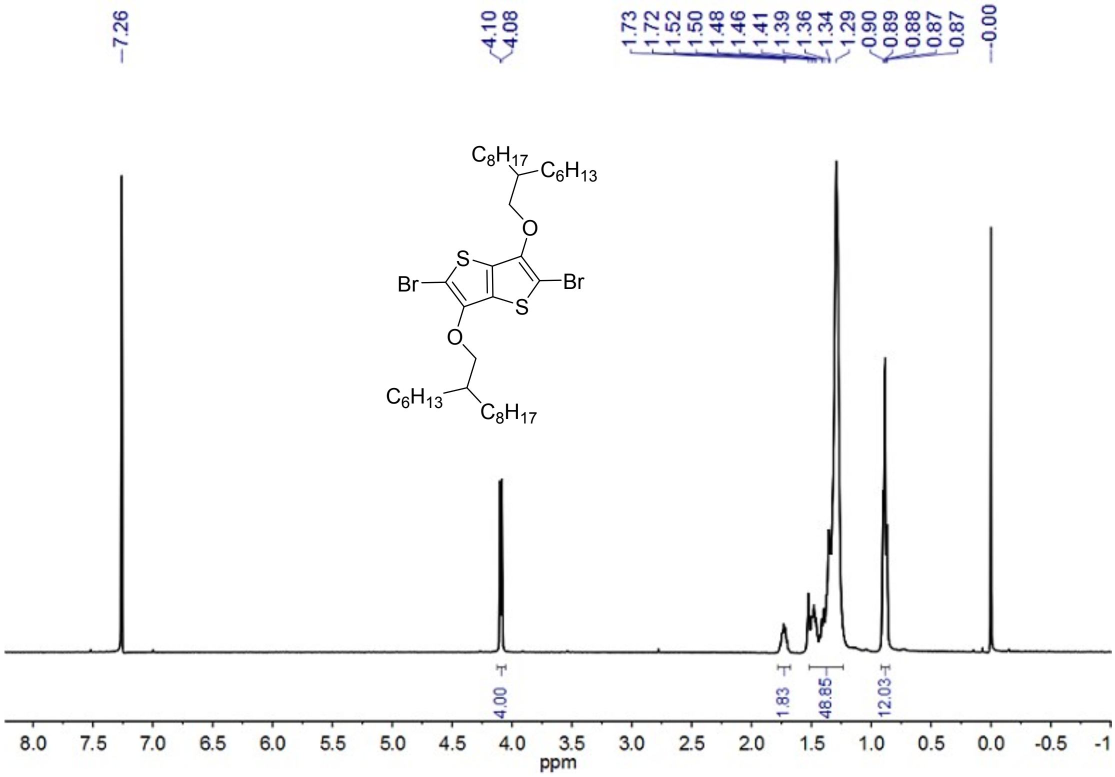


Fig. S9 ^{1}H NMR spectrum of **OTT-Br** ($CDCl_3$, 298 K).

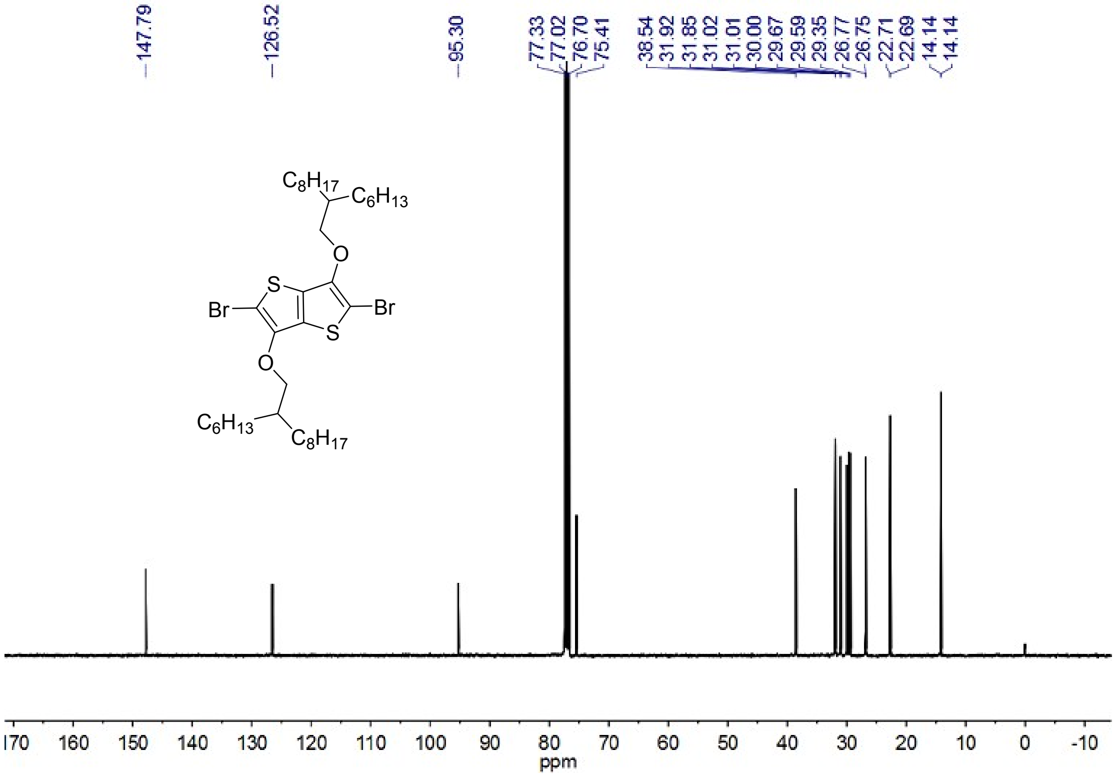


Fig. S10 ^{13}C NMR spectrum of **OTT-Br** ($CDCl_3$, 298 K).

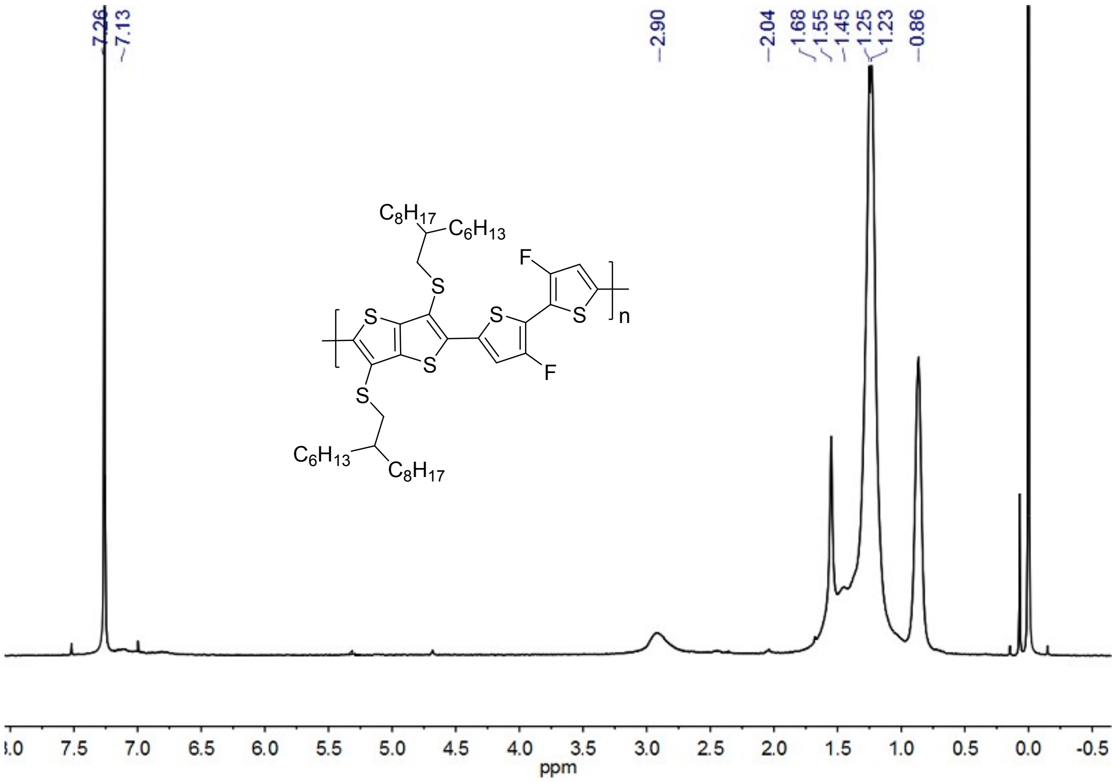


Fig. S11 ^{1}H NMR spectrum of **PSTTF2T** ($CDCl_3$, 298 K).

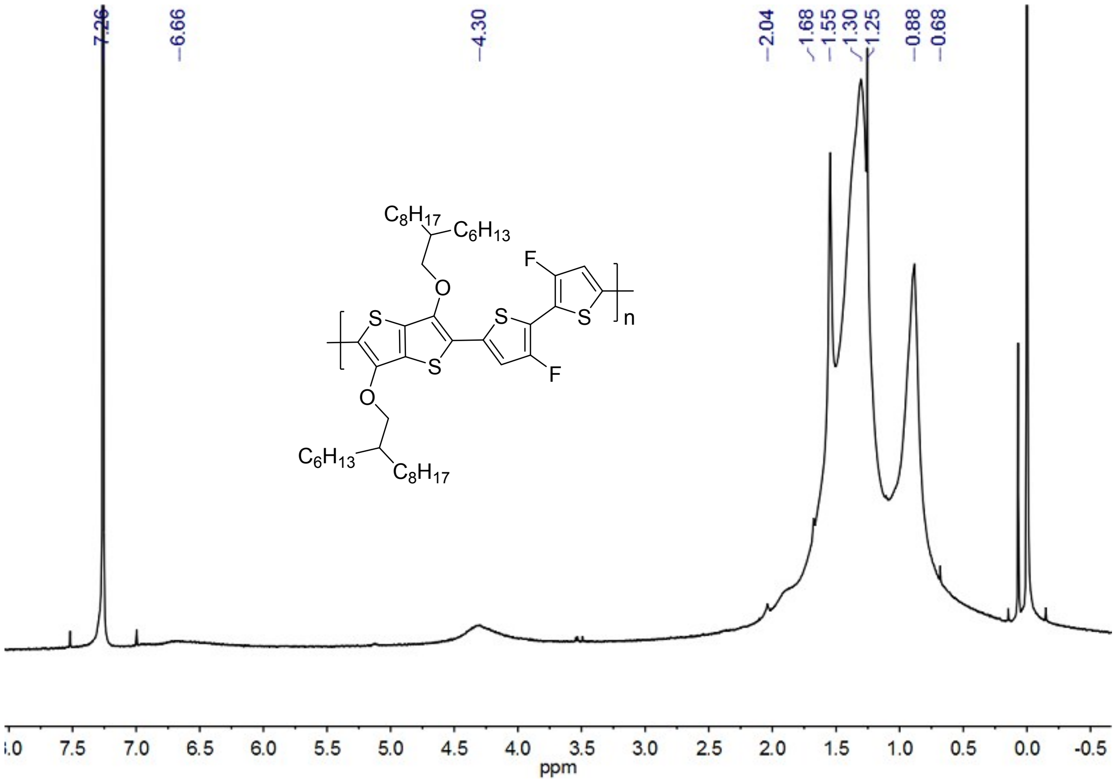
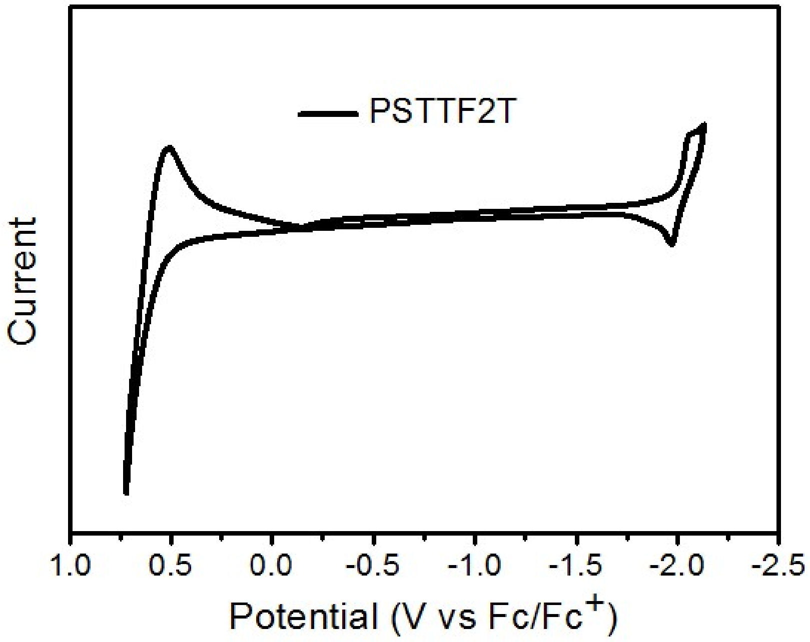


Fig. S12 ^{1}H NMR spectrum of **POTTF2T** ($CDCl_3$, 298 K).

4. CV



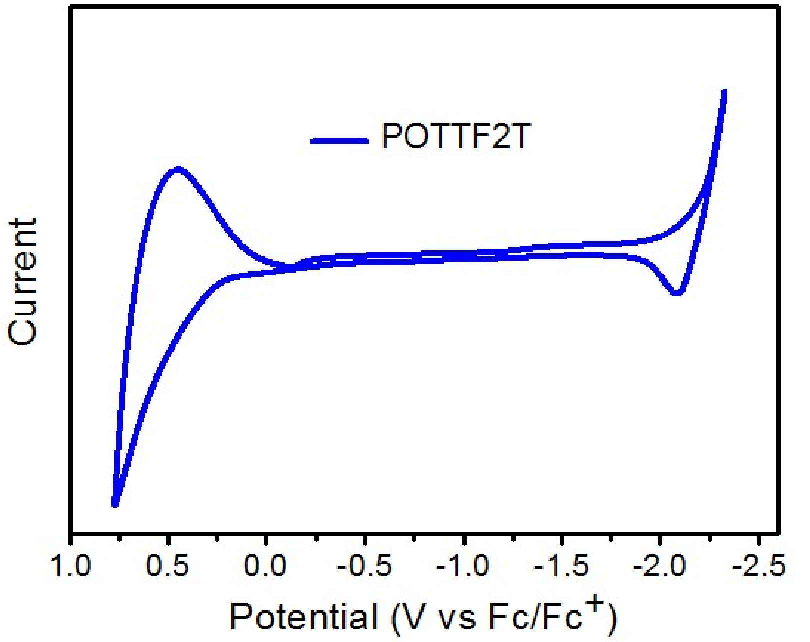


Fig. S13 Cyclic voltammograms for the polymers.

5. XRD

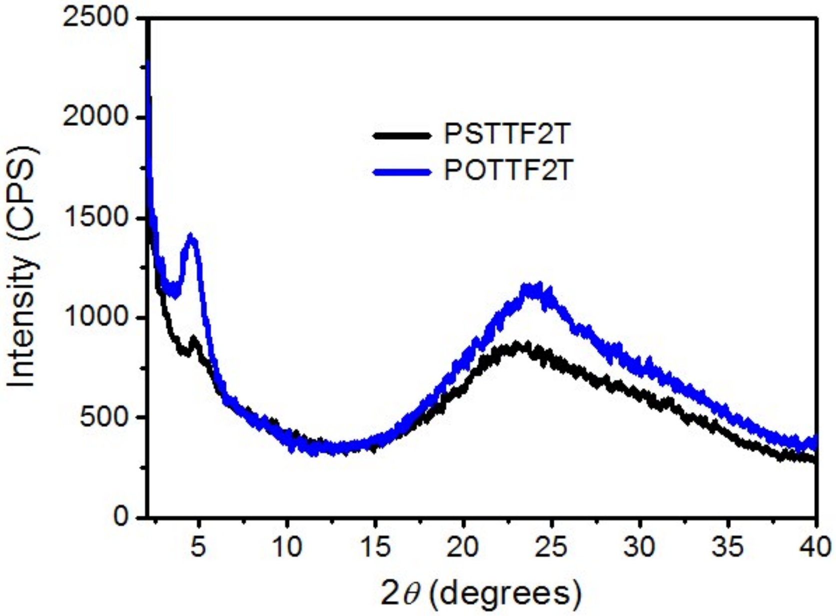


Fig. S14 XRD patterns for PSTTF2T and POTTF2T films.

6. Device fabrication and measurements

Inverted solar cells

The ZnO precursor solution was prepared according to literature.[3] It was spin-coated onto ITO glass (4000 rpm for 30 s). The films were annealed at 200 °C in air for 30 min. ZnO film thickness is ~30 nm. A polymer: acceptor blend in chlorobenzene (CB) with or without DIO additive was spin-coated onto ZnO layer. MoO_3 (~6 nm) and Ag (~80 nm) was successively evaporated onto the active layer through a shadow mask (pressure ca. 10^{-4} Pa). The effective area for the devices is 4 mm^2. The thicknesses of the active layers were measured by using a KLA Tencor D-120 profilometer. *J-V* curves were measured by using a computerized Keithley 2400 SourceMeter and a Xenon-lamp-based solar simulator (Enli Tech, AM 1.5G, 100 mW/cm^2). The illumination intensity of solar simulator was determined by using a monocrystalline silicon solar cell (Enli SRC2020, 2cm×2cm) calibrated by NIM. The external quantum efficiency (EQE) spectra were measured by using a QE-R3011 measurement system (Enli Tech).

Hole-only devices

The structure for hole-only devices is ITO/PEDOT:PSS/active layer/MoO_3/Al. A 30 nm thick PEDOT:PSS layer was made by spin coating an aqueous dispersion onto ITO glass (4000 rpm for 30 s). PEDOT substrates were dried at 150 °C for 10 min. A polymer:acceptor blend in CB with or without DIO additive was spin-coated onto PEDOT layer. Finally, MoO_3 (~6 nm) and Al (~100 nm) was successively evaporated onto the active layer through a shadow mask (pressure ca. 10^{-4} Pa). *J-V* curves were measured by using a computerized Keithley 2400 SourceMeter in the dark.

7. Optimization of device performance

Table S1 Optimization of D/A ratio for PSTTF2T:$PC_{71}BM$ inverted solar cells.[a]

D/A [w/w]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
1:1	0.74	6.28	45.4	2.11 (1.93)[b]
1:1.5	0.75	9.79	59.3	4.38 (4.30)
1:2	0.76	8.97	68.5	4.67 (4.58)
1:2.5	0.76	8.54	72.8	4.73 (4.60)
1:3	0.75	8.70	65.1	4.26 (4.12)

[a] Blend solution: 12 mg/mL in CB with 2 vol% DIO; spin-coating: 1600 rpm for 60 s.

[b] Data in parentheses stand for the average PCEs for 10 cells.

Table S2 Optimization of the active layer thickness for PSTTF2T:$PC_{71}BM$ inverted solar cells.[a]

Thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
165	0.75	10.10	53.3	4.05 (3.91)[b]
142	0.75	9.82	59.0	4.35 (4.29)
129	0.76	9.40	62.3	4.42 (4.32)
116	0.76	8.54	72.8	4.73 (4.60)
105	0.76	8.31	70.2	4.42 (4.32)

[a] D/A ratio: 1:2.5 (w/w); blend solution: 12 mg/mL in CB with 2 vol% DIO.

[b] Data in parentheses stand for the average PCEs for 10 cells.

Table S3 Optimization of DIO content for PSTTF2T:PC$_{71}$BM inverted solar cells.[a]

DIO [vol%]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
0	0.69	1.70	52.5	0.62 (0.54)[b]
1	0.73	7.56	72.9	4.04 (3.57)
2	0.76	8.54	72.8	4.73 (4.60)
3	0.75	8.79	64.4	4.24 (4.02)
4	0.75	8.74	61.5	4.05 (3.99)
5	0.77	8.74	60.1	4.02 (3.94)

[a] D/A ratio: 1:2.5 (w/w); blend solution: 12 mg/mL in CB; spin-coating: 1600 rpm for 60 s.

[b] Data in parentheses stand for the average PCEs for 10 cells.

Table S4 Optimization of D/A ratio for PSTTF2T:ITIC inverted solar cells.[a]

D/A [w/w]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
1:1	0.92	9.29	47.2	4.01 (3.80)[b]
1:1.5	0.92	9.44	54.7	4.75 (4.62)
1:2	0.92	8.44	54.8	4.27 (4.02)

[a] Blend solution: 12 mg/mL in CB; spin-coating: 1600 rpm for 60 s.

[b] Data in parentheses stand for the average PCEs for 10 cells.

Table S5 Optimization of the active layer thickness for PSTTF2T:ITIC inverted solar cells.[a]

Thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
106	0.93	7.29	45.0	3.03 (2.76)[b]
91	0.92	8.83	51.5	4.19 (3.95)
85	0.93	9.67	54.2	4.85 (4.65)
71	0.93	9.80	57.4	5.22 (4.94)
59	0.94	8.28	53.2	4.14 (4.00)

[a] D/A ratio: 1:1.5 (w/w); blend solution: 12 mg/mL in CB.

[b] Data in parentheses stand for the average PCEs for 10 cells.

Table S6 Optimization of DIO content for PSTTF2T:ITIC inverted solar cells.[a]

DIO [vol%]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
0	0.93	9.80	57.4	5.22 (4.94)[b]
0.5	0.95	8.15	47.6	3.69 (3.26)
2	0.80	2.36	35.8	0.68 (0.64)

[a] D/A ratio: 1:1.5 (w/w); blend solution: 12 mg/mL in CB; spin-coating: 2000 rpm for 60 s.

[b] Data in parentheses stand for the average PCEs for 10 cells.

Table S7 Optimization of D/A ratio for POTTF2T:$PC_{71}BM$ inverted solar cells.[a]

D/A [w/w]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
1:1	0.43	5.41	56.4	1.33 (1.28)[b]
1:1.2	0.43	6.76	57.7	1.70 (1.65)
1:1.4	0.43	7.36	58.3	1.85 (1.79)
1:1.6	0.43	8.22	54.8	1.96 (1.86)
1:1.8	0.44	8.52	55.5	2.06 (1.95)
1:2	0.43	8.52	53.3	1.95 (1.84)

[a] Blend solution: 18 mg/mL in CB with 2 vol% DIO; spin-coating: 1200 rpm for 60 s.

[b] Data in parentheses stand for the average PCEs for 10 cells.

Table S8 Optimization of the active layer thickness for POTTF2T:$PC_{71}BM$ inverted solar cells.[a]

Thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
157	0.42	7.30	47.8	1.45 (1.25)[b]
135	0.42	8.09	51.8	1.77 (1.62)
121	0.43	8.34	54.2	1.92 (1.81)
103	0.43	8.78	55.8	2.09 (2.00)
96	0.43	8.74	55.1	2.08 (1.99)
83	0.43	8.53	55.7	2.06 (1.88)

[a] D/A ratio: 1:1.8 (w/w); blend solution: 18 mg/mL in CB with 2 vol% DIO.

[b] Data in parentheses stand for the average PCEs for 10 cells.

Table S9 Optimization of DIO content for POTTF2T:PC$_{71}$BM inverted solar cells.[a]

DIO [vol%]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
0	0.43	1.49	44.0	0.28 (0.27)[b]
1	0.44	6.93	59.3	1.82 (1.76)
2	0.44	8.31	59.1	2.15 (2.03)
3	0.45	8.05	58.3	2.10 (1.92)
4	0.45	7.58	58.6	2.02 (1.95)

[a] D/A ratio: 1:1.8 (w/w); blend solution: 18 mg/mL in CB; spin-coating: 1400 rpm for 60 s.

[b] Data in parentheses stand for the average PCEs for 10 cells.

Table S10 Optimization of D/A ratio for POTTF2T:ITIC inverted solar cells.[a]

D/A [w/w]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
1:1	0.60	6.04	43.1	1.56 (1.53)[b]
1:1.5	0.59	6.50	43.5	1.67 (1.63)
1:2	0.61	5.87	44.4	1.58 (1.41)

[a] Blend solution: 12 mg/mL in CB; spin-coating: 2000 rpm for 60 s.

[b] Data in parentheses stand for the average PCEs for 10 cells.

Table S11 Optimization of the active layer thickness for POTTF2T:ITIC inverted solar cells.[a]

Thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
63	0.59	6.91	42.4	1.73 (1.67)[b]
58	0.60	6.78	45.6	1.85 (1.80)
51	0.60	6.84	43.8	1.79 (1.70)
44	0.59	6.50	43.5	1.67 (1.63)
37	0.60	6.49	41.2	1.61 (1.59)

[a] D/A ratio: 1:1.5 (w/w); blend solution: 12 mg/mL in CB.

[b] Data in parentheses stand for the average PCEs for 10 cells.

Table S12 Optimization of DIO content for POTTF2T:ITIC inverted solar cells.[a]

DIO [vol%]	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
0	0.60	6.78	45.6	1.85 (1.80)[b]
0.5	0.62	5.02	42.6	1.33 (1.26)
1	0.45	2.45	44.9	0.50 (0.47)
2	0.35	0.97	43.4	0.15 (0.14)

[a] D/A ratio: 1:1.5 (w/w); blend solution: 12 mg/mL in CB; spin-coating: 1600 rpm for 60 s.

[b] Data in parentheses stand for the average PCEs for 10 cells.

8. SCLC

Charge carrier mobility was measured by SCLC method. The mobility was determined by fitting the dark current to the model of a single carrier SCLC, which is described by:

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu\frac{V^2}{d^3}$$

where J is the current density, μ is the zero-field mobility of holes (μ_h), ε_0 is the permittivity of the vacuum, ε_r is the relative permittivity of the material, d is the thickness of the blend film, and V is the effective voltage, $V = V_{appl} - V_{bi}$, where V_{appl} is the applied voltage, and V_{bi} is the built-in potential determined by electrode work function difference (here, $V_{bi} = 0.1$ V[4]). The mobility was calculated from the slope of $J^{1/2}$-V plots.

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