

Supplementary Information

Small Band Gap Polymers Incorporating a Strong Acceptor, Thieno[3,2-*b*]thiophene-2,5-dione, with P-Channel and Ambipolar Charge Transport Characteristics

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Synthesis.

3,6-Dibromothieno[3,2-*b*]thiophene (**1**),^{S1} 3-alkyl-2-trimethylsilyl-5-trimethylstannylthiophene (**2**),^{S2} 2-trimethylstannylthiophene (**10**),^{S3} 5,5'-Bis(trimethylstannyl)-2,2'-bithiophene (**11**),^{S4} can be synthesized according to the reported procedure, respectively. All chemicals and solvents are of reagent grade unless otherwise indicated. THF and DMF were purified by a Glass Contour Solvent System, and cyclohexane and toluene were distilled with CaH₂ prior to use. Polymerization was carried out with a microwave reactor, Biotage Initiator. Nuclear magnetic resonance (NMR) spectra were obtained in deuterated chloroform and *o*-dichlorobenzene (for polymers) with TMS as internal reference. High-resolution mass spectrometry was carried out with a LTQ Orbitrap XL (Thermo Fisher Scientific). Molecular weights were determined by gel permeation chromatography (GPC) with a TOSOH HLC-8121GPC/HT at 140 °C using *o*-dichlorobenzene (DCB) as a solvent and calibrated with polystyrene standards.

*3,6-Bis(4-(2-octyldodecyl)-5-(trimethylsilyl)thiophen-2-yl)thieno[3,2-*b*]thiophene (3)*

A mixture of 3,6-dibromothieno[3,2-*b*]thiophene **1** (1.2 g, 4.0 mmol), 3-(2-octyldodecyl)-2-trimethylsilyl-5-trimethylstannylthiophene **2** (6.8 g, 8.0 mmol), tetrakis(triphenylphosphine)palladium (0) (240 mg, 0.2 mmol) in 20 mL of anhydrous DMF were stirred at 90 °C under N₂ atmosphere for 5 h. After cooling to room temperature, x00 mL of saturated KF solution and 100 mL of chloroform were added. The organic layer was washed twice with 100 mL of brine and dried over magnesium sulfate. After removing the solvent, the residue was purified by column chromatography on silica-gel eluted with hexane/CH₂Cl₂ (= 9) to give **3** (4.0 g, quant.) as yellow solid.

¹H-NMR(CDCl₃, 500 MHz): δ (ppm) 7.51 (s, 2 H), 7.30 (s, 2 H), 2.61 (d, 4H, *J* = 7.30), 1.71 (m, 2H), 1.26 (m, 64H), 0.87(m, 12H), 0.38 (m, 18 H). ¹³C-NMR(CDCl₃, 500 MHz): δ (ppm) 150.60, 140.47, 137.44, 133.11, 128.71, 127.66, 121.49, 39.39~0.66. HRMS: Calcd for C₆₀H₁₀₄S₄Si₂

$[M+H]^+$: 1009.66322. Found: 1009.66138.

3,6-Bis(4-(2-decyltetradecyl)-5-(trimethylsilyl)thiophen-2-yl)thieno[3,2-b]thiophene (4)

The same procedure as **3** was performed to yield **4** as yellow solid (6.2 mg, quant).

$^1\text{H-NMR}(\text{CDCl}_3, 500 \text{ MHz})$: δ (ppm) 7.51 (s, 2 H), 7.30 (s, 2 H), 2.61 (d, 4H, $J = 7.30$), 1.71 (m, 2H), 1.26 (m, 80H), 0.87(m, 12H), 0.38 (m, 18 H). $^{13}\text{C-NMR}(\text{CDCl}_3, 500 \text{ MHz})$: δ (ppm) 150.42,

140.58, 137.53, 133.20, 128.80, 127.75, 121.58, 39.48~0.77. HRMS: Calcd for $\text{C}_{68}\text{H}_{120}\text{S}_4\text{Si}_2$

$[M+H]^+$: 1121.78842. Found: 1121.78564.

(5,5'-(2,5-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thieno[3,2-b]thiophene-3,6-diyl)bis(3-(2-octyldodecyl)thiophene-5,2-diyl))bis(trimethylsilane) (5)

To a mixture of **3** (4.0 g, 3.9 mmol), bis(pinacolato)diboron (2.2 g, 8.6 mmol), 4,4'-di-*tert*-butyl-2,2'-bipyridine (209 mg, 0.78 mmol), and $[\text{Ir}(\text{OMe})(\text{COD})]_2$ (258 mg, 0.39 mmol) under N_2 was added dry cyclohexane (10 mL). The resulting mixture was stirred under reflux for 15 h in the dark. After cooling to room temperature and evaporation of cyclohexane, 30 mL of water and 50 mL of chloroform were added. The organic layer was washed twice with 50 mL of brine and dried over magnesium sulfate. After removing the solvent, the residue was purified by column chromatography on silica-gel eluted with hexane to give **5** (4.2 g, ca. 80%) as brown oil, which was used for the next reaction without further purification.

$^1\text{H-NMR}(\text{CDCl}_3, 500 \text{ MHz})$: δ (ppm) 7.62 (s, 2 H), 2.60 (d, 4H, $J = 9.05$), 1.36 (s, 24H), 1.71 (m, 2H), 1.25 (m, 64H), 0.87(m, 12H), 0.38 (m, 18 H). $^{13}\text{C-NMR}(\text{CDCl}_3, 500 \text{ MHz})$: δ (ppm) 149.76,

145.66, 140.49, 135.69, 133.96, 131.58, 84.41, 39.66~0.90. HRMS: Calcd for $\text{C}_{72}\text{H}_{126}\text{B}_2\text{O}_4\text{S}_4\text{Si}_2$

$[M+\text{Na}]^+$: 1283.81558. Found: 1283.81360

(5,5'-(2,5-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thieno[3,2-b]thiophene-3,6-diyl)bis(3-(2-decyltetradecyl)thiophene-5,2-diyl))bis(trimethylsilane) (6)

The same procedure as **5** was performed to yield **6** as brown oil (5.5 g, ca. 80%), which was used for the next reaction without further purification.

$^1\text{H-NMR}$ (CDCl_3 , 500 MHz): δ (ppm) 7.62 (s, 2 H), 2.60 (d, 4H, $J = 9.05$), 1.76 (m, 2H), 1.36 (s, 24H), 1.24 (m, 80H), 0.87(m, 12H), 0.38 (m, 18 H). $^{13}\text{C-NMR}$ (CDCl_3 , 500 MHz): δ (ppm) 149.78, 145.65, 140.48, 135.69, 133.97, 131.58, 84.43, 39.66~0.90. HRMS: Calcd for $\text{C}_{80}\text{H}_{142}\text{B}_2\text{O}_4\text{S}_4\text{Si}_2$ $[\text{M}+\text{Na}]^+$: 1395.94078. Found: 1395.93872.

3,6-Bis(4-(2-octyldodecyl)-5-(trimethylsilyl)thiophen-2-yl)thieno[3,2-b]thiophene-2,5-dione
(TTD2T)

To a mixture of **5** (0.94 g, 0.75 mmol) and Oxone[®] (3.7 mg, 0.58 mmol) under N_2 were added THF (40 mL), acetone (16 mL), and H_2O (8 mL). The resulting mixture was stirred at room temperature for 3 h in the dark and then quenched with aq. $\text{Na}_2\text{S}_2\text{O}_4$. After evaporation of solvents, the residue was partitioned between ethylacetate and H_2O . The organic layer was washed with H_2O and brine and dried over magnesium sulfate. After evaporation of solvent, the residue was subjected to column chromatography on silica gel eluted with hexane/dichloromethane (= 1) to give **TTD2T** (0.16 g) as red solid. Note that TTD2T was obtained as a mixture with the TMS-eliminated compound (TTD2T with X = H), and was directly subjected to the dibromination reaction without further purification. **TTD2T** used for the cyclic voltammetry was isolated by column chromatography (yield = 20%) prior to the measurement.

$^1\text{H-NMR}$ (CDCl_3 , 500 MHz): δ (ppm) 7.68 (s, 2 H), 2.60 (d, 4H, $J = 7.5$), 1.70 (m, 2H), 1.24 (m, 64H), 0.87(m, 12H), 0.38 (s, 18 H). $^{13}\text{C-NMR}$ (CDCl_3 , 500 MHz): δ (ppm) 187.04, 150.39, 146.75, 141.05, 134.72, 132.86, 126.00, 38.85. HRMS: Calcd for $\text{C}_{60}\text{H}_{102}\text{O}_2\text{S}_4\text{Si}_2$ $[\text{M}+\text{H}]^+$: 1039.6379. Found: 1039.6382.

3,6-Bis(4-(2-decyltetradecyl)-5-(trimethylsilyl)thiophen-2-yl)thieno[3,2-b]thiophene-2,5-dione (7)

The same procedure as **TTD2T** was performed using **6** to yield **7** as red solid (178 mg). This compound was obtained as a mixture with the TMS-eliminated compound, and was directly subjected to the dibromination reaction that yields **9** (R = DT) without further purification.

3,6-Bis(5-bromo-4-(2-octyldodecyl)thiophen-2-yl)thieno[3,2-b]thiophene-2,5-dione (8)

N-bromosuccinimide (NBS) (84 mg, 0.48 mmol) was added to a solution of **TTD2T** (180 mg, 0.172 mmol) in THF (13 mL). After the mixture was stirred overnight at room temperature, 20 mL of saturated sodium bicarbonate solution was added. The resulting mixture was extracted with dichloromethane, and washed with brine, and dried over anhydrous magnesium sulfate. The solution was concentrated in vacuo and the residue was purified by column chromatography on silica-gel eluted with hexane to give **8** (156 mg, 86%) as red solid.

¹H-NMR(CDCl₃, 500 MHz): δ (ppm) 7.34 (s, 2 H), 2.52 (d, 4H, *J* = 7.35), 1.66 (m, 2H), 1.25 (m, 64H), 0.87 (m, 12H). ¹³C-NMR(CDCl₃, 500 MHz): δ (ppm) 187.01, 146.75, 143.15, 131.81, 131.33, 125.95, 118.01, 38.62~14.29. HRMS: Calcd for C₅₄H₈₄O₂Br₂S₄ [M-H]⁻: 1049.36372. Found: 1049.36304.

3,6-Bis(5-bromo-4-(2-decyltetradecyl)thiophen-2-yl)thieno[3,2-b]thiophene-2,5-dione (9)

The same procedure as **8** was performed to yield **9** as red solid starting from **7** (160 mg, 18% in two steps from **6**).

¹H-NMR(CDCl₃, 500 MHz): δ (ppm) 7.33 (s, 2 H), 2.52 (d, 4H, *J* = 7.35), 1.66 (m, 2H), 1.25 (m, 64H), 0.88 (m, 12H). ¹³C-NMR(CDCl₃, 500 MHz): δ (ppm) 187.05, 146.79, 143.15, 131.82, 131.33, 125.99, 117.97, 38.61~14.29. HRMS: Calcd for C₆₂H₁₀₀O₂Br₂S₄ [M-H]⁻: 1161.48892. Found: 1161.48962.

3,6-Bis(3-(2-octyldodecyl)-[2,2'-bithiophen]-5-yl)thieno[3,2-b]thiophene-2,5-dione (TTD4T)

To a 10-20 mL microwave pressurized vial equipped with a stirring bar, **8** (25 mg, 0.0237 mmol),

2-trimethylstannylthiophene, **10** (15 mg, 0.0593 mmol), Pd(PPh₃)₄ (0.7 mg), toluene (1 ml) were added. Then the tube was sealed and refilled with argon. The reaction tube was put into a microwave reactor and heated to 180 °C for 1 hour. The reaction solution was added to saturated KF solution and extracted with dichloromethane. The organic layer was washed twice with 10 mL of brine and dried over magnesium sulfate. After removing the solvent, the residue was purified by column chromatography on silica-gel eluted with hexane/CH₂Cl₂ to give **TTD4T** (19 mg, 68%).

¹H-NMR (CDCl₃, 500 MHz): δ (ppm) 7.57 (s, 2 H), 7.39 (dd, 2H, *J* = 1.15, 5.10), 7.24 (dd, 2H, *J* = 1.15, 3.50), 7.10 (dd, 2H, *J* = 3.50, 5.10), 2.73 (d, 4H, *J* = 7.25), 1.71 (m, 2H), 1.25 (m, 64H), 0.87 (m, 12H). ¹³C-NMR (CDCl₃, 500 MHz): 187.39, 146.30, 140.35, 137.87, 135.22, 134.06, 129.67, 127.78, 127.32, 126.84, 126.11, 38.85~14.31. HRMS: Calcd for C₆₂H₉₀O₂S₆ [M+H]⁺: 1059.5343. Found: 1059.5350.

PTTD4T-OD

To a microwave pressurized vial equipped with a stirring bar, **8** (R = OD; 170 mg, 0.30 mmol), **11** (306 mg, 0.30 mmol), Pd(PPh₃)₄ (8.6 mg, 0.075 mmol), toluene (15 ml) were added. Then the tube was sealed and refilled with argon. The reaction tube was put into a microwave reactor and heated to 180 °C for 1 hour. After cooling to room temperature, the reaction solution was poured into 200mL of methanol containing 5 mL of hydrochloric acid, and stirred for 5 hours. Then the precipitated solid was subjected to sequential Soxhlet extraction with methanol, hexane, and chloroform to remove low molecular weight fractions. The residue was extracted with chlorobenzene, and reprecipitated in 200 mL of methanol to yield dark purple solid (323 mg, 98 %, *M_n* = 34200, *M_w* = 62300, PDI = 1.82).

¹H-NMR(*o*-dichlorobenzene-d₄, 500 MHz): δ (ppm) 7.94 (s, 2 H), 3.10 (d, 4H, *J* = 7.35), 2.12 (m, 2H), 1.49 (m, 64H), 1.08 (m, 12H). Two protons at the β-positions of the unsubstituted thiophene

may be obscured by 1,2-dichlorobenzene signals. Anal. Calcd for $C_{62}H_{90}O_2S_6$: C, 70.27; H, 8.56.

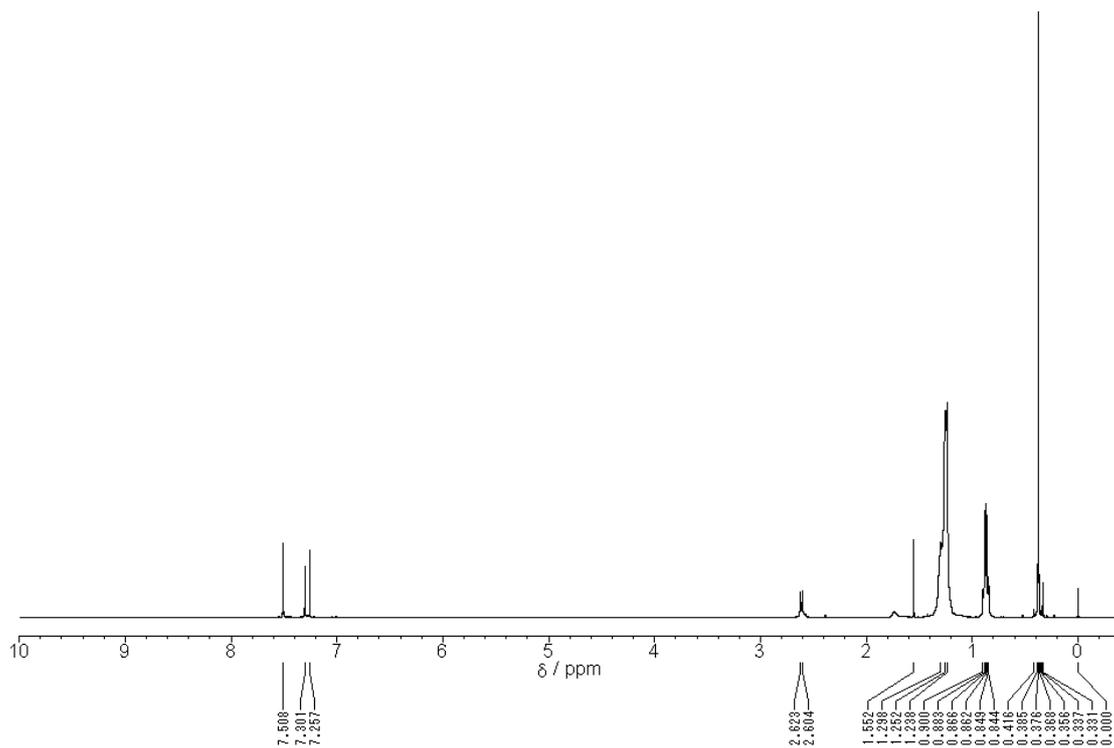
Found: C, 70.05; H, 8.39.

PTTD4T-DT

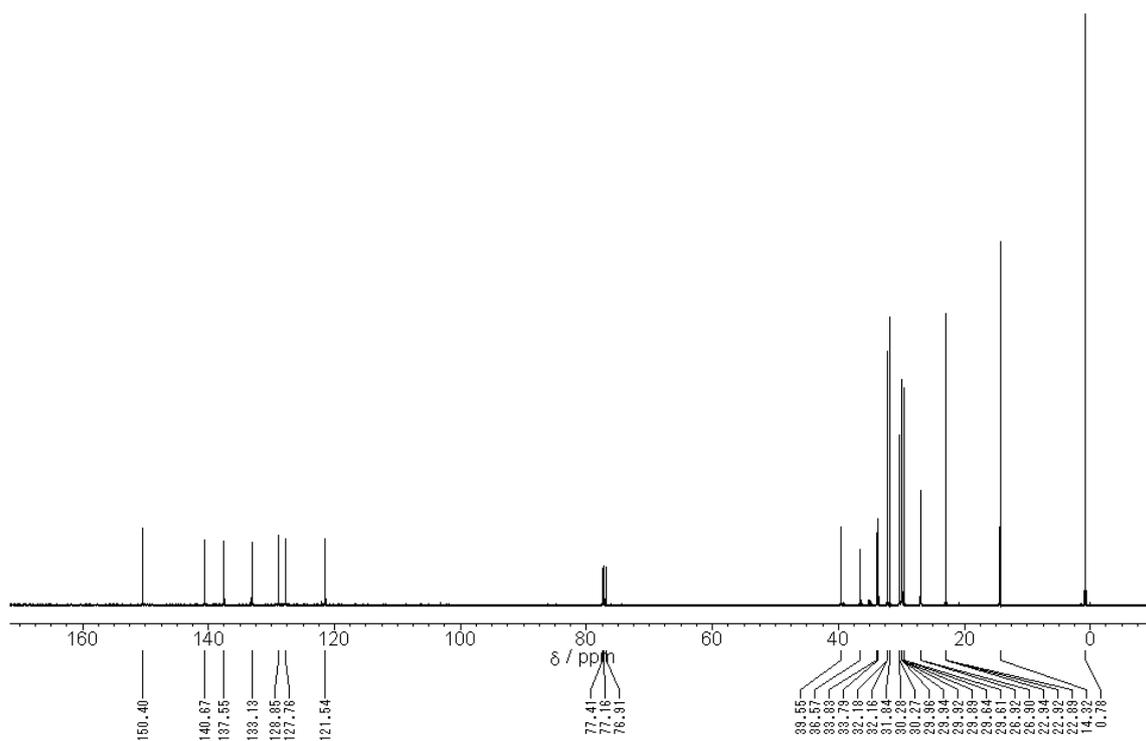
The same procedure as **PTTD4T-OD** was performed using **9** and **11** to yield **PTTD4T-DT** as dark purple solid (98 mg, 85%, $M_n = 33000$, $M_w = 59000$, PDI = 1.79).

1H -NMR(*d o*-dichlorobenzene- d_4 , 500 MHz): δ (ppm) 7.92 (s, 2 H), 3.09 (d, 4H, $J = 7.35$), 2.10 (m, 2H), 1.47 (m, 64H), 1.06 (m, 12H). Two protons at the β -positions of the unsubstituted thiophene may be obscured by 1,2-dichlorobenzene signals. Anal. Calcd for $C_{70}H_{106}O_2S_6$: C, 71.74; H, 9.12.

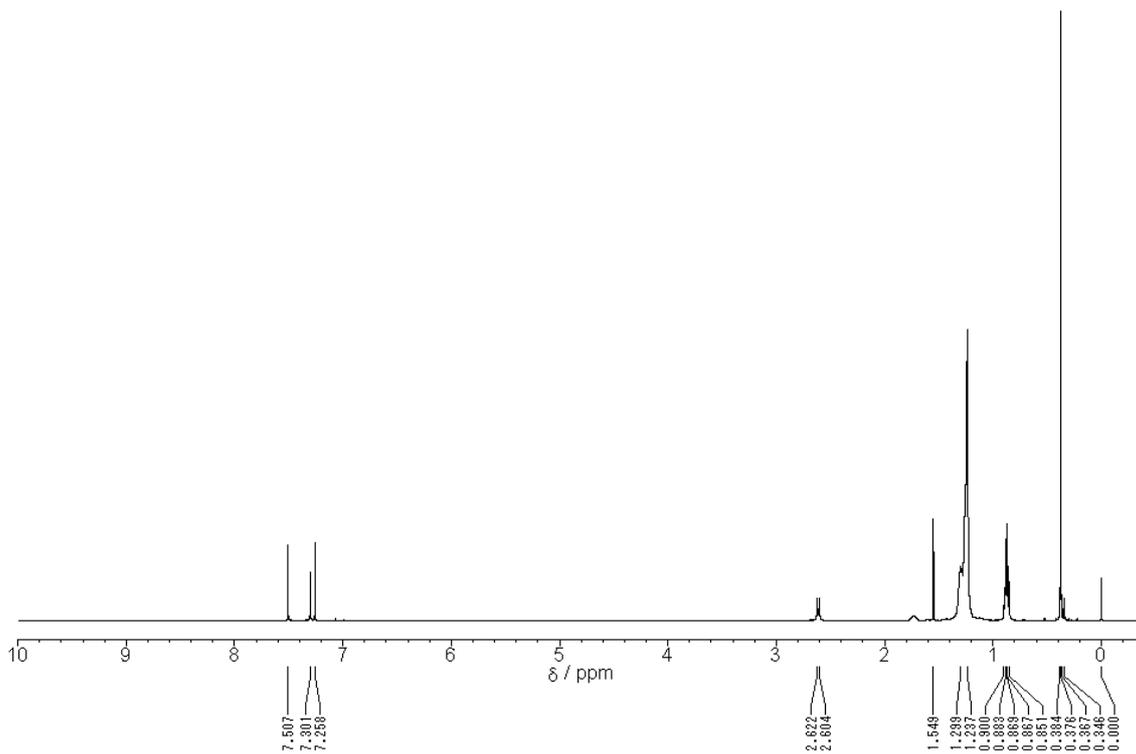
Found: C, 71.34; H, 8.88.



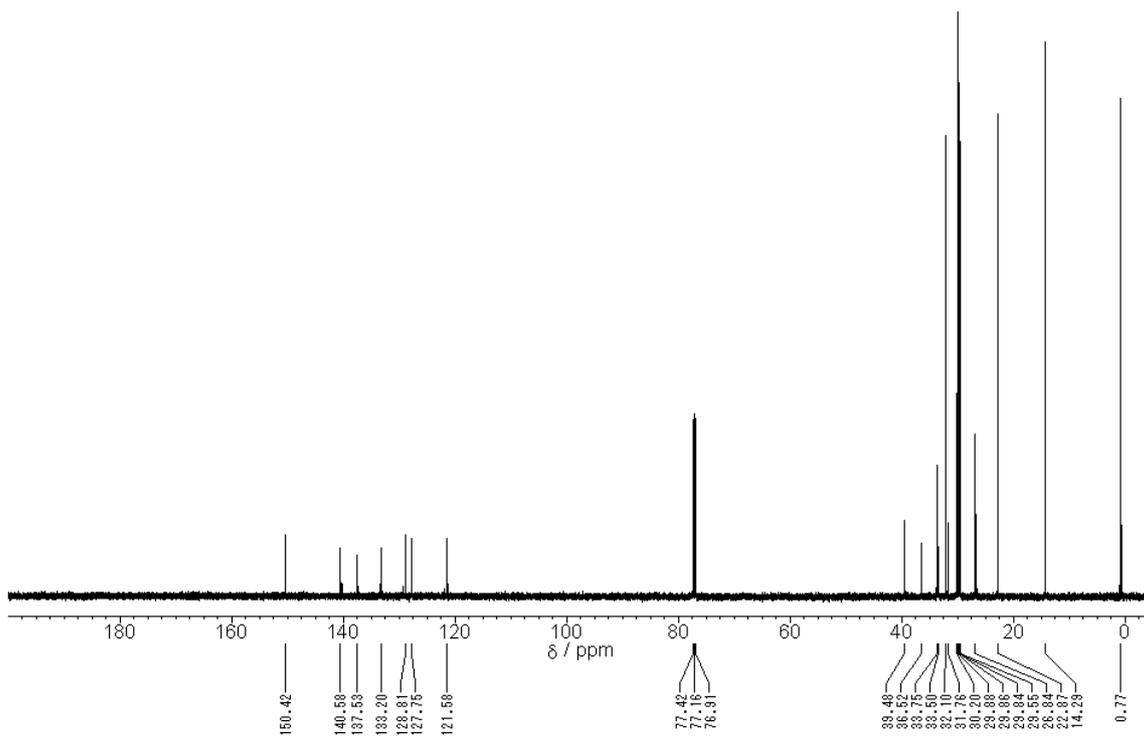
$^1\text{H-NMR}$ spectrum of **3**



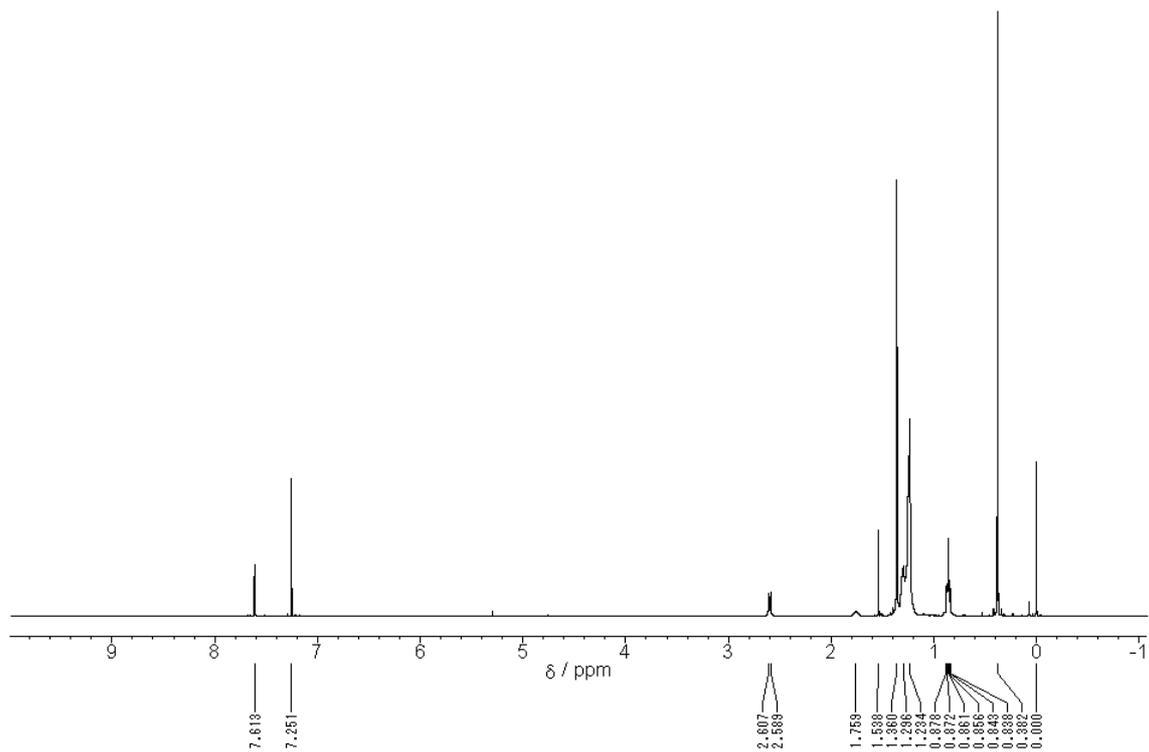
$^{13}\text{C-NMR}$ spectrum of **3**



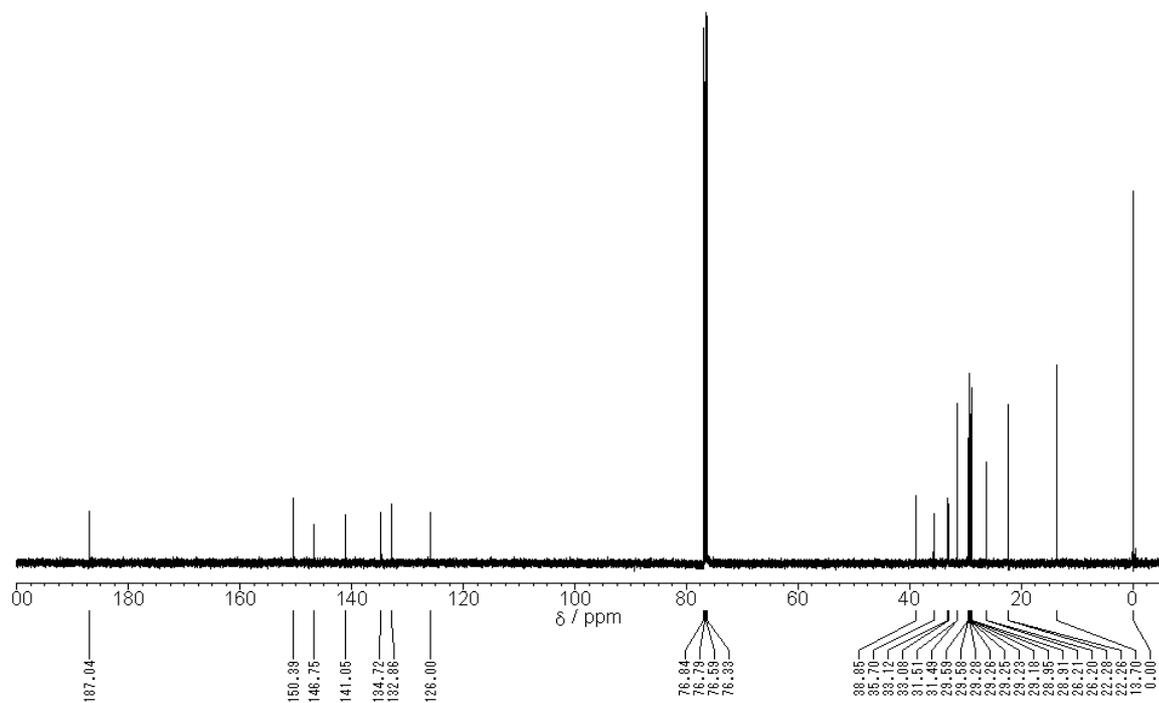
$^1\text{H-NMR}$ spectrum of 4



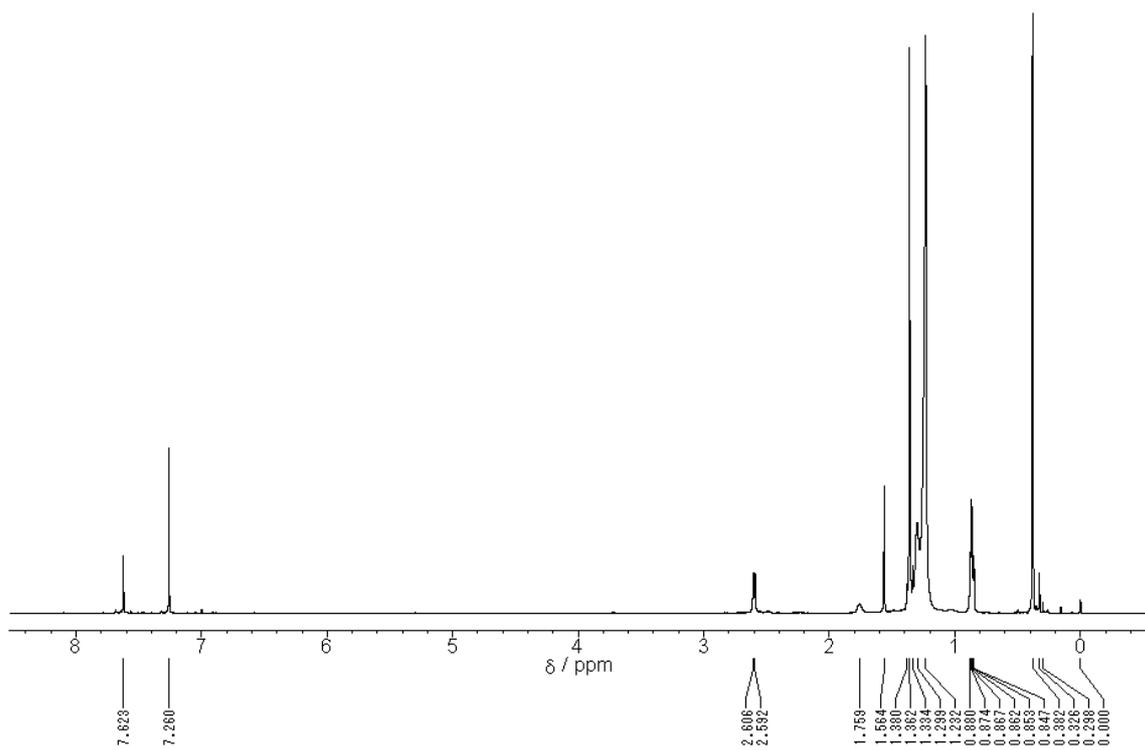
$^{13}\text{C-NMR}$ spectrum of 4



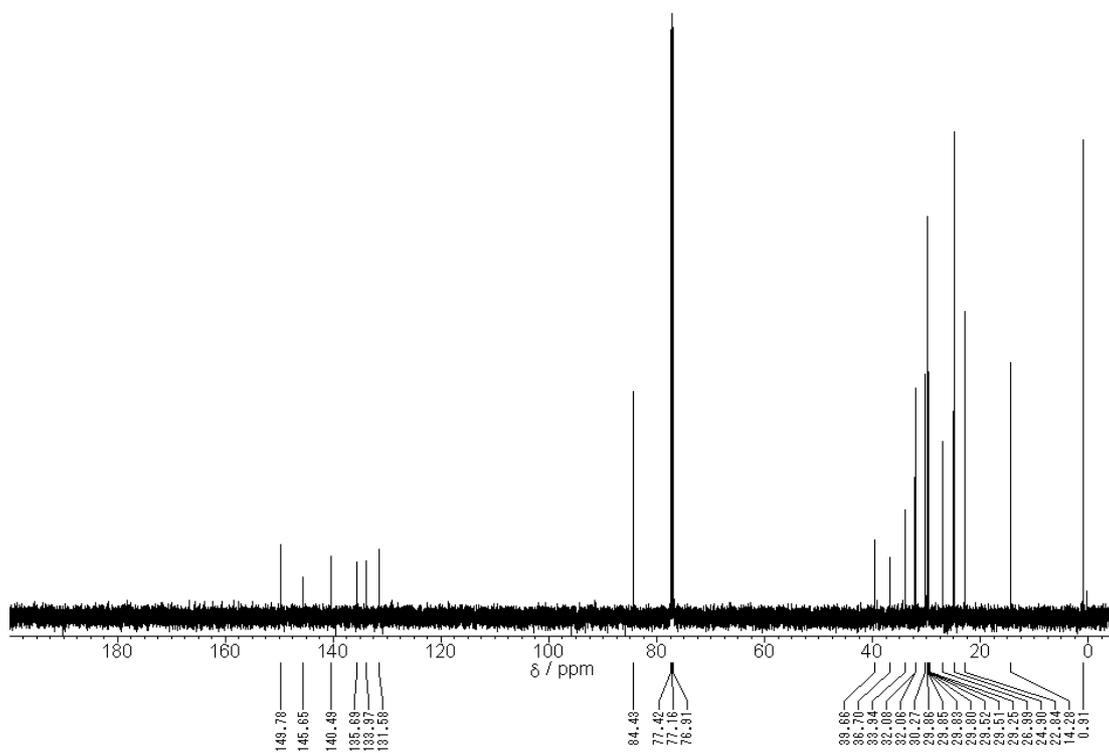
$^1\text{H-NMR}$ spectrum of **5**



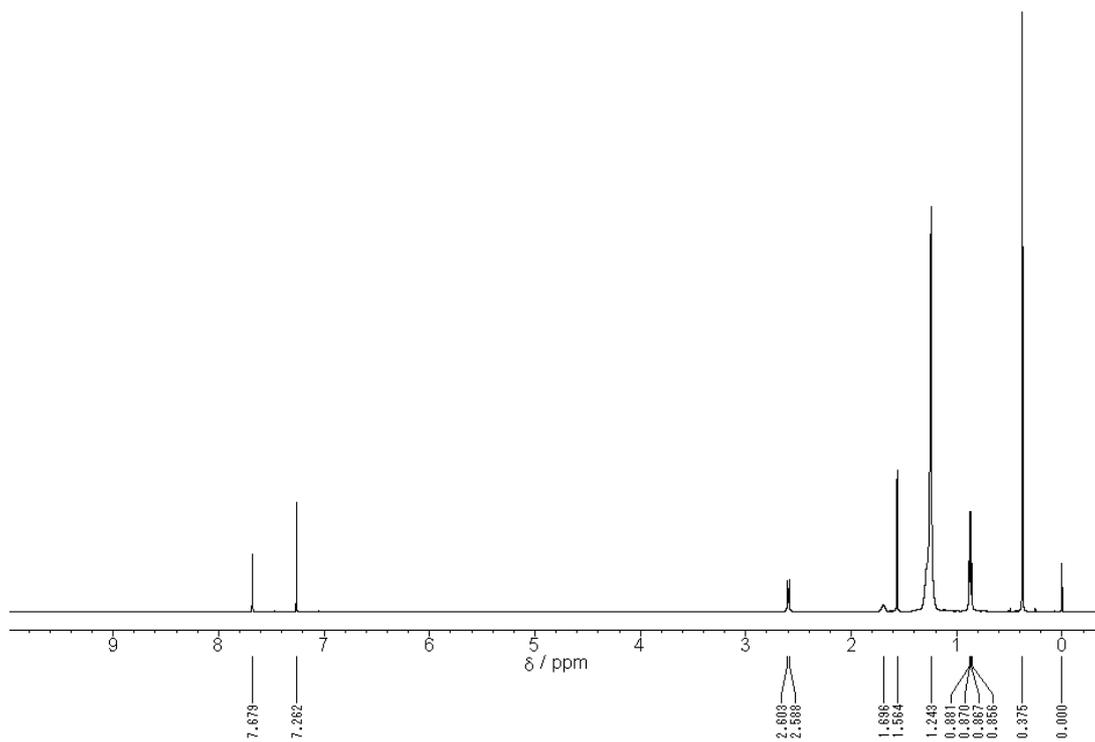
$^{13}\text{C-NMR}$ spectrum of **5**



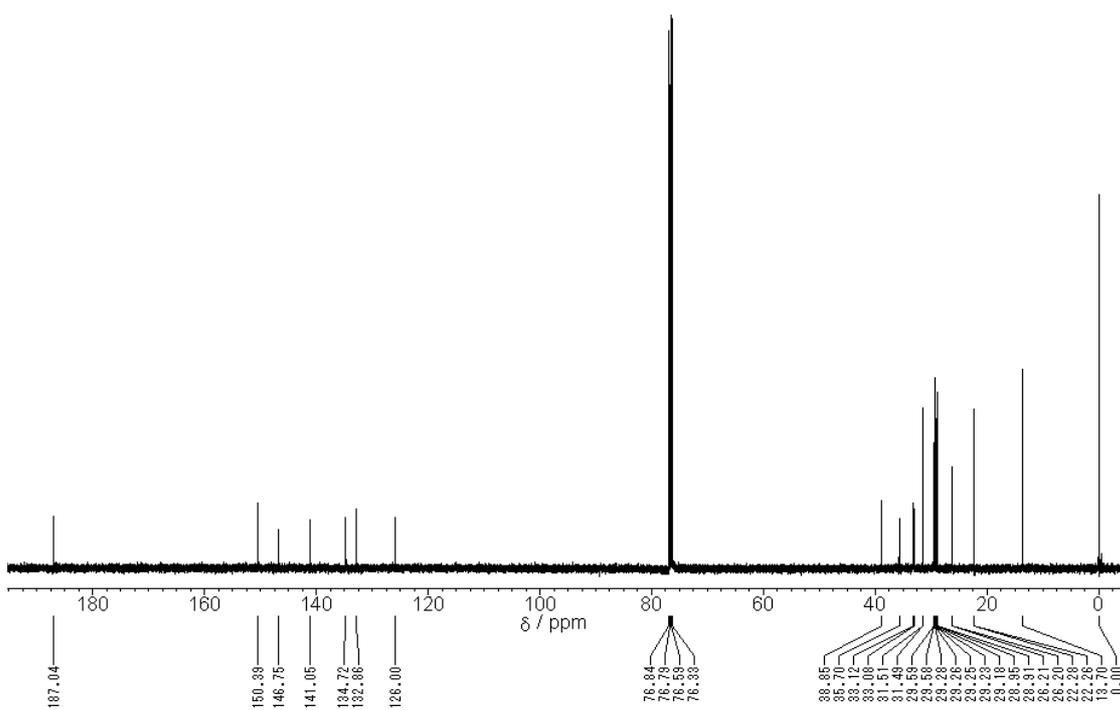
$^1\text{H-NMR}$ spectrum of **6**



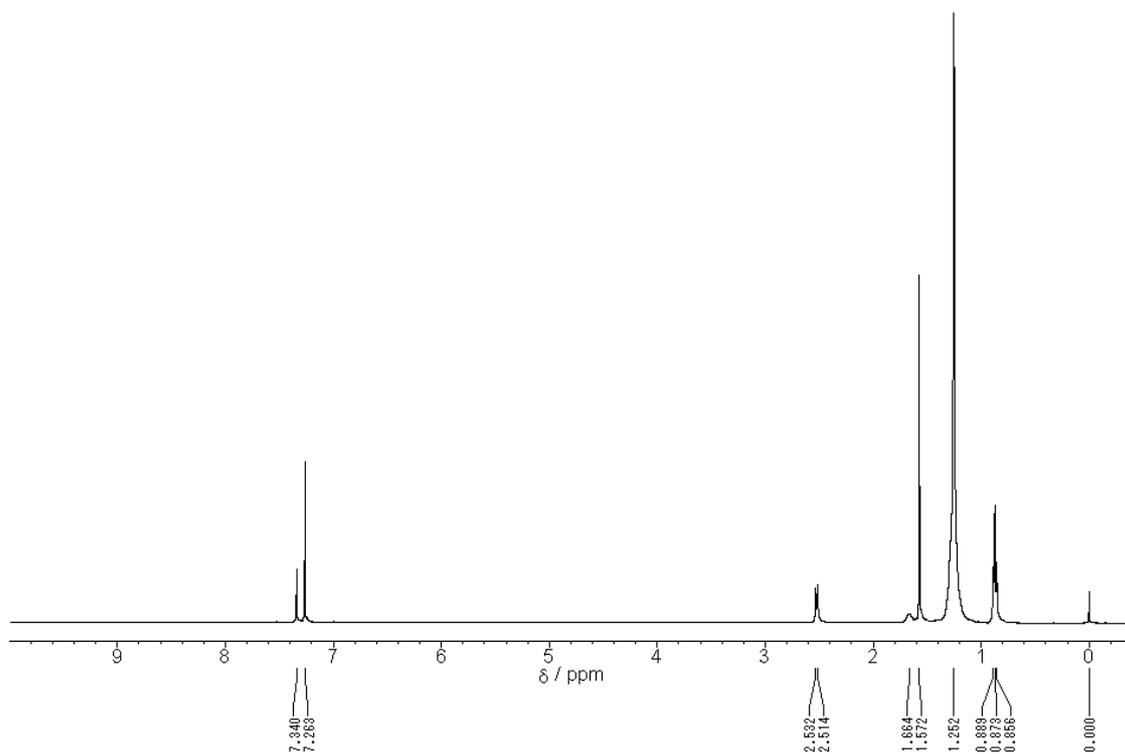
$^{13}\text{C-NMR}$ spectrum of **6**



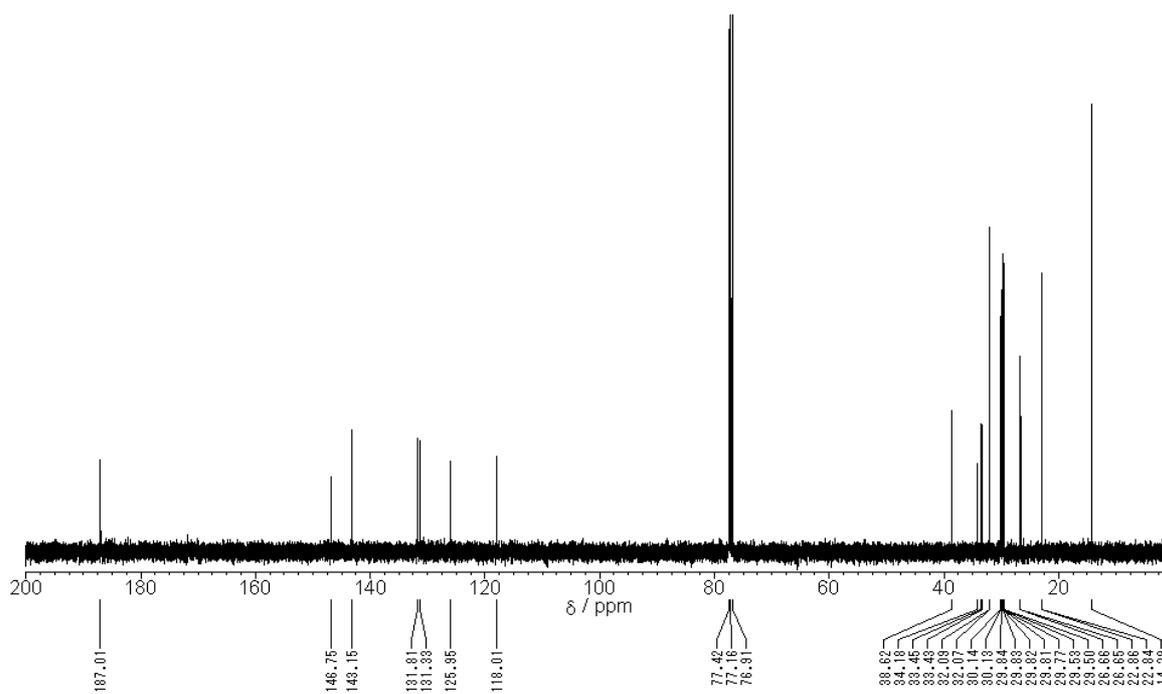
¹H-NMR spectrum of TTD2T



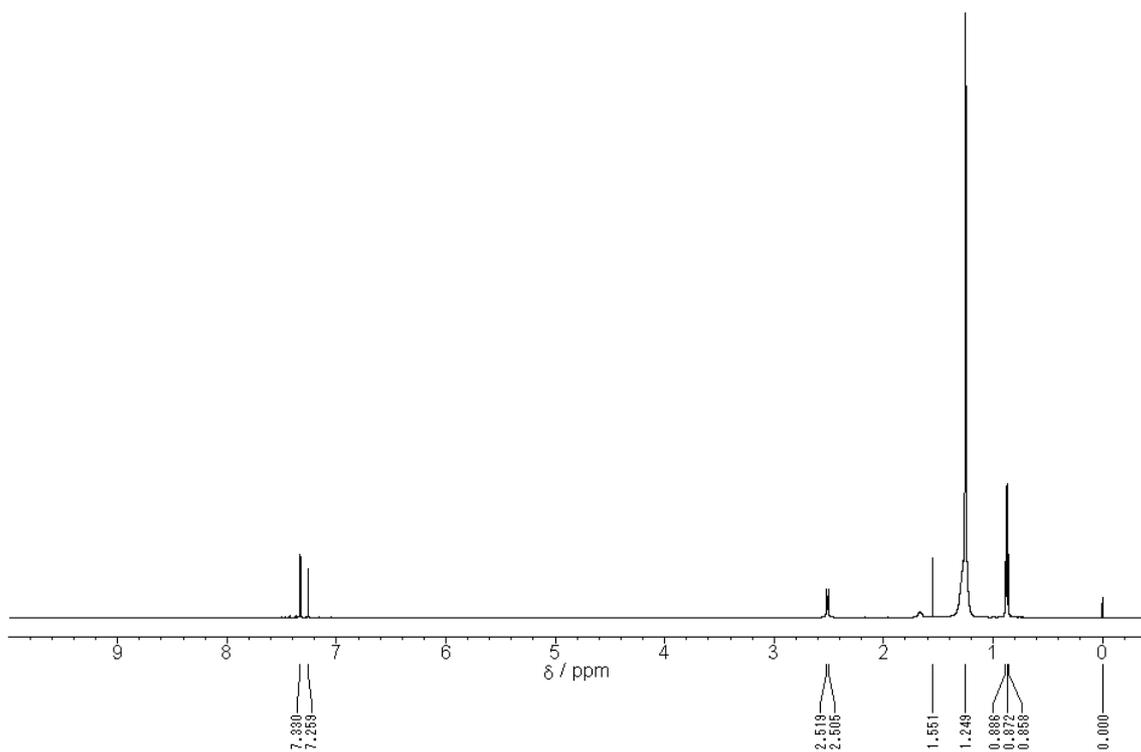
¹³C-NMR spectrum of TTD2T



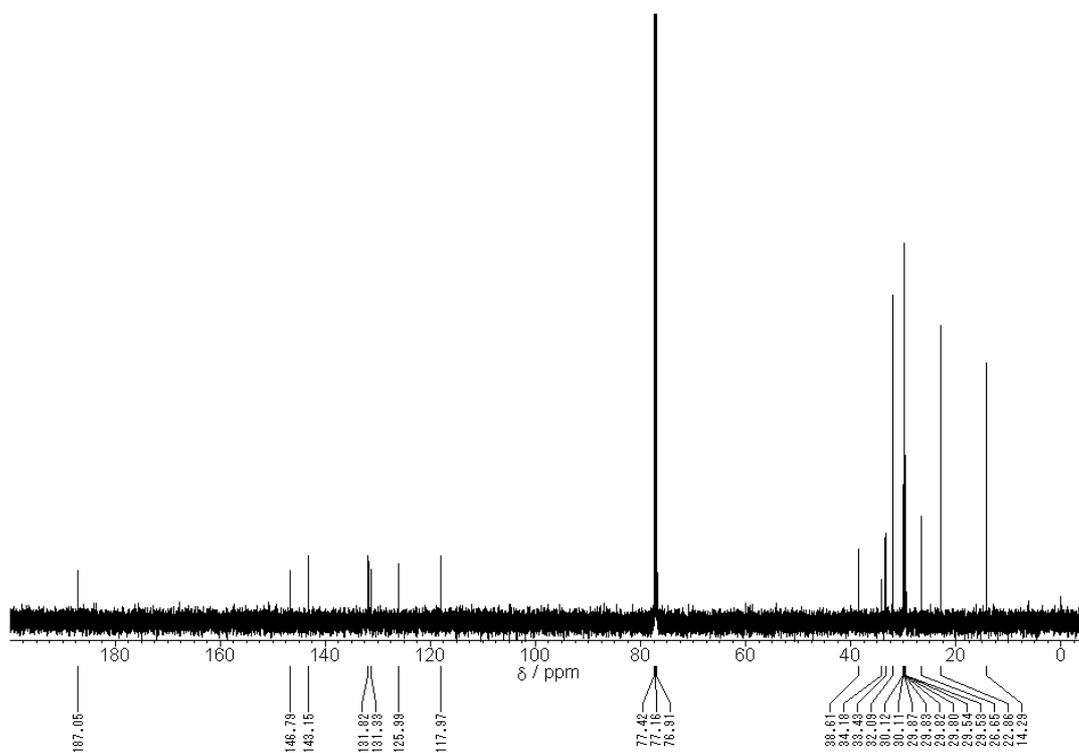
$^1\text{H-NMR}$ spectrum of **8**



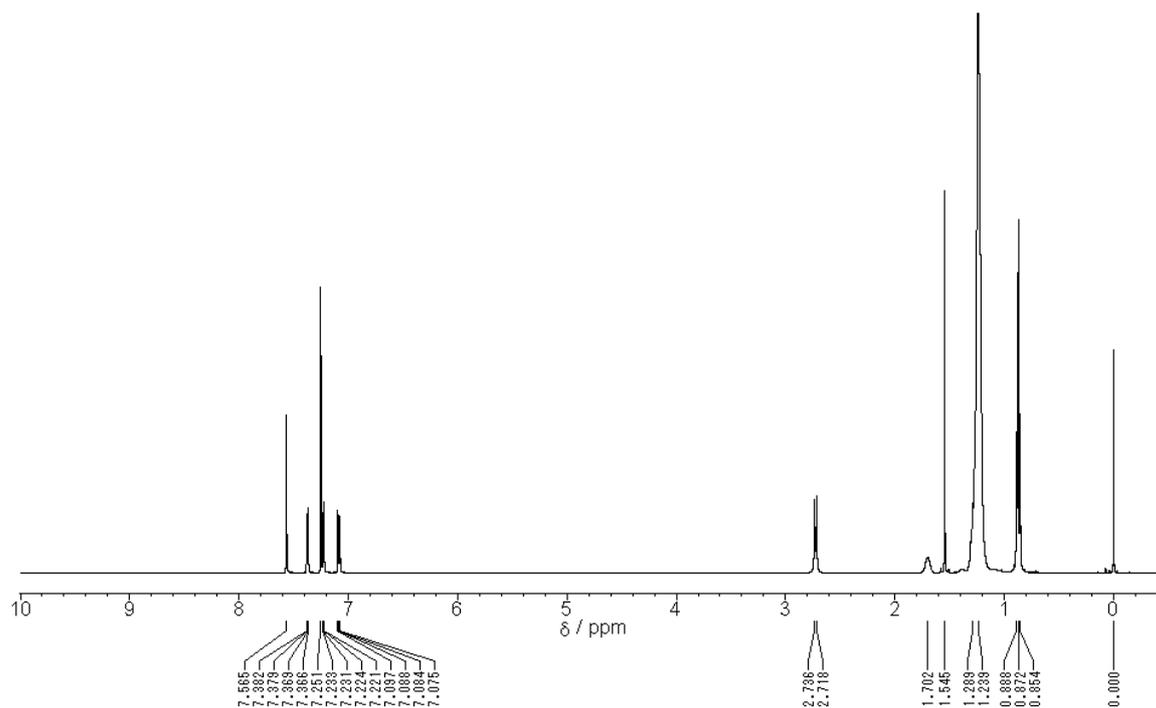
$^{13}\text{C-NMR}$ spectrum of **8**



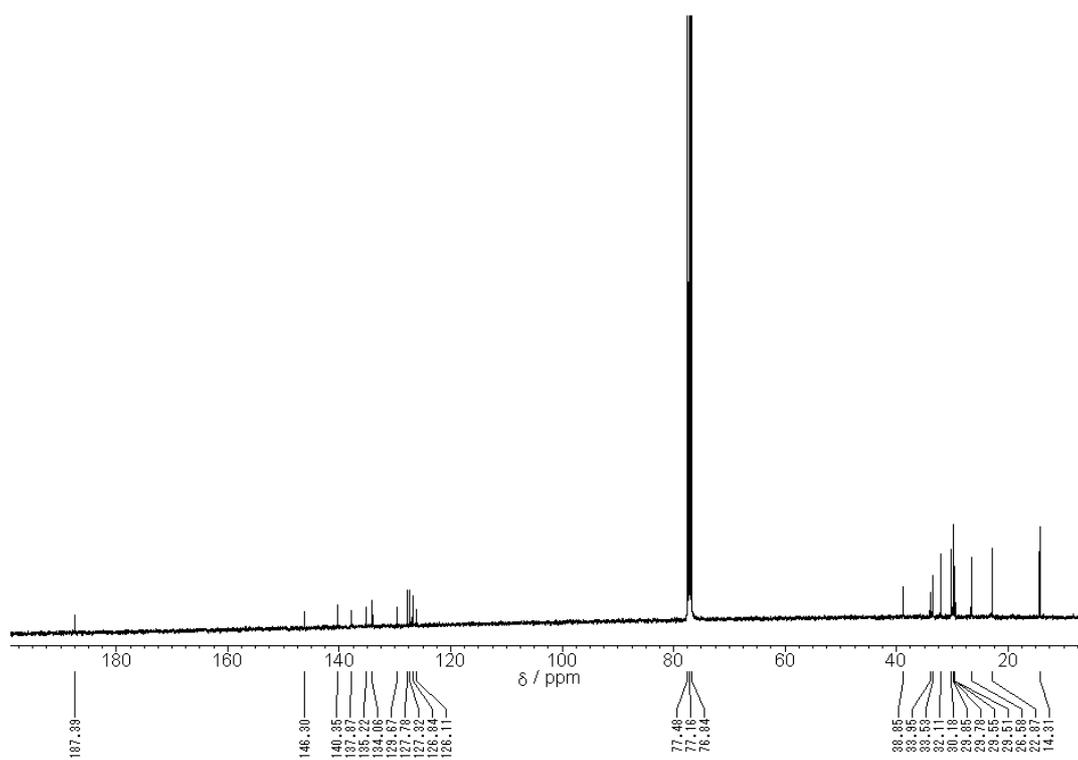
$^1\text{H-NMR}$ spectrum of **9**



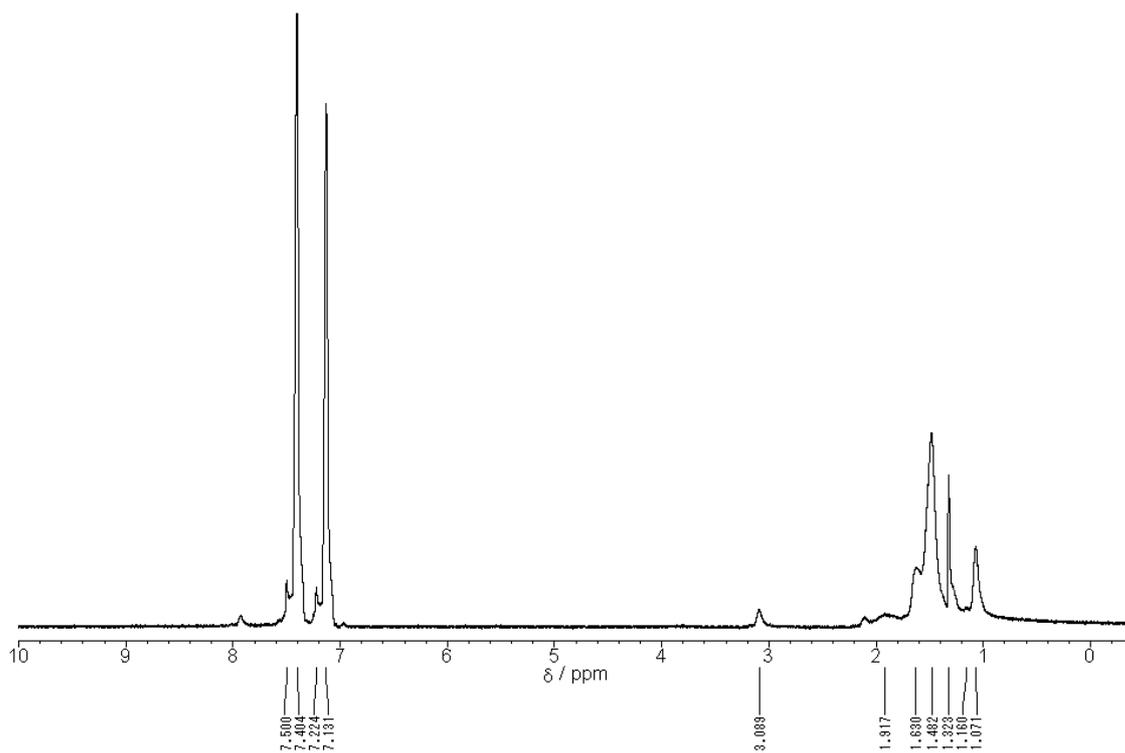
$^{13}\text{C-NMR}$ spectrum of **9**



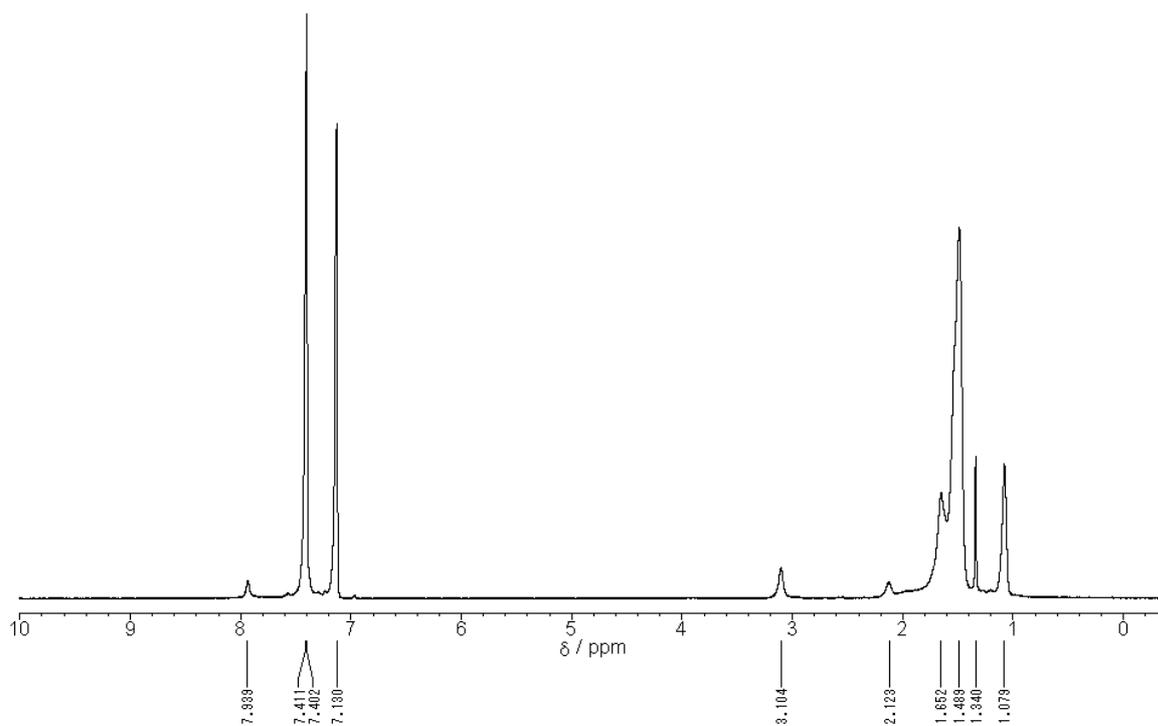
¹H-NMR spectrum of TTD4T



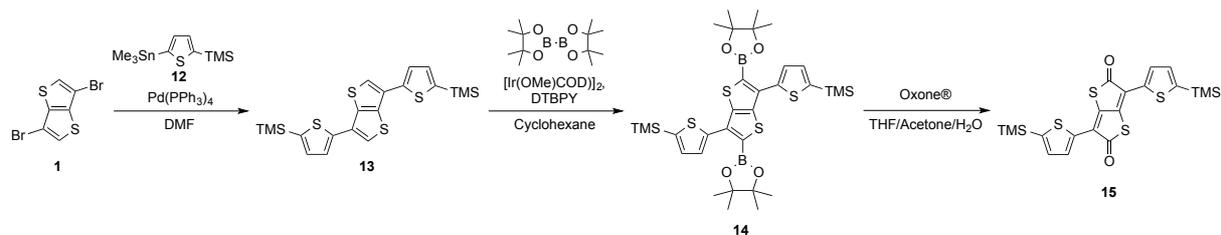
¹³C-NMR spectrum of TTD4T



¹H-NMR spectrum of **PTTD4T-OD**



¹H-NMR spectrum of **PTTD4T-DT**



Scheme S1. Synthesis of the model compound (**15**).

3,6-Bis(5-(trimethylsilyl)thiophen-2-yl)thieno[3,2-b]thiophene (13)

The same procedure as **3** was performed using **1** and **12** to yield **13** as pale yellow solid (79%, 330 mg, 0.74 mmol).

$^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ (ppm) 7.55 (s, 2H), 7.45 (d, 2H, $J = 3.2$), 7.24 (d, 2H, $J = 3.2$).

$^{13}\text{C-NMR}$ (CDCl_3 , 400 MHz): δ (ppm) 142.28, 140.09, 137.66, 134.90, 128.61, 125.39, 122.00, 0.11.

HRMS: Calcd for $\text{C}_{20}\text{H}_{24}\text{S}_4\text{Si}_2$ [$\text{M}+\text{H}$] $^+$: 449.0378. Found: 449.0363.

(5,5'-(2,5-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thieno[3,2-b]thiophene-3,6-diyl)bis(thiophene-5,2-diyl))bis(trimethylsilane) (14)

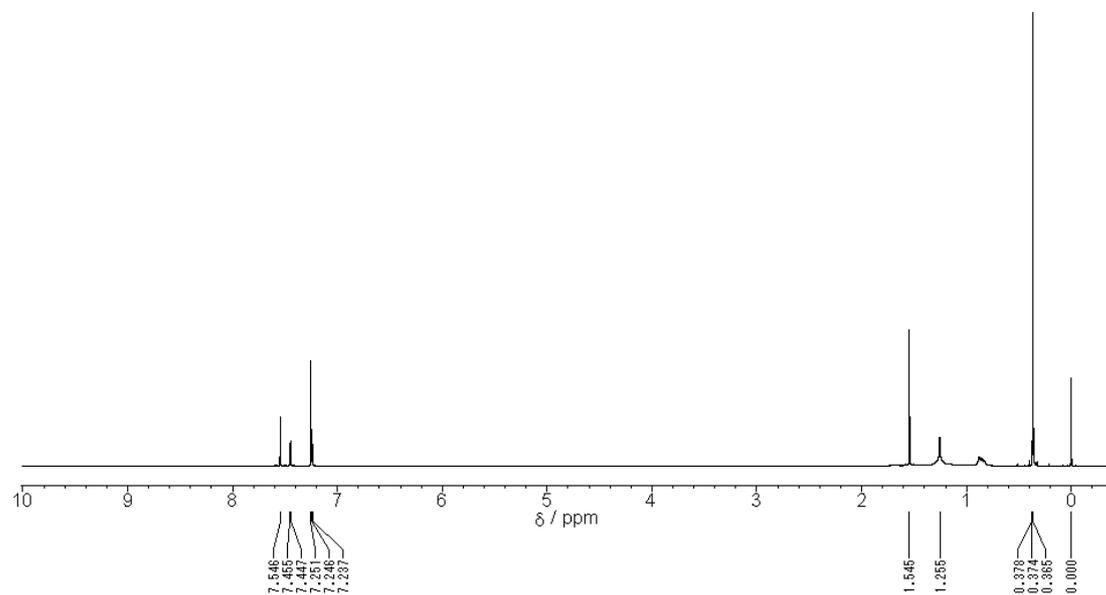
The same procedure as **5** was performed to yield **14** as pale yellow solid (ca. 55%, 200 mg). This compound was subjected to the next reaction without further purification.

3,6-Bis(5-(trimethylsilyl)thiophen-2-yl)thieno[3,2-b]thiophene-2,5-dione (15)

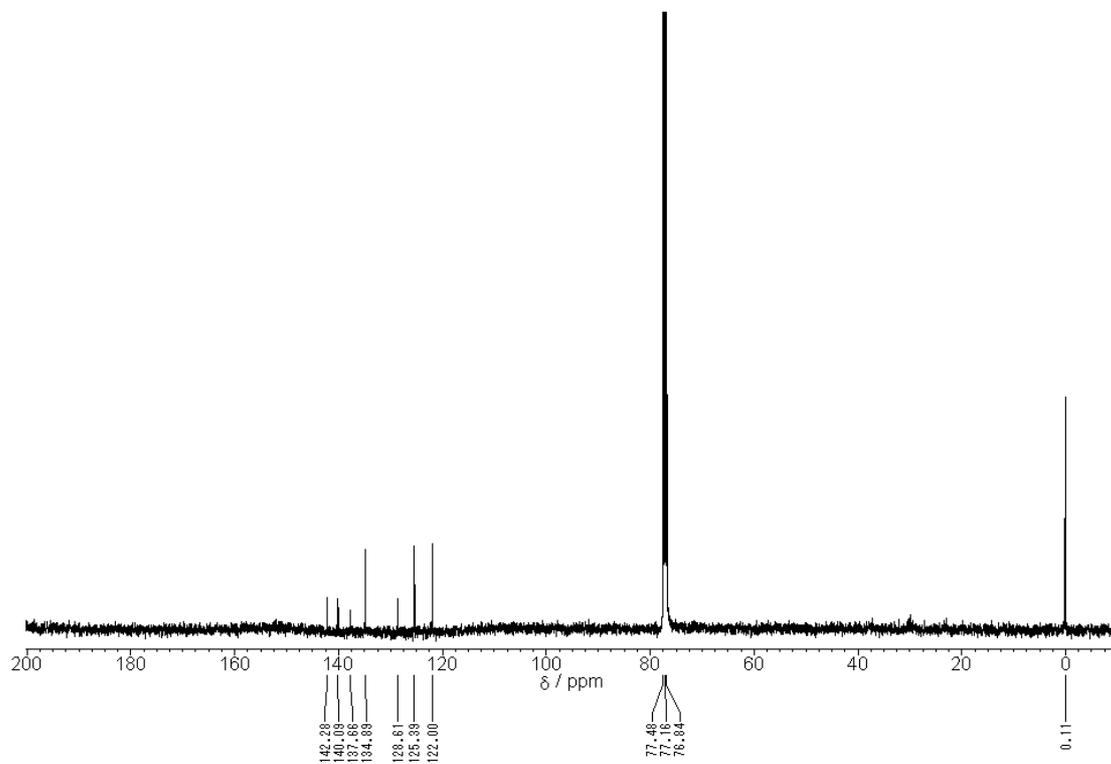
The same procedure as **TTD2T** was performed to yield **15** as red solid (35%, 24 mg, 0.05 mmol).

$^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ (ppm) 7.73 (d, 2H, $J = 3.2$), 7.29 (d, 2H, $J = 3.2$). $^{13}\text{C-NMR}$ (CDCl_3 ,

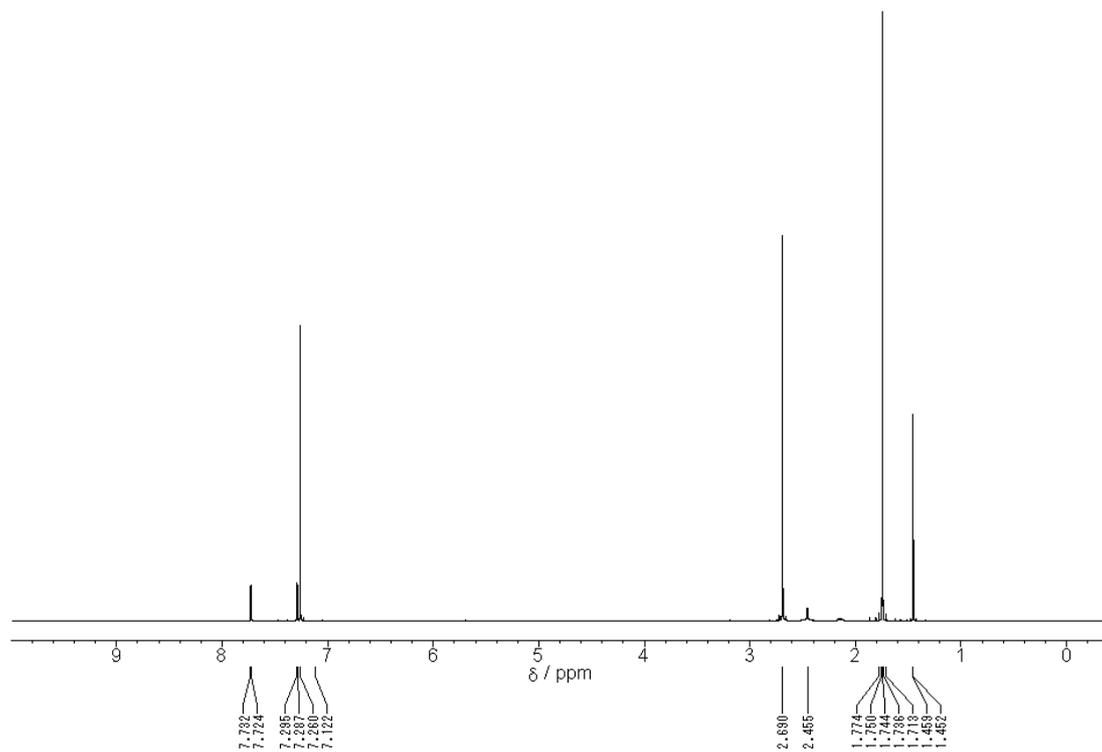
400 MHz): δ (ppm) 187.42, 147.77, 147.72, 136.79, 135.19, 131.32, 126.77, -0.05 . HRMS: Calcd for $\text{C}_{20}\text{H}_{22}\text{O}_2\text{S}_4\text{Si}_2$ [$\text{M}+\text{H}$] $^+$: 479.0119. Found: 479.0120.



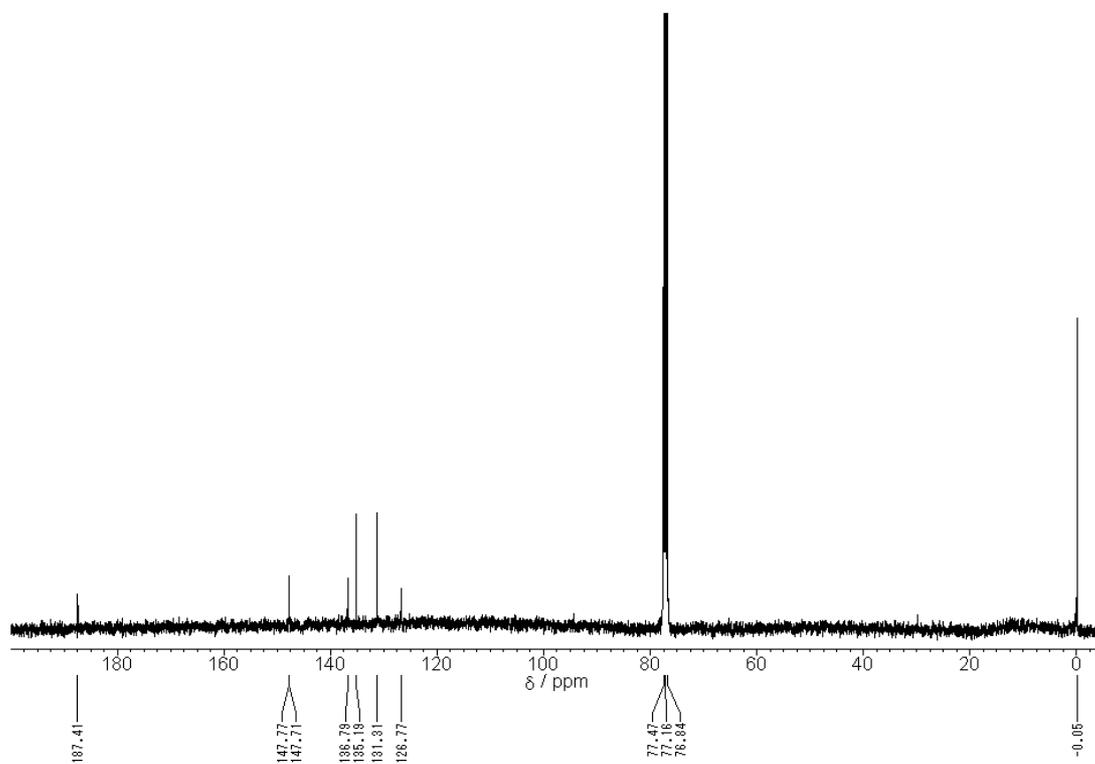
$^1\text{H-NMR}$ spectrum of **13**



$^{13}\text{C-NMR}$ spectrum of **13**



$^1\text{H-NMR}$ spectrum of **15**



$^{13}\text{C-NMR}$ spectrum of **15**

Instrumentation.

UV–vis absorption spectra were measured using a Shimadzu UV-3600 spectrometer. Cyclic voltammograms (CVs) were recorded on a ALS Electrochemical Analyzer Model 612D in dichloromethane containing tetrabutylammonium hexafluorophosphate (Bu_4NPF_6 , 0.1 M) as supporting electrolyte at a scan rate of 100 mV/s. Counter and working electrodes were made of Pt, and the reference electrode was Ag/AgCl. All the potentials were calibrated with the standard ferrocene/ferrocenium redox couple (Fc/Fc^+ : $E^{1/2} = +0.43$ V measured under identical conditions). Thermal analyses were carried out with differential scanning calorimetry (DSC) on an EXSTAR DSC7020 (SII Nanotechnology, Inc.) at 10 °C/min for both heating and cooling processes, and with thermogravimetric analysis (TGA) on an EXSTAR TG/DTA6200 (SII Nanotechnology, Inc.) at 10 °C/min. Ionization potential (IP) was determined from the onset of photoelectron spectra measured by using a photoelectron spectrometer, model AC-2, in air (Riken Keiki Co., Ltd). Dynamic force-mode atomic force microscopy study was carried out on a Nanoscope IIIA MultiMode head on a Nanoscope system (SII Nanotechnology, Inc.). GIXD experiments were conducted at the SPring-8 on beamline BL19B2. The sample was irradiated with an X-ray energy of 12.39 keV ($\lambda = 1$ Å) at a fixed incident angle on the order of 0.12° through a Huber diffractometer, and the GIXD patterns were recorded with a 2-D image detector (Pilatus 300K). Samples for the X-ray measurements were prepared by drop-casting the polymer solution on the FDTS-modified Si/SiO₂ substrate.

OFET Fabrication and Measurement.

Bottom-gate-top-contact (BGTC) devices. All processes except substrate cleaning were performed in inert atmosphere. Heavily doped n^+ -Si (100) wafers with 200-nm-thick thermally grown SiO₂ ($C_i = 17.3$ nF/cm²) were used for the substrate. The Si/SiO₂ substrates were ultrasonicated with acetone and isopropanol for 10 min, respectively, and then were subjected to

UV-ozone treatment for 20 min. The cleaned substrates were treated with FDTS to form a self-assembled monolayer, in which the wafers were exposed to FDTS vapor in a closed desiccator. Polymer layers were then spin-coated from hot (~ 100 °C) 3 g/L DCB solution at 1000 rpm for 10 s and then 2500 rpm for 35 s, and subsequently annealed at 150, 200, 250, 300 °C for 30 min, respectively, under nitrogen. On top of the polymer thin films, Au drain and source electrodes (thickness 80 nm) were deposited in a vacuum through a shadow mask, where the drain–source channel length (L) and width (W) are 40 μm and 3.0 mm, respectively.

Top-gate-bottom-contact (TGBC) devices. All processes except substrate cleaning were performed in inert atmosphere. TGBC devices were fabricated on glass substrates with Cr/Au source and drain electrode, where $L = 50$ μm and $W = 3.0$ mm, deposited via photolithography. The substrates were ultrasonicated with acetone and isopropanol for 10 min, respectively, and then were subjected to UV-ozone for 20 min. Polymer layers were then spin-coated from hot (~ 100 °C) 3 g/L DCB solution, and subsequently annealed at 200 and 300 °C for PTTD4T-OD and -DT, respectively, for 30 min. The CYTOP dielectric layer (2.7 nF/cm²) with ca. 800 nm thickness was spin-coated on top of the polymer layer and then was dried at 120 °C for 1 h. The devices were completed by vacuum evaporation of Al through a shadow mask as gate contacts (~ 50 nm).

Measurements. Current–voltage characteristics of the OFET devices were measured at room temperature in air with a Keithly 4200-SCS semiconductor characterization system. Field-effect mobilities were calculated in the saturation regime ($V_D = -60$ V) of the I_D using the following equation,

$$I_D = (WC_i/2L) \mu (V_G - V_T)^2$$

where C_i is the capacitance of the dielectric layer, I_D is the source–drain current, and V_D , V_G , and V_T are the source–drain, gate, and threshold voltages, respectively. Current on/off ratios ($I_{\text{on}}/I_{\text{off}}$) were

determined from the minimum current around $V_G = 0-20$ V (I_{off}) and the current at $V_G = -80$ V (I_{on}).

The mobility data were collected from more than 10 different devices.

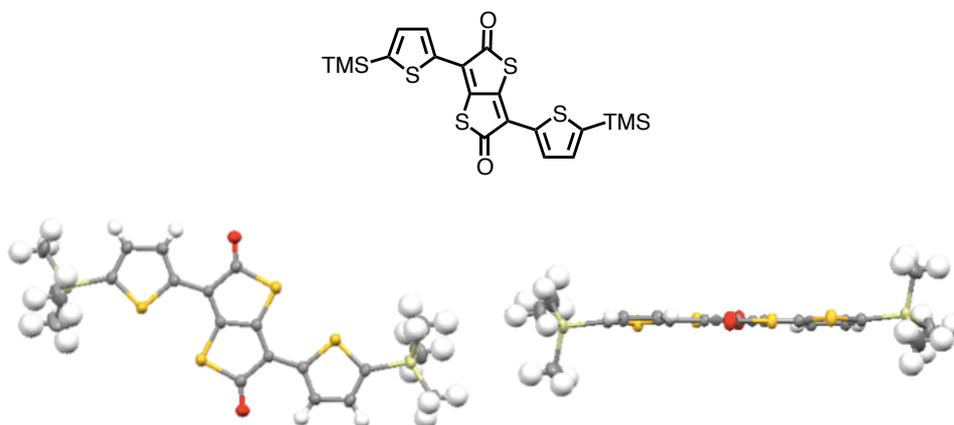


Figure S1. Molecular structure of the model compound (**15**) in the single crystal determined by X-ray analysis.

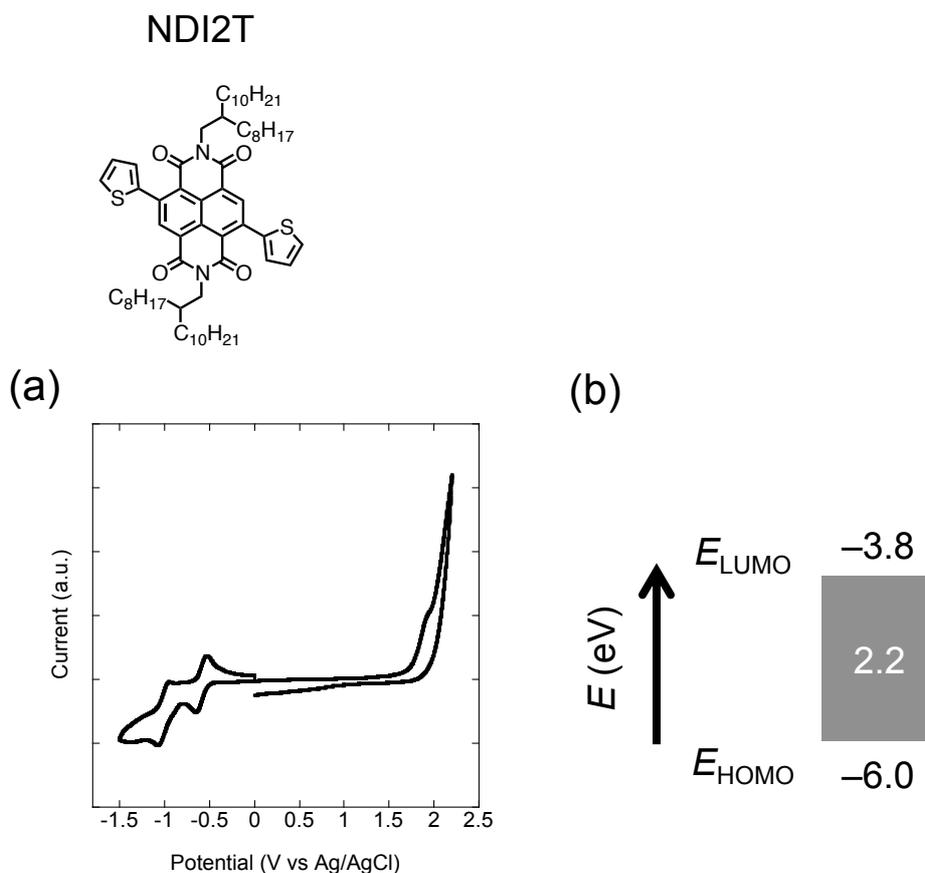


Figure S2. (a) Cyclic voltammograms and (b) energy diagrams of NDI-2T.

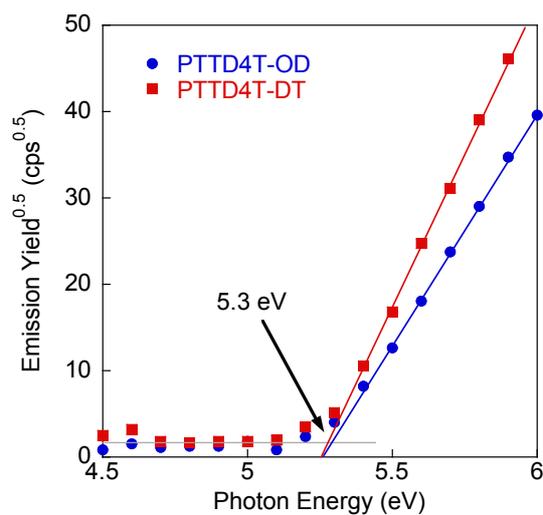


Figure S3. Photoelectron spectra in air of the polymer thin films.

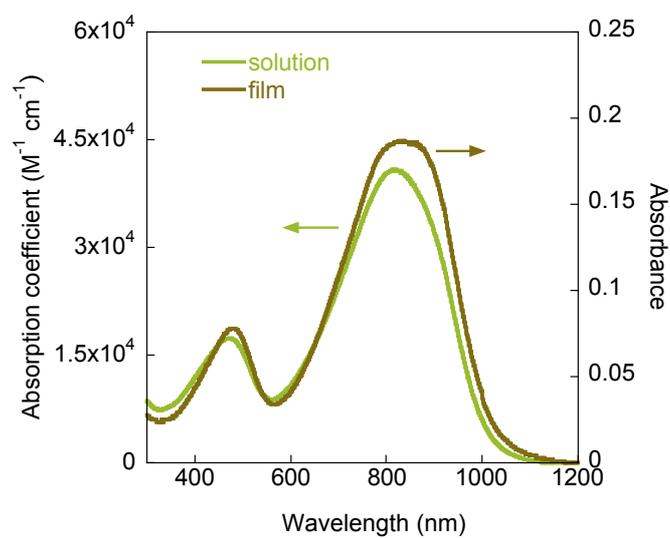


Figure S4. UV-vis absorption spectra of PTTD4T-DT.

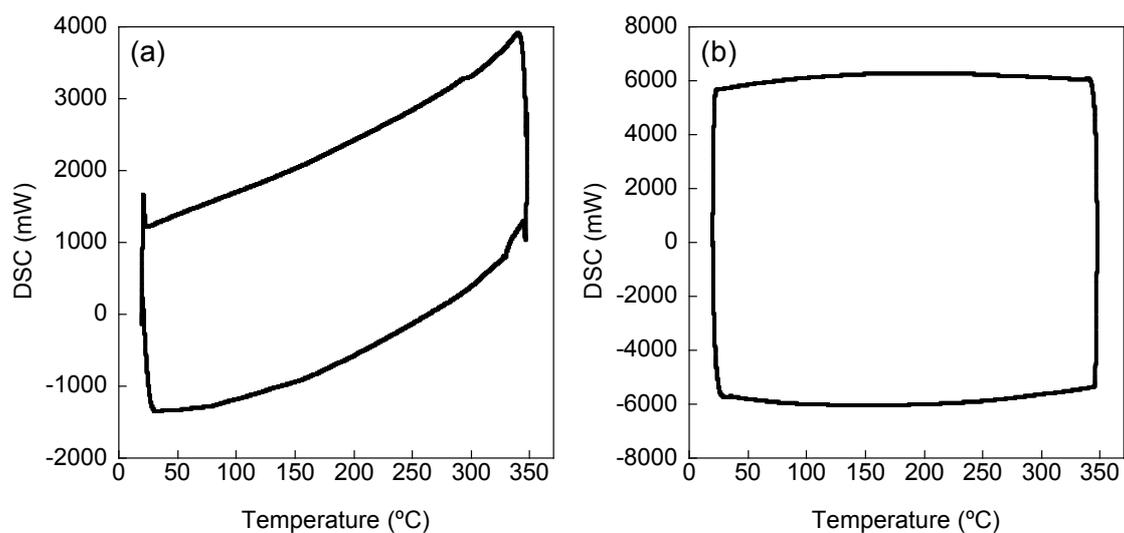


Figure S5. DSC curves of PTTD4T-OD (a) and -DT (b).

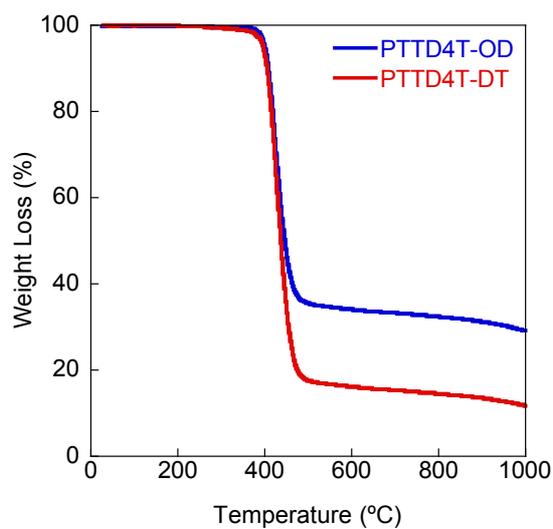


Figure S6. Thermogravimetric curves of the polymers. The temperatures of 5% weight loss for PTTD4T-OD and -DT are 400 and 396 °C, respectively.

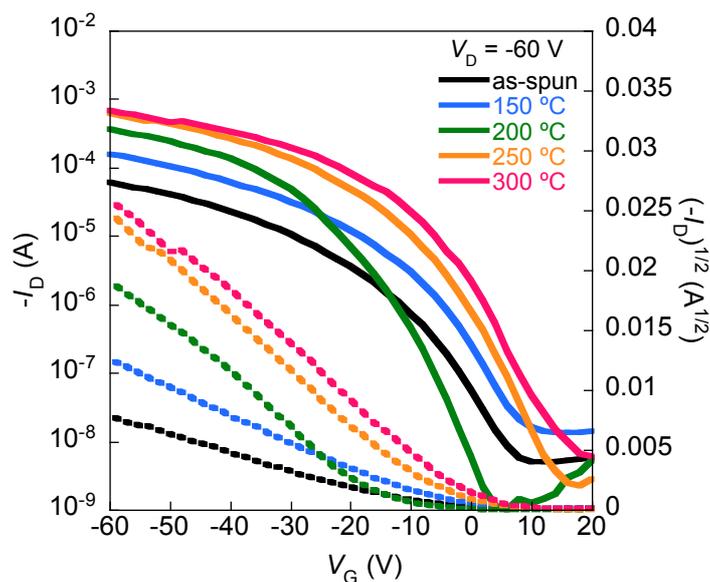


Figure S7. Transfer curves of the BGTC-OFET devices with PTTD4T-OD.

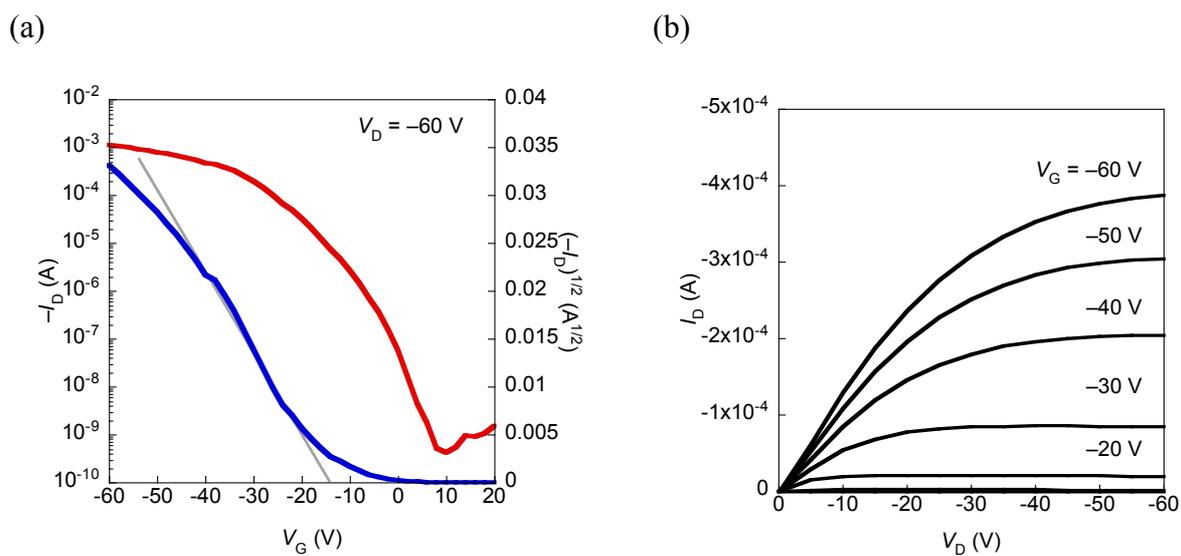


Figure S8. Transfer (a) and output (b) curves of the BGTC-OFET device with PTTD4T-DT annealed at 300 °C that give the maximum hole mobility of $1.38 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The hole mobility was calculated in the saturation regime from the slope obtained by linear fitting of the $(-I_D)^{1/2}$ vs V_G curve in the V_G range from -20 to -40 V.

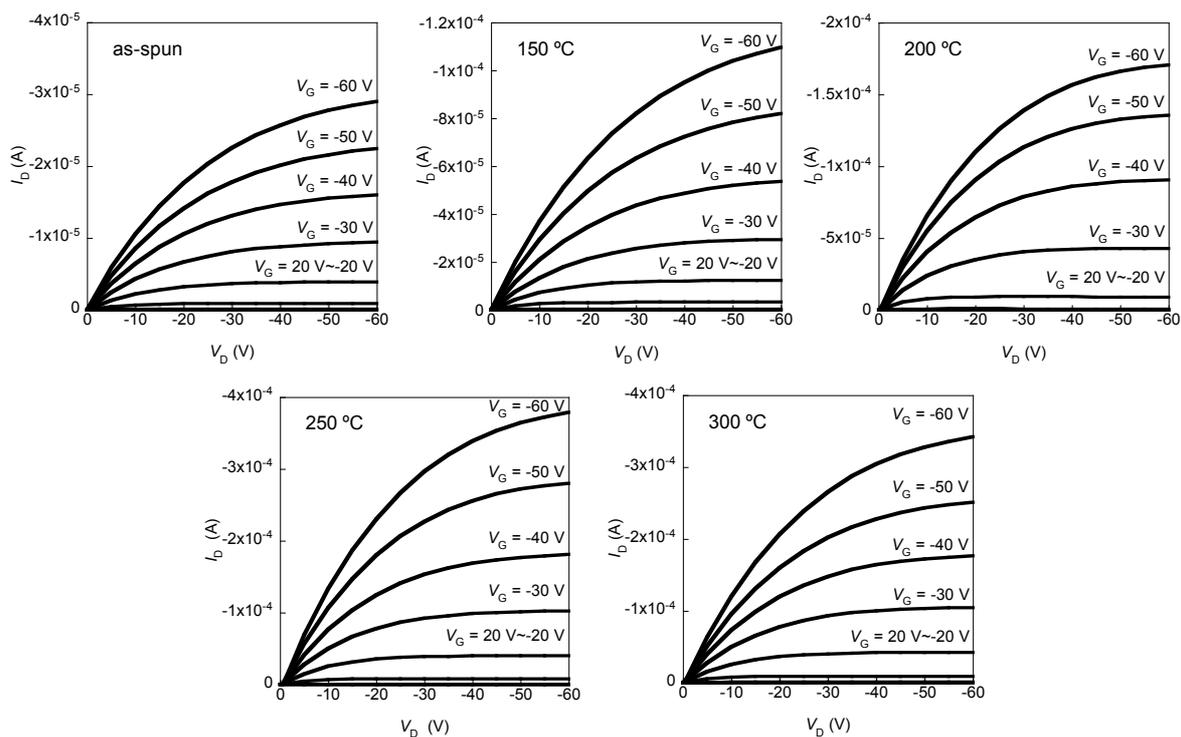


Figure S9. Typical output curves of the BGTC-OFETs with PTTD4T-OD. Annealing temperatures are shown in each chart.

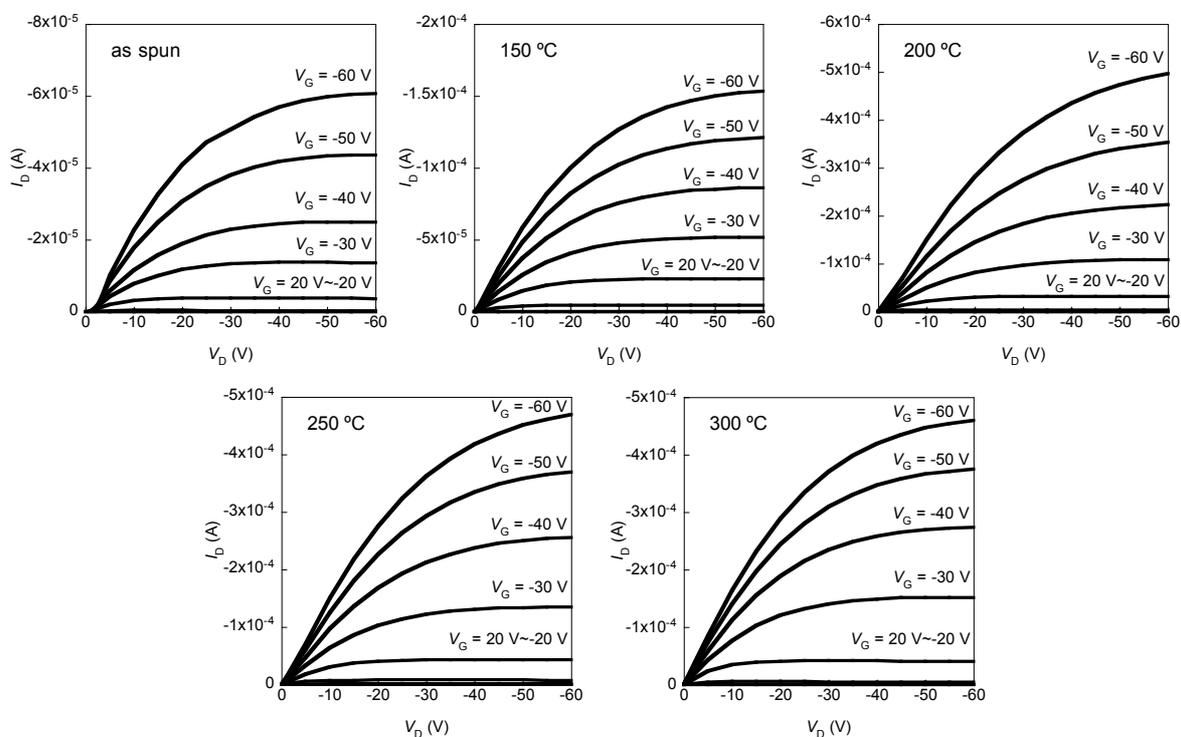


Figure S10. Typical output curves of the BGTC-OFETs with PTTD4T-DT. Annealing temperatures are shown in each chart.

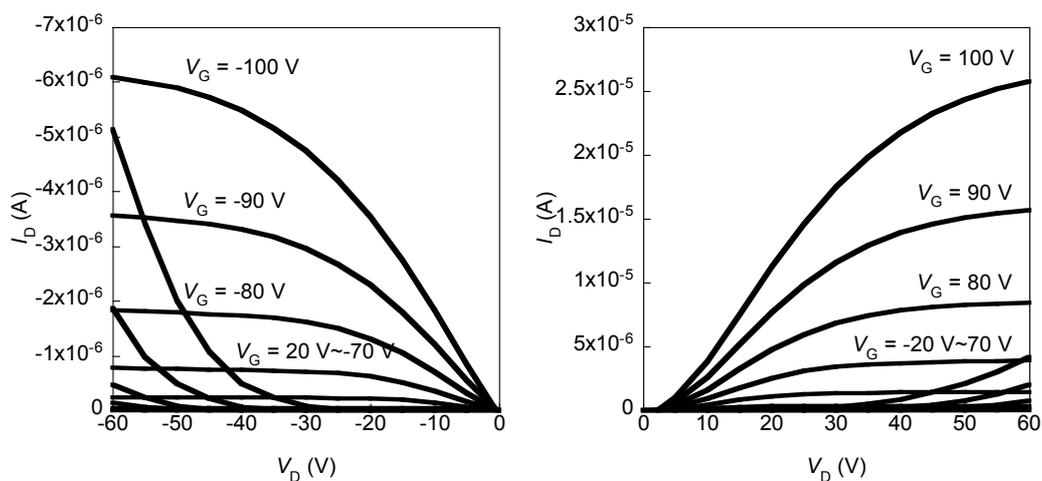


Figure S11. Typical output curves of the TGBC-OFETs with PTTD4T-OD annealed at 200 °C.

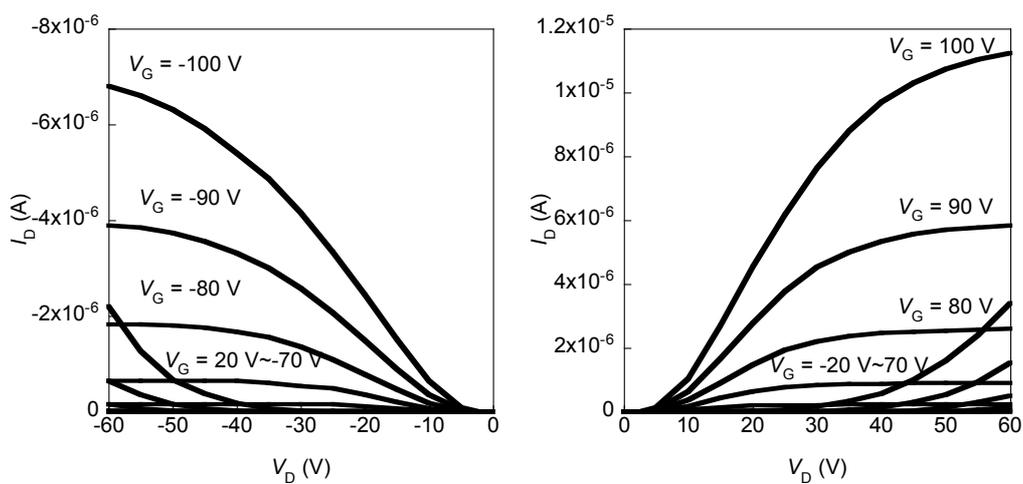


Figure S12. Typical output curves of the TGBC-OFETs with PTTD4T-DT annealed at 300 °C.

Table S1-1. Transistor properties of BGTC devices with PTTD4T-OD

Annealing temperature (°C)	μ_{BGTC} ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) ^a	V_{T} (V) ^b	$I_{\text{on}}/I_{\text{off}}$ ^c
As-spun	0.050 ± 0.020 (0.088)	0 ~ -12.0	~10 ⁵
150	0.14 ± 0.063 (0.26)	-1.3 ~ -10.7	~10 ⁵
200	0.18 ± 0.052 (0.36)	-1.7 ~ -15.8	~10 ⁷
250	0.17 ± 0.078 (0.39)	-2.8 ~ -11.1	~10 ⁵
300	0.23 ± 0.063 (0.35)	-3.1 ~ -14.1	~10 ⁵

Table S1-2. Transistor properties of BGTC devices with PTTD4T-DT

Annealing temperature (°C)	μ_{BGTC} ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) ^a	V_{T} (V) ^b	$I_{\text{on}}/I_{\text{off}}$ ^c
As-spun	0.063 ± 0.038 (0.12)	-5.7 ~ -11.2	~10 ⁵
150	0.15 ± 0.093 (0.21)	-1.8 ~ -11.9	~10 ⁵
200	0.22 ± 0.11 (0.56)	0.9 ~ -17.8	~10 ⁵
250	0.39 ± 0.15 (0.82)	-1.3 ~ -16.2	~10 ⁷
300	0.66 ± 0.29 (1.38)	-1.4 ~ -19.4	~10 ⁸

^aHole mobilities calculated from the saturation regime with different annealing temperatures; average ± standard deviation (maximum value). ^bThreshold voltage. ^cCurrent on and off ratio.

Table S1-3. Transistor properties of TGBC devices with PTTD4T

Polymer	μ_{h} ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) ^a	V_{T} (V)	$I_{\text{on}}/I_{\text{off}}$	μ_{e} ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) ^a	V_{T} (V)	$I_{\text{on}}/I_{\text{off}}$
PTTD4T-OD	0.027 ± 0.0045	-35 ~	~10 ⁴	0.069 ± 0.026	46 ~ 58	~10 ⁴
	(0.034)	-50		(0.13)		
PTTD4T-DT	0.092 ± 0.022	-58 ~	~10 ⁷	0.12 ± 0.043	66 ~ 75	~10 ⁶
	(0.12)	-70		(0.20)		

^aHole (μ_{h}) and electron (μ_{e}) mobilities calculated from the saturation regime; average ± standard deviation (maximum value). The annealing temperature for PTTD4T-OD and -DT are 200 °C and 300 °C.

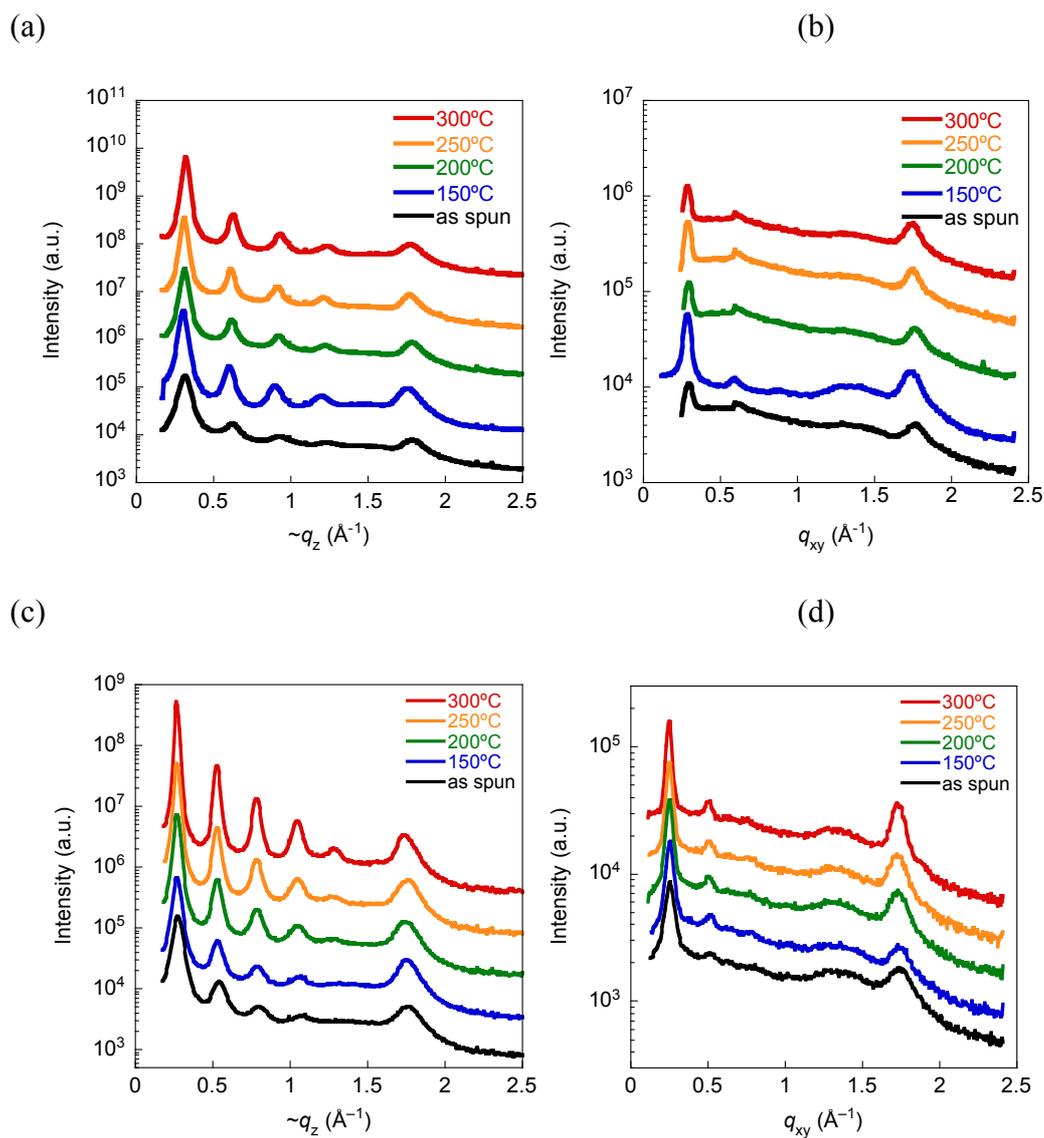


Figure S13. Out-of-plane and in-plane profiles of GIXD cut from 2D images along q_z and q_{xy} direction, respectively. (a), (b) PTTD4T-OD, (c), (d) PTTD4T-DT.

Table S2. Edge-on to face-on crystallite ratio in the PTTD4T-DT thin film at different annealing temperatures.

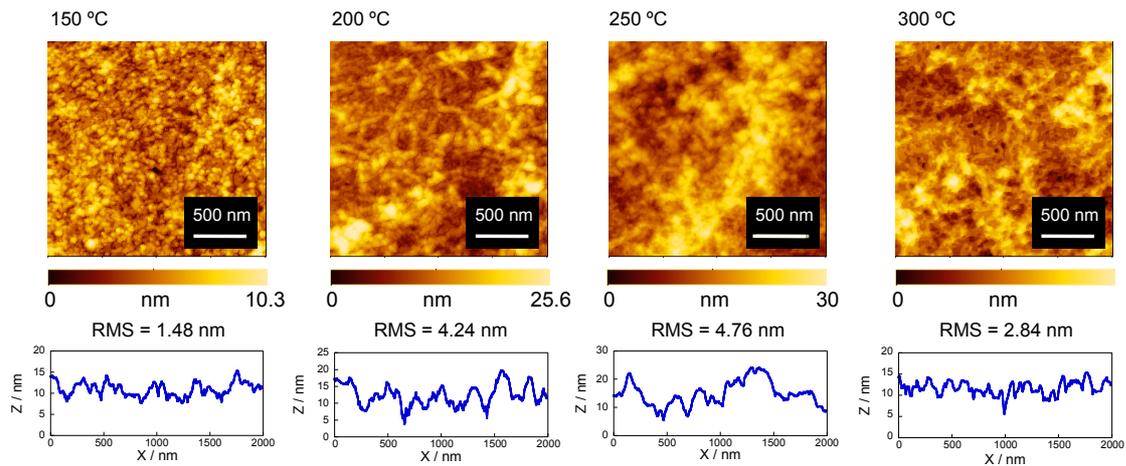
lamellae ^a					π - π stacking ^b				
As spun	150 °C	200 °C	250 °C	300 °C	As spun	150 °C	200 °C	250 °C	300 °C
22.3	18.4	35.7	52.9	104.7	0.25	0.13	0.27	0.28	0.34

^aOut-of-plane (edge-on) to in-plane (face-on) intensity ratio of the lamellar peak. ^bIn-plane (edge-on) to out-of-plane (face-on) intensity ratio of the π - π stacking peak.

Table S3. Coherence length of the crystalline domain determined from the lamellar peak ($q_{xy} \approx 1.73 \text{ \AA}^{-1}$) using the Scherrer equation ($2\pi/[\text{full peak width at half maxima}]$).

Polymer	as spun	150 °C	200 °C	250 °C	300 °C
PTTD4T-OD	9.1	13.4	13.6	15.7	15.6
PTTD4T-DT	10.5	12.9	16.0	18.8	24.1

PTTD4T-OD



PTTD4T-DT

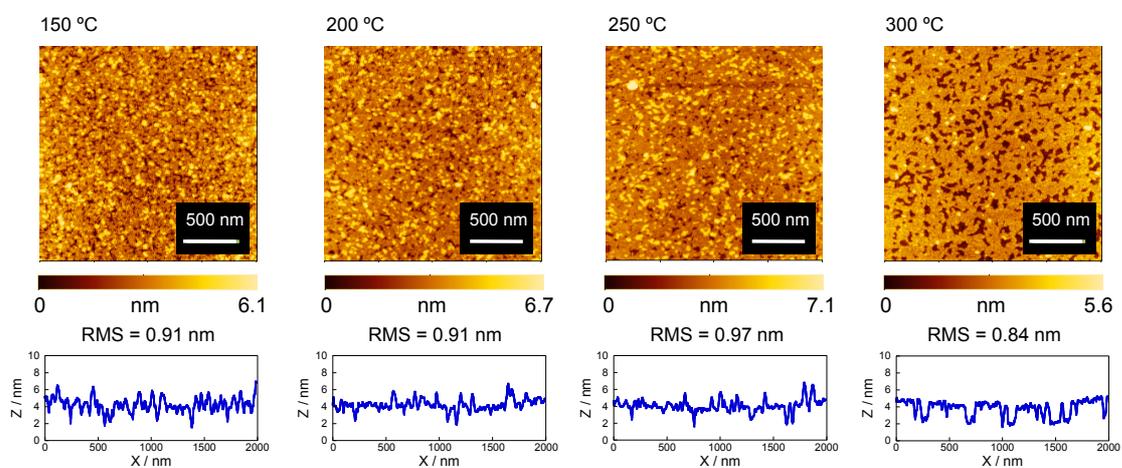


Figure S14. AFM images and cross section profiles of the polymer thin films annealed at 150, 200, 250, and 300 °C.

References.

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