Supplementary Information

5,10-Diborylated naphtho[1,2-*c*:5,6-*c*′]bis[1,2,5]thiadiazole: a ready-to-use precursor for the synthesis of high-performance semiconducting polymers

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Synthesis.

Naphtho[1,2-*c*:5,6-*c*']bis[1,2,5]thiadiazole (NTz) was synthesized according to the reported procedure.[1] 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 CaH_2 prior to use. Polymerization was carried out with a microwave reactor, Biotage Initiator. Nuclear magnetic resonance (NMR) spectra were obtained in deuterated chloroform ($CDCl_3$) and *o*-dichlorobenzene (*o*-DCB-d_4) 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*-DCB as a solvent and calibrated with polystyrene standards.

1. S. Mataka, K. Takahashi, Y. Ikezaki, T. Hatta, A. Tori-i and M. Tashiro, *Bull. Chem. Soc. Jpn*, 1991, **64**, 68-73.

5,10-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphtho[1,2-*c*:5,6-*c*']bis([1,2,5]thiadiazole) [NTz-Bpin$_2$]

To a 200-mL three-neck flask were placed (1,5-cyclooctadiene)(methoxy)iridium(I) dimer (398 mg, 0.60 mmol), 4,4'-di-*tert*-butyl-2,2'-bipyridyl (490 mg, 1.20 mmol), and cyclohexane (150 mL) under an N_2 atmosphere. The mixture was then refluxed for 1 h. Bis(pinacolate)diboron (4.57 g, 18.0 mmol) was added and the mixture was refluxed for 30 min. Naphtho[1,2-c:5,6-c']bis[1,2,5]thiadiazole (NTz) (1.47 g, 6.00 mmol) was added to the mixture, which was then refluxed for 20 h. After the mixture was cooled to room temperature, the precipitate was filtered, washed with methanol, and dried in vacuo. The crude product was purified by recrystallization from chloroform/methyl isobutyl ketone to give NTz-Bpin$_2$ as yellow solid (2.08 g, 70%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.51 (s, 2H), 1.50 (s, 24H). ^{13}C NMR (500 MHz, $CDCl_3$): δ 157.0, 152.7, 136.7, 136.7, 126.7, 84.7, 25.0, 24.9. EI-MS (70 eV) *m/z* 496 (M^+). Anal. Calcd for $C_{22}H_{26}N_4O_4S_2B_2$: C, 53.25; H, 5.28; N, 11.29%. Found: C, 53.03; H, 5.24; N, 11.18%.

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolane)-3-(2-decyltetradecyl)thiophene (2)

To a 100-mL three-neck flask with a dropping funnel were placed **1** (3.00 g, 6.00 mmol) and THF (24 mL) under an N_2 atmosphere. After cooled to –78 °C, 1.64 M *n*-BuLi hexane solution (4.0 mL, 6.60 mmol) was added slowly. After the solution was stirred at –78 °C for 1 h, a solution of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.51 g, 8.10 mmol) in 6 mL of THF was added. The solution was gradually warmed to room temperature, and stirred for 16 h. Saturated NH_4Cl aq. was added, and the mixture was extracted with ethyl acetate. The organic layer was

washed with brine and then dried over anhydrous $MgSO_4$. The solvent was removed by vacuum evaporation, and the residue was purified by column chromatography on silica gel with hexane-dichloromethane (4:1) to give **2** as yellow oil (2.16 g, 66%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 (d, 1H, *J* = 4.7 Hz), 6.97 (d, 1H, *J* = 4.7 Hz), 2.80 (d, 2H, *J* = 7.2 Hz), 1.58 (m, 1H), 1.32 (s, 12H), 1.17–1.30 (m, 40H), 0.88 (t, 6H, *J* = 7.0Hz). ^{13}C NMR (500 MHz, $CDCl_3$): δ 153.8, 131.0, 131.0, 83.5, 40.2, 34.8, 33.4, 31.9, 30.1, 29.7, 29.7, 29.7, 29.4, 26.6, 24.8, 22.7, 14.1. EI-MS (70 eV) *m/z* 546 (M^+). HR-MS (APCI) *m/z* calcd for $C_{34}H_{63}O_2BS$ $[M]^+$ 546.46363, found 546.46484.

3, 3'''-Bis (2-decyltetradecyl)-2,2';5',2'';5'',2'''-quaterthiophene (3)

To a 100-mL three-neck flask with a reflux condenser were placed **2** (2.00 g, 3.66 mmol), 5,5'-dibromo-2,2'-bithiophene (539 mg, 1.66 mmol), and DMF (35 mL) and purged with N_2 for 30 min. Potassium phosphate (2.11 g, 9.96 mmol) and Pd(dppf)Cl_2 (61 mg, 0.08 mmol) were added, and the solution was heated under N_2 at 100 °C for 16 h. After the mixture was cooled to room temperature, saturated NH_4Cl aq. was added, and the mixture was extracted with ethyl acetate. The organic layer was washed with saturated $NaHCO_3$ aq. and brine, and then dried over anhydrous $MgSO_4$. The solvent was removed by vacuum evaporation, and the residue was purified by column chromatography on silica gel with hexane to give **3** as yellow oil (1.57 g, 94%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.18 (d, 2H, *J* = 5.0 Hz), 7.11 (d, 2H, *J* = 3.6 Hz), 7.01 (d, 2H, *J* = 3.4 Hz), 6.90 (d, 2H, *J* = 5.1 Hz), 2.71 (d, 4H, *J* = 7.2 Hz), 1.65–1.73 (m, 2H), 1.16–1.32 (m, 80H), 0.87 (t, 12H, *J* = 6.7 Hz). ^{13}C NMR (500 MHz, $CDCl_3$): δ 139.2, 136.9, 135.3, 130.8, 130.6, 126.8, 123.7, 123.6, 38.9, 33.8, 33.5, 31.9, 30.0, 29.7, 29.7, 29.7, 29.7, 29.4, 26.5, 22.7, 14.1. MS (MALDI-TOF): *m/z* calcd for $C_{64}H_{106}S_4$ $[M]^+$ 1002.72, found 1003.38. HR-MS (APCI) *m/z* calcd for $C_{64}H_{106}S_4$ $[M]^+$ 1002.71719, found 1002.71747.

5,5'''-Dibromo-3,3'''-bis(2-decyltetradecyl)-2,2';5',2'';5'',2'''-quaterthiophene (4)

To a 100-mL three-neck flask with a dropping funnel was placed **3** (1.00 g, 1.00 mmol), and dissolved in chloroform (25 mL). After cooled to 0 °C, a solution of N-bromosuccinimide (357 mg, 2.00 mmol) in 25mL of DMF was added slowly. The solution was gradually warmed to room temperature. After the solution was stirred at room temperature for 3 h, saturated $NaHCO_3$ aq. was added, and the mixture was extracted with hexane. The organic layer was washed with brine and then dried over anhydrous $MgSO_4$. The solvent was removed by vacuum evaporation, and the residue was purified by column chromatography on silica gel with hexane, subsequently by recrystallization from methyl isobutyl ketone to give **4** as a yellow solid (1.06 g, 92%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.09 (d, 2H, *J* = 3.7 Hz), 6.95 (d, 2H, *J* = 3.8 Hz), 6.86 (s, 2H), 2.64 (d, 4H, *J* = 7.2 Hz), 1.59–1.67 (m, 2H), 1.17–1.32 (m, 80H), 0.87 (t, 12H, *J* = 6.8 Hz). ^{13}C NMR (500 MHz, $CDCl_3$): δ 140.0, 137.2, 134.0, 133.1, 132.1, 127.3, 123.8, 110.6, 38.9, 33.7, 33.4, 31.9,

31.9, 30.0, 29.7, 29.7, 29.7, 29.4, 26.5, 22.7, 14.1. MS (MALDI-TOF): *m/z* calcd for $C_{64}H_{105}S_4Br_2$ $[M+H]^+$ 1158.54, found 1158.73; HR-MS (APCI) *m/z* calcd for $C_{64}H_{105}S_4Br_2^+$ $[M+H]^+$ 1158.53821, found 1158.53711.

5,5'-Dibromo-4,4'-bis(2-decyltetradecyl)-2,2'-bithiophene (5)

To a three-neck 200-mL flask with a dropping funnel were placed *i*-Pr_2NH (3.1 mL, 22 mmol) and THF (60 mL) under an N_2 atmosphere. After cooled to –30 °C, 1.6 M *n*-BuLi hexane solution (13.4 mL, 21.3 mmol) was added over 10 min, and the resulting solution was warmed to 0 °C, stirred at the same temperature for 20 min, and then cooled again to –78 °C. A THF solution (15 mL) of **4** (8.2 g, 16.4 mmol) was added dropwise over 30 min at –78 ºC. After the solution was stirred at –78 °C for 1 h, $CuCl_2$ (2.87 g, 21.3 mmol) was added in one portion, and stirred at –78 °C for 20 min. The solution was warmed to room temperature and stirred for 16 h. 2 M HCl aq (50 mL) was added, and the solution was stirred at room temperature for 10 min, and then ethyl acetate (100 mL) was added. The aqueous layer was separated, and extracted with ethyl acetate (30 mL × 2). The combined organic layer was washed with brine (50 mL), dried over anhydrous $MgSO_4$. After the solvent was removed by vacuum evaporation, the residue was purified by column chromatography on silica gel with hexane as the eluent to give **5** as yellow oil (7.45 g, 91%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, 6H, *J* = 6.8 Hz), 0.88 (t, 6H, *J* = 7.0 Hz), 1.20–1.36 (m, 80 H), 1.60–1.64 (m, 2H), 2.44 (d, 4H, *J* = 6.9 Hz), 6.73 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.3, 22.9, 26.7, 29.6, 29.9, 30.1, 31.8, 32.1, 33.5, 34.4, 38.6, 108.6, 125.1, 136.2, 142.4. MS (MALDI-TOF): *m/z* calcd for $C_{56}H_{101}Br_2S_2$ 995.57 $[M+H]^+$, found 995.67.HR-MS (APCI) *m/z* calcd for $C_{56}H_{100}Br_2S_2^+$ $[M]^+$ 994.56277, found 994.56525.

3',4''-Bis(2-decyltetradecyl)-2,2';5',2'';5'',2'''-quaterthiophene (6)

To a 50-mL round-bottom flask with a reflux condenser were placed Mg (42 mg, 1.7 mmol) and ether (4 mL) under an N_2 atmosphere. An ether solution (1 mL) of 2-bromothiophene (250 mg, 1.5 mmol) was then added, and the resulting solution was refluxed for 1 h to completely generate 2-theiney magnesium bromide solution. After cooled to room temperature, the solution was transferred to a solution of **1** (0.50 g, 0.50 mml) and Ni(dppp)Cl_2 (14 mg, 0.025 mmol) in toluene (5 mL) and ether (5 mL), which was then refluxed for 20 h. After cooled to room temperature, saturated NH_4Cl aq. (10 mL) and ethyl acetate (30 mL) were added. The aqueous layer was separated, and extracted with ethyl acetate (20 mL × 3). The combined organic layer was washed with brine (20 mL) and then was dried over anhydrous $MgSO_4$. After the solvent was removed by vacuum evaporation, the residue was purified by column chromatography on silica gel with hexane as eluent, and preparative GPC (JAIGEL 1H–2H, $CHCl_3$ as the eluent) to give **6** (385 mg, 79%) as yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (t, 6H, *J* = 6.5 Hz), 0.87 (t, 6H, *J* = 6.5 Hz), 1.16–1.36 (m, 80

H), 1.62–1.68 (m, 2H), 2.65 (d, 4H, J = 7.0 Hz), 6.95 (s, 2H), 7.06 (dd, 2H, J = 4.4 and 3.8 Hz), 7.12 (d, 2H, J = 3.8 Hz), 7.30 (d, 2H, J = 4.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.3, 22.9, 26.6, 29.5, 29.8, 30.2, 32.1, 33.6, 34.0, 39.0, 125.6, 126.4, 126.9, 127.5, 130.1, 135.1, 136.1, 139.9; MS (MALDI-TOF): m/z calcd for $C_{64}H_{107}S_4$ $[M]^+$ 1002.72, found 1003.09. Anal. Calcd for $C_{64}H_{106}S_4$, C, 76.58; H, 10.64%. Found. C, 76.33; H, 11.00%.

5,5'''-Dibromo-3',4''-Bis(2-decyltetradecyl)-2,2';5',2'';5'',2'''-quaterthiophene (7)

To a 50-mL round-bottom flask was placed **6** (100 mg, 0.10 mmol) and THF (8 mL). After cooled to 0 °C, NBS (36 mg, 0.20 mmol) was added. The solution was gradually warmed to room temperature. After the solution was stirred at room temperature for 10 h, saturated $NaHCO_3$ aq. (10 mL) and $CHCl_3$ (30 mL) were added. The aqueous layer was separated, and extracted with $CHCl_3$ (10 mL × 2). The combined organic layer was washed with brine (10 mL) and dried over anhydrous $MgSO_4$. After the solvent was removed by vacuum evaporation, the residue was purified by flash column chromatography on silica gel with $CHCl_3$ as the eluent, and subsequently by preparative GPC (JAIGEL 1H–2H, $CHCl_3$ as the eluent) to give **6** (108 mg, 93%) as yellow oil.

^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.86–0.89 (m, 12H), 1.19–1.36 (m, 80H), 1.61–1.65 (m, 2H), 2.61 (d, 2H, J = 7.2 Hz), 6.85 (d, 2H, J = 3.9 Hz), 6.93 (s, 2H), 7.00 (d, 2H, J = 3.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 22,7, 26.4, 29.4, 29.7, 30.0, 31.6, 31.9, 33.4, 33.8, 38.8, 112.0, 126.5, 126.8, 129.1, 130.2, 135.2, 137.4, 140.3; MS (MALDI-TOF): m/z calcd for $C_{64}H_{104}S_4Br_2$ $[M]^+$ 1158.54, found 1158.63; HR-MS (APCI) m/z calcd for $C_{64}H_{105}S_4Br_2$: $[M+H]^+$ 1159.54604, found 1159.54443.

PNTz4T (via the Suzuki coupling reaction)

4 (42 mg, 0.036 μmol), NTz-$Bpin_2$ (18 mg, 0.036 μmol), Aliquat 336 (8 mg), and toluene (3.2 mL) were added to a 5 mL reaction vial. The vial was purged with argon for 30 min, and 20% K_2CO_3 aq. (250 mg, 0.362 μmol), tetrakis(triphenylphosphine)palladium(0) (0.83 mg, 0. 72 μmol) were added. The vial was sealed and heated in a microwave reactor at 100 °C for 2 h. After cooling to room temperature, the reaction mixture was poured into a mixture of methanol (100 mL) and concentrated HCl (5 mL), and vigorously stirred for 6 h at room temperature. The precipitate was filtered and subjected to Soxhlet extraction sequentially with methanol, hexane, dichloromethane, chloroform, and finally chlorobenzene. The $CHCl_3$ and chlorobenzene fractions were concentrated and poured into methanol, respectively. The precipitates were collected by filtration to afford the polymer samples (chloroform fraction: 33 mg, 74%. chlorobenzene fraction: 4 mg, 9%) as metallic dark purple solids.

^{1}H NMR (500 MHz, o-DCB-d_4): δ 9.11 (br, 2H), 8.39 (br, 2H), 8.26 (br, 2H), 7.26 (br, 2H), 3.03 (br, 4H), 1.56 (br, 2H), 1.27 (br, 80H), 0.86 (br, 12H). Anal. Calcd for $C_{74}H_{106}N_4S_6$: C, 71.44; H, 8.59; N, 4.50. Found: C, 71.54; H, 8.56; N, 4.40. GPC (o-DCB, 140 °C): M_n = 21,800, M_w = 40,200,

PDI = 1.84 ($CHCl_3$ fraction), M_n = 25,200, M_w = 45,500, PDI = 1.81 (chlorobenzene fraction).

PNTz4Ti

7 (128 mg, 0.11 μmol), NTz-$Bpin_2$ (55 mg, 0.11 μmol), Aliquat 336 (4 drops), and toluene (7 mL) were added to a 5 mL reaction vial. The vial was purged with argon for 30 min, and 5 mL of 2M K_2CO_3 aq., palladium (II) bis(triphenylphosphine) dichloride (3.09 mg, 0.0044 mmol) were added. The vial was sealed and heated in a microwave reactor at 180 °C for 2 h. After cooling to room temperature, the reaction mixture was poured into a mixture of methanol (100 mL) and concentrated HCl (5 mL), and vigorously stirred for 6 h at room temperature. The precipitate was filtered and subjected to Soxhlet extraction sequentially with methanol, hexane, chloroform, 1,1,2-trichloroethane, and finally chlorobenzene. The 1,1,2-trichloroethane and chlorobenzene fractions were concentrated, and poured into methanol, respectively. The precipitates were collected by filteration to afford the polymer samples ($CHCl_3$ fraction: 22 mg, 16%; 1,1,2-trichloroethane fraction: 46 mg, 34%; chlorobenzene fraction: 48 mg, 35%) as metallic dark purple solids.

^{1}H NMR (500 MHz; *o*-DCB-d_4, 90 °C) δ 9.10 (s, 2H), 8.36 (s, 2H), 7.41 (m, 2H), 7.27 (m, 2H), 2.99 (m, 4H), 2.01 (m, 2H), 1.11–1.51 (m, 80H), 0.85 (m, 12H). Anal. Calcd for $C_{74}H_{106}N_4S_6$: C, 71.44; H, 8.59; N, 4.50%. Found. C, 71.49; H, 8.76; N, 4.66%. GPC (*o*-DCB, 140 °C): M_n = 6,200; M_w = 14,400; PDI = 2.31 ($CHCl_3$ fraction). M_n = 12,000; M_w = 18,900; PDI = 1.57 (1,1,2-trichloroethane fraction). M_n = 31,200; M_w = 45,300; PDI = 1.45 (chlorobenzene fraction).

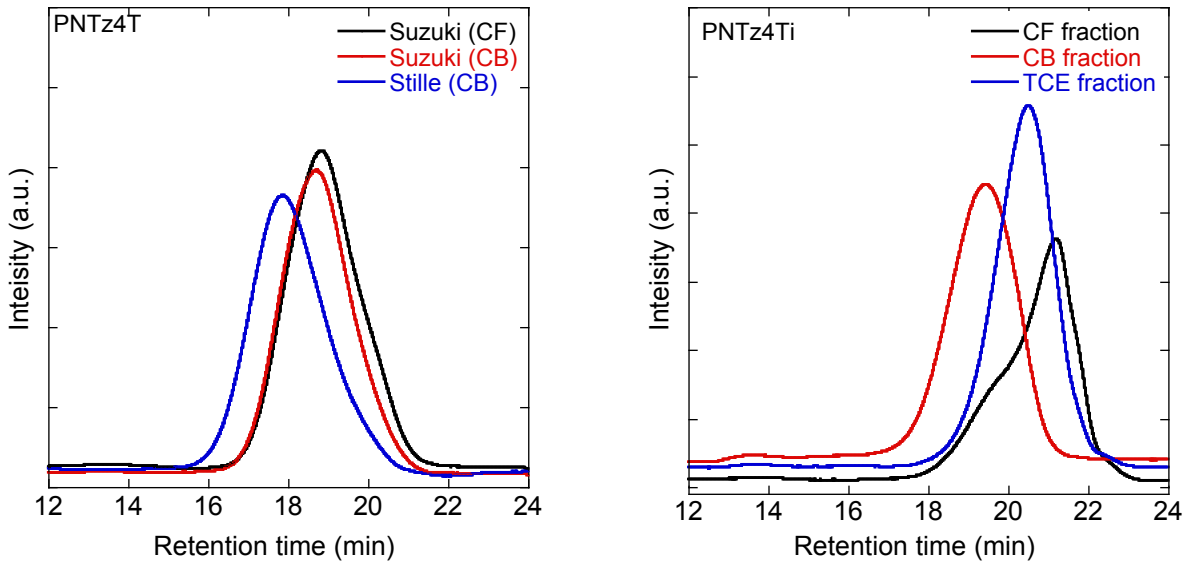
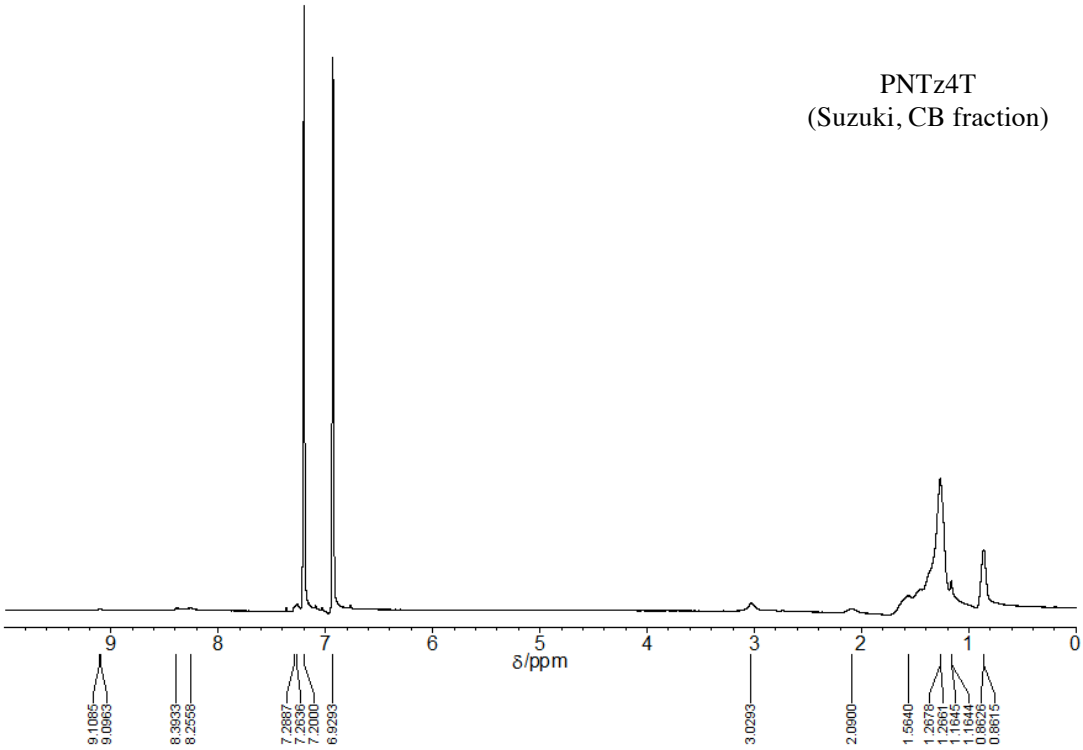
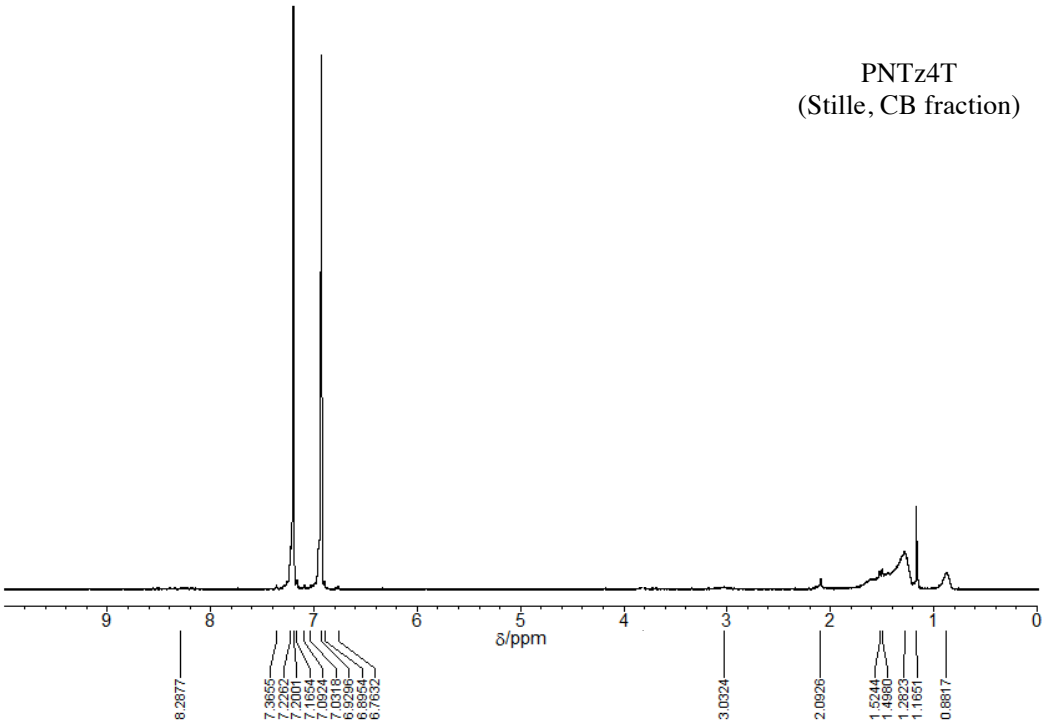


Figure S1. GPC chromatograms of the polymers

PNTz4T
(Suzuki, CB fraction)



PNTz4T
(Stille, CB fraction)



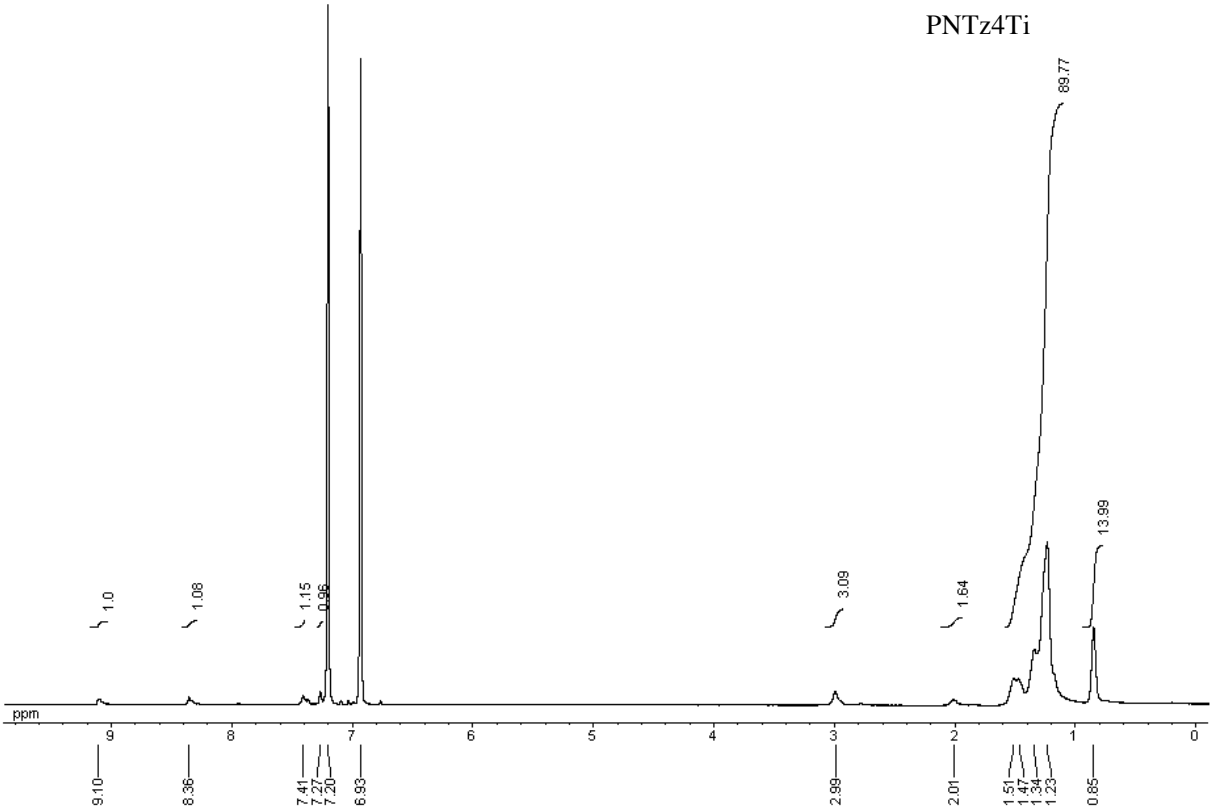


Figure S2. ^{1}H-NMR spectra of the polymers (o-DCB, 90ºC)

Instrumentation.

UV–vis absorption spectra were measured using a Shimadzu UV-3600 spectrometer. GIXD experiments were conducted at the SPring-8 on beamline BL19B2. The sample was irradiated 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). GIXD patterns were recorded with an X-ray energy of 12.39 keV (λ = 1 Å). Samples for the X-ray measurements were prepared by drop-casting the polymer solution on the FDTS-modified Si/SiO_2 substrate.

OFET Fabrication and Measurement.

Fabrication. All processes were performed in air. Heavily doped n^+-Si (100) wafers with 200-nm-thick thermally grown SiO_2 (C_i = 17.3 nF/cm^2) were used for the substrate. The Si/SiO_2 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 1*H*,1*H*,2*H*,2*H*-perfluorodecyltriethoxysilane (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 °C for 30 min under N_2. 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.

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_{on}/I_{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.