Electronic Supplementary Information for

Precision synthesis of fluorene-thiophene alternating copolymer by means of Suzuki-Miyaura catalyst-transfer condensation polymerization: importance of the position of alkyl-substituent on thiophene of biaryl monomer to suppress disproportionation

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Contents

1. Materials

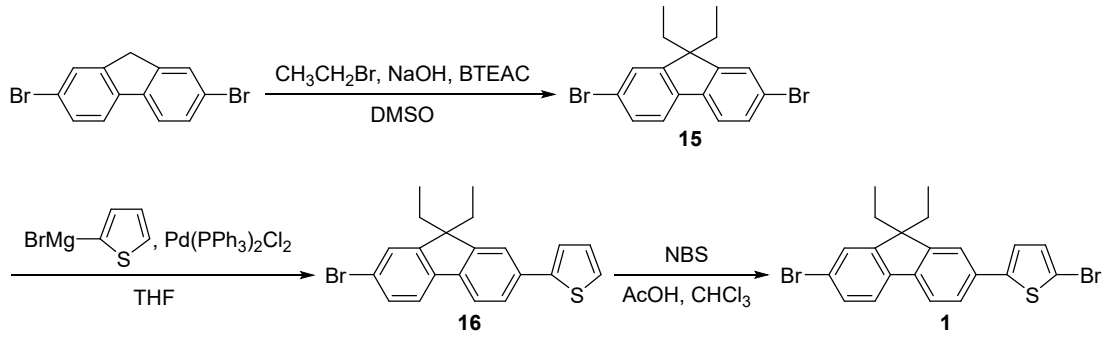
All starting materials were purchased from commercial suppliers (TCI, Aldrich, Wako and Kanto) and used without further purification. Commercially available dehydrated tetrahydrofuran (THF, stabilizer-free, Kanto) was used as a dry solvent. Synthesis of **9**, **12**, **13**, and **14** were prepared according to the literatures.[1-4]

2. General

^{1}H and ^{13}C NMR spectra were obtained on ECA-600 and ECA-500 spectrometers. The internal standard for ^{1}H NMR spectra in $CDCl_3$ was tetramethylsilane (0.00 ppm) and the internal standard for ^{13}C NMR spectra in $CDCl_3$ was the midpoint of $CDCl_3$ (77.0 ppm). IR spectra were recorded on a JASCO FT/IR-410. All melting points were measured with a Yanagimoto hot stage melting point apparatus without correction. Column chromatography was performed on silica gel (Kieselgel 60, 230–400 mesh, Merck) with a specified solvent. Purification of products was carried out by LC908-C60 recycling preparative HPLC (eluent, $CHCl_3$) with two JAIGEL columns (1H-40 and 2H-40). The M_n and M_w/M_n values of polymer were measured with a Tosoh HLC-8320 gel permeation chromatography unit (GPC; eluent, chloroform; calibration, polystyrene standards) with two TSK-gel columns (2 × Multipore HZ-M). MALDI-TOF mass spectra were recorded on a Shimadzu/Kratos AXIMA-CFR plus and Shimadzu AXIMA Confidence in the reflectron ion mode by use of a laser (λ = 337 nm). Dithranol (1,8-dihydroxy-9[10H]-anthracenone) and DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile) were used as the matrix for the MALDI-TOF mass measurements.

3. Model reaction

3-1. Synthesis of **1**



3-1-1. Synthesis of **15**

Into a solution of 2,7-dibromofluorne (0.319 g, 0.985 mmol) and benzyltriethylammonium chloride (BTEAC) (0.0038 g, 0.0167 mmol) in DMSO (3.2 ml) and 50% NaOH aq. (0.8 mL) was added 1-bromoethane (0.26 mL, 3.5 mmol) at room temperature. The mixture was stirred for 24 h, then the reaction was quenched with 1 M HCl. The whole was extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane) to give 0.337 g of **15** as a colorless solid (89%): mp 155.0-156.0 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.53 (s, 1 H), 7.46 (s, 1 H) 7.45 (d, *J* = 2.0 Hz, 1 H), 7.44 (d, *J* = 1.4 Hz, 2 H), 1.99 (q, *J* = 7.5 Hz, 4 H), 0.32 (t, *J* = 7.5 Hz, 6 H).

3-1-2. Synthesis of **16**

All glass apparatus was dried prior to use. Mg metal (0.332 g, 0.0722 mmol) was placed in the flask, and the flask was heated under reduced pressure. The atmosphere in the flask was replaced with argon and cooled to room temperature. Dry THF (15.0 mL) was added under a stream of nitrogen, and the atmosphere in the flask was replaced with argon. A solution of 2-bromothiphene (0.96 mL, 10 mmol) in dry THF (5.0 mL) was added, and the mixture was irradiated with ultrasonic waves for 1 h. Into the mixture was added a solution of **15** (3.862 g, 10.2 mmol) in dry THF (8.0 mL) and a solution of bis(triphenylphosphine)palladium(II) dichloride ($Pd(PPh_3)_2Cl_2$) (0.0719 g, 0.102 mmol) in dry THF (5.0 mL), and the mixture was stirred at room temperature for 24 h. The reaction was quenched with sat. NH_4Cl aq., and the mixture was extracted with $CHCl_3$. The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane) to give 0.0200 g of **16** as an yellow-green viscous oil (35%); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.65 (d, *J* = 8.0 Hz, 1 H), 7.60 (dd, *J* = 8.0 and 2.0 Hz, 1 H), 7.56-7.53 (m, 2 H), 7.47-7.46 (m, 2 H), 7.38-7.37 (m, 1 H), 7.29 (d, *J* = 4.5 Hz, 1 H), 7.10 (dd, *J* = 5.0 and 3.5 Hz, 1 H), 2.09-2.00 (m, 4 H), 0.35 (t, *J* = 7.5 Hz, 6 H).

3-1-3. Synthesis of **1**

N-bromosuccinimide (NBS) (0.662 g, 3.72 mmol) was portionally added into a solution of **16** (1.393 g, 3.63 mmol) in $CHCl_3$ (7.0 mL) and acetic acid (21.0 mL), and the mixture was stirred under reflux for 3 min. The reaction was quenched with aqueous solution of sodium thiosulfate after the mixture was cooled to room temperature. The whole was extracted with $CHCl_3$. The combined organic layers were washed with Na_2CO_3 aq. and

water, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane) to give 1.779 g of **1** as an yellow viscous oil (94%); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.65 (d, *J* = 8.0 Hz, 1 H), 7.56 (dd, *J* = 6.6 and 2.0 Hz, 1 H), 7.50 (dd, *J* = 7.7 and 1.6 Hz, 1 H), 7.47-7.46 (m, 2 H), 7.43 (d, *J* = 1.4 Hz, 1 H), 7.11 (d, *J* = 4.0 Hz, 1 H), 7.05 (d, *J* = 4.0 Hz, 1 H), 2.08-1.98 (m, 4 H), 0.34 (t, *J* = 3.6 Hz, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.3, 150.4, 146.3, 140.4, 139.9, 132.9, 130.9, 130.1, 126.3, 124.8, 123.1, 121.3, 121.1, 119.8, 111.2, 32.7, 8.5; IR (KBr) 1655, 1542, 1456, 1377, 1245, 1132, 1061, 1007, 962, 875, 815, 794 cm^{-1}.

3-2. Synthesis of **4a** and **6a**

All glass apparatus was dried prior to use. **1** (0.547 g, 1.18 mmol), **2** (0.104 g, 0.510 mmol), CsF (0.302 g, 1.99 mmol), 18-crown-6 (1.02 g, 3.88 mmol), and AmphosPd G2 (0.0056 g, 0.0097 mmol) were placed in the flask, and the atmosphere in the flask was replaced with argon. Dry THF (10.0 mL) and distilled water (0.5 mL) were added to the flask via a syringe. The mixture was degassed with argon and stirred at room temperature for 20 h. 5 M HCl was added, and the mixture was extracted with $CHCl_3$. The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by preparative HPLC (eluent: $CHCl_3$) to give 0.013 g of **4a** as an yellow solid (11%) and 0.006 g of **6a** as an yellow solid (3%): **4a**: mp 192.0-194.0 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.77 (d, *J* = 7.8 Hz, 1 H), 7.73 (d, *J* = 7.8 Hz, 1 H), 7.69-7.64 (m, 5 H), 7.60-7.59 (m, 2 H), 7.56 (s, 1 H), 7.47 (t, *J* = 7.8 Hz, 2 H), 7.41 (t, *J* = 7.8 Hz, 2 H), 7.38-7.35 (m, 2 H), 7.33 (d, *J* = 4.2 Hz, 1 H), 7.29 (t, *J* = 7.2 Hz, 1 H), 2.10 (q, *J* = 7.2 Hz, 4 H), 0.40 (t, *J* = 7.2 Hz, 6 H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 158.3, 156.1, 151.0, 146.2, 141.7, 140.2, 133.9, 128.9, 128.8, 127.4, 127.2, 127.1, 125.6, 124.0, 123.8, 119.9, 32.9, 8.6; IR (KBr) 1719, 1686, 1654, 1638, 1543, 1509, 1467, 1261, 806, 756 cm^{-1}. **6a**: mp 149.0-152.0 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.68-7.62 (m, 4 H), 7.57-7.55 (m, 2 H), 7.47-7.46 (m, 2 H), 7.40 (t, *J* = 7.8 Hz, 2 H), 7.36 (d, *J* = 3.6 Hz, 1 H), 7.32 (d, *J* = 3.6 Hz, 1 H), 7.30 (t, *J* = 7.8 Hz, 1 H), 2.09-2.01 (m, 4 H), 0.36 (t, *J* = 7.2 Hz, 6 H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 152.3, 144.0, 140.0, 133.6, 130.1, 128.9, 127.5, 126.2, 125.6, 124.8, 124.0, 120.2, 119.9, 32.7, 8.5; IR (KBr) 1597, 1448, 1402, 1252, 1061, 876, 800, 755 cm^{-1}.

3-3. Synthesis of **4b** and **6b**

All glass apparatus was dried prior to use. **1** (0.140 g, 0.303 mmol), **3** (0.031 g, 0.15 mmol), CsF (0.092 g, 0.60 mmol), and 18-crown-6 (0.318 g, 1.20 mmol) were placed in the flask, and the atmosphere in the flask was replaced with argon. Dry THF (4.0 mL)

and distilled water (0.4 mL) were added to the flask via a syringe, and the atmosphere in the flask was replaced with argon. The mixture was added to a solution of *t*-Bu_3PPd G2 (0.0047 g, 0.0093 mmol) in dry THF (1.0 mL, degassed with argon), and the mixture was stirred at room temperature for 19 h. 5 M HCl was added, and the mixture was extracted with $CHCl_3$. The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by preparative HPLC (eluent: $CHCl_3$) to give 0.012 g of **4b** as a brown solid (34%) and 0.013 g of **6b** as a brown solid (19%): **4b**: mp 162.0-168.0 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.70 and 7.68 (2s, 2 H), 7.61 and 7.60 (2dd, *J* = 8.0 and 2.0 Hz, 2 H), 7.55 and 7.54 (2d, *J* = 8.5 Hz, 2 H), 7.39-7.38 (m, 1 H), 7.30-7.29 (m, 2 H), 7.24-7.22 (m, 2 H), 7.18 (d, *J* = 4.0 Hz, 1 H), 7.11 (dd, *J* = 5.5 and 4.0 Hz, 1 H), 7.04 (dd, *J* = 4.5 and 3.0 Hz, 1 H), 2.10 (q, *J* = 7.5 Hz, 4 H), 0.39 (t, *J* = 7.5 Hz, 6 H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 150.9, 145.0, 143.8, 140.5, 137.5, 136.4, 133.4, 128.1, 127.9, 125.0, 124.7, 124.6, 124.5, 124.3, 123.5, 122.9, 120.2, 120.1, 119.8, 32.8, 8.6; IR (KBr) 1637, 1542, 1509, 1471, 1421, 1265, 839, 800 cm^{-1}. **6b**: mp 182.0-185.0 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.66-7.52 (m, 4 H), 7.47-7.45 (m, 2 H), 7.28 (d, *J* = 4.0 Hz, 1 H), 7.23-7.21 (m, 2 H), 7.17 (d, *J* = 4.0 Hz, 1 H), 7.04 (dd, *J* = 5.0 and 3.5 Hz, 1 H), 2.10-1.99 (m, 4 H), 0.35 (t, *J* = 7.5 Hz, 6 H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 152.3, 140.0, 137.4, 136.6, 130.1, 127.9, 126.2, 124.8, 124.6, 124.4, 123.7, 123.6, 121.0, 120.2, 119.8, 32.7, 8.5; IR (KBr) 1736, 1719, 1702, 1685, 1655, 1637, 1560, 1543, 1509, 1458, 1450, 1262, 1101, 878, 839, 799, 770 cm^{-1}.

3-4. General procedure for model reaction

All glass apparatus was dried prior to use. **1** (0.15 mmol), **2** or **3** (0.30 mmol), CsF (0.625 mmol), 18-crown-6 (1.19 mmol), and AmphosPd G2 or *t*-Bu_3PPd G2 (0.0093 mmol) were placed in the flask, and the atmosphere in the flask was replaced with argon. Dry THF (3.0 mL) and distilled water (0.3 mL) were added to the flask via a syringe. The mixture was degassed with argon and stirred at room temperature for 23 h. 5 M HCl was added, and the mixture was extracted with $CHCl_3$. The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to give brown viscous oil.

3-5. Suzuki-Miyaura coupling reaction of equimolar 2-bromothiophene and 2-bromo-9,9-diethylfluorene with 0.5 equivalent of **2**

All glass apparatus was dried prior to use. **2** (0.15 mmol), 2-bromothiphene (0.15 mmol), 2-bromo-9,9-diethylfluorene (0.15 mmol), CsF (0.62 mmol), 18-crown-6 (1.18 mmol), and *t*-Bu_3PPd G2 or AmPhosPd G2 (0.0091 mmol) were placed in a flask, and the atmosphere in the flask was replaced with argon. Dry THF (3.0 mL) and distilled water

(0.3 mL) were added to the flask via a syringe. The mixture was degassed with argon and stirred at room temperature for 24 h. 5 M HCl was added, and the mixture was extracted with $CHCl_3$ and washed with sat. KCl aq. The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to give yellow viscous oil.

4. Synthesis of PinB-F8T(3)-Br

4-1. Synthesis of **10**

All glass apparatus was dried prior to use. Mg metal 0.30 g (11 mmol) was placed in the flask, and the flask was heated under reduced pressure. The atmosphere in the flask was replaced with argon and cooled to room temperature. Dry THF (10.0 mL) was added under a stream of nitrogen, and the atmosphere in the flask was replaced with argon. A solution of 2-bromo-3-octylthiophene (**7**) (2.77 g, 9.93 mmol) in dry THF (5.0 mL) was added, and the mixture was stirred at room temperature for 1 h. Half of the solution (7.5 mL) was added to a solution of **9** (2.98 g, 5.00 mmol) and Pd(dppf)Cl_2 (0.15 g, 0.20 mmol) in dry THF (80 mL), and the mixture was stirred under reflux for 2 days. The reaction was quenched with water after the mixture was cooled to room temperature. The mixture was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by preparative HPLC (eluent: $CHCl_3$) to give 3.14 g of **10** as a brown viscous oil (88%); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.81 (d, J = 7.7 Hz, 1 H), 7.74 (d, J = 6.3 Hz, 1 H), 7.71 (t, J = 7.7 Hz, 2 H), 7.24 (d, J = 5.1 Hz, 1 H), 7.00 (d, J = 4.8 Hz, 1 H), 2.05-1.91 (m, 4 H), 1.65-1.62 (m, 2 H), 1.39 (s, 12 H), 1.39-1.04 (m, 31 H), 0.86-0.82 (m, 4 H), 0.81-0.79 (m, 6 H), 0.64-0.63 (m, 4 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.5, 148.8, 143.7, 140.1, 138.6, 138.5, 133.9, 133.8, 129.6, 128.8, 128.1, 123.8, 123.4, 120.1, 119.0, 83.7, 55.1, 40.2, 31.9, 31.8, 31.1, 30.4, 30.0, 29.6, 29.5, 29.2, 28.9, 26.5, 24.9, 23.8, 22.7, 22.6, 14.1; IR (neat) 2926, 2855, 1609, 1509, 1459, 1413, 1356, 1312, 1260, 1145, 1082, 1043, 853, 825 cm^{-1}.

4-2. Synthesis of **PinB-F8T(3)-Br**

Into a solution of **10** (2.20 g, 3.10 mmol) in $CHCl_3$ (35 mL) was added a solution of NBS (0.54 g, 3.0 mmol) in $CHCl_3$ (35 mL) and acetic acid (15 mL) at 0 °C, and the mixture was stirred at room temperature for 1 h. The reaction was quenched with water, and the whole was extracted with CH_2Cl_2. The combined organic layers were washed with brine and aqueous solution of sodium thiosulfate, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by preparative HPLC (eluent: $CHCl_3$) to give 1.72 g of **PinB-F8T(3)-Br** as a brown viscous oil (70%); ^{1}H NMR

($CDCl_3$, 600 MHz) δ 7.82-7.80 (m, 1 H), 7.75-7.69 (m, 3 H), 7.34-7.32 (m, 2 H), 6.94 (s, 1 H), 2.60 (t, *J* = 8.0 Hz, 2 H), 1.99-1.97 (m, 4 H), 1.59 (t, *J* = 7.1 Hz, 2 H), 1,39 (s, 12 H), 1.29-1.03 (m, 31 H), 0.90-0.84 (m, 4 H), 0.81 (t, *J* = 7.1 Hz, 6 H), 0.61-0.60 (m, 4 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.6, 150.1, 143.5, 140.5, 140.1, 133.8, 132.2, 128.8, 128.0, 127.8, 123.6, 120.2, 119.1, 110.0, 82.7, 55.2, 40.2, 32.7, 31.8, 31.0, 30.0, 29.5, 29.4, 29.2, 28.8, 24.9, 23.8, 22.7, 22.6, 14.1; IR (neat) 2925, 2854, 1609, 1459, 1412, 1356, 1145, 1082, 964, 825 cm^{-1}.

5. Synthesis of PinB-F8T(4)-Br

5-1. Synthesis of **11**

All glass apparatus was dried prior to use. Into a solution of 3-octylthiophene (**8**) (0.394 g, 2.01 mmol) in dry THF (1.6 mL) was added 1 M solution of 2,2,6,6-tetramethylpiperidinylmagnesium chloride lithium chloride complex in THF (1.5 mL, 1.5 mmol), and the solution was stirred at room temperature for 5 h. The reaction mixture was added to a solution of **9** (0.597 g, 1.00 mmol) and Pd(dppf)Cl_2 (0.015 g, 0.020 mmol) in dry THF (4.8 mL), and the mixture was stirred under reflux for 24 h. The reaction was quenched with water after the mixture was cooled to room temperature. The mixture was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by preparative HPLC (eluent: $CHCl_3$) to give 0.318 g of **11** as a brown viscous oil (45%); ^1H NMR ($CDCl_3$, 600 MHz) δ 7.80 (d, *J* = 7.6 Hz, 1 H), 7.73 (s, 1 H), 7.69-7.67 (m, 2 H), 7.57 (dd, *J* = 8.3 and 1.4 Hz, 1 H), 7.53 (s, 1 H), 7.22 (s, 1 H), 6.88 (s, 1 H), 2.63 (t, *J* = 7.6 Hz, 2 H), 2.04-1.95 (m, 4 H), 1.70-1.65 (m, 2 H), 1.39 (s, 1 H), 1.37-1.02 (m, 30 H), 0.89 (t, *J* = 6.9 Hz, 3 H), 0.80 (t, *J* = 6.9 Hz, 6 H), 0.62-0.58 (m, 4 H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 152.1, 150.0, 144.7, 144.4, 143.7, 140.3, 133.9, 133.8, 128.8, 124.6, 124.4, 120.4, 119.9, 119.2, 118.9, 83.7, 55.2, 40.2, 31.9, 31.8, 30.7, 30.5, 30.0, 29.5, 29.4, 29.3, 29.2, 29.1, 24.9, 23.6, 22.7, 22.6, 14.1, 14.0; IR (neat) 2925, 2854, 1638, 1509, 1459, 1405, 1354, 1145, 820 cm^{-1}.

5-2. Synthesis of **PinB-F8T(4)-Br**

A solution of NBS (0.17 g, 0.96 mmol) in $CHCl_3$ (10 mL) was added into a solution of **11** (0.71 g, 1.0 mmol) in $CHCl_3$ (10 mL) at 0 °C, and the mixture was stirred at room temperature for 1.5 h. The reaction was quenched with water, and the whole was extracted with CH_2Cl_2. The combined organic layers were washed with brine and water, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by preparative HPLC (eluent: $CHCl_3$) to give 0.58 g of **PinB-F8T(4)-Br** as a brown

viscous oil (73%); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.80 (d, J = 7.6 Hz, 1 H), 7.73 (s, 1 H), 7.69-7.67 (m, 2 H), 7.57 (dd, J = 8.3 and 1.4 Hz, 1 H), 7.53 (s, 1 H), 7.22 (s, 1 H), 6.88 (s, 1 H), 2.63 (t, J = 7.6 Hz, 2 H), 2.04-1.95 (m, 4 H), 1.70-1.65 (m, 2 H), 1.39 (s, 1 H), 1.37-1.02 (m, 30 H), 0.89 (t, J = 6.9 Hz, 3 H), 0.80 (t, J = 6.9 Hz, 6 H), 0.62-0.58 (m, 4 H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 152.1, 150.0, 144.7, 144.4, 143.7, 140.3, 133.9, 133.8, 128.8, 124.6, 124.4, 120.4, 119.9, 119.2, 118.9, 83.7, 55.2, 40.2, 31.9, 31.8, 30.7, 30.5, 30.0, 29.5, 29.4, 29.3, 29.2, 29.1, 24.9, 23.6, 22.7, 22.6, 14.1, 14.0; IR (neat) 2926, 2854, 1609, 1491, 1459, 1418, 1355, 1311, 1258, 1145, 1113, 1082, 963, 864, 692 cm^{-1}.

6. General procedure for Suzuki-Miyaura coupling polymerization

All glass apparatus was dried prior to use. Addition of reagents to a reaction flask and withdrawal of a small aliquot of the reaction mixture for analysis were carried out via a syringe from a three-way stopcock under a stream of nitrogen. A round-bottomed flask equipped with a three-way stopcock was heated under reduced pressure, and then cooled to room temperature under an argon atmosphere. Pd initiator **12** or **13** (0.0029 mmol), CsF (0.10 mmol), and 18-crown-6 (0.19 mmol) were placed in the flask, and the atmosphere in the flask was replaced with argon. Dry THF (3.0 mL) and distilled water (0.10 mL) were added to the flask via a syringe, and the mixture was degassed with argon and stirred at room temperature for 1 h. A solution of monomer **PinB-F8T(3)-Br** or **PinB-F8T(4)-Br** (0.024 mmol) in dry THF (1.0 mL, degassed with argon) was added to the mixture of initiator, via a cannula, and the reaction mixture was stirred at room temperature. After a specific time, 6 M hydrochloric acid was added, and the mixture was extracted with $CHCl_3$. The organic layers were washed with sat. KCl aq., dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to give polymer.

7. General procedure for diblock copolymerization

All glass apparatus was dried prior to use. Addition of reagents to a reaction flask and withdrawal of a small aliquot of the reaction mixture for analysis were carried out via a syringe from a three-way stopcock under a stream of nitrogen. A round-bottomed flask equipped with a three-way stopcock was heated under reduced pressure, and then cooled to room temperature under an argon atmosphere. Pd initiator **13** (0.003 mmol) and 18-crown-6 (0.20 mmol) were placed in the flask, and the atmosphere in the flask was replaced with argon. Dry THF (2.0 mL) and 0.96 M solution of CsF (0.1 mL, 0.096 mmol) in distilled water were added to the flask via a syringe, and the mixture was degassed with argon and stirred at room temperature for 1 h. A solution of monomer **PinB-F8T(4)-Br** (0.024 mmol) in dry THF (1.0 mL, degassed with argon) was added to the mixture of

initiator, via a cannula, and the reaction mixture was stirred at room temperature for 1 h. Then, a solution of the second monomer **9** (0.030 mmol) or **14** (0.076 mmol) in dry THF (1.0 mL, degassed with argon) was added to the reaction mixture. After 18-19 h, 6 M hydrochloric acid was added, and the mixture was extracted with $CHCl_3$. The organic layers were washed with sat. KCl aq., dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to give diblock copolymer.

8. General procedure for triblock copolymerization

All glass apparatus was dried prior to use. Addition of reagents to a reaction flask and withdrawal of a small aliquot of the reaction mixture for analysis were carried out via a syringe from a three-way stopcock under a stream of nitrogen. A round-bottomed flask equipped with a three-way stopcock was heated under reduced pressure, and then cooled to room temperature under an argon atmosphere. Pd initiator **13** (0.003 mmol) and 18-crown-6 (0.20 mmol) were placed in the flask, and the atmosphere in the flask was replaced with argon. Dry THF (2.0 mL) and 0.96 M solution of CsF in distilled water (0.1 mL, 0.0096 mmol) were added to the flask via a syringe, and the mixture was degassed with argon and stirred at room temperature for 1 h. A solution of monomer **14** (0.031 mmol) or **9** (0.025 mmol) in dry THF (2.0 mL, degassed with argon) was added to the mixture of initiator via a cannula, and the reaction mixture was stirred at room temperature for 1 h. Then, a solution of the second monomer **PinB-F8T(4)-Br** (0.021 mmol) in dry THF (1.0 mL, degassed with argon) was added, and the reaction mixture was stirred at room temperature for 45 min-1.5 h. Then, a solution of the third monomer **9** (0.027 mmol) or **14** (0.032 mmol) in dry THF (1.0 mL, degassed with argon) was added. After 24-45 h, 6 M hydrochloric acid was added, and the mixture was extracted with $CHCl_3$. The organic layers were washed with sat. KCl aq., dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to give triblock copolymer.

9. Supporting figures

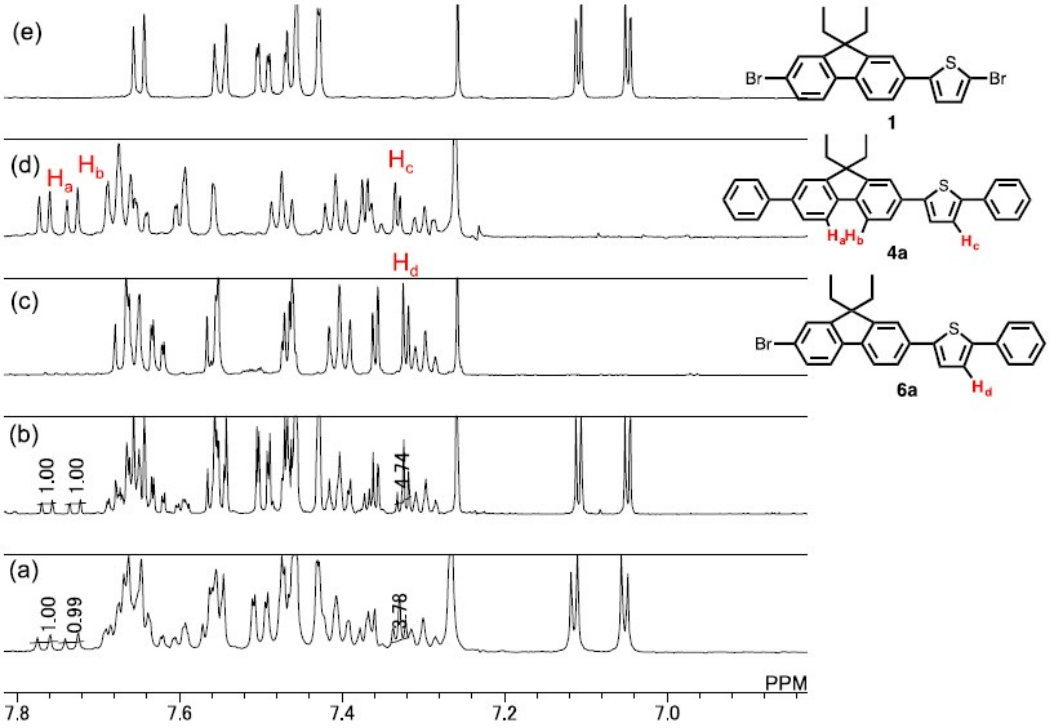


Fig. S1 ^{1}H NMR spectra of the products obtained by Suzuki-Miyaura coupling reaction of **1** with 0.5 equivalent of **2** in the presence of (a) *t*Bu$_3$PPd G2, (b) AmPhosPd G2 and CsF/18-crown-6 at room temperature. Authentic samples of (c) **6a**, (d) **4a**, and (e) **1**.

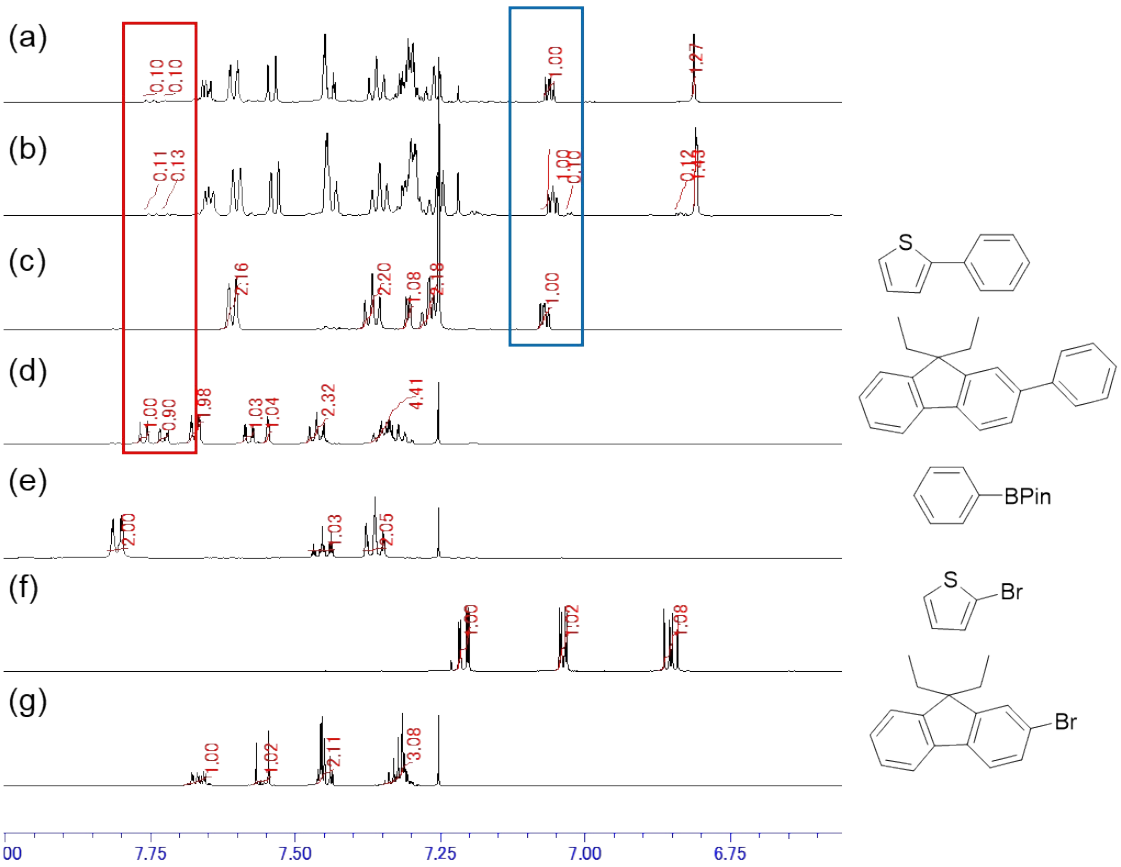


Fig. S2 ^{1}H NMR spectra of the products obtained by Suzuki-Miyaura coupling reaction of equimolar 2-bromothiophene and 2-bromo-9,9-diethylfluorene with 0.5 equivalent of **2** in the presence of (a) *t*Bu$_3$PPd G2, (b) AmPhosPd G2 and CsF/18-crown-6 at room temperature. Authentic samples of (c) 2-phenylthiophene, (d) 9,9-diethyl-2-phenylfluorene, (e) **2**, (f) 2-bromothiophene, and (g) 2-bromo-9,9-diethylfluorene.

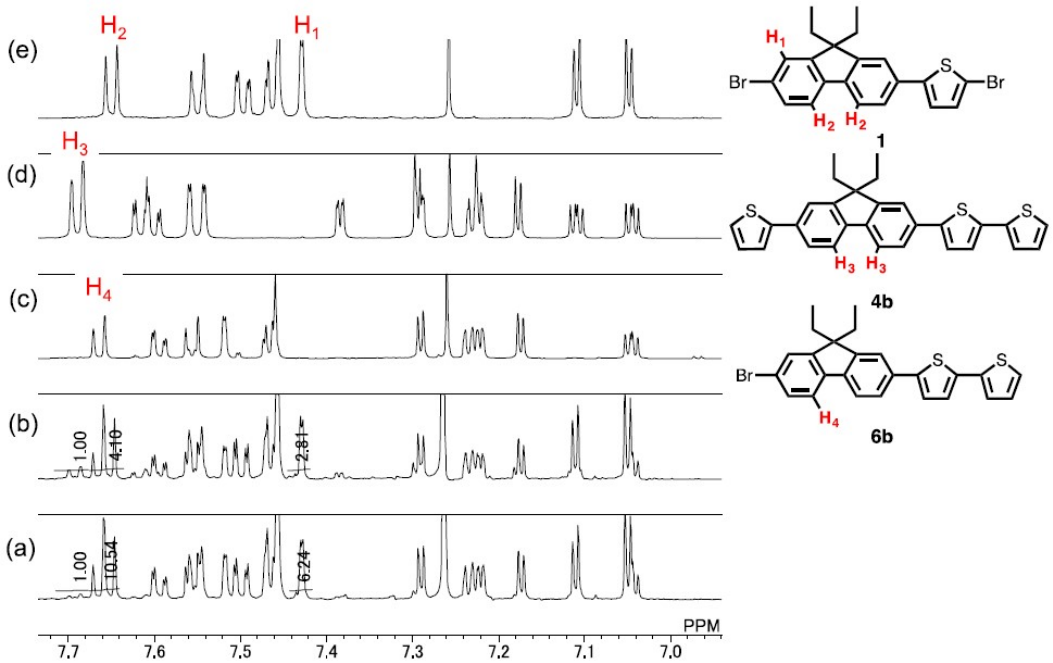


Fig. S3 ^{1}H NMR spectra of the products obtained by Suzuki-Miyaura coupling reaction of **1** with 0.5 equivalent of **3** in the presence of (a) AmPhosPd G2, (b) *t*Bu$_3$PPd G2 and CsF/18-crown-6 at room temperature. Authentic samples of (c) **6b**, (d) **4b**, and (e) **1**.

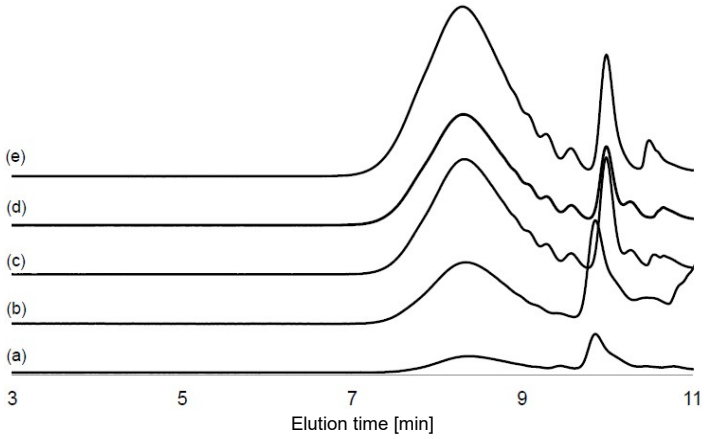


Fig. S4 GPC profiles of P(**F8T(3)8**) obtained by the polymerization of **PinB-F8T(3)8-Br** with 12.5 mol% of Pd initiator **12** in the presence of CsF/18-crown-6 at room temperature for (a) 15 min (M_n = 5750, M_w/M_n = 1.71), (b) 30 min (M_n = 6980, M_w/M_n = 1.64), (c) 2 h (M_n = 7610, M_w/M_n = 1.70), (d) 4 h (M_n = 7690, M_w/M_n = 1.75), and (e) 8 h (M_n = 8130, M_w/M_n = 1.77).

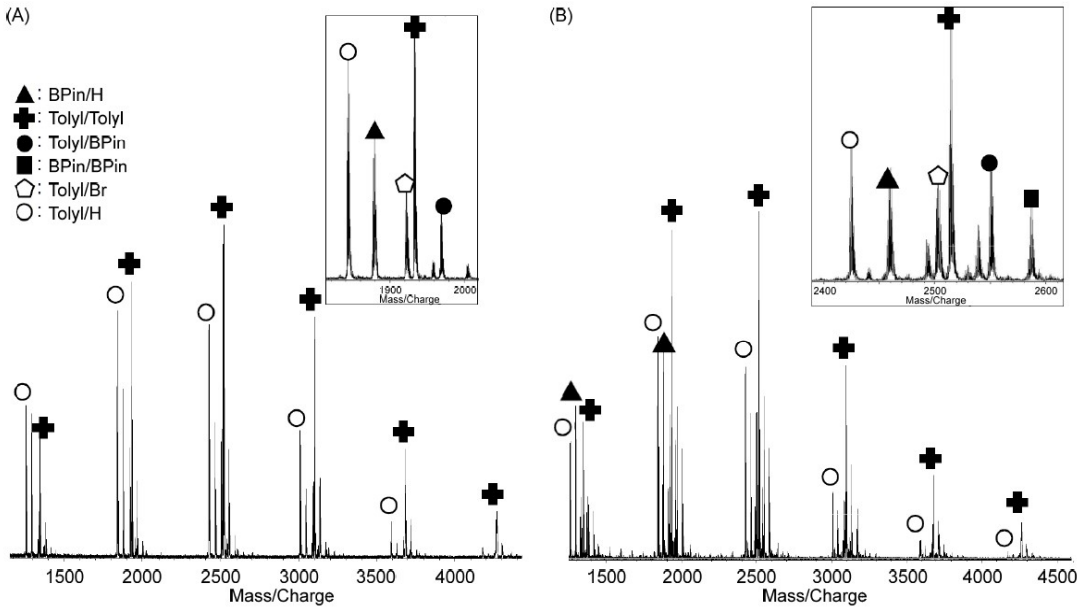


Fig. S5 MALDI-TOF mass spectra of P(**F8T(3)8**) obtained by the polymerization of **PinB-F8T(3)8-Br** with **12** ([**PinB-F8T(3)8-Br**]$_0$/[**12**]$_0$ = 8) in the presence of CsF/18-crown-6 at room temperature for (A) 15 min (M_n = 5750, M_w/M_n = 1.71) and (B) 2 h (M_n = 7610, M_w/M_n = 1.70).

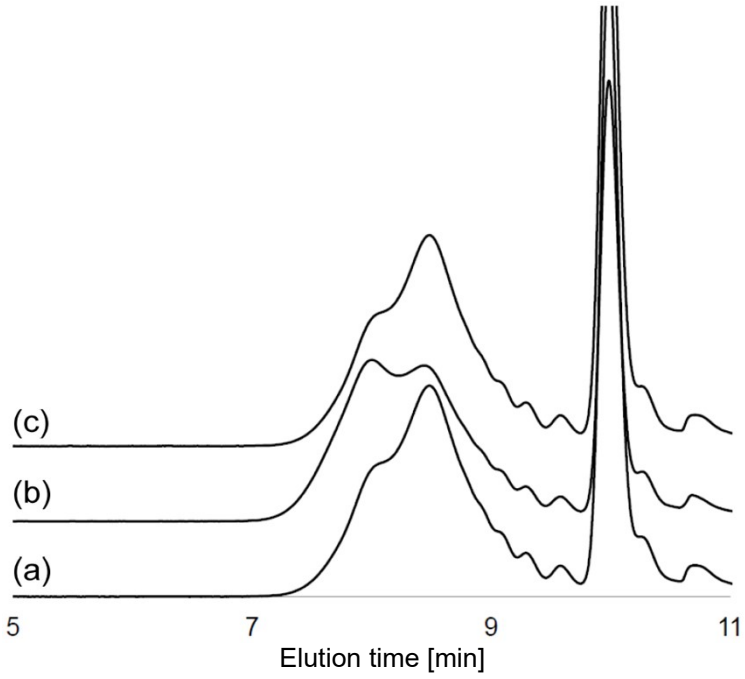


Fig. S6 GPC profiles of P(**F8T(3)8**) obtained by the polymerization of **PinB-F8T(3)8-Br** with 12.5 mol% of Pd initiator **12** in the presence of CsF/18-crown-6 at 0 °C for (a) 2 h (M_n = 7530, M_w/M_n = 1.61), (b) 4 h (M_n = 8780, M_w/M_n = 1.76), and (c) 8 h (M_n = 9240, M_w/M_n = 1.81).

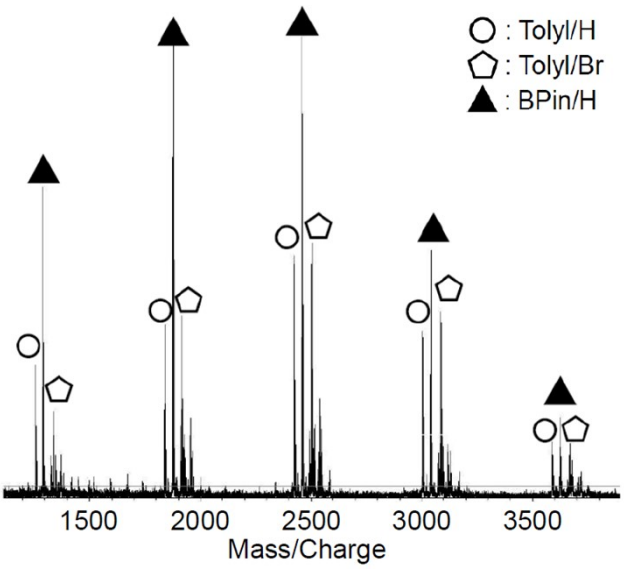


Fig. S7 MALDI-TOF mass spectrum of P(**F8T(3)8**) obtained by the polymerization of **PinB-F8T(3)8-Br** with **12** ([**PinB-F8T(3)8-Br**]$_0$/[**12**]$_0$ = 8) in the presence of CsF/18-crown-6 at 0 °C for 2 h (M_n = 7530, M_w/M_n = 1.61).

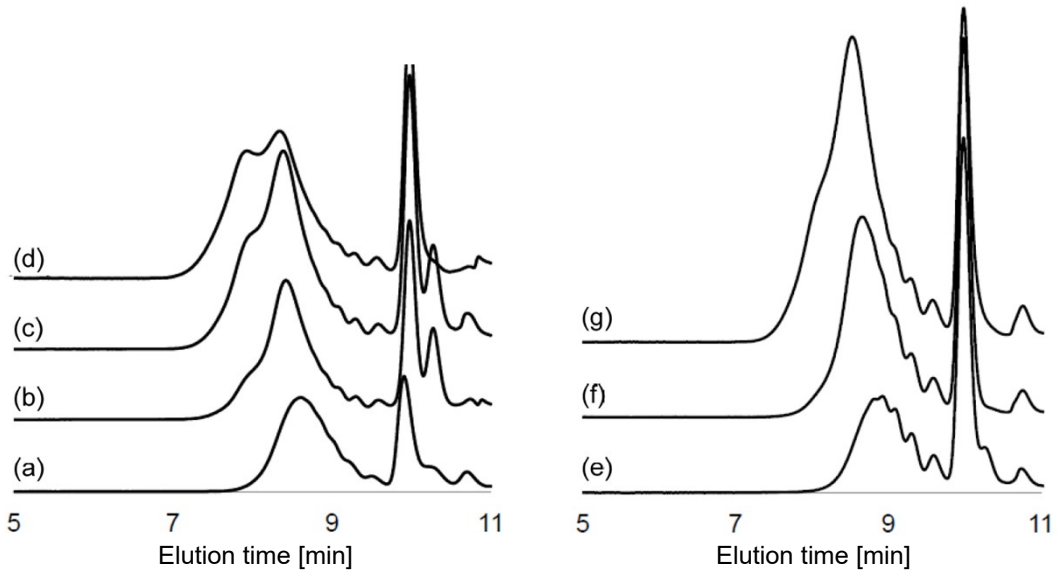


Fig. S8 GPC profiles of P(**F8T(3)8**) obtained by the polymerization of **PinB-F8T(3)8-Br** with 12.5 mol% of Pd initiator **13** in the presence of CsF/18-crown-6 at room temperature for (a) 30 min (M_n= 5830, M_w/M_n = 1.34), (b) 2 h (M_n = 7140, M_w/M_n = 1.57), (c) 4 h (M_n = 8220, M_w/M_n = 1.66), and (d) 8 h (M_n = 9440, M_w/M_n = 1.77), and at 0 °C for (e) 2 h (M_n = 3980, M_w/M_n = 1.33), (f) 4 h (M_n = 5160, M_w/M_n = 1.38), and (g) 8 h (M_n = 6880, M_w/M_n = 1.55).

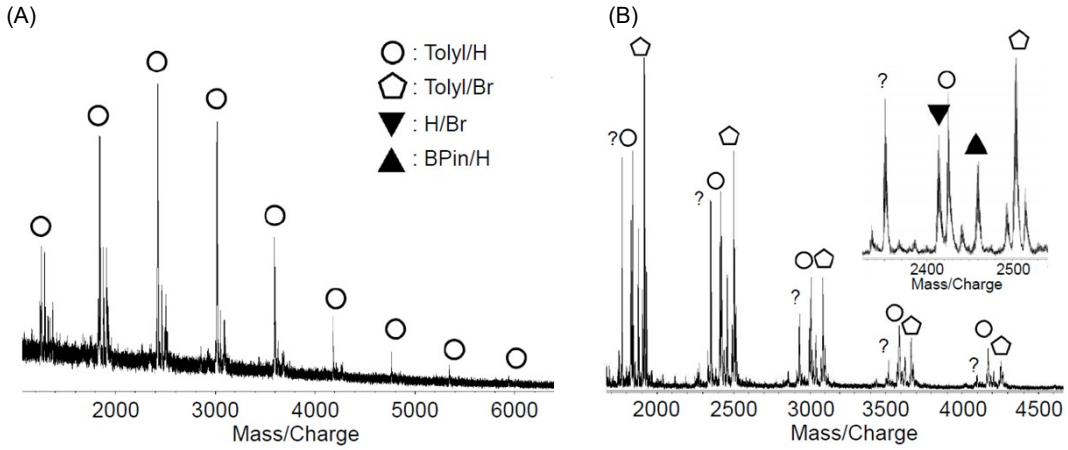


Fig. S9 MALDI-TOF mass spectra of P(**F8T(3)8**) obtained by the polymerization of **PinB-F8T(3)8-Br** with **13** ([**PinB-F8T(3)8-Br**]$_0$/[**13**]$_0$ = 8) in the presence of CsF/18-crown-6 at room temperature for (A) 30 min (M_n = 5830, M_w/M_n = 1.34) and (B) 2 h (M_n = 7140, M_w/M_n = 1.57).

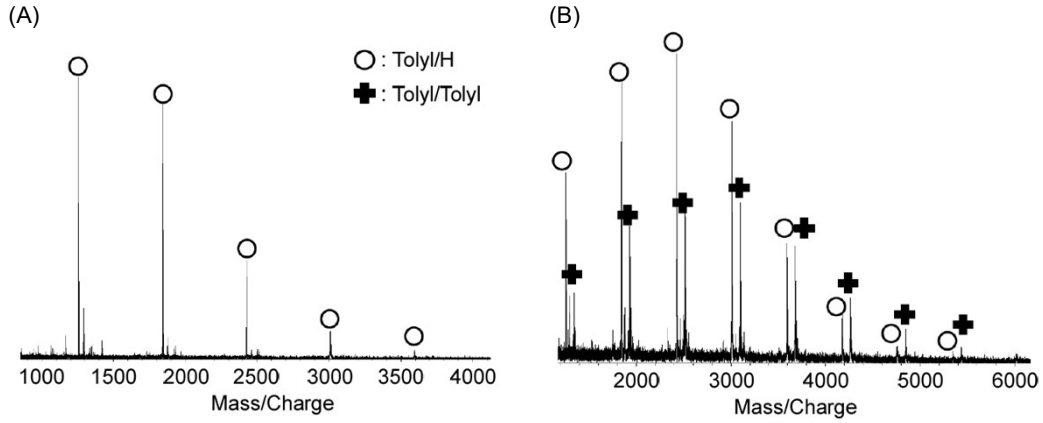


Fig. S10 MALDI-TOF mass spectra of P(**F8T(3)8**) obtained by the polymerization of **PinB-F8T(3)8-Br** with **13** ([**PinB-F8T(3)8-Br**]$_0$/[**13**]$_0$ = 5) in the presence of CsF/18-crown-6 at room temperature for (A) 15 min (M_n = 3900, M_w/M_n = 1.29) and (B) 2 h (M_n = 7030, M_w/M_n = 1.50).

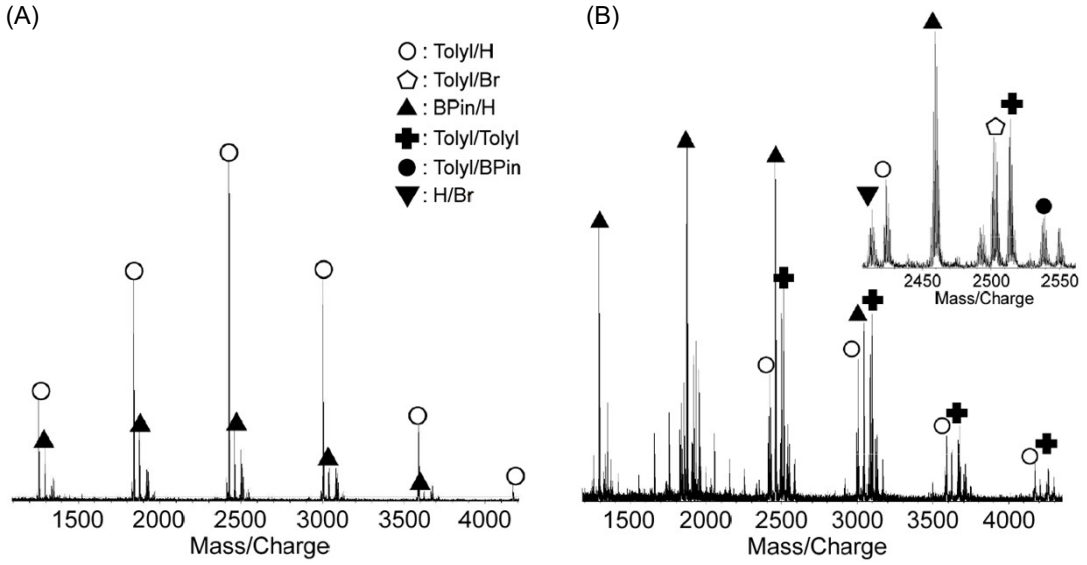


Fig. S11 MALDI-TOF mass spectra of P(**F8T(3)8**) obtained by the polymerization of **PinB-F8T(3)8-Br** with **13** ([**PinB-F8T(3)8-Br**]$_0$/[**13**]$_0$ = 8) in the presence of CsF/18-crown-6 at 0 °C for (A) 2 h (M_n = 3980, M_w/M_n = 1.33) and (B) 8 h (M_n = 6880, M_w/M_n = 1.55).

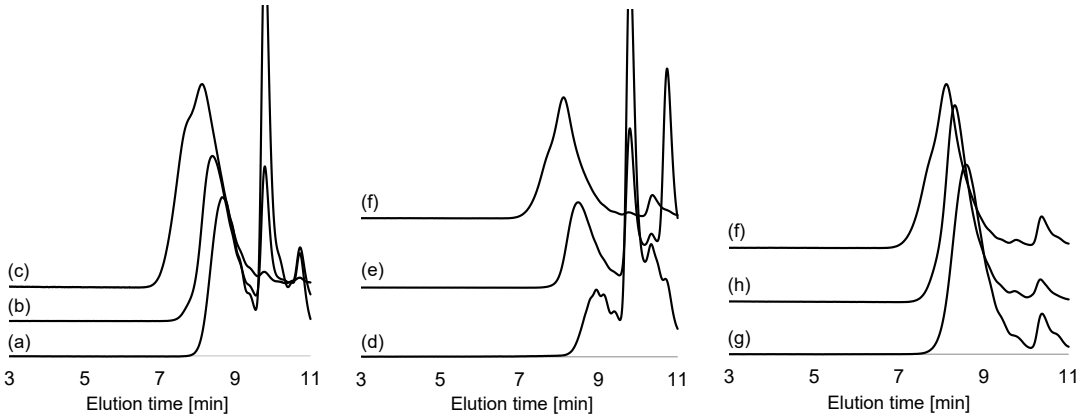


Fig. S12 GPC profiles of P(**F8T(4)8**) obtained by the polymerization of **PinB-F8T(4)8-Br** with 12.5 mol% of Pd initiator **12** in the presence of CsF/18-crown-6 at room temperature for (a) 15 min (M_n = 4470, M_w/M_n = 1.28), (b) 30 min (M_n = 6070, M_w/M_n = 1.47), (c) 24 h (M_n = 10400, M_w/M_n = 1.87), by the polymerization of **PinB-F8T(4)8-Br** with 6.3 mol% of Pd initiator **13** ([**PinB-F8T(4)8-Br**]$_0$/[**13**]$_0$ = 16) in the presence of CsF/18-crown-6 at room temperature for (d) 15 min (conversion of **PinB-F8T(4)8-Br** = 37%, M_n = 3350, M_w/M_n = 1.23), (e) 1 h (conversion of **PinB-F8T(4)8-Br** = 58%, M_n = 5690, M_w/M_n = 1.34), (f) 24 h (conversion of **PinB-F8T(4)8-Br** = 99%, M_n = 10500, M_w/M_n = 1.62), (g) by the polymerization of **PinB-F8T(4)8-Br** with 12.5 mol% of Pd initiator **13** ([**PinB-F8T(4)8-Br**]$_0$/[**13**]$_0$ = 8) in the presence of CsF/18-crown-6 at room temperature for 24 h (conversion of **PinB-F8T(4)8-Br** = 97%, M_n = 5210, M_w/M_n = 1.38), and (h) by the polymerization of **PinB-F8T(4)8-Br** with 8.3 mol% of Pd initiator **13** ([**PinB-F8T(4)8-Br**]$_0$/[**13**]$_0$ = 12) in the presence of CsF/18-crown-6 at room temperature for 26 h (conversion of **PinB-F8T(4)8-Br** = 98%, M_n = 7220, M_w/M_n = 1.42).

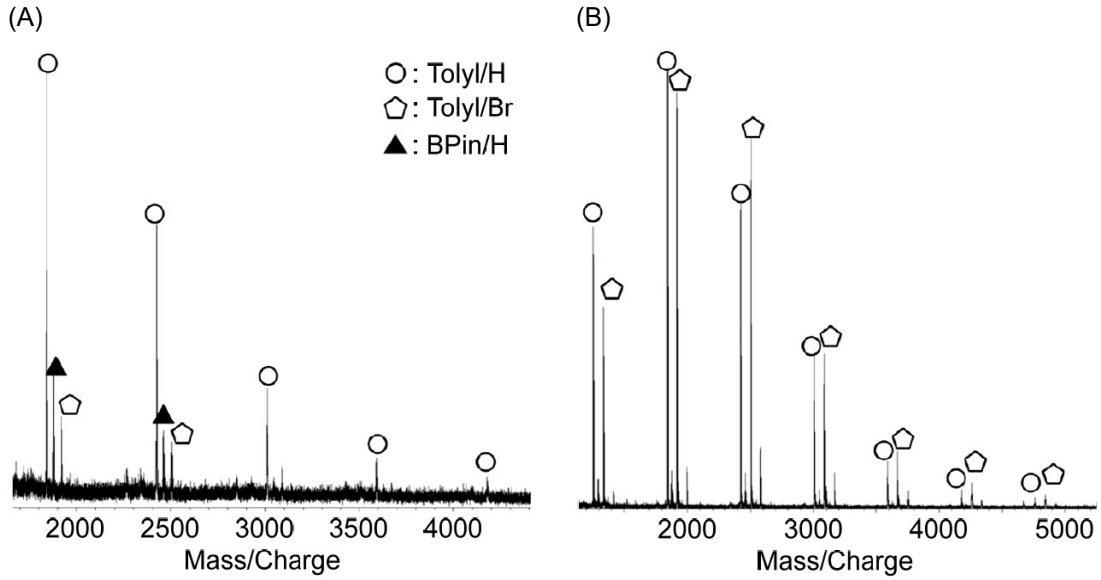


Fig. S13 MALDI-TOF mass spectra of P(**F8T(4)8**) obtained by the polymerization of **PinB-F8T(4)8-Br** with **12** ([**PinB-F8T(4)8-Br**]$_0$/[**12**]$_0$ = 8) in the presence of CsF/18-crown-6 at room temperature for (A) 15 min (M_n = 4470, M_w/M_n = 1.28) and (B) 2 h (M_n = 10400, M_w/M_n = 1.87).

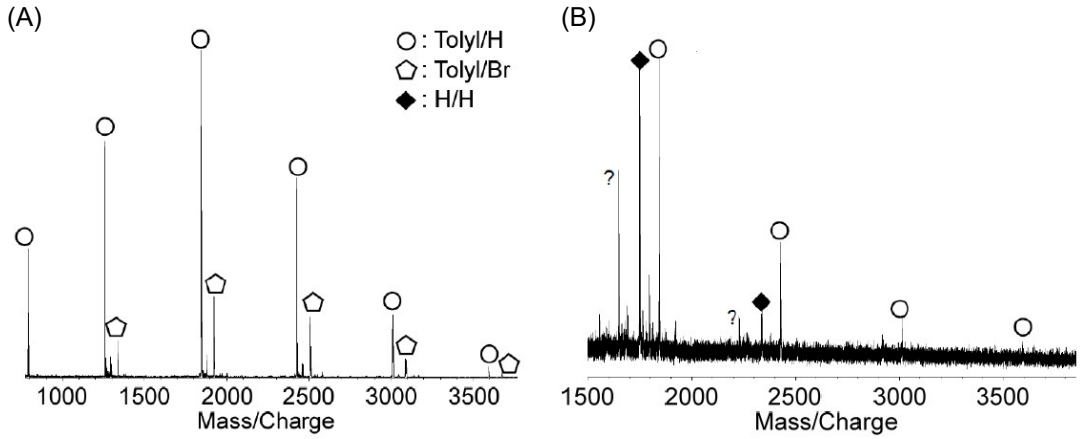


Fig. S14 MALDI-TOF mass spectra of P(**F8T(4)8**) obtained by the polymerization of **PinB-F8T(4)8-Br** with **13** ([**PinB-F8T(4)8-Br**]$_0$/[**13**]$_0$ = 8) in the presence of CsF/18-crown-6 at room temperature for (A) 15 min (M_n = 2250, M_w/M_n = 1.17) and (B) 24 h (M_n = 5550, M_w/M_n = 1.47).

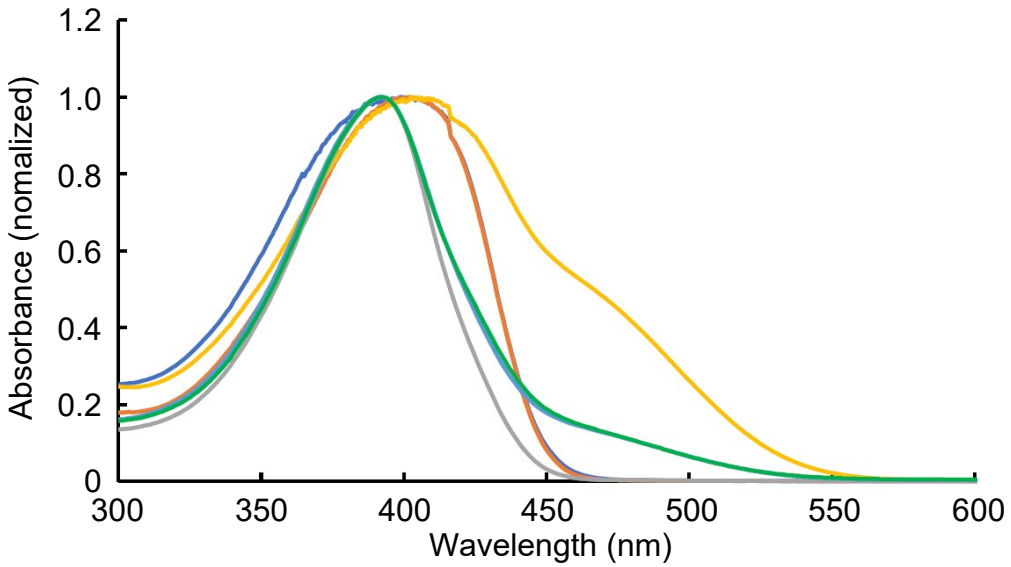


Fig. S15 UV-vis spectra of P(**F8T(3)8**) (dark blue line, M_n = 7320, M_w/M_n = 1.68), P(**F8T(4)8**) (orange line, M_n = 10600, M_w/M_n = 1.63), P(**F8T(4)8**)-*b*-PF8) (gray line, M_n = 12200, M_w/M_n = 2.11), P(**F8T(4)8**)-*b*-P3HT (yellow line, M_n = 8980, M_w/M_n = 1.53), P3HT-*b*-P(**F8T(4)8**)-*b*-PF8 (light blue line, M_n = 8160, M_w/M_n = 1.79), and PF8-*b*-P(**F8T(4)8**)-*b*-P3HT (green line, M_n = 10800, M_w/M_n = 1.66) in $CHCl_3$.

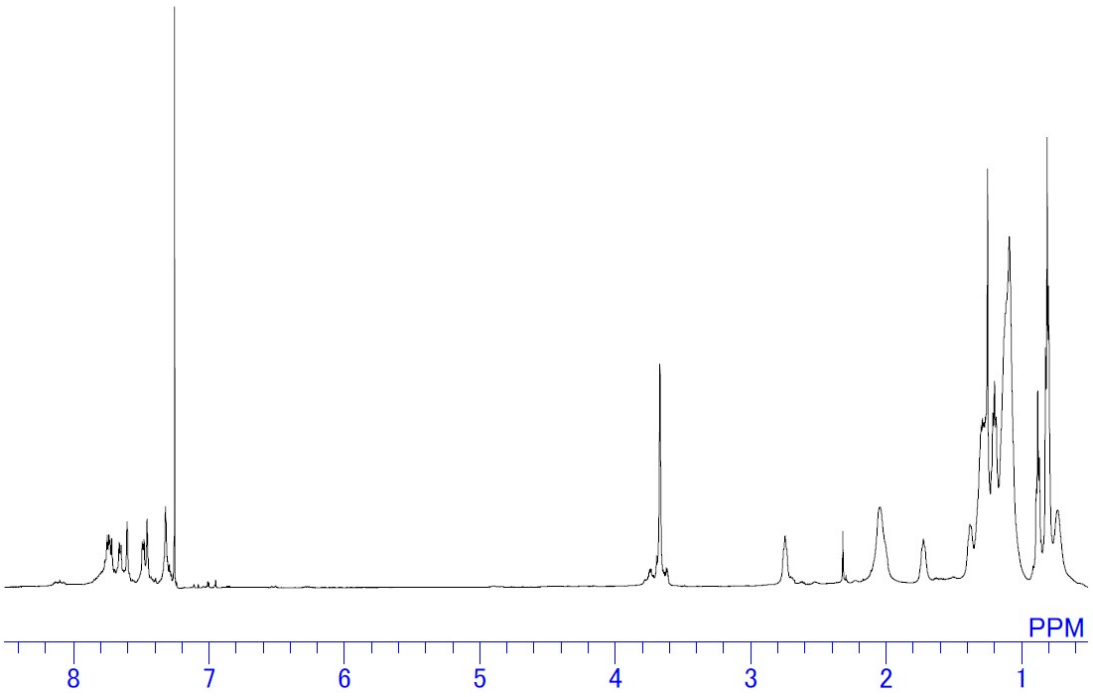


Fig. S16 ^{1}H NMR spectrum of P(**F8T(3)8**) obtained by the polymerization of **PinB-F8T(3)8-Br** with **13** ([**PinB-F8T(3)8-Br**]$_0$/[**13**]$_0$ = 8) in the presence of CsF/18-crown-6.

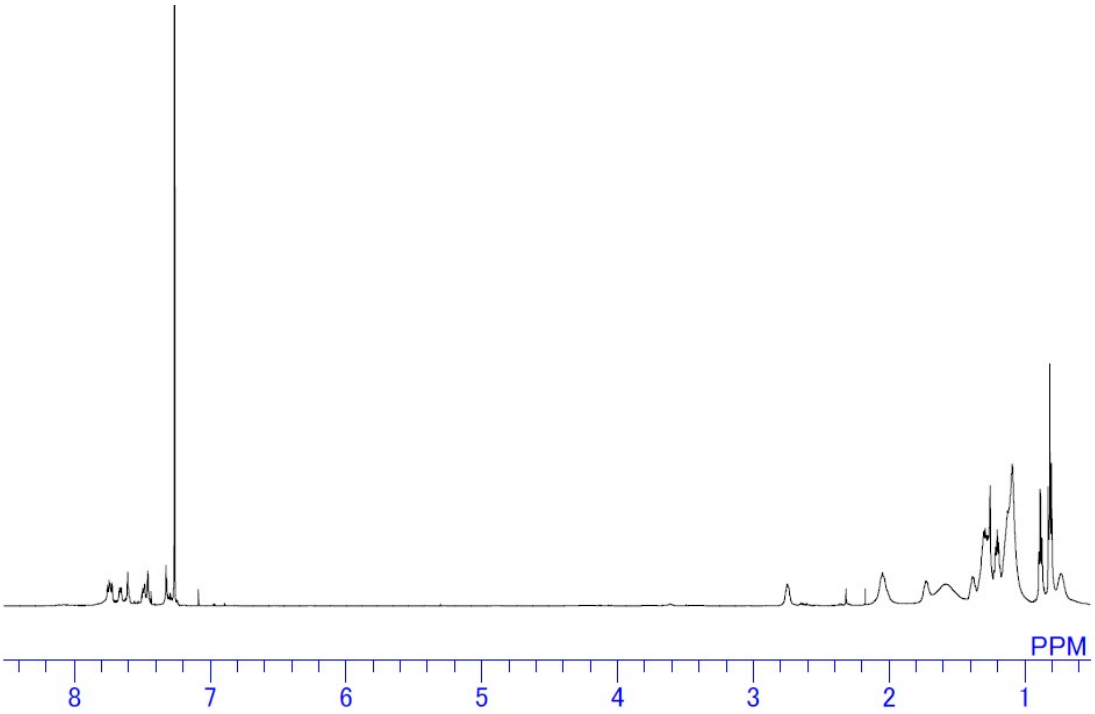


Fig. S17 ^{1}H NMR spectrum of P(**F8T(4)8**) obtained by the polymerization of **PinB-F8T(4)8-Br** with **13** ([**PinB-F8T(4)8-Br**]$_0$/[**13**]$_0$ = 16) in the presence of CsF/18-crown-6.

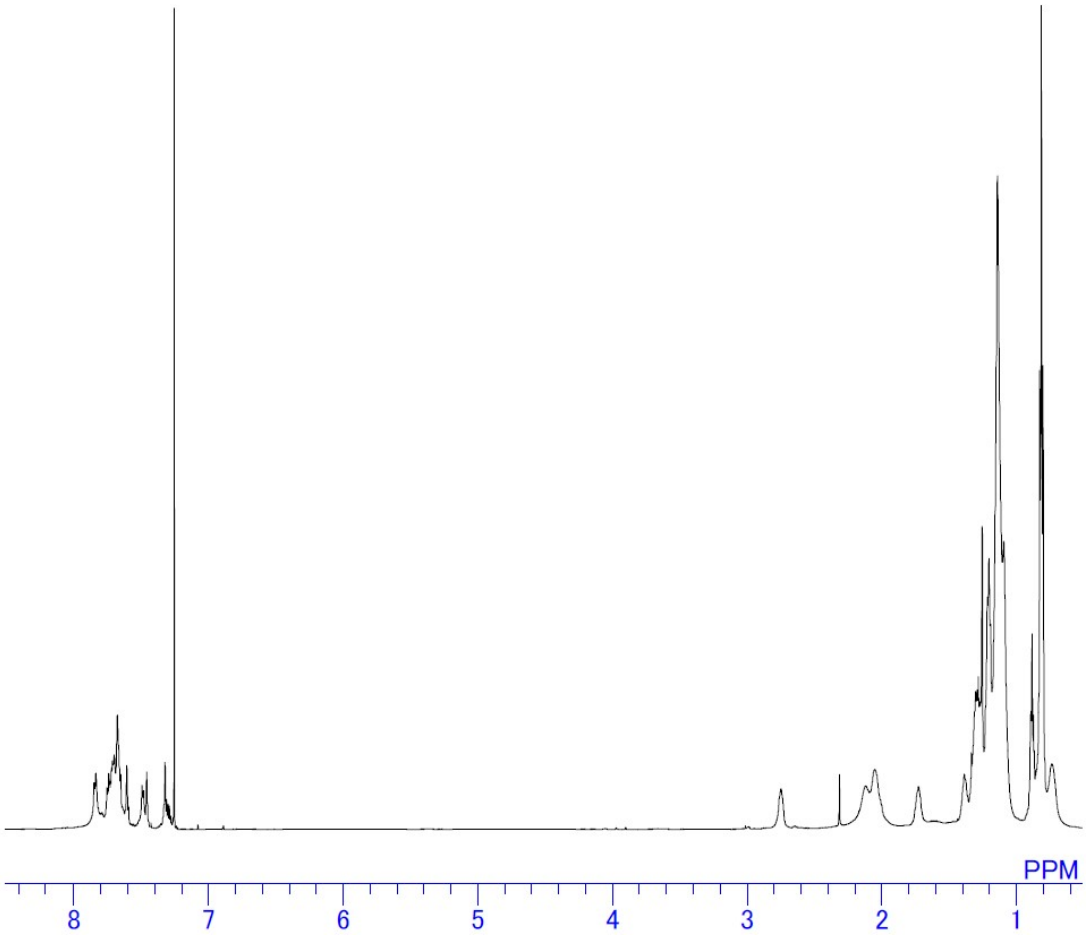


Fig. S18 ^{1}H NMR spectrum of P(**F8T(4)8**)-*b*-PF8 (M_n = 11600, M_w/M_n = 1.97).

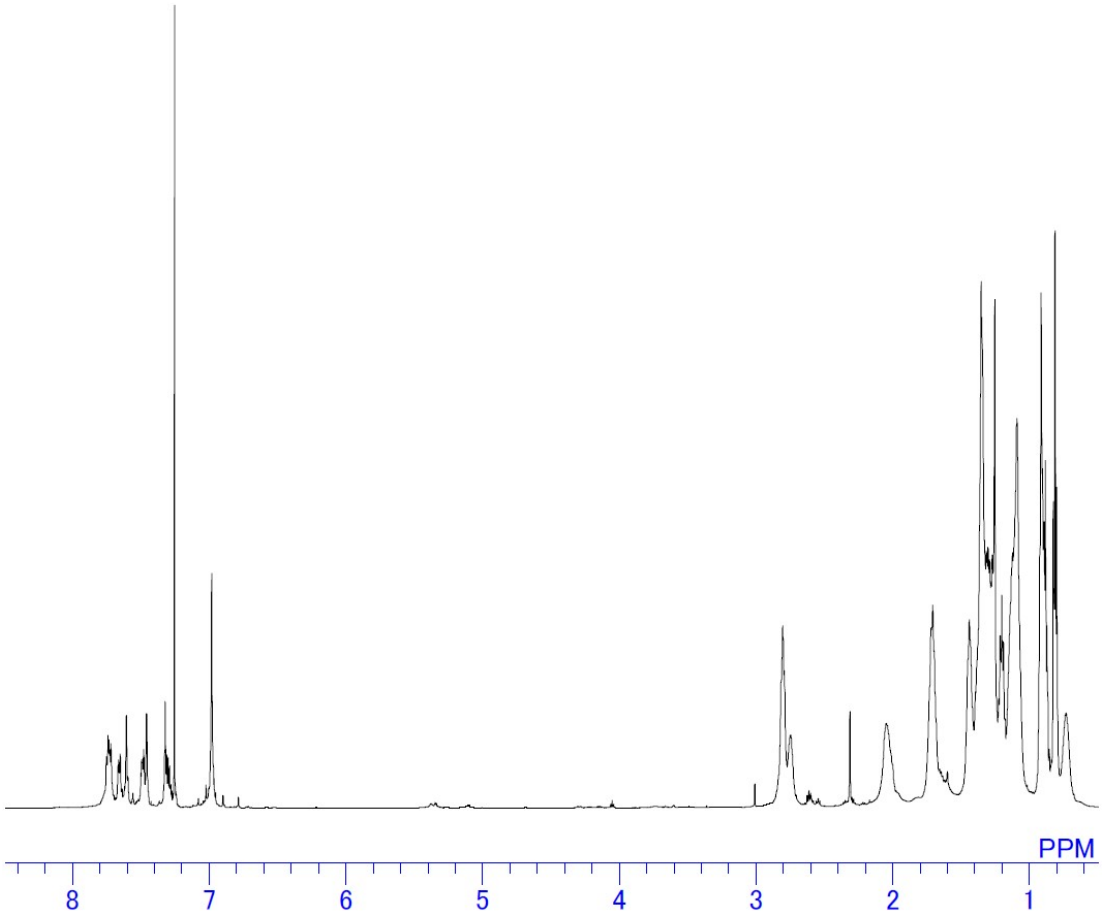


Fig. S19 ^{1}H NMR spectrum of P(**F8T(4)8**)-*b*-P3HT (M_n = 9090, M_w/M_n = 1.43).

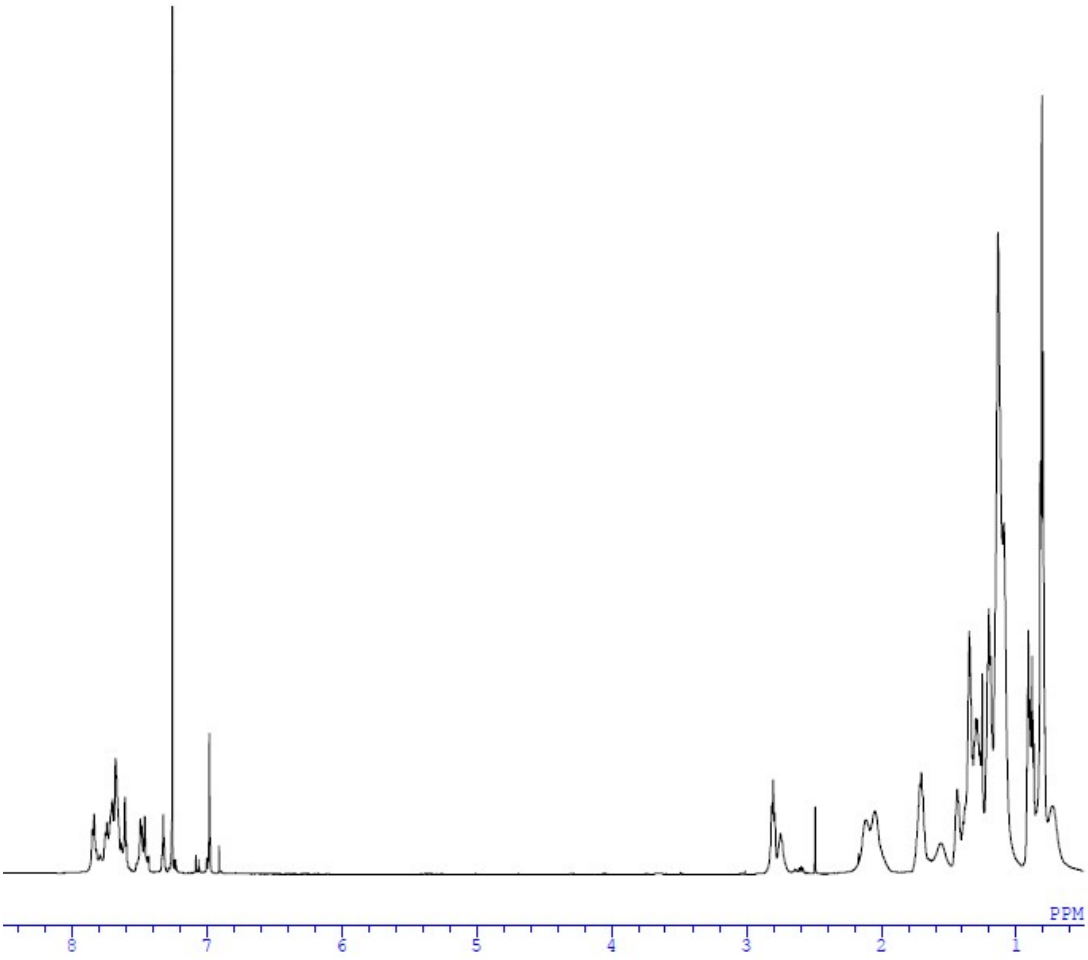


Fig. S20 ^{1}H NMR spectrum of P3HT-*b*-P(**F8T(4)8**)-*b*-PF8 (M_n = 8850, M_w/M_n = 1.68).

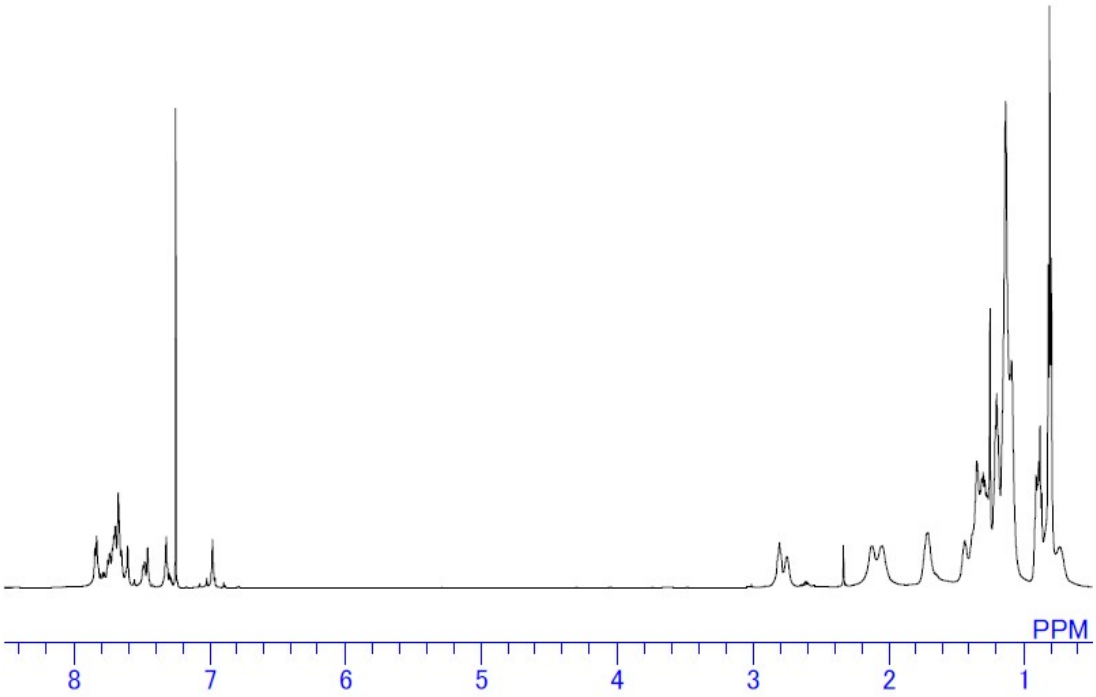


Fig. S21 ^{1}H NMR spectrum of PF8-*b*-P(**F8T(4)8**)-*b*-P3HT (M_n = 11300, M_w/M_n = 1.57).

10. References

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