Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information

Direct Synthesis of π-Conjugated Polymers with Bromoaryl Groups in Side Chains via a Chemoselective Intramolecular Catalyst Transfer System

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General Methods and Materials

Materials: 2,5-Bis(trimethylstannyl)thiophene (**1**, Tokyo Chemical Industry Co., Ltd.) was purified by recrystallization using methanol. Unless otherwise noted, all other reagents were purchased from commercial sources and used without further purification. Deoxidized toluene (FUJIFILM Wako Pure Chemical Co.) was used after N_2 bubbling.

Mass Spectrometry: Field Desorption-Mass Spectroscopy (FD-MS) spectra were recorded on a JEOL JMS-T100GCV mass spectrometer using field desorption ionization. Matrix Assisted Laser Desorption/Ionization-Time of Flight Mass Spectroscopy (MALDI-TOF MS) was performed using a JMS-S3000 (JEOL Ltd., Japan) based on a positive spiral mode at an acceleration voltage of 20 kV. The external mass calibration was performed using a polystyrene standard (M_n = 5,000). Polymer samples in tetrahydrofuran (THF) (10 mg/mL, 10 μL) were mixed with a matrix in THF (DCTB: *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile, 20 mg/mL, 100 μL), and 1.0 μL of the mixed solutions was deposited on a plate, followed by drying under high vaccum condistion (< 10^{-6} torr) before measurement.

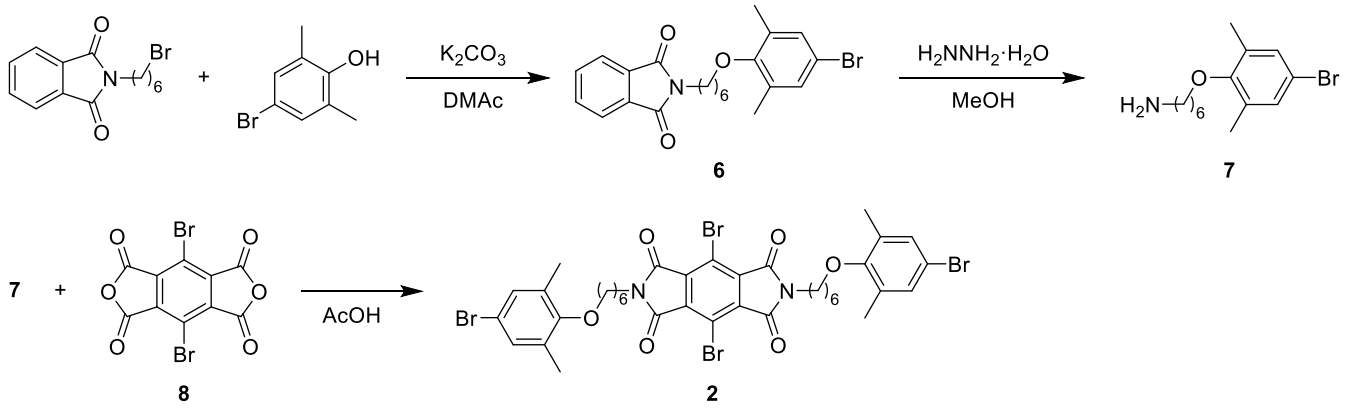
NMR Spectroscopy: ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on a JEOL JNM-ECX400 (working frequencies of 400 MHz for ^{1}H and 101 MHz for ^{13}C), JEOL JNM-ECZ500R (500 MHz for ^{1}H and 126 MHz for ^{13}C), or JEOL JNM-ECZ600R (600 MHz for ^{1}H). Chloroform-*d* ($CDCl_3$) containing tetramethylsilane (TMS) as an internal standard (δH 0.00) and 1,1,2,2-tetrachloroethane-d_2 ($C_2D_2Cl_4$) were used as solvents. ^{1}H NMR spectra for monomer samples were recorded at 25 °C in $CDCl_3$ or $C_2D_2Cl_4$ and polymer samples were recorded at 100 °C in $C_2D_2Cl_4$.

SEC Measurement: Number-average molecular weight (M_n), weight-average molecular weight (M_w), and M_w/M_n were measured by size exclusion chromatography (SEC) using a JASCO GULLIVER HPLC system equipped with a pump (JASCO PU-4580), a column oven (JASCO CO-1565), a UV detector (UV, λ = 254 nm, JASCO UV-4575), and a RI detector (JASCO RI-4030). The column set was as follows: a guard column (Shodex K-G 4A) and two consecutive columns (Shodex K-804L, Shodex K-805L) eluted with chloroform ($CHCl_3$) at 40 °C at a flow rate of 1.0 mL/min. Polystyrene standards were employed for calibration.

Synthetic Procedures and Characterization

All reactions were performed under N_2 flows in oven-dried glassware.

Synthesis of Monomers

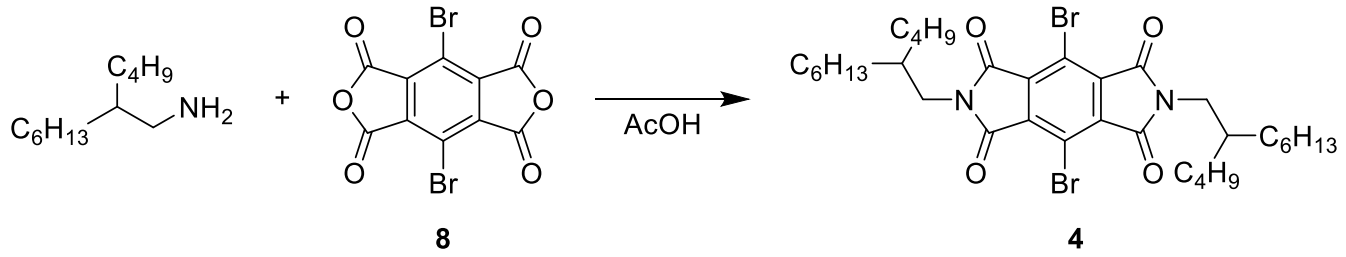


Scheme S1. Synthetic routes for **2**.

*Synthesis of 2-(6-(4-Bromo-2,6-dimethylphenoxy)hexyl)isoindoline-1,3-dione (**6**)*: A mixture of *N*-(6-bromohexyl)phthalimide (2.01 g, 6.48 mmol), 4-bromo-2,6-dimethylphenol (1.56 g, 7.76 mmol), and potassium carbonate (2.29 g, 16.6 mmol) in *N,N*-dimethylacetamide (100 mL) was stirred at 90 °C for 24 h. After cooling to room temperature, dichloromethane (DCM) was added. The organic solution was washed with water and brine and dried over anhydrous magnesium sulfate ($MgSO_4$). After the solvent was removed under reduced pressure, the resulting residue was purified by column chromatography (DCM/Hexane 80:20) to give **7** (1.20 g, 43%) as a colorless liquid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.85-7.83 (m, 2H), 7.71 (q, *J* = 2.7 Hz, 2H), 7.11 (s, 2H), 3.72-3.69 (m, 4H), 2.21 (s, 6H), 1.75 (dq, *J* = 26.8, 7.3 Hz, 4H), 1.58-1.41 (m, 4H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 168.6, 155.2, 134.0, 133.3, 132.2, 131.4, 123.3, 116.1, 72.3, 38.0, 30.2, 28.6, 26.8, 25.8, 16.2. Anal. Calcd for $C_{22}H_{24}BrNO_3$ (%): C, 61.40; H, 5.62; Br, 18.58; N, 3.25 O, 11.15. Found (%): C, 61.52; H, 5.72; N, 3.23.

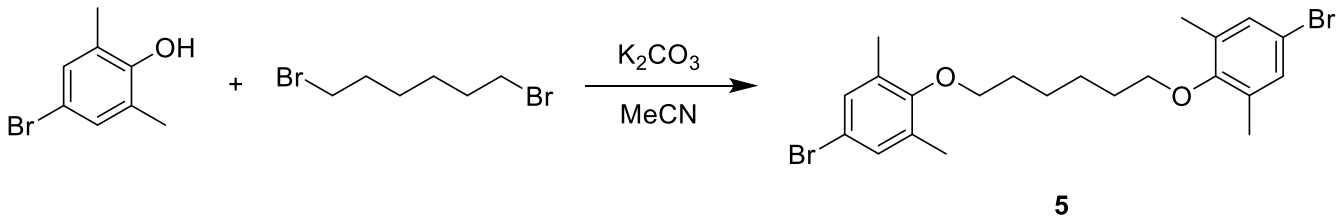
*Synthesis of 6-(4-Bromo-2,6-dimethylphenoxy)hexan-1-amine (**7**)*: A mixture of **7** (0.971 g, 2.26 mmol) and hydrazine monohydrate (0.181 g, 3.62 mmol) in methanol (MeOH) (25 mL) was stirred under reflux condition overnight. After cooling to room temperature, MeOH was removed under reduced pressure, the residue was diluted with DCM, and washed with 1 M potassium hydroxide (KOH) aq. and brine. The organic layer was dried over $MgSO_4$ and concentrated by vacuum evaporation to give **7** (0.432 g, 90%) as a colorless liquid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.13 (s, 2H), 3.72 (t, J = 6.4 Hz, 2H), 2.71 (t, J = 6.9 Hz, 2H), 2.23 (s, 6H), 1.83-1.76 (m, 2H), 1.55-1.37 (m, 6H). 1.11 (s, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 155.1, 133.1, 131.4, 131.3, 131.2, 116.0, 72.3, 42.2, 33.8, 30.3, 26.8, 26.0, 16.1. Anal. Calcd for $C_{14}H_{22}BrNO$ (%): C, 56.01; H, 7.39; Br, 26.60; N, 4.67 O, 5.33. Found (%): C, 55.40; H, 7.48; N, 4.57.

*Synthesis of 4,8-Dibromo-2,6-bis(6-(4-bromo-2,6-dimethylphenoxy)hexyl)pyrrolo[3,4-f]isoindole-1,3,5,7(2H,6H)-tetraone (**2**)*: A mixture of **7** (0.430 g, 1.43 mmol) and dibromopyromellitic dianhydride (**8**) (0.240 g, 0.638 mmol) in acetic acid (AcOH) (20 mL) was stirred under reflux condition overnight. After cooling to room temperature, the precipitation was collected and washed with MeOH. The solid was dried under reduced pressure to give **2** (0.494 g, 82%) as a light yellow solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.07 (s, 4H), 3.76 (t, *J* = 7.2 Hz, 4H), 3.68 (t, *J* = 6.0 Hz, 4H), 2.19 (s, 12H), 1.80-1.74 (m, 8H), 1.59-1.45 (m, 8H). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 163.5, 155.1, 136.1, 133.2, 131.4, 116.2, 114.0, 72.4, 39.2, 29.8, 27.9, 26.7, 26.0, 16.3. Anal. Calcd for $C_{38}H_{40}Br_4N_2O_6$ (%): C, 48.54; H, 4.29; Br, 33.98; N, 2.98 O, 10.21. Found (%): C, 48.90; H, 4.12; N, 3.04.



Scheme S2. Synthetic route for **4**.

*Synthesis of 4,8-Dibromo-2,6-bis(2-butyloctyl)pyrrolo[3,4-f]isoindole-1,3,5,7(2H,6H)-tetraone (**4**)*: A mixture of 2-butyloctan-1-amine (5.00 g, 27.0 mmol) and **8** (4.98 g, 13.2 mmol) in AcOH (75 mL) was stirred under reflux condition overnight. After cooling to room temperature, the precipitation was collected, washed with MeOH, and recrystallized (MeOH/$CHCl_3$ 85:15) to give **4** (7.84 g, 83%) as a light yellow solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 3.62 (d, *J* = 6.9 Hz, 4H), 1.88 (t, *J* = 5.4 Hz, 2H), 1.38-1.26 (m, 33H), 0.88 (dd, *J* = 16.0, 6.9 Hz, 12H). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 163.8, 136.2, 114.2, 43.3, 37.0, 31.9, 31.5, 31.2, 29.7, 28.5, 26.3, 23.0, 22.7, 14.2, 14.2. Anal. Calcd for $C_{34}H_{50}Br_2N_2O_4$ (%): C, 57.47; H, 7.09; Br, 22.49; N, 3.94 O, 9.01. Found (%): C, 57.35; H, 7.08; N, 3.87.

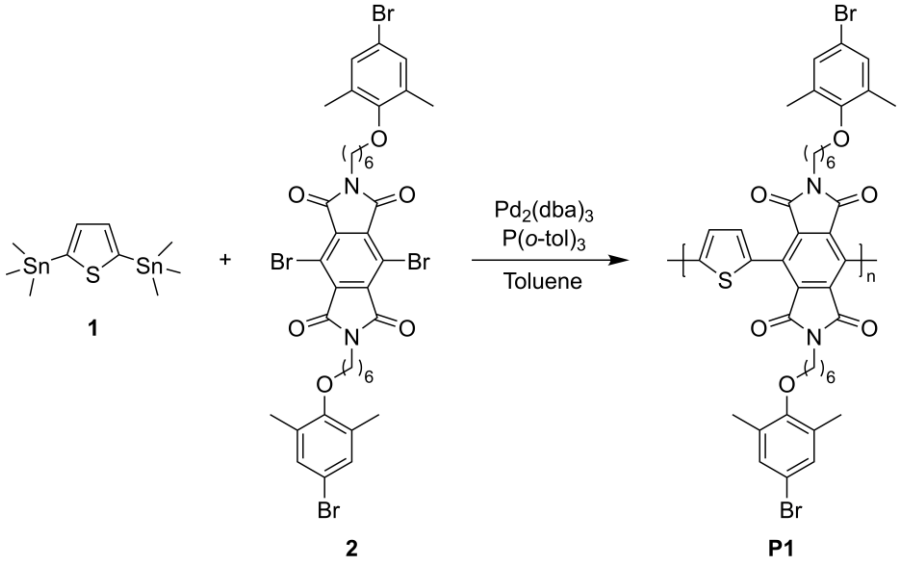


5

Scheme S3. Synthetic route for **5**.

*Synthesis of 1,6-Bis(4-bromo-2,6-dimethylphenoxy)hexane (**5**)*: A mixture of 1,6-dibromohexane (2.55 g, 10.4 mmol), 4-bromo-2,6-dimethylphenol (6.49 g, 32.3 mmol), and potassium carbonate (7.20 g, 52.1 mmol) in acetonitrile (100 mL) was stirred under reflux condition for 24 h. After cooling to room temperature, the precipitation was collected and washed with water (H_2O) and MeOH. The solid was purified by recrystallization (EtOH) to afford **5** (4.47 g, 90%) as a white solid. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.13 (s, 4H), 3.74 (t, *J* = 6.6 Hz, 4H), 2.24 (s, 12H), 1.86-1.80 (m, 4H), 1.60-1.57 (m, 4H). ^{13}C-NMR (126 MHz, $CDCl_3$): δ 155.3, 133.2, 131.5, 131.5, 116.2, 72.4, 30.4, 26.2, 16.2. Anal. Calcd for $C_{22}H_{28}Br_2O_2$ (%): C, 54.56; H, 5.83; Br, 33.00; O, 6.61. Found (%): C, 54.51; H, 5.64.

Synthesis of Polymers

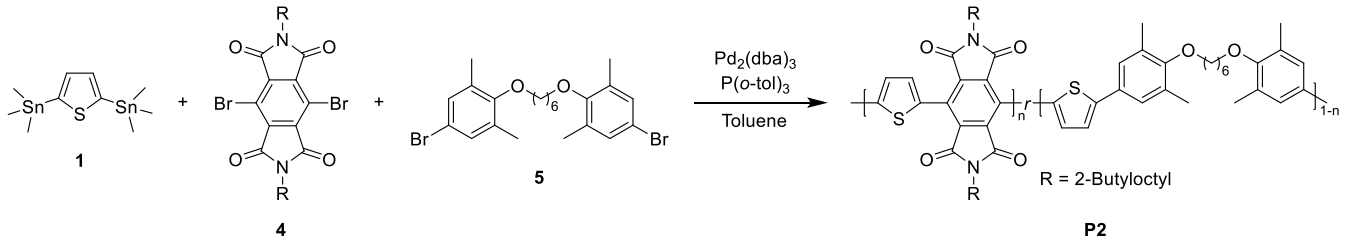


Scheme S4. Synthesis of **P1** by Migita-Kosugi-Stille coupling polymerization between **1** and **2**.

*Synthesis of **P1***: **1** (91.2 mg, 0.222 mmol), **2** (209 mg, 0.222 mmol), $Pd_2(dba)_3$ (12.0 mg, 0.013 mmol), P(*o*-tol)$_3$ (8.5 mg, 0.028 mmol), and deoxidized toluene (20 mL) were added into a two-necked flask, and the mixture was purged with N_2 for 20 min. The reaction was then stirred at 90 °C for 2 h. Sodium dimethyldithiocarbamate dihydrate was added and stirred for another 1 h at room temperature. The solution was poured in methanol to precipitate the polymer. The crude product was dried under reduced pressure to give **P1** as orange powders (189 mg, 99% yield, M_n = 17,000, M_w/M_n = 3.16).

*Synthesis of **P1'***: **1** (85.8 mg, 0.209 mmol), **2** (197 mg, 0.209 mmol), $Pd_2(dba)_3$ (11.5 mg, 0.013 mmol), P(*o*-tol)$_3$ (7.7 mg, 0.025 mmol), and deoxidized toluene (20 mL) were added into a two-necked flask, and the mixture was purged with N_2 for 20 min. The reaction was then stirred at 90 °C for 20 min. Sodium dimethyldithiocarbamate dihydrate was added and stirred for another 1 h at room temperature. The solution was poured in methanol to precipitate the polymer. The crude product was dried under reduced pressure to give **P1'** as orange powders (174 mg, 96% yield, M_n = 7,200, M_w/M_n = 1.96).

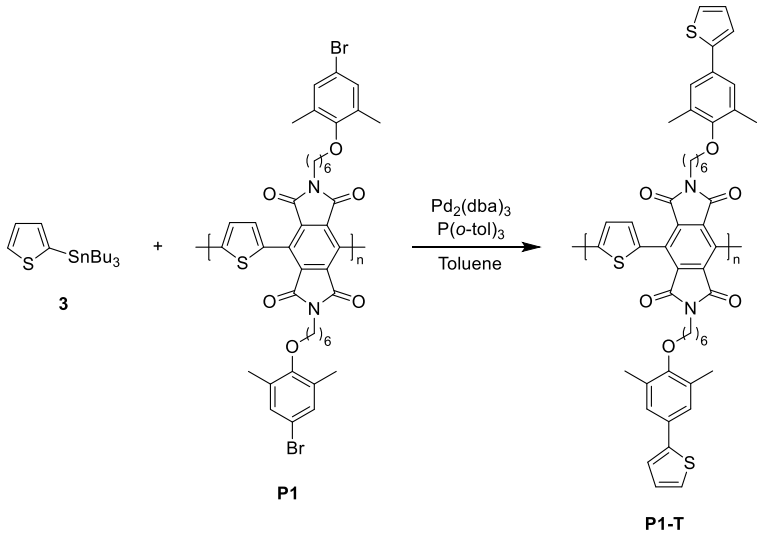
*Synthesis of **P1''***: **1** (60.2 mg, 0.147 mmol), **2** (207 mg, 0.220 mmol), $Pd_2(dba)_3$ (12.6 mg, 0.014 mmol), P(*o*-tol)$_3$ (8.9 mg, 0.029 mmol), and deoxidized toluene (20 mL) were added into a two-necked flask, and the mixture was purged with N_2 for 20 min. The reaction was then stirred at 90 °C for 24 h. Sodium dimethyldithiocarbamate dihydrate was added and stirred for another 1 h at room temperature. The solution was poured in methanol to precipitate the polymer. The crude product was dried under reduced pressure to give **P1''** as orange powders (175 mg, M_n = 11,000, M_w/M_n = 1.97).



Scheme S5. Synthesis of **P2** by ternary copolymerization of **1**, **4**, and **5**.

*Synthesis of **P2***: **1** (152 mg, 0.371 mmol), **4** (132 mg, 0.186 mmol), **5** (87.4 mg, 0.186 mmol), $Pd_2(dba)_3$ (17.0 mg, 18.6 μmol), P(*o*-tol)$_3$ (11.3 mg, 37.1 μmol), and deoxidized toluene (20 mL) were added into a two-necked flask, and the mixture was purged with N_2 for 20 min. The reaction was then stirred at 90 °C for 2 h. Sodium dimethyldithiocarbamate dihydrate was added and stirred for another 1 h at room temperature. The solution was poured in methanol to precipitate the polymer. The crude product was dried under reduced pressure to give **P2** as orange powders (302 mg, 78% yield, M_n = 9,000, M_w/M_n = 2.22).

*Synthesis of **P2'***: **1** (58.6 mg, 0.143 mmol), **4** (102 mg, 0.143 mmol), **5** (67.2 mg, 0.143 mmol), $Pd_2(dba)_3$ (6.5 mg, 7.1 μmol), P(*o*-tol)$_3$ (4.4 mg, 14.5 μmol), and deoxidized toluene (20 mL) were added into a two-necked flask, and the mixture was purged with N_2 for 20 min. The reaction was then stirred at 90 °C for 2 h. Sodium dimethyldithiocarbamate dihydrate was added and stirred for another 1 h at room temperature. The solution was poured in methanol to precipitate the polymer. The crude product was dried under reduced pressure to give **P2** as orange powders (68.9 mg, 46% yield, M_n = 12,000, M_w/M_n = 1.25).



Scheme S6. Synthesis of **P1-T** by post-modification reaction between **3** and **P1**.

*Synthesis of **P1-T***: **3** (6.85 g, 18.4 mmol), **P1** (158 mg), $Pd_2(dba)_3$ (22.7 mg, 0.025 mmol), P(*o*-tol)$_3$ (50.0 mg, 0.164 mmol), and deoxidized toluene (10 mL) were added into a two-necked flask, and the mixture was purged with N_2 for 20 min. The reaction was then stirred at 90 °C overnight. Sodium dimethyldithiocarbamate dihydrate was added and stirred for another 1 h at room temperature. The solution was poured in methanol to precipitate the polymer. The crude product was dried under reduced pressure to give **P1-T** as orange powder (148 mg, 93% yield, M_n = 11,000, M_w/M_n = 2.32).

FD-MS Spectra

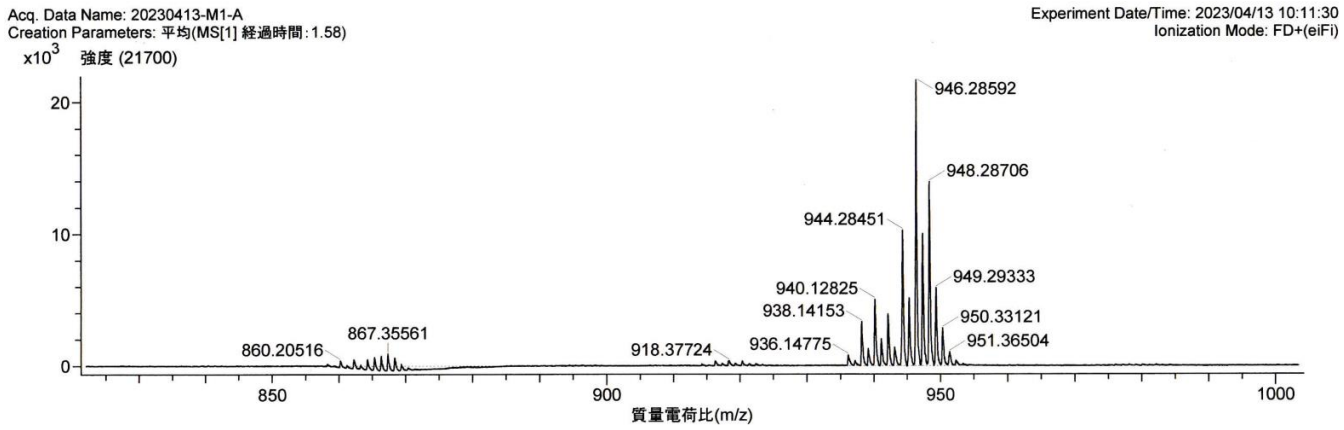


Fig. S1. FD-MS spectrum of crude products obtained by model reaction ([**4**]$_0$/[**2**]$_0$ = 1).

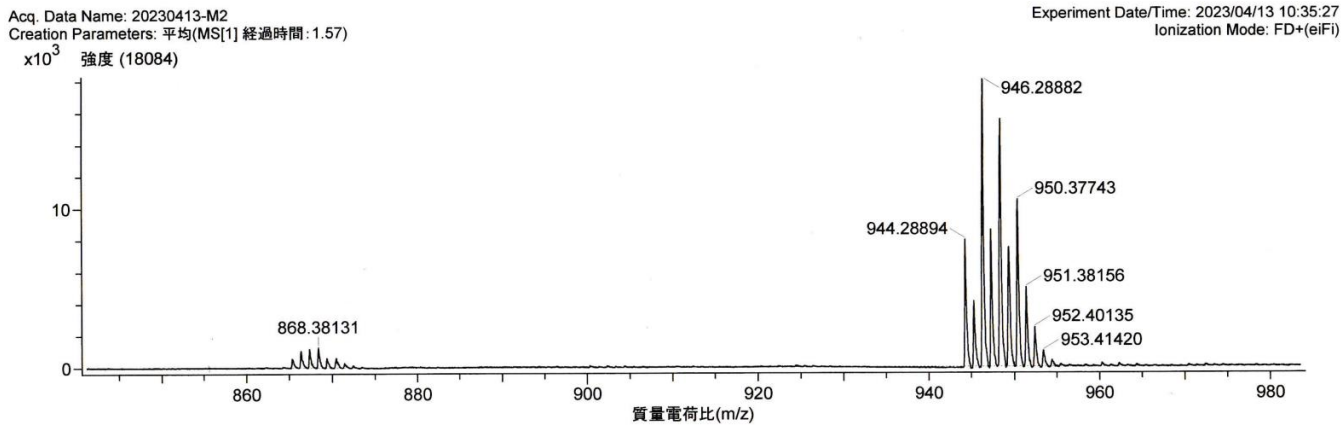


Fig. S2. FD-MS spectrum of crude products obtained by model reaction ([**4**]$_0$/[**2**]$_0$ = 2).

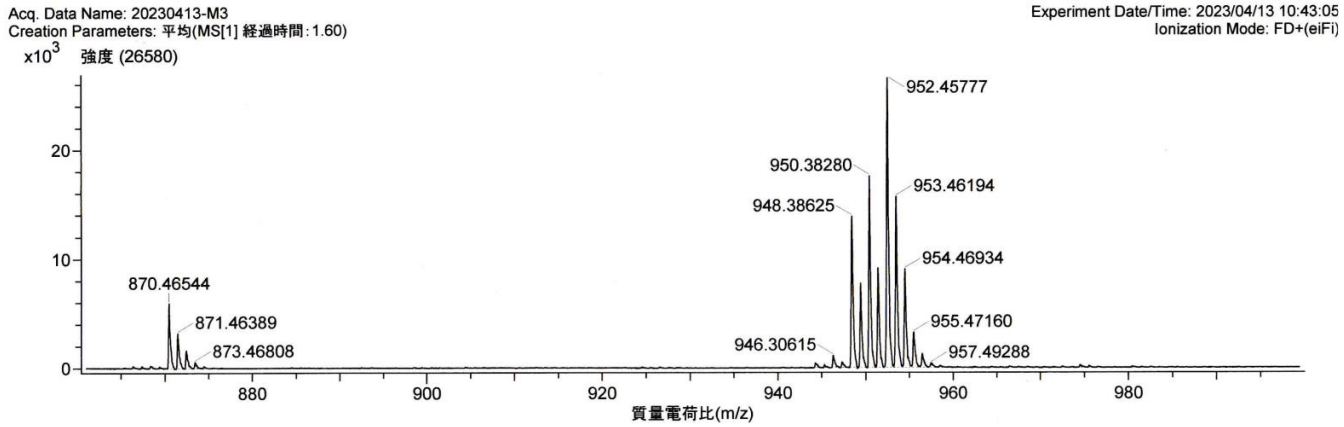


Fig. S3. FD-MS spectrum of crude products obtained by model reaction ([**4**]$_0$/[**2**]$_0$ = 3).

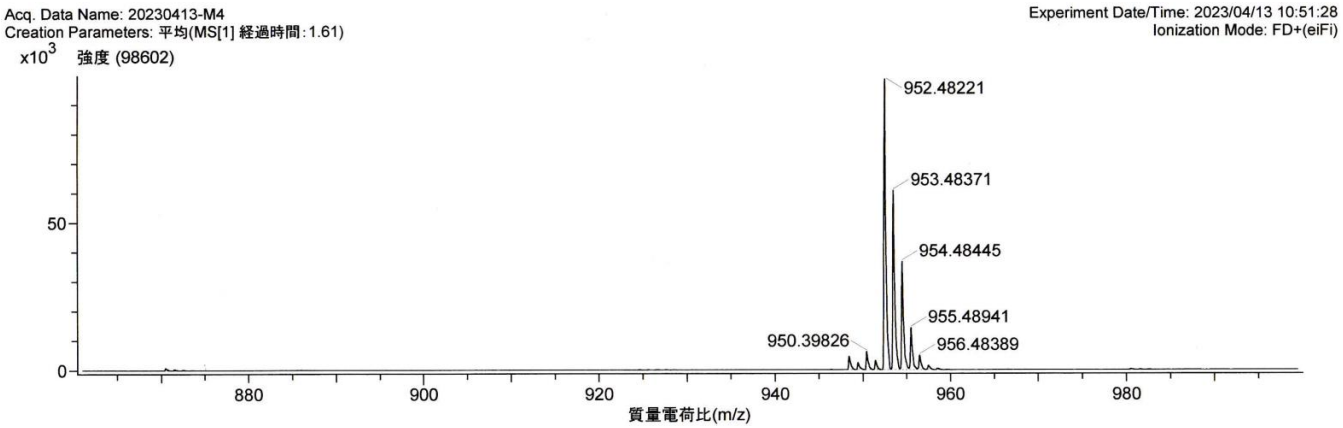


Fig. S4. FD-MS spectrum of crude products obtained by model reaction ([**4**]$_0$/[**2**]$_0$ = 4).

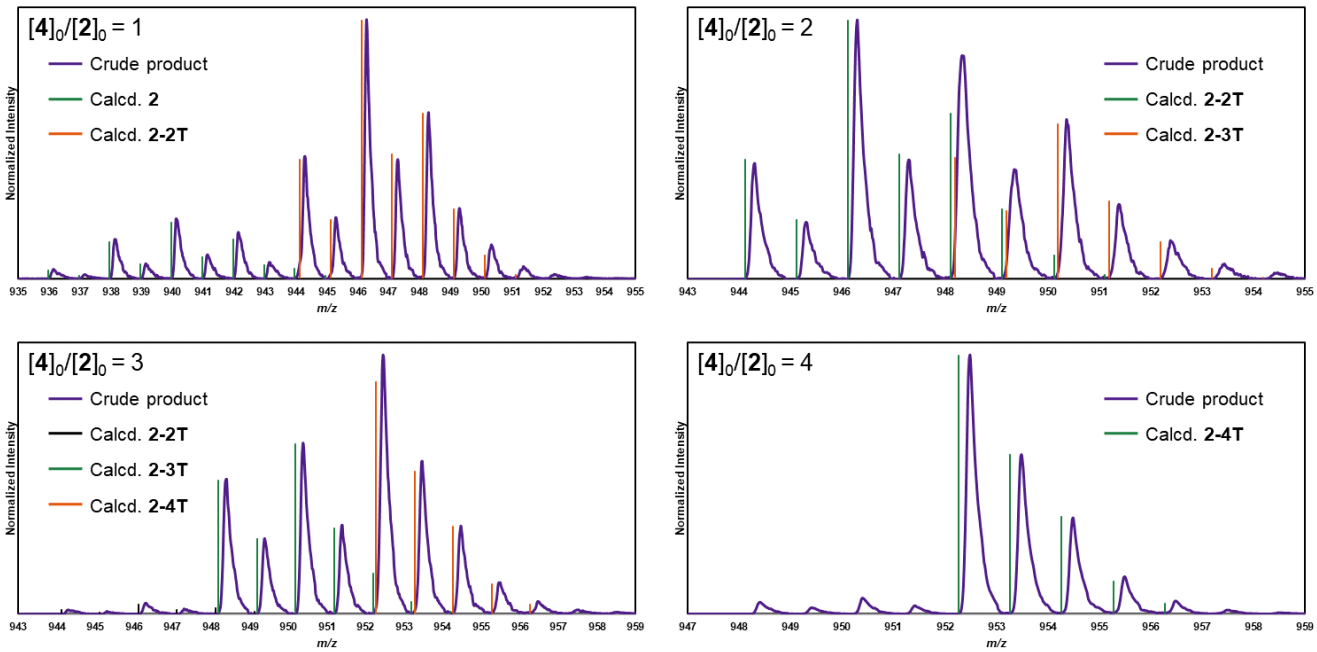


Fig. S5. FD-MS spectra of crude products in model reaction and calculated overlays.

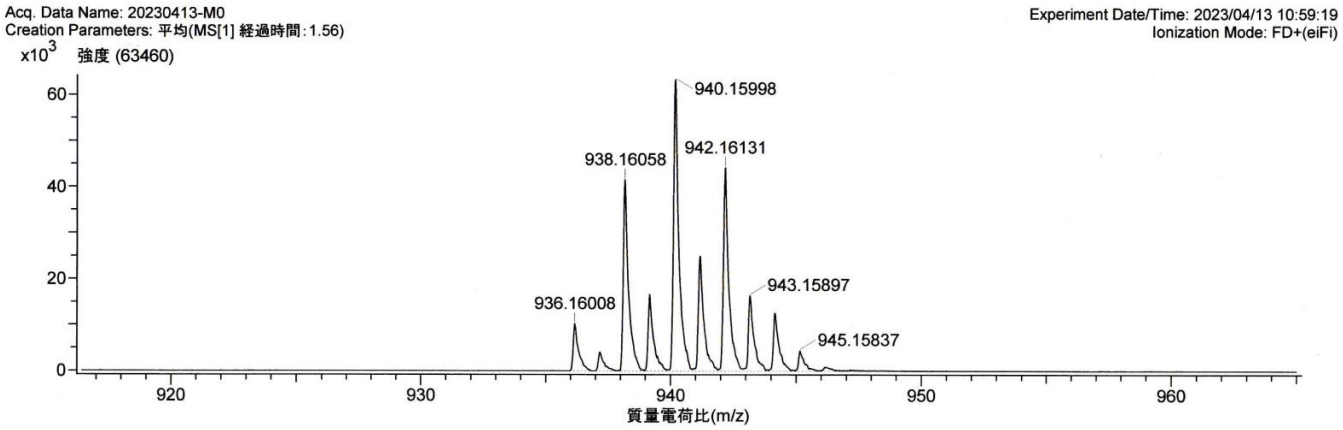


Fig. S6. FD-MS spectrum of **2**.

NMR Spectra

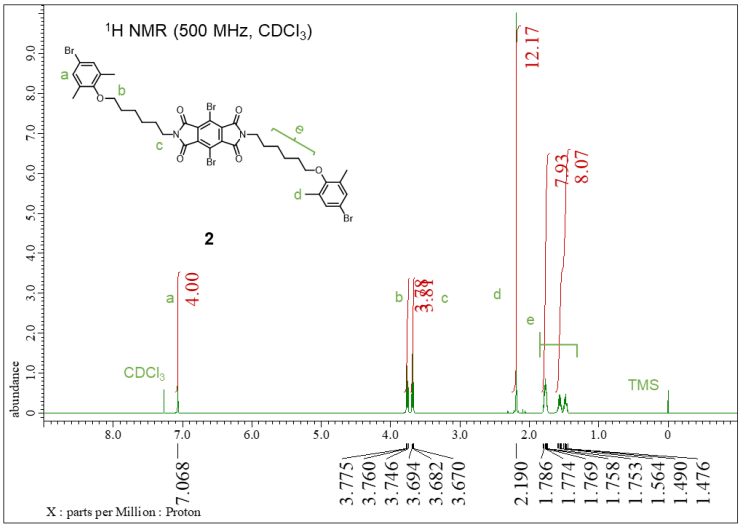


Fig. S7. ^{1}H NMR spectrum of **2**.

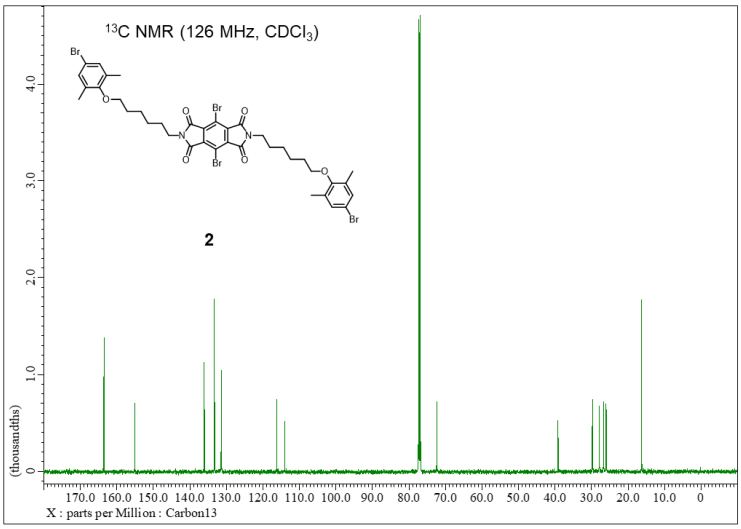


Fig. S8. ^{13}C NMR spectrum of **2**.

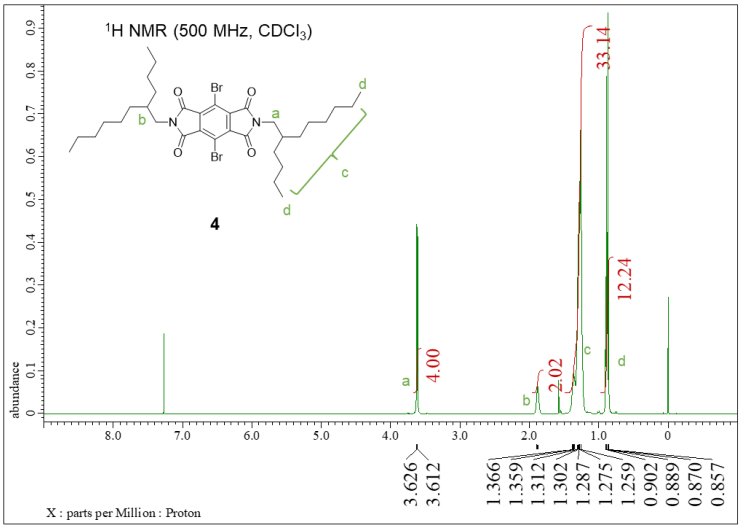


Fig. S9. ^{1}H NMR spectrum of **4**.

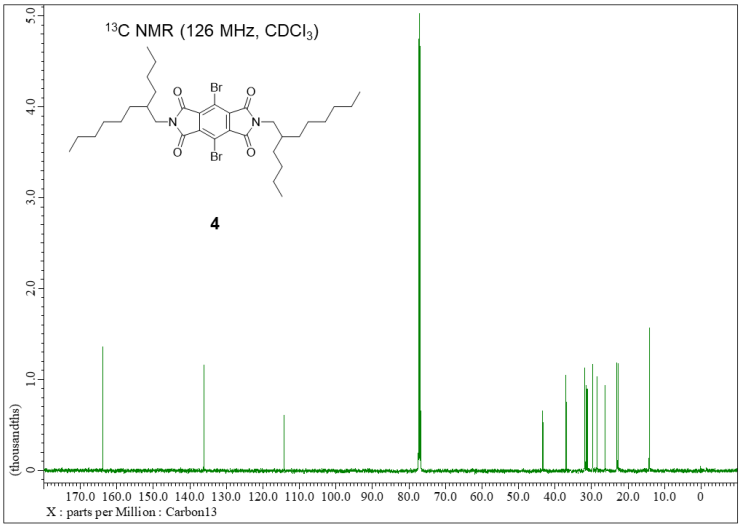


Fig. S10. ^{13}C NMR spectrum of **4**.

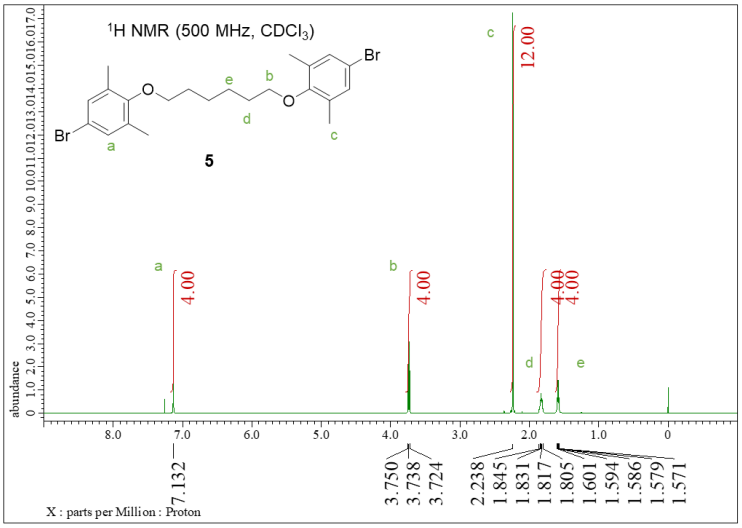


Fig. S11. ^{1}H NMR spectrum of **5**.

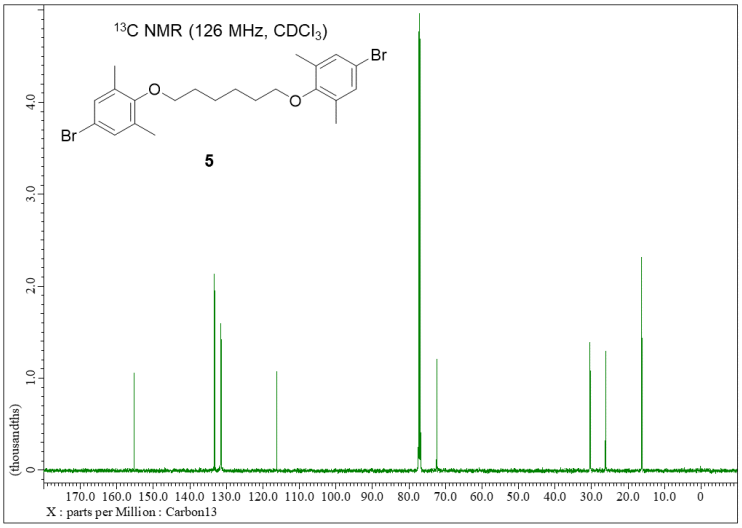


Fig. S12. ^{13}C NMR spectrum of **5**.

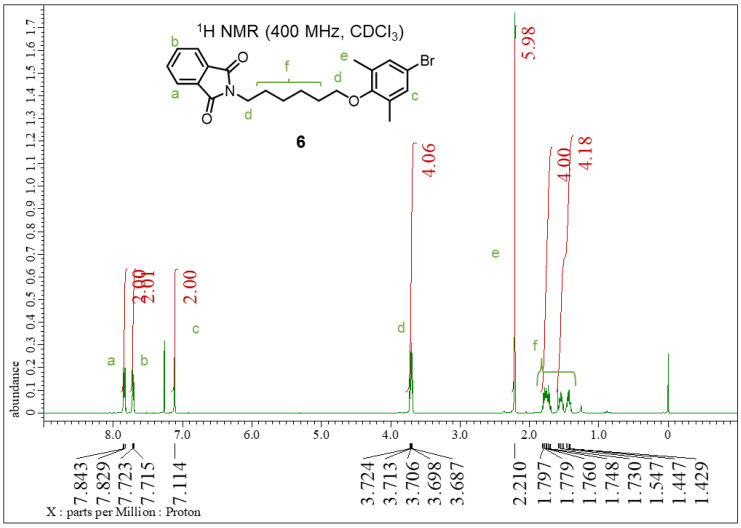


Fig. S13. ^{1}H NMR spectrum of **6**.

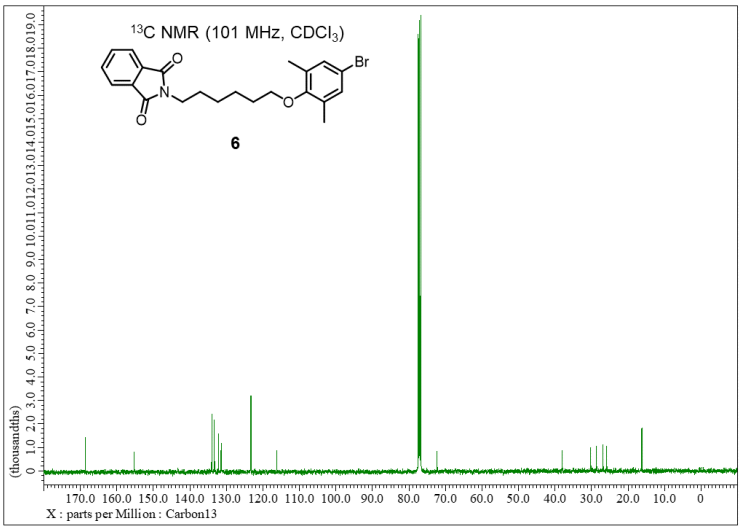


Fig. S14. ^{13}C NMR spectrum of **6**.

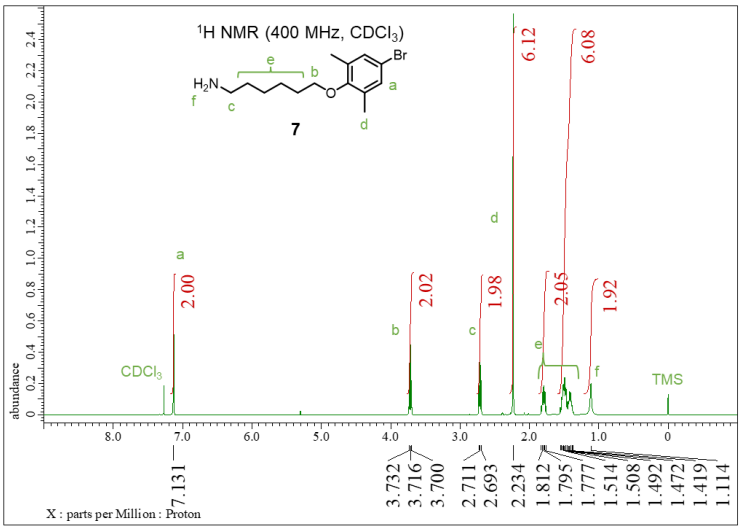


Fig. S15. ^{1}H NMR spectrum of **7**.

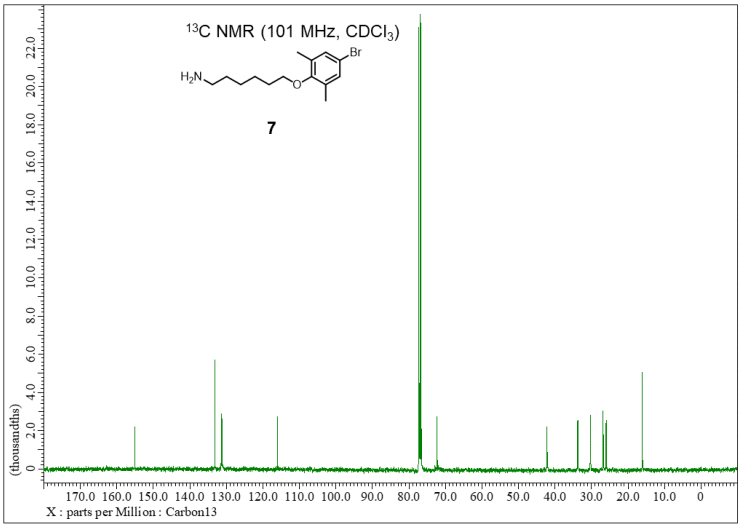


Fig. S16. ^{13}C NMR spectrum of **7**.

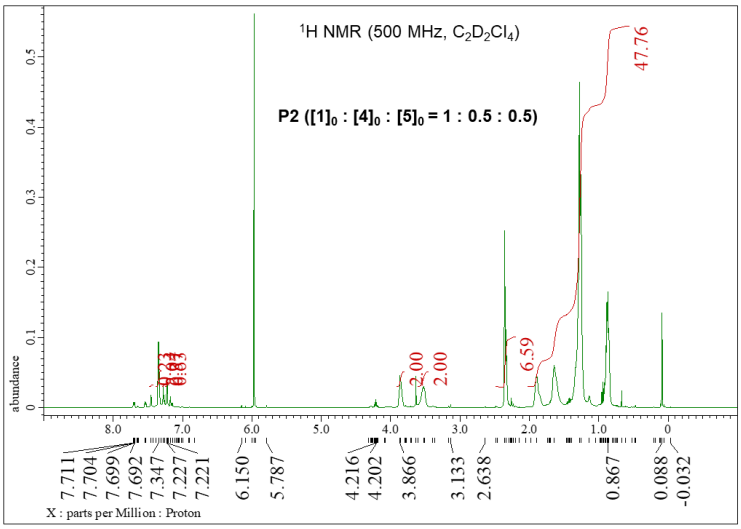


Fig. S17. ^{1}H NMR spectrum of **P2** ($[\mathbf{1}]_0$:$[\mathbf{4}]_0$:$[\mathbf{5}]_0$ = 1:0.5:0.5).

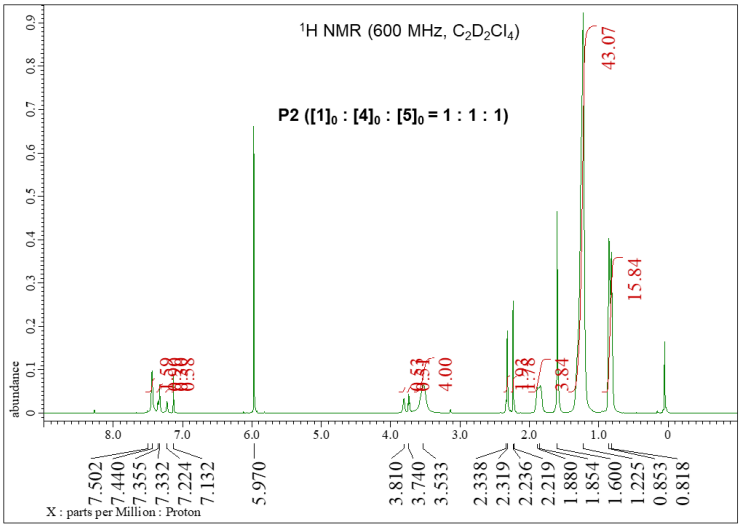


Fig. S18. ^{1}H NMR spectrum of **P2** ($[\mathbf{1}]_0$:$[\mathbf{4}]_0$:$[\mathbf{5}]_0$ = 1:1:1).

SEC Traces

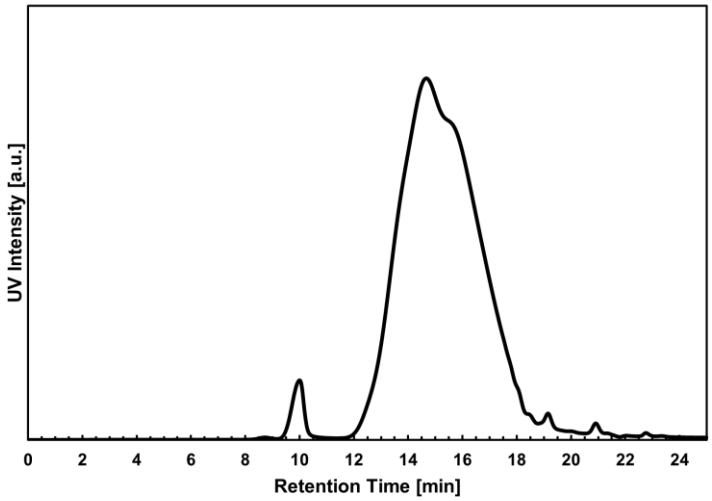


Fig. S19. SEC UV trace of **P1** ([**1**]$_0$:[**2**]$_0$ = 1:1).

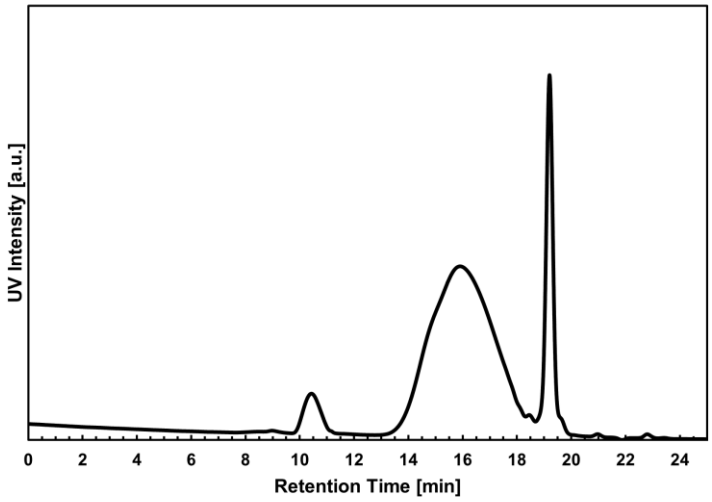


Fig. S20. SEC UV trace of **P1** ([**1**]$_0$:[**2**]$_0$ = 1:1.5).

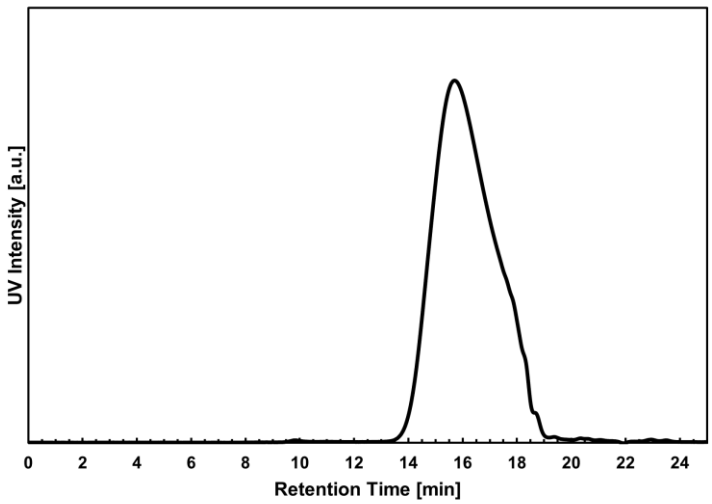


Fig. S21. SEC UV trace of **P2** ([**1**]$_0$:[**4**]$_0$:[**5**]$_0$ = 1:0.5:0.5).

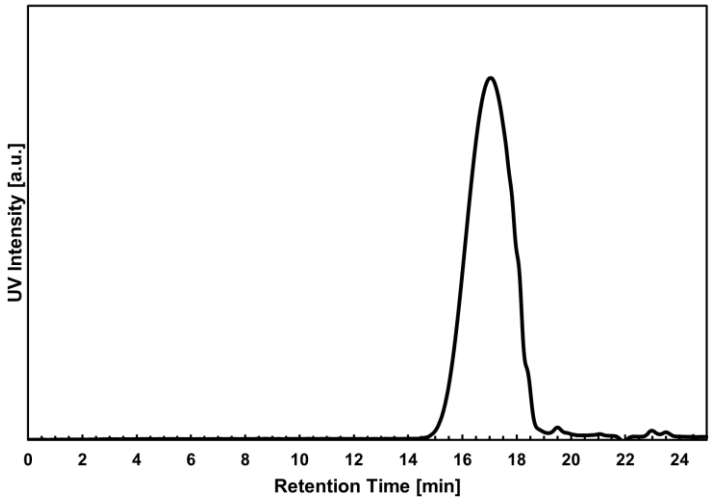


Fig. S22. SEC UV trace of **P2'** ([**1**]$_0$:[**4**]$_0$:[**5**]$_0$ = 1:1:1).

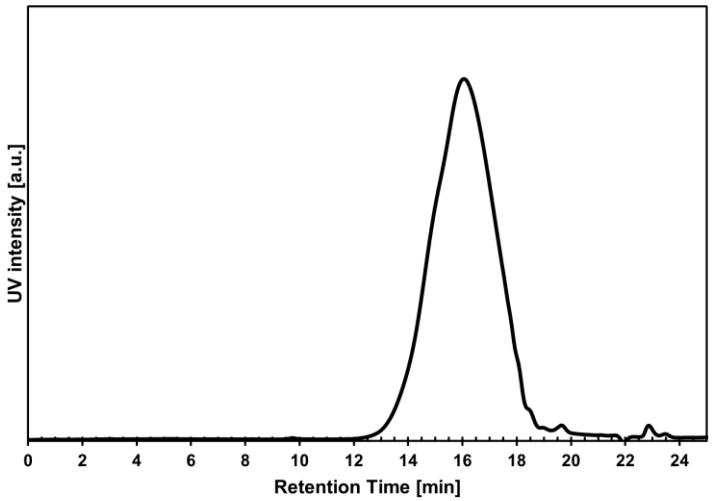


Fig. S23. SEC UV trace of **P1-T**.

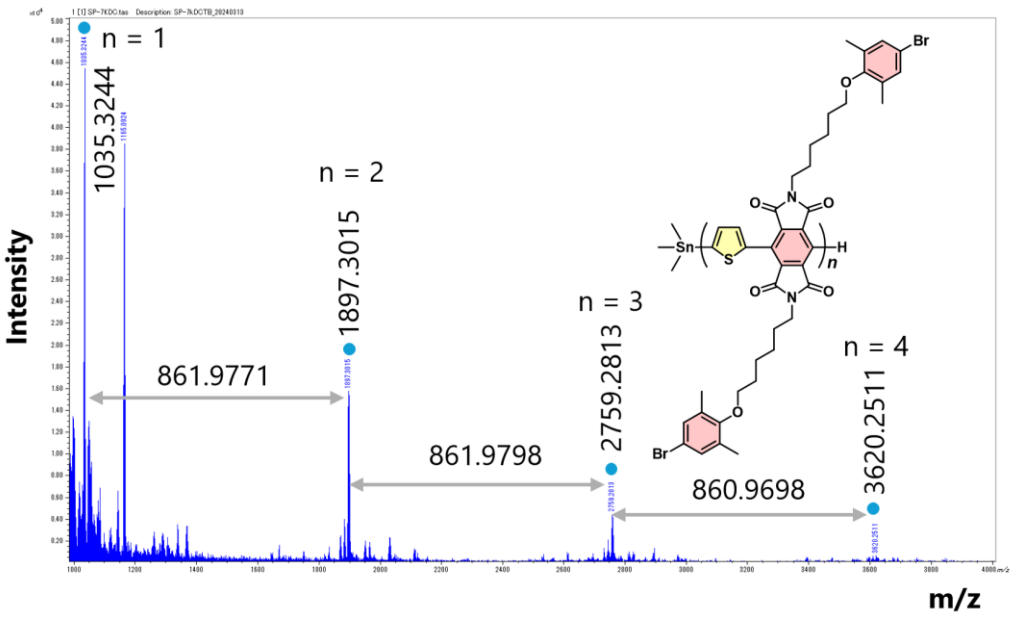


Fig. S24. MALDI-TOF MS spectrum of **P1'**.