Supporting Information

Linear-selective Cross-coupling Polymerization of Branched Oligothiophene by Deprotonative Metalation and Cross-coupling

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Experimental section.

General.

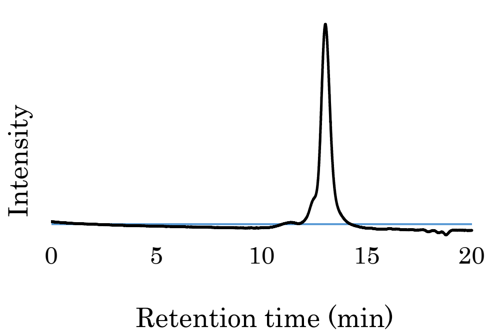
All the reactions were carried out under nitrogen atmosphere with standard Schlenk technique. ^{1}H NMR (300 or 500 MHz) and ^{13}C NMR (125 MHz) spectra were measured on Varian Gemini 300 and Bruker Avance 500 spectrometers as a $CDCl_3$ solution unless noted. The chemical shifts were expressed in ppm with $CHCl_3$ (7.26 ppm for ^{1}H) or $CDCl_3$ (77.0 ppm for ^{13}C) as internal standards. IR spectra were recorded on Bruker Alpha with an ATR attachment (Ge). MALDI-TOF mass spectra were measured by Brucker Daltonics Flexscan ultrafleXtreme. SEC (size exclusion chromatography) analyses were performed with a standard Thermal analyses were carried out with Seiko Instruments Inc., DSC220C (DSC) and RIGAKU Thermo plus EVO2 series (TG). HPLC system equipped with a UV detector using chloroform as an eluent with a Shodex KF-806L or the related column. Molecular weights and molecular weight distributions were estimated on the basis of the calibration curve obtained by 6 standard polystyrenes (M_n = 2630-355000). Elemental analysis was carried out at Quantum Beam Science Center Japan Atomic Energy Agency, Harima, Japan with vario MICRO cube. UV-vis spectra were measured by ALS SEC-2000 UV/VIS spectrometer with SEC-2000 DH. Purification by HPLC with preparative SEC column (JAI-GEL-2H) was performed by JAI LC-9201. For thin layer chromatography (TLC) analyses throughout this work, Merck precoated TLC plates (silica gel 60 F_{254}) were used. Preparation of **3T**-Br_2 (**1a**) and **7T**-Br_4 were performed according to the literature procedure.[1] TMPMgCl·LiCl was prepared by the literature procedure[2] and stored in the freezer as 1.0 M THF solution. $NiCl_2$dppe, and $NiCl_2$dppp were prepared according to the literature procedure.[3] $NiCl_2(PPh_3)$IPr was purchased from Tokyo Chemical Industry Co., Ltd. THF (anhydrous grade) was purchased from Kanto Chemicals Co. Ltd. Other materials were purchased from Aldrich, Tokyo Chemical Industry Co., Ltd., Wako Pure Chemical Industries, Ltd., or Kanto Chemicals Co., Ltd.

General procedure for the polymerization of 3T-Br_2 (1a): To a solution of 1.0 M TMPMgCl·LiCl (0.36 mL, 0.36 mmol) in THF was added **3T**-Br_2 **(1a)** (0.3 mmol, 145.2mg) dropwise at room temperature. After stirring for 3 h, THF (2.64 mL) and $NiCl_2(PPh_3)$IPr (4.68 mg, 0.006 mmol) were successively added. The resulting mixture was allowed to stir at room temperature for 2 h. Hydrochloric acid (1.0 M, 5 mL) and methanol (15 mL) were added to form precipitates. The mixture was filtered and washed with methanol and hexane repeatedly to leave dark purple solid. The product was subsequently washed for 5 h by Soxhlet extractions with methanol, acetone, and hexane, after which the chloroform-soluble fraction was collected by extraction with $CHCl_3$. Then, the solution was concentrated and dried under reduced pressure to afford 130.3 mg of polymer (88%). Molecular weight and molecular weight distribution were estimated by SEC analysis (eluent: $CHCl_3$). SEC analysis showed M_n=21000, PDI = 1.20 in Fig. 1s (a). MALDI-TOF-MS of this polymer was shown in Fig. 1s (c). Peaks with ca. 493 Da interval, which was consistent with **3T**-Br unit, were observed in the mass spectrum. Representative peaks shown as 3041.37 Da and 2961.445 Da indicated the good correspondence with $\text{Br-(3T-Br)}_6\text{-H}$ (78.9+493.58x6+1.01: calcd. for 3041.39 Da) and $\text{H-(3T-Br)}_6\text{-H}$ (1.01+493.58x6+1.01: calcd. for 2963.50 Da), respectively.

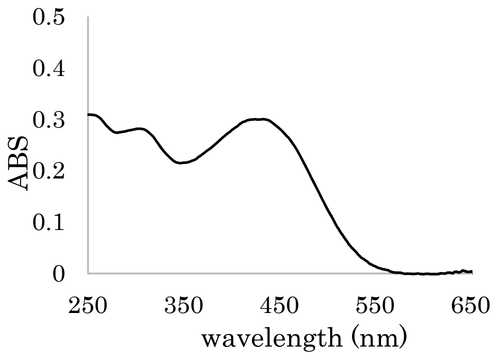
Anal. C: 58.28%; H: 5.96%. Calcd for $\text{Br-(C}_{24}\text{H}_{29}\text{BrS}_3)_n\text{-H}$: C:58.53%, H:5.94%.

^{1}H NMR ($CDCl_3$) δ 0.75-0.95 (m, 6H), 1.23-1.45 (br, 12H), 1.52-1.71 (br, 4H), 2.55 (t, *J* = 6.94 Hz, 2H), 2.76 (t, *J* = 6.94 Hz, 2H), 6.86 (s, H), 7.00 (s, H), 7.06 (s, H)

(a)



(b)



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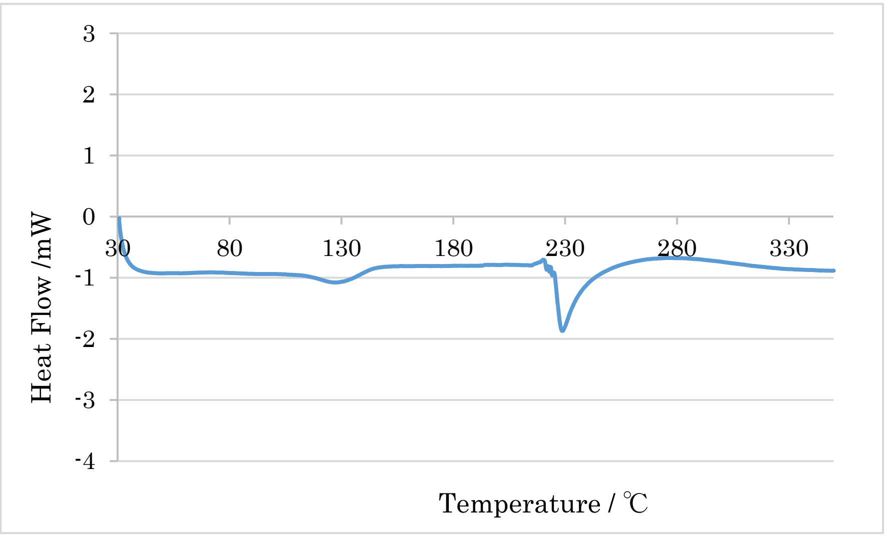

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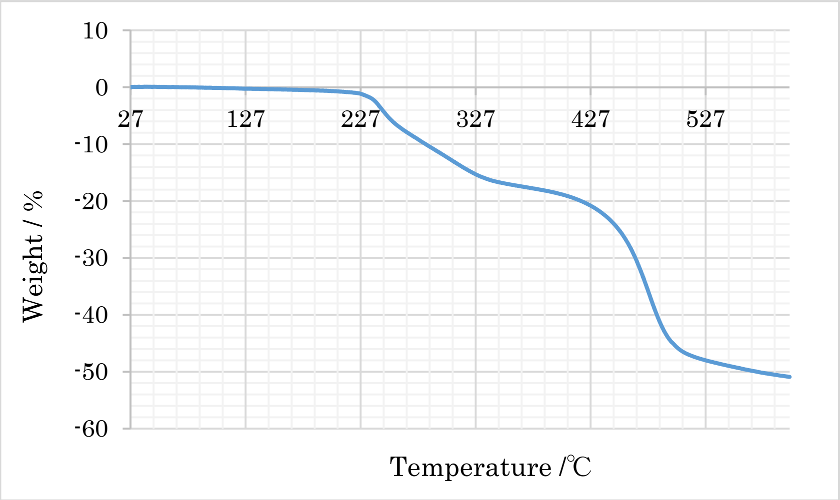


(e)

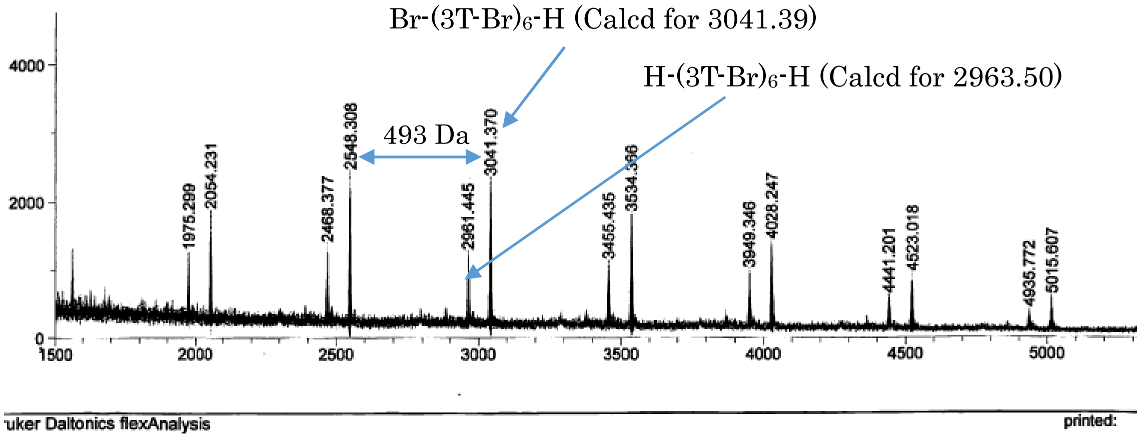


Figure s1. (a) SEC profile of (**3T**-Br)*n* (b) UV-vis spectrum of (**3T**-Br)*n* (c) DSC profile of (**3T**-Br)*n* with heating rate of 10 °C/min. (d) TG profile of (**3T**-Br)*n* with heating rate of 10 °C/min. (e) MALDI-TOF mass spectrum of (**3T**-Br)*n* (catalyst loading: 10 mol%) after treatment of 1 M HCl/MeOH

Studies on the relationship of M_n and catalyst loading: Polymerization of **1a** was carried out in a similar manner as described above with catalyst loading of $NiCl_2(PPh_3)IPr$ as 1.0, 2.0, 3.0, 4.0 mol %, respectively. The isolated polymer was subjected to SEC analysis and M_n and PDI values were estimated from polystyrene standards. The results are summarized in Table 1s.

Table s1. Relationship of M_n and catalyst loading of $NiCl_2(PPh_3)IPr$

catalyst loading (mol%)	isolated yield (conversion)	M_n (PDI)	M_{theor}
1.0	98 (99)	44000 (1.30)	49500
2.0	88 (92)	21000 (1.20)	24700
3.0	93 (95)	15700 (1.23)	16500
4.0	80 (96)	13000 (1.23)	12300

Synthesis of 3T-Cl$_2$ (1b): To a 20 mL Schlenk tube equipped with a magnetic stirring bar were added **3T** (208.4 mg, 0.5 mmol), DMF (3.0 mL), NH_4NO_3 (2.0 mg, 0.025 mmol) and NCS (146.9 mg, 1.1 mmol) and the resulting mixture was stirred at 60 °C overnight. The mixture was quenched with water and the solution was poured into the mixture of diethyl ether/water and two phases were separated. Aqueous phase was extracted with diethyl ether twice and the combined organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude oil, which was purified by chromatography on silica gel (hexanes) to afford 200.9 mg of **3T**-Cl$_2$ **(1b)** (yellow oil, 83%). ^{1}H NMR δ 0.885 (t, J = 6.94 Hz, 3H), 0.888 (t, J = 6.94 Hz, 3H), 1.26-1.37 (m, 12H), 1.51-1.61 (m, 4H), 2.53 (t, J = 6.94 Hz, 2H) , 2.54 (t, J = 6.94 Hz, 2H), 6.77 (s, 1H), 6.84 (s, 1H), 7.08 (d, J = 5.28 Hz, 1H), 7.25 (d, J = 5.28 Hz, 1H); ^{13}C NMR δ 14.09, 14.10, 22.58(×2), 27.92(×2), 28.80, 28.82, 29.53, 29.56, 31.59, 31.61, 124.50, 124.84, 125.69, 127.34, 128.76, 129.23, 130.84, 131.05, 131.71, 133.35, 139.37, 139.58; IR (ATR) 2954, 2925, 2855, 1464, 1406, 1377, 1200, 1177, 1098, 1040, 1027, 876, 837, 796, 780, 729, 696, 642, 619 cm^{-1}; HRMS (DART-ESI+) Calcd for $C_{24}H_{31}{}^{35}Cl_2S_3$ $[M+H]^+$: 485.0965; found: m/z 485.0988.

Polymerization of 3T-Cl$_2$ (1b): To a solution of 1.0 M TMPMgCl·LiCl (0.36 mL, 0.36 mmol) in THF was added **3T**-Cl$_2$(0.3 mmol, 145.2mg) dropwise at room temperature. After stirring for 3 h, THF (2.64 mL) and $NiCl_2(PPh_3)IPr$ (2.34 mg, 0.003 mmol) were successively added. The resulting mixture was allowed to stir at room temperature for 5 h. Hydrochloric acid (1.0 M, 5 mL) and methanol (15 mL) were added to form precipitates. Purification was carried out in a manner described for the polymerization of **3T**-Br$_2$ to afford 111.8 g of (**3T**-Cl)$_n$ (83%). Molecular weight and molecular weight distribution were estimated by SEC analysis (eluent: $CHCl_3$) to show M_n =36000, PDI = 1.42 in Fig. 2s (a).

MALDI-TOF-MS of this polymer was shown in Fig. 2s (b). Peaks with ca. 449 Da interval, which was consistent with **3T**-Cl unit, were observed in the spectrum. A representative peaks shown as 3628.204 Da indicated the good correspondence with Cl-$(3T\text{-}Cl)_8$-H (35.5+449.14x8+1.01: calcd. for 3629.63 Da).

^{1}H NMR δ 0.80-0.93 (m, 6H), 1.20-1.46 (br, 12H), 1.61-1.72 (br, 4H), 2.55 (t, *J* = 7.49 Hz, 2H), 2.77 (t, *J* = 7.49 Hz, 2H), 6.86 (s, 1H), 7.00 (s, 1H), 7.05 (s, 1H)

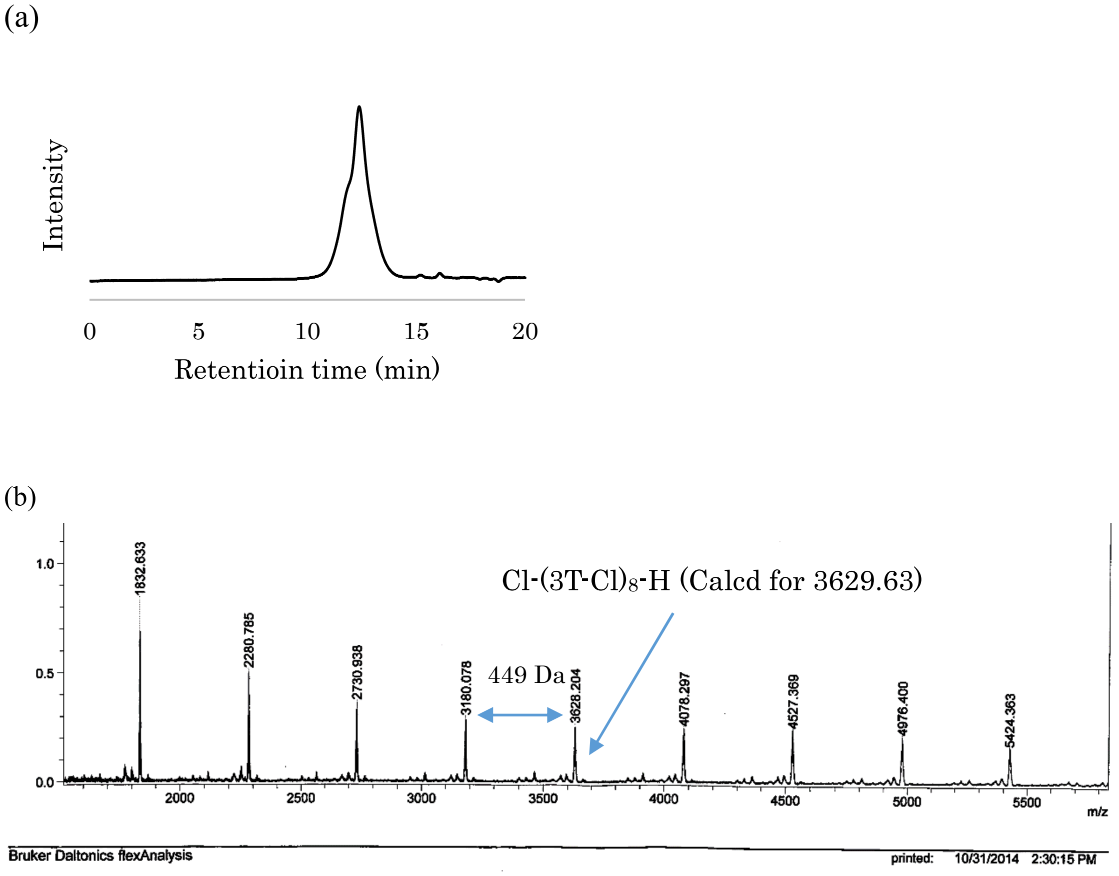


Figure s2. (a) SEC profile of (**3T**-Cl)*n* (b) MALDI-TOF mass spectrum of (**3T**-Cl)*n* (catalyst loading: 10 mol%) after treatment of 1M HCl/MeOH

Synthesis of block copolymer: Polymerization of **3T-**Br_2 **(1a)** (201.1 mg, 0.35 mmol) was carried out in a similar manner described above with 1.0 M TMPMgCl·LiCl (0.42 mmol) and 4 mol % of $NiCl_2(PPh_3)$IPr at room temperature for 2 h. To the resulting mixture the metalated 3-hexylthiophene (25 equiv to Ni) was added and stirring was continued for further 30 min to afford 199 mg of block copolymer (85% yield). The M_n (PDI) of the prepolymer and the obtained block copolymer were estimated to be 13700 (1.09) and 18700 (1.12), respectively by SEC analyses[4] (calcd. prepolymer: 12500; block copolymer: 16700), which suggest the ratio of **3T**-Br and 3-hexylthiophene segments were ca. 1 : 1.08 in Fig. 3s (a). The ratio of those were also estimated by ^{1}H NMR analysis to be ca. 1 : 1.12 in Fig. 3s (c). ^{1}H NMR δ 0.81-0.94 (m, 9H), 1.20-1.42 (br, 18H), 1.58-1.74 (br, 6H), 2.48-2.58 (br, 2H), 2.72-2.84 (br, 2H), 6.86 (s, H), 6.98 (s, H), 7.00 (s, H), 7.05 (s, H)

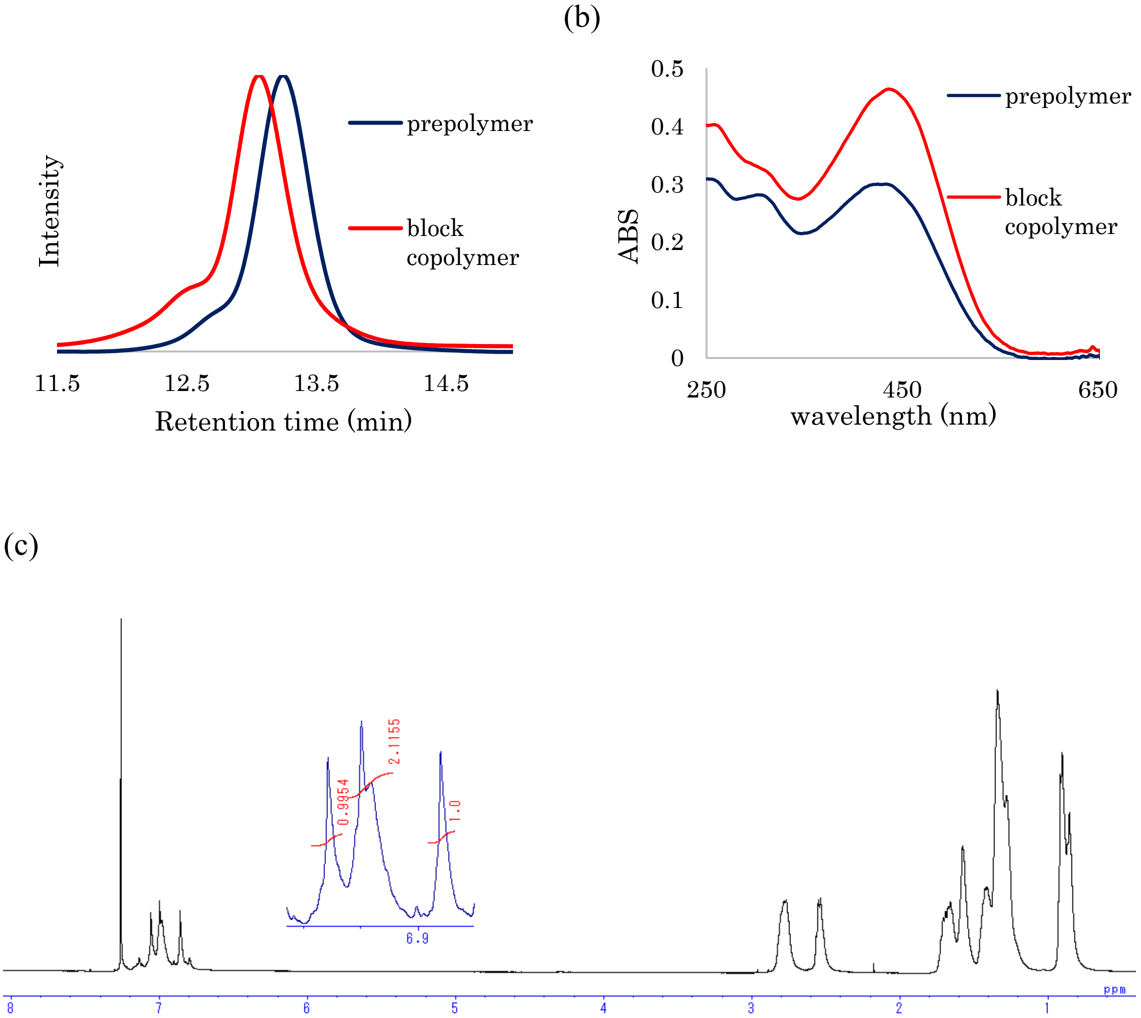
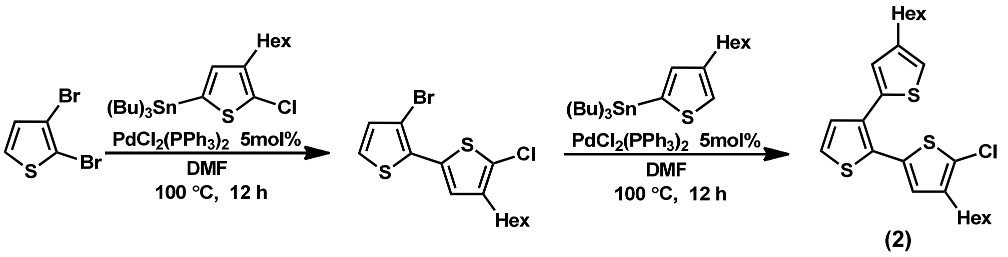


Figure s3. Spectroscopic properties of the prepolymer and the block copolymer: (a) SEC profile; (b) UV-vis absorption spectra in $CHCl_3$; (c) ^{1}H NMR spectrum (block copolymer).

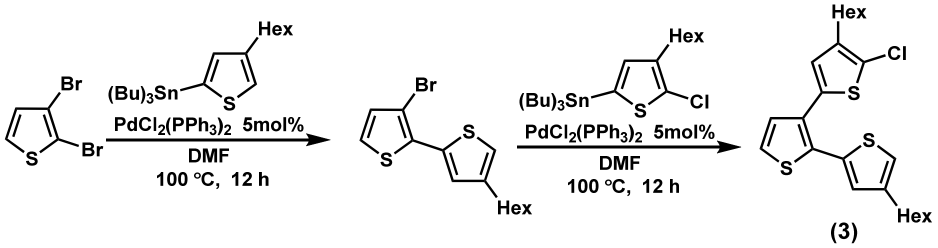
Synthesis of 2-(2-Chloro-3-Hexylthiophen-5-yl)-3-(4-hexylthiophene-2-yl)thiophene (2)



5-(3-Bromothiophen-2-yl)-2-chloro-3-Hexylthiophene: To a 20 mL Schlenk tube equipped with a magnetic stirring bar were added 2-chloro-3-hexyl-5-tributylstannylthiophene (1.61g, 3 mmol), 2,3-dibromothiophene (0.365 mL, 3.3 mmol), $PdCl_2(PPh_3)_2$ (105 mg, 0.15 mmol), and 15 mL of DMF. The mixture was allowed to stir at 100 °C for 12 h. After cooling to room temperature the mixture was quenched with water. The solution was poured into the mixture of diethyl ether/water and two phases were separated. Aqueous phase was extracted with diethyl ether twice. The organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude oil, which was purified by chromatography on silica gel (containing 10 wt% of K_2CO_3) using hexanes as an eluent to afford 807.4 mg of 5-(3-bromothiophen-2-yl)-2-chloro-3-hexylthiophene (74 %). ^{1}H NMR δ 0.89 (t, J = 7.01 Hz, 3H), 1.28-1.39 (m, 6H), 1.60 (quin, J = 7.57 Hz, 2H), 2.57 (t, J = 7.72 Hz, 2H), 6.99 (d, J = 5.36 Hz, 1H), 7.07 (s, 1H), 7.17 (d, J = 5.36 Hz, 1H); ^{13}C NMR δ 14.08, 22.58, 27.94, 28.88, 29.54, 31.58, 107.72, 124.27, 125.30, 127.09, 130.65, 131.79, 131.81, 139.50; IR (ATR) 2953, 2925, 2855, 1513, 1458, 1412, 1376, 1342, 1203, 1145, 1097, 1081, 1040, 857, 833, 801, 758, 700, 649, 609 cm^{-1}; HRMS (DART-ESI+) Calcd for $C_{14}H_{19}{}^{79}Br_1{}^{35}Cl_1S_2$ $[M+H]^+$: 364.9800; found: m/z 364.9794.

2-(2-Chloro-3-hexylthiophen-5-yl)-3-(4-hexylthiophene-2-yl)thiophene (2): To a 20 mL Schlenk tube equipped with a magnetic stirring bar were added 4-hexyl-2-tributylstannylthiophene (914.6 mg, 2 mmol), 5-(3-bromothiophen-2-yl)-2-chloro-3-hexylthiophene (727.4 mg, 2 mmol), $PdCl_2(PPh_3)_2$ (70.2 mg, 0.1 mmol), and 10 mL of DMF. The mixture was allowed to stir at 100 °C for 12 h. After cooling to room temperature the mixture was quenched with water. The solution was poured into the mixture of diethyl ether/water and two phases were separated. Aqueous was extracted with diethyl ether twice. The organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude oil, which was purified by chromatography on silica gel (containing 10 wt% of K_2CO_3) using hexanes as an eluent to afford 703.7 mg of **(2)** (78%). ^{1}H NMR δ 0.885 (t, *J* = 6.94 Hz, 3H), 0.888 (t, *J* = 6.94 Hz, 3H), 1.25-1.37 (m, 12H), 1.51-1.63 (m, 4H), 2.52 (t, *J* = 7.72 Hz, 2H) ,2.56 (t, *J* = 7.72 Hz, 2H), 6.84 (s, 1H), 6.87 (s, 1H), 6.90 (s, 1H), 7.11 (d, *J* = 5.20 Hz, 1H), 7.23 (d, *J* =5.20 Hz, 1H); ^{13}C NMR δ14.09, 14.10, 22.59, 22.60, 27.92, 28.83, 28.92, 29.53, 30.41, 30.43, 31.59, 31.67; IR (ATR) 2954, 2926, 2855, 1521, 1464, 1457, 1406, 1376, 1201, 1092, 1037, 876, 838, 780, 730, 692, 644 cm^{-1}; HRMS (DART-ESI+) Calcd for $C_{24}H_{32}{}^{35}Cl_1S_3$ [M+H]$^+$: 451.1655; found: m/z 451.1370.

Synthesis of 2-(4-hexylthiophene-2-yl)-3-(2-chloro-3-hexylthiophen-5-yl)thiophene (3)



Synthesis of 2,2'-4'-Hexylbithiophene : The reaction was carried out in a similar manner to the preparation of 5-(3-bromothiophen-2-yl)-2-chloro-3-hexylthiophene to yield 806.8 mg of 2,2'-4'-Hexylbithiophene (82%).^{1}H NMR δ 0.91 (t, *J* = 6.94 Hz, 3H), 1.27-1.39 (m, 6H), 1.62 (quin, *J* = 7.65 Hz, 2H), 2.58 (t, *J* = 7.80 Hz, 2H), 6.89 (s, 1H), 6.94 (d, *J* = 5.36 Hz, 1H), 7.05 (d, *J* =5.36 Hz, 1H), 7.26 (s, 1H); ^{13}C NMR δ 14.08, 22.56, 28.92, 30.26, 30.30, 31.59, 107.29, 120.69, 123.82, 127.80, 131.63, 132.51, 133.81, 143.27; IR (ATR) 2953, 2925, 2854, 1507, 1464, 1457, 1410, 1376, 1342, 1206, 1139, 1080, 863, 854, 837, 798, 732, 700, 648, 627, 610 cm^{-1}; HRMS (DART-ESI+) Calcd for $C_{24}H_{18}{}^{81}Br_1S_2$ [M+H]$^+$: 331.0013; found: m/z 330.9997.

Synthesis of 2-(4-hexylthiophene-2-yl)-3-(2-chloro-3-hexylthiophen-5-yl)thiophene (3): The reaction was carried out in a similar manner to the preparation of **(2)** to afford 721.7 mg of **(3)** (80%). ^{1}H NMR δ 0.88 (t, *J* = 6.94 Hz, 3H), 0.89 (t, *J* = 6.94 Hz, 3H) 1.25-1.39 (m, 12H), 1.53 (quin, *J* = 7.57 Hz, 2H), 1.61 (quin, *J* = 7.57 Hz, 2H), 2.51 (t, *J* = 7.65 Hz, 2H) ,2.58 (t, *J* = 7.65 Hz, 2H), 6.76 (s, 1H), 6.92 (s, 1H), 6.97 (s, 1H), 7.10 (d, *J* = 5.28 Hz, 1H), 7.24 (d, *J* =5.28 Hz, 1H); ^{13}C NMR δ 14.10(×2), 22.59, 22.60, 27.91, 28.81, 28.91, 29.55, 30.39, 30.40, 31.62, 31.66, 121.69, 124.10, 124.56, 126.96, 128.99, 129.58, 131.41, 131.92, 133.87, 133.95, 139.19, 143.52; IR (ATR) 2954, 2926, 2854, 1461, 1453, 1377, 1200, 1090, 1045, 1026, 839, 781, 727, 695, 642 cm-1; HRMS (DART-ESI+) Calcd for $C_{24}H_{32}{}^{35}Cl_1S_3$ $[M+H]^+$: 451.1354; found: m/z 451.1355.

Polymerization of 2-(2-chloro-3-hexylthiophen-5-yl)-3-(4-hexylthiophene-2-yl)thiophene (2): The reaction was carried out in a similar manner to that of **3T-**Br_2 **(1a)** to afford **polymer A** in 68% yield. SEC analysis; M_n =22600, PDI = 1.75. ^1H NMR (500 MHz, $CDCl_3$) δ 0.86 (t, *J* =6.94 Hz, 3H), 0.90 (t, *J* =6.94 Hz, 3H), 1.24-1.43 (m, 12H), 1.62 (m, 4H), 2.59 (t, *J* =7.65 Hz, 2H), 2.76 (t, *J* =7.65 Hz, 2H), 6.91 (s, H), 6.978 (s, H), 6.987 (s, H), 7.08 (s, H).

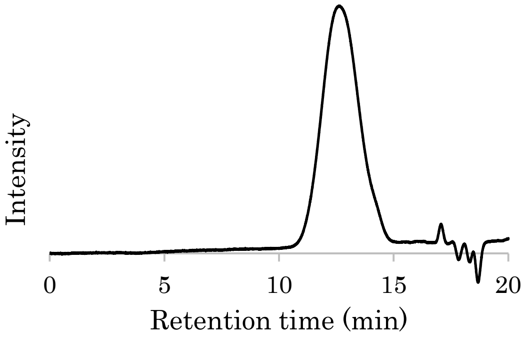


Figure s4. SEC profile of **polymer A**.

Polymerization of 2-(4-hexylthiophene-2-yl)-3-(2-chloro-3-hexylthiophen-5-yl)thiophene (3): The reaction was carried out in a similar manner to that of **3T**-Br_2 **(1a)** to afford **polymer B** in 48% yield. SEC analysis; M_n =11000, PDI = 1.09. ^1H NMR (500 MHz, $CDCl_3$) δ 0.82-0.93 (m, 6H), 1.22-1.44 (br, 12H), 1.57-1.69 (m, 4H), 2.59 (t, *J* =7.49 Hz, 2H), 2.76 (t, *J* =7.49 Hz, 2H), 6.93 (s, H), 6.94 (s, H), 7.03 (s, H), 7.14 (s, H).

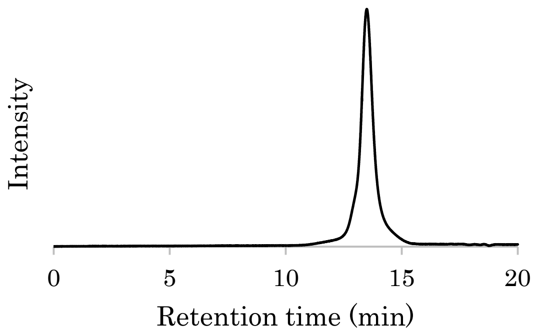
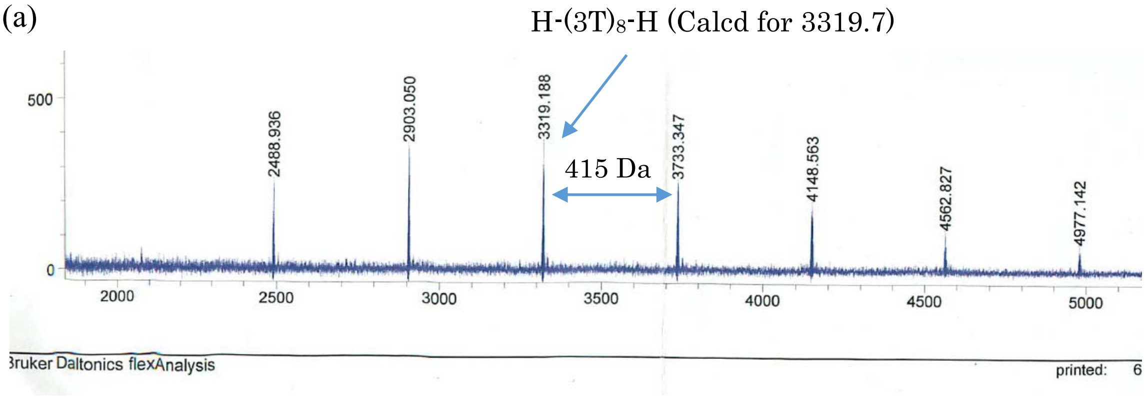


Figure s5. SEC profile of **polymer B**.

Reduction of (3T-Br)*n* with *t*BuMgCl in the presence of nickel catalyst: To a solution of (**3T**-Br)*n* (0.1 mmol, 49.4 mg) in 3 mL of THF were successively added a THF solution of 1.03 M *t*BuMgCl (0.4 mmol, 0.388 mL) and $NiCl_2dppf$ (0.01 mmol, 27.4 mg) and the resulting mixture was stirred at 60 °C for 24 h. The solution was poured into a mixture of 1 M hydrochloric acid and methanol to form a precipitate, which was filtered off. The residue was added to the mixture of hexanes/water and two phases were separated. The organic layer was washed with water repeatedly and dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure afforded 34.2 mg of reddish brown solid. MALDI-TOF MS revealed the bromo group of (**3T**-Br)*n* were completely transformed into the hydrogen atom in Figure 6s (a). The interval of peaks of ca. 415 Da, which was composed of **3T** unit, were observed in the mass spectrum. A representative peak shown as 3319.188 Da indicated the good correspondence with $H\text{-}(3T)_8\text{-}H$ (1.01+414.7x8+1.01: calcd. for 3319.62 Da).

^1H NMR ($CDCl_3$) δ 0.70-1.03 (br, 6H), 1.05-1.48 (br, 12H), 1.50-1.75 (br, 4H), 2.45-2.65 (br, 2H), 2.67-2.85 (br, 2H), 6.91 (s, H), 6.98 (br, 2H), 7.08 (s, H). The debromination protocol was alternatively employed for the estimation on the selectivity of α-α or α-β conjugation described in Figure 3 of the text. Althoguh the NMR spectrum in Figure 6s (b) showed broad siganal probably due to the effect of remaining trace amount of nickel species, the result also suggested that polymerization of **3TBr₂** in the presence of a nickel catalyst proceeded in a α-α selective manner.

(a)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415 Da
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2903.050
3319.188
3733.347
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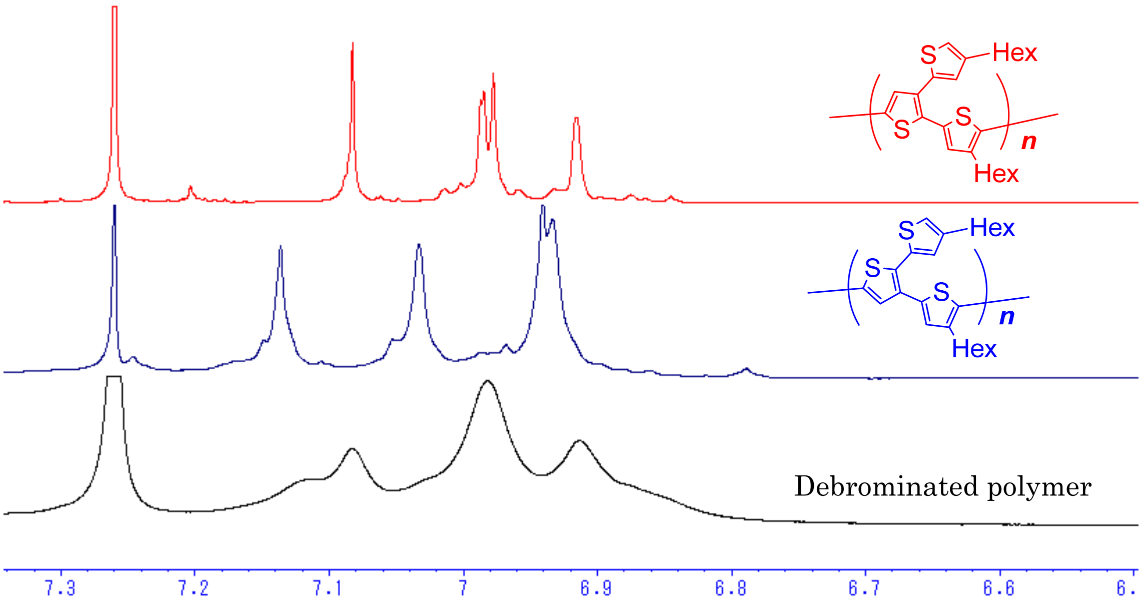
4977.142
2000
2500
3000
3500
4000
4500
5000
ruker Daltonics flexAnalysis
printed: 6

(b)


S
Hex
S
S
Hex
n
S
Hex
S
S
Hex
n
Debrominated polymer
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7.2
7.1
7
6.9
6.8
6.7
6.6
6.

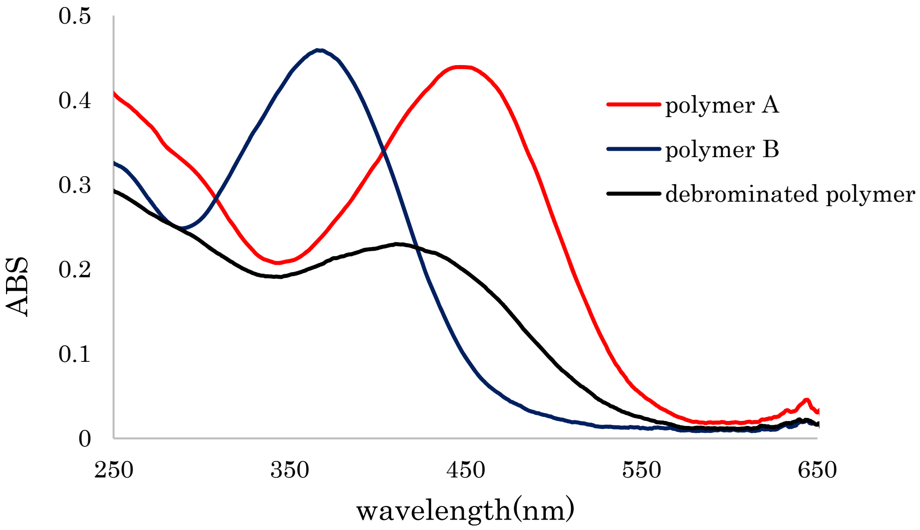


Figure s6. (a) MALDI-TOF mass spectrum of the reduction product from (**3T**-Br)*ₙ* (b) ^{1}H NMR spectrum of polymer **A** (red), **B** (blue) and the reduction product (**3T**-Br)*ₙ* (black). (c) UV-vis absorption spectra of **A**, **B**, and (**3T**-Br)*ₙ*

Transformation of the carbon-bromine bond of (3T-Br)$_n$ with arylboroic acid 4-MeOC$_6$H$_4$B(OH)$_2$: The Suzuki-Miyaura coupling reaction of (**3T**-Br)$_n$ (118.3 mg) with 4-Methoxyphenylboronic acid (145.9 mg, 0.96 mmol) and $PdCl_2(PPh_3)_2$ (8.43 mg, 0.012 mmol) in THF (1.2 mL) was carried out in the presence of 1.2 mL of aqueous K_2CO_3 at 60 °C for 2 days. After cooling to room temperature the reaction mixture was diluted with chloroform**.** The organic layer was washed with water repeatedly and dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure afforded 115.4 mg of reddish brown solid. MALDI-TOF MS spectrum revealed the bromo group of (**3T**-Br)$_n$ were completely transformed into the 4-methoxyphenyl group as shown in Figure 7s. The interval of peaks of ca. 521 Da, which was composed of **3T**-(C_6H_4-OMe) unit, were observed in the mass spectrum. A representative peaks shown as 3125.603 Da and 3231.62 Da indicated the good correspondence with H-(3T-Aryl)$_6$-H (1.01+520.87x6+1.01: calcd. for 3127.24 Da) and Aryl-(3T-Aryl)$_6$-H (107.13+520.87x6+1.01: calcd. for 3233.36 Da), respectively.

^{1}H NMR ($CDCl_3$) δ 0.78-0.91 (br m, 6H), 1.16-1.44 (br m, 12H), 1.52-1.63 (br, 2H), 1.63-1.72 (br, 2H), 2.54-2.64 (br, 2H), 2.74-2.84 (br, 2H), 3.83 (s, 3H), 6.93 (d, *J* =7.49 Hz, 2H), 7.03 (s, H), 7.05 (s, H), 7.15 (s, H), 7.31-7.41 (br, 2H).

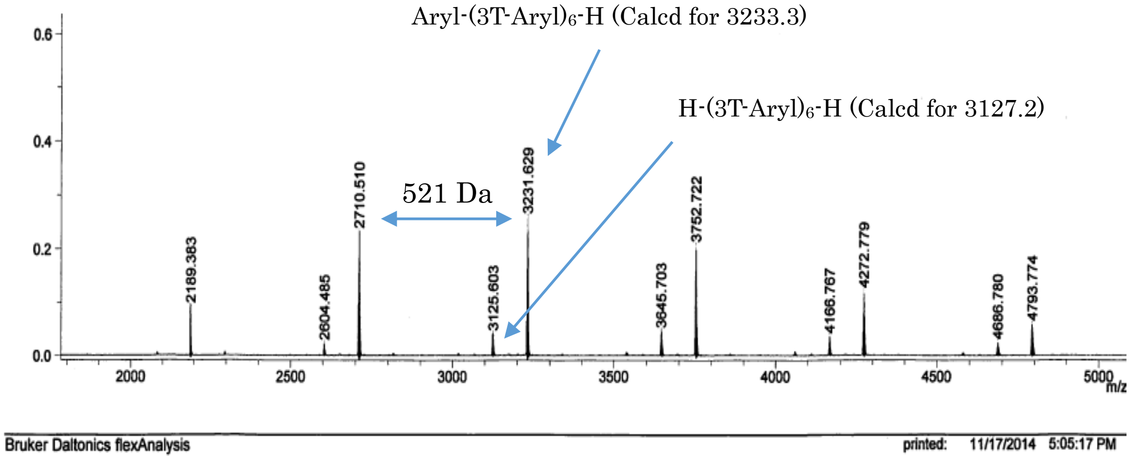
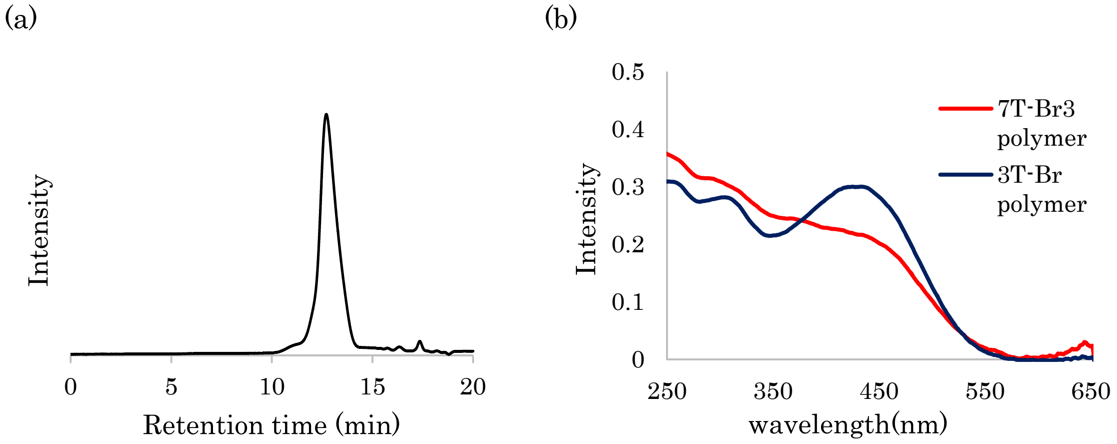


Figure s7. MALDI-TOF mass spectrum of the arylated polymer

Polymerization of 7T-Br$_4$：The reaction was carried out in a similar manner to that of **3T**-Br$_2$ **(1a)**.

Yield; 43%. SEC analysis; M_n =21000, PDI = 1.26. ^{1}H NMR (CDCl$_3$) δ 0.81-0.92 (br m, 12H), 1.21-1.43 (br m, 24H), 1.49-1.72 (m, 8H), 2.45-2.58 (br m, 6H), 2.72-2.82 (br m, 2H), 6.80 (s, H), 6.86 (s, H), 6.87 (s, H), 7.01 (s, H) , 7.14 (s, H) , 7.16 (s, H) , 7.18 (s, H).



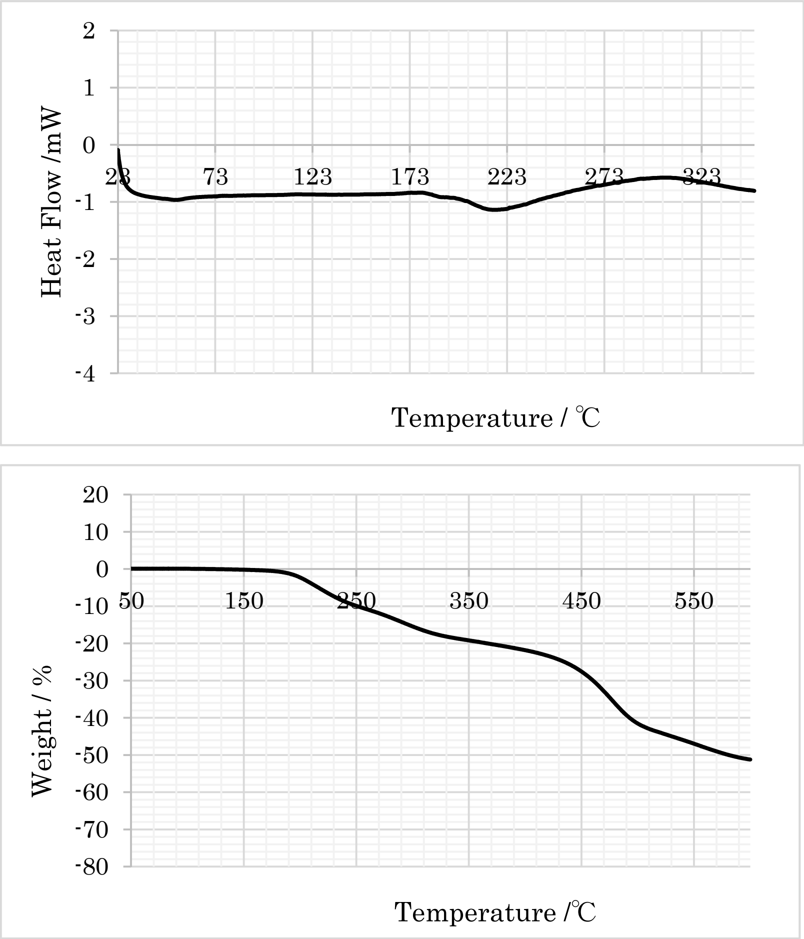


Figure s8. (a) SEC profile of (**7T**-Br_3)$_n$. (b) UV-vis absorption spectra of (**3T**-Br)$_n$ and (**7T**-Br_3)$_n$. (c) DSC profile of (**7T**-Br_3)$_n$. (d) TG profile of (**7T**-Br_3)$_n$.

References

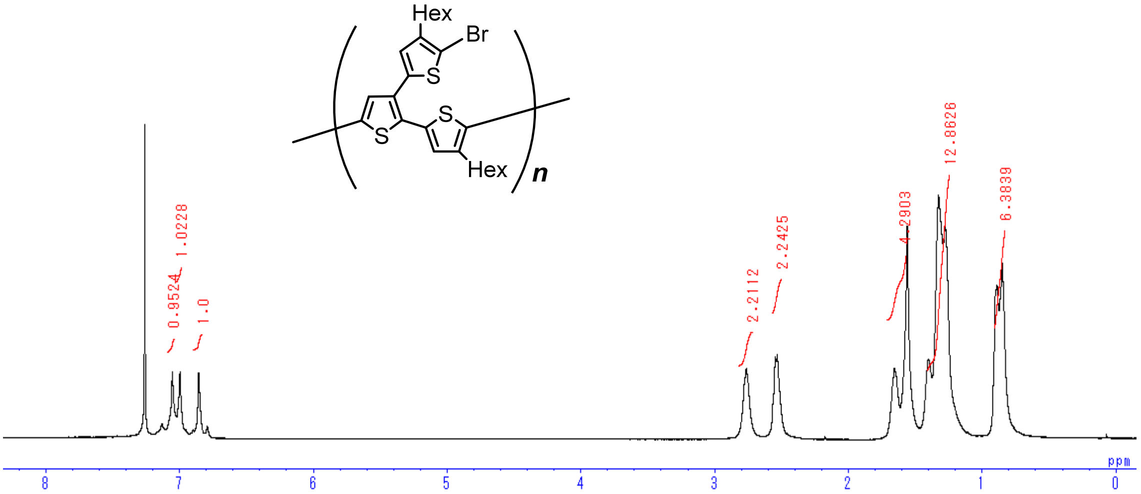
(1) Tanaka, S.; Tanaka, D.; Tatsuta, G.; Murakami, K.; Tamba, S.; Sugie, A.; Mori, A. *Chem. Eur. J.* **2013**, *19*, 1658.

(2) Do, H-Q.; Daugulis, O. *J. Am. Chem. Soc.*, **2009**, *131*, 17052.

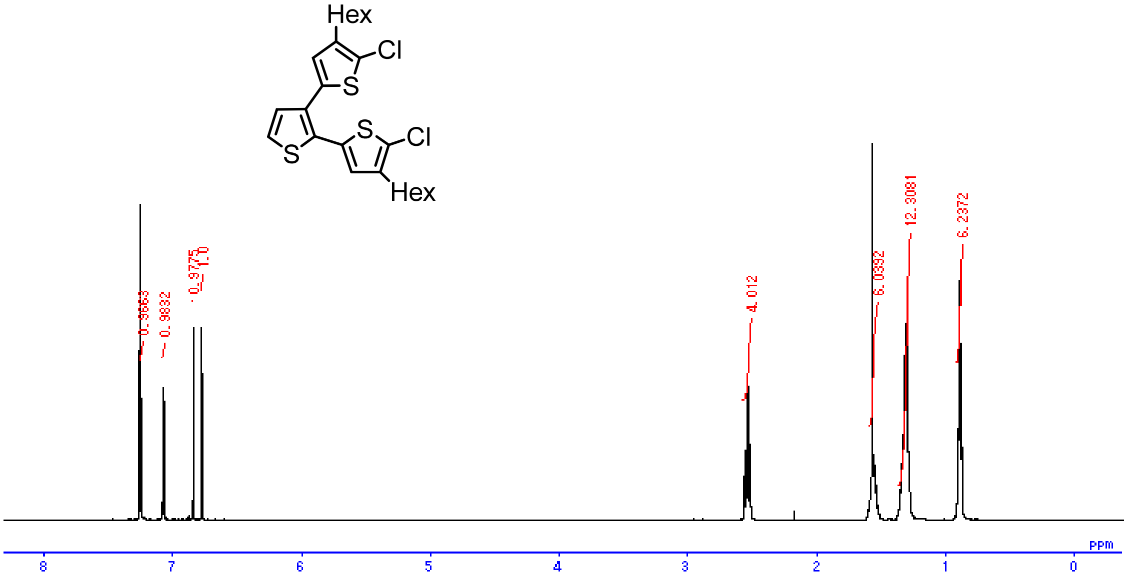
(3) Booth, G.; Chatt, J. *J. Chem. Soc.*, **1965**, 3239.

(4) Small shoulder peaks at the higher molecular weight may be caused by unfavorable coupling reaction between polymer chains probably by nickel catalysis after complete consumption of the monomer although it takes a longer period to result in gelation (see Table 1 of the text).

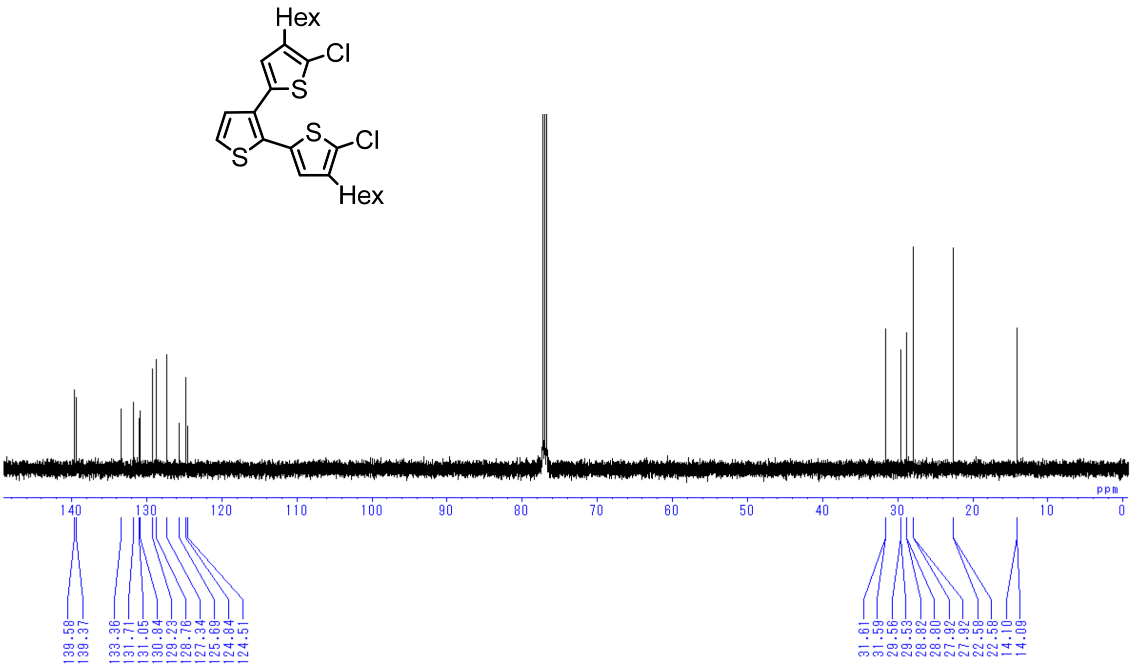
^{1}H NMR spectrum of (**3T**-Br)$_n$



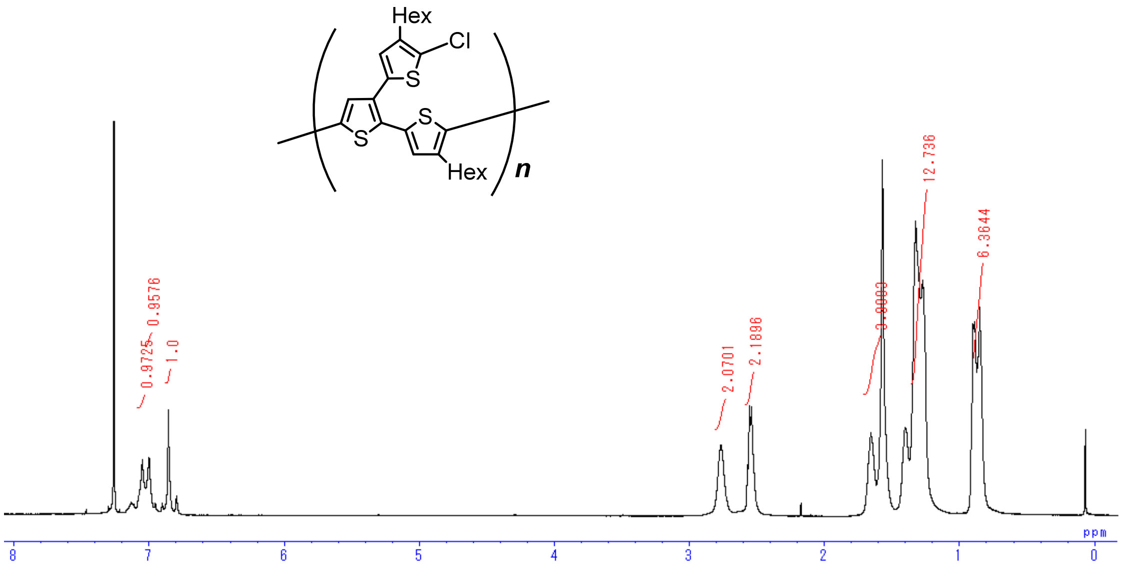
^{1}H NMR spectrum of **3T**-Cl$_2$ (**1b**)



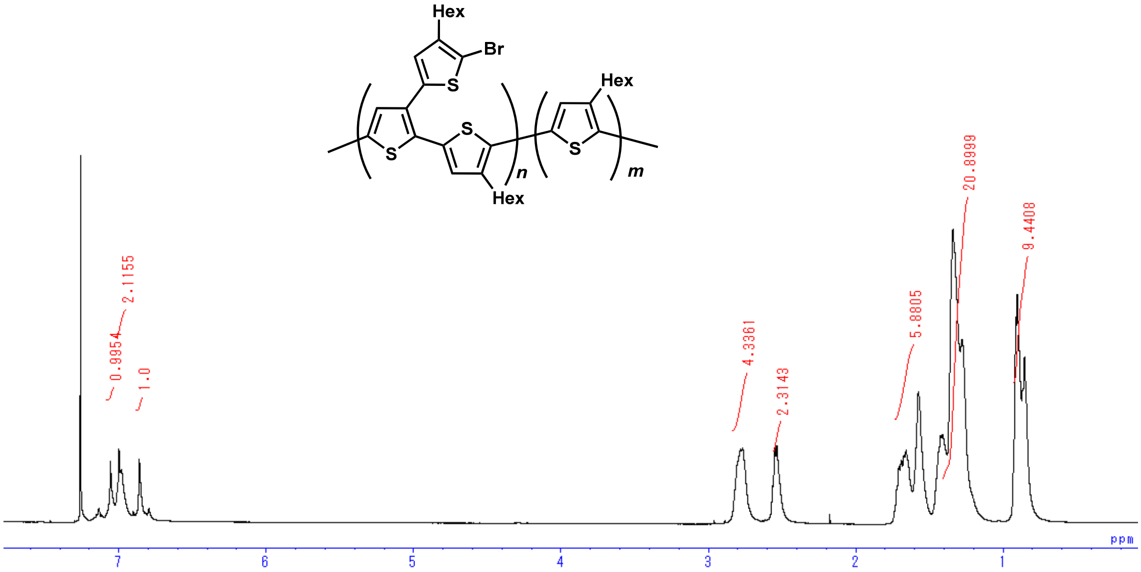
^{13}C NMR spectrum of **3T**-Cl$_2$ (**1b**)



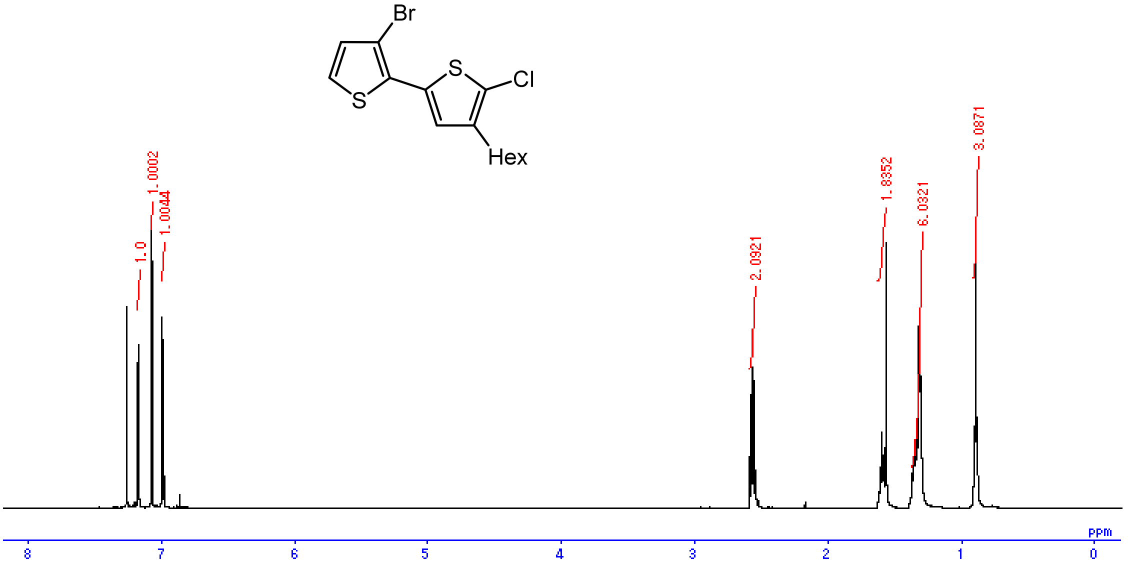
^{1}H NMR spectrum of (**3T**-Cl)$_n$



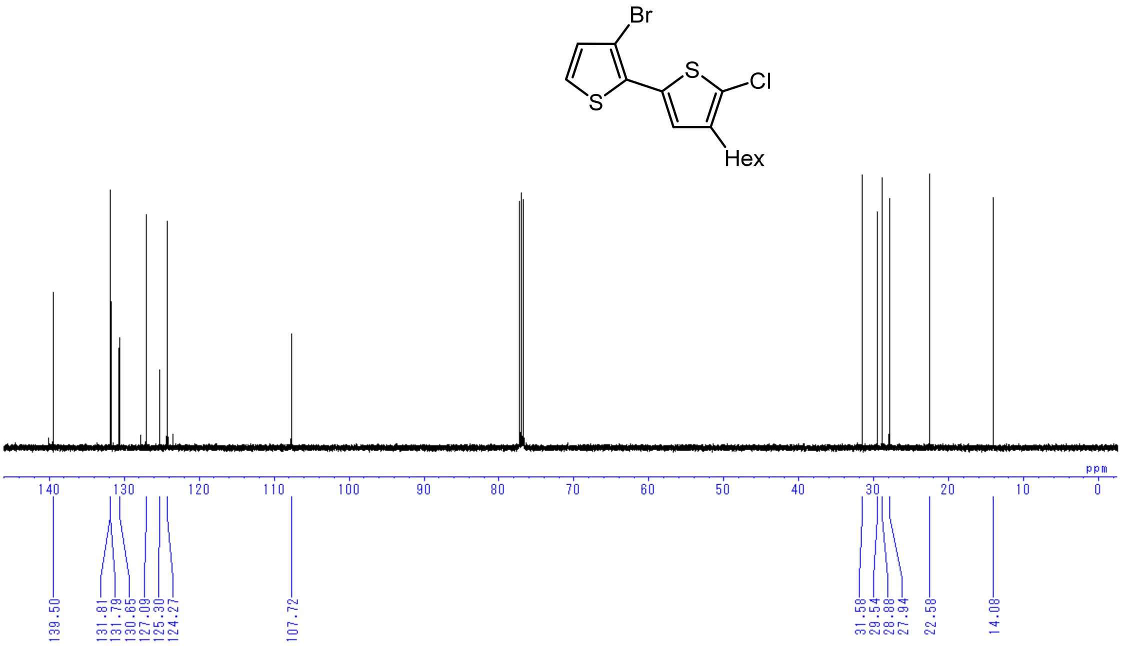
^{1}H NMR spectrum of the block copolymer



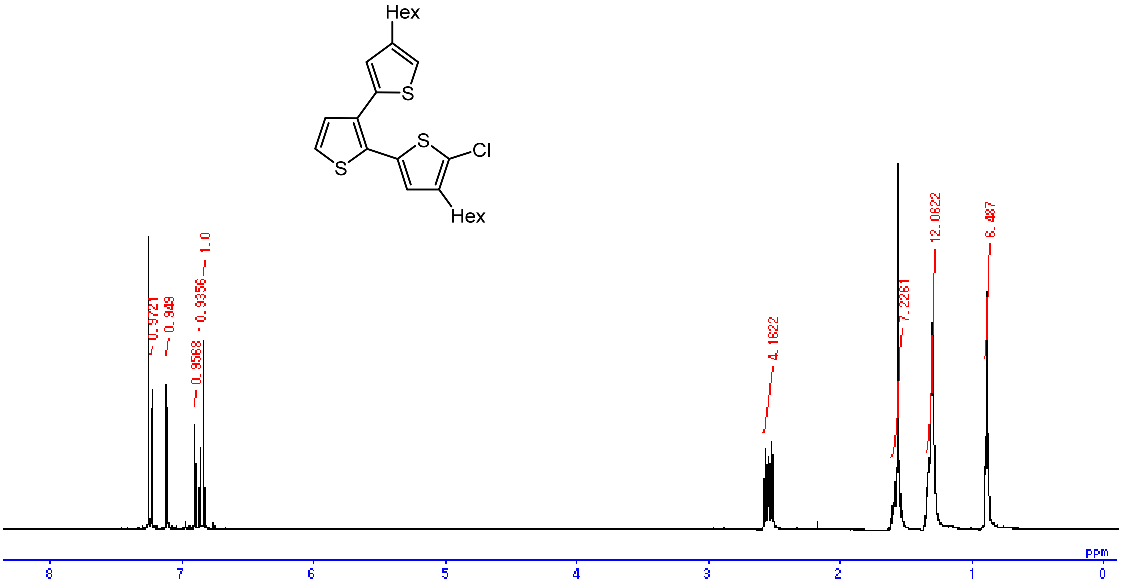
^{1}H NMR spectrum of 5-(3-bromothiophen-2-yl)-2-chloro-3-hexylthiophene



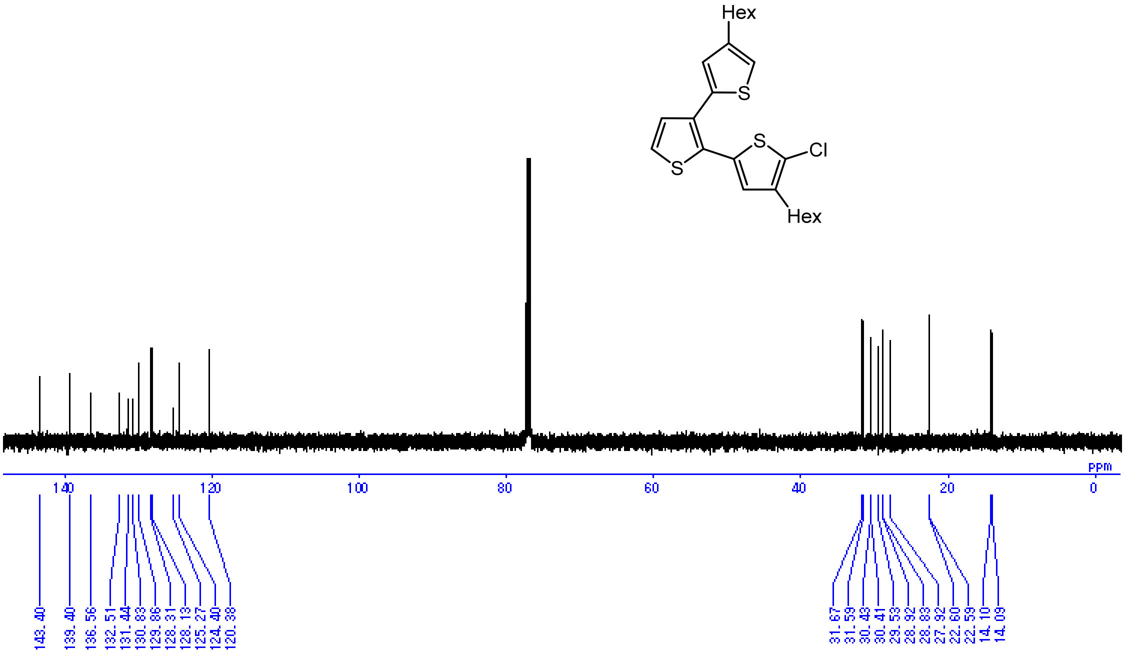
^{13}C NMR spectrum of 5-(3-bromothiophen-2-yl)-2-chloro-3-hexylthiophene



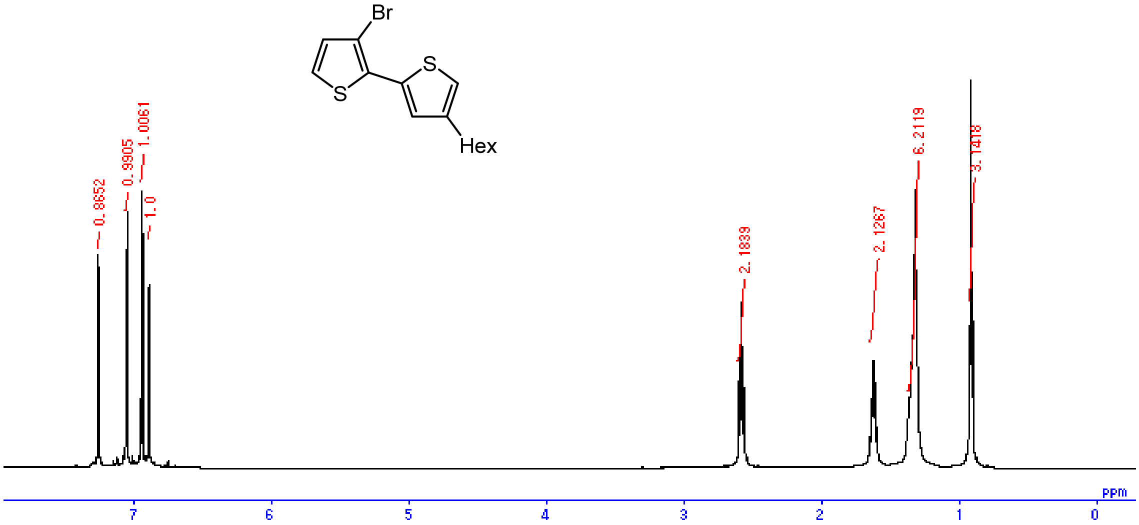
^{1}H NMR spectrum of 2-(2-chloro-3-hexylthiophen-5-yl)-3-(4-hexylthiophene-2-yl)thiophene **(2)**



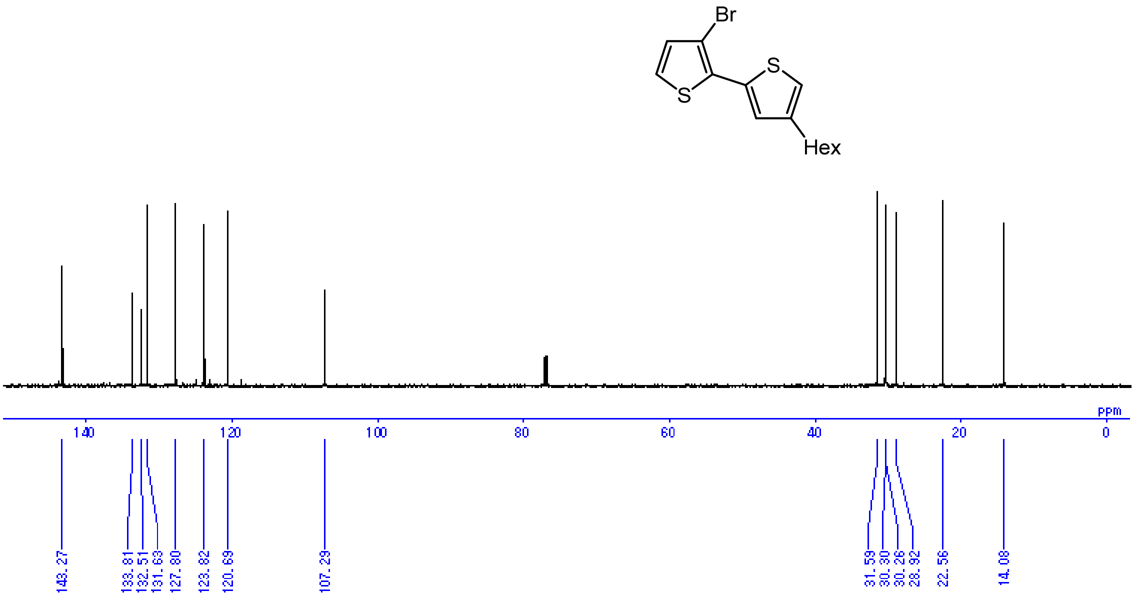
^{13}C NMR spectrum of 2-(2-chloro-3-hexylthiophen-5-yl)-3-(4-hexylthiophene-2-yl)thiophene **(2)**



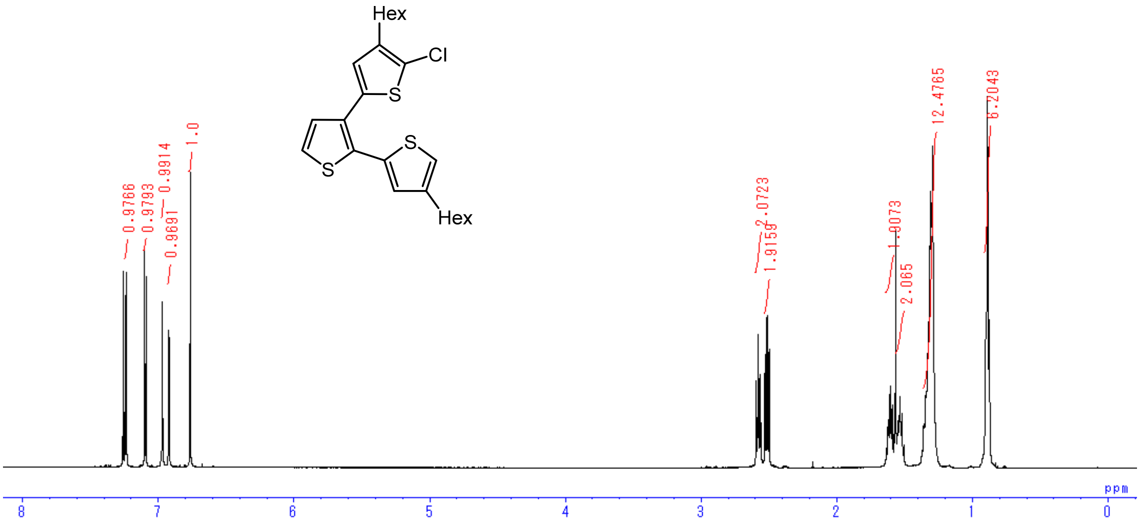
^{1}H NMR spectrum of 2,2'-4'-hexylbithiophene



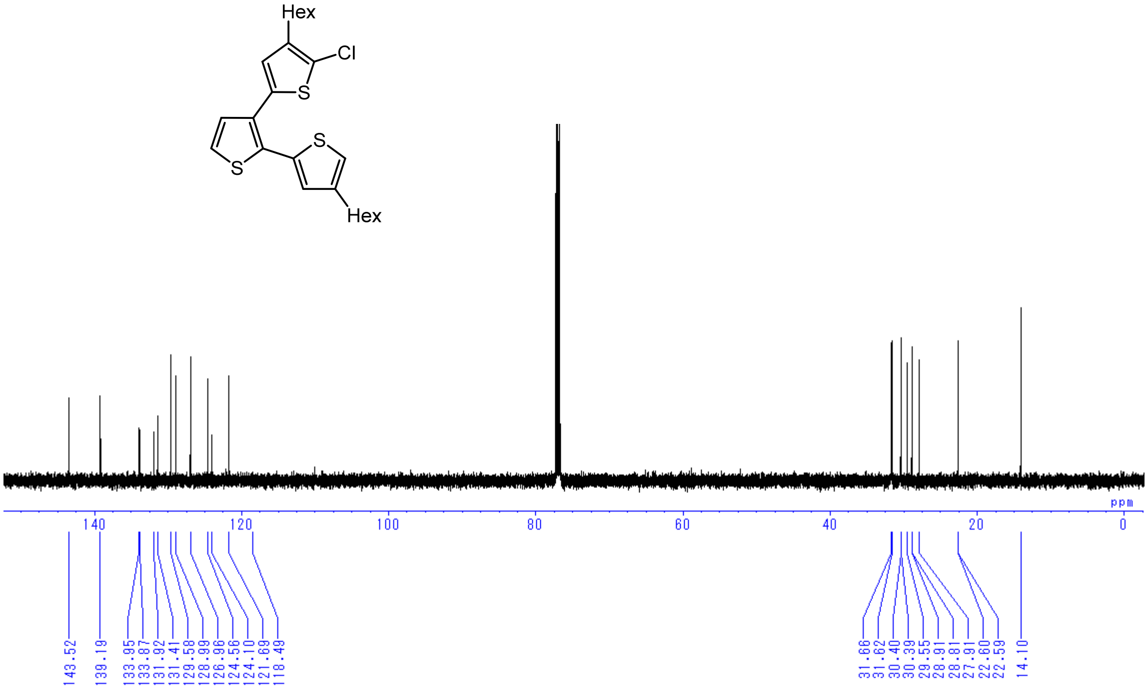
^{13}C NMR spectrum of 2,2'-4'-hexylbithiophene



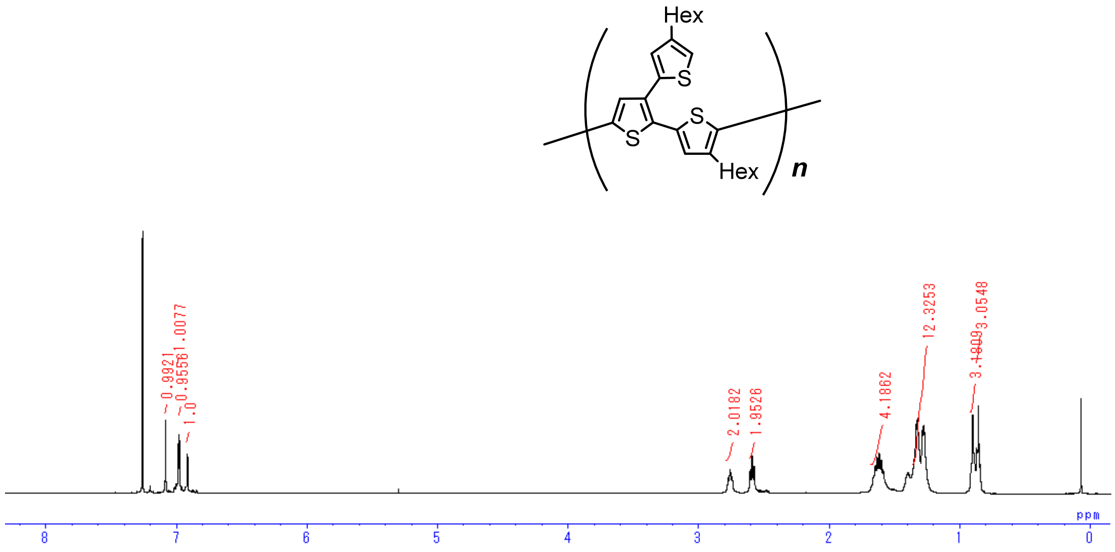
^{1}H NMR spectrum of 2-(4-hexylthiophene-2-yl)-3-(2-chloro-3-hexylthiophen-5-yl)thiophene **(3)**



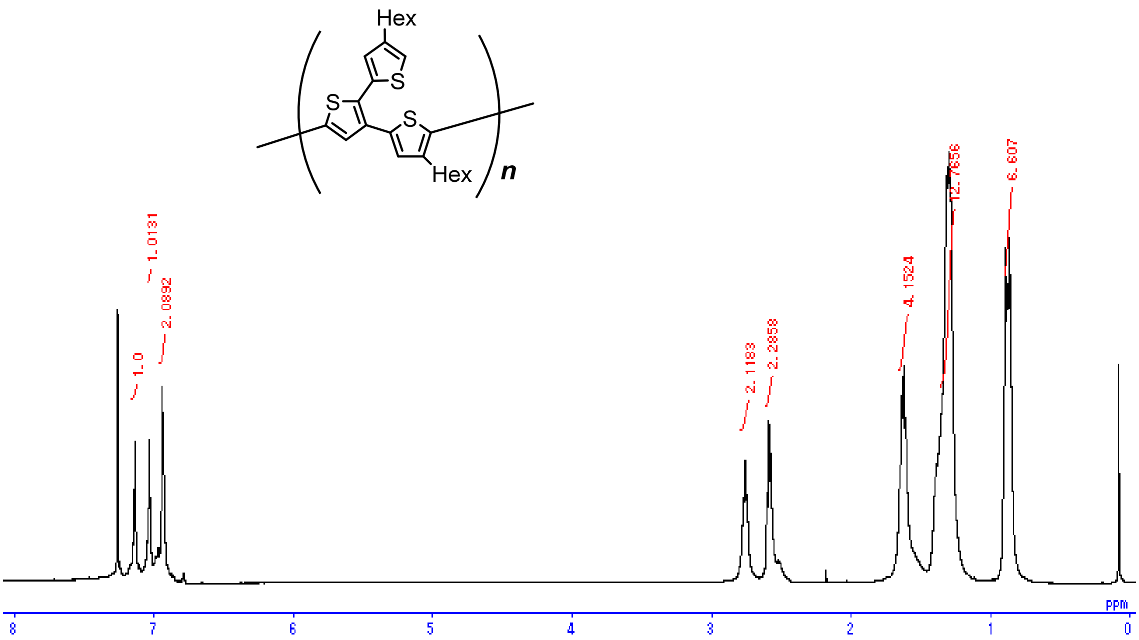
^{13}C NMR spectrum of 2-(4-hexylthiophene-2-yl)-3-(2-chloro-3-hexylthiophen-5-yl)thiophene **(3)**



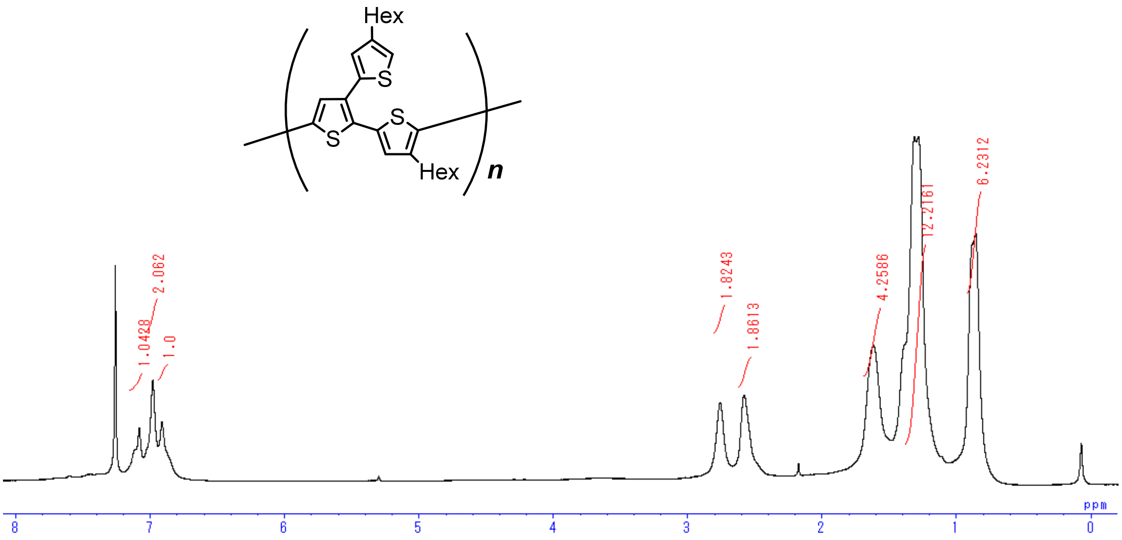
^{1}H NMR spectrum of polymer **A**



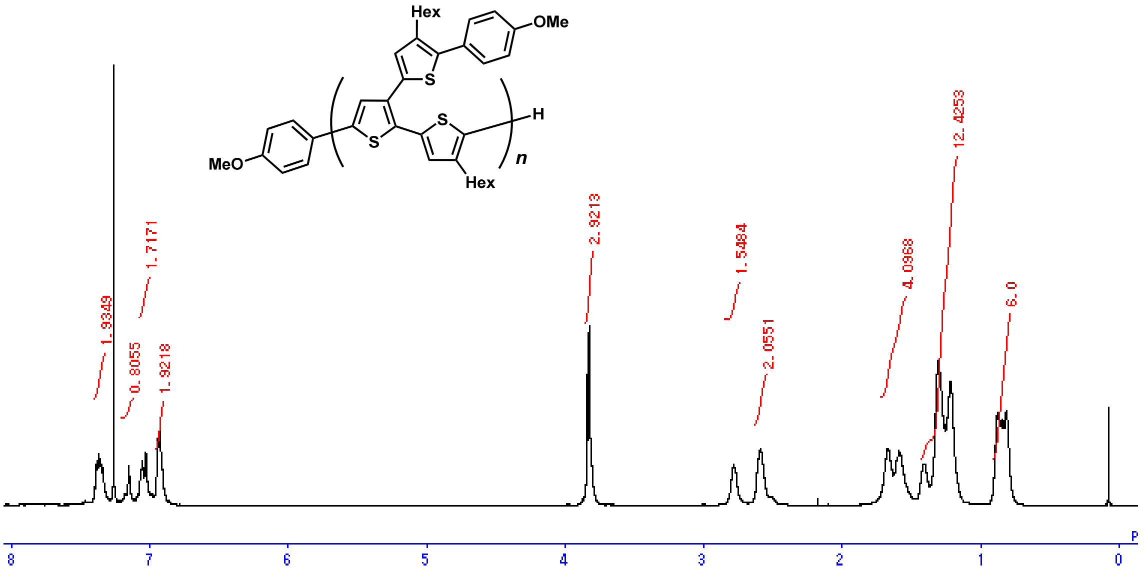
^{1}H NMR spectrum of polymer **B**



^{1}H NMR spectrum of the reduction product from (**3T**-Br)$_n$



^{1}H NMR spectrum of the arylated polymer.



^{1}H NMR spectrum of (**7T**-Br$_3$)$_n$