

Supporting Information

Polythiophene Synthesis via Halogen Dance

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Experimental Section

General.

All the reactions were carried out under nitrogen atmosphere. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were measured on Varian Gemini 300. The chemical shifts were expressed in ppm with CHCl_3 (7.26 ppm for ^1H) or CDCl_3 (77.0 ppm for ^{13}C) as internal standards. IR spectra were recorded on Bruker Alpha with an ATR attachment (Ge). SEC (size exclusion chromatography) analyses were performed with a standard 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 ($M_n = 2630\text{-}355000$). Elemental analyses were carried out at Department of Chemistry, Kobe University with Yanako CHN recorder MT-5 (CH) and at Systems Engineering Co. Ltd. with ICA-2000, Toa DKK. (Br). For thin layer chromatography (TLC) analyses throughout this work, Merck precoated TLC plates (silica gel 60 F₂₅₄) were used. Thiophene derivatives 2,5-dibromo-3-hexylthiophene (**1**) and 2,5-dibromo-3-methylthiophene (**4**) were purchased and used without further purification. Synthesis of 5-bromo-2-chloro-3-hexylthiophene (**6**) was performed by bromination of commercially available 2-chloro-3-hexylthiophene in a manner described in the literature.¹ THF (anhydrous grade) was purchased from Kanto Chemicals Co., Ltd. and stored under nitrogen atmosphere. NiCl_2dppp and NiCl_2dppf were prepared according to the literature procedure.² PEPPSI-SIPr was purchased from Sigma-Aldrich. $\text{NiCl}_2(\text{PPh}_3)\text{IPr}$ was purchased from Tokyo Chemical Industry Co., Ltd. Umicore CX31 and CX32 were kindly donated by Umicore Japan, Ltd.

Transformation of 2,5-dibromo-3-hexylthiophene (1) into 2,4-Dibromo-3-hexylthiophene (2) via halogen dance: To a solution of dicyclohexylamine (0.12 mL, 0.60 mmol) in 5 mL THF was added *n*-butyllithium (1.64 M hexane solution, 0.34 mL, 0.55 mmol) dropwise at $-78\text{ }^\circ\text{C}$. The temperature was gradually raised to $0\text{ }^\circ\text{C}$ and the mixture was allowed to stir for 30 min. To the resulting mixture was added 2,5-dibromo-3-hexylthiophene (**1**, 0.107 mL, 0.50 mmol) and further stirring was continued for 0.5 h at room temperature. The mixture was poured into the mixture of hexane and water to quench the reaction to result in separation into two

phases. Aqueous was extracted by hexanes twice and the combined organic phase was dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure to leave a crude oil, which was subjected to ^1H NMR measurement to estimate conversion of **1** into **2**. (Figure S1)

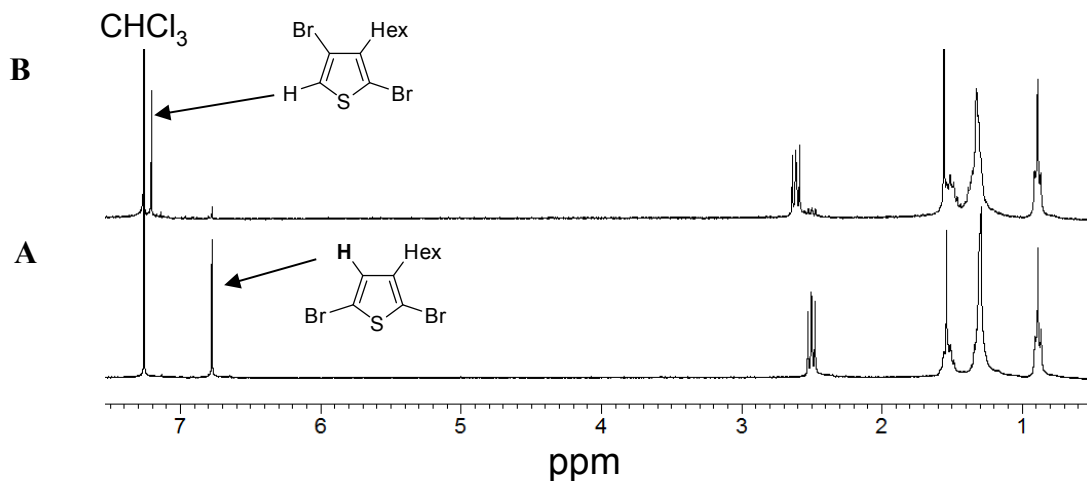


Figure S1. Estimation of conversion of **1** into **2** by ^1H NMR (A): 2,5-Dibromo-3-hexylthiophene (**1**) and (B): 2,4-Dibromo-3-hexylthiophene (**2**).

Figure S2 shows ^1H NMR spectrum of the crude reaction mixture after halogen dance with LDA at $-78\text{ }^\circ\text{C}$ for 5 min and following treatment of the reaction mixture with iodine. The integral values suggest that ca. 45% of **1** is deprotonated. Thus, taken together with this result and the result from Figure S1, the most of 4-lithiated thiophene induced halogen dance even at $-78\text{ }^\circ\text{C}$ in 5 min.

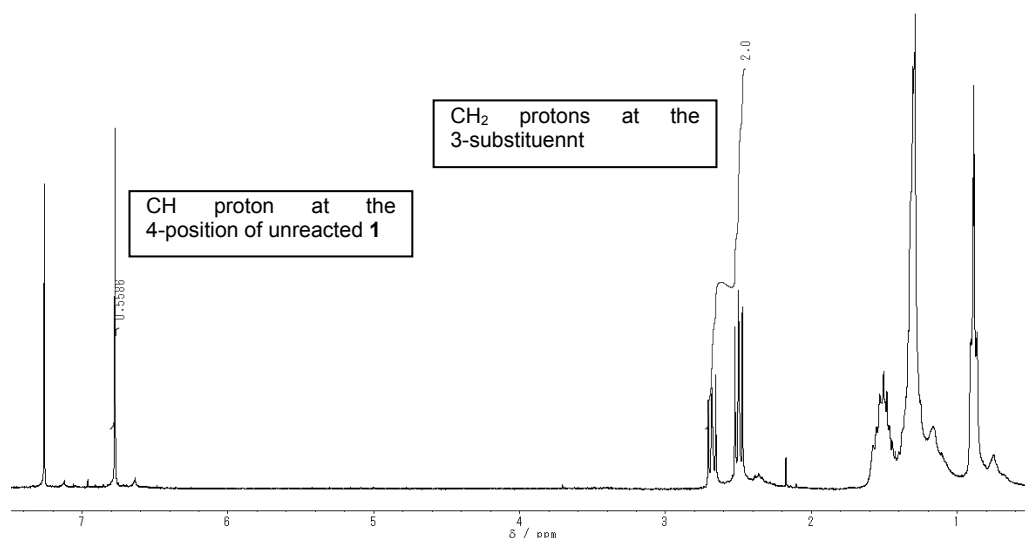


Figure S2. ^1H NMR spectrum of the crude reaction mixture after halogen dance and following iodination.

General Procedure for the halogen dance polymerization: To a solution of diisopropylamine (0.08 mL, 0.60 mmol) in 5.0 mL of THF was added *n*BuLi (1.65 M, 0.55 mmol, 0.33 mL) at $-78\text{ }^\circ\text{C}$. After stirring for 10 min, **1** (0.11 mL, 0.50 mmol) was added dropwise. The temperature of the reaction mixture was gradually raised to $0\text{ }^\circ\text{C}$ and further stirring was continued for 30 min. Then, 2 mol % of $\text{NiCl}_2(\text{PPh}_3)\text{IPr}$ (7.8 mg, 0.01 mmol) was added and the resulting mixture was stirred at $60\text{ }^\circ\text{C}$ for 1 h. The resulting mixture was poured into a mixture of 1 M hydrochloric acid and methanol to form a precipitate, which was washed with methanol repeatedly to leave a crude light yellow solid (94.3 mg, 77%). Further purification was carried out by preparative SEC to remove low-molecular-weight oligomers. The obtained polymer was subjected to elemental analysis (for Br), which showed bromine contents as 32.83% (calcd for $\text{Br}(\text{C}_{10}\text{H}_{13}\text{BrS})_{32}\text{H}$: 33.27%). The molecular weight and the molecular weight distribution of **3** were estimated by SEC analysis ($M_n = 7900$, $M_w/M_n = 1.28$). ^1H NMR (CDCl_3) δ 0.67-0.98 (3H, br s), 0.99-1.76 (8H, br), 2.20-2.93 (2H, br). ^{13}C NMR (CDCl_3) δ 14.1, 22.6, 29.0, 29.4, 31.4, 31.6, 115.8, 129.4, 130.4, 142.7.³ IR (ATR) 626, 645, 678, 836, 910, 1026, 1271, 1339, 1361, 1380, 1396, 1436, 1488, 1512, 1549, 1565, 1642, 1659, 1680, 1690, 1713, 1730, 2864, 2918 cm^{-1} . UV-vis (CHCl_3) $\lambda_{\text{max}} = 357\text{ nm}$. Anal. Calcd for $\text{Br}(\text{C}_{10}\text{H}_{13}\text{BrS})_{32}\text{H}$, C: 48.30; H: 5.30. Found. C: 48.73; H: 5.41.

Poly(4-bromo-3-methylthiophen-2,5-diyl) (5): ^1H NMR (CDCl_3) δ 2.0-2.4 (3H, br). IR (ATR) 636, 668, 725, 835, 1010, 1101, 1175, 1214, 1271, 1339, 1361, 1377, 1511, 1550, 1565, 1611, 1631, 1642, 1659, 1680, 1690, 1713, 1729, 1745, 1767, 1784, 2856, 2925, 2953 cm^{-1} . UV-vis (CHCl_3) $\lambda_{\text{max}} = 339$ nm.

Transformation of poly(4-bromo-3-hexylthiophen-2,5-diyl) (3): To a solution of poly(4-bromo-3-hexylthiophen-2,5-diyl) (**3**, 0.5 mmol, 122.6 mg) in 5.0 mL of THF were successively added a THF solution of 1.03 M *t*BuMgCl (1.0 mmol, 1.03 mL) and NiCl_2dppp (0.025 mmol, 13.6 mg) and the resulting mixture was stirred at room temperature for 24 h. The resulting mixture was poured into a mixture of 1 M hydrochloric acid and methanol to form a precipitate. The mixture was filtered and 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 79.5 mg of reddish brown solid. Conversion of the bromo group of **3** into hydrogen atom was estimated by ^1H NMR analysis, in which the ratio of the proton signal assigned as hydrogen at the 4-position of thiophene vs. methylene signal adjacent to the thiophene ring at the 3-position, as shown in Figure S3. UV-vis spectra of polymer **3** and the transformed product as well as authentic P3HT were shown in Figure S4.

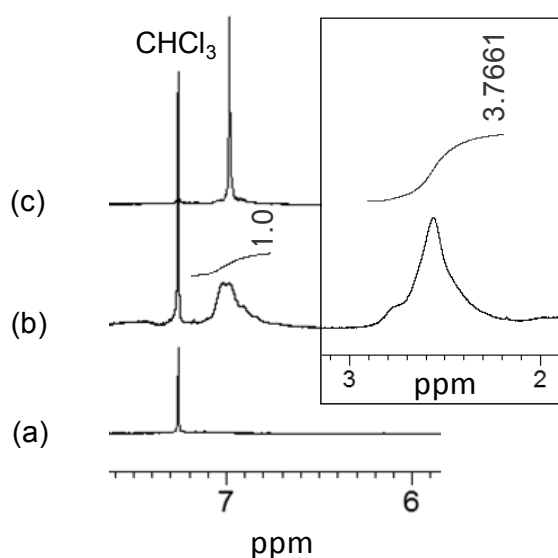


Figure S3. ^1H NMR spectra of (a) polythiophene **3** prepared by halogen dance, (b) polythiophene after reduction, and (c) authentic poly(3-hexylthiophen-2,5-diyl).

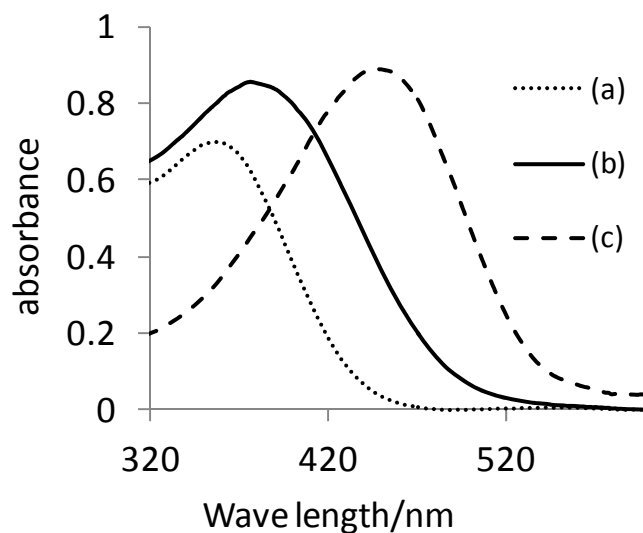
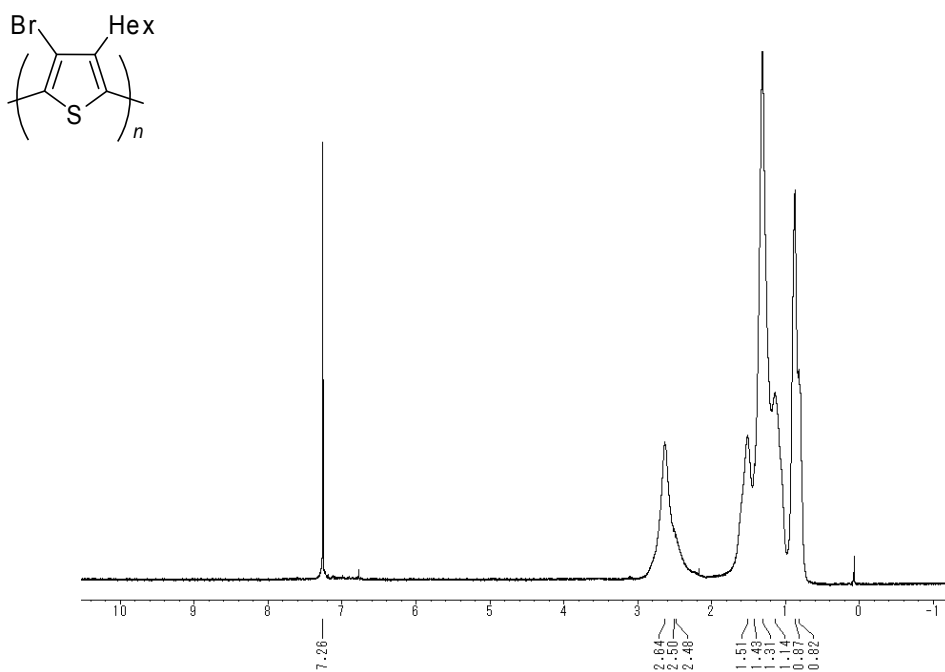
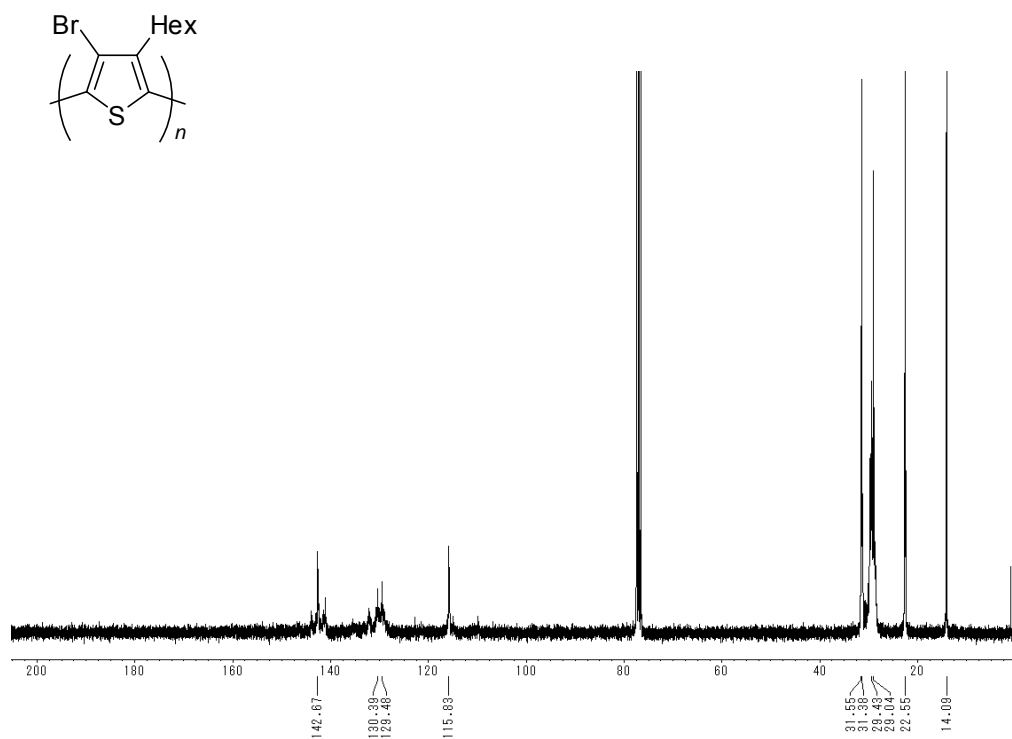
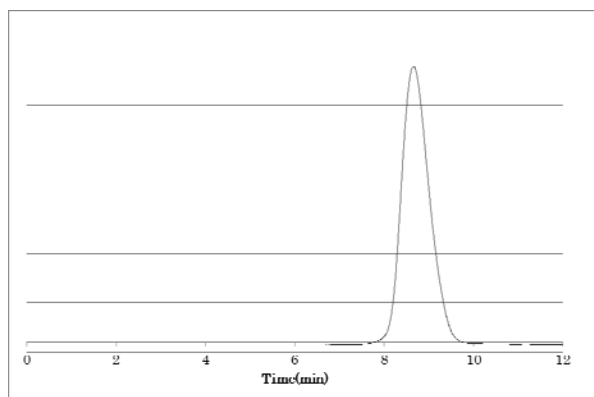


Figure S4. UV-vis spectra of (a) polythiophene **3** prepared by halogen dance, (b) polythiophene after reduction, and (c) authentic poly(3-hexylthiophen-2,5-diyl).

References

- (1) K. Fuji, S. Tamba, K. Shono, A. Sugie and A. Mori, *J. Am. Chem. Soc.*, 2013, **135**, 12208.
- (2) G. Booth and J. Chatt, *J. Chem. Soc.*, 1965, 3239.
- (3) The ^{13}C NMR spectrum shows that there exists unassigned signals, which may come from a small amount of unidentified and undesired side reactions as well as contamination by low-molecular-weight oligomers because of difficulties in purification.

^1H NMR spectrum of poly(4-bromo-3-hexylthiophen-2,5-diyl) (3) **^{13}C NMR spectrum of poly(4-bromo-3-hexylthiophen-2,5-diyl) (3)**

SEC profile of 3 (Table 1, entry 1)**¹H NMR spectrum of poly(4-bromo-3-methylthiophen-2,5-diyl) (5)**