Supporting information for

A Direct Route to Polybromothiophene as a Precursor for Functionalized Polythiophene by Electrooxidative Polymerization

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**General Experimental**

**Materials**

3-Bromo-4-dodecylthiophene (**1**) was prepared by a reported method1. A THF solution of phenylmagnesium bromide was prepared by a reported method2. Iodine (Kanto Chemical, Tokyo, Japan), tetrabutylammonium hexafluorophosphate (Bu4NPF6) (Tokyo Chemical Industry, Tokyo, Japan), dry acetonitrile (MeCN) (Tokyo Chemical Industry, Tokyo, Japan), dry tetrahydrofuran (THF) (Kanto Chemical, Tokyo, Japan), dry diethyl ether (Et2O) (FUJIFILM Wako Chemicals, Tokyo, Japan), hexane solution of *n*-butyllithium (*n*-BuLi) (*ca*. 1.6 mol/L) (Tokyo Chemical Industry, Tokyo, Japan), and [1,3-bis(diphenylphosphino)propane]nickel(II) chloride (Ni(dppp)Cl2) (Tokyo Chemical Industry, Tokyo, Japan) were used as received.

**Instruments**

1H and 13C nuclear magnetic resonance (NMR) spectra were measured on a JEOL (Tokyo, Japan) ECX-400 spectrometer (400 MHz and 100 MHz for 1 H and 13C, respectively). Tetramethylsilane was used as an internal standard for 1 H and 13C NMR spectra. Fourier transform infrared (FT-IR) spectra were measured on a SHIMADZU (Kyoto, Japan) IR Spirit instrument equipped with a Shimadzu QATR-S attenuated total reflection accessory using a diamond prism. UV-vis absorption spectra were measured on a SHIMADZU (Tokyo, Japan) UV-2600. Photoluminescence (PL) spectra were measured on a JASCO (Tokyo, Japan) FP-6100 spectrometer. Size exclusion chromatography (SEC) was performed on a TOSOH (Tokyo, Japan) HLC-8220GPC system equipped with Tosoh TSK-gel G4000HXL, G3000HXL, G2000HXL, and HXL-L tandem columns using THF as an eluent at 40 ºC. Energy dispersive X-ray (EDX) analysis was performed with a system consisting of a JEOL JSM6510A scanning electron microscope equipped with a JEOL JED2300 EDX spectrometer operated at an acceleration voltage of 15 kV. Linear sweep voltammetry (LSV) analysis, cyclic voltammetry (CV) analysis, and constant potential electropolymerization were carried out on a EC FRONTIER (Tokyo, Japan) ECstat-302 potentiostat with a ECboost-4002 power booster. LSV and CV analysis were carried out at the scan rate of 25 mV/s. All the measurements were performed in MeCN containing 0.1 M Bu4NPF6 at ambient temperature using a three-electrode system, with each solution being purged with N2 prior to measurements. The working electrode (WE) was a Pt disk (*f* = 1.6 mm, BAS, Tokyo, Japan), the counter electrode (CE) was a Pt wire (*f* = 0.5 mm, BAS, Tokyo, Japan), and the reference electrode (RE) was an Ag wire (*f* = 1 mm, Nilaco, Tokyo, Japan). The calculation of Mulliken charges was performed by the density functional theory (DFT) calculations, using the level of Becke-three-parameter-Lee-Yang-Parr hybrid (B3LYP) functional and the 6-31G(d) basis set combination on the Gaussian16 program package.3

**Experimental section**

**Electrooxidative polymerization of 1**

Electrooxidative polymerization of **1** was carried out using an undivided glass beaker cell equipped with a working electrode (Pt plate (2 x 2 cm2, Nilaco, Tokyo, Japan)) and a counter electrode (Pt plate (2 x 2 cm2, Nilaco, Tokyo, Japan)), and a quasi-reference electrode (Ag wire (*f* = 1 mm, Nilaco, Tokyo, Japan) at a scan rate of 100 mV s-1 in dry MeCN (10 mL) containing 50 mM **1** and 100 mM supporting electrolyte (Bu4NPF6) at ambient temperature. Electrooxidative polymerizations were conducted with a constant potential mode for 60 seconds at 2.4 V. After the polymerization, the navy-colored polymer film deposited on the working electrode was collected by dissolving in CH2Cl2 and reprecipitated into methanol to give a poly(3-bromo-4-dodecylthiophene) (**2**) in a 26% yield (0.043 g, 0.13 mmol-unit) as a yellow solid.

1H NMR (400 MHz, CDCl3, δ in ppm): 2.90-2.35 (2H, thienyl—C*H*2—CH2—), 1.80-1.50 (2H, thienyl—CH2—C*H*2—), 1.50-1.16 (18H, thienyl—(CH2)2—(C*H*2)9—), 0.96-0.80 (3H, —C*H*3).

13C NMR (100 MHz, CDCl3, δ in ppm): 151.5, 135.8, 128.3, 125.6, 34.3, 32.1, 30.3, 29.8, 29.5, 26.6, 22.8, 21.3, 14.3.

IR (ATR, cm-1): 2952, 2921, 1784, 1728, 1697, 1654, 1456, 1376, 1360, 1269, 1108, 1073, 720.

**Protonation via lithiation** **of 2**

A hexane solution of *n*-BuLi (1.6 M, 0.35 mmol, 0.28 mL) was added to a THF solution of **2** (0.023 g, 0.070 mmol-unit) at –78 °C under N2, and the mixture was kept stirring at that temperature for 15 minutes. Then, methanol (7.90 g, 24.7 mmol) was added to the mixture and kept stirred for 15 minutes at that temperature, and the reaction mixture was warmed slowly to ambient temperature in 2 h. Then, the reaction mixture was poured into water (10 mL). The organic layer was collected, and residual organic substances were extracted three times with dichloromethane (total 50 mL) from the remaining aqueous phase. After drying the combined organic phase over Mg2SO4, the volatile fractions were evaporated, and the residue was precipitated into methanol to give a protonated polymer (**3**) in a >99% yield (0.017 g, 0.068 mmol-unit) as an orange solid.

1H NMR (400 MHz, CDCl3, δ in ppm): 7.1-6.9 (1H, aromatic), 2.84-2.48 (2H, thienyl—C*H*2—CH2—), 1.75-1.49 (2H, thienyl—CH2—C*H*2—), 1.48-1.15 (18H, thienyl—(CH2)2—(C*H*2)9—), 0.95-0.80 (3H, —C*H*3).

IR (ATR, cm-1): 2955, 2922, 2852, 1727, 1456, 1377, 1260, 1121, 1071, 907, 800, 734.

**Phenylation of 2 by Kumada-Tamao coupling reaction**

A THF solution of phenylmagnesium bromide (3.0 M, 0.048 mL, 0.144 mmol) was added to a THF (15 mL) solution of **2** (0.023 mg, 0.091 mmol-unit) and Ni(dppp)Cl2 (1.0 mg, 0.0015 mmol) under N2, and the mixture was refluxed for 12 h. Then, the mixture was kept stirring at room temperature for 6 h. After the reaction, saturated NH4Cl aqueous solution (10 mL) was added to the mixture. The organic layer was collected, and residual organic substances were extracted three times with dichloromethane (total 50 mL) from the remaining aqueous phase. After drying the combined organic phase over Mg2SO4, the volatile fractions were evaporated, and the residue was precipitated into methanol to give a phenylated polymer (**4**) in a >99% yield (0.035 g, 0.11 mmol-unit) as a yellow solid.

1H NMR (400 MHz, CDCl3, δ in ppm): 7.60-7.40 (5H, phenyl), 2.90-2.40 (2H, thienyl—C*H*2—CH2—), 1.80-1.49 (2H, thienyl—CH2—C*H*2—), 1.49–1.00 (18H, thienyl—(CH2)2—(C*H*2)9—), 1.00-0.80 (3H, —C*H*3).

IR (ATR, cm-1): 2959, 2921, 2852, 1727, 1647, 1456, 1360, 1259, 1070, 1015, 795, 700.

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自動的に生成された説明

Figure S1. Linear sweep voltammogram of **1** in 100 mM MeCN solution of Bu4NPF6.

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Figure S2. (a) EDX spectrum, (b) SEM image, and (c, d) elemental mapping images of S and Br of **2**.

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Figure S3. UV-vis absorption spectra of **1** and **2** in CH2Cl2.

Table S1. Optical properties of **1** and **2**.

|  |  |  |  |
| --- | --- | --- | --- |
| Sample | *l*max / nma) | *l*onset / nma) | Band gap / eVb) |
| 1 | 247 | 278 | 4.46 |
| 2 | 339 | 425 | 2.92 |

a) Measured in CH2Cl2. b) Estimated from *l*onset.

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Figure S4. Cyclic voltammograms of (a) **2**, (b) **3**, and (c) **4**.

Table S2. Electronic properties of **2**, **3**, and **4**.

|  |  |  |  |
| --- | --- | --- | --- |
| Polymer | *E*ox / Va) | HOMO / eVb) | LUMO / eVc) |
| 2 | 1.26 | -5.76 | -3.00 |
| 3 | 0.46 | -5.26 | -2.90 |
| 4 | 1.46 | -6.26 | -3.42 |

a) Estimated by CV analysis (film, immersed in MeCN). b) *E* (HOMO) = -(*E*ox + 4.8), where *E*ox is the onset of potential of oxidation, observed in the CV analyses. c) *E* (LUMO) = Optical band gap (film) + HOMO.



Figure S5. 1H NMR spectrum of **2**.

Figure S6. 13C NMR spectrum of **2**.



Figure S7. 1H NMR spectrum of **3**.



Figure S8. 1H NMR spectrum of **4**.

Table S3. Optimized cartesian coordinates of 3-bromo-4-ethylthiophene(**1’**) in the ground-state.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Center Number | Atomic Number | Coordinates / Å | | |
| X | Y | Z |
| 1 | 6 | -1.054372 | -1.416530 | 0.217876 |
| 2 | 6 | -0.131441 | -0.444282 | -0.029616 |
| 3 | 6 | -0.675254 | 0.858697 | -0.299395 |
| 4 | 6 | -2.042632 | 0.815062 | -0.243894 |
| 5 | 16 | -2.658489 | -0.765194 | 0.129606 |
| 6 | 1 | -0.884944 | -2.460634 | 0.436926 |
| 7 | 1 | -2.730672 | 1.634876 | -0.404343 |
| 8 | 6 | 0.141433 | 2.095430 | -0.575164 |
| 9 | 1 | 0.937387 | 1.846432 | -1.288053 |
| 10 | 1 | -0.496325 | 2.841902 | -1.062434 |
| 11 | 35 | 1.739119 | -0.795104 | -0.039047 |
| 12 | 6 | 0.770532 | 2.700128 | 0.692817 |
| 13 | 1 | 1.360962 | 3.588976 | 0.443576 |
| 14 | 1 | -0.002084 | 2.992107 | 1.412372 |
| 15 | 1 | 1.432728 | 1.977048 | 1.179149 |

**References**

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