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Sequential and click-type postfunctionalization of regioregular poly(3-hexylthiophene) for realization of n-doped multiplet state

Yuping Yuan,[a] Wonsung Choi,[b] Hiroyuki Nishide[b] and Tsuyoshi Michinobu*[,c]

[a]*Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, Japan*

[b]*Department of Applied Chemistry, Waseda University, Tokyo 169-8555, Japan*

[c]*Global Edge Institute, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8550, Japan*

*Correspondence Address:

Dr. Tsuyoshi Michinobu

Global Edge Institute, Tokyo Institute of Technology

2-12-1 Ookayama, Meguro-ku, Tokyo 152-8550, Japan

Tel/Fax: +81-3-5734-3774, E-mail: michinobu.t.aa@m.titech.ac.jp

1. Materials

All reagents were purchased from Kanto, Tokyo Kasei, Wako, and Aldrich and used as received. Poly(3-hexylthiophene)[S1] with the molecular weight (M_n) of 9600 and polydispersity (M_w/M_n) of 1.59 and *N*,*N*-dihexyl-4-[(tributylstannanyl)ethynyl]aniline[S2] were synthesized according to the reported methods.

2. Measurements

^{1}H NMR spectra were measured on a JEOL model AL300 spectrometer at 20 °C. Chemical shifts are reported in ppm downfield from $SiMe_4$ using the solvent's residual signal as an internal reference. Infrared (IR) spectra were recorded on a JASCO FT/IR-4100 spectrometer. Gel permeation chromatography (GPC) was measured on a JASCO system equipped with polystyrene gel columns using THF as an eluent at the flow rate of 1.0 mL min^{-1}. Relative molecular weights were determined by comparison with the calibrated standard polystyrenes. Elemental analysis was performed on a PerkinElmer 2400-SeriesII CHNS/O Analyzer. UV-vis-near IR spectra were recorded on a JASCO V-670 spectrophotometer. Electrochemical measurements were carried out at 20 °C in dehydrated CH_3CN or CH_2Cl_2 containing 0.1 M $(nC_4H_9)_4NClO_4$ in a classical three-electrode cell. The working, reference, and auxiliary electrodes were a glassy carbon disk electrode (2 mm in diameter), $Ag/AgCl/CH_3CN/(nC_4H_9)_4NClO_4$, and a platinum wire, respectively. All potentials are referenced to the ferrocene/ferricinium (Fc/Fc^+) couple used as an internal standard. ESR spectra were recorded on a JEOL JES-2XG ESR spectrometer. The signal positions were calibrated with an external standard of Mg^{2+}/MgO (g = 1.981). Electrolytic ESR measurements were performed by the stepwise application of negative voltages to the sample solutions in degassed CH_2Cl_2 (2.9 mM repeat unit^{-1}) containing 0.1 M $(nC_4H_9)_4NClO_4$ at 20 °C.

Magnetization and static magnetic susceptibility were measured with a Quantum Design MPMS-7 SQUID magnetometer (Quantum Design Inc., San Diego, CA, USA). After chemical reduction, the solution samples of poly(anionic radical)s were transferred to a quartz tube in a glove box. The tube was sealed off and then subjected to magnetic measurements. Magnetization was measured from 0.5 to 7 T at 1.8 K in order to estimate the saturated magnetization. Static magnetic susceptibility was measured from 2 to 50 K at a field of 0.5 T. Ferromagnetic magnetization ascribed to the impurities was determined by Honda-Owen plots. Although the quantity was very low, it was subtracted from the overall magnetization. Diamagnetic susceptibility of the sample solution and a part of the tube was estimated from the Curie plots of magnetic susceptibility.

3. Synthetic procedures

P1. To P3HT (0.300 g, 1.81 mmol repeat unit^{-1}) in $CHCl_3$ (20 mL), *N*-bromosuccinimide (NBS) (0.387 g, 2.17 mmol) was added. After the solution was stirred at 20 °C for 15 h, it was heated to 50 °C for 2 h. The reaction mixture was poured into a saturated aqueous $NaHCO_3$ solution (50 mL). The organic layer was washed with water (×5) and dried over $MgSO_4$. Precipitation into MeOH yielded the yellow solid of poly(3-bromo-4-hexylthiophene) (0.440 g, 99%). The analytical data agreed with the reported values.[S3]

To a 30 mL two-necked flask, poly(3-bromo-4-hexylthiophene) (0.196 g, 0.800 mmol) and *N*,*N*-dihexyl-4-[(tributylstannanyl)ethynyl]aniline (0.689 g, 1.20 mmol) were added, and they were dissolved in dehydrated toluene (20 mL). The solution was bubbled with argon for 30 min, and $Pd(PPh_3)_4$ (37 mg, 0.032 mmol) was added. The reaction mixture was heated to 100 °C for 24 h. After cooling to room temperature, $CHCl_3$ was added and the solution was passed through a plug. The solution was concentrated by evaporation and poured into cold MeOH. Reprecipitation from $CHCl_3$ into cold MeOH was performed. The brown solid was collected and washed with MeOH using a Soxhlet extractor. Drying under vacuum yielded the desired polymer (352 mg, 98%).

M_n 23600, M_w/M_n 1.66; ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.87 (br s, 9 H), 1.29 (br s, 18 H), 1.57 (br s, 6 H), 3.25 (br s, 6 H), 6.53 (br s, 2 H), 7.30 ppm (br s, 2 H); IR (neat): 2955.2, 2924.2, 2853.8, 2195.9, 1605.3, 1518.7, 1464.0, 1398.6, 1368.0, 1184.6, 1106.2, 963.7, 812.4, 723.1, 530.2 cm^{-1}; Elemental analysis calcd for $(C_{30}H_{43}NS)_n$: C 80.1, H 9.6, N 3.1; found: C 79.5, H 9.9, N 3.2.

P2. To a 50 mL flask, **P1** (94.6 mg, 0.213 mmol repeat unit^{-1}) and tetracyanoethylene (TCNE) (27.2 mg, 0.213 mmol) were added, and they were dissolved in 1,2-dichloroethane (30 mL). The solution was heated to 60 °C for 6 h. After cooling to room temperature, the reaction mixture was poured into MeOH. Reprecipitation from 1,2-dichloroethane into MeOH was performed. The precipitate was collected and washed with MeOH using a Soxhlet extractor. Drying under vacuum yielded the desired polymer (117.5 mg, 96.5%).

^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.88 (br s, 9 H), 1.31 (br s, 18 H), 1.59 (br s, 6 H), 3.36 (br s, 6 H), 6.65 (br s, 2 H), 7.45 ppm (br s, 2 H); IR (neat): 2953.2, 2928.4, 2856.0, 2209.0, 1600.1, 1465.2, 1412.0, 1362.5, 1181.4, 965.0, 823.0, 723.7, 578.7, 530.3 cm^{-1}; Elemental analysis calcd for $(C_{36}H_{43}N_5S)_n$: C 74.8, H 7.5, N 12.1; found: C 74.3, H 7.8, N 12.5.

4. Electrochemistry

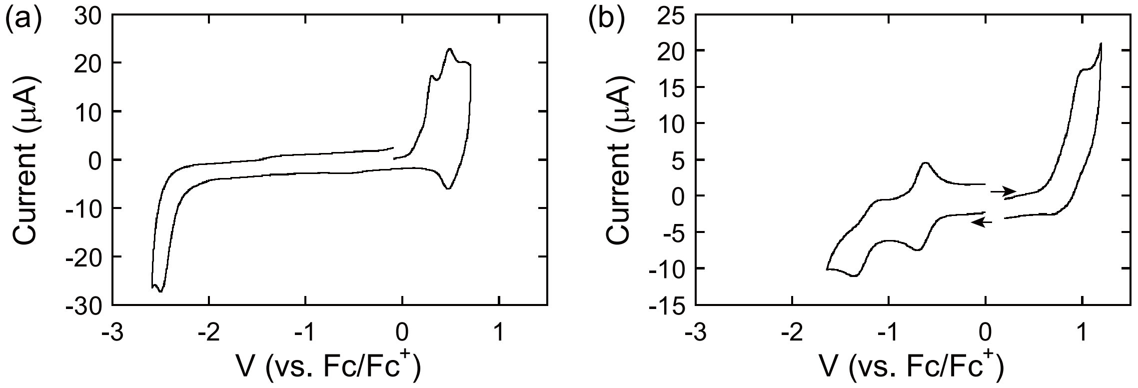

Fig. S1 Cyclic voltammograms of the films of (a) **P1** and (b) **P2** in CH_3CN containing 0.1 M $(nC_4H_9)_4NClO_4$ at 20 °C.

5. n-Doping

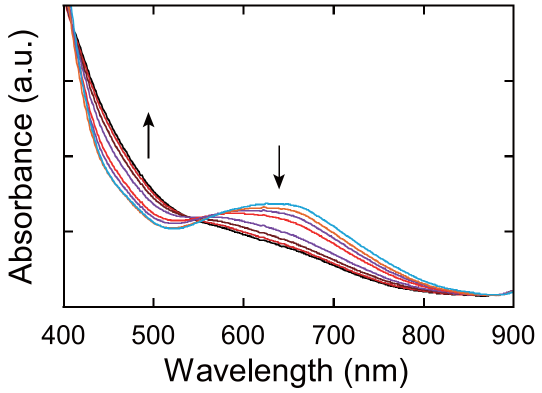

Fig. S2 UV-vis-near IR spectra of **P2** in THF upon the stepwise addition of decamethylcobaltocene under nitrogen.

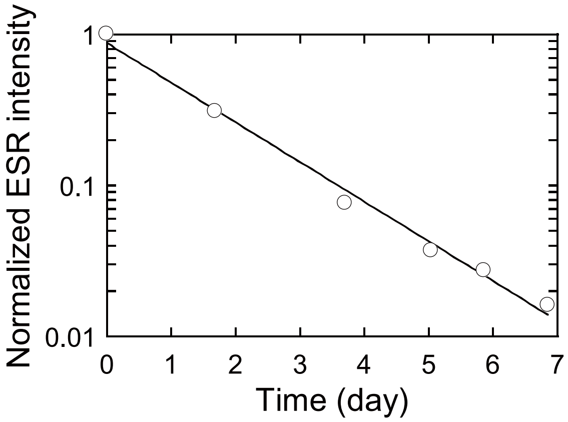

Fig. S3 Time dependent ESR intensity decrease in the polyradical of **P2** in Ar atomosphere at 20 °C.

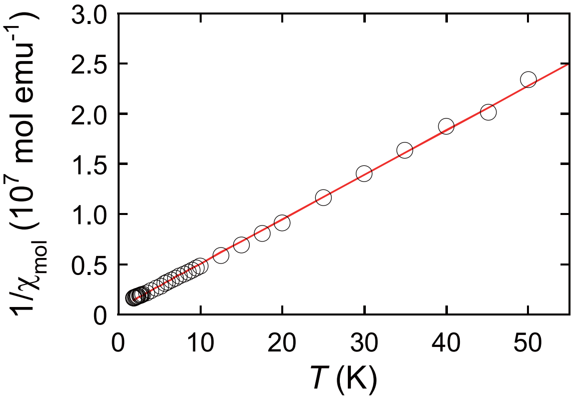

Fig. S4 Plots of $1/\chi_{mol}$ vs. T of the polyradical of **P2** with the spin concentration of 0.17 in THF.

References

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