

SUPPLEMENTARY INFORMATION

Electrochemical Polymer Reaction: Selective Fluorination of a Poly(fluorene) Derivative

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Experimental Section

General Information

NMR spectra were recorded on a JEOL EX-270 spectrometer. UV-vis spectra were obtained on a SHIMADZU UV-1600 spectrophotometer. GPC analyses were performed by a SHIMADZU Prominence GPC system (Shim-pack GPC 803C column), using chloroform as the eluent after calibration with polystyrene standard. IR spectra were obtained on a SHIMADZU FTIR-8100A.

Cyclic voltammetry measurements were recorded on an ALS 600A Electrochemical Analyzer. Preparative electrolysis experiments were carried out with Metronnix Corp. (Tokyo) constant current power supply model 5944 by monitoring electricity with Hokutodenko Coulomb/Amoperehour meter HF-201. EDX analysis was performed with EMAX ENERGY EX-250 (HORIBA). Film thickness was estimated by a KEYENCE Laser Focus Displacement Meter LT-8100. DFT calculation was performed using Gaussian 03 suit of programs by optimization with using the B3LYP/6-31G(d,p) method. The orbital diagrams were generated by using the GaussView program.¹

Materials

Dry solvents were used as received. 2,7-Dibromofluorenone, 9,9-dioctylfluorene-2,7-diboronic acid ester, Pd(PPh₃)₄, *p*-isopropylbenzenethiol, boron trifluoride-ether complex were used as received. Et₄NF·4HF was kindly supplied by Morita Chemical Industries Co. Ltd. (Japan).

Synthesis of PreP1 by Suzuki-Miyaura coupling polymerization (Scheme S1)

2,7-Dibromofluorenone (68 mg, 0.20 mmol) and 9,9-dioctylfluorene-2,7-diboronic acid ester (111 mg, 0.20 mmol) were dissolved in 2 mL of dry toluene under argon. To the solution were added K₂CO₃ (aq) (2.0 M, 1.4 mL), Pd(PPh₃)₄ (3 mg, 0.003 mmol). After stirred for 48 h at 100 °C, the reaction mixture was reprecipitated into a large amount of methanol. **PreP1** was collected by filtration, dried under vacuum, and obtained as an orange powder (120 mg). ¹H-NMR (270 MHz,

CDCl_3): δ 8.1-7.6 (Ar-H, br), 2.11 ($\text{CH}_2(\text{CH}_2)_6\text{CH}_3$, br), 1.25-0.77 ($\text{CH}_2(\text{CH}_2)_6\text{CH}_3$, br). ^{13}C -NMR (270 MHz, CDCl_3): δ 151.9, 142.9, 142.5, 142.4, 140.5, 138.7, 135.2, 133.4, 133.3, 125.7, 123.0, 121.0, 120.9, 120.7, 120.2, 55.6, 40.5, 31.8, 30.1, 29.3, 23.9, 22.7, 14.2. IR (KBr): 2916, 2846, 1695, 1496, 1450, 772 cm^{-1} . Anal. Calcd. for $(\text{C}_{42}\text{H}_{46}\text{O})_n$: C, 88.68; H, 8.51; O, 2.81. Found: C, 87.95; H, 8.24; O, 3.34.

Synthesis of P1 by dithioacetal Formation (Scheme S1)

PreP1 (40 mg) was dissolved in 5 ml of dry dichloromethane under argon atmosphere. 1, *p*-isopropylbenzenethiol (0.68 ml, 4.5 mmol) was added and subsequent addition of boron trifluoride-ether complex (0.30 ml, 2.4×10^{-4} mmol). After the mixture was stirred for 24 h at room temperature, the polymer was reprecipitated into methanol. **P1** was collected by filtration, dried under vacuum, and obtained as a light yellow powder (39 mg). Dithioacetal was quantitatively formed judging from ^1H NMR spectrum. ^1H -NMR (270 MHz, CDCl_3): δ 7.9-6.8 (Ar-H, br), 2.82 ($\text{CH}(\text{CH}_3)_2$, br), 2.11 ($\text{CH}_2(\text{CH}_2)_6\text{CH}_3$, br), 1.25-0.77 (alkyl, br). ^{13}C -NMR (270 MHz, CDCl_3): δ 151.6, 150.4, 150.1, 146.8, 139.8, 136.3, 128.9, 128.1, 127.4, 127.1, 126.4, 123.9, 121.3, 120.1, 120.1, 119.8, 55.4, 40.5, 33.9, 33.8, 32.0, 31.9, 30.2, 30.1, 29.8, 29.4, 24.0, 23.9, 23.8, 22.7, 14.2. IR (KBr): 2927, 2858, 1727, 1446, 1272, 1022, 829 cm^{-1} . Anal. Calcd. for $(\text{C}_{60}\text{H}_{68}\text{S}_2)_n$: C, 84.45; H, 8.03; S, 7.52. Found: C, 82.43; H, 7.23; S, 7.74; Br, 0.94.

General Procedure for Anodic Fluorination

A chloroform solution containing 1 mg of **P1** was casted on the Pt plate electrode (1 cm x 1 cm) and dried under reduced pressure. Et₄NF·4HF (3 mL) was added into plastic test tube, and deaerated by argon bubbling. Pt electrode coated with **P1** film was introduced as an anode and bare Pt plate electrode (1 cm x 1 cm) was used as a cathode. A constant current (10 mA/cm²) was passed at room temperature from 2 F/mol to 24 F/mol. Polymer film was washed by water, methanol and subsequently dried in vacuo and obtained as a yellow film. ¹H-NMR (270 MHz, CDCl₃): δ 7.9-6.8 (Ar-H, br), 2.11 (CH₂(CH₂)₆CH₃, br), 1.25-0.77 (alkyl, br). ¹⁹F-NMR (270 MHz, CDCl₃): δ -33.7 (>CF₂, inner unit), -34.1 (>CF₂, terminal unit). IR (KBr): 2931, 2866, 1713, 1546, 1470, 1230, 775 cm⁻¹.

Scheme S1.

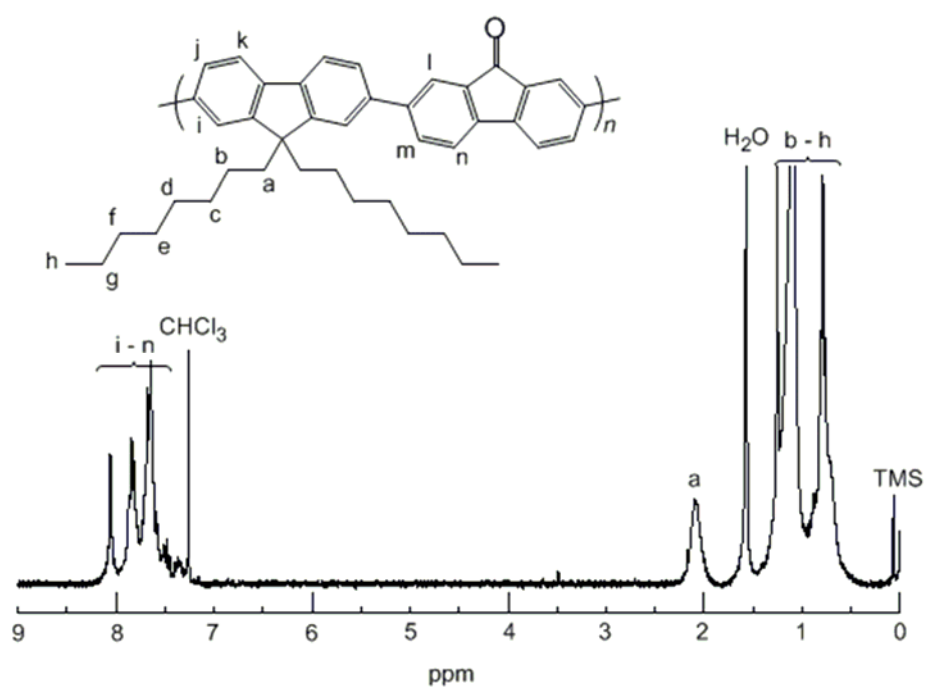
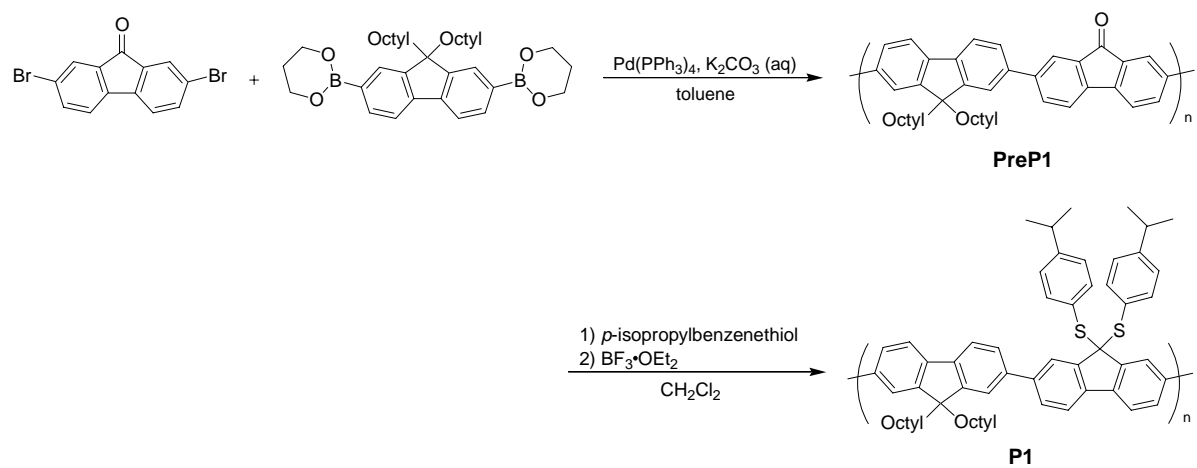


Figure S1. $^1\text{H-NMR}$ spectrum of poly(fluorenone-*alt*-9,9-dioctylfluorene).

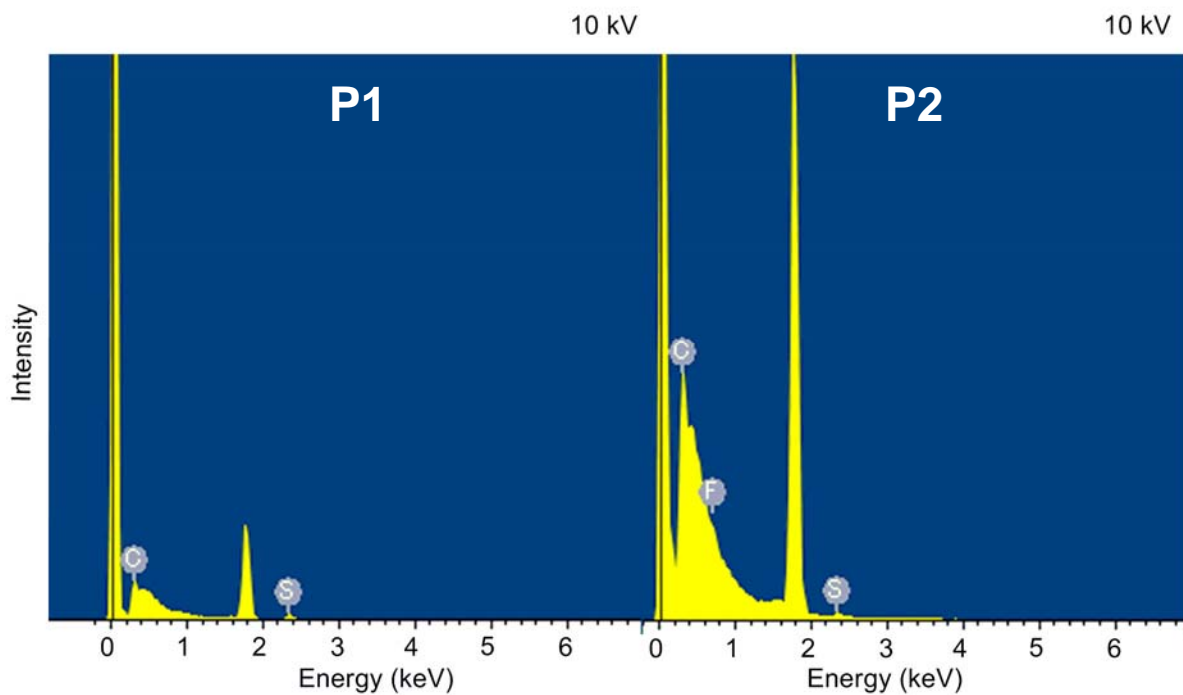


Figure S2. Energy dispersive X-ray (EDX) spectra of **P1** and **P2**.

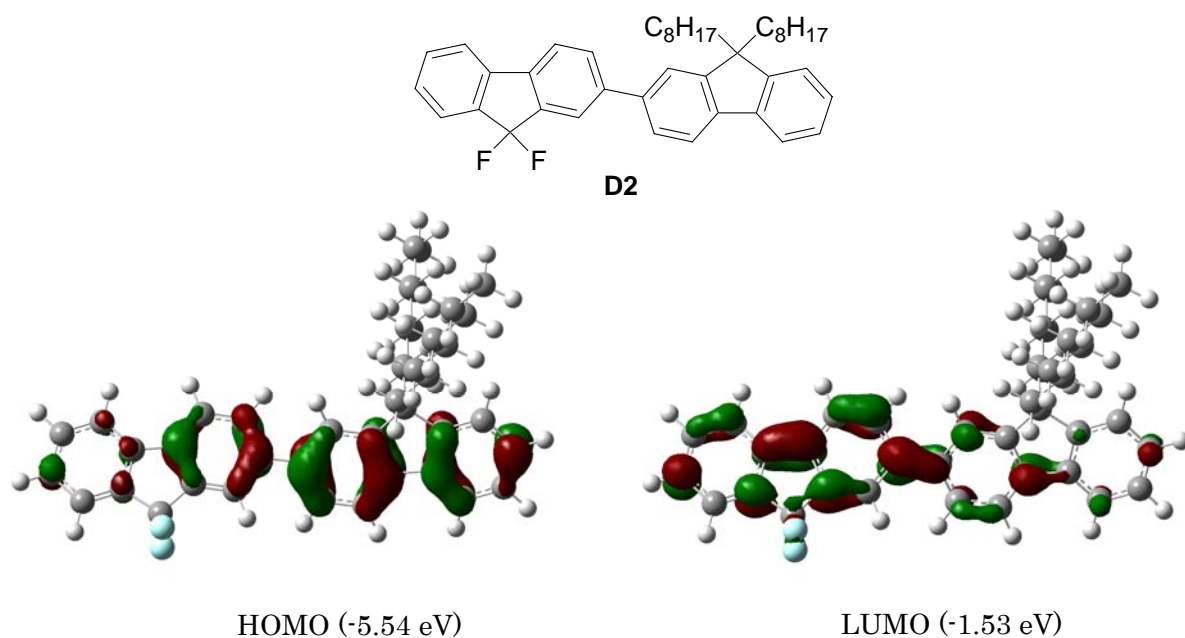


Figure S3. HOMO and LUMO diagrams of **D2**. The molecular orbital surface isovalue is 0.04.

Complete citation for reference 11:

11. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision E.01*; Gaussian, Inc.: Wallingford, CT, 2004.

Reference

1. Dennington II, R.; Keith, T.; Millam, J.; Eppinnett, K.; Hovell, W. L.; Gilliland, R. *GaussView, Version 4.1*; Semichem, Inc.: Shawnee Mission, KS, 2003.