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Supporting Information

Preservation of Main-Chain Conjugation through BODIPY-Containing Alternating Polymers from Electronic Interactions with Side-Chain Substituents by Cardo Boron Structures

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Experimental Sections

Measurements: ^{1}H (400 MHz), ^{13}C (100 MHz), and ^{11}B (128 MHz) NMR spectra were recorded on JEOL JNM-EX400 spectrometers. In ^{1}H and ^{13}C NMR spectra, tetramethylsilane (TMS) was used as an internal standard in $CDCl_3$. ^{11}B NMR spectra were referenced externally with $BF_3{\cdot}OEt_2$ (sealed capillary). Analytical thin-layer chromatography (TLC) was performed with silica gel 60 Merck F254 plates. Column chromatography was performed with a Wakogel C-300 silica gel. Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) values of all polymers were estimated by size exclusion chromatography (SEC) with a TOSOH 8020 series [a dual pump system (DP-8020), a column oven (CO-8020), and a degasser (SD-8020)] equipped with three consecutive polystyrene gel columns [TOSOH TSKgel: G2000H, G3000H and G4000H] and refractive-index (RI-8020) and ultraviolet detectors (UV-8020) at 40 °C. The system was operated at a flow rate of 1.0 mL/min with $CHCl_3$ as an eluent. Polystyrene standards were employed for calibration. UV−vis spectra were recorded on a SHIMADZU UV–3600 spectrophotometer. Fluorescence emission spectra were measured with a HORIBA JOBIN YVON Fluoromax-4P spectrofluorometer, and the absolute quantum yield was calculated by integrating sphere method on a HORIBA JOBIN YVON Fluoromax-P spectrofluorometer. Photoluminescence (PL) lifetime was measured by a Horiba FluoreCube spectrofluorometer system, and excitation was carried out at 375nm using UV diode laser (NanoLED 375 nm). Cyclic voltammetry (CV) was carried out on a BAS ALS-Electrochemical-Analyzer Model 600D with a glassy carbon (GC) working electrode, a Pt counter electrode, an Ag/Ag^{+} reference electrode, and the ferrocene/ferrocenium external reference at a scan rate of 50 mVs^{-1}. Ferrocene (Aldrich Chemical, Co.) was used as received. All reactions were performed under argon atmosphere.

Computational Details: The Gaussian 09 program package[1] was used for computations of the compounds. The optimized structures was obtained by DFT calculation at the B3LYP/6-31G(d) level of theory. TD-DFT calculation was carried out at the B3LYP/6-31G(d) level for the electronic transitions.

Materials: 2,4-Dimethylpyrrole (Tokyo Kasei Kogyo, Co.), decanoyl chloride (Tokyo Kasei Kogyo, Co.), 4-bromoanisole (Tokyo Kasei Kogyo, Co.), 4-bromobenzotrifluoride (Tokyo Kasei Kogyo, Co.), *n*-butyllithium (*n*-BuLi, 1.6 mol/L in hexane, Kanto Chemical, Co., Inc.), boron trifluoride diethyl etherate ($BF_3{\cdot}OEt_2$, Aldrich Chemical, Co.), *N*-iodosuccinimide (NIS, Tokyo Kasei Kogyo, Co.), [9,9-bis(2-dodecyl)-9H-fluorene-2,7-diyl]bisboronic acid (Aldrich Chemical, Co.), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-Phos, Wako Chemical, Co.), tris(dibenzylideneacetone dipalladium(0)) ($Pd_2(dba)_3$, Wako Chemical, Co.), dichloromethane (Wako Chemical, Co.) and toluene (Wako Chemical, Co.) were used as received. Tetrahydrofuran (THF), diethyl ether and triethylamine were purified using a two-column solid-state purification system (Glasscoutour System, Joerg Meyer, Irvine, CA). **B0**[2], **B2**[2] and 2,2'-(3,3'-didodecyl-[2,2'-bithiophene]-5,5'-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)[3] were prepared according to the previous reports.

Synthesis of DM: *n*-BuLi (4.1 mL, 1.55 mol/L in hexane, 6.4 mmol) was added to the solution of 4-bromoanisole (0.80 mL, 6.4 mmol) in THF (120 mL) at −78 °C. The reaction mixture was stirred for 1 h. Then, the solution of **B0** (0.60 g, 1.6 mmol, dissolved in 15 mL of THF) was added to the mixture via a cannula. After the reaction mixture was stirred for 30 min at 0 °C, cooled saturated aqueous solution of ammonium chloride was added. The solution was extracted with dichloromethane, and the organic layer was washed with water and brine. After drying over $MgSO_4$, the solvent was removed by a rotary evaporator. The product was purified by silica gel column chromatography with the mixed solvents of hexane/toluene (1/2) as an eluent. The product was obtained as an orange powder (0.46 g, 52%). ^{1}H NMR (CD_2Cl_2): δ = 7.17 (4H, d, *J* = 7.19 Hz, Ar-*H*), 6.76 (4H, d, *J* = 8.22 Hz, Ar-*H*), 5.97 (2H, s, Ar-*H*), 3.76 (6H, s, -OC*H*$_3$), 3.02 (2H, t, *J* = 7.80 Hz, Ar-C*H*$_2$), 2.45 (6H, s, Ar-C*H*$_3$), 1.80–1.60 (8H, m, Ar-C*H*$_3$, -C*H*$_2$-), 1.49–1.20 (12H, br, -C*H*$_2$-), 0.89 (3H, t, *J* = 6.70 Hz, -C*H*$_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 158.00, 153.02, 147.34, 137.50, 134.87, 132.05, 122.52, 112.85, 55.06, 32.51, 32.03, 30.33, 29.72, 29.70, 29.44, 28.86, 22.81, 17.10, 17.03, 14.21 ppm. ^{11}B NMR (CD_2Cl_2): δ = −0.39 ppm. HRMS (ESI) m/z calcd. $[M+H]^+$: 551.3803, found: 551.3798.

Synthesis of DF: *n*-BuLi (0.92 mL, 1.55 mol/L in hexane, 6.7 mmol) was added to the solution of 4-bromobenzotrifluoride (0.92 mL, 6.7 mmol) in diethyl ether (12.5 mL) at −78 °C. The reaction mixture was stirred for 1.5 h. Then, the solution of **B0** (1.0 g, 2.7 mmol in 25 mL of diethyl ether) was added to the mixture via a cannula. After the reaction mixture was stirred for 1.5 h at −78 °C, methanol was added. The solution was extracted with dichloromethane, and the organic layer was washed with water and brine. After drying over $MgSO_4$, the solvent was removed by a rotary evaporator. The product was purified by silica gel column chromatography with the mixed solvents of hexane/ethyl acetate (50/1) as an eluent. The isolated product was dissolved in a small amount of THF, and the product was reprecipitated from cold methanol to give pure **DF** as a candy-like orange paste (0.19 g, 11%). ^{1}H NMR (CD_2Cl_2): δ = 7.44 (4H, d, *J* = 7.98 Hz, Ar-*H*), 7.35 (4H, br s, Ar-*H*), 6.02 (2H, s, Ar-*H*), 3.06 (2H, t, *J* = 8.22 Hz, Ar-CH_2-), 2.47 (6H, s, Ar-CH_3), 1.70–1.60 (8H, br, Ar-CH_3, -CH_2-), 1.42 (2H, quint, -CH_2-), 1.36–1.20 (10H, br, -CH_2-), 0.88 (3H, t, *J* = 6.94 Hz, -CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 152.81, 147.96, 138.40, 133.65, 131.98, 128.31, 128.00, 126.16, 124.02, 123.99, 123.95, 123.91, 122.83, 32.36, 31.88, 30.12, 29.56, 29.27, 28.82, 22.67, 17.05, 16.90, 14.06 ppm. ^{11}B NMR (CD_2Cl_2): δ = −1.37 ppm. HRMS (APCI) m/z calcd. $[M+H]^+$: 627.3340, found: 627.3336.

Synthesis of F: 4-Bromobenzotrifluoride (1.48 mL, 10.7 mmol) in THF (70 mL) was added to magnesium (0.38 g, 16 mmol) at r.t. under argon atmosphere. The reaction solution was stirred at 60 °C for 30 min. The resulting solution was cooled to r.t. and transferred via a cannula to a solution of **B0** (1.0 g, 2.7 mmol) in THF (50 mL). After the mixture solution was stirred at reflux temperature for 1 h, water was added to the reaction mixture to quench the reaction. The solution was extracted with dichloromethane, and the organic layer was washed with water and brine. After drying over $MgSO_4$, the solvent was removed by a rotary evaporator. The product was purified by column chromatography with hexane/ethyl acetate (24/1). The isolated product was dissolved in a small amount of THF, and the product was reprecipitated from methanol to give pure **F** as

an orange powder (0.75 g, 56%). ^{1}H NMR (CD_2Cl_2): δ = 7.41 (4H, br, Ar-*H*), 6.01 (2H, s, Ar-*H*), 3.09 (2H, br, Ar-C*H*$_2$-), 2.47 (6H, s, Ar-C*H*$_3$), 2.12 (6H, s, Ar-C*H*$_3$), 1.74 (2H, br, -C*H*$_2$-), 1.56–1.52 (2H, m, -C*H*$_2$-), 1.40–1.32 (10H, br, -C*H*$_2$-), 0.89 (3H, t, *J* = 6.94 Hz, -C*H*$_3$) ppm. ^{11}B NMR (CD_2Cl_2): δ = 2.15 ppm. HRMS (ESI) m/z calcd. $[M-H]^-$: 499.2913, found: 499.2918.

Synthesis of MF: 4-Bromoanisole (0.10 mL, 0.80 mmol) in THF (5.5 mL) was added to magnesium (29 mg, 1.2 mmol) at r.t. under argon atmosphere. The reaction solution was stirred at 50 °C for 1.5 h. The resulting solution was cooled to r.t. and transferred via a cannula to a solution of **F** (0.2 g, 0.4 mmol) in THF (7.6 mL). After the mixture solution was refluxed for 3 h, water was added to the reaction mixture to quench the reaction. The solution was extracted with dichloromethane, and the organic layer was washed with water and brine. After drying over $MgSO_4$, the solvent was removed by a rotary evaporator. The product was purified by column chromatography with hexane/toluene (3/1). The isolated product was dissolved in a small amount of THF, and pure **MF** was obtained from the reprecipitation with cold methanol as a candy-like orange paste (96 mg, 41%). ^{1}H NMR (CD_2Cl_2): δ = 7.41 (2H, d, *J* = 7.74 Hz, Ar-*H*), 7.28 (2H, br, Ar-*H*), 7.19 (2H, d, *J* = 7.80 Hz, Ar-*H*), 6.77 (2H, dt, *J* = 8.65, 2.07 Hz, Ar-*H*), 6.00 (2H, s, Ar-*H*), 3.77 (3H, s, -OC*H*$_3$), 3.04 (2H, t, *J* = 8.10 Hz, Ar-C*H*$_2$-), 2.46 (6H, s, Ar-C*H*$_3$), 1.71–1.54 (8H, m, C*H*$_2$, Ar-C*H*$_3$), 1.49–1.20 (12H, br, -C*H*$_2$-), 0.88 (3H, t, *J* = 6.58 Hz, -C*H*$_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 158.21, 152.94, 147.59, 137.91, 134.98, 133.36, 132.36, 132.01, 127.86, 127.54, 126.29, 123.80, 123.77, 123.73, 123.69, 122.62, 112.96, 54.96, 32.37, 31.88, 30.12, 29.56, 29.28, 28.71, 22.67, 17.00, 16.89, 14.05 ppm. ^{11}B NMR (CD_2Cl_2): δ = −0.98 ppm. HRMS (ESI) m/z calcd. $[M+H]^+$: 589.3572, found: 589.3564.

Synthesis of the Iodized Monomers (B0-I, B2-I, DM-I, DF-I and MF-I)

General procedure: **B0** (1.00 g, 2.67 mmol) and *N*-iodosuccinimide (2.40 g, 10.7 mmol) were dissolved in dichloromethane (120 mL) under argon atmosphere. After stirred at r.t. for 0.5 h, the solvent was removed by a rotary evaporator. The mixture was

purified with flash column chromatography with dichloromethane as an eluent. The product **B0-I** was dissolved in a small amount of THF and precipitated from methanol as an orange solid (1.22 g, 73%). ^{1}H NMR ($CDCl_3$): δ = 3.00 (2H, t, *J* = 8.45 Hz, Ar-CH_2-), 2.61 (6H, s, Ar-CH_3), 2.48 (6H, s, Ar-CH_3), 1.70–1.42 (4H, br, -CH_2-), 1.40–1.20 (10H, br, -CH_2-), 0.89 (3H, t, *J* = 6.83 Hz, -CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 155.31, 146.48, 142.24, 131.50, 86.32, 31.84, 31.79, 30.33, 29.50, 29.43, 29.23, 22.64, 18.98, 16.11, 14.05 ppm. ^{11}B NMR ($CDCl_3$): δ = 0.29 ppm. HRMS (ESI) m/z calcd. $[M+H]^+$: 625.0565; found, m/z 625.0566.

B2-I: An orange solid, 86% yield. ^{1}H NMR ($CDCl_3$): δ = 7.33–7.12(8H, br, Ar-*H*), 3.13 (2H, t, *J* = 8.35 Hz, Ar-CH_2-), 2.54 (6H, s, Ar-CH_3), 1.88 (6H, s, Ar-CH_3), 1.66 (2H, quint, *J* = 7.98 Hz, -CH_2-), 1.46 (2H, quint, *J* = 7.43 Hz, -CH_2-), 1.39–1.20 (10H, br, -CH_2-), 0.89 (3H, t, *J* = 6.70 Hz, -CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 153.78, 146.83, 139.71, 133.64, 131.69, 127.42, 126.04, 87.79, 32.22, 31.84, 30.10, 29.65, 29.51, 29.25, 22.65, 19.72, 18.61, 14.05 ppm. ^{11}B NMR ($CDCl_3$): δ = 0.39 ppm. HRMS (ESI) m/z calcd. $[M+H]^+$: 743.1525; found, m/z 743.1518.

DM-I: A red solid, 68% yield. ^{1}H NMR (CD_2Cl_2): δ = 7.17 (4H, br, Ar-*H*), 6.77 (4H, dt, *J* = 8.34 Hz, 2.18 Hz, Ar-*H*), 3.77 (6H, s, -OCH_3), 3.12 (2H, t, *J* = 8.35 Hz, Ar-CH_2-), 2.54 (6H, s, Ar-CH_3), 1.89 (6H, s, Ar-CH_3), 1.66 (2H, quint, *J* = 7.89 Hz, -CH_2-), 1.46 (2H, quint, *J* = 7.39 Hz, -CH_2-), 1.39–1.22 (10H, br, -CH_2-), 0.89 (3H, t, *J* = 6.83 Hz, -CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 158.14, 153.73, 146.67, 139.56, 134.70, 131.63, 112.99, 87.75, 54.94, 32.22, 31.84, 30.11, 29.64, 29.54, 29.26, 22.65, 19.69, 18.57, 14.04 ppm. ^{11}B NMR ($CDCl_3$): δ = 0.88 ppm. HRMS (APCI) m/z calcd. $[M+H]^+$: 803.1736, found: 803.1726.

DF-I: A red solid, 71% yield. ^{1}H NMR (CD_2Cl_2): δ = 7.47 (4H, d, *J* = 7.98 Hz, Ar-*H*), 7.36 (4H, br, Ar-*H*), 3.15 (2H, t, *J* = 8.26 Hz, Ar-CH_2-), 2.56 (6H, s, Ar-CH_3), 1.83 (6H, s, Ar-CH_3), 1.66 (2H, quint, *J* = 7.84 Hz, -CH_2-), 1.46 (2H, quint, *J* = 7.25 Hz, -CH_2-), 1.39–1.20 (10H, br, -CH_2-), 0.89 (3H, t, *J* = 6.55 Hz, -CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 153.73,

147.44, 140.64, 133.57, 131.73, 128.81, 128.49, 125.99, 124.35, 124.31, 124.27, 124.24, 123.28, 88.15, 32.25, 31.84, 30.10, 29.71, 29.52, 29.25, 22.66, 19.80, 18.81, 14.05 ppm. ^{11}B NMR ($CDCl_3$): δ = –0.59 ppm. HRMS (APCI) m/z calcd. $[M+H]^+$: 627.3340, found: 627.3336.

MF-I: A red solid, 66% yield. ^{1}H NMR (CD_2Cl_2): δ =7.45 (2H, d, *J* = 7.74 Hz, Ar-*H*), 7.38–7.23 (2H, br, Ar-*H*), 7.18 (2H, br, Ar-*H*), 6.79 (2H, dt, *J* = 8.65, 2.17 Hz, Ar-*H*), 3.78 (3H, s, -OCH_3), 3.13 (2H, t, *J* = 7.55 Hz, Ar-CH_2-), 2.55 (6H, s, Ar-CH_3), 1.87 (6H, s, Ar-CH_3), 1.64 (2H, br, -CH_2-), 1.53–1.20 (12H, br, -CH_2-), 0.89 (3H, t, *J* = 6.73 Hz, -CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 158.36, 153.73, 147.05, 140.08, 134.84, 133.40, 131.59, 128.25, 127.91, 126.05, 124.06, 124.03, 123.99, 123.95, 123.35, 113.17, 87.96, 54.95, 32.19, 31.83, 30.10, 29.63, 29.50, 29.25, 22.65, 19.74, 18.67, 14.06 ppm. ^{11}B NMR (CD_2Cl_2): δ = −0.29 ppm. HRMS (ESI) m/z calcd. $[M–H]^–$: 839.1359, found: 839.1372.

Synthesis of the Polymers:

PFB0: Water (2.0 mL) was added to the solution of **B0-I** (0.15 g, 0.24 mmol), [9,9-bis(dodecyl)-9H-fluorene-2,7-diyl]bisboronic acid (0,14 g, 0.24 mmol), $Pd_2(dba)_3$ (2.2 mg, 2.4 μmol), S-Phos (3.9 mg, 9.6 μmol) and cesium carbonate (0.78 g, 2.4 mmol) in toluene (2.0 mL). The reaction mixture was stirred at 80 °C for 72 h (**PFB0, PFB2**) or 48 h (**PFDM, PFDF, PFMF**) under argon atmosphere, and poured into a large amount of methanol to collect the polymer by filtration. The precipitate was dissolved in a small amount of THF, and then the product was reprecipitated from ethanol. The polymer collected by filtration was dried in vacuum to give **PFB0** as a red solid (0.19 g, 89%). M_n = 10,200, M_w/M_n = 2.7. ^{1}H NMR ($CDCl_3$): δ = 7.90–7.60 (2H, br, Ar-*H*), 7.40–7.10 (4H, br, Ar-*H*), 3.14 (2H, Ar-CH_2-), 2.66–2.30 (12H, Ar-CH_3), 2.01 (4H, >C(CH_2-)$_2$), 1.77 (2H, -CH_2-), 1.47–0.95 (52H, -C_6H_{12}- and –$C_{10}H_{20}$-), 0.93–0.51 (9H, -CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 152.71, 151.10, 146.88, 139.89, 136.25, 134.44, 132.64, 131.63, 129.21, 125.12, 119.64, 55.22, 40.38, 31.94, 31.88, 30.46, 30.08, 29.66, 29.58, 29.52, 29.39, 29.36, 29.28 ppm. ^{11}B NMR ($CDCl_3$): δ = 8.14 ppm.

PFB2: A red solid, 53% yield. M_n = 6,200, M_w/M_n = 2.2. ^{1}H NMR ($CDCl_3$): δ = 7.90–7.00 (14H, br, Ar-*H*), 3.24 (2H, Ar-CH_2-), 2.44 (6H, Ar-CH_3), 2.01–1.64 (12H, >C(CH_2-)$_2$, -CH_2-, and Ar-CH_3), 1.59–0.78 (55H, -C$_7H_{15}$ and -C$_{10}H_{20}$-), 0.61 (6H, br, -CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 151.93, 150.79, 147.30, 140.97, 139.58, 134.79, 134.03, 133.42, 132.08, 129.55, 127.31, 127.21, 125.62, 125.22, 119.19, 55.15, 55.10, 40.33, 32.49, 31.94, 31.90, 30.30, 29.99, 29.63, 29.53, 29.35, 29.31, 23.92, 22.70, 22.67, 15.75, 15.06, 14.11, 14.08 ppm. ^{11}B NMR ($CDCl_3$): δ = –2.25 ppm.

PFDM: A red solid, 59% yield. M_n = 7,400, M_w/M_n = 1.9. ^{1}H NMR ($CDCl_3$): δ = 7.66 (2H, m, Ar-*H*), 7.51–7.20 (4H, br, Ar-*H*), 7.08 (4H, m, Ar-*H*), 6.83 (4H, m, Ar-*H*), 3.80 (6H, -OCH_3), 3.24 (2H, Ar-CH_2-), 2.44 (6H, Ar-CH_3), 2.90–1.64 (12H, >C(CH_2-)$_2$, -CH_2-, and Ar-CH_3), 1.62–0.78 (55H, -C$_7H_{15}$ and -C$_{10}H_{20}$-), 0.62 (6H, br, -CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 157.77, 151.85, 150.73, 147.14, 139.52, 135.06, 134.66, 133.41, 133.24, 131.94, 129.53, 125.18, 119.15, 112.68, 55.13, 54.91, 40.36, 32.47, 31.94, 31.90, 30.32, 30.30, 29.62, 29.53, 29.36, 29.32, 23.93, 22.70, 22.67, 15.73, 15.04, 14.12, 14.10 ppm. ^{11}B NMR ($CDCl_3$): δ = 0.88 ppm.

PFDF: A red solid, 89% yield. M_n = 6,000, M_w/M_n = 1.7. ^{1}H NMR ($CDCl_3$): δ = 7.79 (2H, m, Ar-*H*), 7.62–7.39 (6H, br, Ar-*H*), 7.32 (2H, m, Ar-*H*), 7.07 (4H, m, Ar-*H*), 3.26 (2H, Ar-CH_2-), 2.45 (6H, Ar-CH_3), 2.13–1.60 (12H, >C(CH_2-)$_2$, -CH_2-, and Ar-CH_3), 1.58–0.78 (55H, -C$_7H_{15}$ and -C$_{10}H_{20}$-), 0.62 (6H, br, -CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 150.94, 150.82, 147.93, 139.75, 135.19, 134.34, 133.86, 132.98, 132.09, 129.52, 126.12, 125.07, 124.03, 123.42, 119.15, 55.22, 40.24, 32.46, 31.90, 31.85, 30.22, 29.97, 29.92, 29.56, 29.50, 29.47, 29.44, 29.31, 29.27, 23.82, 22.65, 15.58, 15.06, 14.06 ppm. ^{11}B NMR ($CDCl_3$): δ = –3.03 ppm.

PFMF: A red solid, 87% yield. M_n = 8,400, M_w/M_n = 2.5. ^{1}H NMR ($CDCl_3$): δ = 7.68 (2H, m, Ar-*H*), 7.59–7.42 (4H, br, Ar-*H*), 7.41–7.27 (2H, m, Ar-*H*), 7.08 (4H, m, Ar-*H*), 6.84 (2H, m, Ar-*H*), 3.80 (6H, -OCH_3), 3.24 (2H, Ar-CH_2-), 2.44 (6H, Ar-CH_3),

2.12–1.59 (12H, >C(CH_2-)$_2$, -CH_2-, and Ar-CH_3), 1.58–0.76 (55H, -C_7H_{15} and -$C_{10}H_{20}$-), 0.62 (6H, br, -CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 158.07, 151.83, 150.82, 147.51, 139.64, 135.14, 134.92, 133.80, 133.20, 132.02, 129.54, 126.25, 125.11, 123.80, 123.55, 119.30, 112.91, 55.17, 54.93, 40.32, 33.95, 32.47, 31.93, 31.88, 30.27, 29.96, 29.60, 29.51, 29.34, 29.30, 23.91, 22.68, 22.66, 15.80, 15.06, 14.10, 14.08 ppm. ^{11}B NMR ($CDCl_3$): δ = 5.30 ppm.

PTB0: A metallic purple solid, 97% yield. M_n = 9,500, M_w/M_n = 1.7. ^{1}H NMR ($CDCl_3$): δ = 6.79 (2H, br, Ar-*H*), 3.11 (2H, Ar-CH_2-), 2.74–2.36 (16H, Ar-CH_3, Ar-CH_2-), 1.81–0.96 (54H, -C_7H_{14}- and –$C_{10}H_{20}$-), 0.93–0.71 (9H, -CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 153.71, 147.49, 142.42, 137.84, 134.20, 131.61, 129.87, 129.41, 126.53, 31.94, 31.84, 30.78, 30.42, 29.72, 29.69, 29.68, 29.64, 29.55, 29.49, 29.37, 29.25, 29.08, 28.94, 22.69, 22.64, 14.67, 14.08, 14.05, 13.49 ppm. ^{11}B NMR ($CDCl_3$): δ = 0.59 ppm.

PTB2: A metallic purple solid, 79% yield. M_n = 11,500, M_w/M_n = 1.8. ^{1}H NMR ($CDCl_3$): δ = 7.45–7.07 (10H, br, Ar-*H*), 6.64 (2H, br, Ar-*H*), 3.20 (2H, Ar-CH_2-), 2.60–2.32 (10H, Ar-CH_3, Ar-CH_2-), 1.93–0.93 (54H, -C_7H_{14}- and –$C_{10}H_{20}$-), 0.92–0.73 (9H, -CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 152.79, 147.89, 142.19, 141.98, 135.14, 135.06, 133.85, 132.06, 129.76, 129.10, 128.71, 128.61, 127.23, 126.62, 125.70, 32.37, 31.94, 31.87, 30.70, 30.25, 29.69, 29.65, 29.60, 29.58, 29.44, 29.38, 29.30, 28.98, 22.71, 22.67, 15.90, 15.20, 14.12, 14.10 ppm. ^{11}B NMR ($CDCl_3$): δ = 5.20 ppm.

PTDM: A metallic purple solid, 90% yield. M_n = 7,800, M_w/M_n = 1.7. ^{1}H NMR ($CDCl_3$): δ = 7.45–7.10 (4H, br, Ar-*H*), 6.86–6.71 (4H, br, Ar-*H*), 6.64 (2H, br, Ar-*H*), 3.78 (6H, -OCH_3), 3.20 (2H, Ar-CH_2-), 2.72–2.30 (10H, Ar-CH_3, Ar-CH_2-), 1.99–1.00 (54H, -C_7H_{14}- and –$C_{10}H_{20}$-), 0.98–0.74 (9H, -CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 157.89, 152.78, 147.67, 141.96, 135.17, 135.01, 134.87, 132.03, 129.73, 129.11, 128.76, 128.61, 126.58, 125.10, 112.77, 54.88, 32.39, 31.93, 31.86, 30.68, 30.25, 29.67, 29.64, 29.59, 29.44, 29.36, 29.29, 28.99, 22.69, 22.65, 15.85, 15.17, 14.09, 14.06 ppm. ^{11}B NMR ($CDCl_3$): δ = –2.44

ppm.

PTDF: A metallic purple solid, 90% yield. M_n = 9,100, M_w/M_n = 1.9. ^{1}H NMR ($CDCl_3$): δ = 7.56–7.30 (8H, br, Ar-*H*), 6.66 (2H, br, Ar-*H*), 3.22 (2H, Ar-CH_2-), 2.72–2.22 (10H, Ar-CH_3, Ar-CH_2-), 1.93–0.95 (54H, -C_7H_{14}- and –$C_{10}H_{20}$-), 0.93–0.75 (9H, -CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 152.61, 148.53, 142.22, 136.03, 134.56, 133.74, 132.05, 129.94, 129.27, 128.75, 128.41, 128.10, 127.07, 126.04, 124.09, 123.33, 32.39, 31.91, 31.84, 30.66, 30.19, 29.64, 29.63, 29.57, 29.54, 29.42, 29.40, 29.34, 29.26, 29.14, 28.97, 22.68, 22.65, 16.00, 15.21, 14.07, 14.06 ppm. ^{11}B NMR ($CDCl_3$): δ = –2.44 ppm.

PTMF: A metallic purple solid, 84% yield. M_n = 11,400, M_w/M_n = 1.8. ^{1}H NMR ($CDCl_3$): δ = 7.55–7.17 (6H, br, Ar-*H*), 6.87–6.75 (2H, br, Ar-*H*), 6.65 (2H, br, Ar-*H*), 3.79 (3H, -OCH_3), 3.21 (2H, Ar-CH_2-), 2.76–2.29 (10H, Ar-CH_3, Ar-CH_2-), 2.02–1.01 (54H, -C_7H_{14}- and –$C_{10}H_{20}$-), 0.98–0.78 (9H, -CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ = 158.16, 152.75, 148.15, 142.27, 142.21, 142.09, 135.53, 134.87, 133.54, 132.08, 129.84, 129.19, 128.62, 127.97, 127.65, 126.82, 126.17, 125.18, 123.86, 123.47, 112.99, 54.92, 32.38, 31.92, 31.84, 30.67, 30.20, 29.66, 29.64, 29.58, 29.42, 29.35, 29.27, 28.98, 22.68, 22.65, 15.93, 15.19, 14.08, 14.06 ppm. ^{11}B NMR ($CDCl_3$): δ = –2.25 ppm.

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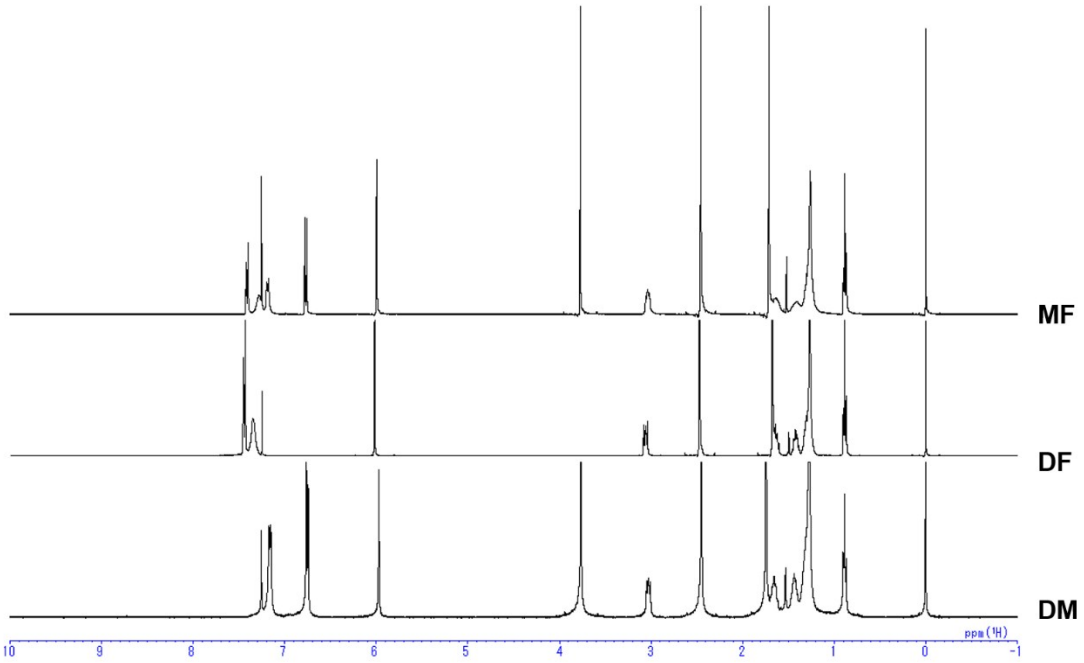
3. Yamane, H.; Tanaka, K.; Chujo, Y. *Tetrahedron Lett.* **2015**, *56*, 6786-6790.

(a)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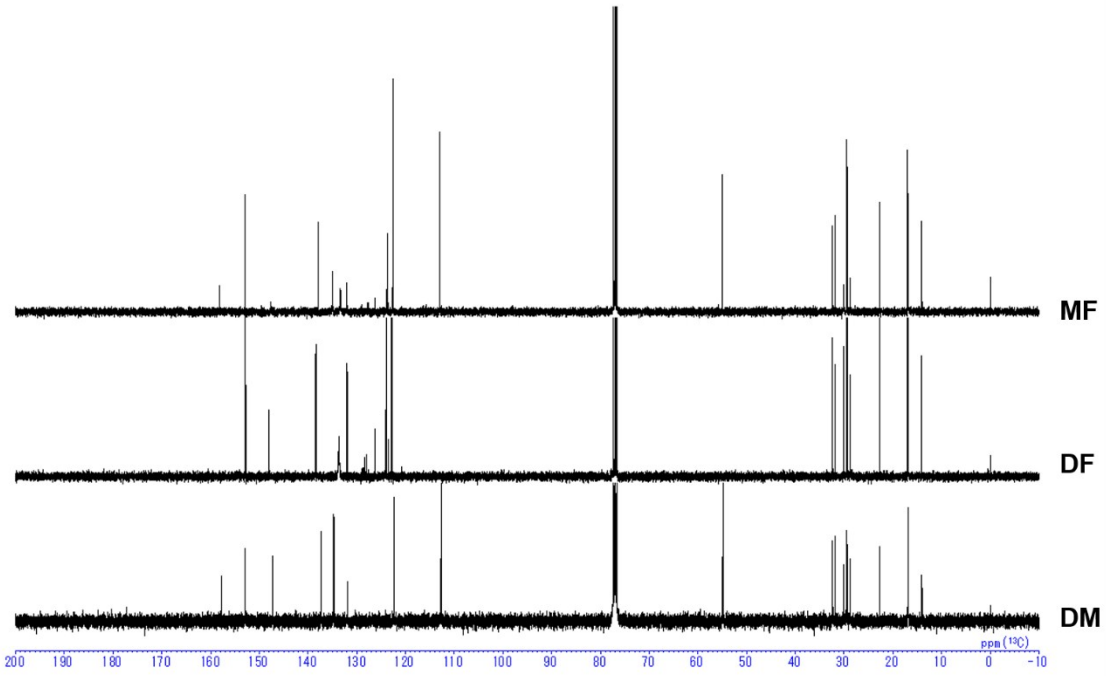
DF
DM
ppm (¹H)
10
9
8
7
6
5
4
3
2
1
0
-1

(b)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DF
DM
ppm (¹³C)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

(c)

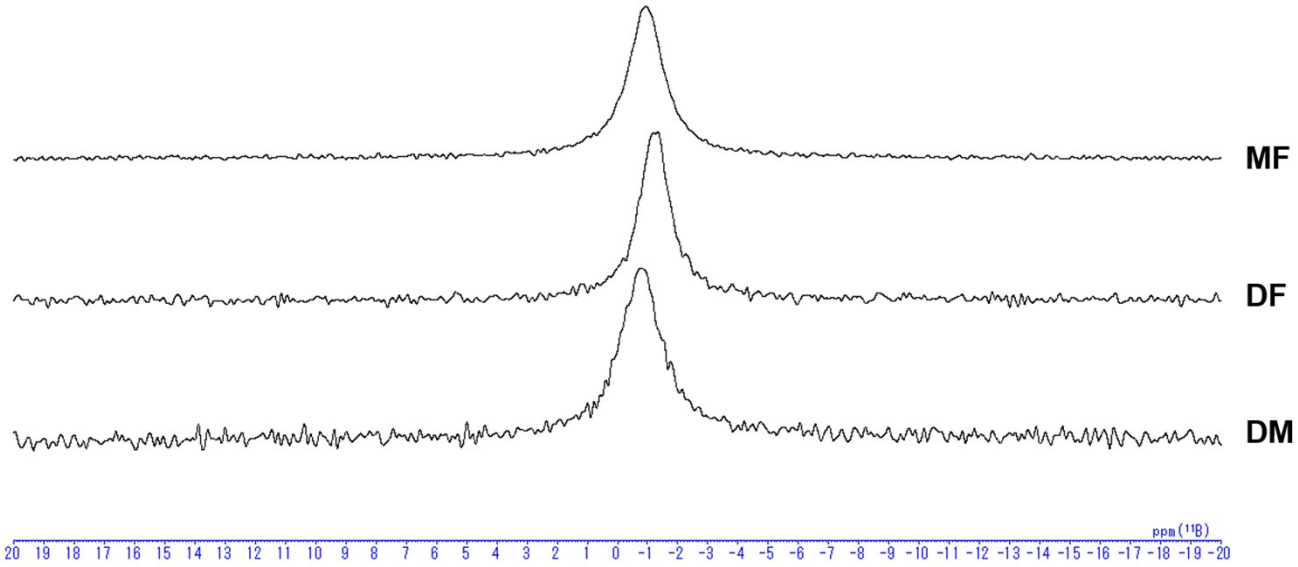
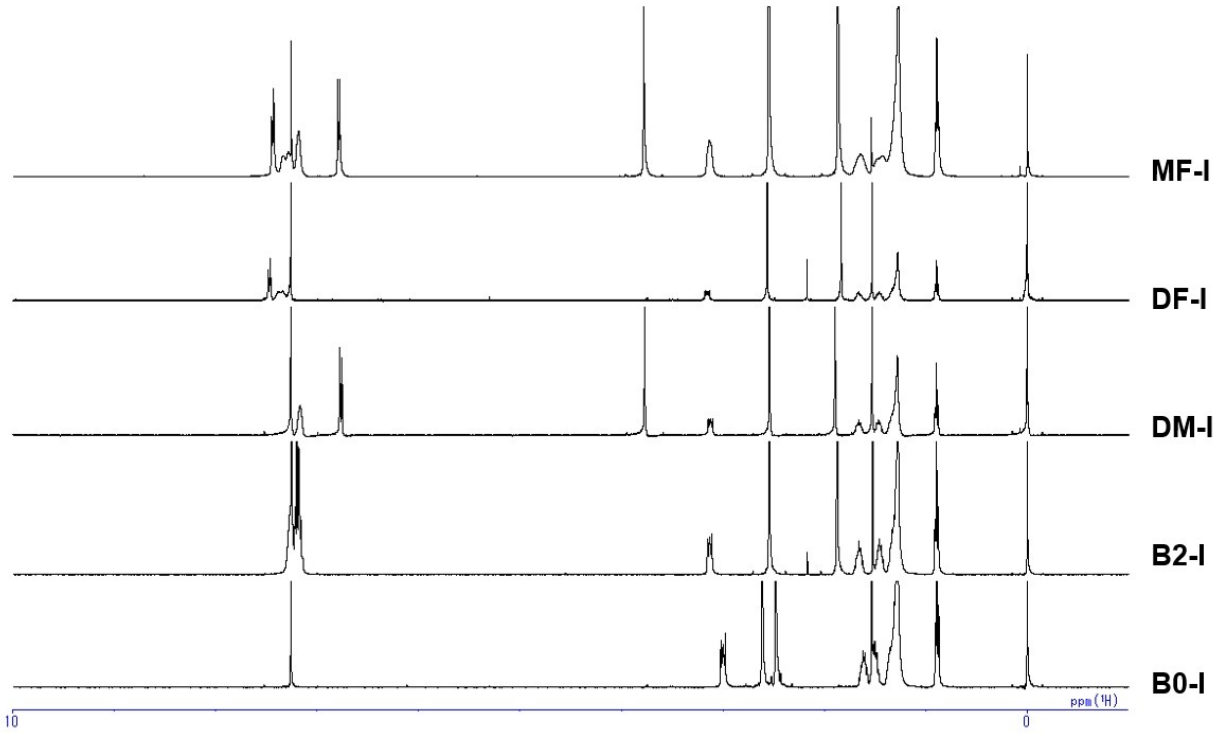


Chart S1. (a) ^{1}H, (b) ^{13}C and (c) ^{11}B NMR spectra of modified BODIPYs.

(a)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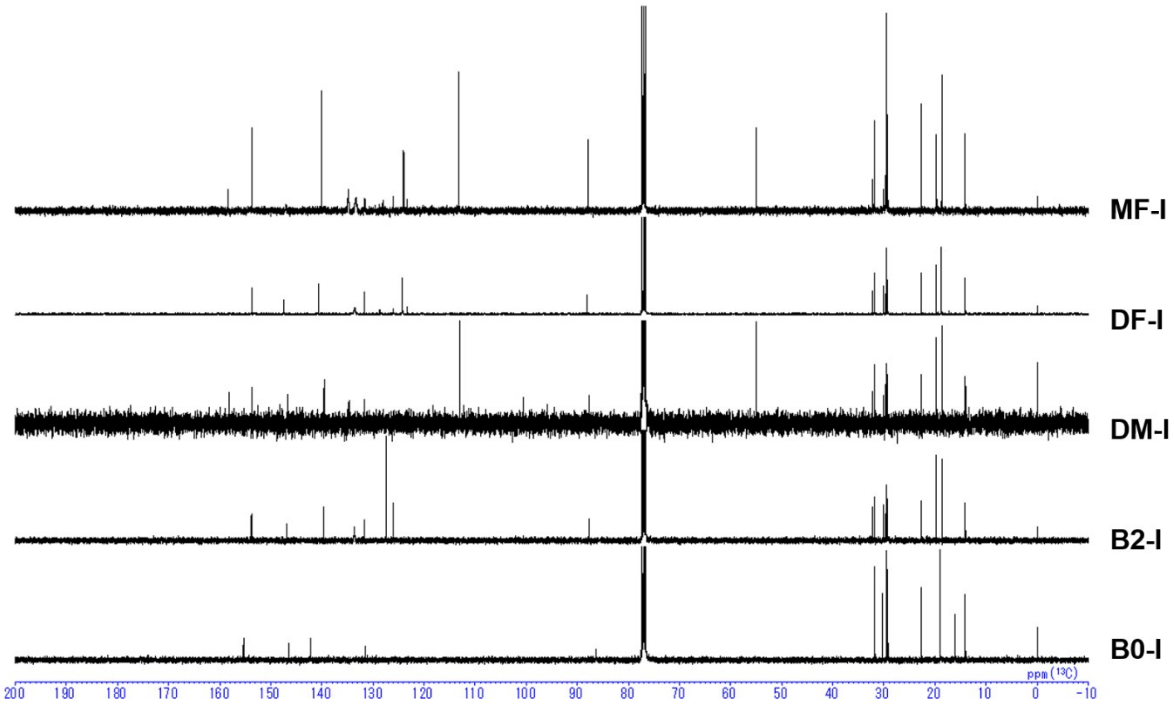
DF-I
DM-I
B2-I
B0-I
ppm(¹H)
10
0

(b)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DF-I
DM-I
B2-I
B0-I
ppm(¹³C)
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(c)

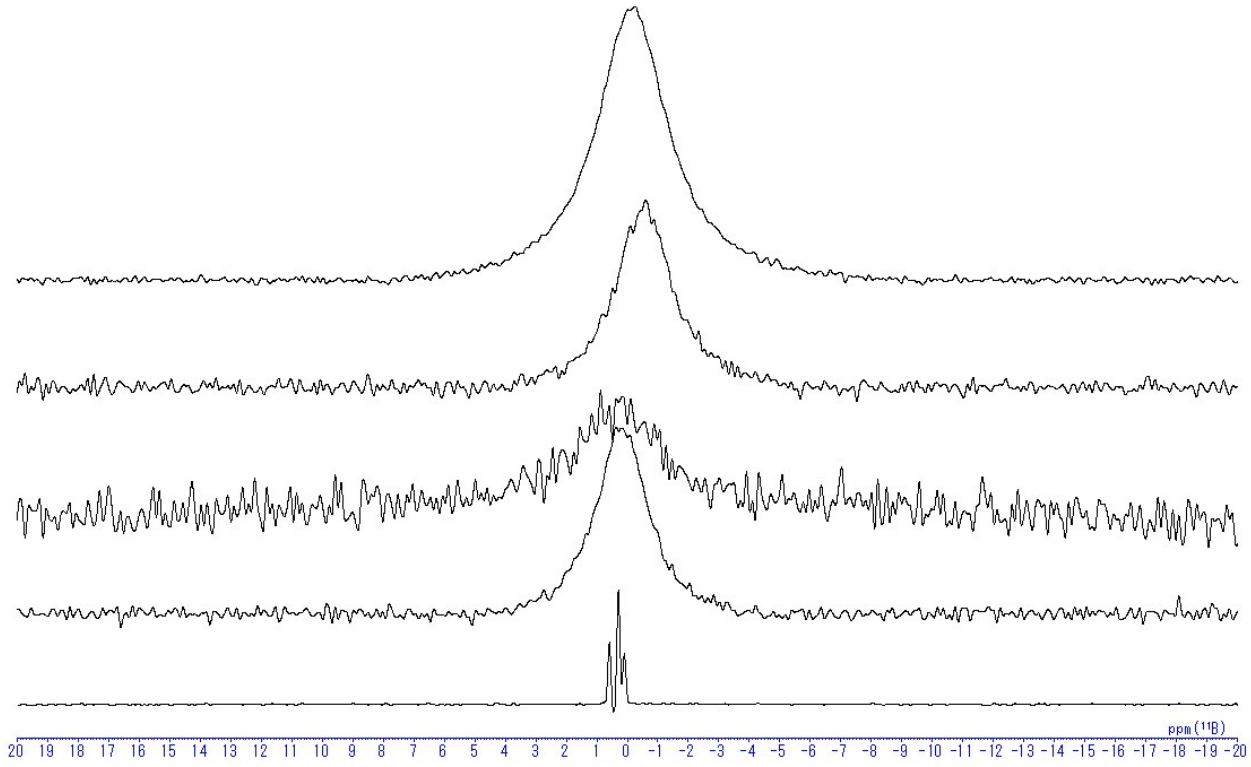
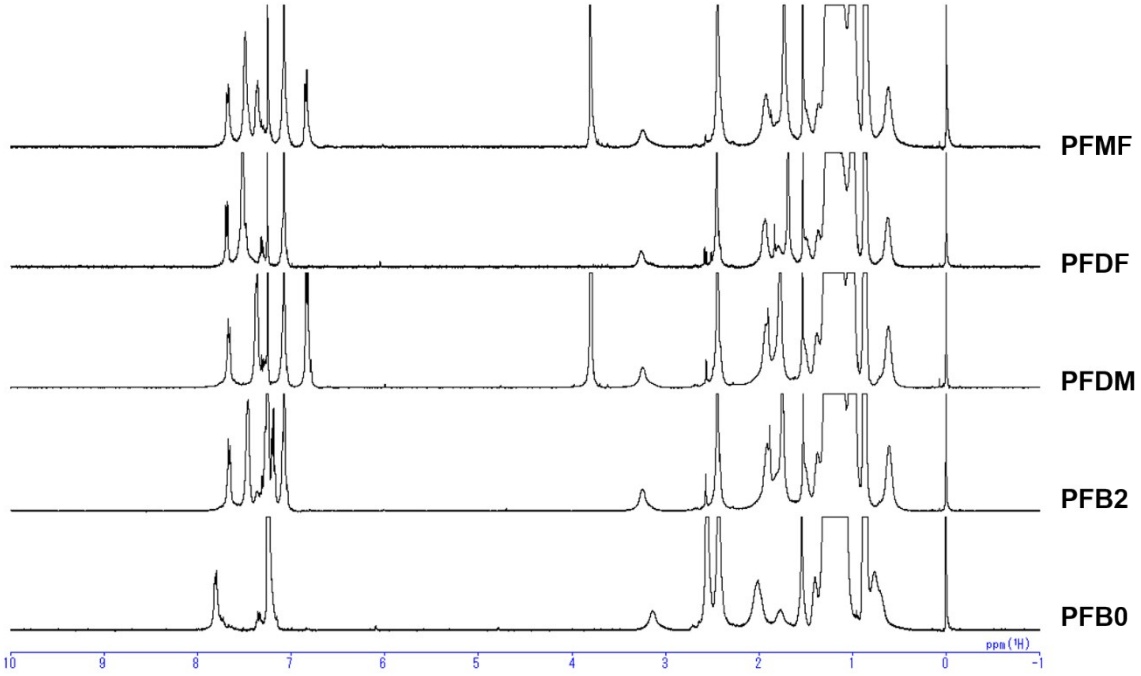


Chart S2. (a) ^{1}H, (b) ^{13}C and (c) ^{11}B NMR spectra of monomers.

(a)


PFMF
PFDF
PFDM
PFB2
PFB0
ppm(¹H)
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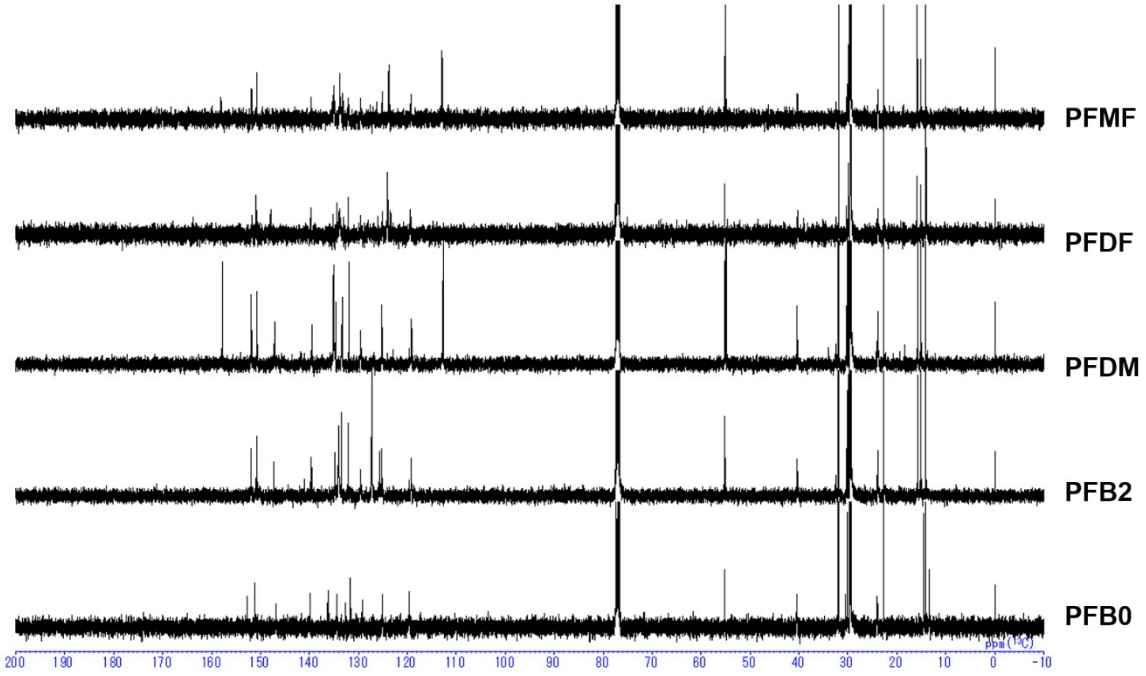
(b)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PFDF
PFDM
PFB2
PFB0
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

(c)

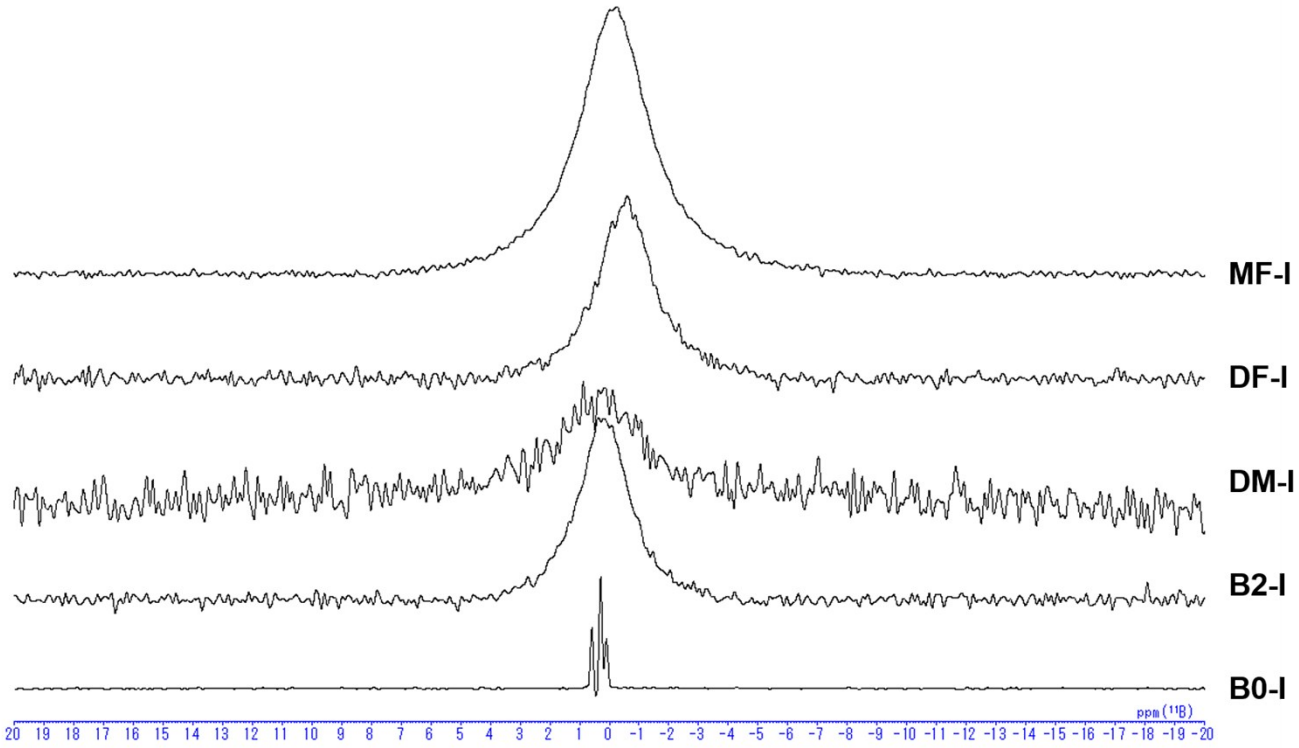
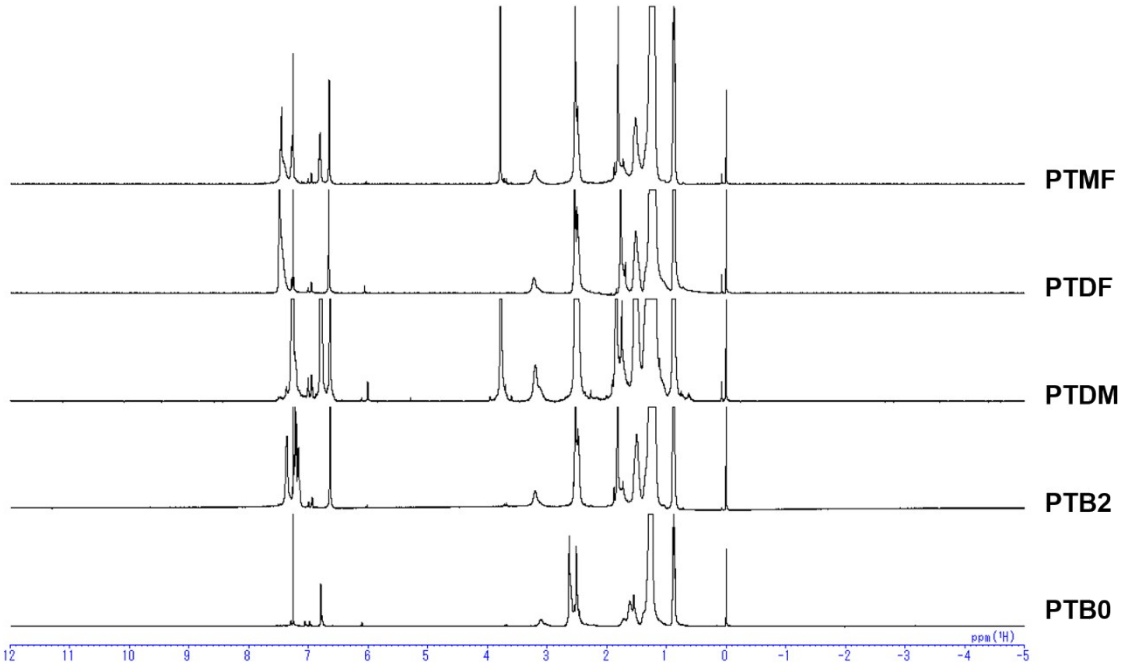
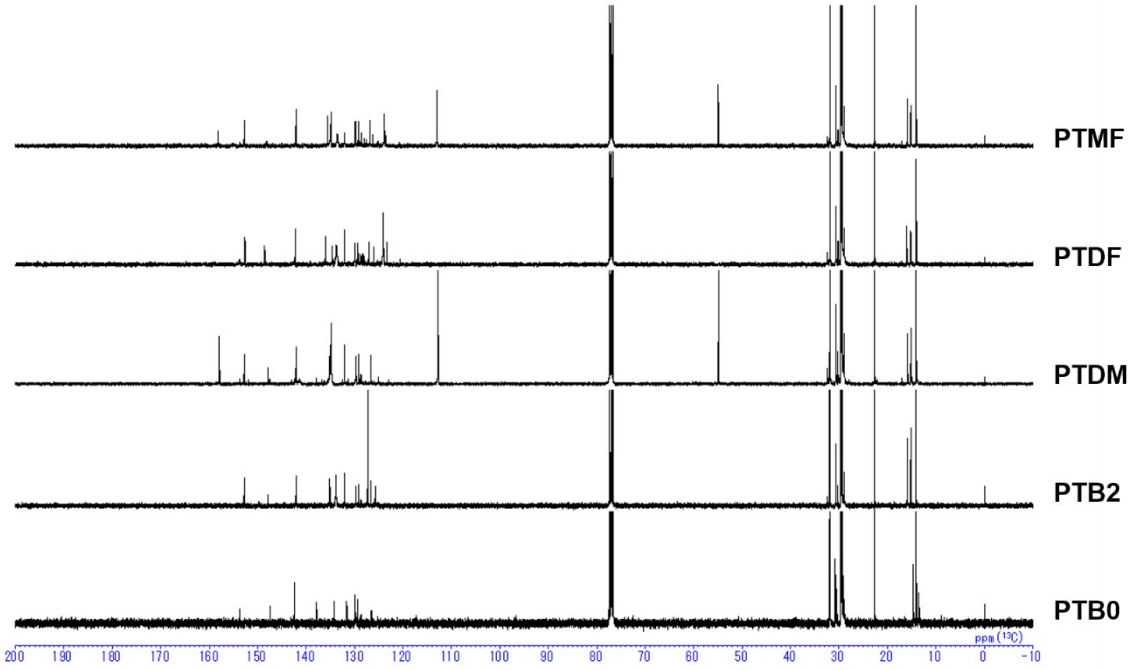


Chart S3. (a) ^{1}H, (b) ^{13}C and (c) ^{11}B NMR spectra of fluorene copolymers.

(a)


PTMF
PTDF
PTDM
PTB2
PTB0
ppm(¹H)
12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5

(b)


PTMF
PTDF
PTDM
PTB2
PTB0
ppm(¹³C)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

(c)

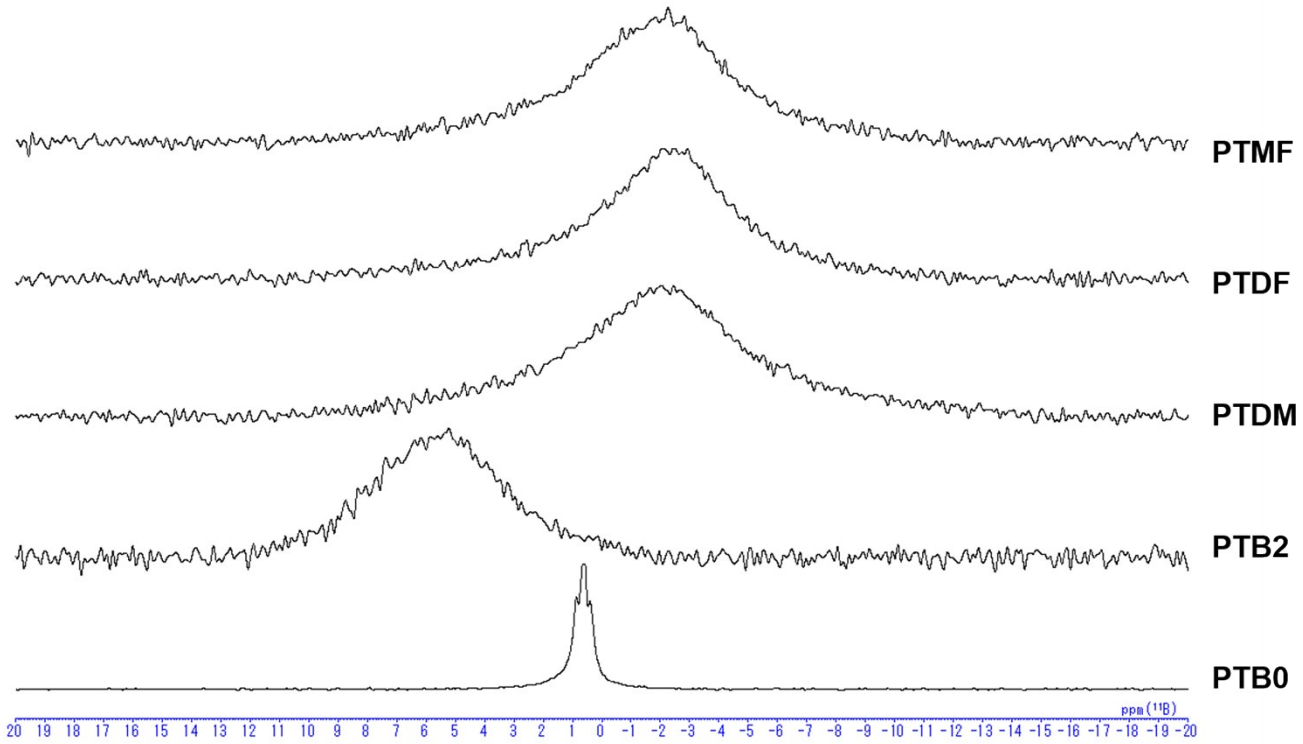
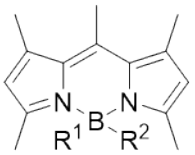
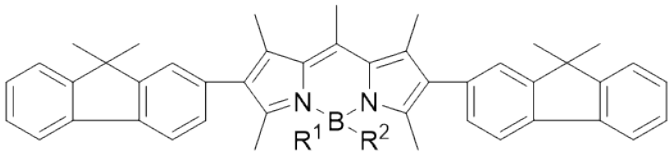


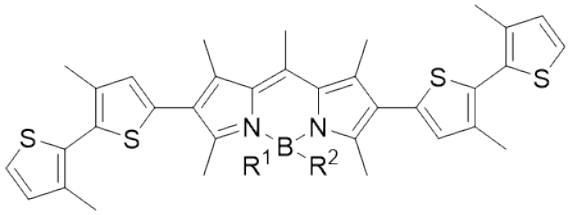
Chart S4. (a) ^{1}H, (b) ^{13}C and (c) ^{11}B NMR spectra of bithiophene copolymers.



B0', **B2'**, **DM'**, **DF'**, **MF'**



PFB0', **PFB2'**, **PFDM'**, **PFDF'**, **PFMF'**



PTB0', **PTB2'**, **PTDM'**, **PTDF'**, **PTMF'**

B0', **PFB0'**, **PTB0'** : $R^1 = R^2 = F$

B2', **PFB2'**, **PTB2'** : $R^1 = R^2 = Ph$

DM', **DMB2'**, **DMB2'** : $R^1 = R^2 = p\text{-MeO-}C_6H_4\text{-}$

DF', **DFB2'**, **DFB2'** : $R^1 = R^2 = p\text{-}CF_3\text{-}C_6H_4\text{-}$

MF', **MFB2'**, **MFB2'** : $R^1 = p\text{-}CF_3\text{-}C_6H_4\text{-}$
$R^2 = p\text{-MeO-}C_6H_4\text{-}$

Figure S1. Structure of the model compounds for DFT caluculation.

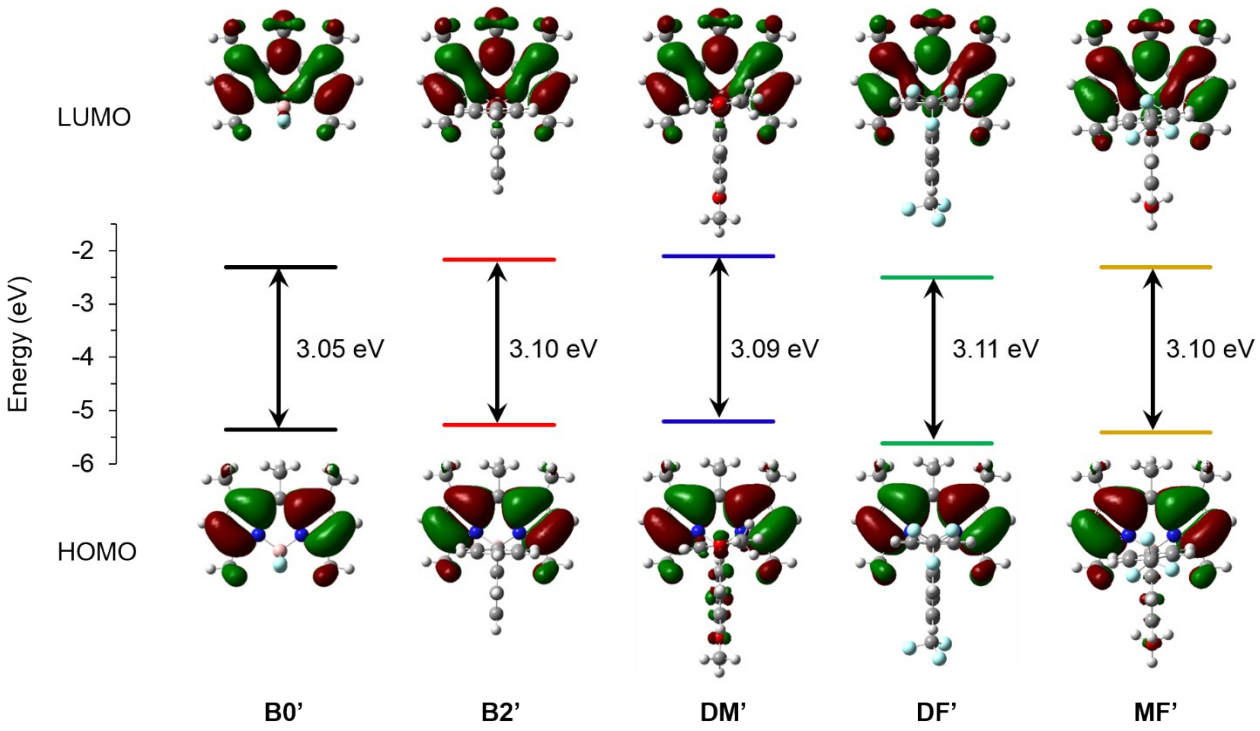


Figure S2. Frontier orbitals and energy diagrams of **B0'**, **B2'**, **DM'**, **DF'** and **MF'**.

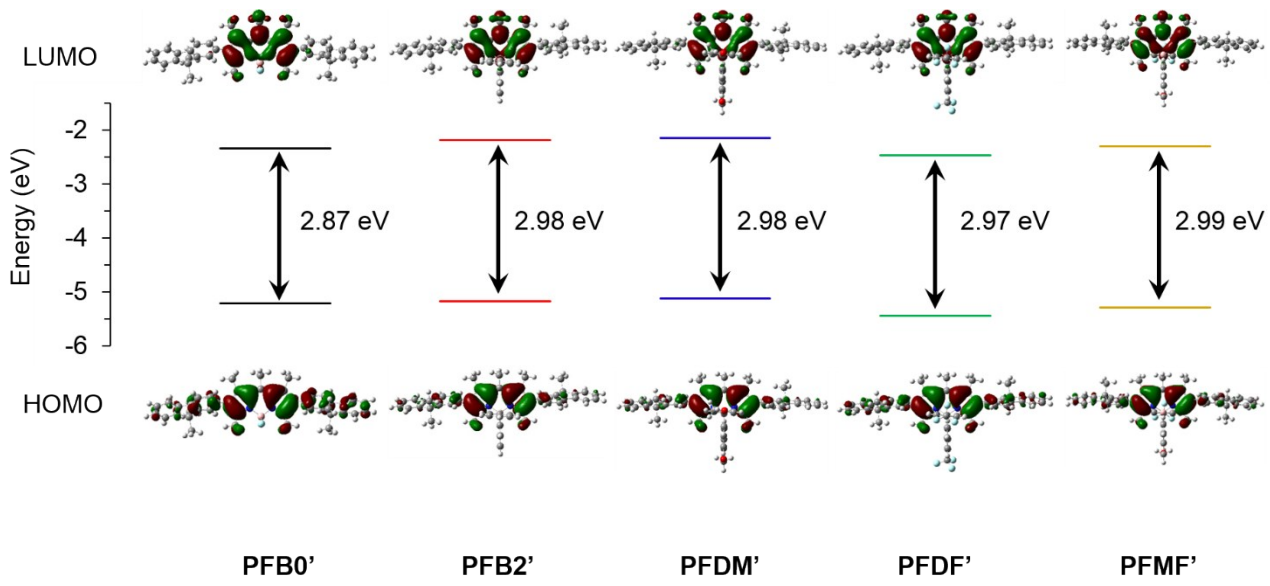


Figure S3. Frontier orbitals and energy diagrams of **PFB0'**, **PFB2'**, **PFDM'**, **PFDF'** and **PFMF'**.

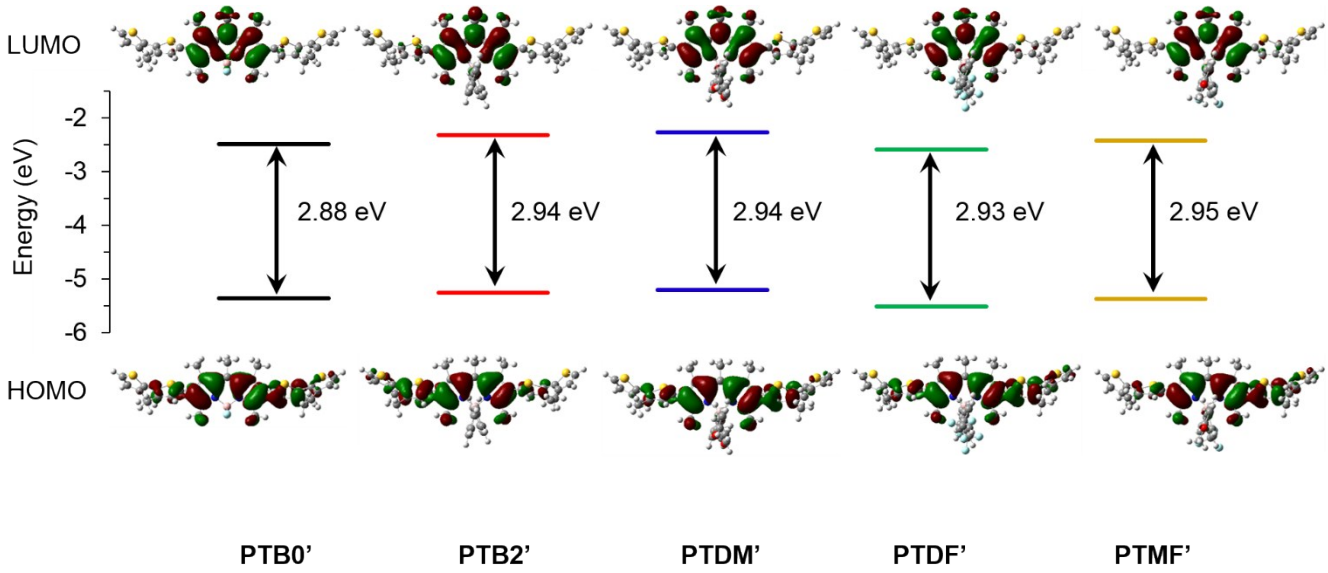


Figure S4. Frontier orbitals and energy diagrams of **PTB0'**, **PTB2'**, **PTDM'**, **PTDF'** and **PTMF'**.

Electrochemical Properties

Cyclic Voltammetry

Electrolyte solution: dichloromethane containing tetrabutylammonium chloride (0.1 M) as an electrolyte.

Counter electrode: glassy carbon.

Reference electrode: Ag/AgCl

Scan condition: scan rate of 0.05 V/s under argon.

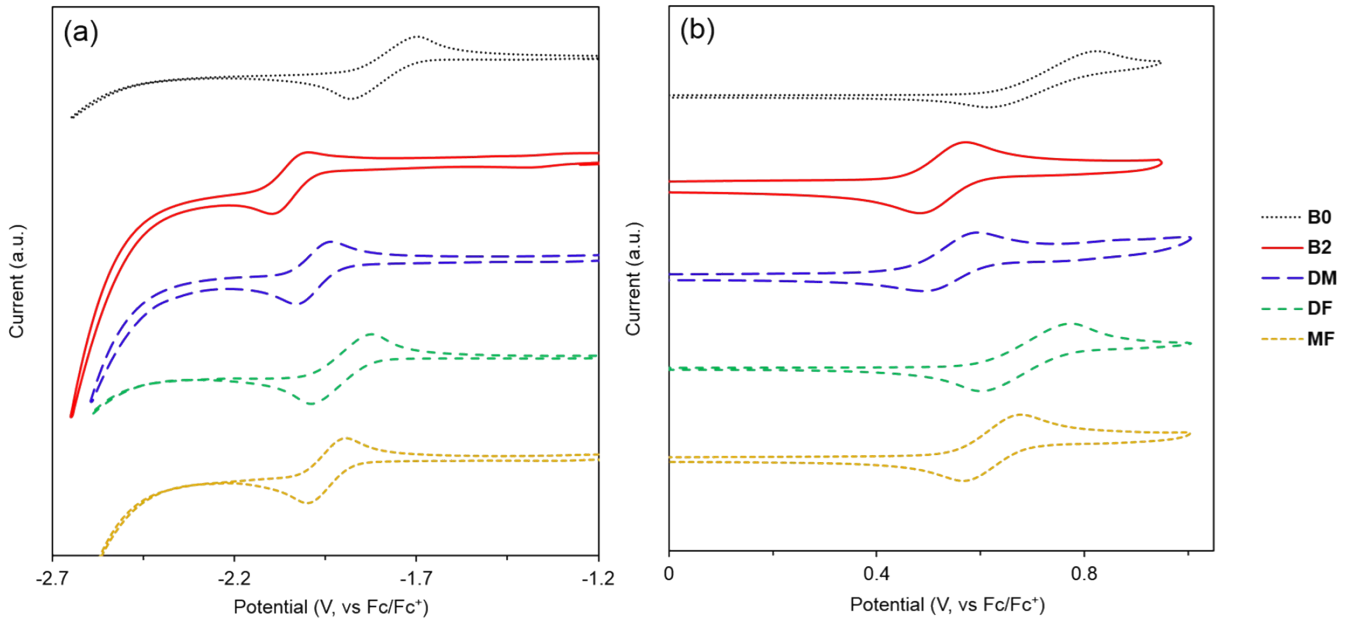


Figure S5. Cyclic voltammograms of the **B0**, **B2**, **DM**, **DF** and **MF** in (a) negative and (b) positive sweeps.

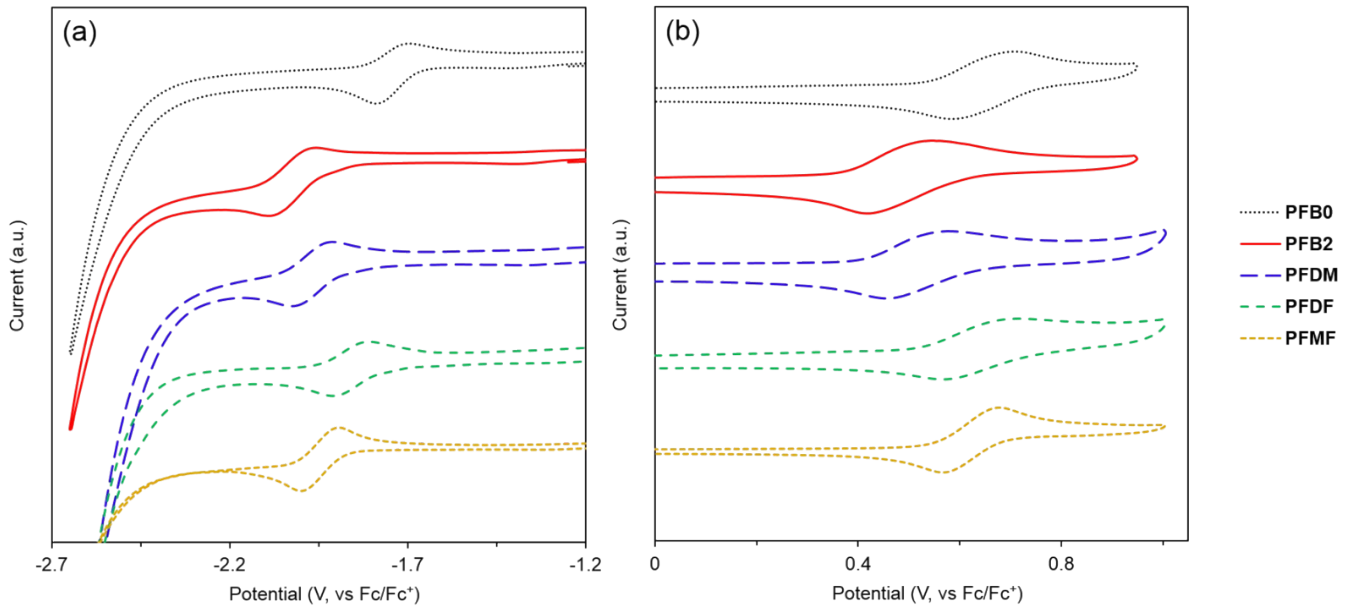


Figure S6. Cyclic voltammograms of the **PFB0**, **PFB2**, **PFDM**, **PFDF** and **PFMF** in (a) negative and (b) positive sweeps.

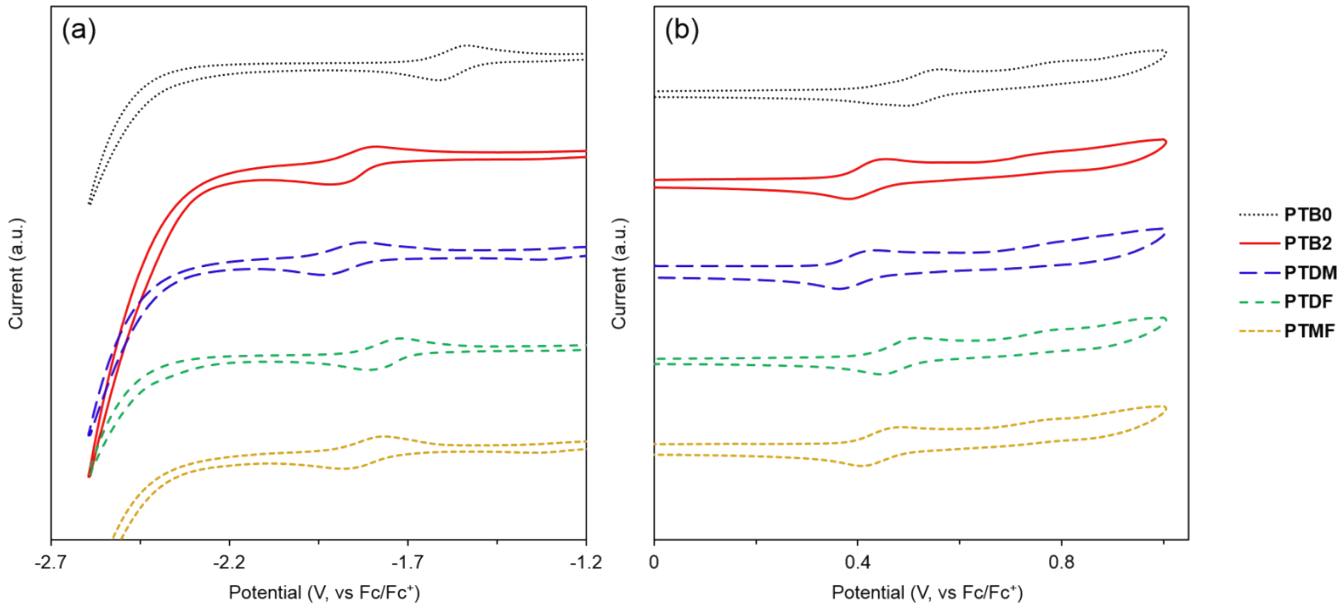


Figure S7. Cyclic voltammograms of the **PTB0**, **PTB2**, **PTDM**, **PTDF** and **PTMF** in (a) negative and (b) positive sweeps.

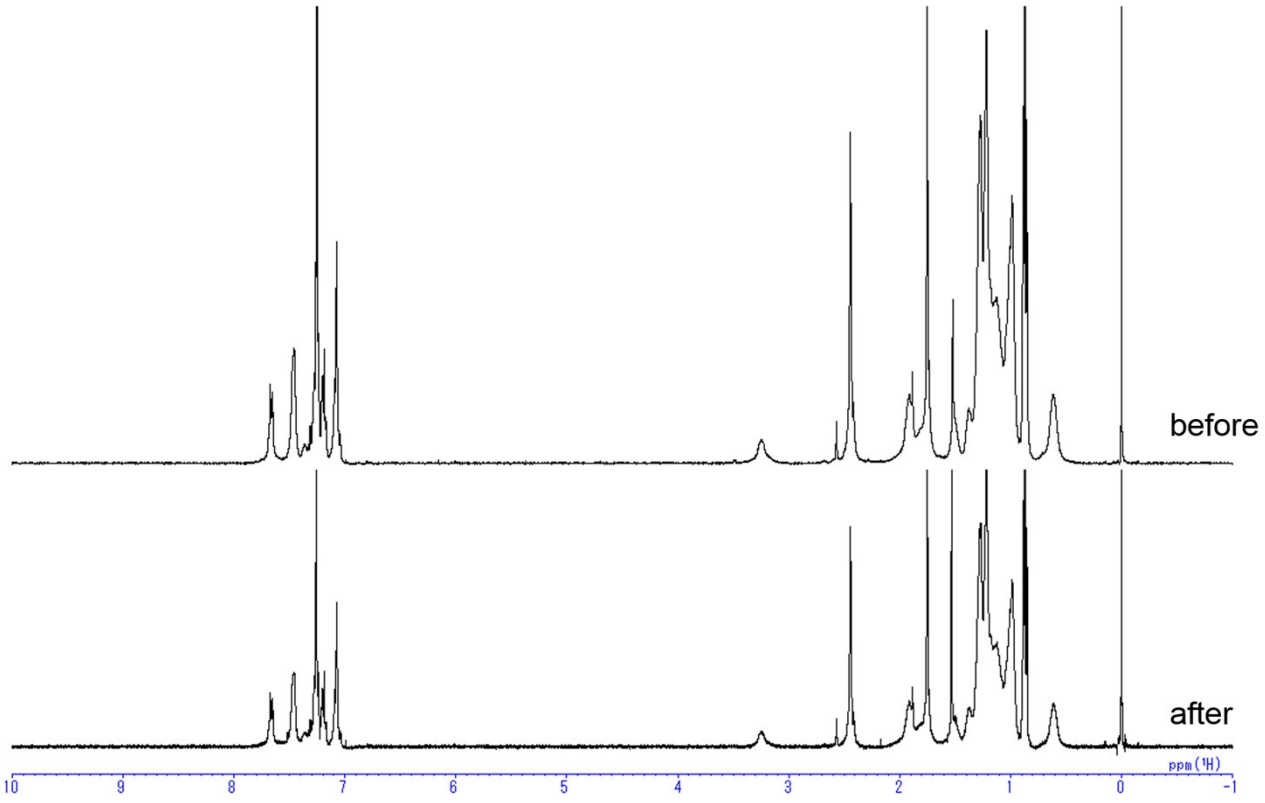


Figure S8. ^{1}H NMR spectra of **PFB2** in chloroform before and after UV (365 nm) irradiation for 30 min at ambient temperature.

	$E_{onset,\ ox}$ [V]	$E_{onset,\ red}$ [V]	E_{HOMO} [eV]	E_{LUMO} [eV]	E_g^{CV} [eV]	λ_{onset} [nm]	E_g^{opt} [eV]
B0	0.64	−1.71	−5.44	−3.09	2.35	512	2.42
B2	0.46	−1.98	−5.26	−2.82	2.44	510	2.43
DM	0.46	−1.91	−5.26	−2.89	2.37	510	2.43
DF	0.60	−1.83	−5.40	−2.97	2.43	510	2.43
MF	0.55	−1.88	−5.35	−2.92	2.43	510	2.43
PFB0	0.54	−1.67	−5.34	−3.13	2.21	576	2.15
PFB2	0.37	−1.92	−5.17	−2.88	2.29	566	2.19
PFDM	0.36	−1.86	−5.16	−2.94	2.23	567	2.19
PFDF	0.52	−1.76	−5.32	−3.04	2.28	566	2.19
PFMF	0.45	−1.81	−5.25	−2.99	2.26	568	2.18
PTB0	0.43	−1.49	−5.23	−3.31	1.92	600	2.07
PTB2	0.37	−1.78	−5.17	−3.02	2.14	587	2.11
PTDM	0.34	−1.80	−5.14	−3.00	2.14	586	2.12
PTDF	0.42	−1.68	−5.22	−3.12	2.10	589	2.11
PTMF	0.38	−1.71	−5.18	−3.08	2.10	588	2.11

Table S1. Results of the electrochemical and optical measurements

[a]The onset wavelength of the UV−vis spectra in chloroform. [b]Optical band gaps were estimated from the corresponding λ_{onset}.