Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information

Selective Modulation of Energy Levels of Frontier Orbitals in Solid-state Luminescent Boron-fused Azomethine Polymers with Orthogonal Orientation to the Main-chains

Masayuki Gon, Misato Kanjo, Shunsuke Ohtani, Kazuo Tanaka* and Yoshiki Chujo

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

E-mail: tanaka@poly.synchem.kyoto-u.ac.jp

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General

^{1}H (400 MHz), ^{13}C (100 MHz) and ^{11}B (128 MHz) NMR spectra were recorded on a JEOL JNM AL400 spectrometer. Samples were analyzed in $CDCl_3$ and CD_2Cl_2. The chemical shift values were expressed relative to tetramethylsilane (TMS) for ^{1}H NMR in $CDCl_3$. For ^{1}H NMR in CD_2Cl_2, internal standards were used. $BF_3{\cdot}OEt_2$ was used as a capillary standard for ^{11}B NMR. Analytical thin-layer chromatography (TLC) was performed with silica gel 60 Merck F254 plates. Column chromatography was performed with Wakogel® C-300 silica gel. UV–vis–NIR absorption spectra were recorded on a SHIMADZU UV-3600i plus spectrophotometer. Photoluminescence (PL) spectra were measured on a HORIBA JOBIN YVON Fluorolog-3 spectrofluorometer. Absolute PL quantum efficiency was measured on a HAMAMATSU Quantaurus-QY Plus. The PL lifetime measurement was performed on a Horiba FluoreCube spectrofluorometer system; excitation was carried out using UV diode lasers (NanoLED 375 nm), and a Horiba DeltaFlex spectrofluorometer system; excitation was carried out using UV diode lasers (DeltaDiode 375 nm). Cyclic voltammetry (CV) was carried out on a BASALS-Electrochemical-Analyzer Model 600D with a grassy carbon working electrode, a Pt counter electrode, an Ag/AgCl reference electrode, and the ferrocene/ferrocenium (Fc/Fc^{+}) external reference at a scan rate of 0.1 V s^{-1}. High-resolution mass (HRMS) spectrometry was performed at the Technical Support Office (Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University), and the HRMS spectra were obtained on a JEOL JMS-MS700 spectrometer for electron ionization (EI), a Thermo Fisher Scientific EXACTIVE spectrometer for electrospray ionization (ESI), a Thermo Fisher Scientific EXACTIVE spectrometer for atmospheric pressure chemical ionization (APCI) and a Bruker Daltonics ultrafleXtreme for matrix assisted laser desorption ionization (MALDI). Gel permeation chromatography (GPC) was carried out on a TOSOH G3000HXI system equipped with three consecutive polystyrene gel columns (TOSOH gels: α-4000, α-3000, α-2500) using chloroform as an eluent after calibration with standard polystyrene samples. TGA was performed on an EXSTAR STA7200RV, a Hitachi High-Tech Science Corporation., with the heating rate of 10 °C/min up to 550 °C under nitrogen flowing (200 mL/min). Photostability test was carried out by UVP Benchtop UV Transilluminator, LMS-20(3UV), 254/302/365nm, 100V, 8W.

Materials

Commercially available compounds used without purification:

2,5-Dibromophenol (**1**) (BLD Pharmatech, Inc.)

$Ca(OH)_2$ (FUJIFILM Wako Pure Chemical Corporation)

Na_2CO_3 (FUJIFILM Wako Pure Chemical Corporation)

$MgSO_4$ (FUJIFILM Wako Pure Chemical Corporation)

1 M HCl for Volumetric Analysis (FUJIFILM Wako Pure Chemical Corporation)

2-Aminobenzyl alcohol (**3**) (Tokyo Chemical Industry Co, Ltd.)

Boron trifluoride diethyl etherate (≥46% BF_3 basis) ($BF_3 \cdot Et_2O$) (Sigma-Aldrich Co. LLC.)

$Pd_2(dba)_2$ (dba = dibenzylideneacetone) (Tokyo Chemical Industry Co, Ltd.)

2-Dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (XPhos) (Strem Chemicals, Inc.)

Dichlorophenylborane (FUJIFILM Wako Pure Chemical Corporation)

Salicylaldehyde (Tokyo Chemical Industry Co, Ltd.)

3-Amino-1-propanol (**5**) (Tokyo Chemical Industry Co, Ltd.)

Phenylboronic acid (FUJIFILM Wako Pure Chemical Corporation)

Commercially available solvents:

EtOH (FUJIFILM Wako Pure Chemical Corporation), $CHCl_3$ (FUJIFILM Wako Pure Chemical Corporation), hexane (FUJIFILM Wako Pure Chemical Corporation), EtOAc (FUJIFILM Wako Pure Chemical Corporation), $CHCl_3$ (deoxidized grade, FUJIFILM Wako Pure Chemical Corporation), toluene (deoxidized grade, FUJIFILM Wako Pure Chemical Corporation), MeCN (super dehydrated grade, FUJIFILM Wako Pure Chemical Corporation), Et_2O (super dehydrated grade, FUJIFILM Wako Pure Chemical Corporation) used without further purification. Et_3N (Kanto Chemical Co., Inc.) purified by passage through solvent purification columns under N_2 pressure.

Compounds prepared as described in the literatures

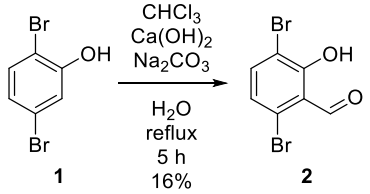
5,5′-Bis(trimethylstannyl)-3,3′-didodecyl-2,2′-bithiophene[1,2]

(9,9-Didodecyl-9*H*-fluorene-2,7-diyl)bis(trimethylstannane)[3]

BAmF[4]

Synthetic Procedures and Characterization

Synthesis of 2 (3,6-dibromo-2-hydroxybenzaldehyde)



To an aqueous mixture of $Ca(OH)_2$ (6.49 g, 87.6 mmol), Na_2CO_3 (22.8 g, 215 mmol) and 2,5-dibromophenol (**1**) (5.04 g, 20.0 mmol), $CHCl_3$ (25 mL, 63 mmol) was added dropwise under N_2 atmosphere. The mixture was refluxed for 5 h. After cooling to room temperature, the mixture was acidified with 1 M HCl aqueous solution. Then, the product was extracted with $CHCl_3$. Organic layer was washed with brine, dried over $MgSO_4$ and evaporated to afford a yellow solid. The solid was purified by chromatography on silica gel with hexane/$CHCl_3$ (v/v = 4/1). In recrystallization procedure (good solvent: $CHCl_3$, poor solvent: hexane), the target compound **2** was collected as a filtrate. After the filtrate was evaporated, further purification was carried out by recrystallization with hexane to afford **2** (0.89 g, 3.2 mmol, 16%) as a yellow solid.

R_f = 0.40 (hexane/$CHCl_3$ = 4/1 v/v). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 12.64 (s, 1H), 10.28 (s, 1H), 7.61 (d, J = 8.3 Hz, 1H), 7.10 (d, J = 8.6 Hz, 1H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz), δ 197.5, 160.4, 140.3, 126.5, 125.1, 118.2, 111.1 ppm. HRMS (APCI) calcd. for $C_7H_3Br_2O_2$ $[M-H]^-$, 276.8505; found: 276.8506.

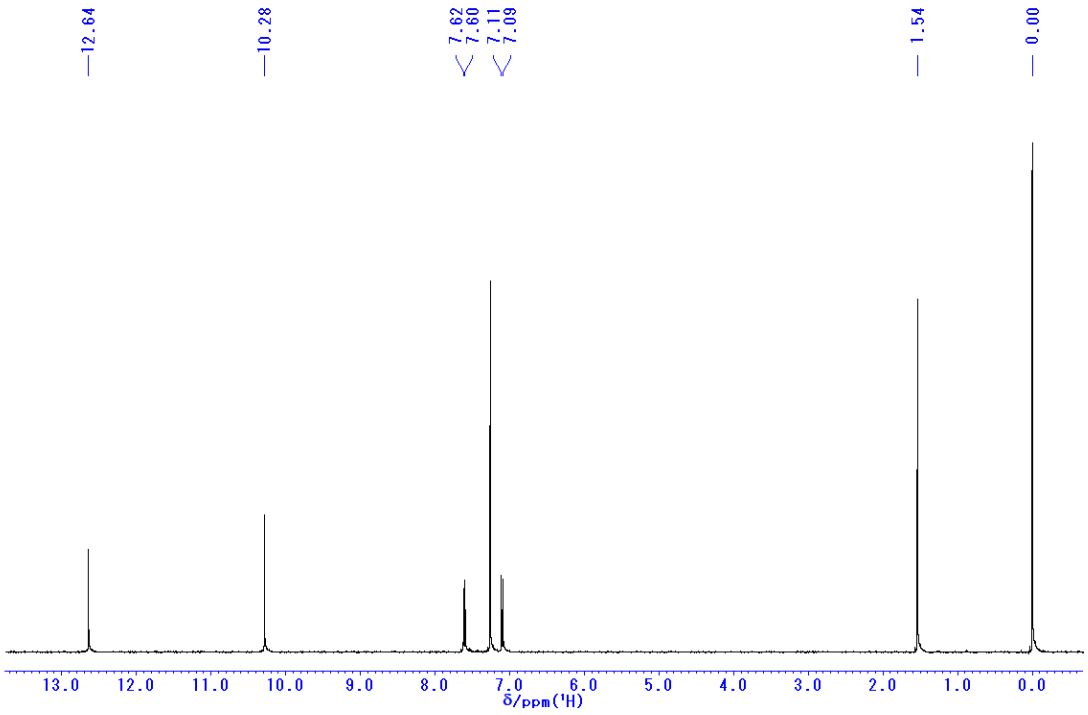


Chart S1. ^{1}H NMR spectrum of **2**, $CDCl_3$, 400 MHz.

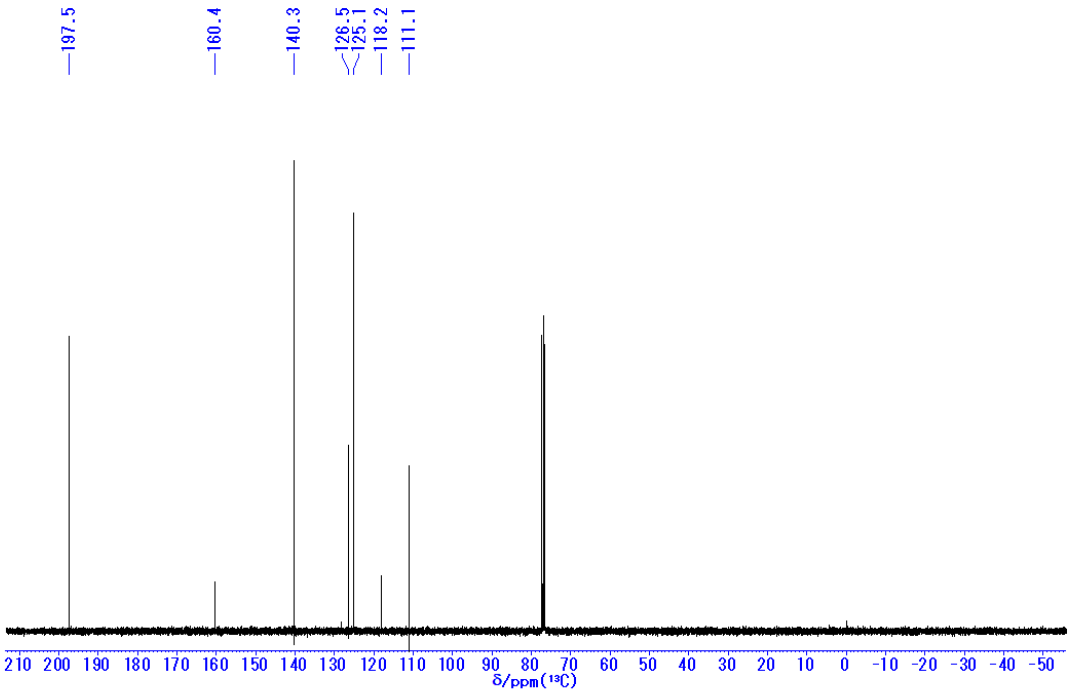
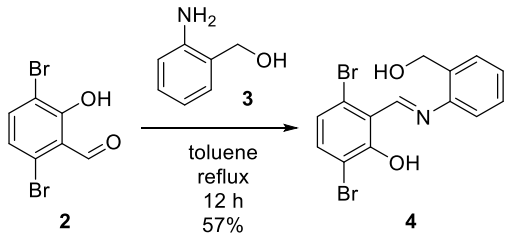


Chart S2. $^{13}C\{^{1}H\}$ NMR spectrum of **2**, $CDCl_3$, 100 MHz.

Synthesis of 4 ((*E*)-3,6-dibromo-2-(((2-(hydroxymethyl)phenyl)imino)methyl)phenol)



2 (0.14 g, 0.498 mmol) and 2-aminobenzyl alcohol (**3**) (0.06 g, 0.498 mmol) were dissolved in toluene (6 mL) under N_2 atmosphere and refluxed for 12 h. Then, the mixture was cooled to room temperature and the solvent was removed by a rotary evaporator. The residue was purified by chromatography on silica gel with hexane/EtOAc (v/v = 4/1) to afford **4** (0.11 g, 0.29 mmol, 57%) as an orange powder.

R_f = 0.30 (hexane/EtOAc = 4/1 v/v). ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 9.10 (s, 1H), 7.55–7.54 (m, 1H), 7.51 (d, J = 8.5 Hz, 1H), 7.44 (dt, J = 7.6, 1.7 Hz, 1H), 7.38 (dt, J = 7.5, 1.5 Hz, 1H), 7.30 (dd, J = 7.8, 1.4 Hz, 1H), 7.06 (d, J = 8.5 Hz, 1H), 4.87 (s, 2H) ppm. Two exchangeable proton peaks at hydroxyl groups were not detected. ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz) δ 162.6, 161.2, 145.0 137.4, 135.3, 129.4, 129.0, 128.4, 125.8, 124.0, 118.7, 118.1, 111.8, 62.2 ppm. HRMS (ESI) $C_{14}H_{12}Br_2NO_2$ calcd. for $[M+H]^+$: 383.9229; found: 383.9238.

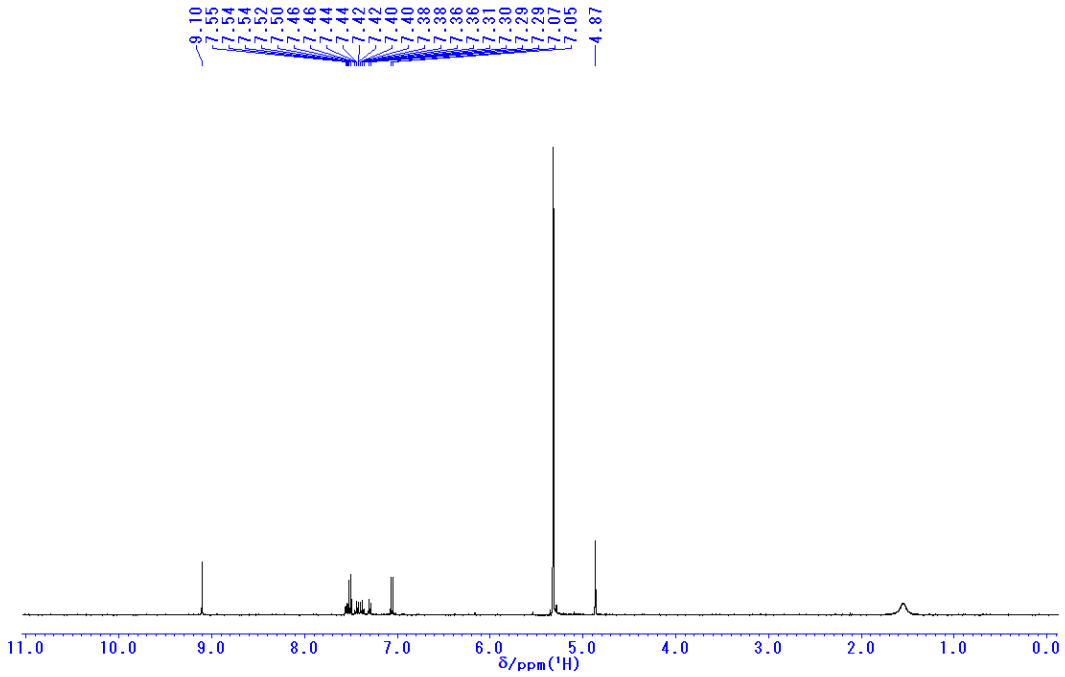


Chart S3. ^{1}H NMR spectrum of **4**, CD_2Cl_2, 400 MHz.

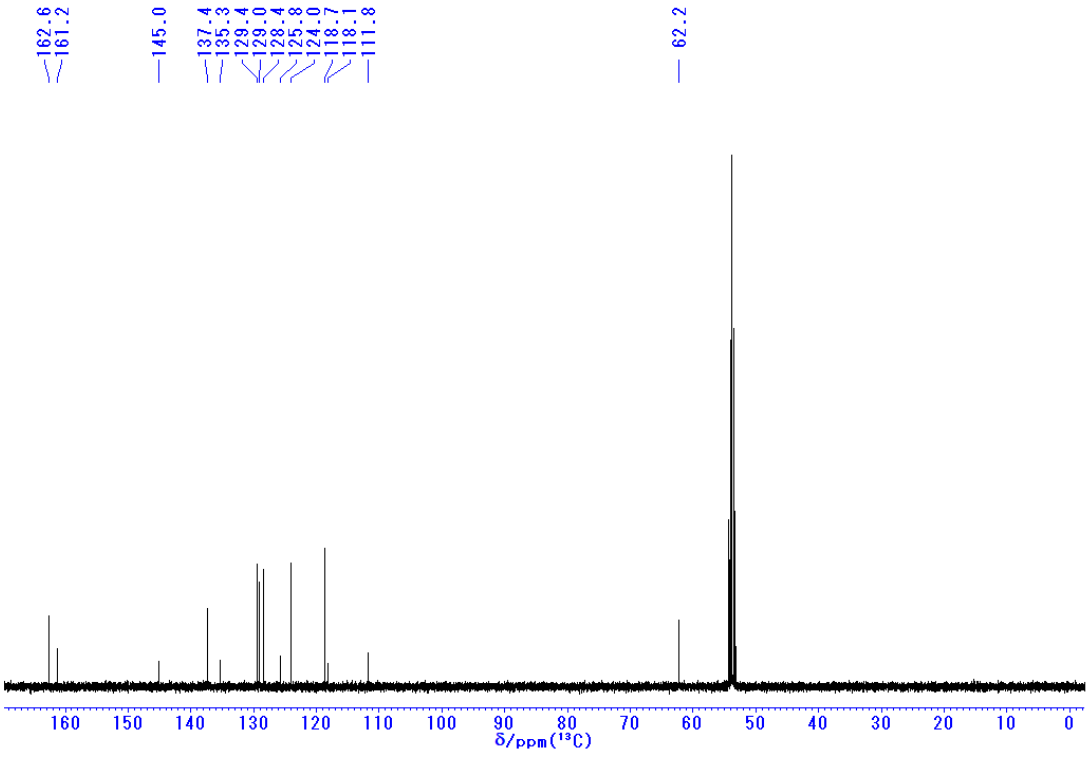
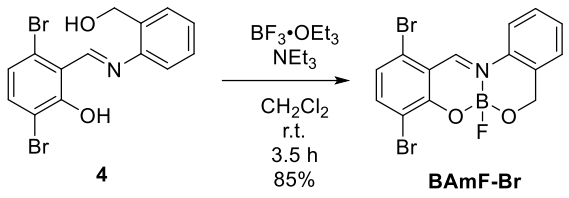


Chart S4. $^{13}C\{^{1}H\}$ NMR spectrum of **4**, CD_2Cl_2, 100 MHz.

Synthesis of BAmF-Br



4 (0.20 g, 0.51 mmol) was dissolved in dry CH_2Cl_2 (15 mL) under N_2 atmosphere and triethylamine (0.7 mL, 5 mmol) was then added to the reaction mixture at room temperature. $BF_3{\cdot}OEt_2$ (0.6 mL, 5. mmol) was added and stirred for 3.5 h at room temperature. The reaction mixture was quenched by H_2O. Then, the product was extracted with CH_2Cl_2. Organic layer was washed with brine, dried over $MgSO_4$ and evaporated to afford **BAmF-Br** (0.18 g, 0.44 mmol, 85%) as a yellow powder.

^{1}H NMR (CD_2Cl_2, 400 MHz) δ 9.14 (s, 1H), 7.75–7.71 (m, 2H), 7.49–7.45 (m, 2H), 7.28–7.26 (m, 1H), 7.17 (d, J = 8.3 Hz, 1H), 5.22 (d, J = 15.6 Hz, 1H), 5.02 (d, J = 15.9 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz) δ 158.0, 153.9, 141.1, 136.2, 135.2, 130.5, 128.6, 127.2, 125.5, 125.5, 117.8, 117.3, 113.4, 63.6 (d, J = 3.29 Hz) ppm. ^{11}B NMR (CD_2Cl_2, 128 MHz) δ 1.31 (d, J = 35.8 Hz) ppm. HRMS (ESI) calcd. for $C_{14}H_9BBr_2FNO_2Na$ $[M+Na]^+$, 433.8969; found: 433.8970.

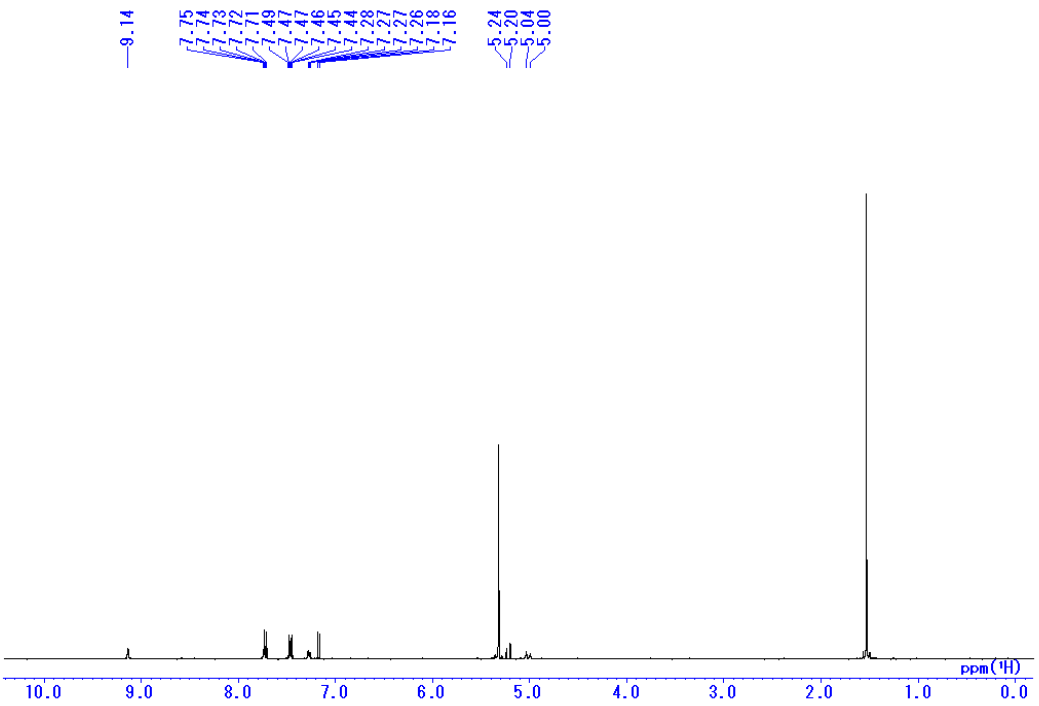


Chart S5. ^{1}H NMR spectrum of **BAmF-Br**, CD_2Cl_2, 400 MHz.

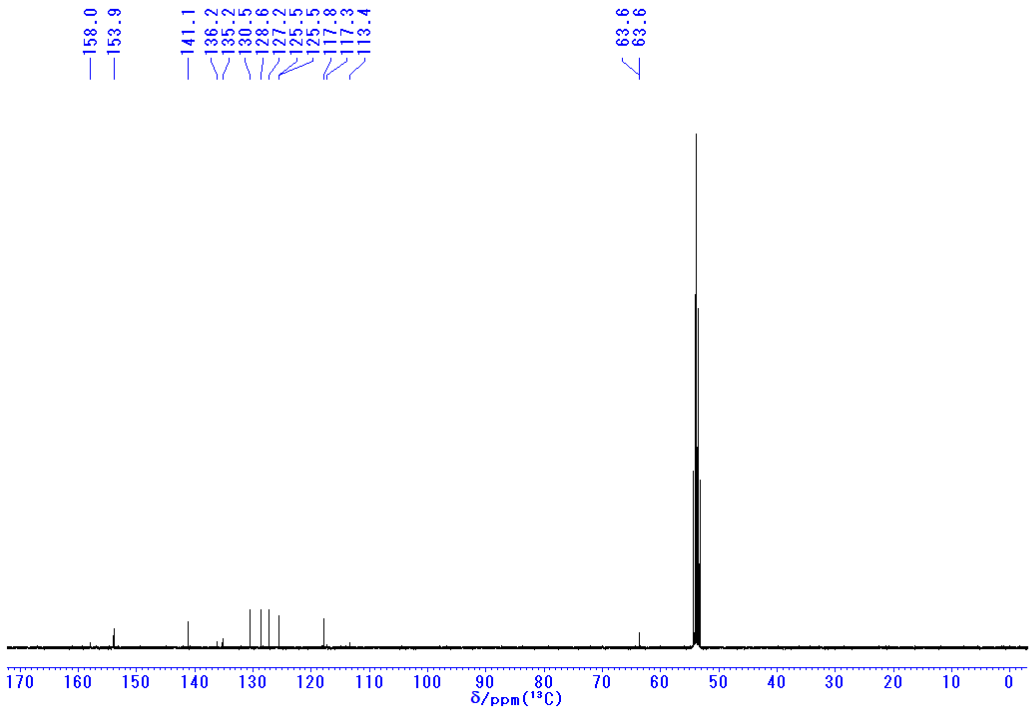


Chart S6. $^{13}C\{^{1}H\}$ NMR spectrum of **BAmF-Br**, CD_2Cl_2, 100 MHz.

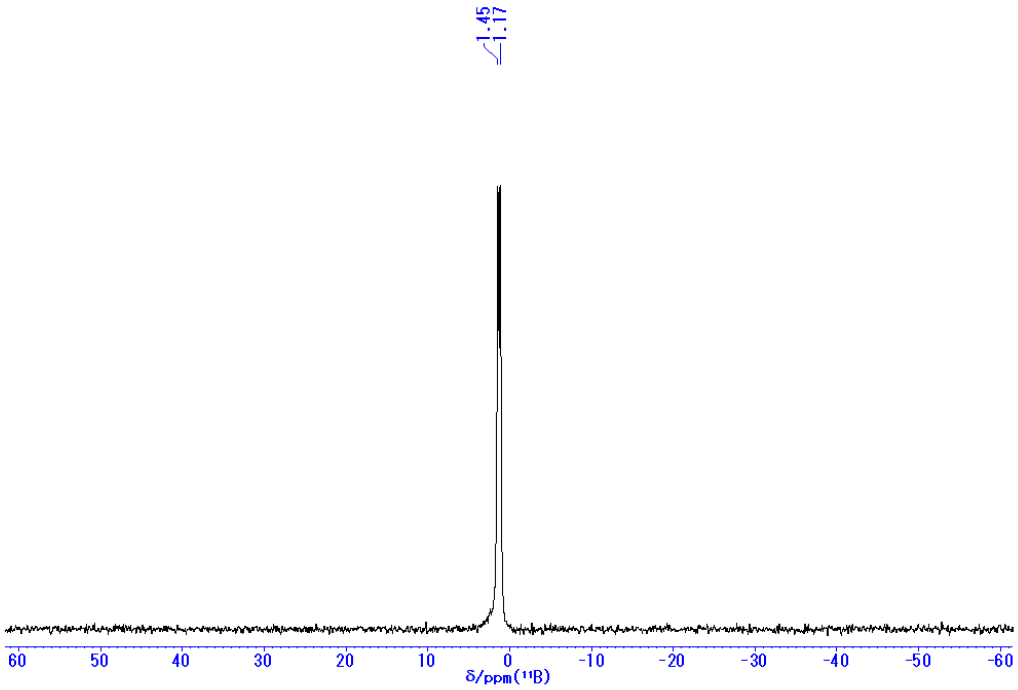
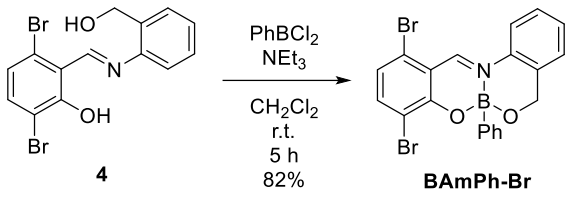


Chart S7. ^{11}B NMR spectrum of **BAmF-Br**, CD_2Cl_2, 128 MHz.

Synthesis of BAmPh-Br



4 (0.10 g, 0.26 mmol) was dissolved in dry toluene (8 mL) under N_2 atmosphere and triethylamine (0.05 mL, 0.4 mmol) was then added to the reaction mixture at room temperature. Dichloro(phenyl)borane (0.1 mL, 0.8 mmol) was added and stirred for 5 h at room temperature. The reaction mixture was quenched by EtOH and concentrated by rotary evaporator. Then, the product was extracted with CH_2Cl_2. Organic layer was washed with brine, dried over $MgSO_4$ and evaporated to afford **BAmPh-Br** (0.10 g, 0.21 mmol, 82%) as a yellow powder.

^{1}H NMR (CD_2Cl_2, 400 MHz) δ 8.95 (s, 1H), 7.73 (d J = 7.8 Hz, 1H), 7.64 (d, J = 7.6 Hz, 1H), 7.50–7.43 (m, 2H), 7.28 (d, J = 7.6 Hz, 1H), 7.19–7.17 (m, 2H), 7.12–7.11 (m, 3H), 7.03 (d, J = 8.6 Hz, 1H), 4.98 (d, J = 15.2 Hz, 1H), 4.85 (d, J = 15.1 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz) δ 159.1, 155.7, 141.0, 138.5, 136.5, 131.4, 130.0, 128.8, 127.7, 127.7, 127.0, 125.5, 124.6, 118.6, 118.5, 113.6, 63.4 ppm. One carbon peak directly connected at boron was not detected. ^{11}B NMR (CD_2Cl_2, 128 MHz) δ 5.20 ppm. HRMS (ESI) clad. for $C_{20}H_{14}BBr_2NO_2Na$ $[M+Na]^+$: 491.9377; found: 491.9379.

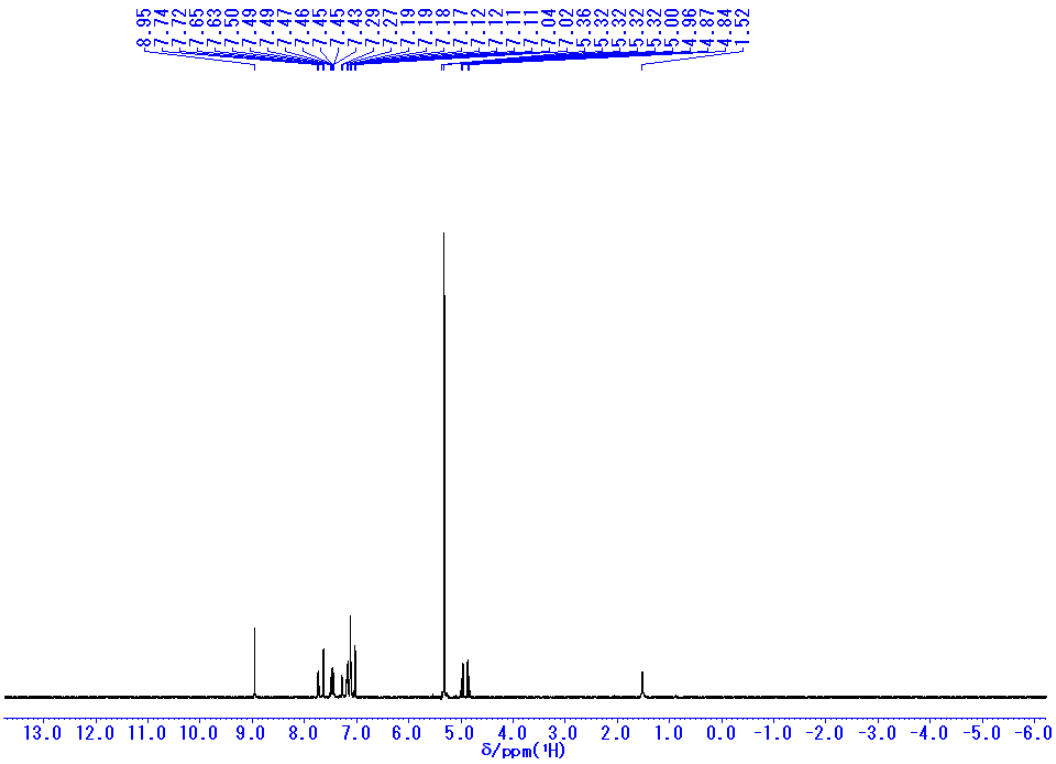


Chart S8. ^{1}H NMR spectrum of **BAmPh-Br**, CD_2Cl_2, 400 MHz.

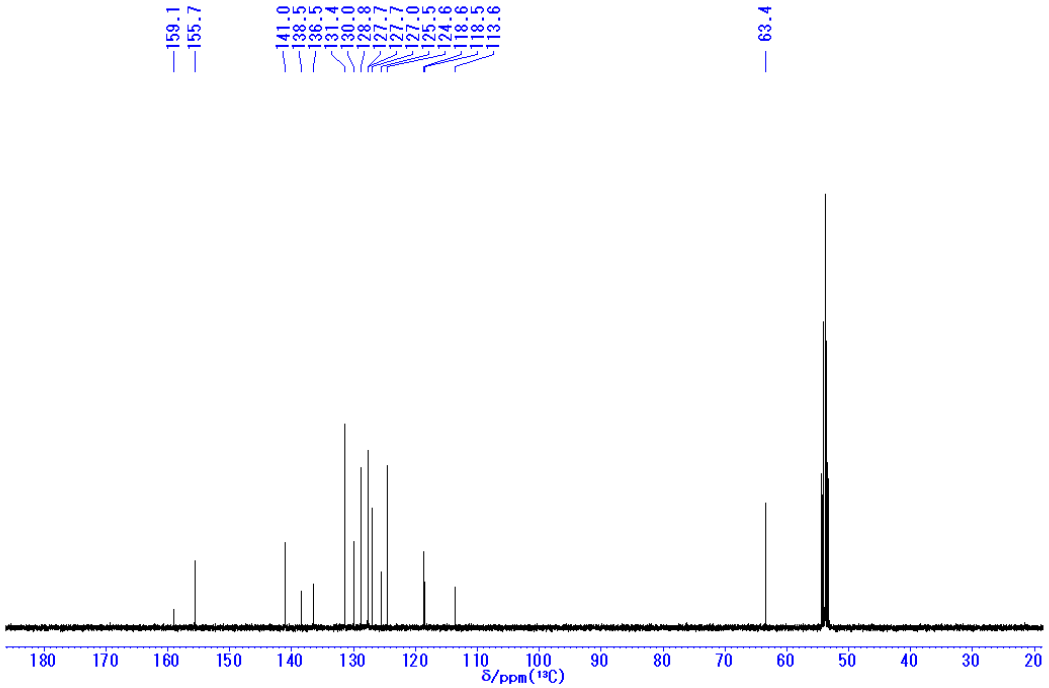


Chart S9. $^{13}C\{^{1}H\}$ NMR spectrum of **BAmPh-Br**, CD_2Cl_2, 100 MHz.

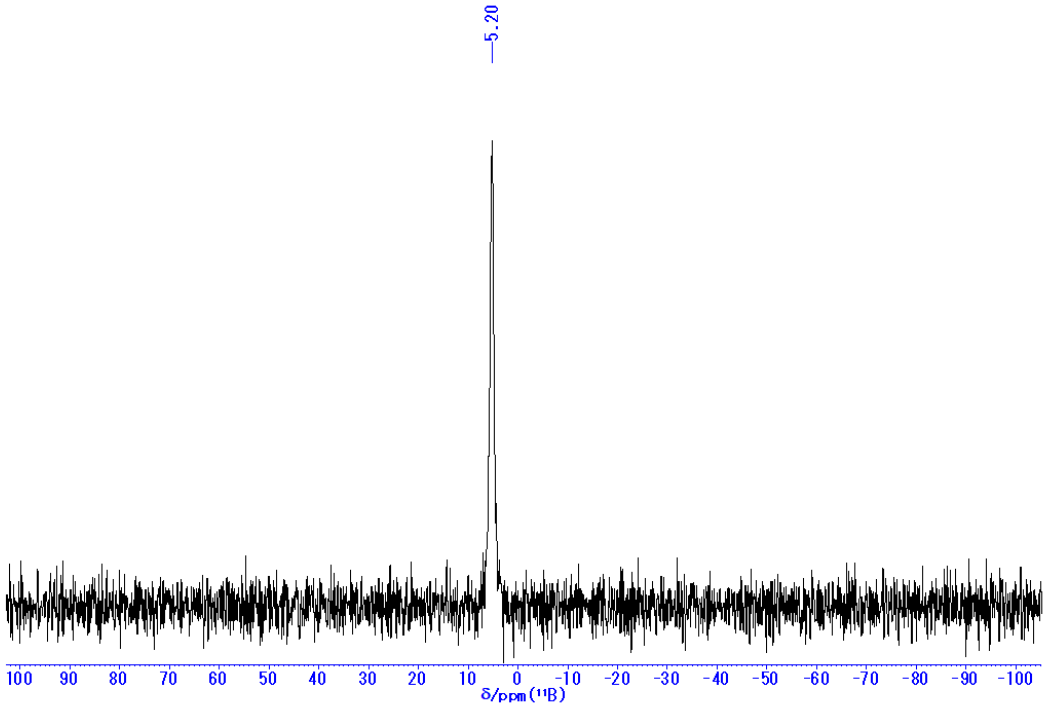
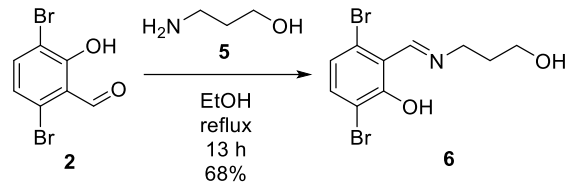


Chart S10. ^{11}B NMR spectrum of **BAmPh-Br**, CD_2Cl_2, 128 MHz.

Synthesis of 6 ((*E*)-3,6-dibromo-2-(((3-hydroxypropyl)imino)methyl)phenol)



2 (0.59 g, 2.13 mmol) and 3-amino-1-propanol (**5**) (0.16 g, 2.13 mmol) were dissolved in EtOH (10 mL) under N_2 atmosphere and refluxed for 13 h. Then, the mixture was cooled to room temperature and the solvent was removed by a rotary evaporator. The residue was purified by reprecipitation (good solvent: $CHCl_3$, poor solvent: hexane) to afford **6** (0.49 g, 1.45 mmol, 68%) as an orange powder.

^{1}H NMR ($CDCl_3$, 400 MHz), δ 15.77 (br, 1H), 8.69 (s, 1H), 7.44 (d, J = 8.3 Hz, 1H), 6.79 (d, J = 8.3 Hz, 1H) 3.85–4.79 (m, 4H), 2.04–1.97 (m, 2H) 1.56 (s, 1H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz), δ 166.8, 165.2, 137.2, 124.6, 120.4, 115.0, 114.8, 59.4, 51.7, 32.4 ppm. HRMS (ESI) calcd. for $C_{10}H_{12}Br_2NO_2$ $[M+H]^+$: 335.9229; found: 335.9233.

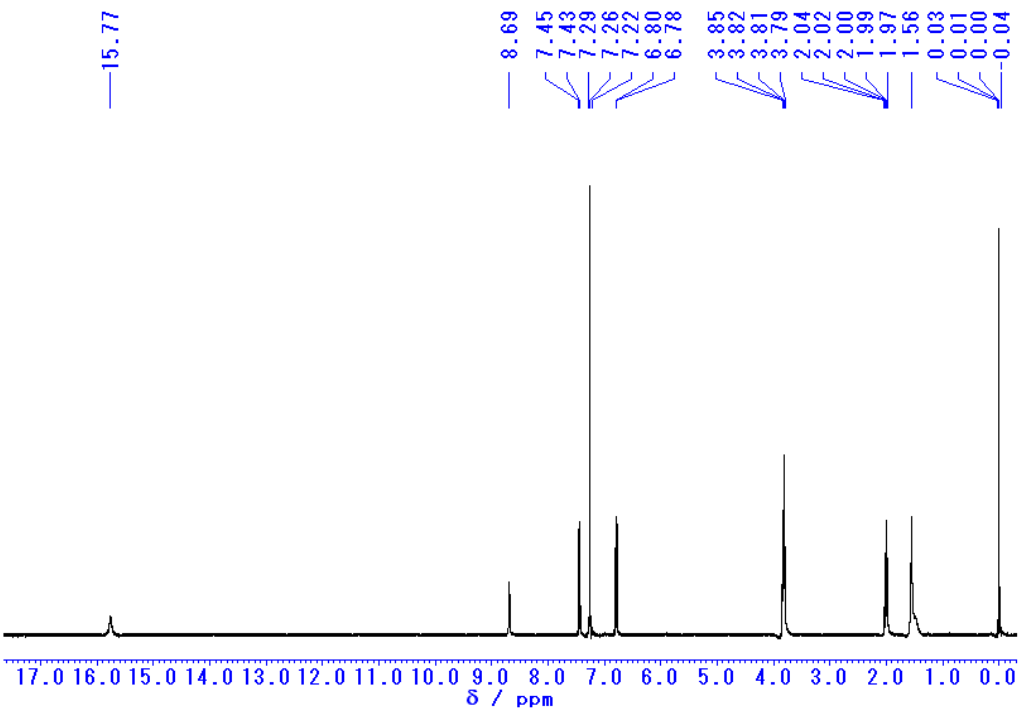


Chart S11. ^{1}H NMR spectrum of **6**, $CDCl_3$, 400 MHz.

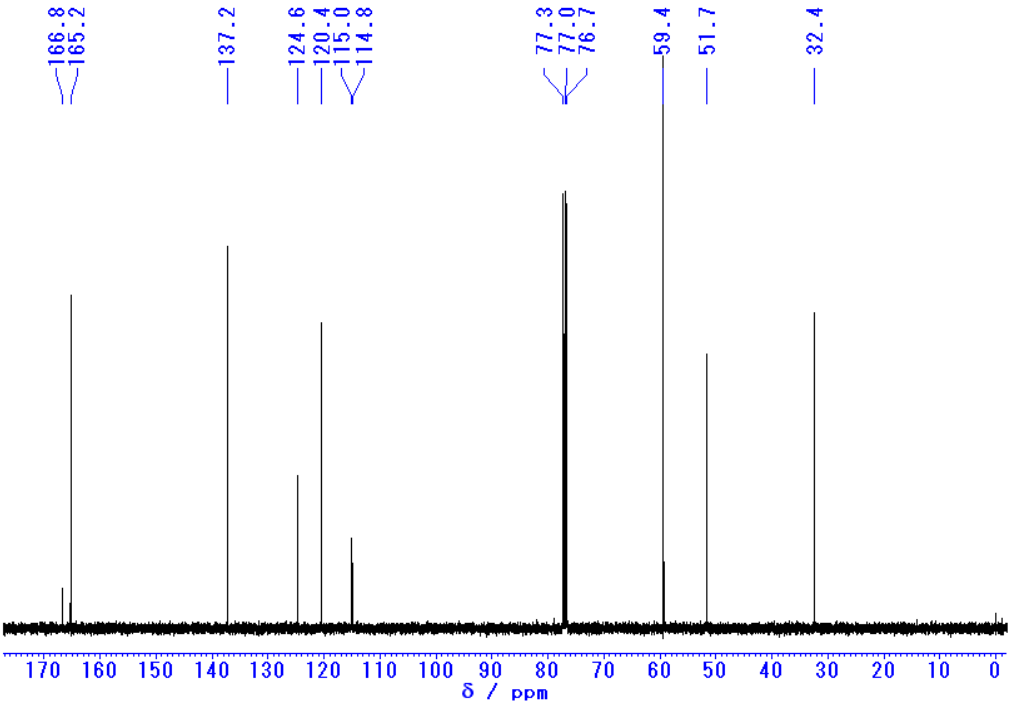
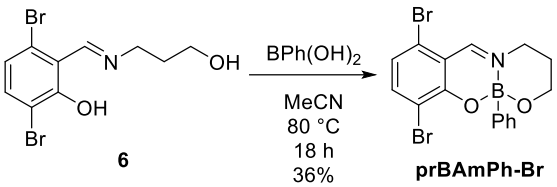


Chart S12. $^{13}C\{^{1}H\}$ NMR spectrum of **6**, $CDCl_3$, 100 MHz.

Synthesis of prBAmPh-Br



6 (0.15 g, 0.44 mmol) and phenylboronic acid (0.21 g, 1.75 mmol) was dissolved in dry MeCN (9 mL) under N_2 atmosphere. The solution was stirred for 18 h at 80 °C. Then, the mixture was cooled to room temperature and the solvent was removed by a rotary evaporator. The residue was washed with Et_2O and purified by recrystallization (good solvent: $CHCl_3$, poor solvent: hexane) to afford **prBAmPh-Br** (0.068 g, 0.16 mmol, 36%) as a pale yellow powder.

^{1}H NMR (CD_2Cl_2, 400 MHz) δ 8.61 (d, J = 1.68 Hz 1H), 7.53 (d J = 8.3 Hz, 1H), 7.37–7.35 (m, 2H), 7.30–7.21 (m, 3H), 6.95 (d, J = 8.3 Hz,1H), 4.07–4.00 (m, 2H), 3.93 (td, J = 11.3, 2.76 Hz, 1H), 3.87–3.83 (m, 1H), 2.20–2.09 (m, 1H), 1.88–1.83 (m, 1H) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz) δ 160.0, 158.3, 140.5, 131.5, 128.1, 127.8, 124.7, 123.7, 116.2, 113.4, 61.5, 56.4, 31.0 ppm. One carbon peak directly connected at boron was not detected. ^{11}B NMR (CD_2Cl_2, 128 MHz) δ 4.91 ppm. HRMS (ESI) calcd. for $C_{16}H_{14}BBr_2NO_2Na$ $[M+Na]^+$: 443.9377; found: 443.9369.

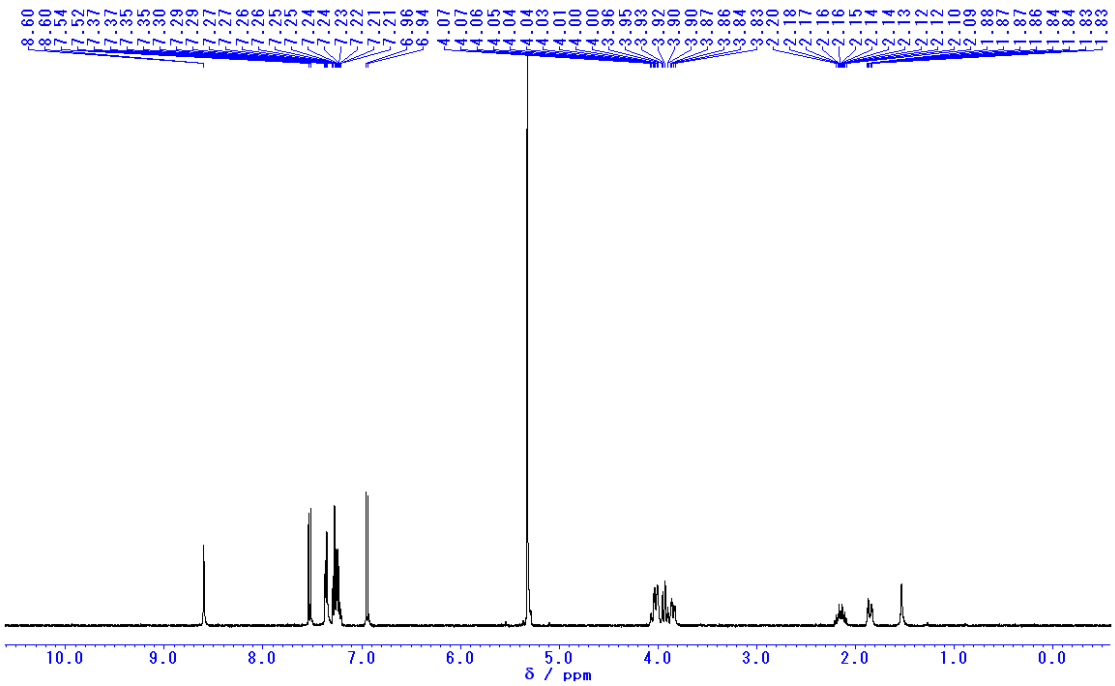


Chart S13. ^{1}H NMR spectrum of **prBAmPh-Br**, CD_2Cl_2, 400 MHz.

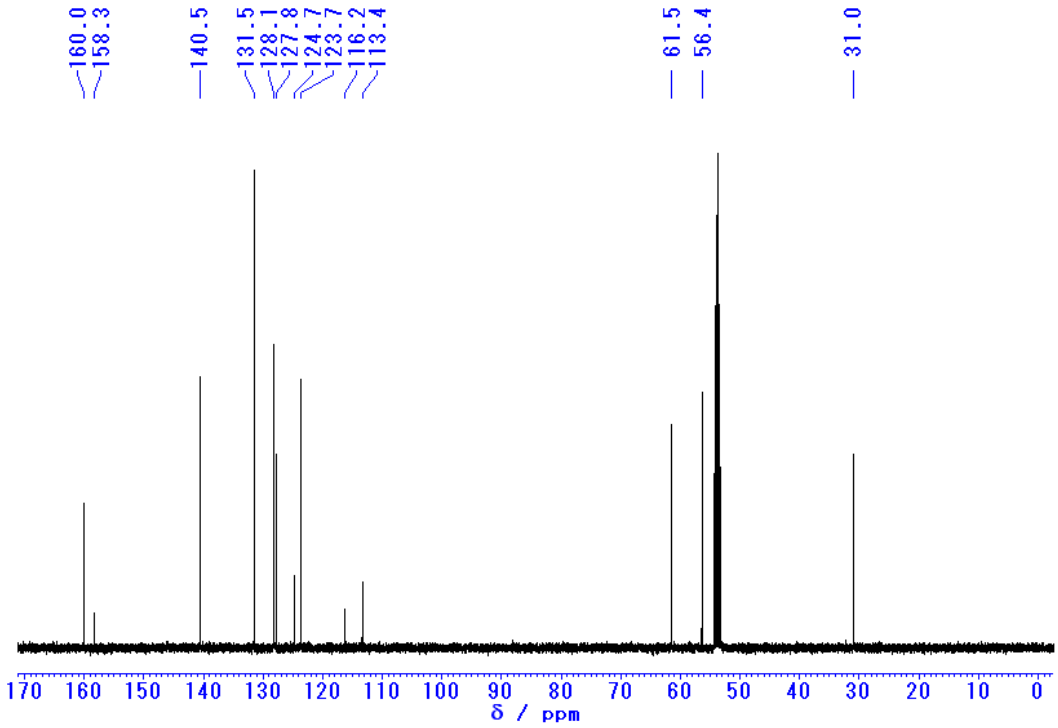


Chart S14. $^{13}C\{^{1}H\}$ NMR spectrum of **prBAmPh-Br**, CD_2Cl_2, 128 MHz.

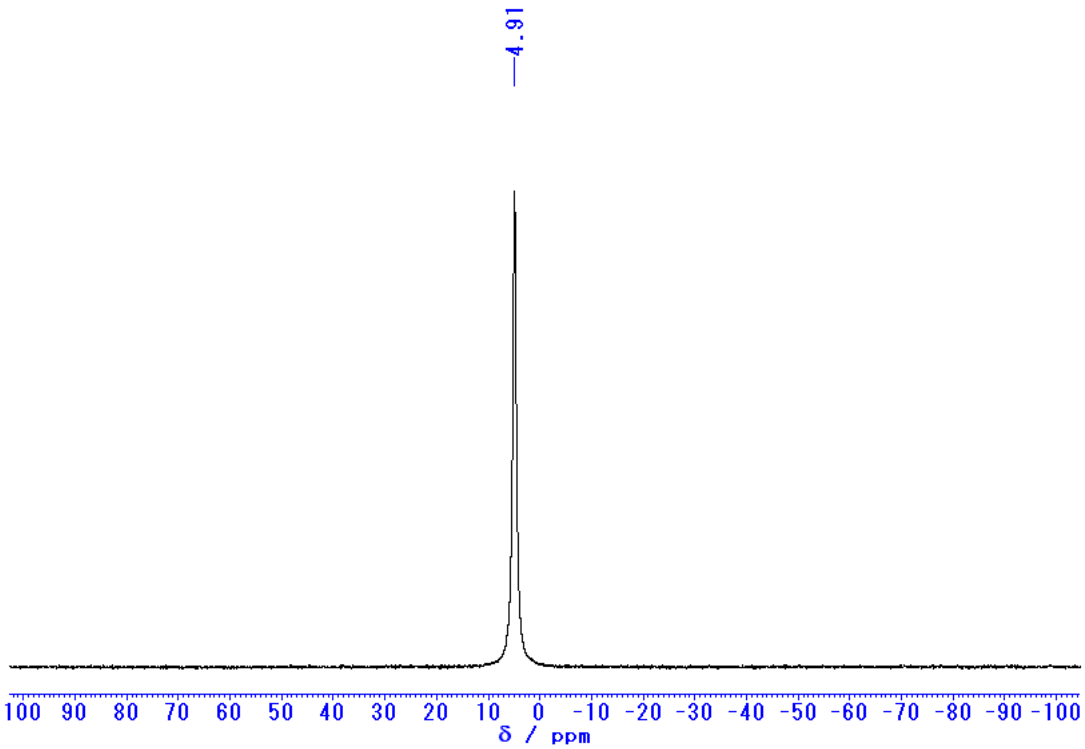
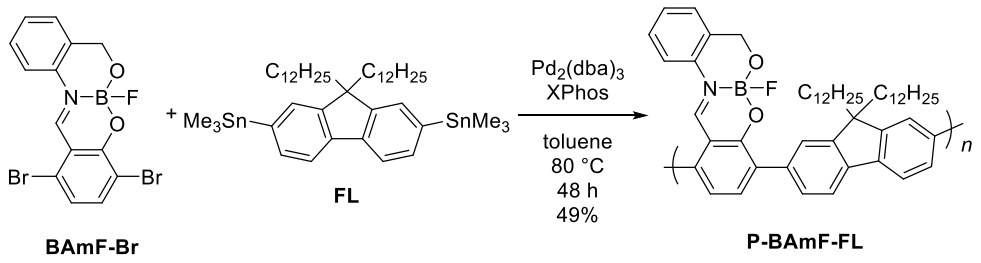


Chart S15. ^{11}B NMR spectrum of **prBAmPh-Br**, CD_2Cl_2, 128 MHz.

Synthesis of P-BAmF-FL



The mixture of **BAmF-Br** (29.9 mg, 0.073 mmol), (9,9-didodecyl-9*H*-fluorene-2,7-diyl)bis(trimethylstannane) (60.1 mg, 0.073 mmol), $Pd_2(dba)_3$ (2.0 mg, 0.0022 mmol), XPhos (2.1 mg, 0.0044 mmol) in toluene (1.5 mL) was stirred at 80 °C for 48 h under N_2 atmosphere. After cooling to room temperature, the solution was purified by alumina column chromatography and poured into a large amount of methanol to collect the polymer by filtration. The polymer collected by filtration was dried *in vacuo* to afford **P-BAmF-BT** (27 mg, 49%) as an orange solid.

M_n = 10,300, M_w = 15,700, M_w/M_n = 1.5. ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 8.90 (s, 1H), 8.07–7.83 (m, 3H), 7.78–7.74 (d, 2H), 7.70–7.55 (m, 2H), 7.45–7.25 (m, 6H), 2.13 (br, 4H), 1.39–0.84 (m, 46H) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100 MHz) 158.2, 151.9, 151.7, 138.3, 136.9, 135.0, 129.3, 129.3, 128.4, 127.2, 127.1, 124.7, 122.2, 120.2, 117.0, 116.4, 63.4, 40.7, 32.3, 32.3, 30.7, 30.5, 30.1, 30.0, 29.9, 29.9, 29.7, 29.7, 24.6, 23.1, 14.3ppm. ^{11}B NMR (CD_2Cl_2, 128 MHz) δ 0.98 ppm.

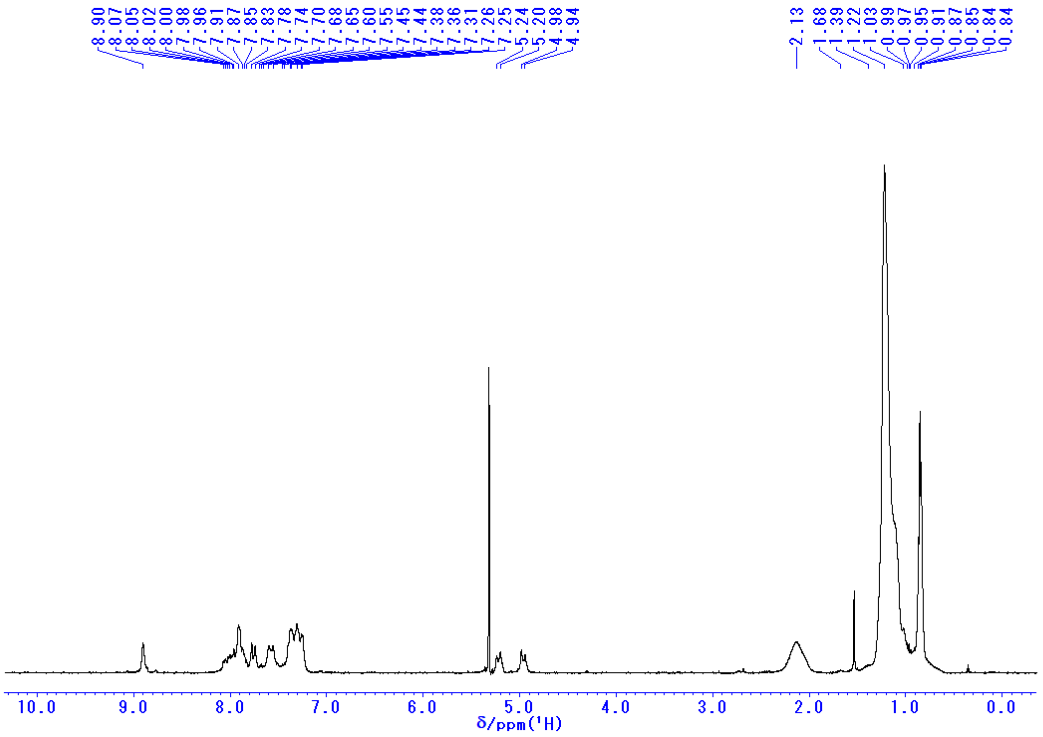


Chart S16. ^{1}H NMR spectrum of **P-BAmF-FL**, CD_2Cl_2, 400 MHz.

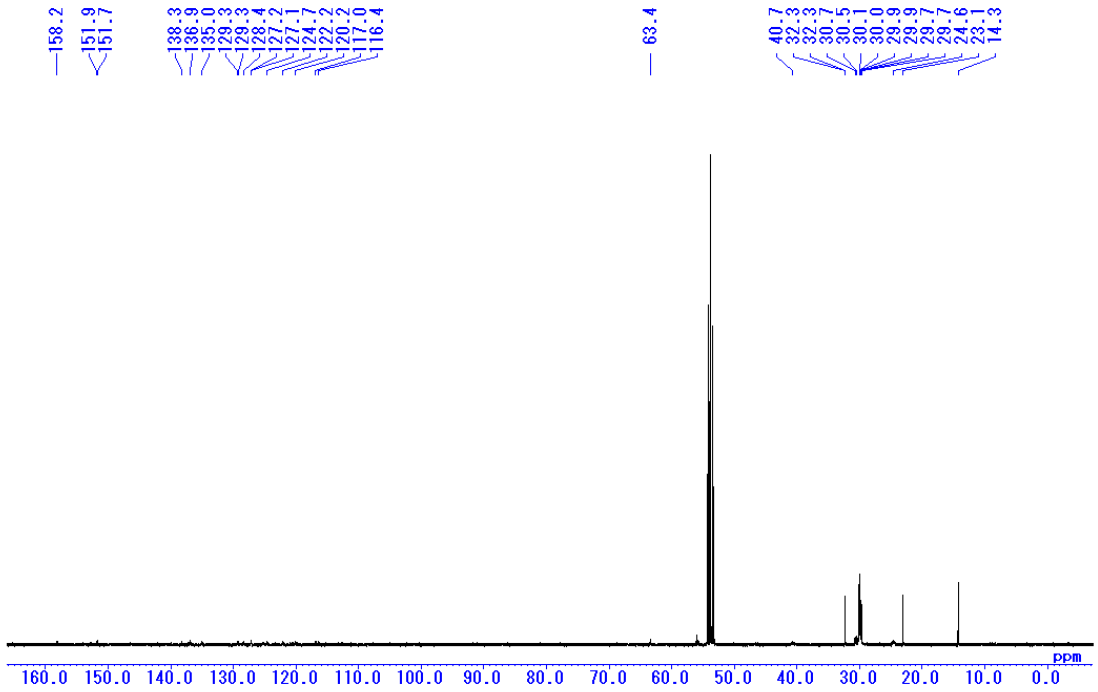


Chart S17. ^{13}C NMR spectrum of **P-BAmF-FL**, CD_2Cl_2, 100 MHz.

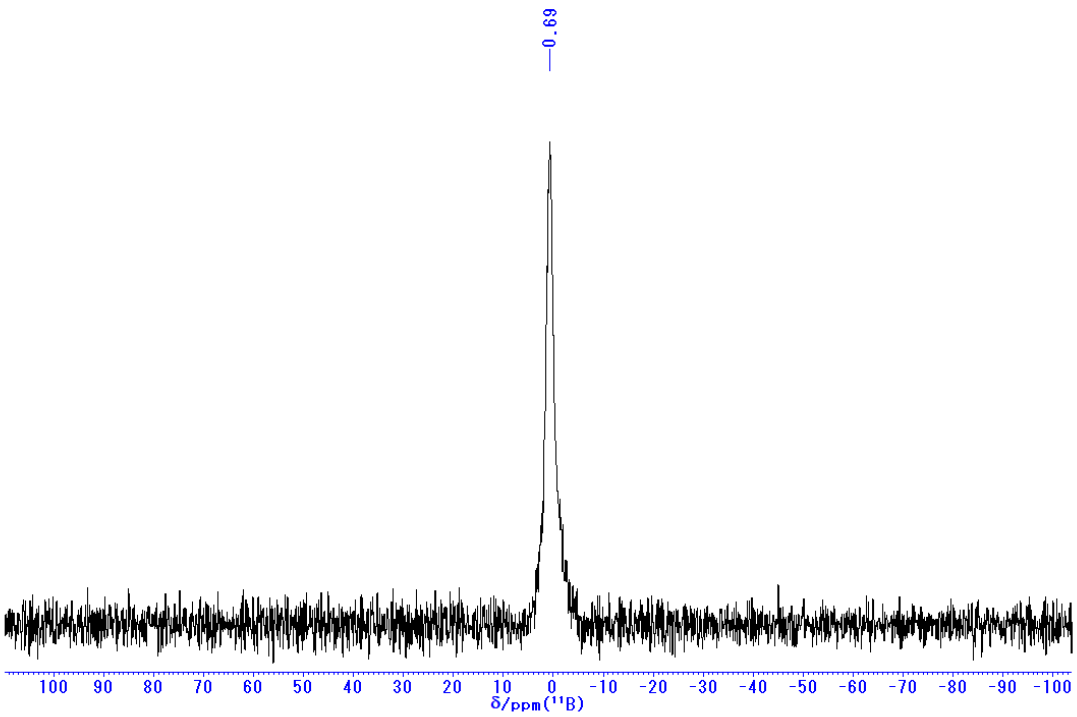


Chart S18. ^{11}B NMR spectrum of **P-BAmF-FL**, CD_2Cl_2, 128 MHz.

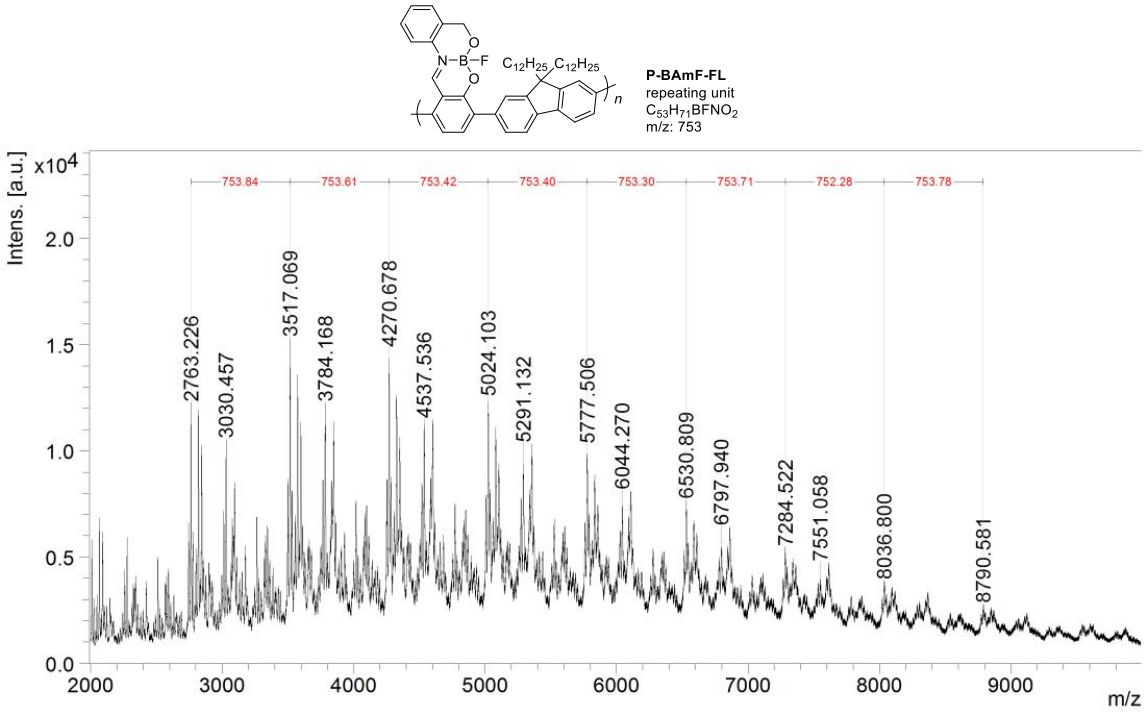
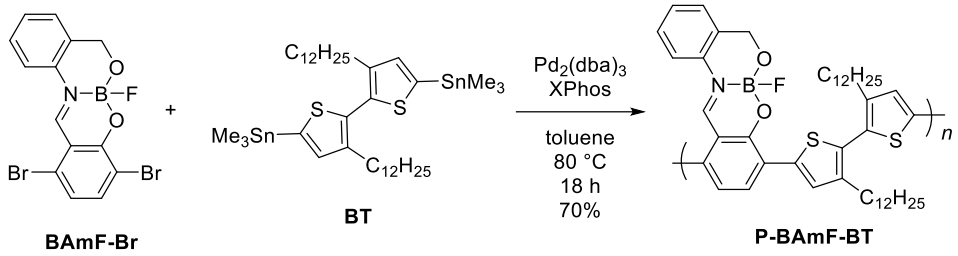


Chart S19. MALDI-TOF mass spectrum of **P-BAmF-FL**. Matrix: DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile), Liner mode.

Synthesis of P-BAmF-BT



The mixture of **BAmF-Br** (19.4 mg, 0.047 mmol), 5,5′-bis(trimethylstannyl)-3,3′-didodecyl-2,2′-bithiophene (38.9 mg, 0.047 mmol), $Pd_2(dba)_3$ (1.3 mg, 0.0014 mmol) and XPhos (1.3 mg, 0.0028 mmol) in toluene (1.0 mL) was stirred at 80 °C for 18 h under N_2 atmosphere. After cooling to room temperature, the solution was purified by alumina column chromatography and poured into a large amount of methanol to collect the polymer by filtration. The polymer collected by filtration was dried *in vacuo* to afford **P-BAmF-BT** (24.7 mg, 70%) as a red solid.

M_n = 20,800, M_w = 39,100, M_w/M_n = 1.9. ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 9.12 (s, 1H), 8.02 (br, 1H), 7.70–7.50 (m, 2H), 7.34 (br, 2H), 7.22 (br, 2H), 7.10–7.06 (m, 1H), 5.21–5.16 (m, 1H), 4.97–4.93 (m, 1H), 2.64 (br, 4H), 1.64 (br, 4H), 1.17 (br, 36H), 0.79–0.76 (br, 6H) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100 MHz) 32.3, 32.3, 30.1, 30.1, 30.1, 30.0, 30.0, 29.9, 29.8, 23.1, 14.3 ppm. The other $^{13}C\{^1H\}$ signals especially in aromatic area were not detected probably because of broadening peaks in a polymer. ^{11}B NMR (CD_2Cl_2, 128 MHz), δ 0.87 (d, J = 28.2 Hz) ppm.

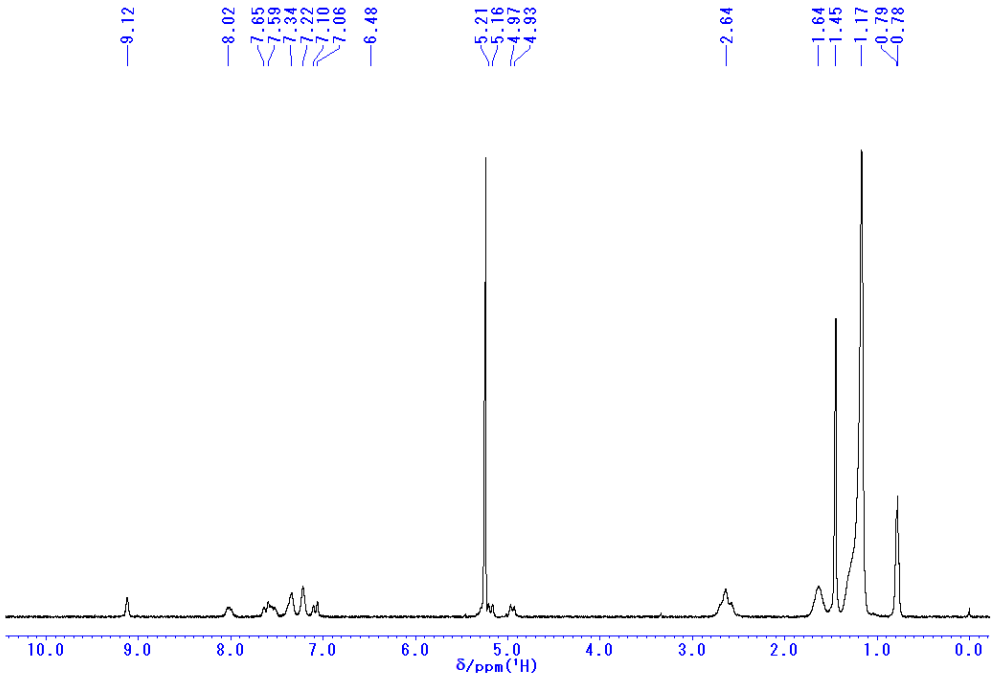


Chart S20. ^{1}H NMR spectrum of **P-BAmF-BT**, CD_2Cl_2, 400 MHz.

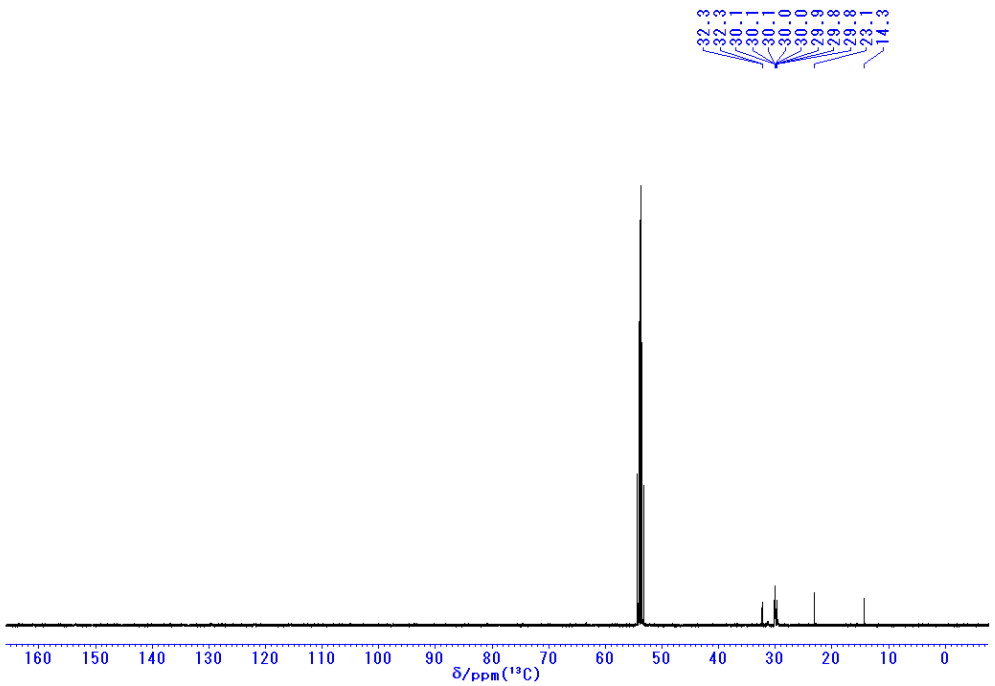


Chart S21. $^{13}C\{^{1}H\}$ NMR spectrum of **P-BAmF-BT**, CD_2Cl_2, 100 MHz.

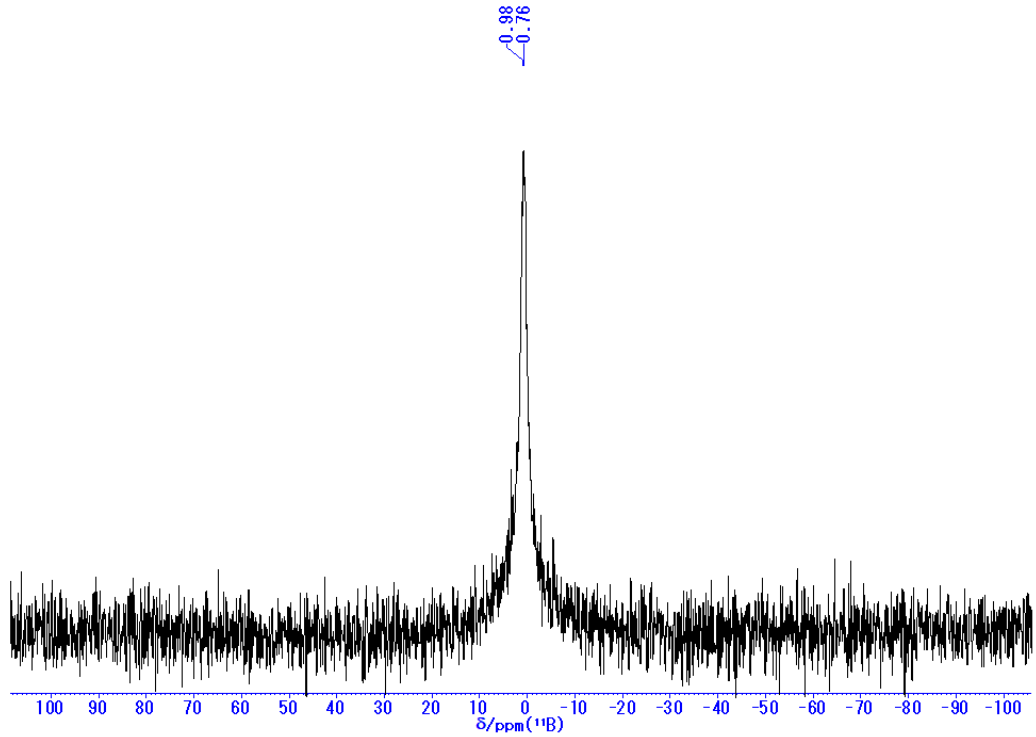


Chart S22. ^{11}B NMR spectrum of **P-BAmF-BT**, CD_2Cl_2, 128 MHz.

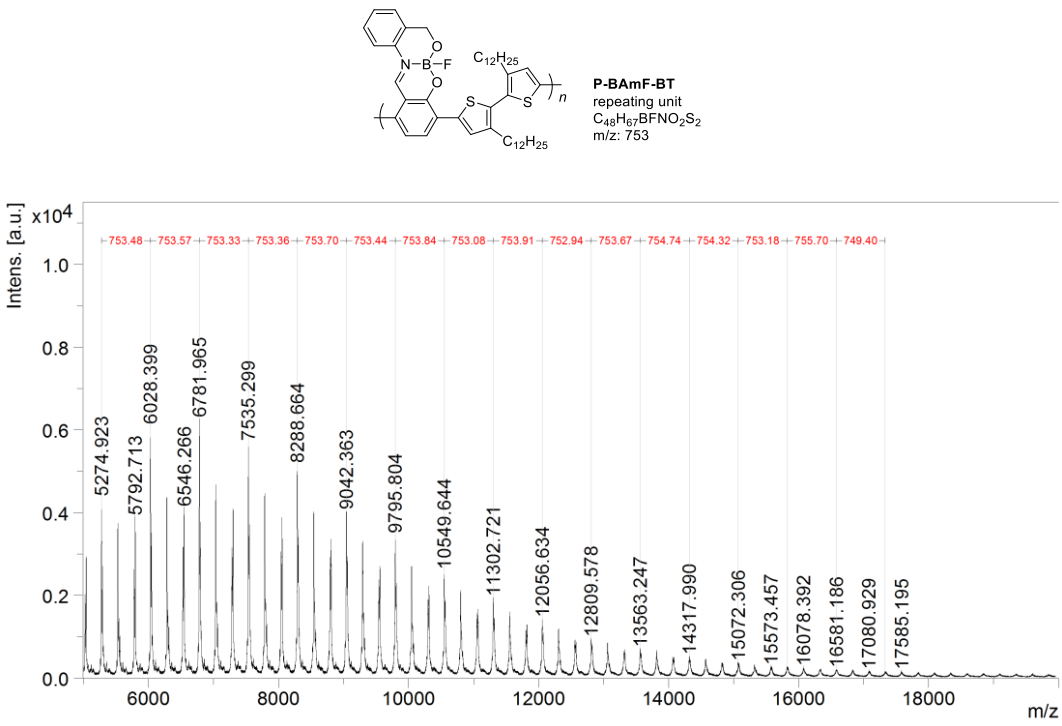
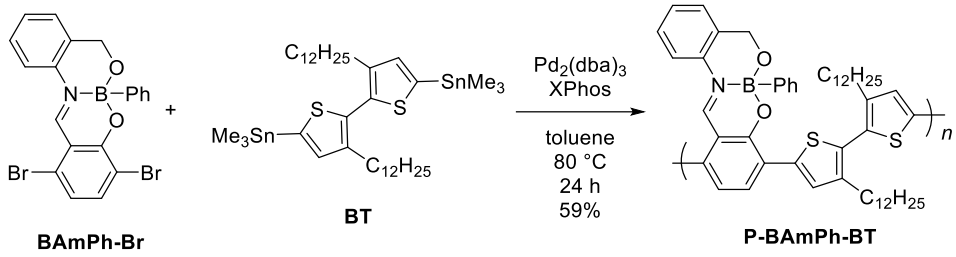


Chart S23. MALDI-TOF mass spectrum of **P-BAmF-BT**. Matrix: DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile), Liner mode.

Synthesis of P-BAmPh-BT



The mixture of **BAmPhBr** (34.1 mg, 0.072 mmol), 5,5′-Bis(trimethylstannyl)-3,3′-didodecyl-2,2′-bithiophene (60.0 mg, 0.072 mmol), $Pd_2(dba)_3$ (2.0 mg, 0.0022 mmol), XPhos (2.1 mg, 0.0044 mmol) in toluene (1.5 mL) was stirred at 80 °C for 24 h under N_2 atmosphere. After cooling to room temperature, the solution was purified by alumina column chromatography and poured into a large amount of methanol to collect the polymer by filtration. The polymer collected by filtration was dried *in vacuo* to afford **p-BAmPh-BT** (34.6 mg, 59%) as a red solid.

M_n = 16,900, M_w = 29,800, M_w/M_n = 1.8. ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 9.05 (s, 1H), 8.04–8.02 (m, 1H), 7.76–7.69 (m, 2H), 7.41–7.39 (m, 4H), 7.27 (d, J = 5.56 Hz, 1H), 7.20–7.15 (m, 4H), 7.08–7.02 (m, 1H), 5.03–5.00 (m, 1H), 4.85 (d, J = 14.4 Hz, 1H), 2.79–7.64 (m, 4H), 1.73 (s, 4H), 1.34–1.24 (m, 36H), 0.90–0.85 (m, 6H) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz) 157.3, 138.8, 136.4, 131.8, 127.7, 126.9, 125.3, 120.5, 63.3, 32.3, 30.2, 30.1, 30.1, 30.1, 30.0, 30.0, 29.9, 29.8, 23.1, 14.3 ppm. The other ^{13}C{^{1}H} signals especially in aromatic area were not detected probably because of broadening peaks in a polymer. ^{11}B NMR (CD_2Cl_2, 128 MHz) δ 2.74 ppm.

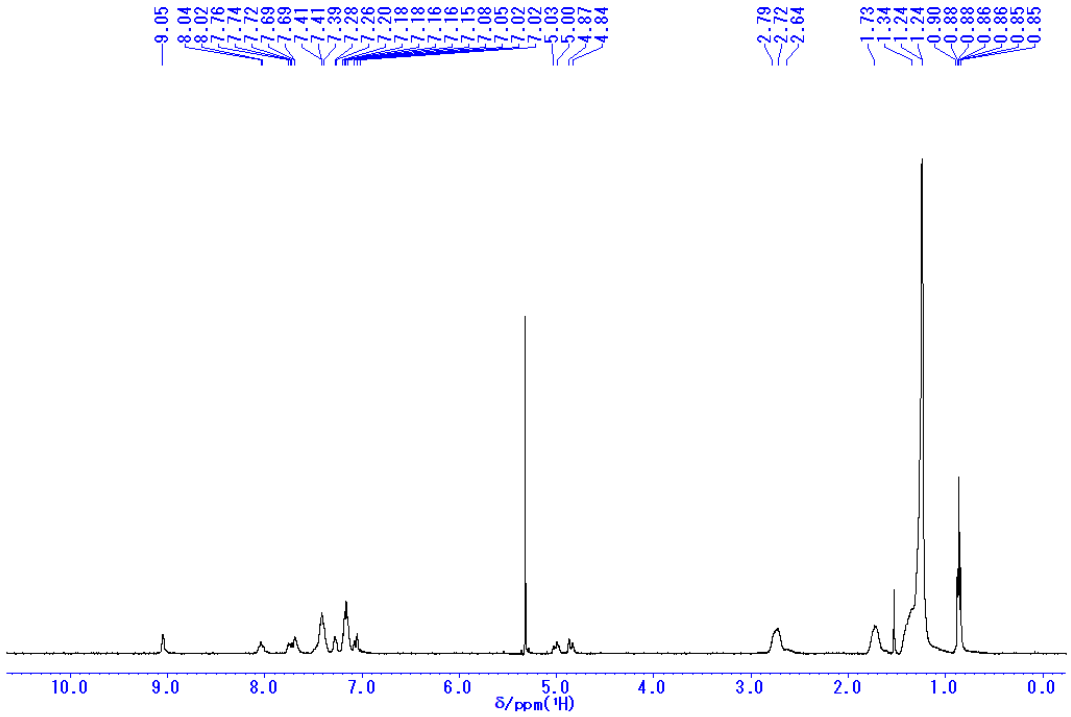


Chart S24. ^{1}H NMR spectrum of **P-BAmPh-BT**, CD_2Cl_2, 400 MHz.

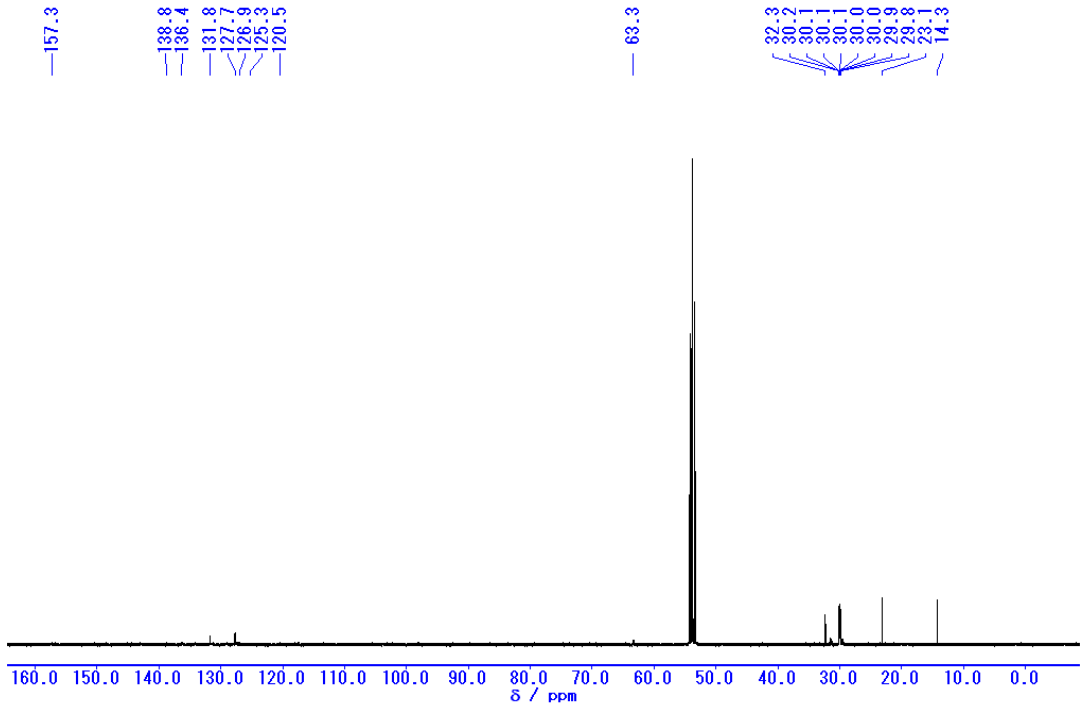


Chart S25. ^{13}C{^{1}H} NMR spectrum of **P-BAmPh-BT**, CD_2Cl_2, 100 MHz.

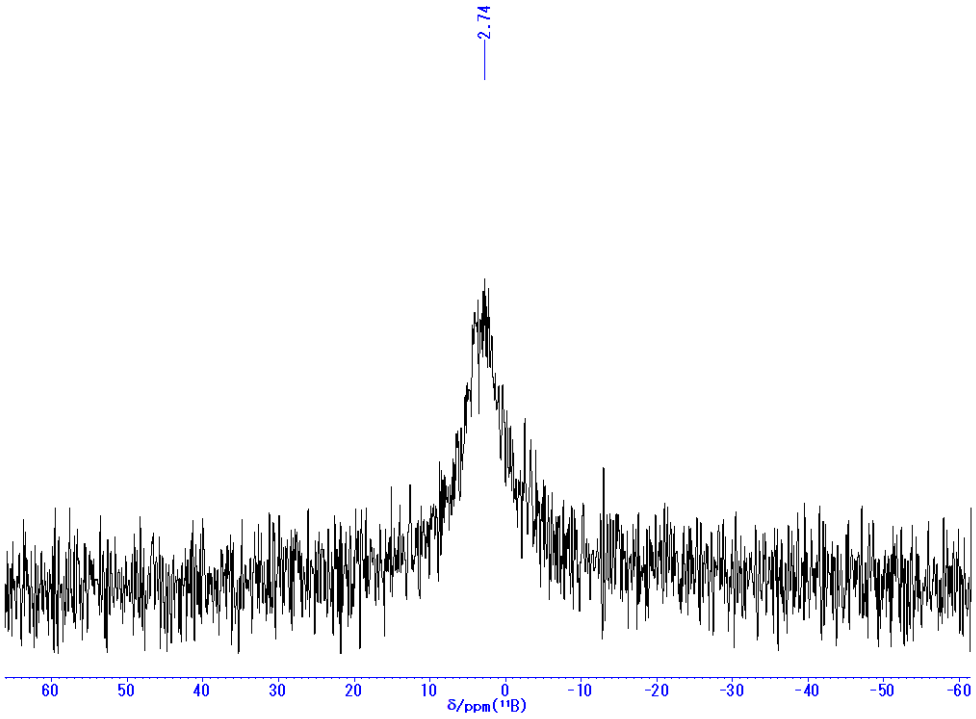


Chart S26. ^{11}B NMR spectrum of **P-BAmPh-BT**, CD_2Cl_2, 128 MHz.

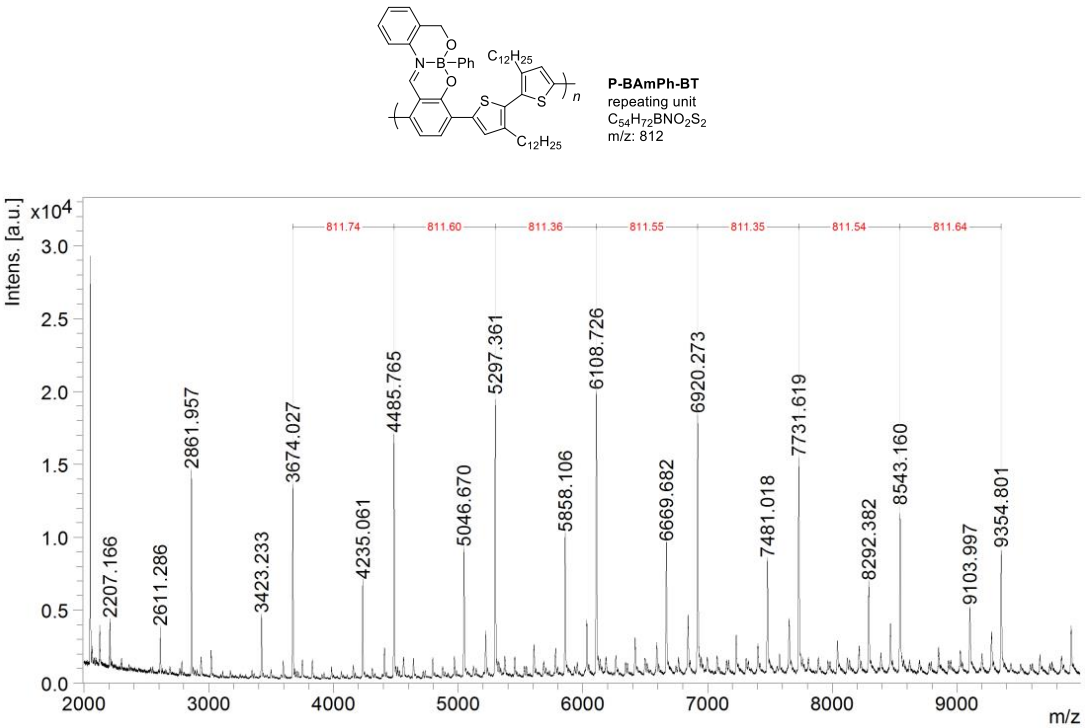
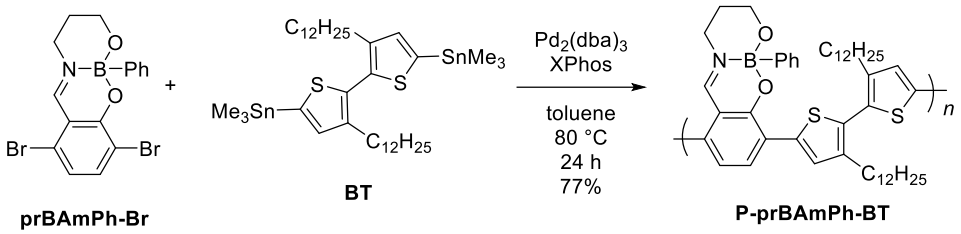


Chart S27. MALDI-TOF mass spectrum of **P-BAmPh-BT**. Matrix: DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile), Liner mode.

Synthesis of P-prBAmPh-BT



The mixture of **prBAmPhBr** (41.2 mg, 0.097 mmol), 5,5′-Bis(trimethylstannyl)-3,3′-didodecyl-2,2′-bithiophene (80.7 mg, 0.097 mmol), $Pd_2(dba)_3$ (2.9 mg, 0.0029 mmol), XPhos (2.8 mg, 0.0058 mmol) in toluene (2 mL) was stirred at 80 °C for 24 h under N_2 atmosphere. After cooling to room temperature, the solution was purified by alumina column chromatography and poured into a large amount of methanol to collect the polymer by filtration. The polymer collected by filtration was dried *in vacuo* to afford **P-prBAmPh-BT** (57.4 mg, 77%) as an orange solid.

M_n = 7,900, M_w = 22,400, M_w/M_n = 2.8. ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 8.60 (d, J = 8.08 Hz, 1H), 7.92–7.87 (m, 1H), 7.55–7.51 (m, 3H), 7.30–7.22 (m, 3H), 7.04–7.01 (m, 2H), 4.08 (br, 2H), 3.88(br, 2H), 2.72–2.56 (m, 4H), 2.17 (br, 1H), 1.84 (br, 2H), 1.64 (br, 3H) 1.25 (br, 36H), 0.88–0.85 (m, 6H) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz) 159.9, 156.7, 142.6, 131.7, 128.1, 127.4, 120.6, 115.3, 115.1, 61.1, 56.0, 32.3, 31.2, 30.1, 30.1, 30.1, 30.0, 29.9, 29.8, 29.5, 23.1, 14.3ppm. The other ^{13}C{^{1}H} signals especially in aromatic area were not detected probably because of broadening peaks in a polymer. ^{11}B NMR (CD_2Cl_2, 128 MHz) δ 3.24 ppm.

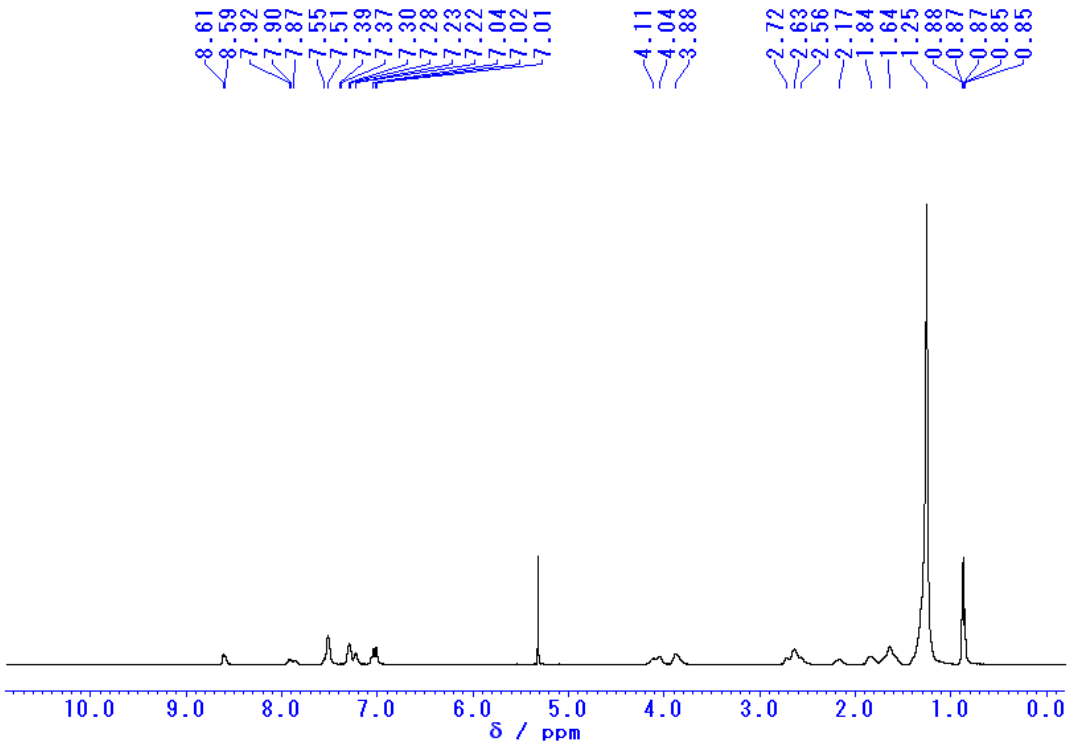


Chart S28. ^{1}H NMR spectrum of **P-prBAmPh-BT**, CD_2Cl_2, 400 MHz.

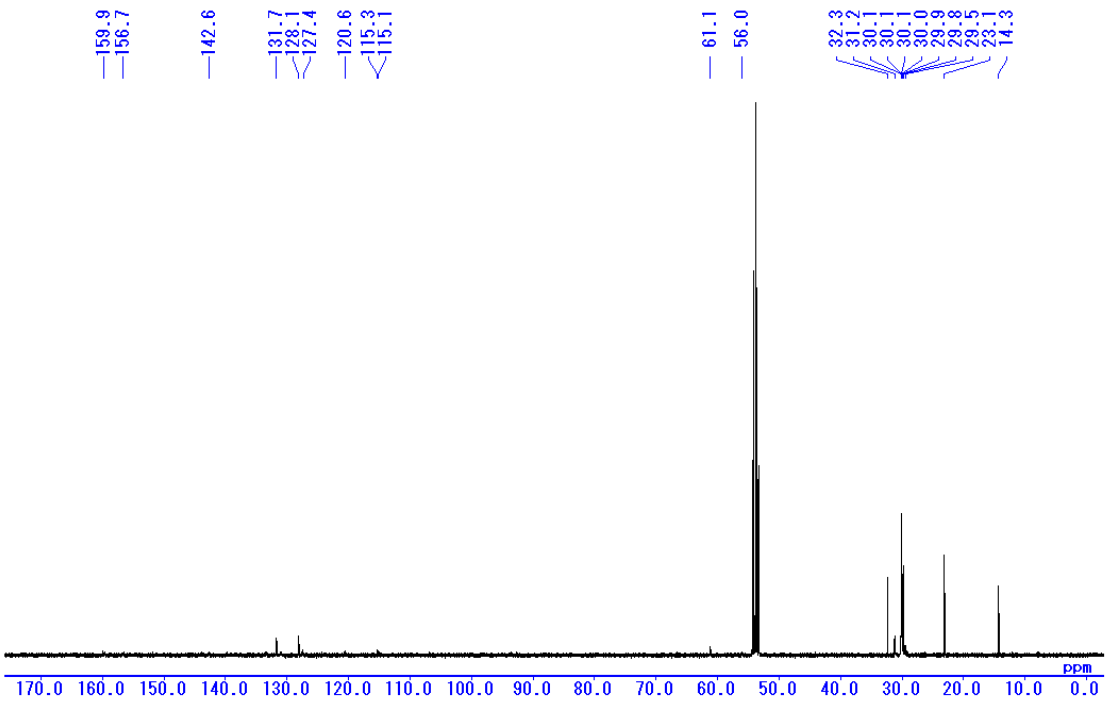


Chart S29. $^{13}C\{^{1}H\}$ NMR spectrum of **P-prBAmPh-BT**, CD_2Cl_2, 100 MHz.

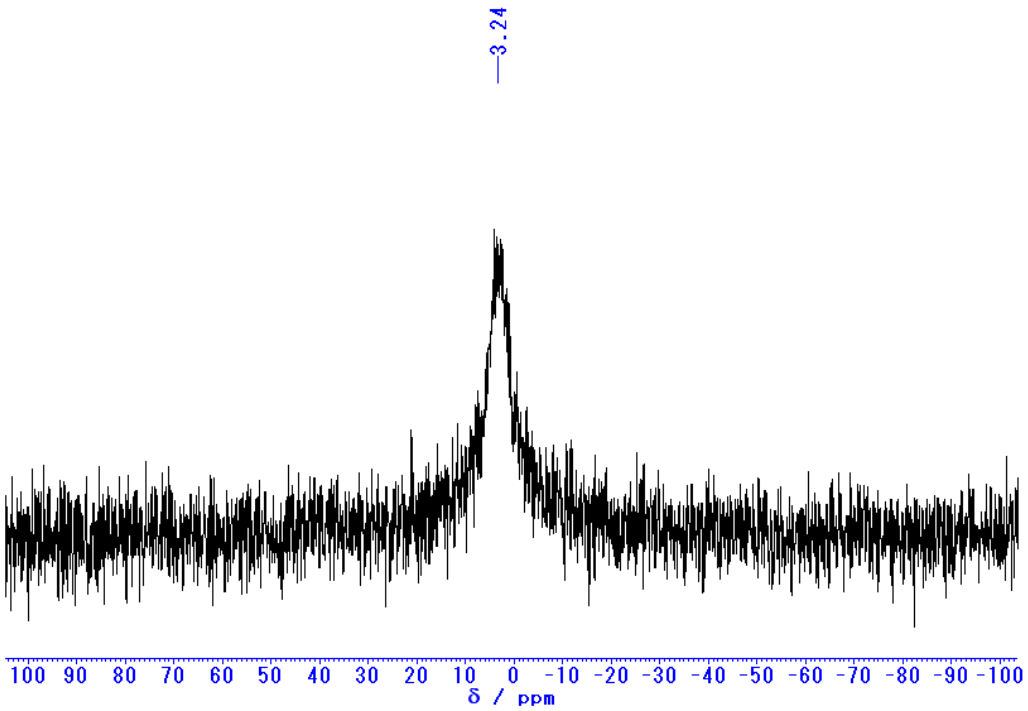


Chart S30. ^{11}B NMR spectrum of **P-prBAmPh-BT**, CD_2Cl_2, 128 MHz.

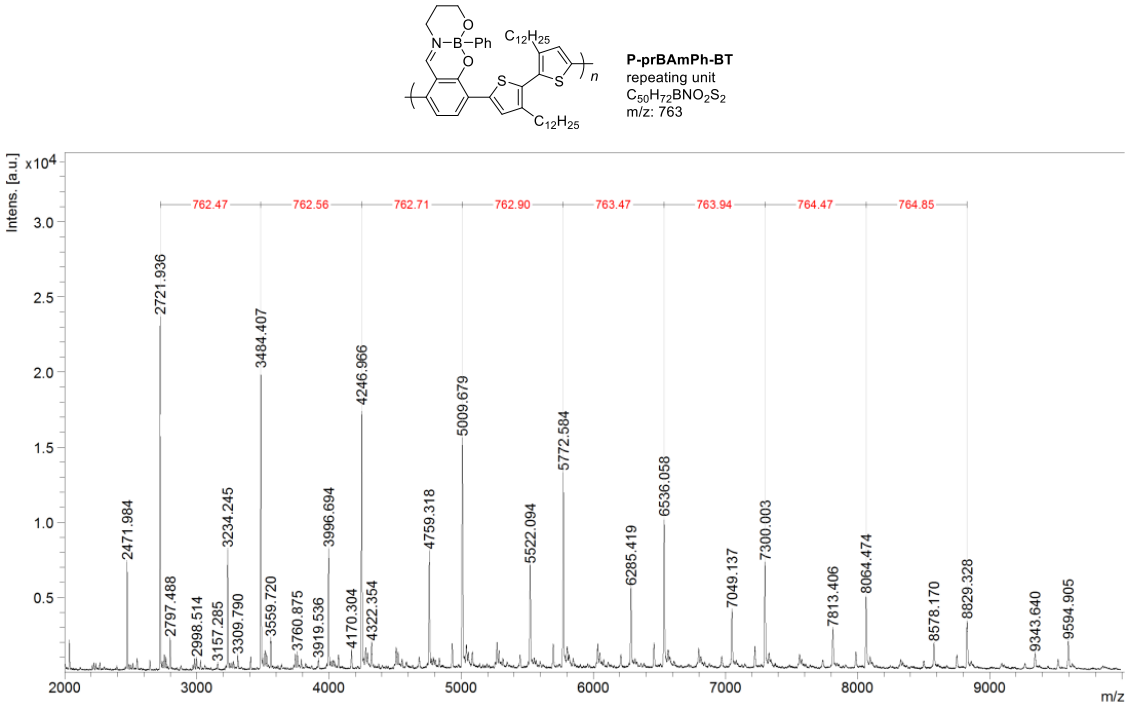
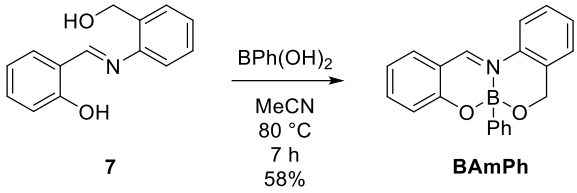


Chart S31. MALDI-TOF mass spectrum of **P-prBAmPh-BT**. Matrix: DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile), Liner mode.

Synthesis of BAmPh



7 (0.20 g, 0.88 mmol) and phenylboronic acid (0.43 g, 3.5 mmol) was dissolved in dry MeCN (18 mL) under N_2 atmosphere. The solution was stirred for 7 h at 80 °C. Then, the mixture was cooled to room temperature and the solvent was removed by a rotary evaporator. The residue was washed with Et_2O and collected by filtration to afford **BAmPh** (0.16 g, 0.51 mmol, 58%) as a yellow solid.

^{1}H NMR (CD_2Cl_2, 400 MHz) δ 8.65 (s, 1H), 7.66 (d, J = 7.6 Hz, 1H), 7.54–7.50 (m, 1H), 7.45 (dd, J = 7.8, 1.7 Hz, 1H), 7.41 (dt, J = 8.3, 0.7 Hz, 1H), 7.36 (td, J = 7.4, 1.3 Hz, 1H), 7.24–7.28 (m, 3H), 7.12–7.06 (m, 3H), 7.00 (d, 8.3 Hz, 1H), 6.92–6.88 (m, 1H), 4.98 (d, J = 15.4 Hz, 1H), 4.87 (d, J = 15.4 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz) δ 161.2, 156.2, 138.8, 138.7, 136.1, 132.6, 131.5, 129.1, 128.4, 127.6, 127.3, 126.8, 120.0, 119.8, 118.0, 117.9, 63.7 ppm. One carbon peak directly connected at boron was not detected. ^{11}B NMR (CD_2Cl_2, 128 MHz) δ 4.91 ppm. HRMS (ESI) calcd. for $C_{20}H_{16}BNO_2Na$ $[M+Na]^+$: 336.1166; found: 336.1159.

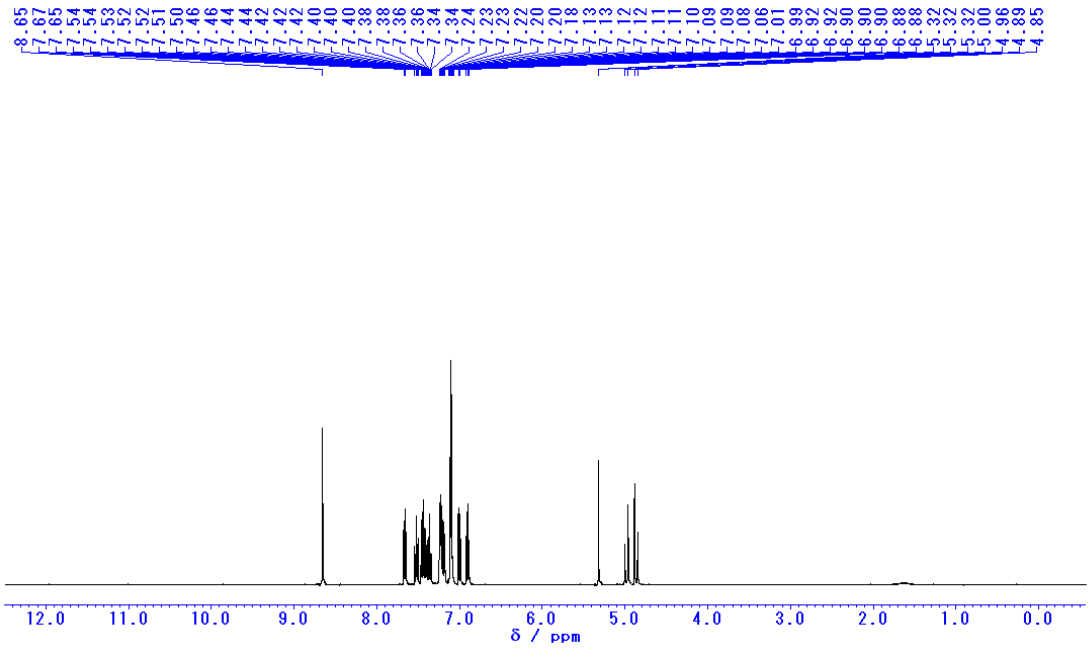


Chart S32. ^{1}H NMR spectrum of **BAmPh**, CD_2Cl_2, 400 MHz.

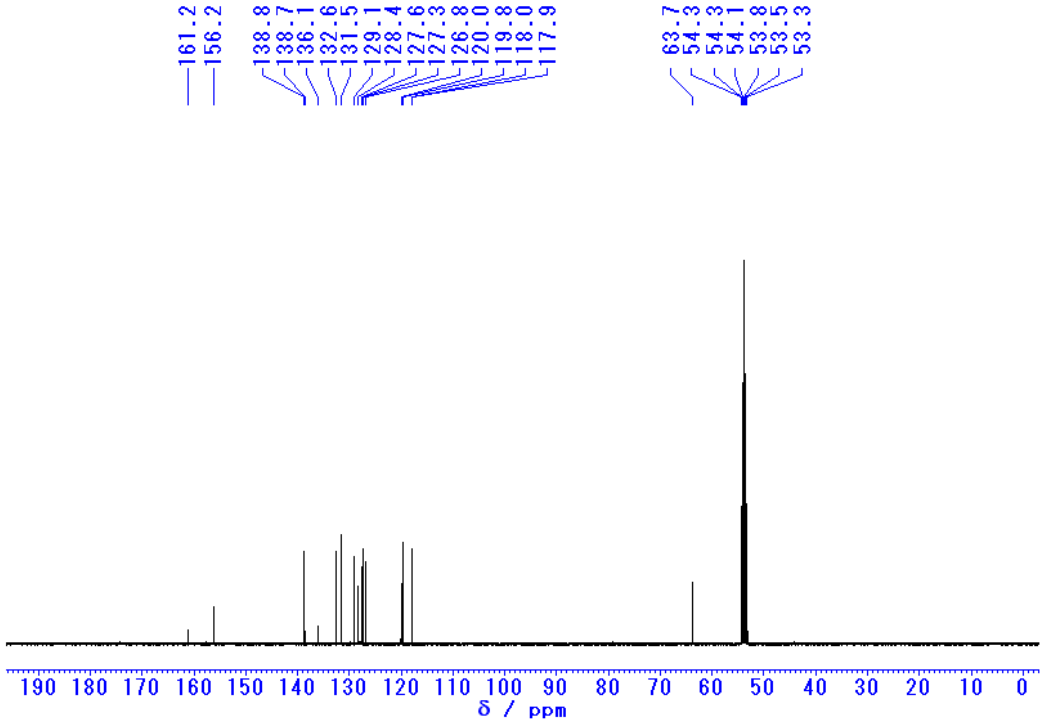


Chart S33. $^{13}C\{^{1}H\}$ NMR spectrum of **BAmPh**, CD_2Cl_2, 100 MHz.

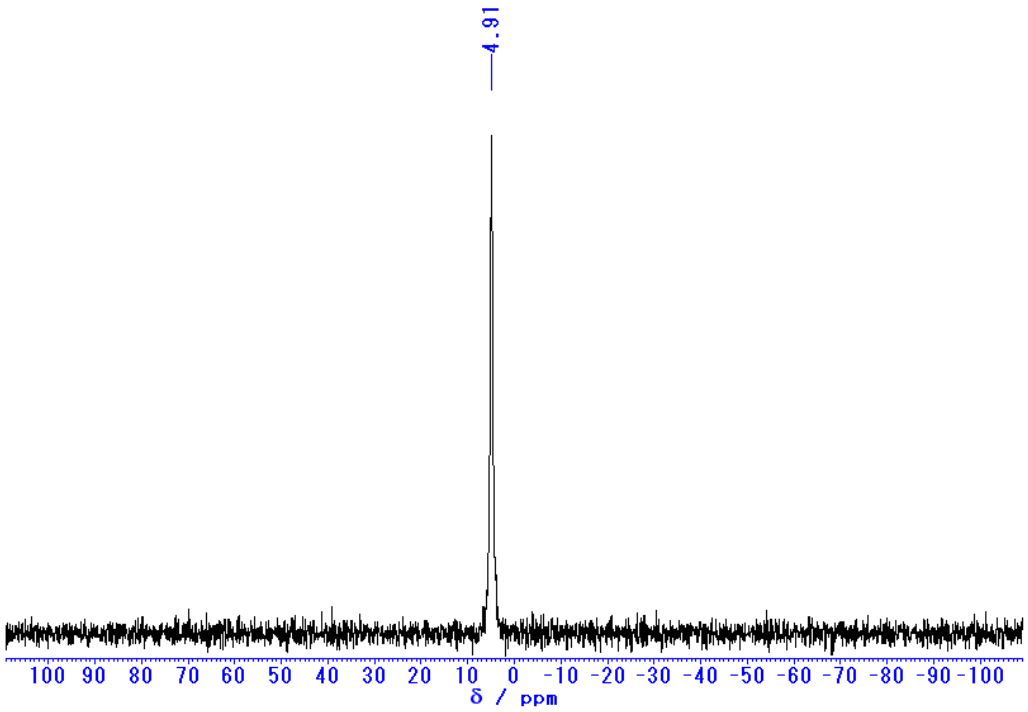
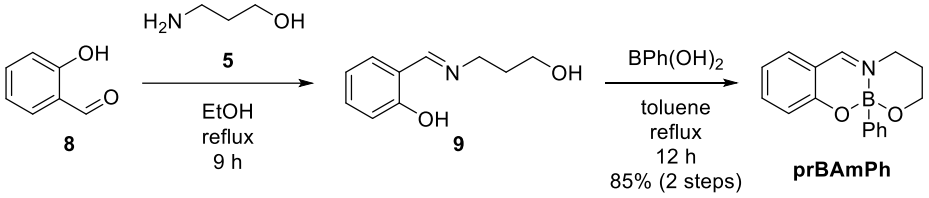


Chart S34. ^{11}B NMR spectrum of **BAmPh**, CD_2Cl_2, 128 MHz.

Synthesis of prBAmPh



2-Hydroxybenzaldehyde (**8**) (0.50 g, 4.1 mmol) and 3-Amino-1-propanol (**5**) (0.31 g, 4.1 mmol) were dissolved in EtOH (12 mL) and refluxed for 9 h. Then, the mixture was cooled to room temperature and the solvent was removed by a rotary evaporator to afford crude **9**.

Crude **9** (0.72 g, 4.0 mmol) and phenylboronic acid (0.57 g, 4.0 mmol) was dissolved in toluene (20 mL). The solution was refluxed for 12 h. Then, the mixture was cooled to room temperature and collected by filtration to afford **prBAmPh** (0.92 g, 3.5 mmol, 85% (2 steps)) as a white solid.

^{1}H NMR (CD_2Cl_2, 400 MHz) δ 8.18 (d, J = 1.2 Hz, 1H), 7.43–7.38 (m, 1H), 7.36–7.31 (m, 3H), 7.28–7.23 (m, 2H), 7.19 (tt, J = 7.2, 1.9 Hz, 1H), 6.82 (ddd, J = 7.7, 7.2, 1.0 Hz, 1H), 6.78–6.75 (m, 1H), 4.00–3.88 (m, 3H), 3.72–3.68 (m, 1H), 2.18–2.06 (m, 1H), 1.79–1.73 (m, 1H) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz), δ 160.8, 160.2, 138.0 131.7, 131.5, 128.1, 127.3, 119.6, 118.9, 116.1, 61.8, 56.0, 31.4 ppm. One carbon peak directly connected at boron was not detected. ^{11}B NMR (CD_2Cl_2, 128 MHz) δ 4.71 ppm. HRMS (ESI) calcd for $C_{16}H_{17}BNO_2$ $[M+H]^+$: 288.1166; found: 288.1163.

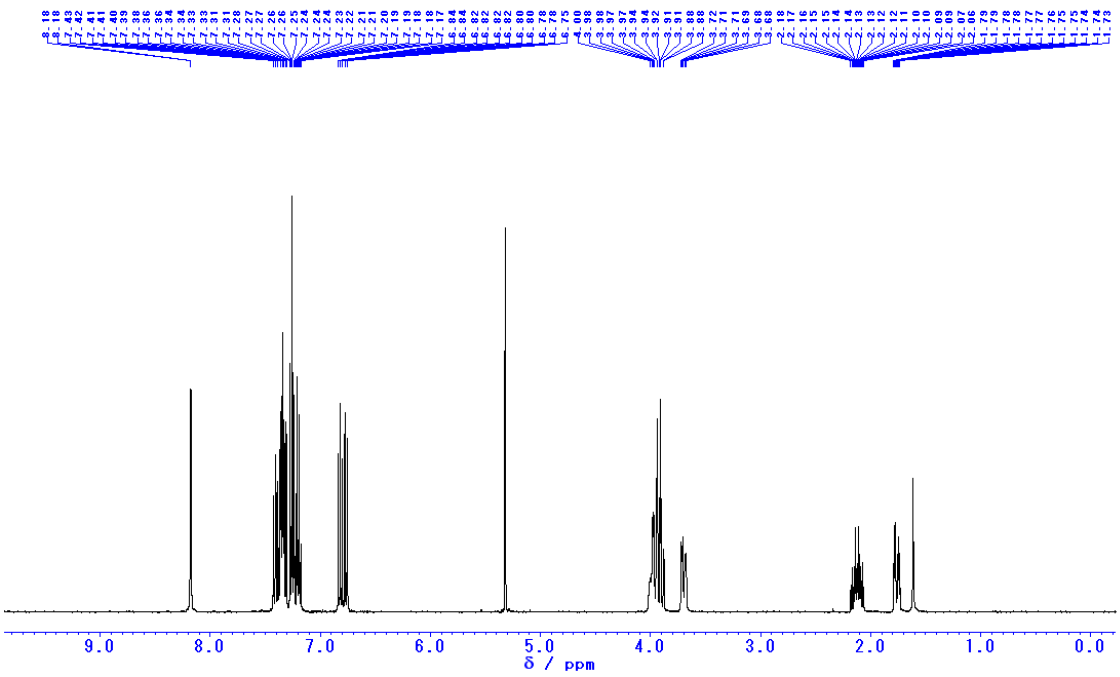


Chart S35. ^{1}HNMR spectrum of **prBAmPh**, CD_2Cl_2, 400 MHz.

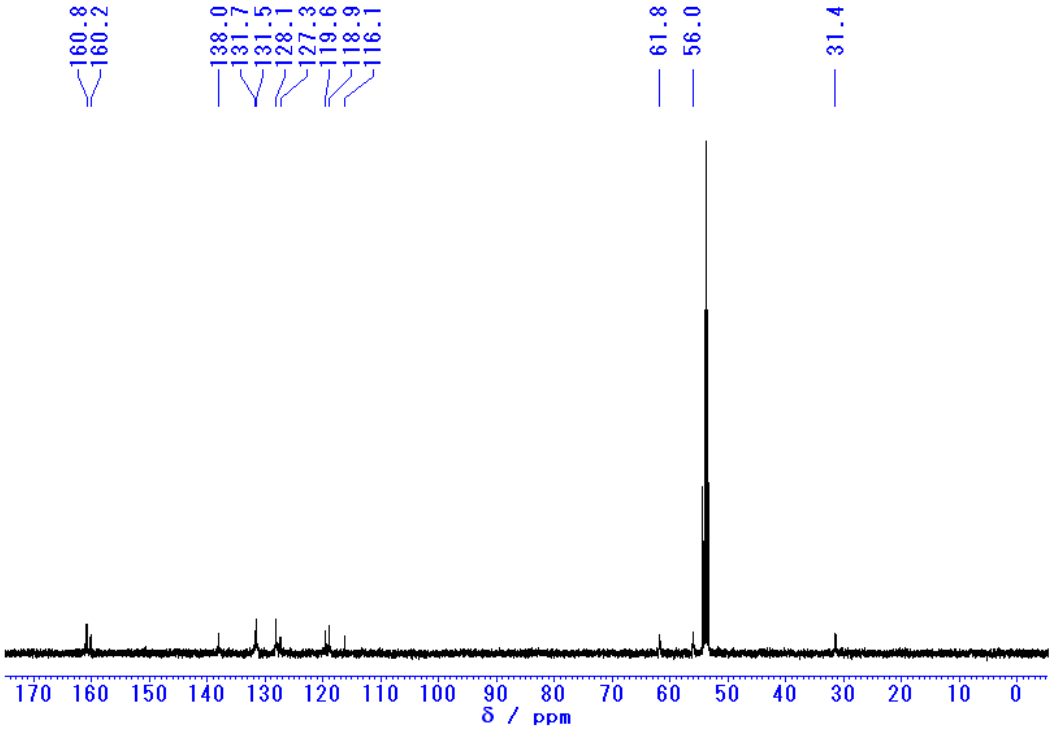


Chart S36. $^{13}C\{^{1}H\}$ NMR spectrum of **prBAmPh**, CD_2Cl_2, 100 MHz.

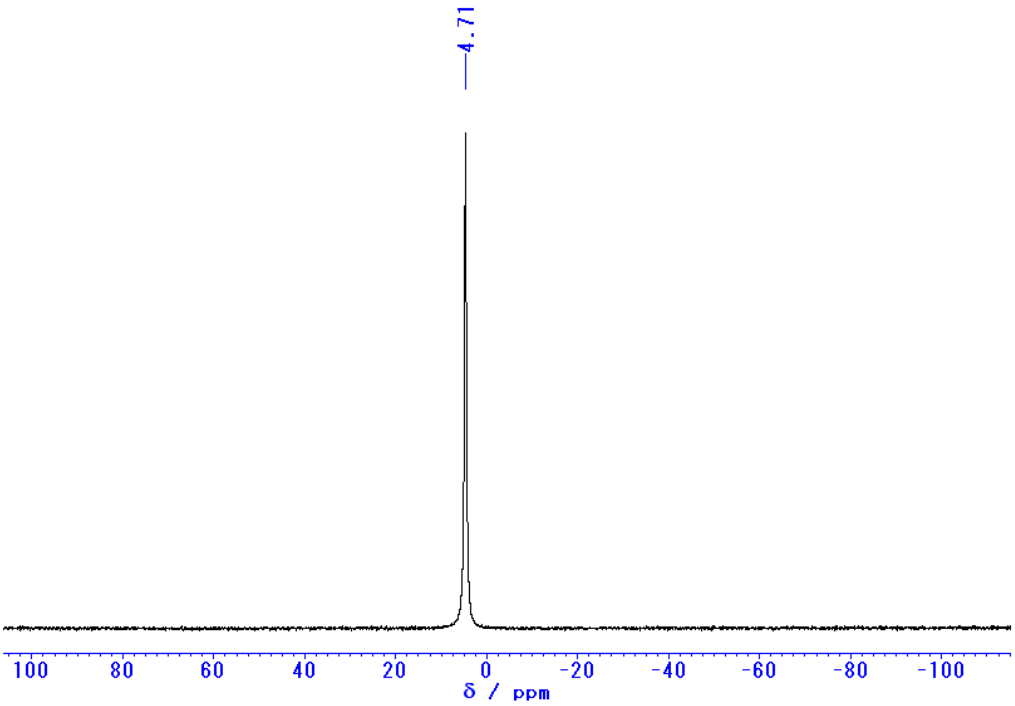


Chart S37. ^{11}B NMR spectrum of **prBAmPh**, CD_2Cl_2, 128 MHz.

Polymer properties depending on the connection positions

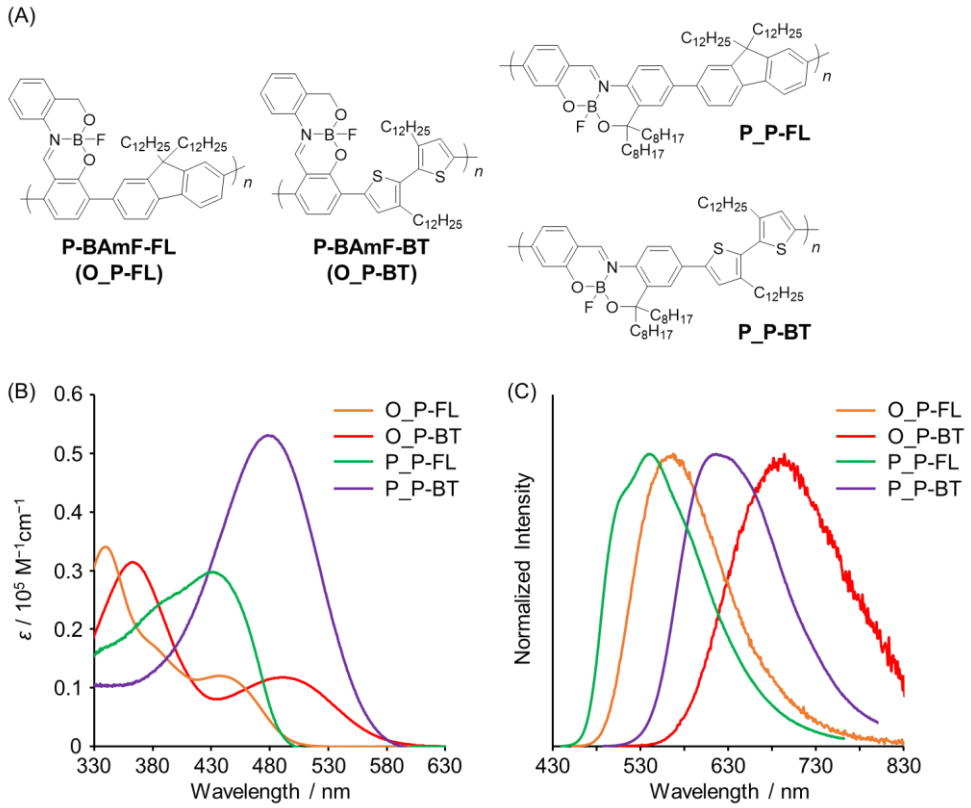


Figure S1. Optical properties of P-BAmF derivatives depending on the connection positions. (A) Chemical structures of P-BAmF derivatives. (B) UV–vis absorption spectra and (C) PL spectra in toluene (1.0×10^{-5} M per repeating unit) and in toluene/$CHCl_3$ = 99/1 v/v (1.0×10^{-5} M per repeating unit), excited at wavelengths of absorption maxima for PL. The data of **P_P-FL** and **P_ P-BT** are cited from ref 4.

Table S1. Optical data and energy levels of molecular orbitals of P-BAmF derivatives

	λ_{abs}[a] /nm	λ_{PL}[a] /nm	Φ_{PL}[a,b] /%	$\lambda_{abs,edge}$[a] /nm	E_{LUMO}[c] /eV	E_{HOMO}[c] /eV
P_O-FL	437	568	18	496	−3.09	−5.59
P_O-BT	491	694	4	575	−3.24	−5.40
P_P-FL[d]	432	538	22	490	−3.18	−5.71
P_P-BT[d]	479	613	51	562	−3.31	−5.51

[a] 1.0×10^{-5} M per repeating unit in toluene, excited at wavelengths of absorption maxima for PL.

[b] Absolute PL quantum yield, excited at wavelengths of absorption maxima.

[c] $E_{g,opt} = 1240/\lambda_{abs,edge}$. $E_{HOMO} = E_{LUMO} - E_{g,opt}$.

[d] From ref 4.

PL lifetime decay curves

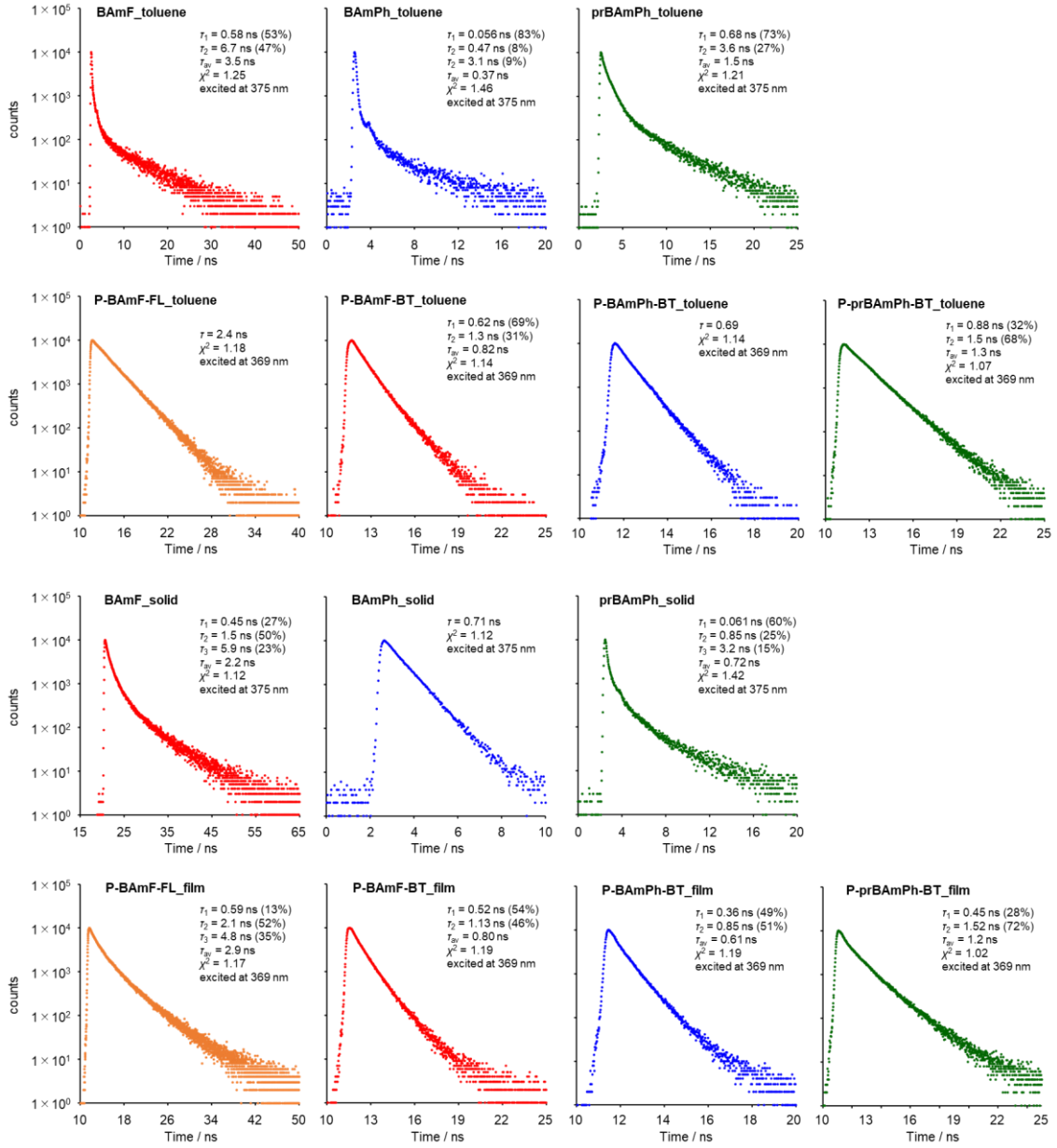


Figure S2. PL lifetime decay curves of BAm derivatives in toluene/$CHCl_3$ = 99/1 v/v (1.0×10^{-5} M) at room temperature, excited by 375 nm LED laser. Their emissions at the PL peak tops were monitored.

Cyclic voltammograms

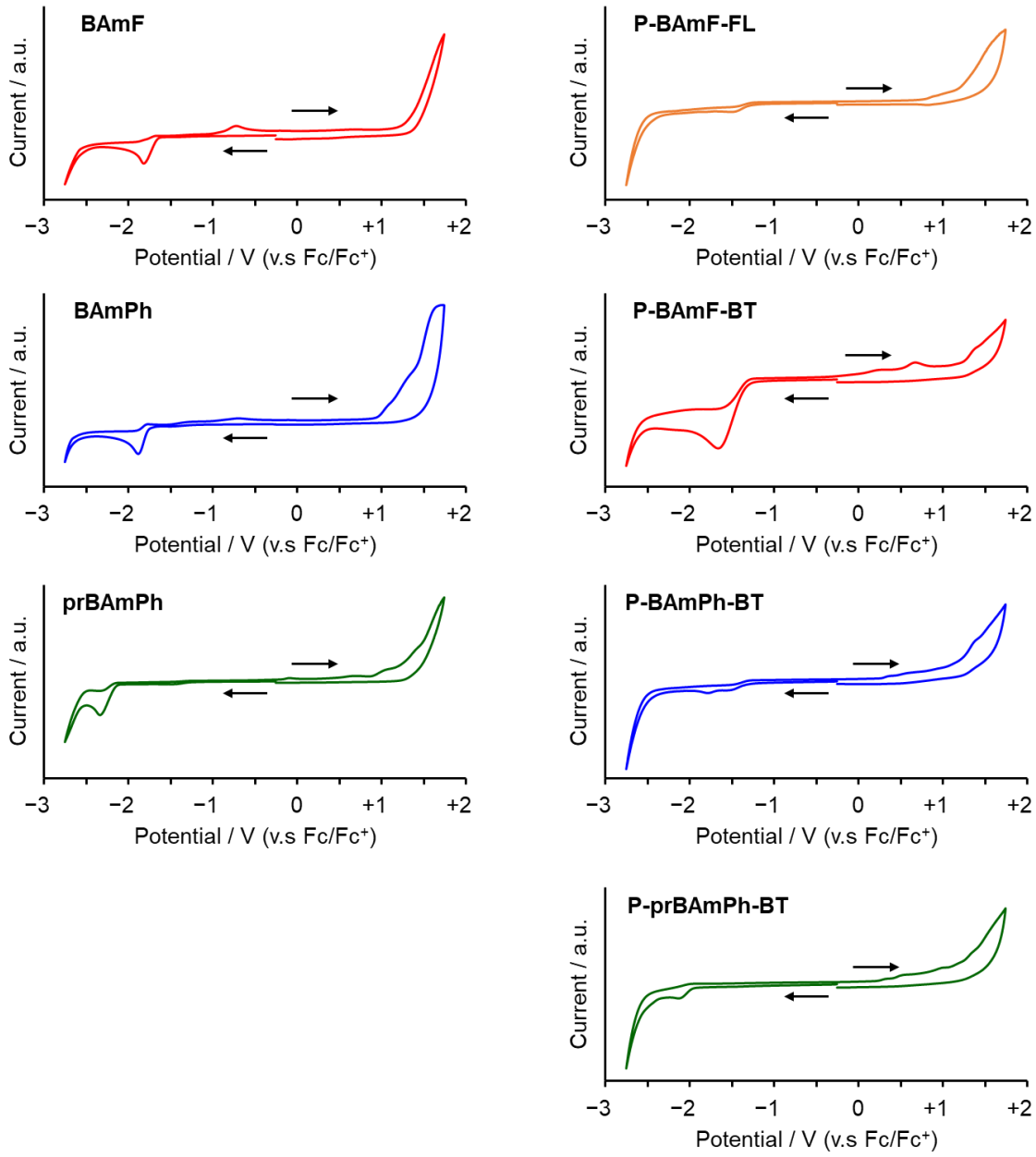


Figure S3. Cyclic voltammograms of BAm derivatives in CH_2Cl_2 (1.0×10^{-3} M) with a grassy carbon working electrode, a Pt counter electrode, an Ag/AgCl reference electrode, and the ferrocene/ferrocenium (Fc/Fc^+) external reference at a scan rate of 0.1 V s^{-1}. The black arrows denote sweep directions (negative scan).

Computational details for theoretical calculation

The Gaussian 16 program package[5] was used for computation. We optimized the structures of the **BAmF**, **BAmPh**, **prBAmPh**, **M-BAmF-FL (O_M-FL)**, **M-BAmF-BT (O_M-BT)**, **M-BAmPh-BT**, **M-prBAmPh-BT**, **P_M-FL**, **P_M-BT**, **M3-BAmF-FL (O_M3-FL)**, **M3-BAmF-BT (O_M3-BT)**, **M3-BAmPh-BT**, **M3-prBAmPh-BT**, **P_M3-FL**, and **P_M3-BT** in the ground S_0 states and calculated their molecular orbitals (Figure S4). Long alkyl chains were converted to methyl groups to save the calculation cost. The density functional theory (DFT) was applied for the optimization of the structures in the S_0 states at B3LYP/6-311G(d,p) level. We calculated the transition energy with optimized geometries in the S_0 states by time-dependent (TD) DFT at B3LYP/6-311G(d,p) level.

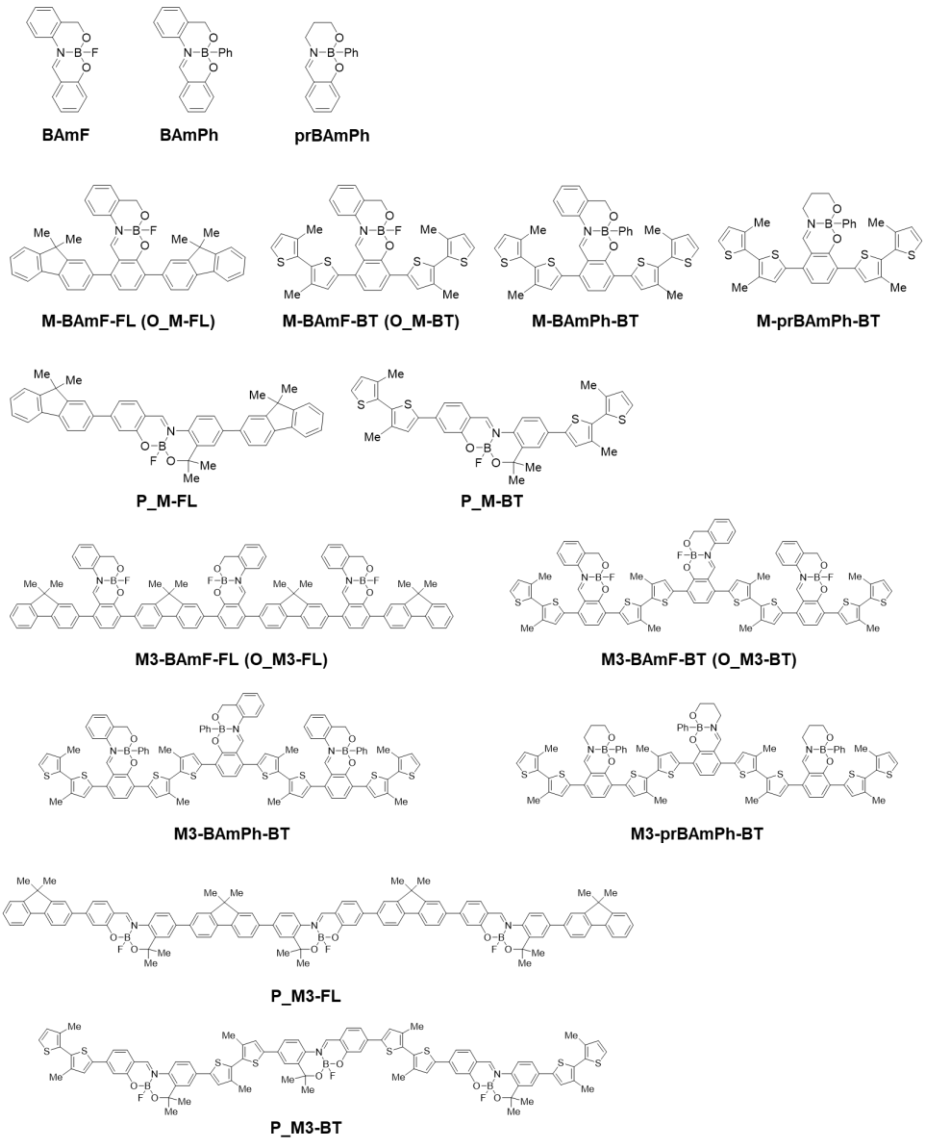


Figure S4. Chemical structures of BAm derivatives for theoretical calculation.

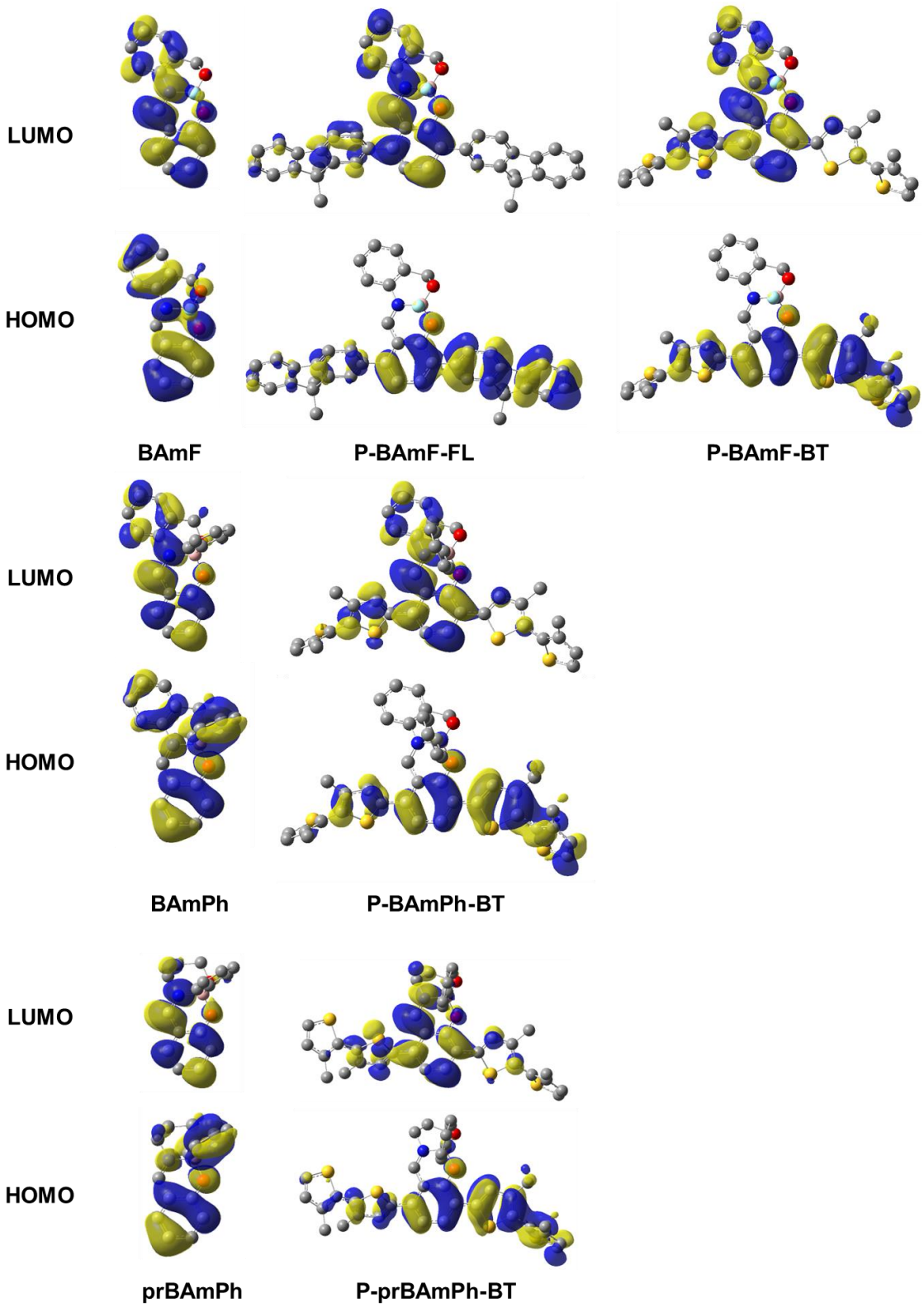


Figure S5. Selected Kohn–Sham orbitals of BAm derivatives obtained with DFT calculations (isovalue = 0.02). Hydrogens were omitted for clarity.

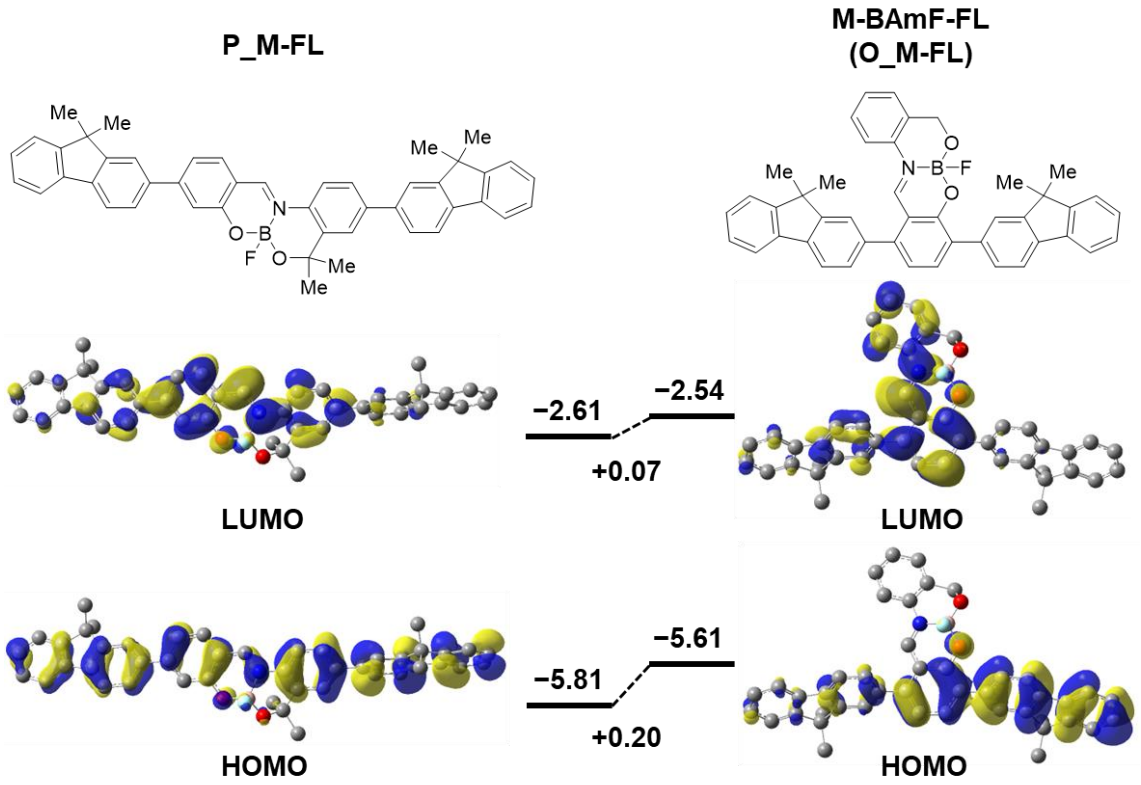


Figure S6. Chemical structures, energy diagrams, and Kohn-Sham orbitals of model compounds of polymers with DFT calculations (isovalue = 0.02). Hydrogens were omitted for clarity.

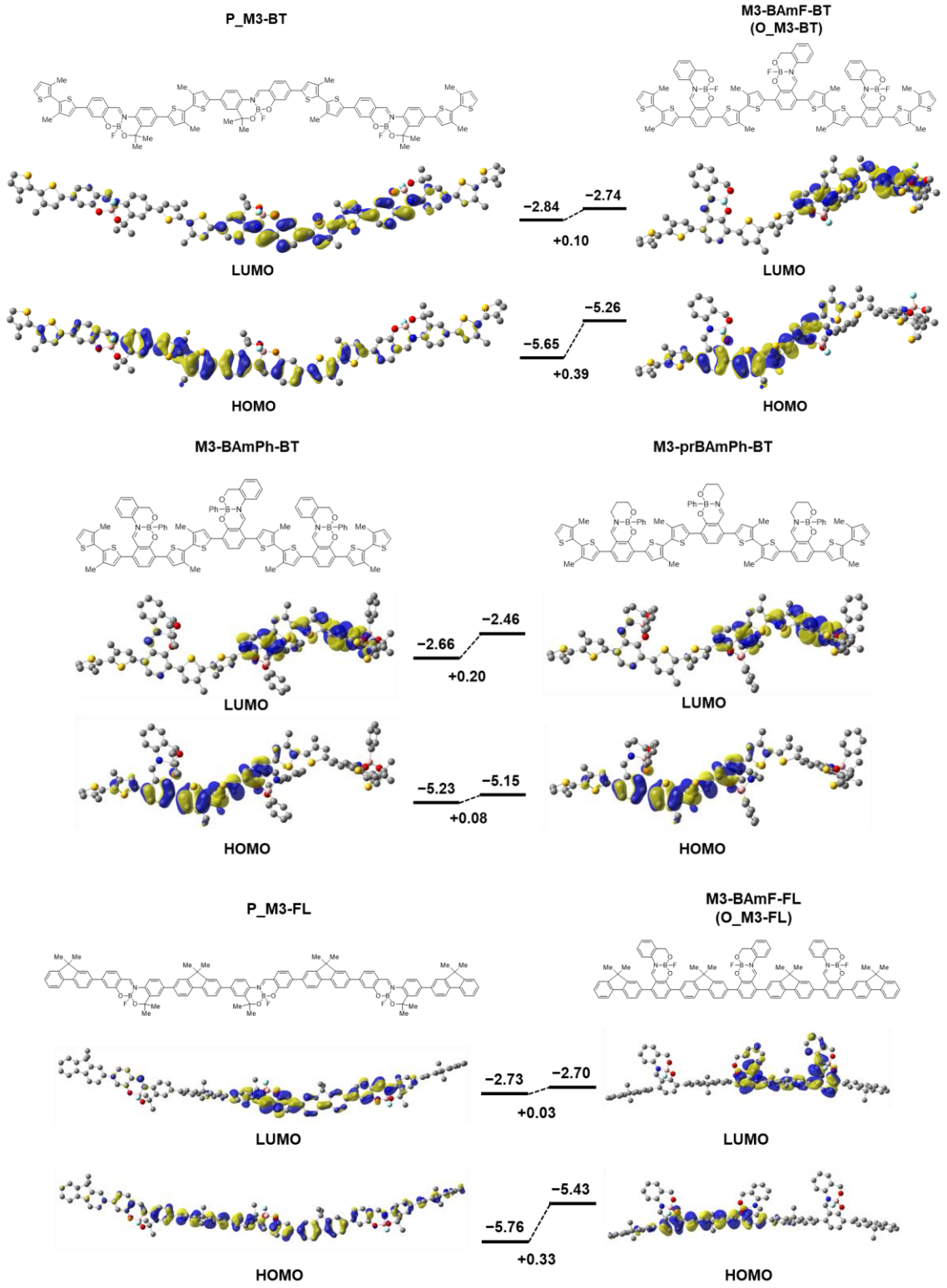


Figure S7. Chemical structures, energy diagrams, and Kohn-Sham orbitals of model oligomers with DFT calculations (isovalue = 0.02). Hydrogens were omitted for clarity.

Thermal stability test

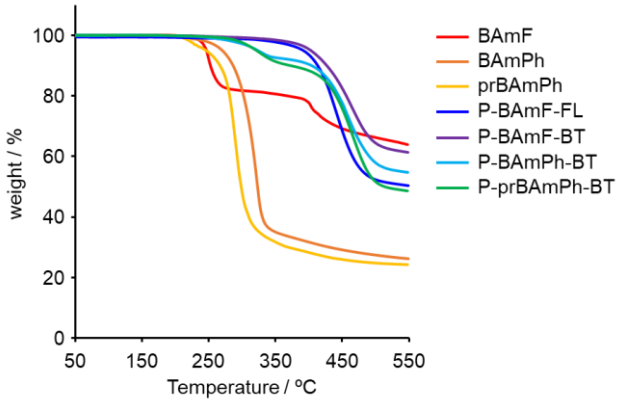


Figure S8. TGA curves of powder samples of BAm derivatives under N_2 (scan rate, 10 °C min^{-1}).

Table S2. Decomposition temperatures of BAm derivatives

	T_{d1} [a] /°C	T_{d2} [b] /°C
BAmF	242	396
BAmPh	296	–
prBAmPh	275	–
P-BAmF-FL	406	–
P-BAmF-BT	414	
P-BAmPh-BT	288	426
P-prBAmPh-BT	293	432

[a] Onset temperature of the first degradation curve calculated from an extrapolation method

[b] Onset temperature of the second degradation curve calculated from an extrapolation method

Photostability test

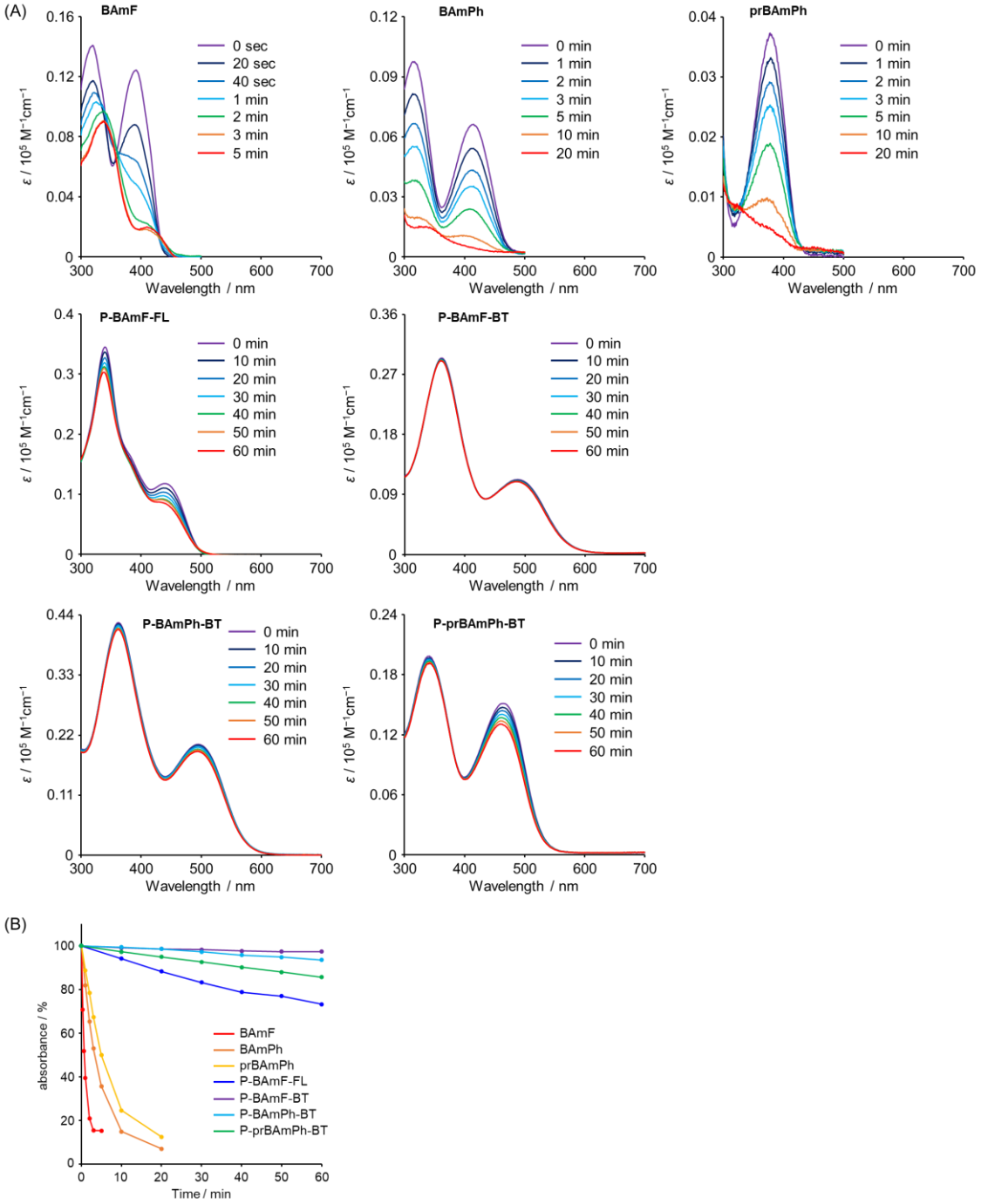


Figure S9. (A) Photostability tests of BAm derivatives in toluene (1.0×10^{-5} M for monomeric units, 1.0×10^{-5} M per repeating units for polymers) irradiated by transilluminator (365 nm). (B) Summary of time-dependent absorbance monitored at the longest absorption band.

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5. Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.