Supporting Information

Pure-Color and Dual-Color Emission from BODIPY Homopolymers Containing the Cardo Boron Structure

Honami Yamane, Kazuo Tanaka and Yoshiki Chujo**

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

Corresponding author E-mail: kazuo123@chujo.synchem.kyoto-u.ac.jp; chujo@chujo.synchem.kyoto-u.ac.jp

Tel: (+81)-75-383-2604. Fax: (+81)-75-383-2605

Experimental Section

General: ^{1}H (400 MHz), ^{13}C (100 MHz) and ^{11}B (128 MHz) NMR spectra were recorded on a JEOL JNM EX400 spectrometer. ^{11}B NMR spectra were referenced externally to $BF_3 \cdot OEt_2$ (sealed capillary). Analytical thin-layer chromatography (TLC) was performed with silica gel 60 Merck F254 plates. Column chromatography was performed with 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 recorded on a HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer, and the absolute quantum yield was calculated by integrating sphere method on the HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer in chloroform.

Synthesis of B2Br: *n*-BuLi (5.2 mL, 1.63 mol/L in hexane) was added to the solution of 1-bromo-4-iodobenzene (2.4 g, 8.5 mmol) in diethyl ether (16 mL) at −78 °C under argon atmosphere. The reaction mixture was stirred for 0.5 h at −78 °C and for 0.5 h at room temperature. Then, the solution of **B0** (0.8 g, 2.1 mmol in 18 mL of diethyl ether) was added to the reaction mixture via cannula at −78 °C. After the reaction mixture was stirred for 0.5 h at −78 °C, methanol was added. The solution was extracted with dichloromethane and washed with water and brine. After the organic phase was dried over $MgSO_4$, the solvent was removed by a rotary evaporator. The silica gel column chromatography with hexane/dichloromethane (9:1) gave **B2Br** as an orange solid (0.41 g, 0.63 mmol, 30 %). ^{1}H NMR ($CDCl_3$): δ = 7.31 (4H, d, *J* = 8.3 Hz), 7.08 (4H, br), 6.00 (2H, s), 3.03 (2H, d, *J* = 8.3 Hz), 2.45 (6H, s), 1.70 (6H, s), 1.67−1.59 (2H, m), 1.42−1.39 (2H,

m), 1.30−1.27 (10H, m), 0.88 (3H, t, J = 6.8 Hz) ^{13}C NMR ($CDCl_3$): δ = 152.7, 147.7, 138.0, 135.3, 131.9, 130.3, 122.7, 122.6, 120.2, 32.3, 31,9, 30.1, 29.5, 29.3, 28.6, 22.6, 17.1, 16.9, 16.9, 14.1 ppm. ^{11}B NMR ($CDCl_3$): δ = −0.98 (br) ppm. HRMS (ESI): Calcd. for $[M+H]^+$, 647.1802; found, m/z 647.1786.

Synthesis of B2A: Water (8.0 mL) was added to the solution of **B2Br** (0.50 g, 0.77 mmol), 10-phenyl-9-anthraceneboronic acid (1.9 g, 3.5 mmol), $Pd_2(dba)_3$ (14 mg, 15 μmol), S-Phos (56 mg, 0.14 mmol) and cesium carbonate (5.0 g, 15 mmol) in toluene (8.0 mL). The reaction mixture was stirred at 80 °C for 24 h under argon atmosphere. The solution was extracted with toluene and washed with water and brine. After the organic phase was dried over $MgSO_4$, the solvent was removed by a rotary evaporator. The product was purified by column chromatography with hexane/dichloromethane (4:1). The isolated product was dissolved in a small amount of CH_2Cl_2, and the product was precipitated from methanol to give pure **B2A** as an orange solid (0.49 g, 64%). ^{1}H NMR ($CDCl_3$): δ = 7.81 (4H, dd, J = 7.2, 3.1 Hz), 7.69−7.48 (18H, m), 7.37 (4H, d, J = 7.8 Hz), 7.32−7.31 (8H, m), 6.18 (2H, s), 3.19 (2H, t, J = 8.3 Hz), 2.59 (6H, s), 2.15 (6H, s), 1.79−1.77 (2H, m), 1.54−1.51 (2H, m), 1.36−1.28 (10H, m), 0.86 (3H, t, J = 6.96 Hz) ppm. ^{13}C NMR ($CDCl_3$): δ = 158.1, 149.2, 147.7, 139.4, 138.4, 137.8, 136.5, 136.0, 133.7, 132.2, 131.4, 130.2, 130.0, 130.0, 128.4, 127.4, 127.3, 126.8, 124.9, 124.6, 122.6, 32.4, 31.8, 30.8, 30.3, 29.6, 29.3, 28.8, 22.6, 17.4, 17.0, 14.0 ppm. ^{11}B NMR ($CDCl_3$): δ = −0.20 (br) ppm. HRMS (APCI): Calcd. for $[M+H]^+$, 995.5470; found, m/z 995.5465.

Synthesis of PB0: $BF_3{\cdot}OEt_2$ (0.33 mL, 0.38 g, 2.7 mmol) was added to a solution of **B0** (0.10 g, 0.27 mmol) and PIFA (0.23 g, 0.53 mmol) in CH_2Cl_2 (2.0 mL) at −78 °C, and the solution was stirred at −78 °C for 1 h. The solution was poured into MeOH (25 mL) and triethylamine (3 mL) to collect desired polymer by filtration. The precipitate was dissolved in a small amount of THF, and further reprecipitated from a large excess of EtOH twice to give **PB0** as a metallic red solid (81 mg, 81%). M_n = 14,000, M_w/M_n = 4.1. ^{1}H NMR ($CDCl_3$): δ = 3.68−1.06 (28H, m), 0.96−0.82 (3H, m) ppm. ^{11}B NMR ($CDCl_3$): δ = 0.59 (br) ppm.

Synthesis of PB2: $BF_3{\cdot}OEt_2$ (0.35 mL, 0.41 g, 2.9 mmol) was added to a solution of **B2** (0.14 g, 0.29 mmol) and PIFA (0.25 g, 0.57 mmol) in CH_2Cl_2 (2.1 mL) at −78 °C, and the solution was stirred at −78 °C for 20 h. The solution was poured into MeOH (30 mL) and triethylamine (3 mL) to collect desired polymer by filtration. The precipitate was dissolved in a small amount of THF, and further reprecipitated from a large excess of EtOH twice to give **PB2** as a purplish red solid (62 mg, 45%). M_n = 11,000, M_w/M_n = 2.6. ^{1}H NMR ($CDCl_3$): δ = 7.48−6.92 (10H, m), 3.35−0.95 (28H, m), 0.93−0.79 (3H, m) ppm. ^{11}B NMR ($CDCl_3$): δ = −1.68 (br) ppm.

Synthesis of PB2A: $BF_3{\cdot}OEt_2$ (0.20 mL, 0.23 g, 1.6 mmol) was added to a solution of **B2A** (0.16 g, 0.16 mmol) and PIFA (0.14 g, 0.32 mmol) in CH_2Cl_2 (1.2 mL) at −78 °C, and the solution was stirred at −78 °C for 6 h. The solution was poured into MeOH (20 mL) and triethylamine (2 mL) to collect desired polymer by filtration. The precipitate was dissolved in a small amount of THF, and the polymeric products were reprecipitated in a large excess of EtOH. To remove monomer and dimers, this procedure was repeated several times, and then **PB2A** was collected as a purplish red solid (43 mg, 27%). M_n = 6,000, M_w/M_n = 2.5. ^{1}H NMR ($CDCl_3$): δ = 7.97−6.60 (34H, m), 3.44−0.36 (31H, m) ppm. ^{11}B NMR ($CDCl_3$): δ = −3.13 (br) ppm.

Calculation of energy transfer efficiency.

The energy transfer efficiency (E_{eff}) was calculated with the equation 1 according to the previous report (*Macromolecules* **2016**, *49*, 8899).

$$E_{eff} = (1 - I_{DA} / I_D) = (1 - \Phi_{DA} / \Phi_D) \quad (1)$$

where I_{DA} is fluorescence intensity of donor (9,10-diphenylanthracene, 813370) in the presence of acceptor (polymer, 193730) and I_D in the absence of acceptor, Φ_{DA} is quantum yield of donor in the

presence of acceptor and Φ_D in the absence of acceptor. In this study, due to low emission intensity, reliable quantum yields were not detectable. Therefore, E_{eff} was calculated from the intensities (76%).

NMR Spectra

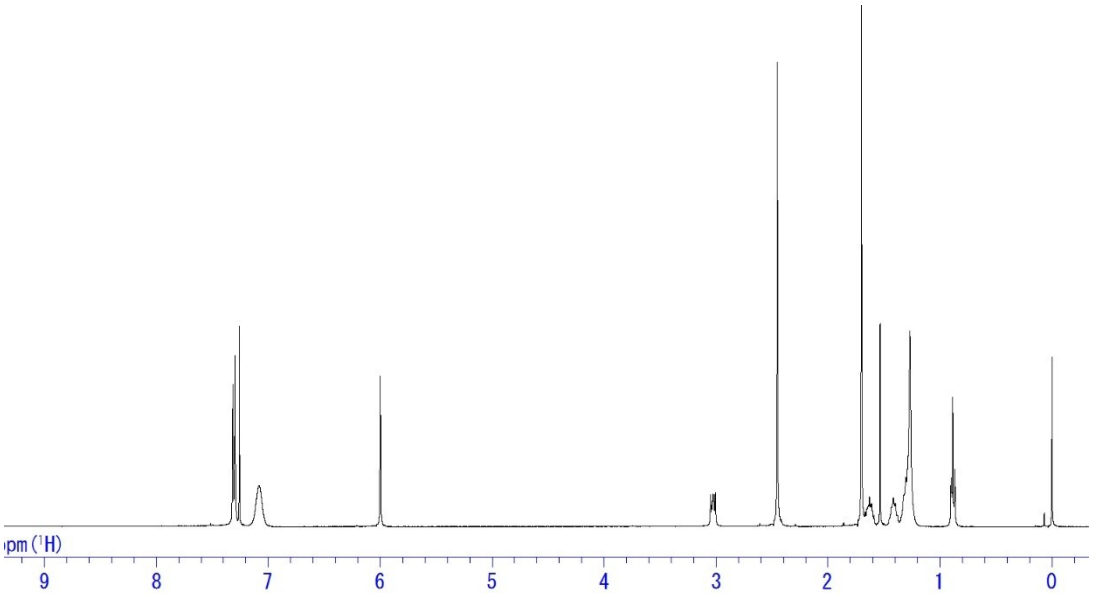

Chart S1. ^{1}H NMR spectrum of **B2Br** in $CDCl_3$.

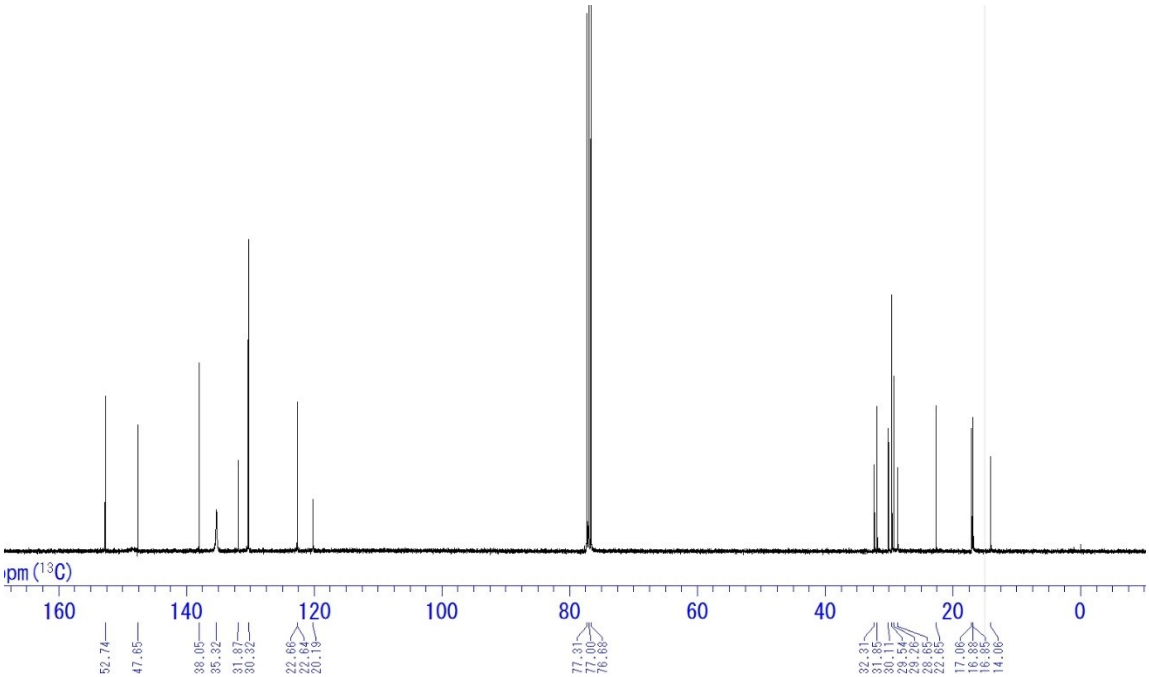

Chart S2. ^{13}C NMR spectrum of **B2Br** in $CDCl_3$.

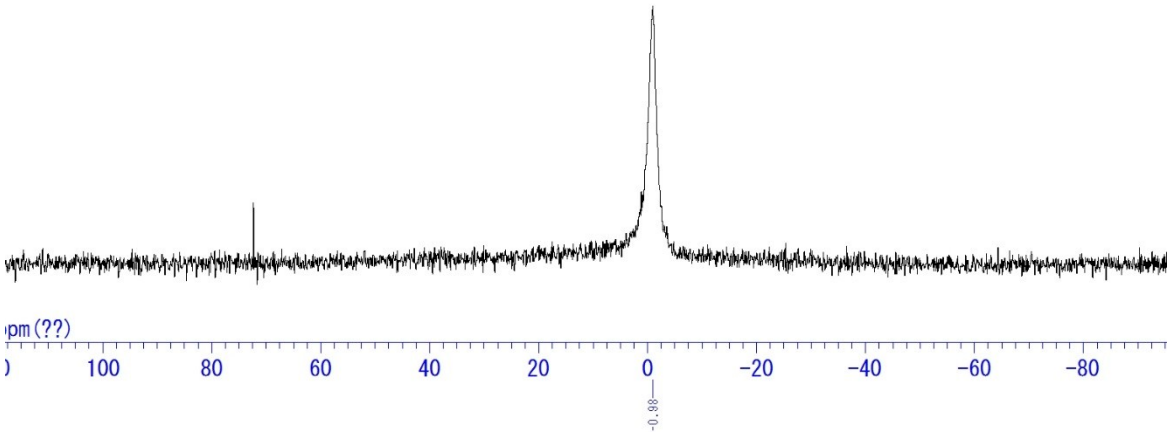

Chart S3. ^{11}B NMR spectrum of **B2Br** in $CDCl_3$.

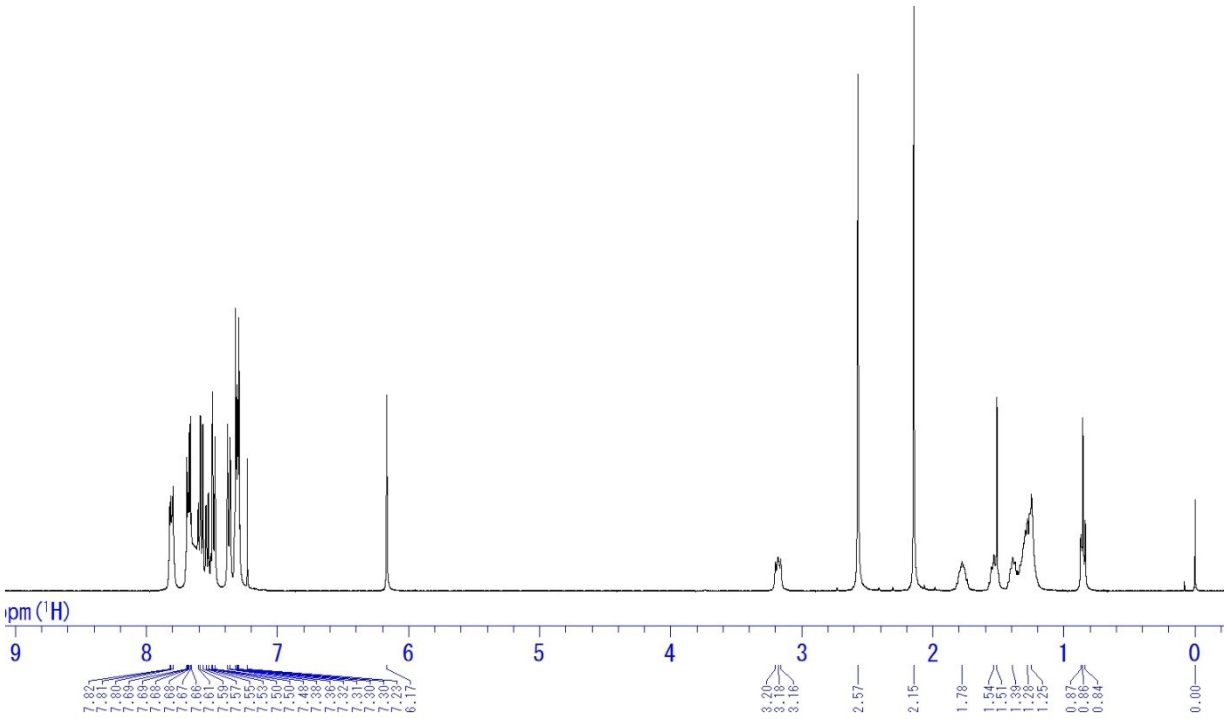

Chart S4. ^{1}H NMR spectrum of **B2A** in $CDCl_3$.

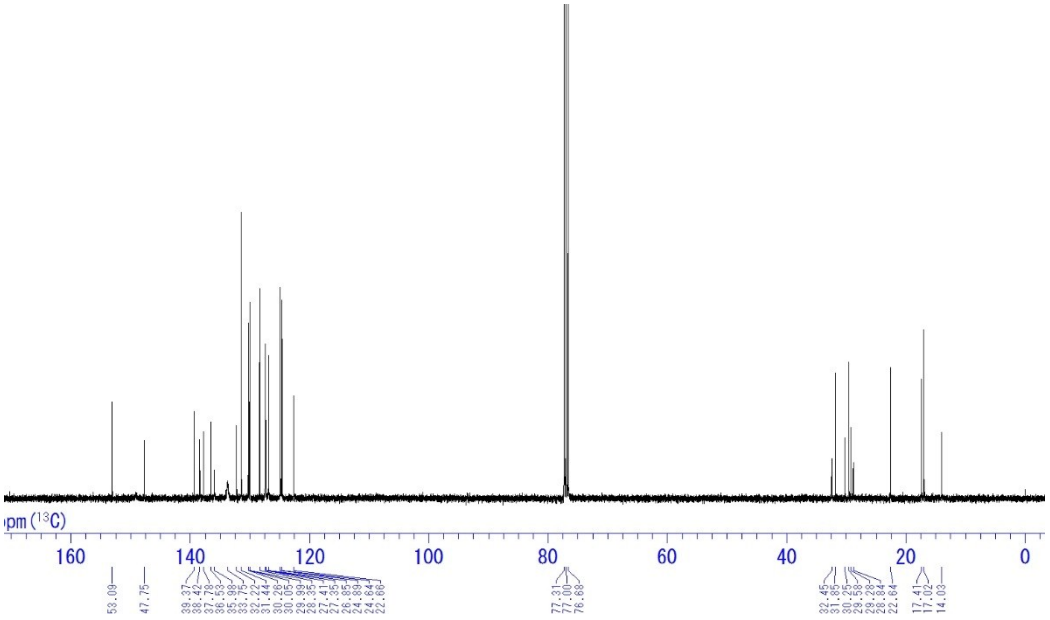

Chart S5. ^{13}C NMR spectrum of **B2A** in $CDCl_3$.

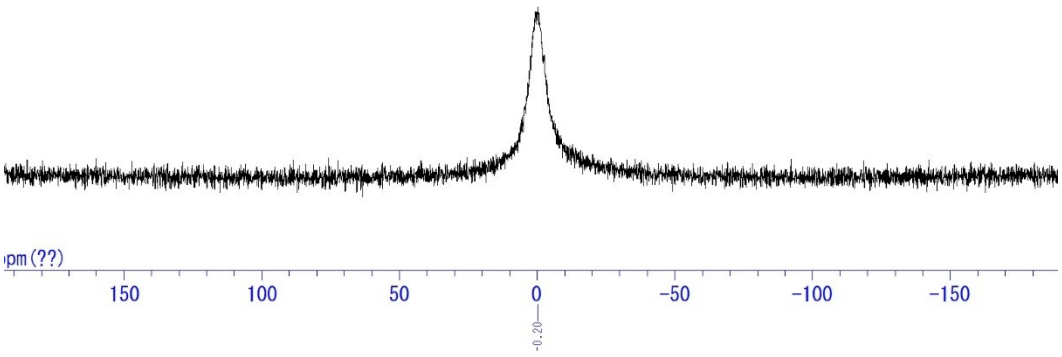

Chart S6. ^{11}B NMR spectrum of **B2A** in $CDCl_3$.

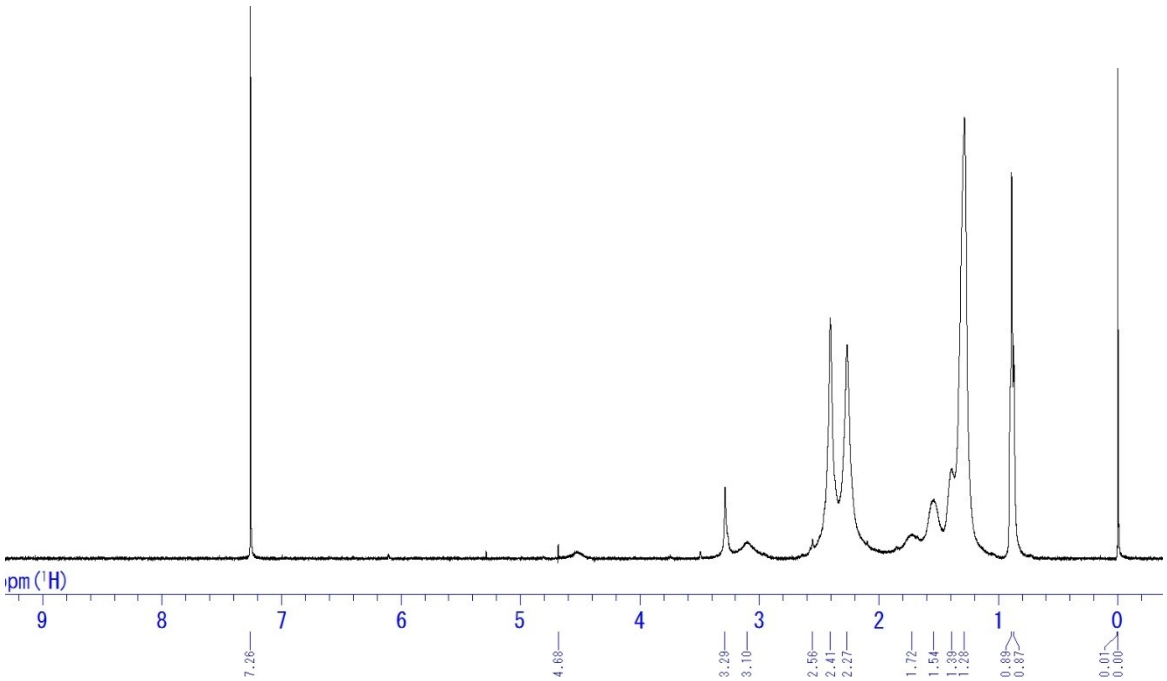

Chart S7. ^{1}H NMR spectrum of **PB0** in $CDCl_3$.

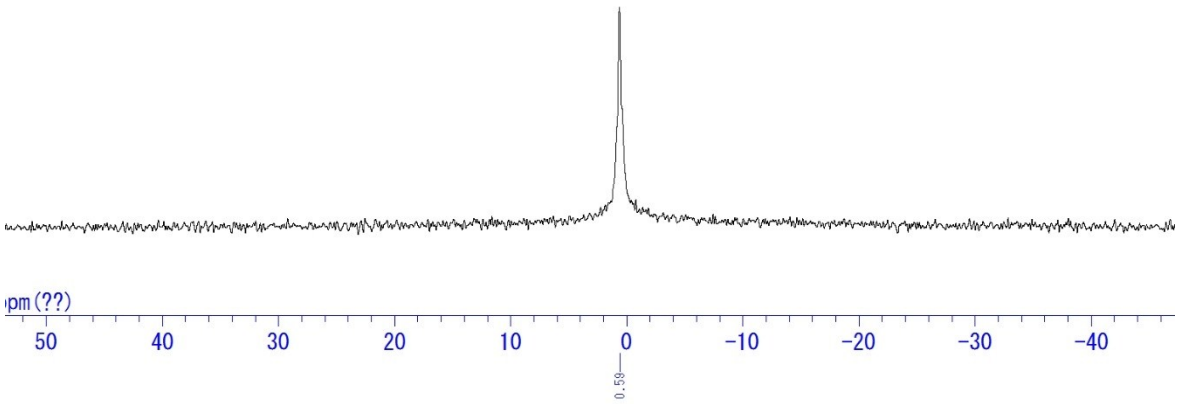

Chart S8. ^{11}B NMR spectrum of **PB0** in $CDCl_3$.

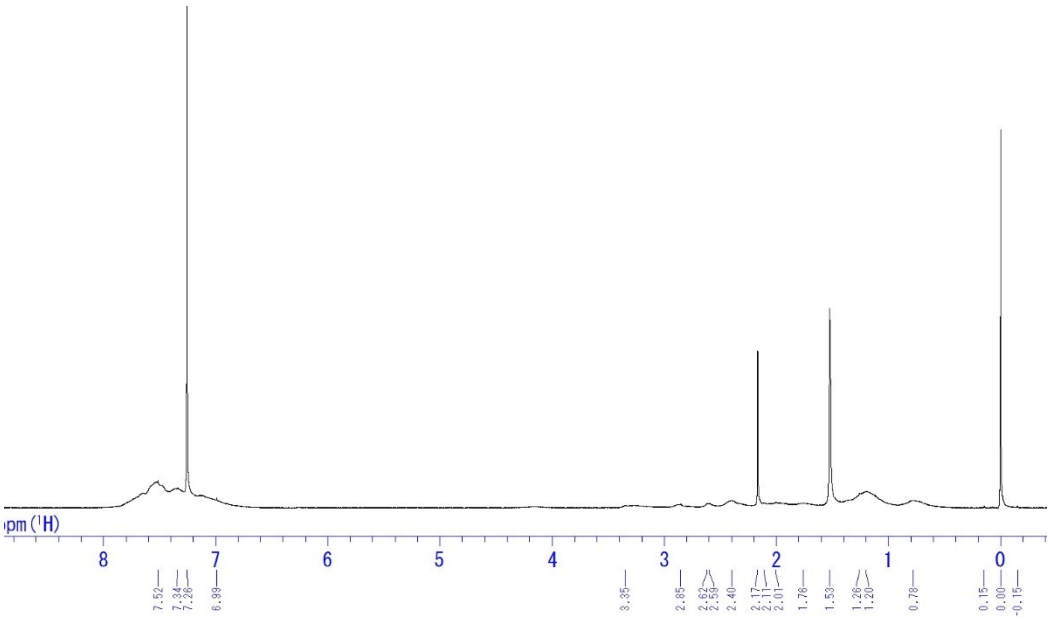

Chart S9. ^{1}H NMR spectrum of **PB2** in $CDCl_3$.

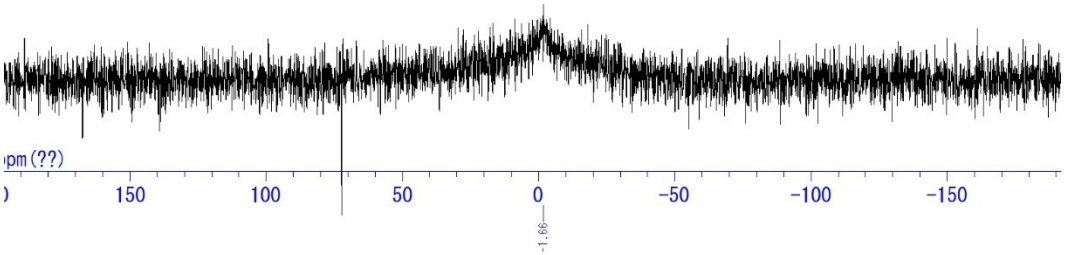

Chart S10. ^{11}B NMR spectrum of **PB2** in $CDCl_3$.

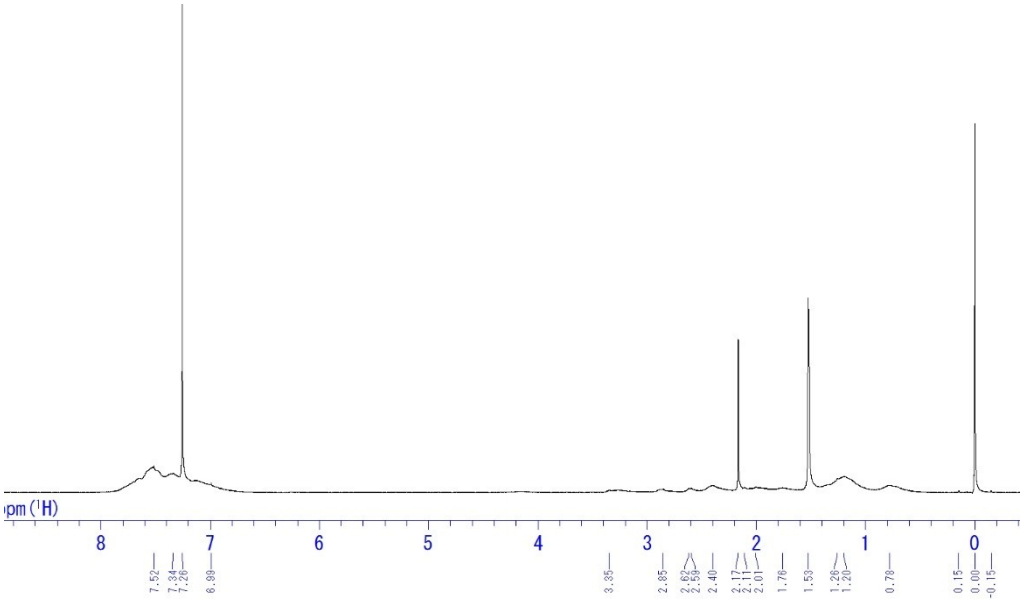

Chart S11. ^{1}H NMR spectrum of **PB2A** in $CDCl_3$.

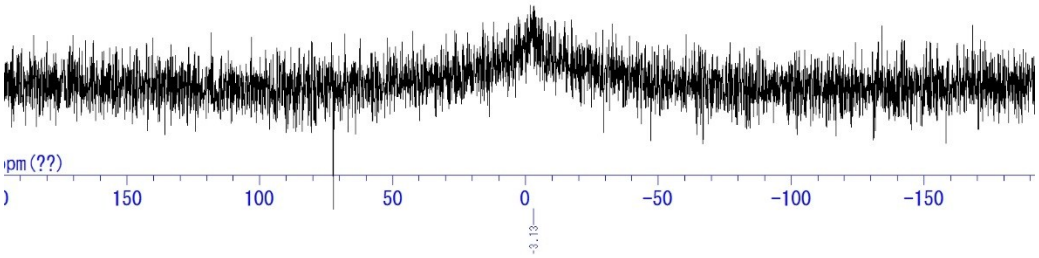

Chart S12. ^{11}B NMR spectrum of **PB2A** in $CDCl_3$.

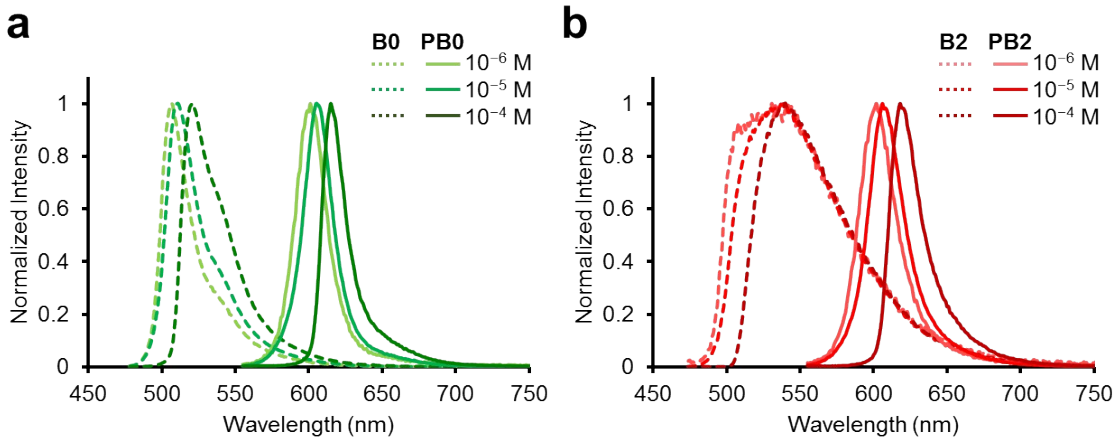

Figure S1. Photoluminescence spectra of the compounds and the polymers with various concentrations in chloroform with the excitation light at 540 nm.

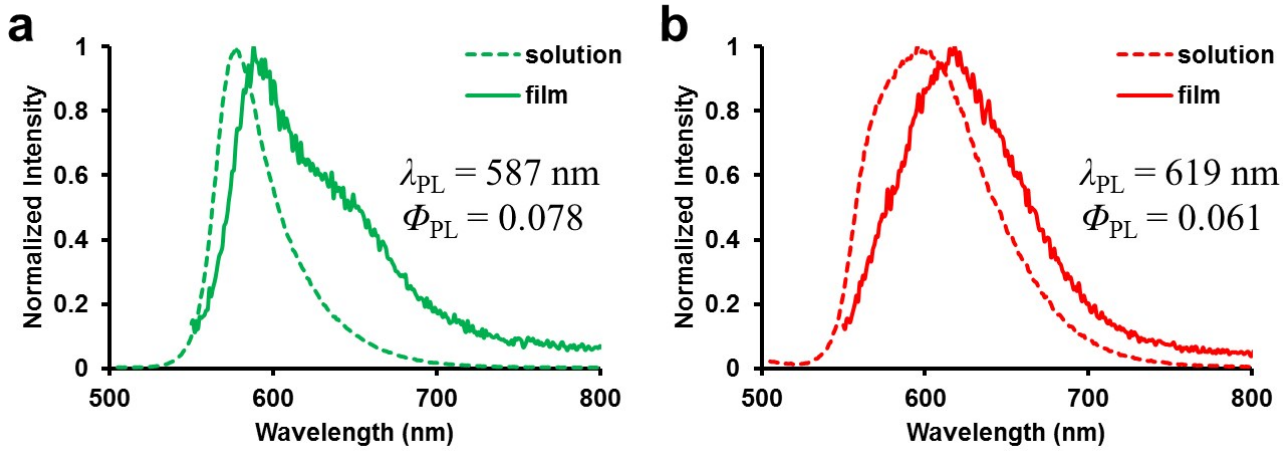

Figure S2. Photoluminescence spectra and luminescent data of (a) **PB0** and (b) **PB2** in the film state with the excitation light at 497 nm. The solution samples were obtained with 10^{-6} M concentration.

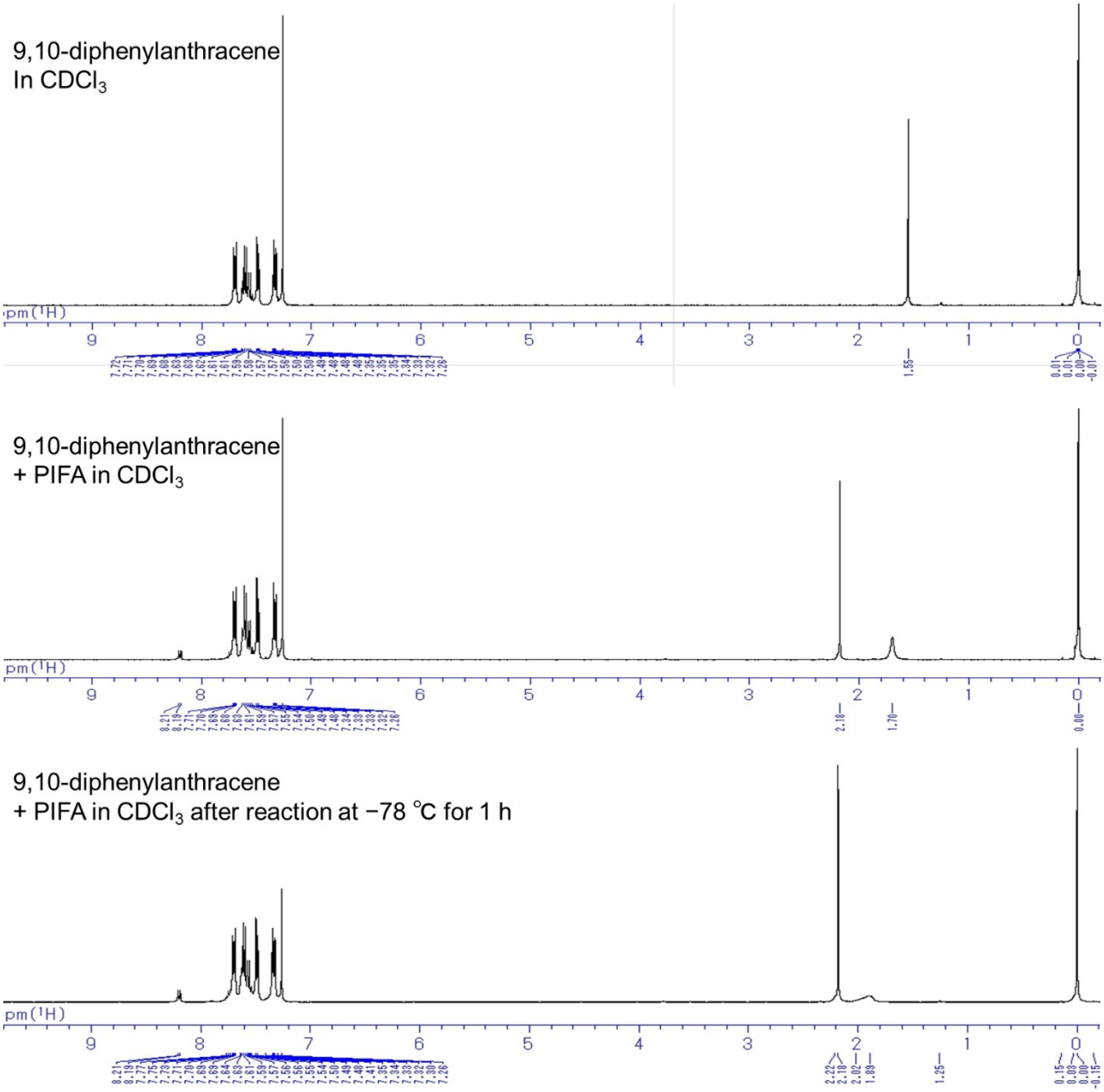

Figure S3. ^{1}H NMR spectra with the solutions containing 9,10-diphenylanthracene and PIFA before and after reactions at −78 °C for 1 h in $CDCl_3$.

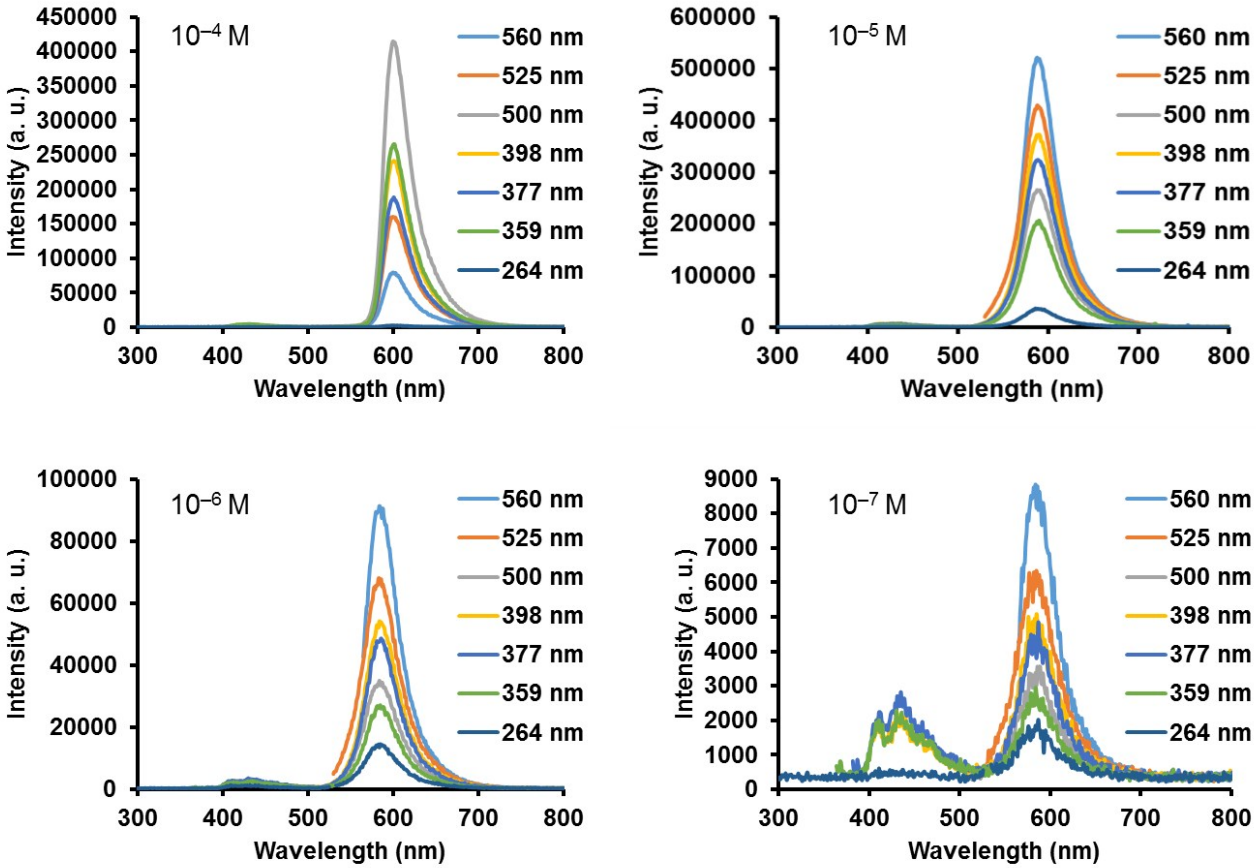

Figure S4. Photoluminescence spectra of **PB2A** with various concentrations and excitation wavelengths in chloroform.