Supporting Information for

Stimuli-Responsive Luminochromic Polymers Consisting of Multi-States Emissive Fused Boron Ketoiminate

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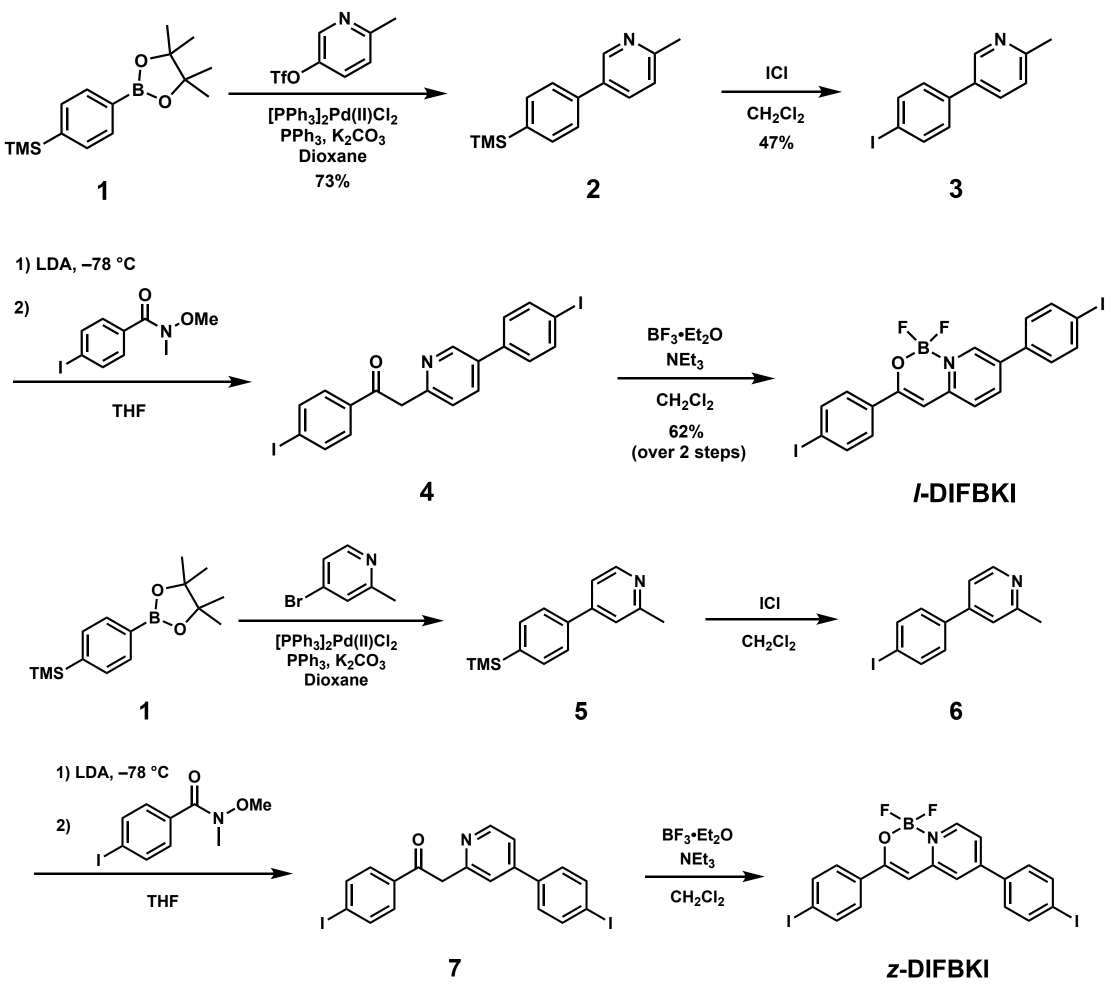
Experimental Section

General: ^{1}H (400 MHz), ^{11}B (128 MHz), and ^{13}C (100 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 $CDCl_3$, and ^{11}B NMR spectra were referenced externally to $BF_3{\cdot}OEt_2$ (sealed capillary). UV−vis absorption spectra were recorded on a SHIMADZU UV-3600 spectrophotometer. Photoluminescence (PL) spectra were measured with a HORIBA JOBIN YVON Fluoromax-4P spectrofluorometer, and photoluminescence quantum yields were calculated by the integrating sphere method. Fluorescence lifetime analyses were carried out on a Horiba FluoreCube spectrofluorometer system; excitation at 375 nm using a UV diode laser (NanoLED-375L). Elemental analysis was performed at the Microanalytical Center of Kyoto University. Cyclic voltammetry (CV) was carried out on a BASALS-Electrochemical-Analyzer Model 600D with a Pt working electrode, a Pt counter electrode, an Ag/Ag^{+} reference electrode, and the ferrocene/ferrocenium external reference at a scan rate of 10 mVs^{-1}. DSC thermograms were carried out on an SII DSC 6220 instrument. The sample on the aluminum pan was heated at the rate of 10 °C/min under nitrogen flowing (50 mL/min). Dynamic light scattering (DLS) was conducted on a FPAR-1000 (Otsuka Electronics Co., Ltd., Japan) to measure the diameters of the PFBT assemblies. The measurements were performed in THF or $CHCl_3$. The diameters were measured with cumulant fits of the correlograms obtained from scattered light intensity. Powder X-ray diffraction (XRD) patterns were taken by using CuKα radiation with Rigaku Miniflex.



Scheme S1. Syntheses of monomers.

Synthesis of 2: A mixture of 2-methyl-5-[(trifluoromethyl)sulfonyloxy]pyridine dried *in vacuo* overnight (0.73 g, 0.41 mL, 3.02 mmol), **1** (1.00 g, 3.62 mmol), $PdCl_2(PPh_3)_2$ (21.2 mg, 0.03 mmol), PPh_3 (15.8 mg, 0.06 mmol) and K_2CO_3 (2.08 g, 15.1 mmol) was placed in a round-bottom flask under Ar atmosphere. To this mixture was added dioxane (5.5 mL), and the solution was stirred at 100 °C for 24 h. The solution was filtrated with celite under suction and extracted with AcOEt (3 × 100 mL). The combined organic layers were washed with water and brine and dried over $MgSO_4$. After filtration, the solvent was removed with a rotary evaporator. The residue was subjected to column chromatography on SiO_2 with chloroform as an eluent. The solvent was evaporated, and **2** (0.53 g, 2.21 mmol, 73%) was obtained as a white solid. $R_f = 0.30$ (chloroform); ^1H NMR ($CDCl_3$, 400 MHz) δ = 8.73 (d, J = 2.4 Hz, 1H), 7.78 (dd, J = 2.4, 8.0 Hz, 1H), 7.63 (d, J = 8.3 Hz, 2H), 7.56 (d, J = 8.3 Hz, 2H), 7.22 (d, J = 8.1 Hz, 1H), 2.60 (s, 3H), 0.30 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 157.3, 147.5, 140.0, 138.3, 134.7, 134.0, 133.7, 126.3, 123.2, 24.1, –1.15 ppm. HRMS (ESI) calcd for $C_{15}H_{20}N_1Si_1$ $[M + H]^+$ 242.1360, found

242.1354.

Synthesis of 3: A CH_2Cl_2 solution (16 mL) of **3** (0.50 g, 2.1 mmol) was cooled to 0 °C under Ar atmosphere. To this stirred solution was added dropwise iodine chloride (1.0 M in CH_2Cl_2, 4.6 mL, 4.6 mmol) by a syringe, and the solution was allowed to warm to room temperature. After the mixture was stirred overnight, the reaction was quenched by 2 M $NaHSO_3$ aq (300 mL). The organic layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with water and brine and dried over $MgSO_4$. After filtration, the solvent was removed *in vacuo*. The residue was subjected to column chromatography on SiO_2 with AcOEt and hexane (v/v = 1/2) as an eluent. The solvent was removed *in vacuo*, and **3** (0.29 g, 0.97 mmol, 47%) was obtained as a white solid. $R_f = 0.35$ (hexane/AcOEt, v/v = 1:2); ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 8.69$ (d, $J = 2.2$ Hz, 1H), 7.79 (d, $J = 8.6$ Hz, 2H), 7.73 (dd, $J = 2.4, 8.0$ Hz, 1H), 7.29 (d, $J = 8.5$ Hz, 2H), 7.22 (d, $J = 8.0$ Hz, 1H), 2.60 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 157.8$, 147.3, 138.1, 137.5, 134.4, 132.7, 128.7, 123.2, 93.6, 24.2 ppm. HRMS (ESI) calcd for $C_{12}H_{11}I_1N_1$ $[M + H]^+$ 295.9931, found 295.9923.

Synthesis of *l*-DIFBKI: A solution of **3** (0.28 g, 0.95 mmol) in THF (3.2 mL) was cooled to –78 °C under Ar atmosphere. To this stirred solution was added dropwise lithium diisopropylamide (1.1 M in THF, 0.83 mL, 0.95 mmol) by a syringe. After the mixture was stirred for 1 h, *N*-methyl-*N*-methoxy-4-iodobenzamide (2.2 mL, 0.87 mmol) was added to the solution dropwise by a syringe. After stirring for 3 h, the reaction was quenched by pouring water (30 mL). The mixture was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with water and brine and dried over $MgSO_4$. After filtration, the solvent was removed with a rotary evaporator. The residue was purified by reprecipitation from chloroform and methanol. The solvent was removed *in vacuo*, and a yellow solid was obtained. The solid was used to the next step without further purification.

To a solution of the solid in CH_2Cl_2 (13 mL) was added NEt_3 (1.3 mL) by a syringe under Ar atmosphere. $BF_3{\cdot}Et_2O$ (1.1 mL, 8.7 mmol) was added dropwise by a syringe and then the mixture was heated to 60 °C. After stirring for 16 h, the reaction was quenched by addition of methanol (50 mL). After filtration, Recrystallization of the precipitate from $CHCl_3$ afforded *l*-DIFBKI (0.31 g, 62%) as a yellow crystal. ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta =$ 8.64 (s, 1H), 8.10 (dd, $J = 2.2, 8.8$ Hz, 1H), 7.86 (d, $J = 8.3$ Hz, 2H), 7.80 (d, $J = 8.6$ Hz, 2H), 7.68 (d, $J = 8.6$ Hz, 2H), 7.40 (d, $J = 8.5$ Hz, 1H), 7.33 (d, $J = 8.6$ Hz, 2H), 6.42 (s, 1H) ppm. ^{13}C NMR (C_4D_8O, 100 MHz) $\delta = 162.1$, 151.0, 140.3, 139.2, 138.5, 138.4, 135.7, 135.1, 134.0, 129.2, 128.6, 123.6, 97.8, 95.5, 93.8 ppm. ^{11}B NMR ($CDCl_3$, 128 MHz) $\delta = 1.47$ ppm. HRMS (ESI) calcd for $C_{19}H_{12}B_1F_2I_2N_1O_1$ $[M + Na]^+$ 595.8962, found 595.8950.

Synthesis of 6: Compound **5** was prepared from 4-bromo-2-methylpyridine (1.60 g, 9.30 mmol), **1** (2.83 g, 10.2 mmol), $PdCl_2(PPh_3)_2$ (130 mg, 0.19 mmol), PPh_3 (97.6 mg, 0.37 mmol) and K_2CO_3 (6.43 g, 46.5 mmol) in dioxane (30 mL) according to the same method with **2**. Yellow oil was obtained and used to the next reaction without further purification.

Compound **6** was prepared from **5** (2.25g 9.30 mmol) and iodine chloride (1.0 M in CH_2Cl_2, 20.5 mL, 20.5 mmol) in 76% after purification (2.09 g, white crystal). ^1H NMR ($CDCl_3$, 400 MHz) δ = 8.55 (d, *J* = 5.2 Hz, 1H), 7.82 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.33 (s, 1H), 7.28 (d, *J* = 1.6 Hz, 1H), 2.63 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 157.8, 147.3, 138.1, 137.5, 134.4, 132.7, 128.8, 123.2, 93.6, 24.2 ppm. HRMS (ESI) calcd for $C_{12}H_{11}I_1N_1$ $[M + H]^+$ 295.9931, found 259.9919.

Synthesis of *z*-DIFBKI: Compound **7** was prepared from **6** (1.20 g, 4.07 mmol), LDA (1.13 M, 3.60 mL, 4.07 mmol), *N*-methyl-*N*-methoxy-4-iodobenzamide (1.08 g, 3.70 mmol) in 90% crude yield (1.76 g, orange solid) according to the same method with **4**.

z-DIFBKIB was prepared from 7 (1.50 g, 2.86 mmol) and $BF_3{\cdot}Et_2O$ (5.29 mL, 42.8 mmol) in NEt_3/CH_2Cl_2 (4 mL/40 mL) as solvent. After silica gel chromatography eluted with hexane: AcOEt (2: 3) and recrystallization, *z*-DIFBKI was obtained as a yellow crystal (1.37 g, 84%). ^1H NMR ($CDCl_3$, 400 MHz) δ = 8.46 (d, *J* = 6.6 Hz, 1H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.80 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 6.7 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 2H), 6.41 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 162.3, 152.7, 151.7, 140.5, 138.8, 137.8, 135.4, 133.8, 128.7, 128.0, 119.3, 118.2, 97.7, 97.6, 93.5 ppm. ^{11}B NMR ($CDCl_3$, 128 MHz) δ = 1.37 ppm.HRMS (ESI) calcd for $C_{19}H_{12}$ $B_1F_2I_2N_1O_1$ $[M + Cl]^-$ 607.8763, found 607.8762.

Synthesis of *l*-PF: A mixture of *l*-DIFBKI (40 mg, 70 μmol), 2,2'-(2-(perfluorooctyl)-5-(trifluoromethyl)-1,4-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (57 mg, 70 μmol), APhos Pd G3 (4.4 mg, 7.0 μmol) and Cs_2CO_3 (0.23 g, 0.70 mmol) was placed in a round-bottom flask under Ar. To this mixture was added toluene (3 mL) and water (3 mL), and the solution was stirred at 80 °C for 24 h. The organic phase was extracted with $CHCl_3$. The combined organic layers were precipitated with methanol. The crude was purified by flash column chromatography on SiO_2 (THF as an eluent), then precipitated into MeOH and *l*-PF (26.8 mg, 44%) was obtained as a yellow solid. ^1H NMR (C_4D_8O, 400 MHz) δ = 8.84 (s, 1H), 8.45 (s, 1H), 8.10 (m, 2H), 7.90–7.80 (br, 4H), 7.70–7.26 (br, 5H), 6.79 (s, 1H) ppm. ^{13}C NMR (C_4D_8O, 100 MHz) δ = 162.30, 162.28, 151.10, 151.07, 142.9, 140.6, 138.7, 138.6, 136.5, 135.7, 134.2, 132.9, 131.7, 131.6, 130.9, 130.7, 130.5, 130.0, 129.8, 127.3, 127.0, 126.8, 126.6, 126.2, 125.5, 123.6, 122.73, 122.70, 94.1, 93.9 ppm. ^{11}B NMR (C_4D_8O, 128 MHz) δ = 1.57 ppm. M_n =

9,400 g/mol, PDI: 2.0, DP: 11.

Synthesis of *l*-PO: A mixture of *l*-DIFBKI (30 mg, 52 μmol), 2,2'-(2,5-bis(dodecyloxy)-1,4-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (37 mg, 52 μmol), APhos Pd G3 (3.3 mg, 5.2 μmol) and Cs_2CO_3 (0.17 g, 0.70 mmol) was placed in a Schlenk flask under Ar atmosphere. To this mixture was added toluene (2.5 mL) and water (2 mL), and the solution was stirred at 80 °C for 12 h. The organic phase was extracted with $CHCl_3$. The combined organic layers were precipitated with methanol. The crude was purified by flash column chromatography on SiO_2 ($CHCl_3$ as an eluent), then precipitated into methanol and *l*-PO (34.8 mg, 87%) was obtained as a yellow solid. ^{1}H NMR (C_4D_8O, 400 MHz) δ = 8.72 (s, 1H), 8.33 (s, 1H), 7.98 (s, 2H), 7.75–7.52 (br, 6H), 7.08 (s, 2H), 6.85 (m, 1H), 6.66 (s, 1H), 3.95 (m, 4H), 1.22 (m, 40H), 0.81 (d, *J* = 6.5 Hz, 6H) ppm. ^{13}C NMR (C_4D_8O, 100 MHz) δ = 163.7, 152.43, 152.41, 152.4, 141.1, 139.2, 139.1, 135.8, 135.4, 135.0 132.1, 132.0, 131.2, 127.7, 127.6, 127.5, 124.4, 117.7, 117.66, 94.4, 71.2, 34.2, 33.7, 31.8, 31.4, 31.2, 31.1, 28.0, 27.9, 27.8, 26.7, 24.3, 15.2 ppm. ^{11}B NMR (C_4D_8O, 128 MHz) δ = 1.56 ppm. M_n: 9,200 g/mol; PDI: 3.4; DP: 12.

Synthesis of *l*-PFL: A mixture of *l*-DIFBKI (30 mg, 52 μmol), 2,2'-(9,9-didodecyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (40 mg, 52 μmol), APhos Pd G3 (3.3 mg, 5.2 μmol) and Cs_2CO_3 (0.17 g, 0.70 mmol) was placed in a Schlenk flask under Ar atmosphere. To this mixture was added toluene (2.5 mL) and water (2 mL), and the solution was stirred at 80 °C for 12 h. The organic phase was extracted with $CHCl_3$. The combined organic layers were precipitated with methanol. The crude was purified by flash column chromatography on SiO_2 ($CHCl_3$ as an eluent), then precipitated into MeOH and *l*-PFL (9.7 mg, 23%) was obtained as a yellow solid. ^{1}H NMR (C_4D_8O, 400 MHz) δ = 8.81 (s, 1H), 8.39 (s, 1H), 8.08 (s, 2H), 7.99–6.98 (br, 13H), 6.72 (s, 1H), 1.51–0.743 (m, 50H) ppm. ^{13}C NMR (C_4D_8O, 100 MHz) δ = 162.7, 152.7, 152.5, 150.9, 144.3, 142.6, 141.8, 141.5, 140.1, 140.0, 139.9, 138.0, 134.7, 134.1, 129.4, 128.6, 128.5, 128.1, 127.6, 127.4, 126.7, 126.6, 123.5, 121.9, 121.2, 121.0, 93.5, 84.1, 56.1, 55.8, 41.0, 40.8, 32.6, 30.7, 30.3, 30.0, 29.5, 23.3, 14.3, 14.2 ppm. ^{11}B NMR (C_4D_8O, 128 MHz) δ = 1.61 ppm. M_n: 9,900 g/mol; PDI: 2.7; DP: 12.

Synthesis of *l*-PBT: A mixture of *l*-DIFBKI (30 mg, 52 μmol), 2,2'-(3,3'-didodecyl-[2,2'-bithiophene]-5,5'-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (40 mg, 52 μmol), APhos Pd G3 (3.3 mg, 5.2 μmol) and Cs_2CO_3 (0.17 g, 0.70 mmol) was placed in a Schlenk flask under Ar atmosphere. To this mixture was added toluene (2.5 mL) and water (2 mL), and the solution was stirred at 80 °C for 12 h. The organic phase was extracted with $CHCl_3$. The combined organic layers were precipitated with methanol. The crude was purified by flash column chromatography on SiO_2 ($CHCl_3$ as an eluent), then precipitated into methanol and *l*-PBT (34.8 mg, 87%) was obtained as a red solid. ^1H NMR (C_4D_8O, 400 MHz) δ = 8.76 (s, 1H), 8.48–6.80 (br, 12H), 6.79–6.00 (br, 1H), 2.61 (s, 4H), 1.62–1.00 (br, 40H), 0.88 (s, 6H) ppm. ^{13}C NMR (C_4D_8O, 100 MHz) δ = 161.4, 150.2, 149.7, 143.9, 143.0, 142.4, 139.3, 139.0, 137.5, 137.1, 136.2, 134.6, 131.7, 130.6, 128.9, 128.5, 126.9, 126.0, 125.7, 125.1, 122.7, 93.5, 84.1, 32.0, 30.8, 30.7, 29.8, 29.7, 29.6, 19.4, 29.2, 28.8, 22.7, 13.5 ppm. ^{11}B NMR ($CDCl_3$, 128 MHz) δ = 1.47 ppm. M_n: 9,300 g/mol; PDI: 4.2; DP: 11.

Synthesis of *z*-PF: A mixture of *z*-DIFBKI (30 mg, 52.4 μmol), 2,2'-(2-(perfluorooctyl)-5-(trifluoromethyl)-1,4-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (42.7 mg, 5.24 μmol), APhos Pd G3 (3.33 mg, 5.24 μmol) and Cs_2CO_3 (0.17 g, 52.4 mmol) was placed in a round-bottom flask under Ar atmosphere. To this mixture was added toluene (3 mL) and water (3 mL), and the solution was stirred at 80 °C for 24 h. The organic phase was extracted with $CHCl_3$. The combined organic layers were precipitated with methanol. The crude was purified by flash column chromatography on SiO_2 (THF as an eluent), then precipitated into MeOH and *z*-PF (44.5 mg, 96%) was obtained as a yellow solid. ^1H NMR ($CDCl_3$, 400 MHz) δ = 8.56 (s, 1H), 8.10 (d, J = 18.0 Hz, 2H), 7.82 (d, J = 18.0 Hz, 2H), 7.74 (dd, J = 7.3, 13.5 Hz, 2H), 7.61 (m, 3H), 7.55–7.50 (br, 2H), 7.44 (d, J = 6.5 Hz, 1H), 6.57 (s, 1H) ppm. ^{13}C NMR (C_4D_8O, 100 MHz) δ = 161.7, 152.6, 151.9, 140.8, 140.6, 140.3, 132.3, 131.1, 130.9, 130.3, 130.0, 129.4, 127.4, 126.8, 126.2, 125.6, 124.8, 122.1, 119.8, 93.7, 77.2 ppm. ^{11}B NMR ($CDCl_3$, 128 MHz) δ = 1.37 ppm. M_n: 9,500 g/mol; PDI: 2.2; DP: 11.

Synthesis of *z*-PO: A mixture of *z*-DIFBKI (30 mg, 52.4 μmol), 2,2'-(2,5-bis(dodecyloxy)-1,4-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (36.6 mg, 5.24 μmol), APhos Pd G3 (3.33 mg, 5.24 μmol) and Cs_2CO_3 (0.17 g, 52.4 mmol) was placed in a round-bottom flask under Ar atmosphere. To this mixture was added toluene (3 mL) and water (3 mL), and the solution was stirred at 80 °C for 24 h. The organic phase was extracted with $CHCl_3$. The combined organic layers were precipitated with methanol. The crude was purified by flash column chromatography on SiO_2 (THF as an eluent), then precipitated into MeOH and *z*-PO (34.3 mg, 86%) was obtained as a yellow solid. ^1H NMR ($CDCl_3$, 400 MHz) δ = 8.50 (s, 1H), 8.04 (dd, J = 3.9, 8.4 Hz, 2H), 7.82–7.72 (br, 6H), 7.57 (br, 2H), 7.07 (dd, J = 3.1, 8.2 Hz, 2H), 6.54 (s, 1H), 3.96 (m, 4H), 1.45–1.35 (br, 4H), 1.25 (s, 36H), 0.87 (m, 6H) ppm. ^{13}C NMR (C_4D_8O, 100 MHz) δ = 163.1, 153.5, 152.7, 152.1, 151.33, 151.31, 150.7, 151.0, 147.1, 141.9, 141.7, 140.9, 135.1, 134.1, 132.9, 131.4, 127.3, 126.5, 119.7, 116.6, 116.5, 93.7, 70.1, 33.2, 32.7, 30.8, 30.5, 30.4, 30.1, 30.0, 27.0, 26.9, 25.6, 23.3, 14.2 ppm. ^{11}B NMR (C_4D_8O, 128 MHz) δ = 1.47 ppm. M_n: 8,600 g/mol; PDI: 1.8; DP: 11.

Synthesis of *z*-PFL: A mixture of *z*-DIFBKI (30 mg, 52.4 μmol), 2,2'-(9,9-didodecyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (39.5 mg, 5.24 μmol), APhos Pd G3 (3.33 mg, 5.24 μmol) and Cs_2CO_3 (0.17 g, 52.4 mmol) was placed in a round-bottom flask under Ar atmosphere. To this mixture was added toluene (3 mL) and water (3 mL), and the solution was stirred at 80 °C for 24 h. The organic phase was extracted with $CHCl_3$. The combined organic layers were precipitated with methanol. The crude was purified by flash column chromatography on SiO_2 (THF as an eluent), then precipitated into MeOH and *z*-PFL (37.9 mg, 88%) was obtained as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.50 (br, 1H), 8.09 (t, J = 7.1 Hz, 2H), 7.90–7.42 (br, 14H), 6.54 (s, 1H), 2.07–2.03 (br, 4H), 1.27–1.05 (br, 40H), 0.84 (m, 6H) ppm. ^{13}C NMR (C_4D_8O, 100 MHz) δ = 162.9, 153.3, 152.8, 152.7, 152.6, 150.7, 144.4, 144.3, 141.0, 140.2, 135.5, 134.6, 134.4, 129.4, 128.6, 128.4, 127.6, 127.5, 126.9, 126.7, 122.0, 119.8, 119.7, 118.7, 93.9, 84.2, 84.1, 56.2, 55.9, 41.0, 32.6, 30.8, 30.7, 30.4, 30.3, 30.1, 30.0, 23.3, 14.2 ppm. ^{11}B NMR ($CDCl_3$, 128 MHz) δ = 1.37 ppm. M_n: 26,000 g/mol; PDI: 6.3; DP: 28.

Synthesis of *z*-PBT: A mixture of *z*-DIFBKI (30 mg, 52.4 μmol), 2,2'-(3,3'-didodecyl-[2,2'-bithiophene]-5,5'-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (39.5 mg, 5.24 μmol), APhos Pd G3 (3.33 mg, 5.24 μmol) and Cs_2CO_3 (0.17 g, 52.4 mmol) was placed in a round-bottom flask under Ar atmosphere. To this mixture was added toluene (3 mL) and water (3 mL), and the solution was stirred at 80 °C for 24 h. The organic phase was extracted with $CHCl_3$. The combined organic layers were precipitated with methanol. The crude was purified by flash column chromatography on SiO_2 (THF as an eluent), then precipitated into MeOH and *z*-PBT (42.0 mg, 98%) was obtained as a yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 8.46 (s, 1H), 7.97 (br, 2H), 7.80–7.67 (br, 6H), 7.52 (s, 1H), 7.35−7.29 (br, 3H), 6.47 (s, 1H), 2.60 (br, 4H), 1.64 (br, 4H), 1.24 (br, 36H), 0.87 (m, 6H) ppm. ^{13}C NMR (C_4D_8O, 100 MHz) δ = 162.4, 152.9, 152.6, 144.8, 144.7, 144.6, 143.3, 144.0, 137.3, 137.2, 137.0, 136.9, 134.6, 128.6, 127.6, 126.9, 126.8, 125.8, 119.7, 118.6, 94.0, 32.7, 31.4, 30.5, 30.4, 30.2, 30.1, 30.0, 29.8, 29.7, 23.3, 14.2 ppm. ^{11}B NMR ($CDCl_3$, 128 MHz) δ = 1.37 ppm. M_n: 14,000 g/mol; PDI: 4.2; DP: 18.

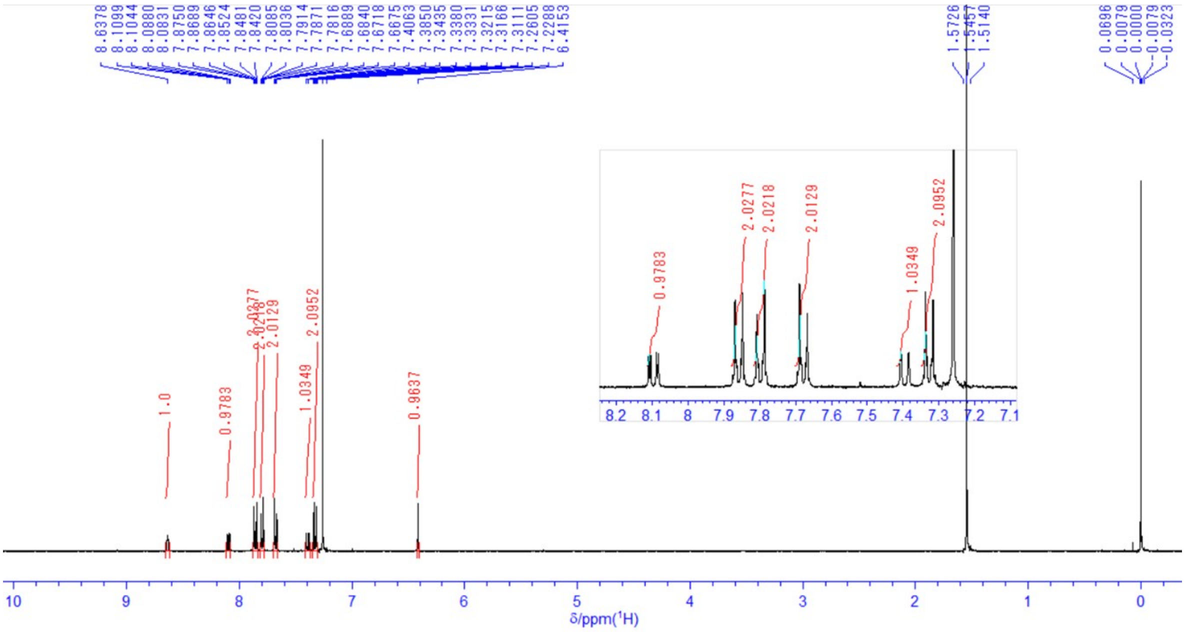


Chart S1. ^{1}H NMR spectrum of *l*-DIFBKI in $CDCl_3$.

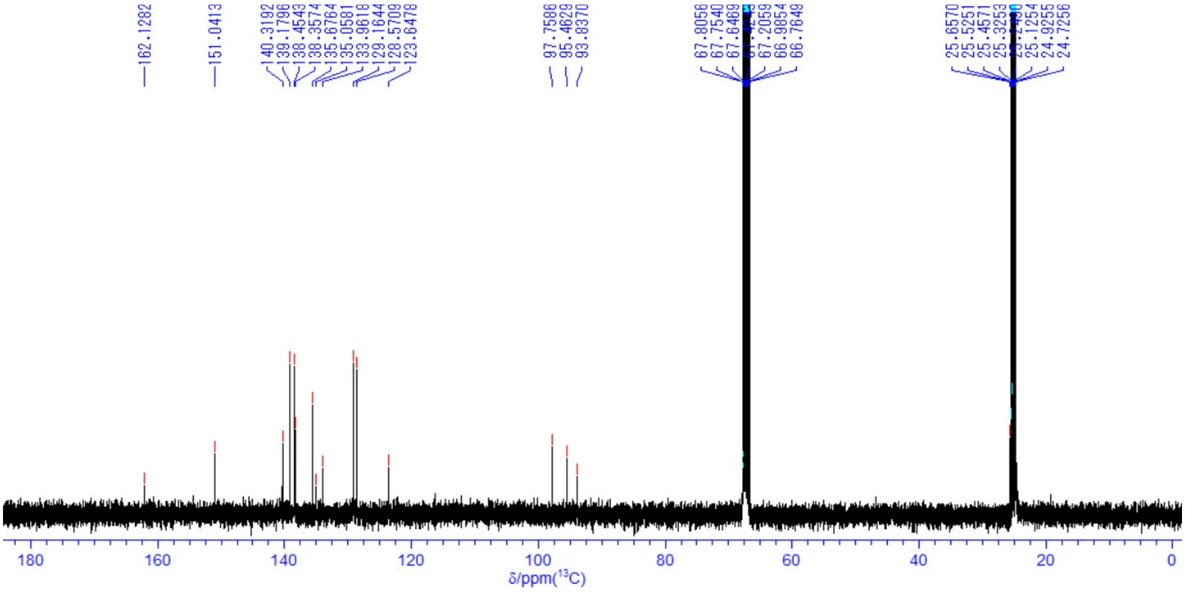


Chart S2. ^{13}C NMR spectrum of *l*-DIFBKI in C_4D_8O.

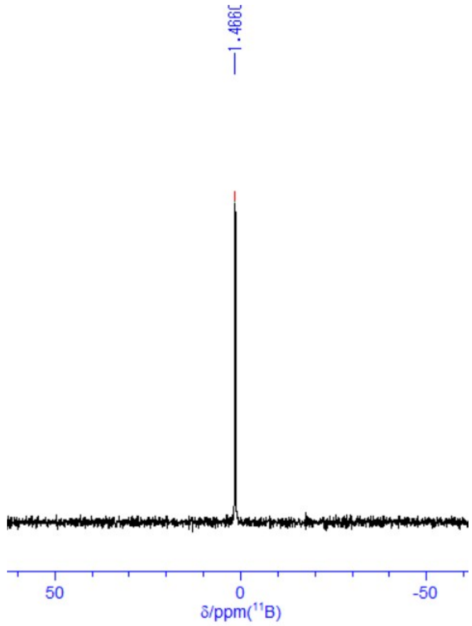


Chart S3. ^{11}B NMR spectrum of *l*-DIFBKI in $CDCl_3$.

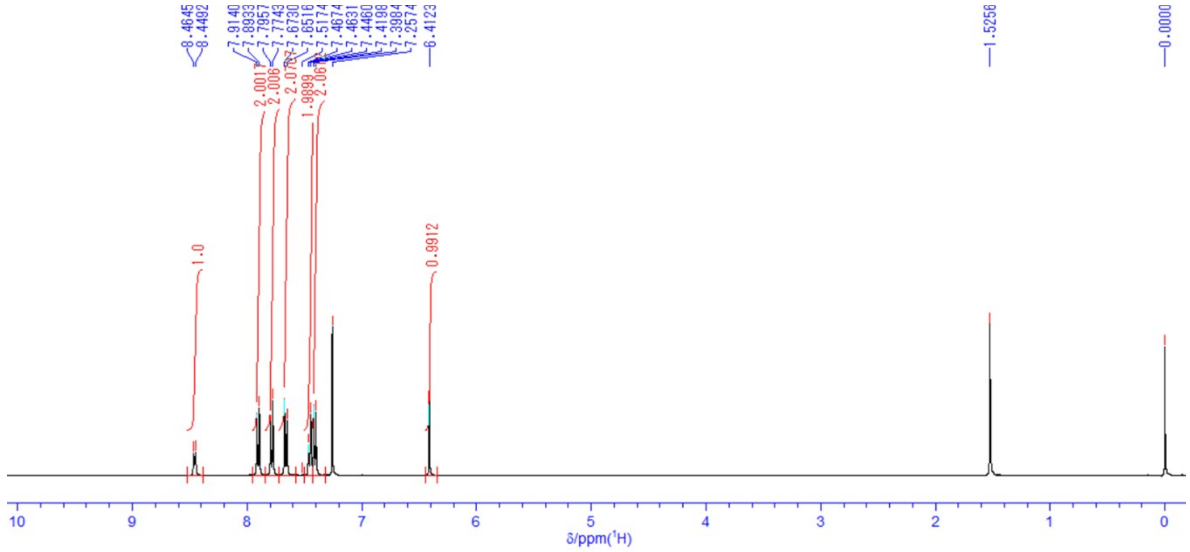


Chart S4. ^{1}H NMR spectrum of *z*-DIFBKI in $CDCl_3$.

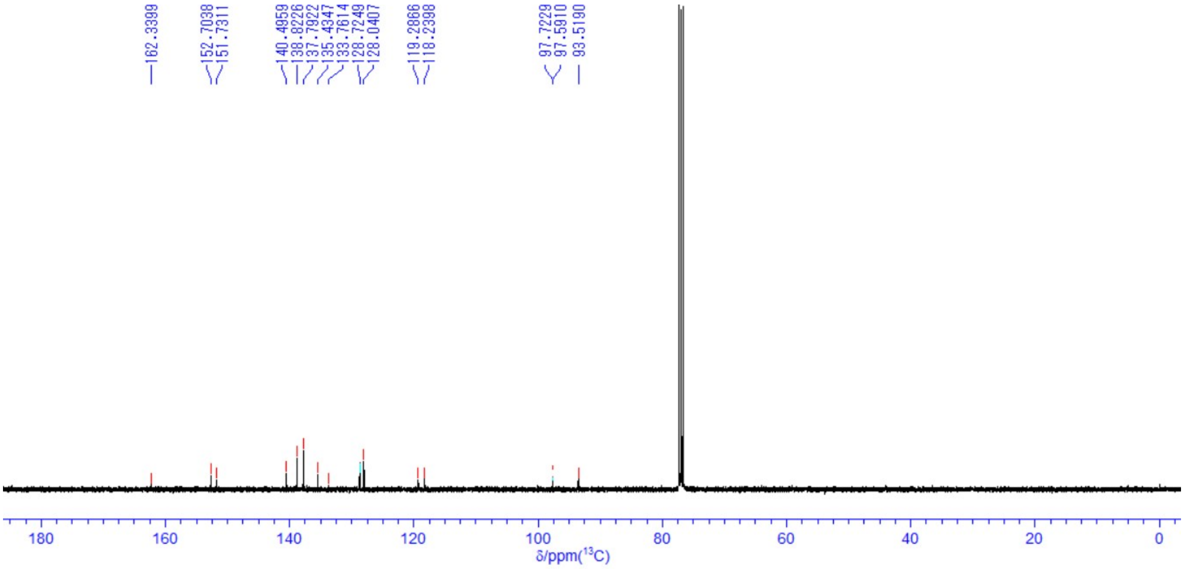


Chart S5. ^{13}C NMR spectrum of *z*-DIFBKI in CDCl$_3$.

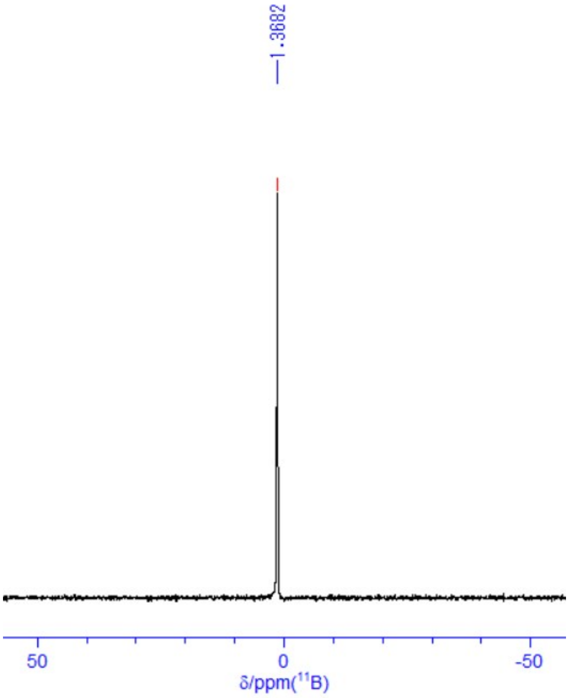


Chart S6. ^{11}B NMR spectrum of *z*-DIFBKI in CDCl$_3$.

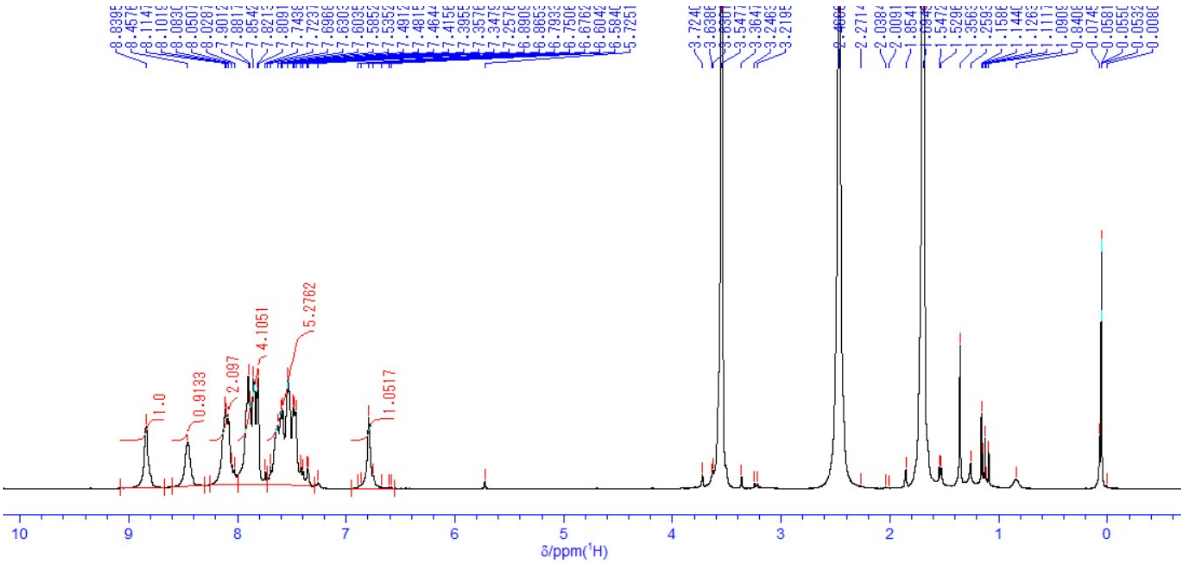


Chart S7. ^{1}H NMR spectrum of *l*-PF in C_4D_8O.

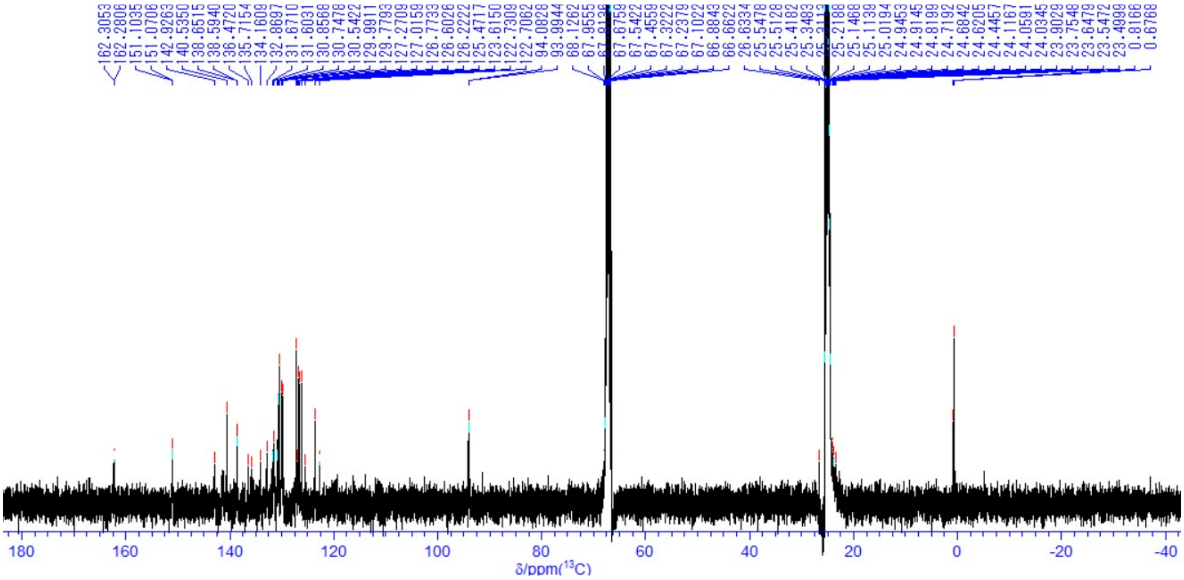


Chart S8. ^{13}C NMR spectrum of *l*-PF in C_4D_8O.

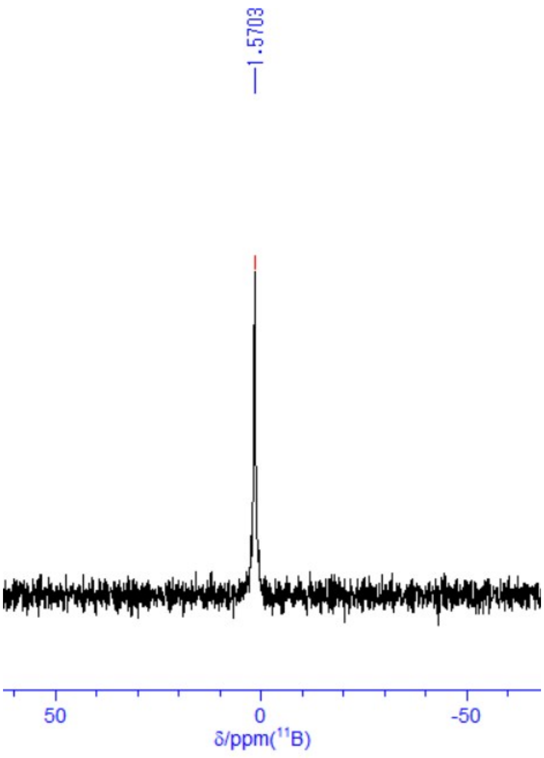


Chart S9. ^{11}B NMR spectrum of *l*-PF in C_4D_8O.

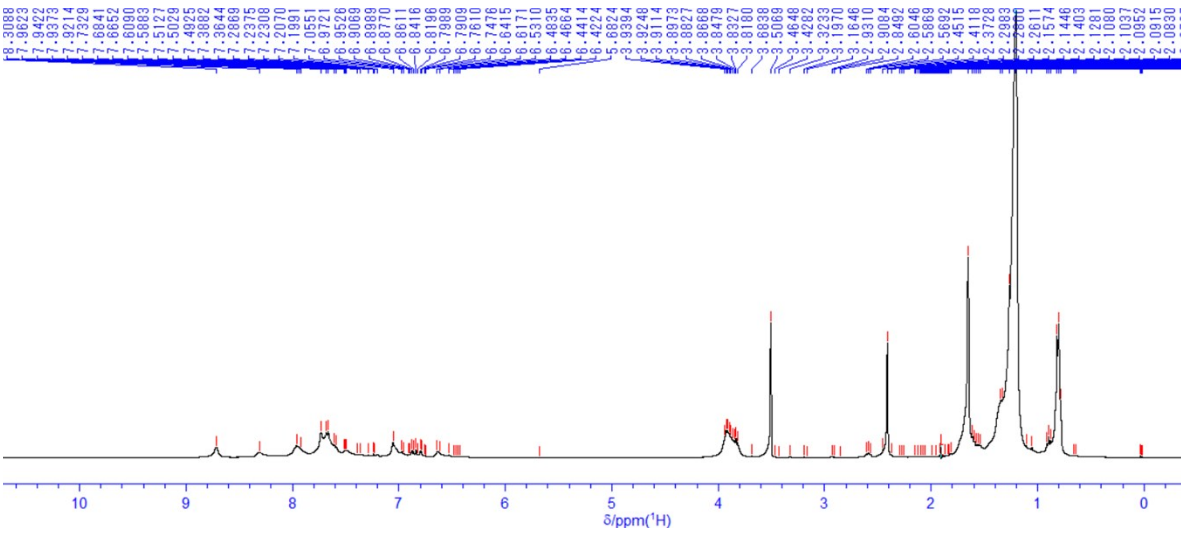


Chart S10. ^{1}H NMR spectrum of *l*-PO in C_4D_8O.

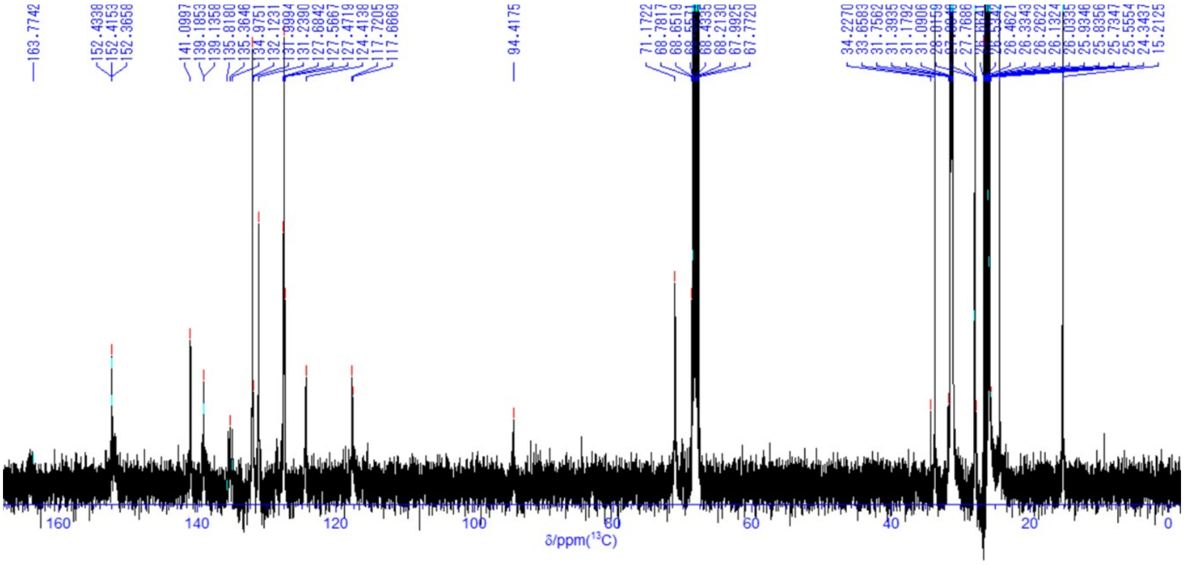


Chart S11. ^{13}C NMR spectrum of *l*-PO in C_4D_8O.

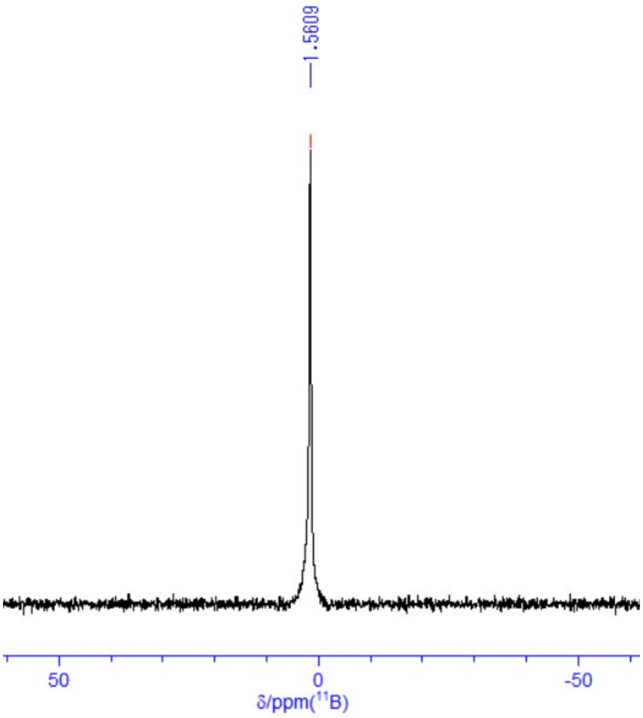


Chart S12. ^{11}B NMR spectrum of *l*-PO in C_4D_8O.

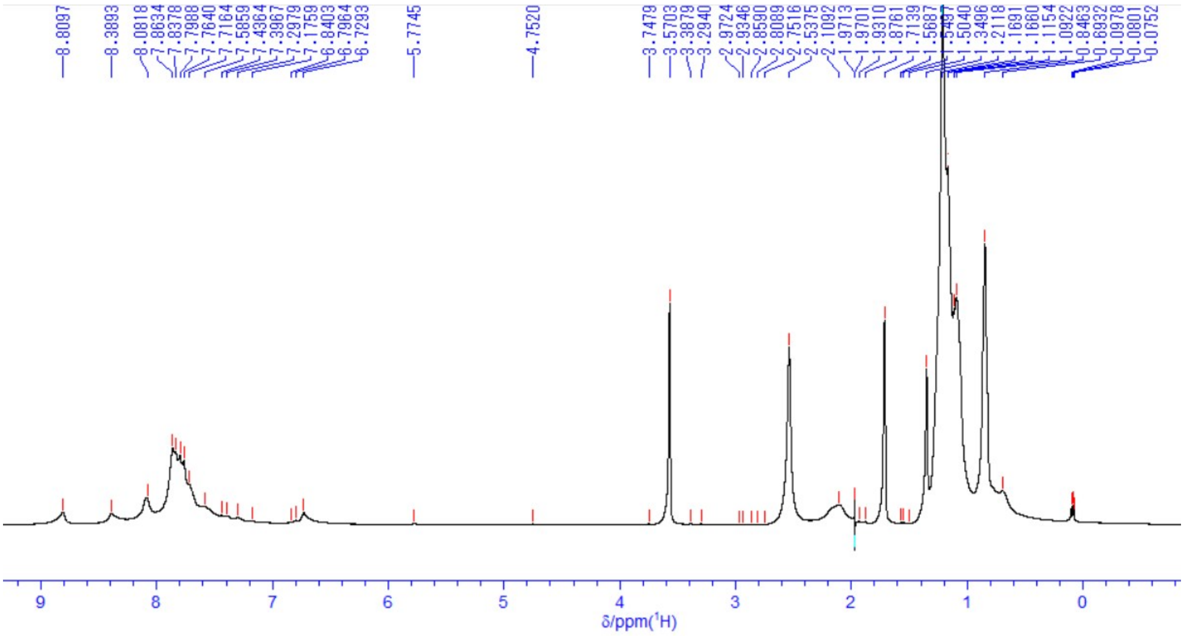


Chart S13. ^{1}H NMR spectrum of *l*-PFL in C_4D_8O.

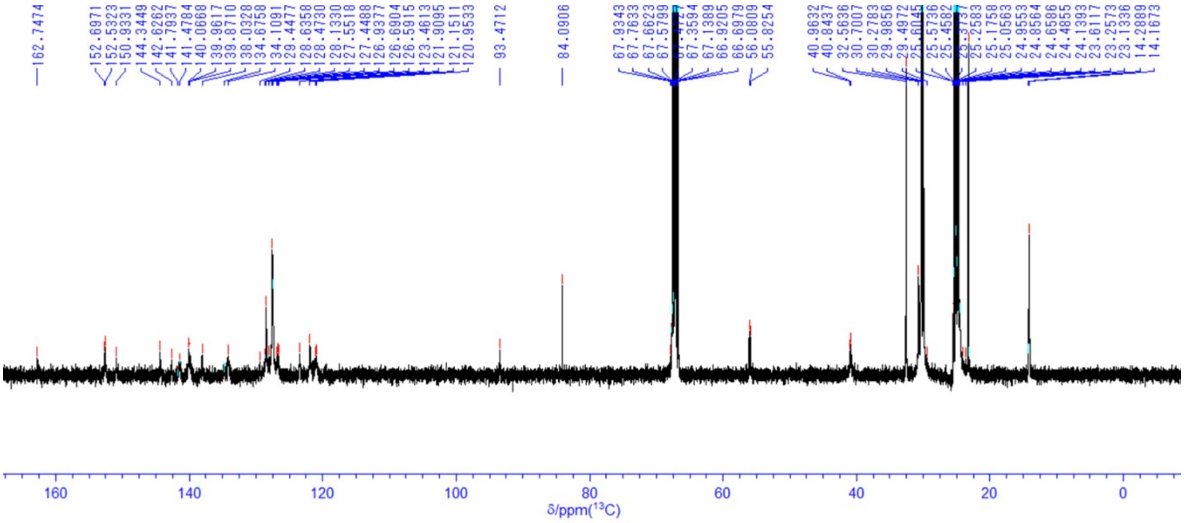


Chart S14. ^{13}C NMR spectrum of *l*-PFL in C_4D_8O.

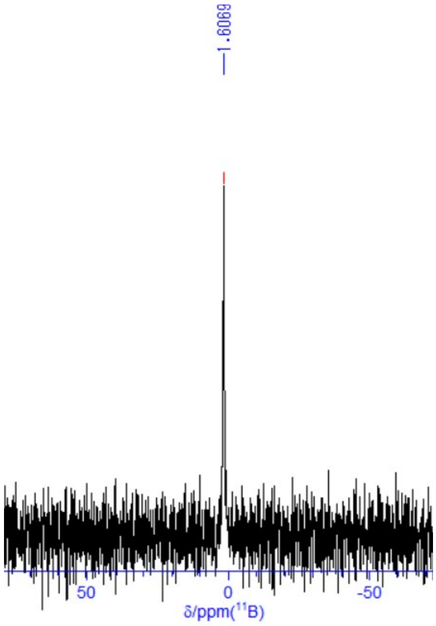


Chart S15. ^{11}B NMR spectrum of *l*-PFL in C_4D_8O.

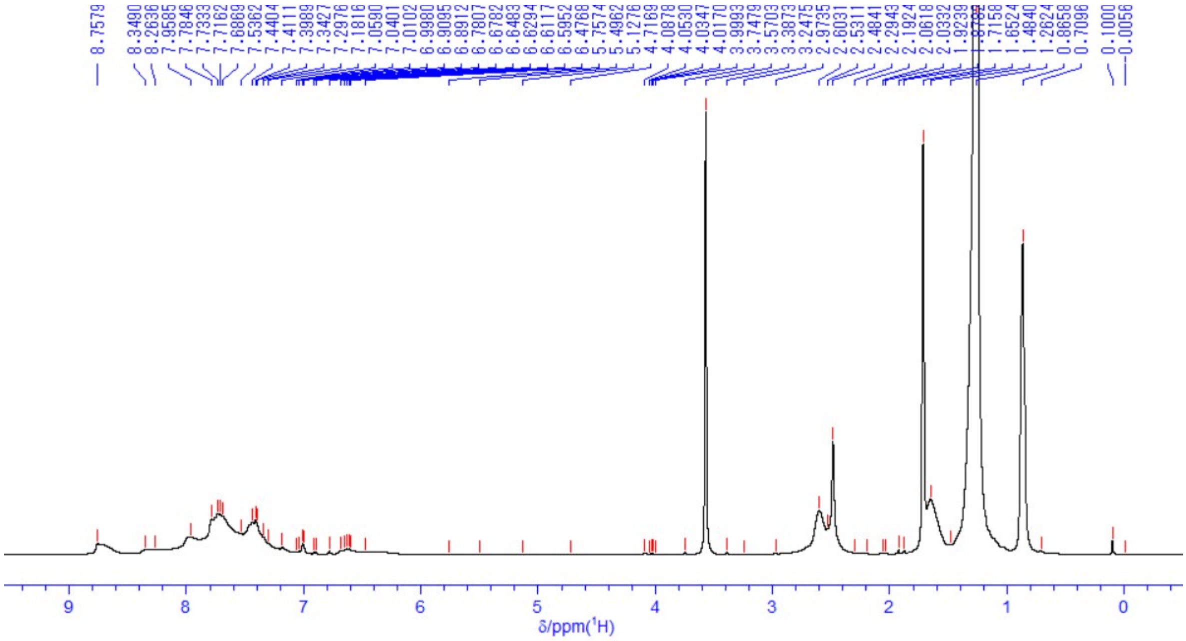


Chart S16. ^{1}H NMR spectrum of *l*-PBT in C_4D_8O.

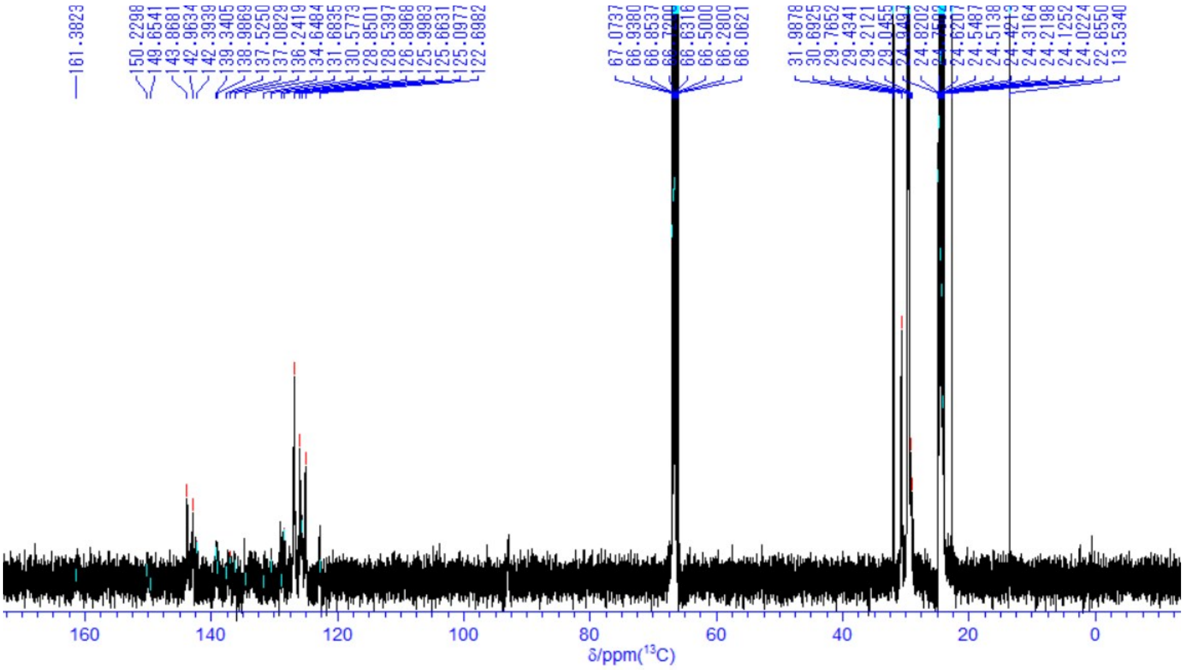


Chart S17. ^{13}C NMR spectrum of *l*-PBT in C_4D_8O.

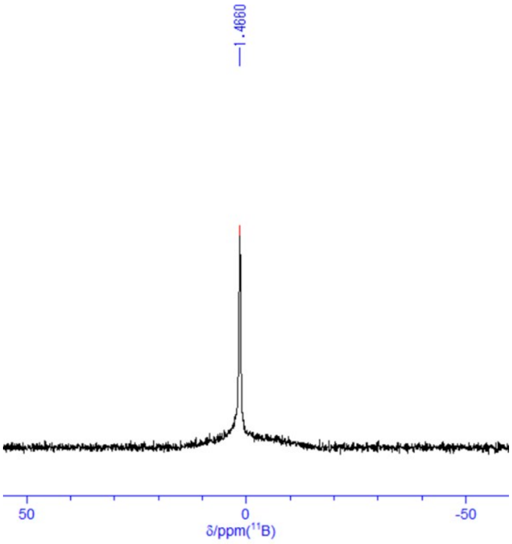


Chart S18. ^{11}B NMR spectrum of *l*-PBT in $CDCl_3$.

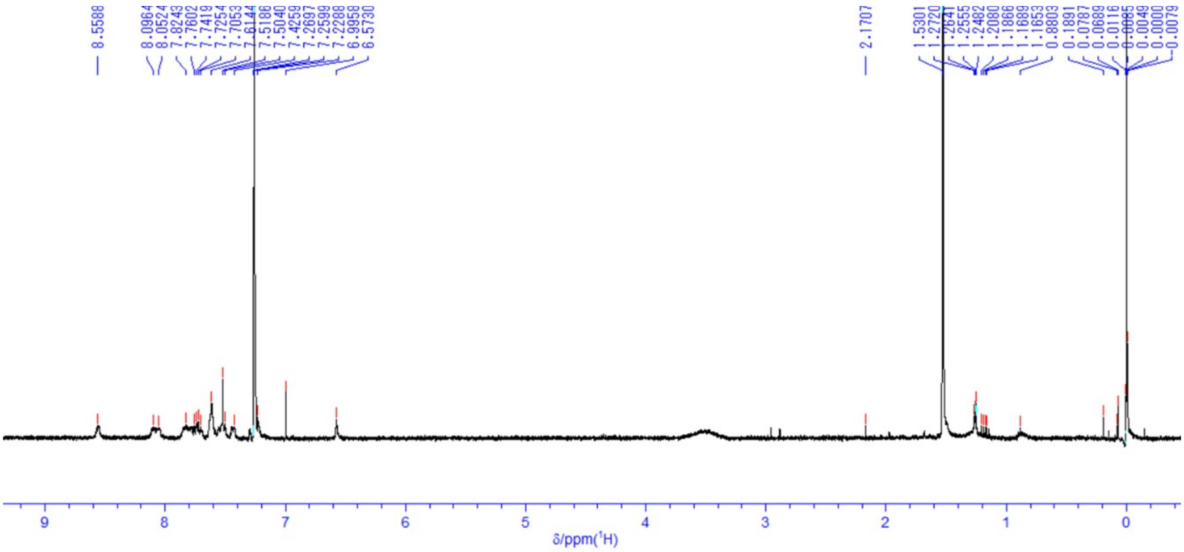


Chart S19. ^{1}H NMR spectrum of *z*-PF in $CDCl_3$.

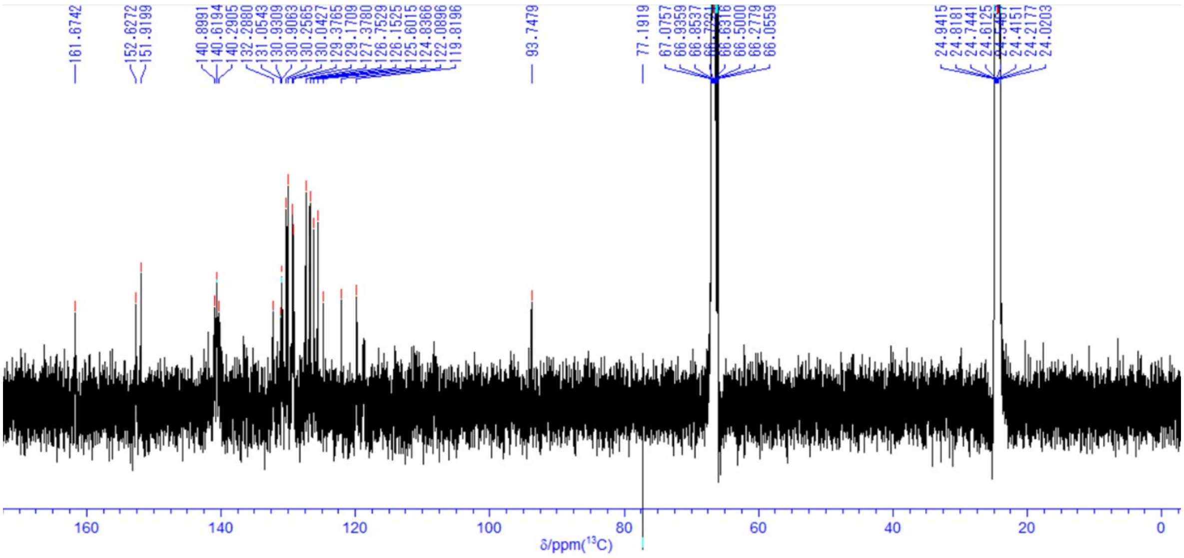


Chart S20. ^{13}C NMR spectrum of *z*-PF in C_4D_8O.

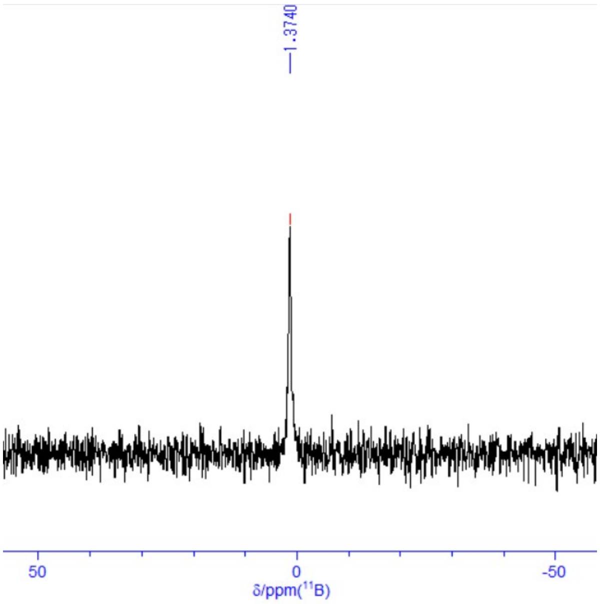


Chart S21. ^{11}B NMR spectrum of *z*-PF in $CDCl_3$.

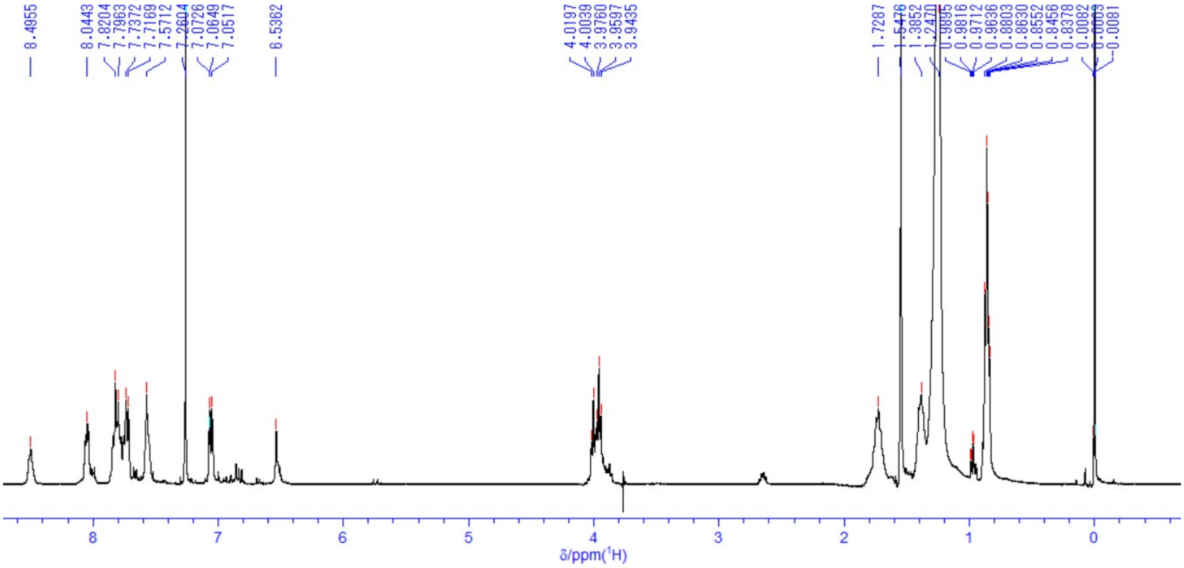


Chart S22. ^{1}H NMR spectrum of *z*-PO in $CDCl_3$.

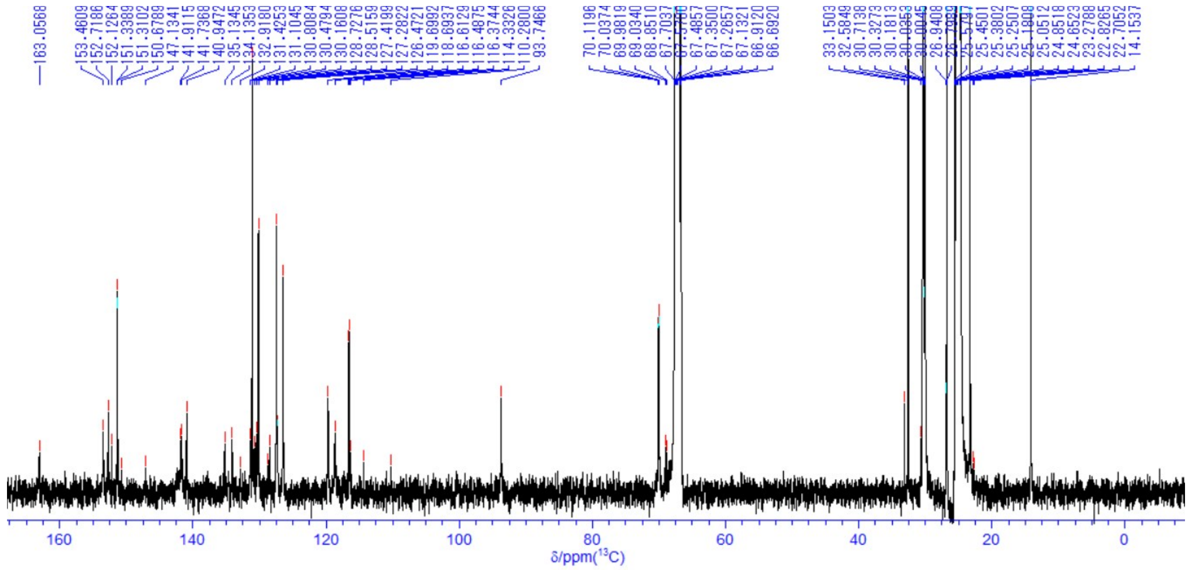


Chart S23. ^{13}C NMR spectrum of *z*-PO in C_4D_8O.

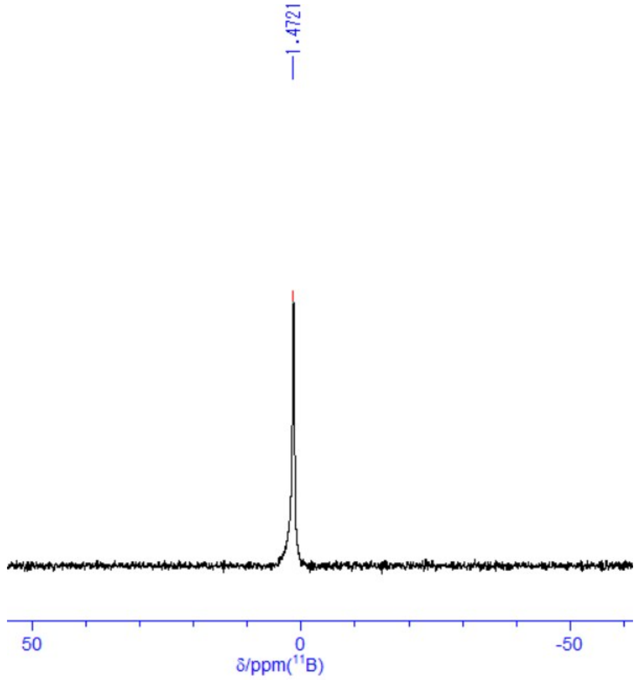


Chart S24. ^{11}B NMR spectrum of *z*-PO in C_4D_8O.

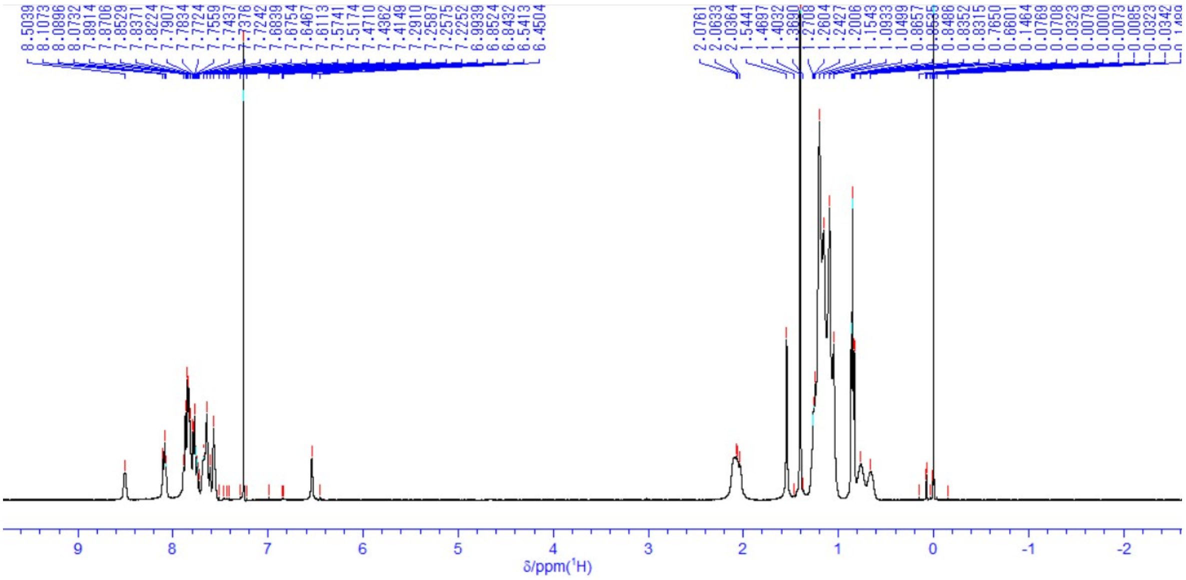


Chart S25. ^{1}H NMR spectrum of *z*-PFL in $CDCl_3$.

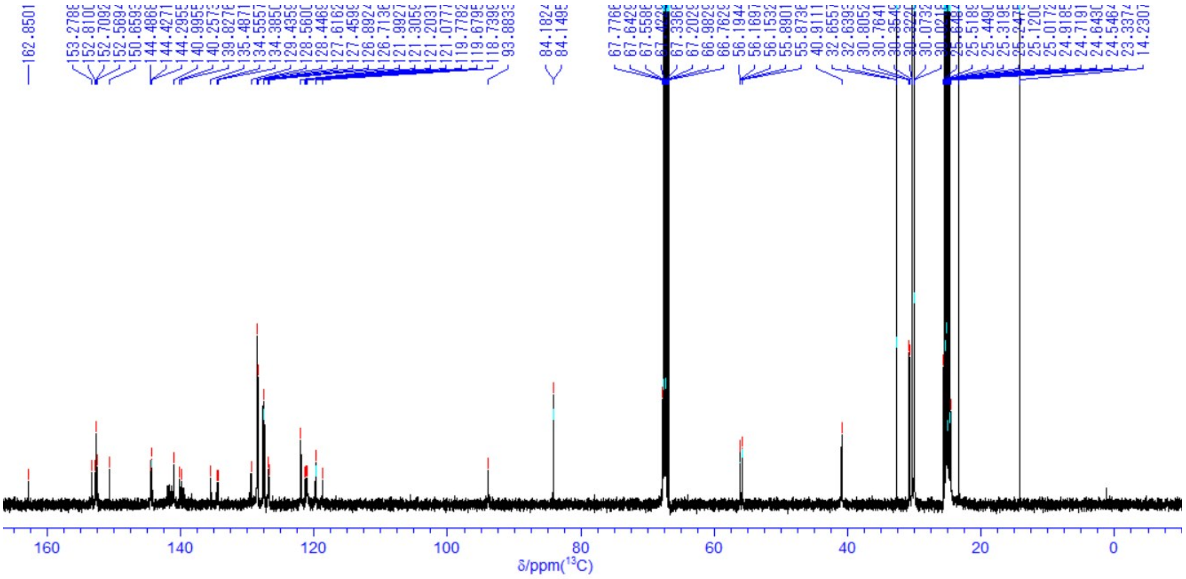


Chart S26. ^{13}C NMR spectrum of *z*-PFL in C_4D_8O.

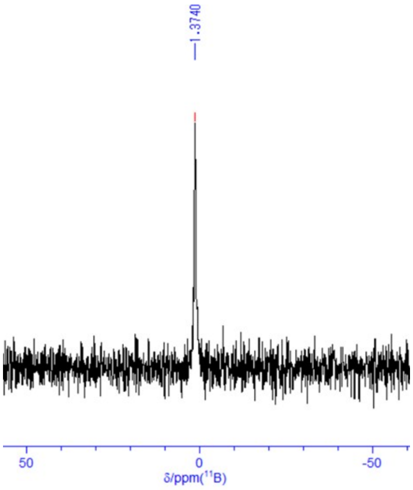


Chart S27. ^{11}B NMR spectrum of *z*-PFL in CDCl$_3$.

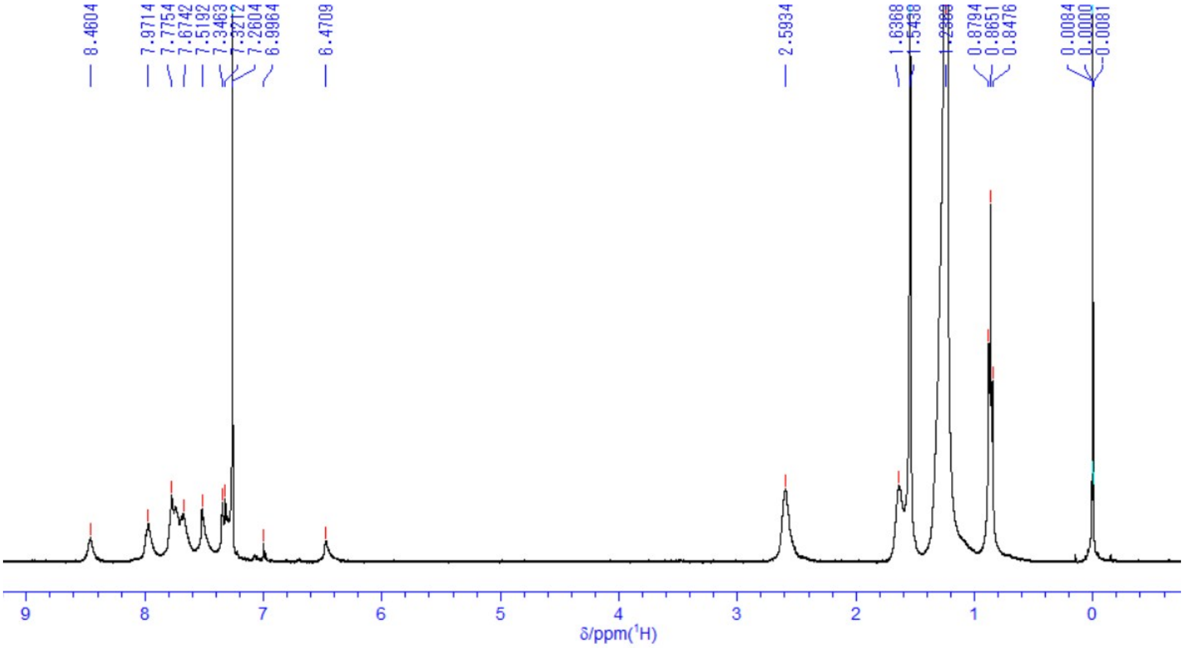


Chart S28. ^{1}H NMR spectrum of *z*-PBT in CDCl$_3$.

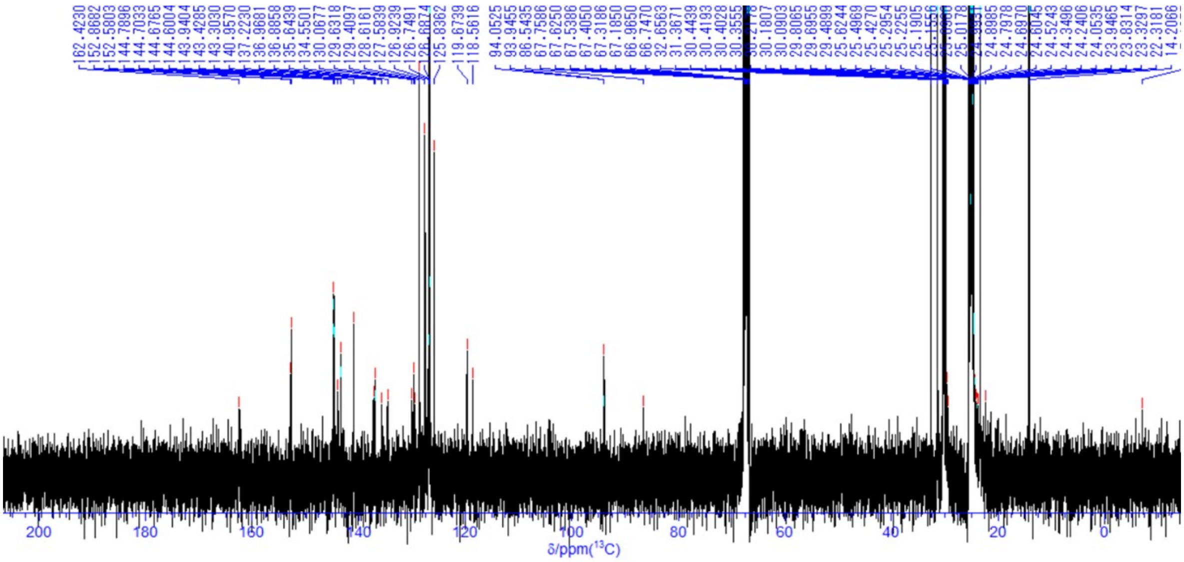


Chart S29. ^{13}C NMR spectrum of *z*-PBT in C_4D_8O.

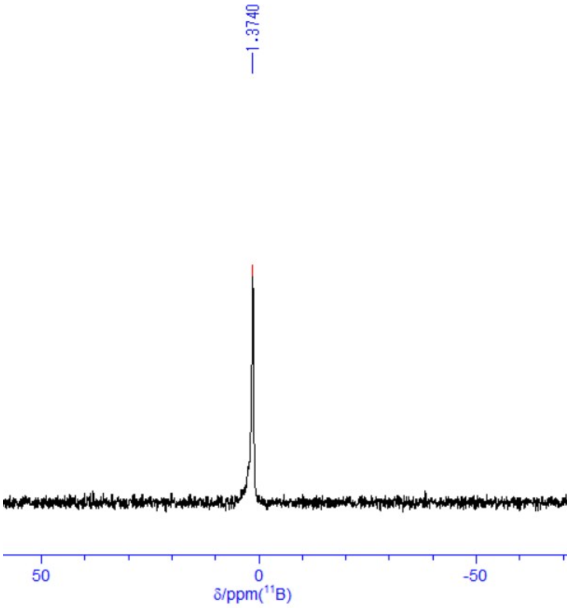


Chart S30. ^{11}B NMR spectrum of *z*-PBT in $CDCl_3$.

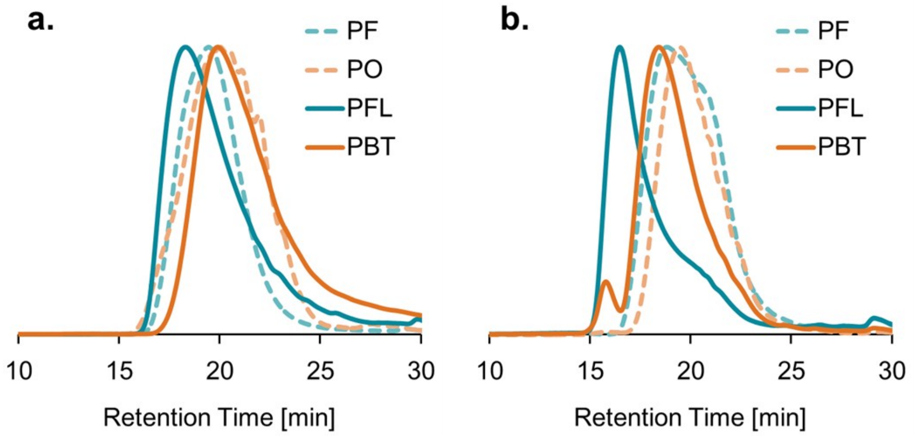


Chart S31. GPC profiles of the polymeric products from (a) *l*- and (b) *z*-DIFBKI.

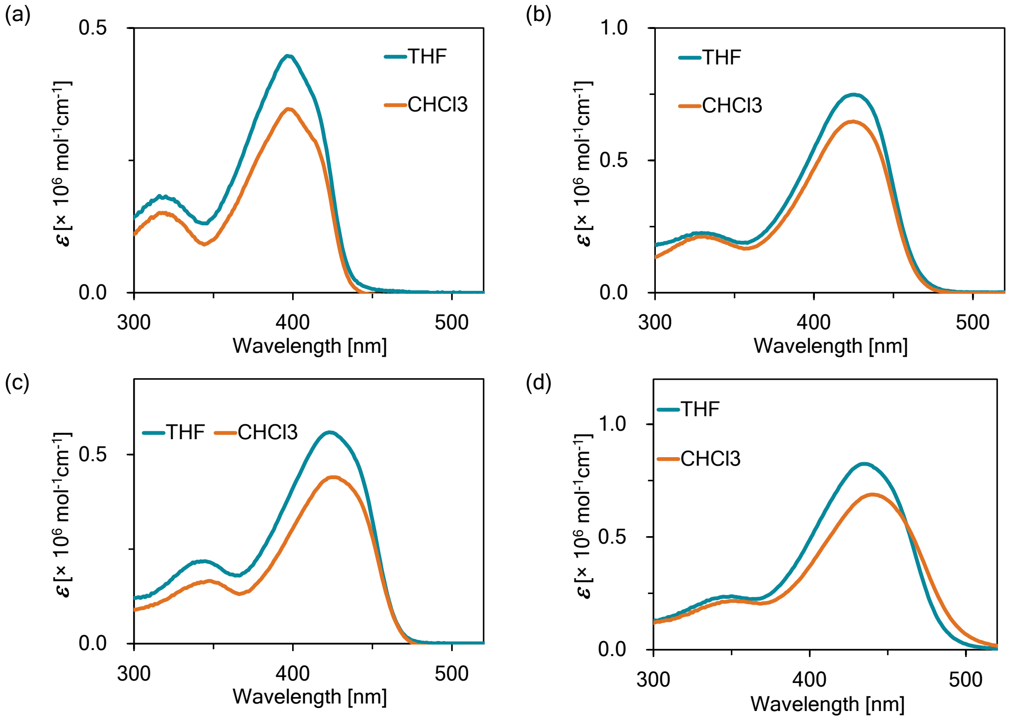


Figure S1. UV−vis absorption spectra of (a) ***l*-PF**, (b) ***l*-PO**, (c) ***l*-PFL** and (d) ***l*-PBT** in THF and CHCl$_3$ (1.0 × 10^{-6} M).

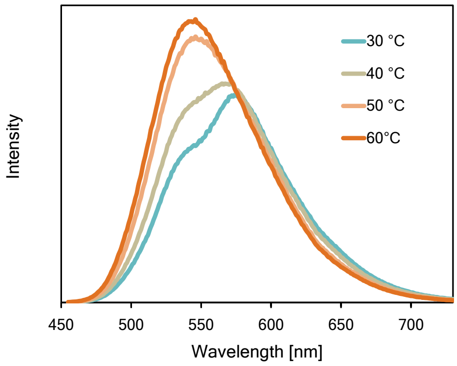


Figure S2. Emission spectra of ***l*-PBT** in CHCl$_3$ with variable temperature.

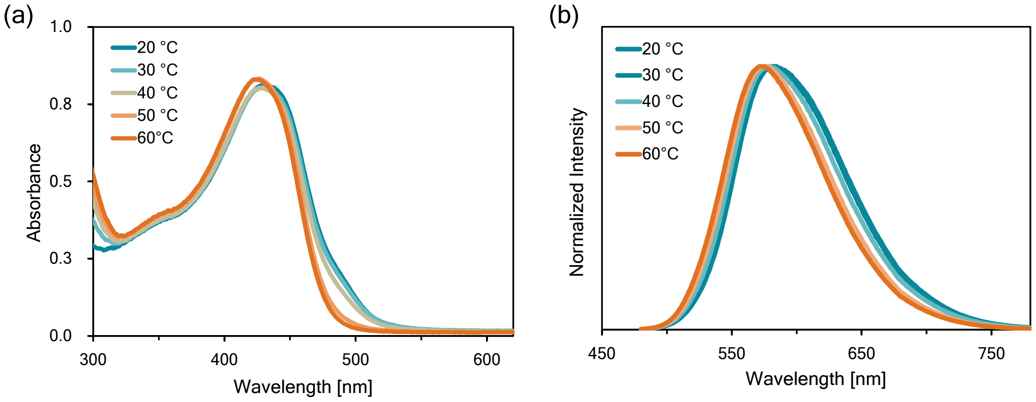


Figure S3. (a) UV−vis absorption and (b) emission spectra of ***z*-PBT** in $CHCl_3$ solution with variable temperature.

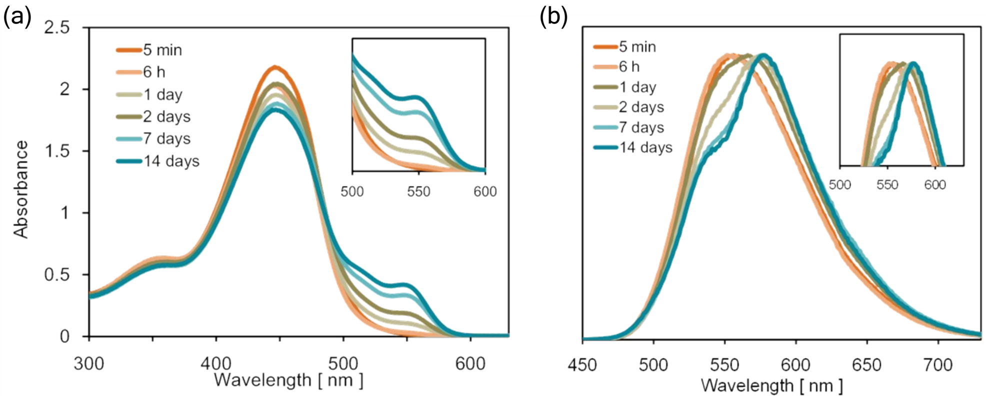


Figure S4. (a) UV−vis absorption and (b) emission spectra of ***l*-PBT** in $CHCl_3$ after heating.

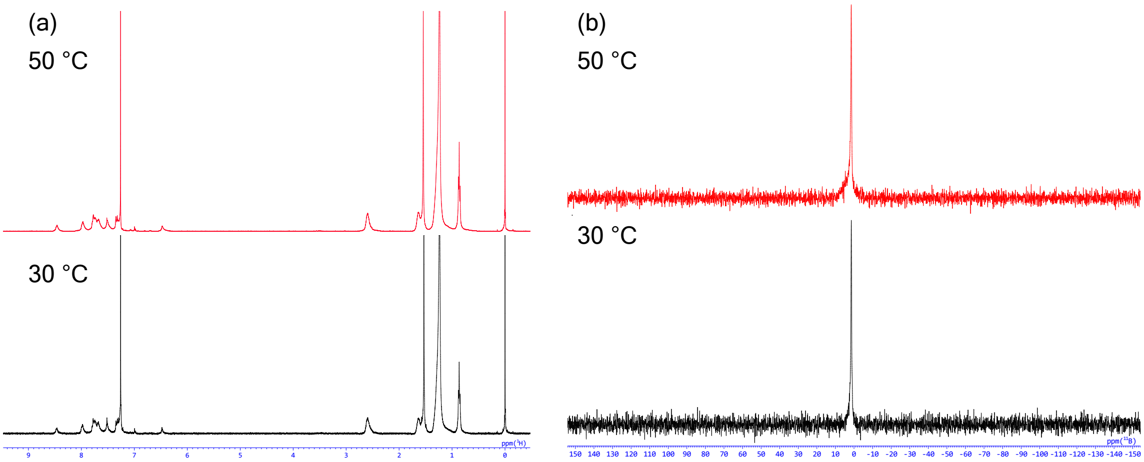


Figure S5. (a) ^{1}H and (b) ^{11}B NMR spectra of ***l*-PBT** in CDCl$_3$ at 30 °C and 50 °C.

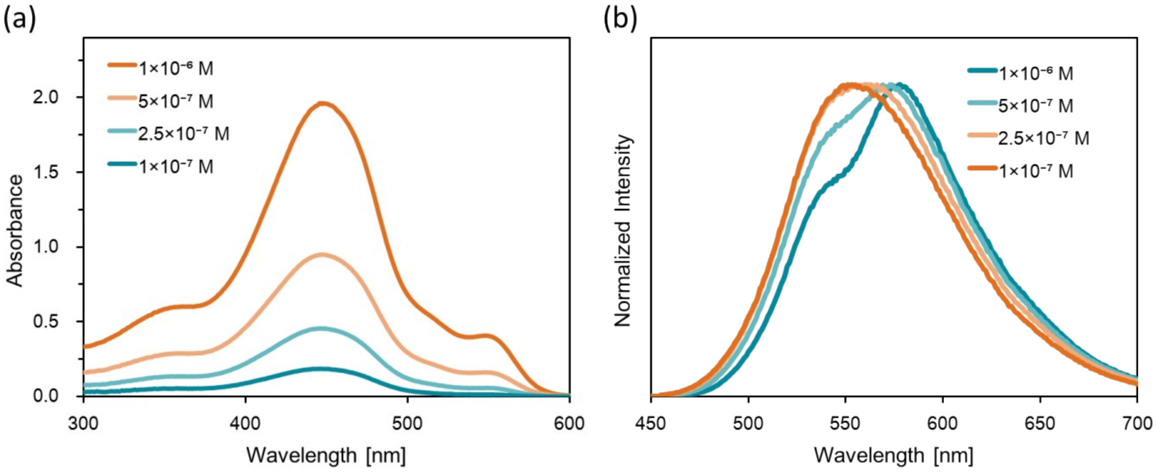


Figure S6. (a) UV−vis absorption and (b) emission spectra of ***l*-PBT** in CHCl$_3$ with variable concentration.

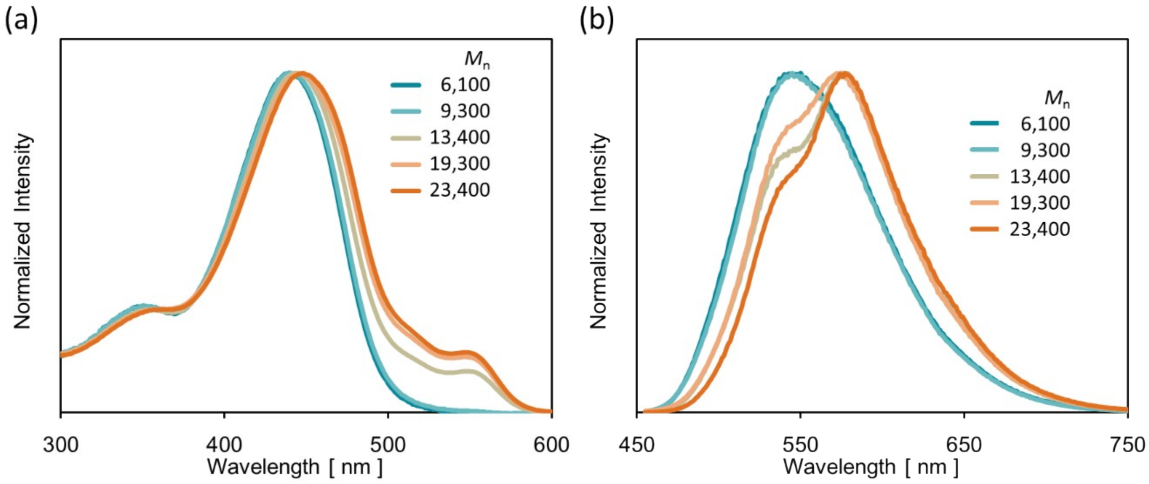


Figure S7. (a) UV−vis absorption and (b) emission spectra of ***l*-PBT** in $CHCl_3$ with variable molecular weight.

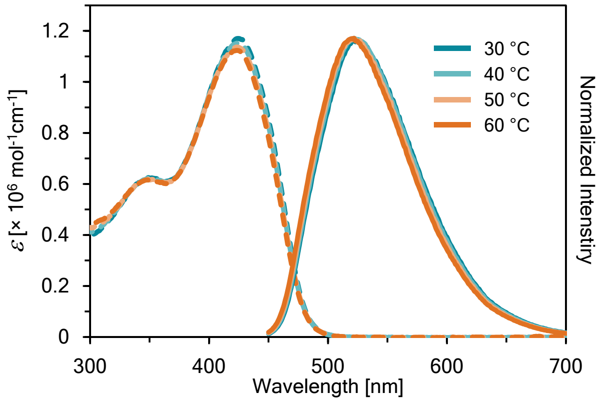


Figure S8. UV−vis absorption and emission spectra of ***l*-PBT** (M_n = 23,400) in THF with variable temperature.

Table S1. Polymerization results

Polymer	Yield [%][a]	M_n[b]	M_w[b]	M_w/M_n	DP[c]
l-PF	44	9,400	18,000	1.9	11
l-PO	87	9,200	30,500	3.3	12
l-PFL	23	9,900	27,000	2.7	11
l-PBT	87	9,300	39,000	4.2	12
z-PF	96	9,500	21,000	2.2	11
z-PO	86	8,600	15,000	1.8	11
z-PFL	88	26,000	170,000	6.3	28
z-PBT	91	14,000	57,000	4.2	18

[a] Isolated yields after precipitation. [b] Estimated by SEC with the polystyrene standards in $CHCl_3$. [c] Average number of repeating units calculated from M_n and molecular weights of repeating units.

Table S2. Optical properties of *l*- and *z*- type copolymers

Polymer	$\lambda_{abs,sol}$ [nm] [a]	ε [× 10^5 $M^{-1}cm^{-1}$] [a]
l-PF	397	4.5
l-PO	424	7.5
l-PFL	424	11.0
l-PBT	435	8.2
z-PF	391	3.4
z-PO	409	5.7
z-PFL	414	22
z-PBT	423	11

[a] Measured in THF solution (1.0×10^{-6} M).

Table S3. Electrochemical properties of the polymers[a]

Polymer	$E_{onset,\ \mathrm{ox}}$ [V][b]	$E_{onset,\ \mathrm{red}}$ [V][c]	$E_{\mathrm{HOMO}}^{\mathrm{CV}}$ [eV][d]	$E_{\mathrm{LUMO}}^{\mathrm{CV}}$ [eV][e]	$E_{\mathrm{gap}}^{\mathrm{CV}}$ [eV][f]
l-PF	0.96	−1.77	−5.99	−3.26	2.73
l-PO	0.86	−1.52	−5.88	−3.51	2.37
l-PFL	0.74	−1.70	−5.76	−3.33	2.43
l-PBT	0.85	−1.26	−5.87	−3.75	2.12
z-PF	0.32	−1.66	−5.35	−3.37	1.98
z-PO	0.85	−1.77	−5.88	−3.26	2.62
z-PFL	0.95	−1.79	−5.98	−3.24	2.74
z-PBT	0.55	−1.74	−5.58	−3.29	2.29

[a] Determined form cyclic voltammogram in MeCN (1×10^{-3} M) with 0.1 M Et_4NPF_6 as supporting electrolyte, Ag/AgCl as a reference electrode, Pt as working and counter electrodes, and a ferrocene/ferrocenium external standard at room temperature with a scan rate at 100 mV/s under Ar. [b] Estimated from the onset of the oxidation waves (vs Fc/Fc$^+$). [c] Estimated from the onset of the reduction waves (vs Fc/Fc$^+$). [d] $E_{\mathrm{HOMO}}^{\mathrm{CV}} = -5.1 - E_{\mathrm{onset,ox}}$. [e] $E_{\mathrm{LUMO}}^{\mathrm{CV}} = -5.1 - E_{\mathrm{onset,red}}$. [f] $E_{\mathrm{gap}}^{\mathrm{CV}} = E_{\mathrm{LUMO}}^{\mathrm{CV}} - E_{\mathrm{HOMO}}^{\mathrm{CV}}$.

Table S4. Emission efficiencies of *l*-PBT in $CHCl_3$ with variable temperature

	30 °C [a]	40 °C [b]	50 °C [b]	60 °C [b]
$\Phi_{\mathrm{PL,sol}}$	49%	51%	60%	62%

[a] Calculated as an absolute value determined using an integrated sphere. [b] Calculated as a relative quantum yield toward the value at 30 °C.

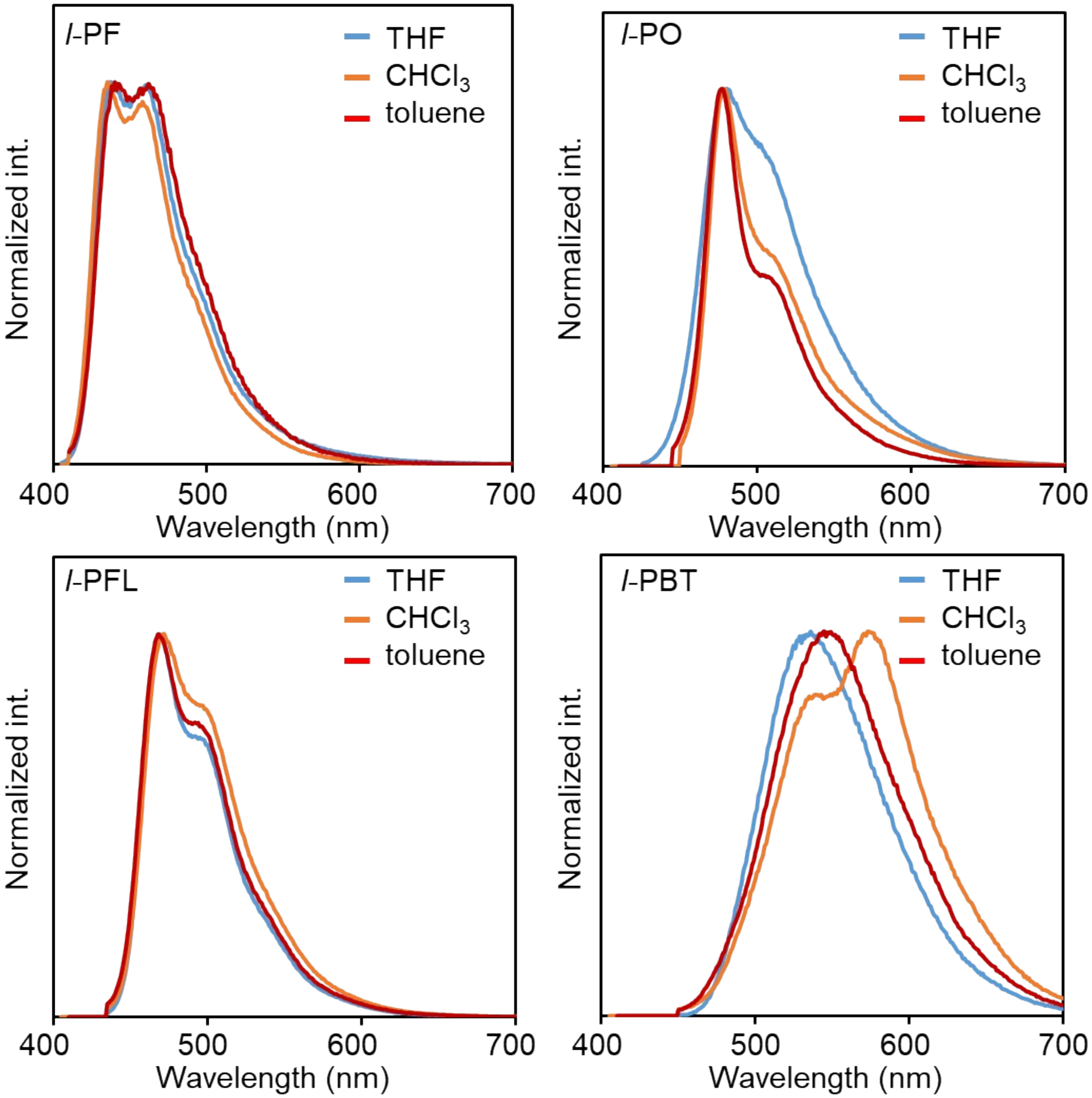


Figure S9. Emission spectra of polymers in various solvents (1.0×10^{-6} M).

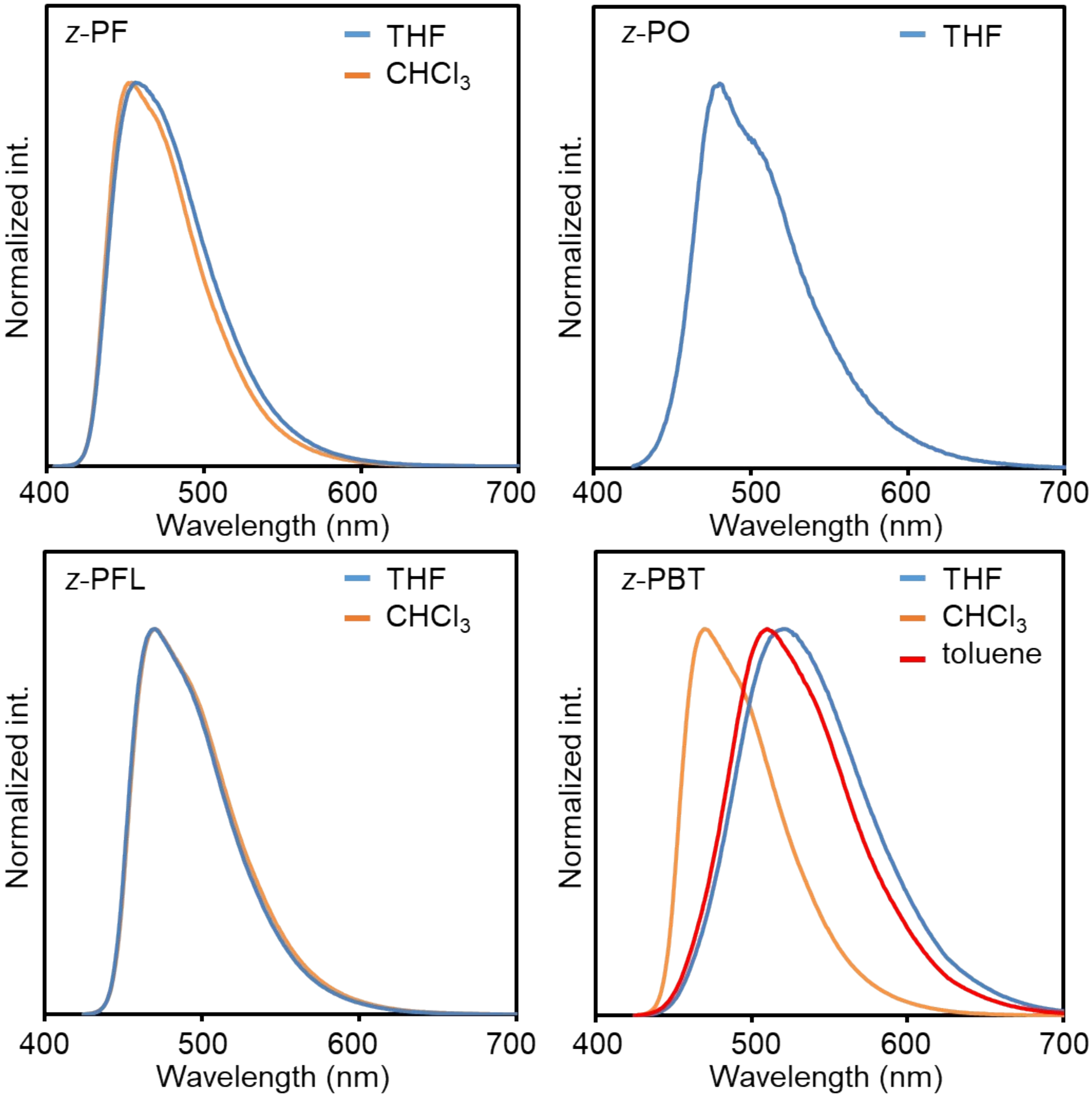


Figure S10. Emission spectra of polymers in various solvents (1.0×10^{-6} M).

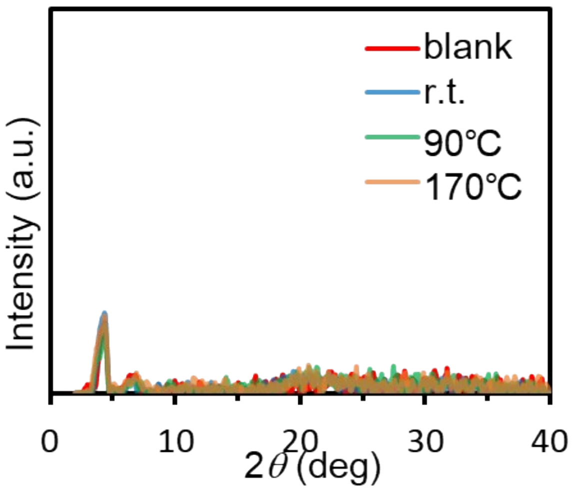


Figure S11. XRD patterns after the annealed samples.