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Facile Modulation of Optical Properties of Diketonate-Containing Polymers by Regulating Complexation Ratios with Boron

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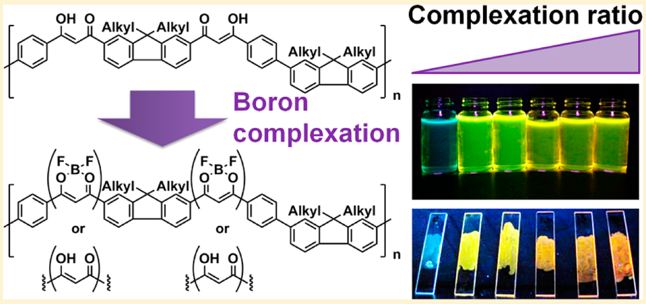
Supporting Information

ABSTRACT: We present the facile modulation of the optical properties of the conjugated polymers via polymer reactions. The polymers composed of diketonate and fluorene were prepared, and boron complexation was performed after polymer synthesis. By changing feed ratios of $BF_3 \cdot Et_2O$, which is a reagent to produce a boron diketonate complex, the series of polymers with various complexation ratios with boron at the diketonate unit can be obtained. These synthesized polymers showed diverse optical properties. In the solution states, the quantum yields of emission were greatly changed by the complexation ratios with boron. Accordingly, the polymers with complexation ratio of 21% present the largest intensity. In addition, the emission color can be tuned by changing the complexation ratios in the films. From blue to orange, the emissions were achieved. It was revealed that induced charge transfer between fluorene and boron diketonate should be the main path for the emission of the synthesized polymers.



INTRODUCTION

Organoboron complex-containing conjugated polymers have gathered attention as a key material for fabricating organic opto- and/or electronic devices.[1] Various unique properties were obtained from the conjugated polymers with tetracoordinate boron-based highly emissive compounds.[2] Particularly, boron diketonate is a versatile building block for preparing functional optical materials.[3] For instance, the regulation of optical properties by physical stimuli was accomplished with the boron diketonate derivatives.[3a] In addition, the aggregation induced emission properties were found from the organoboron complexes with boron diketonate units.[3d] In the poor solvent, the aggregation of the boron diketonate derivative proceeded, leading to the increases of the magnitude of emission intensity. Fraser et al. presented the intelligent optical bioprobes to evaluate the intracellular dissolved oxygen levels. By applying the differences of environment-responsiveness between intrinsic properties of fluorescence and phosphorescence of boron diketonate complexes, the oxygen level can be discriminated quantitatively.[4] We have reported various kinds of highly emissive materials based on boron diketonate-containing polymers.[5] The emissive properties can be modulated.[5a] The strong emission even in the solid states was also observed.[5b]

Fluorene is one of the conventional units for fabricating light-emissive polymers. Since many advantages such as good film formability, solubility in ordinal solvents, stability to environmental changes, and bright emissions in the film states can be obtained, fluorene is known as a suitable platform to construct functional optical materials.[6] Moreover, the modulation of the optical properties of fluorene-containing polymers has been established by combining with various functional units. For example, the emission colors can be drastically tuned by introducing the functional units into the adjacent position via π-conjugation to form charge transfer (CT) states involving to the fluorene unit.[7] By modulating the electron acceptors conjugated with fluorene, the strong emissions were obtained from visible to near-infrared regions. As another example, by changing the feed ratios of the fluorene units to the comonomers, the series of functional optical polymers were synthesized with various ratios of chromophores in the polymer main chains. These polymers showed useful characteristics such as for multicolor materials[8] and a white-light emitter.[9] Furthermore, alternating polymers composed of fluorenes and heterocyclic compounds have been recognized as efficient charge-transporting materials in optoelectronic devices.[10] Thus, not only the construction of conjugation systems but also the modulation of electronic structures are of significance to obtain highly functionalized materials. Although, as mentioned above, there are many examples of the multicomponent polymers with different introduction ratios of each functional unit prepared by changing the feed ratios in the polymerization, there is room to

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develop the modulation of optical properties via the polymer reactions after constructing conjugated main chains. We aimed to establish facile methodology based on polymer reactions to regulate the electronic structures of conjugated polymers for optimizing the device properties and obtaining diverse optical materials.

Herein, we synthesized conjugated polymers composed of diketonate and fluorene in the main chains. The modulation of electronic properties of organoboron-containing polymers was achieved by changing the complexation ratios with boron at the diketonate moiety via polymer reactions. Finally, we prepared a series of emissive polymers with various emission intensities and color variation. This is the first example, to the best of our knowledge, to establish the facile methodology for receiving various functional optical polymers via boron complexation in polymer reactions.

■ EXPERIMENTAL SECTION

General. ^{11}H (400 MHz), ^{13}C (100 MHz), and ^{11}B (128 MHz) NMR spectra were recorded on a JEOL JNM-EX400 spectrometer. ^{1}H NMR spectra used tetramethylsilane (TMS) as an internal standard in $CDCl_3$, ^{11}B NMR spectra were referenced externally to $BF_3 \cdot OEt_2$ (sealed capillary), and ^{13}C NMR spectra used tetrahydrofuran as an internal standard in THF-d_8. The number-average molecular weight (M_n) and the molecular weight distribution [weight-average molecular weight/number-average molecular weight (M_w/M_n)] values of all polymers were estimated by the size-exclusion chromatography (SEC) with a TOSOH G3000HXI system equipped with three consecutive polystyrene gel columns (TOSOH gels: α-4000, α-3000, and α-2500) and ultraviolet detector at 40 °C. The system was operated at a flow rate of 1.0 mL/min, with chloroform as an eluent. Polystyrene standards were employed for the calibration. Recyclable preparative high-performance liquid chromatography (HPLC) was carried out on a Japan Analytical Industry Model LC918R (JAIGEL-1H and 2H columns) and LC9204 (JAIGEL-2.5H and 3H columns) using chloroform as an eluent. UV−vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer. Emission spectra were recorded on a HORIBA Jobin Yvon Fluoromax-4 spectrofluorometer, and absolute quantum yields were determined by the integrating sphere method on the HORIBA Jobin Yvon Fluoromax-4 spectrofluorometer in chloroform.

Synthesis of 2. Dicarboxylic acid (**1**) was prepared according to the previous report.[11] The mixture containing **1** (9.2 g, 19.2 mmol) and concentrated H_2SO_4 (96%, 2 mL) in methanol (180 mL) was refluxed for 16 h. After neutralization with saturated $NaHCO_3$(aq) and evaporation, the residue was dissolved in cyclopentyl methyl ether, and the organic layer was washed with water, saturated $NaHCO_3$(aq), and brine. After drying over Na_2SO_4, volatiles were removed by evaporation. The product **2** was obtained as a white solid (8.9 g, 91%). The authentic sample was purified with recrystallization with THF and methanol. ^{1}H NMR (CD_2Cl_2, ppm) δ: 8.07 (d, J = 1.44 Hz, 2H), 8.06 (d, J = 1.96 Hz, 2H), 7.83 (d, J = 8.56, 2H), 3.93 (s, 6H), 2.12−2.05 (m, 4H), 1.25−0.95 (m, 20H), 0.80 (t, J = 7.20 Hz, 6H), 0.58−0.49 (m, 4H). ^{13}C NMR (CD_2Cl_2, ppm) δ: 167.48, 152.30, 144.89, 130.29, 129.17, 124.55, 120.73, 55.97, 52.41, 40.40, 32.16, 30.25, 29.58, 29.53, 24.13, 22.98, 14.21. HRMS (ESI): calcd for $[C_{33}H_{46}O_4 + H]^+$: m/z 507.3469; found: m/z 507.3475.

Synthesis of 3. In a round-bottom flask with a drop funnel, **2** (3.0 g, 5.9 mmol) and NaH (1.4 mg, 59.3 mmol) were placed under a nitrogen atmosphere. The THF solution (50 mL) containing p-iodobenzaldehyde (3.8 mg, 15.4 mmol) was added dropwise at 50 °C over 30 min, and the solution color gradually turned from yellow to orange. Then, the mixture was stirred at 50 °C for 16 h. After quenching the reaction by adding concentrated HCl (10%) and removing volatiles by evaporation, the residue was dissolved in cyclopentyl methyl ether, and the organic layer was washed with water, saturated $NaHCO_3$(aq), and brine. After drying over Na_2SO_4, volatiles were removed by evaporation. The crude product was purified by the silica gel column chromatography with a mixed eluent containing toluene/n-hexane (1/4). Recrystallization with THF and hexane afforded **3** (1.8 g, 32%) as a yellow solid. ^{1}H NMR (CD_2Cl_2, ppm) δ: 17.05 (s, 2H), 8.05 (d, J = 6.84 Hz, 4H), 7.91−7.88 (m, 6H), 7.76 (d, J = 4.8 Hz, 4H), 6.95 (s, 2H), 2.16−2.12 (m, 4H), 1.20−1.00 (m, 20H), 0.77 (t, J = 7.08 Hz, 6H), 0.65−0.55 (m, 4H). ^{13}C NMR (CD_2Cl_2, ppm) δ: 186.48, 184.85, 152.77, 144.92, 138.44, 135.51, 135.46, 129.00, 127.17, 122.18, 121.13, 100.13, 93.55, 56.21, 40.45, 32.17, 30.26, 29.61, 29.56, 24.21, 22.99, 14.22. HRMS (ESI): calcd for $[C_{47}H_{52}I_2O_4 + H]^+$: m/z 935.2028; found: m/z 935.2034.

Synthesis of Monomer 4. The mixture of **3** (1.5 g, 1.6 mmol), 4-(dimethylamino)pyridine (0.2 g, 1.6 mmol), and di-*tert*-butyl dicarbonate (Boc_2O, 3.5 g, 16 mmol) in 1,4-dioxane (150 mL) was stirred at 40 °C for 24 h. After cooling to room temperature, the reaction solution was directly passed through the silica gel swollen with chloroform. After washing with chloroform and subsequently removing solvents, monomer **4** was obtained (1.2 g, 64%) as a yellow solid. ^{1}H NMR (CD_2Cl_2, ppm) δ: 8.02−7.98 (m, 2H), 7.90−7.86 (m, 4H), 7.84 (d, J = 8.4 Hz, 2H), 7.80−7.79 (m, 4H), 7.49 (d, J = 8.32 Hz, 2H), 7.26 (s, 1H), 7.19 (s, 1H), 2.15−2.05 (m, 4H), 1.53 (s, 18H), 1.25−1.00 (m, 20), 0.78 (t, J = 7.36 Hz), 0.65−0.50 (m, 4H). ^{13}C NMR (CD_2Cl_2, ppm) δ: 188.11, 188.08, 187.84, 187.83, 157.75, 157.70, 155.98. 155.93, 153.05, 152.79, 152.57, 152.32, 150.01, 150.01, 149.93, 144.96, 144.85, 143.58, 143.46, 138.53, 138.51, 138.44, 138.41, 183.33, 138.26, 134.04, 134.03, 134.00, 133.76, 129.92, 128.28, 128.22, 127.94, 126.02, 125.99, 123.03, 123.01, 121.47, 121.17, 120.98, 120.82, 120.67, 110.70, 110.67, 109.43, 109.30, 100.80, 100.78, 97.87, 97.85, 84.523, 84.516, 84.46, 84.45, 56.10, 56.05, 56.00, 40.44, 32.10, 30.29, 30.27, 30.25, 29.62, 29.58, 29.56, 29.55, 27.74, 27.72, 24.21, 22.92, 15.43, 14.18. HRMS (ESI): calcd for $[C_{57}H_{68}I_2O_8 + Na]^+$: m/z 1157.2896; found: m/z 1157.2919.

Synthesis of M0. The mixture containing **4** (650 mg, 0.57 mmol), 9,9-dimethyl-9*H*-fluorene-2-yl-boronic acid (327 mg, 1.37 mmol), 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (S-Phos, 9.4 mg, 0.02 mmol), tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$, 5.2 mg, 6 μmol), and Cs_2CO_3 (1.87 g, 5.73 mmol) in toluene (12 mL) and water (12 mL) was stirred at 80 °C for 16 h. After reaction, an excess amount of cyclopentyl methyl ether was poured to the mixture, and the organic layer was washed with water, saturated $NaHCO_3$(aq), and brine. After drying over Na_2SO_4, volatiles were removed by evaporation. To the solution of the residue in dichloromethane (80 mL), piperidine (113 μL, 1.15 mmol) was added, and then the mixture was stirred at room temperature for 16 h. After neutralization with concentrated HCl (10%), the products in dichloromethane were washed with water, saturated $NaHCO_3$(aq), and brine. After removing volatiles by evaporation, the crude products were purified with the silica gel column chromatography with a mixed eluent containing n-hexane/toluene (1/1). Recrystallization with THF and hexane gave **M0** (379 mg) as a yellow solid in 62% yield. ^{1}H NMR (CD_2Cl_2, ppm) δ: 17.17 (s, 2H), 8.14 (d, J = 8.30 Hz, 4H), 8.10−8.05 (m, 4H), 7.90 (d, J = 8.32 Hz, 2H), 7.84−7.80 (m, 6H), 7.78−7.71 (m, 4H), 7.66 (dd, J_1 = 7.84, J_2 = 1.96 Hz, 2H), 7.48−7.45 (m, 2H), 7.37−7.31 (m, 4H), 7.04 (s, 2H), 2.18−2.10 (m, 4H), 1.52 (s, 12H), 1.21−0.96 (m, 20H), 0.76 (t, J = 6.88 Hz, 6H), 0.62−0.54 (m, 4H). ^{13}C NMR (CD_2Cl_2, ppm) δ: 186.23, 185.48, 155.01, 154.54, 152.79, 146.03, 144.85, 139.89, 139.34, 138.97, 135.80, 134.57, 128.18, 128.06, 127.70, 127.55, 127.14, 126.73, 123.14, 122.20, 121.92, 121.09, 120.87, 120.65, 93.70, 56.26, 47.44, 40.53, 32.20, 30.30, 29.65, 29.60, 27.41, 24.27, 23.02, 14.23. HRMS (ESI): calcd for $[C_{77}H_{79}O_4 + H]^+$: m/z 1067.5973; found: m/z 1067.5987.

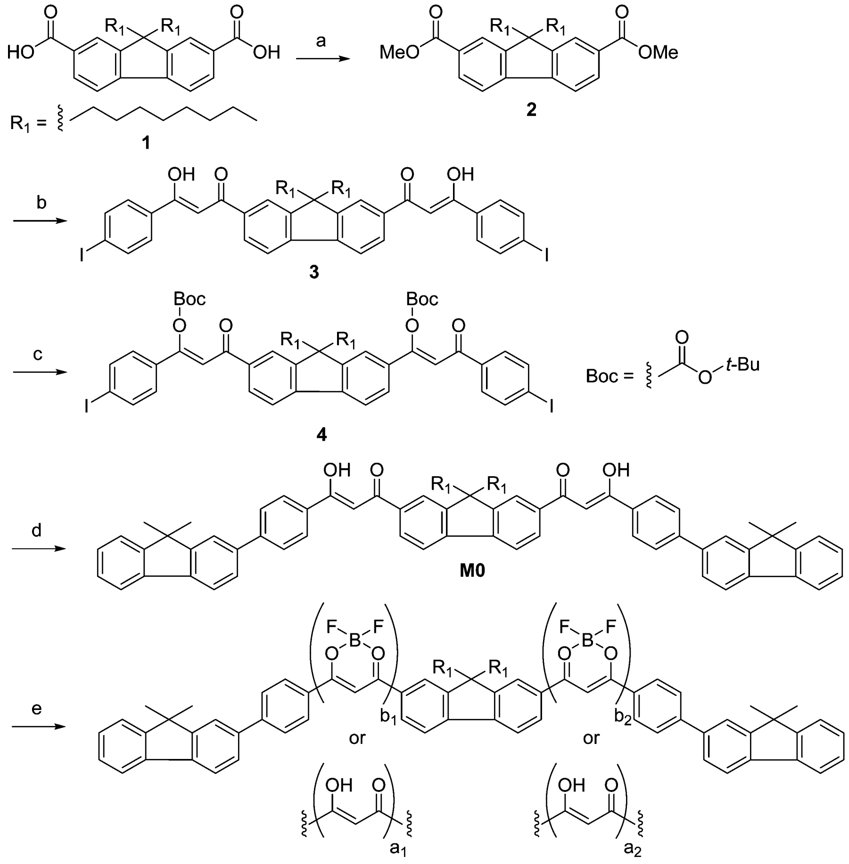
Synthesis of M50 and M100. A typical procedure for boron complexation at the diketonate unit is described here. The mixture containing **M0** (100 mg, 0.09 mmol) and $BF_3 \cdot Et_2O$ (12 μL, 0.09 mmol) in dichloromethane (20 mL) was stirred at room temperature for 6 h. After quenching the reaction by diluting with dichloromethane, the organic layer was washed with water, saturated $NaHCO_3$(aq), and brine. After drying over Na_2SO_4, the products were suspended onto silica gel. The crude product was purified by the silica gel column chromatography with a mixed eluent containing n-hexane/toluene (1/2). The analytical sample of **M50** as an orange sample was separated

Table 1. Polymer Properties of Synthesized Polymers

polymer	yield[a] (%)	M_n[b]	M_w/M_n[b]	$\lambda_{abs,max}$[c] (nm)	$\lambda_{PL,max}$[c,d] (nm)	Φ_{PL}[e]	$\lambda_{PL,max}$[f] (nm)	Φ_{PL}[e,f]
PF0		6500	4.5	404	450	0.098	504	0.004
PF21	77	7800	14.2	407	554	0.326	576	0.019
PF41	76	6700	13.4	413	552	0.314	585	0.013
PF58	75	7300	13.3	461	561	0.235	601	0.012
PF71	70	6700	14.7	464	563	0.219	597	0.010
PF100	76	4400	3.5	470	540	0.209	606	0.019

[a] Isolated yields after boron complexation. [b] Estimated by size-exclusion chromatography (SEC) based on polystyrene standards in chloroform. [c] Measured in chloroform (1.0×10^{-5} M). [d] Excited at the peak wavelength of absorption. [e] Absolute quantum yield. [f] Measured in the solid state; prepared from chloroform solutions.

Scheme 1. Synthetic Scheme of the Monomer and Model Compounds[a]



M50: $(b_1+b_2)/(a_1+a_2+b_1+b_2)\times100=50$
M100: $a_1=a_2=0$

[a] Reagents and conditions: (a) conc H_2SO_4, methanol, reflux, 16 h; (b) *p*-iodobenzaldehyde, NaH, THF, 50 °C, 16 h; (c) Boc_2O, 2,4-dimethylaminopyridine, 1,4-dioxane, 40 °C, 16 h; (d) (i) 9,9-dimethyl-9*H*-fluorene-2-yl-boronic acid, S-Phos, $Pd_2(dba)_3$, Cs_2CO_3, toluene, water, 80 °C, 16 h, (ii) piperidine, dichloromethane, rt, 16 h; (e) BF_2OEt_2, dichloromethane, rt, 6 h.

with HPLC in chloroform and precipitated in methanol (4.2 mg, 4%). The pure **M100** was obtained from the same procedure without HPLC treatment (41 mg, 75%) as an orange solid. **M50**: ^{1}H NMR (CD_2Cl_2, ppm) δ: 17.15 (s, 1H), 8.32 (d, *J* = 8.4 Hz, 2H), 8.25−8.23 (m, 2H), 8.16 (d, *J* = 8.4 Hz, 2H), 8.13−8.09 (m, 2H), 8.00 (d, *J* = 7.80 Hz, 1H), 7.97 (d, *J* = 7.80 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 2H),, 7.88−7.83 (m, 4H), 7.81−7.75 (m, 4H), 7.72 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.69 (dd, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 7.51−7.47 (m, 2H), 7.40−7.34 (m, 5H), 7.06 (s, 1H), 2.23−2.17 (m, 4H), 1.56 (s, 6H), 1.55 (s, 6H), 1.20−1.00 (m, 20H), 0.78 (t, *J* = 7.2 Hz, 6H), 0.65−0.58 (m, 4H). ^{13}C NMR (CD_2Cl_2, ppm) δ: 185.80, 185.78, 183.02, 182.45, 155.12, 155.00, 154.61, 154.52, 153.28, 153.27, 148.79, 147,75, 146.11, 144.03, 140.61, 139.90, 139.30, 138.95, 138.78, 138.56, 136.68, 134.51, 132.08, 131.05, 129.95, 129.14, 128.28, 128.19, 128.07, 128.05, 127.70, 127.58, 127.52, 127.21, 126.92, 126.71, 123.71, 123.15, 123.11, 122.27, 122.03, 121.90, 121.70, 121.50, 120.98, 120.85, 120.76, 120.62, 94.23, 93.83, 56.51, 47.46, 47.41, 40.45, 32.15, 30.24, 29.63, 29.55, 27.39, 27.36, 24.26, 22.97, 14.18. ^{11}B NMR (CD_2Cl_2, ppm) δ: 0.29. HRMS (ESI): calcd for $[C_{77}H_{77}BF_2O_4 + H]^+$: *m/z* 1115.5956; found: *m/z* 1115.5964. **M100**: ^{1}H NMR (C_4D_8O, ppm) δ: 8.50−8.42 (m, 8H), 8.19 (d, *J* = 8.28 Hz, 2H), 8.02 (d, *J* = 8.28 Hz, 4H), 7.95−7.89 (4H, m), 7.84−7.78 (6H, m), 7.54−7.50 (2H, m), 7.38−7.31 (4H, m), 2.35−2.28 (4H, m), 1.58 (s, 12H), 1.25−1.00 (m, 20H), 0.80 (t, *J* = 7.32 Hz, 6H), 0.70−0.58 (m, 4H). ^{13}C NMR (C_4D_8O, ppm) δ: 183.37, 183.34, 155.57, 155.10, 154.05, 149.16, 147.34, 141.17, 139.42, 139.23, 133.94, 132.01, 130.55, 129.91, 128.61, 128.35, 127.95, 127.43, 124.35, 123.47, 122.56, 122.43, 121.34, 121.16, 94.77, 57.19, 47.82, 40.51, 32.70, 30.84, 30.15, 30.13, 27.40, 24.80, 23.42, 14.32. ^{11}B NMR

(CD_2Cl_2, ppm) δ: 0.20. HRMS (ESI): calcd for $C_{77}H_{76}B_2F_4O_4$: m/z 1162.5894; found: m/z 1162.5901.

Synthesis of Polymer PF0. A mixture containing **4** (400 mg, 0.35 mmol), [9,9-bis(2-ethylhexyl)-9*H*-fluorene-2,7-diyl]bisboronic acid (167 mg, 0.35 mmol), S-Phos (5.8 mg, 10 μmol), $Pd_2(dba)_3$ (3.2 mg, 4 μmol), and Cs_2CO_3 (1.15 g, 3.5 mmol) in toluene (10 mL) and water (10 mL) was stirred at 80 °C for 3 h. After reaction, an excess amount of dichloromethane was poured to the mixture, and the organic layer was washed with water, saturated $NaHCO_3$(aq), and brine. After drying over Na_2SO_4, volatiles were removed by evaporation. After dissolving in THF, an excess amount of methanol was poured to precipitate polymers. The mixture products containing **5** and partially deprotected polymers were isolated as a yellow solid by filtration and dried under vacuum (447 mg). The M_n and M_w/M_n of the products were 8800 and 3.1, respectively. The products were directly used for the next step.

To the solution of the products obtained above in dichloromethane (100 mL), piperidine (59 μL, 0.9 mmol) was added, and then the mixture was stirred at room temperature for 24 h. After neutralization with concentrated HCl (10%), the products in chloroform were washed with water, saturated $NaHCO_3$(aq), and brine. After dissolving in THF, an excess amount of methanol was poured to precipitate polymers. Polymer **PF0** was isolated as a yellow solid by filtration and dried under vacuum (230 mg, 55% in two steps). ^{1}H NMR (CD_2Cl_2, ppm) δ: 17.25−17.23 (br, 2H), 8.10−7.83 (br, 20H), 7.10−7.09 (br, 2H), 2.20−2.17 (br, 8H), 1.20−0.59 (br, 60H). ^{13}C NMR (CD_2Cl_2, ppm) δ: 186.05, 185.32, 152.65, 152.07, 146.09, 144.73, 141.40, 138.80, 135.69, 134.45, 128.06, 127.58, 127.03, 126.67, 123.35, 122.10, 121.00, 120.69, 93.64, 56.25, 55.75, 44.84, 40.56, 35.35, 34.32, 32.23, 30.34, 29.67, 29.62, 28.66, 27.63, 24.30, 23.21, 23.06, 14.28, 10.68, 10.65.

Synthesis of PF*n*. Similar procedures were executed for boron complexation at the diketonate unit with the preparation for the model compounds. The mixture containing **PF0** (30 mg, 0.03 mmol of the diketonate unit) and various amounts of $BF_3 \cdot Et_2O$ (0.25, 0.5, 0.65, 0.80, and 1.0 equiv) in dichloromethane was stirred at room temperature for 6 h. After quenching the reaction by diluting with dichloromethane, the organic layer was washed with water, saturated $NaHCO_3$(aq), and brine. After drying over Na_2SO_4, solvents were removed. The residue was dissolved in THF, and an excess amount of methanol was poured to precipitate the polymers. The product was isolated by filtration and dried under vacuum. The resulting polymers were obtained as a yellow powder. The polymer properties are listed in Table 1. **PF100**: ^{1}H NMR (CD_2Cl_2, ppm) δ: 8.34−7.77 (br, 20H), 7.42−7.40 (br, 2H), 2.19−2.16 (br, 8H), 1.00−0.67 (br, 60H). ^{13}C NMR (CD_2Cl_2, ppm) δ: 182.71, 182.67, 153.58, 152.36, 148.92, 146.78, 141.97, 138.28, 132.90, 130.95, 129.99, 129.09, 128.04, 126.99, 123.71, 123.50, 122.05, 121.04, 94.41, 56.82, 55.90, 44.84, 40.52, 35.41, 34.34, 32.21, 30.30, 29.72, 29.63, 28.67, 27.71, 24.37, 23.22, 23.05, 14.28, 10.73, 10.69. ^{11}B NMR (CD_2Cl_2, ppm) δ: 1.17.

Lippert−Mataga Plots. The Lippert equation

$$\nu_{\text{fl}} = \nu_{\text{ab}} - \frac{2\Delta f}{hca^3}(\mu_{\text{E}} - \mu_{\text{G}})^2 + \text{const} \tag{1}$$

where h equals Planck's constant, c equals the velocity of light in a vacuum, a is the Onsager cavity radius, n and ε are the refractive index and the dielectric constant of the solvent, ν_{fl} and ν_{ab} ate the fluorescence and absorption wavelength (expressed in cm^{-1} units), and μ_{E} and μ_{G} are the dipole moment (expressed in Debye units) in the excited and the ground state, respectively

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{4n^2 + 2} \tag{2}$$

while the slope is

$$\text{slope} = -\frac{2\Delta f}{hca^3}(\mu_{\text{E}} - \mu_{\text{G}})^2 \tag{3}$$

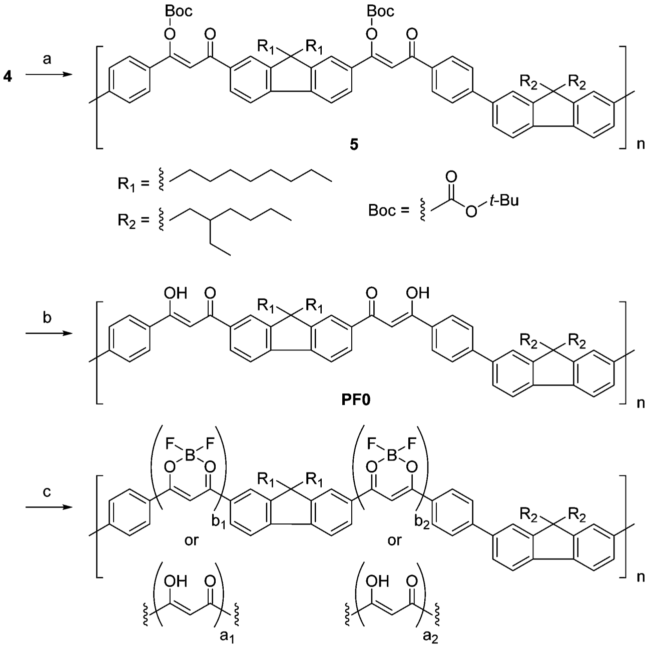
On the basis of the calculation performed above, we can conclude that the single excited state of TP3PY has a larger dipole moment than the ground state.

■ RESULTS AND DISCUSSION

Synthesis of the Monomers. The synthetic outline of monomer **4** and model compounds **M0**, **M50**, and **M100** is shown in Scheme 1. From the fluorene dicarboxylic acid **1**,[11] monomer **4** was synthesized. The alkyl substituent at the 9-position in fluorene critically dominates the reaction yield of the formation of a diketonate structure. When the ethylhexyl-substituted fluorene was used, the desired product was not obtained. To prohibit the metal complexation during the polymerization at diketonate moieties, the Boc group was employed for the protection. Diiodide monomer **4** and the model compounds were characterized by ^{1}H, ^{13}C, and ^{11}B NMR spectroscopies and mass measurements.

Synthesis of the Polymers. The polymerization with diiodide monomers via Suzuki−Miyaura coupling was executed as shown in Scheme 2. The polymer properties determined from the GPC analysis are shown in Table 1. When the fluorene comonomer with two *n*-octyl groups at the 9-position in fluorene was instead used, polymeric products were hardly obtained because of poor solubility of oligomers. Therefore, we used ethylhexyl-substituted fluorene as a comonomer. To remove the metal species originated from the catalyst thoroughly, the reprecipitation and washing with methanol were thoroughly executed. The Boc protected polymer **5** with partially deprotected diketonate units was obtained as a yellow solid. The number-average molecular weights (M_n) and the molecular weight distributions (M_w/M_n) of the polymers, measured by the size-exclusion chromatography (SEC) in

Scheme 2. Synthesis of the Polymers[a]



PFn: $(b_1+b_2)/(a_1+a_2+b_1+b_2)\times 100 = n$ (n = 21, 41, 58, 71, 100)

[a]Reagents and conditions: (a) [9,9-bis(2-ethylhexyl)-9*H*-fluorene-2,7-diyl]bisboronic acid, S-Phos, $Pd_2(dba)_3$, Cs_2CO_3, toluene, water, 80 °C, 3 h, (ii) piperidine, dichloromethane, rt, 24 h; (e) $BF_2 \cdot OEt_2$, dichloromethane, rt, 6 h.

chloroform toward polystyrene standards, were 8800 and 3.1, respectively. The following deprotection of Boc groups also proceeded without formation of undesired precipitation during the reaction. The M_n and M_w/M_n of the resulting product **PF0** were 6500 and 4.5, respectively. The data for structural analysis by ^{1}H and ^{13}C NMR corresponded to those of the monomer and model compounds. Thus, we concluded that the polymers should possess the designed chemical structures, and unexpected conformation or higher-ordered structures were less generated in the solutions.

Boron Complexation at the Diketonate Unit. The introduction of boron into the diketonate moiety was executed with $BF_3{\cdot}Et_2O$ in dichloromethane. The complexation ratios were modulated by changing the feed ratio of $BF_3{\cdot}Et_2O$ to the diketonate unit. After reprecipitation in methanol, the polymers were obtained. The characterization was performed with SCE. The molecular weights of the polymers were not significantly changed after boron complexation. Degradation or scission of the polymer main chain should hardly occur during the reaction. The increases of M_w/M_n were observed except for **PF100**. Cross-linking via boron might proceed under detectable levels in the NMR measurements. The introduction of boron and the formation of boron diketonate were confirmed by ^{11}B NMR measurements. The significant peaks assigned as a tetracoordinate boron were observed at +1.2 ppm.[3] The characteristic peak assigned as the hydroxyl group is obtained around +17 ppm from ^{1}H NMR spectra in dichloromethane.[12] The complexation ratios were calculated from the ratios of the integration area of this peak and that of the proton at the boron diketonate moiety (Figure 1). We obtained the boron-containing polymers in which 21%, 41%, 58%, 71%, and 100% of the diketonate moiety were occupied by boron from the reaction mixture in the presence of 0.25, 0.50, 0.65, 0.80, and 1.0 equiv, respectively, of $BF_3{\cdot}Et_2O$ to the diketonate unit in the polymer **PF0**. These data mean that the boron complexation proceeded quantitatively. In the abbreviations of model compounds and polymers, the numbers represent the complexation ratios.

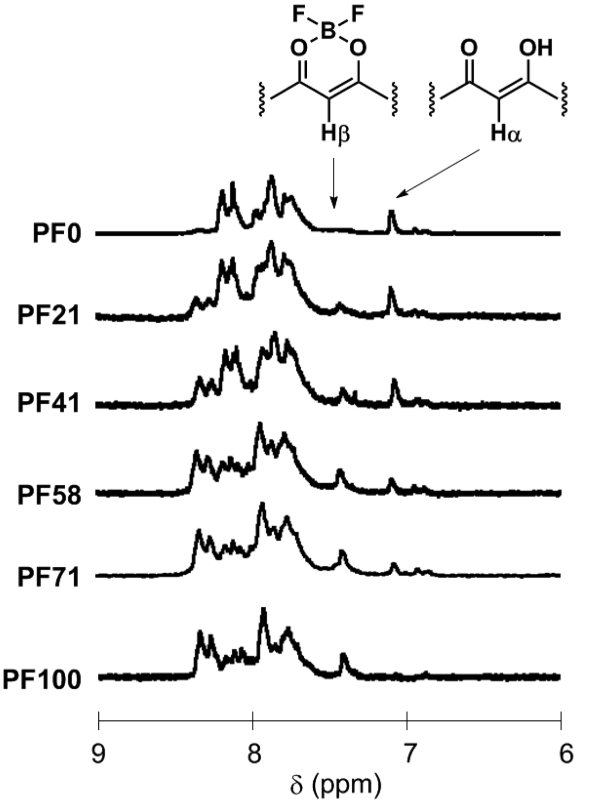


Figure 1. ^{1}H NMR spectra of the polymers with various complexation ratios in dichloromethane-d_2.

Absorption Spectra of the Polymers. The optical properties of the polymers were initially investigated by UV−vis absorption in chloroform solution (Figure 2). The results are summarized in Table 1. The large absorption band with the peak at 404 nm was observed from **PF0**. In contrast, the new absorption band with the peak at 460 nm was observed from the solution containing **PF21**. The magnitude of the absorption at 460 nm increased corresponding to increases of the complexation ratio. By the complexation with boron at diketonate moiety, the electron affinity could be enhanced. Moreover, the structural perturbation should be suppressed by the complexation. As a result, the planarity of the complex can be maintained. These effects play significant roles in the formation of robust conjugation system. The peak positions showed slight shift by increasing complexation ratios from **PF58** to **PF100**. These results are summarized as that boron complexation should contribute to enhancing the electronic coupling between fluorene and diketonate moieties. In addition, the conjugation could be extended within a single fluorene−diketonate pair.

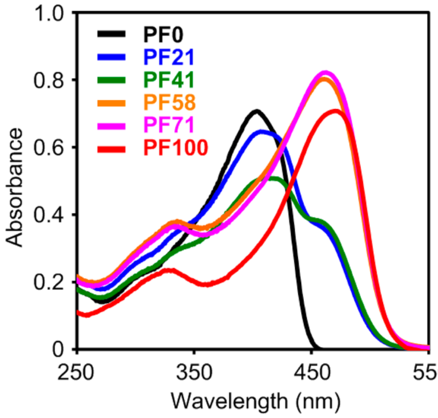


Figure 2. UV−vis spectra of the polymers in chloroform (1.0×10^{-5} M).

Emission Properties of the Polymers. The emission properties of the polymers were compared with various complexation ratios (Figure 3). **PF0** showed weak emission with the peak at 450 nm. In contrast, the introduction of boron at the diketonate moiety greatly induced strong emission bands with the peak around 550 nm. The strong electron coupling between fluorene and boron diketonate could provide significant emission bands. Interestingly, **PF21** showed the largest quantum yields of the polymers. It is presumed that the concentration quenching could occur in the polymers with higher complexation ratios of boron. Similarly as the discussion on the peak positions in absorption spectra from **PF58** to **PF100**, slight peak shifts were observed in the boron-containing polymers. These data also imply the weak correlation between each boron complex. The samples were excited at the peak wavelengths of the absorption. Thereby, the diketonate units should be excited in the samples of **PF21** and

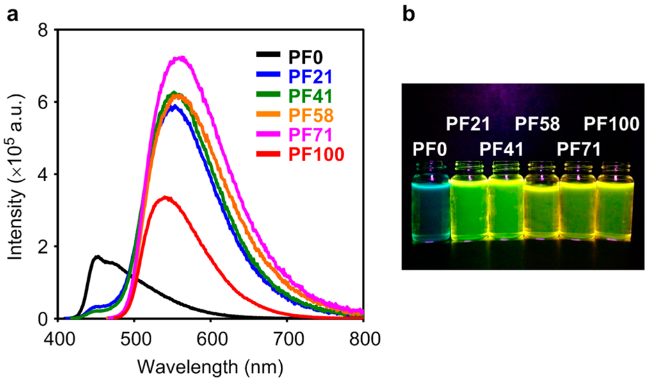


Figure 3. (a) Emission spectra of the polymers in chloroform (1.0 × 10^{-5} M) with various complexation ratios with boron. The excitation wavelengths were at the peak positions in the absorption spectra. (b) Picture of the chloroform solutions of the polymers under UV irradiation (365 nm).

PF41. However, compared to the emission intensity of the boron diketonate units, the emission from the diketonate unit was far smaller. Therefore, it can be said that the discussion on the emission properties concerns to the boron diketonate units.

Optical properties of the polymer films were evaluated. The chloroform solutions of each polymer were cast onto the quartz plate, and the emission spectra were collected. In contrast to the solution states, the emission colors were drastically changed (Figure 4). **PF0** showed the emission band with the peak at 504 nm in the blue region. The orange emission was detected from the cast film with **PF100**. These data can be explained by the speculation that the stacking formation with boron diketonates could induce the bathochromic shift in the emission spectra because of the improved planarity by boron complexation.

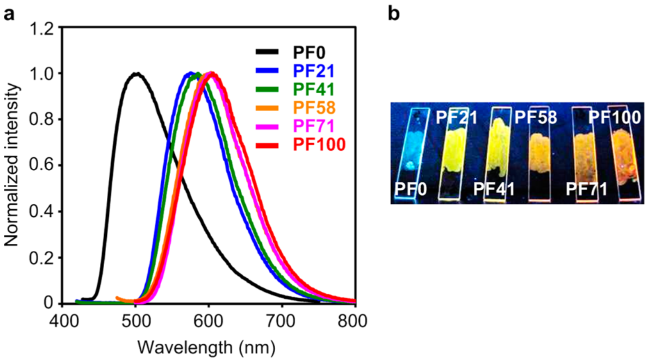


Figure 4. (a) Emission spectra of the polymer films with various complexation ratios with boron. The excitation wavelengths were at the peak positions in absorption spectra in the solutions. (b) Picture of the polymer films under UV irradiation (365 nm).

Emission Mechanism of the Synthesized Polymers. To investigate the emission mechanism from the polymers, the solvent dependency on optical properties was examined (Table 2).[13] The polymers were dissolved in chloroform, THF, DMF, and acetonitrile, and the photoluminescence spectra were monitored with the excitation light at the peaks determined from absorption spectra. The bathochromic shift of the peak position of the emission band and the decrease of the intensity were observed by increasing solvent polarity in the **PF100** sample. In THF, the large emission band with the peak at 535 nm was obtained from **PF100**. In contrast, the small emission was detected with the peak at 598 nm in acetonitrile. According to the Lippert–Mataga plots prepared from the **PF100** samples, the linear relationship between the solvent polarity and the Stokes shifts was obtained (Figure 5a).[14] These data indicate that the emissions from **PF100** should be originated from the CT states with the diketonate unit as an electron acceptor and the fluorene moiety as an electron donor. From **PF0**, weaker correlations between solvent polarity and optical properties were detected than those of **PF100**. Diketonate units could work as a weak electron-accepting group intrinsically.

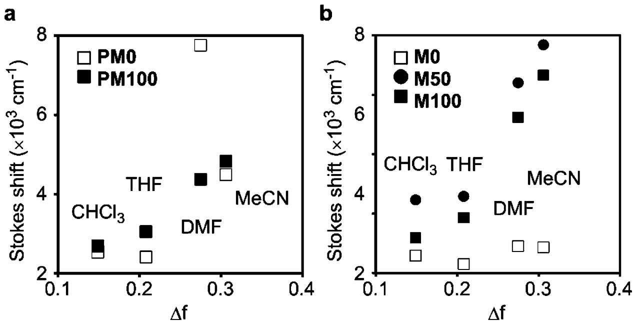


Figure 5. Lippert–Mataga plots of the polymers (a) and model compounds (b) obtained from the data in Table 2. The solvent function Δ*f* was defined in eq 2 for a series of various solvents.

To confirm the influence of the complexation rate on the CT emission involving the boron diketonate complexes, the optical properties of **M0**, **M50**, and **M100** were examined with various types of solvents (Table 2).[15] As similar procedures with the polymers, the compounds were dissolved in the organic solvents with different polarity, and the emission spectra were collected. The similar behaviors to **PF100** were obtained from **M50** and **M100** solutions: The bathochromic shifts of the emission bands and the decreases of the intensity were observed by increasing solvent polarity. In addition, the linear relationships were obtained from the Lippert–Mataga plots

Table 2. Photophysical Properties of Compounds in Various Kinds of Solvents

	chloroform			THF			DMF			acetonitrile		
compd	Φ_{PL}[a]	$\lambda_{PL,max}$[b] (nm)	Stokes shift (cm^{-1})	Φ_{PL}[a]	$\lambda_{PL,max}$[b] (nm)	Stokes shift (cm^{-1})	Φ_{PL}[a]	$\lambda_{PL,max}$[b] (nm)	Stokes shift (cm^{-1})	Φ_{PL}[a]	$\lambda_{PL,max}$[b] (nm)	Stokes shift (cm^{-1})
PF0	0.149	448	2530	0.208	446	2410	0.275	462	7750	0.306	476	4490
PF100	0.209	538	2690	0.244	535	3050	0.010	593	4370	0.015	598	4830
M0	0.186	444	2290	0.115	440	2150	0.213	446	2450	0.200	443	2430
M50	0.845	532	3230	0.807	531	3290	0.154	603	5200	0.150	614	5840
M100	0.781	539	2590	0.614	545	2930	0.010	620	4620	0.005	629	5630

[a] Absolute quantum yield. [b] Measured in the solution (1.0 × 10^{-5} M) with the excitation light at the peak wavelength of absorption.

with **M50** and **M100** (Figure 5b).[14] On the other hand, the **M0** solutions showed slight dependency of optical properties on solvent polarity. These results clearly indicate that the emission bands of boron−diketonate complexes should be originated from the CT emission. Moreover, the electron affinity of the diketonate moiety is enhanced by the boron complexation.

CONCLUSION

The optical properties of the synthesized polymers with various complexation ratios of boron are summarized as follow: Boron complexation enhances the electron acceptability and planarity of the diketonate moiety. Consequently, the strong emission originated from CT by the combination with fluorene and boron diketonate units can be obtained. However, excess increases of complexation ratios induced concentration quenching, resulting in lowering quantum yields. Furthermore, the electronic coupling is valid between a single fluorene and boron diketonate. Thereby, in the solution state, the boron complexation greatly influences on the emission intensity. In contrast, in the film state, the stacking should be formed between boron diketonate units. Finally, the emission colors can be tuned from blue to orange regions by changing the complexation ratios. Our concept presented here is a facile technique to modulate electronic states of conjugated polymers and to optimize properties for receiving advanced materials with functional diversity.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures S1−S4. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(12) See Figure S1 in the Supporting Information.

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