Isolation of π -Conjugated System Through Polyfluorene from Electronic Coupling with Side-Chain Substituents by Cardo Structures

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ABSTRACT: The electronic coupling via the cardo structure in polyfluorene (PFs) was investigated. The series of fluorene units alternatively having alkoxyphenyl as an electron-donating group (EDG) and/or alkyl benzoate as an electron-withdrawing group (EWG) at the cardo carbon were synthesized. From the investigation of optical properties of the polymers containing these fluorene units, it was found that the electronic states of the substituents at the cardo carbons and the PF main chains should be less influenced by the introduction of EDG and/or EWG at the cardo structure. Furthermore, these preservation effects in the cardo-PFs were observed in the film states even after the thermal

INTRODUCTION The polyfluorene (PF) is one of the widely known optical polymers having a bright blue emission.¹⁻⁴ More recently, the robust π -conjugation system through the PF main chain has been recognized as a scaffold for fabricating the advanced optoelectronic materials. For instance, the PF films containing metalloporphyrin as a sensitizer can be used as anti-Stokes fluorescent materials which show the photon upconversion and the generation of higher energy photons than those of the incident light.⁵⁻⁸ As the rigid structure of the PFs can suppress the thermal deactivation of the triplet-excited state produced by the sensitizing reaction under the light irradiation, the singlet-excited state can be efficiently generated via the triplet-triplet annihilation process.⁹ These materials are promising to break through the theoretical limitation on the transition efficiency in the photovoltaic cells.¹⁰ Although construction and elongation of the conjugation systems are still main subjects, the disconnection and isolation of the electronic coupling are also of significance to control a conjugation to receive superior properties from polymers.

Optical properties observed from the solution state are often compromised in the solid states. Particularly, in the case of PFs, the excimer formation, the β -phase conformation, and the interchain interactions are well known as a decay process of an exciton.¹¹⁻¹³ One of the solutions to avoide these

treatment. We conclude that the electronic structures of the PF main chain are highly preserved from the correlations with the substituents at the cardo carbons. This is the first example, to the best of our knowledge, to survey the systematic information on the electronic structures of the cardo-PFs and offer the preservation effect of the optical properties from the introduction of EDGs and EWGs at the cardo carbon. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 000: 000–000, 2012

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processes is an introduciton of functional groups at the 9position. The phenyl groups bonded at the 9-position of a fluorene are three dimensionally arranged to the fluorene unit.^{14–17} The construction of such a tetrahedral bonding carbon into the 9-position of the fluorene, called as a cardo structure, is valid for improving thermal stability and durability against oxidation compared to those of dialkyl-substituted PFs.¹⁸⁻²⁰ In the film states of the dialkyl-substituted PFs, the annealing process should induce the fluorenone formation by oxidation, resulting in a loss of the bright blue emission of PFs.²¹⁻²³ These unfavorable oxidation can be significantly suppressed at the cardo structure. Moreover, owing to the steric hindrance of the bulky phenyl groups, the interchain and/or intrachain aggregations of the main chains are efficiently disturbed. $^{24-27}$ The isolation of the electronic states of the PF main chains resulted in the strong blue emission of the PFs. Thus, the cardo fluorenes are the attractive building block to construct the highly functional polymeric materials.^{28,29}

Using polycardofluorenes as a template to build up functional nanomaterials, the information on the electronic structure and coupling are essential. There are several reports on the energy or charge transfer through the cardo structures with the functional unit-tethered cardo-PFs.^{30,31} Although it was presented that the weak electronic coupling through the

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cardo structures could exist, most of the previous studies mainly focused on the energy transferring between the functional groups tethered to the 9-position of the fluorene and the PF main chains.³² In particular, there is very few systematic information about the substituent effect on the electronic coupling and the extension of the conjugation through the cardo structures in the PFs. For developing the applicability of the PFs as a scaffold for the advanced all-organic devices, the fundamental study on the conjugation through the cardo structure should be necessary.

Herein, to clarify the electronic interaction via the cardo structures particularly the electronic substituent effect, we synthesized and characterized the electronic properties of the PFs with the electron-donating groups (EDGs) and/or the electron-withdrawing groups (EWGs) at cardo structures. The dibromo monomers containing dual alkyl benzoate groups as an EWG, dual alkoxyphenyl groups as an EDG, and single each group were, respectively, prepared, and the corresponding polymers were obtained via Yamamoto coupling. The influence on the optical properties by introducing the substituents was evaluated both in the solution and in the film states. The computer calculation models and the data from cyclic voltammetry (CV) support the discussions on the electronic substituent effect of the PF main chains. This is the first example, to the best of our knowledge, to offer the systematic study on the electronic states of the cardo-PFs.

EXPERIMENTAL

General

¹H NMR and ¹³C NMR spectra were measured with a JEOL EX-400 (400 MHz for ¹H and 100 MHz for ¹³C) spectrometer. Coupling constants (J-value) are reported in hertz. The chemical shifts are expressed in ppm downfield from tetramethylsilane using residual chloroform ($\delta = 7.24$ in ¹H NMR, $\delta =$ 77.0 in ¹³C NMR) as an internal standard. 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. 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. Fluorescence lifetime analysis was carried out on a HORIBA FluoreCube spectrofluorometer system with the excitation light at 375 nm from a UV diode laser (NanoLED-375L). CV spectra were recorded on a BAS ALS electrochemical analyzer model 600D. Fourier transform infrared (FTIR) spectra were obtained using a Shimadzu IRPrestige-21 infrared spectrometer. Thermogravimetric analyses (TGAs) were performed on a Seiko TG/DTA 6200 at a scan rate of 10° C/min.

Materials

Tetrahydrofuran (THF), diethyl ether (Et₂O), and triethylamine (Et₃N) were purified using a two-column solid-state purification system (Glasscontour System, Joerg Meyer, Irvine, CA). 2,7-Dibromo-9-fluorenone, 2,7-dibromofluorene, 1-bromo-4-(diethoxymethyl)benzene, and 2,7-dibromo-9,9dioctyl-9H-fluorene were obtained commercially and used without further purification. 4,4'-(2,7-Dibromo-9H-fluorene-9,9-diyl)diphenol (**1**) and 4-(2,7-dibromo-9-hydroxy-9H-fluoren-9-yl)benzaldehyde (**6**) were prepared according to the literatures.^{33,34} All reactions were performed under nitrogen atmosphere.

2,7-Dibromo-9,9-*bis*(4-(octyloxy)phenyl)-9H-fluorene (2, M1)

Bromooctane (1.52 g, 7.88 mmol) was added to a methanol solution (15 mL) of 1^{33} (2.00 g, 3.94 mmol) and potassium hydroxide (0.44 g, 7.88 mmol). After refluxing for 24 h, the resulting mixture was poured into brine, extracted with cyclopentyl methyl ether (CPME), and dried over anhydrous Na₂SO₄. After evaporation to remove the solvent, the crude product was purified by the silica gel column chromatography with eluent ethyl acetate/*n*-hexane (1/16) to afford **M1** (1.74 g, 61%) as a colorless oil.

¹H NMR (CDCl₃, ppm) 7.54 (d, J = 7.9 Hz, 2H), 7.46 (d, J = 5.0 Hz, 2H), 7.43 (d, J = 3.5 Hz, 2H), 7.04 (d, J = 8.8 Hz, 4H), 6.75 (d, J = 9.0 Hz, 4H), 3.88 (t, J = 6.6 Hz, 4H), 1.73 (dt, J = 7.0 Hz, 4H), 1.46–1.22 (m, 24H), 0.87 (t, J = 7.1 Hz, 6H). ¹³C NMR (CDCl₃, ppm) 158.23, 153.75, 137.83, 136.23, 130.70, 129.26, 128.97, 121.77, 121.48, 114.33, 67.92, 64.36, 31.78, 29.31, 29.24, 29.21, 26.03, 22.63, 14.07. HRMS (EI) calcd for C₄₁H₄₈O₂Br₂: m/z = 730.2021; Found: m/z = 730.2011.

4,4'-(2,7-Dibromo-9H-fluorene-9,9-diyl)dibenzonitrile (3) A mixture of 2,7-dibromofluorene (10.00 g, 30.9 mmol), toluene (15 mL), DMF (50 mL), 18-crown-6-ether (4.08 g, 15.4 mmol), potassium carbonate (10.30 g, 75.1 mmol), and 4-fluorobenzonitrile (8.20 g, 67.7 mmol) was stirred at 140°C for 15 h. After cooling, the solution was dropped into 500 mL of CPME. The product was filtered and washed with water to give **3** 5.76 g (35%) as a yellow solid.

¹H NMR (CDCl₃, ppm) 7.64 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 8.3 Hz, 4H), 7.57 (d, J = 9.3 Hz, 1.7 Hz, 2H), 7.39 (d, J = 1.5 Hz, 2H), 7.23 (d, J = 8.3 Hz, 4H). ¹³C NMR (CDCl₃, ppm) 150.42, 148.63, 138.10, 132.74, 132.11, 129.01, 128.53, 122.45, 122.17, 118.21, 111.84, 65.44. HRMS (FAB⁺) calcd for C₂₇H₁₄Br₂N₂: m/z = 523.9524; Found: m/z = 523.9504.

4,4'-(2,7-DIBROMO-9H-FLUORENE-9,9-DIYL)DIBENZOIC ACID (4)

A mixture of potassium hydroxide (8.50 g, 151.5 mmol) and **3** (5.66 g, 10.8 mmol) in ethanol (25 mL) and distilled water (30 mL) was stirred at 80° C for 3 days. After cooling, the pH value of the reaction mixture was adjusted to nearly 2 by 2N

hydrochloric acid. The generated precipitate was collected by filtration and washed with water to afford 6.03 g of the product (99%) as a white powder.

¹H NMR (DMSO-d₆, ppm) 12.92 (s, 2H), 7.97 (d, J = 7.8 Hz, 2H), 7.87 (d, J = 8.3 Hz, 4H), 7.67 (d, J = 8.7 Hz, 2H), 7.63 (s, 2H), 7.24 (d, J = 8.3 Hz, 4H). ¹³C NMR (DMSO-d₆, ppm) 166.85, 151.46, 148.55, 137.88, 131.53, 129.85, 128.75, 127.83, 123.15, 121.56, 65.24. HRMS (ESI) calcd for C₂₇H₁₆Br₂O₄-H⁺: m/z = 560.9343; Found: m/z = 560.9330.

Dioctyl 4,4'-(2,7-dibromo-9H-fluorene-9, 9-diyl)dibenzoate (5, M2)

Thionyl chloride (15 mL) was added to 4 (1.69 g, 3.0 mmol), and then the solution was refluxed for 3 h. The residual thionyl chloride was removed *in vacuo*. Dibenzoyl chloride was obtained as a red solid and used for the next reaction without further purification. A mixture of dibenzoyl chloride, pyridine (15 mL), octanol (0.78 g, 6.0 mmol), and THF (30 mL) was stirred at room temperature overnight. The resulting mixture was diluted with 1N HCl, and the product was extracted with CPME. The combined organic extracts were washed with brine and dried over anhydrous Na₂SO₄. After removing the solvent, the crude product was purified by silica gel column chromatography with eluent ethyl acetate/ *n*-hexane (1/20) to afford **M2** (1.58 g, 67%) as a colorless oil.

¹H NMR (CDCl₃, ppm) 7.94 (d, J = 8.3 Hz, 4H), 7.62 (d, J = 8.0 Hz, 2H), 7.53 (dd, J = 8.1 Hz, 1.7 Hz, 2H), 7.45 (d, J = 1.7 Hz, 2H), 7.20 (d, J = 8.4 Hz, 4H), 4.29 (t, J = 6.6 Hz, 4H), 1.77–1.67 (m, 4H), 1.44–1.22 (m, 24H), 0.87 (t, J = 7.1 Hz, 6H). ¹³C NMR (CDCl₃, ppm) 166.11, 151.60, 148.81, 138.11, 131.52, 129.96, 129.24, 127.84, 125.49, 121.86, 65.18, 62.31, 31.75, 29.49, 29.20, 29.09, 26.00, 22.60, 14.06. HRMS (APCI) calcd for $[C_{43}H_{48}Br_2O_4+H]^+$: m/z = 787.1992; Found: m/z = 787.1954.

4-(2,7-Dibromo-9-(4-(octyloxy)phenyl)-9H-fluoren-9-yl)benzaldehyde (7)

Trifluoromethanesulfonic acid (5.99 g, 40.0 mmol) was slowly added to a dioxane solution (100 mL) of 6^{34} (13.8 g, 31.1 mmol) and *n*-octyl phenyl ether (7.80 g, 37.8 mmol). After stirring at 70°C for 4 h, the resulting mixture was diluted with saturated aqueous NaHCO₃, and the product was extracted with CPME. The combined organic extracts were washed with brine, and dried over anhydrous Na₂SO₄. After removing the solvent, the crude product was purified by silica gel column chromatography with eluent ethyl acetate/*n*-hexane (1/12) to afford the product **7** (16.0 g, 82%) as a white solid.

¹H NMR (CDCl₃, ppm) 9.88 (s, 1H), 7.70 (d, J = 8.0 Hz, 2H), 7.56–7.50 (m, 4H), 7.44 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 7.7 Hz, 2H), 7.05 (d, J = 7.1 Hz, 2H), 6.77 (d, J = 8.6 Hz, 2H), 3.84 (t, J = 6.3 Hz, 2H), 1.75–1.66 (m, 2H), 1.45–1.19 (m, 12H), 0.86 (t, J = 6.8 Hz, 3H). ¹³C NMR (CDCl₃, ppm) 191.10, 158.33, 152.27, 151.52, 137.78, 135.07, 134.78, 131.04, 129.68, 129.03, 128.72, 128.30, 121.85, 121.60, 114.46, 67.62, 64.96, 31.58, 29.12, 29.01, 28.90, 25.83,

22.45, 13.96. HRMS (MALDI) calcd for $C_{34}H_{32}Br_2O_2$: m/z = 632.07541; Found: m/z = 632.07358.

4-(2,7-Dibromo-9-(4-(octyloxy)phenyl)-9H-fluoren-9-yl)benzoic acid (8)

A mixture of NaClO₂ (2.28 g, 25.2 mmol), NaH₂PO₄ (3.04 g, 25.3 mmol), and H₂O (20 mL) was slowly added to an acetone solution (20 mL) of **7** (2.00 g, 3.15 mmol) and 2-methyl-2-butene (2 mL). After stirring at room temperature for 1 h, the resulting mixture was diluted with 3 N HCl (50 mL), and the product was extracted with CPME. The combined organic extracts were washed with saturated aqueous $Na_2S_2O_3$ twice and dried over anhydrous Na_2SO_4 . The product **8** was obtained as a white powder (1.85 g, 91%).

¹H NMR (DMSO-d₆, ppm) 12.88 (s, 1H), 7.87 (m, 4H), 7.57 (m, 4H), 7.22 (d, J = 7.6 Hz, 2H), 6.99 (d, J = 7.5 Hz, 2H), 6.78 (d, J = 7.8 Hz, 2H), 4.29 (t, J = 6.7 Hz, 2H), 1.65–1.53 (m, 2H), 1.29–1.06 (m, 12H), 0.78 (t, J = 6.6 Hz, 3H). ¹³C NMR (DMSO-d₆, ppm) 166.89, 157.86, 152.45, 149.27, 137.72, 135.12, 131.10, 129.68, 128.64, 127.67, 122.89, 121.36, 114.49, 67.32, 64.60, 31.18, 28.61, 25.46, 22.03, 13.86. HRMS (APCI) calcd for $[C_{34}H_{32}Br_2O_3-H]^-$: m/z = 645.0616; Found: m/z = 645.0645.

Octyl 4-(2,7-dibromo-9-(4-(octyloxy)phenyl)-9Hfluoren-9-yl)benzoate (9, M3)

Thionyl chloride (8 mL) was added to **8** (1.80 g, 2.8 mmol), and the solution was refluxed for 3 h. After the reaction, the residual thionyl chloride was removed *in vacuo*. Benzoyl chloride was obtained as a red solid and used for the next reaction without further purification. A mixture of benzoyl chloride, pyridine (10 mL), octanol (0.36 g, 2.8 mmol), and THF (20 mL) was stirred at room temperature for 3 h. The resulting mixture was diluted with 1N HCl, and the product was extracted with CPME. The combined organic extracts were washed with brine and dried over anhydrous Na₂SO₄. After removing the solvent, the crude product was purified by silica gel column chromatography with eluent ethyl acetate/*n*-hexane (1/25) to afford **M3** (1.92 g, 90%) as a colorless oil.

¹H NMR (CDCl₃, ppm) 7.91 (d, J = 8.5 Hz, 2H), 7.59 (d, J = 8.1 Hz, 2H), 7.49 (d, J = 8.3 Hz, 2H), 7.45 (s, 2H), 7.22 (d, J = 8.5 Hz, 2H), 7.01 (d, J = 8.8 Hz, 2H), 6.78 (d, J = 8.8 Hz, 2H), 4.28 (t, J = 6.6 Hz, 2H), 3.91 (t, J = 6.5 Hz, 2H), 1.79–1.65 (m, 4H), 1.45–1.22 (m, 24H), 0.90–0.84 (m, 6H). ¹³C NMR (CDCl₃, ppm) 166.26, 158.47, 152.71, 149.88, 138.00, 135.29, 131.12, 129.78, 129.45, 129.27, 128.96, 127.90, 121.95, 121.67, 114.57, 68.02, 65.11, 62.34, 31.78, 29.51, 29.31, 29.22, 29.17, 29.10, 28.72, 26.02, 25.75, 22.61, 14.06. HRMS (EI⁺) calcd for C₄₂H₄₈Br₂O₃: m/z = 758.1970; Found: m/z = 758.1941.

Synthesis of Polymer P1

A typical polymerization protocol via Yamamoto coupling¹⁶ is shown and discussed in this section. The solution containing 1,5-cyclooctadiene (COD) (0.16 mL, 1.30 mmol), Ni(COD)₂ (240 mg, 0.87 mmol), and 2,2'-bipyridine (160 mg, 1.02 mmol) in 8 mL of anhydrous DMF was stirred at 60° C





FIGURE 1 Molecular orbital diagrams for the HOMO and LUMO of the models (B3LYP/6-31G(d)//B3LYP/6-31G(d)).

for 30 min under N_2 , and then the monomer **M1** (303 mg, 0.414 mmol) in 4 mL of anhydrous DMF was added. The reaction was stirred at 80°C for 12 h in the dark. The products were reprecipitated several times with a small amount of chloroform into 250 mL of methanol. After celite filtration to remove Ni, the white solid (233 mg, 98%) was precipitated by pouring the chloroform solution of the product into 50 mL of methanol.

¹H NMR (CDCl₃, ppm) 7.72 (2H), 7.53 (4H), 7.15 (4H), 6.74 (4H), 3.87 (4H), 1.71(4H), 1.26 (20H), 0.86 (6H). ¹³C NMR (CDCl₃, ppm) 157.89, 152.75, 140.71, 138.72, 137.87, 129.13, 126.60, 124.75, 120.18, 114.14, 67.97, 64.42, 31.85, 29.41, 29.29, 26.14, 22.70, 14.13. IR (KBr, ν , cm⁻¹): 1246 (Ar—O—R), 1032 (Ar—O—R).

Synthesis of Polymer P2

Similarly to the preparation of **P1**, polymer **P2** was prepared from the monomer **M2** (308 mg, 0.39 mmol) in the presence of Ni(COD)₂ (240 mg, 0.87 mmol), COD (0.16 ml, 1.30 mmol), and bipyridine (160 mg, 1.02 mmol) in 94% yield as a pale green solid (230 mg).

¹H NMR (CDCl₃, ppm) 7.93 (4H), 7.79 (2H), 7.52 (2H), 7.49 (2H), 7.29 (4H), 4.27 (4H), 1.71(4H), 1.39 (4H), 1.24 (16H), 0.85 (6H). ¹³C NMR (CDCl₃, ppm) 166.44, 151.14, 150.43, 141.23, 139.39, 130.06, 129.72, 128.29, 127.64, 124.83, 121.07, 66.10, 65.45, 32.13, 29.57, 29.52, 29.10, 26.37,

22.98, 14.43. IR (KBr, v, cm⁻¹): 1718 (Ar—COO—R), 1273 (Ar—COO—R).

Synthesis of Polymer P3

The polymer **P3** was prepared from the monomer **M3** (338 mg, 0.44 mmol) in the presence of Ni(COD)₂ (240 mg, 0.87 mmol), COD (0.16 mL, 1.30 mmol), and 2,2'-bipyridine (160 mg, 1.02 mmol) in 96% yield as a pale yellow solid (256 mg).

¹H NMR (CDCl₃, ppm) 7.90 (2H), 7.77 (2H), 7.51 (4H), 7.31 (2H), 7.11 (2H), 6.77 (2H), 4.26 (2H), 3.88 (2H), 1.72 (4H), 1.39 (4H), 1.25 (16H), 0.86 (6H). ¹³C NMR (CDCl₃, ppm) 166.30, 159.97, 151.78, 151.32, 140.80, 138.88, 136.63, 129.52, 129.08, 128.03, 126.91, 124.56, 120.46, 114.33, 67.99, 65.10, 65.01, 31.84, 29.39, 29.25, 28.80, 26.12, 26.06, 22.67, 14.11. IR (KBr, ν , cm⁻¹): 1719 (Ar—COO—R), 1273 (Ar—COO—R), 1250 (Ar—O—R), 1020 (Ar—O—R).

Synthesis of Polymer PFO

Similarly to the preparation of **P1**, **PFO** was prepared from 2,7-dibromo-9,9-dioctylfluorene (226 mg, 0.41 mmol) in the presence of Ni(COD)₂ (240 mg, 0.87 mmol), COD (0.16 ml, 1.30 mmol), and 2,2'-bipyridine (160 mg, 1.02 mmol) in 94% yield as a pale green solid (151 mg).

¹H NMR (CDCl₃, ppm) 7.85 (2H), 7.70 (4H), 2.14 (4H), 1.15 (24H), 0.83 (6H). ¹³C NMR (CDCl₃, ppm) 151.43, 140.16,



SCHEME 1 Synthetic scheme of the monomers containing cardo structure. Reagents and conditions: (a) MeSO₃H, phenol, CCl₄, reflux, 48 h; (b) *n*-octyl bromide, KOH, MeOH, reflux, 24 h; (c) 1-cyano-4-fluorobenzene, 18-crown-6, K₂CO₃, DMF, toluene, 140°C, 48 h; (d) KOH, ethanol, water, 80°C, 4 d; (e) (i) SOCl₂, reflux, 3 h, (ii) *n*-octanol, pyridine, THF, room temperature, 3 h; (f) (i) Mg, 4-bromo-1-benzaldehyde diethyl acetal, THF, reflux, 16 h, (ii) 2 N HCl, room temperature, 1 h; (g) *n*-octyl phenyl ether, trifluoro-methanesulfonic acid, 1,4-dioxane, 70°C, 2 h; (h) NaClO₂, NaH₂PO₄, 2-methyl-2-butene, H₂O, acetone, room temperature, 1 h; (j) (i) SOCl₂, reflux, 3 h, (ii) *n*-octanol, pyridine, THF, room temperature, 3 h.

139.66, 125.81, 121.17, 119.59, 55.09, 40.13, 31.54, 29.79, 28.96, 23.72, 22.35, 13.80.

RESULTS AND DISCUSSION

Molecular Orbital Calculations

To estimate the electronic correlation via the cardo structure, we employed the theoretical calculation for the models of the polymers using density functional theory at the B3LYP/6-31G(d)/B3LYP/6-31G(d). The models of the polymers

having the single repeat unit linked the fluorene moiety at both sides. Figure 1 shows lowest unoccupied molecular orbital (LUMO), highest occupied molecular orbital (HOMO), and the resulting structures of the models. It was found that both the HOMOs and the LUMOs in the models were located on the PF main chain. It should be mentioned that the HOMOs and LUMOs of models containing the cardo structures hardly localize on their phenyl groups. There are subtle differences in the energy gaps (E_g) of the models. From these data, we assumed that the EDGs and/or EWGs via the cardo





SCHEME 2 Synthesis of the polymers. Reagents and conditions: (a) Ni(COD)₂, COD, 2,2'-bipyridine, DMF, 80°C, 12 h.

carbon could less significantly affect the electronic states of the PF main chain.

Synthesis of the Monomers

The monomers containing the cardo structures with the dual EDGs, 2,7-dibromo-9,9-bis(4-(octyloxy)phenyl)-9H-fluorene (M1), with the dual EWGs, dioctyl 4,4'-(2,7-dibromo-9H-fluorene-9,9-diyl)dibenzoate (M2), and with the coexisting single EDG and EWG, octyl 4-(2,7-dibromo-9-(4-(octyloxy)phenyl)-9H-fluoren-9-yl)benzoate (M3) were synthesized (Scheme 1). The dibromo fluorene monomers M1 and M2 were prepared according to the previous reports using 2,7-dibromofluorenone and 2,7-dibromofluorene as a starting material, respectively. To obtain the monomer M3, benzaldehyde and subsequently the 4-octyloxyphenyl group were introduced into 2,7-dibromofluorenone. All monomers were characterized by ¹H and ¹³C NMR spectroscopies and mass measurements. The dibromo monomers were obtained as colorless oils with high viscosity without significant fluorescence emissions.

Synthesis of the Polymers

The polymerization with the dibromo monomers via Yamamoto coupling³⁵ was executed as shown in Scheme 2. The polymer properties determined from the GPC analysis are summarized in Table 1. To remove the metal species originated from the catalyst thoroughly, the celite filtration and the following reprecipitation from methanol were repeated at least three times. The polymers P1, P2, P3, and PFO were obtained as pale green or white solids in good yields (94-98%). The solubility in conventional organic solvents seemed to be improved by constructing the cardo structures on the PF main chains. The number-average molecular weights (M_n) and the molecular weight distributions (M_w/M_n) of the polymers, measured by the SEC in chloroform toward polystyrene standards were from 10,500 to 46,600 with 2.8-8.1, respectively. These data suggest that the influence of the polymer ends should be negligible on the optical properties. In addition, the data for structural analysis by ¹H and ¹³C NMR and FTIR measurements were corresponded to those of the monomers. Thus, we concluded that the polymers should possess the designed chemical structures, and unexpected conformation or higher-ordered structures were less obtained in the solutions.

Thermal Properties of the Cardo Structure

The thermal stabilities of the polymers were investigated with TGA. The decomposition temperatures with 5% weight loss are listed in Table 1. The chain scissions in the PF main chain were observed at 403°C in **PFO**. The decomposition was observed at the similar temperature (405°C) from the polymer **P1**. These results indicate that the decomposition of the cardo structures less occurred. The lower decomposition temperatures of **P2** and **P3** would be derived from the degradation at the ester groups at the side chains. From these results, it is presented that the introduction of the cardo structure can contribute to improve thermal stabilities of the PF main chains.

Absorption Spectra of the Polymers

The optical properties of the polymers were initially investigated by UV-vis absorption in CHCl₃ solution and solid thin film state as compared to those of **PFO** (Fig. 2). The results from the absorption and emission spectra are summarized in Table 2. The absorption of **PFO** consists of a π - π * transition

TABLE 1 Polymerization Results

Polymers Yield (%) ^a M_n^b M_w/M_n^b DP ^c T_{5d}^d P1 98 46,600 8.1 81 405 P2 94 10,500 2.8 17 364 P3 96 14,900 3.0 25 365 PFO 94 18,500 4.2 48 403						
P19846,6008.181405P29410,5002.817364P39614,9003.025365PFO9418,5004.248403	Polymers	Yield (%) ^a	$M_{\rm n}{}^{\rm b}$	$M_{\rm w}/M_{\rm n}^{\rm b}$	DPc	$T_{5d}{}^{d}$
P2 94 10,500 2.8 17 364 P3 96 14,900 3.0 25 365 PFO 94 18,500 4.2 48 403	P1	98	46,600	8.1	81	405
P3 96 14,900 3.0 25 365 PFO 94 18,500 4.2 48 403	P2	94	10,500	2.8	17	364
PFO 94 18,500 4.2 48 403	P3	96	14,900	3.0	25	365
	PFO	94	18,500	4.2	48	403

^a Isolated yields after precipitation.

^b Estimated by SEC based on polystyrene standards in chloroform.

^c Degree of polymerization estimated by number-average molecular weight.

 $^{^{\}rm d}$ TGA: heating rate 10 K/min under $N_2;$ values given for weight loss of 5%.



FIGURE 2 UV-vis spectra of the polymers in $CHCl_3$ (1.0 \times 10^{-5} M).

that peaks at about 388 nm both in the solution and in the solid state. Then, the polymers **P1**, **P2**, and **P3** exhibited the strong absorption band in the region from 378 to 394 nm nearby absorption peak of **PF0**. In addition, the absorption onsets of the polymers, which are often used to define the optical gap, are in the range from 414 nm (3.00 eV) to 416 nm (2.99 eV). In particular, the differences in the HOMO-LUMO gaps of the polymers having EDGs, EWGs, or both groups were within 0.01 eV. Moreover, similar results were obtained from the film samples of the cardo-PFs. These results significantly indicate that the electronic structures of the PF main chains should be isolated from the influences from the EDG and the EWG at the cardo sites, and the energy levels of the PF main chains were maintained at the ground states.

Emission Properties of the Polymers

The emission properties of the cardo-PFs were investigated in the solution states (Fig. 3). The polymers were dissolved in chloroform, and the photoluminescence spectra were obtained with the excitation light at 375 nm. All samples

	Solution ^a			Film ^b		
Polymer	λ _{abs,max} (nm)	λ _{PL,max} (nm) ^c	$\Phi_{PL}{}^d$	λ _{abs,max} (nm)	λ _{PL,max} (nm) ^c	Φ_{PL}^{C}
P1	392	418	0.82	394	422	0.22
P2	378	417	0.87	379	420	0.25
P3	383	416	0.90	385	422	0.21
PFO	388	416	0.72	388	439	0.24

^a Evaluated in chloroform (1.0 \times 10⁻⁵ M).

^b Evaluated in the solid state; prepared from chloroform solutions.

^c Excited at 385 nm.

^d Absolute quantum yield.





FIGURE 3 Photoluminescence spectra of the polymers in CHCl3 (1.0 \times 10 $^{-5}$ M).

involving the **PFO** solution showed similar spectra with the peaks at 418, 444, and 475 nm assigned as the 0–0, 0–1, and 0–2 intrachain singlet transition.³⁶ It should be mentioned that the red-shift of the peaks or annihilation was hardly observed in the spectra. The absolute photoluminescence quantum efficiencies of the cardo-PFs are large and the values are >80% (Table 2). These results clearly indicate that the electronic structures at the excitation states were less influenced by the introduction of the substituents at the phenyl groups of the cardo structures. In particular, despite the electron negativity of the PF main chains,^{37–39} the bi-substitued EWGs hardly cause the change in the intrinsic optical properties of the PF main chains. Moreover, electronic interaction between the modified phenyl groups via the cardo carbon should less exist.



FIGURE 4 Photoluminescence spectra of the polymers in the film states.

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FIGURE 5 Photoluminescence spectra of the polymers in the solid state after the thermal treatment at 200° C for 2 h.

The preservation effect of the electronic structures of the PF main chains by the cardo structures was observed in the film states (Fig. 4). The thin films for the measurements were prepared by the spin-coating method with the chloroform solutions of the polymers on the quartz plate. The photoluminescence spectra were measured with the excitation light at the same wavelength as the solutions (375 nm). The shapes of the emission spectra from the cardo-PFs were very similar not only to those of one another but also to the solution states. In particular, the significant red-shift and the broadening of the peaks originated from the excimer formation between the fluorene units was observed only in the PFO film.11 These data indicate that the cardo structure should contribute to the preservation of the electronic states of the PF main chains in the condensed states from the interchain interaction as well as from the electronic correlation via the cardo carbons. In addition, we investigated the optical properties of the films after heating at 200°C for 2 h to induce the oxidation at the fluorene units (Fig. 5). $^{21-23}$ Less significant changes from the films of the cardo-PFs were observed. Only the PFO film after the thermal treatment showed new broad peaks around 520 nm. From the measurements of the emission decay rates, it was found that

the new emission band at 520 nm possessed the longer life time than that of the singlet transition of the PF main chains detected at 420 nm (Table 3). These facts indicate that the thermally induced oxidative degradation in **PFO** should occur.¹³ These results including the TGA experiments can be summarized that the cardo is responsible for various preferable properties of the PFs as optical materials: The thermal stabilities against the production of the keto defect and pyrolysis were enhanced, and the electronic structures, resulting in the optical properties, were efficiently preserved.

Electrochemical Properties

CV (Fig. 6) was employed to investigate the redox behaviors of the polymers and to estimate their HOMO and LUMO energy levels. The measurements were executed with the films of the polymers on a glass substrate-coated indium tin oxide in acetonitrile containing 0.1M lithium perchlorate (LiClO₄) as an electrolyte. Ferrocene was used in this experiment as a reference to calculate the E_{ox} or E_{red} . The HOMO and LUMO levels were calculated using $E_{\rm ox}$ (onset) from the measurements. The values were obtained from the empirical relation $E_{\text{LUMO}} = [(E_{\text{red}} - E_{1/2(\text{ferrocene})}) + 4.8] \text{ eV or } E_{\text{HOMO}} =$ $[(E_{\text{ox}} - E_{1/2(\text{ferrocene})}) + 4.8]$ eV. Table 4 summarizes the results of the measurements with the polymer films. The cardo-PFs approximately showed $E_{\rm HOMO}$ values in the range from -5.85 to -5.88 eV, $E_{\rm gap}$ from 3.20 to 3.24 eV, and E_{LUMO} from -2.64 to -2.65 eV. **PFO** has similar values $(E_{\rm HOMO} = -5.68 \text{ eV}, E_{\rm gap} = 3.05 \text{ eV}$, and $E_{\rm LUMO} = -2.63 \text{ eV}$, respectively). These results also indicate that the cardo-PFs and PFO have almost the HOMO and LUMO at almost same energy levels. From the optical and electrochemical data, it can be concluded that the electronic energy levels of the PF main chains can be highly preserved from the EWG and EDG of the side chains on the cardo structures.

CONCLUSIONS

Three significant issues were obtained from this study. The synthesis of the cardo-PFs introduced by the EDG and/or the EWG at the phenyl groups of the cardo structures was established. The stepwise syntheses to integrate the heterogeneous EDG and EWG pair at the cardo structure were demonstrated. These synthetic protocols can be applied for preparing the dual-functional fluorene-based polymers. The second issue concerns about the influence on the electronic structures of the cardo-PFs. We clearly indicate that the

TABLE 3 Photoluminescence Lifetimes of the Polymers on Emission Wavelength at 520 nm

Thin Film State ^a (% Composition)			Thin Film State ^b (% Composition)				
τ_1/ns	τ_2/ns	τ ₃ /ns	χ ²	τ_1/ns	τ ₂ /ns	τ ₃ /ns	χ^2
5.72 (14)	1.68 (56)	0.42 (30)	3.469	7.83 (49)	2.28 (34)	0.46 (17)	1.625
9.79 (41)	2.20 (20)	0.41 (39)	3.011	9.15 (53)	2.55 (32)	0.43 (15)	1.435
7.30 (13)	1.75 (36)	0.42 (51)	3.223	8.26 (29)	1.72 (45)	0.37 (26)	1.267
8.36 (19)	2.11 (33)	0.48 (48)	5.505	5.23 (73)	1.29 (19)	0.21 (8)	1.040
	$\frac{\text{Thin Fi}}{\tau_1/\text{ns}}$ 5.72 (14) 9.79 (41) 7.30 (13) 8.36 (19)	$\begin{tabular}{ c c c c c } \hline Thin Film Statea (2) \\ \hline $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$ $$	$\begin{tabular}{ c c c c c } \hline Thin Film Statea (% Composite $$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$	$\begin{tabular}{ c c c c } \hline Thin Film State & (& Composition) \\ \hline $$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $

 a 1.0 \times 10 $^{-3}$ M Chloroform solution spin coated at 1,000 rpm for 10 s on quartz glasses.

^b After annealing at 200°C for 2 h.



FIGURE 6 Cyclic voltammograms of the polymers.

optical and electrochemical characteristics were highly preserved from the introduction of the substituents. The bi-substituted EWGs and EDGs caused the subtle changes in the intrinsic properties of the PF main chains, respectively. Moreover, less interaction was observed between the modified phenyl groups via the cardo carbon. Such isolation effects are feasible for conjugating the optical and/or electronic properties of PFs and additional functional units without unexpectedly changing their characteristics. As the third issue, it should be mentioned that the optical properties involving the strong and sharp blue emissions from the PF main chains and the electronic substituent effect were less observed in the film states. Even after the heating treatment to induce the oxidation at the fluorene units, the electronic structures of the PF main chains not only at the ground states but also at the excited states were robustly preserved by the introduction of the cardo structure. From the series of our results, it can be said that the cardo structure is promised to be a suitable scaffold for assembling the functional units to coexist with the preprogrammed multifunctions simultaneously in the solid devices.

TABLE 4 Electronic Energy Levels of the Polymers

	E _{HOMO} (ev)	E _{LUMO} ⁻ (ev)	E _{gap} ⁻ (ev)	Egap ⁻ (ev)
P1	-5.88	-2.64	3.24	2.99
P2	-5.85	-2.64	3.21	3.00
P3	-5.85	-2.65	3.20	3.00
PFO	-5.68	-2.63	3.05	2.99

^a Determined from cyclic voltammograms.

^b Calculated by absorption onsets of the polymers.



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