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Novel Through-Space Conjugated Polymers Consisting of Alternate [2.2]Paracyclophane and Fluorene

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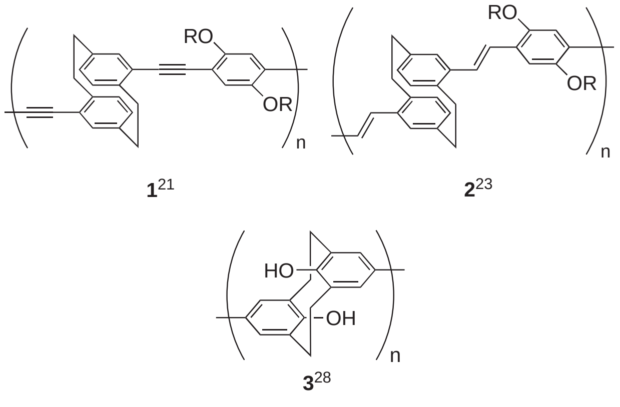
Novel through-space π-conjugated polymers having [2.2]paracyclophane and fluorene units were synthesized by the Suzuki coupling reaction. The polymers possessed good solubility in common organic solvents and good thermal stability. According to the UV–vis absorption spectra, the polymer showed an extension of π-delocalization via the through-space with π–π stacking compared with two kinds of model compounds. All of the polymers exhibited purplish-blue emission with high photoluminescence (PL) efficiencies of 73–81% in solution. The HOMO and LUMO energy levels of the polymer were estimated from the cyclic voltammogram.

[2.2]Paracyclophane, which has two layered benzene rings, has attracted much attention with regard to its structure, reactivity, and physical properties.[1,2] A number of paracyclophane derivatives have been prepared, and their unique properties, especially the structural and electronic properties due to characteristic interactions between the face-to-face π-electron systems, have been investigated in detail.[3–8] In addition, several polymers including a [2.2]paracyclophane skeleton in the main chain[9–12] or in the side chain[13–16] have been prepared so far. However, as to studies of the cyclophane-containing π-conjugated polymers, there have been only a few reports,[17–20] and the structures and properties of these polymers have not been studied, due to their poor solubility in common organic solvents. Recently, we reported on the first preparation and physical properties of well-defined π-conjugated polymers[21–29] having cyclophane derivatives as the key unit. Representative polymers, **1**[21] and **2**,[23] are shown in Chart 1. These polymers showed an extension of π-delocalization via the through-space with π–π stacking according to the UV–vis absorption spectra, and exhibited intense luminescence in solution.

On the other hand, charge transfer is essential to express conductivity and electroluminescence (EL), in which charge-hopping between the π-aromatic systems plays an important role. From this standpoint, Mizogami and Yoshimura reported on the first synthesis of poly(metacyclophane) **3** (Chart 1) by a polycondensation reaction of an oxidative dimer of 8,16-dihydroxy[2.2]metacyclophane. This polymer exhibited a conductivity of 0.25 S cm^{-1} by doping with H_2SO_4 vapor.[30] The incorporation of [2.2]paracyclophane bearing π-stacked benzene rings into the conjugated polymer backbone is expected for not only efficient charge-hopping, but also an effective enhancement of the aromatic content in the obtained materials. Therefore, [2.2]paracyclophane-containing conjugated polymers are promising candidates for high-performance optoelectronic devices.



1[21] **2**[23] **3**[28]

Chart 1.

Fluorene derivatives have a rigid planar structure, and their physical properties and solubility can easily be tuned by substitution at the C9 position. These are important building blocks for constructing blue-emitting polymers due to the high luminescence quantum efficiency and good thermal as well as air stability.[31] In the present study, we prepared novel π-conjugated polymers based on poly(p-phenylene) derivatives having [2.2]paracyclophane and fluorene units alternately in the main chain. Their physical properties, including the thermal, optical, and electrochemical behaviors, were investigated in detail.

Experimental

Materials. Toluene was distilled from sodium under a nitrogen atmosphere. Na_2CO_3, $Pd(PPh_3)_4$, and 2,5-dimethylphenylboronic acid **9** were obtained commercially, and used without further purification. 4,16-Dibromo[2.2]paracyclophane **4**,[32] 9,9-dialkyl-2,7-bis(1,3,2-dioxaborolan-2-yl)fluorene **5a–c**[33] and 9,9-dihexyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)fluorene **7**[34] were prepared as described in the literature. All of the reactions were performed under a nitrogen atmosphere using standard Schlenk techniques.

Measurements. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL EX-400 spectrometer. All samples were analyzed in $CDCl_3$, and the chemical-shift values were expressed relative to Me_4Si as

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an internal standard. UV–vis spectra were obtained on a JASCO V-530 spectrophotometer, and samples were analyzed in $CHCl_3$ at room temperature. Fluorescence emission spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer, and samples were analyzed in $CHCl_3$ at room temperature. Gel permeation chromatography was carried out on a TOSOH UV-8011 and RI-8000 (Shodex K-803L column) using $CHCl_3$ as an eluent after calibration with standard polystyrene. Thermogravimetric analysis (TGA) was made on a Seiko EXSTAR 6000 instrument (10 °C/min). Cyclic voltammetry was carried out under a nitrogen atmosphere using a BAS CV-50W voltammetric analyzer with a 0.10 M CH_3CN solution containing Bu_4NClO_4 as an electrolyte at a scan rate of 100 mV/s. Polymer films were prepared on glass coated with indium-tin oxide (ITO) by spin-coating from the corresponding toluene solutions and dried under vacuum. A platinum wire counter electrode and a Ag/AgCl reference electrode were used. Analytical thin-layer chromatography (TLC) was performed with silica gel 60 Merck F_{254} plates. Column chromatography was performed with Wakogel C-300 silica gel. Purification of the obtained polymers for improvement of the EL device performance was carried out on a recycling preparative HPLC (Japan Analytical Industry Co. Ltd., Model 918R) equipped with JAIGEL-1H and 2H columns (GPC) using $CHCl_3$ as an eluent. EL device fabrication and measurements were performed at Konica Minolta Technology Center, Inc. Low-resolution mass spectra (LRMS) and high-resolution mass spectra (HRMS) were obtained on a JEOL JMS-SX102A spectrometer. Elemental analysis was performed at the Microanalytical Center of Kyoto University.

Polymerization. A typical procedure[35] is as follows. A 50-mL Pyrex flask was charged with **4** (0.11 g, 0.30 mmol), **5a** (0.15 g, 0.30 mmol), $Pd(PPh_3)_4$ (0.035 mg, 0.03 mmol), 2.0 M aqueous Na_2CO_3 (0.50 mL, 1.0 mmol), toluene (8.0 mL), and a stirring bar under a flow of nitrogen. The reaction was carried out at a reflux temperature for 72 h with stirring. To the resulting solution were added AcOEt (10 mL) and H_2O (10 mL), and the organic layer was washed with H_2O several times. The combined organic layer was evaporated and dried in vacuo. This crude polymer was dissolved in toluene and washed three times with aqueous NH_3. The organic layer was dried over $MgSO_4$. After filtration of $MgSO_4$, the solvent was evaporated and dried in vacuo. The residue was dissolved in $CHCl_3$, and the resulting solution was poured into a large amount of MeOH to give a white polymer. The obtained polymer was washed with MeOH several times. After the product was dried under reduced pressure, a white polymer **6a** was obtained.

6a: Yield: 0.14 g, 0.27 mmol, 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.79 (br, 10H), 1.13 (m, 12H), 2.09 (br, 4H), 2.89–3.09 (m, 6H), 3.73 (br, 2H), 6.54 (m, 2H), 6.79 (m, 4H), 7.08 (m, 4H), 7.34–7.80 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.0, 22.1, 23.8, 29.9, 31.4, 33.4, 34.6, 40.7, 55.2, 119.9, 121.5, 125.2, 126.3, 130.1, 133.7, 136.8, 137.6, 138.1, 139.4, 140.8, 151.7.

6b: Yield: 169 mg, 0.24 mmol, 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.47–1.00 (m, 30H), 2.04 (br, 4H), 2.82–3.05 (m, 6H), 3.50 (m, 2H), 6.45–6.66 (m, 6H), 7.21–7.79 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.4, 14.1, 22.7, 27.2, 28.4, 33.0, 33.9, 34.0, 34.5, 44.4, 55.1, 119.5, 125.2, 126.7, 128.5, 128.7, 131.9, 134.8, 136.9, 139.6, 141.0, 142.6, 151.3.

6c: Yield: 137 mg, 0.23 mmol, 77%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.77 (br, 10H), 1.09 (m, 36H), 2.02 (br, 4H), 2.50–3.01 (m, 6H), 3.51 (br, 2H), 6.71 (m, 6H), 7.20–7.84 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7 24.1, 29.6 (overlapping signals), 31.9, 34.7, 40.6, 55.2, 119.8, 126.0, 127.1, 128.5, 128.7, 131.7, 132.0, 134.8, 137.0, 139.7, 142.2, 151.2.

Synthesis of the Model Compounds. 4,16-[Bis(9,9-dihexylfluoren-2-yl)][2.2]paracyclophane (8): A 50-mL Pyrex flask was charged with **4** (1.2 g, 3.3 mmol), **7** (3.1 g, 6.8 mmol), $Pd(PPh_3)_4$ (0.35 mg, 0.3 mmol), aqueous 2.0 M Na_2CO_3 (5.0 mL, 10 mmol), toluene (12 mL), and a stirring bar under a flow of nitrogen. The reaction was carried out at reflux temperature for 48 h with stirring. To the resulting solution were added AcOEt (10 mL) and H_2O (10 mL), and the organic layer was washed with H_2O several times. The combined organic layer was dried over $MgSO_4$. After filtration of $MgSO_4$, the solvent was evaporated and dried in vacuo. The resulting brown residue was subjected to column chromatography on SiO_2 with hexane–$CHCl_3$ (v/v = 3:1, $R_f = 0.75$) as an eluent to give compound **8** (2.1 g, 2.5 mmol, 74%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.70 (m, 10H), 0.83 (m, 10H), 1.05 (m, 12H), 1.20 (m, 12H), 2.04 (m, 8H), 2.73 (m, 2H), 2.89 (m, 2H), 3.05 (m, 2H), 3.55 (m, 2H), 6.67 (d, $J = 8.0$ Hz, 2H), 6.77 (m, 4H), 7.32 (m, 6H), 7.49 (s, 2H), 7.57 (d, $J = 8.0$ Hz, 2H), 7.78 (d, $J = 7.6$ Hz, 2H), 7.84 (d, $J = 7.6$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 14.0, 22.5, 22.8, 29.7, 31.5, 31.6, 34.2, 34.6, 40.5, 55.1, 119.7, 119.8, 122.8, 124.8, 126.8, 127.0, 128.2, 128.9, 132.1, 134.8, 137.0, 139.9, 140.0, 140.9, 142.6, 150.8, 150.9. LRMS (FAB) m/z (relative intensity) = 872 (M^+, 100), 540 ($M^+ - C_{25}H_{52}$, 73). HRMS (FAB): calcd for $C_{66}H_{80}$, 872.6260; found, 872.6256. Anal. Calcd for $C_{66}H_{80}$: C, 90.77; H, 9.23%. Found: C, 90.55; H, 9.47%.

2,7-Bis(2,5-dimethylphenyl)-9,9-dihexylfluorene (10): A 50-mL Pyrex flask was charged with **5a** (0.76 g, 1.5 mmol), **9** (0.60 g, 3.2 mmol), $Pd(PPh_3)_4$ (0.35 mg, 0.3 mmol), aqueous 2.0 M Na_2CO_3 (2.5 mL, 5 mmol), toluene (10 mL), and a stirring bar under a flow of nitrogen. The reaction was carried out at reflux temperature for 48 h with stirring. To the resulting solution were added AcOEt (10 mL) and H_2O (10 mL), and the organic layer was washed with H_2O several times. The combined organic layer was dried over $MgSO_4$. After filtration of $MgSO_4$, the solvent was evaporated and dried in vacuo. The resulting brown residue was subjected to column chromatography on SiO_2 with hexane–$CHCl_3$ (v/v = 3:1, $R_f = 0.67$) as an eluent to give compound **10** (0.63 g, 1.2 mmol, 78%) as a colorless viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.76 (m, 10H), 1.05 (m, 12H), 1.96 (m, 4H), 2.26 (s, 6H), 2.38 (s, 6H), 7.09 (d, $J = 7.6$ Hz, 4H), 7.15 (s, 2H), 7.18 (d, $J = 7.6$ Hz, 4H), 7.23 (s, 2H), 7.26 (d, $J = 8.2$ Hz, 4H), 7.73 (d, $J = 8.2$ Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 20.1, 21.0, 22.5, 23.8, 29.7, 31.5, 40.4, 55.1, 119.2, 123.8, 127.7, 127.8, 130.3, 130.5, 132.2, 135.1, 139.5, 140.7, 142.3, 150.6. LRMS (EI) m/z (relative intensity) = 542 (M^+, 100), 457 ($M^+ - C_6H_{13}$, 13), 373 ($M^+ - C_{12}H_{26}$, 20). HRMS (FAB): calcd for $C_{41}H_{50}$, 542.3913; found, 542.3914. Anal. Calcd for $C_{41}H_{50}$: C, 90.72; H, 9.28%. Found: C, 90.49; H, 9.35%.

Results and Discussion

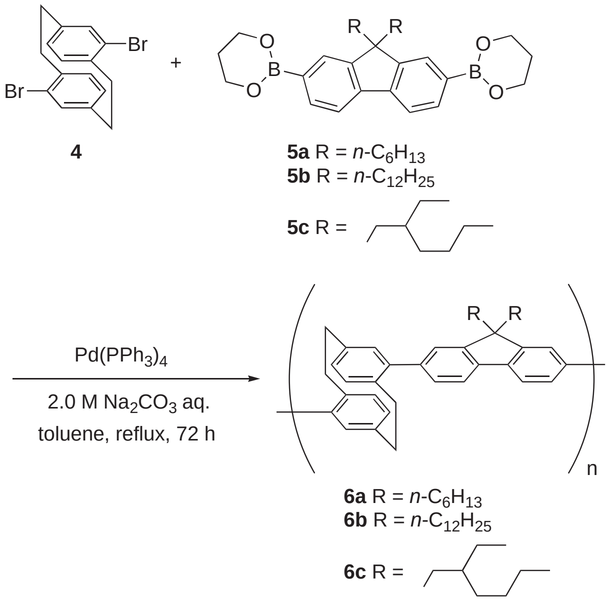
As shown in Scheme 1, monomers **4** and **5a–c** were easily polymerized to the corresponding polymers **6a–c** with $Pd(PPh_3)_4$ in toluene and an aqueous Na_2CO_3 solution at the reflux temperature for 72 h according to the Suzuki coupling reaction method.[35] After the reaction was completed, the organic layer was extracted and washed with H_2O. The organic solvent was evaporated and reprecipitated into a large amount of MeOH to obtain the crude polymers **6a–c**. The polymers

6a–c were dissolved in toluene and washed three times with aqueous NH_3 to remove the palladium species. The corresponding polymers **6a–c** were obtained in good yields of 77–89% as a white powder. The results are summarized in Table 1. All polymers had good solubility in common organic solvents, such as THF, $CHCl_3$, CH_2Cl_2, and toluene. In addition, the polymers could be processed into a pinhole-free thin film by casting or spin-coating from a toluene solution, and were found to be air stable in solution and in the solid state.

Molecular weight measurements were performed by gel-permeation chromatography (GPC) in the eluent $CHCl_3$ using the calibration curve of polystyrene standards, as listed in Table 1. For example, the number-average molecular weight (M_n), the weight-average molecular weight (M_w), and the molecular weight distribution (M_w/M_n) of the polymer **6a** obtained by run 1 were $M_n = 2600$, $M_w = 6500$, and $M_w/M_n = 2.5$, respectively. These polymers were characterized by their ^1H and ^{13}C NMR spectra. For example, in the ^1H NMR spectrum of **6a** in $CDCl_3$ (Fig. 1), the signals of the alkyl side chains dominated in the region of 0.80–2.2 ppm, and the bridged methylenes of a paracyclophane unit appeared at 2.5–3.5 ppm. The signals of the aromatic protons of a [2.2]paracyclophane unit and a fluorene unit appeared at 6.5–7.0 ppm and 7.0–8.0 ppm, respectively.

The thermal stability of polymer **6a** was evaluated by thermogravimetric analysis (TGA) under air; the result is shown in Fig. 2. This polymer possessed good thermal stability with a 10% weight loss temperature at 425 °C, at a heating rate of 10 °C/min. The decomposition of **6a** involved two steps. The first step started around 375 °C, which may be assigned to the thermal decomposition of the alkyl side chain of the polymer, and the second one, which started around 500 °C and completed at 600 °C, is attributed to the decomposition of the polymer backbone. This TGA result reveals that the polymer **6a** has sufficient thermal stability to be applied to light-emitting materials.

The optical properties of polymers **6a–c** are summarized in Table 2. The absorption spectrum of a **6a** solution as a representative polymer is shown in Fig. 3. Polymer **6a** shows a strong absorption peak at 340 nm in $CHCl_3$ at room temperature (run 1), which is the π–π^* transition band of the conjugated polymer backbone. On the other hand, two kinds of model compounds, **8** and **10**, were prepared. The synthetic procedure



Scheme 1.

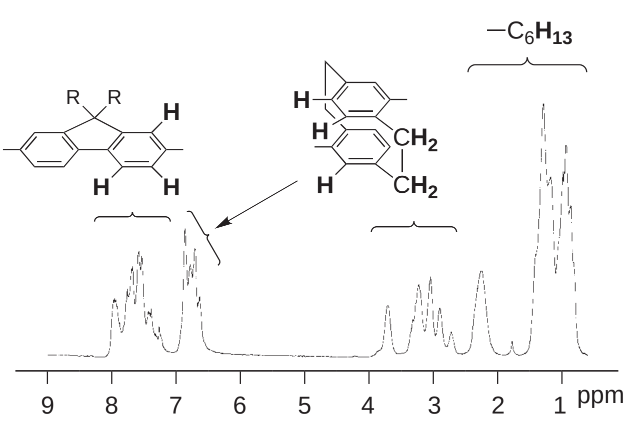


Fig. 1. ^1H NMR spectrum of **6a** in $CDCl_3$.

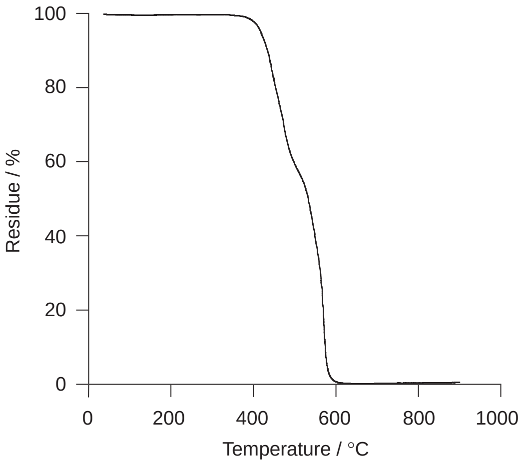


Fig. 2. Thermogravimetric analysis (TGA) of **6a** under air (10 °C/min).

Table 1. Syntheses of the Polymers **6a–c**[a)]

Polymer	R	Yield[b)]/%	M_w[c)]	M_n[c)]	M_w/M_n[c)]
6a	hexyl (**5a**)	89	6500	2600	2.5
6b	dodecyl (**5b**)	80	9900	4100	2.4
6c	2-ethylhexyl (**5c**)	77	5400	2300	2.4

a) Polymerization was carried out at reflux temperature in toluene for 72 h under N_2. b) Isolated yields. c) GPC (THF), polystyrene standards.

Table 2. Optical Properties of the Polymers **6a**–**c**

	Absorption $\lambda_{\max}$$^{a)}$/nm		PL $\lambda_{\max}$$^{a,b)}$/nm		
Polymer	Solution	Film	Solution	Film	$\Phi_{PL}$$^{c)}$
6a	340	339	392	415	0.81
6b	338	339	391	409	0.73
6c	334	333	383	406	0.80

a) Absorption and emission spectra were recorded in dilute $CHCl_3$ solutions at room temperature. b) Excited at absorption $\lambda_{\max}$ (1.0×10^{-6} M). c) PL efficiencies in $CHCl_3$ determined relative to 9-anthracenecarboxylic acid in CH_2Cl_2.

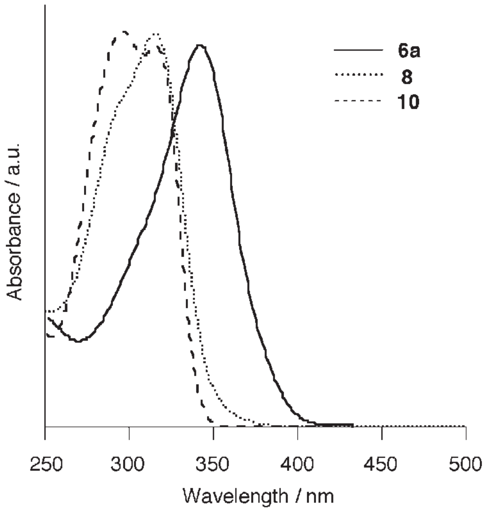
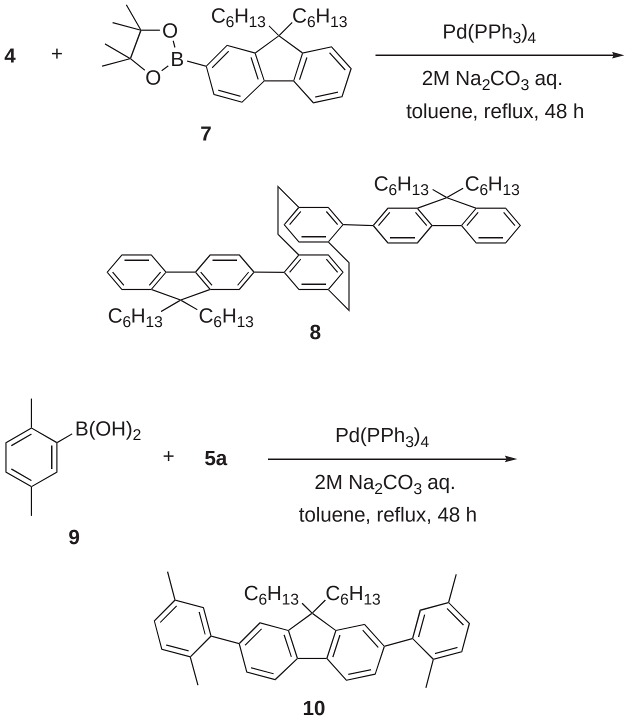


Fig. 3. UV–vis spectra of **6a** and the model compounds **8** and **10** in $CHCl_3$ solution at room temperature.

is outlined in Scheme 2, and the UV–vis absorption spectrum is also shown in Fig. 3. The absorption maximum ($\lambda_{\max} = 340$ nm) and the absorption edge (onset $\lambda = 415$ nm) of polymer **6a** showed a red shift relative to those of two model compounds, **8** ($\lambda_{\max} = 315$ nm, onset $\lambda = 380$ nm) and **10** ($\lambda_{\max} = 314$ nm, onset $\lambda = 350$ nm). This result indicates an extension of the π-delocalization length via the through-space based on face-to-face benzene rings of [2.2]paracyclophane. In addition, the absorption spectrum of the thin film of **6a** showed a peak maximum at 339 nm (Fig. 4). The spectrum and the value are almost the same as those obtained in solution (Fig. 4). Based on the absorption edges of the polymer film, the band gap energy of **6a** is approximately 3.0 eV.

In the fluorescence emission spectra of polymers **6a**–**c** in a dilute $CHCl_3$ solution at room temperature upon excitation at 340 nm, the emission peaks were observed at around 390 nm in the visible purplish-blue region (Table 2). The fluorescence emission spectrum of **6a** is shown in Fig. 4. The polymer solutions showed a high quantum efficiency; for example, **6a** had an efficiency of 0.81 in a $CHCl_3$ solution at room temperature, as demonstrated by using 9-anthracenecarboxylic acid in CH_2Cl_2 as a standard ($\Phi = 0.442$).[36] On the other hand, model compound **10** emitted at 385 nm for the excitation wavelength of 315 nm in $CHCl_3$ (1.0×10^{-6} M). The emission of **10** was slightly blue-shifted compared with that of **6a**, while the absorption maximum of **10** exhibited a relatively large blue shift of approximately 25 nm. These results imply that the excita-



Scheme 2.

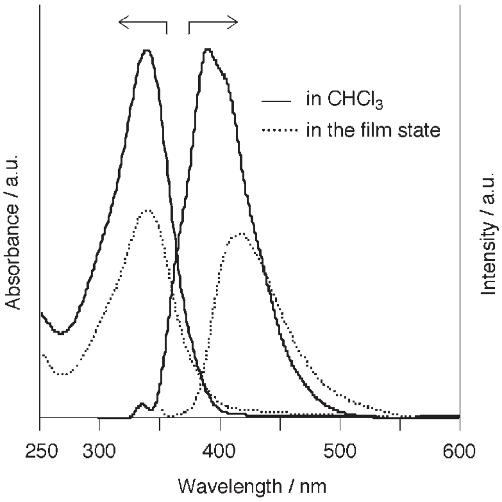
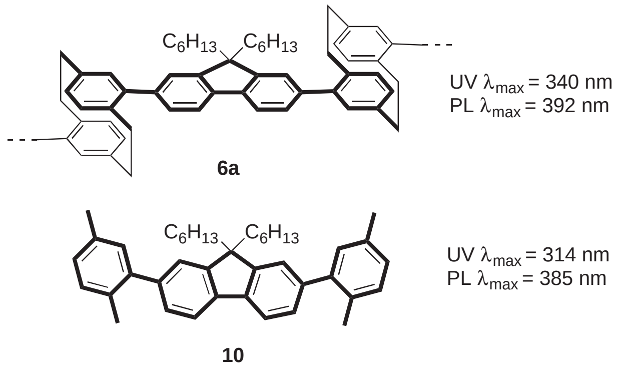


Fig. 4. UV–vis spectra of **6a** in $CHCl_3$ and in the film state, and fluorescence emission spectra of **6a** in $CHCl_3$ and in the film state on excitation at 340 nm.



6a

10

Chart 2.

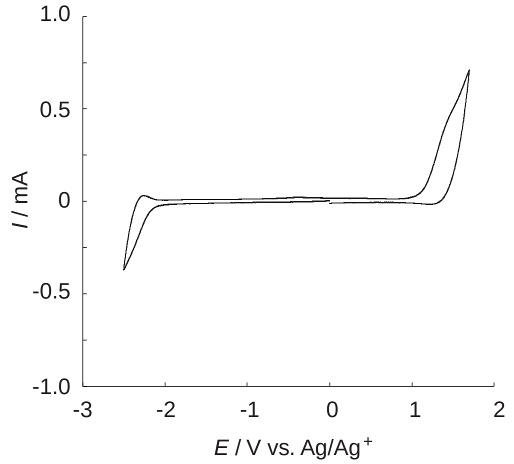


Fig. 5. Cyclic voltammogram of the polymer **6a** film coated on the ITO plate electrode in CH_3CN containing 0.1 M Bu_4NClO_4 as a supporting electrolyte (vs Ag/Ag$^+$) at a scan rate of 100 mV/s.

tion is localized; namely, the model **10** unit of the polymer backbone emits independently of the conjugation length (Chart 2).[3,6] In a solid thin film of **6a**, the emission peak maximum at 415 nm was red-shifted by approximately 25 nm from that in solution (Table 2, Fig. 4). The shapes and peaks of the absorption spectra and emission spectra of **6a–c** were independent of the nature of the alkyl side chains both in solution and in the solid state.

The cyclic voltammetry of polymer **6a** film coated on an ITO glass electrode in a CH_3CN solution of 0.1 M Bu_4NClO_4 was performed in a three-electrode cell using a Pt counter electrode and a Ag/AgCl reference electrode. As shown in the cyclic voltammogram (Fig. 5), the oxidation process gave an onset peak at about 1.0 V vs Ag/Ag$^+$. In a cathodic scan, the onset reduction potential was observed at about -2.0 V. Accordingly, both the HOMO and LUMO energy levels of **6a** could be roughly calculated to be -5.7 and -2.6 eV, respectively.[37] The band gap was estimated to be about 3.1 eV, which is in close agreement with the calculated value of the optical band gap obtained from UV–vis spectrum of **6a** in the film state.

The electroluminescent (EL) properties of polymer **6a** were also examined. The two-layer (ITO/PEDOT-PSS/**6a**/Al) device, where a polymer blend including a conducting polymer PEDOT, poly(3,4-ethylenedioxythiophene), and PSS, poly(4-styrenesulfonic acid), was used as a hole-transport layer, was fabricated. The device exhibited a weak blue light with a turn-on voltage at 13 V when the thickness of the emissive polymer layer was approximately 100 nm. The EL emission maximum and the spectral shape were similar to the PL spectrum. To improve the device performance, BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) was used as a hole-blocking layer on **6a**, and a multi-layered device with a configuration of ITO/PEDOT-PSS/**6a**/BCP/Alq/LiF/Al was fabricated. However, two emission maxima from **6a** (430 nm) and Alq (530 nm) were observed due to the high potential, which resulted in bluish-green emission. The onset potential and brightness are expected to be improved by optimization, e.g., the thickness of the emissive layer, the combination of each charge-transporting layer, and alkyl substituent at the C9 position of the fluorene unit in the polymer backbone.

Conclusion

Novel poly(*p*-phenylene) type π-conjugated polymers having [2.2]paracyclophane and fluorene alternately were prepared by the Suzuki coupling reaction. These polymers were soluble in common organic solvents, and homogeneous thin films were obtained easily by casting or spin-coating from a toluene solution. These polymers possessed good thermal stability. They exhibited strong purplish blue photoluminescence in solution and blue photoluminescence in the solid state. According to the cyclic voltammogram of the polymer **6a**, the HOMO and LUMO energy levels were estimated to be -5.7 and -2.6 eV, respectively. The light-emitting diode of the polymer also emitted blue light with a maximum peak at around 430 nm. However, two emission maxima from the polymer and Alq (530 nm) were observed due to the high potential, which resulted in the bluish-green emission. Further studies on optimization for a high-performance device are now underway.

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