

NOTE

Aromatic-ring-layered polymers composed of fluorene and xanthene

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Polymer Journal (2011) 43, 733–737; doi:10.1038/pj.2011.58**Keywords:** aromatic-ring-layered polymers; conjugated polymers; fluorene; xanthene

INTRODUCTION

Conjugated polymers show intriguing properties such as electrical conductivity,^{1–4} electroluminescence^{5–9} and chemical-sensing ability.^{10–12} Synthesis of new conjugated polymers is an important subject in polymer chemistry as well as in material chemistry, owing to their potential applications in optoelectronic devices. Generally, π -electrons are delocalized throughout the conjugated polymer backbone comprising of sp - and/or sp^2 -carbons. Recently, extensive studies have been conducted on conjugated polymers featuring the incorporation of main group elements. Various unique orbit interactions exist between the main group elements and π -conjugated carbon frameworks, for example, σ - π (or σ^* - π^*) conjugation^{13,14} for Si and p - π^* conjugation^{15–17} for B. Furthermore, the properties of a new class of conjugated polymers that show through-bond conjugation and through-space conjugation in a polymer chain have been investigated. Through-space conjugated polymers were prepared by incorporating pseudo-*para*-^{18–24} and pseudo-*ortho*-substituted²⁵ [2.2]paracyclophane into the conjugated polymer backbone, and their optical and electrochemical properties have been investigated in detail. Recently, pseudo-geminal-substituted [2.2]paracyclophane was used for the synthesis of through-space conjugated polymers, in which the π -electron systems fully overlapped with each other and showed a large Stokes shift.²⁶

Polymers comprising layered π -electron systems have also attracted much attention as novel functional polymers.²⁷ We have previously reported a new synthetic strategy for constructing aromatic ring-layered structures in a polymer main chain by using xanthene or naphthalene as the scaffold. This approach makes it possible to layer various aromatic rings in a single polymer chain; for example, cyclophane-,^{28,29} oligothiophene-³⁰ and anthracene-layered polymers³¹ were synthesized. Expansion of the substrate scope and investigation of the newly developed aromatic ring-layered polymers are of importance in the field of the conjugated polymers. In this study, we used fluorene as the layered aromatic unit and xanthene as the scaffold. Fluorene compounds possess easy functionality, thermal

stability and prominent emitting-property; thus, they are valuable emitters as well as molecular probes to determine the environment via fluorescence spectroscopy due to high-quantum efficiencies and clear vibrational spectra. The fluorene-layered polymers were synthesized by the Sonogashira–Hagihara coupling reaction. The synthetic procedure, characterization and optical properties of the polymers were investigated in detail.

EXPERIMENTAL PROCEDURE

General experimental details

¹H and ¹³C NMR spectra were recorded on a JNM-EX400 instrument (Jeol, Tokyo, Japan) at 400 and 100 MHz, respectively. The chemical shift values were expressed relative to Me₄Si as an internal standard. High-resolution mass spectra were obtained on a JMS-SX102A spectrometer (Jeol, Tokyo, Japan). Gel permeation chromatography was carried out on a Tosoh 8020 instrument (TSKgel G3000HXL column; Tosoh, Tokyo, Japan) using CHCl₃ as an eluent after calibration with standard polystyrene samples. Recyclable preparative high-performance liquid chromatography was performed on a Model 918R (JAIGEL-2.5H and 3H columns; Japan Analytical Industry, Tokyo, Japan) using CHCl₃ as an eluent. Ultraviolet–visible absorption spectra were obtained on a Shimadzu UV3600 spectrophotometer (Shimadzu, Kyoto, Japan). Photoluminescence spectra were obtained on a Horiba FluoroMax-4 luminescence spectrometer (Horiba, Kyoto, Japan). Cyclic voltammetry was carried out on a CV-50W electrochemical analyzer (BAS, Tokyo, Japan) in CH₂Cl₂ containing 0.1 M of the sample and 0.1 M of NBu₄ClO₄ with a glassy carbon-working electrode, a Pt counter electrode, a Ag/AgCl (Ag/Ag⁺) reference electrode and a ferrocene/ferrocenium (Fc/Fc⁺) external reference. Analytical thin-layer chromatography was performed with silica gel 60 Merck F₂₅₄ plates (Merck, Whitehouse, NJ, USA). Column chromatography was performed with Wakogel C-300 silica gel (Wako Pure Chemical Industries, Osaka, Japan). Elemental analyses were carried out on a vario MICRO elemental analyzer (Elementar Analysensysteme GmbH, Hanau, Germany).

Materials

NEt₃ was purchased and purified by passage through purification column under Ar pressure.³² Dehydrated-grade toluene was purchased and used without further purification. Pd(PPh₃)₄, CuI and 2,7-diiodofluorene (**2a**) were

obtained commercially, and used without further purification. 2,7-Di-*tert*-butyl-4,5-diethynyl-9,9-dimethylxanthene (**1**) was synthesized according to the literature's procedure.³³ 2,7-Diiodo-9,9-dialkylfluorenes (**2a–d**) were synthesized according to the literature's procedure,³⁴ and the spectral data matched with the literature's values (**2b**,³⁴ **2c**³⁵ and **2d**³⁶). All reactions were performed under Ar atmosphere.

Polymer synthesis

Typical procedure is as follows.³⁷ 2,7-Di-*tert*-butyl-4,5-diethynyl-9,9-dimethylxanthene (**1**) (57 mg, 0.15 mmol), 2,7-diiodofluorene (**2a**) (45 mg, 0.14 mmol), Pd(PPh₃)₄ (17 mg, 0.015 mmol) and CuI (14 mg, 0.07 mmol) were placed in a Pyrex tube equipped with a magnetic stirrer and a reflux condenser. The equipment was purged with Ar, followed by adding toluene (3.0 ml) and NEt₃ (1.0 ml). The reaction was carried out at 100 °C for 48 h. After cooling, the reaction mixture was filtered by Celite. The filtrate was diluted with CHCl₃, and it was washed with aqueous NH₄OH (25%, 50 ml), brine (50 ml) and water (50 ml). The organic layer was dried over MgSO₄. After removal of MgSO₄, the organic layer was dried. The residue was dissolved in a small amount of CHCl₃ and reprecipitated from a large amount of methanol to afford polymer **3a** as a brown solid (37 mg, 46%).

Polymer **3a** (37 mg, 46%). ¹H NMR (CD₂Cl₂, 400 MHz): δ=1.32 (br), 1.38 (br), 1.70 (br), 3.36 (br), 7.33 (br m), 7.49 (br m) p.p.m. ¹³C NMR (CD₂Cl₂, 100 MHz) δ=31.3, 32.5, 34 (m), 36.4, 85.8, 93.8, 111.1, 119.2, 120.9, 121.8, 128 (m), 130 (m), 140.3, 142.7, 145 (m), 148.4 p.p.m.

Polymer **3b** (68 mg, 62%). ¹H NMR (CD₂Cl₂, 400 MHz): δ=0.77 (br), 1.06 (br), 1.42 (br), 1.72 (br), 2.00 (br), 7.00 (br), 7.22 (br), 7.5 (br m) p.p.m. ¹³C NMR (CD₂Cl₂, 100 MHz) δ=13.9, 22.7, 24.0, 29.7, 31 (m), 34 (m), 40.3, 55.7, 86.3, 94.0, 110.9, 120–131 (m), 140 (m), 145.9, 148.3, 150.5, 153.6 p.p.m.

Polymer **3c** (97 mg, 82%). ¹H NMR (CD₂Cl₂, 400 MHz): δ=0.56 (br), 0.76 (br m), 1.39 (br m), 1.7 (m), 2.03 (br m), 7.0–7.8 (br m) p.p.m. ¹³C NMR (CD₂Cl₂, 100 MHz) δ=10.3, 14.1, 23.0, 28 (m), 31.3, 33–35 (m), 55.4, 86.1, 94.0, 111.0, 120.0, 121.4, 123.9, 127–131 (m), 139.7, 145.8, 148.2, 150.4, 153.4 p.p.m.

Polymer **3d** (108 mg, 80%). ¹H NMR (CD₂Cl₂, 400 MHz): δ=0.85 (br), 1.2 (br m), 1.41 (s), 1.7–2.1 (br m), 7.0–7.8 (br m) p.p.m. ¹³C NMR (CD₂Cl₂, 100 MHz) δ=14.0, 22.8, 24.2, 30 (m), 30–32 (m), 34.6, 40.3, 55.4, 86.1, 94.5, 111.0, 120.1, 123.8, 126–132 (m), 145.8, 148.4, 151.1 p.p.m.

4,5-Bis(2-fluorenyl)-9,9-dimethylxanthene (**4**)

4,5-Diethynyl-9,9-dimethylxanthene³⁸ (65 mg, 0.25 mmol), 2-iodofluorene³⁴ (300 mg, 1.02 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol) and CuI (95 mg, 0.50 mmol) were placed in a Pyrex flask equipped with a magnetic stirrer and a reflux condenser. The equipment was purged with Ar, followed by adding toluene (3.0 ml) and NEt₃ (1.5 ml). The reaction was carried out at 80 °C for 9 h. After cooling, the reaction mixture was diluted with CHCl₃ and filtered by Celite. The filtrate was diluted with CHCl₃, and it was washed with aqueous NH₄OH (25%, 25 ml), brine (25 ml) and water (25 ml). The organic layer was dried over MgSO₄. After removal of MgSO₄, the organic layer was dried. The residue was subjected to column chromatography on SiO₂ with hexane/CHCl₃ (v/v=4:1, R_f 0.1) as an eluent. The obtained compound was purified by recrystallization from CHCl₃ to obtain 4,5-bis(2-fluorenyl)-9,9-dimethylxanthene (**4**) (118 mg, 0.20 mmol, 80%) as a colorless crystal.

¹H NMR (CD₂Cl₂, 400 MHz) δ=1.67 (s, 6H), 3.49 (s, 4H), 7.14 (t, J=7.6 Hz, 2H), 7.19 (m, 4H), 7.24 (t, J=7.2 Hz, 2H), 7.30 (d, J=7.6 Hz, 2H), 7.35 (m, 4H), 7.48 (m, 6H) p.p.m. ¹³C NMR (CD₂Cl₂, 100 MHz) δ=32.4, 34.4, 36.6, 84.9, 94.7, 112.0, 119.4, 119.9, 121.1, 123.1, 124.8, 126.5, 126.7, 127.0, 128.1, 130.4, 130.6, 131.9, 140.6, 141.7, 143.1, 143.4, 150.3 p.p.m. High-resolution mass spectra (fast atom bombardment): m/z calcd. for C₄₅H₃₀O (M⁺): 586.2297, found: 586.2306. Anal. calcd. for C₄₅H₃₀O: C 92.12; H 5.15; O 2.73, found: C 92.01; H 5.15; 2.64.

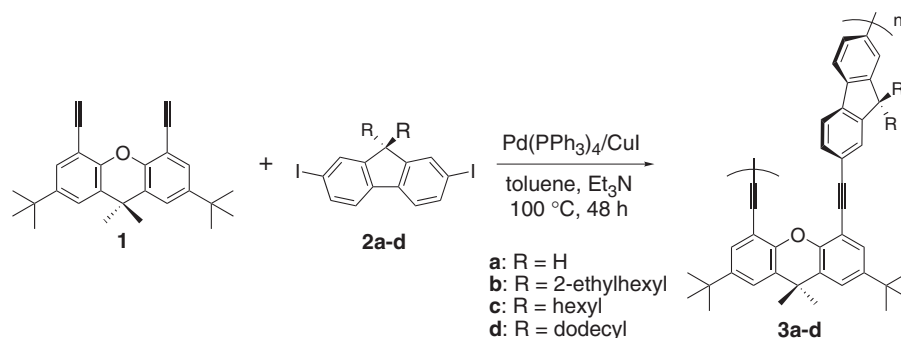
¹H and ¹³C NMR spectra of **3a–d** (Supplementary Figures S1–8) and **4** (Supplementary Figures S9 and 10) are shown in Supplementary Information.

RESULTS AND DISCUSSION

Our approach toward construction of the aromatic-ring-layered structure involves the use of a 2,7-di-*tert*-butyl-9,9-dimethylxanthene skeleton as the scaffold. The synthetic scheme for fluorene-layered polymers **3a–d** is shown in Scheme 1. Treatment of 2,7-di-*tert*-butyl-4,5-diethynyl-9,9-dimethylxanthene (**1**) and 2,7-diiodofluorenes (**2a–d**) in the presence of a catalytic amount of Pd(PPh₃)₄ and CuI yielded a crude polymer, which was purified by reprecipitation from a large amount of MeOH to obtain target polymers **3a–d** in moderate-to-good yields in the form of an orange powder. The polymerization results are summarized in Table 1.

The obtained polymers possessed good solubility in common organic solvents such as CHCl₃, CH₂Cl₂, tetrahydrofuran and toluene, which allows easy characterizations as well as easy film formation by spin-coating. Molecular weight measurements were performed by gel permeation chromatography in CHCl₃ eluent using a calibration curve of polystyrene standards. For example, the number-average molecular weight (*M_n*) and the polydispersity (*M_w*/*M_n*) of polymer **3d** were found to be 2600 and 1.3, as listed in Table 1 (run 4). The structures of polymers were confirmed by ¹H and ¹³C NMR spectroscopy, and all spectra are shown in Supplementary Information. Figure 1 shows the ¹H and ¹³C NMR spectra of polymer **3d** in CD₂Cl₂ as a representative example. In the ¹H NMR spectrum, signals of the dodecyl, *tert*-butyl and methyl protons were observed in the range of 0.8–2.2 p.p.m. Aromatic proton peaks appeared at around 7.5 p.p.m. In the ¹³C NMR spectrum, typical signals for acetylenic carbons were found at 86.1 and 94.5 p.p.m.

To obtain the structural insight into the polymers, we synthesized model compound **4** and subjected it to the single crystal X-ray analysis (Figure 2 and Supplementary Figure S12, data are summarized in Supplementary Table S1). As shown in the top view (Figure 2), the torsion angles of the xanthene scaffold and two fluorene rings are 61.8(3)° and 7.6(3)°, respectively. This result indicates that one fluorene ring and the xanthene scaffold are almost on the same plane to maintain the π-conjugation in the solid state. The distance between the 4-position and the 5-position of xanthene was found to be 4.65 Å, and that between the 2-positions of fluorene was found to



Scheme 1 Synthesis of polymers **3a–d**.

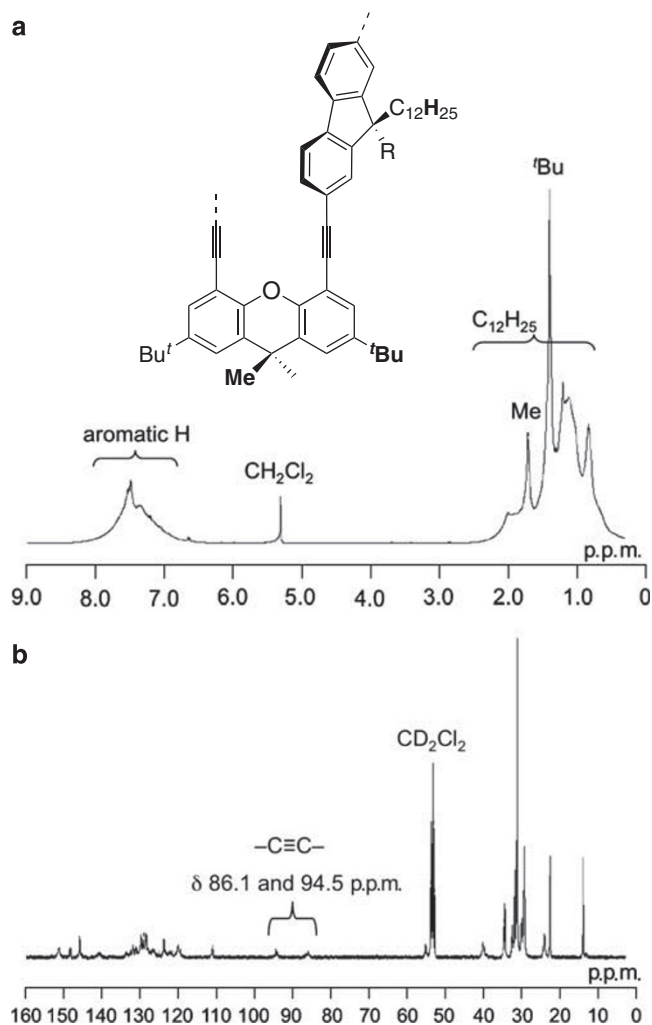


Figure 1 ^1H and ^{13}C NMR spectra of polymer **3d** in CD_2Cl_2 .

Table 1 Results of polymerization

Entry	Polymer	-R	Yield ^a (%)	M_n^b	M_w/M_n^b
1	3a	-H	46	2000	1.1
2	3b	-C ₆ H ₁₃	62	1900	1.1
3	3c	-C ₈ H ₁₇	82	3100	1.3
4	3d	-C ₁₂ H ₂₅	80	2600	1.3

Abbreviations: M_n , number-average molecular weight; M_w/M_n , polydispersity.

^aIsolated yield.

^bEstimated by gel permeation chromatography (CHCl_3) using polystyrene as standards.

be 4.89 Å. However, as shown in Figure 2, the shortest distance between two fluorene rings was approximately 3.5 Å, which is almost equal to the sum of the van der Waals radii of two sp^2 carbon atoms (3.40 Å). The layered fluorene units seem to have sufficient space for twisting in the polymer backbone; a weak π - π interaction among them in solution is expected. In the ^1H NMR spectra of polymer **3a** and compound **4**, signals of the 9-H protons of the fluorene units appeared at $\delta=3.36$ and 3.49 p.p.m., respectively, (Supplementary Figure S11), which are upfield-shifted compared with the signal of fluorene itself ($\delta=3.89$ p.p.m.) The 9-H protons of **3a** and **4**

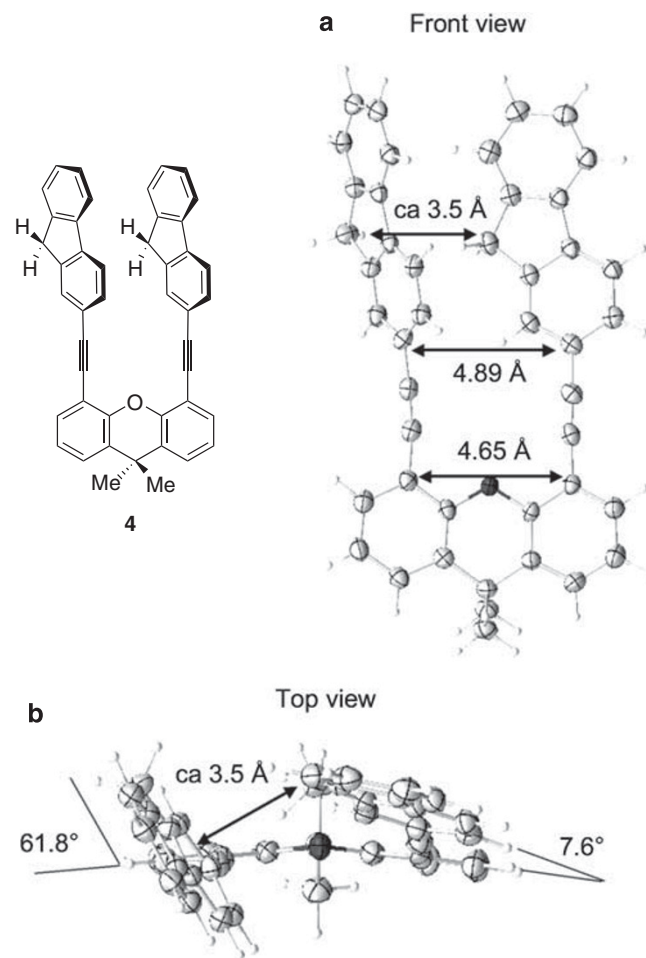


Figure 2 Structure of compound **4** and its ORTEP drawing. Thermal ellipsoids are drawn at the 50% probability level.

Table 2 Optical properties of polymers **3a-d**

Entry	Polymer	$\lambda_{\text{abs,max}}^a$ (nm)	$\lambda_{\text{PL,max}}^b$ (nm)	Φ_{PL}^c
1	3a	323	388, 409	0.40
2	3b	335	390, 411	0.50
3	3c	334	389, 410	0.36
4	3d	348	392, 414	0.28

^aIn CHCl_3 , 1.0×10^{-5} M.

^bIn CHCl_3 , 1.0×10^{-7} M, excited at each absorption maximum.

^cAbsolute photoluminescence quantum efficiency.

have ring current effect of the neighboring fluorene units because of the twist motion of the fluorene units on the xanthen backbone.

The optical properties of polymers **3a-d** were examined, and the results are summarized in Table 2. In addition, the normalized ultraviolet-visible absorption spectra of **3a-d** and **4** in CHCl_3 (1.0×10^{-5} M) are shown in Figure 3a. The absorption maxima of **4** and the polymers were observed at around 315 and 350 nm, respectively. The conjugation lengths of **3a-d** were longer than that of **4**; this is because **3a-d** consist of 2,7-di-substituted fluorine, whereas **4** consists of

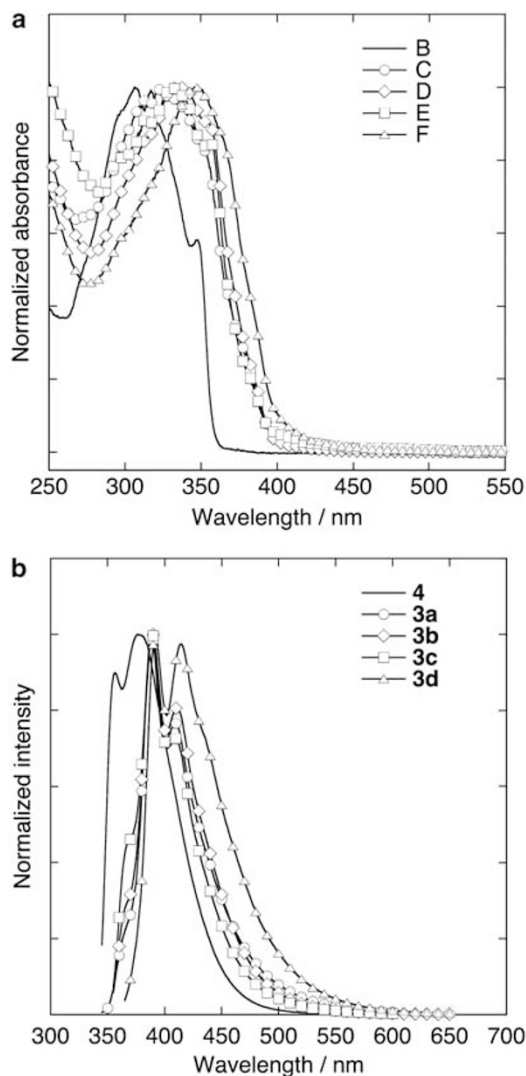


Figure 3 (a) Ultraviolet-visible absorption spectra in CHCl_3 ($1.0 \times 10^{-5} \text{ M}$) and (b) photoluminescence spectra in CHCl_3 ($1.0 \times 10^{-7} \text{ M}$, excited at absorption maxima) of polymers **3a–d** and **4**.

monosubstituted fluorene. The absorption bands of **3a–d** are derived from the S_0 – S_1 transition of 2,7-bis(arylethynyl)fluorene moieties.

Figure 3b shows the photoluminescence spectra of **3a–d** in dilute CHCl_3 solutions ($1.0 \times 10^{-7} \text{ M}$) excited at each absorption maximum. We confirmed that this concentration ($1.0 \times 10^{-7} \text{ M}$) was sufficiently diluted so as to avoid intermolecular interactions among the polymer chains according to the concentration effect. The polymers emitted blue light in the visible range with peak maxima at around 400 nm. The spectra indicated vibrational structures with absolute quantum efficiencies of 0.28–0.50, ruling out excimer formation among the layered fluorene units in the polymer backbone. The π – π interactions among the fluorene units in the polymer chain were weak in the ground and the excited states.

The electrochemical property of the polymers was examined by cyclic voltammetry. The typical cyclic voltammograms, shown in Figure 4, were obtained from a polymer **3d** solution in CH_2Cl_2 containing 0.1 M NBu_4ClO_4 using a glassy carbon-working electrode, Pt counter electrode, Ag/Ag^+ reference electrode and Fc/Fc^+ external reference. As shown in Figure 4, polymer **3d** was readily oxidized with

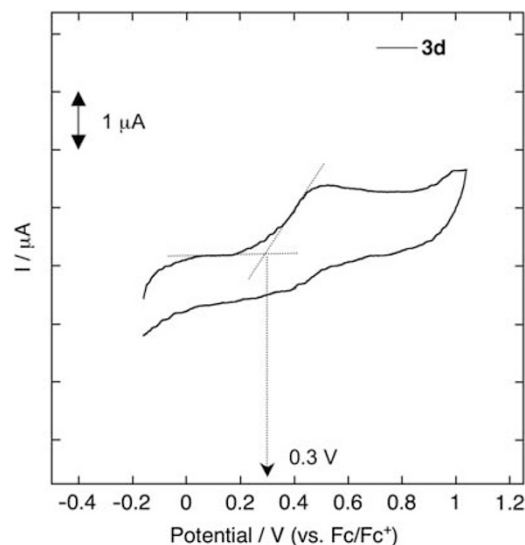


Figure 4 Cyclic voltammogram of polymer **3d** in CH_2Cl_2 (0.1 M) containing NBu_4ClO_4 (0.1 M) using a glassy carbon-working electrode, a Pt counter electrode, a Ag/Ag^+ reference electrode and ferrocene/ferrocenium (Fc/Fc^+) as an external reference.

an oxidation potential (E_{onset}) of approximately 0.30 V (vs Fc/Fc^+) (cyclic voltammetry measurement of **4** was carried out, and the voltammogram is shown in Supplementary Figure S13. The E_{onset} of **4** appeared at around 0.13 V (vs Fc/Fc^+). The slight difference of the E_{onset} values between the polymer and the model compound is probably derived from the number of the electron withdrawing carbon-carbon triple bonds of the fluorene unit.). The highest occupied molecular orbital energy level of the polymer was calculated to be approximately -5.1 eV , and the lowest unoccupied molecular orbital level was estimated to be -2.3 eV according to the highest occupied molecular orbital–lowest unoccupied molecular orbital energy band gap obtained from the ultraviolet-visible absorption spectrum (These values were estimated from the E_{onset} of the polymers and the energy level of Fc/Fc^+ (4.80 eV), namely highest occupied molecular orbital = $-4.80 - E_{\text{onset}}$. For example, see Pommerehne *et al.*³⁹).

In conclusion, we described the synthesis and properties of a new class of aromatic-ring-layered polymer comprising layered fluorene and a xanthene scaffold. The polymers can be prepared in moderate-to-good yields by Sonogashira–Hagihara coupling. The polymers are soluble in common organic solvents and can be spin-coated into thin films from solution. We found that the π – π interactions among the layered fluorene units in the polymer backbone are ineffective in the ground and the excited states; thus, the polymers emit without excimer formation, despite the layered structure. We intend to conduct further studies on the synthesis of various aromatic-ring-layered polymers and fabrication of optoelectronic devices such as light-emitting device and hole-transporting device, in which these polymers find application.

ACKNOWLEDGEMENTS

This work was supported by a Grant-in-Aid for Young Scientists (A) (No. 21685012) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. The financial support from the Kansai Research Foundation of Technology Promotion was also acknowledged.

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Supplementary Information accompanies the paper on Polymer Journal website (<http://www.nature.com/pj>)