Synthesis of optically active green fluorescent π-conjugated fluorene polymers having chiral Schiff bases in the side chain†

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The synthesis of optically active poly(fluorene-*alt*-chiral iminofluorene)s using 1-phenylethylamine as a chiral auxiliary is described. Optically active polyfluorenes were synthesized by the palladium-catalyzed Suzuki–Miyaura coupling polymerization of 9,9′-dioctylfluorene-2,7-bis(trimethyleneborate) with a chiral Schiff base monomer (imino group modified-fluorene). The obtained polymers showed intense green emission with high quantum efficiency. Analysis of the circular dichroism data of the optically active polymers indicates that the polymers exhibit various highly-ordered regular structures in solution.

Introduction

π-Conjugated fluorene polymers exhibit high fluorescence quantum yields in solution or in the solid state; the applicability of π-conjugated polymer-based light-emitting diodes in various devices such as displays has been extensively investigated.[1] At present, tuning the optical properties is of prime importance. The design of π-conjugated polymers involves the modification of a π-conjugated building block, *i.e.*, the replacement of fluorene units by other aromatic compounds such as heterocycles, polycyclic arenes, and substituted arenes.[2] A multi-color display developed using fluorene-based copolymers was designed using the above-mentioned principle.[3] On the other hand, at present, hierarchical structure control is used to design π-conjugated polymers that can be used in novel applications. In particular, optically active polymers are often used as fundamental materials in specific highly-ordered structures.[4] The development of various chiral π-conjugated polymers such as polyacetylene,[5] poly-(*p*-phenylene),[6] polysilane,[7] and polycarbazole[8] has attracted considerable attention. However, little is known about optically active π-conjugated fluorene polymers. For example, Scherf and Neher *et al.*[9] and Fujiki *et al.*[10] have independently reported the synthesis and characterization of a chiral fluorene homopolymer having a chiral auxiliary in its side chain. It is very important to enhance the applicability of chiral fluorene polymers, in particular the use of chiral imino group-substituted fluorene (Schiff base) as a replacement unit for use in functional materials, by means of hybridization of fluorene and other functional π-conjugated building blocks. This type π-conjugated fluorene copolymers exhibit unique properties such as optical activity, a large Stokes' shift, high quantum efficiency, and coordination properties due to the presence of the replacement unit. A Schiff base monomer can be easily prepared by the condensation of a wide variety of chiral amines using 2,7-dibromofluorenone as the starting material. We

now report the synthesis of optically active poly(fluorene-*alt*-chiral iminofluorene)s using 1-phenylethylamine as a chiral auxiliary and investigate their luminescence properties and optical activity by UV–vis, fluorescence, and circular dichroism (CD) spectroscopy.

Experimental

Instruments

All ^{1}H and ^{13}C NMR spectra were recorded using a 400 MHz JEOL LMN-EX400 instrument with tetramethylsilane (TMS) as the internal standard. FT-IR spectra were recorded on a JASCO FT-IR 469 plus spectrometer. Melting points were obtained by a Stuart Scientific Melting Point Apparatus SMP3. Elemental analyses were performed by LECO CHNS-932. High-resolution mass spectra (EI) and EI-MS spectra were obtained using a JEOL JMS700 mass spectrometer. Gel permeation chromatography (GPC) was carried out using a JASCO UV-2075 detector and a JASCO RI-2031 detector (TOSOH TSKgel G3000HXL column) using tetrahydrofuran (THF) as the eluent after calibration with polystyrene standards. TGA was performed using a SII TG/DTA 6200 (SEIKO Instrument Inc.) with a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. DSC was performed using DSC 6220 (SEIKO Instrument Inc.) with a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. UV–vis spectra were recorded using a Beckman Coulter DU800 UV–vis spectrophotometer. Fluorescence spectra were recorded by a JASCO FP-6500 spectrofluorometer. Quantum yields were measured using a Hamamatsu Photonics C9920-02 Absolute PL quantum yield measurement system. Fluorescence lifetimes were carried out using a Hamamatsu Photonics OB 920 fluorescence lifetime spectrometer. CD spectra were measured on a JASCO J-820 spectropolarimeter at 20 °C (1 cm path length cell; sample concentration = 1.0×10^{-5} M. For concentration-dependent measurements, 0.1 and 1 cm path length cells were used for sample concentration of 1.0×10^{-4} M and 1.0×10^{-5} M respectively). Specific optical rotations were measured on a JASCO DIP-1000 digital polarimeter in a 5 cm cuvette. Optically purity was evaluated by HPLC with a chiral column (CHIRAL PAK®AD-H).

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Materials

Unless otherwise noted, all reagents and chemicals were commercially available and used without further purification. 2,7-Dibromofluorenone was obtained from JFE Chemical. 9,9′-Dioctylfluorene-2,7-bis(trimethyleneborate) was obtained from Aldrich. Pd(PPh$_3$)$_4$ and phenylboronic acid were obtained from TCI.

2,7-Dibromo-9-(phenylethylimino)fluorene (1R)

A toluene (120 ml) solution containing 2,7-dibromofluorenone (2.03 g, 6.0 mmol) and R-(+)-1-phenylethylamine (4.76 g, 5 ml, 30 mmol) was added to TiCl$_4$ (1.16 g, 0.64 ml, 6.0 mmol) in toluene (18 ml) under argon atmosphere at 0 °C. The resulting mixture was stirred at room temperature for 1 day. The reaction was quenched by water (120 ml). The crude product was extracted by toluene. The solvent was evaporated and the crude product was recrystallized from MeOH to give yellow solid 1R (1.88 g, 71%). ^{1}H NMR (400 MHz, DMSO-d$_6$, 30 °C): δ 8.21 (d, 1H, H$_a$, J = 1.6), 7.89 (d, 1H, H$_e$, J = 8.0 Hz), 7.87 (d, 1H, H$_b$, J = 1.6 Hz), 7.81 (d, 1H, H$_c$, J = 8.0 Hz), 7.77 (dd, 1H, H$_g$, J = 8.0, 1.6 Hz), 7.70 (dd, 1H, H$_f$, J = 8.0, 1.6 Hz), 7.64 (d, 2H, H$_d$, J = 7.2 Hz), 7.41 (t, 2H, H$_h$, H$_i$, J = 8.0, 7.6 Hz), 7.29 (t, 1H, H$_j$, J = 7.6, 7,2 Hz), 5.79 (q, 1H, J = 6.4 Hz), 1.64 (d, 3H, J = 6.4 Hz) ppm.; ^{13}C NMR (100 MHz, CDCl$_3$): 158.4, 145.3, 141.6, 140.1, 138.4, 133.9, 133.6, 132.4, 130.4, 128.6, 127.0, 126.4, 126.1, 122.5, 121.7, 121.5, 120.6, 60.2, 25.3 ppm.; FT-IR (KBr): 3062, 3024 (Ar–H), 2980, 2923, 2857 (Alkyl–H), 1647 (C=N), 1593 (Ar–H), 1068,(Ar–Br), 811 (–Br) cm^{-1}.; UV–vis (THF): λ$_{max}$ (ε) = 262 (77200) nm.; mp: 117–118 °C.; C$_{19}$H$_{11}$Br$_2$N: Calcd. C, 57.17%; H, 3.43%; N, 3.17%. Found: C, 56.82%; H, 3.41%; N, 3.06%.; MS m/z 441 (M$^{+\cdot}$); HRMS (EI) Calcd for C$_{19}$H$_{11}$Br$_2$N: 438.9571, 440.9552 Found: 438.9560, 440.9544.; [a]$_D^{21.3}$ −12.9 (99% ee). See, Figs S1, S2, S9, and S13 of the ESI.†

2,7-Dibromo-9-(phenylethylimino)fluorene (1S)

^{1}H NMR (400 MHz, DMSO-d$_6$, 30 °C): δ 8.21 (s, 1H), 7.90 (dd, 1H, J = 8.0, 1.6 Hz), 7.88 (s 1H), 7.82 (dd 1H, J = 8.0, 1.6 Hz), 7.78 (d, 1H, J = 8.0), 7.71 (d, 1H, J = 8.0 Hz), 7.64 (d, 2H, J = 7.6 Hz), 7.40 (t, 2H, J = 8.0, 7.6 Hz), 7.29 (t, 1H, J = 7.6, 6.8 Hz), 5.79 (q, 1H, J = 6.4 Hz), 1.64 (d, 3H, J = 6.8 Hz) ppm.; ^{13}C NMR (100 MHz, CDCl$_3$): 158.5, 145.3, 141.7, 140.2, 138.5, 134.0, 133.6, 132.5, 130.5, 128.6, 127.0, 126.5, 126.1, 122.6, 121.8, 121.6, 120.6, 60.2, 25.3 ppm.; FT-IR (KBr): 3058, 3029 (Ar–H), 2971, 2923, 2859 (Alkyl–H), 1647 (C=N), 1593 (Ar–H), 1068(Ar–Br), 816 (–Br) cm^{-1}.; UV–vis (THF): λ$_{max}$ (ε) = 262 (67300) nm.; mp: 116–118 °C.; C$_{19}$H$_{11}$Br$_2$N: Calcd. C, 57.17%; H, 3.43%; N, 3.17%. Found: C, 57.33%; H, 3.28%; N, 3.17%.; MS m/z 441 (M$^{+\cdot}$); HRMS (EI) Calcd for C$_{19}$H$_{11}$Br$_2$N: 438.9571, 440.9560 Found: 438.9572, 440.9552.; [a]$_D^{21.6}$ + 12.90 (98% ee). See, Figs. S3, S10, and S14 of the ESI.†

2,7-Dibromo-9-(phenylethylimino)fluorene (1rac)

^{1}H NMR (400 MHz, DMSO-d$_6$, 30 °C): δ 8.23 (d, 1H, J = 1.6 Hz), 7.92 (d, 1H, J = 8.0 Hz), 7.89 (d, 1H, J = 2.0 Hz), 7.84 (d, 1H, J = 8.0 Hz), 7.79 (dd, 1H, J = 8.0, 1.6 Hz), 7.72 (dd, 1H, J = 8.0, 2.0 Hz), 7.65 (d, 2H, J = 8.0, 7.2 Hz), 7.41 (t, 2H, J = 8.0, 7.2 Hz), 7.29 (t, 1H, J = 7.2 Hz), 5.80 (q, 1H, J = 6.4 Hz), 1.65 (d, 3H, J = 6.8 Hz) ppm.; ^{13}C NMR (100 MHz, CDCl$_3$): 158.3, 145.3, 141.4, 140.0, 138.3, 133.8, 133.5, 132.3, 130.2, 128.5, 127.0, 126.4, 125.9, 122.5, 121.7, 121.4, 120.4, 60.1, 25.3 ppm. FT-IR (KBr): 3072, 3025 (Ar–H), 2962, 2917, 2857 (Alkyl–H), 1637 (C=N), 1592 (Ar–H), 1069,(Ar–Br), 816 (–Br) cm^{-1}.; UV–vis (THF): λ$_{max}$ (ε) = 262 (64500) nm.; mp: 146–147 °C.; C$_{19}$H$_{11}$Br$_2$N: Calcd. C, 57.17%; H, 3.43%; N, 3.17%. Found: C, 56.77%; H, 3.34%; N, 3.23%.; MS m/z 441 (M$^{+\cdot}$); HRMS (EI) Calcd for C$_{19}$H$_{11}$Br$_2$N: 438.9571, 440.9560 Found: 438.9576, 440.9562. See, Figs. S4, S11, and S15 of the ESI.†

Functional polyfluorene with chiral Schiff base (2R)

A mixture of 9,9′-dioctylfluorene-2,7-bis(trimethyleneborate) (0.558 g, 1.0 mmol) and 1R (0.441 g, 1.0 mmol), Pd(PPh$_3$)$_4$ (0.057 g, 0.05 mmol), toluene (10 ml) and 2M Na$_2$CO$_3$ (6 ml) was stirred at 80 °C for 48 h under argon atmosphere. To the resulting mixture was added phenylboronic acid (0.122 g 1.0 mmol), Pd(PPh$_3$)$_4$ (0.052 g, 0.05 mmol), and 2M Na$_2$CO$_3$ (4 ml) at the same temperature and stirred for 1 day. The mixture was poured into MeOH (200 ml) to precipitate a plenty of solid. The obtained solid was collected by filtration and washed with methanol and water. The crude product was dissolved in THF and precipitated in MeOH. The yellow precipitate was collected by filtration and dried in vacuo to give the functional poly-fluorene (2R) (0.628 g, 94%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.29–7.29 (Ar–H), 5.95 (N–C–H) 2.11–0.78 (Alkyl–H) ppm.; FT-IR (KBr): 3058, 3027 (Ar–H), 2924, 2851 (Alkyl–H), 1719, (C=O), 1638 (C=N), 1598 (Ar–C–C), cm^{-1}. See, Figs. S5 and S16 of the ESI.†

Functional polyfluorene with chiral Schiff base (2S)

^{1}H NMR (400 MHz,CDCl$_3$): δ 8.29–7.29 (Ar–H), 5.92 (N–C–H), 2.12–0.78 (Alkyl–H) ppm.; FT-IR (KBr): 3058, 3028 (Ar–H), 2925, 2852 (Alkyl–H), 1718 (C=O), 1641(C=N), 1599 (Ar–C–C), cm^{-1}. See, Figs. S6 and S17.

Functional polyfluorene with chiral Schiff base (2rac)

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.29 − 7.29 (Ar–H), 5.93 (N–C–H), 2.12–0.79 (Alkyl–H) ppm.; FT-IR (KBr): 3058, 3026 (Ar–H), 2925, 2852 (Alkyl–H), 1718 (C=O), 1641 (C=N), 1599(Ar–C–C), cm^{-1}. See, Figs. S7 and S18.

2,7-Diphenyl-9-phenylethyliminofluorene (4)

To a toluene (30 ml) solution of 3 (0.199 g, 0.6 mmol) and DL-1-phenylethylamine (0.94 g, 1 ml, 0.077 mmol) was added a toluene (5 ml) solution of TiCl$_4$ (0.179 g, 0.1 ml, 0.95 mmol) under argon atmosphere at 0 °C. The resulting mixture was stirred at room temperature for 1 day. The reaction was quenched by water (30 ml). The crude product was extracted by toluene. The solvent was evaporated and the obtained precipitate was recrystalized from MeOH. The crude product was recrystallized from MeOH to give yellow solid 4 (0.249 g, 95%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.19–7.25 (21H, Ar–H) 5.85 (q, 1H, J = 6.4), 1.79 (d, 3H, J = 6.4)ppm.; ^{13}C NMR (100 MHz, CDCl$_3$): 161.1, 145.9, 142.6, 141.6, 141.2, 140.9, 139.8, 139.6, 132.5, 130.2, 129.8, 128.9,

128.7, 128.5, 127.6, 127.4, 127.1, 127.0, 126.8, 126.7, 126.6, 121.5, 120.6, 119.6, 60.1, 25.4 ppm; FT-IR (KBr): 3028 (Ar–H), 2967 (Alkyl–H) 1638 (C=N), 1597 (Ar–H), 1458 (–CH$_3$) cm^{-1}.; UV–vis (THF): λ_{max} (ε) = 318 (20100) nm.; mp: 89–90 °C.; C$_{33}$H$_{25}$N: Calcd. C, 91.00%; H, 5.79%; N, 3.22%. Found: C, 90.90%; H, 5.71%; N, 3.12%.; MS m/z 435 (M^{+}); HRMS (EI) Calcd for C$_{33}$H$_{25}$N: 438.1986 Found: 438.1987.

Results and discussion

Synthesis and characterization

Three types of Schiff base monomers (**1R**, **1S**, and **1rac**) were prepared by the TiCl$_4$-mediated condensation of 2,7-dibromo-fluorenone and corresponding 1-phenylethylamines. A chiral Schiff base monomer derived from alkylamine was not applicable because of poor stability against the hydrolysis. Optically active polyfluorenes were synthesized by the palladium-catalyzed Suzuki–Miyaura coupling polymerization of 9,9′-dioctyl-fluorene-2,7-bis(trimethyleneborate) with a chiral Schiff base monomer (imino group modified-fluorene) according to Scheme 1. The obtained polymers (**2R**, **2S**, and **2rac**) were soluble in chloroform, tetrahydrofran (THF), and toluene. From GPC analysis (elution: THF; polystyrene standards), the weight-average molecular weights (M_w) and the polydispersity index (M_w/M_n) of the polymers were determined (Table 1). Although the molecular weights of the obtained polymers were not very high, they were sufficient for the evaluation of their chiroptical properties.

The structures of the polymers were confirmed by ^{1}H NMR and FT-IR spectroscopies. From the FT-IR spectra, it can be
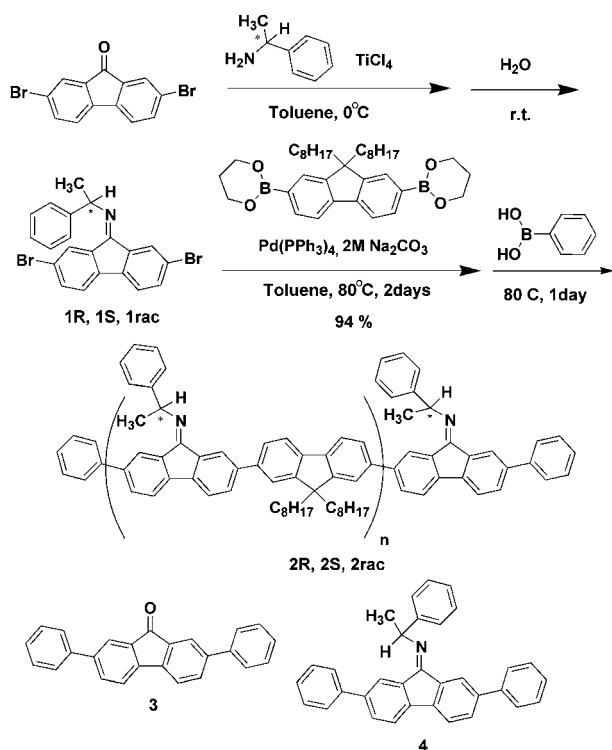
Scheme 1 Synthesis of optically active polyfluorenes with chiral Schiff bases in the side chain.

Table 1 Molecular weights and thermal properties of **2R**, **2S**, and **2rac**

Polymer	M_n	M_w	M_w/M_n	T_g	T_d
2R	4800	10 600	2.2	106.6	397.3
2S	5200	11 000	2.1	84.9	360.2
2rac	3600	71 00	2.0	90.0	389.4

observed that the peaks at 1638–1647 cm^{-1} and 1718 cm^{-1} were attributed to the C=N stretching mode in the Schiff base moiety and the C=O stretching mode in the fluorenone moiety. In contrast, no peaks were observed in the FT-IR spectra of the monomers due to the C=O stretching mode. Therefore, the imine bond was partially hydrolyzed during polymerization. The degree of hydrolyzation determined by FT-IR measurements was estimated to be less than 5%.‡

Differential scanning calorimetric (DSC) and thermogravimetric analyses (TGA) were carried out to determine the thermal transition and degradation behavior of the polymers. The DSC analysis revealed the glass transition temperatures of **2R**, **2S**, and **2rac** (Table 1). From the TG analysis, the 10% weight loss temperatures (T_d) of the polymers during the heating runs were also determined (Table 1), indicating that the polymers exhibited high thermal stabilities.§

Absorption and luminescence properties

From the UV–vis spectra [Fig. 1(b)], it can be observed that the absorption maxima (λ_{max}) of the polymers **2R**, **2S** and **2rac** were 364, 365, and 366 nm, respectively, with molar absorption (λ_{max}) coefficients ε (molarity determined on the basis of the repeating unit) of 73 600, 72 800, and 73 300 M^{-1}cm^{-1}, respectively (Table 2). These absorption maxima were similar to those of polyfluorene chromophores.[1] The UV–vis spectra of the polymers also showed shouldered peaks around 400–500 nm due to weak intramolecular charge transfer (CT) absorption in the ground state between a polyfluorene moiety (donor) and the Schiff base moiety (acceptor).¶

From the fluorescence spectra (Fig. 2), it can be observed that these polymers show intense green emissions at λ_{em} = 530 nm (ϕ = 0.43) (**2R**), 519 nm (ϕ = 0.46) (**2S**), and 523 nm (ϕ = 0.47) (**2rac**), respectively (Table 2), in THF solution (λ_{ex} = 370 nm; c = 1.0 × 10^{-5} M). A large Stokes' shift (**2R**: 266 nm) was observed. In addition, in the case of excitation of the CT absorption band (λ_{ex} = 420 nm), λ_{em} of **2R** was 530 nm. The fluorescence lifetime of the polymers and a conventional

‡ FT-IR spectroscopic analysis revealed that the polymer backbone contained less than 5% of fluorenone units (see Figs. S20 and S21 of the ESI†). We compared the relative length of the C=O stretching peak ($ca.$ 1721 cm^{-1})[12] of **2R** with those of 2,7-dibromofluorenone and **1R** mixed in different ratios.

§ Even though the **2R**, **2S**, and **2rac** polymers are so similar, the observed T_g and T_d values were different. We assume that the difference in molecular weight affects the thermal properties.

¶ From the theoretical calculations using the TD-DFT method at the B3LYP/6-31G(d) level theory, the absorption around 400 nm is assigned to the CT absorption (HOMO → LUMO transition) (Fig. S30 of the ESI†). On the other hand, in the UV–vis spectra (Scheme S31), the λ_{max} (chloroform) is red-shifted by $ca.$ 5 nm relative to λ_{max} (cyclohexane). From these results, the corresponding absorption is "weak" CT absorption.
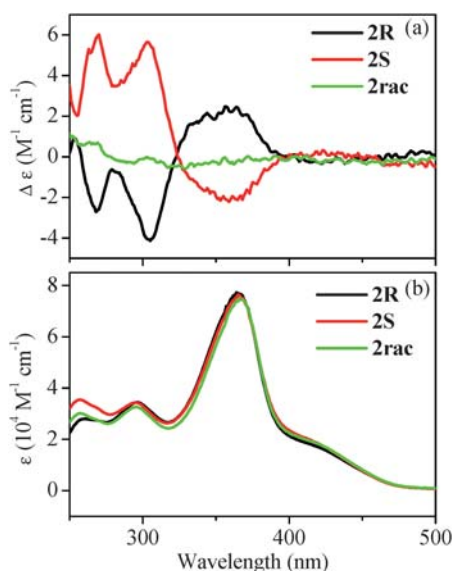
Fig. 1 (a) CD spectra of **2R** (black line), **2S** (red line), and **2rac** (green line) in 10^{-5} M THF solution. (b) UV–vis spectra of **2R** (black line), **2S** (red line), and **2rac** (green line) in 10^{-5} M THF solution.

poly(9,9′-dialkylfluorene) were *ca.* 5 ns and 0.5 ns, respectively. From these results, the green emissions observed in the fluorescence spectra of the polymers were attributed to the intramolecular CT complex in the ground and/or the excited states. In addition, the emission from a small amount of fluorenone moiety in the main chain (<5%) was negligible in the present study.‖,**

CD spectra

Analysis of the circular dichroism (CD) data of the optically active polymers clearly indicates that the polymers exhibit various highly-ordered or regular structures in solution. When the polymers (**2R** and **2S**) were in THF solution at room temperature, Cotton effects ($\Delta \varepsilon = ca.$ 2.5) were clearly observed in the π–π* transition (365 nm) due to the main chain (polyfluorene moiety) (Fig. 1). However, in the cases of the monomers

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‖ In order to evaluate the influence of the fluorescence spectra of the fluorenone moiety, we measured the UV–vis and fluorescence spectra of model monomers 2,7-diphenylfluorenone (**3**) and 2,7-diphenyl-9-phenylethyliminofluorene (**4**) (see Figs. S22 and S23 of the ESI†). From the UV–vis spectra, the model compounds **3** and **4** showed absorption maxima (λ_{max}) at 320 and 318 nm, with a molar absorption coefficient ε (molarity is based on the repeat unit) of 30 900 and 20 100 $M^{-1}cm^{-1}$, respectively (Fig. S22). **3** and **4** had shouldered peaks of 400–500 nm which were assigned to the intramolecular charge transfer (CT) structure band. From the fluorescence spectra, these model compounds showed intense green emissions at λ_{em} = 531 nm (ϕ = 0.12) (**3**) and 498 nm (ϕ = 0.15), respectively, in THF solution (λ_{ex} = 320 nm; c = 1.0 × 10^{-5} M) (Fig. S23). Fluorescence lifetimes of **3** and **4** were 8.32 ns and 2.35 ns, respectively. These values and the fluorenone unit content indicate that the influence of fluorenone moiety in the main chain was negligible.

** In this study, the Suzuki–Miyaura polymerization was carried out under argon atmosphere and basic conditions, therefore, the fluorenone unit might be mainly formed by the hydrolysis of imine. In the case of the synthesis of poly(fluorene-*alt*-9-phenyliminofluorene) under the same reaction conditions, neither the hydrolysis of imine nor the oxidation of fluorene units occurred (K. Asai and G. Konishi, unpublished result).
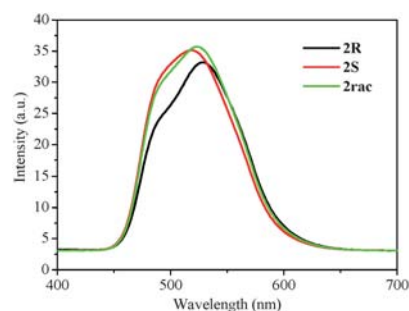
Fig. 2 Fluorescence spectra of **2R** (black line), **2S** (red line), and **2rac** (green line) in 10^{-5} M THF solution (λ_{ex} = 370 nm).

Table 2 Optical properties of **2R**, **2S**, and **2rac**

	UV–vis λ_{max}/nm	ε/M^{-1} cm^{-1}	PL λ_{max}/nm[a]	ϕ[b]	τ/ns[a]	χ^2
2R	364	73 600	530	0.43	5.41	1.043
2S	365	72 800	519	0.46	5.07	1.127
2rac	366	73 300	523	0.47	5.32	1.007

[a] λ_{ex} = 370 nm. [b] λ_{ex} = 370 nm (measured by Hamamatsu Photonics C9920-02 Absolute PL quantum yield measurement system).

1R and **1S** (Fig. S19 of the ESI†), Cotton effects were observed at 253 nm, 271 nm (**1R**), and 252 nm, 271 nm (**1S**) due to the absorption of the phenyl ring-containing chiral auxiliary. Therefore, these results suggest that the Cotton effects which were observed in the polymers, were induced by the chirality of the main chain. In addition, the existence of the main-chain chirality was also supported by the CD data of other optically active polyfluorenes and related polymers.[6,9,10] For example, Fujiki's optically active polycarbazole showed the Cotton effect ($\Delta \varepsilon = ca.$ 2.5) in the π–π* transition region due to the polymer backbone.[8] We also confirmed the similar Cotton effect by a fluorescence-detected circular dichroism (FDCD) spectrum (Fig. S28).

In order to elucidate the origin of the observed Cotton effects, the polymer concentration dependence of the CD and UV–vis absorption signals of **2R** and **2S** in THF were measured (Figs. S26 and S27). Cotton effects of the π–π* transition were not found to change for both concentrations (c = 1.0 × 10^{-4} and 1.0 × 10^{-5} M). Moreover, in order to evaluate the highly-ordered structure formed *via* intermolecular aggregation, the effects of solvent type on the optical properties of **2R** and **2S** were investigated. For this purpose, co-solvent systems consisting of THF and 1-octanol (a poor solvent for the polymers) in different ratios were used; however, solvent dependence in the CD spectra was not observed. From these results, it can be concluded that the observed chiroptical properties are a result of the chirality of the individual polymer chains.

In order to estimate a highly-ordered structure for the polymer, the optimized structure of 2,7-diphenyl-9-phenylethyliminofluorene **4** was investigated by theoretical calculation of density-functional theory (DFT) method at the B3LYP/6-31G level theory (Fig. 3). **4** showed bent-shaped structure (side view). Although as **4** is model compound, this result may suggest that it is possible for polymer **2R** or **2S** to form a helical structure (Table S1).
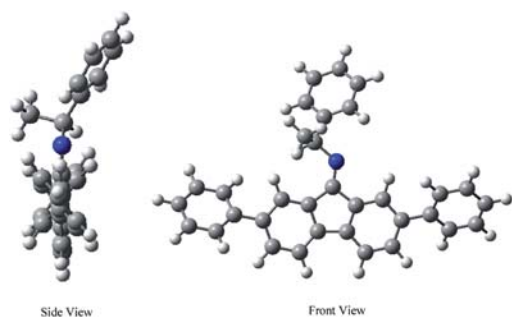
Fig. 3 Optimized structure of **4** [B3LYP/6-31G(d)].

Conclusions

We have successfully synthesized a functional optically active polyfluorene having chiral Schiff base moieties by Suzuki–Miyaura coupling polymerization. The fluorescence spectra of the polymers showed intense green emission with high quantum efficiency. This type of optically active polyfluorene can be easily synthesized from various chiral phenethylamines, and it exhibits metal coordination ability. Therefore, the obtained polymers are expected to be a new class of chiral sensors[11] in which the identification of chiral metal complexes or substrates induces a change in the fluorescence spectra or conformation of the polymer, which in turn results in the development of a spectral signal. In addition, it is important to evaluate the chiroptical properties of the film toward the application of a solid-state device. These viewpoints are now under investigation.

Acknowledgements

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