



# Enhancing the thermal and spectral stabilities of polyfluorene-based blue-light-emitting materials by incorporating pendent spiro-cycloalkyl groups

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## Abstract

We have synthesized polyfluorene-based copolymers containing spiro-cycloalkyl groups functionalized on the C-9 position of alternate fluorene units using the Suzuki coupling reaction. The presence of the rigid spiro-cycloalkyl pendent groups not only hinders the close packing and intermolecular interactions between polymer chains, but also preserves the molecular rigidity of the polymer, leading to polyfluorenes with high glass transition temperatures and improved thermal and spectral stabilities. The results of photoluminescence measurements of the isothermally heated spiro-polyfluorene thin films (150 °C for 20 h) show that the commonly observed aggregate/excimer formation is suppressed effectively in these polymers. Blue electroluminescence was demonstrated in a double-layer LED device using the spiro-derivatized polyfluorene as the emitting layer.

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## 1. Introduction

Since the discovery of poly(phenylene vinylene)-based polymer light-emitting diodes (PLEDs) in 1990 [1], organic light-emitting polymers have been the subject of intensive investigations because their luminescent properties may be fine-tuned by manipulating their chemical structures and because spin-coating and printing processes may be used to prepare large-area-display devices [2–4]. Blue-emitting polymers are of special interest, since they can be used either as a blue light source in full-color displays or as the host material for generating other colors through energy transfer to lower-energy fluorophores [5–7]. Because of their high photoluminescence and electroluminescence efficiencies, polyfluorenes (PF's) are very promising candidates for blue-light-emitting materials [8–12]. A major problem with polyfluorenes, however, is their poor spectral stability; an additional emission band appears between 500 and 600 nm upon exposure to heat [13–16]. This phenomenon leads to a major issue of color instability

of the light emitted from LEDs fabricated with polyfluorenes. The formation of interchain excimers has been suggested as the cause of the undesirable long-wavelength emission. Recently, List et al. reported that keto-defects, which result from the thermal oxidation of the polymers, might also be the source of the low-energy emission bands [17].

Several chemical approaches have been utilized to reduce the excimer formation and enhance the color stability of polyfluorenes, including introducing low-band-gap chromophores to the end and/or middle of the polymer chain [18–21], end-capping with cross-linkable moieties or hole-trapping groups [22,23], and encapsulating the polymer backbone with bulky/dendrimer side chains [24–28]. It has been demonstrated that incorporating alicyclic substituents into the polymer backbone of polyimides improves their solubility effectively without sacrificing their excellent thermal properties, such as their glass transition temperatures ( $T_g$ ) [29,30]. Previous studies also have shown that incorporating spirobifluorene pendent groups in an alternating polyfluorene copolymer enhances both its  $T_g$  and luminescent stability [24]. In light of these observations, we chose to synthesize novel alternating polyfluorene

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copolymers containing spiro-cycloalkanes at the C-9 position of every other fluorene repeating unit. The presence of the rigid spiro-cycloalkyl substituent not only hinders close packing and intermolecular interactions between polymers, but also preserves their molecular rigidity. As a result, the stability of the amorphous state in polymer films can be enhanced by suppressing the formation of aggregates and interchain excimers, leading to polyfluorene-based blue-light-emitting materials with improved thermal and spectral stabilities.

## 2. Experimental section

### 2.1. General directions

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**5**) was synthesized according to a literature procedure [31]. The solvents were dried using standard procedures. All other reagents were used as received from commercial sources, unless otherwise stated.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Varian Unity 300 MHz and a Bruker-DRX 300 MHz spectrometer. Mass spectra were obtained on a JEOL JMS-SX 102A mass spectrometer. Size-exclusion chromatography (SEC) was carried out on a Waters chromatography unit interfaced to a Waters 410 differential refractometer. Three 5- $\mu\text{m}$  Waters styragel columns (300  $\times$  7.8 mm) connected in series in decreasing order of pore size ( $10^4$ ,  $10^3$  and  $10^2$  Å) were used with THF as the eluent. Standard polystyrene samples were used for calibration. Differential scanning calorimetry (DSC) was performed on a SEIKO EXSTAR 6000DSC unit using a heating rate of  $20\text{ }^\circ\text{C min}^{-1}$  and a cooling rate of  $40\text{ }^\circ\text{C min}^{-1}$ . Samples were scanned from 30 to  $300\text{ }^\circ\text{C}$  cooled to  $0\text{ }^\circ\text{C}$ , and then scanned again from 30 to  $300\text{ }^\circ\text{C}$ . The glass transition temperatures ( $T_g$ ) were determined from the second heating scan. Thermogravimetric analysis (TGA) was undertaken on a DuPont TGA 2950 instrument. The thermal stability of the samples was determined in a nitrogen atmosphere, by measuring weight loss while heating at a rate of  $20\text{ }^\circ\text{C min}^{-1}$ . UV-visible spectra were measured with an HP 8453 diode-array spectrophotometer. Photoluminescence (PL) spectra were obtained on a Hitachi F-4500 luminescence spectrometer. The PL quantum yields ( $\Phi_{\text{FL}}$ ) in toluene solutions were measured by excitation of the respective polymer solutions at 365 nm and were compared with the solution emission of 9,10-diphenylanthracene (ca.  $5 \times 10^{-6}$  M solution in cyclohexane,  $\Phi_{\text{FL}} = 0.9$ ).

#### 2.1.1. 1-(2-Biphenyl)-4-tert-butylcyclohexanol (**2a**)

*n*-Butyllithium (2.24 mL, 5.6 mmol, 2.5 M in hexane) was added dropwise to a stirred solution of 2-bromobiphenyl (1.00 g, 4.29 mmol) in dry THF (10 mL) at  $-78\text{ }^\circ\text{C}$  under a nitrogen atmosphere. After the addition was complete, the solution was warmed to room temperature

over 30 min. The mixture was cooled to  $-78\text{ }^\circ\text{C}$  and a solution of 4-*tert*-butylcyclohexanone (**1a**, 0.860 g, 5.58 mmol) in dry THF (3.0 mL) was added dropwise. The solution was then warmed to room temperature and stirred overnight. The reaction contents were quenched with water and diluted with ethyl acetate. The organic phase was washed with water, dried over magnesium sulfate, evaporated, and purified by column chromatography using hexane/ethyl acetate as the eluent to afford the alcohol **2a** (0.60 g, 45%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.74 (s, 9H), 0.92–1.09 (m, 3H), 1.39 (t,  $J = 13.2$  Hz, 2H), 1.58 (d,  $J = 12.6$  Hz, 2H), 2.33 (d,  $J = 12.6$  Hz, 2H), 7.13 (dd,  $J = 7.4$ , 1.4 Hz, 1H), 7.28 (ddd,  $J = 7.2$ , 7.2, 7.2 Hz, 1H), 7.32–7.38 (m, 6H), 7.59 (d,  $J = 7.8$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  24.8, 27.5, 32.2, 39.1, 47.7, 75.2, 126.7, 126.8, 127.1, 127.6, 127.7, 129.5, 133.2, 140.5, 142.6, 144.4. HRMS ( $m/z$ ): [ $\text{M}^+$ ] Calcd for  $\text{C}_{22}\text{H}_{28}\text{O}$ , 308.2140; found, 308.2145.

#### 2.1.2. 1-(2-Biphenyl)-3,3,5,5-tetramethylcyclohexanol (**2b**)

Compound **2b** was prepared from 2-bromobiphenyl and 3,3,5,5-tetramethylcyclohexanone (**1b**) following the procedure described for the preparation of **2a** (79%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.80 (s, 6H), 0.88–0.97 (m, 2H), 1.11 (s, 6H), 1.20–1.42 (m, 2H), 1.66 (m, 2H), 7.05 (dd,  $J = 7.5$ , 1.8 Hz, 1H), 7.18–7.40 (m, 7H), 7.60 (d,  $J = 7.8$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  28.9, 29.0, 31.9, 36.8, 50.4, 51.4, 78.6, 125.9, 126.1, 127.2, 127.6, 128.0, 129.9, 132.8, 140.5, 144.5, 147.9. HRMS ( $m/z$ ): [ $\text{M}^+$ ] Calcd for  $\text{C}_{22}\text{H}_{28}\text{O}$ , 308.2140; found, 308.2138.

#### 2.1.3. Spiro[*tert*-butylcyclohexane-4,9'-fluorene] (**3a**)

A catalytic amount of *p*-toluenesulfonic acid was added to a solution of **2a** (1.20 g, 3.90 mmol) in benzene (10 mL) and the resulting solution was heated under reflux for 10 h. The benzene was evaporated under reduced pressure and the residue was purified by column chromatography using hexane as the eluent afforded **3a** (1.02 g, 90%) as a white solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.04 (s, 9H), 1.37 (m, 1H), 1.59 (d,  $J = 12.6$  Hz, 2H), 1.73–1.90 (m, 4H), 2.05 (td,  $J = 13.2$ , 4.2 Hz, 2H), 7.25–7.42 (m, 5H), 7.71–7.81 (m, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  23.8, 28.0, 33.0, 36.5, 47.7, 50.3, 119.8, 120.2, 123.0, 126.1, 126.7, 127.1, 127.5, 139.5, 140.4, 152.5, 154.0. HRMS ( $m/z$ ): [ $\text{M}^+$ ] Calcd for  $\text{C}_{22}\text{H}_{28}$ , 290.2035; found, 290.2031.

#### 2.1.4. Spiro[(1,1,3,3-tetramethylcyclohexane)-5,9'-fluorene] (**3b**)

Using the procedure described for **3a**, the dehydrative ring closure of **2b** afforded **3b** (96%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.19 (s, 12H), 1.69 (s, 2H), 1.88 (s, 4H), 7.32–7.36 (m, 4H), 7.55–7.60 (m, 2H), 7.69–7.74 (m, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  31.1, 33.8, 46.0, 50.2, 52.3, 119.9, 125.0, 126.8, 127.3, 139.5, 157.0. HRMS ( $m/z$ ): [ $\text{M}^+$ ] Calcd for  $\text{C}_{22}\text{H}_{26}$ , 290.2034; found, 290.2037.

### 2.1.5. Spiro[*tert*-butylcyclohexane-4,9'-(2',7'-dibromofluorene)] (**4a**)

FeCl<sub>3</sub> (catalytic amount) and bromine (0.29 mL, 5.65 mmol) were added in the dark to a stirred solution of **3a** (0.50 g, 1.72 mmol) in chloroform (15 mL) at 0 °C. The solution was stirred at room temperature for 8 h and then poured into aqueous sodium thiosulfate solution and extracted with CHCl<sub>3</sub>. The solvent was evaporated and the residue was purified by column chromatography using hexane as the eluent to give **4a** (0.48 g, 63%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.03 (s, 9H), 1.41 (m, 1H), 1.58 (d, *J* = 12.0 Hz, 2H), 1.72 (td, *J* = 13.2, 3.0 Hz, 2H), 1.86–1.92 (m, 2H), 2.00 (td, *J* = 13.2, 4.2 Hz, 2H), 7.45 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.50 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.52 (d, *J* = 2.1 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 1.6 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 23.6, 27.8, 33.0, 36.1, 47.4, 50.7, 120.9, 121.3, 121.5, 121.7, 126.6, 129.5, 130.3, 130.5, 137.5, 138.3, 153.9, 155.8. HRMS (*m/z*): [M<sup>+</sup>] Calcd for C<sub>22</sub>H<sub>24</sub><sup>81</sup>Br<sub>2</sub>, 450.0204; found, 450.0165; Calcd for C<sub>22</sub>H<sub>24</sub><sup>81</sup>Br<sup>79</sup>Br, 448.0225; found, 448.0236; Calcd for C<sub>22</sub>H<sub>24</sub><sup>79</sup>Br<sub>2</sub>, 446.0244; found, 446.0250.

### 2.1.6. Spiro[(1,1,3,3-tetramethylcyclohexane)-5,9'-(2',7'-dibromofluorene)] (**4b**)

Using the procedure described for **4a**, bromination of **3b** gave **4b** (81%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.12 (s, 12H), 1.60 (s, 2H), 1.76 (s, 4H), 7.39 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 1.4 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 31.0, 33.7, 45.6, 50.0, 53.0, 121.3, 121.5, 128.3, 130.2, 137.4, 158.6. HRMS (*m/z*): [M<sup>+</sup>] Calcd for C<sub>22</sub>H<sub>24</sub><sup>81</sup>Br<sub>2</sub>, 450.0204; found, 450.0248; Calcd for C<sub>22</sub>H<sub>24</sub><sup>79</sup>Br<sup>81</sup>Br, 448.0225; found, 448.0191; Calcd for C<sub>22</sub>H<sub>24</sub><sup>79</sup>Br<sub>2</sub>, 446.0244; found, 446.0246.

### 2.1.7. Preparation of polyfluorene (PF-cyclic<sub>a</sub>)

Aqueous potassium carbonate (2 M, 0.7 mL) and aliquot 336 (40 mg) were added to a mixture of **4a** (200 mg, 446 μmol) and **5** (286 mg, 446 μmol) in distilled toluene (3.0 mL). The mixture was degassed and tetrakis(triphenylphosphine)palladium (15 mg, 2.9 mol%) was added in one portion under N<sub>2</sub>. The solution was then heated at 110 °C for 72 h. The end groups were then capped by heating under reflux for 6 h with benzenboronic acid (108 mg, 0.89 mmol) and then for 6 h with bromobenzene (140 mg, 0.89 mmol). The reaction mixture was then cooled to room temperature and precipitated into a mixture of MeOH and H<sub>2</sub>O (1:1 v/v, 100 mL). The crude polymer was collected and washed with excess MeOH. The resulting polymer was dissolved in THF (2 mL) and reprecipitated into MeOH. The polymer was finally washed for 24 h with Me<sub>2</sub>CO using a Soxhlet apparatus, and dried under vacuum to give PF-cyclic<sub>a</sub> (350 mg, 85%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.76–0.79 (m, 10H), 1.05–1.11 (m, 29H), 1.77–1.80 (m, 3H), 2.01–2.23 (m, 10H), 7.68–7.91 (m, 11H), 8.21 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 14.1, 22.7, 23.7, 24.0, 27.9, 29.3, 29.4, 30.2, 31.8, 33.0, 36.5, 40.7, 47.3, 50.4, 55.5, 120.1, 120.2, 120.5,

121.1, 121.6, 124.7, 126.2, 126.5, 127.3, 128.9, 138.3, 139.1, 139.6, 140.2, 140.4, 140.5, 141.0, 151.7, 151.8, 151.9, 153.2, 154.8.

### 2.1.8. Preparation of polyfluorene (PF-cyclic<sub>b</sub>)

Using the procedure described for PF-cyclic<sub>a</sub>, the copolymerization of monomers **4b** and **5** gave PF-cyclic<sub>b</sub> (89%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.81 (t, *J* = 6.0 Hz, 6H), 0.79–0.83 (m, 4H), 1.13–1.27 (m, 34H), 1.77 (s, 2H), 1.88–2.20 (m, 6H), 7.66–7.85 (m, 12H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 14.2, 22.7, 24.1, 29.4, 30.3, 31.0, 31.9, 33.7, 40.5, 46.0, 50.4, 52.4, 55.3, 120.0, 120.2, 121.8, 123.8, 126.0, 126.2, 127.3, 128.9, 138.2, 140.0, 140.7, 140.8, 152.0, 157.8.

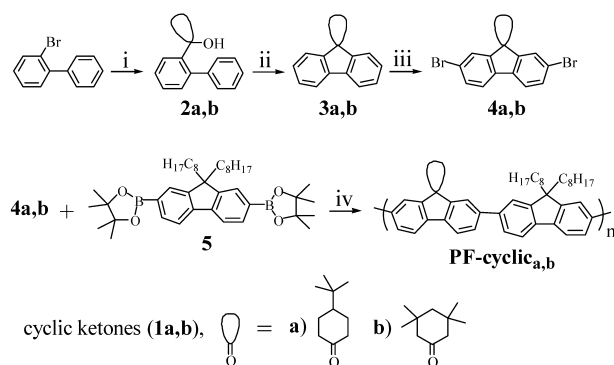
### 2.1.9. Fabrication of light-emitting devices

We fabricated a double-layer LED device with an ITO/polyethylene dioxythiophene:polystyrene sulfonate (PEDOT)/polyfluorene/Ca/Al configuration. The PEDOT (40 nm) was spin-coated directly onto the ITO glass and dried at 150 °C under vacuum for 1 h. Polyfluorene (40–60 nm) was spin-coated on top of the PEDOT layer using toluene as the solvent (1.0 wt%, 2000 rpm), and then dried for 1 h at 70 °C under vacuum. Prior to film casting, the polymer solution was filtered through a Teflon filter (0.45 μm). The Ca cathode (35 nm) was deposited thermally onto the polyfluorene film in vacuo at ≤ 10<sup>-6</sup> Torr. A protection layer of Al (100 nm) was then deposited onto the Ca layer. The film thickness was measured using an Alpha Step Dektak ST surface profiler. The current-voltage-luminance characteristics and EL spectra of the encapsulated device were recorded at room temperature with a computer-controlled DC power supply and a Photo Research PR650 spectrophotometer. The emission area of the device is 0.09 cm<sup>2</sup>, defined by the area overlapped by of the anode and cathode.

## 3. Results and discussion

### 3.1. Synthesis and characterization

Scheme 1 shows the synthetic route used for the preparation of 2,7-dibromofluorene monomers **4a–b** containing a cycloalkyl substituent at the C-9 position. Spirofluorenes **3a–b** were obtained by the reaction of 2-lithiobiphenyl with the appropriate cycloalkanones **1a–b**, followed by dehydrative ring closure of the resulting alcohols **2a–b** in the presence of a catalytic amount of *p*-toluenesulfonic acid. Bromination of the spirofluorenes **3a–b** with Br<sub>2</sub> in presence of FeCl<sub>3</sub> resulted the desired dibromo monomers **4a–b**. The chemical structures of monomers **4a–b** were confirmed by <sup>1</sup>H, <sup>13</sup>C and 2D (<sup>1</sup>H–<sup>13</sup>C heteronuclear multiple-bond-correlation spectroscopy, HMBC) NMR spectroscopy. The 2,7-dibromo substitution pattern present in **4a–b** was established from the HMBC correlation observed between the spiro carbon (C-9) and the



Scheme 1. Reagents: (i) *n*-BuLi, THF, cyclic ketone (1a,b); (ii) *p*-TsOH (cat), benzene; (iii) Br<sub>2</sub>, FeCl<sub>3</sub> (cat), CHCl<sub>3</sub>; (iv) Pd(PPh<sub>3</sub>)<sub>4</sub>/K<sub>2</sub>CO<sub>3</sub>, toluene/H<sub>2</sub>O, aliquat 336.

H-1 proton. The high-resolution mass spectral data also verified the structures of monomers **4a–b**.

As illustrated in Scheme 1, the dioctylfluorene-spiro(cycloalkane-fluorene) alternating copolymers, **PF-cyclic<sub>a</sub>** and **PF-cyclic<sub>b</sub>**, were prepared by a Suzuki coupling reaction between the spiro-dibromides **4a–b** and the diboronate **5**, 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene [31,32]. The copolymerization was carried out using Pd(PPh<sub>3</sub>)<sub>4</sub> as a catalyst in a mixture of toluene and aqueous potassium carbonate in the presence of aliquat 336 as a phase-transfer reagent. When polymerization was complete, the end groups of the polymer chain were capped by heating under reflux sequentially with phenylboronic acid and bromobenzene. <sup>1</sup>H NMR spectra of **PF-cyclic<sub>a</sub>** and **PF-cyclic<sub>b</sub>** exhibit the expected ratio of integrals between the aliphatic and aromatic regions. In the <sup>13</sup>C NMR spectra, the signals appearing in the aliphatic region nearly match those of the aliphatic carbon atoms of the monomers **4a–b** and **5** used in the polymerization reactions. **PF-cyclic<sub>a</sub>** and **PF-cyclic<sub>b</sub>** exhibit good solubility in common organic solvents, such as THF, toluene, and CHCl<sub>3</sub>, even though they incorporate rigid spiro-cycloalkanes. The molecular weights of the spiro-polyfluorene copolymers, calibrated against polystyrene standards, were determined by gel-permeation chromatography (GPC) with THF as the eluent. GPC analysis revealed (Table 1) that the weight-average molecular weights (*M<sub>w</sub>*) are  $5.5 \times 10^4$  and

Table 1  
Molecular weights and thermal properties of polymers **PF-cyclic<sub>a</sub>** and **PF-cyclic<sub>b</sub>**

Polymer	<i>M<sub>w</sub></i> <sup>a</sup>	<i>M<sub>n</sub></i> <sup>a</sup>	<i>M<sub>w</sub></i> / <i>M<sub>n</sub></i>	<i>T<sub>g</sub></i> <sup>b</sup>	<i>T</i> <sub>5%</sub> <sup>c</sup>
<b>PF-cyclic<sub>a</sub></b>	55,000	25,000	2.2	166	421
<b>PF-cyclic<sub>b</sub></b>	39,000	18,000	2.1	132	432

<sup>a</sup> Molecular weight (g/mol) determined by GPC in THF, based on polystyrene standards.

<sup>b</sup> Glass transition temperature (°C) determined by DSC with a heating rate of 20 °C min<sup>-1</sup>.

<sup>c</sup> Temperature (°C) at 5% weight loss measured by TGA with a heating rate of 20 °C min<sup>-1</sup> under a nitrogen atmosphere.

$3.9 \times 10^4$ , with polydispersities (*M<sub>w</sub>*/*M<sub>n</sub>*) of 2.2 and 2.1, respectively, for **PF-cyclic<sub>a</sub>** and **PF-cyclic<sub>b</sub>**.

The glass transition temperatures of **PF-cyclic<sub>a</sub>** and **PF-cyclic<sub>b</sub>** were investigated by differential scanning calorimetry (DSC); the results are presented in Fig. 1 and Table 1. The values of *T<sub>g</sub>* of **PF-cyclic<sub>a</sub>** and **PF-cyclic<sub>b</sub>** are 166 and 132 °C, respectively, and are much higher than that of poly(9,9-dioctylfluorene) (**POF**) (*T<sub>g</sub>* ~ 75 °C) [33]. It is evident that incorporating rigid spiro-cycloalkyl units into the polymer backbone preserves the rigidity of the chain and maintains the high glass transition temperature. For **PF-cyclic<sub>a</sub>**, the presence of the hindered *tert*-butyl groups, which further restrict the rotation of the polymer chain, leads to an additional increase in *T<sub>g</sub>* [34]. The relatively high glass transition temperature is an essential requirement for organic materials used in light-emitting applications [35]. As revealed by thermogravimetric analysis, all the copolymers exhibit high thermal stability, and their 5% weight-loss temperatures in a nitrogen atmosphere are up to ca. 420 °C.

### 3.2. Optical properties

Fig. 2 displays the absorption and photoluminescence (PL) spectra of the alternating copolymers in dilute solutions, which exhibit no noticeable difference in spectral shape from one another. In toluene solutions, **PF-cyclic<sub>a</sub>** and **PF-cyclic<sub>b</sub>** both exhibit a structureless absorption at 385 nm, which is assigned as a  $\pi-\pi^*$  transition contributed by the polyfluorene backbone. The PL spectra ( $\lambda_{\text{exc}} = 385$  nm) display a vibronic fine structure with two emission bands at 414–415 and 438 nm. The values of the absorption and emission maxima for the spiro-polyfluorenes are similar to those obtained for **POF**, which implies that replacing the two flexible octyl chains on every other fluorene unit with a rigid spiro-cycloalkane does not alter the electronic structure of the polyfluorene backbone. The fluorescence quantum yields ( $\Phi_{\text{FL}}$ ) in toluene solutions ( $\lambda_{\text{exc}} = 365$  nm) were estimated by comparison with the standard 9,10-diphenylanthracene (ca.  $5 \times 10^{-6}$  M solution in cyclohexane;

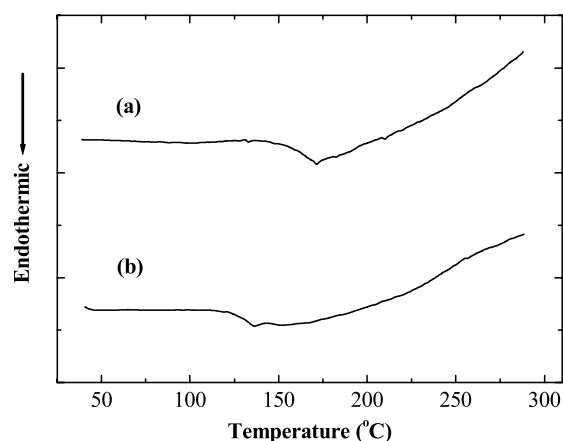


Fig. 1. DSC thermograms of spiro-functionalized polyfluorenes (a) **PF-cyclic<sub>a</sub>** and (b) **PF-cyclic<sub>b</sub>**.

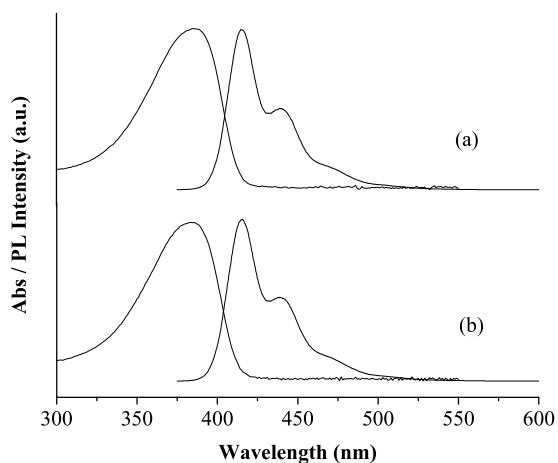


Fig. 2. UV-vis absorption and PL spectra (excited at 385 nm) in toluene of (a) **PF-cyclic<sub>a</sub>** and (b) **PF-cyclic<sub>b</sub>**.

fluorescence quantum yield of 0.90) [36]; the results are listed in Table 2. These PL efficiency values (0.83–0.87) are comparable to that of **POF** (0.89).

Fig. 3 shows the absorption and PL spectra of polymer films spin-coated from toluene solutions onto quartz plates. In comparison to their dilute solutions, the absorption spectra of the thin films have a slight red-shift (1 nm) and the emission spectra show an 11-nm red-shift. It is known that films of polyfluorenes containing flexible alkyl chains exhibit poor spectral stability upon exposure to heat [13–16]. To examine the effect that incorporating spiro-cyclic pendent groups has on the thermal stability of **PF-cyclic<sub>a</sub>** and **PF-cyclic<sub>b</sub>**, the polymer films were heated on a hot plate at 100 and 150 °C under a nitrogen atmosphere for 20 h. The absorption and PL spectra were recorded (Fig. 3) once the films had cooled to room temperature. The annealing-induced spectral change depends on the annealing temperature. When heated at 100 °C, the absorption and PL spectra of both spiro-copolymers are nearly unchanged with the appearance only of a very weak long-wavelength tail in the emission spectra. When the annealing temperature was 150 °C, the absorption spectra of **PF-cyclic<sub>a</sub>** remain unchanged and the emission intensity of the long-wavelength tail is slightly increased. In the case of **PF-cyclic<sub>b</sub>**, the absorption is broadened and the appearance of the long-

Table 2

Optical data and the fluorescence quantum yields of **PF-cyclic<sub>a</sub>**, **PF-cyclic<sub>b</sub>**, and **POF**

Polymer	Solution $\lambda_{\max}$ (nm) <sup>a</sup>		Film $\lambda_{\max}$ (nm) <sup>a</sup>		$\Phi_{\text{FL}}$ <sup>b</sup>
	abs.	em.	Abs.	em.	
<b>PF-cyclic<sub>a</sub></b>	385	414 (438)	386	425 (449)	0.87
<b>PF-cyclic<sub>b</sub></b>	385	415 (438)	386	426 (449)	0.83
<b>POF</b>	387	416 (440)	388	424 (449)	0.89

<sup>a</sup> The data listed in parentheses are the wavelengths of shoulders and subpeaks.

<sup>b</sup> Solution fluorescence quantum efficiency measured in toluene, relative to 9,10-diphenylanthracene ( $\Phi_{\text{FL}} = 0.90$ ).

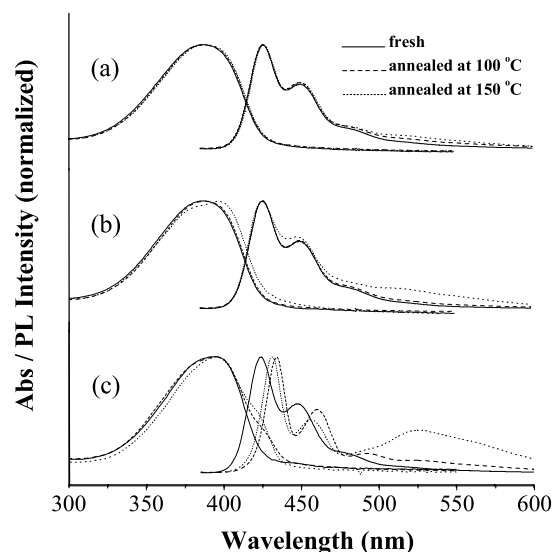


Fig. 3. UV-vis absorption and PL spectra of (a) **PF-cyclic<sub>a</sub>**, (b) **PF-cyclic<sub>b</sub>**, and (c) **POF** films before annealing and after annealing at both 100 and 150 °C for 20 h under a nitrogen atmosphere.

wavelength tail in the emission spectrum becomes more pronounced. The spectral broadening may be due to polymer aggregation during annealing. For comparison, the same experiments were conducted for the film of **POF**. Annealing of the **POF** film at 100 °C led not only to a spectral shift, but also the appearance of an additional emission band between 500 and 600 nm. The spectral instability of **POF** became much more obvious after heating at 150 °C. It is apparent that the spectral stabilities of **PF-cyclic<sub>a</sub>** and **PF-cyclic<sub>b</sub>** are better than that of **POF**. It has been suggested that the formation of aggregates and interchain excimers is the cause of the undesirable emissive color instability of the **POF** film [13–16]. Because of the presence of the spiro-cycloalkyl pendent groups, the steric demand of which restricts the close packing of the polymer chains and reduces the probability of interchain interactions, the tendency for formation of aggregates and excimers in spiro-polymers upon thermal treatment is suppressed. We note that for **PF-cyclic<sub>a</sub>** and **PF-cyclic<sub>b</sub>**, the spectral broadening and enhancement of excimer emission by annealing is  $T_g$ -dependent. Conjugated polymers, such as polyfluorenes, generally are rigid-chain molecules with relatively planar geometries and have a great tendency to pack cofacially in the solid state through molecular chain diffusion [37]. When the polymer is annealed above its  $T_g$ , as in the case of **PF-cyclic<sub>b</sub>**, when annealed at 150 °C, the molecular chains are softened and diffusion becomes relatively easy. Consequently, polymer aggregation and excimer formation are enhanced, resulting in spectral broadening and a pronounced excimer emission.

### 3.3. Electroluminescent devices

To investigate the electroluminescence properties of our

spiro-polyfluorenes, **PF-cyclic<sub>a</sub>**, which has the higher thermal stability of the two, was selected as the emitting material to fabricate polymer light-emitting diodes. We fabricated a double-layer LED device with the configuration ITO/PEDOT/**PF-cyclic<sub>a</sub>**/Ca/Al, where a conducting polymer, PEDOT was used as the hole-injecting layer. The device shows a blue emission without observing any undesirable excimer/aggregate emission at long wavelength. The EL spectra from this device at applied voltages of 7.0 and 9.5 V are shown in Fig. 4(a), with the current-voltage ( $I-V$ ) and light output-voltage ( $L-V$ ) characteristics of the device displayed in the inset. The similarity of the EL and PL spectra indicates that the EL is attributed to an emission from a singlet excited state of **PF-cyclic<sub>a</sub>**. At a bias of 9.5 V, the device exhibits a blue CIE chromaticity ( $x = 0.208$ ,  $y = 0.180$ ). As a comparison, a double-layer LED device based on **POF** was fabricated. In its EL spectra (Fig. 4(b)), an additional band was observed at ca. 550 nm, which is attributed to excimer or aggregate species. At higher applied voltages, the appearance of the emission at long wavelength is more pronounced. The device has a green emission with CIE coordinates measured to be ( $x = 0.309$ ,  $y = 0.387$ ) at an applied voltage of 9.5 V. It is apparent that the emissive color stability of **PF-cyclic<sub>a</sub>** is better than that of **POF**. This is a result of having incorporated the rigid spiro-cycloalkyl pendent groups. However, the presence of the spiro-cycloalkyl substituent may as well reduce intermolecular interactions between polymers. Which, at the same bias voltage, leads to a lower

current density of the **PF-cyclic<sub>a</sub>**-based device than that of the **POF** device, as illustrated in the inset of Fig. 4. It is also noted that the luminescence efficiency of the pristine **POF** device is higher than that of the spiro-cycloalkyl substituted **PF** device.

In conclusion, we have developed novel polyfluorene copolymers, **PF-cyclic<sub>a</sub>** and **PF-cyclic<sub>b</sub>**, with spiro-cycloalkyl groups functionalized on the C-9 position of alternate fluorene units to form a rigid 3-D structure. These polymers possess high values of  $T_g$  and very good thermal stability. The results from the photoluminescence measurements of the isothermally heated spiro-polyfluorene thin films (150 °C for 20 h) reveal that the commonly observed aggregate/excimer formation is effectively suppressed in these polymers. We attribute the improved spectral stability to their high values of  $T_g$  and their spiro-structures that reduce interchain interactions. Blue electroluminescence was demonstrated in a double-layer LED device using **PF-cyclic<sub>a</sub>** as the emitting layer.

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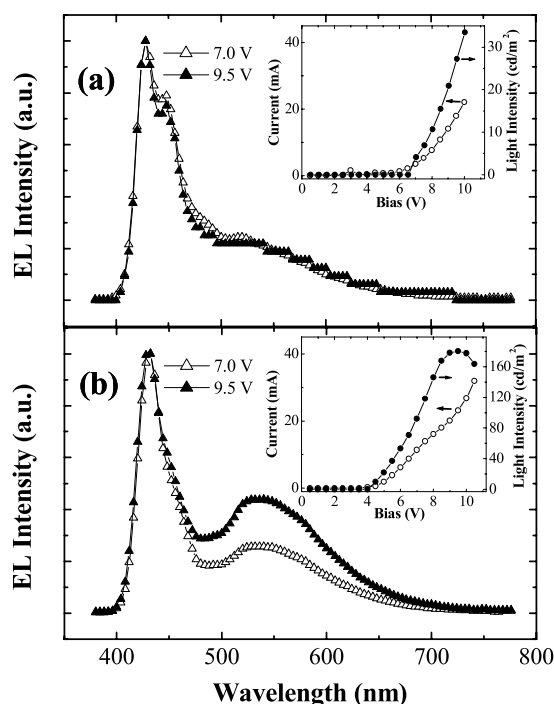


Fig. 4. EL spectra of (a) **PF-cyclic<sub>a</sub>**-based and (b) **POF**-based LED devices at different bias voltages. Inset: current–voltage ( $I-V$ ) and light–voltage ( $L-V$ ) characteristics of (a) the ITO/PEDOT/**PF-cyclic<sub>a</sub>**/Ca/Al device and (b) the ITO/PEDOT/**POF**/Ca/Al device.

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