



# Synthesis of regio- and stereoselective alkoxy-substituted spirobifluorene derivatives for blue light emitting materials

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Received 27 January 2003; revised 11 March 2003; accepted 11 March 2003

**Abstract**—Three new octyloxy substituted spirobifluorenes, 2,7-diphenyl-3',6'-bis(octyloxy)-9,9'-spirobifluorene (DPBSBF, **1a**), 2,7-dibiphenyl-3',6'-bis(octyloxy)-9,9'-spirobifluorene (DBBSBF, **1b**) and 2,7-diterphenyl-3',6'-bis(octyloxy)-9,9'-spirobifluorene (DTBSBF, **1c**) were prepared. All the compounds had been fully characterized by <sup>1</sup>H and <sup>13</sup>C NMR, UV–Vis, DSC, mass spectrometry and gave satisfactory elemental analyses. They possessed good solubility in common organic solvents and good homogeneous film formation. The optical energy band gap of DBBSBF was 3.27 eV between the HOMO energy level, 5.85 eV, measured by UPS and the LUMO, 2.58 eV, calculated from absorption spectrum. A blue organic light emitting diode (OLED) based on the structure of ITO/TPD (60 nm)/DBBSBF (40 nm)/Alq<sub>3</sub> (20 nm)/LiF (1 nm)/Al (100 nm) showed good performance. The luminance of 3125 cd/m<sup>2</sup> was observed at a drive voltage of 12.8 V and the colour coordinate in CIE chromaticity was (0.14, 0.12). The external quantum efficiency was obtained to be 2.8% at 100 cd/m<sup>2</sup>. © 2003 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

Organic electroluminescent materials have recently attracted much interest due to their physical properties and potential applications in light-emitting device and flat panel displays. To develop a blue electroluminescence emitter is essential for the development of a full color display based on the color changing medium technology or the RGB filtered white emission.<sup>1,2</sup> A number of blue electroluminescent materials have been synthesized. A fluorene, planar structure of phenylene, is one of the choice for the blue.<sup>3–6</sup> However, fluorene derivatives show an excimer formation,<sup>7,8</sup> resulting in color impurity and shortening in the lifetime of OLED device. In an efforts to reduce the excimer formation, non-planar molecular structure, 9,9'-spirobifluorene compounds have been introduced as EL materials.<sup>9–11</sup> A series of 9,9'-spirobifluorene derivatives containing symmetrically substituted phenylene groups<sup>12</sup> has been used for blue light emitting materials. The structural feature minimizes the close packing of spiro-annulated molecules in the solid state, resulting in less excimer formation in comparison with fluorene compounds. However, even though they are good candidates for the blue OLED, they still have a problem in

terms of a color purity and material stability for real application in device.

Here we report that regio- and stereoselective alkoxy-substituted spirobifluorene compounds in only one side of fluorene ring were designed and synthesized for the first time. We expect that the unsymmetrically substituted alkoxy groups may reduce intermolecular pi-electron interactions of spirobifluorene moiety and keep stable blue color. We also expect that the substituted alkoxy groups may give a better solubility and a low tendency to crystallize in the device. In this paper, we present our detailed results on synthesis, characterization of DPBSBF **1a**, DBBSBF **1b**, and DTBSBF **1c** and also preliminary results of EL behavior.

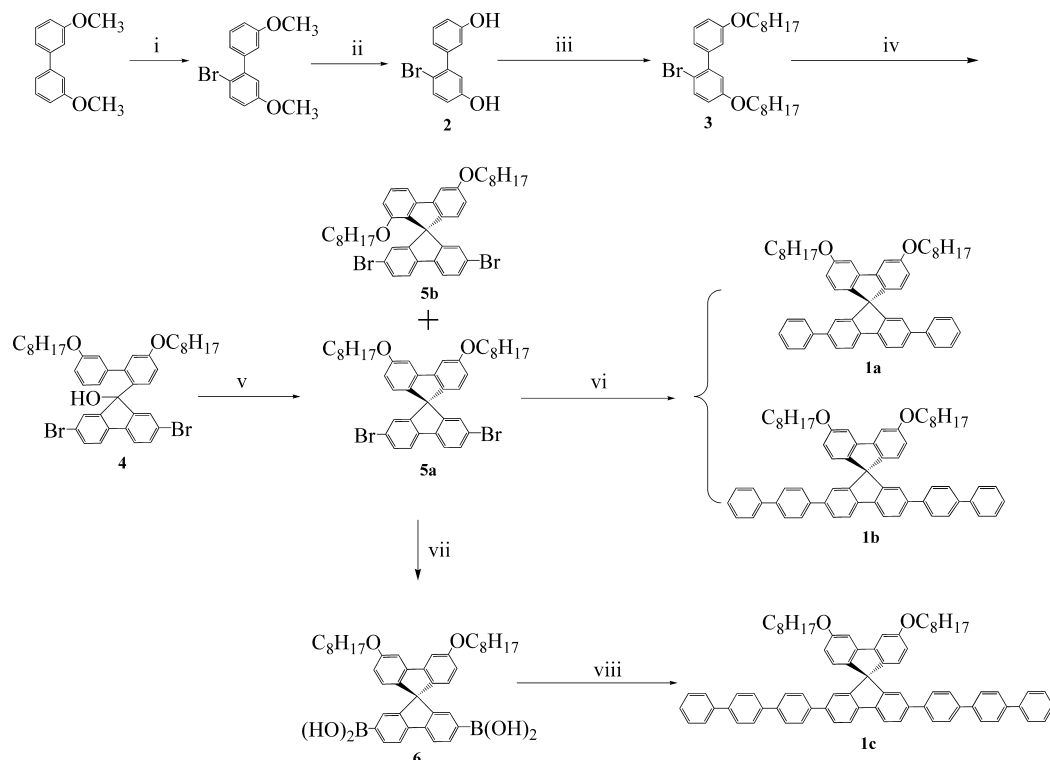
## 2. Results and discussion

### 2.1. Synthesis and characterization

The detailed synthesis of compounds, **1a–c** is sketched in Scheme 1. In order to regioselectively introduce long alkoxy groups at 3' and 6' position of **5a**, we chose 3,3'-dimethoxy biphenyl<sup>13</sup> as a starting material. Compound **2** was prepared from mono-bromination of 3,3'-dimethoxy biphenyl, followed by deprotection of 2-bromo-5,3'-dimethoxy-biphenyl to introduce longer alkoxy chain,<sup>14</sup> and alkylation

**Keywords:** spirobifluorene; blue light emitting material; organic light emitting device.

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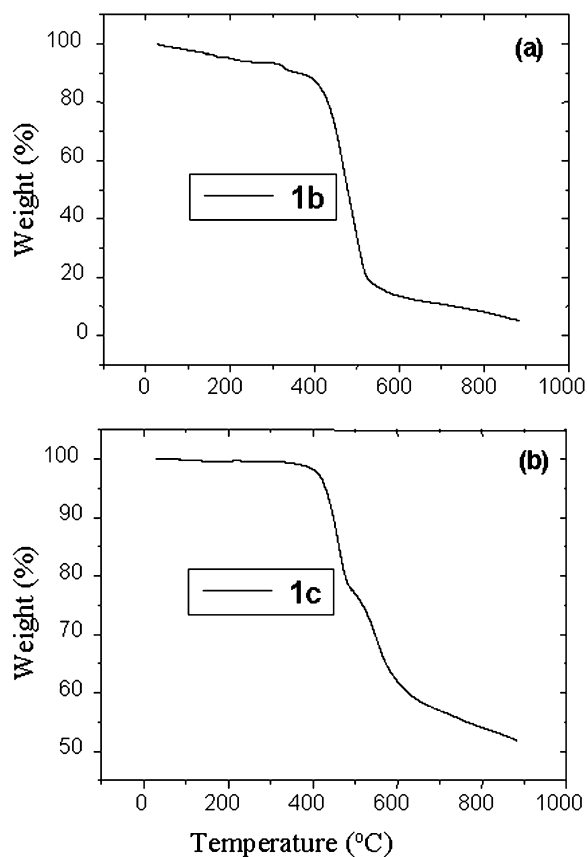


**Scheme 1.** (i) NBS, DMF. (ii)  $\text{BBr}_3$ ,  $\text{CH}_2\text{Cl}_2$ . (iii) 1-Octyl bromide,  $\text{K}_2\text{CO}_3/\text{KI}$ , DMF,  $150^\circ\text{C}$ . (iv)  $t\text{-BuLi}$ , 2,7-Dibromo-fluorene-9-one, THF,  $-78^\circ\text{C}$ . (v)  $\text{HCl}/\text{CH}_3\text{CO}_2\text{H}$ . (vi) Aryl boronic acid,  $\text{Pd}(\text{PPh}_3)_4$ , 2 M- $\text{K}_2\text{CO}_3$ , toluene, reflux. (vii)  $t\text{-BuLi}$ , triisopropylborate. (viii) Iodo terphenyl,  $\text{Pd}(\text{PPh}_3)_4$ , 2 M- $\text{K}_2\text{CO}_3$ , toluene, reflux.

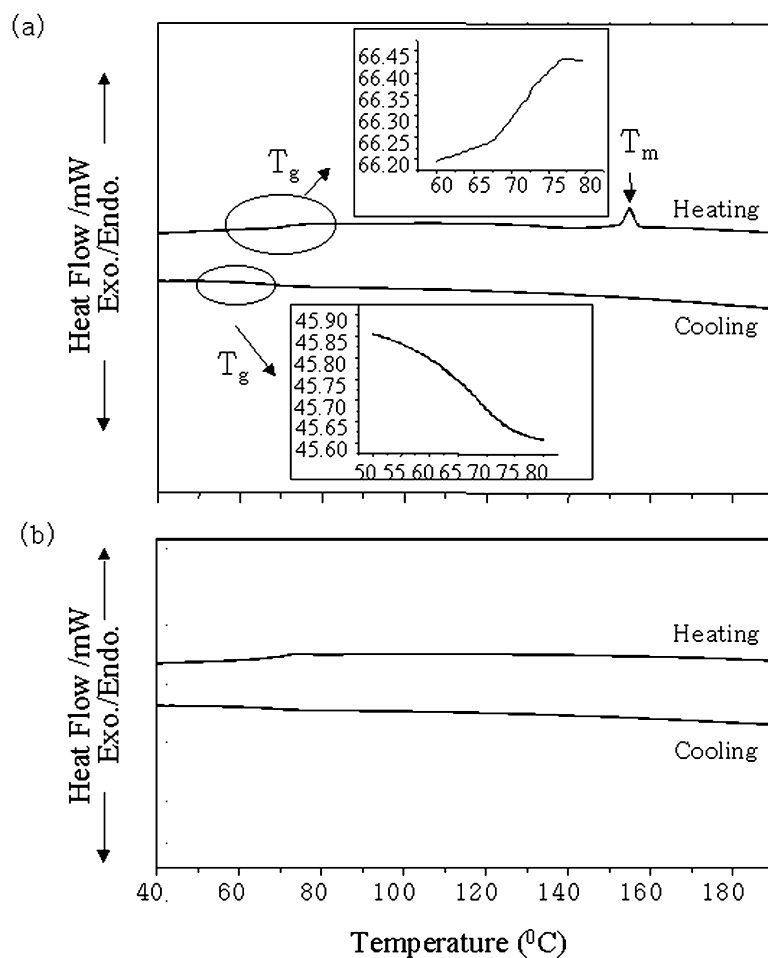
with 1-octyl bromide gave compound **3**. Compound **3** was subjected to halogen–lithium exchange by  $t\text{-BuLi}$  and 2,7-dibromofluorene-9-one was then added to give compound **4**, followed by cyclization to give 2,7-dibromo-3',6'-bis(octyloxy)-9,9'-spirobisfluorene, **5a** and its geometrical isomer, 2,7-dibromo-1',6'-bis(octyloxy)-9,9'-spirobisfluorene, **5b**.<sup>15</sup> Separation of geometrical isomers between major compound **5a** and **5b** can be achieved from column chromatography and/or re-crystallization from a mixed solvent of  $n$ -hexane and dichloromethane. In order to get the higher ratio of one form, **5a**, several stereoselective control experiments were performed by changing cyclization reagent from polyphosphoric acid (PPA) to hydrochloric acid/acetic acid and also by changing the concentration of **4** in hydrochloric acid/acetic acid. The stereoselective control experiments showed that about 10 mmol concentration of **4** in hydrochloric acid/acetic acid (1/50) gave 94% of **5a** over **5b**. DPBSBF **1a** and DBBSBF **1b** were successfully prepared by using Suzuki coupling reaction between 2,7-dibromo-3',6'-bis(octyloxy)-9,9'-spirobisfluorene **5a** and phenylboronic acid and biphenylboronic acid, respectively. In addition, DTBSBF **1c** can be also prepared from Suzuki coupling reaction with 4''-iodo[1,1':4'',1'']terphenyl and spirobisfluorene diboronic acid **6** which was obtained from lithiated 2,7-dibromo-3',6'-bis(octyloxy)-9,9'-spirobisfluorene and isopropylborate. Compounds **1a–c** are soluble in common organic solvents such as  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , THF, toluene, and chlorobenzene.

## 2.2. Thermal and physical properties

The thermal properties of **1a–c** were examined by



**Figure 1.** Thermogravimetric analysis curve of (a) **1b** and (b) **1c**.

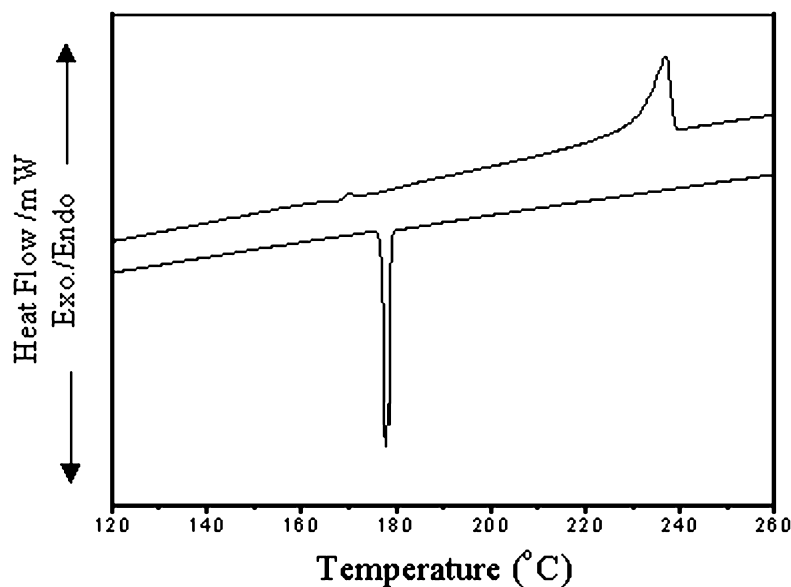


**Figure 2.** (a) The DSC data of **1b** on first heating at 10°C/min and cooling in air, (b) The DSC data of **1b** on second heating at 10°C/min and cooling in air.

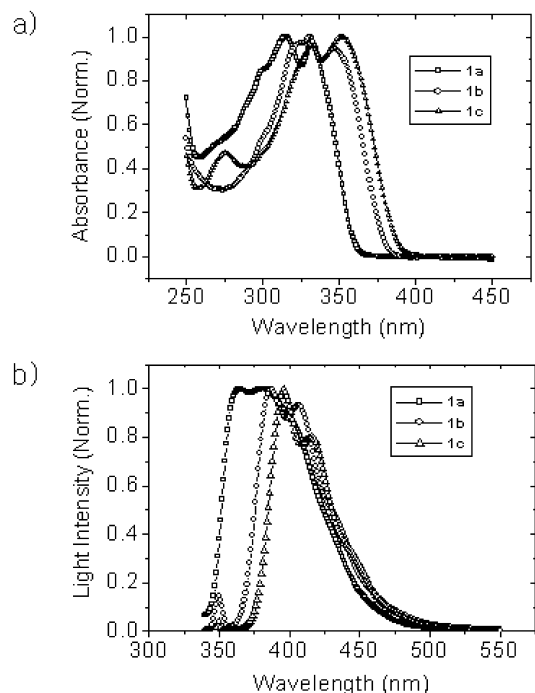
thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere. DSC of **1a** shows the low melting point at 41°C and it easily formed liquid crystalline state at room temperature. Therefore, we did not study the properties of **1a** for organic light emitting

device further. **Figure 1** shows TGA curves of **1b** and **1c**. The TGA curves show that decomposition temperature ( $T_d$ ) of **1b** starts at 388°C and for **1c** at 405°C.

DSC measurements of **1b** depicted in **Figure 2(a)** showed



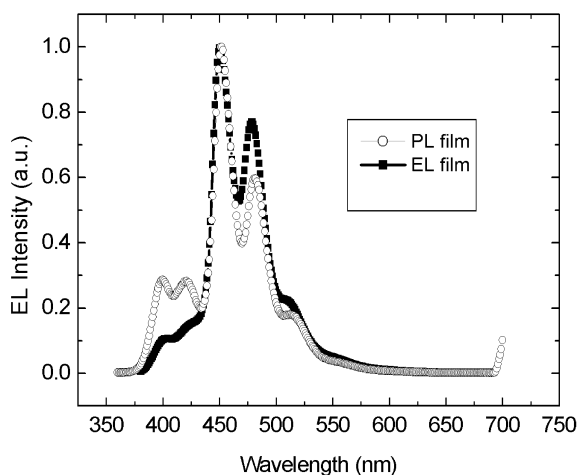
**Figure 3.** The DSC data of **1c** on heating/cooling curves.



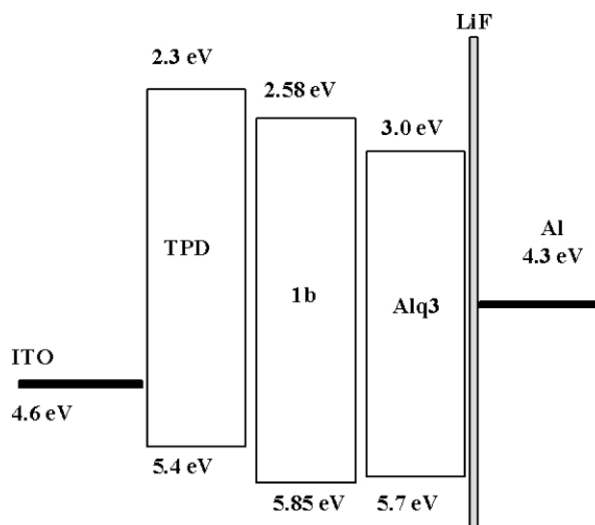
**Figure 4.** (a) and (b) show the UV and photoluminescent (PL) spectra of **1a–c** in  $\text{CHCl}_3$  solution.

that upon the first heating, it revealed the glass transition temperature ( $T_g$ ) of  $70^\circ\text{C}$  on heating and melted at  $158^\circ\text{C}$  to give an isotropic liquid and on cooling, no freezing points were observed except for  $T_g$  at  $60^\circ\text{C}$  on the first cooling.

For second heating in **Figure 2(b)**, there were no melting points observed even though giving enough time to cool in the air and giving a supercooled liquid state for several days. However, DSC measurements of **1c** shown in **Figure 3** revealed the melting point at  $237^\circ\text{C}$  and freezing point at  $180^\circ\text{C}$  on every heating and cooling. These results imply that white solid **1b** forms an amorphous solid state right after first heating. Once becoming amorphous solid state, it does not go back to a crystalline state at all. As a result, the



**Figure 5.** Photoluminescence (PL) spectrum (open circle) of **1b** in film and electroluminescence (EL) spectrum (solid square) of ITO/TPD (60 nm)/**1b** (40 nm)/Alq<sub>3</sub> (20 nm)/LiF (1 nm)/Al (100 nm) fabricated by the vacuum deposition.



**Figure 6.** Band diagram of ITO/TPD/**1b**/Alq<sub>3</sub>/LiF/Al device.

amorphous glassy state of the transparent film of **1b** is a good candidate as an EL material.

### 2.3. PL and EL spectra

The absorption in **Figure 4(a)** and PL spectra in **Figure 4(b)** of **1a–c** dissolved in  $\text{CHCl}_3$  solution exhibit two peaks and are red shift as the chain length of phenylene increases (365, 382 nm for PL spectra of **1a**, 387, 407 nm for PL spectra of **1b**, and 396, 416 nm for PL spectra of **1c**).

**Figure 5** shows the PL and electroluminescence (EL) spectra of **1b** fabricated by using vacuum deposition in film. The PL and EL spectra in film exhibit two peaks at 450 as EL and PL maximum peaks and 470 nm the emission wavelength of PL and EL spectra are almost identical expect relative intensity ratio between two peaks.

### 2.4. Homo, Lumo energy band

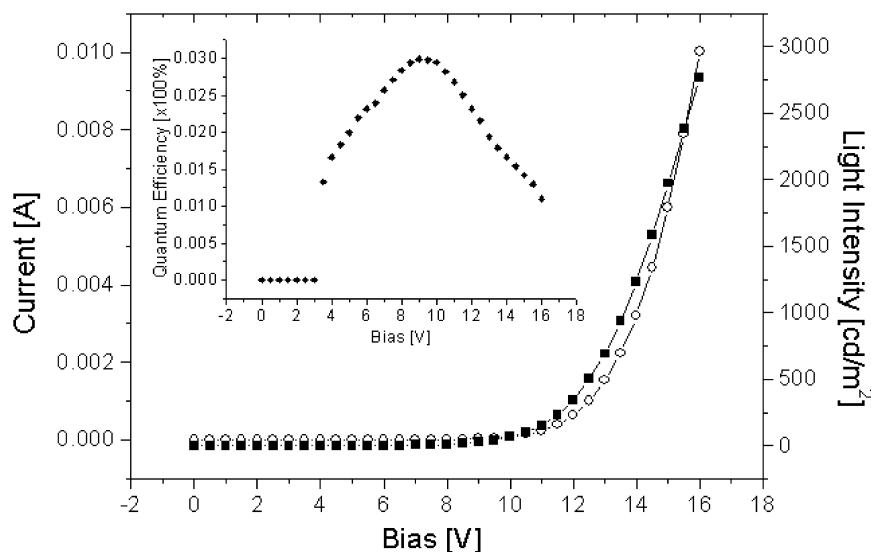
**Figure 6** shows a band diagram of ITO/TPD/**1b**/Alq<sub>3</sub>/LiF/Al device. The optical energy band gap of **1b** was 3.27 eV between the HOMO energy level, 5.85 eV, measured by UPS and the LUMO, 2.58 eV, calculated from absorption spectrum, which was consistent with the result of the optical threshold.

### 2.5. Electroluminescence properties

To investigate the EL properties of the **1b**, the EL device was fabricated in vacuum deposition method. The configuration of the EL device was ITO/TPD (60 nm)/**1b** (40 nm)/Alq<sub>3</sub> (20 nm)/LiF (1 nm)/Al (100 nm). **Figure 7** shows maximum luminance of  $3125 \text{ cd/m}^2$  at a drive voltage of 12.8 V. The luminous efficiency was obtained to be  $0.9 \text{ lm/W}$  at  $100 \text{ cd/m}^2$ . The color coordinate in CIE chromaticity is (0.14, 0.12), which is in a pure blue region. The external quantum efficiency was obtained to be 2.8% at  $100 \text{ cd/m}^2$ .

## 3. Conclusion

In conclusion, the low molecular weight materials, **1a–c**



**Figure 7.** Current–voltage ( $I$ – $V$ ) and light–voltage ( $L$ – $V$ ) characteristics of EL devices fabricated by vacuum deposition method with the configurations of ITO/TPD/**1b**/Alq<sub>3</sub>/LiF/Al (open circle and solid square, respectively). Inset: external quantum efficiency–voltage of **1b** (solid diamond).

having unsymmetrically substituted alkoxy chains were prepared in multi-step synthesis. They are very soluble in common organic solvents. They also possess good film forming properties. We fabricated the blue organic LED by using **1b** with vacuum deposition technique. We can conclude that the unsymmetrically alkoxy substituted spirobifluorenes in comparison with symmetrically substituted spiro-sexiphenyl<sup>12</sup> help preventing intermolecular pi-electron overlap and reducing the excimer formation, resulting in preventing tailing phenomenon of emission wavelength and giving purer blue color emission. From these results, we believe that **1b** is a good candidate for light blue emitting materials in organic LEDs. By using **1b** and **1c**, we are currently investigating on the performance and life time of the device, which will be presented in further papers.

## 4. Experimental

### 4.1. General remarks

NMR spectra were obtained on a Bruker Avance 400 MHz FT NMR spectrometer at room temperature. UV–Vis spectra were recorded on a Perkin–Elmer Lambda 9 UV/Vis spectrometer. Photoluminescence spectra were obtained on a Perkin–Elmer LS 50. Mass spectra were obtained on a Micromass autospec mass spectrometer. Elemental analyses were obtained on a FISON EA 1108. TGA and DSC measurements were carried out using a Perkin–Elmer 7 series thermal analyser system under N<sub>2</sub> at a heating rate of 10 K/min. All the solvents used in this study were purified according to standard methods and THF was distilled from sodium benzophenone-ketyl prior to use. All other chemicals were used as purchased without further purification.

### 4.2. Preparation of alkoxy-substituted spirobifluorene derivatives

#### 4.2.1. 6-Bromo-biphenyl-3,3'-diol (**2**). 2-Bromo-5,3'-di-

methoxybiphenyl can be prepared by literature method.<sup>14</sup> A solution of boron tribromide (137.12 mmol) was slowly added to a solution of 2-bromo-5,3'-dimethoxybiphenyl (22.85 mmol) at 0°C, followed by stirring for 1 h. Purification by silica gel chromatography using 4% ethyl acetate in dichloromethane gave pure 6-bromo-biphenyl-3,3'-diol (yield: 98%).<sup>15</sup> Mp 110–111°C; IR (KBr) 3383.5 (broad), 2925.5, 1566.9, 1466.6, 1314.3, 1182.2, 1023.0, 836.0 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.44 (d, 1H), 7.25 (m, 1H), 6.92–6.68 (m, 5H), 5.73 (s, 1H), 5.54 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 155.0, 154.9, 143.1, 142.3, 133.9, 129.2, 121.8, 118.1, 116.3, 116.2, 114.7, 112.8; MS:  $m/z$  (%) 128 (30), 157 (38), 185 (16), 264 (M<sup>+</sup>, 100). Anal. calcd for C<sub>12</sub>H<sub>9</sub>BrO<sub>2</sub>: C, 54.37; H, 3.42. Found: C, 54.30; H, 3.50.

**4.2.2. 2-Bromo-5,3'-bis(octyloxy)-biphenyl (**3**).** The obtained 6-bromo-biphenyl-3,3'-diol (22.43 mmol), 1-octyl bromide (67.28 mmol), potassium carbonate (134.56 mmol) and potassium iodide (22.43 mmol) were dissolved in dimethylformamide (60 mL), followed by heating for about 24 h at about 150°C. Purification by silica gel chromatography using 4% dichloromethane in hexane gave 2-bromo-5,3'-bis(octyloxy)-biphenyl (6.36 g, yield: 58.1%). Mp 58–59°C; IR (KBr) 2926.5, 2855.1, 1590.0, 1462.8, 1229.4, 698.1 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.49 (d,  $J$ =8.8 Hz, 1H), 7.30 (t,  $J$ =11.0 Hz, 1H), 6.96–6.76 (m, 4H), 6.74 (dd,  $J$ =8.8, 3.1 Hz, 1H), 3.98 (t,  $J$ =6.6 Hz, 2H), 3.91 (t,  $J$ =6.6 Hz, 2H), 1.80–1.74 (m, 4H), 1.44–1.40 (m, 4H), 1.32–1.28 (m, 16H), 0.88 (t,  $J$ =6.8 Hz, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 158.7, 158.3, 143.3, 142.4, 133.6, 128.9, 121.5, 117.2, 115.5, 115.3, 113.9, 112.7, 68.3, 68.1, 31.8, 31.78, 29.36, 29.30, 29.29, 29.23, 29.21, 29.17, 26.1, 26.0, 22.6, 14.1; MS:  $m/z$  (%) 157 (12), 186 (13), 237 (7), 264 (100), 376 (20), 488 (M<sup>+</sup>, 80). Anal. calcd for C<sub>28</sub>H<sub>41</sub>BrO<sub>2</sub>: C, 68.70; H, 8.44. Found: C, 68.70; H, 8.50.

**4.2.3. 9-(5,3'-Bis(octyloxy)-biphenyl-2-yl)-2,7-dibromo-9H-fluorene-9-ol (**4**).** 2-Bromo-5,3'-bis(octyloxy)-biphenyl (1.23 mmol) was dissolved in dried THF (30 mL) and cooled to –78°C. Then, *t*-butyllithium (2.45 mmol) was added slowly. The obtained resultant was stirred for 1 h at

–78°C. After 1 h, 2,7-dibromofluorene-9-one (1.47 mmol) dissolved in dried THF (20 mL) was added slowly, stirred for about 1 h, allowed to warm to room temperature and further stirred at room temperature for about 30 min. Purification by silica gel chromatography using 30–40% dichloromethane in hexane gave 9-(5,4'-bis(octyloxy)-biphenyl-2-yl)-2,7-dibromo-9H-fluorene-9-ol (yield: 68%). Mp 103.5–104°C; IR (KBr) 3445.3, 2925.5, 2855.1, 1596.8, 1467.6, 1227.5, 877.5, 810.0 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.25 (d, *J*=8.8 Hz, 1H), 7.36–7.29 (m, 4H), 7.07–7.02 (m, 3H), 6.54 (t, *J*=7.9 Hz, 1H), 6.48 (d, *J*=2.8 Hz, 1H), 6.39 (dd, *J*=2.6, 1.0 Hz, 1H), 5.65 (t, *J*=2.0 Hz, 1H), 5.61 (d, *J*=7.5 Hz, 1H), 3.94 (t, *J*=6.6 Hz, 2H), 3.52 (t, *J*=6.7 Hz, 2H), 2.41 (s, 1H), 1.76 (m, 2H), 1.59 (m, 2H), 1.42 (m, 4H), 1.34–1.27 (m, 16H), 0.92–0.86 (m, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 158.6, 157.8, 152.9, 142.3, 141.6, 138.5, 138.4, 132.1, 130.4, 128.1, 128.0, 127.9, 127.7, 122.1, 122.0, 121.9, 121.8, 121.6, 117.6, 114.2, 113.3, 113.2, 82.2, 68.5, 67.7, 32.23, 32.18, 29.82, 29.69, 29.67, 29.64, 29.61, 26.42, 26.37, 23.06, 23.03, 14.26, 14.23; MS: *m/z* (%) 186 (18), 201 (54), 313 (34), 425 (41), 635 (18), 732 (10), 748 (M<sup>+</sup>, 100). Anal. calcd for C<sub>41</sub>H<sub>48</sub>Br<sub>2</sub>O<sub>3</sub>: C, 65.78; H, 6.46. Found: C, 65.90; H, 6.50.

**4.2.4. 2,7-Dibromo-3',6'-bis(octyloxy)-9,9'-spirobisfluorene (5a) and 2,7-dibromo-1',6'-bis(octyloxy)-9,9'-spirobisfluorene (5b).** 9-(5,3'-Bis(octyloxy)-biphenyl-2-yl)-2,7-dibromo-9H-fluorene-9-ol (0.5 g, 0.668 mmol) was mixed with acetic acid (50 mL) and hydrochloric acid (1 mL) and stirred for about 22 h at room temperature. Purification by silica gel chromatography using 4% dichloromethane in hexane, followed by recrystallization using a mixed solvent of hexane and dichloromethane gave white solid **5a** (yield: 94%) and **5b** (yield: 6%).

**Compound 5a.** Mp 118.5–119°C; IR (KBr) 2925.5, 2854.2, 1608.4, 1451.2, 1305.5, 1179.3, 1058.7, 807.0 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.60 (d, *J*=8.2 Hz, 2H), 7.44 (dd, *J*=8.1, 1.8 Hz, 2H), 7.29 (d, *J*=2.3 Hz, 2H), 6.82 (d, *J*=1.7 Hz, 2H), 6.66 (dd, *J*=7.1, 3.6 Hz, 2H), 6.56 (d, *J*=8.3 Hz, 2H), 4.02 (t, *J*=6.5 Hz, 4H), 1.80 (m, 4H), 1.47 (m, 4H), 1.31 (m, 16H), 0.88 (t, *J*=3.5 Hz, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 159.7, 151.1, 143.0, 139.6, 139.4, 130.9, 127.3, 124.6, 121.8, 121.2, 114.7, 105.9, 68.3, 64.4, 31.8, 29.37, 29.35, 29.25, 26.11, 22.7, 14.1; MS: *m/z* (%) 425 (11), 505 (14), 617 (5), 730 (M<sup>+</sup>, 100). Anal. calcd for C<sub>41</sub>H<sub>46</sub>Br<sub>2</sub>O<sub>2</sub>: C, 67.40; H, 6.35. Found: C, 67.45; H, 6.40.

**Compound 5b.** Mp 128.5–129°C; IR (KBr) 2925.5, 2854.2, 1585.2, 1456.0, 1267.0, 1058.7, 807.0 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.61 (d, *J*=8.1 Hz, 2H), 7.43–7.30 (m, 5H), 6.83 (s, 2H), 6.64–6.62 (m, 2H), 6.51 (d, *J*=8.2 Hz, 1H), 4.01 (t, *J*=6.5 Hz, 2H), 3.51 (t, *J*=5.9 Hz, 2H), 1.81 (quint, 2H), 1.49 (m, 2H), 1.31–1.24 (m, 12H), 1.08 (m, 4H), 1.02 (m, 4H), 0.88 (m, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 159.6, 155.2, 150.0, 143.5, 143.0, 140.2, 139.3, 134.2, 130.4, 123.0, 126.6, 124.4, 121.4, 120.8, 114.6, 112.1, 111.1, 106.2, 68.3, 67.3, 63.7, 31.9, 31.8, 29.4, 29.3, 29.2, 28.9, 26.1, 25.4, 22.7, 22.7, 14.2, 14.1. MS: *m/z* (%) 425 (6), 506 (15), 730 (M<sup>+</sup>, 100).

**4.2.5. 2,7-Bisphenyl-3',6'-bis(octyloxy)-9,9'-spirobisfluorene (1a).** The compound was prepared under Suzuki

reaction conditions. 2,7-dibromo-3',6'-bis(octyloxy)-9,9'-spirobisfluorene (0.5 g, 0.68 mmol), 4-phenyl boronic acid (0.21 g, 1.71 mmol), tetrakis(triphenylphosphine)palladium (0.24 g, 0.20 mmol), 2 M-sodium carbonate (2.1 mL, 4.10 mmol) and toluene (29 mL) were simultaneously mixed, frozen under liquid nitrogen, evacuated by a vacuum pump and then warmed to room temperature to be melted. This procedure was repeated twice, followed by injection of nitrogen. The mixed solution was refluxed for 2 days and cooled to room temperature. Thereafter, a small amount of distilled water was added, and the organic layer was filtered three times with dichloromethane, dried over sodium sulfate. Then, the dichloromethane was concentrated under reduced pressure. Purification by silica gel chromatography using 10% dichloromethane in hexane, followed by recrystallization using a mixed solvent of hexane and dichloromethane gave white solid **1a** (0.407 g, yield: 82%). UV (CHCl<sub>3</sub>): λ<sub>max</sub> nm (ε, M<sup>-1</sup> cm<sup>-1</sup>), 315 (19400), 332 (18600); IR (KBr) 2925.5, 2854.2, 1608.4, 1463.7, 1224.5, 1176.4, 759.8 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 7.96 (d, *J*=7.8 Hz, 2H), 7.68 (dd, *J*=4.0, 3.9 Hz, 2H), 7.48–7.45 (m, 6H), 7.34–7.32 (m, 4H), 7.26 (m, 2H), 7.02 (d, *J*=1.4 Hz, 2H), 6.71 (d, *J*=1.7 Hz, 4H), 4.07 (t, *J*=6.5 Hz, 4H), 1.85 (m, 4H), 1.53 (m, 4H), 1.44–1.35 (m, 16H), 0.94 (t, *J*=6.8 Hz, 6H); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 160.0, 150.9, 143.6, 141.6, 141.19, 141.18, 140.9, 129.0, 127.6, 127.3, 127.1, 124.9, 122.7, 120.8, 115.0, 106.3, 68.8, 65.3, 32.3, 29.82, 29.81, 29.7, 26.5, 23.1, 14.3; MS: *m/z* (%) 499 (17), 611 (8), 648 (16), 724 (M<sup>+</sup>, 100). Anal. calcd for C<sub>53</sub>H<sub>56</sub>O<sub>2</sub>: C, 87.80; H, 7.79. Found: C, 87.80; H, 7.77.

**4.2.6. 2,7-Dibiphenyl-3',6'-bis(octyloxy)-9,9'-spirobisfluorene (1b).** 2,7-Dibromo-3',6'-bis(octyloxy)-9,9'-spirobisfluorene (0.35 mmol), 4-biphenyl boronic acid (0.89 mmol), tetrakis(triphenylphosphine)palladium (0.11 mmol), 2 M-sodium carbonate (2.13 mmol) and toluene (15 mL) were simultaneously mixed, frozen under liquid nitrogen, evacuated by a vacuum pump and then warmed to room temperature to be melted. The mixed solution was refluxed for 2 days. Purification by silica gel chromatography using 20% dichloromethane in hexane, followed by recrystallization using a mixed solvent of hexane and dichloromethane gave white solid **1b** (yield: 90%). UV (CHCl<sub>3</sub>): λ<sub>max</sub> nm (ε, M<sup>-1</sup> cm<sup>-1</sup>), 331 (22300), 347 (21000); IR (KBr) 2925.5, 2854.2, 1607.4, 1464.7, 1304.6, 1224.6, 1175.4, 816.7, 763.7 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 7.96 (d, *J*=7.9 Hz, 2H), 7.68 (dd, *J*=5.2, 1.7 Hz, 2H), 7.59–7.52 (m, 12H), 7.40–7.38 (m, 8H), 7.01 (d, *J*=1.5 Hz, 2H), 6.68 (d, *J*=1.0 Hz, 4H), 4.04 (t, *J*=6.6 Hz, 4H), 1.80 (m, 4H), 1.48 (m, 4H), 1.40–1.29 (m, 16H), 0.89 (t, *J*=6.9 Hz, 6H); <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 159.3, 150.9, 143.5, 141.4, 140.9, 140.8, 140.2, 140.0, 129.1, 127.7, 127.5, 127.2, 126.9, 124.9, 122.5, 120.8, 114.9, 106.1, 68.7, 65.2, 32.2, 29.8, 29.7, 29.6, 26.4, 23.0, 14.2; MS: *m/z* (%) 651 (21), 764 (7), 877 (M<sup>+</sup>, 100). Anal. calcd for C<sub>65</sub>H<sub>64</sub>O<sub>2</sub>: C, 89.00; H, 7.35. Found: C, 88.85; H, 7.68.

**4.2.7. 3',6'-Bis(octyloxy)-9,9'-spirobisfluorenyl-2,7-bisboronic acid (6).** A solution of 2,7-dibromo-3',6'-bis(octyloxy)-9,9'-spirobisfluorene (0.68 mmol) dissolved in dry-THF (100 mL) was cooled to cooled to –78°C. Then, *t*-butyllithium (3.76 mmol) was added slowly. The reaction

mixture was stirred for 2 h at  $-78^{\circ}\text{C}$ . After 2 h, triisopropylborate (8.2 mmol) was added. The reaction mixture was stirred for an hour at  $-78^{\circ}\text{C}$  and kept to stir overnight while warming to room temperature. Purification by silica gel chromatography using 30–40% ethylacetate in hexane gave **6** (yield: 75.2%). Mp 145–146 $^{\circ}\text{C}$ ; IR (KBr) 3218.7 (broad), 1456.0, 1195.7, 798.4  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (d,  $J=7.6$  Hz, 2H), 7.85 (d,  $J=7.64$  Hz, 2H), 7.62 (d,  $J=2.3$  Hz, 2H), 7.10 (s, 2H), 6.65 (dd,  $J=8.36$ , 2.33 Hz, 2H), 6.46 (d,  $J=8.3$  Hz, 2H), 4.02 (t,  $J=6.3$  Hz, 4H), 1.74 (m, 4H), 1.42 (m, 4H), 1.29 (m, 16H), 0.85 (t,  $J=3.5$  Hz, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  159.0, 148.3, 142.9, 142.8, 140.9, 133.7, 129.2, 124.1, 119.5, 114.6, 106.2, 67.7, 64.1, 31.3, 28.9, 28.7, 25.6, 25.1, 14.0.

**4.2.8. 2,7-Diterphenyl-3'6'-bis(octyloxy)-9,9'-spirobisfluorene (1c).** Compound **6** (0.167 mmol), 4''-iodo-[1,1';4',1'']terphenyl (0.50 mmol), tetrakis(triphenylphosphine)palladium (0.01 mmol) and 2 M-sodium carbonate (1.67 mmol) were mixed, frozen under liquid nitrogen, evacuated by a vacuum pump and then warmed to room temperature to be melted. The mixed solution was refluxed for 2 days and cooled to room temperature. Purification by silica gel chromatography using 10–30% dichloromethane in hexane gave white solid **1c** (yield: 30%). UV ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  nm ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ ), 331 (18600), 350 (18400); IR (KBr) 2925.5, 1610.3, 1462.8, 1222.7, 812.9  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.97 (d,  $J=7.7$  Hz, 2H), 7.68–7.63 (m, 18H), 7.55 (d,  $J=8.4$  Hz, 4H), 7.45 (m, 4H), 7.39 (m, 4H), 7.02 (t,  $J=1.0$  Hz, 2H), 6.69 (d,  $J=1.1$  Hz, 4H), 4.05 (t,  $J=6.6$  Hz, 4H), 1.82 (m, 4H), 1.50 (m, 4H), 1.36–1.27 (m, 16H), 0.89 (t,  $J=6.9$  Hz, 6H);  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  160.0, 151.0, 143.6, 141.5, 141.0, 140.9, 140.6, 140.4, 140.2, 139.7, 139.65, 129.2, 127.77, 127.69, 127.56, 127.45, 127.26, 127.0, 124.9, 122.6, 120.9, 115.0, 106.2, 68.8, 65.3, 32.2, 29.8, 29.7, 26.5, 23.0, 14; MS:  $m/z$  (%) 803 (20), 916 (6), 1001 (21), 1029 ( $\text{M}^+$ , 100). Anal. calcd for  $\text{C}_{77}\text{H}_{72}\text{O}_2$ : C, 89.84; H, 7.05. Found: C, 89.90; H, 7.01.

### 4.3. Fabrication and measurements of EL device

The EL device fabricated by vacuum deposition technique was constructed using a triple layer structure with TPD as the hole injecting layer, **1b** as an emitting layer, and  $\text{Alq}_3$  as an electron transporting layer. The ITO-coated glass substrate was cleaned by sequential ultrasonic sonic washing in acetone, methanol, and deionized water for

15 min, respectively, and finally treated with  $\text{O}_2$  plasma for 5 min after blowing the cleaned substrate with  $\text{N}_2$  for 5 min. TPD, **1b**,  $\text{Alq}_3$ , and LiF/Al layer were evaporated under vacuum. Electroluminescence (EL) spectra were recorded using Minolta CS-1000 and Current–voltage ( $I$ – $V$ ) and radiance–voltage characteristics of the devices were simultaneously measured with a Keithley 2400 Source Measure Unit and a Minolta LS-100. All device testing was carried out at room temperature under ambient atmosphere.

### Acknowledgements

The authors thank the Korean Ministry of Information and Communication for support of this work (Grant No. 2001-s-161).

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