Synthesis of New Spiro[benzo[c]fluorene-7,9′-fluorene] Dimers and Their Optical Properties

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Five novel spiro[benzo[c]fluorene-7,9′-fluorene] based dyes, including 5-[spiro[benzo[c]fluorene-7,9′-fluorene]-5-yl] spiro[benzo[c]fluorene-7,9′-fluorene] (7), 5-[spiro[benzo[c]fluorene-7,9′-fluorene]-9-yl] spiro[benzo[c]fluorene-7,9′-fluorene] (8), 5-[spiro[benzo[c]fluorene-7,9′-fluorene]-2′-yl] spiro[benzo[c]fluorene-7,9′-fluorene] (9), 9-[spiro[benzo[c]fluorene-7,9′-fluorene]-9-yl] spiro[benzo[c]fluorene-7,9′-fluorene] (10), and 2′-[spiro[benzo[c]fluorene-7,9′-fluorene]-2′-yl] spiro[benzo[c]fluorene-7,9′-fluorene] (11) were successfully prepared from the corresponding halogen and boronic acid derivatives through the Suzuki coupling reaction, respectively. Chemical structures were confirmed by 1H nuclear magnetic resonance (NMR), 13C NMR, Fourier transform-infrared spectroscopy, mass spectroscopy, and elemental analysis. The thermal properties were determined by differential scanning calorimetry and thermal gravimetric analysis. The relationships between the optical and electrochemical properties and the combined positions between these dimers were systematically investigated using UV-vis, photoluminescence (PL), and photoelectron spectroscopy. These five dimers exhibited high fluorescent quantum yields and good morphological stability with high glass transition states > 174 °C. Dimer 7 showed a UV absorbance peak at 353 nm, emission PL peak at 424 nm, and quantum efficiency of 0.62 in a cyclohexane solution.

Key Words: Spirodimer, Spiro[benzofluorene-fluorene], High glass transition temperature, Blue host materials, OLED

Introduction

Interest has developed over the last few decades to explore organic semiconductors for various applications, such as organic light-emitting diodes,1-5 field-effect transistors,6,7 nonvolatile memory devices,8,9 and organic solar cells.10-13 Organic semiconductors can be easily used to fabricate large-area devices, and low-cost devices have the advantage of being produced, but has the disadvantage of poor reproducibility and a short lifetime. In particular, the lifetime is very short compared to inorganic-based semiconductor. Thus, many studies have been performed to improve the lifetime of organic semiconductors. Of these studies, using organic semiconductor material with a glass transition temperature that is greater than the operating temperature of the device has been suggested as an effective method to maintain the amorphous state. If the glass transition temperature of the amorphous film is less than the operating temperature of the device, molecular motion increase rapidly, allowing transition to a crystalline state. Crystalline or polycrystalline state films, where grain boundaries act as traps for charge carriers, decrease device lifetime. An important class of spiro compounds as organic semiconductors has been developed to improve morphological stability while retaining the electronic properties. These compounds have several benefits. Spiro linkage between two π-conjugated molecules has the effect of raising the glass transition temperature, because of the rigid structure due to perpendicular arrangement. Furthermore, isolation of the π electron conjugated system, high solubility, and suppression of excimer formation as used solid-state fluorescent dye. Spiro-type derivatives containing fluorene and benzofluorene as OLED fluorescent materials have received a great deal of attention because asymmetrical spiro compounds with a naphthalene group not only can preserve the inherent characteristics of a spiro compound such as morphological stability, high glass transition temperature, and amorphous properties but also provide a variety of substituents on the aromatic ring of spiro molecule resulting in the formation of conjugation controlled OLED host and dopant materials.14-24

In this study, we report the synthesis of novel spiro[benzo[c]fluorene-7,9′-fluorene] (SBFF)-type OLED materials using the Suzuki reaction. Various properties such as UV-Vis absorption, photoluminescence (PL), photoelectron spectroscopy, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA) were evaluated. In addition, the highest occupied molecular orbital (HOMO) and LUMO distribution and energy levels of the six dimers were calculated by density functional theory (DFT) of Becke’s 3-parameters employing Lee-Yang-Parr functional (B3LYP) with 6-31G* basis sets method to compare the experimental data.25-27
Experimental

Materials and Measurements. Tetrakis(triphenylphosphine) palladium(0), n-butyl lithium (2.5 M in hexane), trisopropyl borate, cyclohexane, and 2-methoxyethanol (Aldrich Chem. Co.) were used without further purification. Potassium carbonate and hydrochloric acid (Dukshen Chem. Co.) were used without further purification. Tetrahydrofuran (Dukshen Chem. Co.) was distilled over sodium and calcium hydride.

5-Bromospiro[benzo[c]fluorene-7,9'-fluorene] (1), 9-bromospiro[benzo[c]fluorene-7,9'-fluorene] (2) and 2'-bromospiro[benzo[c]fluorene-7,9'-fluorene] (3) were prepared as reported previously.\(^3\,^5\)

The PL spectra were recorded on a fluorescence spectrophotometer (Jasco FP-6500) and the UV-vis spectra were obtained by means of a UV-vis spectrophotometer (Shimadzu, UV-1601PC). The HOMO energy levels were measured with a low-energy photo-electron spectrometer (Riken-Keiki AC-2). Mass spectra were recorded using a JMS-AX505WA (JEOL) spectrometer in fast atom bombardment (FAB) mode. The \(^1\)H and \(^13\)C nuclear magnetic resonance (NMR) were recorded on Avance 500 (Bruker, 500 MHz) and Unity Inova (Varian, 200 MHz) instruments. Fourier transform-infrared spectra were obtained with a 640-IR (Varian) spectrophotometer and elemental analyses were performed using a EA1110 (CE Instrument). The DSC measurements were performed on a Shimadzu DSC-60 differential scanning calorimeter under nitrogen at a heating rate of 10 °C/min. The TGA measurements were performed on a Shimadzu TGA-50 thermo gravimetric analyzer at a heating rate of 5 °C/min.

Synthesis of Spiro[benzo[c]fluorene-7,9'-fluorene]-5-ylboronic acid (4). A solution of 5-bromo spiro[benzo[c]fluorene-7,9'-fluorene] (0.97 g, 2.18 mmol) in THF (20 mL) was placed into a 100 mL two-necked flask. The reaction flask was cooled to −78 °C and n-BuLi (2.5 M in n-hexane, 1.22 mL) was added slowly dropwise. The solution was stirred at this temperature for 1 h, followed by the addition of a solution of trisopropylborate (6.5 mL) in THF (5 mL) under an argon atmosphere. The resulting mixture was gradually warmed to ambient temperature and quenched by adding saturated, aqueous NaHCO\(_3\) (5 wt %, 50 mL). The mixture was extracted with dichloromethane. The combined organic layers were dried over magnesium sulfate, filtered, and evaporated under reduced pressure. The resulting powdery product was purified a column chromatography with dichloromethane to give a white powder. Spiro[benzo[c]fluorene-7,9'-fluorene]-9-ylboronic acid (4).

Representative Synthesis of 5-[Spiro[benzo[c]fluorene-7,9’-fluorene]-5-yl] spiro[benzo[c]fluorene-7,9’-fluorene] (7). 1 (0.65 g, 1.46 mmol), 4 (0.66 g, 1.61 mmol), tetrakis(triphenylphosphine)palladium(0) and THF (15 mL) were stirred in a two-necked flask under a nitrogen atmosphere for 1 h, and potassium carbonate (0.4 g, 2 M) was added dropwise over 20 min. The resulting mixture was refluxed overnight at 80 °C, and the reaction mixture was extracted with dichloromethane and water. After the organic layer was evaporated in a rotary evaporator, the resulting powder product was purified by column chromatography with dichloromethane/n-hexane to give a white crystalline solid. The other dimers, including 5-[spiro[benzo[c]fluorene-7,9’-fluorene]-9-yl] spiro[benzo[c]fluorene-7,9’-fluorene] (8), 5-[spiro[benzo[c]fluorene-7,9’-fluorene]-2’-yl] spiro[benzo[c]fluorene-7,9’-fluorene] (9), 9-[spiro[benzo[c]fluorene-7,9’-fluorene]-9-yl] spiro[benzo[c]fluorene-7,9’-fluorene] (10), and 2’-[spiro[benzo[c]fluorene-7,9’-fluorene]-2’-yl] spiro[benzo[c]fluorene-7,9’-fluorene] (11) were prepared by similar procedures. The crude products were purified by train sublimation and purity of dimers was measured by HPLC (Young-lin Instrument Co. LTD. Model CTS 30).

5: Yield 72%. \(^1\)H-NMR (200 MHz, CDCl\(_3\)) \(\delta\) 8.95-8.91 (1H, d, Ar-H), 8.55-8.51 (1H, d, Ar-H), 8.14-7.93 (5H, m, Ar-H), 7.81-7.57 (4H, m, Ar-H), 7.45-7.38 (2H, t, Ar-H), 7.14-7.07 (3H, t, Ar-H), 6.70-6.57 (3H, m, Ar-H). Anal. Calcd. for \(C_{29}H_{25}BO_{3}\) (410.27): C, 84.90; H, 4.67; B 2.64. Found: C, 85.09; H, 4.59; B, 3.05. MS (FAB) \(m/z\) 410 [(\(M + 1\))^\(+\)]

6: Yield 70%. \(^1\)H-NMR (200 MHz, CDCl\(_3\)) \(\delta\) 8.84-8.80 (1H, d, Ar-H), 8.43-8.24 (1H, d, Ar-H), 7.91-7.79 (5H, m, Ar-H), 7.60-7.24 (5H, m, Ar-H), 7.21-6.98 (2H, m, Ar-H), 6.78-6.65 (3H, m, Ar-H), 4.40 (2H, s, B-OH). Anal. Calcd. for \(C_{32}H_{29}BO_{2}\) (410.27): C, 84.90; H, 4.67; B 2.64. Found: C, 85.03; H, 4.69; B, 2.76. MS (FAB) \(m/z\) 410 [(\(M + 1\))^\(+\)]
6.60 (d, 2H, Ar-CH-naphthalene), 7.59-7.53 (m, 4H, Ar-CH-benzofluorene), 7.47-7.45 (m, 2H, Ar-CH-benzene), 7.44-7.35 (m, 4H, Ar-CH-benzofluorene), 7.13-7.06 (m, 5H, Ar-CH-benzene), 6.92 (s, 2H, Ar-CH-benzene), 6.79-6.72 (m, 6H, Ar-CH-benzene).

9: Yield 83%. Purity 99.5%. mp 306°C. FT-IR (KBr, cm⁻¹) 3050, 3020 (aromatic C-H).

10: Yield 80%. Purity 99.2%. mp 276°C. FT-IR (KBr, cm⁻¹) 3040, 3020 (aromatic C-H). ¹H-NMR (500 MHz, CDCl₃) δ 8.77-8.75 (d, 2H, Ar-CH-benzofluorene), 8.33-8.32 (d, 2H, Ar-CH-benzofluorene), 7.88-7.86 (d, 6H, Ar-CH-benzene), 7.69-7.66 (t, 2H, Ar-CH-benzofluorene), 7.57-7.56 (d, 2H, Ar-CH-benzofluorene), 7.53-7.48 (m, 4H, Ar-CH-benzene), 7.38-7.35 (t, 4H, Ar-CH-benzofluorene), 7.08-7.05 (t, 4H, Ar-CH-benzofluorene), 6.99 (s, 2H, Ar-CH-benzene), 6.74-6.69 (m, 6H, Ar-CH-benzene).

11: Yield 81%. Purity 99.5%. mp 306°C. FT-IR (KBr, cm⁻¹) 3050, 3020 (aromatic C-H). ¹H-NMR (500 MHz, CDCl₃) δ 8.83-8.82 (d, 2H, Ar-CH-benzofluorene), 8.41-8.39 (d, 2H, Ar-CH-benzofluorene), 7.88-7.86 (d, 2H, Ar-CH-benzofluorene), 7.79-7.77 (d, 2H, Ar-CH-benzofluorene), 7.72-7.68 (m, 4H, Ar-CH-benzofluorene), 7.57-7.52 (m, 4H, Ar-CH-benzene), 7.44-7.41 (t, 2H, Ar-CH-benzofluorene), 7.32-7.29 (t, 4H, Ar-CH-benzene), 7.10-7.07 (t, 2H, Ar-CH-benzofluorene), 7.03-7.00 (t, 2H, Ar-CH-benzofluorene), 6.82 (s, 2H, Ar-CH-benzofluorene), 6.77-6.75 (t, 4H, Ar-CH-benzofluorene), 6.63-6.60 (d, 2H, Ar-CH-naphthalene).

Results and Discussion

Synthesis and Characterization. Dimers 7-11 were prepared in a two-step synthesis as outlined in Scheme 1. In the first step, 1, 2, and 3 were lithiated with n-butyl lithium and consecutively borated with trisopropylboration, followed by aqueous alkali quenching. The resulting SBFF-boronic acids 4, 5, and 6 were obtained with a yield of 70-80%. In the second step, 4, 5, and 6 were coupled with corresponding bromo-SBFFs by the Suzuki reaction in the presence of palladium catalyst to produce SBFF dimers 7-11 as shown in Scheme 1. The crude dimers were purified by column chromatography with dichloromethane/n-hexane until a constant molar excitation coefficient and purity were obtained. The dimers were obtained in good yield (78-80%). The resulting SBFF dimers were identified and characterized by FT-IR, ¹H-NMR, ¹³C NMR, MS, and elemental analysis. The ¹H NMR spectra of the dimers were similar to each other and showed that the aromatic protons were spread over the region between 6.7-8.4 ppm and that the chiral carbon peak was observed at 66.0 ppm in the ¹³C NMR spectra.


Yield 80%. Purity 99.2%. mp 306°C. FT-IR (KBr, cm⁻¹) 3050, 3020 (aromatic C-H). ¹H-NMR (500 MHz, CDCl₃) δ 149.4, 148.3, 148.2, 147.4, 142.9, 141.6, 141.4, 140.9, 136.4, 134.0, 129.6, 129.4, 129.0, 127.9, 127.4, 127.1, 127.0, 125.6, 124.2, 124.0, 123.1, 122.7, 122.2, 120.2, 66.5. Anal. Calcd. for C₃₈H₃₄ (730.80): C, 95.31; H, 4.69. Found: C, 94.65; H, 5.35. MS (FAB) m/z 730 [(M+1)⁺]. UV-vis (THF): λmax (absorption) = 343 nm, λmax (emission) = 417 nm.

results of the elemental analysis and mass spectroscopy also supported the formation of dimers 7-10 and matched well with the calculated data. The FAB mass of the dimers showed [M+1]$^+$ or [M]$^+$ at the same molecular weight range, confirming their molecular weight and chemical structure.

**Thermal Properties.** The thermal properties of the newly synthesized dimers were investigated by DSC and TGA analysis in a nitrogen atmosphere. Table 1 summarizes the DSC data of the five spirodimers. The onset decomposition temperatures were 389, 432, 314, 314 and 374 °C for 7, 8, 9, 10, and 11, respectively. The purified samples of 7-11 showed melting points ($T_m$) of 290, 276, 306, 314, and 306 °C, respectively. No melting points were observed following the second heating, even though it was given enough time to cool in air. Once it became an amorphous solid, it did not revert to the crystalline state. After the sample had cooled to room temperature, a second DSC scan was performed at 10 °C/min and revealed $T_g$ at 207, 213, 205, 195, and 234 °C, respectively, because of their rigid spiro-type backbone. The DSC and TGA thermograms of dimer 7 are shown in Figure 1. The temperature for 5% weight loss at 427 °C on the TGA curve showed the very good thermal stability of dimer 7. As a result, the amorphous glassy state films of the five SBFF dimers were good candidates as organic semiconducting materials.

**Optical Properties.** Table 2 summarizes the optical properties (UV-vis absorption and fluorescence) of the five dimers in tetrahydrofuran. The detailed absorption and fluorescence spectra of the dimers are presented in Figure 2.

The wavelength of the UV-vis absorption band depended on the connection position between the two SBFFs. The benzofluorene/benzofluorene linkage-types of dimers 7, 8, and 10 showed similar conjugation extension. But, as seen in the molecular structure of dimer 7, the spiro[benzo[c]-fluorene-7,9'-fluorene]-5-yl core structure was distorted by the SBFF substituted at the 5-position, leading to a reduction in the degree of SBFF conjugation. For this reason, the UV-Vis absorption band ranges of dimers 8 and 10 compared to that of 7 moved to the short-wavelength region (Figure 2). The distortion of the conjugated structure of the naphthalene increased the optical bandgap of the dimer material, leading to a blue shift in the absorption edge of the UV-vis spectra. The optical band gaps were 3.22, 3.17, and 3.16 eV for 7, 8, and 10.

**Table 1.** Thermal properties of the spirodimers

<table>
<thead>
<tr>
<th>Thermal properties</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_g^a$ (°C)</td>
<td>207</td>
<td>213</td>
<td>205</td>
<td>195</td>
<td>234</td>
</tr>
<tr>
<td>$T_m^b$ (°C)</td>
<td>290</td>
<td>276</td>
<td>306</td>
<td>314</td>
<td>306</td>
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<tr>
<td>$T_d^c$</td>
<td>389</td>
<td>432</td>
<td>314</td>
<td>314</td>
<td>374</td>
</tr>
</tbody>
</table>

*a* Glass transition temperature. *b* Melting temperature. *c* Decomposition temperature.

**Table 2.** Solution (THF) and solid UV-Vis and PL data of the spirodimers

<table>
<thead>
<tr>
<th>Optical properties</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV Max (nm)</td>
<td>353</td>
<td>354</td>
<td>343</td>
<td>354</td>
<td>328, 343$^c$</td>
</tr>
<tr>
<td>Opt. Bg$^a$ (eV)</td>
<td>3.22</td>
<td>3.17</td>
<td>3.24</td>
<td>3.16</td>
<td>3.47</td>
</tr>
<tr>
<td>PL Max (nm)</td>
<td>424</td>
<td>424</td>
<td>417</td>
<td>422</td>
<td>387, 405$^c$</td>
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<tr>
<td>FWHM$^b$ (nm)</td>
<td>68.7</td>
<td>58.9</td>
<td>60.3</td>
<td>59.4</td>
<td>37.5</td>
</tr>
<tr>
<td>Solid PL Max (nm)</td>
<td>435</td>
<td>424</td>
<td>428</td>
<td>436</td>
<td>393</td>
</tr>
<tr>
<td>FWHM (nm)</td>
<td>81.0</td>
<td>63.9</td>
<td>65.2</td>
<td>83.0</td>
<td>50.6</td>
</tr>
</tbody>
</table>

*a* Bandgap was calculated from the absorption edge of solid UV-Vis spectra. *b* Full width at half maximum. *c* Second maximum peak.
and 10, respectively.

Figure 3 shows the structure and optimized angle of dimers 7 and 10 obtained by molecular calculations. It seemed that dimer 7 deviated significantly from the coplanar conformation. In particular, the naphthyl groups formed with the adjacent naphthalene group had a torsion angle of 68°, which allowed the naphthalene unit and the phenyl group to form independent conjugation systems. The torsional angle between the phenyl group and the adjacent phenyl was 36° for 10. The relationship between the absorption and molecular structure is determined to a large extent by the structural dependence of the competing photophysical and photochemical processes.

Dimer 7 exhibited weak absorption in the UV spectrum close to the visible range but very strong fluorescence. In contrast, dimer 8 showed one broad absorption band (with the shoulder) in the visible region located at 320-400 nm and a strong emission band characterized by a 70 nm Stokes shift in THF. When dimer 11 incorporated with fluorene/fluorene units was compared to dimer 9 combined with benzofluorene/fluorene units in the same solvent, the UV-Vis absorption band and the edge of dimer 11 was in a blue shift because the conjugation length of dimer 11 was shorter than that of dimer 9.

The PL spectra of the SBFF dimers were similar except for dimer 11. The fluorescence of 11 combined with fluorene/fluorene unit was blue shifted in comparison with dimers 7 and 9 connecting a benzofluorene/fluorene unit. The blue PL spectrum of dimer 11 was split into two peaks due to a combination of fluorine units as well as isolation of benzofluorene units. The absorption and fluorescence spectra overlapped with each other with nearly mirror images for all of the tested dimers, corresponding to the π→π* transition.

Table 3 summarizes the spectroscopic properties (UV-vis absorption and fluorescence) of the five dimers in cyclohexane, THF, and 2-methoxyethanol. Little influence of the solvents on different polarities was observed. Dimer 7 exhibited fluorescence with a maximum at 424-425 nm in all solvents.

The relative fluorescence quantum yield of dimers 7-11 is summarized in Table 3. The fluorescence quantum of the reference material 9,10-diphenylanthracene in cyclohexane was set to 0.90. All dimers showed fluorescence quantum yields in the range 0.14-0.62. Spiro[benzo[c]fluorene-7,9’-fluoren] substituted at the 5-position showed high PL and QE values of 7 (0.62) and 8 (0.50). But, dimer 11 exhibited the lowest fluorescence quantum yield due to the fluorine/fluorene-type connection, which extended the conjugation length of the dimer. A more accurate QE comparison was possible between dimers 7 and 8 because they had a similar PL spectrum. Dimer 7 had a higher QE than that of dimer 9 (QE: 0.45), even though the two dimers had the same number of naphthalene and phenyl units; this result emphasized the importance of the bond sequence.

Table 3. Optical properties of the spirodimers in different solvents

<table>
<thead>
<tr>
<th>Dimers</th>
<th>( \lambda_{\text{max}} ) (nm)</th>
<th>( \varepsilon_{\text{max}} ) (M(^{-1})cm(^{-1}))</th>
<th>( \lambda_{\text{em}} ) (nm)</th>
<th>Abs Edge(^b) (nm)</th>
<th>( \Phi_F )(^a) (nm)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>C-Hex(^d)</td>
<td>2-ME(^e)</td>
<td>Film</td>
<td>C-Hex(^d)</td>
<td>2-ME(^e)</td>
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<tr>
<td>7</td>
<td>353</td>
<td>353</td>
<td>358</td>
<td>10690</td>
<td>425</td>
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<tr>
<td>8</td>
<td>353</td>
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<td>358</td>
<td>4300</td>
<td>421</td>
</tr>
<tr>
<td>9</td>
<td>343</td>
<td>343</td>
<td>348</td>
<td>12810</td>
<td>425</td>
</tr>
<tr>
<td>10</td>
<td>353, 345, 364</td>
<td>354, 345, 364</td>
<td>364</td>
<td>7320</td>
<td>419</td>
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<tr>
<td>11</td>
<td>329, 343, 328, 343, 348</td>
<td>343, 343, 348</td>
<td>4630</td>
<td>387, 405, 387, 405, 393, 410</td>
<td>390</td>
</tr>
</tbody>
</table>

\(^a\)Fluorescence quantum efficiency relative to 9,10-diphenylanthracene in cyclohexane (\( \Phi_F = 0.90 \)). \(^b\)UV absorption edge. \(^c\)molar extinction coefficient. \(^d\)cyclohexane. \(^e\)2-methoxyethanol
A low-energy photoelectron spectrometer was used to obtain information on the HOMO energies and the charge injection barriers of the dimers. The HOMO energy levels of the five dimers were $-5.96 \sim -6.11$ eV. The HOMO value of dimer 8 ($-6.03$ eV) was different from that of dimer 10 ($-5.96$ eV) due to the conjugation length. According to the DFT calculations and the experimental data from the photoelectron spectra, the calculated HOMO and LUMO energy levels showed a similar trend.

**Conclusions**

Novel spirobenzofluorene dimers based on the SBFF system were successfully prepared by reacting bromo-SBFF derivatives with the corresponding SBFF boronic acids using the Suzuki coupling reaction. These dimers possessed a high glass transition temperature due to the rigid spiro linkage, and have promising potential for applications in organic semiconductors for organic electronic devices. The absorption spectra of the five spirodimers exhibited quite different profiles, which were attributed to a covalently conjugated connection between the naphthalene and benzene groups in the SBFF. Dimer 7 was different from the other dimers, with a maximum absorption peak at 353 nm with no shoulder and a PL of about 424 nm, suggesting that the electronic structure of the conjugated backbone could be affected by suppressing SBFF conjugation. Applications for the blue OLED host materials are now in progress and the results will be presented elsewhere.

**References**


**Figure 4.** HOMO and LUMO distributions of five dimers.

**Table 4.** Experimental and calculated HOMO, LUMO, and energy gap (Bg) by B3LYP/6-31G Method

<table>
<thead>
<tr>
<th></th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
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<tbody>
<tr>
<td>HOMO</td>
<td>-6.01</td>
<td>-6.03</td>
<td>-6.02</td>
<td>-5.96</td>
<td>-6.11</td>
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<tr>
<td>LUMO</td>
<td>-2.79</td>
<td>-2.86</td>
<td>-2.78</td>
<td>-2.80</td>
<td>-2.64</td>
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<tr>
<td>Opt. Bg$^a$ (eV)</td>
<td>3.22</td>
<td>3.17</td>
<td>3.24</td>
<td>3.16</td>
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<tr>
<td>HOMO</td>
<td>-5.17</td>
<td>-5.14</td>
<td>-5.21</td>
<td>-5.12</td>
<td>-5.31</td>
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<tr>
<td>LUMO</td>
<td>-1.43</td>
<td>-1.49</td>
<td>-1.39</td>
<td>-1.52</td>
<td>-1.28</td>
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<tr>
<td>Opt. Bg (eV)</td>
<td>3.74</td>
<td>3.66</td>
<td>3.81</td>
<td>3.61</td>
<td>4.03</td>
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<tr>
<td>Angle$^b$ ($)</td>
<td>68</td>
<td>35</td>
<td>54</td>
<td>36</td>
<td>37</td>
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</tbody>
</table>

$^a$Optimal bandgap. $^b$Optimum angle between two spiro[benzo[c]fluorene-7,9'-fluorene] units

These geometrical characteristics effectively prevent intermolecular interactions between π-systems and, thus, suppress molecular recrystallization, which improves the morphological stability of these molecules. The HOMOs and LUMOs of dimers 7-11 were mostly localized on the connected unit, whereas those of dimer 11 were dispersed over the whole molecule. Bandgaps of the combined fluorene/fluorene unit and the isolated benzofluorene unit could be separated, and, as a result, two peaks were observed in the PL spectrum (Figure 2).

The energy levels of the five dimers including their energy levels in the present study are summarized in Table 4. A low-energy photoelectron spectrometer was used to obtain


