A Novel Ambipolar Spirobifluorene Derivative that Behaves as an Efficient Blue-Light Emitter in Organic Light-Emitting Diodes

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ABSTRACT

A novel ambipolar spiro-configured D−A blue-light emitter bearing hole-transporting diphenylamino groups and electron-transporting phenylbenzimidazole groups was synthesized, characterized, and incorporated into an efficient single-layer organic light-emitting diode (OLED) device exhibiting blue-emission Commission International d’Eclairage (CIE) coordinates of 0.15 and 0.14, a turn-on potential of 4 V, a maximum brightness of 2800 cd/m² at 830 mA/cm² (19 V), and a maximum quantum efficiency of 0.53% (0.61 cd/A).

9,9′-Spirobifluorene-cored compounds have been employed widely in organic light-emitting diodes (OLEDs) displaying a variety of functions.1 A common strategy toward manipulating the electronic structure, emission spectrum, thermal/morphological stability, or charge carrier mobility of 9,9′-spirobifluorene-based materials is through tailoring the nature of the substituents and their substitution patterns about the 9,9′-spirobifluorene unit, e.g., with identical or different substituents positioned on the same or different biphenyl branch.2 Furthermore, to balance the electron−hole recombination efficiency, one promising strategy is that of developing emitters equipped with an electron-donating moiety (D) that facilitates hole injection and/or transport and an electron-withdrawing moiety (A) that improves electron injection and/or transport.3 With appropriate choices of the D and A units, the levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) as well as the emission color of the D−A molecule can be controlled to a fine degree,4 making such systems increasingly attractive for use in a single-layer OLEDs.5 This approach has allowed the development of efficient emitters displaying a range of emission colors.1,6 However, derivatives

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featuring donors on one biphenyl branch spiro-linked to another biphenyl moiety bearing acceptors exhibit low photoluminescence efficiencies as a result of strong photo-induced electron transfer. Thus, a better alternative is to position the D and A moieties on the same biphenyl branch of the spirobifluorene. Unfortunately, strong intramolecular D–A charge transfer normally leads to significant red-shifting of the emission colors, making it difficult to develop efficient blue emitters using this strategy.1-3,6

Herein, we report an efficient spiro-configured D–A bipolar blue emitter, 2,2′-bis(diphenylamino)-7,7′-bis(diphenylbenzimidazole)-9,9′-spirobifluorene (3, Scheme 1). The shift of the emission colors, making it difficult to develop efficient blue emitters using this strategy.1-3,6

Scheme 1 depicts the synthesis of 3. Treatment of 2,2′-dibromo-7,7′-dicarboxyl-9,9′-spirobifluorene with an excess of SOCl2 gave the diacetyl chloride intermediate 1, which was amidated with N-phenyl-o-phenylenediamine in the presence of triethylamine followed by dehydration at 250 °C under vacuum (0.1 Torr) to afford the dibromide 2 (60% for three steps). The diphenylamino groups were introduced through amination of 2 with diphenylamine and NaO-Bu in the presence of catalytic amounts of Pd(OAc)2 and PbBu3, providing 3 in 83% yield. We synthesized the acceptor-only analogue, 2,2′-bis(phenylbenzimidazole)-9,9′-spirobifluorene (5), through a similar path (Scheme S-1, Supporting Information) for the sake of comparison and as an electron-transporting material in subsequent OLED devices.

Table 1 summarizes the physical properties of compounds 3–5. Differential scanning calorimetry (DSC) indicated that these compounds exhibit distinct glass transition temperatures (Tg) within the range from 115 to 165 °C, suggesting that these materials could form homogeneous and amorphous films through thermal evaporation. Thermogravimetric analysis (TGA) indicated that these materials exhibit high decomposition temperatures (Td) within the range from 370 to 477 °C (5% weight loss). We attribute these relatively high morphological and thermal stabilities to the perpendicularly configured spirobifluorene core, which disrupts intermolecular interactions and suppresses the tendency to crystallize.

We first examined the bipolar character of 3 using cyclic voltammetry (CV; Figure S-1 Supporting Information). The electrochemical properties of spirobifluorene derivatives are dependent mainly on their functional substituents. Thus, compound 4 exhibited only reversible oxidation potentials [0.87 and 0.94 V, assigned by differential pulse voltammetry (DPV)], whereas the acceptor-only counterpart 5 displayed reversible reduction potentials (–1.96 and –2.17 V). Merging these two functionalities, the spiro-configured bipolar D–A molecule 3 exhibited both reversible oxidation and reduction behavior but with slight shifts in the potentials. The existence of stable radical cationic and anionic species suggested that it had great potential for efficient electron/hole transport and recombination in OLEDs. We estimated the HOMO energy levels from the oxidation potentials of 3 and 4 in relation to the first reversible oxidation potential (0.74 V in CH2Cl2) of N,N'-bis-(1-naphthyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine (α-NPB), HOMO = –5.3 eV). A band gap energy of 2.86 eV for 3 was calculated from the difference between the reduction and oxidation peak potentials; this value is consistent with the data calculated from the optical absorption threshold. We
red-shifted significantly to 468 nm in MeCN. Because cyclohexane exhibits a maximum signal at 412 nm that was from CH$_2$Cl$_2$ using an integrated sphere system are 0.41 and 0.84, from polarity, we infer that its reduced band gap energy results in emission behavior that is independent of the solvent polarity. We conducted charge-carrier mobility measurements of D and A groups were connected into the extended once the D and A groups were connected into the chromic effect. For example, the emission spectrum of the emission characteristics of relatively insensitive to the dielectric environment, whereas the emission characteristics of 3 revealed a strong solvatochromic effect. For example, the emission spectrum of 3 in cyclohexane exhibits a maximum signal at 412 nm that was red-shifted significantly to 468 nm in MeCN. Because 3 exhibits absorption behavior that is independent of the solvent polarity, we infer that its reduced band gap energy results from $\pi$-orbital interactions between the D and A groups, without evident electronic interactions, in the ground state. The dependence of the emission wavelength of 3 on the solvent polarity is indicative of photoinduced charge transfer occurring in the excited state. Importantly, the photoluminescence quantum yields of 3 measured in thin film and in CH$_2$Cl$_2$ using an integrated sphere system are 0.41 and 0.84, respectively, ensuring the potential use as an efficient emitter.

We conducted charge-carrier mobility measurements of 3–5 using time-of-flight (TOF) techniques at ambient temperature (Figure S-3, Supporting Information). Figure 2 depicts the mobilities plotted as a function of the square root of the electric field; the straight lines follow the nearly universal Poole–Frenkel relationship, $\mu \propto \exp(\beta E^{1/2})$, where $\beta$ is the Poole–Frenkel factor.

The observed hole ($\mu_h = ca. 10^{-4}$ cm$^2$/Vs) and electron ($\mu_e = ca. 3 \times 10^{-6}$ cm$^2$/Vs) mobilities of 3 are comparable to, but slightly lower than, those of its single-chromophore counterparts 4 and 5, respectively. The hybridization of the electron-donating character of the diphenylamino group with the electron-withdrawing character of the phenylbenzimidazole moiety leads to the novel bipolar 3 system exhibiting ambipolar carrier-transport character. The mobilities are compensated to a certain degree, however, by the spiro configuration of the two D–A chromophore branches hindering efficient intermolecular $\pi$-orbital interactions, which is consistent with the observed lower mobilities of 3 and 4 as compared to those of tetraphenylbenzidine (TAD)$_2$ and TBPI, respectively (Figure S-4, Supporting Information).

To examine the potential application of 3 as an emitter in OLEDs, we designed three devices having the configuration ITO/PEDOT-PSS (30 nm)/I: 3 (100 nm): II: 3 (50 nm)/5 (50 nm): III: 4 (40 nm)/3 (30 nm)/5 (30 nm)/LiF (0.5 nm)/Al (100 nm). Table 2 summarizes the device characteristics. The bipolar transport properties and suitable frontier orbital energies of 3 allowed us to realize a blue single-layer device.

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**Table 1. Physical Properties of Spirobifluorene Derivatives 3–5**

<table>
<thead>
<tr>
<th>compd</th>
<th>$T_g$ (°C)</th>
<th>$T_d$ (°C)</th>
<th>$E_{1/2}^{\text{OX}}$ (V)$^a$</th>
<th>$E_{1/2}^{\text{REV}}$ (V)$^a$</th>
<th>HOMO (eV)$^b$</th>
<th>LUMO (eV)</th>
<th>$\Delta E_g$ (eV)</th>
<th>Abs $\lambda_{\text{max}}$ (nm) solution/film</th>
<th>PL $\lambda_{\text{max}}$ (nm) solution/film</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>165</td>
<td>477</td>
<td>0.90, 0.97</td>
<td>$-1.96,-2.17$</td>
<td>$-5.46$</td>
<td>$-2.60$</td>
<td>2.86</td>
<td>307, 386/310, 381</td>
<td>445/460</td>
</tr>
<tr>
<td>4</td>
<td>115</td>
<td>370</td>
<td>0.87, 0.94</td>
<td>$-2.43$</td>
<td>$-5.73$</td>
<td>$-2.43$</td>
<td>3.30</td>
<td>331/331</td>
<td>383/392</td>
</tr>
<tr>
<td>5</td>
<td>154</td>
<td>393</td>
<td>$-$</td>
<td>$-2.13$</td>
<td>$-5.73$</td>
<td>$-2.43$</td>
<td>3.30</td>
<td>331/331</td>
<td>383/392</td>
</tr>
</tbody>
</table>

$^a$ Deduced by differential pulse voltammetry. $^b$ See the text.

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**Figure 1.** UV–vis absorption spectra (dotted lines) and photoluminescence spectra (solid lines) of 3–5 in solid films.

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**Figure 2.** Mobilities of 3–5 vs $E^{1/2}$ (the solid lines are fits to the Poole–Frenkel form).
The EL spectrum of device I is identical to the thin-film PL emission spectrum of 3, with Commission International d’Eclairage (CIE) coordinates of 0.15 and 0.14. This single-layer device exhibits a turn-on potential of 4 V and a maximum brightness of 2800 cd/m² at 830 mA/cm² (19 V) and maximum quantum and power efficiencies of up to 0.53% (0.61 cd/A) and 0.14 lm/W, respectively. Nevertheless, the single-layer device still suffered from imbalanced charge recombination and a possible quenching effect by the cathode, which is a problem encountered frequently in OLED devices. In an attempt to mitigate the cathode quenching effect and improve electron transport into the emitter, in device II we inserted 5 between the 3 layer and the cathode. Both the brightness and EL efficiency were enhanced substantially relative to those of the single-layer device I (Table 2). This result indicates a more balanced electron–hole recombination, which agrees with our TOF observations; i.e., 5 had better electron-transporting capability than 3. Replacing 5 with TPBI, a widely used electron-transporting and hole-blocking layer, led to a lower device efficiency (1.3%, 0.7 lm/W). To further confine the emissive excitons in the 3 layer, we introduced 4 as a hole-transport layer to give the double-heterojunction device III. Figure 3 indicates that the current densities under the same potential decreased in the order III > II > I, suggesting that the double-heterostructure device enhanced the carrier injection and transport properties. Device III exhibited a rather low turn-on voltage of 2.5 V for a blue OLED, with pure emission from 3. This device achieved a high external quantum efficiency (1.57%, 1.9 cd/A), a power efficiency of 1.55 lm/W, and a maximum brightness of ca. 21,000 cd/m² at 13.5 V. Furthermore, the quantum efficiency remained fairly high at high current densities (1.35% at 100 mA/cm²; Figure S-5, Supporting Information).

In summary, we have synthesized and characterized an unprecedented blue-light emitting spiro-configured bipolar molecule (3), equipped with diphenylamino groups as electron donors and phenylbenzimidazole groups as electron acceptors. 3 exhibits a combination of the physical properties originating from its donor and acceptor groups. Its orthogonal molecular configuration is responsible for its high thermal and morphological stabilities. The bipolar character of 3 was evident from its reversible redox potentials, solvatochromic behavior in the excited state, and ambipolar carrier transport properties. These features allowed us to utilize 3 successfully in a single-layer device exhibiting blue-emission CIE coordinates of 0.15 and 0.14, a turn-on potential of 4 V, and a maximum brightness of 2800 cd/m² at 830 mA/cm² (19 V). Employing a double heterostructure of 4/3/5 to confine the excitons in the emissive layer led to a blue OLED device displaying higher performance: brightness reaching as high as 21,000 cd/m², efficiency of up to 1.9 cd/A, and a value of EQE of 1.57%.

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Supporting Information Available: Detailed experimental procedures, spectroscopic characterization of new compounds, cyclic voltammograms, solvent polarity dependent UV–vis and PL spectra, TOF photocurrent transients, and device characteristics. This material is available free of charge via the Internet at http://pubs.acs.org.

Table 2. EL Properties of Devices I–III

<table>
<thead>
<tr>
<th>Device</th>
<th>turn-on voltage (V)</th>
<th>Lₚₑₑₘₐₓ (cd/m²)</th>
<th>Jₚₑₑₘₐₓ (mA/cm²)</th>
<th>ηₑₓₚₑₑₘₐₓ (%)</th>
<th>ηₑₓₚₑₑₘₐₓ (lm/W)</th>
<th>CIE (x, y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>4</td>
<td>2800 (19 V)</td>
<td>830</td>
<td>0.52, 0.61</td>
<td>0.14</td>
<td>0.15, 0.14</td>
</tr>
<tr>
<td>II</td>
<td>3</td>
<td>10600 (17 V)</td>
<td>2500</td>
<td>1.50, 1.68</td>
<td>1.10</td>
<td>0.16, 0.13</td>
</tr>
<tr>
<td>III</td>
<td>2.5</td>
<td>21200 (13.5 V)</td>
<td>3500</td>
<td>1.57, 1.90</td>
<td>1.55</td>
<td>0.16, 0.14</td>
</tr>
</tbody>
</table>

Figure 3. Plots of brightness and current density vs voltage for devices I–III.