Introduction

Considerable progress has been made in organic light-emitting diodes (OLEDs) for full-color displays over the past few decades. Full-color displays require red, green and blue emission with relatively equal stability, efficiency and color purity. Although there are many emitting materials with good efficiency, long lifetime, high brightness and high color purity, the properties of blue OLEDs are relatively poor compared to that of red and green OLEDs. Recently, a range of efficient blue OLEDs using 9,9'-diethyl-2-diphenylaminofluorene derivatives as dopants were reported. In these blue OLEDs, concentration quenching due to excimer formation between the emitting materials reduces the EL performance of the resulting devices dramatically. Therefore, considerable effort has been made to develop blue materials with the bulky moieties to prevent excimer formation. On the other hand, the EL performance is unsuitable for practical applications.

In this paper, a series of blue fluorescent emitters (1-4) based on 9,9'-diethyl-2-diphenylaminofluorene were synthesized and their electroluminescent properties were investigated. In these materials, a styrene unit combined with the diphenylaminofluorene moiety was used to enhance the light-emitting efficiency by providing an extended conjugated structure. In addition, various end-capping groups, such as triphenylmethyl group (1), triphenylsilyl group (2), 2,5-dimethyl-4-phenyl benzene (3) and 3, 5-bis-(2-methylphenyl) group (4) were incorporated to examine the effect of the steric hindrance of the end capping groups to the EL performance. In particular, compared to compound 5 with a biphenyl end-capping group, emitting materials 1-4 have bulky end-capping groups. These groups would reduce the level of molecular aggregation between the emitters which induce the formation of excimer and concentration quenching. Compared to the device using compound 5, the devices using compounds 1-4 exhibited improved EL performance due to the suppressed molecular aggregation by the bulky end-capping groups.

Experimental

Synthesis and Characterization. All reactions were performed under a N₂ atmosphere. The solvents were dried carefully and distilled from the appropriate drying agents prior to use. Commercially available reagents were used without further purification unless stated otherwise. The (7-bromo-9,9-diethylfluoren-2-yl)diphenylamine (A), (7-(di-phenylamino)-9,9-diethylfluoren-2-yl)carbaldehyde (B), (7-(4-bromostyryl)-9,9-diethyl-N,N-diphenyl-9H-fluoren-2-amine (C), diethyl (7-(diphenylamino)-9,9-diethylfluoren-2-yl)methylphosphonate (D), 4-tritylbenzaldehyde (E), 4-triphenylsilylbenzaldehyde (F), p-terphenylphosphonate (I), 2,2'-diphenylamine-9,9-diethylfluoren-7-vinyl-p-terphenyl (J) were synthesized using the methodologies reported elsewhere. The compounds for the blue emitting materials (1-5) were synthesized according to Scheme 1.

General Procedure for the Horner-Wadsworth-Emmons Reaction. Diethyl (7-(diphenylamino)-9,9-diethylfluoren-2-yl)methylphosphonate (D), (270 mg, 0.50 mmol) and 4-tri-
tylenaldehyde (E) (175 mg, 0.50 mmol) in THF (10 mL) placed in an ice bath, followed by the addition of KO\textsubscript{Bu} (0.60 mL, 0.60 mmol) under N\textsubscript{2}. The reaction mixture was stirred for 30 min at 0 °C and 1 h at room temperature. The resulting mixture was quenched with water. The solution mixture was extracted twice with dichloromethane and washed twice with water. The combined organic layers were dried over MgSO\textsubscript{4} and the solvent was removed under reduced pressure to afford the crude product that was purified by column chromatography using silica-gel and recrystallization to give the desired compound.

9.9-Diethyl-N,N-diphenyl-7-(4-tritylstyryl)-9H-fluoren-2-amine (1): (Yield: 30%). \textsuperscript{1}H-NMR (CDCl\textsubscript{3}, 300 MHz): δ ppm 7.78-7.52 (t, J = 8.5 Hz, 3H), 7.47-7.39 (q, J = 19 Hz, 4H), 7.21 (m, 18H), 7.11 (m, 8H), 7.04-6.97 (q, J = 6.2 Hz, 4H), 2.03-1.83 (m, 3H), 0.40-0.35 (t, J = 5.2 Hz, 6H). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}): δ ppm 138.0, 137.9, 137.2, 136.1, 136.0, 134.2, 129.9, 129.3, 127.6, 127.3, 126.1, 125.6, 124.0, 123.8, 122.6, 120.7, 120.5, 119.5, 119.4, 56.1, 32.8, 8.7. FT-IR [ATR]: ν 3029, 2966, 1731, 1590, 1491, 1278, 750, 700. APCI-MS (m/z): 734 [M\textsuperscript{+}], HRMS [EI\textsuperscript{+}] calcd for C\textsubscript{51}H\textsubscript{41}N: 733.3709. Found: 733.3703.

9.9-Diethyl-N,N-diphenyl-7-(4-(triphenylsilyl)styryl)-9H-fluoren-2-amine (2): (Yield: 62%). \textsuperscript{1}H-NMR (CDCl\textsubscript{3}, 300 MHz): δ ppm 7.61-7.51 (m, 12H), 7.47-7.35 (m, 12H), 7.24-7.21 (d, J = 7.2 Hz, 4H), 7.16 (s, 1H), 7.13 (t, J = 8.2 Hz, 5H), 7.04-6.97 (m, 3H), 2.02-1.86 (m, 4H), 0.40-0.36 (t, J = 7.2 Hz, 6H). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}): δ ppm 150.6, 148.1, 138.9, 136.9, 136.5, 136.4, 134.4, 129.8, 129.9, 128.0, 126.0, 124.0, 123.8, 122.6, 120.8, 120.5, 119.4, 119.4, 56.17, 32.8, 8.7. FT-IR [ATR]: ν 3054, 1729, 1591, 1488, 1282, 1110, 749, 699. APCI-MS (m/z): 750 [M\textsuperscript{+}], HRMS [EI\textsuperscript{+}] calcd for C\textsubscript{55}H\textsubscript{45}N: 749.3478. Found: 749.3472.

7-(4-(2,5-Dimethylphenyl)silyl)styryl]-9H-fluoren-2-amine (3): (Yield: 81%). \textsuperscript{1}H-NMR (CDCl\textsubscript{3}, 300 MHz): δ ppm 7.60-7.54 (t, J = 9.1 Hz, 4H), 7.50-7.46 (d, J = 9.8 Hz, 2H), 7.42-7.34 (q, J = 8.7 Hz, 8H), 7.23-7.19 (m, 6H), 7.17-7.11 (t, J = 8.5 Hz, 6H), 7.05-6.97 (q, J = 7.2 Hz, 3H), 2.32-2.27 (d, J = 11.45 Hz, 6H), 2.04-1.86 (m, 4H), 2.02-1.86 (m, 3H). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}): δ ppm 151.7, 150.6, 148.1, 147.4, 141.8, 141.3, 136.3, 135.7, 132.8, 132.8, 132.8, 132.8, 132.9, 128.3, 127.4, 126.9, 126.9, 126.0, 124.0, 123.8, 122.6, 120.7, 120.5, 119.5, 119.4, 56.2, 32.9, 20.1, 20.0, 8.8. FT-IR [ATR]: ν 3004, 2804, 1705, 1533, 1380, 898, 734. APCI-MS (m/z): 672 [M\textsuperscript{+}]. HRMS [EI\textsuperscript{+}] calcd for C\textsubscript{48}H\textsubscript{35}N: 671.3552. Found: 671.3546.

Results and Discussion

Scheme 1 shows the synthetic route of the designed blue fluorescent materials 1-5. The compounds were synthesized by Suzuki cross-coupling and Horner-Wadsworth-Emmons reaction. The Horner-Wadsworth-Emmons reaction between (7-bromo-9,9-diethylfluoren-2-yl)diphenylamine (A) or p-terphenylphosphonate (I) and the corresponding aldehyde afforded the blue emitting materials (1, 2, 4, 5) in moderate yield.\textsuperscript{4} Compound 3 was synthesized by a Suzuki cross-coupling reaction.\textsuperscript{10}

Figure 1 presents the UV-vis absorption and photoluminescence spectra of the blue materials 1-5 in CH\textsubscript{2}Cl\textsubscript{2}. The maximum absorption peaks of compounds 1-5 were 385, 387, 386, 384, and 391 nm, respectively. Figure 1 shows the UV-vis absorption of compounds 1-5 overlapped well with the PL spectrum of a common blue host MADN. The superior matched spectral overlap between the emission of the host and the absorption of dopants 1-5 was enhanced in the order 4 < 1 < 3 < 2 < 5. This means that energy transfer between MADN and the materials is efficient and MADN serves as a host in OLED devices using...
these materials as dopants. In the PL spectra in solution, the maximum emission peaks of compounds 1-5 were 468, 484, 476, 471 and 492 nm, respectively. Compared to compound 5, the emission spectra of compounds 1-4 showed blue shifts due to the shortened $\pi$-conjugation by the distorted structure in the end-capping groups. In particular, compound 3 had a shorter wavelength (476 nm) than compound 5 (492 nm), which may be caused by the dihedral angle between the phenyl groups in compound 3 being more distorted due to the steric effect by the 2,5-dimethyl groups compared to that in compound 5, resulting in a wide band gap. Table 1 summarizes the photophysical properties of compounds 1-5.

**Scheme 1.** Synthetic routes of blue fluorescent materials 1-5. Condition: (a) $n$-BuLi, DMF, THF, −78 °C to 0, 1 h. (b) KO'Bu, THF, 0 °C to room temperature, 1 h. (c) Pd(PPh$_3$)$_4$, K$_2$CO$_3$ (2 M), Aliquat336, Toluene, reflux, 5 h.

**Figure 1.** The UV-vis absorption spectra (a) and PL spectra (b) of compounds 1-5 in dichloromethane ($10^{-5}$ M).
Interestingly, compounds 1-4 all showed a maximum emission wavelength that was blue-shifted (3-30 nm) in the film compared to the solution. The emission quantum yield of these materials was high (Φ = 0.83-0.95), suggesting that these materials have highly efficient electroluminescent properties in OLED devices.

The HOMO/LUMO energy levels of compounds 1-5 in Table 1 are −5.70/−2.78, −5.68/−2.80, −5.73/−2.77, and −5.67/−2.77 eV, respectively. The band gap of the blue materials (1-5) ranged from 2.84 to 2.93 eV, which was narrower than the 3.0 eV of the host material MADN. Figure 2 shows the HOMO and LUMO energy levels of the blue fluorescent materials (1-5), along with the other materials used in the electroluminescent devices, including ITO (Indium Tin Oxide), DNTPD (4,4′-bis(N-(4-(N,N-di-m-tolylamino)phenyl)-N-phenylamino)biphenyl), NPB (4′-bis(N-(1-naphthyl)-N-phenylamino)biphenyl), MADN, Alq3 (tris(8-quinolinolato) aluminum), and LiF: Al. NPB was employed as a hole-transporting layer (HTL) to provide hole injection and transport with DNTPD, whereas the MADN also functioned as a host in the emitting layer (EML) and Alq3 as the electron-transporting layer (ETL).

Table 2 lists the electroluminescent properties of the devices using compounds 1-5 as dopants. Figure 3 shows the EL emission spectra of the OLEDs obtained from MADN and 2% of compounds 1-5 as the emitting layer. All devices exhibited blue emission with the maximum emission wavelength ranging from 448 to 456 nm. The CIE coordinates of devices 1-5 were (0.152, 0.135), (0.151, 0.159), (0.152, 0.139), (0.153, 0.140), and (0.155, 0.165) at 8 V, respectively. Compared to device 5 using compound 5 as a dopant, devices 1-4 using compounds 1-4 as dopants showed improved CIE coordinates due to the shortened π-conjugation in the end-capping groups of compounds 1-4. In particular, devices 1 and 3 using dopants 1 and 3, respectively, exhibited deep blue emission with CIE y values < 0.14. Figure 5(a) and 5(b) present the current density-voltage (J-V) and luminance-voltage (L-V) characteristics of the five devices, respectively. The maximum brightness of these blue OLEDs varied from 6270 cd/m² in device 5 to as high as 8630 cd/m² in device 3.

Figure 5 shows the current density-luminous efficiencies (LE) and power efficiencies (PE) of devices 1-5. All devices showed efficient blue emission. The luminous efficiency of devices 1-5 were 5.86, 8.10, 6.31, 6.18 and 5.85 cd/A at 20 mA/cm², respectively. The power efficiency of devices 1-5

### Table 1: Optical properties of the dopants 1-5

<table>
<thead>
<tr>
<th>Compound</th>
<th>UVλ_{max}{a} [nm]</th>
<th>PLλ_{max}{b} [nm]</th>
<th>FWHM [nm]</th>
<th>HOMO [eV]{c}</th>
<th>LUMO [eV]{c}</th>
<th>E&lt;sub&gt;g&lt;/sub&gt;</th>
<th>Φ{d}</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>385</td>
<td>468/460</td>
<td>70</td>
<td>5.70</td>
<td>2.78</td>
<td>2.92</td>
<td>0.91</td>
</tr>
<tr>
<td>2</td>
<td>387</td>
<td>484/468</td>
<td>76</td>
<td>5.68</td>
<td>2.80</td>
<td>2.88</td>
<td>0.85</td>
</tr>
<tr>
<td>3</td>
<td>386</td>
<td>476/467</td>
<td>74</td>
<td>5.67</td>
<td>2.77</td>
<td>2.90</td>
<td>0.83</td>
</tr>
<tr>
<td>4</td>
<td>384</td>
<td>471/464</td>
<td>71</td>
<td>5.73</td>
<td>2.80</td>
<td>2.93</td>
<td>0.95</td>
</tr>
<tr>
<td>5</td>
<td>391</td>
<td>492/475</td>
<td>78</td>
<td>5.48</td>
<td>2.64</td>
<td>2.84</td>
<td>0.73</td>
</tr>
</tbody>
</table>

{a} Maximum absorption and emission wavelength, measured in CH<sub>2</sub>Cl<sub>2</sub> solution (10<sup>−5</sup> M).

{b} Thin solid film.

{c} Obtained from AC-2 and UV-vis absorption measurements.

{d} Using BDAVBi as a standard; λ<sub>ex</sub> = 360 nm (Φ = 0.86 in CH<sub>2</sub>Cl<sub>2</sub>).

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**Figure 2.** Energy-level diagrams of OLEDs.

**Figure 3.** EL spectra of blue emitting devices 1-5.
were 2.45, 3.36, 2.62, 2.58 and 2.44 lm/W at 20 mA/cm$^2$.

In particular, compared to device 5, devices 1-4 showed improved luminous efficiency. In devices 1-4, the bulky end-capping groups of the dopants in the emitting layers provide the steric hindrance that prevents intermolecular interactions and reduces self-quenching, leading to enhanced EL performance. In addition, the higher quantum yields of devices 1-4 ($\Phi=0.83-0.95$) than device 5 ($\Phi=0.73$) would partially contribute to the improved luminous efficiencies of devices 1-4 compared to device 5. Among devices 1-5, device 2
using dopant 2 with a bulky triphenylsilane moiety exhibited the highest luminous efficiency of 8.10 cd/A at 20 mA/cm² with minute efficiency roll-off within the current density investigated. Presumably, the steric and electronic effects of triphenylsilane end-capping group would contribute to the improved luminous efficiencies of device 2 (38%) as compared to the other devices.

Molecular simulations studies of compounds 1-5 using molecular mechanics (MM2) energy minimization were carried out to further explain the observed differences in electroluminescent properties of devices 1-5 at the molecular level of the dopant materials. Figure 6 shows the energy-minimized structures of compounds 1-5. The calculated dihedral angles between the phenyl rings at energy-minimized structures of compounds 3-5 increased in the order of 5 (33°) < 4 (47°) < 3 (54°). This suggests that intermolecular aggregation was suppressed in the order 5 < 4 < 3 due to steric hindrance. In addition, the bulky triphenylmethyl and triphenylsilyl groups of compounds 1 and 2 would provide large steric hindrance for molecular aggregation, as shown in energy-minimized structures of compounds 1 and 2 in Figure 6. The reduced molecular aggregation prevented the self-quenching between the emitting materials and enhanced the EL performances of the OLED devices.

Conclusions

9,9'-Diethyl-2-diphenylaminofluorene derivatives end-capped with the various bulky aromatic moiety were designed to improve the EL performances of blue OLEDs. Among those, the OLED using dopant 2 exhibited highly efficient blue emission. This device showed a maximum luminance, luminous efficiency, power efficiency and CIE coordinates of 8400 cd/m², 8.10 cd/A at 20 mA/cm², 3.36 lm/W at 20 mA/cm² and (x = 0.151, y = 0.159) at 8 V, respectively. In addition, the OLED using dopant 3 exhibited highly efficient deep blue emission with a maximum luminance, luminous efficiency and power efficiency of 8630 cd/m², 6.31 cd/A at 20 mA/cm² and 2.62 lm/W at 20 mA/cm², respectively. The peak wavelength of the electroluminescence was 448 nm with CIE coordinates of (0.152, 0.139) at 8 V.

Acknowledgments. This research was supported by Basic Science Research Program through the NRF funded by the Ministry of Education, Science and Technology (20100007370).

References and Notes