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Synthesis and characterization of arylamino end-capped silafluorenes for blue to deep-blue organic light-emitting diodes (OLEDs) †

Shao Fu Chen*a, Yuan Tianb, Jinghong Pengb, Huarong Zhanga, Xin Jiang Feng*a, Haixia Zhanga, Xinjun Xuab, Lidong Lib, Jianhua Gaob

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Diphenylamino- or cabazolyl-endcapped silafluorene derivatives which show a wide energy band gap, a high fluorescence quantum yield and high stability have been designed, synthesized, and characterized. Double-layer electroluminescent devices of these silafluorene derivatives exhibited efficient blue emission. The non-doped double-layer OLEDs containing TDMS, TDPS, CDMS, or CDPS exhibited better electroluminescence (EL) efficiencies than those of the devices using the reference emitter DPFL-NPB, among which the best device with TDPS showed a maximum current efficiency of 1.62 cd/A and an external quantum efficiency (EQE) of 1.36%. The solution processed device using TDPS as dopant exhibited high performance with an EQE of 2.48% and an obviously low turn-on voltage of 4 V, as compared to those of the reference device. The replacement of carbon atom of fluorene unit with silicon atom can lower the energy gap effectively and improve thermal stability as well as optical performances. The results indicate that the end-capped arylamino groups affect the OLED performances greatly and aryl or alkyl substitution on 9-position of silafluorene unit is also crucial to the OLED performances of this kind of silafluorenes.

Introduction

The development of materials and device engineering in organic light-emitting diodes (OLEDs) realized the practical applications in OLED displays and solid-state lightings [1-6]. However, blue-emitting materials and devices are still needed to be improved regarding to efficiency, lifetime and color purity as compared to those of green and red emitters and devices. Up to date, blue OLEDs with high external quantum efficiency (EQE) are still limited, because these materials require a high fluorescence yield, a wide energy band gap, a high thermal stability and good thin film morphology [7-12]. As a result, developing blue emitters for OLED applications still remains a challenge [13].

Fluorene derivatives are widely used as OLED materials over the past decades [14-25]. However, long wavelength emission, derived from excimer emission and/or the oxidation of the 9-position on fluorene ring, is a deadly disadvantage for this kind of materials to serve as blue emission materials in OLEDs [26, 27]. To overcome the disadvantages from the latter, silafluorene derivatives have been explored to replace the corresponding fluorene derivatives and exhibited promising properties [28-29]. Furthermore, introduction of arylamino groups, such as diphenylamino- or cabazolyl, are common methods for design of OLED materials [30-34].

The aim of the present work is to study the series of fluorescent arylamino end-capped silafluorene derivatives in which the photonic and electronic properties are systematically varied by chemical modification with different substituent groups on silicon atom and end-capped arylamino groups. To exploit them as emitters in OLEDs, sublimated double-layer devices using TDMS, TDPS, CDMS, and CDPS (Scheme 1) as emitting-layer were fabricated to evaluate their electroluminescent properties by comparison with a commercially available material, DPFL-NPB (9H-Fluorene-2,7-diamine, N,N-di-1-naphthalenyl-N,N,N,9,9,9-tetraphenyl-), among which the device with TDPS exhibits the best performances in the blue region with CIE coordinates of (0.175, 0.144). Further optimization by adding electron-transporting/hole-blocking in different layers, the solution processed devices exhibit enhanced EL performances. The best device with TDPS exhibited a maximum luminance of 550cd/m², an external quantum yield of 2.48%, a maximum luminous efficiency of 2.81cd/A and a low turn-on voltage of 4V.

Results and discussion

Synthesis

The molecular structures of the blue-emitting silafluorene derivatives and their synthetic routes are outlined in Scheme 1. Intermediate 4 was prepared from 2,5-dibromonitrobenzene according to the literature[35]. The target compounds were prepared by Palladium catalyzed Suzuki cross-coupling reaction of (4-(diphenylamino)phenyl)boronic acid, 7 or (4-(9H-carbazol-9-yl)phenyl)boronic acid, 8 with the corresponding silafluorene derivatives 5 and 6. The yields are 69%, 68%, 34%, and 45% for TDMS, TDPS, CDMS, and CDPS, respectively. All the
molecules were fully characterized by NMR spectroscopy, elemental analysis, and high-resolution mass spectrometry and found to be in good agreement with the structures.

Scheme 1 Synthesis of silafluorenes.

Photophysical, electrochemical, and thermal properties

The photophysical, electrochemical, and thermal properties of these silafluorenes are summarized in Table 1 and Table 2. Figure 1a, 1b, and 1c show the absorption and emission characteristics of these materials in toluene, chloroform, and DMF, respectively. All the derivatives show similar absorption spectral features, which are composed of two major absorption bands. The stronger absorption peaks span from 344-378 nm corresponding to the n→π* transition of the π-conjugated cores and the weaker absorption peaks appear around 300 nm due to the n→π* transition of arylamino moieties. In general, the carbazolyl end-capped derivatives exhibit blue-shifted spectra in both absorption and emission as compared with the diphenylamino substituted ones, because the carbazolyl is a weaker electron donor than the diphenylamino group and molecules end-capped with carbazolyl are of more coplanarity. Upon excitation at the absorption maximum, these silafluorene derivatives exhibit strong blue fluorescence with peaks ranging from 394 nm to 462 nm in solution and from 410 nm to 436 nm in thin film. Red-shifts of 14 nm to 21 nm are observed for the emission maxima in thin film compared to those in toluene, indicating the aggregation of molecules in the solid state. Solvatochromism effects are observed for these materials. For instance, the emission maxima of TDPS exhibit solvatochromic shift of 11 nm and 22 nm changing from toluene to chloroform and from chloroform to DMF, respectively, which indicates the intramolecular charge transfer (ICT) properties of these oligomers (see Figure 1d). The fluorescence quantum yields measured in solution are high in the range of 0.57-0.93, while the corresponding quantum yields for powder are 0.26, 0.22, 0.33, and 0.19 for TDMS, TDPS, CDMS, and CDPS, respectively (see Table 1), showing the potential for OLED applications of these materials.
Fig. 1 Absorption and emission of silafluorenes in toluene (a), chloroform (b), and DMF (c) and solvatochromic effect of TDMS (d).

Table 1 Photophysical properties of silafluorene derivatives

<table>
<thead>
<tr>
<th></th>
<th>λ_{abs}^{max} (nm)</th>
<th>λ_{em}^{max} (nm)</th>
<th>Φ_{PL}</th>
<th>λ_{abs}^{max} (nm)</th>
<th>λ_{em}^{max} (nm)</th>
<th>Φ_{PL}</th>
<th>λ_{abs}^{max} (nm)</th>
<th>λ_{em}^{max} (nm)</th>
<th>Φ_{PL}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>371</td>
<td>420</td>
<td>0.86*</td>
<td>371</td>
<td>431</td>
<td>0.74*</td>
<td>371</td>
<td>453</td>
<td>0.69*</td>
</tr>
<tr>
<td>Chloroform</td>
<td>376</td>
<td>426</td>
<td>0.76*</td>
<td>378</td>
<td>436</td>
<td>0.87*</td>
<td>378</td>
<td>462</td>
<td>0.58*</td>
</tr>
<tr>
<td>DMF</td>
<td>344</td>
<td>394</td>
<td>0.75*</td>
<td>345</td>
<td>397</td>
<td>0.76*</td>
<td>344</td>
<td>413</td>
<td>0.58*</td>
</tr>
<tr>
<td>Powder</td>
<td>345</td>
<td>396</td>
<td>0.72*</td>
<td>344</td>
<td>400</td>
<td>0.93*</td>
<td>344</td>
<td>418</td>
<td>0.57*</td>
</tr>
</tbody>
</table>

*excited at the absorption maxima

Table 2 Electrochemical and thermal properties of silafluorene derivatives

<table>
<thead>
<tr>
<th>E_{onset, red} (V)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>E_{a onset} (eV)</th>
<th>T_f (°C)</th>
<th>T_g (°C)</th>
<th>T_d (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TDMS</td>
<td>0.51</td>
<td>-5.22</td>
<td>-2.30</td>
<td>2.92</td>
<td>118</td>
<td>269</td>
</tr>
<tr>
<td>TDPS</td>
<td>0.48</td>
<td>-5.19</td>
<td>-2.34</td>
<td>2.85</td>
<td>-290</td>
<td>490</td>
</tr>
<tr>
<td>CDMS</td>
<td>0.94</td>
<td>-5.65</td>
<td>-2.39</td>
<td>3.26</td>
<td>-380</td>
<td>386</td>
</tr>
<tr>
<td>CDPS</td>
<td>0.89</td>
<td>-5.60</td>
<td>-2.42</td>
<td>3.18</td>
<td>142</td>
<td>383</td>
</tr>
</tbody>
</table>

E_{onset, red} vs Fe/Fc estimated by CV method using platinum disc electrode as a working electrode, platinum wire as a counter electrode, and Ag/AgNO_3 as a reference electrode in dichloromethane using Bu_4NPF_6 (0.1 M) as a supporting electrolyte and all the potentials were calibrated with ferrocene.

t calculated from CV measurements.

e_{a onset} = E_{LUMO} - E_{HOMO}.

e_{onset} estimated by absorption cutoff.

determined by differential scanning calorimeter from re-melt after cooling with a heating rate of 10 °C/min under N_2.

determined by thermal gravimetric analyser with a heating rate of 20 °C/min under N_2.

To probe the redox properties of these arylamino end-capped silafluorenes, cyclic voltammetry (CV) was performed in dichloromethane using Bu_4NPF_6 (0.1 M) as a supporting electrolyte. All the molecules exhibit a reversible one-electron oxidation waves corresponding to the sequential removal of an electron from the triarylimine with E_{onset} of 0.51 V, 0.48 V, 0.94 V, and 0.89 V for TDMS, TDPS, CDMS, and CDPS, respectively (Figure S1, ESI†). By using equation 1 [36], their HOMO energies from onset of first oxidation potentials were estimated as -5.22 eV, -5.19 eV, -5.65 eV, and -5.60 eV for TDMS, TDPS, CDMS, and CDPS, respectively, assuming that the absolute energy level of Fe/Fc redox couple to be 4.8 eV below vacuum. Ferrocene was used as an external standard (0.09 V vs Ag/Ag^+). The energy gaps, determined by absorption cutoff, were -2.92 eV, -2.85 eV, -3.26 eV and, -3.18 eV for TDMS, TDPS, CDMS, and CDPS, respectively. As a result, the LUMO of these molecules, calculated by E_g = HOMO-LUMO, are -2.30 eV, -2.34 eV, -2.39 eV, and -2.42 eV for TDMS, TDPS, CDMS, and CDPS, respectively (see Table 2). The E_g of TDMS has an obvious decrease as compared with that of the corresponding fluorene derivative reported, [37] which manifests that energy gap could be lowered by introduction of silicon atom into 9-position of fluorene unit. The molecular orbital data indicate that the energy gaps of carbazolyl substituted derivatives are obviously high than those of the diphenylamino substituted ones, which are largely derived from the decrease of the corresponding HOMO levels of the carbazolyl substituted derivatives, while the decreases of LUMO levels affect slightly on the increase of the energy gaps. Nevertheless, slight decreases of HOMO and...
LUMO levels still could be observed both in carbazolyl derivatives and diphenylamino derivatives when methyl groups were displaced by phenyl groups on 9-position of the silafluorene units.

\[
E_{\text{HOMO}} = -e(E_{\text{onset(ox,dye)}} - E_{\text{onset(Fc)}} + 4.8)
\]

(1)

Fig. 2 Frontier molecular orbital diagrams and MO values of TDMS, TDPS, CDMS, and CDPS.

DFT (B3LYP, 6-31G (d,p)) calculations for molecular orbitals (MO) of the molecules have been performed by using Gaussian09 package [38]. Figure 2 illustrates the frontier molecular orbitals (HOMO, HOMO–1, LUMO and LUMO+1) and the corresponding values. The HOMOs of all the studied compounds are delocalized on throughout the backbone and electron donating groups. The LUMOs are localized on the backbones of the molecules. While the HOMO–1 and the LUMO+1 are more localized and mainly focused on the donating groups and conjugation cores as compared with HOMO and LUMO, respectively. The charge distribution in unoccupied MO reveals the intramolecular charge transfer in these molecules. The substituents on the silicon atom have no participation in the formation of HOMO and LUMO, which is also consistent with the emission spectra in solution of the materials that diphenyl-substituted derivatives TDPS and CDPS show no obvious red-shift in the emission spectra compared with the dimethyl-substituted ones, TDMS and CDMS, respectively. The resulting energy gaps calculated from HOMO and LUMO are 3.51 eV, 3.46 eV, 3.68 eV, and 3.64 eV for TDMS, TDPS, CDMS, and CDPS, respectively. The theoretical calculation reveals similar trend of energy changes in HOMO, LUMO, and \(E_g\), as compared with those determined by CV and absorption cutoff, when changing the amino group at molecule terminals or substituents on 9-position of the silafluorene units.

The thermal properties of these silafluorenes were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measurements (see Table 2). These silafluorenes exhibit high thermal stabilities with decomposition temperatures (\(T_d\)) higher than 386 °C. In addition, they exhibit high glass transition temperature (\(T_g\)) (Table 2). The high \(T_d\) and \(T_g\) values of these materials suggest stable morphological properties, which is desirable for OLEDs with high thermal stability.

The strong blue emission, good thermal stability, and relatively large energy gap (\(E_g\)) of these silafluorene derivatives imply that these compounds can be employed as potential blue emitters in OLED devices.

Electroluminescence performance

To investigate the EL performance of these materials, non-doped double-layer electroluminescent devices (as shown in Scheme 2, device A) have been fabricated with configuration of ITO/EMI(50nm)/TPBi(20nm)/Ca/Al, where EML = TDMS, TDPS, CDMS, CPDS, and the reference material DPFL-NPB.

1,3,5-tris(4-N-phenylbenzimidazol-2-yl)benzene (TPBi) was used as a hole-blocking layer. Figure 3 depicts the normalized electroluminescence (EL) spectra of the non-doped double-layer OLEDs (Device A). The EL maxima peaked at 458nm and 464nm are in the deep-blue to blue range for the devices of TDMS and TDPS, respectively. The narrow full width half maximum (FWHM, 60nm and 66nm for TDMS and TDPS, respectively and CIE\(_x\),\(_y\) (Commission Internationale de l’Eclairage, (0.156, 0.100) for TDMS and (0.175, 0.144) for TDPS) of these two devices also indicate that devices with TDMS and TDPS exhibit better color purity than those of the devices with CDMS and CDPS. However, the EL spectra of devices using TDPS, CDMS and CDPS as EML became broad to some extent and exhibit long wavelength emission, which maybe derives from the excimer emission in these devices (Figure 3 and Table 3).

Scheme 2 Diagram of the device configurations.

Detailed EL performances of all devices are summarized in Table 3 and figure 4. First of all, double-layer devices with silafluorene emitters have significant better performances in luminance, current efficiency, power efficiency, and external quantum efficiency than those of the device with the reference material as EML. The efficiencies of the device using TDPS as EML are the best. The maximum luminance, current efficiency, power efficiency, and external quantum efficiency are 1.62cd/A, 0.38lm/W, 1792cd/m², and 1.36%, respectively. All these values are several times as high as those of the reference device. Meanwhile, the voltages at a current density of 20mA/cm² are comparable to that of the reference device, which could also be
Moreover, the absorption spectra of silafluorenes in chloroform, film and EL spectra of TDMS, TPMS, CDMS, and CPMS.

Table 3 Summary of EL device performance of silafluorene derivatives based on device A

<table>
<thead>
<tr>
<th>Device</th>
<th>$V_{on}$</th>
<th>$V_{20}$</th>
<th>$\eta_{p,20}$</th>
<th>$\eta_{max}$</th>
<th>$\eta_{p,20}$</th>
<th>$L_{20}$</th>
<th>$L_{max}$</th>
<th>$\text{EQE}^d$</th>
<th>$\lambda_{EL}$(fwhm)$^f$</th>
<th>CIE $(x,y)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TDMS</td>
<td>6.0</td>
<td>10.8</td>
<td>0.51</td>
<td>1.06</td>
<td>0.15</td>
<td>0.23</td>
<td>101</td>
<td>1760</td>
<td>1.19</td>
<td>458(60)</td>
</tr>
<tr>
<td>TDPS</td>
<td>7.4</td>
<td>14.4</td>
<td>1.61</td>
<td>1.62</td>
<td>0.35</td>
<td>0.38</td>
<td>328</td>
<td>1794</td>
<td>1.36</td>
<td>464(66)</td>
</tr>
<tr>
<td>CDMS</td>
<td>13.6</td>
<td>20.0</td>
<td>1.27</td>
<td>1.28</td>
<td>0.20</td>
<td>0.20</td>
<td>271</td>
<td>801</td>
<td>1.32</td>
<td>431(95)</td>
</tr>
<tr>
<td>CDPS</td>
<td>8.4</td>
<td>14.4</td>
<td>0.65</td>
<td>0.74</td>
<td>0.14</td>
<td>0.14</td>
<td>139</td>
<td>2151</td>
<td>0.39</td>
<td>441(166)</td>
</tr>
<tr>
<td>DPFL-NPB</td>
<td>5.2</td>
<td>13.2</td>
<td>0.59</td>
<td>0.59</td>
<td>0.14</td>
<td>0.15</td>
<td>116</td>
<td>375</td>
<td>0.41</td>
<td>465(78)</td>
</tr>
</tbody>
</table>

$^a$Turn on voltage when a brightness of 1 cd/m$^2$ observed.

$^b$Voltage taken at a current density of 20 mA/cm$^2$.

$^c$Current efficiency at a current density of 20 mA/cm$^2$.

$^d$Maximum current efficiency.

$^e$Power efficiency at a current density of 20 mA/cm$^2$.

$^f$Maximum power efficiency.

$^g$Luminance at a current density of 20 mA/cm$^2$.

$^h$Maximum Luminance.

$^i$External quantum efficiency at a current density of 20 mA/cm$^2$.

$^j$Full-width at half-maximum.

observed from the J-V-L curves depicted in Figure 4. Moreover, the good voltage-current density characteristics of the devices also indicates the good hole injection/transporting abilities of these materials. For example, the current densities of device with TDMS are obviously high than those of the reference device at the same voltage. As can be seen in the results, the diphenyl amino substituted derivatives exhibit superior device performances to the carbazolyl substituted ones, which is reasonable that the diphenyl amino substituted silafluorenes have lower $E_g$ and the HOMOs fit ITO better as compared with the carbazolyl substituted ones (Figure 5). On the other hand, replacement of dimethyl groups by diphenyl ones on the 9-position of silafluorene also improves device performances.

The absorption spectra of TDMS and TDPS overlap well with the emission spectrum of PVK (polyvinylcarbazole) around 380 nm, which makes the possibility of these materials to be used as dopants in OLEDs using PVK as host. Moreover, the diphenylamino end-capped silafluorenes exhibited superior properties in device performance to those of carbazolyl end-capped ones in efficiencies and spectra stabilities. To further explore the utilities of the molecules, doped double-layer and triple-layer electroluminescent devices (as shown in Scheme 2) have been fabricated with configuration of ITO/PEDOT:PSS(40nm)/PVK:X(80nm)/Ca/Al, ITO/PEDOT:PSS(40nm)/PVK:X(80nm)/SPPO13(30nm)/Ca/Al, ITO/PEDOT:PSS(40nm)/PVK:OXD-7:X(80nm)/SPPO13(30nm)/Ca/Al, where X = TDMS, TDPS, or DPFL-NPB.
Fig. 4 Current-voltage-brightness, luminance-current density, external quantum efficiency-current density, and power efficiency-current density curves of TDMS, TDPS, CDMS, CDPS and DPFL-NPB.

Fig. 5 Energy levels of emitters and the transporting-layer materials in device A.

Fig. 6 EL spectra of device C with TDMS, TDPS, or DPFL-NPB as dopants.

Table 4 Summary of EL device performance of silafluorene derivatives based on device C

<table>
<thead>
<tr>
<th>Device</th>
<th>( V_{on} ) (^a) (V)</th>
<th>( V_{20} ) (^b) (V)</th>
<th>( \eta_{L,20} ) (^c) (cd/A)</th>
<th>( \eta_{L,max} ) (^d) (cd/A)</th>
<th>( \eta_{P,20} ) (^e) (lm/W)</th>
<th>( \eta_{P,max} ) (^f) (lm/W)</th>
<th>( L_{20} ) (^g) (cd/m(^2))</th>
<th>( L_{max} ) (^h) (cd/m(^2))</th>
<th>( EQE ) (^i) (%)</th>
<th>( \lambda_{EL\text{, fwhm}} ) (^j) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TDMS</td>
<td>8.0</td>
<td>14.4</td>
<td>1.23</td>
<td>1.28</td>
<td>0.68</td>
<td>0.68</td>
<td>256</td>
<td>1050</td>
<td>1.95</td>
<td>434(54)</td>
</tr>
<tr>
<td>TDPS</td>
<td>8.8</td>
<td>16.0</td>
<td>1.65</td>
<td>1.71</td>
<td>0.91</td>
<td>0.91</td>
<td>352</td>
<td>1674</td>
<td>2.12</td>
<td>454(61)</td>
</tr>
<tr>
<td>DPFL-NPB</td>
<td>7.6</td>
<td>13.6</td>
<td>1.19</td>
<td>1.22</td>
<td>0.34</td>
<td>0.34</td>
<td>239</td>
<td>1343</td>
<td>1.31</td>
<td>447(59)</td>
</tr>
</tbody>
</table>

\(^a\)Turn on voltage when a brightness of 1 cd/m\(^2\) observed. \(^b\)Voltage taken at a current density of 20 mA/cm\(^2\). \(^c\)Current efficiency at a current density of 20 mA/cm\(^2\). \(^d\)Maximum current efficiency. \(^e\)Power efficiency at a current density of 20 mA/cm\(^2\). \(^f\)Maximum power efficiency. \(^g\)Luminance at a current density of 20 mA/cm\(^2\). \(^h\)Maximum Luminance. \(^i\)External quantum efficiency at a current density of 20 mA/cm\(^2\). \(^j\)Full-width at half-maximum.
PVK was used as host, while TDMS, TDPS, and DPFL-NPB were used as dopants. SPP013 (2,7-bis(diphenylphosphoryl)-9,9-bispirobifluorene) was used as electron-transporting/hole-blocking material and OXD-7 (1,3-bis(2-(4-tert-butylphenyl)-1,3,4-oxadiazol-5-yl)benzene) was blended into the host matrix to facilitate the electron transport. Poly (3,4-ethylene dioxythiophene) : poly(styrenesulfonate) (PEDOT:PSS) was used as hole-injection layer. EL performances of device B indicated that the efficiencies of device with TDPS increase with the increase of TDPS percentage in the emitting-layer (EML) and the efficiencies are comparable to those of the reference material DPFL-NPB when a 100:20 ratio of PVK:TDPS is used (Table S1 and Figure S2, ESI†). However, the efficiencies of devices with TDMS are obviously lower than those of the references. Based on device B at the 100:20 ratio of host to dopant, an electron-transporting/hole-blocking layer of SPP013 was introduced into device C, the efficiencies of both devices with TDPS and TDMS exhibited significant improvement as compared to those in device B and there was no long wavelength emission observed in the spectra with narrow FWHMs, which may derive from the improvement of charge balance in device C (Figure 6 and table 4). Detailed EL performances of all devices are summarized in Table 4 and Figure 7. Amongst the three devices, device with TDPS as dopant showed the best EL efficiencies with a maximum luminance of 1674 cd/m², an external quantum yield of 2.12%, and a maximum luminous efficiency of 1.71 cd/A, despite of a slightly high turn-on voltage compared with devices using TDMS and DPFL-NPB. To further improve the charge balance and exciton confinement of the device, OXD-7 was blended into the host matrix in the ratio of PVK:OXD-7:X = 3:2:1 and the EL efficiencies of both devices with TDMS and TDPS were enhanced obviously (Table S2, Figure S3, and Figure S4, ESI†). The best device with TDPS exhibited a maximum luminance of 5501 cd/m², an external quantum yield of 2.48%, a maximum luminous efficiency of 2.81 cd/A, and a low turn-on voltage of 4V. However, all the spectra showed larger FWHMs as compared to those in the device C. All these results indicate that EL properties of these molecules could be modified by the 9-position substituents and the end-capped arylamino moieties and that these materials could be served as blue emitters.

Conclusions
In summary, a new homologous series of diphenylamino or carbazolyl end-capped silafluorenes for efficient blue-light emission of non-doped and doped double-layer EL devices have been synthesized and investigated. This class of materials show better promising OLED efficiencies than the commercially used reference DPFL-NPB in the non-doped double-layer devices. The device of ITO/TDPS (50nm)/TPBi(20nm)/Ca/Al gives the best performances in this series and exhibits a maximum current efficiency of 1.61 cd/A, a maximum brightness of 1794 cd/m², and an external quantum efficiency (EQE) of 1.36% with CIE coordinates of (0.175, 0.144) in deep to deep-blue region. The EL performances of the doped multi-layer devices with both TDMS and TDPS could be improved significantly by adding an electron-transporting/hole-blocking layer. In the device of ITO/PEDOT:PSS(40nm)/PVK:TDPS(80nm)/SPP013(30nm)/Ca/Al, TDPS shows promising properties as doping material with...
superior efficiencies to those of the commercially used material DPFL-NPB. Moreover, the devices using TDPS show better performances than those with the other materials in general.

Further improvement could be achieved by adding the electron-transporting materials in the doped emitting-layer for charge balance and excitation confinement. These results indicate that the silafluorene end-capped with diphenylamino group show better electroluminescent efficiencies and stabilities and that introduction of diphenyl groups on 9-position could improve the material properties in OLEDs. Our findings show that these silafluorene derivatives could serve as efficient blue emitters for OLED applications and the properties of the derivatives could be tailored by changing the end-capped groups or the 9-position substituents in the silafluorene unit.

Experimental

Measurements

$^1$H and $^{13}$C NMR spectra were recorded on a Bruker AM 400 spectrometer. Mass spectrometric measurements were recorded by a HP5989 mass spectrometer. UV-vis spectra were obtained on a Varian Cary 200 spectrophotometer. Fluorescence spectra were obtained on a Perkin-Elmer LS55 luminescence spectrometer. The differential scanning calorimetry (DSC) analysis was performed under a nitrogen atmosphere on a TA Instruments DSC 2920. Thermogravimetric analysis was undertaken using a TGA instrument (PE-TGA6). To measure the fluorescence quantum yields ($\Phi_F$), degassed solutions of the compounds in different solvents were prepared and quinine sulfate monohydrate ($\Phi_H^\text{quinine} = 0.58$ or $\Phi_H^\text{quinine} = 0.48$) was used as a standard [39-40], while the absolute quantum yields $\Phi_F$ of the dyes in powder were measured by Edinburgh Photonics FLS920 fluorescence spectrometer. Fluorescence quantum yields in solution were calculated by equation 2 [41-42], where $\Phi_F$, $I_X$, $A_X$, and $n_X$ are quantum yield, fluorescence intensity, absorbance and refractive index of the measured solution and $\Phi_S$, $I_S$, $A_S$, and $n_S$ are the corresponding ones for the standard. Solution concentration was adjusted so that the absorbance of the solution would be lower than 0.1. Cyclic voltammetric (CV) measurements were carried out in a conventional three-electrode cell, using a Pt button working electrode 2 mm in diameter, a platinum wire counter electrode, and a Ag/AgNO$_3$ reference electrode on a computer-controlled EG&G Potentiostat/Galanostat model 283 at room temperature. Reduction CV of all compounds was performed in dichloromethane containing Bu$_4$NPF$_6$ (0.1 M) as the supporting electrolyte.

$$\Phi_F = \left( \frac{I_S}{I_F} \times \frac{A_S}{A_F} \times \left( \frac{n_F}{n_S} \right)^2 \right)$$

Device fabrication

The ITO-coated glass substrates were cleaned by detergent, ultrasound in distilled water, acetone and alcohol sequentially and then treated with ultraviolet-ozone (UVO). For device A, the emitting layer and hole injection/transporting layer were fabricated onto the pretreated ITO glass in sequence under vacuum. For device B, C and D, a layer of 40 nm PEDOT:PSS was spin-coated onto the pretreated ITO substrates, annealed at 150 °C for 15 min, and then followed by an 80 nm emitting layer, annealed at 120 °C for 10 min in a nitrogen filled glove box ($\text{H}_2\text{O} < 0.1 \text{ ppm}$, $\text{O}_2 < 0.1 \text{ ppm}$). For device C and D, SPPO13 was spin-coated after the emitting-layer and annealed at 80 °C for 20 min in a nitrogen filled glove box. Finally, Ca (10 nm)/Al (80 nm) was deposited onto the electron-transporting layer as a cathode by thermal evaporation under a vacuum of $3 \times 10^{-5}$ Torr. The current density–luminance–voltage $(J-L-V)$ and luminous efficiency–current density $(\eta-J)$ characteristics were measured using a Keithley 2612B source-measurement unit and a silicon photodiode that is calibrated by a PR-655 SpectraScan spectrophotometer. Electroluminescent (EL) spectra were recorded on a Maya 2000Pro spectrophotometer (Ocean Optics). CIE coordinates were calculated from the EL spectra.

Acknowledgments

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Notes and references

Silafuorene derivatives are designed for blue OLEDs and tunable efficiencies are investigated by end-capped arylamino groups and substituent groups on silicon atom.

Graphic: