

## 2-Triphenylsilyl-9,10-di-1-naphthalenylantracene and its Application for Blue Organic Light Emitting Diodes

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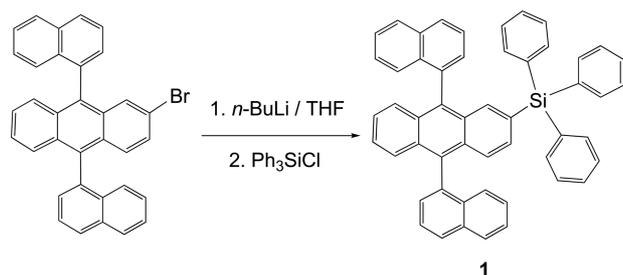
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The red, green, and blue emitters with relatively equal stability, efficiency, and color purity are needed to achieve full-color displays for organic light emitting diode (OLED).<sup>1,2</sup> Compared with red and green emitters,<sup>3,4</sup> further improvement of blue-emitting OLED materials is still required.<sup>5</sup> Generally, it is very difficult to develop new blue-emitting materials with excellent electroluminescence property because of their intrinsic wide band gap. Several blue-emitting OLED materials with high brightness and good stability such as distyrylarylene<sup>6</sup> and anthracene derivatives<sup>7-17</sup> have been developed. In spite of their excellent electronic and optical properties, these organic  $\pi$ -conjugated materials have some problems about device failure and thermal stability. Recently, new silicon-cored anthracene derivatives were reported in the literature to overcome such problems and to improve thermal properties.<sup>18</sup> In this regard, we designed a new blue-emitting anthracene derivative having silicon-substituent such as 2-triphenylsilyl-9,10-di-1-naphthalenylantracene (**1**) to combine two concepts from anthracene derivative with excellent electronic/optical properties and silicon-cored system with improved thermal stability. The introduction of the bulky triphenylsilyl group in 2 position of anthracene and naphthalenyl groups in 9, 10 positions of anthracene may prevent the aggregation of planar anthracenes as well as increase the chemical stability, the thermal stability, and solubility, which results in a bright blue EL emission.

Scheme 1 illustrates the synthetic route for compound **1** via reaction of 2-bromo-9,10-di-1-naphthalenylantracene, which is prepared according to a published procedure,<sup>19</sup> with *n*-BuLi followed by chlorotriphenylsilane. Compound **1** was



Scheme 1. Synthesis of **1**.

obtained as air-stable colorless powder in the yield of 39%. The formation of **1** has been confirmed by <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy and high-resolution mass spectrometry. The thermal property of **1** was investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere. TGA curve showed that **1** exhibits excellent thermal stability with its 5% weight loss temperature ( $\Delta T_{5\%}$ ) at 351 °C, which is stable enough to endure the high temperature for the vacuum vapor deposition. Also, the morphological stability of **1** was monitored by DSC, which was performed from 0 to 450 °C at a heating rate of 10 °C/min and a glass transition temperature ( $T_g$ ) and melting temperature ( $T_m$ ) occurred at 254 °C and 332 °C, respectively. The results of the second scan were recorded to eliminate differences from the sample history. Despite relatively low molecular weight of **1**, its excellent thermal stability might be originated from both the steric protection of triphenylsilyl group and non-planarity of its molecular structure.

As shown in Figure 1, the optical properties of **1** were investigated by means of UV-Vis absorption and photoluminescence (PL) spectroscopy. **1** in dilute toluene solution exhibits the characteristic  $\pi$ - $\pi^*$  transition patterns of the isolated anthracene group ( $\lambda_{\max} = 364, 381, 400$  nm). The similar optical properties with **1** is observed for non-sub-

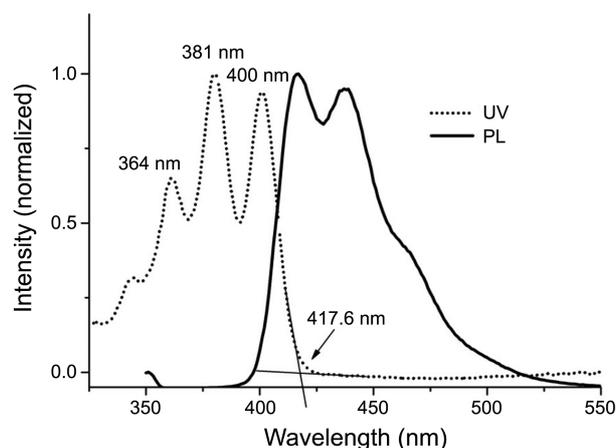
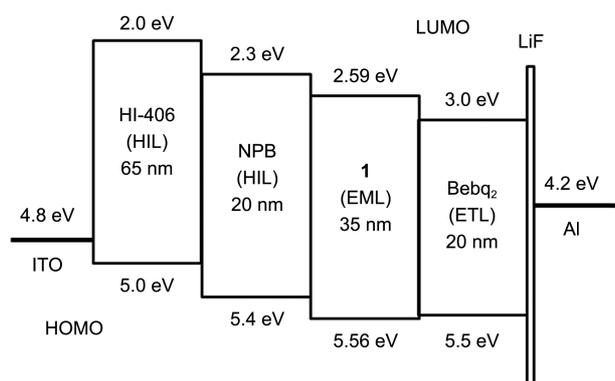


Figure 1. Normalized absorption and fluorescence spectra of **1** in dilute toluene solution.

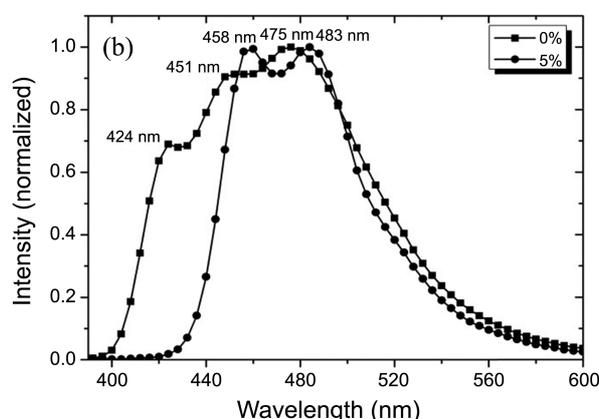
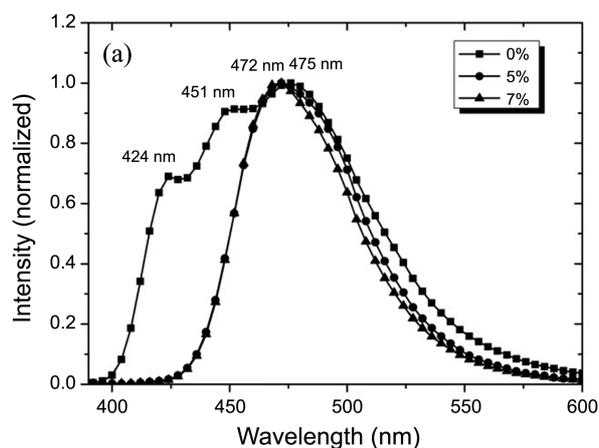


**Figure 2.** Energy diagrams of devices using **1** as a non-doped emitter.

stituted 9,10-di-1-naphthalenylanthracene.<sup>20</sup>

The energy level of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were estimated from the optical band gaps and oxidation onset potentials measured by UV-Vis absorption and cyclic voltammetry (CV).<sup>6-17</sup> HOMO energy level is correlated to ionization potential (IP,  $IP = E_{1/2}^{ox} + 4.8$  eV), and LUMO energy level was obtained by the subtraction of the optical band gap from the IP. From the half-wave oxidation potential ( $E_{1/2}^{ox}$ ) value of 0.76 eV in CV of compound **1**, the energy value of HOMO was calculated to be 5.56 eV ( $= 0.76 + 4.8$ ). According to the UV-Vis edge of the band gap energy ( $1240/417.6 = 2.97$  eV) and IP (5.56 eV), the energy value of LUMO was determined as 2.59 eV ( $= 5.56 - 2.97$ ). Because of the similar HOMO level of **1** and 4,4'-bis[*N*-(1-naphthyl)-*N*-phenylamino]biphenyl (NPB) (*ca.* 5.4 eV), we chose NPB as the hole transport layer (HTL) material.

To investigate the electroluminescence (EL) property of **1**, which was purified by vacuum sublimation before use as the emitting layer (EML), we initially fabricated non-doped blue-emitting device and then we made three different doped blue-emitting devices with BD-142 (5 wt % and 7 wt %) or BD-105 (5 wt %) dopants through successive vacuum deposition of the materials onto indium tin oxide (ITO) glass. Figure 2 shows structure of blue OLED which was fabricated in this study using non-doped **1**. The detailed EL devices have been constructed in the following configuration: ITO/HI-406 (65 nm)/NPB (20 nm)/**1** (35 nm, BD-



**Figure 3.** Normalized EL spectra of the devices at two different dopants such as BD-142 (top) and BD-105 (bottom).

142 (0 wt %, 5 wt %, 7 wt %) or BD-105 (0 wt %, 5 wt %)/Bebq<sub>2</sub> (20 nm)/LiF (1 nm)/Al device, where ITO is the anode; HI-406 (purchased from Idemitsu Kosan Co.) is the hole-injection layer (HIL); NPB is the HTL; the newly purified anthracene derivative **1** is EML; BD-142 (purchased from Idemitsu Kosan Co.) and BD-105 (purchased from Idemitsu Kosan Co.) are dopants; bis(10-hydroxy-benzo[*h*]-quinolinato)beryllium (Bebq<sub>2</sub>) is an electron transporting layer (ETL); a thin LiF serves as an electron injection layer at the Al cathode interface.

As shown in Figure 3, all devices emitted the expected blue light. Figure 3 shows the normalized EL spectra of the devices at different doping materials. EL emission maxima

**Table 1.** Performance of devices

Device architecture	Non-doped	5 wt % BD-142	7 wt % BD-142	5 wt % BD-105
Voltage (V) <sup>a</sup>	5.98	5.51	5.32	5.16
Max Luminance (cd/m <sup>2</sup> ) <sup>b</sup>	422	1322	1345	1326
Max E.Q.E (%) <sup>c</sup>	1.67	4.59	4.89	4.62
Max C.E. (cd/A) <sup>d</sup>	2.11	6.61	6.73	6.63
Max P.E. (lm/W) <sup>e</sup>	1.11	3.77	3.98	4.04
CIE (x, y) <sup>f</sup>	(0.154, 0.184)	(0.135, 0.220)	(0.134, 0.204)	(0.144, 0.213)

<sup>a</sup>Recorded at 20 mA/cm<sup>2</sup>. <sup>b</sup>maximum luminance. <sup>c</sup>maximum external quantum efficiency. <sup>d</sup>maximum luminous current efficiency. <sup>e</sup>maximum power efficiency. <sup>f</sup>Commission Internationale de L'Eclairage

of the device with no doping reagents show three peaks at 424, 451, and 475 nm. However, EL maxima of the device with BD-142 (5 wt % and 7 wt %) or BD-105 (5 wt %) dopants show one peak at 472 nm and two peaks at 458 and 483 nm, respectively. The detailed EL characteristics of the fabricated devices were summarized in Table 1.

The non-doped device exhibited a maximum external quantum efficiency of 1.67% (2.11 cd/A) at 20 mA/cm<sup>2</sup> with Commission Internationale de L'Eclairage (CIE) color coordinates located at (0.154, 0.184). For comparison and optimization purposes, three devices with 5 wt % BD-142, 7 wt % BD-142, and 5 wt % BD-105 dopants were used. Each doped blue-emitting devices showed a maximum external quantum efficiency of 4.59% (6.61 cd/A), 4.89% (6.73 cd/A), and 4.62% (6.63 cd/A) at 20 mA/cm<sup>2</sup>, respectively. The CIE color coordinates appeared at (0.135, 0.220) for 5 wt % BD-142, (0.134, 0.204) for 7 wt % BD-142, and (0.144, 0.213) for 5 wt % BD-105. This result indicates that **1** properly function as an blue emitting materials. But, the overall performance of doped devices showed the better than the non-doped device.

In summary, we have demonstrated that 2-triphenylsilyl-9,10-di-1-naphthalenylanthracene possessed high thermal stability that are suitable as a new emitting material candidate for blue organic light emitting device. The fabricated EL devices containing **1** with doping materials display higher device performances in terms of brightness and luminous and external quantum efficiencies than non-doped device.

### Experimental Section

**General Considerations.** All chemicals were purchased from Aldrich and were used as supplied unless otherwise indicated. 2-Bromo-9,10-di-1-naphthalenylanthracene was prepared according to a published procedure.<sup>19</sup> All reactions were carried out under a nitrogen atmosphere. Tetrahydrofuran (THF) was dried by distilling from sodium-potassium alloy/benzophenone ketyl under a nitrogen atmosphere and stored over the activated molecular sieves 3A.<sup>21</sup> Spectrophotometric-grade chloroform was used as received from Aldrich. CDCl<sub>3</sub> from Cambridge Isotope Laboratories was used after drying over activated molecular sieves (5 Å). <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} spectra were recorded at ambient temperature on a Bruker DPX-300 NMR spectrometer using standard parameters. The chemical shifts are referenced to the peaks of residual CDCl<sub>3</sub> (7.24, <sup>1</sup>H NMR; 77.0, <sup>13</sup>C NMR). HRMS was performed by maXis 4G (Hybrid LC/Q-TOF system). The thermal properties of compound were investigated by TA Instrument TGA2940 system and TA Instrument DSC2910 system under nitrogen atmosphere at a heating rate of 10 °C/min. UV-Vis and photoluminescent spectra were recorded on a Beckman PU 650 and a Jasco FP-750, respectively, in CHCl<sub>3</sub> solvent with a 1-cm quartz cuvette at ambient temperature. Cyclic voltammetry experiment was performed using an AUTOLAB/PGSTAT12 system. Electroluminescent spectra were measured at Dongjin Semichem Co. Ltd.

**Synthesis of Compound 1.** A solution of 2-bromo-9,10-di-1-naphthalenylanthracene<sup>19</sup> (3.61 g, 7.09 mmol) in 70 mL of THF was treated with 5.32 mL of *n*-BuLi (1.6 M solution in THF) at -78 °C. After stirring for 30 min, a solution of triphenylsilyl chloride (2.1 g, 7.09 mmol) in 20 mL of THF was slowly added to the reaction vessel. The reaction mixture was slowly allowed to warm to room temperature. The completeness of the reaction was checked by TLC. All volatiles were evaporated under vacuum, leaving a colorless solid. The desired product **1** was isolated as colorless powder after the recrystallization with MeOH (1.90 g, 38.9%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300.13 MHz) δ 8.07 (d, *J* = 8.2 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.68-7.65 (m, 2H), 7.56-7.44 (m, 7H), 7.41 (s, 1H), 7.32-7.29 (m, 8H), 7.24-7.20 (m, 3H), 7.16 (d, *J* = 7.3 Hz, 4H), 7.13 (d, *J* = 7.3 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.47 MHz) δ 138.03, 136.62, 136.04, 135.02, 133.75, 133.75, 133.70, 133.61, 133.45, 131.28, 131.04, 130.78, 130.70, 130.37, 129.93, 129.30, 129.09, 128.25, 128.20, 128.14, 127.99, 127.59, 127.33, 127.10, 126.71, 126.56, 126.25, 125.99, 125.86, 125.74, 125.57, 125.25, 125.14. HRMS Exact mass calculated for C<sub>52</sub>H<sub>36</sub>Si [M]<sup>+</sup>: 688.2586, found: 688.2577. DSC: *T*<sub>m</sub> = 332 °C, *T*<sub>g</sub> = 254 °C. TGA: Δ*T*<sub>5%</sub> = 351 °C.

**Cyclic Voltammetry.** Cyclic voltammetry measurements were carried out with a three-electrode cell configuration consisting of platinum working and counter electrodes and a Ag/AgNO<sub>3</sub> (0.1 M in acetonitrile) reference electrode at room temperature. The solvent was acetonitrile and 0.1 M tetrabutylammonium hexafluorophosphate was used as the supporting electrolyte. The oxidation potentials were recorded at a scan rate of 50 mV·s<sup>-1</sup> and reported with reference to the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple.

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