



## Orange phosphorescent organic light-emitting diodes using new spiro [benzoanthracene-fluorene]-type host materials

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### ABSTRACT

New spirobenzoanthracene-type orange phosphorescent host materials, 9-(spiro[benzoanthracene-7,9'-fluorene]-2'-yl)-9H-carbazole and 9-(spiro[benzoanthracene-7,9'-fluorene]-3-yl)-9H-carbazole, with stable efficiency roll-off, were prepared by an Ullmann coupling reaction of 2'-bromo-spiro[benzoanthracene-7,9'-fluorene] and 3-bromo-spiro[benzoanthracene-7,9'-fluorene] respectively, with carbazole. Orange phosphorescent organic light-emitting diodes with the configuration of indium tin oxide/*N,N'*-diphenyl-*N,N'*-bis-[4-(phenyl-*m*-tolylamino)-phenyl]-biphenyl-4,4'-diamine/*N,N'*-di(1-naphthyl)-*N,N'*-diphenylbenzidine/Host:Ir(pq)<sub>2</sub>acac/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline/tris(8-hydroxyquinoline)aluminum/LiF/Al were developed using spiro[benzoanthracene-fluorene]-type carbazole derivatives as a host material and Ir(pq)<sub>2</sub>acac as a dopant. A device obtained from 9-(spiro[benzoanthracene-7,9'-fluorene]-2'-yl)-9H-carbazole doped with 3% Ir(pq)<sub>2</sub>acac showed an orange color purity of (0.599, 0.373) and an efficiency of 14.74 cd/A at 6.0 V. The overall result is a device with an external quantum efficiency (EQE) >8.93% at high brightness but an operating voltage of <6.0 V.

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### 1. Introduction

Phosphorescent organic light-emitting diodes (PHOLEDs) have become increasingly important in recent years due to their higher triplet emission efficiency compared with fluorescent OLEDs. An increase in internal efficiency to as high as 100% can be theoretically achieved due to triplet emission, which is particularly important for practical applications in which the device is expected to operate at a low voltage and consume less power [1–5].

However, the quantum efficiency of a PHOLED is considerably reduced at high current density or luminance due to triplet-triplet annihilation [6], triplet-exciton quenching [7], and triplet-polaron quenching [7]. Triplet exciton quenching is caused by the long excited state lifetime of the triplet exciton. Several studies have attempted to minimize the decrease in efficiency at high current density [8–12]. Triplet exciton quenching in the emitting layer is reduced by broadening the recombination zone in the emitting layer [8]. The recombination zone can be controlled using a mixed host system with a broad recombination zone and shows little efficiency roll-off. The exciton density decreases in a mixed host

device due to the broad recombination zone, resulting in reduced probability of exciton quenching. However, the mixed host device is complicated. Therefore, development of a host material that can minimize the efficiency of roll-off is needed.

Carbazole derivatives are photoconductors with good hole transport properties [13–16]. The effectiveness of carbazole-based host materials for use in deep blue PHOLEDs due to the high triplet energy of the carbazole unit has recently been demonstrated [17,18]. Spirobifluorene and spirostilabifluorene derivatives have been used widely as new amorphous host and dopant materials, respectively, possessing high morphological stability [19–25]. Spirobifluorene, with a high glass transition temperature, shows excellent nondispersive hole transporting and ambipolar carrier transporting properties [26,27]. Asymmetrical spiro compounds possessing naphthalene groups not only preserve their inherent characteristics, such as morphological stability, high glass transition temperature, and amorphous properties, but also provide a variety of substituents on the aromatic ring, resulting in the formation of conjugation-controlled OLED host and dopant materials; therefore, spirobenzofluorenes have recently received a great deal of attention as fluorescent materials for OLEDs [28–39]. Spirobenzofluorene/carbazole hybrid material contains a carbazole unit with hole transport properties and a spirobenzofluorene unit with electron transport properties [36]. Therefore, the combination

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of carbazole and spirobenzoanthracene is effective to develop a host material with balanced hole and electron injection.

In this study, new carbazole-based spirobenzoanthracene host materials, 9-(spiro[benzoanthracene-7,9'-fluorene]-2'-yl)-9H-carbazole (**SBAF-2C**) and 9-(spiro[benzoanthracene-7,9'-fluorene]-3-yl)-9H-carbazole (**SBAF-3C**), were prepared by introducing the carbazole moiety at the 2'- and 3-positions on **SBAF**, and their use as orange phosphorescent host materials was evaluated. The device performances of the orange PHOLEDs with the **SBAF-2C** and **SBAF-3C** hosts were investigated based on the red dopant concentration.

## 2. Experimental

### 2.1. Chemicals and instruments

Tetrakis(triphenylphosphine)palladium(0), phenylboronic acid, 9-fluorenone, *n*-butyllithium, carbazole (95%), potassium carbonate (99%), copper powder (99%), dichloromethane, 1,8-diboromonaphthalene, and nitrobenzene (Aldrich Chem. Co., St. Louis, MO, USA) were used without further purification. Ammonia water (Duksan Chem. Co., Seoul, South Korea) was used as received. Tetrahydrofuran was distilled over sodium and calcium hydride.

Photoluminescence (PL) spectra were recorded on a fluorescence spectrophotometer (Jasco FP-6500) and UV-vis spectra were obtained by a UV-vis spectrophotometer (Shimadzu, UV-1601PC). A low-energy photo electron spectrometer (Hitachi High Tech, AC-2) was used to measure energy levels. Fourier transform-infrared (FT-IR) spectra were obtained with a Varian model 640-IR spectrophotometer, and elemental analyses were performed using a Thermo Fisher Flash 2000 elemental analyzer. Differential scanning calorimeter (DSC) measurements were performed on a Shimadzu DSC-60 instrument under nitrogen at a heating rate of 10°C/min. Thermo gravimetric measurements were performed on a Shimadzu TGA-50 analyzer at a heating rate of 10°C/min. Low and high resolution mass spectra were recorded using an HP 6890 and Agilent 5975C MSD in FAB mode.

### 2.2. Preparation of 2'-bromospiro[benzo[de]anthracene-7,9'-fluorene] (2'-bromo-**SBAF**)

1,8-Diboromonaphthalene (10.00 g, 34.95 mmol), phenylboronic acid (4.26 g, 34.95 mmol), tetrakis(triphenylphosphine)palladium(0) (1.7 g, 1.46 mmol), and THF (100 mL) were stirred in a two-necked flask for 30 min. A degassed H<sub>2</sub>O solution of potassium carbonate (3.26 g, 29.1 mmol) was added dropwise to the above solution over a period of 20 min. The resulting solution was heated under reflux overnight at 80°C. The reaction mixture was extracted with dichloromethane and water. Following evaporation of the organic layer with a rotary evaporator, the resulting powdery product was purified by column chromatography using *n*-hexane to give a white crystalline solid.

Yield 73%. Mp 153°C. FT-IR (KBr, cm<sup>-1</sup>) 3054 (aromatic C-H), 652 (aromatic C-Br). <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 7.85–7.83(d, 2H, Ar-CH-naphthalene), 7.76–7.75(d, 1H, Ar-CH-naphthalene), 7.48–7.45(t, 1H, Ar-CH-naphthalene), 7.42–7.40(d, 1H, Ar-CH-naphthalene), 7.38–7.35(m, 3H, Ar-CH-benzene), 7.33–7.31(m, 2H, Ar-CH-benzene), 7.26–7.23(t, 1H, Ar-CH-benzene). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 143.0, 140.5, 136.2, 133.9, 131.3, 130.4, 129.8, 129.0, 129.0, 128.4, 127.5, 127.1, 126.2, 125.4, 120.3, 77.4, 77.2, 76.9, 59.9. Anal. Calcd for C<sub>29</sub>H<sub>17</sub>Br (Mw, 445.35): C, 78.21;H, 3.85;Br, 17.94. Found: C, 78.18; H, 3.82. MS (FAB) *m/z* 445.05 [(M + 1)<sup>+</sup>].

### 2.3. Preparation of spiro[benzo[de]anthracene-7,9'-fluorene] (**SBAF**)

A solution of 1-bromo-8-phenylnaphthalene (8.67 g, 30.6 mmol) in THF (50 mL) was added to a 250 mL two-necked flask. The reaction flask was cooled to -78 °C, and *n*-BuLi (2.5 M in *n*-hexane, 14.68 mL) was added slowly in a dropwise fashion. The solution was stirred at this temperature for 1 h, followed by adding a solution of 9-fluorenone (5.51 g, 30.6 mmol) in THF (30 mL) under an argon atmosphere. The resulting mixture was gradually warmed to ambient temperature and quenched by adding saturated aqueous NaHCO<sub>3</sub> (90 mL). The mixture was extracted with dichloromethane. The combined organic layers were dried over magnesium sulfate, filtered, and evaporated under reduced pressure. A yellow powdery product was obtained. The crude residue was placed in another two-necked flask (100 mL) and dissolved in acetic acid (50 mL). A catalytic amount of aqueous HCl (5 mol%, 12 N) was then added, and the whole solution was heated under reflux for 12 h. After cooling to ambient temperature, the compound was purified as a white powder by silica gel chromatography using dichloromethane/*n*-hexane (2/1).

Yield 87%. Mp 209°C. FT-IR (KBr, cm<sup>-1</sup>) 3056, 3033 (aromatic C-H). <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 8.27–8.26(d, 1H, Ar-CH-naphthalene), 8.22–8.20(d, 1H, Ar-CH-naphthalene), 7.84–7.82(m, 3H, Ar-CH-benzene), 7.68–7.67(d, 1H, Ar-CH-benzene), 7.64–7.61(t, 1H, Ar-CH-naphthalene), 7.37–7.33(t, 2H, Ar-CH-benzene), 7.30–7.26(t, 1H, Ar-CH-naphthalene), 7.20–7.17(t, 1H, Ar-CH-benzene), 7.14–7.11(t, 2H, Ar-CH-fluorene), 6.99–6.96(t, 3H, Ar-CH-benzene), 6.62–6.60(d, 1H, Ar-CH-fluorene), 6.53–6.51(d, 1H, Ar-CH-fluorene). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 156.9, 140.0, 139.0, 137.5, 134.0, 131.9, 130.1, 128.6, 128.3, 127.7, 127.7, 127.7, 126.7, 126.6, 126.3, 125.6, 125.2, 123.5, 120.2, 119.5, 77.4, 77.2, 76.9, 60.0. Anal. Calcd for C<sub>19</sub>H<sub>18</sub> (Mw, 366.14): C, 95.05;H, 4.95. Found: C, 95.01; H, 4.92. MS (FAB) *m/z* 367.14[(M + 1)<sup>+</sup>].

### 2.4. Preparation of 3-bromo spiro[benzo[de]anthracene-7,9'-fluorene]

**SBAF** (3.66 g, 10 mmol) was dissolved in carbon tetrachloride in a two-necked flask; bromine (2.36 g, 15 mmol) was then added slowly in a dropwise fashion over a period of 20 min. The mixture was stirred at room temperature for 3 days. The precipitated solid was filtered and dried *in vacuo* to give the crude product, which was purified by recrystallization from ethyl acetate/*n*-hexane (1/1) to give a white powder.

Yield 79%. Mp 256°C. FT-IR (KBr, cm<sup>-1</sup>) 3053, 3037(aromatic C-H), 748(aromatic C-Br). <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 8.17–8.16 (d, 1H, Ar-CH-naphthalene), 8.11–8.09 (d, 2H, Ar-CH-benzene), 7.94–7.92 (d, 1H, Ar-CH-fluorene), 7.84–7.82 (d, 2H, Ar-CH-benzene), 7.37–7.34 (t, 2H, Ar-CH-benzene), 7.31–7.26 (m, 2H, Ar-CH-benzene), 7.14–7.11 (t, 2H, Ar-CH-benzene) 7.01–6.98 (t, 1H, Ar-CH-fluorene), 6.94–6.93 (d, 2H, Ar-CH-benzene), 6.69–6.67 (d, 1H, Ar-CH-fluorene), 6.53–6.51 (d, 1H, Ar-CH-fluorene). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 156.5, 140.0, 138.9, 138.1, 132.4, 131.3, 130.5, 130.2, 128.9, 128.7, 128.6, 128.6, 127.9, 127.5, 126.2, 126.1, 125.5, 123.4, 122.8, 120.3, 120.0, 77.4, 77.2, 76.9, 66.5, 59.9. Anal. Calcd for C<sub>29</sub>H<sub>17</sub>Br (Mw, 445.35): C, 78.21;H, 3.85;Br, 17.94. Found: C, 78.16; H, 3.81. MS (FAB) *m/z* 445.05 [(M + 1)<sup>+</sup>].

### 2.5. Synthesis of 9-(spiro[benzo[de]anthracene-7,9'-fluorene]-2'-yl)-9H-carbazole (**SBAF-2C**)

A mixture of 2'-bromo-**SBAF** (5.00 g, 11.23 mmol), carbazole (2.00 g, 12.35 mmol), potassium carbonate (3.1 g, 22.45 mmol), and copper bronze (0.71 g, 11.23 mmol) in nitrobenzene (80 mL) was

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