Dyes and Pigments 94 (2012) 304-313

Contents lists available at SciVerse ScienceDirect

Dyes and Pigments



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

Ji-Young Kim<sup>a</sup>, Chil-Won Lee<sup>c</sup>, Jee Geun Jang<sup>b</sup>, Myoung-Seon Gong<sup>a,\*</sup>

<sup>a</sup> Department of Nanobiomedical Science and WCU Research Center of Nanobiomedical Science, Dankook University, Chungnam 330-714, Republic of Korea

<sup>b</sup> Department of Electronics Engineering, Dankook University, Cheonan 330-714, Republic of Korea

<sup>c</sup> Department of Polymer Science and Engineering, Dankook University 126, Jukjeon-dong, Suji-gu, Yongin, Gyeonggi 448-701, Republic of Korea

#### ARTICLE INFO

Article history: Received 1 December 2011 Received in revised form 11 January 2012 Accepted 15 January 2012 Available online 27 January 2012

Keywords: PHOLED Spiro[benzoanthracene-fluorene] Carbazole Orange Host Phosphorescence

#### ABSTRACT

New spirobenzoanthrcene-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', 9-(spiro]-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.

© 2012 Elsevier Ltd. All rights reserved.

PIĞMĔNTS

### 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 spirosilabifluorene 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



<sup>\*</sup> Corresponding author. Tel.: +82 41 5501476; fax: +82 41 5503431. *E-mail address:* msgong@dankook.ac.kr (M.-S. Gong).

<sup>0143-7208/\$ –</sup> see front matter @ 2012 Elsevier Ltd. All rights reserved. doi:10.1016/j.dyepig.2012.01.009

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, 1,8diboromonaphthalene, 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>)  $\delta$  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-CHnaphthalene), 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>)  $\delta$  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>)  $\delta$  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), 7.30–7.26(t, 1H, Ar-CH-naphthalene), 7.20–7.17(t, 1H, Ar-CH-benzene), 6.62–6.60(d, 1H, Ar-CH-fluorene), 6.53–6.51(d, 1H, Ar-CH-fluorene), 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>)  $\delta$  156.9, 140.0, 139.0, 137.5, 134.0, 131.9, 130.1, 128.6, 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>)  $\delta$  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>)  $\delta$  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



Fig. 1. The device configuration and the chemical structure of the materials used in the devices.

heated under reflux with vigorous stirring under a nitrogen atmosphere for 18 h. After removing the solvent *in vacuo*, ammonia solution (80 mL) was added, and the mixture was left to stand for 2 h. Dichloromethane (150 mL) and distilled water (100 mL) were then added, and the organic layer was separated. After evaporation of the organic layer with a rotary evaporator, the resulting powdery product was purified by column chromatography using a mixture of dichloromethane/*n*-hexane (v/v, 1/3) as an eluent to give a white crystalline **SBAF-2C**.

Yield 72%. Mp 261°C. FT-IR (KBr, cm<sup>-1</sup>) 3052, 3037 (aromatic C-H), 1268 (aromatic C-N). <sup>1</sup>H-NMR (500 MHz,CDCl<sub>3</sub>)  $\delta$  8.88–8.87 (d, 1H, Ar-CH-naphthalene), 8.62–8.61 (d, 1H, Ar-CH-naphthalene), 8.05–8.04 (d, 2H, Ar-CH-naphthalene), 7.94–7.92 (d, 1H, Ar-CH-carbazole), 7.82–7.81 (d, 2H, Ar-CH-carbazole), 7.75–7.74 (t, 1H, Ar-CH-carbazole), 7.67–7.66 (d, 2H, Ar-CH-benzene), 7.60–7.58 (t, 1H, Ar-CH-fluorene), 7.37–7.34 (t, 2H, Ar-CH-fluorene), 7.34–7.33 (t, 1H, Ar-CH-fluorene), 7.33–7.32 (d, 1H, Ar-CH-carbazole), 7.28–7.22 (m, 1H, Ar-CH-naphthalene), 7.20–7.18 (m, 3H, Ar-CH-benzene), 7.18–7.14 (t, 2H, Ar-CH-benzene), 7.11–6.99 (s, 1H, Ar-CH-benzene), 6.87–6.84 (d, 2H, Ar-CH-benzene), 6.84–6.82 (d, 1H, Ar-CH-benzene), 6.84–6.82 (d, 2H, Ar-CH-benz

Ar-CH-carbazole). <sup>13</sup>C NMR (CDCl<sub>3</sub>) 152.0, 148.2, 147.5, 142.3, 142.1, 140.8, 136.4, 135.9, 134.3, 129.6, 129.4, 128.2, 128.1, 127.3, 126.4, 126.0, 125.9, 124.1, 124.0, 123.8, 123.5, 122.7, 122.2, 120.4, 120.4, 120.0, 109.9, 77.4, 77.2, 76.9, 60.1. Anal. Calcd for C<sub>41</sub>H<sub>25</sub>N (Mw, 531.64): C, 92.63; H, 4.74; N, 2.63. Found: C, 92.60; H, 4.69; N, 2.68. MS (FAB) m/z 532.6 [(M+1)<sup>+</sup>]. UV-vis (THF):  $\lambda_{max}$  (Absorption) = 345 nm,  $\lambda_{max}$  (Emission) = 395 nm.

# 2.6. Synthesis of 9-(spiro[benzo[de]anthracene-7,9'-fluorene]-3-yl)-9H-carbazole (**SBAF-3C**)

A mixture of 3-bromo-**SBAF** (6.00 g, 13.47 mmol), carbazole (2.47 g, 14.82 mmol), potassium carbonate (3.72 g, 26.95 mmol), and copper bronze (0.85 g, 13.47 mmol) in nitrobenzene (70 mL) was stirred and heated under reflux in a nitrogen atmosphere for 18 h. Following removal of the solvent *in vacuo*, ammonia solution (70 mL) was added, and the mixture was left to stand for 2 h. Dichloromethane (150 mL) and water (100 mL) were added, and the organic phase was separated. The organic solution was washed twice with water (100 mL). Following evaporation of the resulting

solution with a rotary evaporator, the resulting powdery product was purified by column chromatography using a mixture of dichloromethane/hexane (v/v, 1/3) as an eluent to give **SBAF-3C** as a white solid.

Yield 62%. Mp 371°C. FT-IR (KBr, cm<sup>-1</sup>) 3054, 3039 (aromatic C-H), 1268 (aromatic C-N), <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 9.02–9.00 (d. 1H, Ar-CH-benzene), 8.54–8.52 (d, 1H, Ar-CH-carbazole), 8.11–8.10 (d. 1H. Ar-CH-naphthalene). 8.10–8.09 (d. 1H. Ar-CH-carbazole). 7.78-7.77 (d, 1H, Ar-CH-benzene), 7.76-7.75 (d, 2H, Ar-CHcarbazole), 7.52-7.51 (t, 1H, Ar-CH-benzene), 7.37-7.36 (t, 1H, Ar-CH-carbazole), 7.35-7.34 (d, 3H, Ar-CH-benzene), 7.24-7.23 (t, 1H, Ar-CH-carbazole), 7.23-7.22 (t, 1H, Ar-CH-carbazole), 7.20-7.19 (m, 3H, Ar-CH-fluorene), 7.13-7.12 (d, 2H, Ar-CH-benzene), 7.12-7.11 (s, 1H, Ar-CH-fluorene), 6.96–6.87 (d, 1H, Ar-CH-benzene), 6.83–6.81 (m, 3H, Ar-CH-benzene), 6.84–6.82 (d, 1H, Ar-CH-carbazole), <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 150.2, 148.1, 147.5, 142.4, 142.3, 142.1, 137.4, 134.2, 131.3, 130.8, 128.2, 128.1, 127.7, 126.6, 126.0, 125.1, 124.6, 124.4, 124.0, 123.4, 123.3, 123.2, 120.4, 120.4, 119.9, 110.3, 77.4, 77.2, 76.9, 60.1. Anal. Calcd for C<sub>41</sub>H<sub>25</sub>N (Mw, 531.64): C, 92.63; H, 4.74; N, 2.63. Found: C, 92.62; H, 4.70; N, 2.70. MS (FAB) m/z 532.6 [(M+1)<sup>+</sup>]. UV-vis (THF):  $\lambda_{max}$  (Absorption)= 337 nm,  $\lambda_{max}$  (Emission)= 411 nm.

#### 2.7. PHOLED fabrication

PHOLEDs were fabricated with a configuration of (ITO, 150 nm)/N,N'-diphenyl-N,N'-bis-[4-(phenyl-m-tolyl-amino)-phenyl]-biphenyl-4,4'-diamine (DNTPD, 60 nm)/*N*,*N*'-di(1-naphthyl)-N.N'-diphenylbenzidine (NPB, 30 nm)/SBAF-2C or SBAF-3C: iridium(III) bis(2-phenylquinoline)acetylacetonate  $(Ir(pq)_2acac)$ (30 nm, x %)/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP, 5 nm)/tris(8-hydroxyquinoline)aluminum (Alq<sub>3</sub>, 20 nm)/LiF (1 nm)/Al (200 nm) (Fig. 1), in which SBAF-2C or SBAF-3C acted as the phosphorescent host emitter and Ir(pq)<sub>2</sub>acac acted as the dopant material. Alg<sub>3</sub> as the electron-transporting layer, and BCP as the hole/exciton blocking layer. All organic materials, except the dopants, were deposited at a rate of 1 Å/s. Various doping concentrations of  $Ir(pq)_2$  acac were used such as. 1, 3, 5, 7, and 10%. The devices were encapsulated with a glass lid and a CaO getter after cathode deposition. A Keithley 2400 source measurement unit and a CS 1000 spectroradiometer were used to measure current density-voltage-luminance and electroluminescence characteristics of the blue fluorescent OLEDs, respectively.

#### 3. Results and discussion

#### 3.1. Synthesis and characterization

Synthetic routes to SBAF-2C and SBAF-3C are shown in Scheme 1. As the benzoanthrcene was composed of phenyl and naphthalene moieties, it was easy to prepare 3-bromo-SBAF by direct bromination reaction of SBAF with bromine. But it is impossible to brominate at 2'-position, because the rate of



Scheme 1. Synthesis of spirobenzoanthracene precursors for orange phosphorescent host materials.

substitution reaction of bromine on the naphthalene ring was faster than other phenyl ring [39]. Thus, the multi-step synthesis was indispensable to prepare 2'-bromo-**SBAF**. Two bromo compounds were characterized and confirmed by distinctive isotope peak of mass spectrometry. SBAF-2C was prepared through the 1) the Suzuki reaction of 1.8-dibromonaphthalene with phenylboronic acid. 2) the coupling reaction of 8-phenyl-1-lithio-naphthalene and 2-bromofluorenone. 3) the cyclization reaction followed by an amination reaction of naphthalene] with carbazole in the presence of a copper bronze catalyst. SBAF-3C was synthesized by procedures similar to those used to synthesize SBAF-2C, as shown in Schemes 1 and 2. The synthetic yields of SBAF-2C and SBAF-3C were 62% and 72%, respectively. Purity of SBAF-2C and SBAF-3C was >99.5% after purification by column chromatography and train sublimation. The two host materials were completely soluble in common organic solvents, which makes them eligible for solution phase characterization. Chemical structures and compositions of the resulting precursors and **SBAFs** were characterized by <sup>1</sup>HNMR, <sup>13</sup>C-NMR, FT-IR spectriscopy, elemental analysis and gas chromatography-mass spectrometry. The chiral carbon peak was observed at 60.0 ppm in the <sup>13</sup>C NMR spectra. Results of elemental analysis and mass spectroscopy also supported formation of SBAF-2C and SBAF-3C and matched well with the calculated data.

#### 3.2. Optical properties and energy levels

UV-vis absorption and PL spectra of the **SBAF** carbazole derivatives were measured in THF solution (10<sup>-5</sup> mol/L) and in the solid film state (Fig. 2 and Table 1). **SBAF-2C** and **SBAF-3C** showed spiro core absorption peaks at 328 nm and 340 nm, respectively, and the carbazole unit at 291 nm. Solid-state absorption spectra of **SBAF-2C** and **SBAF-3C** differed from those of their solutions. Absorption maxima of **SBAF-2C** and **SBAF-3C** films appeared at 335 and 343 nm and were red-shifted by 7 and 3 nm, respectively. PL maxima of **SBAF-2C** and **SBAF-3C** were 391 and 416 nm in solution, respectively, whereas solid state PL maxima were observed at 399 nm for **SBAF-2C** and 419 nm for **SBAF-3C**. These PL spectra were slightly red-shifted compared with those of spiro[fluorene-7,9'-benzofluorene] analogs (from 366 to 411 nm) [37–39].



Fig. 2. Normalized absorption, photoluminescence spectra and energy diagram of (a) SBAF-2C and (b) SBAF-3C.



Scheme 2. Chemical structures of spirobenzoanthrcene-type orange phosphorescent host materials.

#### Table 1

Thermal properties and EL properties of the devices obtained from two host and  $Ir(pq)_2acac$  dopant materials.

Properties	Host	SBAF-2C	SBAF-3C
	Dopant	Ir(pq) <sub>2</sub> acac	
EL at 7V	λ <sub>max</sub> (nm)	601	603
	FWHM (nm)	86	86
	mA/cm <sup>2</sup>	3.98	4.18
	cd/A <sup>a</sup>	13.98	7.28
	cd/A <sup>b</sup>	14.74 (6 V)	8.04 (6 V)
	lm/W <sup>a</sup>	6.26	3.60
	lm/W <sup>b</sup>	7.70 (6 V)	3.81 (6 V)
	cd/m <sup>2</sup>	521.5	368.4
	CIE-x	0.599	0.616
	CIE-y	0.373	0.374
	EQE(%) <sup>a</sup>	8.50	5.45
	EQE(%) <sup>b</sup>	8.93 (6 V)	4.99 (6 V)
Optical properties	$\lambda_{max} (nm)^{c}$	328	340
	λ <sub>max</sub> (nm) <sup>d</sup>	335	343
	$\lambda_{max} (nm)^{c}$	391.2	415.8
	λ <sub>max</sub> (nm) <sup>d</sup>	399.3	419
Energy levels	Bandgap	3.43	3.15
	HOMO	5.92	5.95
	LUMO	2.49	2.80
	E <sub>T</sub> <sup>e</sup>	2.39	2.30
	Es <sup>f</sup>	3.42	3.11
Thermal properties	Tg <sup>g</sup>	124.5	126.7
	Tm <sup>h</sup>	290.2	286.3
	T <sub>d</sub> <sup>i</sup>	368.5	361

<sup>a</sup> Values at 7 V.

<sup>b</sup> Values at a peak; V<sub>opt</sub>, operating voltage at a specified current.

<sup>c</sup> THF solution.

<sup>d</sup> Solid film.

e Triplet energy.

<sup>f</sup> Singlet energy.

<sup>g</sup> Glass transition temperature.

<sup>h</sup> Melting temperature.

<sup>i</sup> Decomposition temperature.

The hole and electron injection are closely related to the energy level of the host material, and the energy levels of the new host materials were measured by a low energy photo-electron spectrometer and estimated from the absorption edge of their UVvisible spectra. Fig. 3 presents a schematic energy-level alignment of the devices. As shown, HOMO and LUMO of **SBAF-2C** were 5.92 and 2.42 eV, and those of **SBAF-3C** were 5.95 and 2.75 eV, respectively (Table 1). **SBAF-**carbazole (**SBAF-Cz**) host materials had lower LUMO and HOMO values than those of spirobenzofluorene-type phosphorescent host materials [40,41]; therefore, the effect of the carbazole substituent on the parent spirobenzoantnracene-fluorene was weak. Thus, transfer of holes from the hole-transfer layer to the host layer was difficult.

Phosphorescence spectra were obtained at 77K to measure **SBAF-2C** and **SBAF-3C** triplet energy (Fig. 2). **SBAF-2C** and **SBAF-3C** exhibited phosphorescence emission peaks at 518 nm and 539 nm, respectively, and triplet energy was identified as the first energy peak in the phosphorescence spectrum. The calculated triplet energy levels of **SBAF-2C** and **SBAF-3C** were 2.39 eV and 2.30 eV, respectively. The relatively low triplet energy of the two host materials was due to the spirobenzoanthracene group in **SBAF**. **SBAF** triplet energy was slightly higher than that of 9-carbazole-spiro[benzo[c]fluorene-7,9'-fluorene] (541 nm) reported earlier. Therefore, **SBAF** may be better than 9-carbazole-spiro[benzo[c] fluorene-7,9'-fluorene] as a host for orange PHOLED [41].

The energy level of **SBAF-2C** and **SBAF-3C** was determined mainly by the molecular orbital distribution at the molecular level, and a molecular simulation of the two compounds was performed. Fig. 4 (a) shows the HOMO and LUMO distributions of SBAF-2C and SBAF-3C. The HOMO of SBAF-2C was highly delocalized in the carbazole and spirofluorene units, whereas the LUMO of SBAF-2C was distributed only over the spirobenzoanthrcene unit. Therefore, the hole transport property of **SBAF-2C** was determined by the carbazole unit, and the electron transport property was dependent on the SBAF unit. Unexpectedly, the HOMO of SBAF-3C was mostly localized in the carbazole unit with little orbital distribution in the spirobenzoanthracene unit, whereas the LUMO of SBAF-3C was highly delocalized only in the spirobenzoanthracene unit. The carbazole group had a large effect on the HOMO orbital distribution of **SBAF-3C**, indicating that introducing a carbazole group to spirobenzoanthracene was efficient for the PHOLED.

As shown in Fig. 4(b), the carbazole moiety in **SBAF-2C** can be freely rotated, so it can be distorted by  $53^{\circ}$ . Rotation of the carbazole group in **SBAF-3C** was also limited by steric hindrance of



Fig. 3. Energy level diagrams of the devices, (a) SBAF-2C and (b) SBAF-3C doped with Ir(pq)2acac.



Fig. 4. (a) Molecular orbital distribution and (b) optimized geometrical structure of SBAF-2C and SBAF-3C.

spirobenzoanthracene. This lead to distortion of the carbazole core structure (distorted 65°), and delocalization with the carbazole group cannot be guaranteed by either the fluorene or benzoan-thracene groups in **SBAF-2C** and **SBAF-3C**.

### 3.3. Thermal properties

The thermal properties of the **SBAF-Cz** derivatives were evaluated by thermo gravimetric analysis and DSC. Purified **SBAF-2C** and **SBAF-3C** samples showed melting points ( $T_m$ ) of 290.2 and 286.3°C, respectively, (Table 1). No melting points were observed on the second heating scan, even though the specimens were given time to cool in air. Once they become an amorphous solid, they do not revert to the crystalline state. After the samples had cooled to room temperature, a second DSC scan was performed at 10°C/min, which revealed relatively high glass transition temperatures ( $T_g$ ) of 124.5 and 126.7 °C, due the rigid spiro-type backbone. Thermal decomposition temperatures for **SBAF-2C** and **SBAF-3C**, identified as the peaks of the weight loss derivatives, were 368.5 and 361°C, respectively. As a result, the amorphous glassy state of the two host material transparent films makes them good candidates for use as EL materials.

### 3.4. EL properties

Fig. 5 shows normalized EL emission spectra of the devices. EL spectra were obtained from **SBAF-2C** and **SBAF-3C** doped with Ir(pq)<sub>2</sub>acac at various concentrations to determine the optimized dopant concentration. The EL spectra were different from those of PL spectra, suggesting that the different excited state species are

responsible for both the PL and EL emissions, resulting from the triplet emission due to the  $Ir(pq)_2acac$  complex. The EL emission was dominated by the  $Ir(pq)_2acac$  complex emission peak at around 593–603 nm, but a small emission was observed around 460 nm, which originated from the NPB hole transfer layer. The LUMO value of **SBAF-2C** was quite similar to that of NPB. Thus, electrons or excitons were easily transferred to the host.

The small peak in the EL spectra at 420 nm may have originated from the **SBAF-3C** host material, indicating that the energy transfer from the **SBAF-3C** host to the Ir(pq)<sub>2</sub>acac complex was not efficient, even at the optimum dopant concentration used in this experiment. This was caused by a low **SBAF-3C** triplet energy compared with that of **SBAF-2C**.

The full width at half maximum (82–86 nm) was relatively broad compared with that of other spiro[benzofluorene-fluorene] phosphorescent host materials (73 nm) [40,41]. The dependence of the device chromaticity on the current density was measured to evaluate stability (Fig. 6). Converting the EL spectrum into chromaticity coordinates on the CIE 1931 diagram resulted in increased chromaticity stability with an increase in current density and applied voltage. Additionally, the stability of the color coordinates also increased with increasing dopant concentration. In particular, the stability of the CIEy coordinates was better than that of the CIEx.



Fig. 5. Electroluminescence spectra of orange PHOLEDs with (a) SBAF-2C and (b) SBAF-3C as a host according to doping concentration.



Fig. 6. Stability of the chromaticity depicted by CIE coordination.

#### 3.5. OLED properties

Multilayer devices have a structure of ITO (150 nm)/DNTPD (60 nm)/NPB (30 nm)/**SBAF-2C** or **SBAF-3C**:Ir(pq)<sub>2</sub>acac (30 nm, 1, 3, 5, 7, and 10%)/BCP (5 nm)/Alq<sub>3</sub> (20 nm)/LiF (1 nm)/Al (200 nm). Ten different multilayered devices were prepared by changing the dopant concentration. A-1, A-3, A-5, A-7, and A-10 were fabricated with doped **SBAF-2C** using 1, 3, 5, 7, and 10% Ir(pq)<sub>2</sub>acac, respectively, whereas devices B-1, B-3, B-5, B-7, and B-10, made of the **SBAF-2C** host, were doped with 1–10% Ir(pq)<sub>2</sub>acac.

Figs. 7 and 8 show the current density and luminance-voltage curves for the devices. The turn-on voltage was 4.5 V for **SBAF-2C**, whereas the turn-on voltage for the devices obtained from **SBAF-3C** were 6.0 V. The maximum brightness was around 27,390 cd/m<sup>2</sup> (at 552 mA/cm<sup>2</sup>) for the device A-3, 28,440 cd/m<sup>2</sup> (at 653 mA/cm<sup>2</sup>) for the device A-5, and 12,950 cd/m<sup>2</sup> (at 174 mA/cm<sup>2</sup>) for the device A-7. The device A-5 showed the highest brightness, at 28,440 cd/m<sup>2</sup>, which was more than two times that of the device A-7. Both the current density and luminance of the devices using **SBAF-2C** were higher than those of **SBAF-3C** within the same device structure. The phosphorescent device had a lower driving voltage of 4.5 V, required for initiating light emissions, compared with that of other fluorescent OLED [28,29].



Fig. 7. Dependence of current density on the applied voltage of the devices **SBAF-2C** and **SBAF-3C** doped with various concentrations of Ir(pq)<sub>2</sub>acac.

Fig. 8. Dependence of luminance on the applied voltage of the devices SBAF-2C and SBAF-3C doped with various concentrations of  $Ir(pq)_2acac$ .

Increasing the doping concentration to 10 wt% resulted in decreased luminance efficiency due to a concentration quenching effect. Fig. 9 shows the dependence of luminance efficiency on current density for the ten PHOLEDs with different doping concentrations. Maximum luminescence efficiency was obtained for the red PHOLED with a doping concentration of 3%. As a result, the **SBAF-2C** device: 3% Ir(pq)<sub>2</sub>acac showed a luminance efficiency of 14.74 cd/A at 6 V and a quantum efficiency of 8.92%, which was slightly lower than that of the spiro[benzofluorene-fluorene] series [40,41]. Maximum luminance efficiencies of devices B-3, B-5, and B-7 were 6.92 cd/A, 8.04 cd/A, and 6.50 cd/A, respectively. B series devices exhibited lower luminance efficiencies than those of devices obtained from SBAF-2C. Luminance efficiency showed a gradual decrease with <10% luminance efficiency. At low doping concentrations, electron transfer occurred mainly by the host, and SBAF-2C electron transfer seemed to be faster than that of SBAF-3C. Actually, the carbazole moiety was usually adopted as the hole injection and enhancer of hole movement but did not improve the movement of electrons. SBAF-3C was electron rich, because the carbazole moiety contributes an electron. Therefore, SBAF-3C was incapable of accepting an electron around the benzoanthracene

16 SBAF-2C:lr(pq)\_acac (%) - 1% 14 3% Luminance efficiency (cd/A) 5% 12 7% 10% 10 SBAF-3C:lr(pq)<sub>2</sub>acac (%) 1% 8 -D 3% 5% 6 - 7% 10% 4 2 0 0 50 100 150 200 250 300 Current density (mA/cm<sup>2</sup>)

Fig. 9. Luminance efficiency-current density characteristics of the device using SBAF-2C and SBAF-3C.

unit. The HOMO of **SBAF-3C** was delocalized in the cabazole unit, which decreased the hole transporting property.

As the concentration of dopant increased, the NPB peak decreased, because the charge balance was adjusted by the dopant, which considers charge trapping. Energy transfer of the **SBAF-2C** host to the dopant went smoothly, so **SBAF-2C** showed a higher efficiency than that of **SBAF-3C**.

In the B devices group, device B-3 showed the highest luminance efficiency of around 8.04 cd/A (at 368.4 mA/cm<sup>2</sup>). Increasing the doping concentration to 10 wt% resulted in an abrupt increase at the initial state, followed by sudden decreases in luminance efficiency. Due to the mismatch of the charge transport properties and energy level of the host materials, these poor efficiency characteristics of devices using **SBAF-3C** are not unexpected.

Electron transfer from host to dopant in **SBAF-3C** was not favorable because an emission peak from the host was observed. This can also be explained by the triplet energy value. Triplet energy was the same or lower than that of the dopant (Table 1). EL emissions generally occurred by primarily injecting electrons into the dopant. The EL efficiency increased to 5% and then decreased due to concentration quenching, as the doping concentration increased.

The dopant triplet energy was 2.2 eV, and the difference in triplet energy between the host and dopant was smaller than that of **SBAF-2C**. Thus, energy transition was not efficient.

Fig. 10 shows the dependence of the power efficiency on the current density for the ten PHOLEDs with different doping concentrations. The A-3 device exhibited the highest performance at 6.0 V with a maximum power efficiency of 7.70 lm/W at 4.81 mA/ cm<sup>2</sup>, which was ascribed to the larger number of excitons generated in the emitting layer. The high quantum efficiency of the red PHOLED was kept constant up to 300  $cd/m^2$ , irrespective of doping concentration. SBAF-Cz was synthesized as the host for the red PHOLED, and little efficiency roll-off was achieved in the SBAF-Czbased orange PHOLED. In general, quantum efficiency of the PHOLED decreased significantly at high luminance due to triplet exciton quenching [36]. According to one report, efficiency roll-off can be avoided by balancing holes and electron injections from the charge transport layer to the emitting layer [8]. SBAF-Cz has both hole transport and electron transport units; therefore, the hole and electron injection can be balanced. Carbazole plays the role of a hole transport unit, whereas SBAF works as an electron transport



Fig. 10. Power efficiency-current density characteristics of the device using SBAF-2C and SBAF-3C.



unit. Additionally, both holes and electrons can be trapped by the dopant due to HOMO/LUMO differences between **SBAF-Cz** and Ir(pq)<sub>2</sub>acac.

### 4. Conclusion

New spirobenzoanthrcene-type orange phosphorescent host materials, **SBAF-2C** and **SBAF-3C**, were successfully prepared using the amination reaction of 2'-bromo-**SBAF** and 3-bromo-**SBAF** with carbazole. When the device configuration of ITO/DNTPD/NPB/HOST: Ir(pq)<sub>2</sub>acac/BCP/Alq<sub>3</sub>/LiF/Al was constructed, EL emissions of the devices (**SBAF-2C** doped with 3% Ir(pq)<sub>2</sub>acac) were observed at 602 nm. The device obtained using **SBAF-2C**:3% Ir(pq)<sub>2</sub>acac had the highest external quantum efficiency of 8.9% and CIE coordinates of 0.599 and 0.373. Based on these characteristics, these orange host emitting materials are useful for investigating PHOLED with a stable efficiency roll-off.

## Acknowledgment

This research was supported by WCU (World Class University) program through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology (R31-10069).

#### References

- Baldo MA, O'Brien DF, You Y, Shoustikov A, Sibley S, Thompson ME, et al. Highly efficient phosphorescent emission from organic electroluminescent devices. Nature 1998;395:151–4.
- [2] O'Brien DF, Baldo MA, Thompson ME, Forrest SR. Improved energy transfer in electrophosphorescent devices. Appied Physics Letter 1999;74:442–4.
- [3] Baldo MA, Lamansky S, Burrows PE, Thompson ME, Forrest SR. Very highefficiency green organic light-emitting devices based on electrophosphorescence. Applied Physics Letter 1999;75:4–6.
- [4] D'Andrade BW, Forrest SR, Chwang AB. Operational stability of electrophosphorescent devices containing p and n doped transport layers. Applied Physics Letter 2003;83:3858–60.
- [5] Reineke S, Schwartz G, Walzer K, Falke M, Leo K. Highly phosphorescent organic mixed films: the effect of aggregation on triplet-triplet annihilation. Applied Physics Letter 2009;94:163305–7.
- [6] Baldo MA, Adachi C, Forrest SR. Transient analysis of organic electrophosphorescence. II. Transient analysis of triplet-triplet annihilation. Physical Review 2000;B 62:10967–77.
- [7] Kim SH, Jang J, Yook KS, Lee JY. Stable efficiency roll-off in phosphorescent organic light-emitting diodes. Applied Physics Letter 2008;92:023513–5.
- [8] Jeon SO, Yook KS, Joo CW, Lee JY, Ko KY, Park JY, et al. 100% internal quantum efficiency and stable efficiency roll-off in phosphorescent light-emitting diodes using a high triplet energy hole transport material. Applied Physics Letter 2008;93:063306–8.
- [9] Matsushima M, Adachi CA. Suppression of exciton annihilation at high current densities in organic light-emitting diode resulting from energy-level alignments of carrier transport layers. Applied Physics Letter 2008;92:063306–8.
- [10] Schwartz G, Reineke S, Walzer K, Leo K. Reduced efficiency roll-off in highefficiency hybrid white organic light-emitting diodes. Applied Physics Letter 2008;92:053311–3.
- [11] Zang FX, Sum TC, Huan ACH, Li TL, Li WL, Zhu F. Reduced efficiency roll-off in phosphorescent organic light emitting diodes at ultrahigh current densities by suppression of triplet-polaron quenching. Applied Physics Letter 2008;93: 023309–11.
- [12] Aoki A, Tamagawa Y, Miyashita T. Effect of hole transporting film thickness on the performance of electroluminescent devices using polymer Langmuir— Blodgett films containing carbazole. Macromolecules 2002;35:3686–9.
- [13] Kimoto A, Cho JS, Higuchi M, Yamamoto K. Synthesis of asymmetrically arranged dendrimers with a carbazole dendron and a phenylazomethine dendron. Macromolecules 2004;37:5531–7.
- [14] Lu J, Tao Y, D'iorio M, Li Y, Ding J, Day M. Pure deep blue light-emitting diodes from alternating fluorene/carbazole copolymers by using suitable holeblocking materials. Macromolecules 2004;37:2442–9.
- [15] Hwang SW, Chen Y. Photoluminescent and electrochemical properties of novel poly(aryl ether)s with isolated hole transporting carbazole and electrontransporting 1,3,4-oxadiazole fluorophores. Macromolecules 2002;35:5438–43.

- [16] You Y, Kim SH, Jung HK, Park SY. Blue electrophosphorescence from iridium complex covalently bonded to the poly(9-dodecyl-3-vinylcarbazole): suppressed phase segregation and enhanced energy transfer. Macromolecules 2006;39:349–56.
- [17] Jiang J, Jiang C, Yang W, Zhen H, Huang F, Cao Y. High-efficiency electrophosphorescent fluorene-alt-carbazole copolymers N-grafted with cyclometalated Ir complexes. Macromolecules 2006;38:4072–80.
- [18] Salbeck J, Yu N, Bauer J, Weissörtel F, Bestgen H. Low molecular organic glasses for blue electroluminescence. Synthetic Metals 1997;91:209–15.
- [19] O'Brien DF, Burrows PE, Forrest SR, Konne BE, Loy DE, Thompson ME. Hole transporting materials with high glass transition temperatures for use in organic light-emitting devices. Advanced Materials 1998;10:1108–12.
- [20] Katsuma AK, Shirota Y. Novel class of π-electron dendrimers for thermally and morphologically stable amorphous molecular materials. Advanced Materials 1998;10:223–6.
- [21] Ko CW, Tao T. 9,9-Bis{4-[di-(p-biphenyl)aminophenyl]}fluorene: a high Tg and efficient hole transporting material for electroluminescent devices. Synthetic Metals 2002;126:37–41.
- [22] Salbeck J, Bauer J, Weissörtel F. Spiro linked compounds for use as active materials in organic light emitting diodes. Macromolecular Symposia 1997; 125:121–32.
- [23] Xiao H, Leng B, Tian H. Hole transport triphenylamine–spirosilabifluorene alternating copolymer: synthesis and optical, electrochemical and electroluminescent properties. Polymer 2005;46:5707–13.
- [24] Xiao H, Shen H, Lin Y, Su J, Tian H. Spirosilabifluorene linked bistriphenylamine: synthesis and application in hole transporting and two-photon fluorescent imaging. Dyes and Pigments 2007;73:224–9.
- [25] Katsis D, Geng YH, Ou JJ, Culligan SW, Trajkovska A, Chen SH, et al. Spirolinked ter-, penta-, and heptafluorenes as novel amorphous materials for blue light emission. Chemistry Materials 2002;14:1332–9.
- [26] Bach U, Cloedt KD, Spreitzer H, Gratzel M. Characterization of hole transport in a new class of spiro-linked oligotriphenylamine compounds. Advanced Materials 2000;12:1060–3.
- [27] Jeon SO, Jeon YM, Kim JW, Lee CW, Gong MS. Blue organic light-emitting diode with improved color purity using 5-naphthyl-spiro[fluorene-7, 9'benzofluorene]. Organic Eectronics 2008;9:522–32.
- [28] Kim KS, Jeon YM, Kim JW, Lee CW, Gong MS. Blue light-emitting OLED using new spiro[fluorene-7, 9'-benzofluorene] host and dopant materials. Organic Electronics 2008;9:797–804.
- [29] Jeon YM, Kim JW, Lee CW, Gong MS. Blue organic light-emitting diodes using novel spiro[fluorene-benzofluorene]-type host materials. Dyes and Pigments 2009;83:66–71.
- [30] Kim KS, Jeon YM, Lee HS, Kim JW, Lee CW, Jang JG, et al. Blue organic electroluminescent devices based on the spiro[fluorene-7, 9'-benzofluorene] derivatives as host and dopant materials. Synthetic Metals 2008; 158:870-5.
- [31] Kim JH, Jeon YM, Jang JG, Ryu S, Chang HJ, Lee CW, et al. Blue OLEDs utilizing Spiro[fluorene-7, 9'-benzofluorene]-type compounds as hosts and dopants. Bulletin Korean Chemical Society 2009;30:647–52.
- [32] Jeon SO, Lee HS, Jeon YM, Kim JW, Lee CW, Gong MS. Electroluminescent properties of spiro[fluorene-benzofluorene]-containing blue light-emitting materials. Bulletin Korean Chemical Society 2009;30:863–8.
- [33] Kim KS, Jeon YM, Kim JW, Lee CW, Gong MS. Blue light-emitting diodes from 2-(10-naphthylanthracene)-spiro[fluorene-7,9'-benzofluorene] host material. Dyes and Pigments 2009;81:174–9.
- [34] Jeon SO, Jeon YM, Kim JW, Lee CW, Gong MS. Spiro[fluorene-7,9'-benzofluorene] host and dopant materials for blue light-emitting electroluminescence device. Synthetic Metals 2009;159:1147–52.
- [35] Jeon SO, Yook KS, Joo CW, Son HS, Jang SE, Lee JY. High efficiency red phosphorescent organic light-emitting diodes using a spirobenzofluorene type phosphine oxide as a host material. Organic Electronics 2009;10:998–1000.
- [36] Jang SE, Jeon SO, Cho YJ, Yook KS, Lee JY. Stable efficiency roll-off in red phosphorescent organic light-emitting diodes using a spirofluorene-benzofluorene based carbazole type host material. Journal of Luminescence 2010;130:2184-7.
- [37] Lee IH, Gong MS. New fluorescent blue OLED host and dopant materials based on the spirobenzofluorene. Bulletin Korean Chemical Society 2011;32: 1475–82.
- [38] Jeon YM, Lee JY, Kim JW, Lee CW, Gong MS. Deep-blue OLEDs using novel efficient spiro-type dopant materials. Organic Electronics 2010;11: 1844–52.
- [39] Gong MS, Lee HS, Jeon YM. Highly efficient blue OLED based on 9-anthracenespirobenzofluorene derivatives as host materials. Journal Materials Chemistry 2010;20:10735–46.
- [40] Jeon YM, Lee IH, Lee HS, Gong MS. Orange phosphorescent organic lightemitting diodes based on spirobenzofluorene type carbazole derivatives as a host material. Dyes and Pigments 2011;89:29–36.
- [41] Jeon YM, Lee IH, Lee CW, Lee JY, Gong MS. Orange phosphorescent organic light-emitting diodes using a spirobenzofluorene-type phospine oxide as host materials. Bulletin Korean Chemical Society 2010;31:2955–60.