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# Deep blue organic light-emitting diode using non anthracene-type fused-ring spiro[benzotetraphene-fluorene] with aromatic wings

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### ABSTRACT

We prepared three spirobenzotetraphene-based fused-ring spiro[benzo[*ij*]tetraphene-7,9'-fluorene] (**SBTF**) derivatives for use in non anthracene-type deep-blue organic light-emitting diode (OLED) hosts. 3-(2-Naphthyl)-10-naphthylspiro[benzo[*ij*]tetraphene-7,9'-fluorene] (**N-NSBTF**), 3-[4-(2-naphthyl)phenyl]-10-naphthylspiro[benzo[*ij*]tetraphene-7,9'-fluorene] (**NP-NSBTF**), and 3-(phenyl)-10-naphthylspiro[benzo[*ij*]tetraphene-7,9'-fluorene] (**P-NSBTF**), were synthesized *via* multi-step Suzuki coupling reactions. The optimized device structure – ITO/N,N'-bis-[4-(di-*m*-tolylamino)phenyl]-*N*,N'-diphenylbiphenyl-4,4'-diamine (DNTPD, 60 nm)/bis[*N*-(1-naphthyl)-*N*-phenyl]benzidine (NPB, 30 nm)/**NSBTF** hosts: LBD (5%) (20 nm)/aluminum tris(8-hydroxyquinoline) (Alq<sub>3</sub>, 20 nm)/LiF/Al – was characterized by its blue electroluminescence to have a current efficiency of 6.25 cd/A, a power efficiency of 5.07 lm/W, and an external quantum efficiency of 5.24% at 18.7 mA/cm<sup>2</sup> at CIE coordinates of 0.130, 0.149.

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#### 1. Introduction

Many light-emitting dyes have been extensively studied for their ability to produce blue light emissions when used with adequate dopant and host materials in the emissive layer of OLEDs. However, the requirement of a large energy band-gap makes it difficult to fabricate stable, blue OLEDs with high electroluminescence (EL) efficiency and high color purity [1–3].

Anthracene derivatives have been used as blue host materials in OLEDs because they emit blue light and have excellent photoluminescence (PL) and EL properties [4–7]. In addition, anthracene fluorescence can easily change from blue to green by introducing various aromatic substituents at the 9- and 10-positions [8]. Anthracene

http://dx.doi.org/10.1016/j.orgel.2014.08.030 1566-1199/© 2014 Elsevier B.V. All rights reserved. derivatives have been previously reviewed and discussed in terms of their thermal stability and EL performance [9–12], but the color purity is far from adequate for use in full-color organic light emitting diode (OLED) displays.

Only a limited number of materials have been able to provide the appropriate brightness and stability necessary [13–17], and small fluorene-based molecules and polymers have gained much attention for the potential as efficient blue emitters [18,19]. We believe that non-anthracene spirofluorene molecules with high conjugation are effectively avoid molecular aggregation and enhance the efficiency of electron and hole transport.

Spiro[fluorene-7,9'-fluorene] (**SBF**) or spiro[benzo[*c*]fluorene-7,9'-fluorene] (**SBFF**) are interesting fluorescent OLED materials because that can provide for a variety of derivatives. In particular, **SBFF** has an asymmetric spiro core structure with naphthalene and phenyl rings in the spiro molecules. Thus, the substitution of aromatic





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moieties to the **SBFF** core can allow for conjugation controlled OLED host materials, as shown in Scheme 1 [20–23]. More recently, spiro[benzo[*de*]anthracene-7,9'fluorene] (**SBAF**) derivatives have been prepared and implemented as OLED host and dopant materials. The highly conjugated spiro molecules allow for the optical and electrochemical properties to be delicately tuned over a wide range by following the appropriate chemical modification [24,25]. However, more fused and conjugated spiro-compounds have been studied less, particularly spiro[benzo[*ij*]tetraphene-7,9'-fluorene] (**SBTF**) and its derivatives. Only a few examples of applications for **SBTF** derivatives in organic electronics have been published [26,27].

In this study, we developed and characterized a novel 10naphthylspiro[benzo/*ij*]tetraphene-7,9'-fluorene] (NSBTF) core structure for use as a deep-blue, high-fluorescence host material with good thermal and morphological stability. We prepared three new blue host materials that consisted of 3-(2-naphthyl)-10-naphthylspiro[benzo/ii]tetraphene-7,9'fluorene] (N-NSBTF), 3-[4-(2-naphthyl)phenyl]-10-naphthylspiro[benzo/*ij*]tetraphene-7,9'-fluorene] (**NP-NSBTF**), and 3-phenyl-10-naphthylspiro[benzo/ij/tetraphene-7,9'fluorene] (P-NSBTF), and these were characterized using <sup>1</sup>H nuclear magnetic resonance (NMR), <sup>13</sup>C NMR, Fourier transform-infrared (FT-IR) and mass spectroscopy (MS), thermal analysis, and UV-vis and PL spectroscopy. Also, the EL properties of the fabricated multilayered OLEDs were evaluated.

#### 2. Experimental

#### 2.1. Materials and measurements

Tetrakis(triphenylphosphine)palladium(0), (Aldrich Chem. Co., St. Louis, MO, USA), 4-(2-naphthyl)phenyl boronic acid, naphthalene-2-boronic acid, and phenylboronic acid (Frontier Scientific Co., West Logan, UT, USA) were used as received. 3-Bromo-10-naphthylspiro[benzo/ij]tetraphene-7,9'-fluorene] was prepared by a successive Suzuki reaction using corresponding organic boronic acids and halides. 1,6-Bis[(p-trimethylsilylphenyl)amino]pyrene (LBD; band gap, 2.73 eV; HOMO, 5.47 eV;  $\lambda_{max}$  (absorption) = 426 nm;  $\lambda_{max}$  (emission) = 460 nm) was adopted as the deep-blue dopant material. n-Butyllithium (2.5 M solution in hexane), K<sub>2</sub>CO<sub>3</sub>, NaOH and HCl (Duksan Chem. Co., Seoul, South Korea) were used without further purification. Tetrahydrofuran (THF) was purified by distillation over sodium metal and calcium hydride. Photoluminescence (PL) spectra were recorded on a fluorescence spectrophotometer (Jasco FP-6500; Tokyo, Japan) and UV-vis spectra were obtained by a UV-vis spectrophotometer (Shimadzu, UV-1601PC: Tokyo, Japan). Energy levels were measured with a low-energy photo-electron spectrometer (AC-2; Riken-Keiki, Union City, CA, USA). FT-IR spectra were obtained with a Thermo Fisher Nicolet 850 spectrophotometer (Waltham, MA, USA), and elemental analyses were performed using CE Instrument EA1110 (Hindley Green, Wigan, UK). Differential scanning calorimeter (DSC) measurements were performed on a Shimadzu DSC-60 DSC under N<sub>2</sub>. The thermogravimetric analysis (TGA) measurements were performed on a Shimadzu TGA-50 thermogravimetric analyzer. High resolution mass spectra were recorded using an HP 6890 (Brea, CA, USA) and Agilent Technologies 5975C MSD in FAB mode (Palo Alto, CA, USA).

#### 2.2. Preparation of 10-naphthylspiro[benzo[ij]tetraphene-7,9'-fluorene] (**NSBTF**)

A solution of 8-[2-[6-(2-naphthyl)]]naphthyl-1-bromonaphthalene (14.06 g, 30.6 mmol) in THF (100 mL) was added to a 250 mL two-necked flask. The reaction flask was cooled to  $-78 \,^{\circ}$ 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).

**NSBTF:** yield 86%. Mp 333 °C. UV–vis (THF):  $\lambda_{max}$  (absorption) = 362, 379 nm,  $\lambda_{max}$  (emission) = 396, 415 nm. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm) 8.46 (d, 1H), 8.32 (d, 1H), 8.00 (m, 5H), 7.81 (m, 4H), 7.72 (d, 1H), 7.60 (m, 1H), 7.45 (m, 2H), 7.40 (t, 2H), 7.25 (m, 2H), 7.23 (d, 1H), 7.13 (t, 1H), 7.06 (t, 2H), 6.99 (d, 1H), 6.57 (d, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm) 150.4, 148.1, 147.4, 142.8, 142.2,



Scheme 1. Various spiro molecules: Substituent positions on spiro[benzo[c]fluorene-7,9'-fluorene].

140.0, 139.2, 138.4 137.8, 137.2, 136.8, 136.2, 135.2, 134.4, 133.8, 133.2, 130.7, 129.6, 129.2, 128.2, 128.0, 127.8, 127.4, 126.2, 125.8, 125.2, 124.4, 124.0, 123.3, 122.8, 122.4, 120.4, 120.1, 66.5. FT-IR (KBr, cm<sup>-1</sup>) 3060, 3040, 3018 (aromatic C–H). Anal. Calcd. for  $C_{43}H_{26}$  (542.67): C, 95.17; H, 4.83. Found: C, 95.20; H, 4.85. MS (FAB) m/z 543.20 [(M + 1)<sup>+</sup>].

#### 2.3. Representative preparation of 3-(2-naphthyl)-10naphthylspiro[benzo[i,j]tetraphene-7,9'-fluorene] (**N-NSBTF**)

A solution of 3-bromo-10-naphthylspiro[benzo/ij]tetraphene-7,9'-fluorene] (6.22 g, 10 mmol), tetrakis(triphenvlphosphine)palladium(0) (0.59 g, 0.51 mmol), and naphthalene-2-boronic acid (1.72 g, 10 mmol) dissolved in THF (150 mL) was stirred in a double-necked flask for 30 min. K<sub>2</sub>CO<sub>3</sub> (2 M, 150 mL) was added dropwise over 20 min. The resulting reaction mixture was refluxed overnight at 80 °C and then extracted with ethyl acetate and water. After the organic layer was evaporated with a rotary evaporator, the resulting powdery product was purified by column chromatography from  $CH_2Cl_2/n$ -hexane (1/1) to give the yellow crystalline product N-NSBTF. NP-NSBTF and **P-NSBTF** were prepared using similar procedures described above.

**N-NSBTF:** yield 81%. Mp 322 °C. UV–vis (THF):  $\lambda_{max}$  (absorption) = 370, 387 nm,  $\lambda_{max}$  (emission) = 442 nm. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, *ppm*) 8.52 (d, 1H), 8.42 (d, 1H), 8.04 (m, 6H), 7.96 (d, 1H), 7.88 (m, 2H), 7.83 (m, 3H), 7.69 (m, 4H), 7.54 (m, 2H), 7.45 (m, 2H), 7.41 (t, 2H), 7.25 (s, 1H), 7.22 (d, 1H), 7.06 (m, 5H), 6.63 (d, 1H). FT-IR (KBr, cm<sup>-1</sup>) 3060, 3018 (aromatic C–H). Anal. calcd. for C<sub>53</sub>H<sub>32</sub> (668.25): C, 95.18; H, 4.82. Found: C, 95.09; H, 4.81. MS (FAB) *m/z* 669 [(M + 1)<sup>+</sup>].

**NP-NSBTF:** yield 78%. Mp 374 °C. UV–vis (THF):  $\lambda_{max}$  (absorption) = 373 nm,  $\lambda_{max}$  (emission) = 446 nm. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, *ppm*) 8.52 (d, 1H), 8.42 (d, 1H), 8.15 (s, 1H), 8.03 (m, 5H), 7.95 (m, 2H), 7.78 (m, 7H), 7.78 (d, 1H), 7.74 (d, 1H), 7.57 (m, 3H), 7.51 (m, 2H), 7.46 (m, 2H), 7.42 (t, 2H), 7.21 (d, 1H), 7.13 (m, 3H), 7.07 (m, 2H), 6.63 (d, 1H). FT-IR (KBr, cm<sup>-1</sup>) 3060, 3018 (aromatic C–H). anal. calcd. for C<sub>59</sub>H<sub>36</sub> (744.28): C, 95.13; H, 4.87. Found: C, 95.05; H, 4.85. MS (FAB) *m*/*z* 745 [(M + 1)<sup>+</sup>].

**P-NSBTF:** yield 84%. Mp 317 °C. UV–vis (THF):  $\lambda_{max}$  (absorption) = 369, 385 nm,  $\lambda_{max}$  (emission) = 432 nm. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, *ppm*) 8.50 (d, 1H), 8.39 (d, 1H), 8.04 (m, 5H), 7.82 (m, 3H), 7.74 (m, 1H), 7.67 (m, 1H), 7.59 (d, 1H), 7.53 (d, 2H), 7.51 (m, 2H), 7.44 (m, 2H), 7.41 (m, 3H), 7.21 (d, 1H), 7.10 (m, 3H), 7.04 (d, 2H), 6.61 (d, 1H). FT-IR (KBr, cm<sup>-1</sup>) 3060, 3038, 3020 (aromatic C–H). Anal. calcd. for C<sub>49</sub>H<sub>30</sub> (618.23): C, 95.11; H, 4.89. Found: C, 95.09; H, 4.85. MS (FAB) *m/z* 619 [(M + 1)<sup>+</sup>].

### 2.4. OLED fabrication

A basic device configuration of indium tin oxide (150 nm)/*N*,*N*'-bis-[4-(di-*m*-tolylamino)phenyl]-*N*,*N*'-diphenylbiphenyl-4,4'-diamine (DNTPD, 60 nm)/bis[*N*-(1-naphthyl)-*N*-phenyl]benzidine (NPB, 30 nm)/**NSBTF** hosts: LBD (20 nm, 5%)/aluminum tris(8-hydroxyquinoline)(Alq<sub>3</sub>, 20 nm)/LiF (1 nm)/Al (200 nm) was used for device fabrication, as shown in Fig. 1. The organic layers were deposited

sequentially onto the substrate at a rate of 1.0 Å/s by thermal evaporation from heated alumina crucibles. The concentration of the dopant materials was 5%. The devices were encapsulated with a glass lid and a CaO getter after cathode deposition. Current density-voltage luminance and EL characteristics of the blue fluorescent OLEDs were measured with a Keithley 2400 source measurement unit (Cleveland, OH, USA) and a CS 1000 spectroradiometer.

#### 3. Results and discussion

#### 3.1. Synthesis and characterization

Scheme 2 shows the synthetic route to 3-bromo-10-naphthylspiro[benzo/ij]tetraphene-7,9'-fluorene]. Specifically, the Pd-catalyzed Suzuki coupling reaction of 3-bromo-10-naphthylspiro[benzo/ij/tetraphene-7,9'-fluorene] with naphthalene-2-boronic acid, 4-(2-naphthyl)phenyl boronic acid and phenylboronic acid produced high yields (>87%) of N-NSBTF, NP-NSBTF, and P-NSBTF (Scheme 3). Bromination of 10-naphthylspiro[benzo/ij/tetraphene-7,9'-fluorene] with 1.01 equiv. of bromine in carbon tetrachloride solution led to the selective, high-yield formation of 3-bromo-10-naphthylspiro[benzo/ij]tetraphene-7,9'-fluorene] (Figs. S1-S6). The chemical structures and composition of the resulting spiro[benzo/ij]tetraphene-7,9'-fluorene] derivatives were characterized via <sup>1</sup>H NMR, FT-IR, gas chromatography-MS, and elemental analysis (Figs. S7-S15).

#### 3.2. Thermal properties

The thermal behavior of the NSBTF host materials was evaluated by means of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) under a nitrogen atmosphere, and Table 1 summarizes the thermal analysis data for the three compounds. A 5% weight loss was observed at 403, 412, and 398 °C, and the melting points  $(T_m)$  of **N-NSBTF**, **NP-NSBTF**, and **P-NSBTF** were 322, 374, and 317 °C, respectively, but no melting points were observed on the second heating scan, even though they were given enough time to cool in air. Once the compounds became amorphous solids, they did not revert to their crystalline state. After the samples had cooled to room temperature, a second DSC scan showed glass transition temperatures ( $T_g$ ) of 179 °C, 186 °C, and 174 °C for N-NSBTF, NP-NSBTF, and P-NSBTF, respectively, as a result of the rigid spiro-type backbone. The data indicate that these three materials are stable enough to endure the high temperatures of vacuum vapor deposition. As a result, the amorphous glassy state of the transparent films made of the two host materials indicated that these are good candidates for use as EL materials [28].

#### 3.3. Optical properties and energy levels

Fig. 2 shows the UV absorption and PL spectra of **N-NSBTF**, **NP-NSBTF**, and **P-NSBTF** in solution, as well as in the form of solid thin films. Specifically, two maxima were



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

observed in the absorption spectra of the material dissolved in THF. The strong absorption observed at a wavelength of 370 nm, with a shoulder peak at 387 nm, was attributed to the tetraphene moiety and the aromatic substituents in the **SBTF** core. Upon photoexcitation, the PL emission of **N-NSBTF** peaked at approximately 442 nm for the THF solution and at 449 nm for the solid thin film. **NP-NSBTF** had a long conjugation length and showed a red-shifted absorption and PL spectra. On the other hand, **P-NSBTF** had a short conjugation length and showed a blue shift. The spectral shift in the solid state is a result of the different dielectric constants of the surrounding medium [28].

The photophysical properties of these compounds are summarized in Table 1 where it can be seen that all compounds had high PL QE values (**N-NSBTF**, 0.74; **NP-NSBTF**, 0.83; and **P-NSBTF**, 0.71). A more accurate QE comparison was possible for the three host materials because they had similar UV absorption and PL spectra and **NP-NSBTF**  (naphthylphenyl) was found to have a higher QE than **N-NSBTF** (naphthyl) and **P-NSBTF** (phenyl).

Molecular simulation of **N-NSBTF**, **NP-NSBTF**, and **P-NSBTF** was carried out to understand their physical properties at the molecular level. Fig. 3 shows the geometric structure of the three host materials. Rotation of the aromatic substituents in **NSBTF** was limited due to steric hindrance between **SBTF** and the aromatic moiety. This led to distortion (angle, 30–35°) of the aromatic substituents, for which the conjugation can be destroyed by the **SBTF** group in **N-NSBTF**, **NP-NSBTF**, and **P-NSBTF** [29,30].

Molecular simulation also showed the electron distribution of **N-NSBTF**, **NP-NSBTF**, and **P-NSBTF**. Fig. 3 shows the distribution of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of **N-NSBTF**, **NP-NSBTF**, and **P-NSBTF**. The HOMO and LUMO orbitals of the three host materials were concentrated in the tetraphene core, and the fluorene group only played an accessory role. The substituents, such as



a, Triflic anhydride; b, Naphthalene 2-boronic acid; c, Triethyl borate; d, 1,8-Dibromnaphthalene; e, Fluorenone; f, HCl; g, Br<sub>2</sub>/CCl<sub>4</sub>

Scheme 2. Synthetic schemes for the preparation of spiro[benzo[ij]tetraphene-7,9'-fluorene] core.

naphthyl, naphthylphenyl, and phenyl groups on both sides of the spiro[benzotetraphene-fluorene], apparently affected the HOMO and LUMO distribution in the three host materials.

The energy levels of the three host materials used in this study to fabricate the OLEDs are shown in Fig. 4. A lowenergy photoelectron spectrometer was used to obtain information on the HOMO energies of the host and the dopant materials and to examine the charge injection barriers. The energy gaps for N-NSBTF, NP-NSBTF, and P-NSBTF were calculated to be 3.00, 2.98, and 3.03 eV, respectively, which were associated with the substituents at the wings [29]. The HOMO energy levels were -5.82, -5.84 and -5.85 eV for N-NSBTF, NP-NSBTF, and P-NSBTF, respectively, and the HOMO value of dopant LBD (band gap, 2.73 eV; HOMO, -5.47 eV) was quite high compared to those of the hosts. The HOMO values of the three hosts were similar to those of anthracene derivatives (-5.5 to -6.0 eV), such as 2-methyl-9,10-bis(naphthalen-2-yl)anthracene (MADN) and 9,10-di(naphth-2-yl)anthracene (β-ADN).

#### 3.4. EL properties

Fig. 5 shows the EL spectra of the 5% LBD doped Alq<sub>3</sub> devices acting as electron-transporting materials. To elucidate the effective energy transfer from the NSBTF host materials to the LBD dopant, we fabricated a device with the following multilayer structure: ITO/DNTPD (60 nm)/ NPB (20 nm)/NSBTF:LBD 5 wt% (20 nm)/Alq<sub>3</sub> (20 nm)/LiF/ Al where we used DNTPD as the hole-injection layer, NPB as the hole-transport layer, NSBTF derivatives as the fluorescent blue host, LBD as the fluorescent blue dopant, Alq<sub>3</sub> as the electron-transport layers (ETL), and LiF as the electron-injection layer at the LiF/Al cathode interface. The peaks in blue-light emission were observed at a wavelength of 468 nm, which is similar to that of the PL spectrum of NSBTFs, except for a blue shift in the maximum wavelength. The experimental results suggest a similarity in the maximum EL spectra of the three hosts, but these were red-shifted according to the conjugation length (phenyl < naphthyl < naphthylphenyl), as summarized in



Scheme 3. Preparation of spiro[benzo[ij]tetraphene-7,9'-fluorene] host materials. S.K. Kim, B. Yang, Y. Ma, J.H. Lee, J.W. Park, Exceedingly efficient deepblue electroluminescence from new anthracenes obtained using rational molecular design. J. Mater. Chem. 18 (2008) 3376–3384.

Table 1									
UV absorption.	PL.	energy	levels	and	thermal	properties	of NSBTF	host materia	als.

Sample	Properties	NSBTF	N-NSBTF	NP-NSBTF	P-NSBTF
Purity <sup>a</sup>					
HPLC	(%)	99.9	99.9	99.9	99.9
Thermal analysis					
DSC	$T_g$ (°C)	145	179	186	174
	$T_m$ (°C)	333	322	374	317
UV (THF)	Max (nm)	362, 379	370, 387	373	369, 385
	Bg <sup>b</sup> (eV)	3.15	3.00	2.98	3.03
Optical analysis					
PL (THF)	Max (nm)	396, 415	442	446	432
	FWHM <sup>c</sup> (nm)	41	43	61	41
PL (solid)	Max (nm)	428	449	452	444
	FWHM <sup>c</sup> (nm)	48	53	67	49
QE <sup>d</sup>	$\Phi_{f}$	-	0.74	0.83	0.71
Electrical analysis					
AC-2	HOMO (eV)	5.88	5.82	5.84	5.85
	LUMO (eV)	2.73	2.82	2.86	2.82

<sup>a</sup> The purity of the samples were finally determined by high performance liquid chromatography (HPLC) using the above prepared samples after train sublimation.

<sup>b</sup> Bandgap.

<sup>c</sup> Full width at half maximum.

<sup>d</sup> Fluorescence quantum efficiency, relative to 9,10-diphenylanthracene in cyclohexane ( $\Phi_f$  = 0.90).



Fig. 2. UV-vis and PL spectra of spiro[benzo[ij]tetraphene-7,9'-fluorene] derivatives; inset figure shows PL spectra in thin film.

Table 2. This seemed to indicate that the energy transfer from the host to the LBD dopant was quite efficient at the optimum dopant concentration employed in this experiment. A relatively narrow full width half maximum of 34 nm was observed for the  $\beta$ -ADN device with 5% dopant. The EL spectra and chromaticity of our devices, as depicted according to CIE coordination–luminance, were stable with an increasing luminance from 100 to 2000 cd/ m<sup>2</sup>. Little or no change was detected for the different brightnesses in this range.

#### 3.5. OLED device properties

**N-NSBTF**, **NP-NSBTF**, **P-NSBTF**, and commercial  $\beta$ -ADN were evaluated for use as host materials in blue fluorescent OLEDs. Fig. 6 shows the luminance-voltage-current den-

sity characteristics of the OLEDs with an EML composed of the four hosts with 5% LBD dopant. **N-NSBTF** and **NP-NSBAF** showed a higher current density and luminance than **P-NSBAF** and anthracene-type  $\beta$ -ADN did at the same driving voltage. The decrease in the current density and luminance of the **P-NSBTF** device originated from its wide band gap. The **P-NSBTF** band gap was 3.03 eV, compared to the 3.00 eV and 2.98 eV of **N-NSBTF** and **NP-NSBAF**, respectively. The slightly deep HOMO level of the **P-NSBTF** hinders hole injection from the NPB hole transport layer to the emitting layer due to the large energy barrier for hole injection, leading to low current density and low luminance [30].

As shown in Fig. 7, the device with  $\beta$ -ADN with 5% dopant showed a low efficiency. In the case of the **N-NSBTF** device doped with 5% LBD, a maximum brightness of 2205 cd/m<sup>2</sup>



Fig. 3. HOMO and LUMO electronic density distributions of N-NSBTF derivatives, calculated at the DFT/B3LYP/6-31G<sup>\*</sup> for optimization and time dependent DFT (TDDFT) using Gaussian 03.



Fig. 4. Energy diagram of the blue fluorescence devices using NSBTF host materials.

and 5.92 cd/A occurred at 6 V, as seen in Table 2, and a quantum efficiency of 5.19% is maintained at a current density of up to 43.2 mA/cm<sup>2</sup>, as shown in Fig. 8.

In the device, the HOMO level (5.70 eV) of Alq<sub>3</sub> was higher than that of  $\beta$ -ADN (5.95 eV). This difference explains why electron-hole recombination may be unbalanced in the emitting zone of the device. The HOMO level (5.82–5.85 eV) of the three **NSBTF**s was slightly higher than that of  $\beta$ -ADN. This recombination with a higher charge also shifted the blue light-emitting zone to a region close to the ETL (Alq<sub>3</sub>) and, therefore, facilitates electronhole recombination in the 5% doped emitting zone. Consequently, the EL performance of **NSBTF**s was superior to that of  $\beta$ -ADN. The holes injected from a hole transfer layer,  $\alpha$ -NPB, were transferred to the light emitting layer and were trapped at the dopant sites. The LBD dopant had a large capacity to catch holes, and it minimized the loss of holes, resulting in good EL efficiency. Thus, the HOMO level of LBD as a dopant was suitable for hole trapping and hole transport, and the **N-NSBTF** and **NP-NSBAF** host materials were moderate for balancing holes and electrons in the emitting layer.

The maximum external quantum efficiency (EQE) of the device obtained from the **N-NSBTF** device doped with 5% LBD was of 5.19% as shown in Fig. 8. The luminance efficiency increased rapidly to a maximum of approximately 5.92 cd/A at a low current density of 43.2 mA/cm<sup>2</sup> at 6 V.



Fig. 5. Electroluminescence spectra of the devices prepared from NSBTF host materials.

**NP-NSBTF** doped with 5% LBD showed a small decrease in efficiency as the current density increased from 0 to 44.6 mA/cm<sup>2</sup>, i.e., a weak-current-induced fluorescent quenching [31]. The sample reached a current efficiency of 5.84 cd/A, EQE of 5.16%, power efficiency of 4.98 lum/

#### Table 2

Electroluminescence properties of the devices obtained from NSBTF host materials.

W, and CIE coordinates of 0.134 and 0.172 at 6 V. These results suggest that an exciton was formed and that light was emitted at specific thresholds. It should be noted that the efficiencies of these devices showed a small decrease when the luminance increased to  $2018 \text{ cd/m}^2$ .

For the fluorescent host-dopant system, the probability for energy transfer from the excited energy donor to the energy acceptor depends on the overlap of the emission spectrum of the donor with the absorption spectrum of the acceptor. This is evident from the spectral overlap between the PL of **NSBTF** and the UV absorption of LBD [32–36], as shown in Fig. 9.

A combination of good efficiency and color purity enabled the non anthracene-type fused ring spirotetraphene derivatives to be good candidates for use a blue emitters in OLEDs.

The life-time tests were performed at a initial luminance of 5000 cd/m<sup>2</sup>. The life-times of the three new host materials were 139.2 h for **N-NSBTF**, 130.6 h for **NP-NSBTF**, and 119.3 h for **P-NSBTF**. The life-times of **N-NSBTF** (139 h) and **NP-NSBTF** (130 h) were more than those of  $\beta$ -ADN:5% LBD (130–135 h), which can be explained to be a result of a more stable morphology of the **NSBTF** host materials.

Properties	Host	N-NSBTF	NP-NSBTF	P-NSBTF	β-ADN
	Dopant	LBD			
	(%)	5%			
EL at 6 V	$\lambda_{\rm max}$ (nm)	468	467	469	466
	FWHM (nm)	40	42	38	34
	mA/cm <sup>2</sup>	43.2	44.6	18.7	41.8
	cd/A <sup>a</sup>	5.92	5.84	6.25	3.36
	cd/A <sup>b</sup>	6.24 (5.5 V)	6.12 (5.0 V)	6.32 (5.5 V)	3.63 (7.5 V)
	cd/m <sup>2</sup>	2205	2018	1152	1928
	CIE-x	0.130	0.134	0.130	0.142
	CIE-y	0.155	0.172	0.149	0.160
	EQE (%) <sup>a</sup>	5.19	5.16	5.24	2.87
	lum/W	5.02	4.98	5.07	2.14

<sup>a</sup> Values at 6 V.

<sup>b</sup> Values at a highest peak.



Fig. 6. Current density-voltage-luminescence characteristics of the devices using NSBTF host materials doped with 5% LBD.



Fig. 7. Current efficiency-voltage of the devices using NSBTF host materials doped with 5% LBD.



Fig. 8. Quantum efficiency–luminance curves of the devices using NSBTF host materials doped with 5% LBD.



Fig. 9. UV-vis absorption spectrum of LBD and the PL spectrum of three NSBTF host materials N-NSBTF, NP-NSBTF, and P-NSBTF.

#### 4. Conclusion

In summary, we synthesized new spirolbenzoliiltetraphene-7,9'-fluorene]-based host materials and used them to fabricate efficient deep-blue OLEDs. The NSBTF derivatives consisted of a non anthracene-type fused-ring **SBTF** core as well as aromatic substituents at both sides of the SBTF. The device with the optimum structure -ITO/DNTPD (60 nm)/NPB (20 nm)/**NSBTF**:LBD 5 wt% (20 nm)/Alq<sub>3</sub> (20 nm)/LiF (0.5 nm)/Al (100 nm) - was characterized by a high blue EL performance with a current efficiency of 6.25 cd/A, a power efficiency of 5.17 lm/W, and an external quantum efficiency of 5.54% at 18.7 mA/ cm<sup>2</sup> with CIE coordinates of 0.130, 0.149. These results show that non anthracene-type  $\pi$ -conjugated fused-ring aromatic SBTF with aromatic wings can be used as efficient hosts for deep-blue OLEDs.

#### **Appendix A. Supplementary material**

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.orgel.2014.08.030.

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