Cite this: J. Mater. Chem., 2011, 21, 13640

# Efficient deep-blue and white organic light-emitting diodes based on triphenylsilane-substituted anthracene derivatives

Kum Hee Lee,<sup>a</sup> Jeong Keun Park,<sup>a</sup> Ji Hoon Seo,<sup>b</sup> Se Won Park,<sup>b</sup> Young Sik Kim,<sup>\*b</sup> Young Kwan Kim<sup>\*b</sup> and Seung Soo Yoon<sup>\*a</sup>

*Received 12th May 2011, Accepted 4th July 2011* DOI: 10.1039/c1jm12097b

A series of anthracene derivatives with a triphenylsilane end-capping group, (9,9-dimethyl-2-(10phenylanthracen-9-yl)-9*H*-fluoren-7-yl)triphenylsilane (**PAFTPS**), 9,10-bis(9,9-dimethyl-2-(triphenylsilyl)-9*H*-fluoren-7-yl)anthracene (**BFPSA**), (9,9-dimethyl-2-(9,10-diphenylanthracen-2-yl)-9*H*-fluoren-7-yl)triphenylsilane (**DPA-2FTPS**), and (9,10-eiphenylanthracen-2-yl)triphenylsilane (**DPA-2TPS**), have been designed, synthesized, and characterized. A device incorporating **PAFTPS** as the emissive layer exhibited a high external quantum efficiency of 2.02% at 20 mA cm<sup>-2</sup> with color coordinates of (0.152, 0.072) as a non-doped blue emitter. At even higher efficiency, an external quantum efficiency up to 2.32% at 20 mA cm<sup>-2</sup> with color coordinates of (0.155, 0.076) was obtained when doped with the blue fluorescent material, 3-(*N*-phenylcarbazol)vinyl-*p*-terphenyl (**PCVtPh**). Furthermore, an efficient white OLED with an external quantum efficiency, a luminous efficiency and color coordinates of 4.18%, 9.14 cd A<sup>-1</sup> at 1000 cd m<sup>-2</sup> and (0.43, 0.41) at 1000 cd m<sup>-2</sup> was demonstrated by exploiting this highly efficient blue fluorescent material (**PAFTPS**) as a host in the blue emitting layer.

# Introduction

Since the first report by Tang and Vanslyke, there has been huge progress in organic light-emitting diodes (OLEDs) because of their potential applications in full-color flat-panel displays and solid-state illumination sources.<sup>1,2</sup> Therefore, OLED performance has improved remarkably over the past decade.<sup>3–6</sup> For full-color displays, it is essential to have the three primary colors, red, green and blue. However, because of the wide band-gap of blue emitters, blue OLEDs show relatively poor performance compared to red and green OLEDs. For this reason, in the development of new OLEDs, the progress in highly efficient blue-light emitters with good color purity is a great challenge.

Recently, a range of blue emitters have been developed for highly efficient blue OLEDs.<sup>7-9</sup> However, there were few highly efficient deep-blue OLEDs with a CIEy coordinate <0.10, which can be matched to be the national television system committee (NTSC) standard blue (0.14, 0.08).<sup>10–12</sup> Therefore, many researchers aim to develop deep blue-light emitters. Particularly, Park *et al.* reported anthracene derivatives that contain bulky side groups with an excellent external quantum efficiency (EQE) of 7.18% and CIE coordinates of (0.156, 0.088).<sup>13</sup> Also, Lee and Char *et al.* published an excellent blue host material containing silicon-cored anthracene with an external quantum efficiency (EQE) of 6.3% and CIE coordinates of (0.142, 0.149).<sup>14</sup>

Up to now, anthracene derivatives have been used widely to fabricate highly efficient OLEDs due to their outstanding photoluminescence (PL) and electroluminescence (EL) properties.<sup>10,12,15,16</sup> Among these anthracene derivatives, 9,10diphenylanthracene (DPA) is an attractive material for its unity fluorescence quantum efficiency in a dilute solution and high fluorescence in the solid state. However, it is extremely difficult to produce dense films or vapor deposited thin films which tend to crystallize, resulting in a rough surface, grain boundaries or pin holes that can lead to current leakage or catastrophic device failure.<sup>17,18</sup> In general, amorphous thin films (in OLEDs) with high glass transition temperatures  $(T_g)$  are less vulnerable to heat, resulting in more stable devices performance.<sup>19</sup> Consequently, light-emitting materials with high  $T_{g}$  values are desired to retain the film morphology during operation of the device. In this study, triphenylsilane end-capping groups were introduced to the anthracene skeleton to improve the thermal properties, while keeping their advantageous electronic and optical characteristics. The non-planar molecular structure would prevent the close-packing of the molecules in the solid state and enable the formation of smooth and pinhole-free thin films.<sup>10</sup>

This paper reports the synthesis and full characterization of a series of triphenylsilane-substituted anthracene derivatives,

<sup>&</sup>lt;sup>a</sup>Department of Chemistry, Sungkyunkwan University, Suwon, 440-746, Korea. E-mail: ssyoon@skku.edu; Fax: +82 31 290 7075; Tel: +82 31 290 7071

<sup>&</sup>lt;sup>b</sup>Department of Information Display, Hongik University, Seoul, 121-791, Korea. E-mail: kimyk@hongik.ac.kr; Fax: +82 2 3141 8928; Tel: +82 2 3142 3750

(9,9-dimethyl-2-(10-phenylanthracen-9-yl)-9H-fluoren-7-yl)triphenylsilane (PAFTPS), 9,10-bis(9,9-dimethyl-2-(triphenylsilyl)-9H-fluoren-7-yl)anthracene (BFPSA), (9.9-dimethyl-2-(9,10diphenylanthracen-2-yl)-9H-fluoren-7-yl)triphenylsilane (DPA-2FTPS). and (9,10-diphenylanthracen-2-yl)triphenylsilane (DPA-2TPS), as blue host materials for OLEDs. A (9,9dimethyl-9H-fluoren-7-yl) triphenylsilyl or triphenylsilyl group was introduced to various positions of the anthracene skeleton to cause molecular non-planarity. The non-planarity of the molecular structure effectively suppresses the intermolecular interactions, reduces concentration quenching and facilitates the formation of stable, amorphous films. To examine the EL properties of materials PAFTPS, BFPSA, DPA-2FTPS and DPA-2TPS, multilayered OLEDs were fabricated using these blue materials as the emitting layer (non-doped) and host material for 4'-[2-(2-diphenylamino-9,9-diethyl-9H-fluoren-7-yl) vinyl]-p-terphenyl (PFVtPh)<sup>20</sup> (doped) and 3-(N-phenylcarbazol) vinyl-p-terphenyl (PCVtPh)<sup>21</sup> (doped). Furthermore, to expand the applicability of these blue emitting materials PAFTPS, BFPSA, DPA-2FTPS and DPA-2TPS, a white OLED device with the two complementary color emitting layers (e.g., sky-blue and orange) was fabricated. Among many possible OLED device structures to generate white emission from OLEDs based on two complementary colors including a p/n type junction in an asymmetric tandem OLED in series and multi-doping in a single host in single unit OLEDs,<sup>22,23</sup> an OLED device with the structure of the sequential stacking of two complementary color emitting layers in single unit OLEDs using PAFTPS as a skyblue emitting host material is described.

## **Results and discussion**

In this study, we present an integrated investigation encompassing density functional theory (DFT) molecular modeling, material synthesis, and device characterization based on a series of anthracene derivatives with triphenylsilane end-capping groups. Scheme 1 shows the synthetic route of the newly designed host compounds and the structure of the dopant compounds. The host compounds **PAFTPS**, **BFPSA**, **DPA-2FTPS** and **DPA-2TPS** were synthesized by Suzuki cross-coupling reactions between 4,4,5,5-tetramethyl-2-(9,9-dimethyl-2-(triphenylsilyl)-9*H*-fluoren-7-yl)-1,3,2-dioxaborolane and the corresponding arylanthryl bromide compound in moderate yield.

After purification by column chromatography and recrystallization, these newly synthesized blue-emitting materials were purified further by train sublimation at a reduced pressure below 1.33 Pa and fully characterized with <sup>1</sup>H- and <sup>13</sup>C-NMR, infrared, mass spectrometry and element analysis. High-pressure liquid chromatography analysis was carried out to check the purity of materials. These analyses revealed that the purity of blue-emitting materials is at least above 99.0%.

Fig. 1(a) shows the UV-vis absorption spectra of the blue fluorescent materials **PAFTPS**, **BFPSA**, **DPA-2FTPS**, and **DPA-2TPS** in dichloromethane. Fig. 1(b) and 1(c) show the PL emission spectra of the blue fluorescent materials **PAFTPS**, **BFPSA**, **DPA-2FTPS** and **DPA-2TPS** in dichloromethane and quartz plates. Table 1 summarizes the results. In the UV-vis absorption spectra, the maximum absorption wavelengths of **PAFTPS**, **BFPSA**, **DPA-2FTPS** and **DPA-2TPS** appeared at



**Scheme 1** Synthetic routes to host materials and structure of the dopant materials. *Reagents*: (i) *n*-BuLi, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborane, THF; (ii) Pd(PPh<sub>3</sub>)<sub>4</sub>, 2 M K<sub>2</sub>CO<sub>3</sub>, Toluene, Aliquat 336; (iii) *n*-BuLi, THF.

376, 379, 388 and 380 nm, respectively. In addition, the maximum emission wavelengths of PAFTPS, BFPSA, DPA-2FTPS, and DPA-2TPS were observed at 426, 438, 430 and 420 nm, respectively. Compared to the UV-vis and PL spectrum of PAFTPS, DPA-2FTPS showed bathochromic shifts due to the lengthened  $\pi$ -conjugation by the 2-position of the anthracene group. With the same 2-position of the anthracene unit, a red shift in the absorption and PL maxima of DPA-2FTPS was observed compared to DPA-2TPS. This is likely due to an increase in conjugation because of the incorporated spacer of the planar fluorene molecule. The full width at half maximum (FWHM) values of the PL spectra ranged from 51 to 54 nm. Blue emitters PAFTPS, BFPSA, DPA-2FTPS, and DPA-2TPS showed high quantum yields of 0.68, 0.67, 0.68, and 0.84, respectively. Therefore, these compounds are excellent candidates for use as efficient blue-emitting materials in OLEDs. As shown in Fig. 1(c), the emission spectra of the PAFTPS, BFPSA, DPA-2FTPS, and DPA-2TPS in thin films were red-shifted compared to those in a CH<sub>2</sub>Cl<sub>2</sub> solution due to the solid-state effect.<sup>24</sup> Fig. 1(b), which shows the good spectral overlap between the absorption of PFVtPh and the emission of materials PAFTPS, BFPSA, DPA-2FTPS, and DPA-2TPS, suggests adequate energy transfer from PAFTPS, BFPSA, DPA-2FTPS, and DPA-2TPS to PFVtPh by Förster energy transfer would occur. It indicates that PAFTPS, BFPSA, DPA-2FTPS and



Fig. 1 (a) UV-Vis absorption in  $CH_2Cl_2$ , (b) PL emission spectra of blue materials in  $CH_2Cl_2$ , and (c) PL emission spectra of blue materials in thin films.

**DPA-2TPS** perform well as host materials in OLED devices with the **PFVtPh** dopant material.

The highest occupied molecular orbital (HOMO) levels were measured using a photoelectron spectrometer (Riken-Keiki AC-2), and the lowest unoccupied molecular orbital (LUMO) levels were calculated by subtracting the corresponding optical band gap energies from the HOMO values. The HOMO energy levels of compounds **PAFTPS**, **BFPSA**, **DPA-2FTPS** and **DPA-2TPS**  
 Table 1
 Physical properties of the blue materials

	PAFTPS	BFPSA	DPA-2FTPS	DPA-2TPS
$T_{\rm o}/T_{\rm d}/^{\circ}{\rm C}$	140/368	94/490	141/440	89/358
$\lambda_{abs max}/nm^a$	376	379	388	380
$\lambda_{\rm em,max}/\rm{nm}^{a,b}$	426/438	438/451	430/461	420/434
FWHM <sup><i>a,b</i></sup>	52/42	54/47	51/49	52/43
${\Phi_{\mathrm{FL}}}^c$	0.68	0.67	0.68	0.84
$HOMO^d$	-5.86	-5.83	-5.65	-5.90
LUMO	-2.84	-2.89	-2.77	-2.95
$E_{g}^{e}$	3.02	2.94	2.88	2.95

<sup>*a*</sup> Maximum absorption and emission wavelength, measured in CH<sub>2</sub>Cl<sub>2</sub> solution (*ca.* 1 × 10<sup>-5</sup> M). <sup>*b*</sup> Measured in the film. <sup>*c*</sup> Fluorescence quantum yields in CH<sub>2</sub>Cl<sub>2</sub> solution, using DPA as a standard; ( $\Phi = 0.90, \lambda_{ex} = 360$  nm). <sup>*d*</sup> The HOMO energy level was determined by a low-energy photoelectron spectrometer (Riken-Keiki, AC-2). <sup>*e*</sup> E<sub>g</sub> is the band-gap energy estimated from the intersection of the absorption and emission spectra.

were estimated to be -5.86, -5.83, -5.65, and -5.90 eV, respectively. The optical energy band gaps ( $E_g$ ) for these materials were 3.02, 2.94, 2.88, and 2.95 eV, respectively, as determined from the absorption spectra. The LUMO energy levels of compounds **1**, **2**, **3**, and **4** were calculated to be -2.84, -2.89, -2.77, and -2.95 eV, respectively, by subtracting the optical band gaps from the HOMO energy levels.

DFT calculations have been performed to characterize the 3D geometries and the frontier molecular orbital energy levels of **PAFTPS**, **BFPSA**, **DPA-2FTPS**, and **DPA-2TPS** at the B3LYP/ 6-31G\* level by using the Gaussian 03 program.<sup>25</sup> The calculated geometries of **PAFTPS**, **BFPSA**, **DPA-2FTPS**, and **DPA-2TPS** in Fig. 2 show the non-planarity of their molecular structures because of the tetrahedral environment of the tetraphenylsilane group. The non-planar molecular structure provides steric hindrance that prevents the intermolecular interactions between  $\pi$ -systems and suppresses molecular recrystallization, which improves the morphological stability.



**Fig. 2** Three-dimensional structures and calculated HOMO and LUMO density maps of blue materials.



Fig. 3 Energy-level diagrams of non-doped devices 1A-4A.

As shown in Fig. 2, the spatial distributions of electron densities in the HOMO and LUMO for PAFTPS, BFPSA, DPA-2FTPS, and DPA-2TPS are mostly localized on the anthracene moiety. It implies that the absorption and emission process may only be attributed to the  $\pi$ - $\pi$ \* transition centered at the anthracene moiety. The HOMO level is increased with the increase in the number of fluorene groups on the anthracene molecule from **PAFTPS** to **BFPSA**, since the conjugation length of the 9-position of anthracene ring is increased. Apparently, for anthracene such a conjugation effect is stronger for substitution at the 2-, 3-, 6-, and 7-positions than for substitution at the 9- and 10-positions. These results are compatible with the trend of photophysical properties of PAFTPS, BFPSA, DPA-2FTPS, and DPA-2TPS. The calculated HOMO energy levels of PAFTPS, BFPSA, DPA-2FTPS and DPA-2TPS were -5.09, -5.08, -5.04, and -5.11 eV, respectively, which is in good agreement with the experimental values.

The thermal properties of **PAFTPS**, **BFPSA**, **DPA-2FTPS**, and **DPA-2TPS** were measured by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), and are listed in Table 1. The decomposition temperatures ( $T_d$ ), which correspond to a 5% weight loss upon heating during TGA, of blue materials **PAFTPS**, **BFPSA**, **DPA-2FTPS**, and **DPA-2TPS** were 368, 490, 440, and 358 °C, respectively. The glass



Fig. 4 EL spectra of the device 1A–4A at 8 V.

temperatures ( $T_g$ ) of compounds **PAFTPS**, **BFPSA**, **DPA-2FTPS**, and **DPA-2TPS** were determined to be 140, 94, 141, and 89 °C, respectively, by DSC in the second heating scans. The high stability of the amorphous glass state of these compounds was attributed to the non-planarity of their molecular structures. These results clearly show that compounds **PAFTPS** and **DPA-2FTPS** have good thermal stability and very desirable characteristics for OLEDs stability.

To evaluate the applicability of these blue fluorescent materials (PAFTPS, BFPSA, DPA-2FTPS, and DPA-2TPS) as an



**Fig. 5** (a) J-V characteristics, (b) luminous efficiencies, and (c) external quantum efficiencies as a function of current density for the non-doped devices (1A-4A).

emitting layer, non-doped blue emitting devices (1A–4A) were fabricated with the following structure: ITO/NPB (50 nm)/blue materials (30 nm)/Bphen (30 nm)/Liq (2 nm)/Al (100 nm). Fig. 3 shows the HOMO and LUMO energy levels of the blue fluorescent materials, along with those of the other materials used in electroluminescence devices, including ITO, NPB, Bphen and Liq:Al.

The EL spectra of **1A–4A** showed blue emission with peaks at 447, 446, 463 and 448 nm, respectively, as shown in Fig. 4. Narrow EL peaks in the **1A–4A** devices with FWHMs of 55, 56, 60, and 62 nm, respectively, were observed. At a driving voltage of 8 V, the CIE coordinates of devices **2A** and **3A** were (0.159, 0.121) and (0.160, 0.134), respectively. In particular, the CIE coordinates of devices **1A** and **4A** were (0.152, 0.072) and (0.154, 0.092), which is close to the NTSC standard blue color.

Fig. 5 shows the current density–voltage (*J–V*), luminous efficiencies (LE), power efficiencies (PE), and external quantum efficiencies (EQE) of devices **1A–4A**, respectively. Table 2 lists the EL properties of devices **1A–4A** with the low turn-on voltages <4.8 V. Device **1A** exhibited the highest external quantum efficiency of 2.02% (1.39 cd  $A^{-1}$ ) at 20 mA cm<sup>-2</sup> with a maximum luminance of 1347 cd m<sup>-2</sup>, which is higher than the 1.62, 1.29, and 1.43% obtained for devices **2A**, **3A**, and **4A**, respectively. Interestingly, devices **1A–4A** showed improved external quantum efficiencies compared to the device using a common blue emitting material MADN. This suggests that the non-planar molecular structure of triphenylsilane-substituted anthracene derivatives can effectually hinder intermolecular aggregation and prevent the close-packing of the molecules, which can lead to enhanced EL efficiency.

To enhance the EL efficiencies further, these materials (PAFTPS, BFPSA, DPA-2FTPS, and DPA-2TPS) were doped with blue dopant materials (PFVtPh and PCVtPh) at 8 wt% in

 Table 2
 EL performance characteristics of A devices (non-doped)

13644   J. Mater. Chem., 2011, <b>21</b> , 13640–13648
--



Fig. 6 EL spectra of blue OLEDs at 8 V of the doped device; (a) **1B–4B**; and (b) **1C–4C**.

Devices	$LE^{a,b}/cd A^{-1}$	$PE^{a,b}/Im W^{-1}$	EQE <sup><i>a,b</i></sup> (%)	$L^a$ /cd m <sup>-2</sup>	$J^a$ /mA cm <sup>-2</sup>	$V_{\rm on}{}^c/{\rm V}$	$FWHM^d$	EL <sup>d</sup> /nm	$\operatorname{CIE}^{d}(x, y)$
MADN	1.24/0.98	0.98/0.46	1.35/1.25	935	145	4.0	55	442	(0.153, 0.080)
1A	1.73/1.39	1.26/0.69	2.42/2.02	1347	202	4.2	55	447	(0.152, 0.072)
2A	3.01/1.72	1.84/0.67	2.67/1.62	852	135	4.8	56	446	(0.159, 0.121)
3A	1.73/1.52	1.22/0.73	1.41/1.29	1595	215	4.0	60	463	(0.160, 0.134)
4A	1.89/1.22	1.41/0.62	2.06/1.43	981	184	4.2	63	448	(0.154, 0.092)

Table 3 EL performance characteristics of B and C devices (doped)

Devices	$LE^{a,b}/cd A^{-1}$	$PE^{a,b}/lm W^{-1}$	$EQE^{a,b}$ (%)	$L^a$ /cd m <sup>-2</sup>	$J^a/mA \text{ cm}^{-2}$	$V_{\rm on}{}^c/{\rm V}$	$FWHM^d$	EL <sup>d</sup> /nm	$\operatorname{CIE}^{d}(x, y)$
1B	5.17/3.91	4.20/1.76	3.87/2.96	3334	178	3.8	57	451	(0.154, 0.159)
2B	3.03/1.71	2.62/0.84	1.60/0.93	792	120	3.4	81	457	(0.223, 0.266)
3B	4.71/3.58	4.72/2.01	3.23/2.49	2341	196	3.0	63	454	(0.159, 0.174)
4B	4.76/3.71	4.31/2.01	3.41/2.70	2577	174	3.2	60	457	(0.151, 0.174)
1C	2.61/1.68	2.41/0.85	3.37/2.32	1301	174	3.6	52	437	(0.155, 0.076)
2C	3.19/2.11	2.51/0.95	2.19/1.54	1245	159	4.0	64	456	(0.169, 0.166)
3C	3.19/1.86	2.95/0.96	2.63/1.64	1036	149	3.4	62	460	(0.158, 0.128)
4C	0.94/0.94	0.66/0.59	0.91/0.91	899	186	3.4	65	448	(0.163, 0.115)

<sup>*a*</sup> Maximum values. <sup>*b*</sup> At 20 mA cm<sup>-2</sup>. <sup>*c*</sup> Turn-on voltage at 1 cd m<sup>-2</sup>. <sup>*d*</sup> At 8 V.

the same device structure, respectively. Table 3 lists the EL properties of devices **1B–4C**. In terms of the EL efficiency, the **B** devices with **PFVtPh** as the dopant material were more effective than the **C** devices with **PCVtPh** as the dopant material.

As shown in Fig. 1(b), the emission spectra of the host materials 1–4 overlapped better with the absorption spectra of **PFVtPh** than those of **PCVtPh**. This indicates that Förster-type energy transfer enables **PFVtPh** to accept energy from the host materials 1–4 more effectively than **PCVtPh**. This leads to the improved EL efficiency of device **B** compared to device **C**, because the emissions from devices **1B–4C** using host-dopant emitting systems originate from dopant materials by Förstertype energy transfer from the host to dopant.<sup>11</sup>



Fig. 7 (a) J-V characteristics, (b) luminous efficiencies, and (c) external quantum efficiencies as a function of current density for the doped devices (1B-4C).

Fig. 6 shows the EL spectra of the devices B (8 wt% PFVtPhdoped) and C (8 wt% PCVtPh-doped). Fig. 7 shows the J-V, LE, and EQE of the doped devices (1B-4C), respectively. Compared to the corresponding non-doped devices, all **B** devices using **PFVtPh** as a dopant showed improved EL efficiency, whereas the CIE-coordinates were red-shifted. This suggests that the EL emissions of the B devices originate from the emission of PFVtPh by Förster type energy transfer between the dopant and corresponding hosts. The change in CIE coordinates of the B devices would contribute to the differences in the solvation state in solidstate devices using different hosts. Device 1B, which used the (9,9-dimethyl-9H-fluoren-7-yl) triphenylsilyl end-capping group at the 9-position of the anthracene group (PAFTPS) as a host, exhibited the highest EQE of 2.96% with a luminous efficiency and a power efficiency of 3.91 cd A<sup>-1</sup> and 1.76 lm W<sup>-1</sup> at 20 mA cm<sup>-2</sup>, respectively, which is higher than the corresponding values of 0.93%, 2.49%, and 2.70% for devices 2B, 3B, and 4B. At a driving voltage of 8 V, the CIE coordinates of device 1B were (0.154, 0.159). In the case of device C, the best EQE of 2.32%with a luminous efficiency and a power efficiency of 1.68 cd  $A^{-1}$ and 0.85 lm W<sup>-1</sup> at 20 mA cm<sup>-2</sup>, respectively, was obtained in device 1C, which used PAFTPS as a host. In particular, the CIE coordinates of device 1C (0.155, 0.076) were similar to the standard blue emission recommended by the NTSC. As a result, devices 1A, 1B and 1C using PAFTPS showed higher EL performance and color purity in all devices. Interestingly, the EL spectra of device 2B showed shoulder peaks at 594 and 650 nm, which are different from the BFPSA host device. The shoulder peak emission observed in device 2B might be due not only to an excimer from the intermolecular interactions but also to the exciplex in the device interfaces as a result of the ineffective energy transfer from **BFPSA** to the dopant.

Efficient blue emitting materials are needed to realize efficient white light emission from OLEDs. Among the blue emitting materials (**PAFTPS**, **BFPSA**, **DPA-2FTPS**, and **DPA-2TPS**) in this study, **PAFTPS** is the most suitable candidate owing to its high EL efficiency and color purity. Multilayered WOLEDs were fabricated with the device **1D** structure as follows: ITO/DNTPD



Fig. 8 External quantum efficiency–current density curves of the WOLEDs fabricated from DAF-ph and **PAFTPS** (inset) EL spectra of the WOLEDs at 1000 cd m<sup>-2</sup>.

(60 nm)/NPB (20 nm)/CBP:iridium(III) bis(5-acetyl-2-phenylpyridine)acetylacetonate (Ir(acppy)<sub>2</sub>acac) (8 wt%, 5 nm)/CBP (5 nm)/**PAFTPS**: 1,4-bis(2-diphenylamino-9,9-diethylfluoren-7-ylethenyl)benzene (DAF-ph) (5 wt%, 25 nm)/Bphen (30 nm)/ Liq (2.0 nm)/Al (100 nm). In this study, the blue material DAFph was used as a dopant in a **PAFTPS** host in the blue emitting layer.<sup>26</sup> In addition, CBP was used as the host material for the dopant and Ir(acppy)<sub>2</sub>(acac) in the red emitting layer.<sup>27</sup> Fig. 8 shows the EQE and EL spectra of the WOLEDs at 1000 cd m<sup>-2</sup>. Device **1D** with CIE coordinates of (0.43, 0.41) exhibited a luminous efficiency, a power efficiency and an external quantum efficiency of 9.14 cd A<sup>-1</sup>, 3.44 lm W<sup>-1</sup> and 4.18%, respectively, at 1000 cd m<sup>-2</sup>. This study demonstrates that an anthracene derivative **PAFTPS** has excellent properties for efficient blue fluorescent OLEDs as well as white OLEDs.

## Conclusions

Four anthracene derivatives with triphenylsilane end-capping groups, which have enhanced thermal and morphological stability, were synthesized. The **PAFTPS**-based non-doped device exhibited efficient blue emission with CIE coordinates of (0.152, 0.072), which are very close to the NTSC standard. In addition, an efficient deep blue OLED with color coordinates of (0.155, 0.076) was obtained using **PAFTPS** as a host and 3-(*N*-phenylcarbazol)vinyl-*p*-terphenyl (**PCVtPh**) as a blue dopant. Furthermore, an efficient white OLED with a external quantum efficiency, luminous efficiency and color coordinates of 4.18%, 9.14 cd A<sup>-1</sup> at and (0.43, 0.41) at 1000 cd m<sup>-2</sup> was fabricated by exploiting this highly efficient blue fluorescent material (**PAFTPS**) as a host in the blue emitting layer.

## **Experimental section**

#### General information

Unless stated otherwise all solvents were dried using standard procedures and all reagents were used as received from commercial sources. All reactions were performed under a N<sub>2</sub> atmosphere. 9,10-Dibromoanthracene, 2-bromo-9,10-diphenylanthracene (D), and chlorotriphenylsilane were used as received from Aldrich or TCI. (2-Bromo-9,9-dimethyl-9H-fluoren-7-yl) triphenylsilane (A),<sup>28</sup> 10-bromo-9-phenylanthracene (C),<sup>29</sup> 4'-[2-(2-diphenylamino-9,9-diethyl-9H-fluoren-7-yl)vinyl]-p-terphenyl (PFVtPh),<sup>20</sup> and 3-(N-phenylcarbazol)vinyl-p-terphenyl (PCVtPh)<sup>21</sup> were prepared using a method reported elsewhere. The <sup>1</sup>H- and <sup>13</sup>C-nuclear magnetic resonance (NMR) spectra were recorded on a Varian Unity Inova 300Nb spectrometer. All FT-IR spectra were recorded using a Bruker VERTEX70 FT-IR spectrometer. Elemental analysis (EA) was measured using an EA 1108 spectrometer. The low resolution mass spectra were measured using a Jeol JMS-AX505WA spectrometer in FAB mode and a JMS-T100TD (AccuTOF-TLC) in positive ion mode. The UV-Vis absorption and photoluminescence spectra of the newly designed host materials were measured in a CH<sub>2</sub>Cl<sub>2</sub> solution (10<sup>-5</sup> M) using a Shimadzu UV-1650PC and an Amincobrowman series 2 luminescence spectrometer. The fluorescent quantum yields were determined in a CH<sub>2</sub>Cl<sub>2</sub> solution at 293 K against 9,10-diphenylanthracene as the standard ( $\Phi = 0.90$ ).<sup>30</sup> The ionization potentials (or HOMO energy levels) of the

compounds were measured using a low-energy photo-electron spectrometer (Riken-Keiki, AC-2). The LUMO energy levels were estimated by subtracting the energy band gap from the HOMO energy levels. The energy band gap was determined by the on-set absorption energy from the absorption spectra of the materials. The thermal properties were measured by thermogravimetric analysis (TGA) (DTA-TGA, TA-4000) and differential scanning calorimetry (DSC) (Mettler Toledo; DSC 822) under N<sub>2</sub> at a heating rate of 10 °C min<sup>-1</sup>. A heat-cold-heat method was used with an initial heating rate of 10 °C min<sup>-1</sup>, rapidly quenched-cooled in liquid nitrogen, and finally heated at a rate of 10 °C min<sup>-1</sup>.

#### General procedure for the Suzuki cross-coupling reaction

4,4,5,5-Tetramethyl-2-(9,9-dimethyl-2-(triphenylsilyl)-9*H*-fluoren-7-yl)-1,3,2-dioxaborolane (1.2 or 2.4 mol) and the corresponding arylanthryl bromide derivatives (1.0 mol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.04 mol), aqueous 2.0 M K<sub>2</sub>CO<sub>3</sub> (10.0 mol), Aliquat 336 (0.1 mol), and toluene were mixed in a flask, and heated under reflux for 4 h. After the reaction was complete, the reaction mixture was extracted with ethyl acetate and washed with water. The organic layer was dried with anhydrous MgSO<sub>4</sub> and filtered with silica gel. The solution was then evaporated. The crude product was then recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/EtOH.

(9,9-Dimethyl-2-(10-phenylanthracen-9-yl)-9*H*-fluoren-7-yl)triphenylsilane (PAFTPS). Yield: 89%, <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.96 (d, J = 7.5 Hz, 1H), 7.85 (d, J = 7.5 Hz, 1H), 7.79 (dd, J = 3.3 Hz, 6.9 Hz, 2H), 7.73–7.69 (m, 3H), 7.65 (dd, J = 1.8 Hz, 8.1 Hz, 7H), 7.61–7.55 (m, 4H), 7.51–7.46 (m, 4H), 7.45–7.41 (m, 7H), 7.40–7.38 (m, 1H), 7.33 (dd, J = 3.3, 6.9 Hz, 4H), 1.51 (s, 6H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 154.5, 153.4, 140.8, 139.3, 138.7, 138.5, 137.8, 137.4, 136.7, 135.7, 134.8, 133.2, 131.6, 130.7, 130.5, 130.2, 130.1, 129.9, 128.7, 128.2, 127.7, 127.3, 126.1, 125.3, 125.2, 120.5, 119.8, 47.3, 27.4. FT-IR (ATR cm<sup>-1</sup>): 2981, 2972, 1738, 1429, 1387, 1055, 1033, 1013, 771, 703; MS (FAB<sup>+</sup>, *m/z*): 704 [M<sup>+</sup>]; Anal. Calcd: C, 90.30; H, 5.72. Found: C, 89.18; H, 6.05%.

**9,10-Bis(9,9-dimethyl-2-(triphenylsilyl)-9***H***-fluoren-7-yl)anthracene (BFPSA). Yield: 86%, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): \delta (ppm) 7.97 (d, J = 7.8 Hz, 2H), 7.86 (d, J = 7.2 Hz, 2H), 7.79 (dd, J = 3.3 Hz, 6.9 Hz, 4H), 7.30 (s, 2H), 7.67–7.63 (m, 12H), 7.61–7.60 (m, 2H), 7.56 (d, J = 6.9 Hz, 2H), 7.49–7.38 (m, 20H), 7.35 (dd, J = 3.3 Hz, 6.9 Hz, 4H), 1.52 (s, 12H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): \delta (ppm) 154.5, 153.4, 140.7, 138.7, 138.5, 137.8; 136.7, 135.7, 134.8, 133.2, 130.7, 130.4, 130.3, 129.8, 128.1, 127.3, 125.3, 120.4, 119.8, 47.3, 27.4; FT-IR (ATR, cm<sup>-1</sup>): 2970, 1738, 1366, 1217, 1108, 815, 770, 746, 700; MS (FAB<sup>+</sup>,** *m/z***): 1078 [M<sup>+</sup>]; Anal. Calcd: C, 89.01; H, 5.79. Found: C, 87.53; H, 5.96%.** 

(9,9-Dimethyl-2-(9,10-diphenylanthracen-2-yl)-9*H*-fluoren-7-yl)triphenylsilane (DPA-2FTPS). Yield: 82%, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.95 (s, 1H), 7.80 (d, J = 9.1 Hz, 1H), 7.71–7.65 (m, 7H), 7.60 (d, J = 7.5 Hz, 11H), 7.55–7.53 (m, 5H), 7.52–7.50 (m, 2H), 7.44–7.38 (m, 5H), 7.37–7.32 (m, 6H), 1.42 (s, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 154.8, 153.4, 140.9, 140.5, 139.3, 139.2, 138.6, 137.9, 137.7, 137.3, 136.7, 135.7, 134.7, 133.1, 131.7, 131.6, 130.6, 130.4, 130.2, 129.8, 129.3, 128.7, 128.1, 127.9, 127.8, 127.3, 127.2, 126.7, 125.4, 125.3, 124.8, 121.8, 120.9, 119.8, 47.2, 27.4; FT-IR (ATR, cm<sup>-1</sup>): 2970, 1739, 1428, 1374, 1108, 817, 744, 699; MS (FAB<sup>+</sup>, m/z): 780 [M<sup>+</sup>]; Anal. Calcd: C, 90.73; H, 5.68. Found: C, 89.6; H, 5.85%.

(9,10-Diphenylanthracen-2-yl)triphenylsilane (DPA-2TPS). Yield: 55%, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.94 (s, 1H), 7.74–7.67 (m, 3H), 7.61–7.52 (m, 4H), 7.50–7.47 (m, 8H), 7.39 (dd, J = 2.4 Hz, 6.6 Hz, 5H), 7.36–7.28 (m, 10H), 7.26–7.25 (m, 1H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 138.1, 136.5, 134.2, 131.6, 131.3, 130.5, 129.7, 129.4, 128.6, 128.4, 128.0, 127.7, 127.4, 127.2, 125.9, 125.5, 125.2; FT-IR (ATR, cm<sup>-1</sup>): 2970, 2948, 1739, 1366, 1217, 1033, 760, 746, 697 cm<sup>-1</sup>; MS (EI<sup>+</sup>, *m/z*): 589 [M<sup>+</sup> H]; Anal. Calcd: C, 89.75; H, 5.48. Found: C, 87.4; H, 5.92.

4,4,5,5-Tetramethyl-2-(9,9-dimethyl-2-(triphenylsilyl)-9H-fluoren-7-yl)-1,3,2-dioxaborolane (B). To (2-bromo-9,9-dimethyl-9H-fluoren-7-yl)triphenylsilane (1.4 g, 2.64 mmol) in anhydrous THF (40 mL) was added n-BuLi (1.9 mL of a 1.6 M solution in hexane, 4.74 mmol) within 30 min at -78 °C. After an additional 2-isopropoxy-4,4,5,5,-tetramethyl-1,3,2-dioxaborolane hour, (0.8 mL, 3.96 mmol) was added and reaction mixture and allowed to warm to room temperature. Water was the added, followed by the usual extractive workup with ethyl acetate. The combined organic layers were dried with anhydrous MgSO<sub>4</sub>, filtered, and evaporated to dryness. The crude product was purified by column chromatography with silica gel using ethyl acetate/hexane (1: 20, v/v), affording a white solid at yield of 860 mg (57%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 7.87 (s, 1H), 7.80–7.79 (m, 1H), 7.74 (dd, J = 2.5, 7.4 Hz, 2H), 7.65–7.59 (m, 7H), 7.53 (dd, J = 0.8, 7.6 Hz, 1H), 7.44–7.85 (m, 9H), 1.44 (s, 6H), 1.38 (s, 12H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ (ppm) 153.8, 153.4, 142.2, 140.7, 136.7, 135.5, 134.7, 134.1, 133.8, 130.7, 129.8, 129.0, 128.1, 120.1, 119.9, 84.1, 47.1, 27.3, 25.2; FT-IR (ATR, cm<sup>-1</sup>): 2972, 1461, 1423, 1356, 1144, 1108, 959, 907, 704; MS (EI<sup>+</sup>, *m*/*z*):578 [M<sup>+</sup>].

# **OLED** fabrication and measurement

To fabricate the OLEDs, 100 nm thick indium-tin-oxide (ITO) thin films (sheet resistivity =  $30 \Omega$ ) on glass substrates were used. The ITO-coated glass was cleaned in an ultrasonic bath in the following sequence: acetone, methyl alcohol, distilled water. The substrates were then stored in isopropyl alcohol for 48 h and dried with a  $N_2$  gas gun. The substrates were treated with  $O_2$ plasma under  $1.96 \times 10^{-1}$  Pa at 125 W for 2 min.<sup>31</sup> All organic materials and metals were deposited under high vacuum (6.70  $\times$  $10^{-5}$  Pa). The OLEDs were fabricated in the following sequence: ITO/4,4'-bis(*N*-(1-naphthyl)-*N*-phenylamino)biphenyl (NPB) (50 nm)/blue-emitting materials (30 nm)/4,7-diphenyl-1,10-phenanthroline (Bphen) (30 nm)/lithium quinolate (Liq) (2 nm)/Al (100 nm), NPB as the hole-transporting layer, Bphen as the electron-transporting layer, and Liq:Al as the composite cathode. The current density (J), luminance (L), luminous efficiency (LE), and CIE chromaticity coordinates of the OLEDs were measured using a Keithley 2400, Chroma meter CS-1000A. The electroluminance was measured using a Roper Scientific Pro 300i.

# Acknowledgements

This research was supported by Basic Science Research Program through the NRF funded by the Ministry of Education, Science and Technology (20110004655).

# Notes and references

- 1 C. W. Tang and S. A. Vanslyke, Appl. Phys. Lett., 1987, 51, 913.
- 2 M. A. Baldo, M. E. Thompson and S. R. Forrest, *Nature*, 2000, **403**, 750.
- 3 S. R. Forrest, Nature, 2001, 428, 911.
- 4 J. K. Park, K. H. Lee, S. Kang, J. Y. Lee, J. S. Park, J. H. Seo, Y. K. Kim and S. S. Yoon, *Org. Electron.*, 2010, **11**, 905.
- 5 K. H. Lee, J. H. Seo, Y. K. Kim and S. S. Yoon, J. Nanosci. Nanotechnol., 2009, 9, 7099.
- 6 K. H. Lee, S. M. Kim, J. Y. Kim, Y. K. Kim and S. S. Yoon, Bull. Korean Chem. Soc., 2010, 31, 2884.
- 7 K. H. Lee, L. K. Kang, J. Y. Lee, S. Kang, S. O. Jeon, K. S. Yook, J. Y. Lee and S. S. Yoon, *Adv. Funct. Mater.*, 2010, **20**, 1345.
- 8 K. T. Wong, Y. Y. Chien, R. T. Chen, C. F. Wang, Y. T. Lin, H. H. Chiang, P. Y. Hsieh, C. C. Wu, C. H. Chou, Y. O. Su, G. H. Lee and S. M. Peng, *J. Am. Chem. Soc.*, 2002, **124**, 11576.
- 9 J. Luo, Y. Zhou, Z. Q. Niu, Q. F. Zhou, Y. G. Ma and J. Pei, J. Am. Chem. Soc., 2007, 129, 11314.
- 10 Y. H. Kim, D. C. Shin, S. H. Kim, C. H. Ko, H. S. Yu, Y. D. Chae and S. K. Kwon, *Adv. Mater.*, 2001, **13**, 1690.
- 11 S. J. Lee, J. S. Park, K. J. Yoon, Y. I. Kim, S. H. Jin, S. K. Kang, Y. S. Gal, S. W. Kang, J. Y. Lee, J. W. Kang, S. H. Lee, H. D. Park and J. J. Kim, *Adv. Funct. Mater.*, 2008, **18**, 3922.
- 12 Y. H. Kim, H. C. Jeong, S. H. Kim, K. Yang and S. K. Kwon, Adv. Mater., 2001, 13, 1690.
- 13 S.-K. Kim, B. Yang, Y. Ma, J.-H. Lee and J.-W. Park, J. Mater. Chem., 2008, 18, 3376.
- 14 Y.-Y. Lyu, J. Kwak, O. Kwon, S.-H. Lee, D. Kim, C. Lee and K. Char, Adv. Mater., 2008, 20, 2720.
- 15 P. I. Shih, C. Y. Ghuang, C. H. Chien, E. W. G. Daiu and C. F. Shu, *Adv. Funct. Mater.*, 2007, **17**, 3141.
- 16 K. H. Lee, J. N. You, H. J. Kwon, Y. K. Kim and S. S. Yoon, *Mol. Cryst. Liq. Cryst.*, 2010, 530, 48.
- 17 I. B. Berlan, Handbook of Fluorescence Spectra of Aromatic Molecules, Academic Press, New York, 2nd edn, 1971.
- 18 M. D. Joswick, I. H. Campbell, N. N. Barashkov and J. P. Ferraris, J. Appl. Phys., 1996, 80, 2883.
- 19 B. E. Konne, D. E. Loy and M. E. Thompson, *Chem. Mater.*, 1998, 10, 2235.
- 20 K. H. Lee, Y. S. Kwon, L. K. Kang, G. Y. Kim, J. H. Seo, Y. K. Kim and S. S. Yoon, Synth. Met., 2009, 159, 2603.
- 21 J. H. Seo, K. H. Lee, B. M. Seo, J. R. Koo, S. J. Moon, J. K. Park, S. S. Yoon and Y. K. Kim, Org. Electron., 2010, 11, 1605.
- 22 T.-W. Lee, T. Noh, B.-K. Choi, M.-S. Kim, D. W. Shin and J. Kido, *Appl. Phys. Lett.*, 2008, **92**, 043301.
- 23 T.-W. Lee, O. O. Park, H. N. Cho, J.-M. Hong, C. Y. Kim and Y. C. Kim, *Synth. Met.*, 2001, **122**, 437.
- 24 J. Salbeck, F. Weissörtel, N. Yu, J. Baner and H. Bestgen, Synth. Met., 1997, 91, 209.
- 25 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T. Vreven, Jr, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson,

W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03, Revision B05*, Gaussian, Inc., Pittsburgh, PA, 2003.

- 26 S. O. Kim, K. H. Lee, G. Y. Kim, J. H. Seo, Y. K. Kim and S. S. Yoon, *Synth. Met.*, 2010, 160, 1259.
- 27 J. H. Seo, J. H. Seo, J. H. Park, Y. K. Kim, J. H. Kim, G. W. Hyung, K. H. Lee and S. S. Yoon, *Appl. Phys. Lett.*, 2007, **90**, 203507.
- 28 M. A. Lee, H. J. Kwon, Y. J. Cho, B. O. Kim, S. M. Kim and S. S. Yoon, *KR Pat.*, 857023, 2008.
- 29 Y.-I. Park, J.-H. Son, J.-S. Kang, S.-K. Kim, J.-H. Lee and J.-W. Park, *Chem. Commun.*, 2008, 2143.
- 30 D. F. Eaton, in *Handbook of Organic Photochemistry*, ed. J. C. Scaiano, CRC Press, Boca Raton, FL, 1989, vol. I.
- 31 C. C. Wu, J. C. Sturm and A. Khan, Appl. Phys. Lett., 1997, 70, 1348.