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# Molecular Crystals and Liquid Crystals

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# Synthesis and Electroluminescent Properties of Blue-Light-Emitting Arylene Derivatives End-Capped with Thiophene Groups

# SUHYUN OH,<sup>1</sup> KUM HEE LEE,<sup>1</sup> SEUL ONG KIM,<sup>1</sup> JI HOON SEO,<sup>2</sup> YOUNG KWAN KIM,<sup>2</sup> AND SEUNG SOO YOON<sup>1,\*</sup>

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In this study, four blue fluorescent arylenes end-capped with thiophene derivatives have been synthesized. To explore electroluminescent properties of these molecules, multilayer OLEDs device structure of ITO/NPB/EML/BPhen/Al were fabricated. Two multilayer devices, using **3–4**, showed the efficient deep blue emissions with CIE<sub>xy</sub> of (0.159, 0.092) and (0.151,0.082) at 9.0 V, and the external quantum efficiencies of 1.60 and 0.80%, respectively. A PFVtPh doped-device exhibited the highly efficient blue emission with a maximum luminance of 3480 cd m<sup>-2</sup> at 9.0 V, the external quantum efficiency of 5.23%, and CIE<sub>xy</sub> of (0.151, 0.185) at 9.0 V.

**Keywords** blue OLEDs; fluorescence; host; suzuki cross-coupling reaction; thiophene group

## Introduction

A variety of efficient electroluminescence materials have been investigated over the past two decades because of their promising applications in full-color flat-panel displays [1–3]. Compared to red and green materials, many efforts are still needed to further improve the performance of blue-light-emitting materials because high-performance blue-light-emitting materials exhibiting ideal color purity, good stability, and high fluorescence efficiency remain relatively rare [4–6]. Some of the blue-emitting materials that have been developed include: anthracene [7–11], carbazole [12–14], oligoquinoline [15], others [16,17]. However, EL performances of these blue emitters are still needed to be improved.

Thiophene-based materials have attracted considerable attention because of their potential applications in the area of organic light emitting diodes [18] as they possess good chemical stability and high carrier mobility [19–21]. Recently, a benzothiophenesubstituted compound was reported to have a better electroluminescence performance than a well-known MADN host [22]. In this study, the synthesis and electroluminescent properties of four arylene derivatives, 9,10-bis(benzothiophen-2-yl)anthracene (1), 1,4bis(benzothiophen-2-yl)naphthalene (2), 4,4'-bis(benzothiophen-2-yl)binaphthyl (3), and 4,4'-bis(5-methylthiophen-2-yl)binaphthyl (4) are reported. These new emitters are based

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on arylene emitting units end-capped with thiophene derivatives. In materials 1-3, arylene emitting moieties such as anthracene, naphthalene, and 1,1'-binaphthylene are end-capped with two benzothiophenes to test the effect of the core emitting units on their electroluminescent properties. Furthermore, in materials **3** and **4**, 1,1'-binaphthylene emitting core are connected with two benzothiophenes and 5-methylthiophenes, respectively, to study the effect of the end-capping groups on their electroluminescent properties. As will be seen in below, we evaluate the structural effects of the fluorescent materials on the various thermal and photophysical properties. Also, we demonstrate highly efficient OLEDs using two of these materials, **3** and **4**.

## Experimental

#### Materials and Measurements

All palladium-mediated cross-coupling reactions were performed under a N2 atmosphere. Solvents were carefully dried and distilled from appropriate drying agents prior to use. Thianaphthene-2-boronic acid, 5-methyl-2-thiopheneboronic acid, 9,10dibromoanthracene, and 1,1'-naphthyl were used as received from Aldrich or TCI. The 4,4'-dibromo-1,1'-binaphthyl [23], 9,10-bis(benzothiophen-2-yl)anthracene (1) and 4'-[2-(2-diphenylamino-9,9-diethyl-9H-fluoren-7-yl)vinyl]-p-terphenyl (PFVtPh) were synthesized according to previously reported literature [1,2]. <sup>1</sup>H-NMR spectra were recorded on a Varian Unity Inova 300Nb spectrometer in CDCl<sub>3</sub> as the solvent. The FT-IR spectra were recorded using a Bruker VERTEX70 FT-IR spectrometer. Elemental analysis (EA) was measured using an EA 1108 spectrometer. Low- and high-resolution mass spectra were measured using a Jeol JMS-600 spectrometer in the EI mode and a JMS-T100TD (AccuTOF-TLC) in the positive ion mode. The UV-vis absorption spectra were measured in a dichloromethane solution (10<sup>-5</sup> M) using a Shimadzu UV-1650PC. Photoluminescence spectra were obtained on an Aminco-Browman series 2 luminescence spectrometer. Fluorescent quantum yields were determined in a CH2Cl2 solution at 293 K against the host ( $\Phi_{\text{DPA}} = 0.90$ ) as a standard. Thermal properties were measured using thermogravimetric analysis (TGA) (DTA-TGA, TA-4000 or DTA-6100) under nitrogen at a heating rate of  $10^{\circ}$ C min<sup>-1</sup>. The HOMO (highest occupied molecular orbital) energy levels were determined with cyclic voltammetry (CV) in solutions of 0.1 M supporting electrolyte (tetra-n-butylammonium hexafluorophosphate,  $\text{TBAPF}_{6}$ ) and 1.0 mM substrate in dry dichloromethane under an argon atmosphere, using ferrocene as an internal standard. The LUMO (lowest unoccupied molecular orbital) energy levels were calculated by subtracting the corresponding optical band gap energies from the HOMO energy values. The energy band gaps were determined from the intersection of the absorption and photoluminescence spectra. LUMO (lowest unoccupied molecular orbital) energy levels were calculated by subtracting the corresponding optical band gap energies from the HOMO energy values.

#### Synthesis

General Procedure for the Suzuki Cross-Coupling Reaction. A mixture of thianaphthene-2boronic acid (690 mg, 3.88 mmol), corresponding dibromoarylene (0.97 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (112 mg, 0.097 mmol), Na<sub>2</sub>CO<sub>3</sub> (411 mg, 3.88 mmol) in H<sub>2</sub>O (10 mL), THF (30 mL) and toluene (30 mL) were heated at 85°C under N<sub>2</sub> for 14 h. After the reaction had finished, the solution was extracted twice with toluene. The combined organic layers were washed with brine and dried over MgSO<sub>4</sub>. After filteration and evaporation of the solvent, the crude product was purified by column chromatography (silica gel, hexane:dichloromethane, 10:1).

*1,4-bis(benzothiophen-2-yl)naphthalene* (2): Yield: 78.8%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  8.40–8.37 (m, 2H), 7.93 (d, J = 7.2 Hz, 2H), 7.88 (d, J = 6.7 Hz, 2H), 7.71 (s, 2H), 7.58–7.54 (m, 2H), 7.52–7.51 (m, 2H), 7.45–7.35 (m, 4H); FT-IR (ATR, cm<sup>-1</sup>): 3006, 1738, 1366, 1229, 1033, 827, 770, 744; EIMS (*m*/*z*): 393 [M<sup>+</sup>]. HRMS-TOF (M<sup>+</sup>+H) Calcd for C<sub>26</sub>H<sub>17</sub>S<sub>2</sub> 393.0772, found: 393.0754; Anal. Calcd for C<sub>26</sub>H<sub>16</sub>S<sub>2</sub> C 79.55, H 4.11, S 16.34, found: C 79.03, H 4.17 S 18.28.

4, 4'-bis(benzothiophen-2-yl)binaphthyl (3): Yield: 82.5%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  8.42 (d, J = 8.5 Hz, 2H), 7.94 (d, J = 7.6 Hz, 2H), 7.92–7.89 (m, 2H), 7.79 (d, J = 7.2 Hz, 2H), 7.59–7.55 (m, 6H), 7.52–7.49 (m, 2H), 7.48–7.34 (m, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  142.4, 140.6, 140.5, 139.3, 133.4, 132.7, 132.1, 128.2, 127.5, 127.3, 126.8, 126.6, 126.3, 124.8,124.6, 124.6,123.9,122.4. FT-IR (ATR, cm<sup>-1</sup>): 3007, 1738, 1376, 1216, 1032, 833, 767, 744. EI-MS (*m*/*z*): 519 [M<sup>+</sup>]. HRMS-TOF (M<sup>+</sup>+H) Calcd for C<sub>36</sub>H<sub>23</sub>S<sub>2</sub> 519.1241, found 519.1232; Anal. Calcd for C<sub>36</sub>H<sub>22</sub>S<sub>2</sub> C 83.36, H 4.28, S 12.36, found: C 82.77, H 4.30, S 13.34.

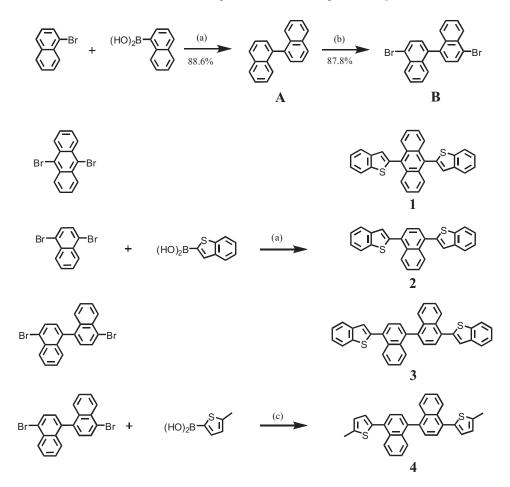
4,4'-bis(5-methylthiophen-2-yl)binaphthyl (4): A mixture of 4,4'-dibromo-1,1'binaphthyl (300 mg, 0.73 mmol), 5-methyl-2-thiophene boronic acid (310 mg, 2.18 mmol), K<sub>3</sub>PO<sub>4</sub> (309 mg, 1.46 mmol), Pd<sub>2</sub>dba<sub>3</sub> (2 mol%) and SPhos (8 mol%) was heated to 80 °C in n-butanol with stirring for 12 h. The crude product was purified via flash column chromatography on silica gel (Hexanes) to provide the title compound in a 36.6% yield (119 mg) as a white solid. Yield: 36.6%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  8.59 (d, J = 8.7 Hz, 2H), 7.66,7.64 (d, J = 7.2 Hz, 2H), 7.52–7.46 (m, 6H), 7.34–7.30 (m, 2H), 7.13–7.12 (d, J = 3.3 Hz, 2H), 6.89–6.88 (m, 2H), 2.61 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  140.4, 139.4, 138.4, 133.2, 132.8, 131.9, 127.5, 127.4, 127.3, 127.0, 126.2, 126.1, 126.0, 125.6, 15.4. EIMS (*m*/*z*): 447[M<sup>+</sup>]. HRMS-TOF (M<sup>+</sup>+H). Calcd for C<sub>30</sub>H<sub>22</sub>S<sub>2</sub>: 446.6257, found: 446.6251.

## Fabrication of OLEDs

To fabricate OLEDs, indium-tin-oxide (ITO) thin films coated on glass substrates were used, which had 30  $\Omega$  per square of sheets resistivity with 100 nm of thickness. The ITO-coated glass was cleaned in an ultrasonic bath by the following sequence: acetone, methyl alcohol, and distilled water; it was then stored in isopropyl alcohol for 48 h and dried by a N2 gas gun. The substrates were treated by  $O_2$  plasma under  $2.0 \times 10^{-2}$  torr at 125 W for 2 min [24]. All organic materials and metals were deposited under high vacuum (5  $\times$  10<sup>-7</sup> torr). Two types of multilayer devices, A and B, were fabricated as follows: (device A) ITO/NPB (50 nm)/blue-emitting material 3-4 (30 nm)/Bphen (30 nm)/Liq (2 nm)/Al; (device B) ITO/NPB (50 nm)/8% PFVtPh: compound 3-4 (30 nm)/Bphen (30 nm)/Liq (2 nm)/Al. where NPB were used as the hole -transporting layer, Bphen as the electron-transporting layer, and Liq: Al as the composite cathode. The CIE coordinates of the OLEDs were measured with a Keithly 2400, Chroma meter CS-1000A. Electroluminescence was measured using a Roper Scientific Pro 300i. The current-voltage-luminance (J-V-L) characteristics, luminous efficiency (LE), Power efficiency (PE), and CIE chromaticity coordinates of the devices were measured using a Keithly 2400 source measurement unit and Chroma meter CS-1000A. Electroluminescence was measured using a Roper Scientific Pro 300i.

#### **Results and Discussion**

Scheme 1 shows the structure and synthetic route of the designed blue fluorescent materials **1–4**. These blue light emitting materials were synthesized by Suzuki coupling reaction between the boronic acid and dibromoarylene afforded the target compounds with moderate yields. After the conventional purifications such as column chromatography and recrystallization, these newly synthesized blue-emitting materials (**1–4**) were purified further by train sublimation at a reduced pressure, below  $10^{-3}$  Torr, and fully characterized with <sup>1</sup>H and <sup>13</sup>C NMR, FT-IR, and low- and high-resolution mass spectrometry.



Scheme 1. Molecular structures and synthetic routes of new host materials (1–4). Condition: (a)  $Pd(PPh_3)_4$ ,  $Na_2CO_3(2M)$ , THF/toluene, reflux, 14 h. (b)  $Br_2/CH_2Cl_2$ , rt, 2 h. (c)  $Pd_2dba_3$ ,  $K_3PO_4$ , XPhos, n-Butanol, reflux, 14 h.

High-temperature resistance is a desired feature of OLED materials because of the unavoidable joule heating under device operating conditions. The thermal properties of **1–4** were measured by thermogravimetric analysis (TGA, TA-4000 or DTA-6100) under nitrogen rate of  $10^{\circ}$ C min<sup>-1</sup>, and are listed in Table 1. The TGA thermogram of the compounds is shown in Fig. 1. All compounds under a nitrogen atmosphere, with the exception of **2**, showed decomposition temperatures (T<sub>d</sub>: corresponding to 5% weight loss)

Compound	$\begin{array}{c} Abs^a\lambda_{max}\\ [nm] \end{array}$	PL <sup>a</sup> λ <sub>max</sub> [nm]	PL <sup>b</sup> λ <sub>max</sub> [nm]	HOMO [eV]	LUMO [eV]	Band gap [eV]	$\Phi^{ m c}$	$T_d \ [^\circ C]^d$
1	380	451, 63	462	5.70	2.66	3.04	0.05	358
2	329	440, 69	450	5.81	2.33	3.48	0.22	248
3	322	439, 68	441	5.82	2.56	3.26	0.56	384
4	328	436, 67	438	5.74	2.48	3.26	0.34	340
MADN	377	425, 54	447	5.50	2.50	3.00	0.54	397

 Table 1. Photophysical data of blue host materials 1–4

<sup>a</sup>CH<sub>2</sub>Cl<sub>2</sub> solution (10<sup>-5</sup> M). <sup>b</sup>Thin film. <sup>c</sup>Using 9,10-diphenylanthracene (DPA) as a standard;  $\lambda_{ex} = 360 \text{ nm}$  ( $\Phi = 0.90$  in CH<sub>2</sub>Cl<sub>2</sub>). <sup>d</sup>Td: the decomposition temperature (5% loss weight).

higher than  $340^{\circ}$ C. The data demonstrates that the thermal stability of these materials improves as the size of the aryl groups at the core unit. The excellent thermal stability of compound **3** may be attributed to a rigid benzothiophenyl-substituted binaphthyl unit in the molecular core structure. Presumably, the non-coplanar molecular structure of **3** resulting from the large distortional angle of the 1,1'-binaphthyl units would enable to form thermally stable amorphous thin films.

UV-vis absorption and photoluminescent (PL) spectra of **1–4** in dichloromethane are shown in Fig. 2, and the results are summarized in Table 1. Compound **1** exhibited a UV-vis absorption peaks at 380 nm with the characteristic vibronic peaks of isolated anthracene, while compounds **2–4** showed shorter main absorption peaks at 329, 322, and 328 nm, respectively. Figure 2(b) shows the emission spectra of blue materials **1–4** with a PL maximum of 439–451 nm. The PL emission spectra of **2–4** are almost identical, whereas the PL spectrum of **1** is red-shifted with a peak at 451 nm. This is likely due to the increase in  $\pi$ -conjugation length by the anthracene group. Also, PL studies on film of **1–4** were also performed to examine the emission in the condensed phase. Particularly, the film of

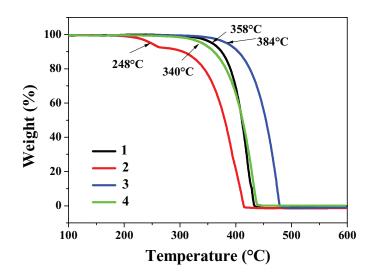


Figure 1. TGA curves of new blue host materials recorded at a heating rate of  $10^{\circ}$ C min<sup>-1</sup>.

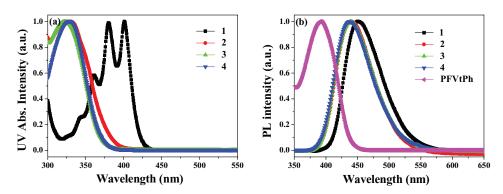


Figure 2. (a) The absorption spectra of new host materials, (b) The emission spectra of new host materials and absorption spectrum of dopant material (PFVtPh) in  $CH_2Cl_2$ .

compounds 3 and 4 exhibited the PL spectra, which are similar to those in the solution state. Thus, compounds 3 and 4 do not appear to reveal severe aggregation due to the nonplanar binaphthyl moieties. In Fig. 2(b), the emission spectra of blue materials 1–4 overlap the absorption spectrum of PFVtPh, indicating that it can more effectively accept energy from materials 2–4 through a Förster-type energy transfer. Particularly, emission spectra of compounds 2–4 showed a favorable overlap with the apsorption of a common blue dopant (PFVtPh), respectively. Thus, this implies that 2–4 can act as good host materials in devices using PFVtPh as a dopant. The quantum yields of compounds 1–4 are given in Table 1. The fluorescence quantum yield of compounds 1–4 in dichloromethane solution at 298 K was measured using ( $\Phi = 0.90$ ) as a calibration standard. The overall quantum yields of all compounds, with the exception of 1, was high ( $\Phi = 0.22-0.56$ ), suggesting that these materials have highly efficient electroluminescent properties in OLED devices.

The highest occupied molecular orbital (HOMO) energy levels of the compounds were calculated using cyclic voltammetry, using a three-electrode cell with ferrocene (4.8 eV) [25] as the internal standard. The respective values of the HOMOs for **1–4** thus calculated were 5.70, 5.81, 5.82, and 5.74 eV, respectively. The four compounds also possessed wide optical energy band gaps between 3.04 - 3.48 eV. From the HOMO values and the optical band gap energies available from the intersection of the absorption and photoluminescence spectra, the LUMO energies of **1–4** were calculated as: 2.66 (**1**); 2.33 (**2**); 2.56 (**3**); 2.46 eV(**4**). These compounds possessed higher energy band gaps than these of PFVtPh (2.82 eV), implying that energy transfer from materials **1–4** to PFVtPh through a Förster energy transfer was expected, indicating them as good host materials in OLED devices using PFVtPh as a dopant.

Compounds **3** and **4** were selected for electroluminescence measurement because of suitable emission wavelengths and higher quantum yields. Two types of multilayer devices, **A** and **B**, were fabricated as follows: (device **A**) ITO/ NPB (50 nm)/ **3** or **4** (30 nm)/ Bphen (30 nm)/ Liq (2 nm)/ Al; (device **B**) ITO/ NPB (50 nm)/ 8% PFVtPh: compound **3** or **4** (30 nm)/ Bphen (30 nm)/ Liq (2 nm)/ Al. Particularly, **B** types of devices were fabricated to test the usefulness of **3** and **4** as the host materials and improve the EL efficiencies of **A** type of devices by doping with the suitable dopant. The schematic device structures and energy level diagrams are shown in Fig. 3. The performance characteristics of these devices are summarized in Table 2. The EL spectra of devices are shown in Fig. 4. The

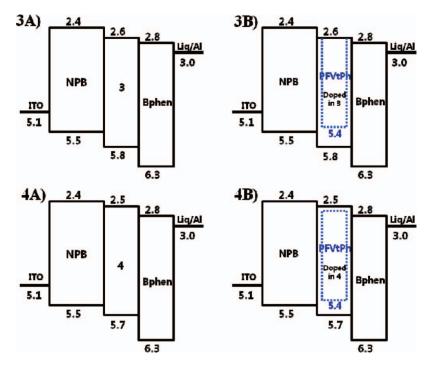


Figure 3. Energy-level diagrams of OLEDs.

current density-voltage (*J*-*V*) and luminance-voltage (*L*-*V*) characteristics for non-doped and doped (8% PFVtPh) devices are shown in Fig. 5(a). Variations in the luminous and power efficiencies of device **A**, as a function of the current density, are shown in Figs 6(a) and (b). The device **3A** using was found to be more efficient than the device **4A**. Presumably, the higher quantum yield of **3** ( $\Phi = 0.56$ ) than that of **4** ( $\Phi = 0.34$ ) would contribute the better EL efficiencies of device **3A** than device **4A**. Device **3A** showed the efficient blue emission with a maximum luminous efficiency of 1.19 cd A<sup>-1</sup>, a maximum quantum efficiency of 1.60% and CIE coordinates of (0.159, 0.092). In order to increase EL efficiencies, these materials were doped with the blue fluorescent dopant PFVtPh at a

Table 2. Electroluminescent characteristics of the devices A (non-doped) and B (doped)

Device	Von <sup>a</sup>	Max. <i>L</i> [cd m <sup>-2</sup> ]	Device efficiency $[cd \ A^{-1}, \\ lm \ W^{-1}, \%]^b$	$\begin{array}{c} \text{Max. efficiency} \\ [\text{cd } A^{-1}, \\ \text{lm } W^{-1}, \%] \end{array}$	EL, FWHM [nm]	CIE [ <i>x</i> , <i>y</i> ] at 9V
3A 3B	3.3 3.0	457	0.97, 0.48, 1.28	, ,	444, 60	0.159, 0.092 0.151, 0.185
3B 4A	5.0 5.6	3465 428	0.56, 0.23, 0.79	0.58, 0.27, 0.80	459, 60 448, 62	0.151, 0.082
4B MADN-A	4.0 4.0	2134 954	3.28, 1.28, 2.05 1.08, 0.48, 0.98	3.61, 2.06,2.27 1.35, 1.01, 1.45	463, 64 442, 55	0.149, 0.219 0.153, 0.080
MADN-B	3.0	13330	9.76, 6.02, 6.40	10.1, 9.86, 6.65	457, 60	0.152, 0.192

<sup>a</sup>Turn-on voltage at 1cd/m<sup>2</sup>. <sup>b</sup>At current density of 20 mAcm<sup>-2</sup>.

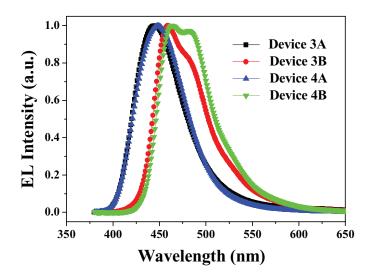


Figure 4. EL spectra of blue emitting devices 3A-4B.

concentration of 8% in the same device structure shown in Fig. 3. Because materials **3** and **4** have higher energy gaps (3.26 eV) compared to the band gap of PFVtPh ( $E_g \sim 2.83 \text{ eV}$ ), it is possible that efficient Förster energy transfer takes place from **3** and **4** to PFVtPh. Thus, the emission of device **3B** and **4B** would originate from the PFVtPh dopant by an efficient energy transfer from host **3–4** (Fig. 2). Also, compared to device **A**, the higher EL efficiencies of device **B** excluded the possible contribution of host **3** to the emission of device **3B**. In addition, the hole-trapping, followed by the direct recombination with electrons at the dopant sites, could additionally contribute to the enhanced EL efficiency. Particularly, PFVtPh dopant in device **3B** can act as a hole trap because the HOMO level of PFVtPh is near 5.4 eV, as measured with a AC-2 photoelectron spectrometer, which is higher than the host material **3** (5.82 eV). As a result, device **3B** shows the highly efficient blue emission with a maximum luminous efficiency of 7.58 cd A<sup>-1</sup>, a maximum quantum efficiency of 5.18% and the CIE coordinates of (0.151, 0.185). Notably, doped-devices **3B** and **4B** showed higher EL efficiency than non-doped devices **3A** and **4A**, which may be due partly to the effective exciton formation on dopant materials. This study clearly

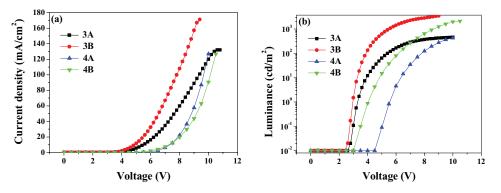
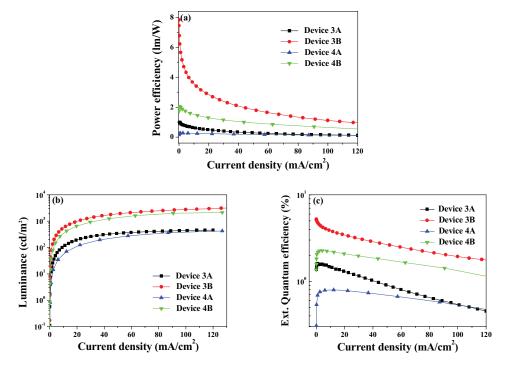


Figure 5. J-V characteristics (a) and L-V characteristics (b) of the devices 3A-4B.



**Figure 6.** Power efficiencies (a), luminous efficiencies (b), and external quantum efficiencies (c) as a function of voltage for the devices **3A–4B**.

suggests that efficiencies of blue OLEDs can be improved by doping with the suitable dopant in a host. Interestingly, compared device **MADN B**, the CIE coordinates of device **3B** the improved from (0.152, 0.192) to (0.151,0.185). Presumably, the different solvation of dopant PFVtPh in MADN and compound **3** would contribute to the improved the blue color coordinates of device **3B**. This study clearly demonstrates the excellent properties of host material **3**, containing thiophene groups, for application in deep blue emitting materials in OLEDs.

### Conclusions

We demonstrated synthesis and electroluminescent properties of blue fluorescent arylene derivatives end-capped with benzothiophene and thiophene groups. A facile synthesis of these arylene derivatives was achieved with palladium-catalyzed Suzuki cross coupling as a key step. The non-doping OLED device using the compound **3** showed the efficient deep blue emission with a maximum luminance efficiency of 1.19 cd  $A^{-1}$ , a maximum external quantum efficiency of 1.60% and CIE coordinate of (0.159, 0.092) at 9.0 V. Moreover, using the compound **3** as a blue host for the PFVtPh dopant, device **3B** furnished a efficient blue OLED with a maximum luminous efficiency of 7.58 cd  $A^{-1}$  (4.90 cd  $A^{-1}$  at 20 mA cm<sup>-2</sup>), maximum power efficiency of 7.82 lm W<sup>-1</sup> (2.80 lm W<sup>-1</sup> at 20 mA cm<sup>-2</sup>), maximum external quantum efficiency of 5.23% (3.42% at 20 mA cm<sup>-2</sup>), and CIE coordinate of (0.151, 0.185) at 9.0 V.

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