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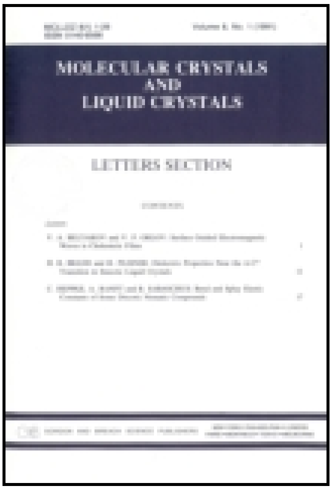

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Two Anthracene-Containing Materials for Blue Organic Light-Emitting Diodes

Seung Soo Yoon[a], Hye Jeong Kim[a], Young Kwan Kim[b], Song Eun Lee[b] & Seok Jae Lee[b]

[a] Department of Chemistry, Sungkyunkwan University, Suwon, Korea

[b] Department of Information Display, Hongik University, Seoul, Korea

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Two Anthracene-Containing Materials for Blue Organic Light-Emitting Diodes

SEUNG SOO YOON,[1,*] HYE JEONG KIM,[1]
YOUNG KWAN KIM,[2] SONG EUN LEE,[2] AND SEOK JAE LEE[2]

[1]Department of Chemistry, Sungkyunkwan University, Suwon, Korea
[2]Department of Information Display, Hongik University, Seoul, Korea

*We have designed and synthesized anthracene-benzene-anthracene containing blue emitters **1-3** end-capped with the various aryl groups using Suzuki cross coupling reaction. Multilayered OLEDs with the device structure of ITO/NPB (50 nm)/blue emitters (**1-3**) (40 nm)/Alq$_3$ (15 nm)/Liq/Al were fabricated by using the compounds as blue emitting materials. All devices showed efficient blue emissions. Particularly, a highly efficient blue OLED was fabricated, showing the maximum luminance of 4674 cd/m^2 at 9.5 V, the luminous efficiency of 1.95 cd/A, the power efficiency of 0.93 lm/W, the external quantum efficiency of 2.05% at 200 cd/m^2 and CIEx,y coordinates of (0.163, 0.096) at 8.5V.*

Keywords Organic light-emitting diode; full-color display; blue fluorescence; anthracene; Suzuki cross-coupling reaction; excimer

Introduction

Over the past decades, significant progress has been made in organic light-emitting diodes (OLEDs) because of their potential application in full-color flat-panel displays and solid-state lighting [1]. For full-color displays, it is required to high EL efficiencies of red, green and blue emitters. Among the three primary-color emitters (red, green and blue) in OLEDs, blue light-emitting materials are still rare because of wide band gaps [2, 3].

Recently, anthracene derivatives have been studied to be excellent candidates in efficient blue OLEDs [4, 5, 6, 7]. However, it is needed to be improved EL efficiencies and color purity for the practical applications [8, 9, 10, 11]. Among diphenylanthracene derivatives, blue OLED with fluorescent 1,4-Bis(10-phenylanthracen-9-yl)benzene reported high EL efficiencies of 3.16 cd/A, 1.60 lm/W, 1.80% at 20 mA/cm^2 [12].

In this study, we have synthesized three blue emitters **1-3** based on Anthracene-Benzene-Anthracene core units with the various end-capping groups such as phenyl and naphthyl groups; 1,4-Bis(10-phenylanthracen-9-yl)benzene (**1**), 1,4-Bis(10-(1-naphthyl)anthracen-9-yl)benzene (**2**), 1,4-Bis(10-(2-naphthyl)anthracen-9-yl)benzene (**3**). Anthracene has excellent photoluminescence (PL) and thermal stability as an emitting material. Furthermore, the end-capping groups of **1-3** such as phenyl and naphthyl groups

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[*] Address correspondence to Prof. Seung Soo Yoon Department of Chemistry Sungkyunkwan University 300, Cheoncheon-dong, Jangan-gu, Suwon, Gyeonggi-do, 440-746 Korea (ROK). Tel.: (+82)31-290-7071; Fax: (+82)31-290-7075. E-mail: ssyoon@skku.edu

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would induce the non-planar structural features of **1**-**3**, which prevent the intermolecular interaction and the self-aggregation of **1**-**3** in solid state devices [13, 14]. Therefore, these materials **1**-**3** with two anthracene moieties end-capped with phenyl and naphthyl groups have been expected to be excellent candidates in efficient blue OLEDs.

Experimental

Synthesis

General Procedure for the Suzuki Cross Coupling Reaction: the corresponding 10-arylanthracen-9-yl-boronic acid; 10-phenylanthracen-9-ylboronic acid (1.52 g, 5.09 mmol), 10-(1-naphthyl)anthracen-9-ylboronic acid or 10-(2-naphthyl)anthracen-9-ylboronic acid (1.77 g, 5.09 mmol) and 2,4-dibromobenzene (0.5 g, 2.12 mmol), Pd(PPh$_3$)$_4$ (980 mg, 0.08 mmol), aqueous 2.0 M Na$_2$CO$_3$ (3.2 ml, 6.3 mmol), ethanol, and toluene were mixed in a flask under N$_2$ gas. The mixture was refluxed for 4 h. After the reaction was completed, water was added to quench the reaction. After cooling, the crude solid was collected by filtration, washed with water and ethanol. The product was purified recrystallization from CH$_2$Cl$_2$/EtOH.

1,4-Bis(10-phenylanthracen-9-yl)benzene (**1**) Yield: 82%. ^{1}H-NMR (CDCl$_3$) δ : 7.99 (d, 3H, Ar-***H***), 7.77 (d, 4H, Ar-***H***), 7.74 (s, 3H, Ar-***H***), 7.67-7.58 (m, 7H, Ar-***H***), 7.56-7.47 (m, 9H, Ar-***H***), 7.44-7.38 (m, 5H, Ar-***H***) ^{13}C-NMR (CDCl$_3$) δ : 139.3, 138.4, 137.1, 131.6, 131.5, 130.2, 130.2, 128.6, 127.7, 127.3, 127.2, 125.4, 125.3, 125.3 FT-IR (ATR) cm^{-1}: 3061(Ar CH), 2360, 2341, 1736, 1440(Ar C=C), 1368, 764, 702(Monosubst. oop). MS (APCI$^+$) m/z 582 (M$^+$).

1,4-Bis(10-(1-naphthyl)anthracen-9-yl)benzene (**2**) Yield: 74%. ^{1}H-NMR (CDCl$_3$) δ: 8.10 (d, 3H, Ar-***H***), 8.05 (d, 5H, Ar-***H***), 7.85 (dd, 3H, Ar-***H***), 7.81 (dd, 2H, Ar-***H***), 7.74 (t, 3H, Ar-***H***), 7.64 (dd, 2H, Ar-***H***), 7.53-7.47 (m, 10H, Ar-***H***), 7.33-7.26 (m, 6H, Ar-***H***) ^{13}C-NMR (CDCl$_3$) δ: 138.5, 137.4, 137.0, 135.4, 133.9, 133.8, 131.7, 131.0, 130.3, 129.4, 128.4, 128.3, 127.4, 127.2, 126.8, 126.5, 126.2, 125.8, 125.5, 125.4 FT-IR (ATR) cm^{-1}: 2964(Ar CH), 2355, 1740, 1442(Ar C=C), 1221, 1056, 869(Para-subst. oop), 934, 763, 696(Monosubst. oop). MS (APCI$^+$) m/z 682 (M$^+$).

1,4-Bis(10-(2-naphthyl)anthracen-9-yl)benzene (**3**) Yield: 86%. ^{1}H-NMR (CDCl$_3$) δ: 8.12 (d, 3H, Ar-***H***), 8.07-8.01 (m, 8H, Ar-***H***), 7.97-7.94 (m, 2H, Ar-***H***), 7.80 (d, 4H, Ar-***H***), 7.77 (s, 3H, Ar-***H***), 7.68 (dd, 2H, Ar-***H***), 7.64-7.61 (m, 4H, Ar-***H***), 7.54-7.48 (m, 4H, Ar-***H***), 7.42-7.36 (m, 4H, Ar-***H***) ^{13}C-NMR (CDCl$_3$) δ: 138.4, 137.3, 137.2, 136.8, 133.6, 133.0, 131.6, 130.4, 130.3, 130.2, 129.7, 128.3, 128.2, 128.1, 127.3, 127.2, 126.6, 126.4, 125.4, 125.4 FT-IR (ATR) cm^{-1}: 3118(Ar CH), 2929(aliphatic CH), 1739, 1442(Ar C=C), 1370, 1222, 862(Para-subst. oop), 772, 694(Monosubst. oop). MS (APCI$^+$) m/z 682 (M$^+$).

Fabrication of OLED

For fabricating OLEDs, indium-tin-oxide (ITO) thin films coated on glass substrates were used, which was 30 square of the sheet resistivity, and 100 nm of thickness. The ITO-coated glass was cleaned in an ultrasonic bath by the following sequence: acetone, methyl alcohol, distilled water, and stored in isopropyl alcohol for 48 h and dried by a N$_2$ gas gun. The substrates were treated by O$_2$ plasma under 2.0×10^{-2} torr at 125 W for 2 min. All organic materials and metals were deposited under high vacuum (5×10^{-7} torr). The OLEDs were fabricated in the following sequence: ITO /4,4′-Bis(N-(1-naphthyl)-N-phenylamino)biphenyl (NPB) (50 nm) /Blue emitting materials (**1-3**) (40 nm)

/Tris(8-hydroxyquinolinato)aluminium (Alq_3) (15 nm) /Lithium quinolate (Liq) (2 nm) /Al (100 nm), NPB as the hole-transporting layer, Alq_3 as the electron-transporting layer, and Liq:Al as the composite cathode.

Measurements

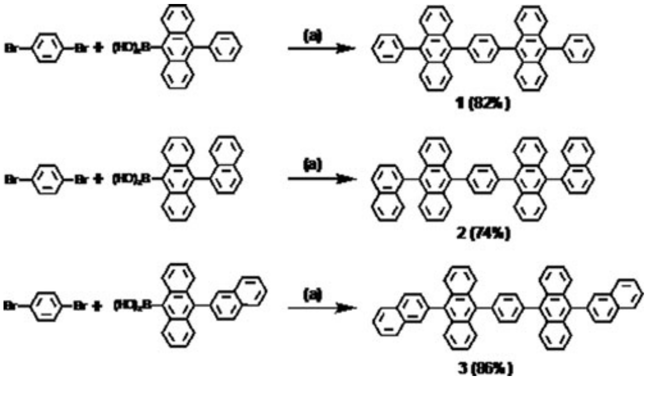
^{1}H- and ^{13}C-NMR were recorded on a Varian Unity Inova 300Nb spectrometer. FT-IR spectra were recorded using a Bruker VERTEX70 FT-IR spectrometer. Low- resolution mass spectra were measured using a Jeol JMS-600 spectrometer in the APCI mode.

The UV-Vis absorption and photoluminescence spectra were measured in dichloromethane (10^{-5} M) using Shimadzu UV-1650PC and Aminco-Browman series 2 luminescence spectrometers. The fluorescence quantum yields of the emitting materials were determined in dichloromethane at 293 K against DPA (9,10-diphenylanthracene) as a reference ($\Phi_{DPA} = 0.90$). The HOMO (highest occupied molecular orbital) energy levels were measured with a low-energy photoelectron spectrometer (Riken-Keiki, AC-2). The energy band gaps were determined from the intersection of the absorption and photoluminescence spectra. The LUMO (lowest unoccupied molecular orbital) energy levels were calculated by subtracting the corresponding optical band gap energies from the HOMO energy values.

The current density (J), luminance (L), luminous efficiency (LE) power efficiency (PE), external quantum efficiency (EQE) and CIE chromaticity coordinates of the OLEDs were measured with a Keithly 2400, Chroma meter CS-1000A. Electroluminance was measured using a Roper Scientific Pro 300i.

Results and Discussion

The synthetic method of the designed blue fluorescent materials **1-3** and its structures are shown Scheme 1. The compounds **1-3** are prepared by Suzuki cross coupling reaction between the corresponding 10-arylanthracene-9-boronic acid and 2,4-dibromobenzene with moderate yields (74-86%). After the conventional purification such as recrystallization, these blue materials **1-3** were fully characterized with ^{1}H- and ^{13}C-NMR, and mass spectroscopy.



Scheme 1. Synthesis of blue materials (**1-3**). (a) $Pd(PPh_3)_4$, 2M Na_2CO_3, toluene, EtOH, reflux, 4 h.

Figure 1 shows the UV-vis absorption and PL emission spectra of blue fluorescent materials **1–3** in dichloromethane solutions and on quartz plate films. The absorption

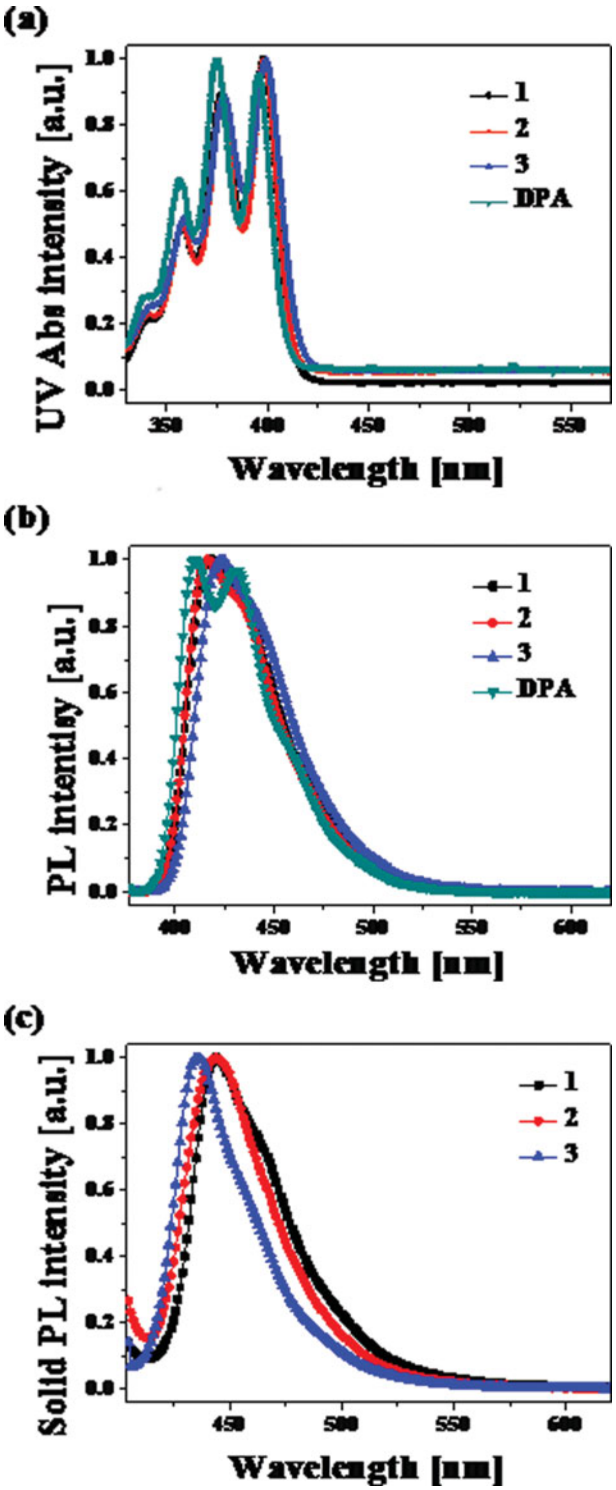


Figure 1. (a) The absorption spectra, (b) emission spectra in solution and (c) emission spectra in solid state film of blue materials (**1-3**).

Table 1. Optical properties of blue materials (**1-3**)

Compound	UV_{max} ^{a} [nm]	PL_{ma} ^{a} [nm]	PL_{max} ^{b} [nm]	FWHM [nm]	HOMO/ LUMO [eV]	E_g [eV]	Φ^c [%]
1	398	417	444	56	−5.85/−2.79	3.06	0.85
2	398	417	444	50	−5.82/−2.76	3.06	0.84
3	399	424	435	51	−5.80/−2.77	3.03	0.80

a. CH_2Cl_2 solution (10^{-5} M). b. Thin film. c. Using DPA(9,10-diphenylanthracene) as a standard; $\lambda_{ex} = 360$ nm ($\Phi = 0.90$ in CH_2Cl_2). Ref. 18

spectra of the compounds in CH_2Cl_2 solution show the characteristic vibronic band from the $\pi-\pi^*$ transitions of the isolated anthracene group (λ_{max} are about 358, 378 and 398 nm) [15, 16]. As shown in Table 1,blue fluorescent materials **1-3** showed blue emission with maximum emission wavelengths at 417, 417 and 424 nm in solution. In comparison with material **3**, the emission spectra of **1** and **2** in solution showed blue shifted emissions by 7 nm due to the shorter π-conjugation length of **1** and **2**. On the contrary, the emission spectra in solid state films is slightly red shifted by 11-27 nm in comparison with the solution PL spectra due to the solid state effect [17].

The energy band gaps of the blue fluorescent materials **1-3** ranged from 3.03 to 3.06 eV, and The HOMO energy levels of compounds **1-3** measured by AC-2 are −5.85, −5.82 and −5.80 eV, respectively. The LUMO energy levels are −2.79, −2.76, −2.77 eV, respectively. These blue emitters **1-3** show good quantum yields of 0.85, 0.84 and 0.80, which are expected to show high efficient electroluminescent properties in OLED devices.

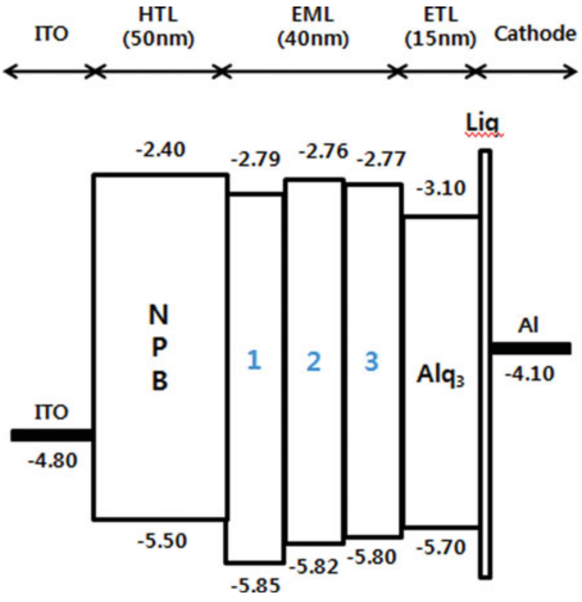


Figure 2. Energy levels diagram of compounds (**1-3**) used in the OLED fabrication.

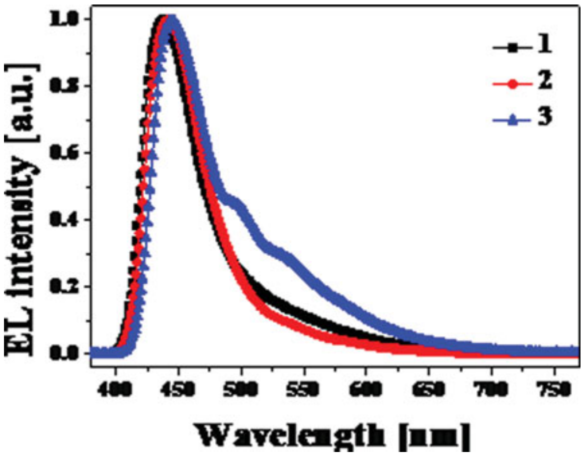


Figure 3. EL spectra of the devices **1-3**.

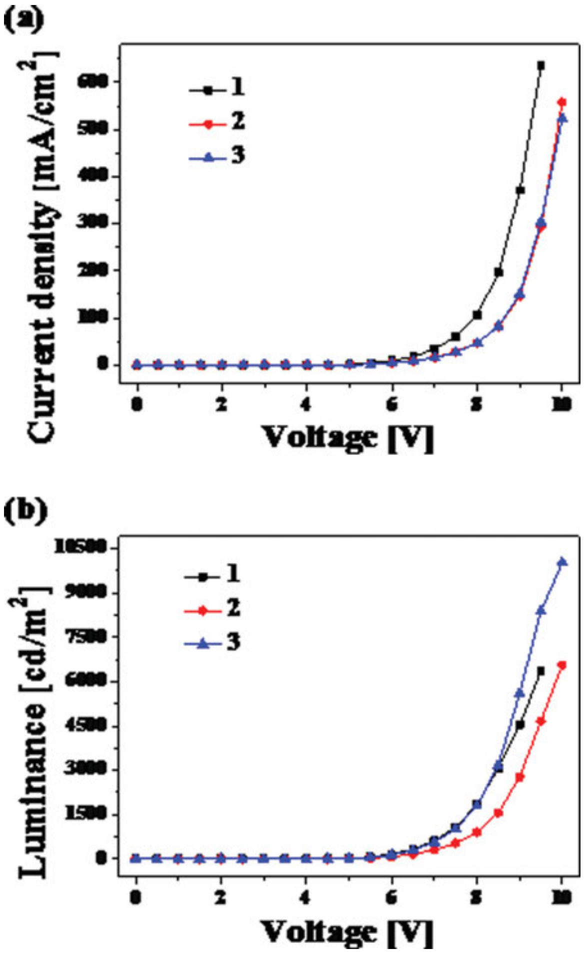


Figure 4. (a) *Current density-Voltage (J-V)* and (b) *Luminance-Voltage (L-V)* curves.

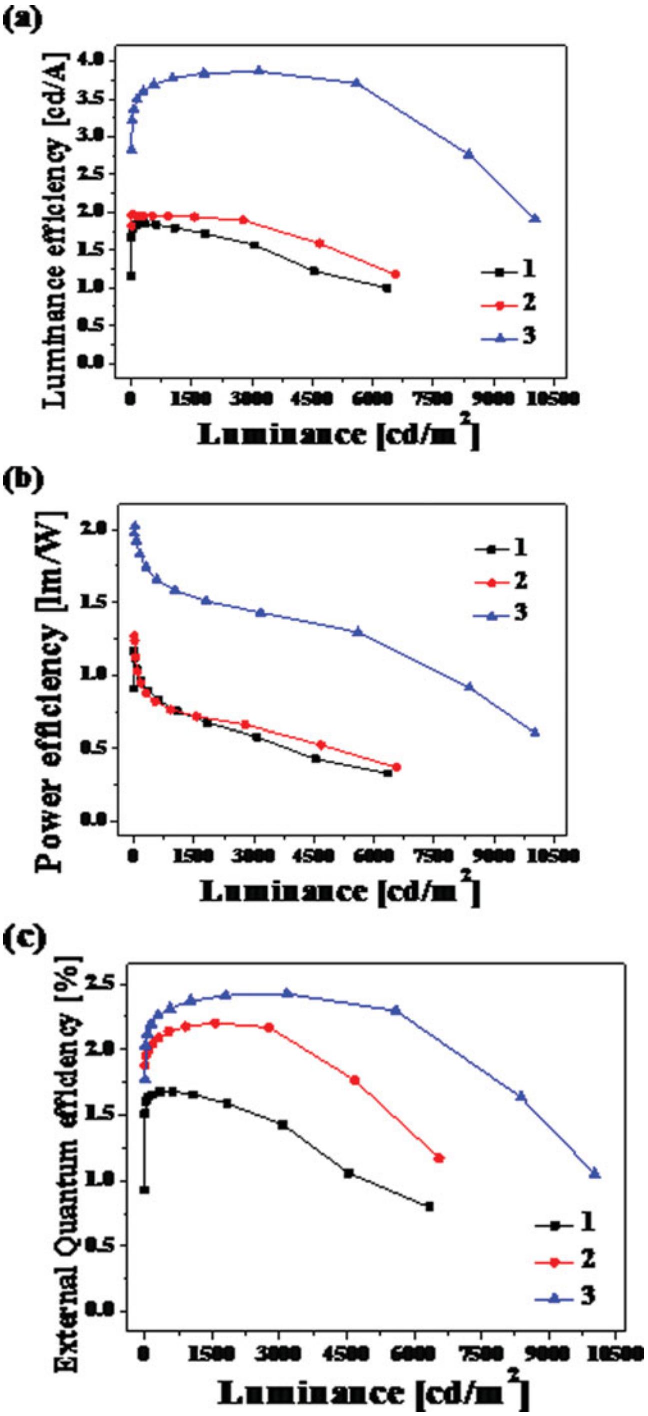


Figure 5. (a) Luminous efficiencies, (b) power efficiencies and (c) external quantum efficiencies as a function of luminance for the devices **1-3**.

Table 2. EL performance characteristic of the devices **1-3**

Device	$\lambda_{,max}$ / FWHM [a] [nm]	J [b] [mA/cm^2]	L [b] [cd/m^2]	LE [c/d] [cd/A]	PE [c/d] [lm/W]	EQE [c/d] [%]	CIE [e] (x,y)
1	437 / 52	636	6349	1.85 / 1.84	1.16 / 0.95	1.68 / 1.66	(0.179, 0.127)
2	444 / 53	294	4674	1.97 / 1.95	1.27 / 0.93	2.20 / 2.05	(0.163, 0.096)
3	444 / 55	303	8383	3.86 / 3.52	2.02 / 1.79	2.42 / 2.22	(0.197, 0.197)

a. Emission maximum and FWHM of EL emission spectra. b. Current density and Luminance at 9.5 V. c. Maximum values. d. At 200 cd/m^2. e. Commission Internationale d'Énclairage (CIE) at 8.5 V

Figure 2 shows the energy level diagrams of devices using compounds **1-3**. We have fabricated in the following sequence: ITO /4,4′-Bis(N-(1-naphthyl)-N-phenylamino)biphenyl (NPB) (50 nm) /Blue emitting materials (**1-3**) (40 nm) /Tris(8-hydroxyquinolinato)aluminium (Alq$_3$) (15 nm) /Lithium quinolate (Liq) (2 nm) /Al (100 nm), NPB as the hole-transporting layer, Alq$_3$ as the electron-transporting layer, and Liq:Al as the composite cathode.

As shown in Figure 3, the devices **1-3** exhibit blue emission at 437-444 nm, which are similar to PL spectra of materials **1**-**3** in solid state films. All devices show blue emission with CIE$_y$ < 0.20. The CIE coordinates of devices **1-3** were (0.179, 0.127), (0.163, 0.096), and (0.197, 0.197), respectively at a driving voltage of 8.5 V. Presumably, 1-naphthyl end-capping groups of material **2** in device **2** would prevent the unfavorable crystallization and excimer formation in the film state and thus lead to the most deep blue emission of device **2**.

Figure 4 shows current density-voltage-luminance (*J*-*V*-*L*) characteristics of the devices **1-3**. The device **3** exhibits a maximum brightness of 8383 cd/m^2 and a current density of 303 mA/cm^2 at a voltage of 9.5 V.

The luminous and power efficiencies and external quantum efficiencies of devices **1–3**, as a function of the luminance, are shown in Figure 5. The maximum luminous efficiencies were 1.84, 3.32 and 3.52 cd/A, maximum power efficiencies of 0.95, 0.93, and 1.79 lm/W, and maximum external quantum efficiencies 1.66, 2.05 and 2.22% at 200 cd/m^2, respectively. The device **3** has the high efficiencies because its HOMO energy level is closer to that of NPB as the hole transporting layer and has lower hole-injection energy barrier than those of other devices **1-2**. This study suggests that the emitting materials **1**-**3** have the excellent properties for blue OLEDs.

Conclusions

We have synthesized two anthracene-containing blue emitters **1-3** based on Anthracene-Benzene-Anthracene moieties using Suzuki cross coupling reaction. Their electroluminescent properties were investigated by fabrication of multilayered OLEDs. All devices showed efficient blue emissions. Particularly, the device **3** shows the high efficiencies with the luminous efficiency of 3.52 cd/A, the power efficiency of 1.79 lm/W, the external quantum efficiency of 2.22% at 200 cd/m^2. Moreover, the device **2** is deep-blue region CIE$_{x,y}$ coordinates of (0.163, 0.096) at 8.5V and exhibit high efficiencies of 3.32 cd/A, 0.93 lm/W and 2.05%. This study clearly suggests that the emitting materials **1**-**3** have the excellent properties for blue OLEDs.

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