



# Blue Emitters Based on Anthracene-Aryl-Anthracene Moieties End-Capped with 1-Naphthyl Groups for Organic Light-Emitting Diodes

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We have designed emitters based on Anthracene-Aryl-Anthracene moieties end-capped with 1-naphthyl groups. In particular, a device showed blue EL properties with luminous and power efficiencies of 1.95 cd/A and 0.93 lm/W at 200 cd/m<sup>2</sup> respectively, and CIE coordinates of (0.16, 0.10) at 7.0 V.

Keywords: Organic Light-Emitting Diode, Blue Fluorescence, Anthracene, Suzuki Reaction.

Delivered by Publishing Technology to: Chinese University of Hong Kong IP: 109.161.209.100 On: Mon, 07 Dec 2015 15:33:06 Copyright: American Scientific Publishers 2. EXPERIMENTAL DETAILS

#### **1. INTRODUCTION**

Organic light-emitting diodes (OLED) have been attracting considerable attention due to its potential applications in organic flat-panel displays and solid-state lighting.<sup>1</sup> For full-color display applications, blue, green, and red emitters that have high emission, efficiencies and color purity are required. Particularly, it is needed to be improved EL efficiencies and color purity of blue emitting materials for the practical applications.<sup>2,3</sup> In this study, we have designed and synthesized four emitters 1-4 based on Anthracene-Aryl-Anthracene moieties end-capped with 1-naphthyl groups. Anthracene derivatives have excellent photoluminescence (PL) and thermal stability as an emitting material.<sup>4,5</sup> Furthermore, the end-capping groups of compounds 1-4 such as 1-naphthyl groups would induce the non-planar structural features of compounds 1-4, which prevent the intermolecular interaction and the self-aggregation in solid state devices. Furthermore, two anthracene moieties end-capped with 1-naphtyl groups in compounds 1-4 were connected through by the various aryl-spacer groups such as *m*-phenylene, *p*-phenylene, 1,4biphenylene and 2,7-dimethylfluorene. Therefore, compounds 1-4 may expect to be excellent candidates in efficient OLEDs.

## 2.1. Synthesis

General Procedure for the Suzuki Cross Coupling Reaction 9-(1-naphthyl)anthracen-10-yl-boronic acid (2.4 mol) and the corresponding aryl bromides (1.0 mol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.04 mol), aqueous 2.0 M Na<sub>2</sub>CO<sub>3</sub> (10.0 mol), ethanol, and toluene were mixed in a flask. 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<sub>2</sub>Cl<sub>2</sub>/EtOH.

### 2.1.1. 1,3-bis(10-(naphthalen-1-yl)anthracen-9-yl) Benzene (1)

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) [ $\delta$  ppm]: 8.06 (*s*, 8 H), 8.01–7.92 (*m*, 3 H), 7.80–7.77 (*m*, 3 H), 7.72–7.68 (*m*, 3 H), 7.62 (*s*, 1 H), 7.52–7.45 (*m*, 13 H), 7.14–7.05 (*m*, 3 H). MS (APCI<sup>+</sup>) m/z 682 (M<sup>+</sup>).

## 2.1.2. 1,4-bis(9-(1-naphthyl)anthracene-10-yl) Benzene (2)

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) [ $\delta$  ppm]: 8.12 (d, J = 8.1 Hz, 3 H), 8.06 (d, J = 8.4 Hz, 5 H), 7.86 (dd, J = 6.9 Hz, 3 H), 7.82 (dd, J = 6.6 Hz, 2 H), 7.77 (t, J = 7.5 Hz, 3 H), 7.65

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Park et al.

Blue Emitters Based on Anthracene-Aryl-Anthracene Moieties End-Capped with 1-Naphthyl Groups for OLED



**Scheme 1.** Structure and synthetic routes of compounds (1–4). (a) 9-(1-naphthyl)anthracen-10-yl-boronic acid,  $Pd(PPh_3)_4$ , 2 M  $Na_2CO_3$ , Toluene, EtOH, reflux, 4 h.

(*dd*, *J* = 6.6 Hz, 2 H), 7.53–7.47 (*m*, 10 H), 7.33–7.26 (*m*, 6 H). MS (APCI<sup>+</sup>) m/z 682 (M<sup>+</sup>).

#### 2.1.3. 4,4'-bis(9-(1-naphthyl)anthracene-10yl)Biphenyl (3)

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) [ $\delta$  ppm]: 8.10–8.03 (*m*, 8 H), 7.92 (*d*, *J* = 8.7 Hz, 4 H), 7.77–7.69 (*m*, 6 H), 7.63 (*dd*, *J* = 6.9 Hz, 2 H), 7.53–7.47 (*m*, 6 H), 7.42–7.37 (*m*, 4 H), 7.29–7.23 (*m*, 8 H). MS (APCI<sup>+</sup>) m/z 759 (M<sup>+</sup>).

### 2.1.4. 10-(9,9-dimethyl-2-(10-(naphthalen-1yl)anthracen-9-yl)-9H-fluoren-7-yl)-9-(naphthalen-1-yl)Anthracene (4)

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) [ $\delta$  ppm]: 8.13 (t, J = 7.5 Hz, 2 H), 8.10 (d, J = 8.5 Hz, 2 H), 8.04 (d, J = 8.0 Hz, 2 H), 7.91 (d, J = 9.0 Hz, 4 H), 7.74–7.70 (m, 4 H), 7.63–7.60 (m, 4 H), 7.50–7.48 (m, 6 H), 7.40–7.36 (dd,



Figure 1. The absorption spectra and emission spectra in solution of blue materials (1–4).

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Table I. Optical properties of	compounds $(1-4)$ .
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Compound	UV	$\mathrm{PL}^{a}$	$\mathrm{PL}^b$	FWHM	НОМО	LUMO	$E_g$	$\Phi^c$
1	398	417	442	44	-5.85	-2.68	3.17	0.58
2	398	417	442	50	-5.82	-2.76	3.06	0.84
3	377	419	442	49	-5.88	-2.83	3.05	0.77
4	396	425	442	49	-5.85	-2.73	3.12	0.46

*Notes*: <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 DPA(9,10-diphenylanthracene) as a standard;  $\lambda_{ex} = 360 \text{ nm} (\Phi = 0.90 \text{ in CH}_2\text{Cl}_2).$ 



Figure 2. EL spectra of the devices (1-4).

J = 6.5 Hz, 4 H), 7.28–7.26 (m, 4 H), 7.23–7.21 (m, 4 H). MS (APCI<sup>+</sup>) m/z 799 (M<sup>+</sup>).

#### 2.2. OLED Fabrication and Measurement

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<sub>2</sub> gas gun. The substrates were treated by O<sub>2</sub> plasma under  $2.0 \times 10^{-2}$  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)



Figure 3. Luminous efficiencies and power efficiencies as a function of luminance for the devices (1–4).

Blue Emitters Based on Anthracene-Aryl-Anthracene Moieties End-Capped with 1-Naphthyl Groups for OLED

Park et al.

Table II.	EL properties of devices (1-4).								
Device	$\lambda_{\max}$ [nm]	$J^a$ [mA/cm <sup>2</sup> ]	$L^a$ [cd/m <sup>2</sup> ]	$LE^{b/c}$ [cd/A]	$PE^{b/c}$ [lm/W]	$\operatorname{CIE}^d(x,y)$			
1	442, 498, 537	74	1513	2.10/2.06	1.09/0.91	(0.23, 0.26)			
2	442	147	2781	1.97/1.95	1.27/0.93	(0.16, 0.10)			
3	553	225	4009	3.32/3.32	2.49/1.90	(0.41, 0.54)			
4	442, 538	150	2798	3.91/3.90	2.63/2.08	(0.30, 0.45)			

Notes: "Current density and luminance at 9.0 V; "Maximum values; "At 200 cd/m2; "Commission Internationale d'Énclairage (CIE) at 7.0 V.

biphenyl (NPB) (50 nm)/Blue emitting materials (1– 4) (40 nm)/Tris(8-hydroxyquinolinato)aluminium (Alq<sub>3</sub>) (15 nm)/Lithium quinolate (Liq) (2 nm)/Al (100 nm), NPB as the hole-transporting layer, Alq<sub>3</sub> as the electrontransporting layer, and Liq:Al as the composite cathode. All EL properties of the OLEDs were measured with a Keithly 2400, Chroma meter CS-1000A. Electroluminance was measured using a Roper Scientific Pro 300i.

#### 3. RESULTS AND DISCUSSION

Scheme 1 shows the synthetic route of the designed blue fluorescent materials **1–4** and its structures. The compounds **1–4** were synthesized using the Suzuki cross coupling reaction between the 9-(1-naphthyl)anthracenyl-10-boronic acid and the corresponding aryl bromides with moderate yields (70–86%).

Figure 1 shows the UV-vis absorption and PL emission spectra of compounds 1-4 in dichloromethane solutions and on quartz plate films. The absorption spectra of compounds 1-4 in CH<sub>2</sub>Cl<sub>2</sub> solution show the characteristic vibronic band from the transitions of anthracene group.<sup>6</sup> As shown in Table I, compounds 1-4 showed blue emission with maximum emission wavelengths at 417, 417, 419 and 425 nm in solution. Compared to the PL spectra of compound 1 and 2, compounds 3 and 4 showed red-shifts (2 and 8 nm) due to the longer  $\pi$ -conjugation lengths. Solid state PL wavelengths of compound 1-4 showed red shifts rather than solution PL wavelengths (ca. 14–27 nm) due to the solid state effect.<sup>7</sup>

Figure 2 shows the EL spectra of devices 1–4. Device 2 shows the EL spectrum with the maximum peak at 442 nm. This device exhibits the deep blue emission with the CIE coordinates of (0.16, 0.10). However, the EL spectra of the other devices 1, 3 and 4 show the interesting features. Device 1 shows the main emission peak at 442 nm and the small shoulder peaks at 498 and 537 nm with the CIE coordinates of (0.23, 0.13). In some multilayer OLEDs, a bimolecular recombination state called an electromers or electroplexes were usually formed at relatively high electric fields.<sup>8</sup> The existence of the electromers or electroplexes in OLEDs usually leads to a red-shifted and broadened emission spectrum.<sup>9</sup> Therefore, this result imply the possibility of formation of a species such as an electromers or electroplexes during the electroluminescence process in device 1.<sup>10</sup> The devices 3 and 4 exhibits mainly the greenish emission at 553 nm and 538 nm due to forming significant portions of electromers or electroplexes with the CIE coordinates of (0.41, 0.54) and (0.30, 0.45), respectively at a driving voltage of 7.0 V. Intriguingly, the degree of the electroplexes at the the Alq<sub>3</sub>/Emission layer interface formation in OLED devices are greatly dependent on the structural changes of the emitting materials with the similar HOMO/LUMO energy levels within 0.15 eV.

The luminous and power efficiencies and external quantum efficiencies of devices **1–4** as a function of the luminance are shown in Figure 3 and Table II.

The devices 1–4 exhibited the luminous efficiencies of 2.06, 1.95, 3.32 and 3.90 cd/A and the power efficiencies of 0.91, 0.93, 1.90 and 2.08 lm/W at 200 cd/m<sup>2</sup>, respectively. Interestingly, devices 3 and 4 have the better EL efficiencies than devices 1 and 2. Presumably, the efficient formation of electromers or electroplexes in devices 3 and 4 would contribute to the improved EL efficiencies in comparison with the devices 1 and 2.<sup>5</sup>

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#### 4. CONCLUSION

In this study, we have synthesized two anthracenecontaining blue emitters **1–4** based on Anthracene-Aryl-Anthracene moieties using Suzuki cross coupling reaction. Their EL properties were investigated by fabrication of multilayered OLEDs. All devices showed efficient EL efficiencies from blue to green emissions. Particularly, the device **2** showed the efficient deep-blue emission with  $\text{CIE}_{(x,y)}$  coordinates of (0.16, 0.10) at 7 V, 1.95 cd/A and 0.93 lm/W at 200 cd/m<sup>2</sup> respectively. These results suggest that anthracene derivatives with 1-naphtyl groups have excellent electroluminescent properties in efficient OLEDs.

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J. Nanosci. Nanotechnol. 15, 5242-5245, 2015

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