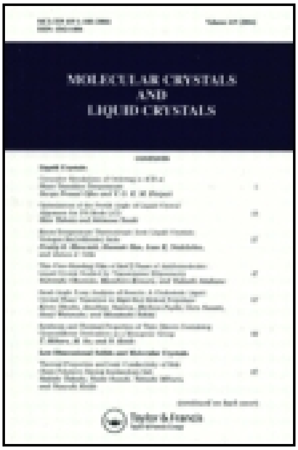

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Asymmetric Monotriphenylamine-Substituted Anthracenes for Blue-Organic Light-Emitting Diodes

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Asymmetric Monotriphenylamine-Substituted Anthracenes for Blue-Organic Light-Emitting Diodes

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A series of blue fluorescent materials based on asymmetric mono-triphenylamine-substituted anthracenes have been synthesized and characterized using spectroscopic analysis. Multilayered organic light-emitting diodes (OLED) were fabricated using these materials as dopants. A maximum luminance of 27900 cd/m^2 at 11 V and a luminous efficiency of 10.1 cd/A at 20 mA/cm^2 were achieved. The peak wavelength of the electroluminescence was 459 nm with CIE coordinates of (0.174, 0.288) at 10 V and the device also showed a stable color chromaticity at various voltages.

Keywords: asymmetric mono-triphenylamine-substituted anthracenes; blue fluorescent materials; organic light-emitting diode

INTRODUCTION

Recently, the development of highly efficient blue OLEDs has attracted considerable interest due to their practical applications in flat panel displays and lighting [1–3]. A variety of blue-emitting materials based on anthracenes have been reported. Particularly, 9,10-diarylanthracene-derivatives were described as very efficient blue host materials [4]. In addition, symmetric diarylamine-substituted anthracene derivatives

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were disclosed as efficient blue emitting materials, but their electroluminescent properties were not excellent [5].

In this work, we designed and synthesized new blue fluorescent materials (**1–4**) based on asymmetric mono-triphenylamine-substituted anthracene moieties. In these materials, various aryl and triphenylamino groups with different chromophoric conjugation at the 9- and 10-positions of anthracene were asymmetrically introduced. Herein, the synthesis and electroluminescent properties of these new materials, when doped in a suitably matched OLED host, are described.

EXPERIMENTAL

Synthesis

N-{4-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)styryl]phenyl}-*N*-phenylbenzenamine [6], 1,1-diphenyl-2-(4-dihydroxyboronphenyl) ethane [7], and 10-(naphthalen-2-yl)anthracen-9-ylboronic acid [8] were prepared according to literature methods.

Synthesis of **5**: A mixture of 9,10-dibromoanthrathene (234 mg, 0.69 mmol), *N*-{4-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)styryl] phenyl}-*N*-phenylbenzenamine (300 mg, 0.63 mmol), and $Pd(PPh_3)_4$ (32 mg, 0.03 mmol) in toluene (15 mL), Aliquit336 (0.02 mL, 0.06 mmol), and 2.0 M aqueous potassium carbonate (3.0 mL) was stirred at reflux under nitrogen for 5 h. The solution was then extracted twice with EA. The combined organic layers were washed with brine and $MgSO_4$. After filtration and evaporation of the solvent, the crude product was purified by column chromatography (silica gel, hexanes: CH_2Cl_2, 10:1) to give the desired compound as a green solid (220 mg, 58%). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) 8.61 (d, $J = 8.9$ Hz, 2 H), 7.74–7.69 (m, 4 H), 7.62–7.57 (m, 2 H), 7.46 (d, $J = 8.6$ Hz, 2 H), 7.44–7.36 (m, 4 H), 7.31–7.25 (m, 4 H), 7.20–7.02 (m, 10 H); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ (ppm) 147.8, 147.8, 137.8, 137.5, 137.4, 131.8, 131.6, 131.3, 130.5, 129.6, 129.0, 128.1, 127.7, 127.7, 127.2, 126.8, 126.6, 125.8, 124.8, 123.8, 123.4, 123.0; V_{max} (KBr)/cm^{-1} 3029, 1589, 1510, 1491, 1330, 1279, 1026, 963, 936, 829, 756, 697; FAB-MS $m/z = 601$ [M$^+$]; HRMS-FAB [M$^+$] calcd for $C_{40}H_{28}BrN$ 601.1405: found 601.1406.

Synthesis of **1**: A mixture of **5** (542 mg, 0.90 mmol), phenylboronic acid (131 mg, 1.08 mmol), and $Pd(PPh_3)_4$ (41 mg, 0.03 mmol) in toluene (15 mL), ethanol (5.0 mL), and 2.0 M aqueous sodium carbonate (5.0 mL) was stirred at reflux under nitrogen for 24 h. The solution was extracted twice with EA. The combined organic layers were then washed with brine and $MgSO_4$. After filtration and evaporation of the solvent, the crude product was purified by column chromatography (silica gel, hexanes:CH_2Cl_2, 5:1) and recrystallization from CH_2Cl_2:EtOH to give the desired compound as a yellow solid (426 mg, 79%). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.79–7.67 (m, 6 H), 7.64–7.55 (m, 2 H), 7.50–7.47 (m, 4 H), 7.45 (d, $J = 2.6$ Hz, 2 H), 7.37–7.26 (m, 9 H), 7.20 (d, $J = 6.9$ Hz, 2 H), 7.16–7.11 (m, 5 H), 7.08–7.03 (m, 3 H); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ (ppm) 147.8, 147.7, 139.3, 138.3, 137.4, 137.1, 132.0, 131.8, 131.6, 130.1, 129.3, 128.8, 128.7, 127.7, 127.3, 127.2, 127.0, 126.6, 125.3, 124.8, 123.8, 123.4; V_{max} (KBr)/cm^{-1} 3060, 3027, 1589, 1513, 1492, 1329, 1312, 1279, 830, 771, 753, 696; FAB-MS $m/z = 599$ [M$^+$]; HRMS-FAB [M$^+$] calcd for $C_{46}H_{33}N$ 599.2613: found 599.2610.

Synthesis of **2**: The synthetic procedure used was similar to that described for **1**. Starting from **5** (427 mg, 0.71 mmol) and 2-naphthaleneboronic acid (146 mg, 0.85 mmol), the desired compound was obtained as a yellow solid (300 mg, 65%). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) 8.08 (d, $J = 8.4$ Hz, 1 H), 8.04–8.01 (m, 1 H), 7.98 (s, 1 H), 7.94–7.90 (m, 1 H), 7.81–7.70 (m, 6 H), 7.63–7.56 (m, 3 H), 7.51–7.46 (m, 4 H), 7.37–7.26 (m, 8 H), 7.20 (d, $J = 6.8$ Hz, 2 H), 7.16–7.03 (m, 8 H); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ (ppm) 147.8, 138.3, 137.2, 136.8, 133.0, 132.0, 131.7, 130.5, 130.3, 130.2, 129.8, 129.6, 128.8, 128.2, 127.7, 127.3, 127.0, 126.7, 126.6, 125.4, 125.3, 124.8, 123.8, 123.3, 116.5; V_{max} (KBr)/cm^{-1} 3059, 3025, 1590, 1512, 1507, 1492, 1279, 831, 772, 764, 753, 696; FAB-MS $m/z = 649$ [M$^+$]; HRMS-FAB [M$^+$] calcd for $C_{50}H_{35}N$ 649.2770: found 649.2769.

Synthesis of **3**: The synthetic procedure applied was similar to that described for **1**. Starting from **5** (500 mg, 0.83 mmol) and 1,1-diphenyl-2-(4-dihydroxy boronphenyl)ethene (300 mg, 0.99 mmol), the desired compound was obtained as a greenish solid (310 mg, 48%). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) 7.77–7.67 (m, 6 H), 7.47–7.39 (m, 9 H), 7.37–7.28 (m, 15 H), 7.18 (d, $J = 7.0$ Hz, 2 H), 7.15–7.02 (m, 11 H); ^{13}C-NMR ($CDCl_3$, 125 MHz) δ (ppm) 147.8, 147.7, 143.7, 143.2, 140.7, 138.3, 137.7, 137.1, 137.1, 137.1, 136.9, 132.0, 131.8, 131.3, 130.6, 130.1, 130.1, 129.8, 129.6, 129.1, 128.8, 128.6, 128.1, 127.9, 127.9, 127.7, 127.2, 127.0, 126.6, 125.3, 125.2, 124.8, 123.8, 123.4; V_{max} (KBr)/cm^{-1} 3058, 3026, 1589, 1512, 1493, 1392, 1325, 1314, 1277, 824, 769, 750, 696; FAB-MS $m/z = 777$ [M$^+$]; HRMS-FAB [M$^+$] calcd for $C_{60}H_{43}N$ 777.3396: found 777.3405.

Synthesis of **4**: The synthetic procedure employed was similar to that described for **1**. Starting from 10-(naphthalen-2-yl)anthracen-9-ylboronic acid (500 mg, 1.43 mmol) and 4-bromotriphenylamine (421 mg, 1.3 mmol), the desired compound was obtained as a yellow solid (480 mg, 67%). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm) 8.08 (d,

$J = 8.2$ Hz, 1 H), 8.04–8.01 (m, 1 H), 7.98 (s, 1 H), 7.93–7.90 (m, 1 H), 7.88 (d, $J = 8.8.$ Hz, 2 H), 7.72 (d, $J = 8.6$ Hz, 2 H), 7.63–7.59 (m, 3 H), 7.42–7.38 (m, 4 H), 7.35–7.27 (m, 12 H), 7.11–7.07 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm) 148.1, 147.4, 137.4, 137.0, 136.9, 133.7, 133.0, 132.9, 132.4, 130.5, 130.4, 129.8, 129.7, 128.3, 128.2, 128.2, 127.4, 127.3, 126.7, 126.5, 125.4, 125.3, 125.0, 123.4; V_{max} (KBr)/cm^{-1} 3063, 1592, 1510, 1489, 1438, 1370, 1329, 1287, 1270, 815, 756, 700; FAB-MS $m/z = 547$ [M$^+$]; HRMS-FAB [M$^+$] calcd for $C_{42}H_{29}N$ 547.2300: found 547.2303.

OLED FABRICATION AND MEASUREMENT

For OLED fabrication, indium-tin-oxide (ITO) thin films coated on glass substrates were used, which were 30 Ω/square of the sheet resistively and 1000 Å thick. The ITO-coated glass was cleaned in an ultrasonic bath through the following sequence: washes with acetone, methyl alcohol, and distilled water, storage in isopropyl alcohol for 48 h, and drying with a N_2 gas gun. The substrates were treated by O_2 plasma under 2×10^{-2} Torr at 125 W for 2 min. All organic materials and metal were deposited under high vacuum (5×10^{-7} Torr). The OLEDs were fabricated in the following sequence: ITO/*N,N′*-diphenyl-*N,N′*-(2-naphthyl)-(1,1′-phenyl)-4,4′-diamine (NPB) (500 Å)/2-methyl-9,10-di(2-naphthyl)anthracene (MADN):Blue dopants (15%) (300 Å)/4,7-diphenyl-1,10-phenanthroline (Bphen) (300 Å)/lithium quinolate (Liq) (20 Å)/Al (1000 Å).

Measurements

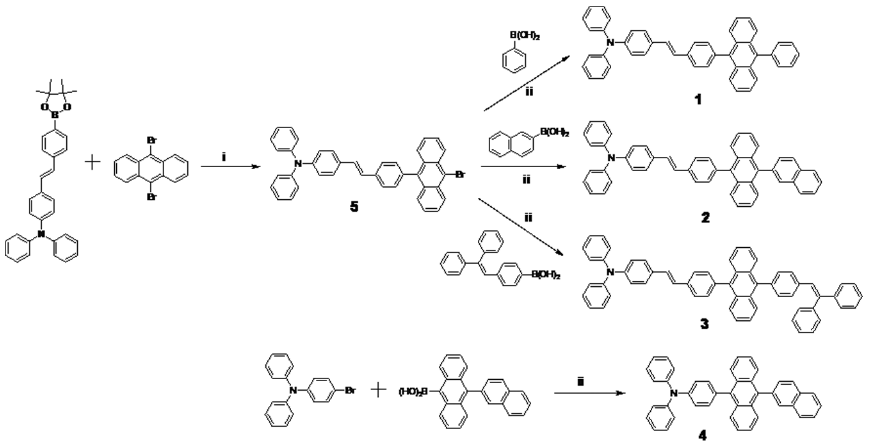
^{1}H- and ^{13}C-NMR were recorded on Varian (Unity Inova 300 Nb or Unity Inova 500 NB) spectrometers. FT-IR spectra were recorded using a Thermo Nicolet Avatar 320 FT-IR Spectrometer. Low- and high-resolution mass spectra were measured using a Jeol JMS-AX505WA spectrometer in the FAB mode. The UV-Vis absorption and photoluminescence spectra of the new dopants were measured in dichloromethane (10^{-5} M) using Sinco S-3100 and Amincobrowman series 2 luminescence spectrometers. The current density (J), luminance (L), luminous efficiency (LE), 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 routes of the new blue dopants are shown in Scheme 1. The materials were characterized by ^{1}H- and ^{13}C-NMR, FT-IR, and low- and high-resolution mass spectroscopy.

The UV-Vis absorption and photoluminescence (PL) spectra of these new fluorescent materials were compared with 2-methyl-9,10-di(2-naphthyl) anthracene (MADN) in dichloromethane, Figure 1(a) and 1(b), and the results summarized in Table 1. The maximum absorption peak wavelengths are located at 398, 398, 399, and 398 nm, respectively. The PL spectra of these materials were also similar, between 492 and 504 nm. The emission wavelength of compound **4** is blue-shifted around 10 nm with respect to that of the others, which is due to the absence of styryl bridge and thus shortening of the chromophoric conjugation length. The emission quantum yields of **1–4** were 0.59, 0.70, 0.57, and 0.57, respectively, as determined using BDAVBi, which has a value of 0.86, as a reference [9].

In order to investigate the electroluminescent properties, we fabricated four devices with the same configurations were fabricated, except employing 15% **1–4** as a dopant within a MADN host in the emitting layers. Figure 2 shows that devices had a maximum luminance of 20500, 27900, 19100, and 6650 cd/m^2 at 11 V, respectively. As shown in Figure 3, the devices have a luminous efficiency of 8.49, 10.1, 7.34, and 5.84 cd/A at 20 mA/cm^2, respectively, and in Figure 4,



i) Pd(PPh$_3$)$_4$, 2M K$_2$CO$_3$, Aliquit 336, Toluene, 5h, reflux ii)Pd(PPh$_3$)$_4$, 2M Na$_2$CO$_3$, Ethanol, Toluene, 24h, reflux

SCHEME 1 Syntheses of compounds **1–4**.

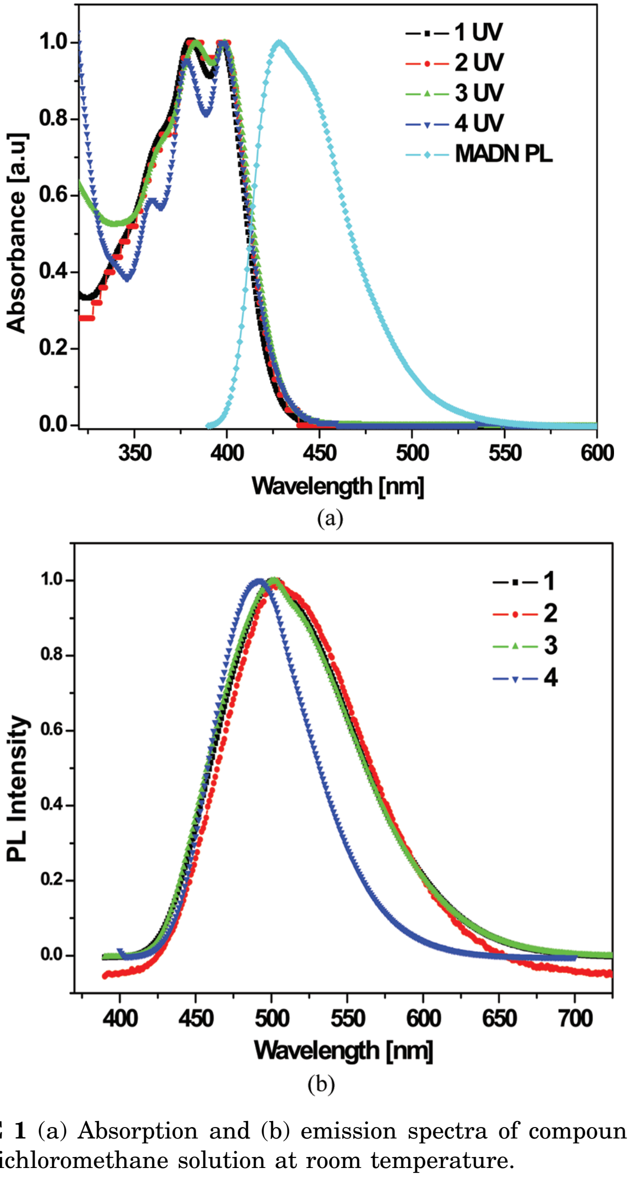


FIGURE 1 (a) Absorption and (b) emission spectra of compounds **1–4** in a 10^{-5} M dichloromethane solution at room temperature.

respective power efficiencies of 4.94, 6.08, 4.12, and 3.30 lm/W at 20 mA/cm^2.

Notably, the device performances of the **2** dopped device are much better than those of **1**, **3**, and **4**, probably due to its higher fluorescent

TABLE 1 Characteristics of OLEDs Using Blue Dopants (**1**–**4**)

	UV [nm]	PL [nm]	Φ_f	LE [cd/A] @20 mA/cm^2	PE [lm/W] @20 mA/cm^2	CIE$_{x,y}$ @10 V
1	388, 398	502	0.59	8.49	4.94	(0.160, 0.239)
2	383, 398	504	0.70	10.1	6.08	(0.174, 0.288)
3	383, 399	502	0.57	8.61	4.12	(0.160, 0.237)
4	398	492	0.57	5.84	3.30	(0.140, 0.205)

emission quantum yield, as shown in Table 1. CIE coordination of the OLEDs using blue dopants were found at (0.160, 0.239) for **1**, (0.174, 0.288) for **2**, (0.160, 0.237) for **3**, and (0.140, 0.205) for **4** at 10 V, respectively. Device employing **4** as a dopant shows deeper blue emission than the others, which is well compatible with the results of solution PL measurement. The color chromaticities of the OLEDs were stable under various voltages. OLEDs using dopant **4** exhibited the bluest emission given the shortening of the chromophoric conjugation and the hypsochromic shift of dopant fluorescence as well.

Previous studies suggest that the efficient energy transfer between host and dopant play a key role in the efficiency of OLEDs. These imply that the efficiencies of blue dopants (**1–4**) may be improved by using a new wide band gap host to achieve emission maximum peaks around 400 nm, similar to the absorption maximum peaks of dopants

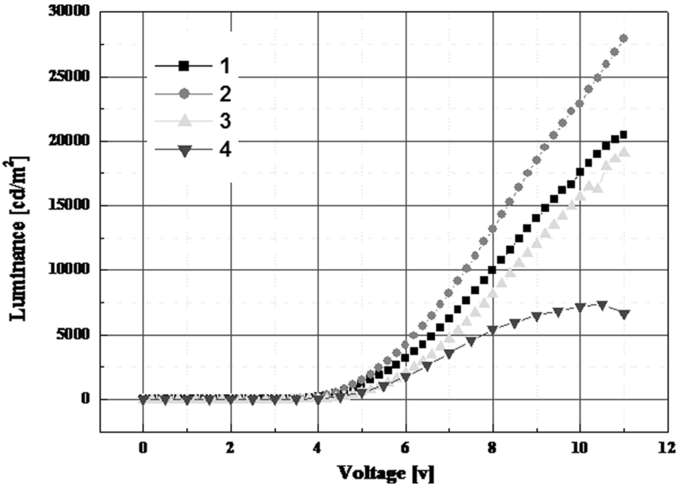


FIGURE 2 The luminance vs. voltage relationship of devices using compounds **1–4** as dopants.

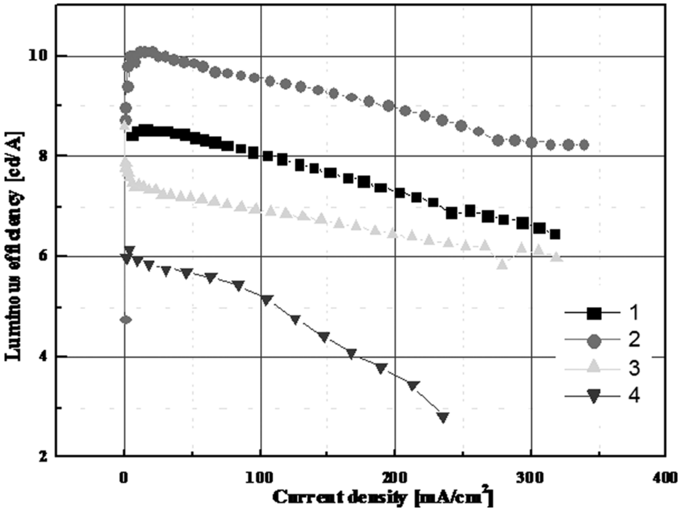


FIGURE 3 The Luminous efficiency of devices using compounds **1–4** as dopants with respect to the applied current density.

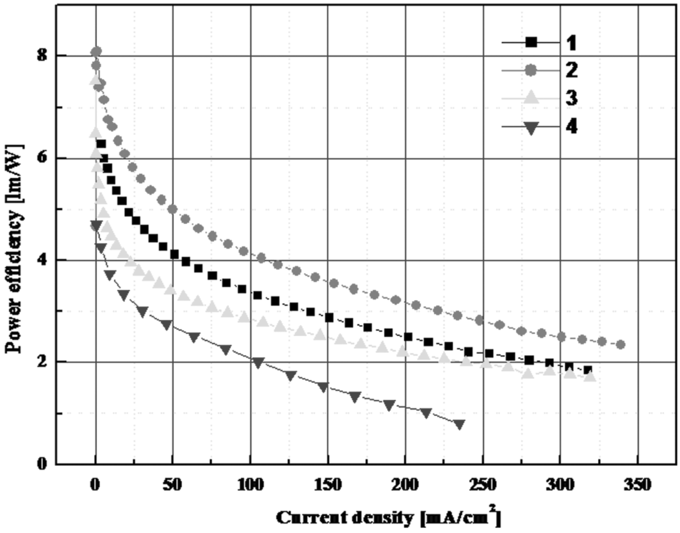
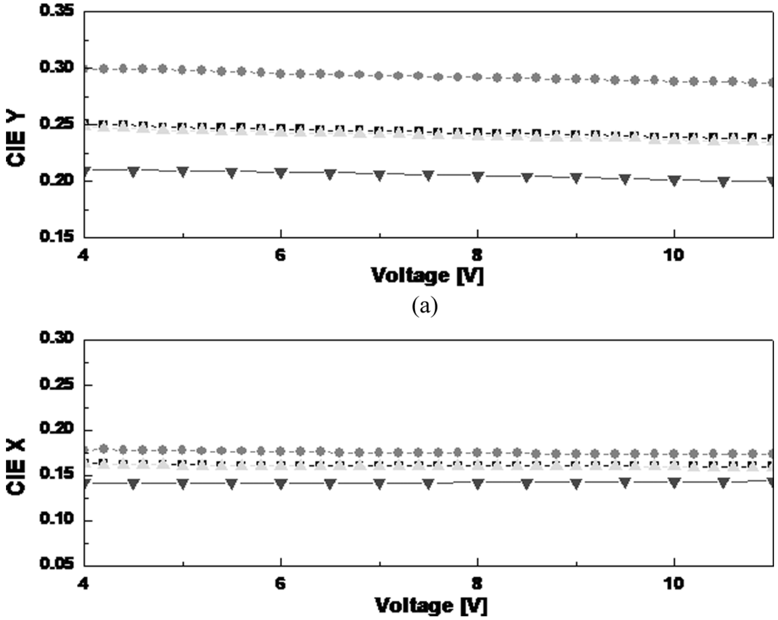


FIGURE 4 The power efficiency of devices using compounds **1–4** as dopants with the applied current density.



(a)

(b)

FIGURE 5 CIE X and Y coordinate on the devices using compounds **1–4** as dopants with the operating voltages.

(**1–4**) and thus providing a matched spectral overlap between the emission of the host and the absorption of the dopants. Works in this direction as well as the optimization of device structures to develop highly efficient blue OLEDs are in progress.

CONCLUSIONS

Blue fluorescent materials based on asymmetric mono-triphenylamine-substituted anthracenes have been synthesized and characterized. By using these materials as dopants, high-efficiency blue OLEDs were fabricated. Among those, a device using **2** shows a maximum luminance of 27900 cd/m^2 at 11 V and a luminous efficiency of 10.1 cd/A at 20 mA/cm^2. With future studies centered on device optimization and development of wide band gap host materials to improve luminous efficiency and color chromaticity, these materials would be excellent blue dopants for future OLED display applications.

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