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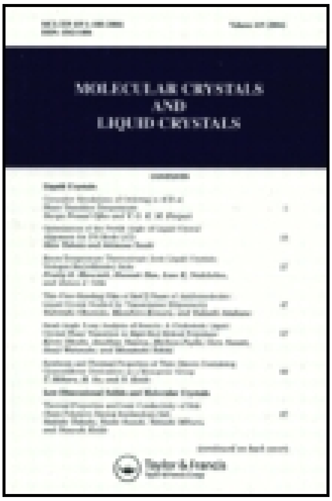

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Synthesis and Electroluminescent Properties of Blue Fluorescent Triphenylamine Substituted Anthracene Derivatives for OLEDs

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Synthesis and Electroluminescent Properties of Blue Fluorescent Triphenylamine Substituted Anthracene Derivatives for OLEDs

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We describe the electroluminescent properties of blue fluorescent materials based on mono(triphenylamino)anthracene derivatives synthesized via *Suzuki cross coupling reactions. To explore the electroluminescent properties of materials* **1–3**, *multilayered OLEDs were fabricated and all devices exhibited efficient blue emissions. Among those, device* **1**, *with CIE* x,y *coordinates of (0.159, 0.166) at 12.0 V, exhibited the best performance, with a maximum luminance of 7306 cd/m^2 at 12.0 V, and luminous and power efficiencies of 4.95 cd/A and 1.83 lm/W at 20 mA/cm^2, respectively.*

Keywords Blue fluorescent materials; mono(triphenylamino)anthracene derivatives; multilayered OLEDs; Suzuki cross-coupling reaction

Introduction

The development of highly efficient organic light-emitting diodes (OLEDs) has attracted significant attention recently due to its potential application in flat panel displays [1–4]. In this regards a variety of new emitting materials have been developed to fill the requirements of three primary color (red, green, blue) emitters for full color OLED displays [5]. However, blue-emitting materials still receive considerable attention, because its wide band gap is such that highly efficient deep blue emitting materials are difficult to produce. Recently, a variety of blue-emitting materials based on anthracene have been reported [6–16]. Among these are mono(triarylamino)-substituted anthracene derivatives. For example, Tao et al. have reported that 9-mono(triphenylamino)-10-pyrenyl anthracene derivatives exhibited efficient blue emission with a maximum efficiency of up to 7.9 cd/A in a nondoped

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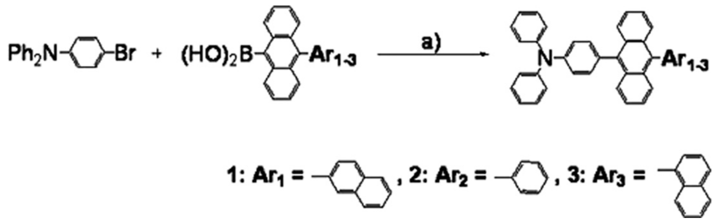


Figure 1. Synthetic routes to blue fluorescent materials (**1–3**). Conditions: a) $Pd(PPh_3)_4$, K_2CO_3 (2 M in H_2O), Aliquat 336, Toluene, reflux.

device [17]. However, for practical applications, the properties of these emitting materials need to be improved.

In this study, a series of blue fluorescent materials (**1–3**) based on mono(triphenylamino) anthracene (Figure 1) were synthesized, and their electroluminescent properties were investigated in doping system using ADN as a host [7].

Experimental

Materials and Characterization

9-(naphthalen-2-yl)-10-(4-triphenylamine)anthracene (**1**) and 9-phenyl-10-(4-triphenylamine) anthracene (**2**) were prepared according to literature methods [18]. ^{1}H- and ^{13}C-NMR were recorded using a Varian (Unity Inova 300NB) or Varian (Unity Inova 500NB) spectrometer at 300 MHz and 500 MHz, respectively. Low- and high-resolution mass spectra were recorded using a Jeol JMS-AX505WA spectrometer in FAB mode or Jeol JMS-600 spectrometer in EI mode.

9-(naphthalen-1-yl)-10-(4-triphenylamine)anthracene (**3**). A solution of 4-bromo-*N,N*-diphenylaniline (0.64 mmol), 10-phenylanthracen-9-ylboronic acid (0.84 mmol), tetrakis(triphenyl phosphine)palladium (0.02 mmol), Aliquat 336 (0.05 mmol) and aqueous 2.0 M K_2CO_3 (5.20 mmol) in toluene were heated at 120°C under Ar atmosphere for 4 h. After the solution cooled, the product was extracted with CH_2Cl_2. The CH_2Cl_2 solution was washed with brine and H_2O, and then dried on $MgSO_4$. Evaporation of the solvent, followed by recrystallization with $CHCl_3$/hexane, gave **3** (92%) as a yellow solid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ ppm 8.06 (d, $J = 8.2$ Hz, 1H), 8.01 (d, $J = 8.2$ Hz, 1H), 7.89 (d, $J = 8.8$ Hz, 2H), 7.70 (t, $J = 7.0$ Hz, 1H), 7.56 (d, $J = 7.0$ Hz, 1H), 7.51–7.15 (m, 21H), 7.12–7.06 (m, 2H); ^{13}C-NMR (500 MHz, $CDCl_3$): ppm 148.0, 147.4, 137.6, 137.1, 135.0, 133.9, 133.8, 132.8, 132.4, 130.9, 130.3, 129.6, 129.4, 128.4, 128.3, 127.3, 127.2, 126.9, 126.5, 126.2, 125.8, 125.4, 125.2, 124.9, 123.4, 123.3, 123.2; IR (KBr): ν 3037, 1592, 1509, 1493, 1374, 1326, 1279, 936, 762, 755, 738, 697 cm^{-1}; EI-MS $m/z = 547$ [M$^+$]; HRMS-TOF [M$^+$ + H] Anal. calcd for $C_{50}H_{53}N_2$ 547.2300: found 547.2273.

Physical Measurements

The UV-Vis absorption and photoluminescence spectra of these newly designed dopants were measured in CH_2Cl_2 solution (10^{-5} M) using a Sinco S-3100 and Amincobrowman series 2 luminescence spectrometer, respectively. The HOMO energy levels were determined by low energy photoelectron spectrometry

(Riken-Keiki AC-2). LUMO energy levels were estimated by subtracting the energy gap from the HOMO energy levels.

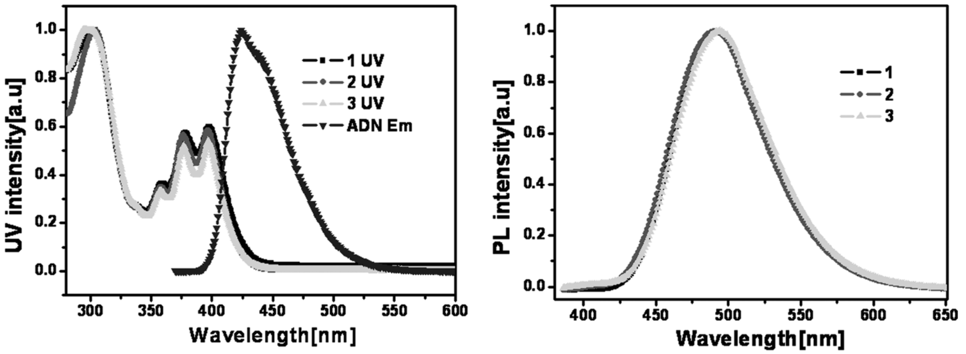
OLED Fabrication and Measurement

For fabricating the OLEDs, indium-tin-oxide (ITO) thin films coated on glass substrates were used, with a sheet resistivity of 30 Ω/square and a thickness of 100 nm. The ITO-coated glass was cleaned in an ultrasonic bath by the following sequence of solvents: acetone, methyl alcohol, and distilled water, and kept in isopropyl alcohol for 48 h and dried by N_2 gas gun. The substrates were treated by O_2 plasma treatment under the conditions of 2×10^{-2} Torr at 125 W for 2 min [22]. 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*′-(1-napthyl)-(1,1′-phenyl)-4,4′-diamine (NPB) (50 nm)/9,10-di(2-naphthyl)anthracene (ADN): Blue dopant materials (30 nm, 2%)/tris(8-hydroxyquinoline) aluminum (Alq_3) (20 nm)/lithium quinolate (Liq) (2 nm)/Al (100 nm). The current density (*J*), luminance (*L*), luminous efficiency (*LE*), and CIE chromaticity coordinates of the OLEDs were measured with a Keithley 2400 and Chroma Meter CS-1000A. Electroluminance was measured using a Roper Scientific Pro 300i.

Results and Discussion

Figure 1 shows the molecular structures of the dopant compounds used in this study. Compounds **1–3** were synthesized *via* Suzuki cross-coupling reactions between 4-bromo-triphenylamine and corresponding arylanthracene boronic acid compounds with moderate yields. After conventional purifications such as column chromatography and recrystallization, the newly synthesized blue-emitting materials (**1–3**) were purified further by train sublimation at reduced pressure, below 10^{-3} torr, and fully characterized using ^{1}H- and ^{13}C-NMR, infrared (IR), and low- and high-resolution mass spectrometry. High-pressure liquid chromatography (HPLC) analysis revealed that the purity of the blue-emitting materials (**1–3**) was at least 99.0%.

Figure 2 shows the absorption (a) and emission (b) spectra of each of compounds **1–3** in CH_2Cl_2 solution. The photophysical data are summarized in Table 1. The absorption spectra have two major bands in the range of



(a) (b)

Figure 2. (a) The absorption and (b) emission spectra of compounds **1–3**.

Table 1. Optical properties of Compounds (**1–3**)

Compound	UV_{max}[a] [nm]	PL_{max}[b] [nm]	FWHM [nm]	HOMO/LUMO[c] [eV]	E_g	Φ[d]
1	397	492	74	5.71/2.82	2.89	0.67
2	396	492	50	5.75/2.83	2.92	0.72
3	397	494	75	5.63/2.68	2.95	0.72

[a,b] Maximum absorption or emission wavelength, measured in CH_2Cl_2 solution.
[c] Obtained from AC-2 and UV-vis absorption measurements.
[d] Using BDAVBi as a standard; $\lambda_{ex} = 360$ nm ($\Phi = 0.86$ in CH_2Cl_2 solution).

360–400 nm. The peaks at 360–400 nm with a characteristic vibronic pattern are attributed to the π-π^* transitions of the anthracene core [19,20]. The absorption bands at 280–350 nm can be interpreted as the combination of the n-π^* transition of triarylamine moieties and the π-π^* transitions of the substituted aryl groups on the anthracene core [21]. These compounds **1–3** all have similar emission properties in CH_2Cl_2 solution, each with a maximum peak at 492–494 nm, in the blue region. We calculated the fluorescence quantum yield (Φ) of **1–3** in the CH_2Cl_2 solution to be 0.67, 0.72 and 0.72, respectively, using BDAVBi ($\Phi = 0.86$ in CH_2Cl_2 solution) as a standard [22], suggesting that these materials were expected to have highly efficient electroluminescent properties in OLED devices. Their full widths at half maximum (FWHM) were 74, 50 and 75 nm, respectively, in CH_2Cl_2 solution. The edge of the UV-Vis spectra was used to calculate the band gap of these blue materials. The calculated HOMO-LUMO energy gaps (E_g) for **1–3** were 2.89, 2.92, and 2.95 eV, respectively. The highest occupied molecular orbital (HOMO) levels were determined by 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 and LUMO energy levels for blue fluorescent materials varied from −5.63 to −5.75 eV and −2.68 to −2.83 eV, respectively (Table 1). In particular, the blue material dopant **1**, with a substituted 2-naphthylanthracene unit had lower HOMO (−0.08 eV) and LUMO energy levels (−0.14 eV) in comparison with dopant **3**, with a substituted 1-naphthylanthracene core. These results suggest that 2-position of naphthylanthracene group decreases the HOMO and LUMO energy levels through the effective π-conjugation.

The device performance of the blue fluorescent materials was studied by doping these materials in the ADN host at a 2% concentration. Figure 3 shows the device structure and relative HOMO/LUMO energy levels of the materials used in this study. NPB was employed as a hole-transporting layer (HTL) to provide hole transport, and also functioned as host in the emitting layer (EML), while Alq_3 was used as the electron-transporting layer (ETL) [23,24].

Figure 4 shows the EL emission spectra of the OLEDs obtained from devices **1–3**, and indicate that doped devices exhibited deeper blue than nondoped devices. All devices exhibited blue emissions with maximum emission peaks at 460, 456, and 458 nm for device **1**, **2**, and **3** (Table 2). Interestingly, there is a blue shift in EL spectra of the device **3** as compared to device **1**, because the steric effect of the 1-naphthalene group of dopant **3** decreases the π-conjugation length. The CIE (Commission Internationale de l'Eclairage) coordinates of devices **1–3** were (0.16, 0.17), (0.15, 0.14), and (0.15, 0.14), respectively, which were close to the NTSC

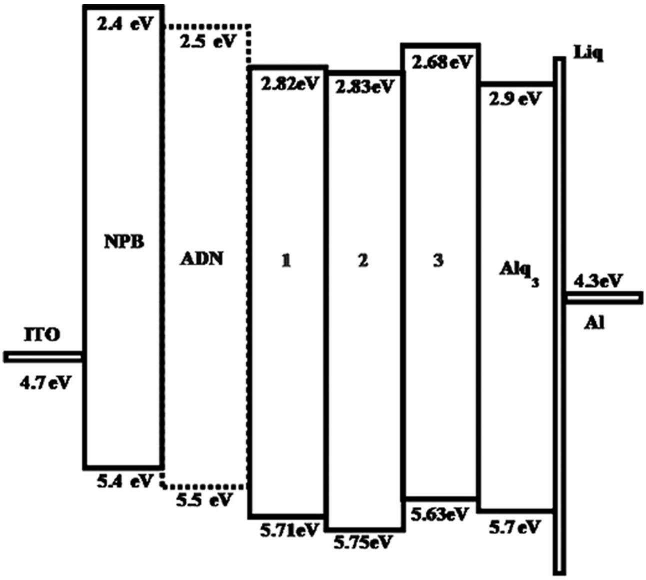


Figure 3. Energy-level diagram of the materials in devices **1–3**.

standard blue ($x = 0.15$, $y = 0.16$). However, the CIE coordinates of the nondoped devices corresponding to **1** and **2** were (0.14, 0.21), (0.14, 0.20) respectively, which indicates that the doped devices exhibited a deeper blue color than the nondoped device because the dopant materials functioned as a carrier trap in the doping system.

All devices **1–3** showed efficient blue emission, with results summarized in Table 2. The device **3**, which uses dopant **3** containing 1-naphtyl unit, exhibited CIE coordinates of (0.15, 0.14) at 12 V, a luminance of 7225 cd/m^2 at 12 V, a luminous efficiency of 4.62 cd/A, and a power efficiency of 1.81 lm/W at 20 mA/cm^2. Intriguing, similar results were obtained in the device **2** and **3**. In other words,

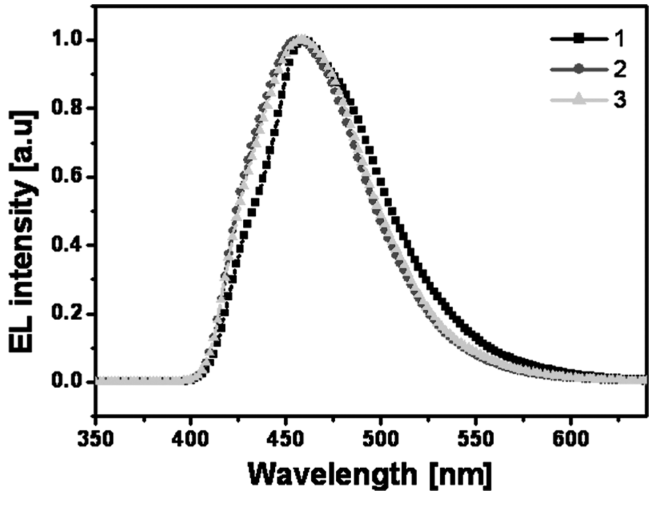
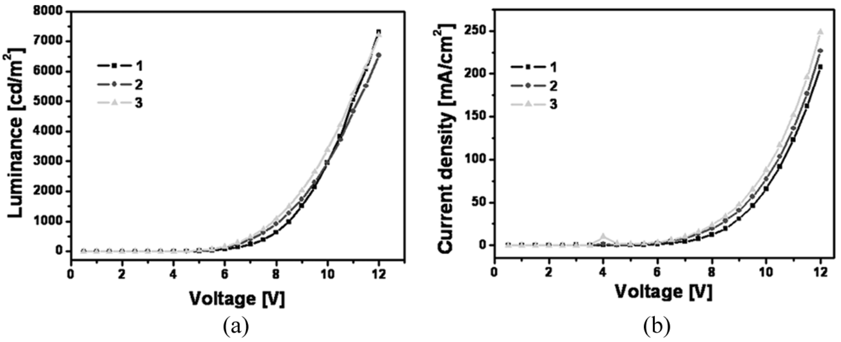
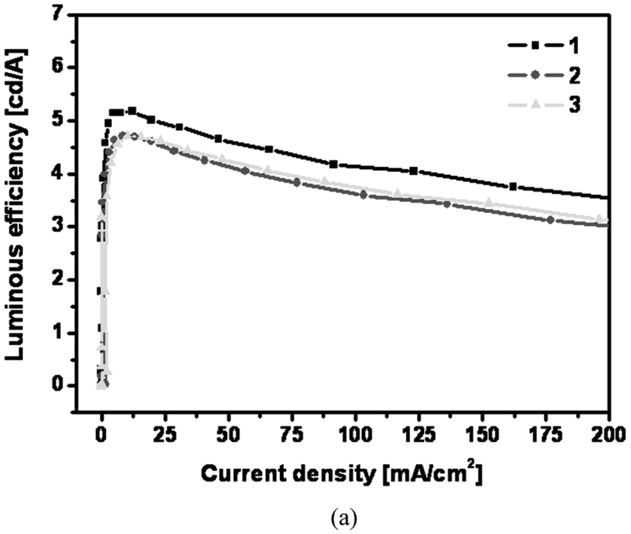


Figure 4. Electroluminescence (EL) spectra of the devices **1–3**.

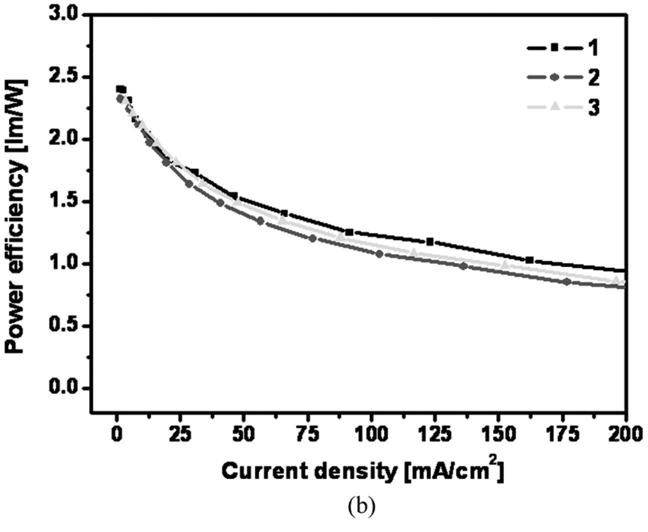


(a) (b)

Figure 5. (a) *L-V* characteristics and (b) *I-V* characteristics of the devices **1–3**.



(a)



(b)

Figure 6. (a) Luminous and (b) Power efficiencies as a function of current density for the devices **1–3**.

Table 2. EL performance characteristic of devices (**1–3**)

Device	EL_{max}[a] [nm]	L[b] [cd/m^2]	LE[c] [cd/A]	Max LE[d] [cd/A]	PE[e] [lm/W]	Max PE[f] [lm/W]	CIE[a] (*x, y*)
1	460/472[g]	7306	4.95	5.18/5.5[g]	1.83	3.72/3.5[g]	(0.16, 0.17) (0.14, 0.21)[g]
2	456/470[g]	6541	4.61	4.71/4.0[g]	1.81	2.30/4.0[g]	(0.15, 0.14) (0.14, 0.20)[g]
3	458	7225	4.62	4.71	1.81	2.29	(0.15, 0.14)

Device (ITO/NPB/ADN: blue dopant materials **1–3** (2%)/Alq_3/Liq/Al).

[a] Value collected at 12.0 V.

[b] Maximum luminance at 12.0 V.

[c] Luminous efficiency at 20 mA/cm^2.

[d] Maximum luminous efficiency.

[e] Power efficiency at 20 mA/cm^2.

[f] Maximum power efficiency.

[g] Nondoped device with a configuration of ITO/NPB (50 nm)/EML/TPBI (30 nm)/LiF/MgAg [17].

device **2**, employing compound **2** with a phenyl substituent as a dopant material, indicated deep blue emission with CIE coordinates of (0.15, 0.14) at 12.0 V, the maximum luminance of 6541 cd/m^2 at 12.0 V, and the luminous and power efficiencies of 4.61 cd/A and 1.81 lm/W at 20 mA/cm^2, respectively. The EL performances of devices **1–3** are sensitive to the structure of blue dopant materials in the emitting layer. Among those, a device using dopant **1** comprising 2-naphtyl moiety exhibited the best performance, with the maximum luminance of 7306 cd/m^2 at 12.0 V, and the luminous and power efficiencies of 4.95 cd/A and 1.83 lm/W at 20 mA/cm^2, respectively. However, the EL performances of the doped systems were not improved over those of undoped systems. This indicates that energy transfer between host (AND) and dopants (**1–3**) is not efficient because the absorption of dopants (**1–3**) do not overlap effectively with the emission of a common host (ADN) as shown in Figure 1 (a). This study implies that the effective energy transfer between host and dopant is a key factor in improving the EL performances in a doped system.

Conclusions

In conclusion, highly efficient blue dopant materials based on mono(triphenylamino) anthracene derivatives were synthesized *via* Suzuki cross-coupling. Multilayered OLEDs were fabricated with the device structure of ITO/NPB/2% anthracene-triphenylamine derivatives **1–3** doped in ADN/Alq_3/Liq/Al. All devices exhibited efficient blue emissions. Among those, device **1**, with CIE *x*, *y* coordinates of (0.16, 0.17) at 12.0 V, exhibited the best performance, with maximum luminance of 7306 cd/m^2 at 12.0 V, and luminous and power efficiencies of 4.95 cd/A and 1.83 lm/W at 20 mA/cm^2, respectively.

Acknowledgments

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