

Blue-Light-Emitting Bis(diarylamino)stilbene Derivatives: Synthesis, Photophysical Properties, and Highly Efficient OLEDs

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New electroluminescent materials, 4,4'-bis(2-naphthyl-4-tert-butylphenylamino)-stilbene (1), 4,4'-bis(4-tert-butylphenyl-3,5-di-tert-butylphenylamino)stilbene (2), and 4,4'-bis(di-4-tert-butylphenylamino)stilbene (3) were synthesized and characterized. To evaluate the electroluminescent properties of these compounds, multi-layered OLED devices 1-3 were designed. By employing blue dopant 1 into a multilayer device, it was possible to achieve a maximum luminance of 8861 cd m⁻² at 12.0 V, a luminous efficiency of 6.82 cd A⁻¹ at 20 mA cm⁻², a power efficiency of 2.72 lm W⁻¹ at 20 mA cm⁻², and CIE_{x,y} coordinates of (x=0.158,y=0.187) at 10.0 V. These results demonstrated the superiority of these bis(diarylamino)-stilbene derivatives in organic light-emitting devices.

Keywords Bis(diarylamino)stilbene; blue fluorescent materials; Buchwald-Hartwig cross-coupling reaction; organic light-emitting diode

Introduction

Organic light-emitting diode (OLED) displays are considered the next generation flat-panel display because OLEDs have the advantages of low-driving-voltage, high efficiency, and possibility for flexible and large-area display applications [1,2]. Research on OLEDs has focused on the improvement of device performance by introducing highly efficient materials. In particular, there has been considerable interest in developing the performance of blue OLEDs, which is relatively poor compared with that of red and green OLEDs [3]. It is therefore important to develop high-performance blue-light-emitting materials with good color purity and intense luminescent efficiency. Out of small molecules, several classes of materials based on anthracenes [4,5], distyrylarylenes [6], oligofluorenes [7], spirobifluorenes [8,9],

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metal chelates [10], and others [11–13] have been explored as possible blue OLEDs. However, blue emitters are necessary to improve full color display performance.

In this study, the synthesis and electroluminescent properties of three stilbene derivatives, 4,4'-bis(2-naphthyl-4-*tert*-butylphenylamino)stilbene (**1**), 4,4'-bis(4-*tert*-butylphenyl-3,5-di-*tert*-butylphenylamino)stilbene (**2**), and 4,4'-bis(di-4-*tert*-butylphenylamino)stilbene (**3**) are reported. Since *trans*-4,4'-bis(diarylamino)stilbene derivatives have promising photoluminescent and electroluminescent properties [14,15], they have served in various applications, including organic light-emitting diodes. In the three different blue dopant materials studied here, sterically bulky *tert*-butyl groups were introduced into the diarylamine moiety to prevent intermolecular π - π stacking interactions and thus reduce concentration quenching. We herein demonstrate highly efficient blue OLEDs using these new blue emitters.

Experimental

Materials and Measurements

All reactions were performed under a nitrogen atmosphere. Commercially available reagents were used without further purification unless otherwise stated. ^1H - 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- and high-resolution mass spectra were measured using a Jeol JMS-600 spectrometer in the FAB mode and a JMS-T100TD (AccuTOF-TLC) in the positive ion mode.

Synthesis

Synthesis of 4,4'-bis(2-naphthyl-4-tert-butylphenylamino)stilbene (1). To a toluene (10 mL) solution of 4,4'-bis(4-*tert*-butylphenylamino)stilbene (0.60 g, 1.26 mmol) was added 2-bromonaphthalene (0.58 g, 2.78 mmol), sodium *tert*-butoxide (0.36 g, 3.78 mmol), Pd_2dba_3 (0.058 g, 0.063 mmol), and (2-biphenyl)di-*tert*-butylphosphine (0.038 g, 0.13 mmol) under N_2 . The resulting solution was heated to reflux for 18 h. The reaction mixture was extracted with toluene, washed with aqueous NaCl solution, and dried with MgSO_4 . After filtration and evaporation of the solvent, the crude product was purified by column chromatography (silica gel, hexanes:EtOAc = 15:1) and recrystallization from THF:MeOH to give the desired compound as a bright green solid (0.81 g, 88.3%). ^1H -NMR (CDCl_3 , 300 MHz) [δ ppm]: 7.74 (d, J = 7.6 Hz, 2H), 7.69 (d, J = 8.8 Hz, 2H), 7.58 (d, J = 7.6 Hz, 2H), 7.45 (s, 2H), 7.39–7.32 (m, 8H), 7.30–7.26 (m, 6H), 7.07 (dd, J = 2.2, 8.7 Hz, 8H), 6.96 (s, 2H), 1.32 (s, 18H). ^{13}C -NMR (CDCl_3 , 75 MHz) [δ ppm]: 147.5, 146.5, 145.6, 145.0, 134.7, 132.1, 130.3, 129.1, 127.8, 127.4, 127.2, 126.8, 126.5, 126.4, 124.7, 124.6, 124.5, 124.0, 120.4, 34.6, 31.7. FT-IR [ATR]: ν = 3028, 2962, 1629, 1506, 1363, 1294, 965, 851, 747, 652 cm^{-1} . FAB-MS (m/z): 726 [M^+]. HRMS-TOF ($\text{M}^+ + \text{H}$) Anal. calcd for $\text{C}_{54}\text{H}_{51}\text{N}_2$ 727.40522; found: 727.40056.

Synthesis of 4,4'-bis(4-tert-butylphenyl-3,5-di-tert-butylphenylamino)stilbene (2). The synthetic procedure used was similar to that described for **1** and the desired compound was obtained as a bright green solid (0.41 g, 56.0%). ^1H -NMR (CDCl_3 , 300 MHz) [δ ppm]: 7.33 (d, J = 8.5 Hz, 4H), 7.26–7.23 (m, 4H), 7.09 (s, 2H), 7.05–7.01 (m, 8H), 6.96–6.94 (m, 6H), 1.32 (s, 18H), 1.25 (s, 36H). ^{13}C -NMR

(CDCl₃, 75 MHz) [δ ppm]: 151.9, 147.7, 147.0, 145.6, 145.2, 131.3, 127.1, 126.5, 126.1, 123.8, 123.0, 119.8, 117.3, 35.1, 34.5, 31.7, 31.6. FT-IR [ATR]: ν = 2962, 1650, 1510, 1329, 1306, 1248, 833, 712, 623 cm⁻¹. FAB-MS (m/z): 850 [M⁺]. HRMS-TOF (M⁺ + H) Anal. calcd for C₆₂H₇₉N₂ 851.62433; found: 851.62405.

Synthesis of 4,4'-bis(di-4-tert-butylphenylamino)stilbene (3). The synthetic procedure used was similar to that described for **1** and the desired compound was obtained as a bright green solid (0.33 g, 67.3%). ¹H-NMR (CDCl₃, 300 MHz) [δ ppm]: 7.32 (d, J = 8.7 Hz, 4H), 7.25 (d, J = 8.7 Hz, 8H), 7.04–7.00 (m, 12H), 6.91 (s, 2H), 1.31 (s, 36H). ¹³C-NMR (CDCl₃, 75 MHz) [δ ppm]: 147.5, 145.9, 145.1, 131.5, 127.2, 126.6, 126.3, 124.2, 123.2, 34.5, 31.7. FT-IR [ATR]: ν = 3031, 2959, 1603, 1509, 1364, 1323, 1282, 826, 696, 629 cm⁻¹. FAB-MS (m/z): 738 [M⁺]. HRMS-TOF (M⁺ + H) Anal. calcd for C₅₄H₆₃N₂ 739.49913; found: 739.49416.

Physical Measurements

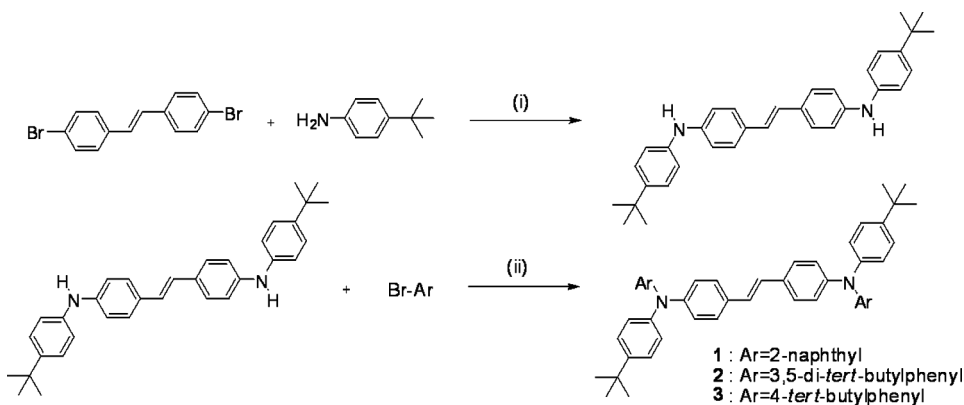
The UV-Vis absorption and photoluminescence spectra of the new dopant materials were measured in dichloromethane (10⁻⁵ M) using Sinco S-3100 and Amincobrowman series 2 luminescence spectrometers. The fluorescence quantum yields of the emitting materials were determined in dichloromethane at 293 K against BDAVBi as a reference (Φ = 0.86). HOMO (highest occupied molecular orbital) energy levels were determined with a low-energy photoelectron spectrometer (Riken-Keiki, AC-2).

OLED Fabrication and Characterization

For fabricating OLEDs, indium-tin-oxide (ITO) thin films coated on glass substrates were used, which were 30 Ω /square of the sheet resistivity at a 1000 Å thickness. The ITO-coated glass was cleaned in an ultrasonic bath by the following sequences: acetone, methyl alcohol, distilled water, storage in isopropyl alcohol for 48 h, drying by an N₂ gas gun. The substrates were treated by O₂ plasma treatment at 2 $\times$ 10⁻² Torr at 125 W for 2 min. All organic materials and metals were deposited under high vacuum (5 $\times$ 10⁻⁷ Torr). The OLEDs fabricated in this study had a configuration of indium tin oxide (ITO)/4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (NPB) (700 Å)/9,10-di(2-naphthyl)anthracene (ADN): blue dopants **1–3** (300 Å: 2%)/tris(8-hydroxyquinolino)aluminum (Alq₃) (300 Å)/lithium quinolate (Liq) (10 Å)/Al. All of the optical and electrical properties of OLEDs such as the current density, luminance, luminous efficiency and CIE coordinate characteristics were measured with a Keithly 236, LS-50B, and MINOLTA CS-100A, respectively.

Results and Discussion

Scheme 1 shows the synthetic routes of the all compounds used in this study. As shown in Scheme 1, we prepared bis(diarylamino)stilbene derivatives **1–3** via Buchwald-Hartwig cross-coupling reactions using Pd₂dba₃, *t*-BuONa, and the JohnPhos ligand (dba: dibenzylideneacetone, JohnPhos: (2-biphenyl)di-*tert*-butylphosphine). A Pd-catalyzed coupling reaction of these species delivered the desired stilbenes **1–3** with yields in the range of 56–88%. All the compounds were characterized by ¹H- and ¹³C-NMR, FT-IR, and low- and high-mass spectroscopy.



Scheme 1. Synthetic routes of compounds **1–3**. Condition (i), (ii): $\text{Pd}_2(\text{dba})_3$ (5 mol %), (2-biphenyl)di-*tert*-butylphosphine (10 mol %), *t*-BuONa (3.0 eq), toluene, 120°C, 18 hr.

Figure 1a shows the normalized optical absorption spectra of the three dopant materials and emission of the host material in the dichloromethane solution. A good spectral overlap was observed between the emission of the host (ADN) and the absorption of the dopant materials **1–3**. These observations indicate that the blue materials **1–3** can effectively accept energy from the ADN host material by Förster-type energy transfer. The energy transfer efficiency is highly dependent on the spectral overlap between the emission of the host and the absorption of the dopant, so these materials should be expected to have highly efficient electroluminescent properties in OLED devices. The absorption spectra show maximum peaks in the 396–400 nm range. These absorption bands are thus associated with $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of the stilbene derivatives. The normalized PL emission spectra of the compounds **1–3** are shown in Figure 1b. Blue emissions with a PL maximum of 452–456 nm were observed. Notably, the three blue materials show very similar UV (396–400 nm) and photoluminescence (452–456 nm) spectra. The similarity of absorption and emission spectra in the blue materials reflect the fact that

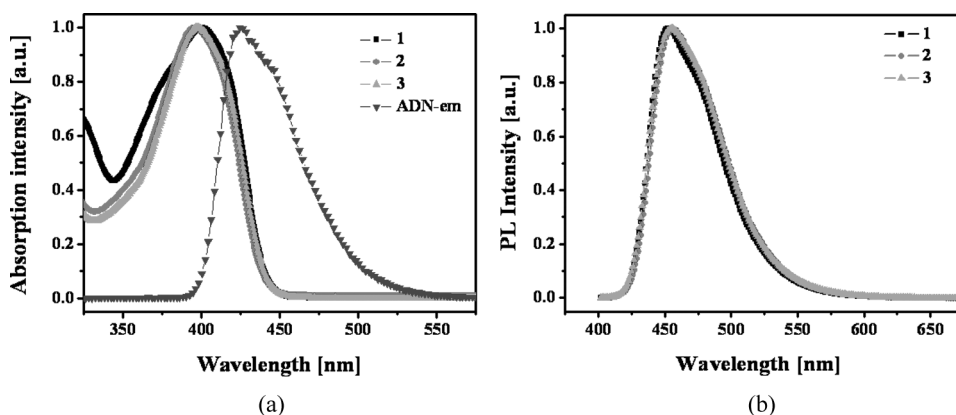


Figure 1. (a) UV-vis absorption and (b) photoluminescence spectra of compounds **1–3** in a 10^{-5} M dichloromethane solution.

Table 1. Photophysical data for the compounds **1–3**

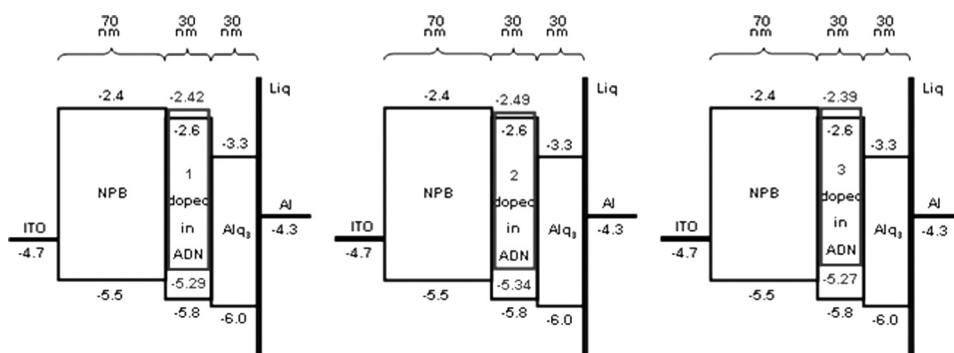
Compound	UV λ_{max} [a] [nm]	PL λ_{max} [b] [nm]	FWHM [nm]	HOMO [c] [eV]	LUMO [c] [eV]	E_g	Φ [d]
1	400	452	58	5.29	2.42	2.87	0.82
2	398	456	60	5.34	2.49	2.85	0.92
3	396	456	60	5.27	2.39	2.88	0.99

[a,b] Maximum absorption and emission wavelength, measured in CH_2Cl_2 solution. [c] Obtained from AC-2 and the intersection of the absorption and photoluminescence spectra. [d] Using BDAVB_i as a standard; $\lambda_{\text{ex}} = 360$ nm ($\Phi = 0.86$ in CH_2Cl_2).

the effective conjugation length in these molecules is the same, since the *t*-butyl unit have no influence on conjugation length. The FWHM of the spectra is very narrow at 58–60 nm, and these blue-light-emitting bis(diarylamino)stilbene derivatives have very high PL quantum yields of 0.82–0.99, suggesting that these materials are expected to have highly efficient electroluminescent properties in OLED devices.

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of compounds **1–3** are shown in Table 1 and Figure 2. The HOMO energy levels were measured with an AC-2 photoelectron spectrometer and the LUMO levels calculated by subtracting the corresponding optical band gap energies from the HOMO values. The HOMO/LUMO energy levels of compounds **1–3** are 5.29/2.42, 5.34/2.49, and 5.27/2.39, respectively. Compounds **1–3** show a slight difference between the HOMO and LUMO energy levels. Because N-substituted phenyl and naphthyl end groups are in a distorted π -orbital plane of the stilbene core unit, these aryl units contribute little to the molecular conjugation level. As expected, this result causes similar electron delocalization of blue-light-emitting materials **1–3**, and these compounds have almost the same energy levels. Their optical energy band gaps (E_g) are 2.87, 2.85, and 2.88 eV, respectively, as determined from the intersection of the absorption and photoluminescence spectra.

To evaluate the EL properties of using these compounds as dopants in the emitting layer, multilayered devices **1–3** were fabricated with the structure of (ITO)/

**Figure 2.** Relative energy-level alignments and layer thickness of OLEDs.

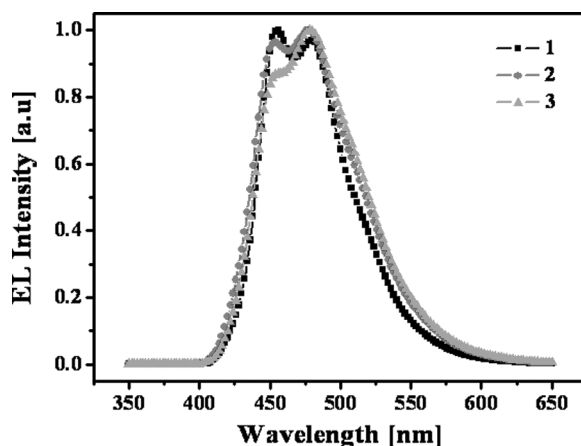


Figure 3. Electroluminescence spectra of devices 1–3.

4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (NPB) (70 nm)/9,10-di(2-naphthyl)anthracene (ADN): blue dopants **1–3** (30 nm: 2%)/tris(8-hydroxyquinolino)aluminum (Alq₃) (30 nm)/lithium quinolate (Liq) (1 nm)/Al, in which ITO served as the substrate, ADN acted as a host material, NPB as a hole transport material, and Alq₃ as an electron transport material.

The EL emission spectra of the devices **1–3** with emitting layers consisting of the ADN host doped with dopants **1–3** are shown in Figure 3. All three stilbene-based devices exhibited blue emissions in the region of 454–456 nm, with a vibrational shoulder at 478–480 nm. The corresponding CIE coordinates are $x=0.158$, $y=0.187$ for **1**, $x=0.165$, $y=0.208$ for **2**, and $x=0.170$, $y=0.230$ for **3**. The device employing dopant **1**, with a narrower FWHM and shorter emission wavelength, shows $\text{CIE}_y=0.187$ in the deeper blue region.

The current density-voltage (J - V) and luminance-voltage (L - V) characteristics of the three stilbene OLEDs are shown in Figure 4a and b, respectively. The key performance parameters of the devices and EL emission characteristics are summarized in

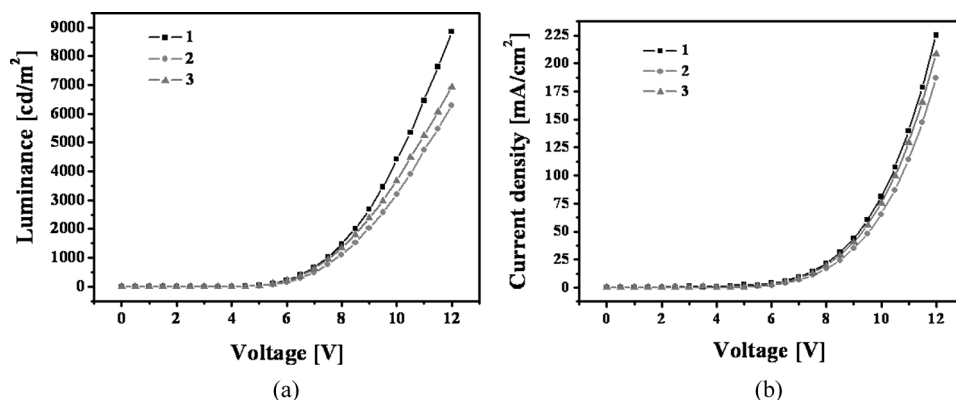


Figure 4. (a) Current density versus applied electric voltage and (b) luminance versus applied electric voltage characteristics of devices 1–3.

Table 2. Electroluminescence data for the devices 1–3

Device	EL _{max} [nm]	J [mA/cm ²] [a]	L [cd/m ²] [b]	L. E. [cd/A] [c]/[d]	P. E. [lm/W] [c]/[d]	CIE (x,y) [e]
1	456/480	225.0	8861	7.01/6.82	3.27/2.72	(0.158, 0.187)
2	454/478	186.7	6296	7.39/6.49	3.92/2.49	(0.165, 0.208)
3	456/478	208.3	6934	7.56/6.73	3.85/2.64	(0.170, 0.230)

[a, b] The maximum current density and luminance, [c] Maximum values, [d] At 20 mA/cm², [e] Commission Internationale d'Éclairage (CIE) coordinates at 10.0 V.

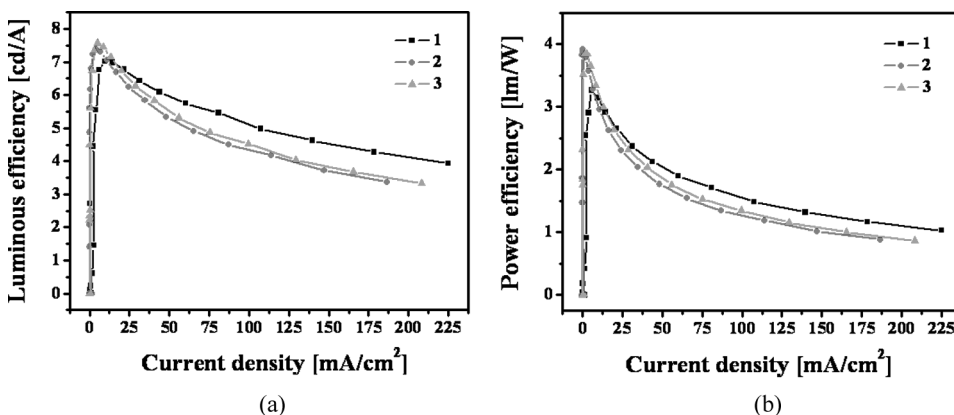
**Figure 5.** (a) Luminous efficiencies and (b) power efficiencies as a function of current density for the devices 1–3.

Table 2. The maximum brightness of the stilbene-based blue OLEDs varied from 6296 cd m⁻² in device 2 to as high as 8861 cd m⁻² in device 1. Variations in the luminous and power efficiencies of devices 1–3, as a function of the current density, are shown in Figure 5a and b. These devices show high luminous efficiencies, between 7.01–7.56 cd A⁻¹, as blue emitters because of the superior matched spectral overlap between the emission of the host and the absorption of the dopant, as shown in Figure 1. In particular, compound 1 with 2-naphthyl end groups gave the best device performance among the three stilbene derivatives 1–3. The maximum brightness of this device was 8861 cd m⁻², with a luminous efficiency of 6.82 cd A⁻¹ at 20 mA cm⁻² and power efficiency of 2.72 lm W⁻¹ at 20 mA cm⁻². The EL parameters for blue dopant 1 reflect its promising application in OLED devices. This study clearly suggests that not only the high quantum yield of the dopant, but also the superior matched spectral overlap between the emission of the host and the absorption of the dopant can improve efficiencies of blue OLEDs composed of a host and dopant.

Conclusions

In summary, new blue-light-emitting bis(diarylamino)stilbene derivatives 1–3 containing bulky *tert*-butyl groups were designed and synthesized. The stilbenes each

exhibited very high photoluminescence quantum yield. By employing blue dopant **1** into a multilayer device structure, it was possible to achieve a maximum luminance of 8861 cd m^{-2} at 12.0 V, a luminous efficiency of 6.82 cd A^{-1} at 20 mA cm^{-2} , a power efficiency of 2.72 lm W^{-1} at 20 mA cm^{-2} , and CIE_{x,y} coordinates of ($x=0.158$, $y=0.187$) at 10.0 V. These results demonstrate the superiority of these bis(diarylamino)stilbene derivatives in OLED devices.

Acknowledgments

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (20090073679).

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