

Molecular Engineering of Blue Organic Light Emitting Materials Based on Diarylamino-fluorene

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Abstract

We demonstrated the efficient blue organic light-emitting diodes (OLEDs) by employing diarylamino-fluorene derived blue fluorescent molecules as dopants. Among those, a device exhibited blue emission with the luminous efficiency of 11.2 cd/A at 20 mA/cm², the external quantum efficiency of 9.7% at 20 mA/cm², and the CIE_{x,y} coordinates of (x=0.163, y=0.259) at 8V

1. Introduction

For full-color OLED display application, it is essential to deliver a set of primary RGB emitters with sufficient high luminous efficiency, properly balanced color chromaticity, as well as sufficient operational stability. Such a set of emitters has been demonstrated by using a guest-host doped emitting system which encompasses a single or co-host matrix dispersed with various highly fluorescent or phosphorescent guest dopants leading to electroluminescence (EL) with the desirable hues.[1]

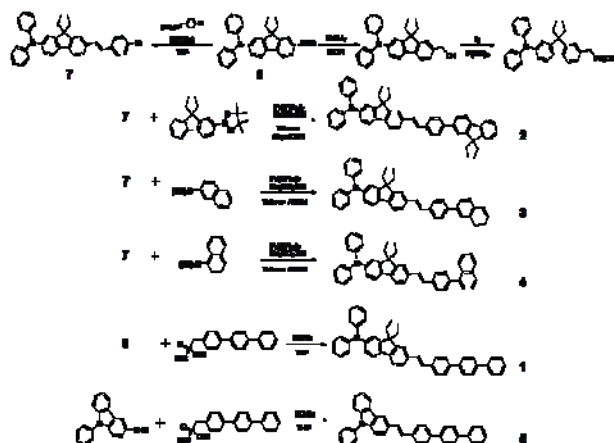
Several studies have been conducted on blue OLEDs using materials such as metal complexes [2], oxadiazoles [3], distyrylarylene derivatives [4,5]. But it is difficult to develop blue OLEDs having the sufficient electroluminescent properties for display application, due to the intrinsic characteristic having a wide band gap irrespective of the type of materials.

In the present work, we have designed and synthesized a new class of blue emitter 1~5 based on diarylamino-fluorene derivatives. Because of their high photoluminescence quantum yields both in solution and solid-state, these diarylamino-fluorene based materials are expected to have highly efficient electroluminescent properties. [6]

2. Experimental

2.1 Synthesis.

Synthesis of 1~5 were outlined in Scheme 1.



Scheme 1. Molecular structures and synthetic route for diarylamino-fluorene derived materials

N,N-Diphenylamino-9,9-diethyl-fluorene-7-vinyl-p-terphenyl (1).

To a mixture of 7-(diphenylamino)-9,9-diethyl-fluorene-2-carbaldehyde (350 mg, 0.92 mmol) and *p*-terphenylphosphonate (384 mg, 0.92 mmol) in 8 mL of anhydrous THF at 0 °C was added dropwise 1.38 mL of 1.0 M KO^t-Bu (1.38 mmol) in THF under N₂. The reaction mixture was stirred for 10 min at 0 °C followed by 1 h at room temperature and quenched with water. The solution mixture was filtered with water. The filtered solid was dissolved with CH₂Cl₂, dried over Na₂SO₄, filtered with silica-gel and then the solvent was removed under reduced pressure to afford a crude product. The crude product was

recrystallization from $\text{CHCl}_3/\text{EtOH}$ affording 457 mg (77.0%) of the pale yellow solid. ^1H NMR (300 MHz, CDCl_3 , δ): 7.74-7.69 (m, 4H), 7.67-7.61 (m, 6H), 7.60 (d, $J = 13$ Hz, 1H), 7.57 (d, $J = 13$ Hz, 1H), 7.51-7.44 (m, 4H), 7.39-7.34 (m, 1H), 7.28-7.21 (m, 6H), 7.14-7.10 (m, 5H), 7.05-6.99 (m, 3H), 1.99 (q, $J = 7.3$ Hz, 4H), 0.39 (t, $J = 7.3$ Hz, 6H); ^{13}C NMR (300 MHz, CDCl_3 , δ): 151.9, 150.7, 148.2, 147.5, 141.5, 140.9, 140.3, 139.8, 139.7, 137.0, 136.6, 135.8, 129.7, 129.4, 129.1, 127.8, 127.6, 127.5, 127.3, 127.1, 126.2, 124.1, 123.9, 122.7, 120.8, 120.6, 119.6, 119.5, 56.3, 33.0, 8.8; MS(EI^+) m/z 643 (M^+); HRMS(EI^+) Calce for $\text{C}_{49}\text{H}_{41}\text{N}$: 643.3239 (M^+). Found: 643.3248.

(E)-2-N,N-Diphenylamino-9,9-diethyl-fluoren-7-vinyl-2'-9',9' - diethyl-fluorene (2).

A mixture of (E)-7-(4-bromostyryl)-9,9-diethyl-N,N-diphenyl-fluoren-2-amine (378 mg, 0.66 mmol), 2-(9,9-diethyl-9H-fluorene-2-yl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (300 mg, 0.86 mmol), tetrakis(triphenylphosphine)palladium(0) (30 mg, 0.026 mmol), 2M K_2CO_3 (6 mL) added Toluene and Aliquat336 was refluxed at 130°C for 2-3h. At the conclusion of the reaction, the mixture was extraction with ethyl acetate. The organic layer was washed with brine and dried (MgSO_4). The reaction mixture was concentrated and the residue was purified by chromatography (MC/Hex) to afford 334 mg (yield 71%). ^1H NMR (300 MHz, CDCl_3 , δ): 8.80(s, 1H), 7.94-7.85 (m, 3H), 7.79 (d, $J = 6.7$ Hz, 1H), 7.75 (d, $J = 10$ Hz, 2H), 7.64 (s, 1H), 7.61 (d, $J = 8.4$ Hz 2H), 7.56 (d, $J = 6.7$ Hz, 2H), 7.55 (s, 1H), 7.53-7.48 (m, 4H), 7.3-7.2 (m, 4H), 7.13 (d, $J = 8.5$ Hz, 5H), 7.10-6.98 (m, 3H), 2.17-2.00 (m, 8H), 0.41-0.34 (m, 12H); ^{13}C NMR (300 MHz, CDCl_3 , δ): 152.0, 151.0, 150.8, 150.5, 148.4, 147.6, 141.5, 141.2, 140.9, 139.9, 136.9, 136.8, 136.0, 129.5, 127.7, 127.5, 127.2, 126.3, 126.1, 124.2, 124.0, 123.3, 122.9, 121.6, 120.9, 120.7, 120.3, 120.1, 119.7, 102.5, 56.5, 56.4, 34.9, 33.1, 8.9.

(E)-2-N,N-Diphenylamino-9,9-diethyl-fluoren-7-vinyl-2' naphthalene (3).

A mixture of (E)-7-(4-bromostyryl)-9,9-diethyl-N,N-diphenyl-fluoren-2-amine (570 mg, 0.525 mmol), 2-Naphthaleneboronic acid (135 mg, 0.8 mmol), tetrakis(triphenylphosphine)palladium(0) (25 mg, 0.021 mmol), Na_2CO_3 (560 mg, 5.25 mmol) in H_2O (2.63 mL) and solvent [toluene (5.26 mL) and EtOH (2.63 mL)] was refluxed at 130°C for 2-3h. At the conclusion of the reaction, the mixture was extraction with ethyl acetate. The organic layer was washed with brine and dried (MgSO_4). The reaction mixture was concentrated and the residue was purified by chromatography (EA/Hex) to afford 203 mg

(yield 62.9%). ^1H NMR (300 MHz, CDCl_3 , δ): 8.1 (s, 1H) 7.95-7.87 (m, 3H), 7.81-7.75 (t, $J = 9.2$ Hz, 3H), 7.68-7.48 (m, 10H), 7.32 (d, $J = 7.3$ Hz, 5H), 7.13(d, $J = 8.5$ Hz, 4H), 7.05-6.99 (m, 3H), 2.05-1.89 (m, 4H), 0.42-0.37 (t, $J = 6.8$ Hz, 6H); ^{13}C NMR (300 MHz, CDCl_3 , δ): 152.0, 150.8, 148.3, 147.6, 141.6, 1140.3, 138.8, 137.1, 136.7, 135.9, 133.0, 129.8, 129.5, 128.8, 128.5, 127.9, 127.4, 127.2, 126.7, 126.3, 125.8, 125.6, 124.2, 122.8, 120.9, 120.7, 119.6, 56.4, 33.0, 8.9.

(E)-2-N,N-Diphenylamino-9,9-diethyl-fluoren-7-vinyl-1' naphthalene (4).

The reaction described for the synthesis of **3** was carried out starting with (E)-7-(4-bromostyryl)-9,9-diethyl-N,N-diphenyl-fluoren-2-amine (800 mg, 1.4 mmol) and naphthaleneboronic acid (362 mg, 2.1 mmol). 320 mg (yield 27%). ^1H NMR (300 MHz, CDCl_3 , δ): 8.1 (s, 1H) 7.96-7.88 (m, 3H), 7.81-7.77 (t, $J = 9.0$ Hz, 3H), 7.68-7.48 (m, 10H), 7.31 (d, $J = 7.2$ Hz, 5H), 7.13 (d, $J = 8.5$ Hz, 4H), 7.04-6.98 (m, 3H), 2.05-1.89 (m, 4H), 0.42-0.37(t, $J = 6.8$ Hz, 6H); ^{13}C NMR (300 MHz, CDCl_3 , δ): 152.0, 150.8, 148.4, 147.6, 141.6, 140.2, 138.3, 137.1, 136.7, 135.9, 134.1, 133.0, 129.9, 129.5, 128.8, 128.6, 128.0, 127.4, 127.3, 126.7, 126.3, 125.8, 125.7, 124.2, 124.0, 122.9, 121.0, 120.8, 119.7, 56.4, 33.1, 9.0

(E)-9-phenyl cabazole-3-vinyl-p-terphenyl (5).

The reaction described for the synthesis of **1** was carried out starting with 9-phenyl-9H-carbazole-3-carbaldehyde (170 mg, 0.627 mmol) and *p*-terphenylphosphonate (238 mg, 0.627 mmol). 290 mg (93.2%). ^1H NMR (300 MHz, CDCl_3 , δ): 8.31 (s, 1H), 8.20 (d, $J = 7.6$ Hz, 1H), 7.43 (d, $J = 4.7$ Hz 3H), 7.68-7.62 (m, 8H), 7.61 (d, $J = 4.1$ Hz, 3H), 7.51-7.31 (m, 10H), 7.26(s, 1H); ^{13}C NMR (300 MHz, CDCl_3 , δ): 141.6, 141.0, 140.3, 140.0, 139.5, 137.8, 137.3, 130.2, 129.9, 129.8, 129.0, 128.4, 127.8, 127.7, 127.6, 127.5, 127.3, 127.2, 127.0, 126.4, 126.2, 125.1, 125.0, 124.1, 123.6, 120.6, 120.4, 118.8, 110.3, 110.2, 29.9, 1.2, 0.2.

2.2. UV-Vis and PL Characterization

The UV-Vis absorption and photoluminescence spectra of these new dopants were measured in dichloromethane (10^{-5} M) using Sinco S-3100 and Amincobrowman series 2 luminescence spectrometer, respectively.

2.3 Measurement of Energy level

The ionization potentials (or HOMO energy levels) of five blue materials were determined by low energy photo-electron spectrometry (Riken-Keiki AC-2).

LUMO energy levels were estimated by subtracting the energy gap from the HOMO energy levels.

2.4. Device fabrication

For fabricating OLEDs, the indium-tin-oxide (ITO) thin films coated on glass substrates were used, which was $30 \Omega / \text{square}$ of the sheet resistivity and 1000 \AA of thickness. The ITO coated glass was cleaned in an ultrasonic bath by the following sequences: in acetone, methyl alcohol, distilled water and kept in isopropyl alcohol for 48 hours and dried by N_2 gas gun. The substrates were treated by O_2 plasma treatment with the conditions of 2×10^{-2} Torr at 125 W for 2 minutes [7]. All organic materials and metal were deposited under high vacuum (5×10^{-7} Torr). The OLEDs were fabricated in the following sequence: 9,10-di(2-naphthyl)anthracene (MADN) : Blue dopants (15 %) / 4,7-diphenyl-1,10-phenanthroline (BPhen) (300 \AA) / lithium quinolate (Liq) (20 \AA) / Al (1000 \AA).

3. Results and discussion

Fig. 1(a) shows UV-Vis spectra of the maximum absorption wavelengths of new designed dopant 1~5 at $\lambda_{\text{max}} = 392, 393, 393, 396,$ and 397 nm , respectively, in dichloromethane. Especially, the effective spectra overlap between the emission of the host (MADN) and the UV-absorption of the dopants 1~4 were observed. This indicates that the effective energy transfer between host (MADN) and dopants 1~4 are possible and thus good device performances are expected.

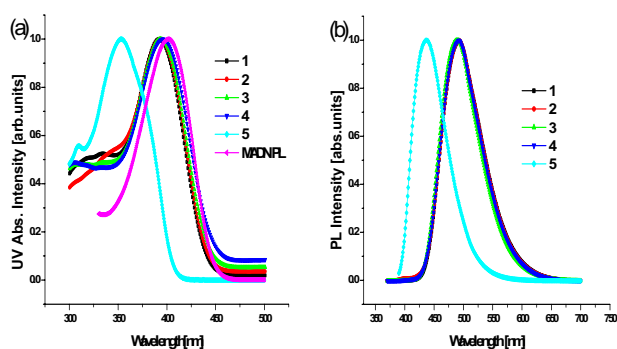


Fig.1. Solution UV-Vis absorption spectra (a) and PL spectra (b) of 1~5 in dichloromethane.

Figure 1(b) depicts the blue fluorescence spectra of

1~5, which have the maximum emission wavelengths at 492, 490, 493, 492, and 436 nm, respectively, in dichloromethane, when they were excited around 392~397 nm. Notably, the emission wavelength of compound 5 is blue-shifted around 28 nm with respect to that of compound 1. Compared with 1, 5 have carbazole instead of diphenylamino group in fluorene moiety of materials. This carbazole group makes LUMO energy level of 5 be 0.7 eV higher than that of 1 and thus fluorescence spectra of 5 be blue shifted.

The optical properties and energy levels of five materials are listed in **Table 1**.

Table 1. Optical properties and energy levels of 1~5 materials.

	1	2	3	4	5
Optical					
Ab _{max} (nm)	392	393	393	396	397
Em _{max} (nm)	492	490	493	492	436
Energy level					
HOMO(eV)	5.4	5.5	5.4	5.5	5.1
LUMO (eV)	2.6	2.7	2.6	2.7	1.9
E _g (eV)	2.8	2.8	2.8	2.8	3.2

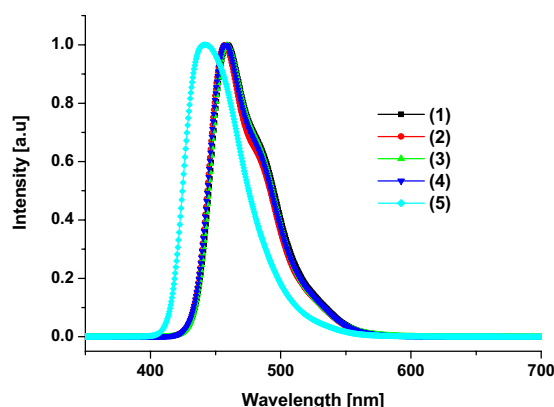


Fig.2. EL spectra of 1~5 at 10V

As shown in **Fig. 2**, OLEDs based on 1~5 emit blue electroluminescence $\lambda_{\text{max}} = 460, 457, 459, 459,$ and 430 nm , respectively. Notably, device employing 5 as a dopant shows deeper blue emission than the others, which is due to carbazole group.

Fig. 3(a) shows the luminance-voltage characteristic of the devices. The maximum luminances of devices employing dopants 1~5 were 28900, 27600, 27400, 27700, and 4773 cd/m^2 at 12 V, respectively. The maximum luminous efficiencies were 11.6, 11.4, 9.7, 10.2 and 2.74 cd/A , respectively

as shown in Fig. 3(b).

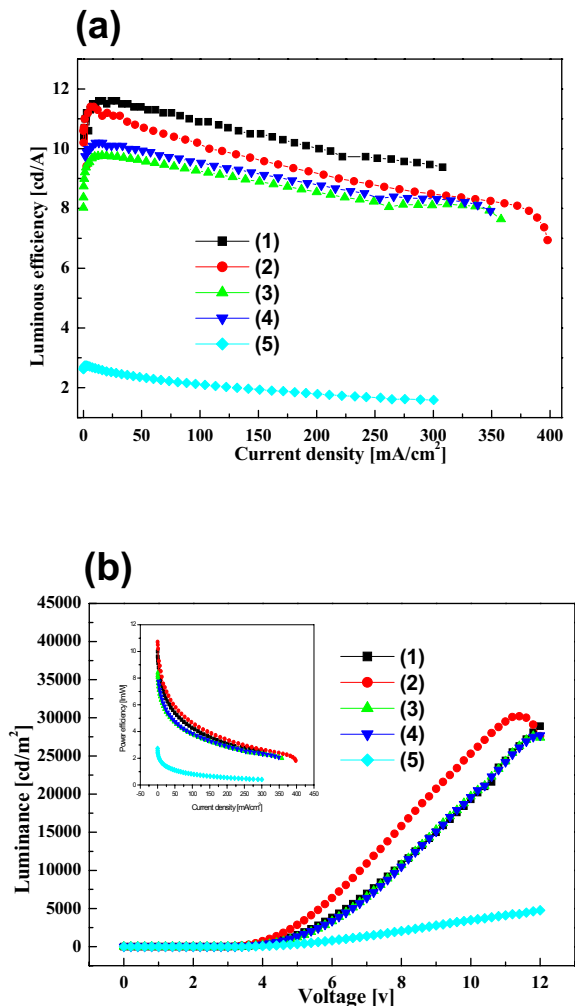


Fig. 3 (a) Luminance efficiency vs. current density characteristics. (b) Luminance vs. voltages characteristics. (Inset: Power efficiency vs. current density characteristics)

All EL performance characteristics of devices employing dopants **1~5** are summarized in **Table 2**.

The luminance efficiency were 11.5, 11.2, 9.8, 10.1, 2.6 cd/A at 20 mA/cm² and power efficiency were 6.7, 7.3, 5.7, 5.9, 1.5 lm/W at 20 mA/cm² for devices (**1~5**), respectively. The external quantum efficiencies for devices (**1~5**) were 8.9, 9.7, 8.4, 8.1 and 3.7 % at 20 mA/cm², respectively. The CIE (Commission Internationale de l'Eclairage) coordinates of these devices made of **1~5** were (0.173, 0.281), (0.163, 0.259), (0.170, 0.275), (0.167, 0.277), and (0.160, 0.150), respectively.

Table 2. EL performance characteristics of 1~5 devices

	Luminance [cd/m ²] @ 12V	Luminous Efficiency @ 20mA/cm ² [cd/A]	Power Efficiency @ 20mA/cm ² [lm/W]	Quantum Efficiency @ 20mA/cm ² [%]	EL Spectra [λ _{nm}]	CIE (x, y) @ 8V
(1)	28900	11.5	6.7	8.9	460	(0.173, 0.281)
(2)	27600	11.2	7.3	9.7	457	(0.163, 0.259)
(3)	27400	9.8	5.7	8.4	459	(0.170, 0.275)
(4)	27700	10.1	5.9	8.1	458	(0.167, 0.277)
(5)	4773	2.6	1.5	3.7	430	(0.160, 0.150)

Notably, the efficiencies of OLED devices of (**1~4**) have much higher than that of **5** due to good matched spectral overlap between the emission of the host and the absorption of the dopants shown in **Figure 1**, and thus the effective formation of dopants excitons in blue emitting layer of devices. This clearly suggests that the efficient energy transfer between host and dopant play a key role in efficiency in OLED.

4. Summary

A series of highly efficient blue emitters based on diarylamino-fluorene has been synthesized and fully characterized. By using **2** as emitting layer, high-efficiency blue OLEDs were fabricated, showing the maximum luminance of 27600 cd/m² at 12 V, the luminous efficiency of 11.2 cd/A at 20 mA/cm², the external quantum efficiency of 9.7% at 20 mA/cm² and the CIE_{x,y} coordinates of (x=0.163, y=0.259) at 8V. With future studies to improve the color purity, **2** may prove to be an excellent blue-light emitter for future OLED display applications.

5. References

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