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Highly efficient blue OLEDs based on diphenylaminofluorenylstyrenes end-capped with heterocyclic aromatics

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ABSTRACT

In this paper, we have designed four diphenylaminofluorenylstyrene derivatives end-capped with heterocyclic aromatic groups, such as 9-phenylcabazole, 4-dibenzofuran, 2-benzoxazole, 2-quinoxaline, respectively. These materials showed blue to red fluorescence with maximum emission wavelengths of 476–611 nm, respectively, which were dependent on the structural and electronic nature of end-capping groups. To explore the electroluminescent properties of these materials, multilayer OLEDs were fabricated in the following sequence: ITO/DNTPD (40 nm)/NPB (20 nm)/2% doped in MADN (20 nm)/Alq_3 (40 nm)/Liq. (1 nm)/Al. Among those, a device exhibited a highly efficient blue emission with the maximum luminance of 14,480 cd/m^2 at 9 V, the luminous efficiency of 5.38 cd/A at 20 mA/cm^2, power efficiency of 2.77 lm/W at 20 mA/cm^2, and $CIE_{x,y}$ coordinates of (0.147, 0.152) at 8 V, respectively.

1. Introduction

Organic light-emitting diodes (OLEDs) have attracted a great deal of attention given their potential application in full color flat-panel displays and light sources [1–4]. For the full color OLEDs, the proper red, green and blue emitting materials need. Since blue materials have the wide energy band gaps comparing to red or green emitting materials, it has difficulties in improving color purity, high efficiency, and long operation time [5]. Thus, current studies have mainly focused on the development of efficient blue emitting materials to fulfill high efficiency and deep blue simultaneously. Recently, we reported that a series of diphenylaminofluorene derivatives had the excellent potentials as the efficient blue emitters for OLEDs [6,7]. Although these materials showed high efficiency, further development will be needed for the saturated deep blue color OLEDs.

In this paper, we report the synthesis and electroluminescent properties of four emitting materials based on the diphenylaminofluorenylstyrene derivatives with various heteroaromatic end-capping groups as shown in Fig. 1. In compounds **1**–**4**, diphenylamino groups were introduced to enhance the hole transporting properties and improve the charge balance in the emitting layers. Compounds **1** and **2** have a chemical structure with a diphenylaminofluorenylstyrene emitting core end-capped with electron-donating groups, such as 9-phenylcabazole and 4-dibenzofuran, whereas compounds **3** and **4** have the same emitting core end-capped with electron-withdrawing groups, such as 2-benzoxazole and 2-quinoxaline, respectively. As will be seen in below, the photophysical and electroluminescent properties of these materials (**1**–**4**) were dependent on the structural and electronic nature of end-capping groups. In addition, 9-phenylcabazole and 4-dibenzofuran groups are incorporated in diphenylaminofluorenylstyrene skeleton of materials **1** and **2**, to study the substituent effect of electron-donating groups on the electroluminescence properties of the devices using them as emitting materials. Also, an OLED device using **1** exhibited blue emission with the high efficiencies and blue color chromaticity.

2. Experimental

2.1. Synthesis and characterization

2-Bromo-9-phenylcarbazole, 2-chlorobenzoxazole, 2-chloroquinoxaline, 4-formylbenzene boronic acid were used as received from Aldrich or TCI. The (7-(diphenylamino)-9,9-diethylfluorene-2-yl)methylphosphonate (A), and 7-(4-bromostyryl)-9,9-diethyl-*N*,*N*-diphenyl-fluorne-2-amine (C) was synthesized according to previously reported literature [7–10]. ^1H NMR spectra were recorded on a Varian Unity Inova 300Nb spectrometer in $CDCl_3$ as the solvent. Low- and high-resolution mass spectra were measured using a Jeol JMS-600 spectrometer in the EI mode and a JMS-T100TD (AccuTOF-TLC) in the positive ion mode. The UV–vis absorption and photoluminescence spectra of the dopant materials were measured in dichloromethane (10^{-5} M) using a Sinco S-3100

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and Aminco-Browman series 2 luminescence spectrometer, respectively. The fluorescence quantum yields of the blue materials were determined in dichloromethane at 293 K against BDAVBi as a reference ($\Phi = 0.86$) [11].

General procedure for the Horner–Wadsworth–Emmons reaction of **1**, **3** and **4**: to a solution of (7-(diphenylamino)-9,9-diethylfluorene-2-yl)methylphosphonate (A) (1.5 mmol) and corresponding aldehyde (1.5 mmol) in THF in an ice bath, potassium-*tert*-butoxide (2.3 mmol) was added under nitrogen [11]. The reaction mixture was stirred for 30 min at 0 °C, followed by 1 h at room temperature, and quenched with water. The solution mixture was extracted with ethyl acetate and washed twice with water. The combined organic layers were dried over $MgSO_4$ and the solvent removed under reduced pressure to afford a crude product that was purified by column chromatography with silica gel from CH_2Cl_2/hexane. Diphenylaminofluorenylstyrene derivatives were synthesized from (7-(diphenylamino)-9,9-diethylfluorene-2-yl)methylphosphonate (A) and the corresponding aryl aldehyde according to this procedure.

General procedure for the synthesis of compound **2**: to a toluene (10 mL) solution of 4,4′-bis(3,5-di-tertbutylphenylamino) stilbene (0.85 mmol) were added aryl bromide (2.13 mmol), sodium *tert*-butoxide (2.73 mmol), $Pd(PPh_3)_4$ (0.01 mmol), and ethanol. The reaction mixture was heated and stirred at 120 °C under N_2 for 4 h. The reaction mixture was extracted with toluene, washed with aqueous NaCl solution, dried with $MgSO_4$. Evaporation of the solvent under reduced pressure to afford a crude product that was purified by column chromatography with silica gel from CH_2Cl_2/hexane.

2-*N*,*N*-Diphenylamino-9,9-diethyl-fluorene-7-styryl-3′-9′-phenylcarbazole (**1**): yield 50%. ^1H NMR (300 MHz, $CDCl_3$, δ): 9.40 (s, 1H), 8.22–8.20 (d, *J* = 7.5 Hz, 1H), 7.76–7.71 (m, 2H), 7.68–7.43 (m, 14H), 7.36–7.29 (m, 3H), 7.23 (s, 4H), 7.14–7.11 (d, *J* = 8.4 Hz, 5H), 7.05–6.99 (m, 4H), 2.03–1.89 (m, 4H), 0.42–0.37 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 151.7, 150.5, 148.1, 147.3, 141.5, 141.2, 141.0, 136.1, 135.8, 133.0, 128.5, 127.7, 127.5, 126.9, 126.6, 125.4, 124.8, 124.5, 124.0, 123.6, 123.3, 121.0, 120.6, 120.4, 120.0, 118.8, 118.5, 56.2, 32.9, 8.7. HRMS [EI$^+$] calcd for $C_{55}H_{44}N_2$: 732.3504, found: 732.3501.

2-*N*,*N*-Diphenylamino-9,9-diethyl-fluorene-7-styryl-4′-dibenzofuran (**2**): yield 75%. ^1H NMR (300 MHz, $CDCl_3$, δ): 7.99–7.90 (m, 4H), 7.70–7.68 (d, *J* = 8.4 Hz, 2H), 7.64–7.60 (m, 2H), 7.58–7.57 (d, *J* = 4.5 Hz, 1H), 7.54–7.46 (m, 3H), 7.44–7.41 (d, *J* = 7.4 Hz, 1H), 7.39–7.21 (m, 8H), 7.18–7.12 (m, 5H), 7.05–6.98 (m, 3H), 2.05–1.88 (m, 4H), 0.42–0.38 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 156.3, 151.8, 150.6, 148.1, 147.4, 141.4, 137.3, 136.5, 135.7, 135.4, 130.2, 129.3, 129.0, 128.5, 128.1, 127.2, 126.8, 126.2, 125.1, 124.6, 123.4, 120.0, 118.9, 56.2, 32.9, 8.8, 8.7. HRMS [EI$^+$] calcd for $C_{49}H_{39}NO$: 647.3032, found: 647.3027.

2-*N*,*N*-Diphenylamino-9,9-diethyl-fluorene-7-styryl-2′-benzoxazole (**3**): yield 63%. ^1H NMR (300 MHz, $CDCl_3$, δ): 8.28–8.25 (d, *J* = 8.4 Hz, 2H), 7.71–7.68 (d, *J* = 8.4 Hz, 2H), 7.61–7.59 (d, *J* = 8.1 Hz, 2H), 7.56–7.53 (d, *J* = 8.4 Hz, 2H), 7.50–7.49 (m, 1H), 7.38–7.35 (m, 2H), 7.32–7.29 (d, *J* = 7.2 Hz, 2H), 7.15–7.12 (d, *J* = 8.7 Hz, 6H), 7.08–7.00 (m, 4H), 2.02–1.89 (m, 4H), 0.41–0.34 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 163.1, 151.8, 150.8, 150.6, 148.1, 147.5, 142.4, 141.9, 140.9, 136.3, 135.1, 129.5, 129.2, 128.1, 127.0, 126.7, 125.7, 124.2, 123.9, 120.8, 119.9, 56.1, 32.8, 8.7. HRMS [EI$^+$] calcd for $C_{44}H_{36}N_2O$: 608.2828, found: 608.2821.

2-*N*,*N*-Diphenylamino-9,9-diethyl-fluorene-7-styryl-2′-quinoline (**4**): yield 73%. ^1H NMR (300 MHz, $CDCl_3$, δ): 9.38 (s, 1H), 8.26–8.23 (d, *J* = 8.4 Hz, 2H), 8.18–8.11 (m, 2H), 7.83–7.78 (m, 1H), 7.76–7.73 (d, *J* = 8.4 Hz, 2H), 7.64–7.50 (m, 5H), 7.31–7.29 (d, *J* = 6.9 Hz, 1H), 7.25–7.2 (m, 3H), 7.17–7.10 (m, 5H), 7.08–6.99 (m, 5H), 2.03–1.86 (m, 4H), 0.42–0.33 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 163.1, 151.8, 150.8, 150.6, 148.1, 147.5, 142.4, 141.9, 140.9, 136.3, 135.1, 129.5, 129.2, 128.1, 127.0, 126.7, 125.7, 124.2, 123.9, 120.8, 119.9, 56.1, 32.8, 8.7. HRMS [EI$^+$] calcd for $C_{45}H_{37}N_3$: 619.2987, found: 619.2983.

2.2. Device fabrication and measurements

OLEDs using red dopants in the emitting layers were fabricated by vacuum (10^{-7} torr) thermal evaporation onto pre-cleaned ITO coated glass substrates. The structure was as follows: ITO/DNTPD (40 nm)/NPB (20 nm)/MADN: 2% blue dopants **1** and **2** (20 nm)/Alq_3 (40 nm)/Liq. (1.0 nm)/Al. The current density (*J*), luminance (*L*), luminous efficiency (LE), power efficiency (PE), and the CIE chromaticity coordinates of the OLEDs were measured with Keithly 2400, Chroma meter CS-1000A. Electroluminescence was measured using a Roper Scientific Pro 300i.

3. Results and discussion

Four materials (**1**–**4**) were base on a diphenylaminofluorenylstyrene core structure with the heterocyclic aromatic end-capping groups such as 9-phenylcarbazole, 4-dibenzofuran, 2-benzoxazole, and 2-quinoxaline, respectively. The molecular structures and synthetic routes of new materials are shown in Fig. 1(a). These compounds were prepared *via* the Horner–Wadsworth–Emmons reaction and Suzuki cross-coupling reaction. The molecular structures of the compounds **1**–**4** were characterized by ^1H and ^{13}C NMR, and high-resolution mass spectroscopy.

The UV–vis absorption spectra of fluorescent materials **1**–**4** in dichloromethane are shown in Fig. 2. Compounds **1**–**4** show a main absorption peak in the 390–408 nm range and good spectral overlap was observed between the emission of the common blue host (MADN) and the absorption of materials **1**–**4**. These observations indicate that the blue materials **1**–**4** can effectively accept energy from the MADN host material by Förster-type energy transfer. These imply that these materials **1**–**4** would work as the highly efficient dopants in OLED devices using MADN host.

The normalized PL emission spectra of materials **1**–**4** are shown in Fig. 2. The maximum emission peaks of these materials increased in the order of **1**(476 nm) < **2**(493 nm) < **3**(543 nm) < **4**(611 nm). The emission spectra of these materials showed a gradual red shift with the increase of the electron accepting properties of the end-capped groups. For example, compared to material **1** with the electron-donating carbazole group, the observed red shift in the emission spectra of materials **3** and **4** may arise from the electron accepting properties of 2-benzoxazole and 2-quinoxaline in the end-capping groups. Also, compound **2** had a shorter emission maximum wavelength (493 nm) than compound **3** (543 nm), which may be rationalized from the fact that the 4-dibenzofuran end-capping group in compound **2** has the smaller electron accepting property than 2-benzoxazole in compound **3**. Charge transfer band in these type materials **1**–**4** would contribute to the differences in energy band-gaps. The contribution of charge transfer band is increased in the order of **1** < **2** < **3** < **4**, which is dependent on the electron-accepting capabilities of the end-capping groups of materials **1**–**4**. These are in good agreement with the trends of the PL spectra of materials **1**–**4**.

The quantum yields of materials **1**–**4** were 0.81, 0.85, 0.52, and 0.02, respectively. The full width at half maximum (FWHM) of materials **1**–**4** were 73, 79, 100, and 126, respectively. The HOMO energy levels of **1**–**4** were measured using a low-energy photo-electron spectrometer (Riken-Keiki AC-2). The HOMO/LUMO energy levels of **1**–**4** were −5.33/−2.46, −5.56/−2.73, −5.54/−2.88, and −5.54/−2.93, respectively. In addition, the respective optical energy band gaps (E_g) of **1**–**4** were 2.87, 2.83, 2.66, and 2.61 eV, as determined from the absorption spectra.