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Highly Efficient Blue Light-Emitting Materials Based on Arylamine Substituted DPVBi Derivatives

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A series of arylamine substituted DPVBi derivatives (**1–4**) were synthesized via the Horner-Wadsworth-Emmons reaction. Their electroluminescent properties were examined by fabricating a multilayer OLED device with the following structure: ITO/DNTPD (40 nm)/NPB (20 nm)/2% DPVBi derivatives (**1–4**) doped in MADN (20 nm)/Alq_3 (40 nm)/Liq (1.0 nm)/Al. All devices showed efficient blue emission. In particular, a high efficiency blue OLED was fabricated using compound **1** as a dopant in the emitting layer. The maximum luminance, luminous efficiency, power efficiency and CIE coordinates of the blue OLED using compound **1** as a dopant were 16110 cd/m^2 at 10 V, 10.1 cd/A at 20 mA/cm^2, 4.37 lm/W at 20 mA/cm^2, and ($x = 0.197$, $y = 0.358$) at 8 V, respectively. Moreover, a device using compound 4 as the dopant exhibited efficient deep blue emission with a luminance, luminous efficiency, power efficiency and CIE coordinates of 7005 cd/m^2 at 10 V, 6.25 cd/A at 20 mA/cm^2, 2.50 lm/W at 20 mA/cm^2 and ($x = 0.151$, $y = 0.143$) at 8 V, respectively.

Keywords: Blue OLEDs, DPVBi Derivatives, Horner-Wadsworth-Emmons Reaction.

1. INTRODUCTION

Blue light-emitting materials have attracted considerable interest in academic and industrial fields for applications to light-weight, low-cost, flexible large-area OLED (organic light-emitting diode) displays.[1] However, blue-emitting materials with a high EL efficiency of 3.1–6.5%, deep-blue color with Commission Internationale de l'Eclairage (CIE) y coordinate <0.15, and long operational lifetime are difficult to develop due to the wide bandgap of blue-emitting materials.[2] DPVBi (4,4′-bis(2,2-diphenylvinyl)biphenyl) is a deep blue-emitting material for OLEDs with the CIE coordinates of (0.15, 0.08).[3] However, the EL efficiencies of devices using DPVBi are unsuitable for widespread use. In addition, DPVBi has a low glass transition temperature (T_g; ~64 °C) and a tendency to crystallize.[4] Therefore, devices using DPVBi have problems with their operational lifetime.

This paper describes the synthesis and electroluminescent properties of arylamine-substituted DPVBi derivatives (**1–4**). In these materials, the DPVBi core was combined with arylamine units, which have enhanced hole-transporting properties,[5] and the EL performances of the devices using them as emitting materials showed significant improvement. Moreover, the bulky 1,1′-diphenyl groups could prevent intermolecular interactions of the emitting materials and contribute to high EL efficiency through the suppression of concentration quenching.[6]

Among the four different blue materials, compounds **1** and **2** have two diphenylamine groups at the DPVBi emitting core, whereas the other two materials **3** and **4** had the same emitting core with a diphenylamine and carbazole group, respectively, to allow an examination of the amine-substituents effects on device performances of blue fluorescent OLEDs. As described herein, blue OLEDs with high efficiency and deep blue color chromaticity were developed using these novel blue materials based on DPVBi.

2. EXPERIMENTAL DETAILS

2.1. Synthesis of Materials

Diethyl (4′-(2,2,-diphenylvinyl)biphenyl-4-yl) methylphosphonate (**A**)[7] (515 mg, 1.06 mmol) and bis[4-(diphenylamino)phenyl]- methanone (**B**)[8] (551 mg, 1.06 mmol) in THF (35 mL) placed in an ice bath, KO^{t}Bu (1.17 mL, 1.17 mmol) was added under N_2. The reaction mixture was stirred for 30 min at 0 °C, followed by 1 h at room temperature and quenched with water. It was extracted twice with CH_2Cl_2 and washed twice

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with water. The organic layers were dried with anhydrous $MgSO_4$ and filtered. The crude mixture was purified through column chromatography using silica-gel and recrystallization to give the desired compound. The tetraethyl biphenyl-4,4′-diylbis(methylene)diphosphonate (C),[7] (4-(diphenylamino)phenyl)(phenyl)methane (D),[9] and (4-(9-carbazole-9-yl)phenyl)(phenyl)methane (E)[10] were synthesized as reported previously.

1: (Yield: 60%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ ppm 7.37–7.32 (m, 11H), 7.30–7.27 (m, 5H), 7.25–7.23 (m, 6H), 7.14–7.08 (m, 14H), 7.05–6.99 (m, 11H), 6.90 (s, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ ppm 147.9, 147.8, 147.5, 147.3, 143.6, 142.9, 142.2, 140.7, 138.5, 137.3, 136.6, 134.5, 131.5, 130.6, 130.2, 130.1, 129.5, 129.0, 128.5, 128.5, 128.0, 127.8, 127.7, 126.5, 126.4, 126.2, 124.8, 124.7, 123.8, 123.3, 123.2. APCI-MS (m/z): 845 [M^+]. HRMS [EI^+] calcd for $C_{64}H_{48}N_2$: 844.3817, found: 844.3793. Anal. calcd for C 90.96, H 5.73, N 3.31; found: C 90.90, H 5.69, N 3.37. mp 229 °C.

2: (Yield: 72%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ ppm 7.43-7.38 (m, 4H), 7.36–7.31 (m, 8H), 7.30–7.21 (m, 8H), 7.20–7.18 (m, 2H), 7.17–7.08 (m, 12H), 7.05–6.97 (m, 12H), 6.94–6.92 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ ppm 147.8, 147.8, 137.3, 134.3, 131.5, 130.6, 130.2, 130.1, 129.5, 129.0, 128.4, 128.0, 127.7, 126.4, 124.8, 123.6, 123.2, 123.2. APCI-MS (m/z): 845 [M^+]. HRMS [EI^+] calcd for $C_{64}H_{48}N_2$: 844.3817, found: 844.3799. Anal. calcd for C 92.96, H 5.73, N 3.31; found: C 92.92, H 5.71, N 3.35. mp 124 °C.

3: (Yield: 35%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ ppm 7.40–7.29 (m, 15H), 7.25–7.23 (m, 7H), 7.15–7.12 (m, 6H), 7.09–7.06 (m, 5H), 7.03–6.70 (m, 5H), 6.92 (s, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ ppm 147.8, 147.3, 143.7, 143.6, 142.9, 142.7, 140.7, 139.0, 138.8, 137.0, 136.6, 134.3, 131.5, 130.6, 130.2, 130.2, 129.5, 129.0, 128.5, 128.0, 127.8, 127.7, 126.5, 126.4, 124.8, 123.6, 123.2, 123.2. APCI-MS (m/z): 678 [M^+]. HRMS [EI^+] calcd for $C_{52}H_{39}N$: 677.3083, found: 677.3077. Anal. calcd for C 92.13, H 5.80, N 2.07; found: 92.10, H 5.76, N 2.05. mp 202 °C.

4: (Yield: 53%). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ ppm 8.68–8.65 (d, $J = 8.1$ Hz, 2H), 7.85–7.83 (d, $J = 7.8$ Hz, 5H), 7.58–7.50 (d, $J = 8.1$ Hz, 3H), 7.44–7.35 (m, 9H), 7.19–7.09 (m, 8H), 6.96–6.91 (t, $J = 7.8$ Hz, 2H), 6.74–6.72 (d, $J = 7.8$ Hz, 6H), 6.67–6.64 (d, $J = 7.5$ Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ ppm 143.6, 143.2, 143.5, 141.0, 140.6, 138.8, 136.8, 136.8, 132.2, 130.6, 130.3, 130.3, 130.2, 129.2, 129.1, 129.0, 128.7, 128.5, 128.0, 127.8, 127.8, 127.4, 126.9, 126.6, 126.5, 126.5, 126.2, 126.2, 123.7, 123.7, 120.6, 120.3, 120.2, 110.1. EI-MS (m/z): 676 [M^+]. HRMS [EI^+] calcd for $C_{52}H_{37}N$: 675.2926, found: 675.2919. Anal. calcd for C 92.41, H 5.52, N 2.07; found: C 92.38, H 5.47, N 2.12. mp 114 °C.

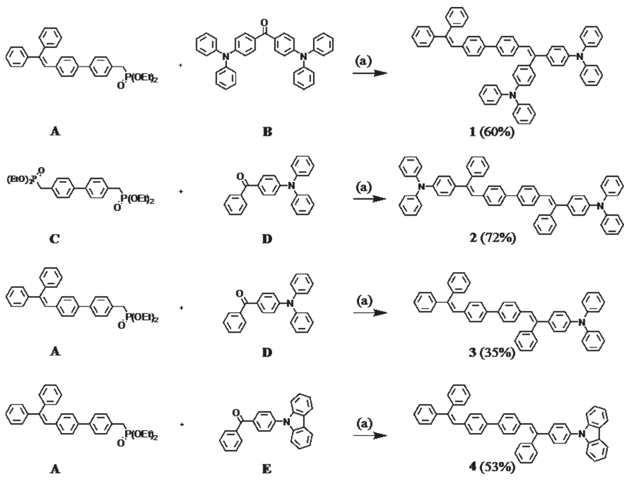
2.2. Device Fabrication and Characterization

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 100 nm 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 N_2 gas gun. The substrates were treated by O_2 plasma treatment at 2×10^{-2} Torr at 125 W for 2 min. All organic materials and metals were deposited under high vacuum (5×10^{-7} Torr). The OLEDs fabricated in this paper had a configuration of ITO/DNTPD (40 nm)/NPB (20 nm)/MADN: Blue dopants **1–4** (2%, 20 nm)/Alq_3 (40 nm)/Liq (1.0 nm)/Al. The CIE coordinates of the OLEDs were measured with a Keithly 2400, Chroma meter CS-1000A. Electroluminance was measured using a Roper Scientific Pro 300i. The UV-vis absorption spectra were measured in a dichloromethane solution (10^{-5} M) using a shimadzu UV-1650PC. The HOMO energy levels were measured with a low-energy photo-electron spectrometer (Riken-Keiki, AC-2).The energy band gaps were determined from the intersection of the absorption and photoluminescence spectra. LUMO (lowest unoccupied molecular orbital) energy levels were calculated by subtracting the corresponding optical band gap energies from the HOMO energy values.

3. RESULTS AND DISCUSSION

Blue compounds **1–4** were synthesized by Horner-Wadsworth-Emmons reactions between the phosphonate compounds and the corresponding carbonyl compounds in moderate yield,[7] as shown in Scheme 1.

Figure 1 presents the UV-vis absorption and photoluminescence (PL) spectra of the blue materials **1–4** in CH_2Cl_2.



Scheme 1. Synthetic routes of blue fluorescent materials **1–4**. Condition: (a) KO^{t}Bu, THF, 0 °C to room temperature, 30 min.

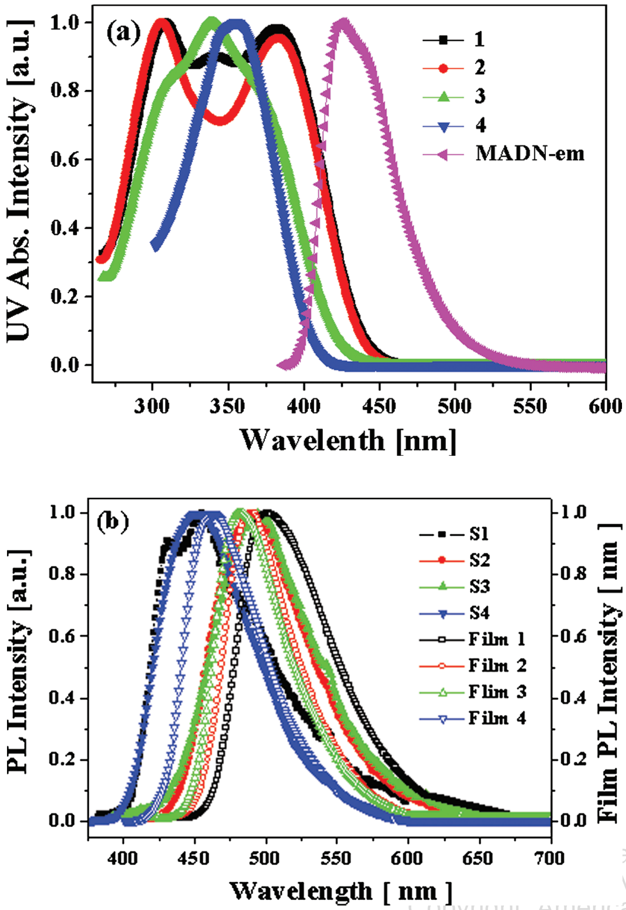


Fig. 1. (a) The absorption and (b) solution and film emission spectra of compounds **1–4**.

The maximum absorption peaks of compounds **1–4** were located at 382, 383, 338, and 354 nm, respectively.

Figure 1(a) shows that the UV-vis absorption of the compounds **1–4** overlapped well with the PL spectrum of a common blue host MADN. This indicates that host in OLED devices using these materials as dopants. In the PL spectra in solution, the maximum emission peaks of compounds **1–4** were observed at 456, 492, 494, and 451 nm, respectively. In thin film states, the maximum peaks of compounds **1–4** ranged from 461 to 498 nm, which is similar to those in the dilute solution states. This suggests that molecular aggregation was restrained effectively in compounds **1–4** by the bulky substituent in the DPVBi emitting core.

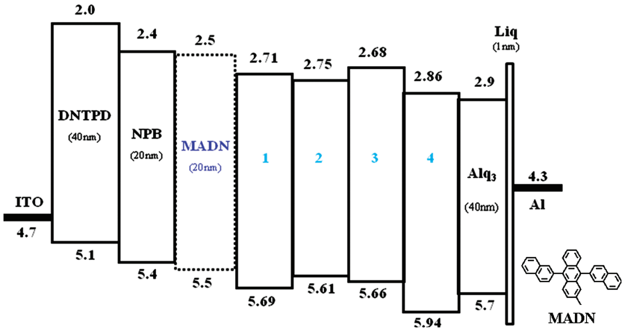


Fig. 2. Energy-level diagrams of OLEDs.

The HOMO/LUMO energy levels of compounds 1–4 were $-5.69/-2.71$, $-5.61/-2.75$, $-5.66/-2.68$, and $-5.94/-2.86$ eV, respectively. The bandgap of the blue materials (**1–4**) ranged from 2.86 to 3.08 eV. Figure 2 shows the HOMO and LUMO energy levels of blue fluorescent materials (**1–4**), along with the other materials used in the electroluminescent devices, including ITO, DNTPD, NPB, MADN, Alq$_3$, and LiF: Al.

Table II summarizes the electroluminescent properties of the devices using compound **1–4** as dopants. All devices exhibited blue emission with a maximum emission wavelength from 454 to 472 nm, as shown in Figure 3(a). Among devices **1–4**, device **4** using dopant **4** with a carbazole moiety showed the deepest blue emission with a CIE$_y$ value <0.15. This is compatible with the results of PL studies in the solution and thin film states, in which compound **4** showed the most blue-shifted emission peaks in both states compared to compounds **1–3**. The incorporation of a carbazole moiety was expected to turn the LUMO energy level to the increase band gap (average 0.14 eV) of the light-emitting materials.

Figure 3(b) shows the current density-luminous efficiencies (LE) and power efficiencies (PE) characteristics of devices **1–4**. All devices showed efficient blue emission. The arylamine moieties with the good hole-transporting properties and the bulky 1,1′-diphenyl groups of compounds **1–4** would lead to efficient blue emission by

Table I. Physical properties of compounds **1–4**.

Compound	1	2	3	4
UV$\lambda^{a}_{\max}$[nm]	382	383	338	354
PL$\lambda^{a/b}_{\max}$[nm]	465/498	492/489	494/481	451/461
FWHM [nm]	99	83	90	79
HOMO[eV]	5.69	5.61	5.66	5.94
LUMO[eV]	2.71	2.75	2.68	2.86
E$_g$	2.98	2.86	2.98	3.08
Φ^c	0.035	0.035	0.032	0.081

[a] CH$_2$Cl$_2$ solution (10^{-5} M). [b] Thin solid film. [c] Using BDAVBi as a standard; λ_{ex} = 360 nm ($\Phi = 0.86$ in CH$_2$Cl$_2$).

Table II. EL performance characteristic of the doped-devices **1–4**.

Device	1	2	3	4
$\lambda^{EL}_{\max}$[nm]	472	466	458	454
L^a [cd/m^2]	16110	10420	7180	7005
LE [cd/A]	10.1^b	8.65^b	6.12^b	6.27^b
	10.1^c	8.56^c	6.08^c	6.25^c
PE [lm/W]	5.08^b	3.96^b	2.86^b	2.72^b
	4.37^c	3.41^c	2.53^c	2.50^c
CIE^d (x, y)	(0.197, 0.358)	(0.185, 0.248)	(0.161, 0.182)	(0.151, 0.143)

[a] Maximum luminance. Values were obtained at 10 V. [b] Maximum value. [c] At 20 mA/cm^2. [d] CIE (x, y) at 8.0 V.

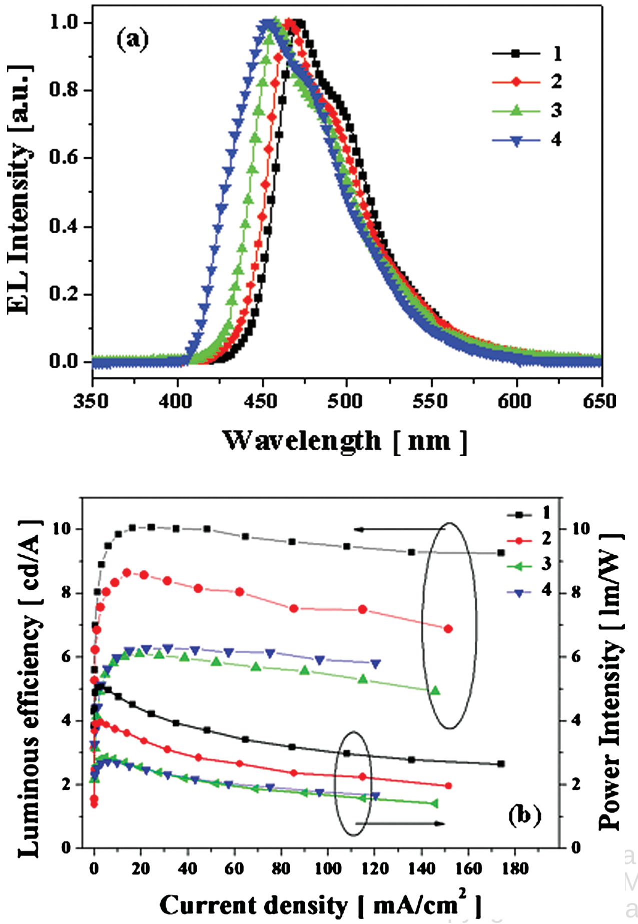


Fig. 3. (a) EL spectra of the devices **1–4**, and (b) the luminous, and power efficiencies as a function of current density for the devices **1–4**.

enhancing the carrier balances and suppressing concentration quenching. The luminous efficiency of devices **1–4** were 10.1, 8.56, 6.08, and 6.25 cd/A at 20 mA/cm^2, respectively. The power efficiency of devices **1–4** were 4.37, 3.41, 2.53, and 2.50 lm/W at 20 mA/cm^2, respectively. Devices **1** and **2** showed higher EL efficiency than devices **3** and **4**, which may be due partly to the effective exciton formation on dopant materials **1** and **2** through energy transfer between the MADN host material and the dopant within the devices. The overlap of the emission spectra of the MADN host with the absorption spectra of dopants **1** and **2** was better than those with dopants **3** and **4**, as shown in Figure 1. This suggests that exciton formation on the dopant materials was more effective in devices **1** and **2** than devices **3** and **4**. This indicates that effective energy transfer between the host and dopant play an important role in the highly efficient blue OLEDs.

4. CONCLUSION

Blue-emitting dopants based on arylamine substituted DPVBi derivatives were synthesized. Among those, an OLED using dopant **1** exhibited highly efficient blue emission. The device showed the maximum luminance, best luminous efficiency, power efficiency and CIE coordinates of 16,110 cd/m^2 at 10 V, 10.1 cd/A at 20 mA/cm^2, 4.37 lm/W at 20 mA/cm^2, and (0.197, 0.358) at 8 V. In addition, the OLED using dopant **4** exhibited a highly efficient deep blue emission with a maximum luminance, luminous efficiency and power efficiency of 7,005 cd/m^2 at 10 V, 6.25 cd/A, and 2.50 lm/W at 20 mA/cm^2. The peak wavelength of the electroluminescence was 454 nm with CIE coordinates of (0.151, 0.143) at 8 V.

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