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Bipolar 9-linked carbazole-π-dimesitylborane fluorophores for nondoped blue OLEDs and red phosphorescent OLEDs

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ABSTRACT

Three dimesitylborane-containing fluorophores with various π-conjugated systems attached at the 9th position of carbazole, namely, 9-(4′-bromobiphenyl-4-yl)-9*H*-carbazole (Cz^9Ph_2B), 9-(4-(5-(dimesitylboryl)thiophen-2-yl)phenyl)-9*H*-carbazole (Cz^9ThPhB), and 9-(4-(4-(dimesitylboryl)styryl)phenyl)-9*H*-carbazole (Cz^9SB) were synthesized and their photophysical and electroluminescent properties were investigated for application in nondoped blue OLEDs as well as red phosphorescent OLEDs (PhOLEDs). The electron-accepting dimesitylboryl group and various π-conjugated segments appended to the electron-donating carbazole moiety impart the three fluorophores with bipolar transporting ability, and their energy levels are matched with those of the adjacent carrier-transporting layers. These bulky fluorophores are thermally stable with glass transition temperatures and degradation temperatures reaching up to 105 and 383 °C, respectively. In addition, efficient nondoped Cz^9PhThB- and Cz^9SB-based blue OLEDs with maximum currents of 1.51 and 4.03 cd A^{-1} and external quantum efficiencies (EQE) of 2.30 and 4.72% were achieved, respectively. Notably, the Cz^9Ph_2B-based red PhOLEDs exhibits a relatively low turn-on voltage (3.3 V) and high electroluminescence efficiencies (maximum current = 23.12 cd A^{-1} and EQE = 14.10%). Their performance is superior to that of the corresponding device using conventional 4,4′-*N*,*N*′-dicarbazolbiphenyl as the host material. Moreover, a maximum brightness of 39700 cd m^{-2} was also achieved.

1. Introduction

Organic light-emitting diodes (OLEDs) have attracted great attention owing to their application in full-color flat panel displays and solid-state lighting [1–3]. Since Tang and Van Slyke reported the first multilayered OLEDs, much research has been directed to improve the OLED performance in terms of their efficiency, color stability, and lifetime [4,5]. To meet the demand of commercial application, three primary colors, blue, green, and red are basically required. During the past few decades, green and red electroluminescence (EL) devices have been improved significantly; however, for full-color application, there is an ongoing search for efficient materials (including host or dopant materials) for developing EL devices based on all three primary colors with appropriate Commission Internationale de l'Eclairage (CIE) coordinates [6–8]. Different classes of core structures have been studied and used as the skeletal backbone for constructing emitters for OLEDs. Among these materials, carbazole-based compounds are one of the promising candidates, owing to their large triplet energy, good hole-transporting ability, and relatively weak π-donor ability [9–13]. The large triplet energy is useful for their application as host materials in phosphorescent organic light-emitting diodes (PhOLEDs). A weak π-donating property is particularly useful in generating short-wavelength emissions, which is advantageous for designing blue light-emitting materials. Moreover, to achieve bipolarity, various electron-accepting moieties such as pyridine, triazole, trazine, phenanthroline, oxadiazole, benzimidazole, phosphine oxide, and phosphine sulfide, are included in the molecular designs based on carbazole [14–26]. Another class of electron-acceptors, boron-containing derivatives, has attracted

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significant attention owing to the vacant *p*-orbital of the boron atom. These derivatives possess electron-transporting capability and have been demonstrated to be useful for various applications such as nonlinear optics, anion sensing, and luminescent devices [11,27–31]. Using a steric protection method in which the boron center is appended with bulky substituents, compounds that are claimed to be stable under air and moisture were prepared [27]. A representative example of the steric protection strategy is the use of dimesitylboryl group, wherein the boron atom is protected effectively by two *ortho*-methyl substituted mesityl groups. As such, this moiety has been extensively employed as an electron acceptor for constructing air-stable organoboron materials. Considering that the electron-accepting ability of the boryl group plays an important role in determining the overall performance of the material, incorporation of this moiety is expected to lead to further improvements in OLEDs. Moreover, with the nonplanar structure of the dimesitylboryl moiety in the molecular framework, the π-π stacking between the molecules can be diminished and thus the fluorescence quantum yield is increased. According to these considerations, three dimesitylborane-containing fluorophores with various π-conjugated systems attached at the 9th position of carbazole, viz., 9-(4′-bromobiphenyl-4-yl)-9*H*-carbazole (Cz^9Ph_2B), 9-(4-(5-(dimesitylboryl)thiophen-2-yl)phenyl)-9*H*-carbazole (Cz^9ThPhB), and 9-(4-(4-(dimesitylboryl)styryl)phenyl)-9*H*-carbazole (Cz^9SB), were synthesized and their photophysical and electroluminescent properties were investigated toward application in nondoped blue OLEDs. Further, because of their large triplet energies, these compounds are suitable host materials for PhOLED application; therefore, red PhOLEDs were fabricated and their EL properties were also examined.

2. Material and method

2.1. Materials

All chemicals were obtained from Aldrich, Alfa Aesar, and TCI Chemical Co., and were used as received unless otherwise noted. All the solvents, including *o*-dichlorobenzene (*o*-DCB), tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), and toluene were freshly distilled and dried over appropriate drying agents before use. The hole-transporting material, di-[4-(*N*,*N*-ditolyl-amino)phenyl]cyclohexane (TAPC), and electron-transporting material, 1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene (TmPyPB), were purchased from Lumtec Corp., and used without purification.

2.2. 9-(4-bromophenyl)-9H-carbazole (Cz^9PhBr)

The Cz^9PhBr was synthesized according to a previously published procedure [32,33]. Briefly, under nitrogen atmosphere, 9*H*-carbazole (5.02 g, 30 mmol), 1,4-dibromobenzene (14.14 g, 60 mmol), K_2CO_3 (16.54 g, 120 mmol), Cu powder (1.92 g, 30 mmol), 18-crown-6 (3.73 g, 15 mmol), and anhydrous *o*-DCB (150 mL) were taken in a 500 mL two-neck flask. The mixture was stirred and then heated to reflux for 12 h. After cooling, the resulting mixture was filtered and the collected organic solvent was removed by distillation under reduced pressure. The residue was extracted with ethyl acetate and water. The organic layer was collected and dried over magnesium sulfate. The product was purified further by silica gel chromatography using hexanes as the eluent, to obtain Cz^9PhBr as a white solid (7.02 g, 73%). ^1H NMR (300 MHz, $CDCl_3$, δ/ppm): 8.15 (d, $J = 7.5$ Hz, 2H), 7.73 (d, $J = 8.4$ Hz, 2H), 7.36–7.47 (m, 6H), 7.30 (t, $J = 7.2$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, δ/ppm): 140.66, 136.86, 133.16, 128.76, 126.15, 123.57, 120.93, 120.47, 120.30, 109.61. HRMS (*m*/*z*): calcd for $C_{18}H_{12}BrN$:321.0153. Found: 321.0162.

2.3. 9-(4′-bromobiphenyl-4-yl)-9H-carbazole (Cz^9Ph_2Br)

Cz^9Ph_2Br was synthesized using the same procedure described for Cz^9PhBr using 9*H*-carbazole (5.02 g, 30 mmol), 4,4′-dibromobiphenyl (18.63 g, 60 mmol), K_2CO_3 (16.54 g, 120 mmol), Cu powder (1.92 g, 30 mmol), 18-crown-6 (3.73 g, 15 mmol), and anhydrous *o*-DCB (150 mL), affording Cz^9Ph_2Br as a white solid (5.36 g, 45%). ^1H NMR (300 MHz, $CDCl_3$, δ/ppm): 8.16 (d, $J = 7.5$ Hz, 2H), 7.78 (d, $J = 8.4$ Hz, 2H), 7.62–7.66 (m, 4H), 7.31 (t, $J = 6.6$ Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, δ/ppm): 140.77, 139.17, 139.01, 137.26, 132.07, 128.69, 128.31, 127.43, 125.99, 123.47, 121.96, 120.34, 120.06, 109.76. HRMS (*m*/*z*): calcd for $C_{24}H_{16}BrN$: 397.0466. Found: 397.0464.

2.4. 4-(9H-carbazol-9-yl)benzaldehyde (Cz^9PhCHO)

In a 250 mL two-necked flask, anhydrous DMF (100 mL) was added to a mixture of 9*H*-carbazole (8.40 g, 50 mmol) and potassium *tert*-butoxide (5.52 g, 50 mmol). The mixture was stirred at 110 °C for 30 min under nitrogen atmosphere. Then, 4-fluorobenzaldehyde (1.24 g, 10 mmol) was added and stirred for 36 h. Then, the reaction mixture was cooled to room temperature and the reaction solvent was removed by distillation under reduced pressure. The residue was extracted with ethyl acetate and water. Further purification was carried out by silica gel chromatography to afford Cz^9PhCHO as a light yellow solid (9.30 g, 68%). ^1H NMR (300 MHz, $CDCl_3$, δ/ppm): 10.11 (s, 1H), 8.12–8.16 (m, 4H), 7.79 (d, $J = 8.4$Hz, 2H), 7.51 (d, $J = 7.5$ Hz, 2H), 7.44 (t, $J = 7.2$ Hz, 2H), 7.33 (t, $J = 7.8$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, δ/ppm): 191.03, 143.39, 140.07, 134.64, 131.42, 126.82, 126.34, 124.00, 120.88, 120.56, 109.81. HRMS (*m*/*z*): calcd for $C_{19}H_{13}NO$: 271.0997. Found: 271.0996.

2.5. 9-(4-(thiophen-2-yl)phenyl)-9H-carbazole (Cz^9PhTh)

A mixture of Cz^9PhBr (3.22 g, 10 mmol), 2-(tri-butylstannyl)thiophene (3.74 g, 10 mmol), and $PdCl_2(PPh_3)_2$ (0.35 g, 0.5 mmol) was dissolved in anhydrous toluene (100 mL) and the mixture was refluxed for 48 h. After cooling, the reaction mixture was poured into ice water and then extracted with dichloromethane. The combined organic extracts were dried over magnesium sulfate and the organic solvent was removed by distillation under reduced pressure. Finally, the residue was purified by column chromatography on silica gel to afford Cz^9PhTh as a white solid (2.34 g, 72%). ^1H NMR (300 MHz, $CDCl_3$, δ/ppm): 8.14 (d, J = 7.8 Hz, 2H), 7.70 (d, $J = 8.7$ Hz, 2H), 7.56 (d, $J = 8.4$ Hz, 2H), 7.39–7.44 (m, 5H), 7.28–7.35 (m, 3H), 7.12 (t, $J = 3.9$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ143.44, 140.78, 136.82, 133.56, 128.29, 127.47, 127.28, 126.03, 125.38, 123.63, 123.46, 120.38, 120.07, 109.83. HRMS (*m*/*z*): calcd for $C_{22}H_{15}NS$:325.0925. Found: 325.0928.

2.6. 9-(4-(4-bromostyryl)phenyl)-9H-carbazole (Cz^9SBr)

Previously reported procedures were employed for the synthesis of Cz^9SBr [9]. Under nitrogen atmosphere and at −20 °C, a solution of 4-bromobenzyltriphenylphosphonium bromide (3.07 g, 10 mmol) in anhydrous THF (20 mL) was added in portions over a period of 10 min to a mixture of sodium hydride (0.36 g, 15 mmol) in anhydrous THF (80 mL). After 10 min, a mixture of Cz^9PhCHO (2.71 g, 10 mmol) and dry THF (50 mL) was added to the reaction mixture and stirred for another 8 h at room temperature under nitrogen atmosphere. The resulting product was poured into water, neutralized with dilute hydrochloric acid, and extracted with dichloromethane. Then, the obtained organic layer was dried over magnesium sulfate. After the organic solvent was removed by distillation under reduced pressure, the residue was purified by column chromatography on silica gel to yield Cz^9SBr as a green-yellow solid (2.92 g, 70%). ^1H NMR (400 MHz, $CDCl_3$, δ/ppm): 8.12 (d, $J = 7.5$ Hz, 2H), 7.69 (d, $J = 9.0$ Hz, 2H), 7.54 (d, $J = 8.4$ Hz, 2H), 7.49 (d, $J = 8.4$ Hz, 2H), 7.37–7.45 (m, 6H), 7.25 (t, $J = 8.1$ Hz, 2H), 7.16 (d, $J = 16.5$ Hz, 1H), 7.07 (d, $J = 16.5$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.74, 137.14, 136.10, 136.06, 131.90, 128.39, 128.27, 128.08, 127.88, 127.25, 125.99, 123.46, 121.65, 120.35,