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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 (Cz⁹Ph₂B), 9-(4-(5-(dimesitylboryl)thiophen-2-yl) phenyl)-9*H*-carbazole (Cz⁹ThPhB), and 9-(4-(4-(dimesitylboryl)styryl)phenyl)-9*H*-carbazole (Cz⁹SB) 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 Cz⁹PhThB- and Cz⁹SB-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 Cz⁹Ph₂B-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 solidstate 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)-9H-carbazole (Cz⁹Ph₂B), 9-(4-(5-(dimesitylboryl)thiophen-2-yl)phenyl)-9H-carbazole (Cz⁹ThPhB), and 9-(4-(4-(dimesitylboryl)styryl)phenyl)-9H-carbazole (Cz⁹SB), 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 (Cz⁹PhBr)

The Cz⁹PhBr was synthesized according to a previously published procedure [32,33]. Briefly, under nitrogen atmosphere, 9H-carbazole (5.02 g, 30 mmol), 1,4-dibromobenzene $(14.14 \text{ g}, 60 \text{ mmol}), K_2 \text{CO}_3$ (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 twoneck 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 Cz⁹PhBr as a white solid (7.02 g, 73%). ¹H NMR $(300 \text{ MHz}, \text{ CDCl}_3, \delta/\text{ppm})$: 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); ¹³C NMR (75 MHz, CDCl₃, 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 C18H12BrN:321.0153. Found: 321.0162.

2.3. 9-(4'-bromobiphenyl-4-yl)-9H-carbazole (Cz⁹Ph₂Br)

Cz⁹Ph₂Br was synthesized using the same procedure described for

Cz⁹PhBr using 9*H*-carbazole (5.02 g, 30 mmol), 4,4'-dibromobiphenyl (18.63 g, 60 mmol), K₂CO₃ (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 Cz⁹Ph₂Br as a white solid (5.36 g, 45%). ¹H NMR (300 MHz, CDCl₃, 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). ¹³C NMR (75 MHz, CDCl₃, 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 C₂₄H₁₆BrN: 397.0466. Found: 397.0464.

2.4. 4-(9H-carbazol-9-yl)benzaldehyde (Cz⁹PhCHO)

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 C2⁹PhCHO as a light yellow solid (9.30 g, 68%). ¹H NMR (300 MHz, CDCl₃, δ /ppm): 10.11 (s, 1H), 8.12–8.16 (m, 4H), 7.79 (d, *J* = 8.4Hz, 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); ¹³C NMR (75 MHz, CDCl₃, 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 C₁₉H₁₃NO: 271.0997. Found: 271.0996.

2.5. 9-(4-(thiophen-2-yl)phenyl)-9H-carbazole (Cz⁹PhTh)

A mixture of Cz⁹PhBr (3.22 g, 10 mmol), 2-(tri-butylstannyl)thiophene (3.74 g, 10 mmol), and PdCl₂(PPh₃)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 Cz⁹PhTh as a white solid (2.34 g, 72%). ¹H NMR (300 MHz, CDCl₃, 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); ¹³C NMR (75 MHz, CDCl₃) δ 143.44, 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 C₂₂H₁₅NS:325.0925. Found: 325.0928.

2.6. 9-(4-(4-bromostyryl)phenyl)-9H-carbazole (Cz⁹SBr)

Previously reported procedures were employed for the synthesis of $Cz^{9}SBr$ [9]. Under nitrogen atmosphere and at -20 °C, a solution of 4bromobenzyltriphenylphosphonium 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 Cz⁹PhCHO (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 Cz⁹SBr as a green-yellow solid (2.92 g, 70%). ¹H NMR (400 MHz, CDCl₃, 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); ¹³C NMR (100 MHz, CDCl₃) 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,

120.05, 109.81. HRMS (m/z): calcd for C₂₆H₁₈BrN: 423.0623. Found: 423.0624.

2.7. 9-(4'-dimesitylboryl)biphenyl-4-yl)-9H-carbazole (Cz⁹Ph₂B)

A solution of 2.5 M n-butyllithium (10 mmol, 4 mL) in n-hexane was added to a solution of Cz⁹Ph₂Br (3.98 g, 10 mmol) in anhydrous THF (100 mL) at -78 °C. The mixture was stirred for 1 h and dimesitylboron fluoride (2.68 g, 10 mmol) was slowly added. Stirring was continued for 1 h at -78 °C and for further 12 h at room temperature. The reaction mixture was quenched with water and then extracted with dichloromethane. The organic layer was dried over magnesium sulfate. filtered, and evaporated to drvness under reduced pressure. The crude product was purified by column chromatography to obtain Cz⁹Ph₂B as a white solid (3.01 g, 53%). ¹H NMR (300 MHz, CDCl₃, δ/ppm) δ 8.16 (d, J = 7.8 Hz, 2H), 7.89 (d, J = 8.1 Hz, 2H), 7.64–7.70 (m, 5H), 7.40–7.49 (m, 5H), 7.30 (t, J = 6.6 Hz, 2H), 6.86 (s, 4H), 2.33 (s, 6H), 2.06 (s, 12H); ¹³C NMR (75 MHz, CDCl₃, δ/ppm) δ 145.05, 143.42, 141.86, 140.99, 139.85, 138.87, 137.45, 137.33, 128.78, 128.37, 127.46, 126.68, 126.13, 123.60, 120.49, 120.17, 109.96, 23.50, 21.23. HRMS (*m/z*): calcd for C₄₂H₃₈BN: 567.3097. Found: 567.3101. Anal. Calcd. for C42H38BN (%): C, 88.88; H, 6.75; N, 2.47; found: C, 88.98; H, 6.79; N, 2.48.

2.8. 9-(4-(5-(dimesitylboryl)thiophen-2-yl)phenyl)-9H-carbazole (Cz⁹PhThB)

Cz⁹PhThB was synthesized according to a method reported previously [32], using Cz⁹PhTh (3.25 g, 10 mmol), 2.5 M *n*-butyllithium (10 mmol, 4 mL) in *n*-hexane, dimesitylboron fluoride (2.68 g, 10 mmol), and anhydrous THF (100 mL), to yield Cz⁹PhThB as a white solid (3.44 g, 60%). ¹H NMR (300 MHz, CDCl₃, δ /ppm): 8.15 (d, J = 7.8 Hz, 2H), 7.90 (d, J = 8.4 Hz, 2H), 7.54–7.60 (m, 3H), 7.38–7.51 (m, 5H), 7.28–7.35 (m, 2H), 6.86 (s, 4H), 2.33 (s, 6H), 2.19 (s, 12H). ¹³C NMR (75 MHz, CDCl₃, δ /ppm): 155.89, 150.14, 141.88, 141.28, 141.02, 140.78, 138.78, 137.82, 133.25, 128.37, 127.70, 127.49, 126.18, 125.92, 123.65, 120.52, 120.23, 109.90, 23.65, 21.41. HRMS (*m*/z): calcd for C₄₀H₃₆BNS: 573.2662. Found: 573.2668. Anal. Calcd. for C₄₀H₃₆BNS (%): C, 83.76; H, 6.33; N, 2.44; found: C, 83.52; H, 6.40; N, 2.44.

2.9. 9-(4-(4-(dimesitylboryl)styryl)phenyl)-9H-carbazole (Cz⁹SB)

Cz⁹SB was prepared using the same procedure described for Cz⁹Ph₂B using Cz⁹SBr (4.24 g, 10 mmol), 2.5 M *n*-butyllithium (10 mmol, 4 mL) in *n*-hexane, dimesitylboron fluoride (2.68 g, 10 mmol), and anhydrous THF (100 mL), to obtain a white solid (3.50 g, 59%). ¹H NMR (300 MHz, CDCl₃, δ /ppm): 8.16 (d, *J* = 7.8 Hz, 2H), 7.76 (d, *J* = 8.7 Hz, 2H), 7.50–7.62 (m, 6H), 7.38–7.49 (m, 4H), 7.19–7.35 (m, 4H), 6.85 (s, 4H), 2.33 (s, 6H), 2.05 (s, 12H); ¹³C NMR (75 MHz, CDCl₃, δ /ppm): 145.64, 141.87, 140.98, 140.86, 140.57, 138.79, 137.23, 136.40, 129.55, 129.40, 128.33, 128.15, 127.33, 126.30, 126.12, 123.59, 120.48, 120.18, 109.98, 23.63, 21.40. HRMS (*m*/z): calcd for C₄₄H₄₀BN: 593.3254. Found: 593.3260. Anal. Calcd. for C₄₄H₄₀BN (%): C, 89.03; H, 6.79; N, 2.36; found: C, 88.99; H, 6.76; N, 2.41.

2.10. Instrumentation

General. ¹H NMR spectra were recorded on a Varian Unity Inova 300WB NMR spectrometer at room temperature. Elemental analyses were performed on an Elementar Vario EL III elemental analyzer. High-resolution mass spectrometry (HRMS) was performed with a Finnigan/ Thermo Quest MAT 95XL mass spectrometer. Differential scanning calorimetry (DSC) was carried out using a SEIKO SII Model SSC5200 at a scanning rate of 10 °C min⁻¹ in the temperature range of 30–250 °C

under a nitrogen flow. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA-7 analyzer at a scanning rate of 10 °C min⁻¹ in the temperature range of 30-800 °C under nitrogen atmosphere. UV-visible absorption spectra were recorded on Hewlett-Packard 8453 spectrometer and fluorescence and EL spectra were recorded on a Hitachi F-7000 spectrophotometer. Energy levels were determined by low energy photo-electron spectrometry using a Riken-Keiki AC-2 Photoelectron Spectrometer. The sample was prepared by vacuum deposition on clean indium tin oxide (ITO)-coated glass substrates. The photoluminescence quantum yield (Φ_f) was determined from the corrected fluorescence spectrum of the individual substances in diluted deoxygenated 10^{-6} M ethyl acetate solution using the standard, coumarin 1 according a process reported previously [34]. In addition, Φ_f of the material in the solid film state was determined by the integrating-sphere method described by Mello et al. [11,35] All the EL devices were fabricated as follows: Glass substrates (with a sheet resistance of $15 \Omega \text{ sq}^{-1}$) coated with ITO were patterned lithographically, then sequentially cleansed with a detergent, ultrasonicated in acetone and isopropyl alcohol, and dried on a hot plate at 120 °C for 5 min, and finally treated with oxygen plasma for 5 min. For the EL devices, 4.4'bis[N-(1-naphthyl)eN-phenylamino] biphenyl (NPB) or di-[4-(N,N-ditolyl-amino)phenyl]cyclohexane (TAPC) was used as the hole transporting material, Cz⁹Ph₂B, Cz⁹ThPhB, or Cz⁹SB was used as the emitter for nondoped blue OLEDs whereas Cz⁹Ph₂B was used as the host material for red PhOLEDs, 1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene (TmPyPB) or 1,3,5-tris(N-phenyl benzimidizol-2-yl)benzene (TPBI) was the electron-transporting layer, dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) was used as the hole-blocking material, and lithium fluoride (LiF) and Al electrode were used as the cathode. All the materials were deposited sequentially on top of the ITO glass substrate through a shadow mask, without breaking the vacuum. The thermal evaporation of the organic materials was carried out using ULVAC Cryogenics at a chamber pressure of 10^{-6} Torr. Current-voltage-luminescence (IeV-L) characteristics and CIE color coordinates of the devices were measured simultaneously using a Keithley 2400 source meter and a Newport 1835C optical meter equipped with a Newport 818-ST silicon photodiode, respectively. All electrical measurements were made in air.

3. Results and discussion

3.1. Synthesis and characterization

The synthetic routes of the three designed fluorophores, viz., Cz⁹Ph₂B, Cz₉PhThB, and Cz⁹SB, are illustrated in Scheme 1. The synthesis of the intermediate, Cz⁹PhTh was carried out as described elsewhere, whereas the intermediate, Cz⁹Ph₂Br was prepared using 9Hcarbazole and 4,4'-dibromobiphenyl through Ullmann coupling reaction. Another intermediate, Cz⁹SBr, was obtained by reacting Cz⁹PhCHO with 4-bromobenzyltriphenylphosphonium bromide via the Wittig reaction. The three target fluorophores were synthesized by treating Cz⁹PhTh, Cz⁹Ph₂Br, and Cz⁹SBr with *n*-butyllithium and dimesitylboron fluoride, following a same synthetic procedure. The chemical structures of these fluorophores (Cz⁹Ph₂B, Cz₉PhThB, and Cz⁹SB) were confirmed by ¹H NMR, ¹³C NMR, and molecular mass data (Figure S1–S9). These fluorophores showed good solubility in common organic solvents such as ethyl acetate, THF, chloroform, and toluene. This high solubility is possibly owing to the slightly twisted conformation due to the introduction of nonplanar dimesitylboryl group, which increases the steric hindrance of the molecule. Fig. 1 shows the thermal properties of these fluorophores, determined by DSC and TGA measurements. The glass transition temperatures (T_g) together with the thermal decomposition temperatures (T_d) are summarized in Table 1. As shown in Fig. 1(a), the DSC curves displayed no indication of crystallizing or undergoing melting phase transition up to 250 °C, only a weak endothermic transition was observed, corresponding to the glass



Scheme 1. Synthetic scheme of Cz^9Ph_2B , Cz^9PhThB , and Cz^9SB . Reaction condition: (a) 1,4-Dibromo-aryl, Cu, K_2CO_3 , 18-crown-6-ether, *o*-dichlorobenzene, reflux, 12 h. (b) 4-Fluorobenzaldehyde, K_2CO_3 , DMF, 110 °C, 36 h. (c) 2-(Tributylstannyl)thiophene, $PdCl_2(PPh_3)_2$, toluene, reflux, 48 h. (d) 4-Bromobenzyltriphenylphosphonium bromide, NaH, THF, 0 °C, 8 h. (e) *n*-BuLi, dimesitylboron fluoride, THF, -78 °C.



Fig. 1. (a) DSC thermograms and (b) TGA curves of Cz⁹-based fluorophores.

Table 1						
Thermal,	photophysical	and	electrochemical	properties	of fluorophore	s.

Fluorophore	T _g (°C)	T _d (°C)	λ_{\max}^{abs} (nm) a/b	λ_{\max}^{PL} (nm) a/b	E ^{opt} (V) c	HOMO/LUMO (eV) d	Φ _f (%) b/e
Cz ⁹ Ph ₂ B	105	364	340/348	438/414	3.03	- 6.01/-2.98	38/91
Cz ⁹ PhThB	103	383	371/387	451/439	2.83	- 5.92/-3.09	45/100
Cz ⁹ SB	98	341	367/378	465/453	2.79	- 5.91/-3.12	33/64

a. Measured in THF solution.

b. In thin film state.

c. Optical band gap was estimated from the wavelength of the optical edge of the thin film.

d. The HOMO energy levels determined by low-energy photoelectron spectrometry. The LUMO energy levels were calculated according to: LUMO = E_g^{opt} + HOMO (eV).

e. Relative to 10^{-6} M ethyl acetate solution of Coumarin 1.

transition phase. This implies that these fluorophores are amorphous in nature. The amorphous characteristic of the materials is ascribed to the twisted conformation of the molecules due to the nonplanar dimesitylboryl group. The T_g values corresponding to Cz^9Ph_2B , Cz^9PhThB , and Cz^9SB are 105, 103, and 98 °C, respectively. Cz^9Ph_2B showed the highest T_g among the materials, which is attributed to the rigid diphenyl ring in the bridge. The thermal stability of these fluorophores is indicated by their high T_d , as depicted in Fig. 1(b); the T_d values (corresponding to 5% weight loss) of these fluorophores are approximately 364, 383, and 341 °C corresponding to Cz^9Ph_2B , Cz^9PhThB , and Cz^9SB , respectively. All the fluorophores clearly showed favorable thermal stability up to 340 °C, which is suffice for their application in OLEDs.

3.2. Photophysical properties

Fig. 2 displays the absorption spectra of these fluorophores in THF solutions and in thin films. The corresponding absorption data of these fluorophores are summarized in Table 1. In solution, all the fluorophores exhibited two absorption peaks; the absorption band at the shorter wavelength originated from the π - π * transition of the fluorophore backbone whereas the absorption band at the longer wavelength is assigned to the intramolecular charge transfer from the carbazole moiety acting as the donor to the dimesitylboryl group acceptor



Fig. 2. UV–Vis absorption spectra of $\mathrm{Cz}^9\text{-}\mathsf{based}$ fluorophores in THF solutions and thin films.



Fig. 3. PL spectra of Cz⁹-based fluorophores in THF solutions and thin films.

[36]. Apparently, the absorption maximum is red-shifted with an increase in the conjugation length between the carbazole and dimesitylboryl moieties. Cz⁹PhThB showed the longest absorption peak wavelength, which is ascribed to the electron-rich thiophene ring together with the effect of the conjugation length in comparison to the other fluorophores. A similar trend was observed for these fluorophores in the thin film state. The structure-property relationship followed the same trend, and thus, the Cz⁹PhThB showed the longest absorption maximum among the fluorophores. The photoluminescence of these fluorophores in THF solutions and in thin films are plotted in Fig. 3 and the corresponding data including the fluorescence quantum yields (Φ_f) are also listed in Table 1. These compounds in the solution state provide blue luminescence with the wavelength maximum in the range of 438-465 nm, whereas the wavelength maxima in thin film state are in the range of 414–453 nm Cz⁹SB showed a longer wavelength maximum than that of Cz⁹PhThB, implying that Cz⁹SB is more coplanar than Cz⁹PhThB, and this is further revealed by the fluorescence quantum yields. As shown in Table 1, the Φ_f values in the solution state are 91, 100, and 64% for Cz⁹Ph₂B, Cz⁹PhThB, and Cz⁹SB, respectively, whereas the Φ_f values in the thin film state are 38, 45, and 33%, following the same sequence as in the solution state. The Cz⁹SB exhibited lower Φ_f than that of Cz⁹PhThB in the thin film state, and this suggests that Cz^9SB has stronger intermolecular $\pi\pi$ interactions of the molecules than those of Cz⁹PhThB, which is consistent with the PL results. Notably, all

the fluorophores exhibited high Φ_f in the thin film state, which is favorable for OLED application. The HOMO energy levels of these fluorophores were determined by low-energy photoelectron spectrometry. The measured HOMO levels for Cz⁹Ph₂B, Cz⁹PhThB, and Cz⁹SB are -6.01, -5.92, and -5.91, respectively. Similar to the absorption properties, the HOMO levels are affected by the electron-donating ability and conjugation length of the fluorophore; therefore, Cz⁹Ph₂B showed the lowest HOMO level amongst the three fluorophores. The LUMO energy levels of these fluorophores were estimated from their HOMO levels and the energy bandgaps that were determined from the UV-vis absorption threshold. The LUMO levels of Cz⁹Ph₂B, Cz⁹PhThB, and Cz^9SB are -2.98, -3.09, and -3.12, respectively. Apparently, these fluorophores exhibit wide bandgaps and this is suitable for their use as blue emitters or as host materials in PhOLED applications. To provide a better insight into the geometries and electron-state-density distributions of these fluorophores, DFT calculation at B3LYP/6-31G(d) level was performed, as provided in Figure S10-S12. The HOMO state density of the three fluorophores mainly distributes on the carbazole and π -bridge moieties, spreading slightly on the boron atom. On the other hand, the LUMO state electron density mainly locates on dimesitylboryl and π -bridge groups with a minor contribution from the carbazole unit. Obviously, the HOMO and LUMO of the three fluorophores are well overlapping, leading to the ambipolar property and efficient fluorescence of these fluorophores [37,38]. The calculated HOMO levels were -5.35, -5.33, -5.28 eV, while the LUMO levels were -1.85, -2.02, -2.08 eV for Cz^9Ph_2B , Cz^9PhThB , and Cz^9SB , respectively. The predicted HOMO and LUMO energies show good agreement with the experimental results although there are some discrepancies existing between the calculations and experiments. The dihedral angles between the carbazole plane and π -bridge moiety were predicted to be 56°, 54° and 53° for Cz⁹Ph₂B, Cz⁹PhThB, and Cz⁹SB, respectively, while the dihedral angles between π -bridge moiety and dimesitylboryl group were 25°, 16°, and 22° for Cz⁹Ph₂B, Cz⁹PhThB, and Cz⁹SB, respectively. The twisted conformation of the molecules implied the amorphous characteristics and wide bandgaps of these fluorophores. In addition, the relative low dihedral angle between π-bridge moiety and dimesitylboryl group of the Cz⁹PhThB indicated Cz⁹PhThB showed stronger π - π interactions of the molecules than the others, and thus the Cz⁹PhThB exhibited the longest absorption maximum among the fluorophores.

3.3. EL properties

To assess the utility of these fluorophores for nondoped blue OLEDs and red PhOLEDs, multilayer devices with various device configuration were fabricated and investigated. Fig. 4 shows the nondoped blue (devices A–C) and phosphorescent red (device D) device configurations along with the energy alignments of Cz⁹Ph₂B, Cz⁹PhThB, and Cz⁹SB. The electroluminescent characteristics of these devices are depicted in Fig. 5 and the corresponding performance data are summarized in Table 2. First, the Cz⁹Ph₂B-based device (device A) was fabricated in multilayer configuration, with the device structure of ITO/PEDOT:PSS (40 nm)/TAPC (40 nm)/Cz₉Ph₂B (20 nm)/TPBI (40 nm)/LiF (1 nm)/Al (100 nm). Under the applied voltage, device A emits near the ultraviolet region with the peak wavelength centered at 416 nm. Device A exhibits a maximum luminance, current, and external quantum efficiency of $770\,cd\,m^{-2},\ 0.30\,cd\,A^{-1},\ and\ 1.65\%,\ respectively.$ The very similar λ_{max} observed in the EL and PL ($\lambda_{max} = 414 \text{ nm}$) spectra of Cz⁹Ph₂B in the thin film state indicates that the observed EL arises solely from the emitter layer. However, an undesired shoulder emission at ~380 nm is observed in device A, which is attributed to the emission from TPBI. The emission contribution from TPBI indicates leakage of holes from Cz⁹Ph₂B owing to the relatively low HOMO energy level of Cz⁹Ph₂B. In order to prevent the same issue in other devices, TPBI was replaced by TmPyPB in devices B and C, owing to the low HOMO energy level of TmPyPB. The thickness of each layer in devices B and C were the same



Fig. 4. Energy level diagrams for device A – device D.



Fig. 5. EL characteristics of device A - device C.

Device	host	λ_{\max}^{EL} (nm)	$V_{on}^{a}(V)$	L_{\max}^{b} (cd m ⁻²)	$\eta_{c(\max)}^{b}$ (cd A ⁻¹)	$\eta_{ext(\max)}^{b}$ (%)	$\eta_{p(\max)}^{b}$ (lm W ⁻¹)	CIE (<i>x</i> , <i>y</i>) at 7 V
А	-	415	4.8	770	0.30	1.65	0.17	0.16, 0.03
В	-	443	3.4	7650	1.51	2.30	1.13	0.15, 0.07
С	-	452	5.9	7110	4.03	4.72	1.73	0.15, 0.10
D	CBP	622	4.0	25800	17.40	13.01	8.28	0.66, 0.33
	Cz ⁹ Ph ₂ B	621	3.3	39700	23.12	14.10	10.67	0.67, 0.33

a. Voltages at 1 cd m^{-2} .

b. The maximum values.

as in device A, except that the electron transporting material was replaced by TmPyPB. The EL properties of the optimized Cz⁹PhThB-based device (device B) are also shown in Fig. 5. Device B emits pure blue light with the peak wavelength centered at 442 nm and the CIE_{x v} coordinates of (0.15, 0.07). Comparing this with the PL spectrum of the $Cz^{9}PhThB$ thin film ($\lambda_{max} = 439 \text{ nm}$) clarifies that the emission originates from Cz⁹PhThB. Further, the EL spectrum exhibited a slight redshift compared to the PL spectrum. This can be explained by the spacecharge-induced spectral shift originating from the space charge redistribution in response to the dipole moment change under electronic excitation. Notably, device B reaches a maximum brightness of 7650 cd m⁻² with a full-width at half-maximum (FWHM) of 60 nm, a maximum current efficiency of $1.51 \text{ cd } \text{A}^{-1}$, and a maximum external quantum efficiency (EQE) of 2.30%. The Cz⁹SB-based device (device C) emitted blue light with a peak wavelength at 452 nm, with the CIE_{x,v} coordinates of (0.15, 0.10) and a FWHM of 70 nm, providing a maximum brightness of 7110 cd m⁻², a maximum current efficiency of 4.03 cd A^{-1} , and a maximum EQE of 4.72%. Similarly, the similarity between the EL and PL spectra in thin film state of Cz⁹SB reveals that the observed EL comes mainly from the emitter. The FWHM of EL in device C is broader than that in device B, implying that the intermolecular π - π interactions in Cz⁹SB are stronger than that in Cz⁹PhThB, which agrees with the Φ_F results. Interestingly, the Cz⁹SBbased device exhibited better device performance than that of the Cz⁹PhThB-based device. We attribute this to the better π - π interactions of Cz⁹SB that enhances the charge mobility between the molecules, thereby improving the device performance. This also indicates that the bulky structure with high Φ_f and strong π - π interactions which facilitate good charge mobility are in a trade-off relationship in OLEDs.

Based on the high fluorescence Φ_f and wide bandgap of Cz⁹Ph₂B, red PhOLEDs were fabricated to access the utility of Cz⁹Ph₂B for potential application as a host material for red PhOLED. For comparison, a device based on the commonly used host material, 4,4'-N,N'-dicarbazolbiphenyl (CBP), was also fabricated in the same device configuration. The devices were fabricated in the configuration of ITO/ PEDOT:PSS (40 nm)/NPB (30 nm)/EML (40 nm)/BCP (6 nm)/Alq₃ (30 nm)/LiF (1 nm)/Al (100 nm), as depicted in Fig. 4. Here, "EML" refers to a layer of Cz⁹Ph₂B or CBP doped with 10 wt% Ir(piq)₃. Ir(piq)₃ was chosen as the red phosphor, because of its commercial availability and reliability, as reported elsewhere [39-41]. The EL spectra of these red-emitting devices and the current density-voltage-luminance characteristics together with the efficiency curves are illustrated in Fig. 6 and Fig. 7, respectively, and the EL data are listed in Table 2. As shown in Fig. 6, both devices show red electrophosphorescence exclusively from $Ir(piq)_3$, with the maximum signal intensity at ~621 nm, indicating the excellent confinement of carriers within the emitting layer. The Cz⁹Ph₂B-based device exhibited a relatively lower operating voltage compared to that of the CBP-based device, which is presumably due to the lower energy barrier between BCP and Cz⁹Ph₂B than that between BCP and CBP. Notably, the Cz⁹Ph₂B-based phosphorescent device exhibited improved performance with enhanced brightness and emission efficiency compared to those of the CBP-based phosphorescent device (Fig. 7). A maximum current efficiency of 23.12 cd A^{-1} and a



Fig. 6. EL spectra of device D using CBP and Cz⁹Ph₂B as host.

maximum EQE of 14.10% with a brightness of 39700 cd m^{-2} were achieved from the Cz⁹Ph₂B-based phosphorescent device, whereas the CBP-based phosphorescent device showed a maximum current efficiency of 17.40 cd A^{-1} and a maximum EQE of 13.01% with a brightness of 25800 cd m⁻². Compared to the CBP-based device, an increase of almost 33, 11, and 55% were obtained in current efficiency, EQE, and brightness, respectively, for the Cz⁹Ph₂B-based device. The excellent performance of the Cz⁹Ph₂B-based red phosphorescent device can be ascribed to its bipolar nature that enhanced the charge transport property and the wide bandgap of Cz⁹Ph₂B, as revealed by the theoretical calculations. In addition, the relatively small electron injection barrier at the Alq₃/BCP/Cz⁹Ph₂B interface (Fig. 4) owing to the lowlying LUMO level of Cz⁹Ph₂B is responsible for a higher current density in the Cz⁹Ph₂B-based device compared to that in the CBP-based device and finally results in the enhancement of the device performance. Notably, the device using Cz⁹Ph₂B as host showed less efficiency roll-off with increased current density than that of device that used the CBP host, which implies that the Cz⁹Ph₂B-based phosphorescent device exhibits more charge balance at a high current density than that of CBPbased device.

4. Conclusion

In summary, three dimesitylborane-containing fluorophores with various π -conjugated systems attached at the 9th position of carbazole, referred as Cz⁹Ph₂B, Cz⁹ThPhB, and Cz⁹STB were designed and synthesized for application in nondoped blue OLEDs and red PhOLEDs. All these fluorophores were thermally stable and provided strong emissions both in the solution and thin film states. Importantly, Cz⁹ThPhB and Cz⁹STB are promising as nondoped blue emitters with maximum current efficiencies of 1.51 and 4.03 cd A⁻¹ and external quantum efficiencies of 2.30 and 4.72%, respectively. Notably, the red PhOLEDs using Cz⁹Ph₂B as the host material displayed a low efficiency roll-off,



Fig. 7. (a) Current density–voltage–luminance and (b) external quantum efficiency–current density–current efficiency curves of device D.

with a relatively low turn-on voltage (3.3 V), a maximum brightness of 39700 cd m^{-2} , and high electroluminescence efficiencies (current, 23.12 cd A^{-1} and EQE, 14.10%). Their performance is superior to that of the corresponding device using conventional CBP as the host material. The finding here provide a molecular platform for achieving high EL efficiency in blue OLEDs and red PhOLEDs applications.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.

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