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Carbazole/fluorene copolymers with dimesitylboron pendants for blue light-emitting diodes

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ABSTRACT

A series of random and alternating carbazole/fluorene copolymers with various dimesitylboron-containing carbazole derivative contents were synthesized by Suzuki polymerization for use as a light-emitting layer in blue light-emitting diodes. Two carbazole derivatives, CzPhB and CzPhThB consisted of a carbazoyl group as the donor and a dimesitylboron group as the acceptor group, separated by phenyl and phenylthiophene groups π -conjugated systems, respectively. The copolymers exhibited good thermal stability and blue emission in both solution and the solid state. Moreover, the CzPhB/fluorene and CzPhThB/fluorene copolymers exhibited a higher PL quantum efficiency than the fluorene-based homopolymer (POF). Higher brightness and larger current efficiency were observed for the CzPhB/fluorene and CzPhThB/fluorene copolymer-based devices compared to the POF-based device. Additionally, the CzPhThB/fluorene copolymer-based devices had better EL performances than the CzPhB/fluorene copolymer-based devices. The turn-on voltage, maximal brightness, and highest luminescence efficiency of the carbazole/fluorene copolymer-based devices were found to be 4.5–8.5 V, 436 cd/m², and 0.51 cd/A, respectively.

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1. Introduction

In the past decades, polymer light-emitting diodes (PLEDs) have received attention because of their applications in full-color flat panel displays and solid state lighting sources [1,2]. PLEDs have a number of advantages over inorganic or organic small moleculebased light-emitting diodes, including easy processing, low operating voltages, low cost fabrication, and high flexibility [3]. For a full-color display, the need to develop more stable and highly efficient three primary color (red, green, and blue) emitters is important for allowing PLEDs to become commercial products [4]. Of particular interest are blue light-emitting materials, which can serve as either blue light sources in a full-color display or as host materials for lower energy fluorescent or phosphorescent dyes [5–8]. Therefore, developing stable blue EL materials with high efficiency and excellent Commission Internationale de L'Enclairage (CIE) coordinates (y-coordinate value < 0.15) is essential to realizing such applications.

Conjugated polyfluorenes (PFs) have evolved to be the most promising candidates for blue-emitting materials for PLEDs because of their highly efficient blue emission in photoluminescence (PL) and electroluminescence (EL), excellent thermal and chemical stability, and good solubility in common organic solvents [9–13]. However, an undesired emission appearing in the long-wavelength division (from 500 to 600 nm) of the emission spectra of PF homopolymers not only hampers the EL efficiency, but impairs the color purity. Either the formation of aggregates/ excimers or degradation of the polymers during operation of the PF-based PLEDs has been proposed as the source of this problem [14-16]. The long-wavelength emission could be curtailed by introducing bulky substituents or long alkyl chains at the C-9 position of the fluorene unit through copolymerization with appropriate co-monomers or the attachment of bulky end-capping groups, among others [17–24]. Additionally, most PF-type polymers with low highest occupied molecular orbital (HOMO) levels have a high energy barrier to hole-injection from the anode, resulting in imbalanced charge mobility and subsequent low quantum efficiency [25,26]. Chemical structure modification of PFs by incorporating electron-donor moieties, such as triarylamine, carbazole, and thiophene groups, seems to improve the deficiency in hole-injection properties [20,27,28]. It is well-known that



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attaching a carbazole moiety to the molecular scaffold can significantly enhance the thermal stability and HOMO energy level of light-emitting polymers (LEPs). Moreover, the 3-, 6- or 9-position of the carbazole moiety can be easily functionalized, and thus the photo-physical properties of the polymers can be tuned [29–32]. N-arylated carbazoles, in which a phenyl or napthyl group is attached at the 9-position of the carbazole, have shown excellent thermal stability and good electro-optical properties in smallmolecule OLEDs [33]. As far as the conjugated polymer is concerned, the imbalanced transport properties between the holes and electrons are another crucial factor deciding the efficiency of PLEDs. Due the poor electron-mobility of LEPs, the attachment of electrondeficient groups (such as pyridine, benzothiadiazole, quinoxalines, and oxadiazole, etc.) onto a polymer chain has proven to be an effective methodology to promote its electron transport capabilities [34–37]. Several studies have also demonstrated that boranederivatives are potential luminescent and electron-transporting materials [38-40]. The air and moisture stabilities of electrondeficient arylboranes can be improved by incorporating the noncoplanar dimesityl group into the molecules [41-43]. Moreover, the non-coplanar structure of dimesitylborane could hinder the molecular close packing in the solid state. A stable amorphous film was formed for a dimesitylborane moiety containing carbazole derivative [40]. Although arylborane-containing fluorophores have been successfully developed as light emitters, only a few arylborane moieties containing LEPs have been proposed for PLED applications [44-47]. Chujo et al. synthesized a series of alternating copolymers by the hydroboration polymerization of aromatic divnes and mesitylborane [44]. Blue emission was observed for the copolymers in dilute solution state. The copolymers containing boron atoms in the main-chains are expected to act as electrondeficient π -conjugated systems, where π -conjugation length is extended via the vacant *p*-orbital of the boron atom [44]. However, the EL properties of the main chain organoboron polymer-based emitting layers have not been investigated. In addition, Yamaguchi and coworkers reported a series of highly emissive diborylphenylene containing poly(arylenethyynylene)s [45,46]. The presence of bulky diarylboryl substituents not only acts as a good electron-accepting unit, but also prevents the interaction and aggregation between the polymer backbones. However, these poly (arylenethyynylene)s exhibited sky-blue to green emission as thin films due to the strongly intramolecular charge transfer (ICT) transition from the π -conjugated backbone to the diborylphenylene unit. EL properties of the poly(arylenethyynylene)s were not discussed even through the fact that highly absolute quantum yields were observed for these polymer-based thin films [46]. More recently, two N-p-(diarylboryl)phenyl-substituted polycarbazoles were reported by Lambert et al. [47]. Although the authors demonstrated a light-emitting device based on N-p-(diarvlborvl)phenvl-substituted 3.6-linked polycarbazoles, but only the EL spectrum was shown in the literature.

Base on the above, highly blue emissive conjugated polymers could be obtained by the incorporation of the electron-deficient arylborane unit into the conjugated polymers [44–47]. It is important to note that EL properties have never been discussed for these arylborane unit containing conjugated polymers. In addition to the bipolar structure in the polymer, the conjugation length in both side-chain moiety and polymer backbone should be taken into account for pursuing a polymer-based device with excellent EL performances. In this study, a series of random and alternating carbazole/fluorene copolymers with various contents of dimesitylboron-containing carbazole derivatives were designed and synthesized for use as blue emitters in PLEDs because the bipolar carbazole- π -dimesitylboron unit exhibits a high PL quantum efficiency in both solution and the solid state [40]. Two carbazole derivatives, CzPhB and CzPhThB consisted of a carbazoyl group as the donor and a dimesitylboron group as the acceptor group, separated by phenyl and phenyl-thiophene groups π -conjugated systems, respectively. Incorporating the bipolar carbazole derivative as the pendant of the conjugated polymer was favorable for improvement of the charge-injection/transporting characteristics of the PF. Excellent EL properties were expected for these carbazole/ fluorene copolymer-based PLEDs. The thermal stability, electrochemical properties, photo-physical behavior, and EL performances of the carbazole/fluorene copolymer-based devices are discussed in detail as the chemical structures and carbazole derivative content of the copolymers are taken into account.

2. Experimental

2.1. Materials

All reactions and manipulations were performed in a nitrogen atmosphere using standard Schlenk techniques. All chromatographic separations were carried out on silica gel. 9H-carbazole, 1,4-dibromobenzene, N-bromosuccinimide (NBS), copper powder and 18-crown-6 were purchased from Acros Co. Potassium carbonate (K₂CO₃) was bought from Fisher Scientific. Tetrakistriphenylphosphine palladium(0) [Pd(PPh₃)₄] was purchased from Strem Chemicals. 2.7-Dibromo-9,9-dioctylfluorene (compound **3**), n-butyl lithium and dimesitylboron fluoride were obtained from Aldrich Co. *o*-Dichlorobenzene (DCB) was bought from TEDIA. Tetrahydrofuran (THF) and toluene were purified by distillation from sodium in the presence of benzophenone. Detailed synthetic procedures for the carbazole derivatives (CzPhB and CzPhThB) and carbazole/fluorene copolymers are report hereafter and are shown in Schemes 1 and 2.

2.2. Synthesis of monomers

2.2.1. Synthesis of 9-(4-bromophenyl)-9H-carbazole (compound 1) [48]

A stirred mixture of 9*H*-carbazole (5.02 g, 30 mmol), 1,4-dibromobenzene (14.13 g, 60 mmol), K₂CO₃ (16.56 g, 120 mmol), Cu powder (1.94 g, 30 mmol) and 18-crown-6 (3.71 g, 15 mmol) in DCB (120 ml) was degassed with nitrogen for 1 h. The reaction mixture was then refluxed under a nitrogen atmosphere for 16 h. The crude mixture was filtered, and the residue was washed with dichloromethane. The combined filtrates were then evaporated to dryness. The product was purified by flash column chromatography (silica gel, hexane) to give compound 1 (7.0 g, yield = 73%) as a white solid. ¹H NMR (600 MHz, CDCl₃): δ [ppm]: 7.26–7.31 (m, 2H), 7.35–7.38 (m, 3H), 7.40–7.45 (m, 3H), 7.72 (d, *J* = 8.7 Hz, 2H), 8.13 (d, *J* = 7.8 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃): δ [ppm]: 109.53, 120.20, 120.37, 120.87, 123.47, 126.07, 128.71, 133.10, 136.79, 140.60. HRMS (*m/z*): calcd for C₁₈H₁₂BrN: 321.0153. Found: 321.0162. Anal. calcd for C₁₈H₁₂BrN: C, 67.10; H, 3.75; N, 4.35. Found: C, 67.45; H, 3.73; N, 4.21.

2.2.2. Synthesis of 9-(4-(thiophen-2-yl)phenyl)-9H-carbazole (compound 2)

50 mL of anhydrous toluene was added to a mixture of compound 1 (3.22 g, 10 mmol) and 2-thiopheneboronic acid (2.77 g, 10 mmol). After 10 mL of 2 M aqueous K_2CO_3 was added to the stirred mixture, the reaction mixture was degassed with nitrogen for 1 h. Then Pd (PPh₃)₄ (0.03 g, 0.05 mmol) was added to the mixture. The solution was further refluxed under a nitrogen atmosphere for 48 h. After the reaction solution was cooled to room temperature, the whole mixture was poured into water, and the organic layer was separated and washed with water. The organic extracts were dried over MgSO₄ and concentrated by rotary evaporation. After the solvent was



Scheme 1. Synthetic routes of monomers.

evaporated, the crude product was further purified by column chromatography on silica gel using hexane as the eluent to yield compound 2 (2.34 g, yield = 72%) as a white solid. ¹H NMR (600 MHz, CDCl₃): δ [ppm]: 7.12 (t, *J* = 3.9 Hz, 1H), 7.28–7.35 (m, 3H), 7.39–7.44 (m, 5H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.7 Hz, 2H), 8.14 (d, *J* = 7.8 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃): δ [ppm]: 109.76, 120.01, 120.31, 123.42, 123.57, 125.30, 125.97, 127.22, 127.41, 128.22, 133.51, 136.77, 140.74, 143.39. HRMS (*m*/*z*): calcd for C₂₂H₁₅NS: 325.0925.

Found: 325.0923. Anal. calcd for $C_{22}H_{15}NS$: C, 81.20; H, 4.65; N, 4.30. Found: C, 81.25; H, 4.30; N, 4.28.

2.2.3. Synthesis of 9-(4-(dimesitylboryl)phenyl)-9H-carbazole (compound 3)

Under a nitrogen atmosphere, n-butyl lithium (4.4 ml, 11 mmol, 2.5 M in hexane) was added to a solution of compound 1 (3.2 g, 10 mmol) in dry THF (50 mL) at -78 °C. After 1 h of stirring,



Scheme 2. Synthetic routes of the carbazole/fluorene copolymers.

dimesitylboron fluoride (3.0 g, 11 mmol) in 15 mL of THF was added slowly to the reaction mixture, which was stirred for a further 12 h. The reaction mixture was then cooled to room temperature and quenched with 2 N HCl. The solution was extracted with ethyl acetate and the organic layer was dried over MgSO₄, filtered, and evaporated to yield a crude solid. The crude product was purified by column chromatography to afford a white solid of compound 3 (3.42 g, yield = 70%). ¹H NMR (600 MHz, CDCl₃): δ [ppm]: 2.08 (s, 12H), 2.31 (s, 6H), 6.85 (s, 4H), 7.28 (t, I = 8.1 Hz, 2H), 7.40 (t, I = 8.1 Hz, 2H), 7.49 (d, I = 7.8 Hz, 2H),7.56 (d, I = 8.4 Hz, 2H), 7.73 (d, I = 8.1 Hz, 2H), 8.12 (d, I = 7.2Hz, 2H). ¹³C NMR (75 MHz, CDCl₃): δ [ppm]: 21.24, 23.51, 109.94, 120.22, 120.34, 123.66, 125.89, 125.98, 126.89, 127.2, 128.309, 137.95, 138.89, 140.37, 140.83. FABMS (*m*/*z*): calcd for C₃₆H₃₄BN: 491.2784. Found: 491.2786. Anal. calcd for C₃₆H₃₄BN: C, 87.98; H, 6.97; N, 2.85. Found: C, 87.57; H, 7.11; N, 2.38.

2.2.4. Synthesis of 9-(4-(5-(dimesitylboryl)thiophen-2-yl)phenyl)-9H-carbazole (compound 4)

Compound 2 (3.25 g, 10 mmol), n-butyl lithium (4.4 mL, 11 mmol, 2.5 M in hexane) and dimesitylboron fluoride (3.0 g, 11 mmol) were allowed to react according to the procedure for compound 3. A pale yellow solid of compound 4 was obtained (3.44 g, Yield = 60%). ¹H NMR (600 MHz, CDCl₃): δ [ppm]: 8.15 (d, *J* = 7.8 Hz, 2H), 7.90 (d, *J* = 8.7 Hz, 2H), 7.54–7.59 (m, 3H), 7.47–7.49 (m, 5H), 7.41–7.45 (m, 2H), 6.86 (s, 4H), 2.32 (s, 6H), 2.18 (s, 12H). ¹³C NMR (75 MHz, CDCl₃): δ [ppm]: 21.23, 23.48, 109.73, 120.12, 120.34, 123.49, 125.75, 126.01, 127.32, 127.52, 128.20, 133.11, 137.66, 138.61, 140.62, 140.86, 141.70, 155.73. HRMS (*m*/*z*): calcd for C₄₀H₃₆BNS: 573.2662. Found: 573.2658. Anal. calcd for C₄₀H₃₆BNS: C, 83.76; H, 6.33; N, 2.44. Found: C, 83.59; H, 6.77; N, 2.07.

2.2.5. Synthesis of 3,6-dibromo-9-(4-(dimesitylboryl)phenyl)-9H-carbazole (compound 5, CzPhB)

N-Bromosuccinimide (3.92 g, 22 mmol) was added portion wise to a solution of compound 3 (4.91 g, 10.00 mmol) in THF (80 mL). The mixture was stirred at room temperature under a nitrogen atmosphere for 16 h. The whole mixture was then poured into water, and the organic layer was separated and washed with water. The organic extracts were dried over anhydrous Na₂SO₄, filtered, and evaporated to yield a crude solid. The crude product was further purified by column chromatography using silica gel and eluting with hexane to afford a white solid, compound 5 (4.01 g, yield = 62%). ¹H NMR (600 MHz, CDCl₃): δ [ppm]: 2.08 (s, 12H), 2.32 (s, 6H), 6.86 (s, 4H), 7.32 (d, J = 9.0 Hz, 2H), 7.31–7.48 (m, 4H), 7.74 (d, J = 8.4 Hz, 2H), 8.15 (s, 2H). ¹³C NMR (75 MHz, CDCl₃): δ [ppm]: 21.26, 23.53, 111.65, 113.32, 123.24, 124.18, 125.70, 128.34, 129.42, 138.02, 139.04, 139.33, 140.78.FABMS (*m*/*z*): calcd for C₃₆H₃₂BBr₂N: 647.0995. Found: 647.1002. Anal. calcd for C₃₆H₃₂BBr₂N: C, 66.60; H, 4.97; N, 2.16. Found: C, 66.48; H, 5.17; N, 1.92.

2.2.6. Synthesis of 3,6-dibromo-9-(4-(5-(dimesitylboryl)thiophen-2-yl)phenyl)-9H-carbazole (compound 6, CzPhThB)

N-Bromosuccinimide (3.92 g, 22.0 mmol) and compound 4 (5.73 g, 10.0 mmol) were allowed to react according to the procedure for compound 5. A pale yellow solid, compound 6 (CzPhThB) was obtained (4.08 g, Yield = 56%). ¹H NMR (600 MHz, CDCl₃): δ [ppm]: 2.17 (s, 12H), 2.32 (s, 6H), 6.86 (s, 4H), 7.24 (d, *J* = 8.7 Hz, 2H), 7.44–7.48 (m, 4H), 7.50–7.54 (m, 3H), 7.86 (d, *J* = 8.4 Hz, 2H), 8.16 (d, *J* = 1.8 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃): δ [ppm]: 21.24, 23.48, 111.42, 113.25, 123.24, 124.01, 125.95, 127.16, 127.68, 128.22, 129.47, 133.79, 136.55, 138.67, 139.57, 140.83, 141.05, 141.64, 150.29, 155.18. FABMS (*m*/*z*): calcd for C₄₀H₃₄BBr₂NS: 729.0872. Found: 729.0887. Anal. calcd for C₄₀H₃₄BBr₂NS: C, 65.69; H, 4.69; N, 1.92. Found: C, 65.63; H, 5.08; N, 1.39.

2.3. Synthesis of carbazole/fluorene copolymers

2.3.1. Synthesis of PFCzPhB10

As shown in Scheme 2, the carbazole/fluorene copolymers were prepared via the standard Suzuki polycondensation reaction, as previously reported [49]. A stirred mixture of compound 5 (0.13 g, 0.2 mmol), compound 7 (0.44, 0.8 mmol), compound 8 (0.64 g, 1 mmol). Pd(PPh₃)₄ (0.035 g, 3 mol %), an aqueous solution of K_2CO_3 (2 M, 12 mL), and anhydrous toluene (30 mL) was degassed with nitrogen for 1 h. The mixture was heated to 90 °C and stirred under a nitrogen atmosphere for 48 h. After cooling to room temperature, the whole mixture was poured into methanol, and the precipitated polymer was filtered out. The crude product was then dissolved in a small amount of THF and precipitated several times with methanol. The polymer was further purified by a Soxhlet extraction in acetone for 24 h. A pale yellow solid product PFCzPhB10 was obtained in 61% yield (0.49 g). ¹H NMR (600 MHz, CDCl₃): δ [ppm]: 0.78-0.86 (br, 54H), 0.90-1.35 (br, 216H), 2.06-2.18 (br, 48H), 2.34 (s, 6H), 6.88 (s, 4H), 7.58-7.90 (m, 62H), 8.35-8.52 (br, 2H). Anal. Found (%) for PFCzPhB10 [(C₃₆H₃₂NB)_{0.1}(C₂₉H₄₀)_{0.9}]: C, 89.55; H, 9.85; N, 0.35. Found: C, 88.99; H, 10.84; N, 0.38.

2.3.2. Synthesis of PFCzPhB30

With the same procedure as that described for the synthesis of copolymer PFCzPhB10, compound 5 (0.39 g, 0.6 mmol), compound 7 (0.22 g, 0.4 mmol) and compound 8 (0.64 g, 1 mmol) were used to prepare copolymer PFCzPhB30. A pale yellow solid was obtained in 63% yield (0.53 g). ¹H NMR (600 MHz, CDCl₃): δ [ppm]: 0.60–0.86 (br, 14H), 0.90–1.30 (br, 56H), 2.05–2.15 (br, 21H), 2.34 (s, 6H), 6.86 (s, 4H), 7.47–7.98 (br, 22H), 8.35–8.52 (br, 2H). Anal. Found (%) for PFCzPhB30 [(C₃₆H₃₂NB)_{0.3}(C₂₉H₄₀)_{0.7}]: C, 89.3; H, 9.0; N, 1.0. Found: C, 88.5; H, 9.56; N, 0.12.

2.3.3. Synthesis of PFCzPhB50

With the same procedure as that described for the synthesis of copolymer PFCzPhB10, compound 5 (0.65 g, 1 mmol) and compound 8 (0.64 g, 1 mmol) were used to prepare copolymer PFCzPhB50. The PFCzPhB50 polymer was obtained as a pale yellow solid after drying under vacuum at 60 °C overnight (0.45 g, yield = 51%). ¹H NMR (600 MHz, CDCl₃): δ [ppm]: 0.74–0.88 (br, 6H), 1.0–1.2 (br, 24H), 1.80–2.10 (br, 16H), 2.31–2.40 (d, 6H), 6.86 (s, 4H), 7.50–8.10 (m, 14H), 8.50–8.62 (br, 2H). Anal. Found (%) for PFCzPhB50 [C₆₅H₇₂NB]: C, 88.96; H, 8.2; N, 1.6. Found: C, 88.12; H, 9.52; N, 1.48.

2.3.4. Synthesis of PFCzPhThB10

With the same procedure as that described for the synthesis of copolymer PFCzPhB10, compound 6 (0.15 g, 0.2 mmol), compound 7 (0.44 g, 0.8 mmol) and compound 8 (0.64 g, 1 mmol) were used to prepare copolymer PFCzPhThB10. A pale yellow solid was obtained in 66% yield (0.54 g). ¹H NMR (600 MHz, CDCl₃): δ [ppm]: 0.77–0.88 (br, 54H), 0.95–1.27 (br, 216H), 2.05–2.18 (br, 48H), 2.38 (s, 6H), 6.83 (s, 4H), 7.31–7.48 (m, 2H), 7.57–7.88 (m, 62H), 8.30–8.60 (d, 2H). Anal. Found (%) for PFCzPhThB10 [(C₄₀H₃₄NBS)_{0.1}(C₂₉H₄₀)_{0.9}]: C, 88.92; H, 9.70; N, 0.34; S, 0.79. Found: C, 88.17; H, 9.69; N, 0.30; S, 0.74.

2.3.5. Synthesis of PFCzPhThB30

With the same procedure as that described for the synthesis of copolymer PFCzPhB10, compound 6 (0.44 g, 0.6 mmol), compound 7 (0.22 g, 0.4 mmol) and compound 8 (0.64 g, 1 mmol) were used to prepare copolymer PFCzPhThB30. A pale yellow solid was obtained in 65% yield (0.58 g). ¹H NMR (600 MHz, CDCl₃): δ [ppm]: 0.60–0.92 (br, 14H), 0.95–1.20 (br, 56H), 1.80–2.18 (br, 21H), 2.36 (s, 6H), 6.82 (s, 4H), 7.34–7.50 (m, 2H), 7.55–7.97 (m, 22H), 8.30–8.60 (br, 2H). Anal. Found (%) for PFCzPhThB30 [(C₄₀H₃₄NBS)_{0.3}(C₂₉H₄₀)_{0.7}]:

C, 87.53; H, 8.63; N, 0.95; S, 0.72. Found: C, 87.45; H, 8.60; N, 0.89; S, 0.68.

2.3.6. Synthesis of PFCzPhThB50

With the same procedure as that described for the synthesis of copolymer PFCzPhB10, compound 6 (0.73 g, 1 mmol) and compound 8 (0.64 g, 1 mmol) were used to prepare copolymer PFCzPhThB50. A pale yellow solid was obtained in 44% yield (0.42 g). ¹H NMR (600 MHz, CDCl₃): δ [ppm]: 0.60–0.92 (br, 6H), 0.92–1.25 (br, 24H), 1.80–2.10 (br, 16H), 2.25–2.38 (br, 6H), 6.82 (s, 4H), 7.34–7.50 (br, 2H), 7.50–7.98 (m, 14H), 8.30–8.60 (br, 2H). Anal. Found (%) for PFCzPhThB50 [C₆₉H₇₄NBS]: C, 86.36; H, 7.72; N, 1.46; S, 0.34. Found: C, 86.31; H, 7.94; N, 1.36; S, 0.32.

2.4. Instruments

¹H NMR spectra were recorded on a Bruker AMX-600 MHz spectrometer, and elemental analysis was carried out on an elemental analyzer (Elementar Vario EL III). Mass spectra were carried out on a Finnigan/Thermo Quest MAT mass spectrometer. Gel permeation chromatography (GPC) measurements were performed on a Waters chromatograph (Waters 1515 plus Autosampler) using two Waters Styragel linear columns with polystyrene as a standard and THF as the eluent. Glass transition temperatures (Tgs) were measured by differential scanning calorimetry (TechMax Instruments DSC 6220) in a nitrogen atmosphere at a heating rate of 10 °C/min. Thermogravimetric analysis (TGA) of the polymers was measured under a nitrogen atmosphere at a heating rate of 20 °C/min by using a Thermo-gravimetric analyzer (VersaTherm thermo-gravimetric analyzer). The UV-vis absorption and PL spectra were recorded on a Shimadzu UV-1240 spectrophotometer and an Acton Research Spectra Pro-150 spectrometer, respectively. Cyclic voltammetric (CV) measurements were conducted on a CHI model611D with the use of a three-electrode cell, in which an ITO sheet, a platinum wire and silver/silver nitrate (Ag/Ag⁺) were used as the working electrode, counter electrode and reference electrode, respectively. All electrochemical experiments were performed in deoxygenated acetonitrile (CH₃CN) solution with 0.1 M tetrabutylammonium perchlorate (Bu_4NCl_6) as the electrolyte.

2.5. EL device fabrication and electro-optical characterization

The PLED structure in this study was ITO glass/hole-transporting material (HTM)/copolymer/TPBI/LiF/Al. The ITO-coated glass, with a sheet resistance of 8 Ω /sq, was purchased from Applied Film Corp. Glass substrates with patterned ITO electrodes were washed well and cleaned with an O₂ plasma treatment. A thin film (60 nm) of HTM poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS, CH8000, Bayer) was formed on the ITO layer of a glass substrate by the spin-casting method and dried at 130 °C for 1 h. Light-emitting layers were then spin-coated (1500 rpm) from the LEP solutions (10 mg/mL) onto the HTM layer and dried at 80 °C for 1 h in a glove box. LEP solutions were prepared with 1,2-dichloroethane (DCE). The hole-blocking and electron-transporting material, TPBI, was evaporated to a thickness of 30 nm in a vacuum chamber. Finally, a thin LiF (1 nm) cathode was thermally deposited onto the light-emitting layer, followed by the deposition of Al (120 nm) metal as the top layer, in a highvacuum chamber. After the electrode deposition, the PLED was transferred from the evaporation chamber to a glove box purged with high-purity nitrogen gas to keep oxygen and moisture levels below 1 ppm. The device was then encapsulated with glass covers sealed with UV-cured epoxy glue in the glove box. The deposition rate of the cathode was operated with a quartz thickness monitor (FU-12CR). The EL spectra, luminescence, and current-voltage characteristics of the devices were measured on a programmable electrometer with current and voltage sources (Keithley 2400) and a Newport Optics 1835C luminance spectrophotometer.

3. Results and discussion

3.1. Synthesis and Characterization

Scheme 1 illustrates the synthetic routes of the monomer and carbazole/fluorene copolymers. Compound 1 was synthesized from carbazole and 1,4-dibromobenzene through an Ullmann coupling reaction [48] and then further reacted with thiophen-2-ylboronic acid via Suzuki coupling to obtain compound 2. Compound 1 and compound 2 were then further reacted with *n*-BuLi in THF at -78 °C, followed by the addition of dimesitylboron fluoride to give compounds 3 and 4, respectively. Compounds 5 (CzPhB) and 6 (CzPhThB) were obtained through bromination at the 3- and 6positions of carbazole compounds 3 and 4 with NBS in THF at room temperature, respectively. A series of CzPhB/fluorene and CzPhThB/ fluorene copolymers (PFCzPhB and PFCzPhThB) were synthesized via Suzuki coupling reaction of the appropriate diboronates and dibromo compounds in toluene at 90 °C for 48 h in the presence of Pd(PPh₃)₄ and 2 M K₂CO₃. The chemical structures of the conjugated polymers were verified by ¹H NMR spectroscopy, and the spectra of PFCzPhB50 and PFCzPhThB50 are shown in Fig. 1. The signals in the ranges of 0.79-2.27 ppm were assigned to the dihexyl chains, whereas the peaks at 6.38-8.52 ppm were attributed to the protons of the fluorene and carbazole rings. The absorption peak of proton *i* was observed at 2.2–2.4 ppm, which corresponds to the protons of methyl groups in the dimesitylboryl moiety. The characteristic peak at around 0.6–0.9 ppm was assigned to the protons of the methyl group in dihexyl chains of the fluorene unit. According to the ¹H NMR spectrum of PFCzPhB50, the integral values of protons *i* and *a* are about 8.13 and 8.43, respectively. This demonstrates that the molar percentage of the CzPhB unit was about 50% for PFCzPhB50. In the case of PFCzPhThB50, the integration values of peaks *i* and *a* are about 7.82 and 7.53, respectively, meaning the amount of the CzPhThB unit was about 50% for PFCzPhThB50. The molar ratio of the carbazole derivative and 9,9-dioctylfluorene in the copolymers according to ¹H NMR are summarized in Table 1. The chemical shifts and relative intensities of the signals are in agreement with the proposed structures for the carbazole/fluorene copolymers. The molar ratio of the carbazole derivative and 9,9-dioctylfluorene in the copolymers according to ¹H NMR are summarized in Table 1. The chemical shifts and relative intensities of the signals are in agreement with the proposed structures for the carbazole/fluorene copolymers.

The number- and weight-average molecular weights $(M_n$ and $M_{\rm W}$) of the carbazole/fluorene copolymers are summarized in Table 2. The M_n and M_w of copolymers PFCzPhB10-PFCzPhB50 were in the range of 11.7-16.3 and 26.3-38.5 kg/mol, respectively, while the $M_{\rm p}$ of the poly(9,9-dioctylfluorene) (POF) was 19.2 kg/mol and the M_w for POF was 38.1 kg/mol. For copolymers PFCzPhThB10-PFCzPhThB50, the $M_{\rm p}$ and $M_{\rm w}$ were in the range of 8.4–14.6 and 18.2-36.5 kg/mol, respectively. Generally, the thermal stability of conjugated polymers plays an important role in the operating stability of a PLED. Operational lifetime of a PLED is directly related to the thermal stability of the LEP. Therefore, high $T_{\rm g}$ and $T_{\rm d}$ are important requisites for application of an LEP in outdoor displays. TGA and DSC thermograms of the copolymers are shown in Fig. 2. The temperatures at which five percent weight loss occurred for the copolymers are summarized in Table 1. The T_ds of PFCzPhB10-PFCzPhB50 were found to be approximately 408-412 °C, while the copolymers PFCzPhThB10-PFCzPhThB50 had a T_ds in the range of 340–425 °C. Thermal stability is affected by the molecular weight



Fig. 1. ¹H NMR spectra of (a) PFCzPhB50 and (b) PFCzPhThB50.

and the chemical structure of the conjugated polymer backbone. The conjugated polymers with low molecular weight possess low thermal stability. For example, PFCzPhThB50 has the lowest molecular weight and showed the lowest T_d of all of the polymers. The T_g of the POF was about 100 °C, while the T_g s values of CzPhB/ fluorene copolymers were around 83-92 °C. For the CzPhThB/fluorene copolymers, the $T_{\rm g}$ s values were in the range of 105–117 °C. The results indicated that the CzPhThB/fluorene copolymers showed a slightly higher T_g than the CzPhB/fluorene copolymers. This can presumably be attributed to the more rigid molecular segment of the CzPhThB/fluorene copolymers compared to those of the CzPhB/fluorene copolymers. In addition, the solubilities of the conjugated polymers in organic solvents are summarized in Table 2. The carbazole/fluorene copolymers were completely soluble in most organic solvent at room temperature, including toluene, THF, DCE, chloroform (CHCl₃), and chlorobenzene (CB). However, the copolymers were only partially soluble in 1,4-dioxane and

dimethylacetamide at room temperature, but completely soluble after a mild heating procedure.

3.2. Photo-physical properties

UV–vis absorption and PL spectra of the carbazole/fluorene copolymers in DCE (1×10^{-5} M) solution and thin films are shown in Fig. 3. The photo-physical properties of the copolymers are itemized in Table 3. All polymers exhibited only a distinct absorption band, which was attributed to the π – π * electronic transition of the conjugated polymer backbones. In dilute DCE solution, the absorption maximum wavelengths (λ_{max}) of the PFCzPhB10, PFCzPhB30, and PFCzPhB50 were 376, 365 and 344 nm, respectively, while PFCzPhThB10, PFCzPhThB30, and PFCzPhThB50 were located at 378, 366, and 356 nm, respectively. Notably, with an increase of carbazole– π -boron units in the polymer main chain, the absorbance spectra of CzPhB/fluorene and the CzPhThB/fluorene

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Compositions, molecular weights, and thermal properties of the carbazole/fluorene
copolymers.

Copolymers	Cz-π-B unit (%) ^a	Cz-π-B unit (%) ^b	M_n (×10 ³)	$M_{\rm w}$ (×10 ³)	PDI (M_n/M_w)	<i>T</i> d (°C)	T_{g} (°C)
POF	_	_	19.2	38.1	1.98	432	100
PFCzPhB10	10	12	16.3	38.5	2.36	408	92
PFCzPhB30	30	29	12.0	26.3	2.19	412	83
PFCzPhB50	50	50	11.7	29.3	2.51	409	86
PFCzPhThB10	10	11	14.6	36.5	2.49	425	105
PFCzPhThB30	30	31	9.3	21.1	2.28	420	108
PFCzPhThB50	50	50	8.4	18.2	2.16	340	117

^a Molar ratio of carbazole unit in feed monomer mixture.

^b Molar ratio of carbazole unit calculated from ¹H NMR spectra.

copolymers exhibited a blue-shift, which was also found in previous reports on the analogous fluorene-carbazole copolymers [32]. Such a hypsochromic shift is probably attributable to interruption of the π -conjugation along the polymer backbone caused by the meta-linkage between the fluorene unit and the carbazole- π -boron unit. This would result in the conjugation length of the polymer being shortened [20]. Additionally, the absorption spectra of PFCzPhB10 and PFCzPhThB10 were similar to that of POF due to the minimal content of carbazole- π -boron units in the backbone. However, as the content of the carbazole- π -boron units increased to 50%, the spectral characteristics of PFCzPhB50 ($\lambda_{max} = 344 \text{ nm}$) and PFCzPhThB50 ($\lambda_{max} = 356 \text{ nm}$) were assigned to the combined electronic contribution from the carbazole and fluorene segments, which indicated that the electronic configurations of both units in the copolymers were almost mixed. Similar absorption results were previously reported for a 3,6-linked carbazole-fluorene/spirofluorene alternating copolymer [32]. Therefore, the absorption



Fig. 2. TGA (a) and DSC (b) thermograms of the copolymers.

Table 2
Solubility of the carbazole/fluorene copolymers in the organic solvents

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Copolymers	Toluene	THF ^a	DCE ^a	CHCl ₃ ^a	CB ^a	1,4-dioxane	DMAc ^a
POF	++ ^b	++	++	++	++	+- ^b	+-
PFCzPhB10	++	$^{++}$	++	++	$^{++}$	+-	+-
PFCzPhB30	++	$^{++}$	$^{++}$	++	$^{++}$	++	+-
PFCzPhB50	++	$^{++}$	$^{++}$	++	$^{++}$	++	+-
PFCzPhThB10	++	$^{++}$	$^{++}$	++	$^{++}$	+-	+-
PFCzPhThB30	++	$^{++}$	$^{++}$	++	$^{++}$	++	+-
PFCzPhThB50	++	++	++	++	++	++	+-

^a Organic solvents: Tetrahydrofuran (THF), 1,2-dichloroethane (DCE), chloroform (CHCl₃), chlorobenzene (CB), and dimethylacetamide (DMAc).

^b The solubility was measured in the concentration of 1 mg/mL; ++: soluble at room temperature; +-: partially soluble at room temperature.

results of the copolymers confirmed that changing the content of the 3,6-linked carbazole units could effectively manipulate the maximal absorption wavelength of the copolymer. In addition, the maximum absorption values of the copolymers in a thin film were red-shifted slightly compared to those of the copolymers in DCE solution. These results were attributed to the interactions and $\pi - \pi$ stacking between the polymer chains.

When irradiated with UV light at 350 nm, the PL emission colors of the copolymers in solution and as thin films ranged from blue to green. In dilute DCE solution, the main emission peaks of copolymers PFC2PhB10, PFC2PhB30, and PFC2PhB50 were 417, 470, and 474 nm, respectively. As shown in Fig. 3, the PL spectrum of the PFC2PhB10 showed maximum correspondence to the 0–0 transition at around 420 nm, with a well defined vibronic feature (0–1 transition) at around 436 nm, which is almost identical to that of POF [11]. On the other hand, PFC2PhB30 showed a sky-blue emission peak at 470 nm, with a shoulder emission peak at 418 nm, while PFC2PhB50 demonstrated a featureless vibronic PL spectrum,



Fig. 3. UV–vis and PL spectra of the carbazole/fluorene copolymers in (a) DCE solution and (b) thin films.

reflecting their different electronic features. Accordingly, upon increasing the content of the CzPhB moiety, the PL spectra of the CzPhB/fluorene copolymers revealed a relatively intensive emission peak at around 470 nm in dilute DCE solutions. This result can be explained as follows: partial ICT from fluorene segments to the carbazole- π -boron units occurred with an increasing content of 3.6-linked carbazole- π -boron units in the polymer main chain [50]. As a result, the relative intensity of the emission peak at 470 nm was strikingly enhanced. Such ICT behavior had been observed in other conjugated polymers with donor-acceptor segments [51]. In DCE solution, the main emission peaks of copolymers PFCzPhThB10, PFCzPhThB30, and PFCzPhThB50 were at 440, 495, and 503 nm, respectively. The PL emission maximum values of the CzPhThB/fluorene copolymers exhibited a large red-shift compared to those of the CzPhB/fluorene copolymers. This PL trend was also observed for the copolymers in the thin film state. Such differences in PL spectra between CzPhB/fluorene and the CzPhThB/fluorene copolymers may be attributed to incorporation of the thiophene moiety at the 9-position of carbazole, which not only enhances the strength of the ICT effect via its high delocalization properties, but also extend the side-chain conjugation length at the 9-position of the carbazole [52]. On the other hand, thin films of CzPhB/fluorene and CzPhThB/fluorene copolymers showed small red-shifts in their PL maxima upon increasing the carbazole- π -boron unit content. This could be due to less π -stacking aggregation in the polymer backbone because of the meta-linkage of the carbazole and/or the non-planar structures of the dimesitylboryl groups. Furthermore, with increasing carbazole- π -boron unit content. PL maxima of the copolymers in DCE solution exhibited a largely red-shifted as compared to those of the copolymers as thin films. This is due to the solvatochromic effect of the copolymers in polar organic solvent [47]. Lambert et al. reported that the PL spectra of N-p-(diarylboryl) phenyl-substituted 3,6-linked polycarbazoles show significant solvatochromic shifts in polar organic solvents with respect to the PL spectra of the copolymers as thin films [47]. Therefore, the large red-shift was possibly caused by the dipole-dipole interaction between the polar solvent (DCE) and bipolar side chains of CzPhB/ fluorene and CzPhThB/fluorene copolymers.

The PL quantum efficiencies ($\Phi_{\rm fl}$) of the carbazole/fluorene copolymers in DCE are summarized in Table 4. The $\Phi_{\rm fl}$ values of these copolymers were measured in dilute DCE solution by comparing their emission with that of a standard solution of 9,10-diphenylanthracene in cyclohexane ($\Phi_{\rm fl}=0.90$) at room temperature. Accordingly, the $\Phi_{\rm fl}$ values of POF, PFCzPhB10, PFCzPhB30, and PFCzPhB50 were 58, 60, 63, and 53%, respectively, while the $\Phi_{\rm fl}$ values of PFCzPhThB10, PFCzPhThB30, and PFCzPhThB50 were 72, 69, and 65%, respectively. The CzPhB/fluorene and CzPhThB/fluorene copolymers show higher $\Phi_{\rm fl}$ values than the POF. This was attributed to the dual fluorescence arising from a fluorescent delocalized state of the POF backbone and from a fluorescent ICT between the dimesitylboron and carbazole groups. However, the $\Phi_{\rm fl}$ values of the copolymers decreased upon increasing the carbazole derivative content (CzPhB or CzPhThB) in the polymer main chain. Increasing the high meta-linkage carbazole moiety content results in interruption of the π -conjugation along the polymer backbone, and thus, the effective conjugation length of the polymer is shortened. Therefore, the $\Phi_{\rm fl}$ values of the copolymers decreased slightly with increasing carbazole derivative content

The PL stability of the CzPhB/fluorene and CzPhThB/fluorene copolymers as solid films was further investigated by thermal annealing at 200 °C for 1 h. As shown in Fig. 4, the annealed polymer film exhibited a new broad green emission peak at about 528 nm, which was attributed the formation of low-energy excimer aggregates at high temperature [53,54]. High thermal energy causes the chain conformation to be altered to a higher inter-chain

Table 3

C	ptical	properties	of the	carbazole	/fluorene	copoly	mers.

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	Copolymers	$\lambda_{\max}^{UV} (nm)^a$	$\lambda_{max}^{UV} (nm)^{b}$	$\lambda_{\max}^{PL} (nm)^{c}$	$\lambda_{\max}^{PL} (nm)^d$	$\Phi_{\mathrm{fl}}(\%)^{\mathrm{e}}$
	POF	382	391	420, 442, 470	440, 460, 484	58
	PFCzPhB10	376	384	417, 439, 468	420, 436	60
	PFCzPhB30	365	372	418, 470	422, 435	63
	PFCzPhB50	344	351	474	431	53
	PFCzPhThB10	378	384	441, 466, 498	439, 462	72
	PFCzPhThB30	366	370	419, 495	456	69
	PFCzPhThB50	356	352	501	464	65

^a Maximal absorption wavelength of the copolymers in DCE.

^b Maximal absorption wavelength of the copolymers as solid film.

^c Maximal PL wavelength of the copolymers in DCE.

^d Maximal PL wavelength of the copolymers as solid film.

 $^{\rm e}~$ PL quantum efficiency ($\Phi_{\rm fl})$ of the copolymers in DCE.

order or packing density. An aggregation or excimer was likely formed among the polymer chains, which led to the occurrence of an inter-chain exciton emission at longer wavelengths. However, a relatively lower intensity of green emission peak was observed for the CzPhB/fluorene and CzPhThB/fluorene copolymers with higher carbazole moiety contents. A greater PL stability was observed for both the CzPhB/fluorene and CzPhThB/fluorene copolymers compared to that of the POF homopolymer. This was attributed to suppression of the polymer chain packing and aggregation due to the presence of kink linkages between the fluorene unit and carbazole- π -boron unit and/or the presence of non-coplanar dimesitylboryl groups as pendants [41,42]. Therefore, better PL stability was obtained for the carbazole/fluorene copolymer with higher carbazole units.

3.3. Electrochemical properties

CV was employed to investigate the electrochemical behavior and to estimate the HOMO and LUMO energy levels of the copolymers. The HOMO levels of the copolymers were calculated from the onset potential of oxidation (E_{onset}^{ox}) by assuming the absolute energy level of ferrocene at -4.8 eV below the vacuum level. The LUMO levels were calculated from the HOMO energy level and the absorption edge [55,56]. The oxidation and reduction behaviors of the copolymers are shown in Fig. 5. The CV curves of all copolymers showed broad spectra with single quasi-reversible oxidation and reduction waves. The electrochemical properties of the copolymers are summarized in Table 4. The Eox on served at about 1.01, 0.84, and 0.78 V for PFCzPhB10, PFCzPhB30, and PFCzPhB50, respectively. Moreover, the optical band gaps ($E_{\alpha}s$) of copolymers PFCzPhB10, PFCzPhB30, and PFCzPhB50, determined from the absorption edge, were 2.89, 2.91, and 2.96 eV, respectively. Therefore, the LUMO levels of PFCzPhB10, PFCzPhB30, and PFCzPhB50 were 2.82, 2.63, and 2.53 eV, respectively, while the HOMO levels were 5.72, 5.55 and 5.49 eV. In addition, the values of Eox for PFCzPhThB10, PFCzPhThB30, and PFCzPhThB50 were about 1.04, 0.87 and 0.85 V, respectively. Moreover, Egs of copolymers PFCzPhThB10, PFCzPhThB30, and PFCzPhThB50 were

Table 4
Electrochemical properties of the carbazole/fluorene copolymers

Copolymers	$E_{\rm ox} (V)^{\rm a}$	LUMO (eV)	HOMO (eV)	$E_{g}^{opt} (eV)^{b}$
POF	1.08	-2.96	-5.78	2.82
PFCzPhB10	1.01	-2.82	-5.72	2.89
PFCzPhB30	0.84	-2.63	-5.55	2.91
PFCzPhB50	0.78	-2.53	-5.49	2.96
PFCzPhThB10	1.04	-2.93	-5.75	2.82
PFCzPhThB30	0.87	-2.78	-5.58	2.80
PFCzPhThB50	0.85	-2.19	-5.56	2.77

^a Onset oxidation potential versus Ag/AgNO₃.

^b Estimated from the UV-vis absorption edge.



Fig. 4. PL spectra of the carbazole/fluorene copolymers as thin films after being treated at 200 $^\circ C$ for 1 h.

2.89, 2.91, and 2.96 eV, respectively. Hence, the LUMO levels of PFCzPhThB10, PFCzPhThB30, and PFCzPhThB50 were 2.93, 2.78, and 2.79 eV, respectively, while the HOMO levels were 5.75, 5.78, and 5.56 eV. Using the same approach, the LUMO and HOMO levels of POF were about 2.90 and 5.76 eV, respectively. The CV results indicated that the Eox values of the copolymers decreased upon increasing the content of the electron-rich carbazole derivative. Moreover, with the same carbazole unit content, higher E_{onset}^{ox} values were observed for the CzPhThB/fluorene copolymers compared to those of the CzPhB/fluorene copolymers. When compared to the phenyl-linked CzPhB moiety, better conjugation of the phenyl/ thiophene linkage results in a poor electro-donating capacity of the CzPhThB moiety. Therefore, higher Eox values were observed for the CzPhThB/fluorene copolymers. In addition, the Egs of CzPhB/ fluorene copolymers were increased by increasing the CzPhB unit content, while the Egs of the CzPhThB/fluorene copolymers were decreased upon increasing CzPhThB content. For the CzPhB/fluorene-based copolymers, the meta/kink-linkage between the fluorene unit and carbazole- π -boron units resists π -conjugation along the polymer backbone [20]. Moreover, the presence of the dimesitylboryl group reduced the coplanarity of the carbazole-based pendant and polymer backbone. Therefore, the Egs of the copolymers were increased with increasing CzPhB unit content. Nevertheless, the coplanarity between the pendant and backbone would increase because of the enhancement of the effective conjugation length and rigidity of the pendants. A decrease of the E_{gs} of CzPhThB/fluorene copolymers with increasing pendant content was



Fig. 5. CV spectra of the carbazole/fluorene copolymers in the thin film state.



Fig. 6. EL spectra of the carbazole/fluorene copolymer-based devices.

attributed to improved coplanarity between the phenyl/thiophenelinked carbazole moiety and polymer backbone. Apart from that, higher LUMO and HOMO levels were observed for the carbazole/ fluorene copolymers compared to the POF homopolymer due to incorporation of the electron-rich unit into the polymer backbone. A higher HOMO level is favorable for hole-injection to the lightemitting layer from an ITO transparent anode [20].

3.4. EL properties of carbazole/fluorene copolymers-based devices

For the carbazole/fluorene copolymers, the HOMO levels increased with increasing carbazole- π -boron unit content, and thus facilitated hole-injection into the copolymer-based light-emitting layer from the indium tin oxide anode. However, the LUMO energy levels were also enhanced upon increasing the carbazole- π -boron unit content. A higher LUMO level will result in the poor electron injection to the light-emitting layer from the cathode. Therefore, multilayer devices were fabricated with the configuration of ITO/ PEDOT/copolymer/TPBI (30 nm)/LiF(1 nm)/Al (120 nm) in this work. An electron injection/transporting layer of TPBI was inserted into the light-emitting layer and cathode interface for better electron and hole charge balance. The EL spectra of the CzPhB/fluorene and CzPhThB/fluorene copolymer-based devices are shown in Fig. 6. The EL emission maximum wavelength, full width at halfmaximum (fwhm) of EL, and CIE coordinates of the carbazole/fluorene copolymer-based devices are summarized in Table 5. The EL spectra showed a main emission peak at around 426-438 and 442–466 nm, respectively, for the CzPhB/fluorene and CzPhThB/ fluorene copolymer-based devices, without any shoulder emission of an excimer or exciplex at around 500 nm. Not much difference was observed for the maximal EL emission wavelengths of the PLEDs in comparison with the maximal PL emission wavelengths of

Table 5

Electroluminescence properties of the carbazole/fluorene copolymers-based devices.

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	Copolymers	λ ^{EL} (nm)	fwhm (nm)	$V_{\rm on} (V)^{\rm a}$	Max luminance (cd/m ²)	Max efficiency (cd/A)	CIE (x, y) ^b
	POF	436	22	6.5	130	0.23	(0.17, 0.08)
	PFCzPhB10	426	48	6.0	101	0.18	(0.17, 0.09)
	PFCzPhB30	430	52	8.0	92	0.26	(0.16, 0.07)
	PFCzPhB50	438	60	8.5	94	0.22	(0.18, 0.13)
	PFCzPhThB10	442	58	6.5	445	0.51	(0.16, 0.11)
	PFCzPhThB30	454	56	5.5	414	0.34	(0.16, 0.13)
	PFCzPhThB50	466	70	6.5	288	0.19	(0.21, 0.21)

^a Turn-on voltage at 1 cd/m².

^b CIE (x, y): Commission Internationale de L'Eclairage coordinates.



Fig. 7. Current density versus voltage of the carbazole/fluorene copolymer-based devices.

the copolymers in the solid state. Nevertheless, the fwhm values of the EL emission peaks were increased upon increasing the carbazole- π -dimesitylborane content in the CzPhB/fluorene and CzPhThB/fluorene copolymer-based devices. This is because partial emission was contributed from the light-emitting side-chain conjugated pendants. The CIE coordinates of the PFCzPhB10-, PFCzPhB30- and PFCzPhB50-based devices were (0.17, 0.09), (0.16, 0.07), and (0.18, 0.13), respectively, while the CIE coordinates of PFCzPhThB10, PFCzPhThB30 and PFCzPhThB50 were (0.16, 0.11), (0.16, 0.13), and (0.21, 0.21), respectively. High color purities of the PLEDs indicated that these carbazole/fluorene copolymers are good candidates for use as blue-emitting layers in PLEDs.

The EL properties of the CzPhB/fluorene and CzPhThB/fluorene copolymer-based devices are shown in Figs. 7–9. The turn-on voltages of the CzPhB/fluorene and CzPhThB/fluorene copolymer-based devices were about 6.0–8.5 V and 5.5–6.5 V, respectively. The maximum brightness of the CzPhB/fluorene and CzPhThB/fluorene copolymer-based devices were about 92–101 cd/m² and 288–445 cd/m², while the current efficiencies were about 0.18–0.26 cd/A and 0.19–0.51 cd/A, respectively. Moreover, the POF-based device showed a maximum brightness of 130 cd/m² and current efficiency of 0.23 cd/A. The EL performances of POF-based device were poorer than those reported in the literature [11,25]. This is attributed to the low molecular weight of POF. Low molecular weight led to the poor thin film quality and low brightness and small current efficiency of the POF-based device [54]. Clearly, the carbazole/fluorene copolymer-based



Fig. 8. Luminescence versus voltage of the carbazole/fluorene copolymer-based devices (applied voltage: 11 V).



Fig. 9. Current efficiency versus current density of the carbazole/fluorene copolymerbased devices.

devices showed the better EL performances than the POF-based devices, especially for the CzPhThB/fluorene copolymer-based devices. The better EL performance of the carbazole/fluorene copolymer-based devices was attributed to dual fluorescence arising from the polymer backbone and the carbazole- π -boron unit. The reduction of polymer chain aggregation via incorporation of the carbazole- π boron unit into the polymer backbone is another reason for the better EL performance of the devices. In addition, higher brightness and larger current efficiency were observed for the CzPhThB/fluorene copolymer-based devices compared to those of the CzPhB/fluorene copolymer-based devices. This is because the phenyl/thiophenelinked CzPhThB unit possesses a longer effective conjugation length than the phenyl-linked CzPhB unit, and thus better EL performances were observed with the CzPhThB/fluorene copolymer-based devices. Apart from that, lower values of brightness and current efficiency were observed for the devices fabricated from the CzPhThB/fluorene copolymers with higher CzPhThB contents. Interruption of the π -conjugation along the polymer backbone via the incorporation of a high meta-linkage carbazole moiety content occurs in these cases, and thus the EL performances of the PLEDs are reduced.

4. Conclusion

A series of novel carbazole/fluorene copolymers with dimesitylboron pendants were synthesized by Suzuki coupling. Excellent thermal stability was observed for the copolymers due to incorporation of the rigid carbazole- π -boron (CzPhB and CzPhThB) pendants in the fluorene-based backbone. The CzPhB/fluorene and CzPhThB/fluorene copolymers showed a higher PL quantum efficiency than the POF. Moreover, higher brightness and larger current efficiency were observed for the CzPhB/fluorene and CzPhThB/fluorene copolymer-based devices compared to the POF-based devices, which was attributed to the dual fluorescence arising from the polymer backbone and the carbazole- π -boron pendants. The reduction of polymer chain aggregation via incorporation of the rigid pendants into the polymer backbone is another reason for the better EL performance of the carbazole/fluorene copolymerbased devices. In addition, the phenyl/thiophene-linked CzPhThB unit possesses a longer effective conjugation length than the phenyl-linked CzPhB unit, and thus the CzPhThB/fluorene copolymer-based devices had better EL performance than the CzPhB/ fluorene copolymer-based devices. It was concluded that the EL properties of the copolymer-based devices were strongly dependant on the effective conjugation length and content of the carbazole- π -boron pendant.

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