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New carbazole-substituted anthracene derivatives based non-doped blue light-emitting devices with high brightness and efficiency



PIGMENTS

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ABSTRACT

A series of anthracene and 2-*tert*-butyl–substituted anthracene derivatives featuring 9-ethyl-9H-carbazol-3-yl or 4-(9-ethyl-9H-carbazol-3-yl)phenyl groups were synthesized for use as light-emitting layer in sky-blue organic light emitting devices (OLEDs). Efficient conjugation between the carbazole and anthracene unit resulted in strong blue emissions and high quantum efficiencies of anthracene derivatives in solution. Electroluminescence (EL) properties of non-doped OLEDs incorporated with these anthracene derivatives, along with an electron-transporting layer (ETL), tri-(8-hydroxyquinoline) aluminum (Alq₃) or 1,3,5-tris(N-phenyl benzimidizol-2-yl)benzene (TPBI) were investigated. The OLEDs incorporated with TPBI provided superior EL performance than did those incorporated with Alq₃. A holeblocking layer 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) was inserted at the interface of light emitting layer and ETL to enhance the EL performance for the OLED with Alq₃ as ETL. High brightness (37423 cd/m²), and great current efficiency (5.89 cd/A) were observed for the 4-(9-ethyl-9H-carbazol-3yl)phenyl-substituted anthracene derivatives based OLEDs.

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1. Introduction

Organic light-emitting diodes (OLEDs) have attracted much attention because of their excellent performance and great potential in flat-panel displays [1–6]. In full-color displays, pure blue emission is very difficult to achieve because a larger energy band gap is required as compared to green or red light-emitting materials. In order to fabricate the OLED with excellent performance, the dopant—host system is often adopted. However, electrolumines-cence (EL) properties, including color purity, are extremely sensitive to the dopant concentration, and the thickness of light-emitting layer [7–10]. In addition, precise control of the dopant concentration using co-evaporation methods is not an easy task. The development of high performance blue-light-emitting materials for nondoped OLEDs is one of the effective approaches to circumvent such fabrication problems [9,11,12].

Several small-molecule emitters, including pyrene [13,14], oxadiazole [15,16], carbazole [17,18], fluorene [19,20], and anthracene derivatives [21–36], were reported for applications in nondoped type blue OLEDs. Several anthracene derivatives attached with electron-donating or -withdrawing moieties at C9 and C10 positions, exhibiting hole-transporting/light-emitting or electrontransporting/light-emitting properties were reported [21-29]. A direct substitution of either strong electron-withdrawing or electron-donating groups at C9 and C10 positions changes the electron density on the anthracene ring and consequently enhances the conjugation length and photoluminescence (PL) performance of the anthracene derivative [23]. Particularly high brightness and large current efficiency were observed for the triphenylamine moieties attached anthracene derivative based OLEDs [24,25]. Moreover, the attachment of bulky side-groups to the anthracene core can prevent $\pi - \pi^*$ stacking interactions of the molecules in the solid state and reduce self-quenching effects [27,28]. Various electron-donating and -accepting groups were attached to tertbutyl substituted anthracene derivatives for use as blue emitters in OLEDs [21,27-32]. In addition, a series of OLEDs based on the anthracene derivatives attached with N-phenylcarbazole, triphenylphosphine, tetraphenylethylene, or oxadiazole exhibiting deep



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blue emission were reported in literature [30,32–35]. However, the brightness and current efficiency of these OLEDs are not among the high numbers. In fact, it is very difficult for the anthracene derivative based non-doped blue OLEDs to achieve all of the benchmark features at once (high brightness, great current efficiency, deep blue emission, and excellent operational stability) [21–36]. Apart from that, the conjugated side-group effect on the EL performance of anthracene derivatives has not been thoroughly discussed. Therefore, it is important to further discuss the chemical structure effect of the anthracene derivatives on the photo-physical properties, electrochemical behavior, and EL performance for developing practical blue emitters.

In general, the incorporation of a carbazole moiety into a molecular scaffold can significantly improve the glassy-state durability and thermal stability of an organic compound [17,35]. Moreover, the 3, 6, and 9 positions of the carbazole moiety can be readily functionalized, allowing the fine-tuning of the electro-optical properties of the molecules [37-44]. Recently, we synthesized a series of Narylated carbazole moiety attached anthracene derivatives for use as blue emitters in nondoped-type OLEDs [45]. Chemical structures of the N-arylated carbazole moiety attached anthracene derivatives are shown in Fig. S1. However, the EL properties of the anthracene derivative based OLEDs were only moderate, which is attributed to the relatively poor conjugation of the anthracene derivatives attached with the N-arylated carbazole moieties. The feature of poor conjugation affected the photophysical properties and electrochemical behaviors of the blue emitter negatively, and subsequently resulted in poor EL performance for OLEDs. With that in mind, a more efficient conjugation would be obtained for the attachment of C3-position of carbazolyl groups onto the C9 and C10 positions of anthracene unit. In this study, we designed and synthesized a series of anthracene and 2-tert-butyl-substituted anthracene derivatives featuring carbazole moieties as side groups-9,10-bis(9-ethyl-9Hcarbazol-3-yl)anthracene (Cz3An), 2-tert-butyl-9,10-bis(9-ethyl-9H-carbazol-3-yl)anthracene (Cz3Ant), 9,10-bis[4-(9-ethyl-9Hcarbazol-3-yl)phenyl]anthracene (Cz3PhAn) and 2-tert-butyl-9,10bis[4-(9-ethyl-9H-carbazol-3-yl)phenyl]anthracene (Cz3PhAnt) for use as light-emitting layers in blue OLEDs. EL properties of nondoped OLEDs incorporating these anthracene derivatives, with tri-(8-hydroxyquinoline)aluminum (Alq₃) or 1,3,5-tris(N-phenyl benzimidizol-2-yl)benzene (TPBI) as electron transporting layer (ETL) were investigated. In order to improve the EL performance of OLEDs, a hole-blocking layer (HBL), 2,9-dimethyl-4,7-diphenyl-1,10phenanthroline (BCP) was inserted at the interface of light emitting layer and ETL for these anthracene derivatives based nondoped-type blue emitting OLEDs. In addition, we analyzed the influence of the attached carbazole moieties on the thermal stability, electro-chemical properties, photo-physical behavior, and EL performances of the anthracene derivative-based devices.

2. Experimental section

2.1. Materials

All reactions and manipulations were performed under a N₂ atmosphere using standard Schlenk techniques. All chromatographic separations were performed using SiO₂. Anthraquinone and 2-tert-butylanthraquinone were obtained from SHOWA. Compounds 9-ethyl-carbazole, 1,4-dibromobenzene, tributylchlorostannane, palladium(II) acetate (Pd(OAc)₂), and *n*-butyl lithium (*n*-BuLi), *N*, *N*-dimethylformamide (DMF), and toluene were obtained from Aldrich and used as received. N-bromosuccinimide (NBS), potassium iodide (KI), and sodium hypophosphite monohydrate (NaHPO₂) were purchased from Acros. Tetrahydro-furan (THF) was purified through distillation from Na in the presence of benzophenone. The syntheses of intermediates (CzBr, CzSn, and CzPhBr) and carbazole-substituted anthracene derivatives (Cz3An, Cz3Ant, Cz3PhAn, and Cz3PhAnt) are presented in Schemes 1 and 2.

2.2. Synthesis

2.2.1. 3-Bromo-9-ethyl-9H-carbazole (CzBr)

N-bromosuccinimide (1.77 g, 10 mmol) in 10 mL DMF was added dropwise to a DMF (25 mL) solution containing 9-ethyl-9H-carbazole (1.95 g, 10 mmol) at 0 °C in a nitrogen atmosphere. The reaction mixture was reacted for 8 h, then quenched with water, and extracted with ethyl acetate (EA). The organic layer was dried over anhydrous magnesium sulfate followed by solvent evaporation in a rotary evaporator. A solid crude product was recrystallized in ethanol to afford a white solid product. The white solid product yield was 80.0% (2.19 g). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 1.41 (t, *J* = 7.2 Hz, 3H), 4.26 (q, *J* = 7.2 Hz, 2H), 7.24 (d, *J* = 8.7 Hz, 1H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.41 (d, *J* = 8.26 Hz, 1H), 7.50 (d, 1H), 7.57(dd, *J* = 8.6, 1.8 Hz, 1H), 8.08 (d, *J* = 7.3 Hz, 1H), 8.27 (s, 1H). ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 140.3, 138.6, 128.3, 126.4, 124.7, 123.2, 121.9, 120.7, 119.3, 111.6, 109.9, 108.8, 37.6, 13.8.

2.2.2. 9-Ethyl-3-(tributylstannyl)-9H-carbazole (CzSn)

A solution of CzBr (2.73 g, 10 mmol) in dry THF (50 mL) was stirred at -78 °C under N₂ for 10 min and then n-BuLi (2.5 M in hexane, 4.0 mL) was added dropwise. The mixture was maintained at -78 °C with continued stirring for a further 1 h, at which point the tributylchlorostannane (3.26 g, 10 mmol) was added dropwise. After warming to room temperature and stirring for 24 h, methanol was added to quench the reaction. The solution was partitioned between EA and water; the organic phase was collected, dried (MgSO₄), filtered, and evaporated to dryness. The residue was purified chromatographically (SiO₂; EA/hexanes) to provide a brown solid (3.41 g, 71.0%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 0.85–1.00(s, 9H), 1.16–1.69 (t, 3H), 4.40(q, *J* = 6.8 Hz, 2H), 7.27–7.63(m, 5H), 8.09–8.27(m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 140.1, 139.5, 133.2, 128.3, 126.3, 125.5, 120.3, 118.7, 37.3, 29.2, 27.4, 13.7, 9.7, 8.7.

2.2.3. 3-(4-Bromo-phenyl)-9-ethyl-9H-carbazole (CzPhBr)

A solution of CzSn (4.84 g, 10 mmol), 1,4-dibromobenzene (2.3 g, 10 mmol), Pd(OAc)₂ (0.01 g, 0.045 mmol) in dry toluene (100 mL) was stirred and reacted at 120 °C under N₂ for 48 h. After cooling to room temperature, the solution was evaporated to dryness. The



Scheme 1. Synthetic routes of compounds CzBr, CzSn, and CzPhBr.



Scheme 2. Synthetic routes of Cz3An, Cz3Ant, Cz3PhAn, and Cz3PhAnt.

cold water was then added to the mixture and finally extracted with EA. The organic phase was collected, dried (MgSO₄), filtered, and evaporated to dryness. The crude product was purified chromatographically (SiO₂; EA/hexanes) to provide a white solid (2.50 g, 72.0%). ¹H NMR(400 MHz, CDCl₃) δ (ppm): 1.47(t, *J* = 7.2 Hz, 3H), 4.41(q, *J* = 7.2 Hz, 2H), 7.26(t, *J* = 7.4 Hz, 1H), 7.45-7.51(m, 3H), 7.59(s, 4H), 7.67(dd, *J* = 8.4, 1.8 Hz, 1H), 8.16(d, *J* = 7.7 Hz, 1H), 8.28(s, 1H). ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 141.0, 140.3, 139.5, 131.7, 130.9, 128.8, 125.9, 124.8, 123.4, 122.9, 120.4, 119.0, 118.7, 108.7, 108.6, 37.6, 13.8.

2.2.4. 9,10-Bis(9-ethyl-9H-carbazol-3-yl)anthracene (Cz3An)

A solution of CzBr (2.73 g, 10 mmol) in dry THF (500 mL) was stirred at -78 °C under N2 for 10 min and then n-BuLi (2.5 M in hexane, 4.8 mL) was added dropwise. A solution of anthraquinone (1.04 g, 5 mmol) in THF (20 mL) was then added dropwise to the mixture at -78 °C. The resulting mixture was warmed to room temperature and stirred for 24 h. After the reaction had finished, methanol was added to the mixture, which was then partitioned between dichloromethane (DCM) and water. The combined organic fractions were dried (MgSO₄) and the volatiles evaporated under reduced pressure. The residue was added to a mixture of KI (2.99 g, 18 mmol), NaHPO₂ (2.96 g, 34 mmol) and AcOH (50 mL) and then the mixture was heated under reflux for 24 h. After the reaction had finished, the mixture was poured into water, and the precipitate was filtered off and washed with plenty of water. The yellowish crude product was purified chromatographically (SiO₂; hexane/CH₂Cl₂) to give a yellow solid (2.93 g, 52.0%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 1.56–1.59 (t, J = 7.2 Hz, 6H), 4.49–4.52 (q, J = 8.2 Hz, 4H), 7.27–7.30 (q, J = 3.46 Hz, 6H), 7.50–7.51 (m, 4H), 7.58–7.65 (m, 4H), 7.78–7.81 (q, J = 3.33 Hz, 4H), 8.05–8.09 (m, J = 6.4 Hz, 2H), 8.23 (s, 2H). ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 131.1, 129.9, 129.4, 128.9, 127.7, 126.2, 125.0, 123.6, 120.9, 119.3, 108.9, 108.6, 38.1, 14.2. HRMS (m/z): Calcd for C₄₂H₃₂N₂: 564.26, Found: 564.26 (M+). Anal. Calcd for C₄₂H₃₂N₂: C, 89.33; H, 5.71; N, 4.96, Found: C, 89.20; H, 5.90; N, 4.66.

2.2.5. 2-tert-Butyl-9,10-bis(9-ethyl-9H-carbazol-3-yl)anthracene (Cz3Ant)

A solution of CzBr (2.73 g, 10 mmol) in dry THF (500 mL) was stirred at -78 °C under N₂ for 10 min and then n-BuLi (2.5 M in hexane, 4.8 mL) was added dropwise. A solution of 2-tert-butylanthraquinone (1.31 g, 5 mmol) in THF (20 mL) was then added dropwise to the mixture at -78 °C. The resulting mixture was warmed to room temperature and stirred for 24 h. After the reaction had finished, methanol was added to the mixture, which was then partitioned between DCM and water. The combined organic fractions were dried (MgSO₄) and the volatiles evaporated under reduced pressure. The residue was added to a mixture of KI (2.99 g, 18 mmol), NaHPO₂ (2.96 g, 34 mmol) and AcOH (50 mL) and then the mixture was heated under reflux for 24 h. After the reaction had finished, the mixture was poured into water and the precipitate filtered off and washed with plenty of water. The yellowish crude product was purified chromatographically (SiO₂; hexane/CH₂Cl₂) to give a yellow solid (3.22 g, 52.0%). ¹H NMR(400 MHz, CDCl₃) δ (ppm): 1.19 (s, 9H), 1.54–1.58 (t, 6H), 4.50–4.52 (q, J = 2.6 Hz, 4H), 7.25–7.28 (m, 4H), 7.38–7.41 (dd, J = 9.2, 1.6 Hz, 1H), 7.52–7.50 (t, *J* = 3.8 Hz, 4H), 7.56–7.64 (m, 4H), 7.73–7.78 (m, 4H), 8.04–8.09 (q, J = 6.7 Hz, 2H), 8.23–8.21 (d, J = 8.0 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 147.2, 140.6, 139.6, 137.7, 137.5, 131.1, 130.8, 130.6, 129.8, 129.3, 127.5, 127.3, 126.1, 126.0, 124.8, 124.5, 123.4, 123.2, 123.1, 121.8, 120.8, 119.2, 108.8, 108.5, 38.0, 35.1, 31.0, 14.2. HRMS (m/ z): Calcd for C₄₆H₄₀N₂: 620.32, Found: 620.32 (M+). Anal. Calcd for C₄₆H₄₀N₂: C, 88.99; H, 6.49; N, 4.51, Found: C, 89.27; H, 6.53; N, 4.22.

2.2.6. 9,10-Bis[4-(9-ethyl-9H-carbazol-3-yl)phenyl]anthracene (Cz3PhAn)

Cz3PhAn was obtained as a yellow solid (3.58 g, 50.0%) after using a procedure similar to that described above for Cz3An. ¹H NMR(400 MHz, CDCl₃) δ (ppm): 1.49 (t, 6H), 4.43–4.45 (q, *J* = 7.2 Hz, 4H), 7.25–7.29 (m, 2H), 7.37–7.39 (dd, *J* = 6.8, 3.2 Hz, 4H), 7.46–7.61 (m, 10H), 7.85–7.97 (m, 10H), 8.19–8.21 (d, *J* = 7.6 Hz, 2H), 8.50 (s, 2H). ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 141.6, 140.9, 140.0, 137.4, 132.4, 132.1, 130.5, 128.3, 127.9, 127.5, 127.4, 127.3, 126.2, 125.5, 125.4, 125.3, 124.0, 123.9, 120.8, 119.4, 109.1, 109.0, 38.0, 14.1. HRMS (m/z): Calcd for C₅₄H₄₀N₂: 716.32, Found: 716.32 (M+). Anal. Calcd for C₅₄H₄₀N₂: C, 90.47; H, 5.62; N, 3.91, Found: C, 90.28; H, 5.24; N, 3.75.

2.2.7. 2-tert-Butyl-9,10-bis[4-(9-ethyl-9H-carbazol-3-yl)phenyl] anthracene (Cz3PhAnt)

Cz3PhAnt was obtained as a yellow solid (3.63 g, 47.0%) after using a procedure similar to that described above for Cz3Ant. ¹H NMR(400 MHz, CDCl₃) δ (ppm): 1.29 (s, 9H), 1.48–1.52 (m, 6H), 4.44–4.45 (q, *J* = 7.2 Hz, 4H), 7.26–7.29 (t, *J* = 7.4 Hz, 2H), 7.34–3.36 (dd, *J* = 6.8, 3.6 Hz, 2H), 7.44–7.61 (m, 11H), 7.76–7.99 (m, 10H), 8.19–8.22 (q, *J* = 4.3 Hz, 2H), 8.53–8.50 (d, *J* = 11.6 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ (ppm): 147.5, 141.4, 141.1, 140.7, 139.8, 137.5, 137.0, 136.7, 132.3, 132.1132.0, 130.5, 130.2, 123.0, 128.9, 127.4, 127.3, 127.0, 126.1, 125.4, 125.1, 124.9, 123.8, 123.4, 121.5, 120.8, 119.2, 109.0, 108.9, 37.9, 35.2, 31.0, 14.1. HRMS (*m*/*z*): Calcd for C₅₈H₄₈N₂: 772.38, Found: 772.38 (M+). Anal. Calcd for C₅₈H₄₈N₂: C, 90.12; H, 6.26; N, 3.62, Found: C, 90.12; H, 6.60; N, 3.90.

2.3. Measurements

¹H and ¹³C NMR spectra were recorded using a Varian Gemini NMR spectrometer operated at 400 and 125 MHz, respectively. Elemental analysis was performed using an elemental analyzer (Elementar Vario EL III). High-resolution mass spectra were recorded using a Finnigan/Thermo Quest MAT mass spectrometer. Glass transition temperatures $(T_{o}s)$ were measured under N₂ using a differential scanning calorimeter (TechMax Instruments DSC 6220) operated at a heating rate of 10 °C min⁻¹. Thermogravimetric analysis (TGA) was performed under a N₂ atmosphere using a thermogravimetric analyzer (VersaTherm thermogravimetric analyzer) operated at a heating rate of 10 °C min⁻¹. UV-Vis absorption and PL spectra were recorded using a Shimadzu UV-1240 spectrophotometer and an Acton Research Spectra Pro-150 spectrometer, respectively. We measured the fluorescence quantum yields ($\Phi_{\rm fl}$) of the four anthracene derivatives in dilute CHCl₃ solution by comparing their emissions with that of a standard solution of DPA in cyclohexane ($\Phi_{\rm fl} = 0.90$) at room temperature [29]. In addition, solid state Φ_{fl} values of vacuum-deposited thin films were determined by the integrating-sphere method described by de Mello et al. [46]. Cyclic voltammetry (CV) was conducted using a CHI model611D apparatus and a three-electrode cell, in which an indium tin oxide (ITO) sheet, a Pt wire, and silver/silver nitrate (Ag/ Ag⁺) were used as the working electrode, counter electrode, and reference electrode, respectively. All electrochemical experiments were performed using deoxygenated MeCN solutions containing 0.1 M tetrabutylammonium perchlorate (TBAP) as the electrolyte.

2.4. EL device fabrication and electro-optical characterization

Fabrication of OLEDs was conducted through high-vacuum thermal evaporation of the organic materials onto ITO-coated glass (sheet resistance: 15 Ω /square; Applied Film Corp). Glass substrates with patterned ITO electrodes were washed well and then cleaned through O₂ plasma treatment. Furthermore, a LiF layer was thermally deposited onto the organic material layer, followed by Al metal deposition as the top layer in a high-vacuum chamber. OLED configurations in this study were (type A) ITO/4,4'-bis[*N*-(1-naphthyl)-*N*-phenylamino]biphenyl (NPB, 30 nm)/anthracene derivative (30 nm)/tri-(8-hydroxyquinoline)aluminum (Alq₃, 30 nm)/LiF (0.5 nm)/Al (150 nm), (type B) ITO/NPB (30 nm)/anthracene (TPBI, 30 nm)/LiF (0.5 nm)/Al (150 nm), (type C) ITO/NPB (30 nm)/

anthracene derivative (30 nm)/2,9-dimethyl-4,7-diphenyl-1,10phenanthroline (BCP, 10 nm)/Alq₃ (30 nm)/LiF (0.5 nm)/Al (150 nm), and (type D) ITO/NPB (40 nm)/anthracene derivative (30 nm)/BCP (10 nm)/TPBI (30 nm)/LiF (0.5 nm)/Al (150 nm), where NPB, the anthracene derivative, BCP, and Alq₃ (or TPBI) were the hole-transporting layer (HTL), blue light-emitting layer, holeblocking layer (HBL), and electron-transporting layer (ETL), respectively. The cathode deposition rate was determined using a quartz thickness monitor (STM-100/MF, Sycon). The thin film thickness was determined using a surface texture analysis system (3030ST, Dektak). UV-Vis spectra of the organic thin films were measured using a Hewlett-Packard 8453 spectrometer equipped with a photodiode array detector. PL and EL spectra were recorded using a Hitachi F-4500 fluorescence spectrophotometer. Currentvoltage characteristics were measured using a programmable electrometer equipped with current and voltage sources (Keithley 2400). Luminance was measured with a BM-9 luminance meter (Topcon).

3. Results and discussion

3.1. Synthesis and characterization

Schemes 1 and 2 illustrate the routes for the syntheses of the anthracene derivatives containing carbazole moieties. The carbazole-substituted anthracene derivatives Cz3An, Cz3Ant Cz3PhAn, and Cz3PhAnt were synthesized through reactions of anthraquinone or 2-tert-butylanthraquinone with various carbazole derivatives. The chemical structures of these compounds were confirmed by ¹H and ¹³C NMR spectroscopy, elemental analysis, and high-resolution mass spectrometry. The relative intensities of the signals in the various spectra were in agreement with the proposed structures of these anthracene derivatives. The operational stability of an OLED is directly related to the thermal stability of the light-emitting layer. Thus, high T_g and thermal degradation temperature (T_d) are desirable for a light-emitting material to be utilized in OLEDs. Fig. 1 presents DSC thermograms of the carbazole-substituted anthracene derivatives; Table 1 summarizes their values of T_g , crystallization temperature (T_c), melting temperature (T_m) , and T_d . DSC results indicate that no transition was observed at temperature below 350 °C in the second-heating scan for Cz3An and Cz3Ant. The melting peak was observed at 422 °C for Cz3PhAn. The tight molecular stacking resulted in the high T_m value



Fig. 1. DSC thermograms of Cz3An, Cz3Ant, Cz3PhAn, and Cz3PhAnt.

Table 1								
Thermal propert	ties, UV–Vis al	osorption, and	PL emission ar	nd quantum ef	ficiency of the carb	oazole-substituted an	thracence derivati	ves.
Compound	$T (\circ C)^{a}$		$T (\circ C)^{a}$	T. (°C)b	abs (nm)d	abs (nm)e) ^{PL} (nm) ^{d,e}	F\A/F

Compound	$T_g (^{\circ}C)^a$	$T_c (^{\circ}C)^{a}$	$T_m (^{\circ}C)^a$	$T_d (^{\circ}C)^{b}$	$\lambda_{\max}^{abs} (nm)^d$	λ ^{abs} (nm) ^e	$\lambda_{\max}^{PL}(nm)^{d,e}$	FWHM of PL (nm) ^{d,e}	$\Phi_f(\%)^{\mathrm{f},\mathrm{g}}$
Cz3An	n.a. ^c	n.a.	n.a.	448	397, 378, 355	443	450/456	61/52	71/24
Cz3Ant	n.a.	n.a.	n.a.	401	397, 378, 354	444	453/455	60/44	83/27
Cz3PhAn	n.a.	n.a.	422	495	397, 378, 359	445	440/458	62/53	72/25
Cz3PhAnt	169	238	344	486	397, 378, 358	446	444/457	61/51	85/28

^a Determined by DSC at heating rate and cooling rate of 10 °C/min and 50 °C/min under nitrogen.

^b Determined by TGA at heating rate of 10 °C/min under nitrogen. (T_d : at 5% loss weight.)

^d Measured in dilute DCM solution.

^e Measured in solid film.

 $^{\rm f}$ PL quantum efficiency ($\Phi_{\rm fl}$) of the compounds, measured in CHCl₃ solution using 9,10-diphenylanthracene as a standard.

 g PL quantum efficiency ($\Phi_{\rm fl}$) of the compounds, measured as solid film using 9,10-diphenylanthracene as a standard.

of Cz3PhAn. The glass transition (169 °C), and re-crystallization (238 °C) and melting (344 °C) peaks were clearly observed in the heating-scan for the anthracene derivative Cz3PhAnt. As compared to Cz3PhAn, the incorporation of the tert-butyl groups on the C2 position of anthracene unit led to the lower values of T_g and T_m of Cz3PhAnt. Nevertheless, the presence of the sterically bulky carbazole side groups meant that these carbazole-substituted anthracene derivatives exhibited higher value of T_g than those of the well-known blue-emitting materials DPVBi (64 °C) [16] and MADN (120 °C) [47]. Consequently, these carbazole-substituted anthracene derivatives were capable of forming the morphologically stable and uniform amorphous films required to improve the efficiencies and lifetimes of OLEDs. In addition, the values of T_d of Cz3An, Cz3Ant, Cz3PhAn, and Cz3PhAnt were 448, 401, 495, and 486 °C, respectively. The values of T_d of Cz3PhAn and Cz3PhAnt are much higher than those of Cz3An and Cz3Ant, which is attributed to the presence of more aromatic rings in the molecules of Cz3PhAn and Cz3PhAnt. Moreover, higher thermal stability was observed for the Cz3PhAn and Cz3An relative to those of the Cz3PhAnt and Cz3Ant. This is due to the close molecular stacking of Cz3PhAn and Cz3An in the absence of the tert-butyl groups on the C2 position of anthracene units. It is also important to note that these carbazolesubstituted anthracene derivatives show higher thermal stability than that of the 9,10-diphenylanthracene (DPA, $T_d = 241 \ ^{\circ}$ C).

3.2. Photophysical properties

Fig. 2 presents UV-Vis absorption and PL spectra of the carbazole-substituted anthracene derivatives in dilute DCM solutions and as solid films. The UV-Vis absorption spectra of the emitters in solution were measured at a concentration of 10^{-5} M; the thickness of the emitter layer for the UV-Vis absorption measurements was approximately 100 nm. Table 1 summarizes the maximal absorption and PL emission wavelengths of the carbazolesubstituted anthracene derivatives. The maximal absorption wavelengths of the anthracene derivatives appeared in the range from 280 to 320 nm due to carbazole-centered transitions [48], along with moderately weak absorptions in the ranged from 350 to 425 nm (characteristic vibronic patterns attributed to the $\pi - \pi^*$ transition of anthracene [49]). In solution, the maximal absorption wavelengths (corresponding to the $\pi - \pi^*$ transition of anthracene) of Cz3PhAn and Cz3PhAnt were slightly red-shifted as compared with those of the Cz3An and Cz3Ant. Moreover, as thin film state, the onset absorption wavelength of Cz3PhAn and Cz3PhAnt were also slightly red-shifted when compared with those of the Cz3An and Cz3Ant. This implies that the conjugation of the carbazolesubstituted anthracene derivatives was somewhat enhanced via the incorporation of a phenyl ring between the carbazole and anthracene units. In addition, relative to the absorption behavior of the anthracene derivatives in solution, the maximal absorption wavelengths corresponding to the carbazole-centered transitions were slightly red-shifted for the three anthracene derivatives in thin film state, presumably because of the interactions and aggregation of the molecules in thin film state.

Upon excitation at 350 nm, these anthracene derivatives exhibited deep-blue emissions with PL maxima at *ca.* 440–453 nm in dilute DCM solution. The maximum emission wavelength of the PL (λ_{max}^{PL}) and the full width at half-maximum (FWHM) of the PL were dependent on the chemical structure of the carbazole-substituted anthracene derivative. The difference of λ_{max}^{PL} was not significant



Fig. 2. UV–Vis absorption and PL spectra of Cz3An, Cz3Ant, Cz3PhAn, and Cz3PhAnt ((a) UV–Vis absorption spectra and (b) PL spectra).

^c n.a.: not available.

for Cz3An and Cz3Ant in solution. Moreover, a slightly red-shift of λ_{max}^{PL} was observed for Cz3An and Cz3Ant in the thin film state. As compared to the Cz3An and Cz3Ant, the Cz3PhAn and Cz3PhAnt exhibited blue-shifts of approximately 10 nm when in solution. The free rotation of the phenyl ring interrupted the conjugation between the carbazole and anthracene units for Cz3PhAn and Cz3PhAnt. As a result, a blue shifting of λ_{max}^{PL} was observed for Cz3PhAn and Cz3PhAnt. Relative to the PL spectra of the samples in the dilute solutions, however, the emission spectra of Cz3PhAn and Cz3PhAnt in the thin film state exhibited red-shifts of 12-16 nm. The differences in the PL spectra of the compounds in solution and as thin film suggested the presence of intermolecular interactions or aggregation in thin film states. In the thin film state, the values of λ_{max}^{PL} of the Cz3PhAn and Cz3PhAnt were slightly red-shifted as compared with those of Cz3An and Cz3Ant. This implies that the conjugation lengths of these anthracene derivatives were slightly enhanced by the incorporation of a phenyl ring between the carbazole and anthracene groups. On the other hand, the FWHM values of the PL emission band were almost the same for these anthracene derivatives in the solution state, while the FWHM values varied slightly in the thin film state for these anthracene derivatives with different chemical structures. With the incorporation of the *tert*-butyl group at the C2 position of the anthracene unit, the FWHM of Cz3Ant was smaller than that of Cz3An. The steric hindrance of the *tert*-butyl group on the peripheral anthracene group reduced the degree of intermolecular $\pi - \pi$ stacking of Cz3Ant, leading to the smaller FWHM value of the PL emission band. Furthermore, the FWHM value of Cz3PhAn was slightly larger than that of Cz3An. The incorporation of a phenyl ring between the carbazole and anthracene units enhanced the degree of intermolecular $\pi - \pi$ stacking of Cz3PhAn and Cz3PhAnt, leading to the larger FWHM value of the PL emission band. Apart from that, the λ_{max}^{PL} values of anthracene derivatives attached with the carbazolyl groups at C3-positions were slightly larger than those the anthracene derivatives attached with N-arylated carbazole moieties. The λ_{max}^{PL} values of the anthracene derivatives attached with N-arylated carbazole moieties are summarized in Table S1 (Supporting Information).

The blue emitters Cz3An, Cz3Ant, Cz3PhAn, and Cz3PhAnt in solution exhibited high quantum yields of 0.71, 0.83, 0.72, and 0.85, respectively. Moreover, the values of $\Phi_{\rm fl}$ of Cz3An, Cz3Ant, Cz3PhAn, and Cz3PhAnt in thin film state were 0.24, 0.27, 0.25, and 0.28, respectively. Relative to the $\Phi_{\rm fl}$ values of anthracene derivatives in dilute solution, lower $\Phi_{\rm fl}$ values in thin film state were attributed to the intermolecular $\pi - \pi$ stacking and PL quenching of these anthracene derivatives. The values of Φ_{fl} of Cz3Ant and Cz3PhAnt were larger than that of Cz3An and Cz3PhAn. This is because the incorporation of the tert-butyl group on the anthracene unit would possibly reduce the degree of intermolecular $\pi - \pi$ stacking of Cz3Ant and Cz3PhAnt, leading to the lower PL emission quenching of carbazole-substituted anthracene derivatives. In addition, the conjugation lengths of the anthracene derivatives were slightly enhanced via inserting a phenyl ring between the carbazole and anthracene units. Therefore, the Φ_{fl} values of Cz3PhAn and Cz3PhAnt were slightly larger than those of Cz3An and Cz3Ant, respectively. Furthermore, the presence of bipolar structure in these carbazole-attached 2-tert-butyl-substituted anthracenes would lead to larger $\Phi_{\rm fl}$ values when compared with other 2-*tert*butyl-substituted anthracene derivatives in literature [21,28,32].

3.3. Electrochemical properties of carbazole-substituted anthracene derivatives

We employed CV to investigate the electrochemical behavior (Fig. 3) and to estimate the energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital



Fig. 3. CV spectra of Cz3An, Cz3Ant, Cz3PhAn, and Cz3PhAnt.

(LUMO) of the carbazole-substituted anthracene derivatives. Fig. 4 presents the energy band diagram of the carbazole-substituted anthracene derivatives along with BCP, TPBI and Alq₃. The electrochemical properties of the anthracene derivatives are summarized in Table 2. The oxidation potentials ($E_{\rm ox}^{\rm on}$) of Cz3An, Cz3Ant, Cz3PhAn, and Cz3PhAnt were 0.76, 0.78, 0.80, and 0.84 V, respectively. From these values, the HOMO levels of the anthracene derivatives were calculated according to the following equation:

HOMO =
$$-e\left(E_{\text{ox}}^{\text{on}} - E_{\text{ox}, \text{ ferrocene}}^{\text{on}} + 4.8\right)(eV)$$

where 4.80 eV is the energy level of ferrocene below the vacuum level and the E_{0x}^{on} of ferrocene/ferrocene⁺ is 0.08 V in 0.1 M Bu₄NClO₄–MeCN solution. The HOMO levels were obtained as -5.48, -5.50, -5.52 and -5.56 eV for Cz3An, Cz3Ant, Cz3PhAn, and Cz3PhAnt, respectively. The HOMO energy levels of Cz3PhAn and Cz3PhAnt were slightly lower than those of the Cz3An and Cz3Ant. The incorporation of a phenyl ring between the carbazole and anthracene units would dilute the density of the electron-rich carbazole moiety. As a result, lower HOMO energy levels were observed for Cz3PhAn and Cz3PhAnt. In addition, the HOMO energy levels of carbazole-substituted anthracene derivatives are slightly higher than those of 9,10-di(2-naphthyl)anthracene (ADN, -5.8 eV) [22,26]. The incorporation of electron-rich



Fig. 4. Energy levels of the blue emitters (Cz3An, Cz3Ant, Cz3PhAn, and Cz3PhAnt), hole-transporting layer (NPB), electron-transporting layer (Alq₃ and TPBI), hole-blocking layer BCP, and cathode (LiF/Al). (For interpretation of the references to co-lor in this figure legend, the reader is referred to the web version of this article.)

 Table 2
 Electrochemical behaviors of the carbazole-substituted anthracence derivatives.

Compound	$E_{\text{onset}}^{\text{ox}} (\text{eV})^{\text{a}}$	$E_g (\mathrm{eV})^\mathrm{b}$	HOMO (eV) ^c	LUMO (eV) ^d
Cz3An	0.76	2.80	-5.48	-2.68
Cz3Ant	0.78	2.79	-5.50	-2.71
Cz3PhAn	0.80	2.79	-5.52	-2.73
Cz3PhAnt	0.84	2.78	-5.56	-2.78

^a $E_{1/2}^{\text{ox}}$ = the onset potential of oxidation peak.

^b Determined from UV–Vis absorption spectra.

^c Determined by cyclic voltammeter in 0.1 M TBAP/DCM.

^d LUMO = HOMO - E_g .

carbazole moieties onto the C9 and C10 positions of anthracene enhances the HOMO energy levels of anthracene derivatives [17]. The high HOMO energy levels of carbazole-substituted anthracene derivatives would certainly facilitate hole-injection from an ITO transparent anode to the light-emitting layer [50]. Because of this, better EL performances from OLEDs based on the carbazolesubstituted anthracene derivatives in this study would be achieved. On the other hand, the LUMO energy levels of Cz3An, Cz3Ant, Cz3PhAn, and Cz3PhAnt were –2.68, –2.71, –2.73, and –2.78 eV, respectively. The difference of the LUMO energy levels between the anthracene derivatives and TPBI (–2.70 eV) was smaller than that between the anthracene derivatives and Alq₃ (–3.30 eV) [21]. This indicates that TPBI would exhibit superior electron-injection characteristics to those of Alq₃. Moreover, the difference of the HOMO energy levels between the anthracene derivatives and TPBI



Fig. 5. Energy levels and configurations of the OLEDs (Device A: ITO/4,4'-bis[*N*-(1-naphthyl)-*N*-phenylamino]biphenyl (NPB, 30 nm)/anthracene derivative (30 nm)/tri-(8-hydroxyquinoline)aluminum (Alq₃, 30 nm)/LiF (0.5 nm)/Al (150 nm); Device B: ITO/ NPB (30 nm)/anthracene derivative (30 nm)/1,3,5-tris(N-phenyl benzimidizol-2-yl) benzene (TPBI, 30 nm)/LiF (0.5 nm)/Al (150 nm); Device C: ITO/NPB (30 nm)/anthracene derivative (30 nm)/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP, 10 nm)/ Alq₃ (30 nm)/LiF (0.5 nm)/Al (150 nm), and Device D: ITO/NPB (40 nm)/anthracene derivative (30 nm)/BCP (10 nm)/TPBI (30 nm)/LiF (0.5 nm)/Al (150 nm)).

(-6.20 eV) was larger than that between the anthracene derivatives and Alq₃ (5.70 eV), implying that TPBI showed a better holeblocking characteristic than Alq₃ [51]. Consequently, superior EL performance could be realized if TPBI was to be used as ETL in OLEDs based on these anthracene derivatives. The band gap energies of Cz3An, Cz3Ant, Cz3PhAn, and Cz3PhAnt were 2.80, 2.79, 2.79, and 2.78 eV, respectively. The band gap energies of these anthracene derivatives were slightly decreased with the incorporation of a phenyl ring between the carbazole and anthracene units,



Fig. 6. Brightness, EL efficiency, and EL spectra of Cz3An, Cz3Ant, Cz3PhAn, and Cz3PhAnt-based type-A devices (Devices A-I – A-IV).

corresponding to the enhancement of the conjugation length of the anthracene derivative. On the other hand, smaller band gap energies, lower LUMO levels, and higher HOMO levels were observed for these 9-ethyl-9H-carbazol-3-yl or 4-(9-ethyl-9H-carbazol-3-yl) phenyl groups substituted anthracene derivatives when compared with the anthracene derivatives attached with the N-arylated carbazole moieties in literature [45]. The $E_{\text{ox}}^{\text{on}}$ values, band gap energies, LUMO levels, and HOMO levels of the anthracene derivatives attached with N-arylated carbazole moieties are summarized in Table S1 (Supporting Information).

3.4. EL properties of devices based on carbazole-substituted anthracene derivatives

The fluorophores Cz3An, Cz3Ant, Cz3PhAn, and Cz3PhAnt appeared to be promising blue-emitting materials for OLED applications based on their photophysical and electrochemical properties. To determine the EL properties of these fluorophores, we fabricated a series of non-doped devices using Alq₃ (or TPBI) as ETL and BCP as HBL. The energy levels and configurations of the Cz3An, Cz3Ant, Cz3PhAn, and Cz3PhAnt based OLED devices are shown in Fig. 5. Fig. 6 present the brightness, EL efficiency (current and external quantum efficiency), and EL spectra of the OLEDs (Device A-I - A-IV) based on the carbazole-substituted anthracene derivatives; the key EL performance data of the non-doped devices are summarized in Table 3. The Alq₃ was used as ETL for the Devices A-I - A-IV. For Devices A-I - A-IV, the Cz3Ant based Device A-II exhibited higher brightness and larger EL efficiency (current and external quantum efficiency) than the Cz3An based Device A-I (Fig. 6(a,b)). The presence of *tert*-butyl groups on the anthracene unit inhibited the aggregation and $\pi - \pi^*$ stacking of the anthracene derivatives, thereby improving the EL performance of the OLEDs. As a result, the brightness and EL efficiency of the Cz3Ant based Device A-II were much higher than those of the Cz3An based Device A-I. In addition, higher brightness and larger efficiency were observed for the Cz3PhAn based Device A-III as compared to the OLEDs based on Cz3An and Cz3Ant (Devices A-I and A-II). CzPhAn with one more phenyl ring between the carbazole and anthracene units exhibited longer conjugation length than those of the Cz3An and Cz3Ant. Moreover, CzPhAn exhibits a lower LUMO energy level than those of the Cz3An and Cz3Ant, which is favorable for the electron-

EL properties of the carbazole-sul	stituted anthracence	derivatives based OLEDs.

injection into ETL from cathode. As a result, better EL perfor-
mance was observed for the Device A-III in comparison with those
for Devices A-I and A-II. Furthermore, as compared to Devices A-I
and A-II, longer conjugation length of CzPhAn resulted in a larger
value of the maximal EL wavelength (λ_{max}^{EL}) of Device A-III
(Fig. 6(c)). The Cz3PhAn based device showed a larger FWHM value
of EL emission than did the Cz3An and Cz3Ant based devices, which
is attributed to the lower HOMO energy level of Cz3PhAn. Lower
HOMO energy level of Cz3PhAn favored the hole-transporting from
light-emitting layer to Alq3 ETL, leading to the EL emission partially
contributed from Alq ₃ . Green emission from Alq ₃ at wavelength
ranged from 530 to 600 nm was observed not only for the Cz3PhAn
based devices, but for the Cz3An and Cz3Ant based devices as well.
Additionally, poor EL performance was obtained for the Cz3PhAnt
based Device A-IV as compared to the Cz3PhAn based Device A-III.
The incorporation of the tert-butyl group on the anthracene unit
disrupted the order packing of Cz3PhAnt, which was not favorable
for the charge transfer between the molecules [45,52]. Apart from
that, low HOMO energy level led to the hole-transporting from the
Cz3PhAnt layer into ETL. Consequently, lower brightness and
smaller EL efficiency were achieved for Device A-IV. In addition, a
lowest turn-on voltage was observed for the Device A-IV as
compared to those for the Devices $A-I - A$ -III. This is due to the fact
that Cz3PhAnt exhibited the lowest HOMO energy level among
these carbazole-substituted anthracene derivatives.

As TPBI was used as ETL, the EL properties were improved significantly for the carbazole-substituted anthracene derivatives based OLEDs (Fig. 7). The EL efficiency of the Devices B-I – B-IV were much higher than those of the Devices A-I - A-IV. Moreover, the FWHM values of the Devices B-I – B-IV were much smaller than those of the Devices A-I - A-IV (Fig. 7(c)). The EL emissions of Devices B-I – B-IV were blue-shifted as compared to those of the Devices A-I - A-IV. Devices B-I - B-IV also exhibited better color purities than those of the Devices A-I – A-IV. This is attributed to the better blocking effect of TPBI for OLEDs. Low HOMO energy level of TPBI would block the holes to transfer from blue emitter layer to ETL. As a result, higher EL efficiency and better color purity were obtained for Devices B-I - B-IV. Nevertheless, TPBI exhibits a lower electron-transporting capacity than Alq₃. Therefore, the brightness values of Devices B-I – B-IV were slightly lower than those of Devices A-I – A-IV. In addition, the brightness values of the

Devices ^a	EML	$V_{\mathrm{on}}{}^{\mathrm{b}}(\mathrm{V})$	Max. luminance (cd/m ²)	Max. efficiency (cd/A)	FWHM ^c (nm)	λ_{\max}^{EL} (nm)	$CIE (x,y)^d$
Device A-I	Cz3An	3.1	8937	1.88	110	489	(0.21,0.36)
Device A-II	Cz3Ant	3.1	12841	3.35	110	494	(0.22,0.38)
Device A-III	Cz3PhAn	3.1	37423	4.02	120	504	(0.23,0.40)
Device A-IV	Cz3PhAnt	2.4	25669	2.94	114	500	(0.23,0.39)
Device B-I	Cz3An	3.3	12270	5.09	68	468	(0.15,0.22)
Device B-II	Cz3Ant	3.1	5136	5.37	68	468	(0.15,0.21)
Device B-III	Cz3PhAn	3.2	33118	5.84	72	470	(0.16,0.24)
Device B-IV	Cz3PhAnt	3.1	19290	4.35	70	470	(0.15,0.20)
Device C-I	Cz3An	4.0	4847	3.38	68	470	(0.13,0.22)
Device C-II	Cz3Ant	3.0	4324	3.92	72	474	(0.17,0.26)
Device C-III	Cz3PhAn	3.0	25419	4.52	82	472	(0.18,0.28)
Device C-IV	Cz3PhAnt	3.0	23049	4.65	72	470	(0.16,0.23)
Device D-I	Cz3An	3.5	9394	4.80	80	474	(0.16,0.27)
Device D-II	Cz3Ant	3.0	2987	5.74	74	474	(0.15,0.26)
Device D-III	Cz3PhAn	3.5	30049	5.37	80	472	(0.18,0.27)
Device D-IV	Cz3PhAnt	3.0	17977	5.89	74	474	(0.17,0.25)

^a Device A: ITO/NPB (30 nm)/anthracene derivative (30 nm)/Alq₃ (30 nm)/LiF (0.5 nm)/Al (150 nm); Device B: ITO/NPB (30 nm)/anthracene derivative (30 nm)/TPBI (30 nm)/LiF (0.5 nm)/Al (150 nm); Device C: ITO/NPB (30 nm)/anthracene derivative (30 nm)/BCP (10 nm)/Alq₃ (30 nm)/LiF (0.5 nm)/Al (150 nm); Device D: ITO/NPB (30 nm)/anthracene derivative (30 nm)/Alq₃ (30 nm)/LiF (0.5 nm)/Al (150 nm); Device D: ITO/NPB (30 nm)/anthracene derivative (30 nm)/Alq₃ (30 nm)/LiF (0.5 nm)/Al (150 nm); Device D: ITO/NPB (30 nm)/

^b Turn-on voltage at 1 cd/m².

Table 3

^c Under an applied voltage of 8 V.

^d Commission International de L'Eclairage coordinates; under an applied voltage of 8 V.

Cz3Ant based Device B-II and Cz3PhAnt based Device B-IV were lower than those of the Cz3An based Device B-I and Cz3PhAn based Device B-III, correspondingly. This is because the incorporation of the *tert*-butyl group on the anthracene unit reduced the charge transfer capacity in light-emitting layer. Therefore, lower brightness values were found for the Devices B-II and B-IV. On the other hand, larger turn-on voltages were observed for the Devices B-I – B-IV as compared to those for Devices A-I - A-IV. As shown in Fig. 7(c), EL spectra were not changed significantly with increasing

applied voltage (8-12 V). This implies that these carbazolesubstituted anthracene derivatives based non-doped OLEDs exhibited good blue color stability.

In order to improve the EL properties, BCP as HBL was inserted between the blue emitter layer and ETL Alq₃ (or TPBI) for the carbazole-substituted anthracene derivatives based non-doped OLEDs (Devices C-I – C-IV and Devices D-I – D-IV). Figs. 8 and 9 present EL properties of these OLEDs (Devices C-I – C-IV and Devices D-I – D-IV). EL efficiency and color purity were improved significantly as the Alq₃ based OLEDs (Devices C-I - C-IV) were incorporated with HBL BCP (Fig. 8). In fact, the EL efficiency and



Fig. 7. Brightness, EL efficiency, and EL spectra of Cz3An, Cz3Ant, Cz3PhAn, and Cz3PhAnt-based type-B devices (Devices B-I - B-IV).





Fig. 8. Brightness, EL efficiency, and EL spectra of Cz3An, Cz3Ant, Cz3PhAn, and Cz3PhAnt-based type-C devices (Devices C-I - C-IV).

color purity of Devices C-I – C-IV were much better than those of Devices A-I – A-IV. However, the brightness was slightly reduced by the incorporation of BCP HBL between the blue emitter layer and Alq₃ for devices C-I – C-IV. The turn-on voltages of Devices C-I – C-IV did not vary significantly as compared to those of Devices A-I – A-IV. In addition, the improvement of EL properties was not significant as BCP HBL was inserted between the blue emitter layer and TPBI ETL for the carbazole-substituted anthracene derivatives



Fig. 9. Brightness, EL efficiency, and EL spectra of Cz3An, Cz3Ant, Cz3PhAn, and Cz3PhAnt-based type-D devices (Devices D-I – D-IV).

based OLEDs (Devices D-I - D-IV; Fig. 9). The insertion of BCP reduced the electron-injection activities from TPBI to blue emitter layer because of the presence of the energy barrier between the light emitting layer and BCP. As shown in Fig. 9, the EL efficiency was not further enhanced, while the brightness was reduced for the Devices D-I - D-IV as compared to those for Devices B-I - B-IV. In addition, the EL spectra of Devices C-I – C-IV and Devices D-I – D-IV are shown in Figs 8(c) and 9(c). The green emission was slightly enhanced with increasing applied voltage for Cz3An based Device C-I and Cz3Ant based Device C-II. This implies that the charge recombination was occurred at the Alq₃ layer under higher applied voltages (>10 V). The color purity of the Cz3PhAn based Device C-III and Cz3PhAnt based Device C-IV was more stable than those of the Cz3An based Device C-I and Cz3Ant based Device C-II. Furthermore, the color stability was improved by inserting BCP HBL between the blue emitter layer and TPBI ETL (Fig. 8(c)). As compared to the Devices B-I - B-IV (Fig. 7(c)), the color purity was not improved by inserting BCP HBL between the blue emitter layer and TPBI ETL for Cz3An, Cz3Ant, and Cz3PhAn based Devices D-I - D-IV (Fig. 9(c)). This is attributed to the presence of the microcavity effect in the multilayer structure of the blue OLEDs [53]. The color purities of the 9-ethyl-9H-carbazol-3-yl or 4-(9-ethyl-9H-carbazol-3-yl)phenyl groups containing anthracene derivatives based OLEDs were not exactly matched the saturated deep-blue CIE chromaticity coordinates. Nevertheless, the non-doped OLED based on the anthracene derivatives attached with the carbazolyl groups at C3positions exhibited much better EL performance (brightness and current efficiency) than the OLEDs based on the anthracene derivatives attached with N-arvlated carbazole moieties [45]. The EL properties of the OLEDs fabricated from N-arylated carbazole moieties attached anthracene derivatives are summarized in Table S2 (Supporting Information).

4. Conclusion

Excellent EL performance was observed for the Cz3An, Cz3Ant, Cz3PhAn, and Cz3PhAnt based nondoped sky-blue OLEDs, which is attributed to the efficient conjugation of the anthracene unit attached with the carbazolyl group at C3-position. Better conjugation results in the lower LUMO and higher HOMO energy levels of the anthracene derivative, which is favorable for the electron- and hole-injection from the electrodes to the light-emitting layer. As a result, the non-doped OLED based on the anthracene derivatives attached with the carbazolyl groups at C3-postions exhibited much better EL performance than the OLEDs based on the anthracene derivatives attached with N-arylated carbazole moieties. In addition to the efficient conjugation of the carbazole moieties substituted anthracenes, the optimal design of the OLED architecture is also a deciding factor for the EL performance.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2013.06.025.

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