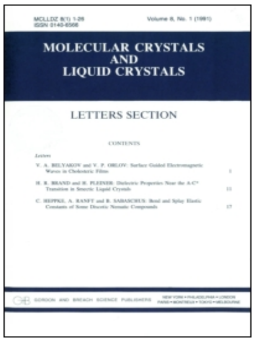
MOLECULAR CRYSTALS AND LIQUID CRYSTALS

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9,10-Diphenylanthracene derivative substituted with indole moiety for blue organic light-emitting diodes

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ABSTRACT

In order to develop blue emitters in organic light-emitting diodes (OLEDs), we synthesized two materials, 9-(9,10-diphenylanthracen-6-yl)-9*H*-carbazole and 1-(9,10-diphenylanthracen-6-yl)-1*H*-indole by Buchwald–Hartwig reactions. To investigate their electroluminescent performances, multilayer devices were fabricated by following structure: indium-tin-oxide (ITO) (180 nm) / *N*,*N*′-di(1-naphthyl)-*N*,*N*′-diphenyl-(1,1′-biphenyl)-4,4′-diamine (NPB) (50 nm) / blue emitters (30 nm) / 4,7-diphenyl-1,10-phenanthroline (Bphen) (30 nm) / lithium quinolate (Liq):Al (100 nm). A device using 1-(9,10-diphenylanthracen-6-yl)-1*H*-indole exhibited an efficient blue emission with luminous, power, and external quantum efficiency of 3.11 cd/A, 1.60 lm/W, and 2.82% at 20 mA/cm^2, respectively and CIE (x, y) coordinates of (0.15, 0.13) at 6.0 V.

KEYWORDS
Blue OLED; anthracene; carbazole; indole; Buchwald–Hartwig reactions

1. Introduction

Organic light-emitting diodes (OLEDs) have many attractive advantages such as low-driving voltage, solid-state lighting, and wide view angle [1]. For these characteristics, OLEDs have attracted the public eyes in scientific and commercial fields, and been regarded as next-generation displays due to the promise of applications for the full-color and flat-panel displays [2]. In order to achieve them, highly efficient red, green, and blue emitters with tremendous thermal stabilities, long life-time, and good color-purity are indispensible. Compared to the advances of red and green emitters, the development of blue emitters with high electroluminescent (EL) efficiency needs to be further progressed because of their intrinsic weakness; they have wide energy band gap and thus charge-injection from the near layer is difficult comparing to red and green emitters [3–4].

Most recent researches about blue emitters have been used fluorescent organic materials based on anthracene [5–7, 15–16]. Especially, 9,10-diphenylanthracene (DPA) is considered as a representative anthracene derivative because of its high quantum yield in solution state ($\Phi = 0.90$) and worthy EL properties in OLED device. However, this material has also disadvantages of characteristics as a blue emitter and its EL performances should be improved [8].

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In this work, as the continuing efforts for the efficient blue emitters based on anthracene derivatives, we designed and synthesized two materials, 9-(9,10-diphenylanthracen-6-yl) -9*H*-carbazole (**1**) and 1-(9,10-diphenylanthracen-6-yl)-1*H*-indole (**2**) by Buchwald–Hartwig reactions. For improved carrier balances in OLED devices, the well-known electron-rich and -donating arylamino groups such as carbazole and indole groups are incorporated at the C-2 position of 9,10-diphenylanthracene which enhance hole- transporting abilities. Furthermore, the arylamine moieties have noteworthy thermal stabilities with amorphous film forming abilities [9, 17]. Therefore, these materials would have improved EL performances for blue OLEDs.

2. Experimental details

Synthesis and characterization

2-Bromo-9,10-diphenylanthracene was synthesized according to literature [10]. ^{1}H NMR and ^{13}C NMR were recorded on Bruker Avance III 500 MHz NMR spectrometer. FT-IR spectra were recorded using a Bruker VERTEX70 FT-IR spectrometer. Low- and high-resolution mass spectra were measured using Jeol JMS-AX505WA spectrometer in APCI mode.

9-(9,10-diphenylanthracen-6-yl)-9H-carbazole (1)

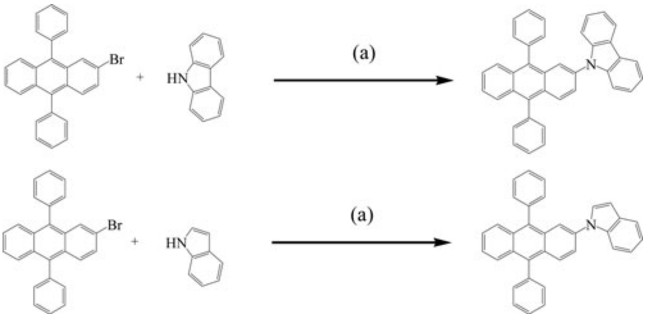
2-bromo-9,10-diphenylanthracene (1.0 mmol), 9*H*-carbazole (1.5 mmol), Tris(dibenzylideneacetone)dipalladium(0) (0.05 mmol), dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (0.08 mmol), sodium *tert*-butoxide (3.0 mmol) and anhydrous toluene (14 ml) were mixed in a flask. The mixture was refluxed at 120°C for 4 h. After the reaction finished, the reaction mixture was extracted with toluene and washed with water. The organic layer was dried with anhydrous $MgSO_4$ and filtered with silica gel. The solution was then evaporated. The crude product was purified recrystallization from CH_2Cl_2/EtOH. Yield: 60%. ^{1}H NMR ($CDCl_3$, 500 MHz, δ); 8.11 (d, $J = 8.0$ Hz, 2 H), 7.91 (d, $J = 9.0$ Hz, 1 H), 7.88 (s, 1 H), 7.77–7.73 (m, 2 H), 7.67–7.64 (m, 2 H), 7.60 (d, $J = 7.0$ Hz, 1 H), 7.58–7.55 (m, 4 H), 7.54–7.51 (m, 4 H), 7.46 (d, $J = 7.0$ Hz, 1 H), 7.43 (d, $J = 8.5$ Hz, 2 H), 7.40–7.38 (m, 3 H) 7.37 (d, $J = 8.5$ Hz, 2 H); ^{13}C NMR ($CDCl_3$, 500 MHz, δ); 140.7, 138.7, 138.5, 137.5, 137.2, 134.2, 131.3, 131.2, 131.1, 130.5, 130.2, 130.2, 129.2, 128.7, 128.6, 127.8, 127.8, 127.1, 127.0, 125.9, 125.6, 125.4, 124.4, 123.8, 123.4, 120.3, 120.0, 109.8; FT-IR [ATR]: ν (cm^{-1}) 3026, 2378, 2351, 2312, 1740, 1368, 1270, 1216; APCI-MS (*m/z*): 495 [M^{+}].

1-(9,10-diphenylanthracen-6-yl)-1H-indole (2)

Yield: 72%. ^{1}H NMR ($CDCl_3$, 500 MHz, δ); 7.85 (d, $J = 9.5$ Hz, 1 H), 7.76 (s, 1 H), 7.74–7.71 (m, 2 H), 7.66–7.62 (m, 3 H), 7.61–7.57 (m, 3 H), 7.54–7.51 (m, 7 H), 7.39–7.33 (m, 3 H), 7.20–7.13 (m, 2 H), 6.65 (s, 1 H); ^{13}C NMR ($CDCl_3$, 500 MHz, δ); 138.7, 138.6, 137.5, 137.0, 136.2, 135.7, 131.2, 131.2, 130.6, 130.1, 130.0, 129.3, 129.0, 128.6, 128.5, 128.2, 127.8, 127.8, 127.7, 127.1, 126.9, 125.6, 125.2, 122.7, 122.4, 121.1 120.5, 120.0, 110.6, 103.8; FT-IR [ATR]: ν (cm^{-1}) 3055, 1521, 1467, 1211, 1125, 1022, 763, 739, 703; APCI-MS (*m/z*): 446 [M^{+}].

Physical measurements

The UV–Vis absorption and photoluminescence (PL) spectra of these materials were measured in dichloromethane (10^{-5} M) using Shimadzu UV-1650PC and Aminco-Bowman series 2 luminescence spectrometers. The fluorescent quantum yield were determined in



Scheme 1. Structures and synthetic routes of compounds **1** and **2**. (a) $Pd_2(dba)_3$, XPhos, NaOt-Bu, toluene, reflux, 120°C, 4 h.

dichloromethane solution at 293 K against DPA as a reference ($\Phi = 0.90$) [11]. The highest occupied molecular orbital (HOMO) energy levels were measured with a low energy photoelectron spectrometry (Riken-Keiki AC-2). The energy band gaps were determined from the intersection of the absorption and photoluminescence spectra. The lowest unoccupied molecular orbital (LUMO) energy levels were estimated by the energy band gap and the HOMO energy levels.

OLED fabrication and measurements

For fabricating OLEDs, the indium-tin-oxide (ITO) thin films coated on glass substrates were used, which was 30 Ω / square of the sheet resistivity. The ITO coated glass was cleaned in an ultrasonic bath by the following sequences: in acetone, methyl alcohol, distilled water and kept in isopropyl alcohol for 48 hours and dried by N_2 gas gun. The substrates were treated by O_2 plasma treatment with the conditions of 2×10^{-2} Torr at 125 W for 2 minutes. All organic materials and metal were deposited under high vacuum (5×10^{-7} Torr). The OLEDs were fabricated in the following sequence: indium-tim-oxide (ITO) / *N*,*N*'-di(1-naphthyl)-*N*,*N*'-diphenyl-(1,1'-biphenyl)-4,4'-diamine (NPB) (50 nm) / blue light-emitting materials (**1** and **2**) (30 nm) / 4,7-diphenyl-1,10-phenanthroline (Bphen) (30 nm) / lithium quinolate (Liq):Aluminium (Al) (100 nm) (Device **A** and **B**). All of the properties of the OLEDs such as current density (*J*), luminance (*L*), luminous efficiency (LE), power efficiency (PE), external quantum efficiency (EQE), and the CIE chromaticity coordinates of OLEDs were measured with Keithley 2400, Chroma meter CS-1000A. Electroluminescence was measured using Roper Scientific Pro 300i.

3. Results and discussion

The synthetic scheme and chemical structures of materials (**1** and **2**) are shown in the Scheme 1. They were synthesized by Pd-catalyzed Buchwald–Hartwig reactions between 2-bromo-9,10-diphenylanthracene and arylamino groups such as 9*H*-carbazole or 1*H*-indole with good yields. Their chemical structures were characterized by ^{1}H-, ^{13}C-NMR, FT-IR, and mass spectrometer.

Figure 1 illustrates the UV–Vis absorption and photoluminescence (PL) spectra of materials **1** and **2** at room temperature in diluted CH_2Cl_2 solutions and thin films; their physical data are shown in the Table 1. In UV–Vis spectra in CH_2Cl_2, the higher-intensity bands in both compounds **1** and **2** around 310–350 nm may be attributed to the delocalized π–π^*

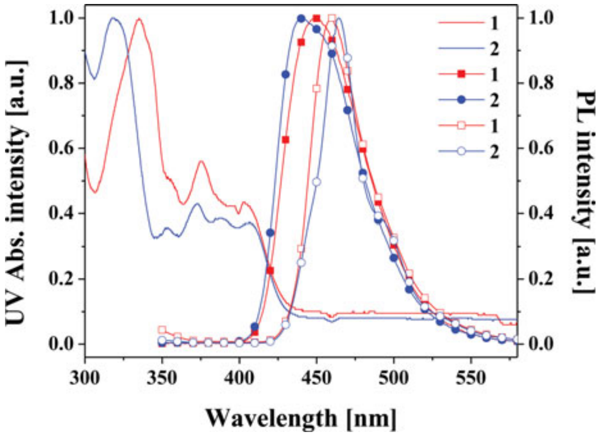


Figure 1. UV–Vis absorption spectra (no symbol), PL spectra in CH_2Cl_2 (closed symbol), and in thin films (opened symbol) of blue emitters **1** and **2**.

Table 1. Physical properties of compounds **1** and **2**.

Compound	UV_{max} [a] [nm]	PL_{max} [a] [nm]	FWHM [a/b] [nm]	HOMO / LUMO [c] [eV]	E_g [d] [eV]	Φ [e]
1	335	451 / 460	58.8 / 42.1	− 5.81 / −2.86	2.95	0.73
2	318	439 / 464	58.2 / 30.2	− 5.70 / −2.73	2.97	0.68

[a] In CH_2Cl_2 (10^{-5} M). [b] Solid thin film on quartz plates. [c] The HOMO energy level was determined by low-energy photoelectron spectrometer (Riken-Keiki, AC-2) and the LUMO = HOMO + ΔE. [d] Using DPA as a standard; $\lambda_{ex} = 360$ nm ($\Phi = 0.90$ in CH_2Cl_2).

transition of corresponding arylamino groups and the lower-intensity bands in them around 350–400 nm are derived from the characteristic π–π^* transition of anthracene moiety. The maximum wavelength (λ_{max}) in PL spectra of materials **1** and **2** in CH_2Cl_2 were 451 nm and 439 nm, respectively. Compared to λ_{max} of compound **2** with indole moiety, that of compound **1** shows red-shifted emissions due to the extended π-conjugation including carbazole moiety. The full widths at half maximum (FWHM) values in solution state are 42.1 nm and 30.2 nm, respectively. Compared to PL spectra of compounds **1** and **2** in CH_2Cl_2, each value of λ_{max} of compounds **1** and **2** in thin film state shows red-shifts due to the effect of molecular packing in the solid states.

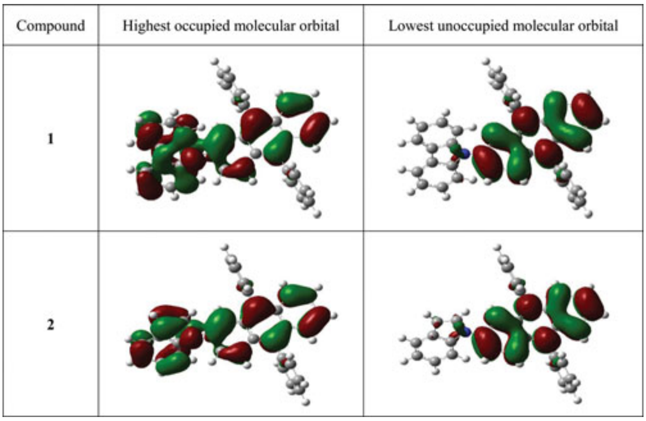


Figure 2. Frontier molecular orbitals of compounds **1** and **2**.

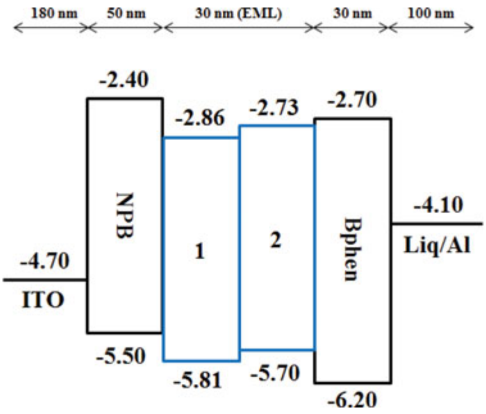


Figure 3. Energy-level diagrams of the materials used in devices **A** and **B**.

The HOMO energy levels of compounds **1** and **2** measured by a photoelectron spectrometer (Riken-Keiki AC-2) are −5.81 and −5.70 eV, respectively. Compound **2** exhibits shallower HOMO level than that of compound **1** due to the increased electron-donating ability of lone-pair electrons at nitrogen atom in indole moiety compared to in carbazole moiety [12]. The energy band gaps (E_g) of the materials **1** and **2** are 2.95 and 2.97 eV, respectively. The LUMO energy levels which were calculated by the HOMO energy levels with their corresponding E_g values are −2.86 and −2.73 eV, respectively.

To understand the photophysical properties of the compounds **1** and **2** at the molecular level, density functional theory (DFT) calculations of compounds **1** and **2** were carried out using the Becke's three parameterized Lee–Yang–Parr (B3LYP) functional with 6–31G∗basis sets using a suite of Gaussian programs, as shown in the Figure 2. In both compounds **1** and **2**, the electron clouds in HOMOs spread anthracene over carbazole or indole units; they indicate that chromophores are a combination anthracene and arylamino groups. On the other hands, those in LUMOs are distributed only anthracene unit; it means that the only lumophores are anthracene units.

To investigate the EL properties of these materials **1** and **2**, devices **A** and **B** using materials **1** and **2** as emitters were fabricated with a following structure: ITO (180 nm) / NPB (50 nm) / blue emitters **1** or **2** (30 nm) / Bphen (30 nm) / Liq:Al (100 nm) (Devices **A** or **B**); ITO, NPB, Bphen, and Liq:Al are used as an anode, hole-transporting layer (HTL), electron-transporting layer (ETL), and a cathode, respectively. The HOMO and LUMO energy-level diagrams of all the materials used in the EL devices are illustrated in Figure 3 and their EL properties are summarized in Table 2.

Figure 4 shows the EL spectra of devices **A** and **B** which exhibit blue fluorescence with λ_{max} values of 456 and 447 nm, respectively. The EL emission spectra of devices **A** and **B** show similar trend with the PL emission spectra of materials **1** and **2**. This means that the

Table 2. EL properties of devices **A** and **B**.

Device	L_{max} [a] [cd/m^2]	LE[a]/[b] [cd/A]	PE[a]/[b] [lm/W]	EQE[a]/[b] [%]	$\lambda_{,max}$ [c] [nm]	CIE[c]/[d] (x, y)
A	3502	3.60 / 3.54	2.08 / 1.90	2.67 / 2.63	456	(0.16, 0.16)
B	3344	3.31 / 3.11	2.46 / 1.60	3.04 / 2.82	447	(0.15, 0.13)

[a] Maximum value.
[b] Value at 20 mA/cm^2.
[c] At 6.0 V.
[d] Commission Internationale d'Éclairage (CIE).

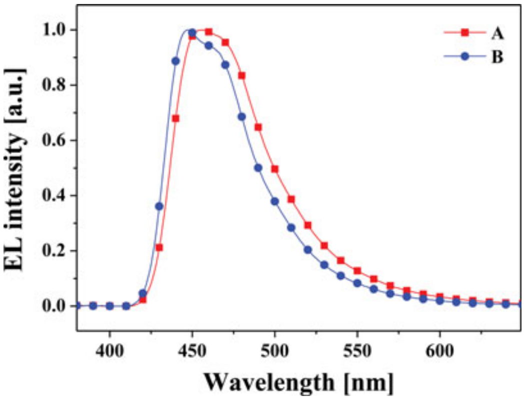


Figure 4. EL spectra of blue OLEDs **A** and **B** at 6.0 V.

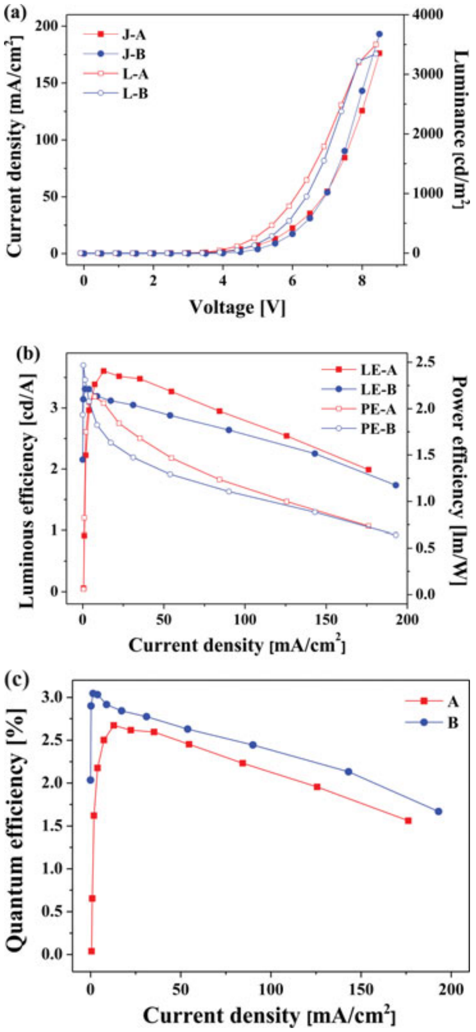


Figure 5. (a) *J-V-L* characteristics, (b) luminous efficiencies and power efficiencies, and (c) external quantum efficiencies of the devices **A** and **B**.

emissions from devices **A** and **B** are originated from the singlet excitons in the corresponding emitters **1** and **2**. The CIE coordinates of devices **A** and **B** are (0.16, 0.16) and (0.15, 0.13) at 6.0 V, respectively. Particularly, device **B** showed efficient deep-blue emission.

Figure 5 shows *J-V-L* characteristics, luminous efficiencies (LE), power efficiencies (PE), and external quantum efficiencies (EQE) of the devices **A** and **B**, respectively. Particularly, device **B** has better EL efficiencies than device **A**. This phenomenon may have been attributed by effective charge-carrier injection, especially holes-injection. In device **B**, hole could be easily injected to the EML from the HTL through the shallower HOMO energy level of **2** than that of compound **1** in device **A**. Furthermore, the hole-blocking capability in device **B** is larger than that in device **A**, because the energy barrier between the EML and the ETL in device **B** is higher than that in the device **A**. Therefore, holes are effectively injected in the emitting layer and prevented from leakages to the ETL in device **B** in comparison with device **A** [13]. These would leads to more efficient EL performances in device **B** than device **A**. Interestingly, device **A** shows the higher values of LE than device **B**, even though EQE of device **B** is higher than that of device **A**. This is the result from the differences in luminance by what color they are. The luminance is under control with the visual recognition from the emission or reflection from the light sources and their values are increased in order of blue $<$ red $<$ green. Thus, device **B** whose CIE coordinates are located in deeper blue region shows lower LE value than that of device **A**, although it has the higher EQE values [14, 18].

4. Conclusion

In summary, a series of highly efficient blue light-emitting materials was synthesized by Buchwald–Hartwig reactions. Particularly, the device **B** using compound **2**, which has shallow HOMO energy level (−5.70 eV), exhibiting the efficient blue emission with high LE, PE, and EQE values of 3.11 cd/A, 1.60 lm/W, 2.82% at 20 mA/cm^2, respectively, with CIE coordinates of (0.15, 0.13) at 6.0 V. This study demonstrates that arylamine substituted 9,10-diphenylanthracene derivatives would have the excellent properties as emitters for efficient blue OLEDs.

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