



High efficiency non-doped deep-blue and fluorescent/phosphorescent white organic light-emitting diodes based on an anthracene derivative



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ABSTRACT

A deep-blue fluorescent emitter 9-(4-(10-phenylanthracene-9-yl)phenyl)-9H-carbazole (PhPC) has been synthesized and applied in organic light-emitting diode (OLED). The monochromatic device based on PhPC shows a deep-blue emission peaked at 436 nm and has CIE coordinates of (0.15, 0.05). The device has a maximum external quantum efficiency of 3.6% and a maximum current efficiency of 1.8 cd A⁻¹. Performance of the deep-blue emitting OLED is among the best of reported non-doped fluorescence deep-blue organic light-emitting diodes (OLEDs) with a CIEy around 0.05. A fluorescent/phosphorescent (F/P) white OLED has been fabricated by using PhPC as a deep blue fluorescent emitter. The device shows maximum efficiencies of 27.6 lm W⁻¹, 35.1 cd A⁻¹, and a maximum EQE of 17.4% with CIE coordinates of (0.35, 0.43).

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1. Introduction

White organic light-emitting diodes (WOLEDs) have been widely investigated for their applications in flat panel displays and solid-state lightings [1]. In the early days, various approaches have been devised to realize WOLEDs, such as all-fluorescence WOLEDs and all-phosphorescent WOLEDs [2]. WOLEDs based on all-fluorescent emitters usually have lower efficiencies, because fluorescent emitters are theoretically capped to have a fluorescent quantum efficiency of about 25% due to singlet-triplet statistics [3]. While, fully phosphorescent WOLEDs have obtained the highest reported efficiencies for the ability of capturing both singlet and triplet excitons to achieve a 100% internal quantum efficiency [4]. As we all know, performance of blue phosphorescent emitters is generally behind those of green and red phosphorescent emitters [5]. For example, lifetimes of typical blue phosphorescent emitters such as iridium(III)bis[(4,6-difluorophenyl)-pyridinato-N,C2']picolinate (FlrPic) are clearly not long enough [6]. Besides, the color purity of FlrPic based devices is always compromised

because it is actually a blue-green emitter with two peaks at 472 and 500 nm, respectively [7]. Therefore, high performance blue fluorescent emitters are often used in combination with phosphorescent emitters of other colors for enhancing operation stability and color gamut [8].

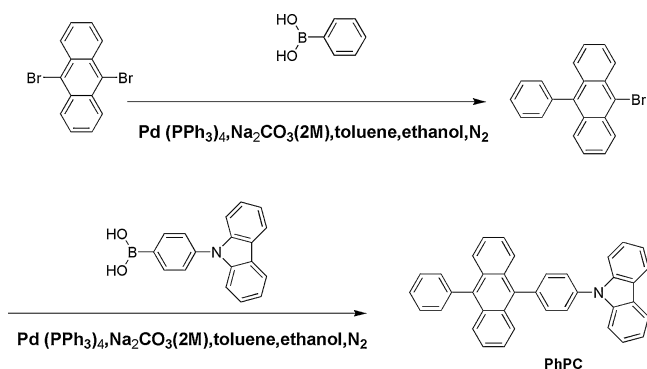
It is therefore important to develop efficient and stable deep blue fluorescent materials. In addition to enhancing the color gamut, deep blue materials can also lower the power consumption in a full-color display [9]. However, according to the European Broadcasting Union (EBU) standard blue CIE coordinate of (0.15, 0.06), there have been few reports on deep blue OLEDs used in WOLEDs that can match the emission with y coordinate lower than 0.06 with high efficiency [10–15].

In this work, we applied a phenylcarbazole end-capped asymmetrical anthracene derivative, 9-(4-(10-phenylanthracene-9-yl)phenyl)-9H-carbazole (PhPC) as a deep blue emitter in both blue and white OLEDs. While PhPC has been used as a host material, its fluorescence performance has not been reported [16]. Using PhPC, we have fabricated a high efficiency non-doped deep-blue OLED with emission peaked at 436 nm and CIE of (0.15, 0.05). The maximum external quantum efficiency and current efficiency of the device reaches 3.6% and 1.8 cd A⁻¹, respectively. Performance of the deep-blue emitting OLED is among the best reported non-doped fluorescence deep-blue organic light-emitting diodes

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Scheme 1. Synthetic route of PhPC.

(OLEDs) with a CIE_y around 0.05. Considering deep blue emitter can easily modulate color-balancing to achieve white OLEDs, a F/P hybrid white OLED has been fabricated by using PhPC as a deep blue emitter. The white device shows the maximum luminous efficiencies of 27.6 lm W⁻¹, 35.1 cd A⁻¹ and EQE of 17.4% along with the CIE coordinates of (0.35, 0.45).

2. Experimental details

2.1. Material synthesis

The anthracene derivative was synthesized according to the procedures in Scheme 1 using two-step Suzuki coupling reactions. All solvents used in the reaction were purified by routine procedures. Other reagents in the scheme were used as received from commercial sources.

2.2. 9-Bromo-10-phenylanthracene (1)

9,10-Dibromoanthracene (5 mmol), phenyl boronic acid (5 mmol), Pd (PPh₃)₄ (0.5 mmol), aqueous Na₂CO₃ (2.0 M, 15 mL), ethanol (10 mL), and toluene (30 mL) were mixed in a flask. The mixture was degassed and refluxed for 24 h under a nitrogen atmosphere. After cooling, the solvent was evaporated under vacuum and the product was extracted with dichloromethane (CH₂Cl₂). The CH₂Cl₂ solution was washed with water and dried with MgSO₄. Evaporation of the solvent, followed by column chromatography on silica gel, gives a pale yellow product. Yield: 85%. MS (*m/z*): 332 (M⁺).

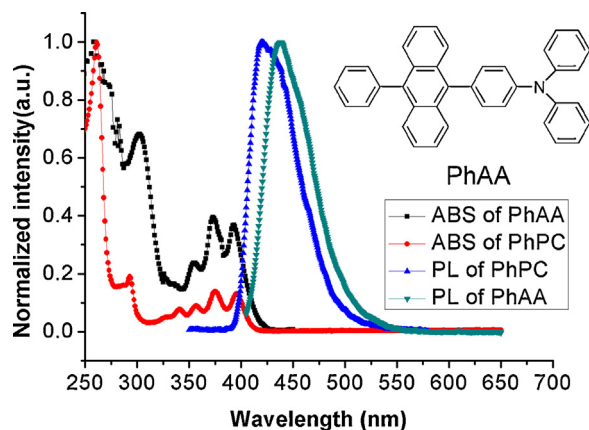


Fig. 1. Absorption and photoluminescence spectra of PhPC and PhAA.

2.3. 9-(4-(10-phenylanthracene-9-yl)phenyl)-9H-carbazole (PhPC)

Compound **1** (3 mmol), *N*-phenylcarbazole boronic acid (4 mmol), Pd(PPh₃)₄ (0.3 mmol), aqueous Na₂CO₃ (2.0 M, 10 mL), ethanol (15 mL), and toluene (25 mL) were mixed in a flask. The mixture was degassed and refluxed for 24 h under nitrogen and in dark. After cooling, the solvent was evaporated under vacuum and the product was extracted with dichloromethane (CH₂Cl₂). Evaporation of the solvent, followed by recrystallization using CH₂Cl₂/ethanol, gives PhPC as a white product. Yield: 86%. ¹H NMR (CDCl₃, 300 MHz): δ 7.34–7.47 (m, 6H), 7.50–7.55 (m, 4H), 7.55–7.62 (m, 3H), 7.68–7.76 (m, 6H), 7.83–7.86 (m, 4H), 8.21–8.23 (d, 2H). MS (*m/z*): 495 (M⁺). Elemental analysis: calcd for C₃₈H₂₅N: C, 92.12; H, 5.05; N, 2.83. Found: C, 92.07; H, 5.09; N, 2.65.

2.4. Measurements and OLEDs fabrication

Absorption and fluorescence spectra were recorded using a PerkinElmer Lambda 2S UV–vis spectrophotometer and a PerkinElmer LS50B luminescence spectrophotometer, respectively. Glass transition temperature (T_g) was determined with differential scanning calorimeters (DSC) using a PerkinElmer DSC7 at a heating rate of 20 °C min⁻¹. The highest occupied molecular orbital (HOMO) energy was measured with ultraviolet photoelectron spectroscopy (UPS), while the lowest unoccupied molecular orbital (LUMO) energy was determined from difference between the HOMO energy and the lowest energy absorption edge of the UV absorption spectra. OLEDs were fabricated via vacuum deposition on ITO glass substrates with a sheet resistance of 30 Ω per square. The ITO substrate was carefully cleaned, then dried in an oven at 120 °C, and finally treated with UV-ozone before loading into a deposition chamber. The devices were fabricated by sequentially evaporating organic layers and metal cathode onto the ITO substrate with a rate of 2–4 Å s⁻¹ and a pressure below 5 × 10⁻⁶ mbar. EL spectra and CIE color coordinates were measured with a Spectrascan PR650 photometer. Current-voltage-luminescence characteristics were measured with a computer-controlled Keithley 236 Sourcemeter under ambient atmosphere.

3. Results and discussions

Scheme 1 shows the synthetic route and the chemical structure of 9-(4-(10-phenylanthracene-9-yl)phenyl)-9H-carbazole (PhPC). The compound can be synthesized with a high yield via two-steps Suzuki coupling reactions according to reported procedure [17]. Molecular structure of PhPC is verified with ¹H NMR spectrometry, elemental analysis (EA) and mass spectrometry (MS).

Thermogravimetric analysis (TGA) of PhPC shows a decomposition temperature (T_d, corresponding to 5% weight loss) of 320 °C. The compound shows no obvious glass transition temperature upon analysis with two-time heat differential scanning calorimetry (DSC). UV–vis absorption and photoluminescence spectra in dilute dichloromethane solution are shown in Fig. 1.

To study the influences of different substituents at the 9-position of the middle anthracene core of the compound, we have prepared another compound PhAA with a structure (Fig. 1)

Table 1

Key physical data of PhPC and PhAA.

	T _g /T _d (°C)	Emission peak (nm) ^a	HOMO (eV)	LUMO (eV)	E _g (eV)	Φ ^b
PhPC	–/320	420/431	5.9	2.9	3.0	0.89
PhAA	104/–	438/457	5.7	2.9	2.8	0.44

^a Is emission peak in CH₂Cl₂ solution and as film.

^b Is fluorescence quantum yield in dilute CH₂Cl₂ using 9,10-diphenyl-anthracene (Φ = 0.9) as a standard.

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