



Excellent deep-blue emitting materials based on anthracene derivatives for non-doped organic light-emitting diodes



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ABSTRACT

Two deep-blue emitting materials 2-*tert*-butyl-9,10-bis(3,5-diphenylphenyl)anthracene (An-1) and 2-*tert*-butyl-9,10-bis(3,5-diphenylbiphenyl-4'-yl)anthracene (An-2) were successfully synthesized by the Pd-catalyzed Suzuki coupling reaction. Both of these compounds have high thermal stabilities and show strong deep-blue emission as solid-state film as well as in *n*-hexane solution. Two non-doped electroluminescent devices employing An-1 and An-2 as emitting layers were fabricated by vacuum vapor deposition. These devices exhibited highly efficient and stable deep-blue emission with high color purity. The CIE coordinate and maximum EQE of An-1 based device are 4.2% and (0.16, 0.06), respectively. Device based on An-2 achieved a maximum EQE of 4.0% and a CIE coordinate of (0.16, 0.10).

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1. Introduction

As the next generation flat-panel displays, organic light-emitting diodes (OLEDs) have many unique advantages, such as low driving voltage, high efficiency, excellent flexibility, vivid color, wide viewing angle et al., and have been attracting considerable scientific and commercial attention since the pioneering works by Tang [1–3]. Stable and color pure three primary colors (red, green and blue) emitters with high emission efficiency are required for the full-color OLEDs. Moreover, a blue emitter is particularly important, because it not only can give blue emission but also can be utilized to generate green and red emissions through energy transfer in OLEDs, and robust blue emitters can also cut down the power consumption and extend the color gamut for full-color OLEDs [4–6]. However, developing desirable blue emitters remains a great challenge because of their intrinsic wide band gap,

and thus the performance of blue OLEDs is still obviously inferior to those of red and green ones to date [4–6].

Color purity is one of key criteria for the high-quality displays. According to the standards of National Television System Committee (NTSC) and European Broadcasting Union (EBU), the Commission Internationale de l'Éclairage (CIE) coordinate of blue emission should be (0.14, 0.08) and (0.15, 0.06), respectively, which are at the deep-blue area of CIE chromaticity diagram. Thus, OLEDs capable of giving a deep-blue emission are highly desired considering the practical application. In recent years, various kinds of fluorescent emitters, such as anthracene derivatives [7–13], fluorene derivatives [14–17], pyrene derivatives [18–21], D- π -A type intramolecular charge transfer compounds [22–33], and so forth [34–43], have been investigated to improve the performance of deep-blue OLEDs. To obtain high electroluminescence (EL) efficiency, many OLEDs adopted the host-guest system [4,6]. Although the use of dopant emitters in the host-guest system can improve the EL efficiency, the intrinsic phase separation of doped devices would lead to a poor stability during operation [4,6], and the addition of dopants is usually a complicated and expensive process for the mass production of OLEDs. Obviously, the non-doped deep-

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blue OLEDs with a single-component host emitting layer are more pragmatic for application.

Anthracene is an excellent building block for constructing deep-blue emitting materials, its derivatives have many outstanding physical properties, such as high photoluminescence yield, good thermal stability, and superior electrochemical properties [44]. In this paper, we synthesized and studied two deep-blue emitting anthracene derivatives 2-*tert*-butyl-9,10-bis(3,5-diphenylphenyl)anthracene (An-1) and 2-*tert*-butyl-9,10-bis(3,5-diphenylbiphenyl-4'-yl)anthracene (An-2) (Scheme 1). In An-1 and An-2, the bulky groups 3,5-diphenylphenyl and 3,5-diphenylbiphenyl are introduced at 9- and 10-position of the anthracene backbone, respectively, which can enhance the non-planarity of molecular structures and thermal stability of materials. Although the compound An-2 was reported by Lee et al. when we carried out the studies in this paper, they focused on the solution process performance of this compound and did not study its EL performance [45]. We investigated the photophysical, thermal and electrochemical properties of An-1 and An-2 in detail. The non-doped electroluminescent devices based on An-1 and An-2 showed highly efficient and stable deep-blue emissions, the CIE coordinate and maximum external quantum efficiency (EQE) are (0.16, 0.06) and 4.2% for An-1 based device, (0.16, 0.10) and 4.0% for An-2 based device.

2. Experimental

2.1. General information

Commercially available reagents were used without purification unless otherwise stated. The ^1H NMR spectra and ^{13}C NMR spectrum were recorded on Bruker Avance 400 spectrometer. Elemental analysis was performed on a Vario III elemental analyzer. Mass spectra were obtained on a Bruker Microflex spectrometer. The absorption and photoluminescence spectra were recorded on a Hitachi U-3010 UV–Vis spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer, respectively. Cyclic voltammetry (CV) was performed on a CHI620C electrochemical analyzer, and the electrolytic cell is a conventional three-electrode cell consisting

of a Pt working electrode, a Pt wire counter electrode and an Ag/AgCl reference electrode. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a TA instrument TGA2050 and a TA instrument DSC2910, respectively, with a heating rate of 10 °C/min under the nitrogen atmosphere. Density functional theory (DFT) calculations were performed using Gaussian 09 with the B3LYP/6-31G(d) method.

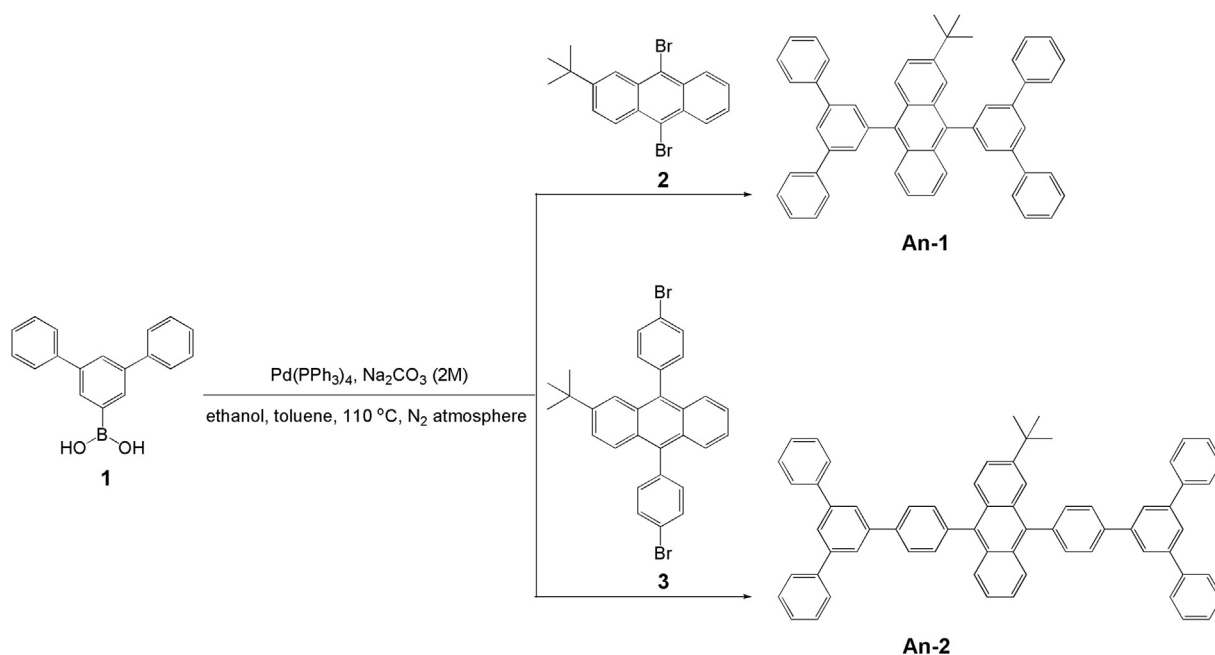
2.2. Synthesis

2.2.1. Synthesis of An-1

3,5-Diphenylphenyl boronic acid **1** (605 mg, 2.2 mmol), 2-*tert*-butyl-9,10-dibromoanthracene **2** (392 mg, 1.0 mmol) and tetrakis(triphenylphosphine)palladium (50 mg) were mixed in toluene (35 mL), then Na_2CO_3 (2 M, 10 mL) and ethanol (10 mL) were added under the nitrogen atmosphere. The mixture reacted at 110 °C under the nitrogen atmosphere overnight. After cooling, the resulting solution was extracted with dichloromethane, the combined organic solution was dried over anhydrous MgSO_4 and evaporated with a rotary evaporator. The crude product was purified by column chromatography using dichloromethane/petroleum ether (1:10 v/v) as eluent to give a white powder (yield: 497 mg, 72%). ^1H NMR (500 MHz, CDCl_3) δ (ppm): 8.03 (2H, s), 7.89–7.84 (3H, m), 7.79–7.75 (13H, m), 7.50–7.46 (9H, m), 7.40–7.34 (6H, m), 1.29 (9H, s). TOF-MS: 690.213. ^{13}C NMR (125 MHz, CDCl_3) δ (ppm): 147.60, 141.83, 141.76, 140.99, 140.91, 140.23, 136.76, 136.57, 130.15, 129.97, 129.69, 129.16, 129.12, 128.93, 128.61, 127.62, 127.37, 127.34, 127.04, 127.01, 126.82, 125.16, 125.09, 125.05, 124.96, 124.92, 121.15, 35.03, 30.83. TOF-MS: 690.314. Anal. Calcd. For $\text{C}_{54}\text{H}_{42}$: C, 93.87; H, 6.13. Found: C, 93.72; H, 6.15.

2.2.2. Synthesis of An-2

The synthesis and purification procedures of An-2 are similar to those of An-1. 3,5-Diphenylphenyl boronic acid **1** reacted with 2-*tert*-butyl-9,10-di(4-bromophenyl)anthracene **3** to give the crude product. The pure An-2 was obtained as pale green powder by column chromatography using dichloromethane/petroleum ether (1:8 v/v) as eluent, yield is about 78%. ^1H NMR (500 MHz, CDCl_3)



Scheme 1. Synthesis and molecular structures of An-1 and An-2.

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