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Two non-doped blue emitters for electroluminescent devices: Preparation, photophysics and electroluminescence

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Two blue emitters, 2,7-bis(9-benzyl-9*H*-carbazol-2-yl)pyrene and 2,7-bis(4-(5-phenyl-1,3,4-oxadiazol-2-yl)phenyl)pyrene, were synthesized by a Suzuki coupling reaction. Photophysical studies show that the two emitters have excellent optical and electron transfer properties. The emission peaks of the two emitters are 430 nm and 439 nm with 87.5% and 68.6% fluorescence quantum yields in chloroform, respectively. The emitters both have good thermal stability (Td > 330 °C, Tg > 160 °C). Electrochemical Redox properties of the emitters were measured by cyclic voltammetry, and the highest occupied molecular orbital and the lowest unoccupied molecular orbital levels are in good agreement with the results of theoretical calculations. Additionally, non-doped blue organic light-emitting diodes with these emitters have been achieved with the Commission International de l'Éclairage (x,y) coordinates of (0.17, 0.11) and (0.16, 0.15) respectively, which are very close to the National Television System Committee standard blue. Remarkably, the performance of device A (2,7-bis(9-benzyl-9*H*-carbazol-2-yl) pyrene) offers balanced performance and without any significant disadvantages.

1. Introduction

Organic light-emitting diodes (OLEDs) have been developed rapidly due to the advantages of the low drive voltage, high luminance and high efficiency [1–5]. Red, green and blue light plays a very important role in the full-color display, as they are the three primary colors. To date, green and red OLEDs materials have been widely reported [6–15]. Due to the low energy consumption lighting, white OLEDs materials have also been developed rapidly [16–22]. In comparison with other shades of OLED materials, it is difficult to obtain high-efficient blue or deep blue OLEDs because of the necessary wide band gaps. Hence, it is always a large challenge to design and achieve blue OLEDs. Based on these requirements, recently, the development speed of blue OLEDs is also very fast and many different types of blue OLEDs have been reported. Carbazole and its derivatives have been widely used as good hole-transport materials in the preparation of blue OLEDs [23–28]. Fluorene and its derivatives can be used as efficient blue emitters in the preparation of blue OLEDs [23,28–35]. Moreover, chrysene derivatives [36], anthracene derivatives [37–39], triphenylamine derivatives [40], naphthalene derivatives [41,42] and other simple polymers [43–46] have also been used in OLEDs. Apart from these organic molecules, some metal complexes can be also used in OLEDs. Florian [47], Wong [48], Adachi [49] amongst other researchers have succeeded in using iridium (III) complexes to prepare blue OLEDs. Moreover, some other transition-metal complexes have also been successful in OLED applications [50].

Compared with other conjugated aromatic compounds, the pyrene functional group offers a high quantum yield, excellent electron mobility and hole-injection ability. However, pyrene itself has a strong tendency towards crystallization. Due to the $\pi-\pi$ stack forming the excited molecule, its fluorescence emission may be red-shifted over 480 nm and with pyrene derived molecules it is difficult to form a stable amorphous thin film, which makes pyrene itself unsuitable for blue OLEDs [51,52]. Therefore, it is imperative to modify pyrene structures with some specific functional groups. Rao and his coworkers have successfully appended an electron transport group to blue emitting pyrene derivatives. But the CIE$_y$ of these compounds are over 0.2, and the thermal stability of these compounds are not good [53]. Mullen and his coworkers successfully prepared a dark blue emitter with pyrene and carbazole units, but the brightness of corresponding OLED is low (<1000 cd m^{-2}) [24]. Tao and his coworkers also prepared pyrene derivatives with 4-(2,2-diphenyl-vinyl)phenyl group [54]. The performances of

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combined devices are good, but they are not deep blue OLEDs. Similarly, other researchers also designed and developed some pyrene derivatives as blue OLEDs materials [55–58]. These obtained pyrene emitters have their own particular characteristics, but more or less have their disadvantages, such as either larger CIE$_y$, lower brightness or emitting violet light. Additionally, hole-transfer and electron-injection properties of emitters are two important parameters for OLEDs materials.

Based on the current case, the aim of our work is to achieve excellent blue emitters with hole-transfer or electron-injection groups. Hence, we designed and synthesized two novel pyrene emitters with 9-benzyl-9-*H*-carbazole (hole-transfer group) and 2,5-diphenyl-1,3,4-oxadiazole (electron-injection group), respectively. The test results of photophysical and electroluminescence properties display that the two compounds as emitters of OLEDs emit blue light. Noticeably, the device based on 2,7-bis(9-benzyl-9*H*-carbazol-2-yl)pyrene (BCP) emitter has good properties including higher brightness, pure blue light and good stability.

2. Experimental

2.1. Materials

Unless otherwise stated, all chemical reagents were obtained from commercial suppliers and were used without further purification. The following reagents: Pd(dppf)Cl$_2$, bis(pinacolato) diboron, *N*-bromosuccinimide, phosphoryl chloride, Pd(PPh$_3$)$_4$, 4-bromobenzoyl chloride, phenylhydrazine, *N*-benzylcarbazole and 1,6-dibromopyrene were all purchased from Aldrich (Steinheim, Germany).

2.2. Characterization

^{1}H NMR and ^{13}C NMR were measured on a Bruker ARX400 spectrometer with chemical shifts reported as ppm (TMS as an internal standard). The UV–vis absorption and fluorescence emission spectra were taken on a HITACHI UH5300 and F-4600 spectrophotometers, respectively. The excitation and emission slit widths were both 5.0 nm. High-resolution mass spectra (HRMS) were acquired on an Agilent 6510 Q-TOF LC/MS instrument (Agilent Technologies, Palo Alto, CA) equipped with an electrospray ionization (ESI) source. IR-spectroscopy measurements were performed on a FTIR8400S spectrophotometer, using KBr pellets. Elemental analyses were measured on a EuroVector EA3000 elemental analyzer. The glass transition temperatures of compounds were determined by DSC using a DSC-Q10 instrument under a nitrogen atmosphere. The decomposition temperature corresponding to 5% weight loss was detected using a Perkine Elmer Pyris 1 TGA thermal analyzer. The melting points of compounds were recorded on a WRS-3 instrument with a 3 °C/min heating rate. Cyclic voltammetry (CV) measurements were determined on a three-electrode AUTOLAB (model PGSTAT30) workstation in a solution of Bu$_4$NClO$_4$ (0.1 M) in acetonitrile at a scan rate of 50 mV/s at room temperature.

2.3. Device fabrication

The multilayer OLEDs were fabricated by vacuum-deposition method. Organic layers were fabricated by high-vacuum (5×10^4 Pa) thermal evaporation onto a glass (3 cm × 3 cm) substrate percolated with an ITO layer, which was used as anode. The hole-transfer layer (HTL) was poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT: PSS). The electron-blocking layer was 4,4-bis(*N*-carbazolyl)-1,10-biphenyl (CBP). The emitting layer was BOP and BCP, respectively. The electron-transport layer (ETL) was 1,3,5-tris(*N*-phbenylbenzimidazol-2-yl) benzene (TBPI). The cathode was LiF/Al. All organic layers were sequentially deposited. Thermal deposition rates for organic materials, LiF and Al were 0.5 Å s^{-1}, 0.5 Å s^{-1}and 1.0 Å s^{-1}, respectively. The active areas of these devices were 9 mm^2. The electroluminescent spectra were measured on a Hitachi MPF-4 fluorescence spectrometer. The voltage–current density characteristics of OLEDs were recorded on Keithley 2400 Source Meter. The characterization of luminance-voltage was measured with a 3645 DC power supply combined with a 1980 A spot photometer and was recorded simultaneously. All measurements were done at room temperature.

2.4. Synthesis procedures of BCP and BOP

Compounds of 9-benzyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-carbazole and 2-phenyl-5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,4-oxadiazole were prepared according to the previous reported works [59–61].

2.4.1. 2,7-bis(9-benzyl-9H-carbazol-2-yl)pyrene (BCP)

A mixture with 1,6-dibromopyrene (0.9 g, 2.5 mmol), 9-benzyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-carbazole (1.92 g, 5.0 mmol) in dioxane (50.0 mL) and 2.0 M K$_2$CO$_3$ (10.0 mL) was stirred for 30 min at room temperature under nitrogen atmosphere. Then, Pd(PPh$_3$)$_4$ (0.1 g) catalyst was quickly added to the suspension and heated to 110 °C for 48 h under nitrogen atmosphere. The reaction mixture was cooled to room temperature, poured into the ice water (200 mL), filtered and then purified by column chromatography on silica gel with dichloromethane/petroleum ether (1/1, v/v) as the eluant to afford BCP as faint yellow solids (1.149 g 64.5%), m.p. 275–277 °C. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.42 (s, 2H), 8.34–8.31 (d, *J* = 12.0 Hz, 2H), 8.26–8.22 (m, 4H), 8.19–8.06 (m, 6H), 7.76–7.73 (t, *J* = 6.0, 6.0 Hz, 2H), 7.67–7.59 (t, *J* = 8.0, 8.0 Hz, 2H), 7.56–7.45 (m, 4H), 7.36–7.04 (m, 10H), 5.65 (s, 4H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 141.21, 140.03, 138.56, 137.18, 132.50, 130.23, 128.87, 128.33, 127.57, 126.54, 126.12, 125.42, 123.24, 122.39, 120.56, 119.44, 108.70, 46.83. IR (KBr, υcm^{-1}):(arene C–H) 3083, 3030; (aliphatic C–H) 2920, 2856; (C=C, Ar) 1625, 1601; (C–N, Ar) 1477, 1466. Element Analysis for C$_{54}$H$_{36}$N$_2$ (Mol. Wt.: 712.90) calcd.: C, 90.98; H, 5.09; found: C 91.12; H 4.98. HRMS-ESI for C$_{54}$H$_{36}$N$_2$ (*m*/*z*) 713.53 [M+1].

2.4.2. 2,7-bis(4-(5-phenyl-1,3,4-oxadiazol-2-yl)phenyl)pyrene (BOP)

The BOP was synthesized according to the above method. The crude produce was purified by column chromatography on silica gel with ethyl acetate/dichloromethane (1/12, v/v) as the eluant to afford BOP as a pale fawn solid (0.905 g 56.3%), m.p. 285–287 °C, respectively. ^{1}H NMR (CDCl$_3$, 400 MHz) *δ* 8.50 (d, *J* = 6.4 Hz, 2H), 8.41 (d, *J* = 4.8, 2H), 8.39–8.25 (m, 8H), 8.14 (d, *J* = 12.0 Hz, 2H), 8.03 (d, *J* = 8.0 Hz, 2H), 7.89 (d, *J* = 8.0 Hz, 4H), 7.62 (m, 6H). ^{13}C NMR (CDCl$_3$, 100 MHz) *δ* 164.71, 135.34, 131.77, 129.08, 127.00, 126.06, 125.97, 123.89, 84.25, 25.03. IR (KBr, υcm^{-1}): (arene C–H) 3043; (C=C, Ar) 1612, 1630; (C=N) 1546; (C–O–C) 1078, 1296. Element Analysis for C$_{44}$H$_{26}$N$_4$O$_2$ (Mol. Wt.: 642.72) calcd.: C, 82.23; H, 4.08; N, 8.72; found: C, 82.48; H, 4.51; N, 8.64; HRMS-ESI for C$_{44}$H$_{26}$N$_4$O$_2$ (*m*/*z*): 643.48 [M+1].

3. Results and discussion

3.1. Synthesis and photophysical properties of BCP and BOP

The synthetic routes used to prepare blue emitters BCP and BOP were showed in Scheme 1. The two compounds also were