Dyes and Pigments 92 (2011) 732–736

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Novel pyrene derivatives: Synthesis, properties and highly efficient non-doped deep-blue electroluminescent device

Zhiqiang Wang [a], Chen Xu [a,*], Weizhou Wang [a], Xinming Dong [b], Bangtun Zhao [a], Baoming Ji [a,*]

[a] College of Chemistry and Chemical Engineering, Luoyang Normal University, Luoyang 471022, People's Republic of China
[b] Department of Chemistry, Zhengzhou University, Zhengzhou 450052, People's Republic of China

ARTICLE INFO

Article history:
Received 21 February 2011
Received in revised form
8 June 2011
Accepted 20 June 2011
Available online 1 July 2011

Keywords:
Pyrene derivatives
Organic light emitting devices
Deep-blue emission
Luminescence
Quantum chemical calculations
Thermal properties

ABSTRACT

Two novel pyrene derivatives 1,6-bis(3,5-diphenylphenyl)pyrene (BDPP) and 1,6-bis(2-naphthyl)pyrene (BNP) were synthesized and characterized by ^{1}H NMR, ^{13}C NMR, mass spectrum and elemental analysis. The compounds BDPP and BNP exhibit bright blue emission with high fluorescence quantum yields. The quantum chemical calculations show that BDPP has a higher non-coplanar structure compared to BNP. The electrochemical properties and energy levels of the compounds were investigated by cyclic voltammetry. BDPP exhibits a high thermal stability with the decomposition temperature of 440 °C and the glass transition temperature of 139 °C. The non-doped device based on BDPP achieves a very stable deep-blue emission with a maximum efficiency of 3.26 cd/A. The 1931 CIE coordinates (0.15, 0.11) of this device are very close to the National Television System Committee blue standard.

1. Introduction

Since the pioneering works on organic light emitting devices (OLEDs) by the Kodak [1] and Cambridge groups [2], OLEDs have been attracting considerable attention due to their potential application in flat-panel displays, solid-state lighting sources and backlights for liquid-crystal displays. For the full-color OLEDs, highly efficient and stable three basic colors (red, green, and blue) emission are needed. However, it is much more difficult to produce a high-performance blue emission for its intrinsic characteristic of having a wide bandgap irrespective of the type of materials [3]. Although the electroluminescence (EL) efficiency can be significantly improved by using dopant emitters, the addition of dopants implies additional complexity and cost for the mass production of OLEDs. In addition to efficiency and stability, color purity is another important essential for OLEDs. However, the non-doped deep-blue OLEDs with the Commission Internationale de l'Eclairage (CIE) coordinates matched to the National Television System Committee (NTSC) standard (0.14, 0.08) are still rare [4]. In addition, it is well known that the power consumption of a full-color OLED is highly dependent upon the color of blue emission, and the deeper the blue color (smaller CIE y -value) is, the lower the power consumption of the device is [4]. Thus, developing highly efficient and stable non-doped deep-blue OLEDs continues to receive considerable attention [5–10].

Due to the large conjugated aromatic characteristic, pyrene not only has high fluorescence efficiency, but also has high carrier mobility. Recently, some pyrene derivatives have been used in blue OLEDs in order to improve the hole-transporting ability for the electron-rich characteristic of pyrene [11–13], but the performances of those devices are not satisfactory in efficiency, stability and color purity. In view of these findings and our continuous interest in non-doped deep-blue OLEDs [4,14], we designed and synthesized two novel pyrene derivatives BDPP and BNP. The quantum chemical calculations were carried out to investigate their stereostructures and electronic structures. The photophysical properties, electrochemical properties and thermal properties of the compounds were contrastively studied. The non-doped device, ITO/PEDOT:PSS (30 nm)/NPB (30 nm)/BDPP (30 nm)/TPBI (30 nm)/CsF (2 nm)/Mg:Ag, shows a stable deep-blue emission with high EL efficiency. The 1931 CIE coordinates (0.15, 0.11) of this device are very close to the National Television System Committee (NTSC) blue standard.

---

* Corresponding authors. Tel./fax: +86 379 65523821.
E-mail addresses: xubohan@163.com (C. Xu), lyhxxjbm@126.com (B. Ji).

0143-7208/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2011.06.025

2. Experimental

2.1. Chemicals and instruments

Commercially available reagents were used without purification unless otherwise stated. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ solution on a Bruker Avance 400 spectrometer with tetramethylsilane (TMS) as the internal standard. Elemental analysis was performed on a Vario III elemental analyzer. Mass spectrum was 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. TGA and DSC measurements were performed on a TA instrument TGA2050 and TA instrument DSC2910, respectively, with a heating rate of 10 °C/min (0 °C is corresponding to 273.15 K, 1 °C = 1 K) under the nitrogen atmosphere. Cyclic voltammetry was performed on a CHI620C electrochemical analyzer.

2.2. Synthesis

BDPP was synthesized by the Suzuki coupling reaction (Fig. 1). 1,6-Dibromopyrene **1** (1.0×10^{-3} mol), 3,5-diphenylphenyl boronic acid **2** (2.2×10^{-3} mol) and tetrakis(triphenylphosphine)palladium [$Pd(PPh_3)_4$] (0.12×10^{-3} mol) were mixed in toluene (20×10^{-6} m^3), then Na_2CO_3 (2 M, 5×10^{-6} m^3) and ethanol (5×10^{-6} m^3) were added during stirring. The mixture was refluxed under the nitrogen atmosphere for 24 h. After cooling, precipitate was collected by filtration and purified by column chromatography (eluent = dichloromethane/hexane, 1:10 v/v). The product was recrystallized in toluene (yield: 0.34 g, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.33 (2H, d, J = 9.2), 8.25 (2H, d, J = 7.6), 8.10 (4H, t, J = 7.4), 7.95 (2H, s), 7.87 (4H, s), 7.77 (8H, d, J = 7.6), 7.49 (8H, t, J = 7.4), 7.40 (4H, t, J = 7.2); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 142.48, 142.10, 141.19, 137.86, 130.79, 129.18, 129.08, 128.60, 128.02, 127.89, 127.78, 127.58, 125.55, 125.45, 125.21, 124.81; TOF-MS: m/z = 658.74; Anal. Calcd. for $C_{52}H_{34}$: C, 94.80; H, 5.20; Found: C, 94.74; H, 5.22.

The synthesis of BNP is similar to that of BDPP, yield: 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.27 (2H, s), 8.25 (2H, s), 8.12 (2H, s), 8.11 (1H, s), 8.09 (2H, s), 8.07 (2H, s), 8.04 (1H, s), 7.96–8.01 (4H, m), 7.82 (1H, d, J = 1.6), 7.78 (1H, d, J = 1.7), 7.58–7.60 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 139.01, 133.67, 132.76, 130.72, 129.53, 129.26, 129.10, 128.32, 128.20, 128.00, 127.97, 127.77, 126.58, 126.32, 125.57, 124.74; TOF-MS: m/z = 454.48; Anal. Calcd. for $C_{36}H_{22}$: C, 95.12; H, 4.88; Found: C, 95.08; H, 4.86.

2.3. OLED fabrication and measurements

Indium-tin-oxide (ITO)-coated glass substrates were cleaned with isopropyl alcohol and deionized water, then dried in an oven over 393 K, and finally treated with UV-ozone. A 30 nm (1 nm = 1×10^{-9} m) thick film of poly (3, 4-ethylenedioxy thiophene) doped with poly (styrene sulfonate) (PEDOT:PSS) was spin-coated on the ITO glass substrates. After dried at 393 K for 30 min under nitrogen atmosphere, the substrate was transferred to the vacuum deposition system with a base pressure of $<5 \times 10^{-7}$ torr (1 torr = 133.322 Pa). The device was fabricated by evaporating organic layers onto the PEDOT layer sequentially with an evaporation rate of 0.1–0.2 nm/s. The Mg:Ag alloy cathode was prepared by co-evaporation of Mg and Ag at a volume radio of 10:1. EL spectra and 1931 CIE color coordinates were measured with a spectrascan PR650 photometer and the current-voltage-luminance characteristics were measured with a computer-controlled Keithley 2400 SourceMeter under ambient atmosphere.

3. Results and discussion

3.1. Quantum chemical calculations

To gain insight into the stereostructures and the electronic structures of BDPP and BNP, quantum chemical calculations were carried out by using the B3LYP/6-31G(d) method [15]. In BDPP, the 3,5-diphenylphenyl substituents at the 1- and 6- positions are twisted toward the pyrene backbone to a angle of 56.7°, and the twist angles between adjacent benzene rings in 3,5-diphenylphenyl group are 37.6° and 37.9°, respectively, which indicates BDPP has a highly non-coplanar structure. The non-coplanar structure can limit the intermolecular interactions and facilitate the formation of stable amorphous thin films. In BNP, the twist angle between 2-naphthyl substituents and pyrene backbone is 54.9°, the lesser twist angle implies that BNP has

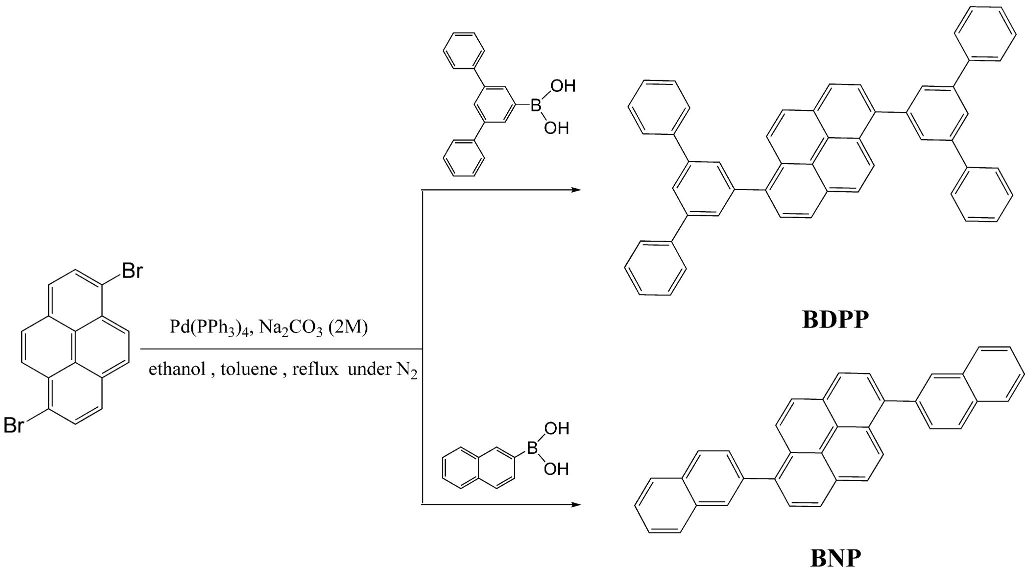

Fig. 1. Synthetic route of BDPP and BNP.

larger π-delocalization due to the more coplanar configuration compared to BDPP. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of BDPP are almost concentrated on the pyrene backbone (Fig. 2a), which implies that its emission and absorption are mostly controlled by the pyrene unit. As shown in Fig. 2b, the 2-naphthyl groups make a considerable contribution to the HOMO and LUMO of BNP.

3.2. Photophysical properties

The absorption and photoluminescence (PL) spectra of BDPP and BNP were measured in dilute dichloromethane solution (Fig. 3), the corresponding data were summarized in Table 1. The absorption spectra of BDPP and BNP exhibit the characteristic vibronic pattern of the substituted pyrene group (λ_{max} = 361 nm for BDPP, λ_{max} = 365 nm for BNP). The additional absorption bands (λ_{max} = 255 nm, 275 nm, 287 nm for BDPP, λ_{max} = 226 nm, 249 nm, 285 nm for BNP) can be assigned to the substituents at the 1- and 6-positions of the central pyrene core. Upon excitation of the pyrene moiety (at 361 nm for BDPP, at 365 nm for BNP), the PL spectra show structureless emission peaks at 404 nm and 413 nm for BDPP and BNP, respectively. It can be found that the absorption and PL spectra of BNP show obvious red-shift compared to those of BDPP, which can be attributed to the larger π-delocalization of BNP according to the quantum chemical calculation results. The PL quantum yields in dichloromethane solution were measured to be 0.82 for BDPP and 0.87 for BNP, respectively, by using 9,10-diphenylanthrancene as the reference standard [16]. The PL spectra of the solid thin films red-shifted 37 nm and 51 nm compared to those of dichloromethane solution for BDPP and BNP, respectively. Whereas the fluorescence emission of the films (λ_{max} = 441 nm for BDPP, λ_{max} = 464 nm for BNP) are obvious shorter than that of the typical pyrene excimer emission (480–500 nm) [17]. Thus, the red-shift is probably due to the aggregation of pyrene moiety and the difference in dielectric constant of the environment [13,18].

3.3. Electrochemical properties

The electrochemical properties of BDPP and BNP were investigated by cyclic voltammetry in CH_2Cl_2 solution containing tetrabutylammonium hexafluorophosphate (0.1 M) with a scan rate of 0.05 V/s. The electrolytic cell was a conventional three-electrode cell consisting of a Pt working electrode, a Pt wire counter electrode and Ag/AgCl reference electrode. As shown in Fig. 4, both BDPP and BNP exhibit reversible oxidation process with half-wave oxidation potentials ($E^{ox}_{1/2}$) of 1.29 V and 1.25 V (vs. Ag/AgCl), respectively. The HOMO energy levels were calculated by using the energy level value of −4.8 eV for ferrocene (Fc) with respect to zero vacuum level [19–21]. The LUMO energy levels were estimated according to the HOMO energy level values in combination with the band gaps derived from the absorption band edges (Table 1).

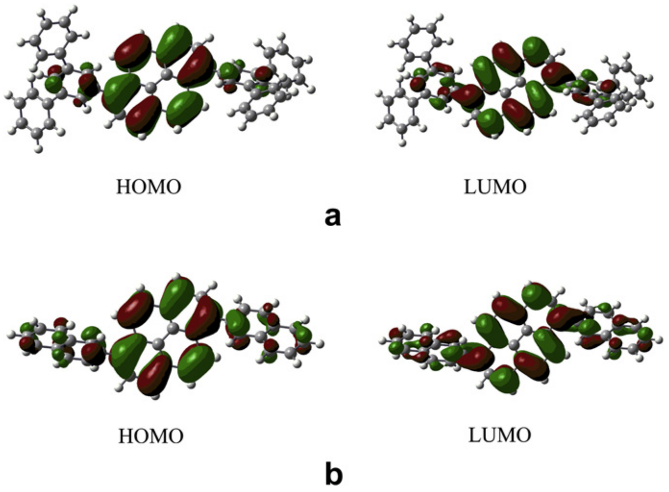

Fig. 2. Calculated stereostructures and HOMO and LUMO for BDPP (a) and BNP (b).

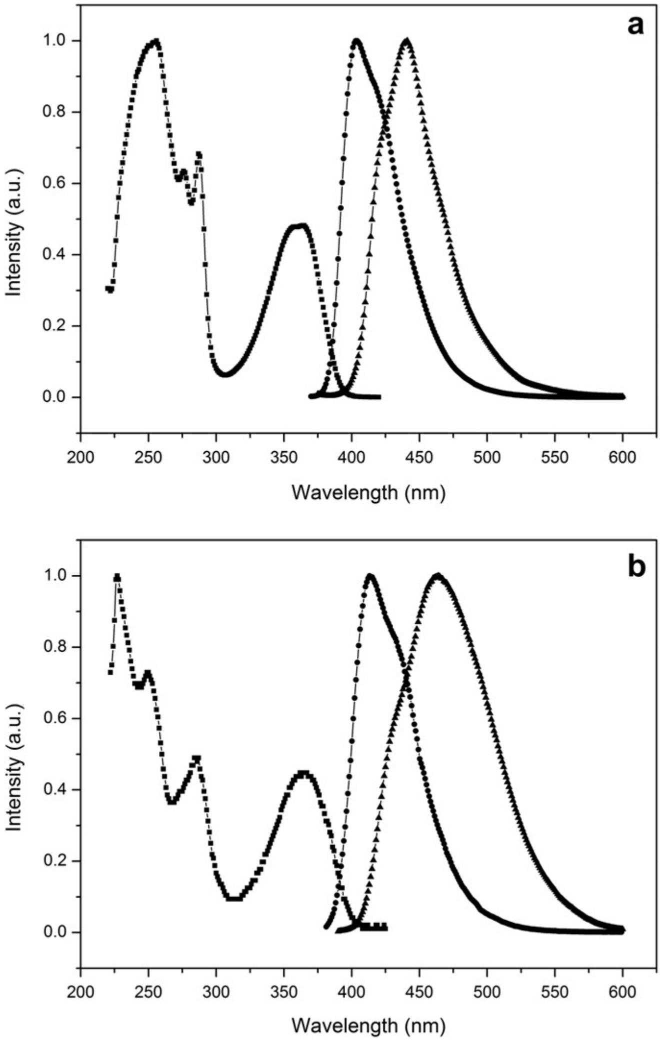

Fig. 3. The absorption (-■- in CH_2Cl_2 solution) and photoluminescence (-•- in CH_2Cl_2 solution, -▲- solid thin film) spectra of BDPP (a) and BNP (b).

Table 1
Key physical data of BDPP and BNP.

Compounds	Absorption (nm)	PL (nm)		HOMO (eV)	LUMO (eV)	T_g (°C)
		Solution[a]	Film[b]			
BDPP	255, 275, 287, 361	404	441	−5.62	−2.47	139
BNP	226, 249, 285, 365	413	464	−5.58	−2.51	n.o.

n.o. = Not observed.
[a] In dilute dichloromethane solution.
[b] Prepared by vacuum deposition (100 nm).

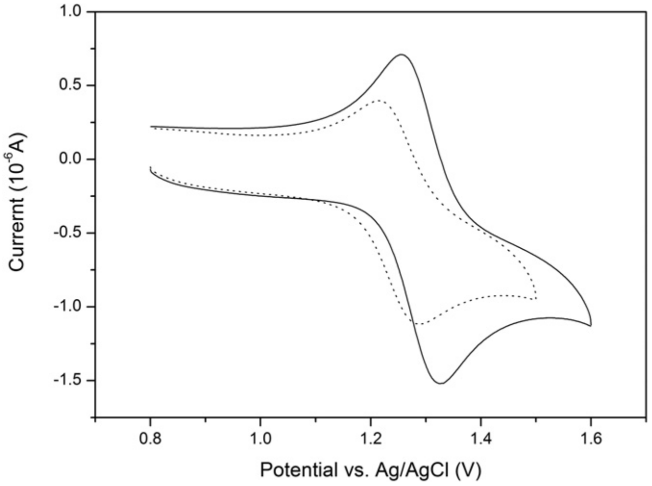

Fig. 4. The cyclic voltammograms of BDPP (solid line) and BNP (dot line).

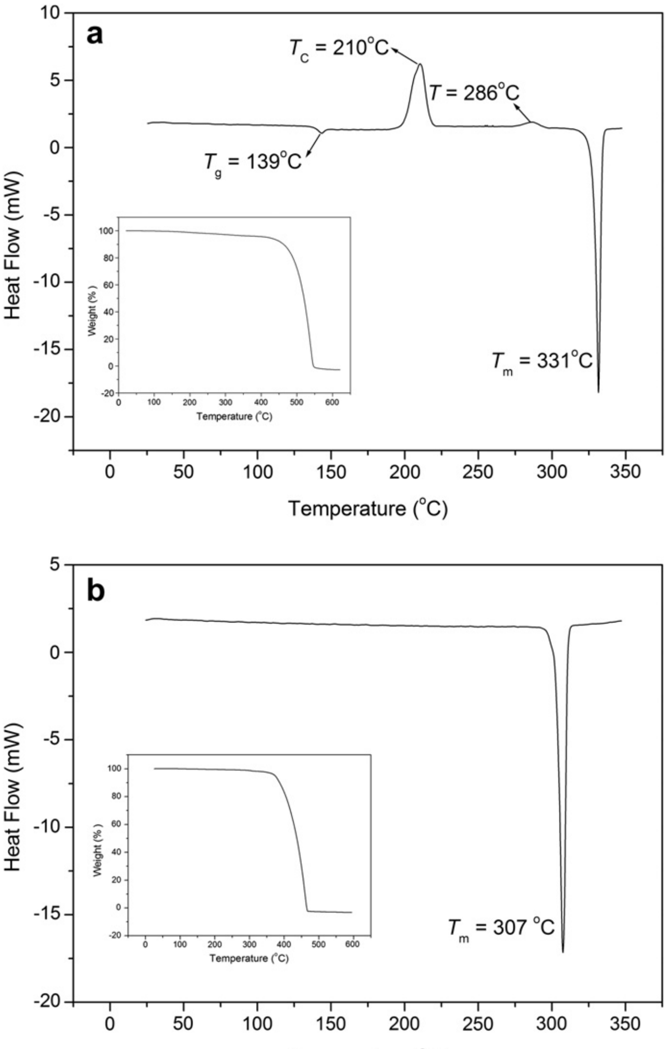

Fig. 5. The DSC and TGA (insert) curves of BDPP (a) and BNP (b).

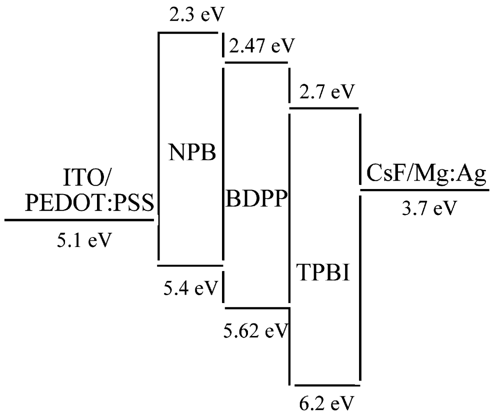

Fig. 6. The relative energy level alignments of the BDPP based device.

3.4. Thermal properties

The thermal properties of BDPP and BNP were investigated using thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) with a heating rate of 10 °C/min under the nitrogen atmosphere. Both the two compounds exhibit high thermal stability, the decomposition temperatures (T_d) which correspond to a 3% weight loss upon heating during TGA, are around 440 °C and 391 °C for BDPP and BNP, respectively. DSC measurements were performed from 25 °C to 350 °C under the nitrogen atmosphere. BDPP melted at 331 °C (T_m) upon the first heating process, and then was rapidly cooled by liquid nitrogen to form a amorphous glassy state. When the glassy sample was heated again, a glass transition occurred at 139 °C (T_g) (Fig. 5a). The high T_g of BDPP is presumably due to its non-coplanar structure. Upon further heating beyond T_g, an exothermic crystallization was observed at 210 °C (T_c), and then an exothermic solid–solid phase transition was observed at 286 °C. For BNP, the T_m appeared at 307 °C, however, no glass transition was observed (Fig. 5b).

3.5. Electroluminescent properties

For the higher performance of BDPP compared to BNP, we fabricated the non-doped device based on BDPP with the configuration of

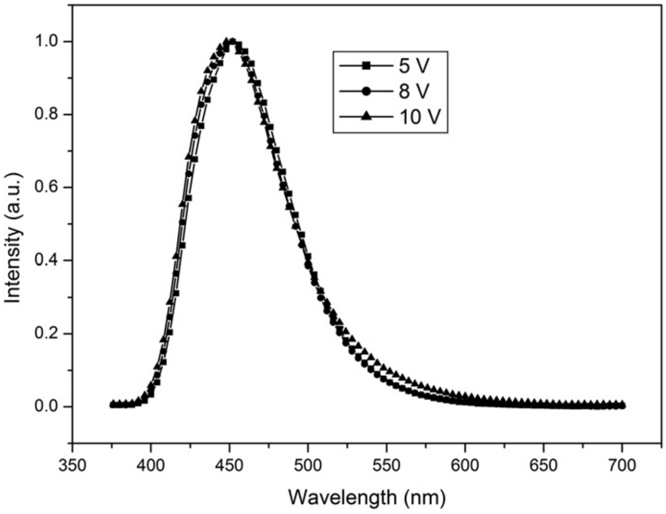

Fig. 7. The EL spectra of the BDPP based device at different applied voltages.

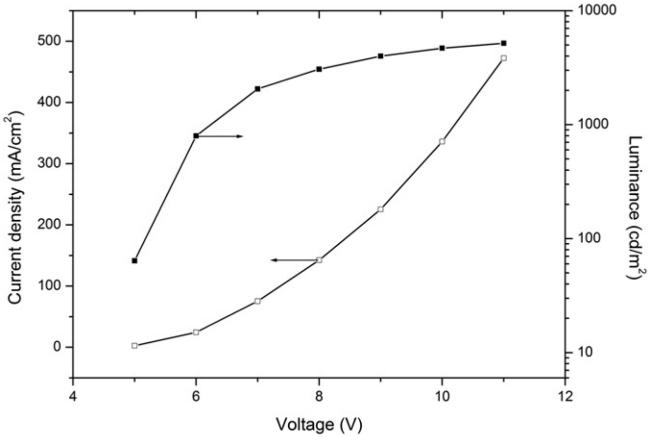

Fig. 8. The current density-voltage-luminance characteristics of the BDPP based device.

ITO/PEDOT:PSS (30 nm)/NPB (30 nm)/BDPP (30 nm)/TPBI (30 nm)/CsF (2 nm)/Mg:Ag. ITO (indium-tin-oxide) and CsF/Mg:Ag are the anode and the cathode, respectively; PEDOT:PSS is the hole injection layer; 4,4′-bis[N-(1-naphthyl)-N-phenyl amino] biphenyl (NPB) is the hole-transporting layer; 1,3,5-tris(N-phenylbenzimidazol)benzene (TPBI) is used as the electron transporting and hole blocking layer; BDPP was used as the emitting layer. The relative energy level alignments of the device are shown in Fig. 6.

Fig. 7 shows the normalized EL spectra of this device at different applied voltages. The emission peaks are all at 451 nm, and the EL spectra show no emission at longer wavelength from the exciplex species, which could be attributed to the non-coplanar structure of BDPP because of introducing the bulky 3,5-diphenylphenyl substituents. The 1931 CIE coordinates (0.15, 0.11) of this device are very close to the NTSC blue standard. While increasing the applied voltage from 5 V to 10 V, the EL spectra and the CIE coordinates show very little change, which is highly desirable for OLEDs.

The current density-voltage-luminance characteristics of the device are shown in Fig. 8. The turn-on voltage (at a luminance of 1.0 cd/m^2) is about 4.5 V, and the maximum luminance is 5184 cd/m^2 at a voltage of 11 V with a current density of 473 mA/cm^2. The device achieves a maximum efficiency of 3.26 cd/A at 6 V with a current density of 24.5 mA/cm^2 and a luminance of 798 cd/m^2. The efficiency is comparable to the best of the non-doped blue OLEDs based on pyrene derivatives [13,14]. The high EL efficiency may be attributed to the high fluorescence quantum yield and non-coplanar structure of BDPP. In addition, the small carriers injection barriers, 0.22 eV at NPB/BDPP interface and 0.23 eV at BDPP/TPBI interface (Fig. 6), can facilitate the electron and hole injection into the emitting layer and result in a high EL efficiency.

4. Conclusions

In conclusion, two novel pyrene derivatives BDPP and BNP were synthesized and characterized. Both the compounds BDPP and BNP exhibit bright blue emission with high fluorescence quantum yields. The quantum chemical calculations, photophysical properties and thermal properties show BDPP has a higher performance compared to BNP. The non-doped device based on BDPP exhibits very stable deep-blue emission with the CIE coordinates of (0.15, 0.11) and a maximum efficiency of 3.26 cd/A. The high efficiency and stability of the device indicate that BDPP is a promising emitting material for non-doped deep-blue OLEDs.

Acknowledgment

This work was supported financially by the National Natural Science Foundation of China (NO.20872057, 20902043 and 20872058).

References

[1] Tang CW, Van Slyke SA. Organic electroluminescence diode. Applied Physics Letter 1987;51:913–5.
[2] Burroughes JH, Bradley DDC, Brown AR, Marks RN, Friend RH, Burn PL, et al. Light-emitting diodes based on conjugated polymers. Nature 1990;347:539–41.
[3] Kim YH, Jeong HC, Kim SH, Yang K, Kwon SK. High-purity-blue and high-efficiency electroluminescent devices based on anthracene. Advanced Functional Materials 2005;15:1799–805.
[4] Zheng CJ, Zhao WM, Wang ZQ, Huang D, Zhang XH, Lee CS, et al. Highly efficient non-doped deep-blue organic light-emitting diodes based on anthracene derivatives. Journal of Materials Chemistry 2010;20:1560–6.
[5] Kim YH, Shin DC, Kim SH, ko CH, Yu HS, Kwon SK, et al. Novel blue emitting material with high color purity. Advanced Materials 2001;13:1690–3.
[6] Shen WJ, Dodda R, Wu CC, Wu FI, Liu TH, Shu CF, et al. Spirobifluorene-linked bianthracene: a efficient blue emitter with pronounced thermal stability. Chemistry of Materials 2004;16:930–4.
[7] Gao ZQ, Li ZH, Xia PF, Wong MS, Cheah KW, Chen CH, et al. Efficient deep-blue organic light-emitting diodes: arylamine-substituted oligofluorenes. Advanced Functional Materials 2007;17:3194–9.
[8] Chien CH, Chen CK, Hsu CF, Shu CF, Chou PT, Lai CH. Multifunctional deep-blue emitter comprising an anthracene core and terminal triphenylphosphine oxide groups. Advanced Functional Materials 2009;19:560–6.
[9] Liao SH, Shiu JR, Liu SW, Yeh SJ, Chen YH, Chen CT, et al. Hydroxynaphthyridine-derived group III metal chelates: wide band gap and deep blue analogues of green Alq$_3$ (Tris(8-hydroxyquinolate)aluminum) and their versatile applications for organic light-emitting diodes. Journal of American Chemical Society 2009;131:763–77.
[10] Wu CH, Chien CH, Hsu FM, Shih PI, Shu CF. Efficient non-doped blue-light-emitting diodes incorporating an anthracene derivative end-capped with fluorene groups. Journal of Materials Chemistry 2009;19:1464–70.
[11] Jia WL, Cormick TM, Liu QD, Fukutani H, Motala M, Wang RY, et al. Diarylamino functionalized pyrene derivatives for use in blue OLEDs and complex formation. Journal of Materials Chemistry 2004;14:3344–50.
[12] Tang C, Liu F, Xia YJ, Lin J, Xie HL, Huang W, et al. Fluorene-substituted pyrenes–novel pyrene derivative as emitters in nondoped blue OLEDs. Organic Electronics 2006;7:155–62.
[13] Wu KC, Ku PJ, Lin CS, Shih HT, Wu FI, Huang MJ, et al. The photophysical properties of dipyrenyl benzenes and their application as exceedingly efficient blue emitters for electroluminescent devices. Advanced Functional Materials 2008;18:67–75.
[14] Wang ZQ, Xu C, Wang WZ, Fu WJ, Niu LB, Ji BM. Highly efficient undoped deep-blue electroluminescent device based on a novel pyrene derivative. Solid-State Electronics 2010;54:524–6.
[15] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, et al. Gaussian 03, revision A1. Pittsburgh, PA: Gaussian Inc.; 2003.
[16] Danel K, Huang TH, Lin JT, Tao YT, Chuen CH. Blue-emitting anthracenes with end-capping diarylamines. Chemistry Materials 2002;14:3860–5.
[17] Winnik FM. Photophysics of preassociated pyrenes in aqueous polymer solutions and in other organized media. Chemical Reviews 1993;93:587–614.
[18] Salbeck J, Yu N, Baner J, WeissÖrtel F, Bestgen H. Low molecular organic glasses for blue electroluminescence. Synthetic Metals 1997;91:209–15.
[19] Pommerehne J, Vestweber H, Guss W, Mahrt RF, Porsch M, Daub J. Efficient two layer leds on a polymer blend basis. Advanced Materials 1995;7:551–4.
[20] Thelakkat M, Schmidt HW. Synthesis and properties of novel derivatives of 1,3,5-tris(diarylamino)benzenes for electroluminescent devices. Advanced Materials 1998;10:219–23.
[21] Zhang XW, Gao J, Yang CL, Zhu LN, Li ZA, Zhang KJ, et al. Highly efficient iridium(III) complexes with diphenylquinoline ligands for organic light-emitting diodes: synthesis and effect of fluorinated substitutes on electrochemistry, photophysics and electroluminescence. Journal of Organometallic Chemistry 2006;691:4312–9.