Pure blue and white light electroluminescence in a multilayer organic light-emitting diode using a new blue emitter*

Wei Na(魏 娜)[a)b)], Guo Kun-Ping(郭坤平)[a)b)], Zhou Peng-Chao(周朋超)[a)b)], Yu Jian-Ning(于建宁)[b)], Wei Bin(魏 斌)[b)], and Zhang Jian-Hua(张建华)[b)†]

[a)] *School of Materials Science and Engineering, Shanghai University, Shanghai* 200072, *China*
[b)] *Key Laboratory of Advanced Display and System Applications of Ministry of Education, Shanghai University, Shanghai* 200072, *China*

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We characterized the 6,12-bis{[N-(3,4-dimethylphenyl)-N-(2,4,5-trimethylphenyl)]amino} chrysene (BmPAC), which has been proven to be a blue fluorescent emission with high EL efficiency. The blue fluorescent device exhibits good performance with an external quantum efficiency of 5.8% and current efficiency of 8.9 cd/A, respectively. Using BmPAC, we also demonstrate a hybrid phosphorescence/fluorescence white organic light-emitting device (WOLED) with high efficiency of 36.3 cd/A. In order to improve the relative intensity of blue light, we plus a blue light-emitting layer (BEML) in front of the orange light emitting layer (YEML) to take advantage of the excess singlet excitons. With the new emitting layer of BEML/YEML/BEML, we demonstrate the fluorescence/phosphorescence/fluorescence WOLED exhibits good performance with a current efficiency of 47 cd/A and an enhanced relative intensity of blue light.

Keywords: BmPAC, high efficiency, blue organic light emitting diodes, white organic light-emitting diodes

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1. Introduction

White organic light-emitting diodes (WOLEDs) have been extensively studied due to the unique merits of fabrication of large-scale for solid-state lighting sources and full-color displays.[1–5] At present, WOLEDs have already found application in color flat panel displays. Nevertheless, in the illuminant and lighting domains, the understanding of the performance characteristics of WOLEDs (e.g., efficiency, stability, and lifetime) is still not sufficient.[6,7]

The luminous efficiency of organic light emitting diodes (OLEDs) has been greatly improved in recent years.[8–12] Certainly, very high efficiency in OLEDs cannot be realized without the use of phosphorescent OLED technology since all electrically generated singlet and triplet excitons can be harvested by phosphorescent emitters.[13–16] However, the development of phosphorescent WOLEDs is severely limited by the absence of efficient blue phosphorescent emitters for their intrinsic properties, for example: the operational lifetimes are not as long as expected for this class of materials, the cost is comparatively high, and blue phosphorescent emitters are relatively rare compared with the large number of green or red phosphorescent emitters. In addition, the external quantum efficiency (EQE) of true blue OLEDs is not so high and they often exhibit a serious efficiency roll-off at high driving current density due to triplet-triplet annihilation.[17] In 2006, Forrest *et al.* proposed a hybrid fluorescent/phosphorescent route to realize efficient WOLEDs.[1] In this design, high efficiency WOLEDs can be achieved with the blue fluorescence substituting for the blue phosphors. Based on the above, the enthusiasm of electro-phosphorescence (PhOLEDs) might diminish and that for electro-fluorescent OLEDs might revive instead.[17–19]

Recently, searching for high performance materials, driving the further development of OLEDs, has gained increasing attention. There is a considerable need for the preparation of novel pure-blue light-emitting materials exhibiting high efficiency. In this paper, we characterize the 6,12-bis{[N-(3,4-dimethylphenyl)-N-(2,4,5-trimethylphenyl)]amino}chrysene (BmPAC), which has been proven to be a blue emission with high efficiency. In addition, a hybrid WOLED consisted of blue fluorescent light emitting layer (BEML) /yellow phosphorescent light emitting layer (YEML)/BEML was presented for high efficiency and mild roll-off properties at high luminance.

2. Experiment

2.1. Materials and synthesis

In this paper, we selected the blue emitter (BmPAC) as the dopant to the ADN. Fig. 1(a) illustrates the chemical structure of the fluorescent material BmPAC that we have synthesized, the detailed synthetic procedure is depicted in Fig. 1(b). In this compound, with the aim of obtaining highly efficient fluorescence, chrysene with a super big aromatic ring as core center

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†Corresponding author. E-mail: jhzhang@staff.shu.edu.cn

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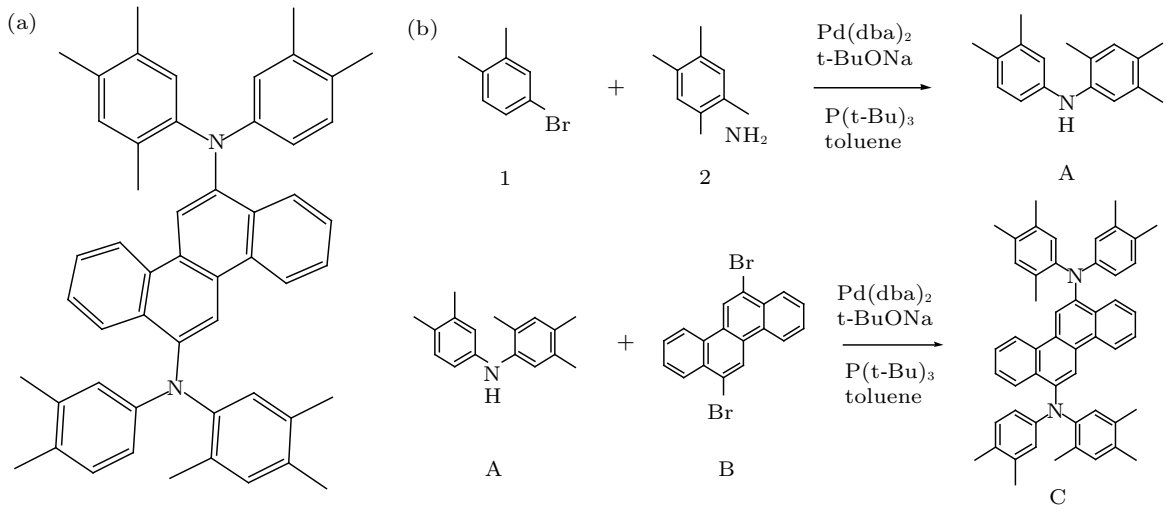


Fig. 1. (a) Molecular structure of fluorescent material BmPAC. (b) Synthesis process of BmPAC.

was introduced, and a diphenylamine derivative was connected at position 6 and 12 of chrysene to enhance conductivity and stability. This compound was obtained via a facile two step preparation, the detailed procedures are as follows.

We dissolved 1.85 g (10 mmol) of 3,4-dimethylphenyl,1.35 g (10 mmol) of 2,4,5-trimethylphenyl,1.06 g (11 mmol) of sodium tert-butoxide in 50 ml of toluene in a 100 ml round flask. Then, 0.46 g (0.5 mmol) of Palladium dibenzyliden amine and 0.75 ml (1.15 mmol) of tert-butyl phosphorus were added into the flask. The mixture was refluxed for 12 h under a nitrogen flow. After the reaction was completed, the mixture was washed with water, the organic layer was treated with a Silica gel column, obtaining a compound A of 1.91 g (yield: 80%). We dissolved 4.78 g (20 mmol) of compound A, 3.86 g (10 mmol) of compound B, 2.12 g (22 mmol) of sodium tert-butoxide in 50 ml of toluene in a 100 ml round flask. Then 0.92 g (1 mmol) of Palladium dibenzyliden amine and 1.5 ml (2.3 mmol) of tert-butyl phosphorus were added into the flask. The mixture was refluxed for 12 h under a nitrogen flow. After the reaction was completed, the mixture was filtered and then washed with water and ethanol, obtaining a compound C of 5.97 g (yield: 85%).

2.2. OLED fabrication and measurement

We have fabricated OLEDs in three different configurations, named: devices A, B, and C. The architectures of these devices are shown as follows:

Device A: ITO/2T-NATA(45 nm)/NPB(3 nm)/TCTA (2 nm)/ADN:(3 wt %)BmPAC(15 nm)/Bphen(30 nm)/LiF (0.3 nm)/Al(100 nm).

Device B: ITO/2T-NATA(45 nm)/NPB(3 nm)/TCTA (2 nm)/Ga(pyimd)$_3$:(10 wt %)(bt)$_2$Ir(acac)(2 nm)/Ga(pyimd)$_3$ (6 nm)/ADN:(1 wt%)BmPAC(5 nm)/Ga(pyimd)$_3$(2 nm)/Bphen (28 nm)/LiF(0.3 nm)/Al (100 nm).

Device C: ITO/2T-NATA(45 nm)/NPB(3 nm)/TCTA (2 nm)/ADN:(1 wt %)BmPAC(10 nm)/Ga(pyimd)$_3$(6 nm) /Ga(pyimd)$_3$:(10 wt %)(bt)$_2$Ir(acac)(2 nm)/Ga(pyimd)$_3$(6 nm) /ADN:(1 wt %)BmPAC(5 nm)/Ga(pyimd)$_3$(2 nm)/Bphen (28 nm)/LiF(0.3 nm)/Al(100 nm).

In these devices, 4,4,4-{N-(2-naphthyl)-N-phenylamino}-triphenylamine (2T-NATA) is used as the hole-injection layer (HIL), N, N′-diphenyl-N, N′-bis(1-naphthyl)-1, 1′-biphenyl-4, 4″-diamine(NPB) acts as the hole-transport layer (HTL) and 4,7-diphenyl-1,10-phenanthroline (Bphen) acts as the electron-transport layer (ETL). In addition, we utilize 1,4-bis[N-(1-naphthyl)-N′-phenylamino]-4,4-diamine/9,10-di(2-naphthyl)anthracene(ADN) doped in 1 wt% BmPAC, as the blue light emitting layer (BEML). Yellow lumophore bis(2-phenylbenzothiazolato)(acetylacetonate)iridium bt$_2$Ir(acac) is doped into host material tris [2-(2-pyridyl)imidazole]gallium(III) Ga(pyimd)$_3$ as the yellow emitting layer (YEML). With the energy gap of the two hosts, there was exciton-blocking layer of Ga(pyimd)$_3$ between the emissive layers to confine the diffusion of excitons and improve the stability of the Commission Internationale de L'Eclairage (CIE) coordinates.[20] The device architectures of devices A, B, and C are shown in Fig. 2.

The OLED devices were fabricated by conventional vacuum deposition of the organic layers and cathode onto an ITO (15 Ω/sheet, 150 nm) coated glass substrate under a base pressure lower than 2×10^{-4} Torr (1 Torr = 1.33322×10^2 Pa). The substrates were successively cleaned in detergent, de-ionized water, acetone, and isopropanol. Immediately prior to loading into a custom-made high vacuum thermal evaporation chamber, the substrates were exposed to a UV-ozone environment for 15 min. The typical deposition rates were 0.6 Å/s, 0.1 Å/s, and 5.0 Å/s for organic materials, lithium fluoride (LiF), and aluminum (Al), respectively.

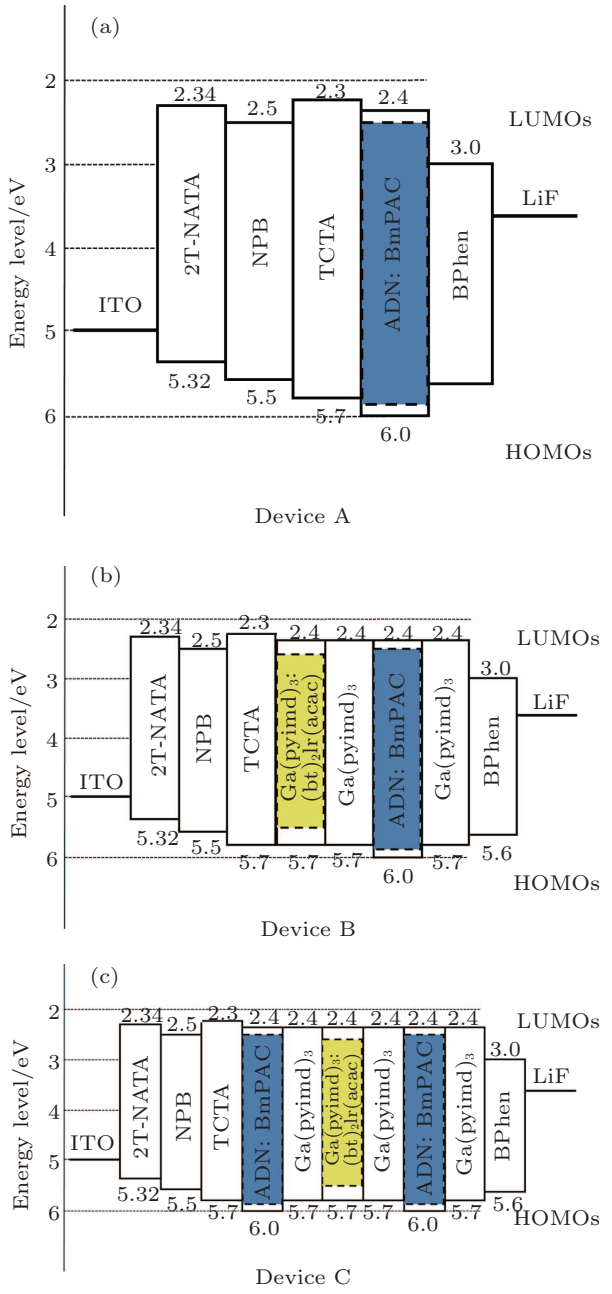


Fig. 2. (color online) The device structures of OLED and energy levels of organic functional materials. (a) Device A; (b) device B; (c) device C.

The photoluminescence spectra were recorded on a HITACHI F-4500 florescence spectrophotometer. The current–voltage–luminescence characteristics were measured by a Keithley 2400 source meter and a PR-650 luminance color meter. The luminance and spectra of each device were measured in the direction perpendicular to the substrate.

3. Results and discussion

The photophysical properties of the 3 wt% BmPAC doped in ADN film (120 nm) and pure BmPAC film (120 nm) were measured, as shown in Fig. 3. The PL peak of the doped BmPAC is 452 nm while the none-doped one is 462 nm, and we could find a significant blue shift.

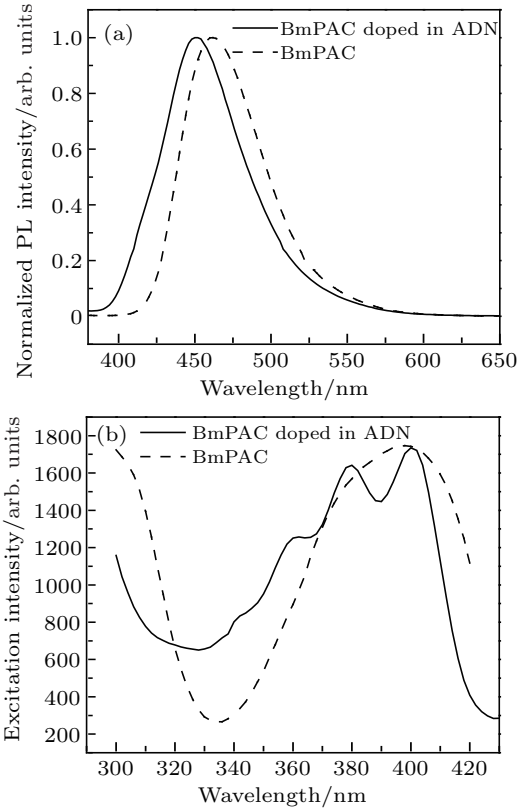


Fig. 3. (a) PL spectrum of 3 wt% BmPAC doped in ADN and pure BmPAC (120 nm). (b) Excitation spectrum of 3 wt% BmPAC doped in ADN and pure BmPAC (120 nm).

Figure 4 reveals the electroluminescent (EL) properties of device A, including current density–voltage–luminance (*J*–*V*–*L*) characteristics, external quantum efficiency characteristics and EL spectra, current efficiency–voltage–power efficiency characteristics. A dominant emission with a peak at $\lambda_{max} = 464$ nm is observed at all brightnesses, which is the location of the emission peak from BmPAC. The highest luminance of 13500 cd/m^2 at 8.5 V, the highest current efficiency of 8.9 cd/A, and the maximum EQE of 5.8% (17.6 mA/cm^2) are arrived, which is a respectable result among blue fluorescent devices.[21–23]

To further study the light-emitting characteristics of BmPAC in WOLEDs, we designed and fabricated device B. The device performances are shown in Fig. 5. The maximum current efficiency of 36.3 cd/A and power efficiency of 22.9 lm/w (11.4% external quantum efficiency) are obtained, respectively. The maximum luminance is 11820 cd/m^2. Additionally, device B shows a current efficiency of 34.4 cd/A at 100 cd/m^2, or 35.6 cd/A at 1000 cd/m^2. The normalized EL spectra of device B at different luminance have been shown. For ease of analysis, the spectra are normalized at a wavelength of 564 nm, which is the location of all emission peaks. For device B, a dominant emission with a peak at $\lambda_{max} =$ 564 nm accompanied by a vibronic sideband at about 606 nm and a slight emission at the wavelength of 460 nm are observed at all brightnesses. Obviously, the dominant emission

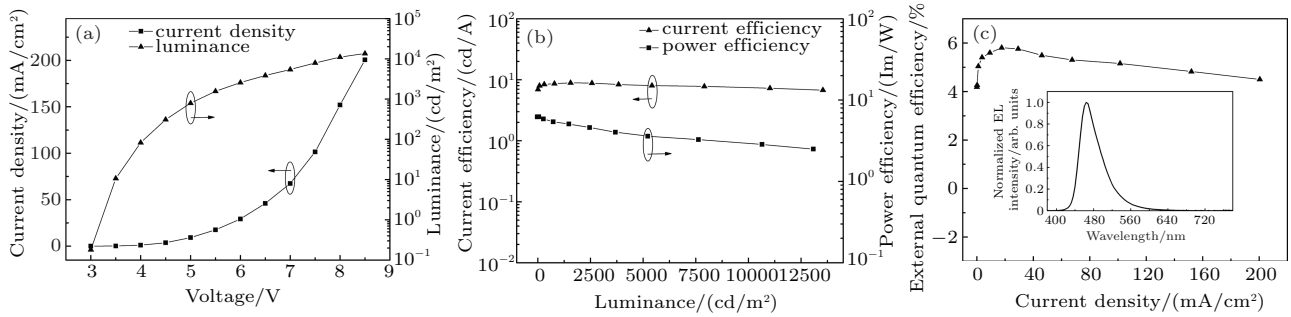


Fig. 4. (a) Current density and luminance plotted against the applied voltage for device A. (b) Current efficiency and power efficiency plotted against luminance for device A. (c) External quantum efficiency plotted current density for device A. Inset: spectra of device A at the luminance of 100 cd/m^2.

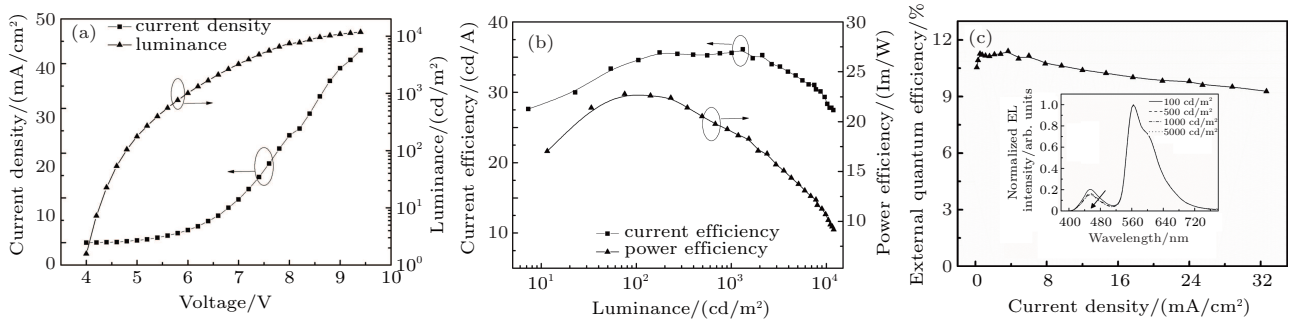


Fig. 5. (a) Current density and luminance plotted against the applied voltage for device B. (b) Current efficiency and power efficiency plotted against luminance for device B. (c) External quantum efficiency plotted current density for device B. Inset: spectra of device B.

with a vibronic sideband is ascribed to $(bt)_2Ir(acac)$, while the slight emission is ascribed to BmPAC. Furthermore, no unexpected emission is observed, indicating efficient energy transfer both from $Ga(pyimd)_3$ to $(bt)_2Ir(acac)$ and from ADN to BmPAC.[23–25] The spectra are normalized at the peak wavelength of the orange light. We find that the intensity of orange emission is about five times as high as that of blue emission. The higher concentration and stronger trapping ability of $(bt)_2Ir(acac)$ compared with BmPAC is the main reason for the higher intensity of the orange emission. As the brightness increases, there is a certain degree of reduction of blue emission, which is dominated by the shift of the recombination area. Specifically, the initial recombination concentrates lies to the $Ga(pyimd)_3$/ADN interfaces due to the relatively low electron mobility under low-voltage, it then extends to the subsequent layers ($Ga(pyimd)_3$ and YEML here) because the electric field strongly enhances the electron mobility of Bphen as the voltage increases.[12]

In order to increase the relative intensity of blue light or solve the problem of weak blue light caused by the transfer of exciton recombination zone, we designed and fabricated device C. Considering the diffusions for both singlet excitons and triplet excitons,[26,27] the singlet and triplet excitons were transferred to BEML and YEML, respectively. Additionally, parts of the singlet excitons were transferred to YEML and then annihilated. Compared with device B, device C added another blue light-emitting layer, on the left side of orange layer, which was used to recycle the excess exciton to give more blue light.

Figure 6 illustrates the characteristics of device C, which exhibits a lower turn-on voltage compared with devices A and B. The turn-on voltage for device C is about 2.6 V, while 3.5 V for device A and 4 V for device B. This result suggests that there is an optimal energy level match between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of each organic layer in device C.[28] The HOMO level of TCTA is intermediate between those of NPB and ADN, there is a large barrier to hole injection from NPB directly into $Ga(pyimd)_3$, whereas there are two smaller barriers from NPB into TCTA and from TCTA into ADN. The maximum current efficiency and power efficiency is 47 cd/A, 56.8 lm/W (16.3% external quantum efficiency), respectively. The current efficiency is 40.2 cd/A at 100 cd/m^2, or 36.1 cd/A at 1000 cd/m^2, which is a relatively higher result for WOLEDs and much higher than that of device B. Improved efficiency can be attributed to the increased utilization of excitons, the added BEML used the singlet excitons, which is wasted in device B, to re-emit blue light. This is also the reason for the enhancement of the blue light in device C, in which the orange light is just 2.5 times more than the blue. Interestingly, the emission from blue lumophore, despite being weak with respect to the orange light, has a dramatic effect on the CIE coordinates. The CIE coordinates for devices held at a luminance of 100 cd/m^2 are (0.46, 0.43) and (0.40, 0.40) for devices B and C, respectively. Obviously, the added blue light-emitting layer plays a crucial role in enhancing the quality of the lighting source.

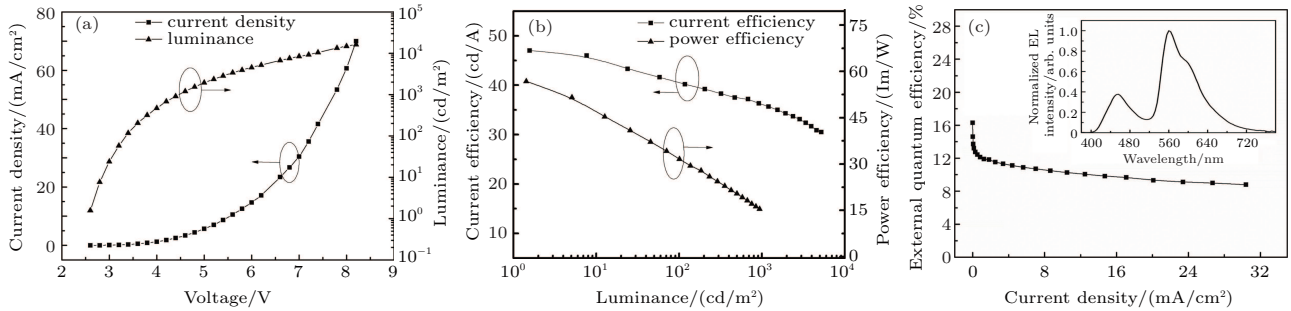


Fig. 6. (a) Current density and luminance plotted against applied voltage for device C. (b) Current efficiency and power efficiency plotted against luminance for device C. (c) Extern al quantum efficiency plotted current density for device C. Inset: spectra of device C at the luminance of 100 cd/m^2.

Furthermore, the luminance of device C is 5200 cd/m^2 with an efficiency of 30.5 cd/A at 17.1 mA/cm^2 (9.68% external quantum efficiency). A comparative mild roll-off property is presented in Fig. 6,[29], which corresponds to the wide charge carrier distribution and extended exciton recombination region due to the BEML/YEML/BEML structure.

4. Conclusions

In summary, we have characterized the BmPAC, which has been proven to be a superior blue fluorescent material with high EL efficiency and has provided the opportunity of the blue material. The current efficiency and external quantum efficiency of the blue device (device A) reached 8.9 cd/A and 5.8%, respectively, which is a respectable result among blue fluorescent devices. In addition, we use the blue material to achieve a high efficiency WOLED, with the emitting layer of BEML/YEML/BEML. The maximum current efficiency and external quantum efficiency were achieved 47 cd/A and 16.3%, respectively. The luminance of device C is 5200 cd/m^2 with an efficiency of 30.5 cd/A at 17.1 mA/cm^2(9.68% external quantum efficiency), a comparative mild roll-off property is also presented. These results demonstrate that the emitting layer of BEML/YEML/BEML represents a promising structure in achieving high brightness, high efficiency and stability for WOLED. Nevertheless, further research of the novel blue material BmPAC and the improvement of physical properties for the new WOLED structure are urgently needed.

References

[1] Sun Y, Giebink N C, Kanno H, Ma B, Thompson M E and Forrest S R 2006 *Nature* **440** 908
[2] So F, Kido J and Burrows P 2008 *Mrs. Bull.* **33** 663
[3] Service R F 2005 *Science* **310** 1762
[4] Kido J, Kimura M and Nagai K 1995 *Science* **267** 1332
[5] D'Andrade B W and Forrest S R 2004 *Adv. Mater.* **16** 1585
[6] Wan J, Zheng C J, Fung M K, Liu X K, Lee C S and Zhang X H 2012 *J. Mater. Chem.* **22** 4502
[7] Zhang L J, Hua Y L, Wu X M, Wang Y and Yin S G 2008 *Chin. Phys. B* **17** 3097
[8] Yu J N, Zhang M Y, Li C, Shang Y Z, Lü Y F, Wei B and Huang W 2012 *Chin. Phys. B* **21** 083303
[9] Reineke S, Lindner F, Schwartz G, Seidler N, Walzer K, Lüsem B and Leo K 2009 *Nature* **459** 234
[10] Schwartz G, Reineke S, Rosenow T C, Walzer K and Leo K 2009 *Adv. Funct. Mater.* **19** 1319
[11] Hou L D, Li W, Duan L and Qiu Y 2008 *Chin. Phys. Lett.* **25** 1457
[12] Kondakova M E, Deaton J C, Pawlik T D and Giesen D J 2010 *J. Appl. Phys.* **107** 014515
[13] Wang Q, Ding J Q, Ma D G, Cheng Y X, Wang L X, Jing X B and Wang F S 2009 *Adv. Funct. Mater.* **19** 84
[14] Sun Y and Forrest S R 2007 *Appl. Phys. Lett.* **91** 263503
[15] Ma B, Djurovich P I, Garon S, Alleyne B and Thompson M E 2006 *Adv. Funct. Mater.* **16** 2438
[16] Wang Q, Ding J Q, Cheng Y X, Wang L X and Ma D G 2009 *J. Phys. D: Appl. Phys.* **42** 065106
[17] Wei B, Liu J Z, Zhang Y, Zhang J H, Peng H N, Fan H L, He Y B and Gao X C 2010 *Adv. Funct. Mater.* **20** 2448
[18] Sivasubramaniam V, Brodkorb F, Hanning S, Loebl H P, Elsbergen V V, Boerner H, Scherf U and Kreyenschmidt M 2009 *J. Fluor. Chem.* **130** 640
[19] Chang C F, Cheng Y M, Chi Y, Chiu Y C, Lin C C, Lee G H, Chou P T, Chen C C, Chang C H and Wu C C 2008 *Angew. Chem. Int. Ed.* **47** 4542
[20] Lei G T, Wang L D and Qiu Y 2006 *Appl. Phys. Lett.* **88** 103508
[21] Chi C C, Chiang C L, Liu S W, Yueh H, Chen C T and Chen C T 2009 *J. Mater. Chem.* **19** 5561
[22] Wei Y and Chen C T 2007 *J. Am. Chem. Soc.* **129** 7478
[23] Yu J N, Lin H, Wang F F, Lin Y, Zhang J H, Zhang H, Wang Z X and Wei B 2012 *J. Mater. Chem.* **22** 22097
[24] Park Y S, Jeong W I and Kim J J 2011 *J. Appl. Phys.* **110** 124519
[25] O'Brien D F, Baldo M A, Thompson M E and Forrest S R 1999 *Appl. Phys. Lett.* **74** 442
[26] Hofmann S, Rosenow T C, Gather M C, Lüsem B and Leo K 2012 *Phys. Rev. B* **85** 245209
[27] Lebental M, Choukri H, Chénais S, Forget S, Siove A, Geffroy B and Tutiš E 2009 *Phys. Rev. B* **79** 165318
[28] Kanno H, Ishikawa K, Nishio Y, Endo A, Adachi C and Shibata K 2007 *Appl. Phys. Lett.* **90** 123509
[29] Chopra N, Swensen J S, Polikarpov E, Cosimbescu L, So F and Padmaperuma A B 2010 *Appl. Phys. Lett.* **97** 033304