Bi-layer non-doped small-molecular white organic light-emitting diodes with high colour stability

Bi-layer non-doped small-molecular white organic light-emitting diodes with high colour stability

Shuming Chen[1]**, Zujin Zhao**[2]**, Zhiming Wang**[3]**, Ping Lu**[3]**,
Zhao Gao**[3]**,Yuguang Ma**[3] **and Ben Zhong Tang**[2] **and Hoi-Sing Kwok**[1,4]

[1] Center for Display Research and Department of Electronic and Computer Engineering, The Hong Kong
University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China
[2] Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay,
Kowloon, Hong Kong, China
[3] Key Laboratory for Supramolecular Structure and Materials of Ministry of Education, Jilin University,
Changchun 130023, People's Republic of China

E-mail: eekwok@ust.hk

Abstract

Bi-layer non-doped white organic light-emitting diodes (WOLEDs) with hole-transporting
layer 4-(4-(1,2,2-triphenylvinyl)phenyl)-7-(5-(4-(1,2,2-triphenylvinyl)phenyl)thiophen-
2yl)benzo[c][1,2,5]thiadiazole (BTPETTD) as a red emitter and electron-transporting layer
4,4′-bis(1-phenyl-1H-phenanthro[9,10-d]imidazol-2-yl)biphenyl (DDPi) as a blue emitter are
demonstrated. The blue emission is due to direct recombination of excitons in DPPi, while the
red emission originates not only from the direct recombination of excitons in BTPETTD but
also from a colour down-conversion process by absorbing blue emission and re-emitting red
photons. The combination of blue emission and red emission yields an efficient and extremely
stable white colour, regardless of driving voltages. In our demonstration, a bi-layer WOLED
with an efficiency of 4.2 cd A^{-1} at 1000 cd m^{-2}, 1931 Commision International de L'Eclairage
coordinates of (0.31, 0.31) and a high colour rendering index of 92 over a wide range of
driving voltages is obtained.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

White organic light-emitting diodes (WOLEDs) have been
a subject of intensive research in recent years due to their
potential applications in flat panel displays and solid-state
lighting [1–16]. To realize white light emission, two or
three emitters which emit complementary colours [1, 2] or
three primary colours [3–6] can be employed. The emitters,
either fluorescent [2, 4] or phosphorescent [1, 3, 5, 6] dyes,
in general, have to be doped into wide band-gap hosts to
reduce the aggregation-induced quenching effect. Hence,
the white light emissive layers typically consist of multi-
host layer with each host layer doped with a single colour

dopant [1–6], or single-host layer with several dopants [7–9].
Either multi-host-layer or single-host-layer WOLEDs require
several kinds of functional materials and complex fabrication
processes, rendering the WOLEDs more expensive than their
monochromatic counterpart. Moreover, both multi-host-
layer and single-host-layer WOLEDs suffer from low colour
stability, i.e. the white colour changes as the driving voltage
is changed. This effect is probably due to the shifting of the
recombination zone in multi-host-layer structures [10, 11], or
due to field-dependent charge trapping effect in single-host-
layer structures [12].

A variety of novel structures, such as non-doped
WOLEDs [13], colour down-conversion phosphor WOLEDs
[14], exciplex/excimer WOLEDs [15] and single-molecular
WOLEDs [16] have been proposed to simplify the fabrication

---

[4] Author to whom any correspondence should be addressed.

process, cut down the material cost and enhance the colour stability of WOLEDs. However, most reports employed multi-layer (>3) structures [1–16]. Is it possible to get white light from a simple bi-layer structure? Conventional bi-layer OLEDs, such as the classical TPD/Alq$_3$ structure [17], emit monochromatic light despite the fact that both TPD and Alq$_3$ are capable of emitting colours. This has to do with the distribution of excitons inside the bi-layer structure. If both layers can be forced to emit light, then there is a good possibility of obtaining a WOLED in a simple bi-layer device.

In this work, we present a bi-layer non-doped WOLED which contains only two layers. Using the hole-transporting layer (HTL) as a red emitter and the electron-transporting layer (ETL) as a blue emitter, a bi-layer non-doped WOLED can be demonstrated. In such bi-layer WOLEDs, most excitons recombine in the blue emitter and thus produce the blue emission directly, while some excitons are captured by the red emitter, thus generating the red emission. Additionally, some of the blue emission is converted to red emission by either a colour down-conversion process, and/or interface Förster energy transfer. The combination of blue emission and red emission yields an efficient and extremely stable white colour, regardless of driving voltages. In our demonstration, a bi-layer WOLED with an efficiency of 4.2 cd A^{-1} at 1000 cd m^{-2}, a 1931 Commision International de L'Eclairage (CIE) coordinates of (0.31, 0.31) and a high colour rendering index (CRI) of 92 over a wide range of driving voltages is obtained. Bi-layer WOLEDs may be desirable for mass production due to their simple structure and capability of reducing material cost.

2. Experimental

The hole-transporting material/red emitter 4-(4-(1,2,2-triphenylvinyl)phenyl)-7-(5-(4-(1,2,2-triphenylvinyl)phenyl)thiophen-2yl)benzo[c][1,2,5]thiadiazole (BTPETTD), and the electron-transporting material/blue emitter 4,4′-bis(1-phenyl-1H-phenanthro[9,10-d]imidazol-2-yl)biphenyl (DPPi) were synthesized according to [18] and [19], respectively. The molecular structure and energy level of BTPETTD and DPPi are shown in figure 2(a). The organic and metal layers were deposited on 80 nm thick ITO coated glass in a multi-source vacuum chamber at a base pressure of 5×10^{-7} Torr. The current density–voltage characteristics of the devices were measured by the HP4145B semiconductor parameter analyser. The forward direction photons emitted from the devices were detected by placing a calibrated UDT PIN-25D silicon photo-diode very close to the top of the devices. The luminance and external quantum efficiency of the devices were inferred from the photocurrent of the photodiode. The electroluminescence (EL) spectra were obtained with a PR650 spectrophotometer.

3. Results and discussion

The bi-layer non-doped WOLEDs were composed of HTL and ETL, which serve as the red-emitting layer and blue-emitting layer, respectively. Hence the EL performance and the carrier

transporting ability of the emitters were tested first. Four devices were fabricated with the following structures:

(1) red & HTL: ITO/BTPETTD 80 nm/TPBi 40 nm/LiF 0.5 nm/Al 100 nm,
(2) red: ITO/NPB 60 nm/BTPETTD 20 nm/TPBi 40 nm/LiF 0.5 nm/Al 100 nm,
(3) blue & ETL: ITO/NPB 60 nm/DPPi 60 nm/LiF 0.5 nm/Al 100 nm,
(4) blue: ITO/NPB 60 nm/DPPi 20 nm/TPBi 40 nm/LiF 0.5 nm/Al 100 nm,

where 2, 2′, 2″-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzinidazole) (TPBi) and N, N′-Bis(naphthalen-1-yl)-N,N′-bis(phenyl)-benzidine (NPB) serve as ETL and HTL, respectively. In devices 'red & HTL', BTPETTD serves as the red emitter as well as HTL; similarly, DPPi functions as the blue emitter and ETL for devices 'blue & ETL'. The schematic illustration of the device structures are shown in figure 1(a). Figure 1(b) shows the current density–voltage–luminance characteristics of the devices. Although a large carrier injection barrier exists while adopting BTPETTD as HTL and DPPi as ETL due to the high HOMO level (6.1 eV) of BTPETTD and low LUMO level (2.3 eV) of DPPi, devices 'red & HTL' and 'blue & ETL' exhibit reduced driving voltages and turn on voltages compared with devices 'red' and 'blue', respectively. For example, at a current density of 100 mA cm^{-2}, devices 'red & HTL' and 'blue & ETL' require a driving voltage of 8.4 V and 7.4 V, significantly lower than 10.2 V and 8.8 V for devices 'red' and 'blue', respectively. Such improved performance may be mainly due to the higher hole mobility of BTPETTD and electron mobility of DPPi, compared with that of NPB and TPBi, respectively, thus resulting in a reduced driving voltage. This assumption can further be verified by investigating the efficiency–luminance characteristics of the devices. As shown in figure 1(b), devices 'red & HTL' exhibit a lower efficiency than devices 'red'; for example, at a luminance of 1000 cd m^{-2}, devices 'red & HTL' show an efficiency of 3.5 cd A^{-1} and 1.7 lm W^{-1}, substantially lower than 7 cd A^{-1} and 3.2 lm W^{-1} for devices 'red', which may be attributed to the higher hole injection current in devices 'red & HTL' leading to an imbalance of hole and electron injection. While devices 'blue & ETL' show a higher efficiency of 6.7 cd A^{-1} and 4.2 lm W^{-1} at 1000 cd m^{-2} than 5.8 cd A^{-1} and 1.9 lm W^{-1} for devices 'blue', which is expected due to the enhanced electron injection by utilizing DPPi as the ETL, leading to reduced driving voltages and more balanced hole and electron injection. Figure 1(c) shows the EL spectra of the devices. Devices 'red & HTL' and 'blue & ETL' show identical spectra to that of devices 'red' and 'blue', indicating that the excitons recombine in BTPETTD and DPPi, thus generating a red emission with peak at 592 nm and a blue emission with peak at 465 nm, respectively. The photos of devices 'red & HTL' and 'blue & ETL' are shown in figure 2(a).

The excellent carrier transporting ability and EL performance of BTPETTD and DPPi render them to be ideal candidates for constructing bi-layer non-doped WOLEDs. To test this assumption, bi-layer WOLEDs with structures ITO/BTPETTD d_1 nm/DPPi 60 nm/LiF 0.5 nm/Al 100 nm
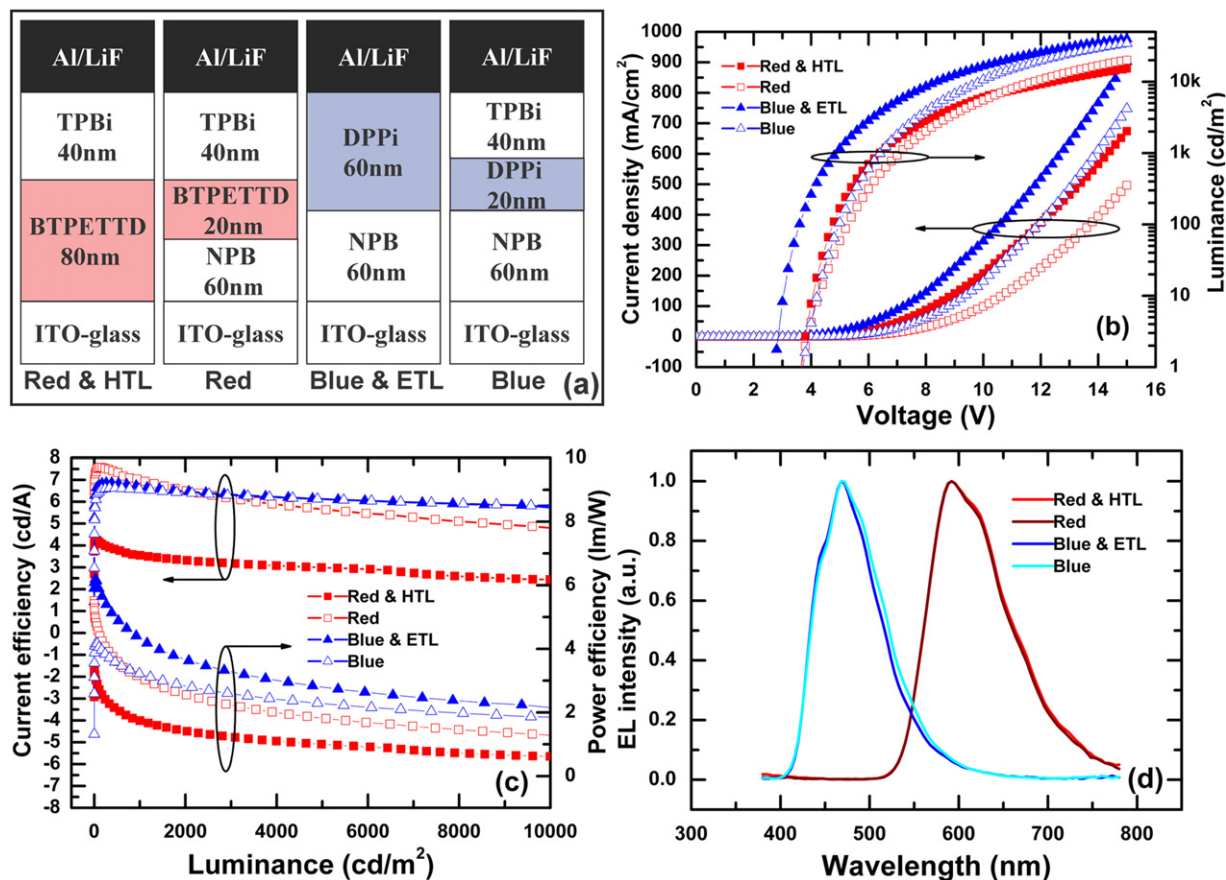
J. Phys. D: Appl. Phys. **44** (2011) 145101

S Chen *et al*

Figure 1. (*a*) Schematic illustration of the device structures, (*b*) current density–luminance–voltage characteristics, (*c*) efficiency–luminance characteristics, (*d*) EL spectra of the devices.

were fabricated with BTPETTD thickness d_1 ranging from 60 to 140 nm. Figure 2(*b*) shows the EL spectra of the bi-layer WOLEDs with different BTPETTD thicknesses. Two main emission peaks located at 465 nm and 592 nm, originating from DPPi and BTPETTD, respectively, can be clearly observed. In an organic semiconductor, the hole mobility in general is larger than the electron mobility, most excitons are therefore formed inside the DPPi layer, resulting in a stronger blue emission than the red emission. To get a more balanced white colour, the red emission should be enhanced; thus the thickness of BTPETTD was tuned to obtain an enhanced red emission. However, unlike the blue emission, which originates solely from direct recombination of excitons in DPPi, the generation of red emission may be mainly due to two different mechanisms: (1) direct recombination of excitons in BTPETTD. As shown in figure 2(*a*), the electrons may be easily trapped by the BTPETTD thanks to the high LUMO level of BTPETTD. The trapped electrons recombine with holes and hence generate the red emission. It should be noted that a barrier-free BTPETTD/DPPi interface is essential in obtaining the white light emission, for the excitons can be distributed in both layers. Devices with barrier interface, such as the classical bit-layer TPD/Alq$_3$, can only emit monochromatic colours because the excitons are confined in the Alq$_3$ layer. Additionally, the red emission may also be generated by mechanism (2): a colour down-conversion process (i.e. a photoluminescence (PL) process) by absorbing blue emission and re-emitting red

photons, and/or interface Förster energy transfer from blue emission to red emission. Figure 2(*c*) shows the absorption spectrum of BTPETTD as well as the PL spectrum of DPPi. Good overlap between absorption spectrum of BTPETTD and PL spectrum of DPPi in the region 400–550 nm can be clearly observed, indicating that effective energy down-conversion by PL process and/or interface Förster energy transfer may take place [20]. To verify this assumption, a 12 nm TcTa, serving as an electron-blocking layer due to its extremely low electron mobility [21], was inserted between BTPETTD and DPPi. By doing so, the excitons are confined in the DPPi layer thus eliminating the red emission due to direct recombination of excitons in BTPETTD. However, red emission still can be observed as shown in figure 2(*c*), indicating that the BTPETTD can absorb the blue emission and convert to red emission effectively. As the thickness of BTPETTD is increased, more blue energy is absorbed by the BTPETTD and converted to red emission, resulting in an increased red emission.

Therefore, the overall red emission in bi-layer WOLEDs is contributed by dual channels of excitons' direct recombination and PL process. To distinguish the contribution due to these two different routes, the total red emission and the red emission due to the PL process are extracted from the spectra of the bi-layer WOLEDs (as shown in figure 2(*b*)) and the spectra of the tri-layer WOLEDs with 4, 4′, 4″-Tris(carbazol-9-yl)triphenylamine (TcTa) interlayer (as shown in figure 2(*c*)), respectively. By subtracting the PL spectra of DPPi, the red
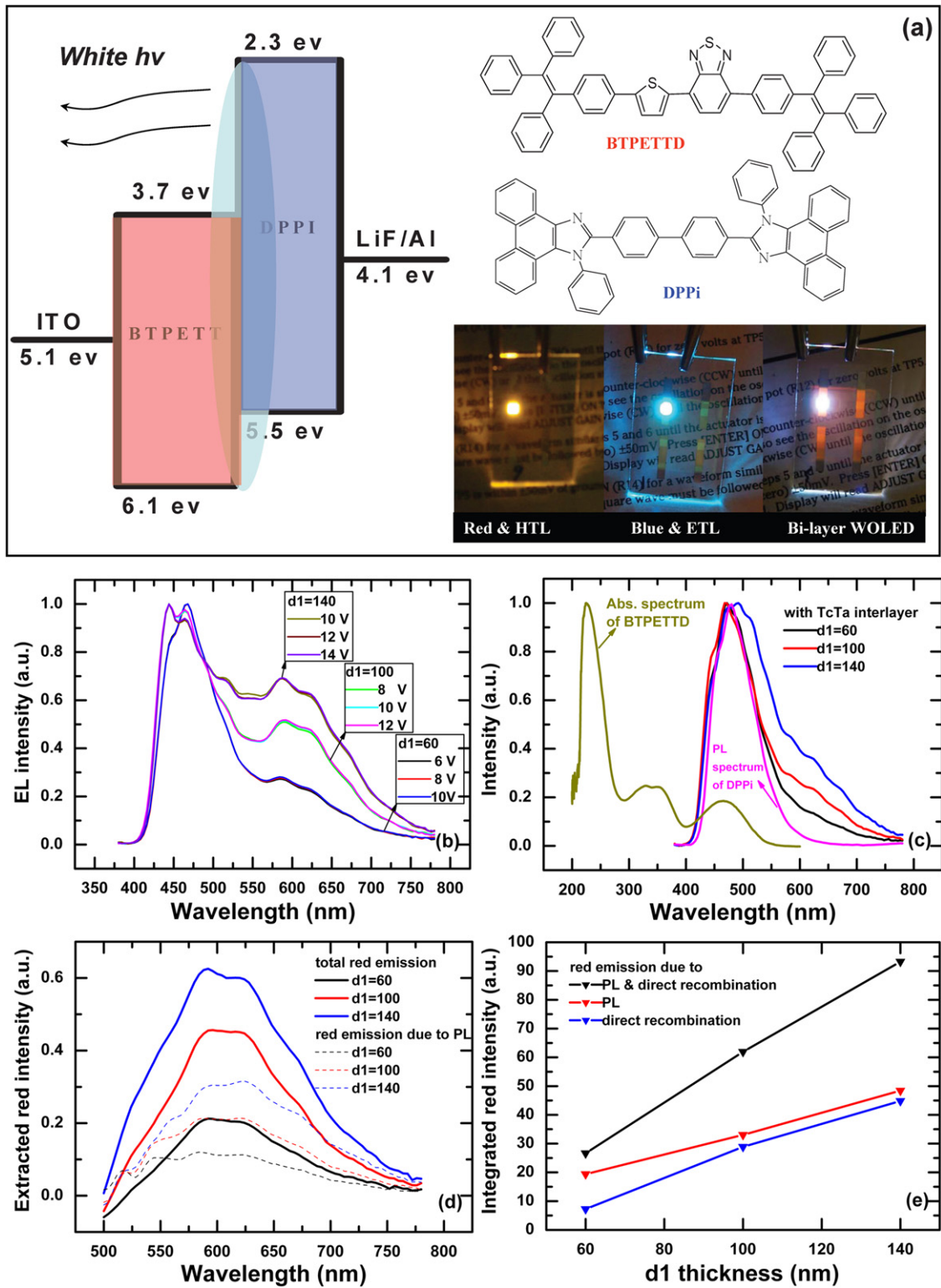
Figure 2. (*a*) Energy level (measured by cyclic voltammetry) and molecular structure of the emitters; right bottom: photos of OLED based on BTPETTD (red & HTL), DPPi (blue & ETL) and BTPETTD/DPPi (bi-layer WOLED), (*b*) EL spectra of the bi-layer WOLEDs with different thicknesses of BTPETTD, (*c*) absorption spectrum of BTPETTD and EL spectra of tri-layer WOLEDs with TcTa interlayer, (*d*) extracted red spectra from the spectra of bi-layer WOLEDs and tri-layer WOLEDs, (*e*) integrated red intensity due to different generation channels.

spectra can be extracted as shown in figure 2(*d*). By integrating the area of the extracted red spectra, the red intensity can be obtained. The red intensity due to direct recombination can further be obtained from the difference of the total red intensity

and the red intensity due to the PL process. Figure 2(*e*) shows the integrated red intensity due to PL & direct recombination, PL and direct recombination, respectively, as a function of BTPETTD thickness. Obviously, the red intensity due to
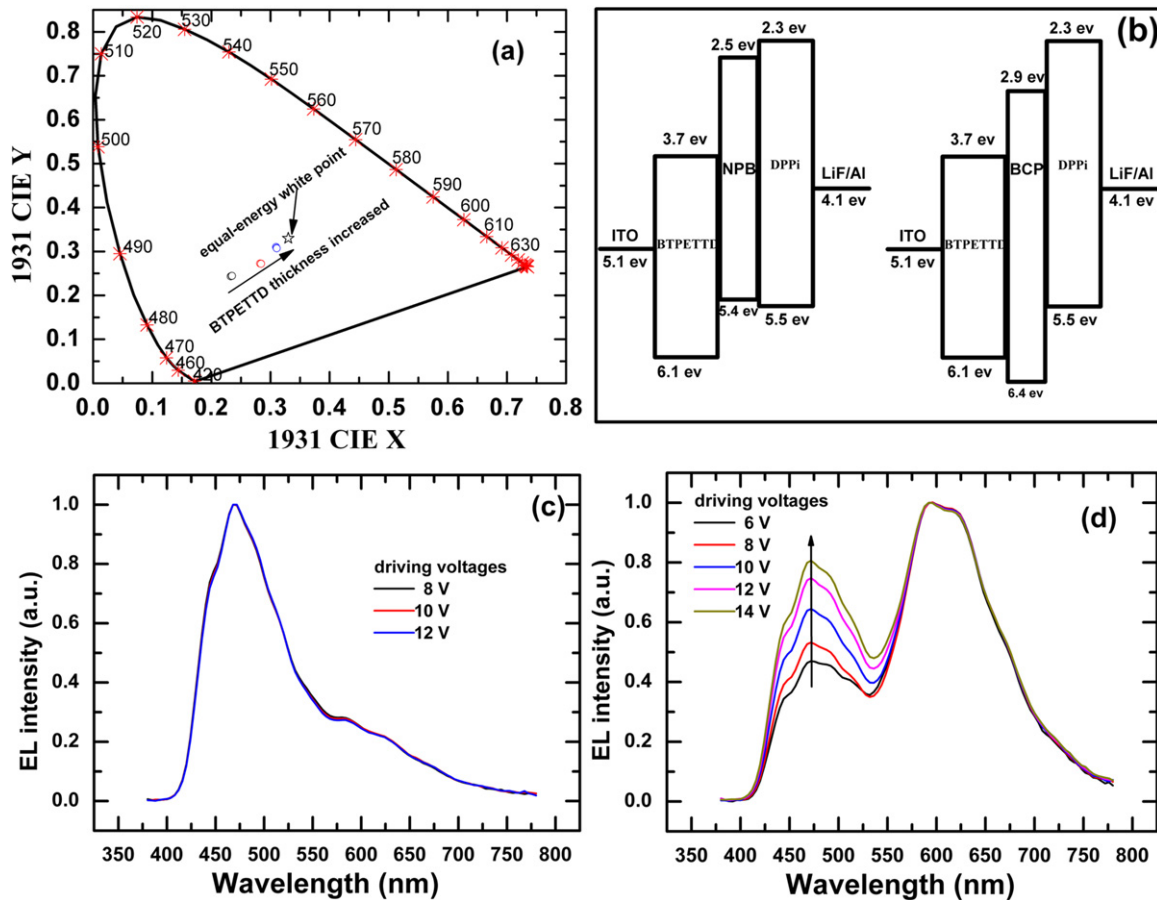
Figure 3. (*a*) CIE coordinates of the bi-layer WOLEDs with different thicknesses of BTPETTD, (*b*) energy level of the materials employed, (*c*) EL spectra of tri-layer WOLEDs with NPB interlayer, (*d*) EL spectra of tri-layer WOLEDs with BCP interlayer.

the PL process is linearly enhanced with an increase in BTPETTD thickness, because more blue energy is absorbed by the BTPETTD and converted to red emission, resulting in a linearly increased red emission. Similarly, the red intensity due to direct recombination exhibits a monotonic enhancement, indicating that more excitons are recombined in the BTPETTD layer as the thickness of BTPETTD is increased. Since the hole concentration drops significantly along the HTL [22], the fraction of holes transported to the DPPi layer is reduced with an increase in BTPETTD thickness, leading to a reduced blue emission and hence an enhanced red/blue emission ratio. For example, the red emission due to direct recombination contributes 27%, 46% and 48% to the overall red emission, as the thickness of BTPETTD is increased from 60 nm, 100 nm to 140 nm, respectively.

Figure 3(*a*) shows the CIE coordinates of the bi-layer WOLEDs with different thicknesses of BTPETTD. By increasing the thickness of BTPETTD, the CIE coordinates are moved close to an equal-energy white point, shifting from (0.23, 0.24) and (0.28, 0.27) for BTPETTD thicknesses of 60 nm and 100 nm, respectively, to (0.31, 0.31) for a BTPETTD thickness of 140 nm. The bi-layer WOLEDs with 140 nm BTPETTD exhibit a colour-correlated temperature of 6887 K and a high CRI of 92. Surprisingly, unlike conventional multi-layer WOLEDs, which suffer from colour changing at different driving voltages due to the shift of

recombination zone [10, 11], the bi-layer WOLEDs exhibit extremely stable colour regardless of the driving voltages, as shown in figures 2(*b*) and 3(*a*). Such phenomena may be partially due to the barrier-free BTPETTD/DPPi interface. As the holes can move from BTPETTD to DPPi freely, and the electrons see no barrier on travelling from DPPi to BTPETTD, the distribution profile of excitons remains almost unchanged regardless of the driving voltages. To verify this assumption, a 12 nm NPB and a 12 nm 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) interlayer was inserted between the 60 nm BTPETTD and 60 nm DPPi. The energy level of the materials employed is shown in figure 3(*b*). As seen from figure 3(*c*), the introduction of the bi-polar material NPB [23] does not create a new barrier for holes and electrons, and thus the white spectra remain unchanged regardless of the voltages as expected due to the barrier-free interface. However, by introducing the 12 nm BCP interlayer, a hole barrier is created and the main exciton formation position is located at the interface of BTPETTD/BCP. As the driving voltage is increased, more holes can tunnel through BCP and recombine in DPPi, resulting in an increased blue emission as shown in figure 3(*d*). Hence, a barrier-free interface is essential in obtaining colour stable WOLEDs; moreover, the red emission by the colour down-conversion process is also voltage-independent [14]; thus the bi-layer WOLEDs with their red photons harvested by dual channels of excitons' direct
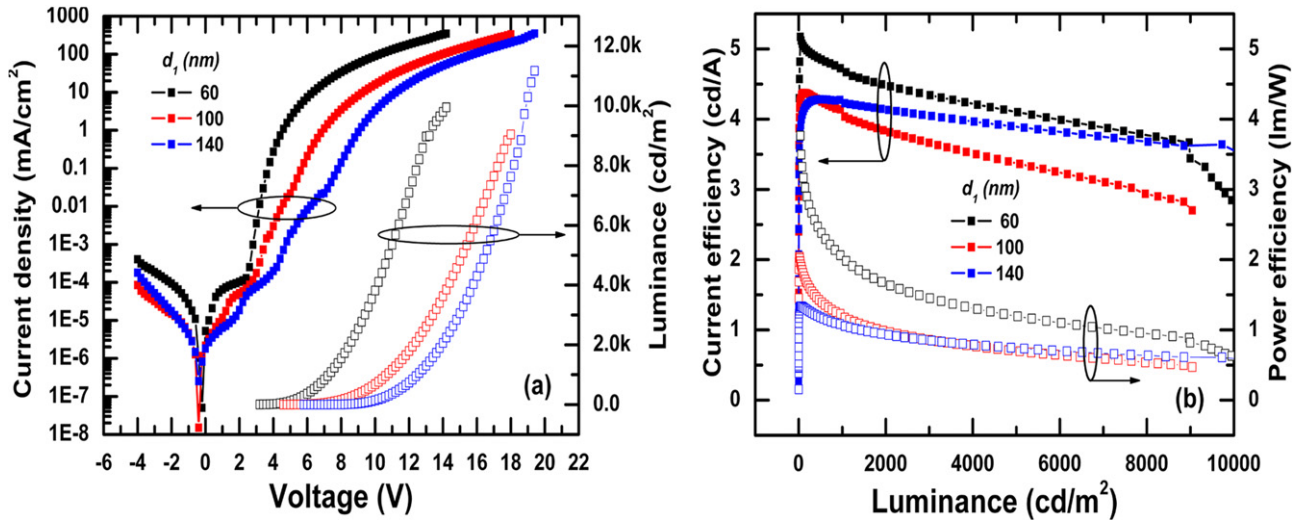
Figure 4. (*a*) Current density–luminance–voltage and (*b*) efficiency–luminance characteristics of the bi-layer WOLEDs with different thicknesses of BTPETTD.

Table 1. Performance of the devices.

Device	V (V) at 1 cd m^{-2}	V (V) at 1 kcd m^{-2}	η_L (cd A^{-1}) at 1 kcd m^{-2}	η_P (lm W^{-1}) at 1 kcd m^{-2}	CIE (x, y) at 8 V	CIE (x, y) at 12 V	CRI
$d_1 = 60$ nm	3	7.3	4.6	2	(0.23, 0.24)	(0.23, 0.24)	-
$d_1 = 100$ nm	5.4	10.8	4.1	1.2	(0.28, 0.27)	(0.28, 0.27)	-
$d_1 = 140$ nm	7.6	12.6	4.2	1.1	(0.31, 0.31)	(0.31, 0.31)	92

recombination and colour down-conversion process exhibit extremely stable colour regardless of driving voltages.

Figure 4(*a*) shows the current density–luminance–voltage characteristics of the bi-layer WOLEDs with different BTPETTD thicknesses. The driving voltages increase as the BTPETTD thickness increases, which is expected due to the larger resistance induced by the thicker layer. For example, at a luminance of 1000 cd m^{-2}, devices with 140 nm BTPETTD exhibit a driving voltage of 12.6 V, significantly higher than 10.8 V and 7.3 V for devices with 100 nm and 60 nm BTPETTD, respectively. Figure 4(*b*) shows the efficiency–luminance characteristics of the devices. At a luminance of 1000 cd m^{-2}, devices with 60 nm BTPETTD show a current efficiency of 4.6 cd A^{-1} (2.7%, 2 lm W^{-1}), slightly higher than 4.1 cd A^{-1} (2.3%, 1.2 lm W^{-1}) and 4.2 cd A^{-1} (2.3%, 1.1 lm W^{-1}) for devices with 100 nm and 140 nm BTPETTD, respectively, mainly due to the optical interference effect as the thickness of the BTPETTD increases; the resonant wavelength is shifted to the low-efficiency bluer region. The key characteristics of the devices are listed in table 1. It should be pointed out that the device performance was not optimized, but fabricated to demonstrate the concept of bi-layer WOLEDs. Further optimization, for example, p-doping of the BTPETTD layer to reduce the driving voltages [24, 25], inserting an exciton confinement layer to avoid the loss due to leakage [26], employing new emitters with high carrier mobility and fluorescent quantum efficiency, applying an out-coupling technique [27], can be employed to boost the device performance.

4. Summary

In conclusion, bi-layer non-doped WOLEDs with HTL as a red-emitting layer and ETL as a blue-emitting layer are demonstrated. With such a special configuration, most excitons recombine in DPPi and generate blue emission. The red emission is a result of direct recombination of excitons in BTPETTD, as well as colour down-conversion from blue to red photons. The reverse configuration, i.e. with blue emitter DPPi as the HTL and red emitter BTPETTD as the ETL, does not produce white colour. Only red emission is obtained due to the existence of a charge barrier at the interface which confines the excitons in the BTPETTD layer, as well as a lack of colour conversion. The combination of blue emission and red emission yields an extremely stable white colour regardless of driving voltages, mainly attributable to the barrier-free BTPETTD/DPPi interface and voltage-independent property of the colour down-conversion process. The bi-layer non-doped WOLEDs may be desirable for mass production due to their simple structure and capability of cutting down material cost.

Acknowledgment

References

[1] Ho C-L, Lin M-F, Wong W-Y, Wong W-K and Chen C H 2008 *Appl. Phys. Lett.* **92** 083301

[2] Kim Y M, Park Y W, Choi J H and Ju B K 2007 *Appl. Phys. Lett.* **90** 033506

[3] Reineke S, Lindner F, Schwartz G, Seidler N, Walzer K, Lüssem B and Leo K 2009 *Nature* **459** 234

[4] Zhang Z, Wang Q, Dai Y, Liu Y, Wang L and Ma D 2009 *Org. Electron.* **10** 491

[5] Park Y-S, Kang J-W, Kang D M, Park J-W, Kim Y-H, Kwon S-K and Kim J-J 2008 *Adv. Mater.* **20** 1957

[6] Sun Y and Forrest S R 2007 *Appl. Phys. Lett.* **91** 263503

[7] Wang Q, Ding J, Ma D, Cheng Y, Wang L, Jing X and Wang F 2009 *Adv. Funct. Mater.* **19** 84

[8] Chuen C H and Tao Y T 2002 *Appl. Phys. Lett.* **81** 4499

[9] Chu T-Y, Chen J-F, Chen S-Y and Chen C H 2006 *Appl. Phys. Lett.* **89** 113502

[10] Kim C-H and Shinar J 2002 *Appl. Phys. Lett.* **80** 2201

[11] Kim S H, Jang J and Lee J Y 2007 *Appl. Phys. Lett.* **91** 123509

[12] Gather M C, Alle R, Becker H and Meerholz K 2007 *Adv. Mater.* **19** 4460

[13] Chen S, Zhao Z, Tang B Z and Kwok H S 2010 *J. Phys. D: Appl. Phys.* **43** 095101

[14] Chen S and Kwok H S 2011 *Org. Electron.* **12** 677

[15] Tong Q-X, Lai S-L, Chan M-Y, Tang J-X, Kwong H-L, Lee C-S and Lee S-T 2007 *Appl. Phys. Lett.* **91** 023503

[16] Tu G, Mei C, Zhou Q, Cheng Y, Geng Y, Wang L, Ma D, Jing X and Wang F 2006 *Adv. Funct. Mater.* **16** 101

[17] Tang C W and VanSlyke S A 1987 *Appl. Phys. Lett.* **51** 913

[18] Zhao Z, Lam W Y and Tang B Z 2010 *Curr. Org. Chem.* **14** 2109

[19] Wang Z, Lu P, Gao Z and Ma Y, unpublished

[20] Zhang D and Ma D 2007 *Appl. Opt.* **46** 2996

[21] Kang J W, Lee S H, Park H D, Jeong W L, Yoo K M, Park Y S and Kim J J 2007 *Appl. Phys. Lett.* **90** 223508

[22] Crone B K, Campbell I H, Davids P S, Smith D L, Neef C J and Ferraris J P 1999 *J. Appl. Phys.* **86** 5767

[23] Tse S C, Kwok K C and So S K 2006 *Appl. Phys. Lett.* **89** 262102

[24] Xie G, Meng Y, Wu F, Tao C, Zhang D, Liu M, Xue Q, Chen W and Zhao Y 2008 *Appl. Phys. Lett.* **92** 093305

[25] Zhou X, Pfeiffer M, Blochwitz J, Werner A, Nollau A, Fritz T and Leo K 2001 *Appl. Phys. Lett.* **78** 410

[26] Yook K S, Jeon S O, Joo C W and Lee J Y 2008 *Appl. Phys. Lett.* **93** 113301

[27] Chen S and Kwok H S 2010 *Opt. Express* **18** 37