

All Non-Dopant RGB Composing White Organic Light-Emitting Diodes

Shi-Jay Yeh, Hung-Yang Chen, Min-Fei Wu, Li-Hsin Chan, Chih-Long Chiang,
Hsiu-Chih Yeh, Chin-Ti Chen

Institute of Chemistry, Academia Sinica, Taipei, Taiwan 11529, R. O. C.
Phone: +886-2-27898542, E-mail: cchen@chem.sinica.edu.tw

Jiun-Haw Lee^{b,*}

Graduate Institute of Electro-Optical Engineering and Department of Electrical
Engineering, National Taiwan University, Taipei, Taiwan 10617, R. O. C.

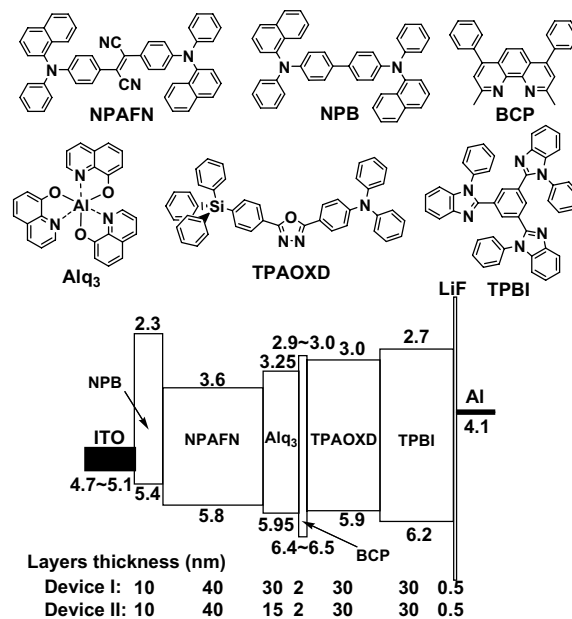
Abstract

All non-dopant white organic light-emitting diodes (WOLEDs) have been realized by using solid state highly fluorescent red bis(4-(*N*-(1-naphthyl)phenylamino)phenyl)fumaronitrile (NPAFN) and amorphous bipolar blue light-emitting 2-(4-diphenylamino)phenyl-5-(4-triphenylsilyl)phenyl-1,3,4-oxadiazole (TPAOXD), together with well known green fluorophore tris(8-hydroxyquinolino)aluminum (Alq₃). The fabrication of multilayer WOLEDs did not involve the hard-to-control doping process. Two WOLEDs, Device I and II, different in layer thickness of Alq₃, 30 and 15 nm, respectively, emitted strong electroluminescence (EL) as intense as 25,000 cd/m². For practical solid state lighting application, EL intensity exceeding 1,000 cd/m² was achieved at current density of 18-19 mA/cm² or driving voltage of 6.5-8 V and the devices exhibited external quantum efficiency (η_{ext}) of 2.6~2.9% corresponding to power efficiency (η_p) of 2.1~2.3 lm/W at the required brightness.

1. Introduction

Recently, we have successfully developed a few bright (electroluminescence (L) of 8000~12400 cd/m²) and efficient (external quantum efficiency, η_{ext} , of 2.4-3.6% or η_p of 0.9-1.8 lm/W) non-doped red OLEDs based on extraordinary red light-emitting materials.^[1-4] NPAFN (Scheme 1) is one of those rare materials that have an unusual property of aggregation-induced emission (AIE) and it was adopted here as non-dopant red light-emitting material for WOLEDs.^[5] In addition to NPAFN, we have also explored a new type of blue fluorophore, TPAOXD (Scheme 1), which is bipolar in nature but is an authentic amorphous molecular material.^[6] High-performance (maximum brightness ~20,000 cd/m²

and maximum external quantum efficiency ~2.4%) blue (1931 Commission Internationale de L'Éclairage, CIE_{x,y} of $x = 0.16$ and $y = 0.18$) OLEDs containing TPAOXD as the non-dopant blue emitter was found to be relatively stable with little decay of external quantum efficiency at ~2.3% from low to high current density (10~500 mA/cm²).^[7] In this work, three devices A, B, and C, were fabricated to test the idea of bright and efficient all non-dopant WOLEDs using NPAFN, Alq₃, and TPAOXD for red, green, and blue emitters, respectively (see photoluminescence, PL, spectra in Figure 1).



Scheme 1. Chemical structures and their relative energy level (HOMO and LUMO) diagram of NPAFN, Alq₃, TPAOXD, NPB, BCP, and TPBI. Layer structures of Device I and II are also

schematically shown here with the layer thickness indicated therein.

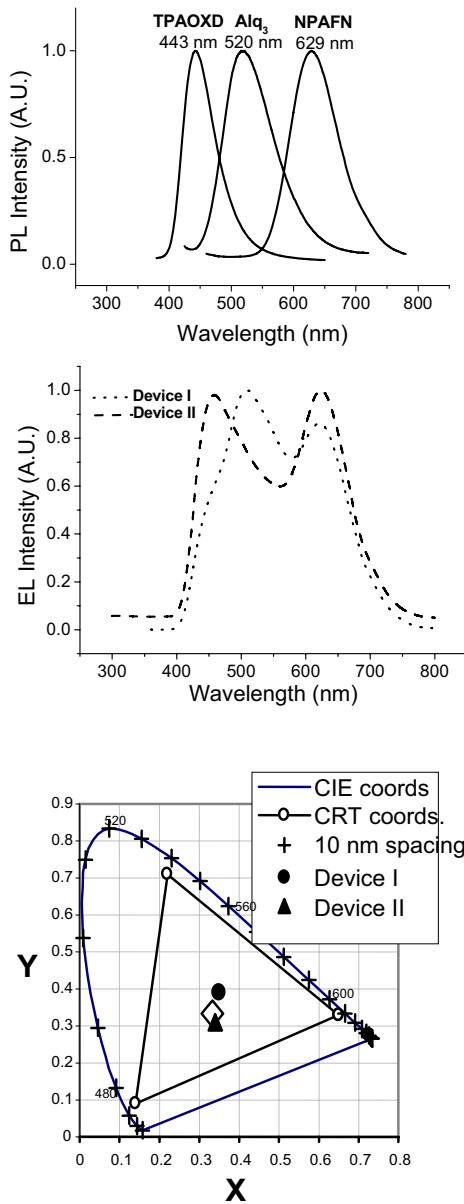


Figure 1. Normalized photoluminescence spectra of vacuum thermal deposited thin films of **TPAOXD**, **Alq₃**, and **NPAFN**; EL spectra (center) and 1931 CIE coordinates (bottom) of Device I and II at driving voltage of 8 V. CRT (cathode ray tube) coordinates mean the standard red-green-blue color coordinates of CRT screen (traditional color television screen).

2. Results

In current case, 2 nm layer of **BCP** is thin enough that just partially blocks the hole from entering **TPAOXD** and hence allows the charge recombination and/or exciton diffusion on it. This permits the blue emission ($\lambda_{max} \sim 460$ nm) from **TPAOXD** in EL spectra (Figure 1). CIE coordinates of it is (0.35, 0.39), which is just fine for the requirement of white OLED. Higher color purity of white EL has been achieved by adjusting the thickness of **Alq₃** layer. In Device II, the thickness of **Alq₃** layer was further reduced to half (15 nm) from 30 nm of Device I. Having both thin layers of green light-emitting **Alq₃** and hole-blocking **BCP**, Device II showed significant increase of the blue emission from **TPAOXD** as well as the decrease of green emission from **Alq₃** (Figure 1). Such changes of relative contribution of emission color rendered virtually white EL of Device II as indicated by the CIE coordinates (0.34, 0.31) (Figure 1). In principle, all non-dopant WOLED with any CIE coordinates as close as to standard white (0.33, 0.33) can be achieved with the variation of the thickness of **Alq₃** and **BCP** layers.

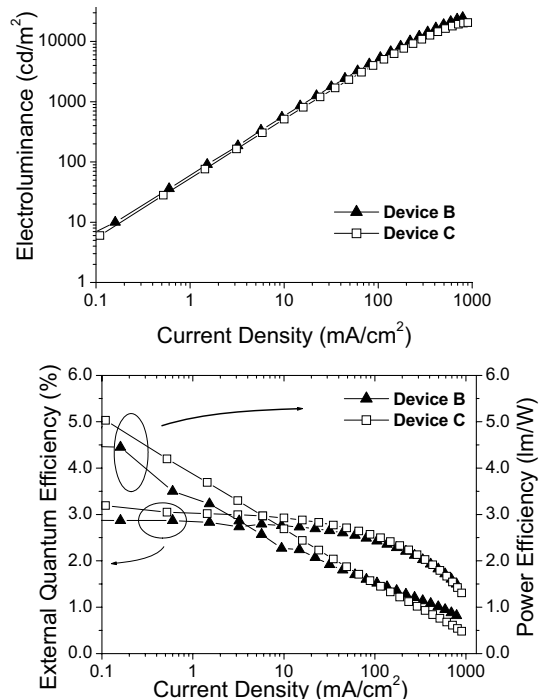
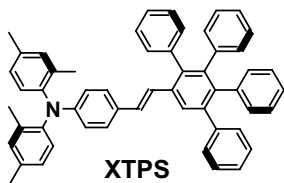


Figure 2. Electroluminescence (L)—current density (I)—efficiency (η_{ext} and η_p) characteristics of Device I and II.

WOLEDs reached 1000 cd/m^2 of EL intensity, the general requirement for solid state lighting application, at a reasonable current density range of $18\sim 19 \text{ mA/cm}^2$ (Figure 2), which corresponded to $6.5\sim 8 \text{ V}$ for Device I and II. The maximum EL intensity of $25,000 \text{ cd/m}^2$ was observed for Device B at 790 mA/cm^2 and 15 V . At low current density near 0.1 mA/cm^2 , high η_{ps} over 5 lm/W were observed for Device II and slightly lower $4.0\text{--}4.5 \text{ lm/W}$ were found for Device I, although both devices display a roll-off of η_p at elevated current density (Figure 2). However, high η_{ext} s of $2.9\sim 3.3\%$ remained relatively stable with only slight decay to $2.6\sim 2.9\%$ (corresponding to $2.1\sim 2.3 \text{ lm/W}$) when the current density up to 20 mA/cm^2 (or 1000 cd/m^2 lighting intensity). Even at relatively high current density of 100 mA/cm^2 (where WOLED showed EL intensity of $\sim 5,000 \text{ cd/m}^2$, Figure 2), η_{ext} s stayed reasonably high around $2.4\sim 2.6\%$. The rather current-stable external quantum efficiency can be partially attributed to the relatively stable blue emitter **TPAOXD**. Similar stability of η_{ext} was previously known for blue OLEDs based on amorphous **TPAOXD**.^[39] Containing both electron-poor oxadiazole and electron-rich triphenylamine moieties, bipolar **TPAOXD** possesses electro-transporting characteristic, which is crucial for a good performance WOLEDs here. We have fabricated the same WOLED by using **XTPS** (*trans*-4-(bis(2,4-dimethylphenyl)amino)-2',3',4',5'-tetraphenylstilbene), another highly efficient (maximum external quantum efficiency up to 4.1%) non-dopant blue light ($\lambda_{max}^{EL} \sim 462 \text{ nm}$) emitter.^[8] However, the **XTPS**-containing WOLEDs performed poorly. Unlike bipolar **TPAOXD**, **XTPS** is stilbene-type triarylamine (Scheme 2) and preferentially transports hole instead of electron. This is not appropriate for using **XTPS** as blue light-emitting material that is insufficient for electron-transporting in current devices.



Scheme 1. Chemical structure of **XTPS**.

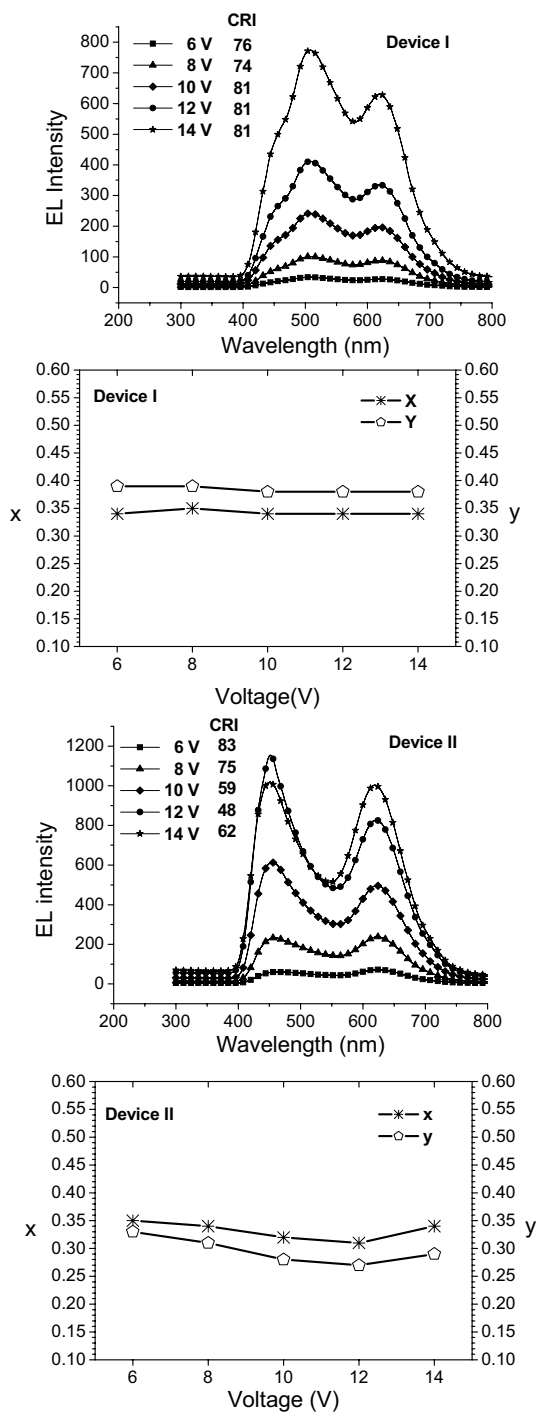


Figure 3. The voltage dependency of EL spectra and CIE coordinates (x , y), and CRIs of Device I and II under different voltage of 6, 8, 10, 12, and 14 V.

Device I was unusual stable regarding CIE coordinates and CRIs. The CIE coordinates of Device B were virtually unchanged with CIE coordinates $x = 0.34\sim 0.35$ and $y = 0.38\sim 0.39$ at the driving voltage

range of 6-14 V. (Figure 3). CRIs of Device I were rather high in the range of 74-81 and they also remained reasonably steady in the driving voltage between 6 and 14 V (Figure 3). However, we noted that Device II was less stable considering either CIE coordinates or CRIs. With increasing driving voltage, CIE coordinates of Device C shifted to smaller figures and CRIs dropt to smaller numbers from 83 to less than 50 (Figure 3). This is in sharp contrast to Device I. Furthermore, Device II exhibited complicate up and down of CIE coordinates and CRIs when driving voltage varied from 6 to 14 V. Usually, such nonlinear changes imply that there are at least two different processes that are responsible for the color changes of devices. For Device II, blue EL first increased in intensity relative to the red EL (CIE coordinates changed to smaller figures) when the driving voltage was raised from 6 to 12 V (Figure 3). Significant decrease of blue EL was then observed when driving voltage was further up to 14 V (Device II in Figure 3). It is not so clear at the moment that why Device I is more stable in general than Device II. We can surmise that it is probably due to the instability of blue **TPAOXD** because the device having thinner Alq₃ tends to have more portion of blue EL from **TPAOXD**.

3. Conclusion

In summary, we have studied the EL properties of a series of multilayer OLEDs containing all non-dopant emitters. Devices with the structure configuration of ITO/NPB/NPAFN/Alq₃/BCP/TPAOXD/TPBI/LiF/Al emit color-balanced white EL. The success of the all non-dopant WOLEDs here hinges on the unusual AIE red emitter of NPAFN as well as the amorphous bipolar blue emitter **TPAOXD**. Green light-emitting Alq₃ also plays a crucial role of white color purity and stability of non-dopant WOLEDs. Under the condition of sufficient amount of blue EL contributed

to the color-balanced WOLED, a thick Alq₃-containing device can cover most of the charge-recombination zone and reduce the number of exciton migrating into blue **TPAOXD**. The relatively unstable blue EL from **TPAOXD** is limited and CIE- or CRI-stability can thus be enhanced. WOLEDs, particularly the thick (30 nm) Alq₃-containing Device I, has been demonstrated to show satisfactory performances, including EL intensity, efficiency, CRIs, and voltage-stable white EL, which are comparable with or better than conventional electrofluorescence-based WOLEDs that are exclusively based on hard-to-control doping process.

4. Acknowledgements

This work was supported by Academia Sinica and National Science Council of Taiwan.

5. References

- [1] W. -C. Wu, H. -C. Yeh, L. -H. Chan, C. -T. Chen, *Adv. Mater.* 14 (2002) 1072.
- [2] H. -C. Yeh, S. -J. Yeh, C. -T. Chen, *Chem. Commun.* (2003) 2632.
- [3] H. -C. Yeh, L. -H. Chan, W. -C. Wu, C. -T. Chen, *J. Mater. Chem.* 14 (2004) 1293.
- [4] C. -L. Chiang, M. -F. Wu, D. -C. Dai, Y. -S. Wen, J. -K. Wang, C. -T. Chen, *Adv. Funct. Mater.* 15 (2005) 231.
- [5] J. Chen, B. Xu, X. Ouyang, B. Tang, Y. Cao, *J. Phys. Chem. A* 108 (2004) 7522.
- [6] L. -H. Chan, H. -C. Yeh, C. -T. Chen, *Adv. Mater.* 13 (2001) 1637.
- [7] L. -H. Chan, R. -H. Lee, C. -F. Hsieh, H. -C. Yeh, C. -T. Chen, *J. Am. Chem. Soc.* 124 (2002) 6469.
- [8] C. -T. Chen, C. -L. Chiang, Y. -C. Lin, L. -H. Chan, C. -H. Huang, Z. -W. Tsai, C. -T. Chen, *Org. Lett.* 5 (2003) 1261