Electroluminescence and negative differential resistance studies of TPD:PBD:Alq₃ blend organic-light-emitting diodes

M A MOHD SARJIDAN, S H BASRI, N K ZA'ABA, M S ZAINI and W H ABD MAJID*

Low Dimensional Materials Research Centre, Department of Physics, University of Malaya,
50603 Kuala Lumpur, Malaysia

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Abstract. Ternary system of single-layer organic-light-emitting diodes (OLEDs) were fabricated containing tris(8-hydroxyquinoline) aluminium (Alq₃) blended with N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine and 2-(4-biphenyl)-5-phenyl-1,3,4-oxadiazole small molecules. Electroluminescence properties were investigated with respect to blend systems. Significant improvement in turn-on voltage and luminance intensity was observed by employing the blends technique. Negative differential resistance (NDR) characteristics observed at a low voltage region in blended OLED is related to the generation of guest hopping site and phonon scattering phenomenon. However, luminescence of the devices is not altered by the NDR effect.

Keywords. Organic-light-emitting diodes; Alq₃; TPD; PBD; electroluminescence; negative differential resistance.

1. Introduction

Shirakawa *et al*¹ have successfully synthesized the first semi-conducting polymer in 1977. Since then, many reports on organic semiconductor have been published to date, especially in relation to their application. In 1987, Tang and VanSlyke² have reported the first organic-light-emitting diode (OLED) with high efficiency using a small molecule of tris(8-hydroxyquinoline) aluminium (Alq₃). The research and development of OLEDs technology expanded from display application towards lighting application. OLEDs have drawn intensive interest for the next generation of flat-panel displays owing to their great response time,³ high contrast,⁴ wide viewing angle,⁵ low power consumption⁶ and low cost.⁷ However, the objective to have a high-performance, long life and low-cost device is still yet to be fully achieved.

Solution-processing method is an easier and relatively cheaper^{8,9} as compared to the other physical fabrication method, such as the thermal evaporation technique. This method is also suitable for fabrication of a large-area OLEDs, especially through the print-screen technique.¹⁰ Blending method has been used in many fabrication of OLED based on the solution-processed OLEDs^{9,11–16} in order to improve the performance of an OLED such as the turn on voltage^{17,18} and the current and luminance efficiency.¹⁹

Usually, an electron transporting material is blended with a hole transporting material to promote a more balance carrier injection and transportation in the organic layer.^{20,21} For example, due to low mobility of hole, lanthanide complexes

such as europium and samarium are commonly blended with a hole transporting material, for instance, poly-N-vinylcarbazole (PVK) to achieve a high mobility of hole.^{22–24} Another advantage of the blend technique is that the chemical and thermal properties of the materials can be significantly improved²⁵ and this is important especially in order to form a more stable thin film.

In this work, we introduce a new ternary system of N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD):2-(4-biphenyl)-5-phenyl-1,3,4-oxadiazole (PBD):Alq₃ blend to improve the Alq₃-based OLED. The devices were fabricated in an open air environment to simplify the preparation method and also to produce a cheaper OLEDs. Due to excellent hole and electron transportation properties of TPD²⁶ and PBD,²⁷ respectively, they have been used as a host blend for the Alq₃-based OLED in this work. Using current density–voltage–luminance (*J–V–L*) characteristic, the effects of different blend system on Alq₃-based OLED were investigated. Such ternary OLED has never been reported before.

2. Experimental

Alq₃, TPD and PBD used as an organic blend of the emissive layer were purchased from Sigma-Aldrich. Figure 1a shows the molecular structure of the materials. The organic blend solution was prepared by dissolving the Alq₃, TPD:Alq₃ and TPD:PBD:Alq₃ with the weight ratio of 1, 1:1 and 1:1:1, respectively. The concentration of the solutions was fixed at 10 mg ml⁻¹, while chloroform was used as a solvent. Single-layer OLEDs were constructed as ITO/PEDOT:PSS/Blend/Al, while ITO and PEDOT:PSS act

* Author for correspondence (q3haliza@um.edu.my)

Figure 1. (a) Molecular structure of Alq₃, TPD and PBD and (b) single-layer OLED structure fabricated in this work.

as the bulk anode layer, Alq₃–organic blend as the emissive layer and Al as the metal cathode. Glass coated with ITO layer was patterned by etching some parts of the ITO with hydrochloric acid boiled for 15 min. The substrate was then ultrasonically cleaned in a solution of Decon 90, followed by deionized water, acetone and isopropanol. The cleaned ITO was purged with nitrogen gas for drying without further surface treatment. The PEDOT:PSS layer was then spin coated onto the substrate at 7000 r.p.m. in 40 s and heated at 100°C in 1 min to remove the residual water. An emissive layer was deposited by the spin-coating method with a spin speed of 1500 r.p.m. for 40 s to produce a thickness of 80 nm. Finally, a top Al metal electrode was deposited by the thermal evaporation technique in a vacuum environment of 2.5×10^{-5} mbar with a deposition rate of 0.2 nm s^{-1} to perform an active area of $2.6 \times 10^{-5} \text{ m}^2$. All devices were prepared in room environment without encapsulation. Figure 1b shows the structure of the fabricated device.

The J – V – L characteristics were measured using a chroma meter CS-200 (Konica Minolta) powered by source measure unit (Keithley 2400). All characterizations of the device performance were performed at room temperature without encapsulation.

3. Results and discussion

The logarithm plot of current density–voltage (J – V) characteristics of the single-layer OLEDs are shown in figure 2. The current density of OLEDs increases with the increase in

the blend elements in the emissive layer. This provides the evidence that the blending method enhances the mobility of the OLED, as reported in Blochwitz *et al.*²⁸ From figure 2, the anomalous J – V characteristic is observed at a low-driven voltage ranging from 2.5 to 6 V for TPD:PBD:Alq₃ device, which is similar to that reported by Berleb *et al.*²⁹ and Manca *et al.*³⁰ This feature is called negative differential resistance (NDR). It has been discussed that the NDR effect in OLED-doped system was related to guest hopping sites (GHSs) and phonon scattering.³¹ In addition, it has been reported that molecular blends will generate hopping site in the TPD-blended system.³² The same argument has been discussed for OLEDs base on NPD/poly-Alq₃ blends, in which hopping-type bipolar charge transport was considered.³³ Thus, it is suggested that GHS was formed in the TPD:PBD:Alq₃ OLED system.

Figure 3 shows a schematic diagram of carrier pathways and electroluminescence (EL) mechanism of TPD:PBD:Alq₃ blend OLEDs. In a very low voltage region (0–2 V), holes and electrons are injected from anode and cathode, respectively, and travel through GHS. More injection at a higher bias (2.5–4.5 V) results in a rapid current rise. After 4.5 V of bias, the holes and electrons are still travelling through GHS; however, at the same time, they recombine at the Alq₃ molecule to generate phonons. These energetic phonons then scatter the carriers to decrease the mobility and current, simultaneously,³⁴ which result in NDR phenomenon. This behaviour is not observed in the very low bias, indicating that the number of generated phonons is too small to affect the mobility of the carriers. For bias above 6 V, the applied electric field is sufficient enough to facilitate the transportation

of holes and electrons through highest occupied molecular orbital (HOMO) level of TPD and lowest unoccupied molecular orbital (LUMO) level of PBD, respectively. The recombination of carriers was then occurring in the Alq₃ molecule (from LUMO to HOMO level of Alq₃) to release photon energy as an emission. High amount of phonons in the system also explains the rapid Joule heating process in such a blend OLED. It is postulated that the generation of GHS is an important feature that cause the reduction in the effective barrier height where injection mechanism is enhanced.

It can also be seen that the NDR characteristic occurred at a higher voltage for the TPD:PBD:Alq₃ (4.5 V) as compared to that of TPD:Alq₃ (2 V) device. This suggest that the

Figure 2. Log J –Log V plot of single-layer OLEDs.

concentration of GHS is higher in TPD:PBD:Alq₃ device as compared to that of TPD:Alq₃ due to more elements in the blend system. Thus, high voltage is required to be applied in order for charged carrier to fill the GHS before the phonon emission occurs, and then produces the NDR phenomena. It can also be observed that the negative gradient of NDR is larger in TPD:PBD:Alq₃ as compared with TPD:Alq₃ devices. There are two factors that contribute to this property; the high concentration of GHS and improvement of current density in the blend device. It is noted that the blend system may improve charge carrier.¹⁴ However, the carrier mobility is rapidly reduced due to high intensity of phonon emission at high voltage. For TPD:Alq₃ device, the concentration of GHS is lower and carrier mobility is lower as compared to that of TPD:PBD:Alq₃, thus the NDR characteristic has occurred at a lower voltage and thus the negative gradient is lower.

Figure 4 shows the luminance intensity with respect to driven voltage supplied to the OLED device with different blend system. The turn-on voltage (when $L = 1 \text{ cd m}^{-2}$) obtained was reduced for TPD:PBD:Alq₃ blend (5 V) as compared to that of the pure Alq₃ device (15 V). The maximum luminance (before the voltage drops due to Joule heating) was significantly improved from $8 \pm 1 \text{ cd m}^{-2}$ for Alq₃ OLED up to $347 \pm 10 \text{ cd m}^{-2}$ for TPD:PBD:Alq₃ blend OLED. The percentage of increment is calculated to be 41.7%. In TPD:PBD:Alq₃-based OLED, the Alq₃ molecule is acting as a luminescence centre, while TPD and PBD act as a hole transporting molecule and an electron transporting blend molecule, respectively. Thus, the amount of charge carriers (hole and electron) that have been injected into the organic layer of TPD:PBD:Alq₃ OLED became more balanced as compared to Alq₃ and TPD:Alq₃ OLEDs. The

Figure 3. Schematic diagram of charge carrier pathways and EL mechanism of TPD:PBD:Alq₃ OLEDs.

Figure 4. L - V characteristic of single-layer OLEDs.

accumulation of the balance charge carriers creates more exciton and more recombination of the exciton occurs due to the Coulomb interaction, resulting in the significant increase in luminance of the OLED device. The current efficiency, η , can be directly understood as the ratio of luminance, L (cd m^{-2}), emitted with respect to the amount of current density applied, J (A m^{-2}). A maximum η is obtained to increase from $1.1 \pm 0.2 \text{ cd A}^{-1}$ for Alq_3 to $2.7 \pm 0.7 \text{ cd A}^{-1}$ for TPD:PBD:Alq_3 OLEDs. The increase in the current efficiency indicated that the TPD and PBD played an important role in facilitating the enhancement of the exciton formation by trapping and transporting more carriers inside the Alq_3 emissive molecule. It is also noted that the NDR characteristic does not affect the luminescence properties of the blend OLED because the turn-on voltage of the device is higher than that of the NDR region.

Figure 5 shows *Commission Internationale de l'Eclairage* (CIE) coordinate plot of the single-layer blend OLEDs. The emission of light from all blend OLEDs was observed within green light region. Interestingly, the CIE coordinates were shifted towards the higher value of x -axis and downward to the lower value of y -axis. This shift indicates that there is a change in colour tone from pure green towards yellowish-green when the Alq_3 -based OLED was blended with the TPD and PBD molecules. The colour shift is related to complex charge transfer from TPD and PBD molecules to Alq_3 molecule exciton formation in the blend system. The shift in colour due to charge transfer also has been reported in other blend OLEDs.^{15,35} These results can also confirm that the Alq_3 molecules remain as a centre of luminescence even in the blended OLEDs.

4. Conclusions

The TPD:PBD:Alq_3 blend OLED exhibits the highest maximum luminance and current efficiency as compared to the

Figure 5. CIE coordinate plot of single-layer OLEDs.

TPD:Alq_3 - and Alq_3 -only devices, which can be related to a more balance charged carrier accumulated in the recombination region, as hole and electron transporting molecules were blended into Alq_3 molecule. Introducing TPD and PBD molecules in Alq_3 single-layer OLEDs also result in the significant reduction in hole barrier height, which improves the injection mechanism of hole at anode-organic interface. An anomalous current characteristic was observed in TPD:PBD:Alq_3 OLEDs, where the device exhibits the highest NDR at a low voltage region. The occurrence of NDR is related to the generation of GHS and phonon scattering phenomenon. Concentration of GHS and carrier conductivity properties in the blend system are suggested to be the major factor in determining the position and gradient size of NDR, respectively. However, the NDR does not alter the luminance and current efficiency of the device at high voltage region.

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References

1. Shirakawa H, Louis E J, MacDiarmid A G, Chiang C K and Heeger A J 1977 *J. Chem. Soc. Chem. Commun.* **16** 578
2. Tang C W and VanSlyke S A 1987 *Appl. Phys. Lett.* **51** 913
3. Dawson R M A et al 1998 *The impact of the transient response of organic light emitting diodes on the design of active matrix OLED displays*. Paper presented at the Electron Devices Meeting, 6–9 December 1998. IEDM '98. Technical Digest International
4. Singh R, Narayanan Unni K N, Solanki A and Deepak 2012 *Opt. Mater.* **34** 716

5. Choy W C H and Ho C Y 2007 *Opt. Express* **15** 13288
6. Sempel A and Büchel M 2002 *Org. Electron.* **3** 89
7. Xie G *et al* 2010 *Org. Electron.* **11** 407
8. Hebner T R, Wu C C, Marcy D, Lu M H and Sturm J C 1998 *Appl. Phys. Lett.* **72** 519
9. Valadares M *et al* 2009 *Mater. Sci. Eng. C* **29** 571
10. Lee D H, Choi J S, Chae H, Chung C H and Cho S M 2009 *Curr. Appl. Phys.* **9** 161
11. Reyes R, Cremona M, Teotonio E E S, Brito H F and Malta O L 2004 *Chem. Phys. Lett.* **396** 54
12. Cossiello R F, Cirpan A, Karasz F E, Akcelrud L and Atvars T D Z 2008 *Synth. Met.* **158** 219
13. Yap C C, Yahaya M and Salleh M M 2008 *Curr. Appl. Phys.* **8** 637
14. Yap C C, Yahaya M and Salleh M M 2009 *Curr. Appl. Phys.* **9** 722
15. Camurlu P *et al* 2009 *Synth. Met.* **159** 41
16. Kim S-J *et al* 2011 *Org. Electron.* **12** 492
17. Lee W J *et al* 2003a *Solid-State Electron.* **47** 927
18. Xie G *et al* 2008 *Appl. Phys. Lett.* **92** 093305
19. Nie H, Zhang B and Tang X Z 2007 *Chin. Phys.* **16** 730
20. Chopra N *et al* 2008 *Appl. Phys. Lett.* **93** 143307
21. Kao P-C, Lin J-H, Wang J-Y, Yang C-H and Chen S-H 2011 *J. Appl. Phys.* **109** 094505
22. Zhang T *et al* 2005 *J. Appl. Phys.* **98** 063503
23. Fang J, Chan Choy C, Ma D and Ou E C W 2006 *Thin Solid Films* **515** 2419
24. Kin Z, Kajii H, Hasegawa Y, Kawai T and Ohmori Y 2008 *Thin Solid Films* **516** 2735
25. Costela A *et al* 2004 *Chem. Phys. Lett.* **387** 496
26. Kalinowski J and Szybowska K 2008 *Org. Electron.* **9** 1032
27. Lee C E *et al* 2001 *Curr. Appl. Phys.* **1** 107
28. Blochwitz J, Pfeiffer M, Fritz T and Leo K 1998 *Appl. Phys. Lett.* **73** 729
29. Berleb S, Brütting W and Schwoerer M 1999 *Synth. Met.* **102** 1034
30. Manca J *et al* 1998 *Opt. Mater.* **9** 134
31. Fang Y K *et al* 2008 *J. Phys. Chem. Solids* **69** 738
32. Lee W J *et al* 2003b *Solid-State Electron.* **47** 1127
33. Kim Y S, Jung S Y, Koh K H, Lee S and Ko K Y 2008 *J. Korean Phys. Soc.* **53** 3563
34. Nan G, Yang X, Wang L, Shuai Z and Zhao Y 2009 *Phys. Rev. B* **79** 115203
35. de Deus J F *et al* 2011 *Org. Electron.* **12** 1493