Aging-induced Recombination Zone Shift in Mixed-Host Organic Light-emitting Devices

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ABSTRACT

In this paper, we have demonstrated the time-dependent distribution of recombination-rate of a mixed-host (MH) organic light-emitting devices (OLEDs) by co-evaporating an ultra thin red-emitting doped layer (probe). With various probe position, the intensity ratio of red to green directly indicates the exciton distribution in MH layer. If the position of probe insertion is that of maximum recombination-rate, the driving voltage is also reduced which can be explained by the increase of the recombination current. From spectral and J-V analyses, the maximum recombination-rate position is 10 nm to the hole transporting layer when MH-OLED is not aged. After 48 hours of the DC aging test, the changes in the red to green intensity ratio of different devices are different. After 96 hours aging, this ratio does not change further among all devices, indicative of the achievement of steady state of recombination-rate distribution. The organic materials degrade more when it locates near the maximum of the recombination-rate.

Keywords: organic light-emitting device, mixed hosts, lifetime

1. INTRODUCTION

The academic researches and the commercial applications of organic light-emitting devices (OLEDs) blossomed from two decades ago[1 2]. Since the invention of multiple thin (less than micrometer) organic films structure opened the gateway to the practical applications. Accompanying the build-up of device physics and the development of novel organic materials and fantastic device structure, it is believed OLED has the potential of being the next generation of display technology. However, the short device operational lifetime still limits the application field so far[3]. Through the intensive improvement on the fabrication process, all factors from the unstable environment can be dramatically suppressed[4]. However, the intrinsic degradation of organic material is inevitable. To improve, mixed-host (MH) OLEDs have been demonstrated as one of the effective methods to elongate the operational lifetime[5].

In a conventional hetero-junction (HJ) OLED, the interface of the hole transporting layer (HTL) and emitting layer (EML) provide a barrier to confine carriers which improves the device efficiency. Due to this barrier, the high local electric field which is built by holes in HTL and electrons in EML deteriorates the materials near the interface. Also, the highly accumulated holes in the EML near the interface form chemically unstable cations, thus accelerating the formation of non-radiative trapping centers and results in luminance decay and voltage increase of an OLED[6]. Unlike hetero-junction devices, MH devices are able to broaden exciton distribution and to blur the interface between layers because of providing low injection barrier from both electron transporting layer (ETL) and HTL to EML. The significant prolongation in device lifetime is attributed to the blurring of interface barrier. Using this technology, carrier mobilities can be easily modulated by selecting organic materials or mixing two hosts with different ratios[7 8]. Typically, the bipolar carrier transporting behavior of the MH-EML can effectively reduce the driving voltage of an OLED[9]. Nevertheless, in the absence of the carrier confinement of the conventional HJ structure, the MH-OLED usually exhibits a higher carrier leakage and thus lower current efficiency. Besides, the bipolar characteristic of the EML extend the recombination zone from narrow region at the interface into the wider region inside the EML.

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Organic Light Emitting Materials and Devices X, edited by Zakya H. Kafafi, Franky So,
Proc. of SPIE Vol. 6333, 63331A, (2006) · 0277-786X/06/$15 · doi: 10.1117/12.678317

There are numerous methods to deduce the spatial exciton distribution, as well as the corresponding width in organic layer[10 11 12 13]. In this paper, the insertion of an ultra-thin doped layer was chosen to measure the exciton distribution. The major principle of using this method is illustrated below: first, insert a thin and emissive dopant with the emission color different from the matrix emission at different positions. If the probe approaches the maximum recombination-rate position, the intensity ratio of dopant to matrix (red to green in this paper) component in the spectra will show an obvious increase. Therefore, through the analysis of the green and red emission from the matrix and dopant material of the EML, we can determine the exciton distribution. By examining the evolution of spectra from various probe positions, the spatial distribution can be plotted. This probe is guaranteed to be very thin to avoid its effects on carrier transport. In this paper, the experiment details are given in section 2. Experimental results and the related discussions are presented in section 3. Finally, a summary is drawn in section 4.

2. EXPERIMENT

In all devices, N,N'-diphenyl-N,N'-bis(1-napthyl)-1,1'-biphenyl-4,4'-diamine (NPB), tris-(8-hydroxyquinoline) aluminum (Alq_3), and 4-(dicyanomethylene)-2-tert-butyl-6-1,1,7,7- tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTB) were used as the HTL, ETL, and red-emitting probe material, respectively; our backboned device structure without DCJTB was ITO/NPB (30nm)/NPB: Alq_3 (40nm)/Alq_3 (20nm)/LiF (1.2nm)/Al (150nm). All organic materials were thermally evaporated under high-vacuum (~3×10^{-6} torr) condition. The MH structure consists of a volume ratio of NPB: Alq_3 = 1:1. A very thin DCJTB probe (1.2 nm) with 2 vol. % is co-evaporated at the different positions within the MH layer to measure the exciton distribution. Device configuration is schemed in Fig. 1. The device with the probe position x ranging from 0 to 35 nm, in steps of 5 nm, is label as 1 to 8. The location of probe in Device 9 is just at the interface of EML/ETL, i.e., x=38.8. Device 10 is a reference device without DCJTB probe.

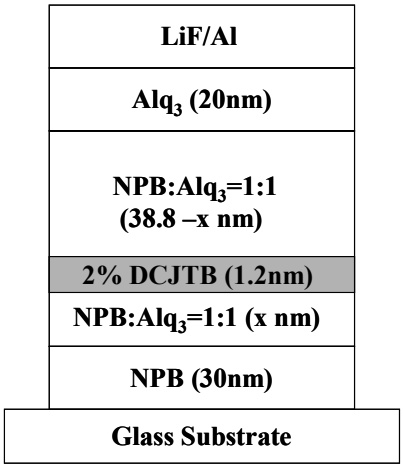


Fig. 1 Scheme of device configuration. Shaded region indicates 2% DCJTB was co-doped in MH-EML with the total thickness of 40 nm.

3. RESULTS AND DISCUSSIONS

Fig. 2 shows the driving voltage and red-to-green intensity ratio with respect to probe position. The red-to-green intensity ratio reflects the exciton distribution since the light is generated from the radiatively recombination of exciton. We can see that the peak of exciton concentration is 10 nm to the NPB side. The driving voltage of reference device 10 is about 8.5V at 100 mA/cm^2. If the thin probe layer serves as the trapping site, the driving voltage of device 10 should be the lowest. However, the voltage reduction in device 2, 3, 4 was observed. The largest voltage reduction is 2V. The

driving voltages of other devices are comparable to that of device 10. It indicates that dopant in this method is no longer a trap for carrier. Here, we propose a possible mechanism to explain the low driving voltages of devices 3 and 4 where the probes locate near the peak of the exciton concentration: since the recombination rate constant of DCJTB is higher than Alq3[14], the recombination current can be enhanced due to the increasing recombination rate constant. Equivalently, the driving voltage is lowered. Consequently, the inverse of the voltage reduction indicates the recombination-rate distribution, since the cause of this behavior comes from the recombination current.

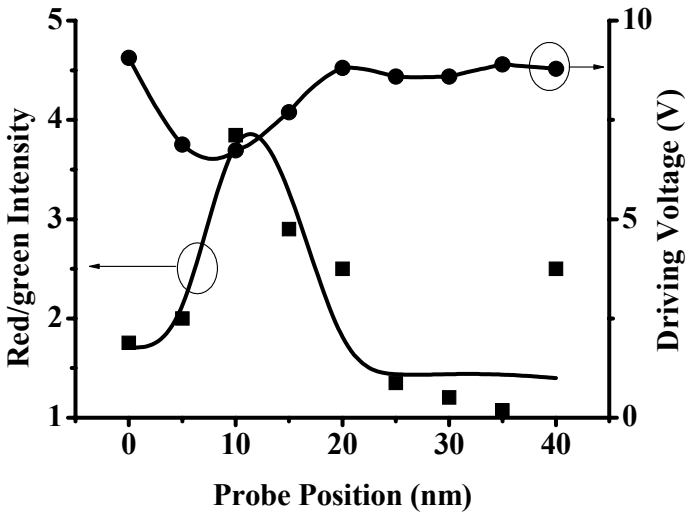
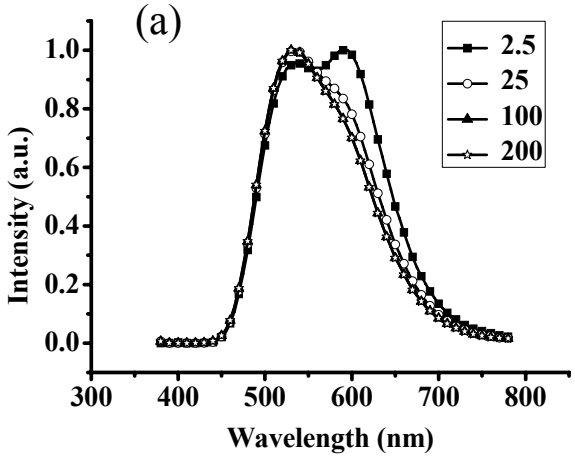


Fig. 2 (Squared symbols) Intensity ratio of red/green at 2.5 mA/cm^2 versus probe position. (Circle symbols) Driving voltage at 100 mA/cm^2 versus probe position. The curves are the guides for eyes.

Fig. 3 shows the electroluminescence (EL) spectra of device 7 (probe in inserted at 10 nm from the EML/ETL interface) with different current densities at 0, 48 and 96 hours. From 0 to 48 hrs, the relative intensity of green component decreases. Since the probe position is not at the maximum recombination-rate position, DCJTB is less deteriorated than Alq3. It suggests that the degradation of materials are faster at the maximum recombination-rate position. Further, from 48 to 96 hrs, the spectra do not change with aging time. It implies that the steady state of degradation in MH-EML is achieved. The process from initial state to the steady state can be described as follows: At the beginning, the degradation is most serious at the maximum recombination-rate position. As time goes by, the recombination zone becomes flatter and flatter. Therefore, after 48 hours, the extent of degradation everywhere in MH-EML is identical.



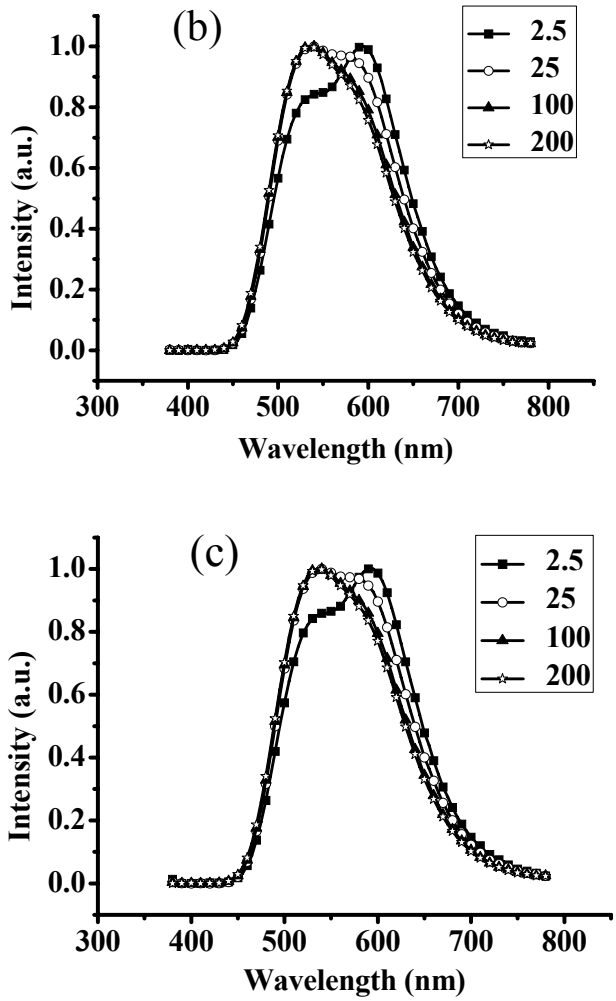


Fig. 3 Evolution of spectra of device 7 with aging time of 0 (a), 48 (b), 96 (c) hrs. The inset indicates the injection current density (mA/cm^2).

The spectral evolutions of device 3 and 5 were then examined following the similar procedure describe above. However, device 3 and 5 has opposite trend compared to device 7, which is the relative intensity of green component increases after the aging of 48 hours. In device 3 where the probe is right at the maximum recombination-rate position, regardless of the degradation of Alq3 or DCJTB at this position, the increase in green-to-red intensity ratio supports that the initial degradation at the recombination-rate position is most serious. In device 5, the abovementioned behavior was also observed. Although its probe is not at the maximum recombination-rate position, the green-to-red intensity ratio still increases. It is likely that the maximum recombination-rate position could shift toward cathode side during the aging period. Among all examined devices, the spectra do not change after aging time of 48 hours. In EL measurement mentioned above, the carrier transport and recombination processes affect the red and green emission. To further study the intrinsic material degradation. Photoluminescence (PL) experiments were conducted. Fig. 4 shows the PL spectra of devices 1, 3 and 9, respectively. The discrepancy of spectra before and after aging signifies the amount of degradation of materials. As can be obviously seen, the DCJTB intensity relative to the Alq3 varies with different probe position. As probe approaches the maximum recombination-rate position, the difference (before – after) of the red intensity is larger, such as device 1 and 3. In the case that the probe is distant from maximum recombination-rate position, the relative red difference of the red intensity is smaller, such as device 9. This behavior also provides another evidence for faster degradation occurring at the maximum recombination-rate position.

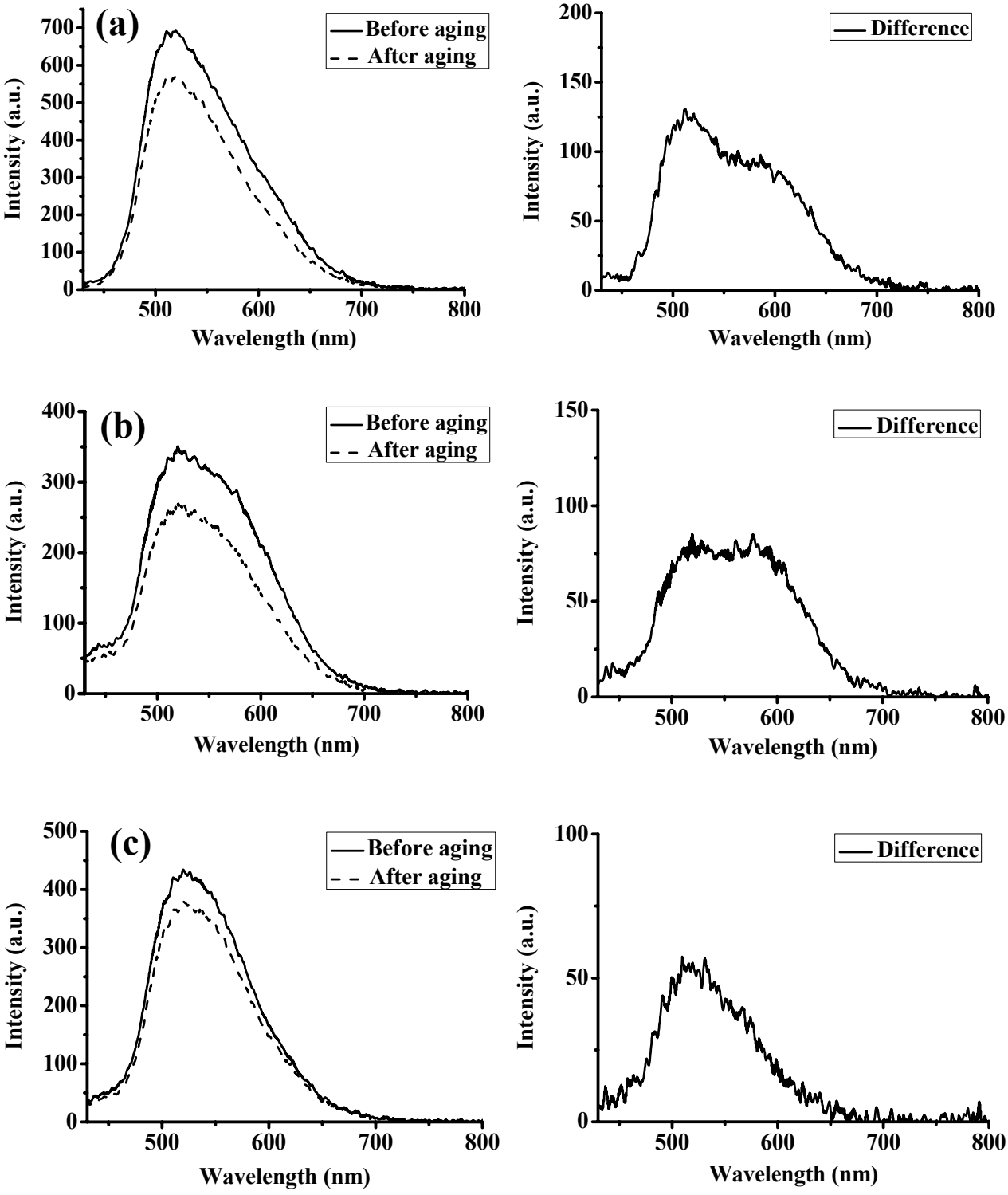


Fig. 4 Left figures are the PL spectra before and after aging of device 1 (a), 3 (b), 9 (c). Rights figures are the discrepancy of the PL spectra before and after aging.

4. SUMMARY

In the MH-OLED where its EML consists of NPB:Alq3=1:1, the maximum recombination-rate position was determined to be at 10 nm away from NPB side. In addition, the well-known broaden recombination-rate distribution in MH-OLED is concretely observed. Examining this distribution by inserting ultra thin DCJTB probe, we observed the enhancement of recombination current, leading to driving voltage reduction. Both EL and PL evolution with aging time support that at the initial stage of degradation, the rate of degradation at the maximum recombination-rate position is fastest. From the EL spectra evolution, we could deduce that the recombination-rate distribution become flatter after aging.

ACKNOWLEDGMENT

This work was financially supported by Aixtron Corporation.

REFERENCES

1 C. W. Tang, and S. A. VanSlyke, *Appl. Phys. Lett.* **51**, 913 (1987).
2 C. W. Tang, S. A. Vanslyke, and C. H. Chen, *J. Appl. Phys.* **65**, 3610 (1989).
3 V. E. Choong, S. Shi, J. Curless, C. L. Shieh, H. C. Lee, F. So, J. Shen, and J. Yang, *Appl. Phys. Lett.*, **75**, 172 (1999)
4 A. B. Chwang, R. C. Kwong, and J. J. Brown, *Appl. Phys. Lett.*, **80**, 725 (2002)
5 D. Ma, C. S. Lee, S. T. Lee, and L. S. Hung, *Appl. Phys. Lett.*, **80**, 3641 (2002)
6 D. Y. Kondakov, J. R. Sandifer, C. W. Tang, and R. H. Young, *J. Appl, Phys.*, **93**, 1108 (2003)
7 L.-B. Lin, S. A. Jenekhe, and P. M. Borsenberger, *Appl. Phys. Lett.*, **69**, 3495 (1996)
8 J. Shen, and J. Yang, *J. Appl. Phys.*, **87**, 3891 (2000)
9 J. H. Lee, C. I Wu, S. W. Liu, C. A. Huang, and Y. Chang, *Appl. Phys. Lett.* **86**, 103506 (2005)
10 C. W. Tang, S. A. Vanslyke, and C. H. Chen, *J. Appl. Phys.* **65**, 3610 (1989)
11 J. Kalinowski, L. C. Palilis, W. H. Kim, and Z. H. Kafafi, *J. Appl. Phys*. **94**, 7764 (2003)
12 C. Qiu, H. Chen, M. Wong, and H. S. Kwok, *IEEE Trans. Electron Devices* **49**, 1540 (2002)
13 J. Kalinowski, *Organic Light Emitting Diodes: Principles, Characteristics and Processes*, Marcel Dekker, New York, 2005
14 L. S. Hung, and C. H. Chen, *Mater. Sci. Eng.* **R 39**, 143 (2002)