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Citation: Applied Physics Letters **94**, 023306 (2009); doi: 10.1063/1.3072616
View online: http://dx.doi.org/10.1063/1.3072616
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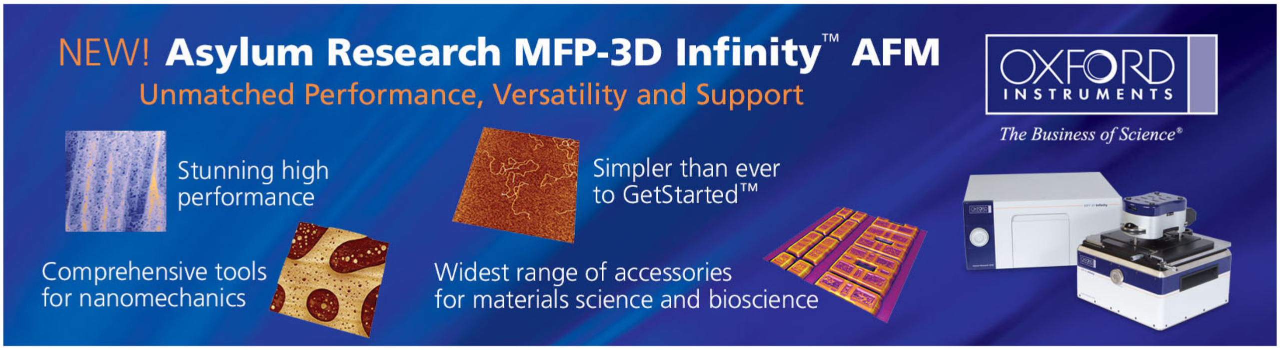

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APPLIED PHYSICS LETTERS **94**, 023306 (2009)

Study of efficient and stable organic light-emitting diodes with 2-methyl-9,10-*di*(2-naphthyl)anthracene as hole-transport material by admittance spectroscopy

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(Received 4 November 2008; accepted 27 December 2008; published online 16 January 2009)

An organic light-emitting device with enhanced efficiency sby employing 2-methyl-9,10-*di*(2-naphthyl)anthracene (MADN) as hole-transport material (HTM) has been developed. The admittance spectroscopy studies indicate that using MADN as HTM can reduce the amount of hole carriers injected into the device leading to a well-balanced carrier recombination. The green fluorescent 10-(2-benzothiazolyl)-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1H,5H,11H-benzo[l]pyrano-[6,7,8-ij]quinolizin-11-one doped *tris*(8-quinolinolato)aluminum device achieved a current efficiency of 21.8 cd/A and a power efficiency of 10.4 lm/W at 20 mA/cm^2 that are 65% higher than those of the control device. The green-doped device also achieved a long half-decay lifetime of 22 000 h at an initial brightness of 500 cd/m^2. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3072616]

Since Tang and VanSlyke developed the multilayer organic light-emitting devices (OLEDs),[1] tremendous efforts have been directed toward improving the device performance. It was recognized that the external quantum efficiency (EQE) of OLEDs depends heavily on the efficiency of carrier injection and recombination as well as the balance of the holes and electrons.[2,3] Therefore, in order to achieve maximal efficiency, a well-balanced carrier recombination in the emission layer is a must inside the device.

However, OLEDs in general do not necessarily provide the configuration to achieve a balanced carrier injection/transportation that leads to recombination. One of the reasons is that the injected hole is usually more mobile than the injected electron under the same electric field. For instance, the hole mobility of the most commonly used hole-transport material (HTM), N,N'-bis-(1-naphthyl)-N,N'-diphenyl,$1,1'$-biphenyl-$4,4'$-diamine (NPB), is 5.1×10^{-4} cm^2 V^{-1} s^{-1},[4] which is three orders higher than the electron mobility of the commonly used electron-transport material (ETM), *tris*(8-quinolinolato)aluminum (Alq$_3$) with charge mobility of $10^{-7}-10^{-6}$ cm^2 V^{-1} s^{-1} depending on the electric field.[5–7] Moreover, it has been reported that the fluorescent quencher of Alq$_3$ cationic species would easily be produced when considerable quantities of hole carriers exist, resulting in the deterioration of the device lifetime.[8–10] Thus, there were many attempts to identify practical ETMs.[11,12] However, they are often of limited use because of undesirable thermal stability or morphological properties. Up until recently, formal reports with full disclosure on really efficient and stable ETMs are still rare and sketchy. One notable example is reported by Sanyo Electric Co., which utilized 9,10-bis[4-(6-methylbenzothiazol-2-yl)phenyl]anthracene as ETM and had achieved a highly efficient fluorescent green and red doped device.[13,14]

Consequently, finding a way of reducing the number of holes or increasing the number of electrons reaching the emission layer is considered one of the most direct and economic solutions to improve device efficiency. Recently, it was found that the hole mobility can be efficiently controlled by incorporating the composite hole transporting layer (c-HTL) of NPB:copper phthalocyanine (CuPc) (1:1) to balance the charge carriers from which the device efficiency can be significantly enhanced.[15] However, the fabrication process is complicated, which requires precise control and in particular, using the environmentally unfriendly CuPc.

In our previous work, 2-methyl-9,10-*di*(2-naphthyl)anthracene (MADN) has been developed and used as an efficient blue host material, which has a stable thin-film morphology and a wide energy bandgap.[16] Moreover, MADN was shown to exhibit an ambipolar transporting ability.[17] By time-of-flight measurements, values of electron and hole mobilities of MADN have been found to be $(2-4)\times 10^{-7}$ and $(3-5)\times 10^{-7}$ cm^2 V^{-1} s^{-1}, respectively. Due to the comparable hole mobility of MADN and electron mobility of Alq$_3$, it is expected that by using MADN as HTM, the issues of excess hole carriers mentioned earlier can be circumvented. In this letter, we study the electrical characteristics of current-voltage (I-V) dependence and admittance spectroscopy of devices in which conventional NPB is replaced with MADN and find that it could simultaneously improve the carrier recombination in the device and significantly enhance the device efficiency and operational lifetime as well.

In our experiments, the following 10-(2-benzothiazolyl) - 1,1,7,7 - tetramethyl - 2,3,6,7 - tetrahydro-1H,5H,11H-benzo[l]pyrano -[6,7,8- ij]quinolizin-11-one (C545T) green-doped OLED devices whose structure was indium tin oxide (ITO)/CF$_x$/HTM(60 nm)/

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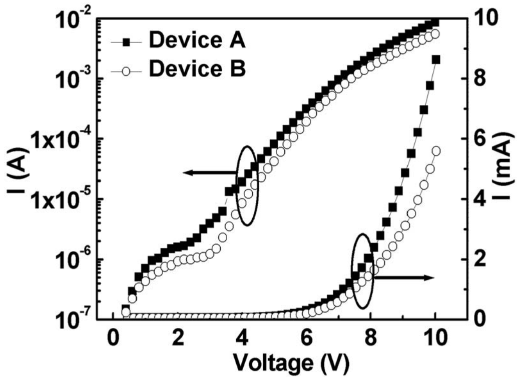

FIG. 1. Current-voltage (I-V) characteristics of devices A and B in linear scale and logarithmic scales.

Alq_3:1%C545T/(37.5 nm)/Alq_3(37.5 nm)/LiF(1 nm)/Al(150 nm) were fabricated, where CF_x and Alq_3 were used as the hole injection material[18] and ETM, respectively. The HTMs of devices I and II were NPB and MADN, respectively. For studying the transport phenomenon and electrical characteristics, two additional hole-only devices were also fabricated. The structures of hole-only devices A and B were ITO/CF_x/NPB(30 nm)/Alq_3(60 nm)/Al(150 nm) and ITO/CF_x/MADN(30 nm)/Alq_3(60 nm)/Al(150 nm), respectively.

Figure 1 shows the current-voltage (I-V) characteristics of the hole-only devices. Higher operational voltage and smaller current density dependency were observed in device B with MADN as compared to that of device A. For instance, the turn-on voltages of hole-only devices A and B are 2.4 and 3.0 V, respectively. Figure 2 shows the room temperature conductance/frequency-frequency (G/F-F) spectra at zero bias for devices A and B. In Fig. 2, both the curves show two distinct G/F peaks, which are proportional to the dielectric loss. The loss peak can be described by the classical Debye frequency response, which is given by

$$\frac{G(F)}{F} = \frac{A/F_p}{1+(F/F_p)^2},$$

where the amplitude A is a temperature-dependent constant and F_p is the peak frequency. Based on the theory of admittance spectroscopy with an equivalent circuit model of the studied hole-only devices,[19] the low-frequency loss peak is assigned to be associated with the single resistance-capacitance (RC) time constant of the HTM layer, and the high-frequency peak is associated with the RC time constant of parasitic series resistance.[20] For comparison, higher resistance of HTM layer was observed in device B, resulting in a smaller current condition observed in Fig. 1; the higher resistance of HTM layer in device B can be ascribed to lower hole mobility of MADN. Moreover, the increase in operation voltage upon using MADN as HTM can be explained by a larger energy barrier between ITO and MADN. The inset in Fig. 2 plots ln(F) versus 1000/T derived from the low-frequency peak of the G/F-F measurements at various temperatures, which yield the activation energies (E_a) of HTM layers for devices A and B. As shown, E_a of MADN is 0.655 eV, which is larger than that of NPB (0.238 eV). As a result, the larger E_a increases the band offset between the ITO anode and HTM layer, which in turn retards hole injection from ITO to MADN as compared that to NPB. In addition, higher resistance and larger hole injection energy barrier in the device with MADN as HTM can reduce the amount of hole transported into the doped Alq_3 emitting layer under the same applied bias as compared that to NPB. Therefore, it is expected that a well-balanced charge carrier can be achieved by introducing MADN as HTM in OLED devices.

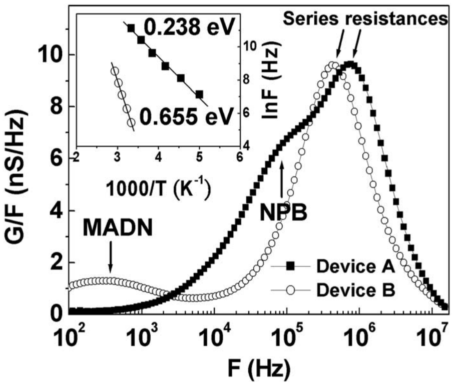

FIG. 2. Conductance/frequency-frequency (G/F-F) spectra of devices A and B. Inset: ln(F) vs 1000/T derived from Fig. 2 at various temperatures.

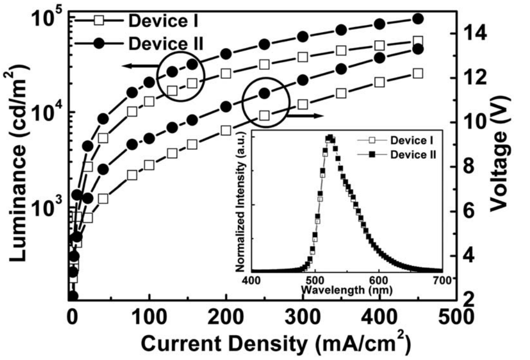

FIG. 3. Luminance-current density-voltage (L-J-V) characteristics of devices I and II. Inset: normalized electroluminescent spectra of devices I and II at 20 mA/cm^2.

Figure 3 shows the dependence of luminance-current density-voltage (L-J-V) characteristics of the C545T devices. It is noted that the voltage required at a given current density of device II with MADN as HTM is higher than that of the standard device, which is in complete agreement with the independent results derived from I-V measurement and admittance spectra. Although the drive voltage was slightly increased by using MADN as HTM, the performance of device II was considerably enhanced. For instance, the luminances of devices I and II at 20 mA/cm^2 were 2646 cd/m^2 (at 5.7 V) and 4366 cd/m^2 (at 6.6 V), respectively. Device II achieved 21.8 cd/A and 10.4 lm/W with an EQE of 5.8% at 20 mA/cm^2, whose current efficiency has been improved by 65% as compared to that of standard device I (13.2 cd/A), as shown in Fig. 4. Furthermore, the introduction of MADN as HTM would not impact the emission color, which is essentially identical to that of the standard device with a Commission Internationale d'Eclairage ($CIE_{x,y}$) coordinates of (0.30, 0.64) as shown in the inset of Fig. 3. It can also be observed that the current efficiency of device II is sustained at 21.3 cd/A (under 450 mA/cm^2), suffers essentially no current-induced quenching, and there is no color shift with respect to

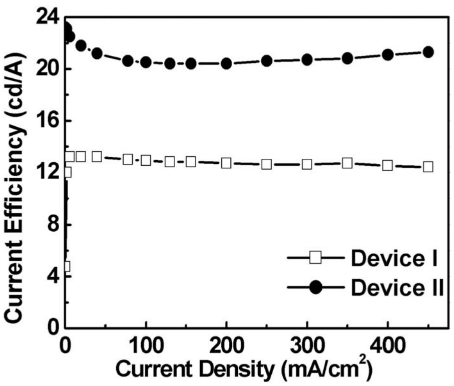

FIG. 4. Current efficiency vs current density characteristics of devices I and II.

varying drive currents, as the CIE$_{x,y}$ coordinates only shift from (0.304, 0.647) at 2 mA/cm^2 to (0.303, 0.637) at 450 mA/cm^2 with ΔCIE$_{x,y}=\pm(0.001,0.01)$. The enhancement in the device performance and the apparent resistance to changes in both current efficiency and emission color under various drive current densities can be attributed to the well-balanced charge carriers for recombination in device II.

Device II with MADN as HTM also showed exceptionally long operational stability as shown in Fig. 5. The $t_{1/2}$ [the times for the luminance to drop to 50% of initial luminance (L_0)] of device II measured at constant current densities of 20 mA/cm^2 (L_0=4366 cd/m^2), 40 mA/cm^2 (L_0=8469 cd/m^2), and 60 mA/cm^2 (L_0=12 387 cd/m^2) were 612, 202, and 110 h, respectively. Assuming scalable Coulombic degradation of ($L_0^n \times T_{1/2}$=const) under accelerated drive conditions[21] and by estimation of extrapolated profile, the $t_{1/2}$ of device II driving at a L_0 value of 500 cd/m^2 is projected to be about 22 000 h. The remarkably long operational lifetime is attributed to the improved recombination probability of charge carriers in the emission layer that leads to much reduced fluorescent quencher of Alq$_3$ cationic radical produced by excess hole in the emitter.

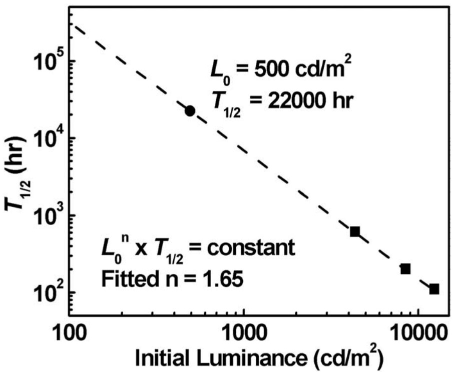

FIG. 5. Extrapolated half life of device II.

Carrier recombination, as well as the balance of holes and electrons, is considered to be one of the most important factors that determine the EQE of OLEDs. Here, we have developed a simple method of introducing MADN as HTM because MADN has a comparable hole mobility to the electron mobility of Alq$_3$ to improve the balance of charge carriers in OLED devices. In addition, *I-V* measurement and admittance spectra indicate that MADN layer has higher resistance and higher energy barrier (E_a) with respect to ITO anode, which can efficiently reduce the excess injected holes and further improve the hole/electron recombination efficiency, giving rise to the remarkably high EQE and current efficiency of 5.8% and 21.8 cd/A and a long operational lifetime of C545T-doped OLED device.

This work was supported by the National Science Council of Taiwan (Grant No. NSC 97-2218-E-009-003). The authors also thank e-Ray Optoelectronics Technology Co., Ltd. of Taiwan for generously supplying some of the OLED materials studied in this work.

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