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Highly stable organic light-emitting devices with a uniformly mixed hole transport layer

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Highly stable organic light-emitting devices were made by using a uniformly mixed hole transport layer (UM-HTL) composed of a mixture of 2-methyl-9,10-di(2-naphthyl)anthracene (MADN) and *N*,*N*′-bis(1-naphthyl)-*N*,*N*′-diphenyl,1,1′-biphenyl-4,4′-diamine (NPB) in a 3:7 (MADN:NPB) ratio. The lifetime of 10-(2-benzothiazolyl)-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1*H*,5*H*,11*H*-benzo[*l*]-pyrano[6,7,8-*ij*]quinolizin-11-one doped green device with UM-HTL can be greatly improved to 2.7 times longer than that of the conventional device (NPB based HTL) without impacting on its driving voltage and emissive color significantly. This improvement in stability can be attributed to the fact that the unstable $[Alq_3^+]$ species formed by electro-oxidation have been effectively suppressed. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2137453]

Since Tang *et al.* developed the heterojunction device structure in 1987, organic light emitting devices (OLEDs) are considered as one of the most attractive technologies for flat panel display and future lighting applications.[1] As a result, it attracts many scientists to pay attention in improving OLED performance. One of the key issues needed to be resolved is the device lifetime. For commercial flat panel display application, it is well known that a lifetime ($t_{1/2}$) of at least 10 000 hours is required under continuous dc stress at an initial luminance of at least 100 cd/m^2.[2]

According to previous studies, factors influencing OLEDs stability can be distinguished into two parts.[2] One is extrinsic, such as dark spot growth due to moisture/oxygen permeation which may be controlled by good encapsulation/desiccation methodology.[3,4] The other is the intrinsic property which relates fundamentally to material stability, carrier transport, and device structure[5–8] that are by far more complicated and still without clear and adequate solution. In 1999, Aziz *et al.* demonstrated that *tris*(8-hydroxyquinoline) aluminum (Alq_3) cationic species caused by the excess of holes resided in Alq_3 is a main unstable factor that determines the stability of Alq_3 based device.[9] Therefore, suppressing the accumulation of excess holes by somehow slowing down the hole mobility seems to be a good way of improving device stability.

Doping of the hole transporting layer (HTL) is commonly used as one of the methods performed to reach this goal.[5,10–14] The underlying principle is that the highest occupied molecular orbital (HOMO) of the dopant material must be lower than that of the HTL material in order to produce hole traps that reduces hole mobility.[12,13] However, there are two disadvantages: (1) it is too sensitive with respect to dopant concentration variations, (2) most of the dopant materials used, such as rubrene (E_g=2.2 eV) (Refs. 5 and 10) or DSA-Ph (E_g=2.7 eV),[14] often has relative small energy band gap, which cannot totally eliminate the problem of dopant emission when doped in the HTL.

In order to circumvent the problems mentioned earlier, we chose a wide energy gap material, 2-methyl-9, 10-*di*(2-naphthyl)anthracene (MADN) (E_g=3.0 eV), to mix with HTL for managing the holes for recombination. In addition to the advantage of wide energy gap, the HOMO of MADN is 5.5 eV (measured by cyclic voltammetry),[15] which is higher than that of *N*,*N*′-*bis*(1-naphthyl)-*N*,*N*′-diphenyl-1,1′-biphenyl-4,4′-diamine (NPB) (HOMO=5.4 eV) and will not be expected to reduce the hole mobility significantly unless under high doping concentration.[12,13] Hence, a wider range of mixed concentration of MADN and NPB can be used to attenuate the hole mobility. Here, we report the optimal concentration of MADN mixed with NPB has been determined to be around 30%, and the mixed layer in this new type of device structure is hitherto named as *uniformly mixed hole transport layer* (UM-HTL). Moreover, the effect of the UM-HTL positioned at various part of the HTL has also been studied. It was found that when the UM-HTL was positioned adjacent to the emission layer (EML), the emission color of the device was not affected and the device lifetime could be enhanced to about 2.7 times longer than that of the conventional OLED structure.

In our experiment, green devices with structure of indium-tin-oxide (ITO)/hole injection layer (HIL)/HTL (60 nm)/EML (37.5 nm)/electron transporting layer (ETL) (37.5 nm)/LiF (1 nm)/Al (200 nm) have been fabricated. Here, CF_x, NPB, Alq_3, 10-(2-benzo-thiazolyl)-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1*H*,5*H*,11*H*-benzo[*l*] pyrano [6,7,8-*ij*]quinolizin-11-one (C-545T), and LiF/Al were employed as HIL, HTL, ETL/emission layer, green dopant material, and cathode, respectively. The emission layer was composed of 1% C-545T doped with Alq_3. To study the effect and illustrate the advantage of the UM-HTL, we fabricated five types of devices with the UM-HTL placed strategically at various positions of the HTL. As a benchmark, the conventional device with single NPB HTL (60 nm) was des-

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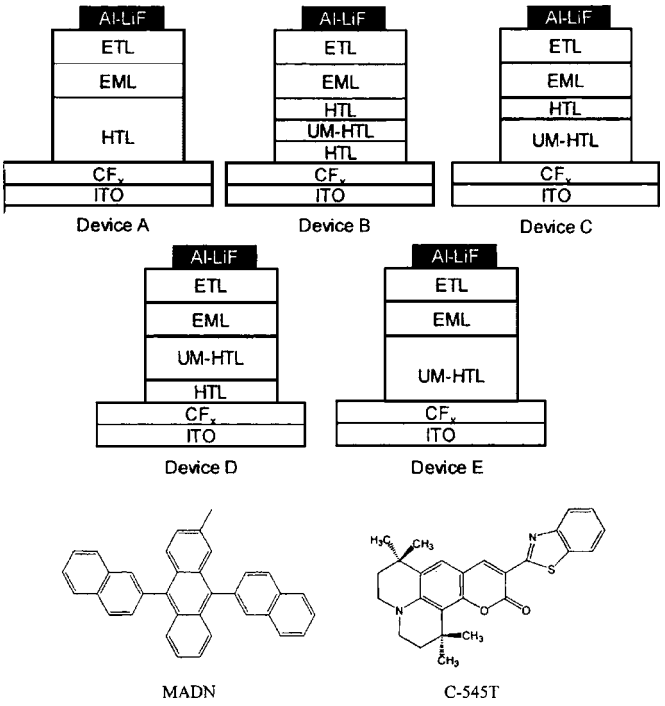

FIG. 1. The schematic device structures and molecular structures of key materials.

ignated as device A. In device B, the HTL was divided into three sections in which the UM-HTL (15 nm) was placed in-between two undoped NPB layers each of 15 nm thick. In device C, the HTL was divided into two sections in which UM-HTL (45 nm) was positioned in-between the hole-injection CF_x and the undoped NPB layer (15 nm). In device D, the HTL was also divided into two parts in that the UM-HTL (45 nm) was positioned in-between the undoped NPB layer (15 nm) and the EML. Finally, in device E, the entire HTL was replaced by the UM-HTL. Detailed device architectures and the molecular structures of key organic materials under study are shown in Fig. 1. Three additional hole-only devices were also fabricated to investigate the effect of the UM-HTL on hole mobility. The structure was ITO/NPB (30 nm)/MADN:NPB (100 nm)/NPB (30 nm)/Al with different MADN:NPB ratios of 0%, 30%, and 60%.

The ITO-coated glass was pretreated by oxygen plasma, and then coated with a polymerized fluorocarbon film (CF_x).[16] Devices were fabricated under the base vacuum of about 10^{-6} Torr in a thin-film evaporation coater following a published protocol. All devices were hermetically sealed prior to testing. The active area of the electroluminescent (EL) device, defined by the overlap of the ITO and the cathode electrodes, was 9 mm^2. The current-voltage-luminance characteristics of the devices were measured with a diode array rapid scan system using a Photo Research PR650 spectrophotometer and a computer-controlled programmable dc source. The device lifetime measurement was performed at a constant drive current density of 20 mA/cm^2.

Figure 2 shows the plots of current density versus voltage (J-V) for three hole-only devices. It can be seen that the voltage at a given current density is increased when the ratio of mixed MADN concentration is high. This result shows that the hole transporting property was indeed changed when high concentration of MADN was mixed. Figure 3 shows the plots of luminance efficiency versus current density of

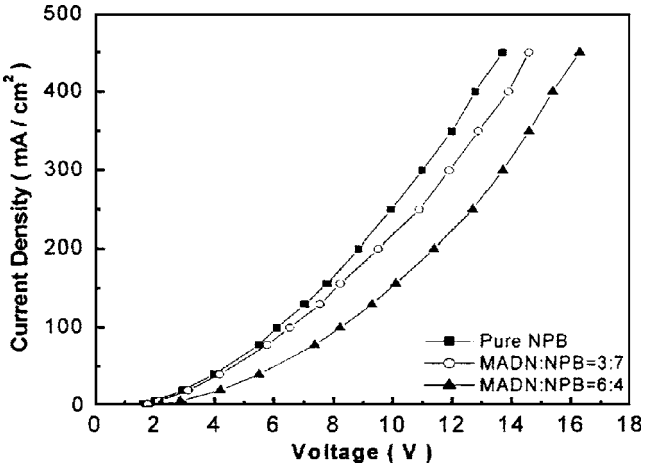

FIG. 2. J-V of three hole only devices.

C-545T doped green devices. Under 20 mA/cm^2, the current efficiency is 12.5, 13.8, 14.0, 12.7, and 12.9 cd/A for devices A, B, C, D, and E, respectively. It is found that the current efficiencies of devices B and C where the UM-HTL is not in contact with EML are all higher than that of the other devices, which means that the position of UM-HTL will have a dominant effect on the recombination efficiency. In the inset of Fig. 3, it shows that emission peak is mainly from C-545T disregarding whether the UM-HTL is in contact with the EML or not.

The operational stability of these OLEDs driven under constant current density of 20 mA/cm^2 is shown in Fig. 4. The t_{80} (the time for the luminance to drop to 80% of initial luminance) and initial luminance (L_0) for devices A, B, C, D, and E were 75 h @ L_0=2500 cd/m^2, 100 h @ L_0=2760 cd/m^2, 110 h @ L_0=2800 cd/m^2, 195 h @ L_0=2540 cd/m^2, and 195 h @ L_0=2580 cd/m^2, respectively. The best stability is found in devices D and E and the overall EL performance of these devices is summarized in Table I.

It is noteworthy that these UM-HTL devices and their associated EL performance can be categorized into two groups: (I) with UM-HTL *not* in contact with EML (devices B and C), and (II) with UM-HTL in contact with EML (devices D and E). Comparing (I) and (II), the increase in efficiency of group (I) can be attributed to the reduced hole

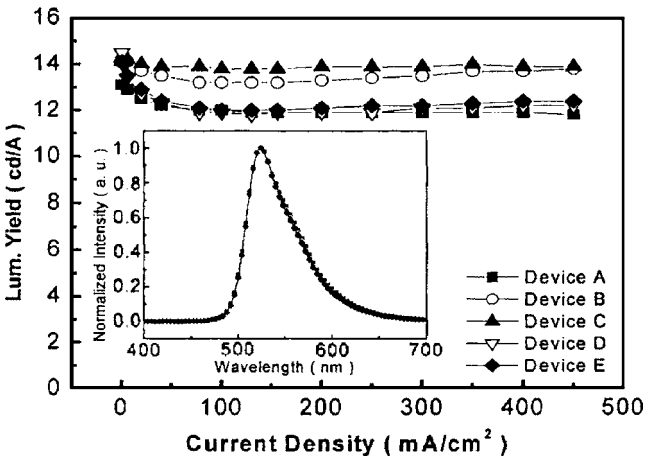

FIG. 3. Current efficiency vs current density characteristics and emission spectra (20 mA/cm^2) (inset) of C-545T doped green device with a different placement of the UM-HTL.

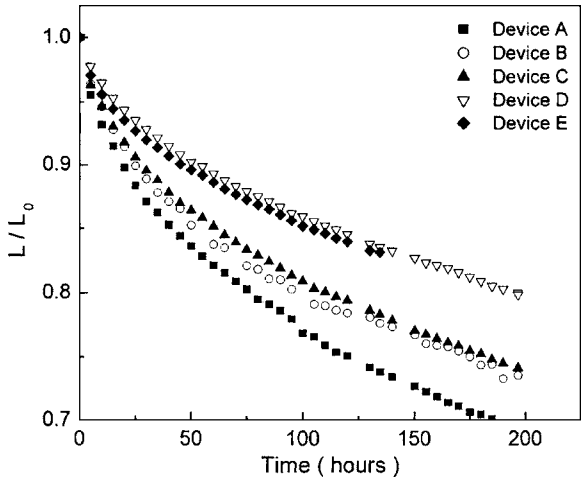

FIG. 4. Operational stability of the OLEDs driven at room temperature under constant current density of 20 mA/cm^2.

mobility which improves the recombination probability in the emitter. However, the current efficiency of group (II) with the removal of the undoped NPB in-between the UM-HTL and EML is somewhat reduced. This presumably can be rationalized by the fact that NPB with a lowest unoccupied molecular orbital (LUMO) at 2.3 eV can act as electron blocking.[17] The electron blocking ability is attenuated when the concentration of MADN with a higher LUMO at 2.5 eV in the mixed layer is increased. As a result, the electron injection to the LUMO of MADN in the UM-HTL becomes possible and in turn may reduce the probability of carrier recombination in the emitting layer leading to a slightly lower current efficiency.

On the other hand, group (II) shows amazing improvement in device lifetime, compared with group (I). It means there is another mechanism operating in addition to the decreased hole mobility. As mentioned before, electron transport to the LUMO of MADN is possible, which means carrier recombination in a MADN molecule at the UM-HTL/EML interface is also possible. This will prevent the excess holes from accumulating in the EML which increases the propensity of producing the unstable Alq_3 cationic species. In addition, the MADN exciton can deliver its energy to the EML by Förster energy transfer as well,[10] which is why there is no MADN peak found in the inset of Fig. 3.

TABLE I. EL performance of C-545T doped green devices with different placement of the UM-HTL measured under 20 mA/cm^2.

Device	Voltage (V)	1931 CIE x	1931 CIE y	Lum. yield (cd/A)	Lifetime enhancement factor (t_{80})[a]
A	6.0	0.32	0.64	12.5	1
B	5.9	0.31	0.64	13.8	1.5
C	5.6	0.31	0.64	14.0	1.6
D	5.9	0.31	0.64	12.7	2.7
E	5.8	0.31	0.64	12.9	2.7

[a]See Refs. 7 and 14.

In conclusion, we have demonstrated that the hole transporting property can be modified by mixing high concentration of MADN in the HTL. Moreover, we have also shown that the stability of these C-545T doped devices incorporating the UM-HTL can be improved significantly. The UM-HTL may be advantageously implemented as a single layer in contact with the EML without influencing the emission color and still shows improvement in device lifetime. The improvement of device lifetime can be attributed to the fact that the unstable $[Alq_3^+]$ species have been effectively suppressed.

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