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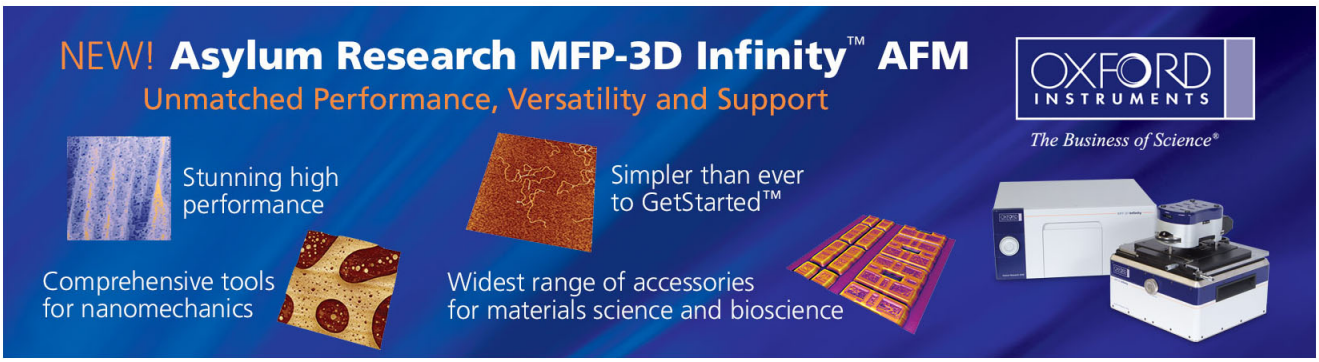

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HTML ABSTRACT + LINKS

Improved stability of organic electroluminescent devices by doping styrylamines in hole or electron transporting layer

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The stability of green organic electroluminescent devices has been improved by doping styrylamine derivate, *p*-bis(*p*-*N*,*N*-diphenyl-aminostyryl)benzene (DSA-Ph) in hole or electron transporting layer. Compared with the undoped device, the stability of the electron transporting layer has increased by a factor of 1.8 without affecting the electroluminescence efficiency of 11 cd/A and color ($CIE_{x,y}$=0.34, 0.62). The enhanced stability is believed to derive from the hole trapping nature of DSA-Ph which can reduce the residual hole carriers in *tris*(8-hydroquinolinato)aluminum (Alq_3) and suppress the formation of fluorescent quencher of Alq_3 cationic species. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1881796]

The stability of organic electroluminescent device (OLED) continues to be one of the major concerns in the commercialization of this wonderful display technology of the future. For mobile display applications, it is generally assumed that a half life ($t_{1/2}$) of at least 10 000 h, at an initial brightness of 100 cd/m^2, is needed.[1] There are two primary factors that are believed to cause most OLED degradation. One is the formation and growth of dark spots which were attributed to the gradual corrosion of the highly reactive cathode by moisture and oxygen,[1,2] which, however, can be suppressed by incorporating desiccant and careful encapsulation of the device.[3]

The other factor is the formation of fluorescent quencher of *tris*(8-hydroquinolinato)aluminum (Alq_3) cationic species[4–6] which result from the fact that the hole carriers are often intrinsically more mobile than the electron carriers in conventional Alq_3 based OLED structure. Recently, it has been shown that one of the solutions was to interpose a copper phthalocyanine (CuPc) layer between the indium tin oxide (ITO) anode and the hole transporting layer (HTL), such as *N*,*N*'-*bis*(1-naphthyl)-*N*,*N*'-diphenyl,1,1'-biphenyl-4,4' -diamine (NPB).[7] One of the functions of CuPc is believed to impede hole carrier injection into the HTL thus leading to better balance of hole/electron for radiative recombination. As a result, the device stability was a significant improvement albeit often at the expense of considerable operational voltage increase.

It had been reported that doping of HTL can also improve device stability.[8–11] One of the commonly used materials was 5,6,11,12-tetraphenylnathracene (rubrene), owing to its high hole-transporting mobility ($6–7\times10^{-3}$ cm^2/V s) and lower ionization potential (I_p=5.3 eV) as compared to that of the NPB (I_p=5.4 eV). Rubrene has been shown to slow down the transport of hole carriers by trapping and de-trapping mechanism in HTL.[12] But, its relatively small band gap energy (E_g=2.2 eV) tends to limit its application in blue and green OLED devices not to mention the drawbacks of its propensity for easy oxidative degradation.[13]

Recently, we have developed a highly stable and efficient blue OLED by employing a styrylamine dopant, *p*-bis(*p*-*N*,*N*-diphenyl-aminostyryl)benzene (DSA-Ph) in a stable blue host material 2-methyl-9,10-*di*(2-naphthyl)anthracene (MADN) as emitter.[14] At about 5% doping concentration, two different excitation mechanisms were proposed to rationalize the observed electroluminescence (EL) performance. One is the Förster energy transfer from MADN to DSA-Ph while the other is the direct carrier trapping by DSA-Ph. The phenomenon was attributed for the most part to the higher hole-transporting mobility (10^{-3} cm^2/V s) of DSA-Ph and lower ionization potential (I_p=5.4 eV) than those of the host MADN (I_p=5.5 eV). It also indicates that DSA-Ph has essentially the same transport and hole trapping properties as rubrene except that the energy band gap (E_g=2.7 eV) is larger.

One of the best green dopants used in many of today's OLED prototypical products is 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 (abbreviated as C-545T). When doped in Alq_3 hosted OLED device, it displayed high EL efficiency (10.4 cd/A) and color (0.31, 0.65), however, the device stability was not satisfied for the commercial requirement.[15] In this letter, we demonstrate that the device stability of C-545T doped green OLED can be greatly improved by doping a styrylamine derivative, DSA-Ph in HTL or electron transporting layer (ETL). We will also present evidence that the effect of DSA-Ph doped in HTL or ETL is associated with the reduction of the residual hole carriers in Alq_3 that suppress the formation of the unstable Alq_3 cationic quencher.

In this study, a series of OLED structures of [ITO/CF_x/HTL(150 nm)/emission layer (37.5 nm)/ETL (37.5 nm)/LiF (1 nm)/Al(200 nm)] was fabricated, in which NPB and Alq_3 were used as a hole and electron transport material to form the HTL and ETL, respectively. DSA-Ph was doped in different portions into the HTL or

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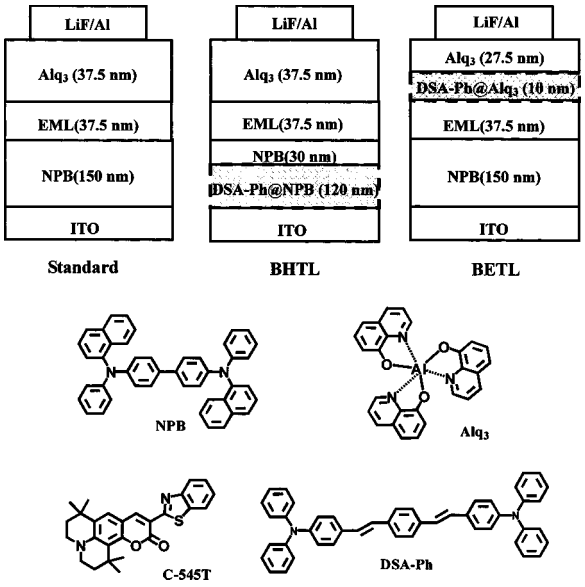

FIG. 1. The schematic device structures and the molecular structure of the organic materials.

ETL that resulted in two distinctive kinds of device configuration abbreviated as *BHTL* and *BETL*, while keeping the total thickness of the HTL (150 nm) and ETL (37.5 nm) constant. For comparison purposes, the undoped HTL and ETL devices were served as a standard reference. In the BHTL, the HTL was partitioned into two regions, a thick (120 nm) doped region (8% DSA-Ph in NPB) and a thin (30 nm) undoped region. In the BETL, the ETL was partitioned into two regions, a thin (10 nm) doped region (8% DSA-Ph in Alq_3) and a thick (27.5 nm) undoped region. The emission layer was composed of 1% C-545T doped with Alq_3. The schematic device structures and the molecular structure of the organic materials are shown in Fig. 1. The ITO-coated glass was loaded on the grounded electrode of a parallel-plate plasma reactor, pretreated by oxygen plasma, and then coated with a polymerized fluorocarbon film. The devices were fabricated under the base vacuum of about 10^{-6} Torr in a thin-film evaporation coater following a published protocol.[7] All devices were hermetically sealed prior to testing. The active area of the 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 measurements were performed in a glovebox at a constant drive current density of 20 mA/cm^2.

The EL efficiencies of the standard, BHTL, and BETL are 10.1, 10.9, and 10.4 cd/A, respectively, at 20 mA/cm^2. It appears that the EL efficiency was not affected by doping

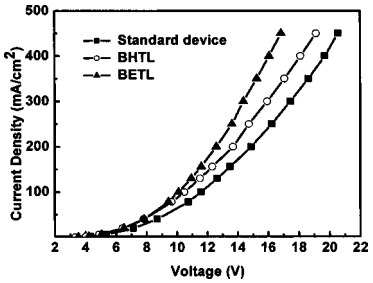

FIG. 2. The current density-voltage (*I-V*) characteristics of the standard, BHTL, and BETL devices.

DSA-Ph in either HTL or ETL. Figure 2 shows the current density-voltage (*I-V*) characteristics for the standard, BHTL, and BETL. It is found that the driving voltage of the BHTL and BETL are lower than that of the standard device. Consequently, the BHTL and BETL have higher power efficiency of 5.3 lm/W at 6.5 V and 5.0 lm/W at 6.4 V, respectively, than that of the standard device of 4.6 lm/W at 7.1 V. The detailed EL performances are summarized in Table I.

Figure 3 shows the EL spectra of the standard, BHTL, and BETL which are similar to the green emission (λ_{max} =528 nm) originated from the fluorescence of C-545T by Förster energy transfer from Alq_3.[15] The lack of any DSA-Ph emission in the BHTL indicates that electron injection and transport and/or energy transfer through the 30 nm undoped NPB layer must be negligible. This is attributed to the higher electron affinity of NPB (EA=2.3 eV) than that of Alq_3 (EA=2.8 eV). Similarly, the lack of DSA-Ph emission in the BETL is probably also due to higher EA of DSA-Ph (EA=2.7 eV) than that of Alq_3.

The device stability tests of the standard, BHTL, and BETL are shown in Fig. 4, presented in changes of normalized luminance versus device operating time at constant current density of 20 mA/cm^2. The initial brightness (L_0) of the standard, BHTL, and BETL were 2020, 2180, and 2080 cd/m^2, respectively. Under this driving condition, the t_{80} (the time for the luminance to drop to 80% of its initial brightness) of the standard, BHTL, and BETL devices was 60, 80, and 110 h. Thus, the life extension factor at t_{80} of BHTL and BETL, compared with that of standard device, is estimated to be 1.3 and 1.8, respectively.

The improved device stability, in the BHTL, can be attributed to DSA-Ph doped in NPB in the form of a sublayer HTL that can slow down the hole transport by trapping and de-trapping mechanism leading to better hole/electron balance. As a result, it can improve the recombination probability of h/e in EML and reduce the formation of fluorescent quencher of Alq_3 cationic radical due to oxidation induced by excess hole. It is also interesting to note that in general transport by trapping and de-trapping tends to increase the driving voltage as well.[9,11] However, in our BHTL, this phe-

TABLE I. EL performance of standard, BHTL, and BETL devices driven at 20 mA/cm^2.

	Voltage	Lum. yield	Efficiency	CIE	
Device	(V)	(cd/A)	(lm/W)	*x*	*y*
Standard	7.1	10.1	4.6	0.36	0.60
BHTL	6.4	10.9	5.3	0.35	0.61
BETL	6.5	10.4	5.0	0.34	0.62

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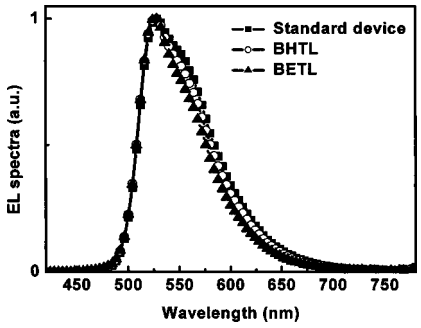

FIG. 3. EL spectra of the standard, BHTL, and BETL devices.

nomenon was not observed. It suggests that the trapping and de-trapping of holes in our BHTL probably was not as severe, which might be due to the fact that the ionization potentials of both DSA-Ph and NPB are *isoenergetic* at $I_p \sim 5.4$ eV. This is also reflected on the much higher doping concentration of DSA-Ph (8%) than that of rubrene-doped (5%)[11] needed to maximize their device stability.

The improved device stability of the BETL is more significant than that of the BHTL. It suggests that the residual hole carriers (which were not recombined with electron carriers in the EML) can be further trapped by the DSA-Ph doped in Alq_3 which is the layer adjacent to the EML. In turn, it also can induce electron injection through Alq_3 and eventually lead to increased electron concentration in the ETL layer doped with DSA-Ph. Therefore, the high concentration of Alq_3 anion can immediately quench the residual hole carrier which was trapped by the DSA-Ph. This conception explains why the improvement in device stability was no longer observed when the positions of the DSA-Ph doped ETL and the undoped ETL were interchanged. The conclusion is also consistent with the unchanged EL spectrum and the lower driving voltage of the BETL than that of the standard device.

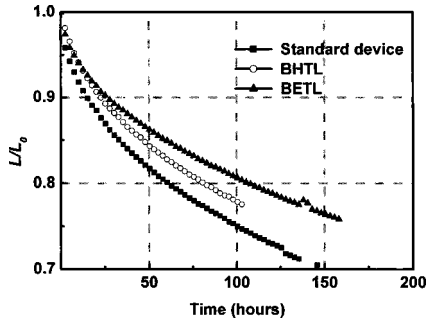

FIG. 4. The device stability tests of the standard, BHTL, and BETL devices.

In summary, we have demonstrated that the device stability of fluorescent C-545T doped green OLED by doping the styrylamine derivative, DSA-Ph, in either HTL or ETL can be significantly improved by a factor of 1.3 and 1.8, respectively, as compared with that of the standard device. The enhanced stability is suggested to derive from the hole trapping nature of DSA-Ph which can reduce the residual hole carriers in Alq_3 by slowing down hole transport in HTL of the BHTL or in the case of BETL by increasing the concentration of the Alq_3 anion in ETL which can reduce the excess hole carriers as well.

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