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Stable styrylamine-doped blue organic electroluminescent device based on 2-methyl-9,10-di(2-naphthyl)anthracene

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We have developed a highly efficient and stable blue organic electroluminescent (EL) device based on a blue fluorescent styrylamine dopant, p-bis(p-N,N-diphenyl-aminostyryl)benzene, in a morphologically stable high band-gap host material, 2-methyl-9,10-di(2-naphthyl)anthracene, which achieved an EL efficiency of 9.7 cd/A and 5.5 lm/W at 20 mA/cm^2 and 5.7 V, with Commission Internationale d'Eclairage coordinates of (x=0.16, y=0.32). The blue-doped device achieved a half-decay lifetime ($t_{1/2}$) of 46 000 h at an initial brightness of 100 cd/m^2. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1804232]

In recent years, there has been considerable interest in developing blue organic electroluminescent (EL) devices with high efficiency, deep blue color, and long operational lifetime. It is well known that the EL efficiency, color, and operational stability of organic EL devices can be significantly improved with the use of a doped emitter.[1,2] To date, there are two major blue-doped emitter systems that have been applied in both area-color and full-color organic EL devices. One was reported by Hosokawa *et al.*, in 1995, which utilized a class of distyrylarylene derivatives (known as DPVBi) as blue host material and styrylamine (known as BCzBV) as dopant. The device efficiency recorded then was about 3.4 cd/A producing bright emission in the blue-green region.[3] Further improvement of this system was later published in Ref. 4, in which the EL efficiency reached 10.2 cd/A at 1.89 mA/cm^2 with a 1931 Commission Internationale d'Eclairage (CIE$_{x,y}$) coordinates of (0.174, 0.334) and a half-life of 20 000 h at an initial brightness (L_o) of 100 cd/m^2. When oligoamine was used as a hole injection layer for this device, the operational lifetime can be further improved to 10 000 h with L_o=500 cd/m^2.[4] It appears that the sky-blue emission was specifically designed by Idemistu for application of color-changing media (CCM) technology for full-color organic EL devices.[5,6]

The other major blue-doped emitter was developed by Shi and coworkers at Kodak, in 2002, which utilized the diphenylanthracene derivatives 9,10-di(2-naphthyl)anthracene (ADN) as blue host and 2,5,8,11-tetra(*t*-butyl)-perylene (TBP) as dopant to generate a somewhat deeper blue emission of CIE$_{x,y}$ (0.154, 0.232). The blue EL device was reported to produce an EL efficiency of around 3.5 cd/A with a half-life of 4000 h at an initial light output of 700 cd/m^2.[7] However, the thin film of ADN is later found to be morphologically unstable and tends to crystallize under prolonged electrical stress or annealing at elevated temperature.[8] It is likely that, due to the potential pin-hole formation during operation, this inherent morphological instability could ac-celerate the decay of the device and reduce the lifetime of the device.[9]

Recently, we molecularly engineered a blue host material based on ADN, which bears a relatively small *methyl* substituent at *C*-2 position of the anthracene moiety with the purpose of disrupting the symmetry of ADN and suppressing the problematic crystallization without altering the LUMO/HOMO relationship. The thin-film morphology of 2-methyl-9,10-*di*(2-napthyl)anthracene (MADN) had been shown to be considerably more robust than that of ADN, albeit with a slightly lower luminance efficiency of 1.4 cd/A with a deep blue CIE$_{x,y}$ (0.15,0.10).[10] We find its efficiency can be greatly improved by a judicious choice of a styrylamine type of blue dopant, such as p-bis(p-N,N-diphenyl-amino-styryl)benzene (DSA-Ph) and report herewith this blue-doped emitter system which achieved a high EL efficiency of 9.7 cd/A at 20 mA/cm^2 and 5.7 V with CIE$_{x,y}$ (0.16,0.32) and a half-decay lifetime ($t_{1/2}$) of 46 000 h with an initial brightness of 100 cd/m^2.

The energy diagram of the blue-doped EL device and the molecular structure of MADN and DSA-Ph are depicted in Fig. 1. The CF$_x$, N,N'-bis-(1-naphthyl)-N,N'-diphenyl,1,1'-biphenyl-4,4'-diamine (NPB), and *tris*(8-quinolinolato)aluminium (Alq_3) were used as the hole injection material,[11] hole transport, and electron-transport material, respectively. After a routine cleaning procedure, the indium-tin-oxide (ITO)-coated glass was loaded on the grounded electrode of
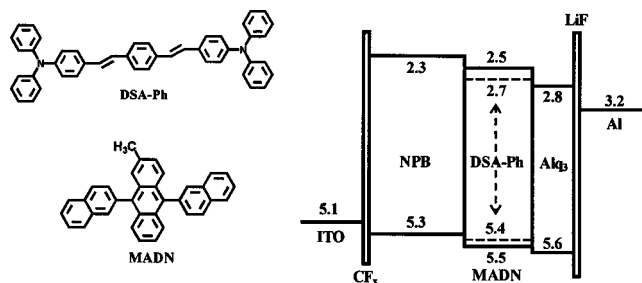

FIG. 1. Energy diagram of blue-doped device and the molecular structure of MADN and DSA-Ph.

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TABLE I. EL performances of undoped and DSA-Ph-doped devices driven at 20 mA/cm^2. (The values in the quotation mark were driven at 200 mA/cm^2.)

DSA-Ph (v%)	Voltage (V)	Lum yield (cd/A)	Efficiency (lm/W)	CIE	
				x	y
0	6.2	1.4	0.7	0.15	0.10
1	6.1	9.8	5.0	0.16	0.31
3	5.7	9.7	5.5	0.16	0.32
5	4.9 (10.9)	4.2 (7.5)	2.7 (2.2)	0.16 (0.16)	0.36 (0.35)

a parallel-plate plasma reactor, pretreated by oxygen plasma, and then coated with a polymerized fluorocarbon film.[11] Devices were fabricated under the base vacuum of about 10^{-6} Torr in a thin-film evaporation coater following a published protocol.[12] A multilayer structure of NPB/EML/Alq_3/LiF/Al was deposited on the substrate by resistive heating with a thickness of 70, 40, 10, 1, and 200 nm for NPB, EML, Alq_3, LiF, and Al, respectively. In the evaporation of EML, the fluorescent dopant was codeposited at a molar ratio of 1%–5%. 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 glove box at a constant drive current density of 20 mA/cm^2.

The detailed EL performances are summarized in Table I. The voltage, luminance yields, color coordinates, and power efficiencies were measured at 20 mA/cm^2. The EL efficiency of the undoped MADN device is 1.4 cd/A and 0.7 lm/W at 6.2 V with a CIE$_{x,y}$ (0.15,0.10). The optimum DSA-Ph concentration in MADN is about 3%, providing an EL efficiency of 9.7 cd/A and 5.5 lm/W at 5.7 V with a CIE$_{x,y}$ (x=0.16, y=0.32) that is 2.4 times higher than that of DSA-Ph/DPVBi guest/host system of 4.1 cd/A reported by Park *et al.*[13] in 2004. We believe this enhancement in efficiency is likely due to the fact that the solution PL efficiency of MADN is 2.6 times higher than that of DPVBi.

Figure 2 shows the EL spectra of the undoped and 3% DSA-Ph-doped devices (driven at 20 mA/cm^2), along with the corresponding solid PL spectra of MADN:DSA-Ph (3%) film. The spectrum of the undoped device exhibits one dominating peak at 452 nm with a full width at half maximum (FWHM) of 64 nm, while that of the doped device exhibits
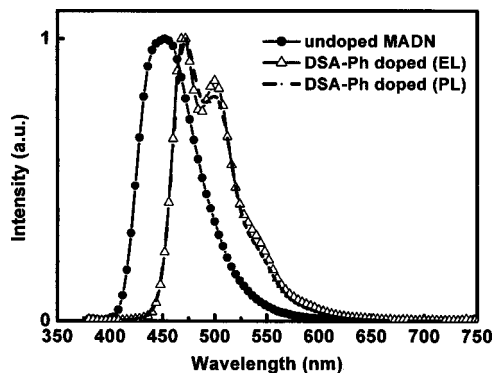
a major peak at 464 nm and a shoulder peak at 490 nm with a FWHM of 56 nm. From the similar PL/EL spectra shown, we conclude that the emissive states of both EL and solid PL are identical, and the emission from MADN is essentially quenched in the EL spectrum of the 3% DSA-Ph-doped device. Therefore, it suggests that the Förster energy transfer from the MADN host to the DSA-Ph dopant is very efficient.[1,14]

Figure 3 shows the dependency of the EL efficiency on the drive current density for the undoped and DSA-Ph-doped devices. For the 3% DSA-Ph-doped device, the EL efficiency rises sharply at low current density to a maximum of EL efficiency (cd/A) and then displays a nearly flat response from 10 to 450 mA/cm^2. This result implies the absence of the *current-induced quenching* and a highly balanced recombination of the hole and electron in this blue-doped emitter system that is rarely observed in the blue-doped emitter published to date.[3,7,8,10,15] For the more concentrated 5% DSA-Ph-doped device, the EL efficiency rises only slowly and reaches a plateau EL efficiency of about 7.5 cd/A at 200 mA/cm^2. This phenomenon is quite different from that observed in the 3% DSA-Ph-doped device. We suggest that there are two different excitation mechanisms operating at the low and high current density, respectively. At low current density, the dominant excitation mechanism is in self-recombination in the dopant as carrier trap.[16] But, in high current density, the excitation mechanism is included not only in self-recombination in the dopant, but also the Förster energy transfer from host to dopant.

The current density-voltage (I–V) characteristics for the undoped and DSA-Ph-doped devices are shown in Fig. 4. Turn-on voltage for 1 mA/cm^2 current injection were recorded at 4.4, 4.3, 4.0, and 3.0 V for the undoped and 1%, 3%, and 5% DSA-Ph-doped devices, respectively. It is noteworthy that the applied voltage decreases considerably for the doped device in comparison with the undoped device. We
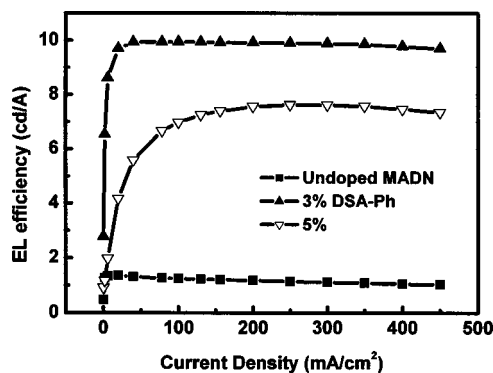

FIG. 2. EL spectra of the undoped and 3% DSA-Ph-doped device and solid PL of 3% doped DSA-Ph.

FIG. 3. The dependency of the EL efficiency on the drive current density for the undoped and DSA-Ph-doped devices.
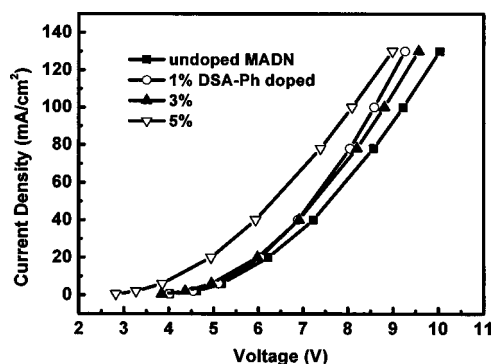
FIG. 4. Current density-voltage (*I–V*) characteristics for undoped and DSA-Ph-doped devices.

attribute the lowering of turn-on voltage to the styrylamine-like dopant, which has a high hole-transporting mobility $(10^{-3} \text{ cm}^2/\text{V s})^{17}$ and a low ionization energy $(I_p = 5.4 \text{ eV})$ that lies between those of NPB and MADN, as shown in Fig. 1. As a result, it provides the hole injection a more effective pathway from HTM to dopant and from dopant to EML host molecule than the injection directly from HTM to EML in the undoped device. Furthermore, it evidently shows that the dominant excitation mechanism of the 5% DSA-Ph-doped device at low current density is in self-recombination in the dopant as alluded to before.

The device operational stability for the 3% DSA-Ph-doped device is shown in Fig. 5 with an initial brightness of 1980 cd/m^2 and a driving voltage of 6 V. It shows that the relative luminance (L/L_0) of the 3% DSA-Ph-doped device has reached to about 0.75 and the driving voltage has increased 0.5 V, after a continued operation for 1000 h. By estimation of its extrapolated profile, it is concluded that the half-decay lifetime $(t_{1/2})$ of 3% DSA-Ph-doped device is about 2400 h $(L_o = 1940 \text{ cd/m}^2)$. Assuming the scalable law
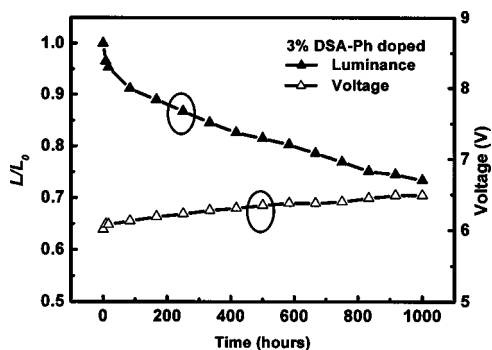
of Coulombic degradation,[12] for driving at L_0 of 100 cd/m^2, the half-decay lifetime $(t_{1/2})$ of the 3% doped device is projected to be over 46 000 h.

In summary, we have developed a useful blue-doped emitter system, which is composed of a styrylamine dopant (DSA-Ph) and an anthracene derivative (MADN) as host material. The DSA-Ph dopant can provide an effective pathway for the hole injection into EML. Once the DSA-Ph doping concentration is higher than 5%, the doping of holes on the DSA-Ph molecules becomes possible in which two different excitation mechanisms results at low and high current density.

FIG. 5. Device operational stability for 3% DSA-Ph-doped device.

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