15.1: Asia Display/IMID '04: Development of Highly Efficient and Stable Blue Organic Electroluminescent Devices

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Abstract

We have developed a highly efficient and stable blue organic electroluminescent device (OLED) based on the blue fluorescent p-bis(p-N,N-diphenyl-aminostyryl)benzene (DSA-Ph) dopant in a morphologically stable high-bandgap host material, 2-methyl-9,10-di(2-naphthyl)anthracene (MADN), which achieved an EL efficiency of 9.7 cd/A and 5.5 lm/W at 20 mA/cm² and 5.7 V with a Commission Internationale d'Eclairage coordinates of (x = 0.16, y = 0.32). This sky blue device which could also alleviate the problematic current induced quenching at high current achieved a half-decay lifetime ($t_{1/2}$) of 46,000 h at an initial brightness of 100 cd/m².

1. Introduction

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 OLED products. One was originally reported by Hosokawa *et al.*, in 1995, which utilized a class of distyrylarylene (DSA) derivatives (known as DPVBi) as blue host material and styrylamine (SA) (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 SID'02, in which the EL efficiency reached 10.2 cd/A at 1.89 mA/cm² with a 1931 Commission Internationale d'Eclairage ($CIE_{x,y}$) coordinates of (0.174, 0.334) and a half-lifetime of 20,000 hours at an initial brightness (L_o) of 100 cd/m². When an oligo-amine was used as hole injection layer for this device, the operational lifetime can be further improved to 10,000 h with L_o = 500 cd/m².[4] It appears that the sky-blue emission was specifically designed by Idemistsu for adaptation of color-changing media (CCM) technology for full-color OLEDs.[5,6]

The other major blue-doped emitter was developed by Shi and coworkers at Kodak in 2002, which utilized the diphenylanthracene (DPA) 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 half-life of 4,000 h at initial light output of 700 cd/m².[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 accelerate the decay of the device and reduce the lifetime of the device.[9]

Recently, we have molecularly engineered a new blue host material based on ADN, which bears a relatively small *methyl*-substituent at the 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 judicious choice of a styrylamine type of blue dopant, such as *p-bis*(*p*-*N,N*-diphenyl-aminostyryl)benzene (DSA-Ph) and report herewith this new blue-doped emitter system which achieved a high EL efficiency of 9.7 cd/A at 20 mA/cm² 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/m². In addition, we will also benchmark our EL performance and device stability against that of the same dopant in Idemitsu's state-of-the-art blue host distyrylarylene derivative, 9,10-*di*[4-(2,2-diphenylvinyl)phenyl]-anthracene (DPVPA).

2. Experimental

The molecular structure of MADN, DPVPA, DSA-Ph and blue-doped EL device are depicted in Figure 1. 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,[11] hole transport, and electron transport materials, respectively. After a routine cleaning procedure, the indium-tin-oxide (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.[11] Devices were

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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 co-deposited at an optimum molar ratio of 3%. 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.

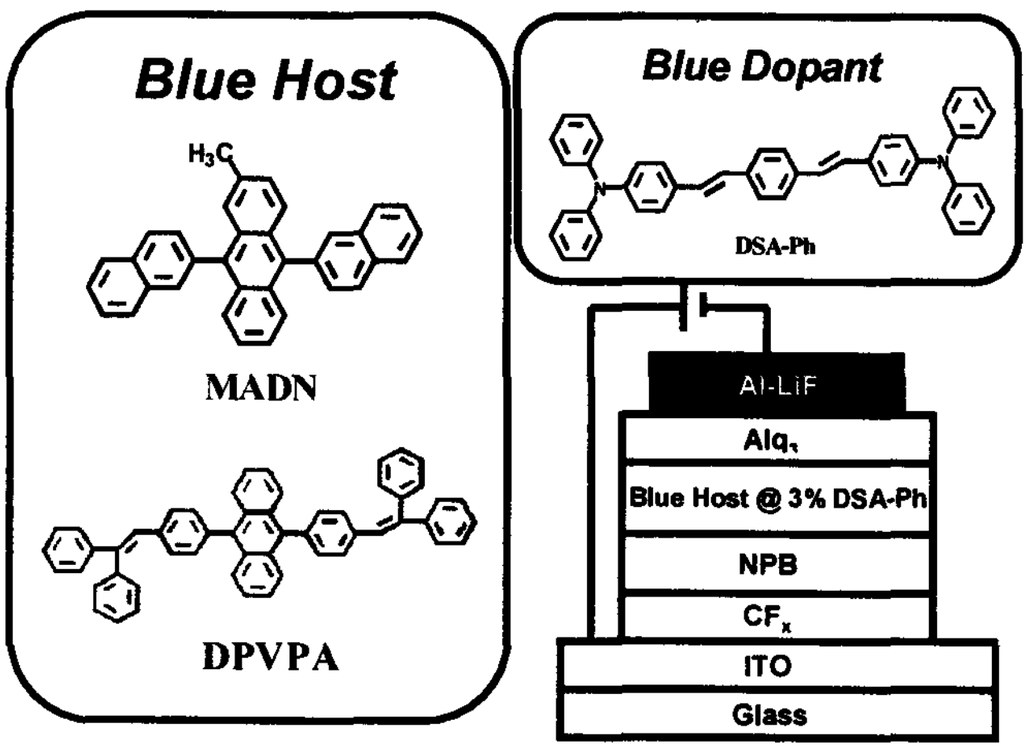


FIG. 1. Structures of blue EL device and materials

3. Results and discussion

The EL spectra of DSA-Ph doped in hosts MADN and DPVPA are compared in Figure 2 and their EL performances are summarized in Table I. The EL efficiency of the undoped MADN and DPVPA were 1.4 and 4.0 cd/A, respectively, and the color of the undoped MADN is found to be more saturated than that of DPVPA device with a $CIE_{x,y}$ (0.15, 0.10) vs (0.14, 0.17). When doped with 3% DSA-Ph, the current efficiencies were increased to 9.7 and 10.2 cd/A with a $CIE_{x,y}$ (0.16, 0.32) and (0.16, 0.35), respectively. From their EL spectra, the emission from MADN and DPVPA are essentially quenched in each of the 3% DSA-Ph doped device suggests that the Förster energy transfers from MADN and DPVPA host to DSA-Ph dopant are both very efficient. [13]

Table I. EL performances of undoped and 3% DSA-Ph doped devices for MADN and DPVPA driven at 20 mA/cm^2.

Host	device	Voltage (V)	Lum. yield (cd/A)	Efficiency (lm/W)	CIE	
					x	*y*
MADN	undoped	6.2	1.4	0.7	0.15	0.10
	doped	5.7	9.7	5.5	0.16	0.32
DPVPA	undoped	7.3	4.0	1.7	0.14	0.17
	doped	6.7	10.2	4.8	0.16	0.35

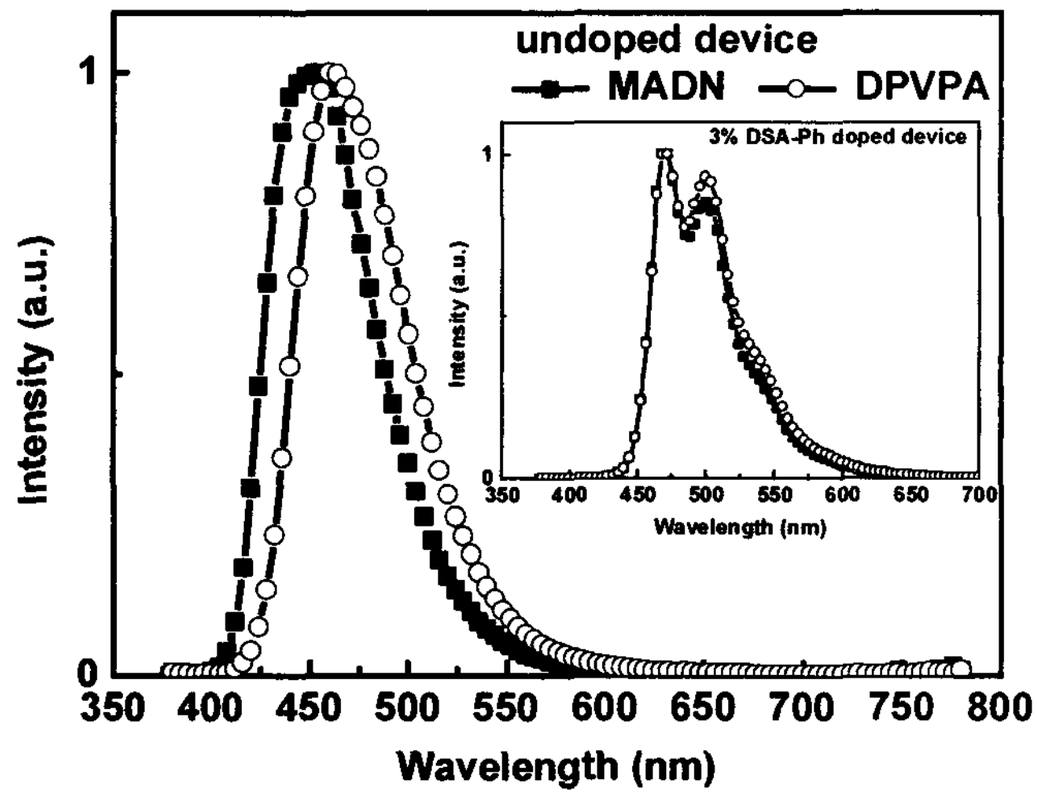


FIG. 2. The EL spectra of the undoped and 3% DSA-Ph doped devices for MADN and DPVPA.

Figure 3 shows the current density-voltage characteristics of the undoped and 3% DSA-Ph doped devices for MADN and DPVPA. The driving voltage (driven at 20 mA/cm^2) of the undoped MADN and DPVPA devices were 6.2 and 7.3 V, which were decreased to 5.7 and 6.7 V, respectively, upon doping with 3% DSA-Ph. It is noteworthy that the driving voltage decreases considerably for the doped devices in comparison with the undoped devices. We attribute the lowering of drive voltage to the styrylamine-like dopant, which has a high hole-transporting mobility (10^{-3} cm^2/V s)[14] and a low ionization potential (I_p = 5.4 eV) that lies in-between those of NPB and MADN or DPVPA. As a result, it provides hole-injection a more effective pathway from HTM to dopant and from dopant to EML host molecule than the corresponding injection directly from HTM to EML in the undoped device.

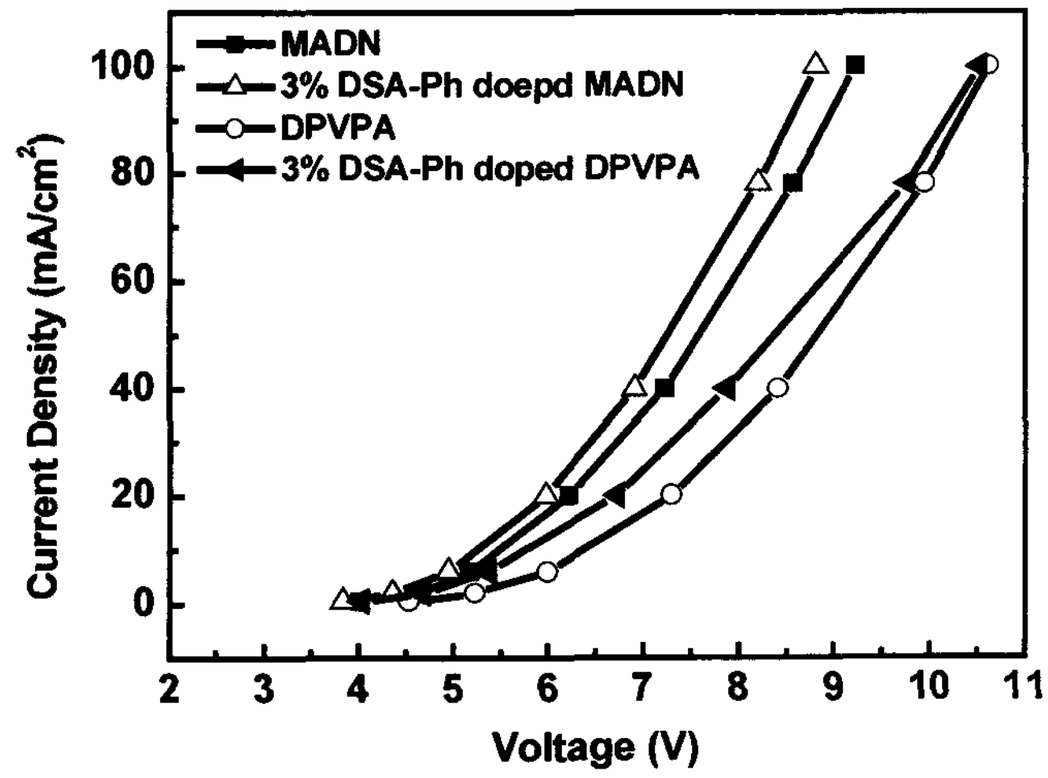


FIG. 3. The current density-voltage characteristics of undoped and doped devices for MADN and DPVPA.

Figure 4 shows the dependency of the EL efficiency on the drive current density for 3% DSA-Ph doped MADN and DPVPA devices. For the DSA-Ph doped MADN device, the EL efficiency rises sharply at low current density to a maximal efficiency of 9.7 cd/A which remains essentially "constant" from 10 to 450 mA/cm^2, that translates to a luminance range of from 100 to 43,000 cd/m^2. This result implies the absence of the *current induced quenching (CIQ)* at high current drive conditions and a highly balanced recombination of the hole and electron in this blue-doped emitter system using MADN as blue host. On the contrary, in the DPVPA doped device, the EL efficiency appears to also rise quickly at low current density to a maximum of EL efficiency of 10.2 cd/A. But, it shows a "descending" trend with increasing current density, which suggests significant *CIQ* at high luminance – a common foe often found in many of today's blue OLEDs.

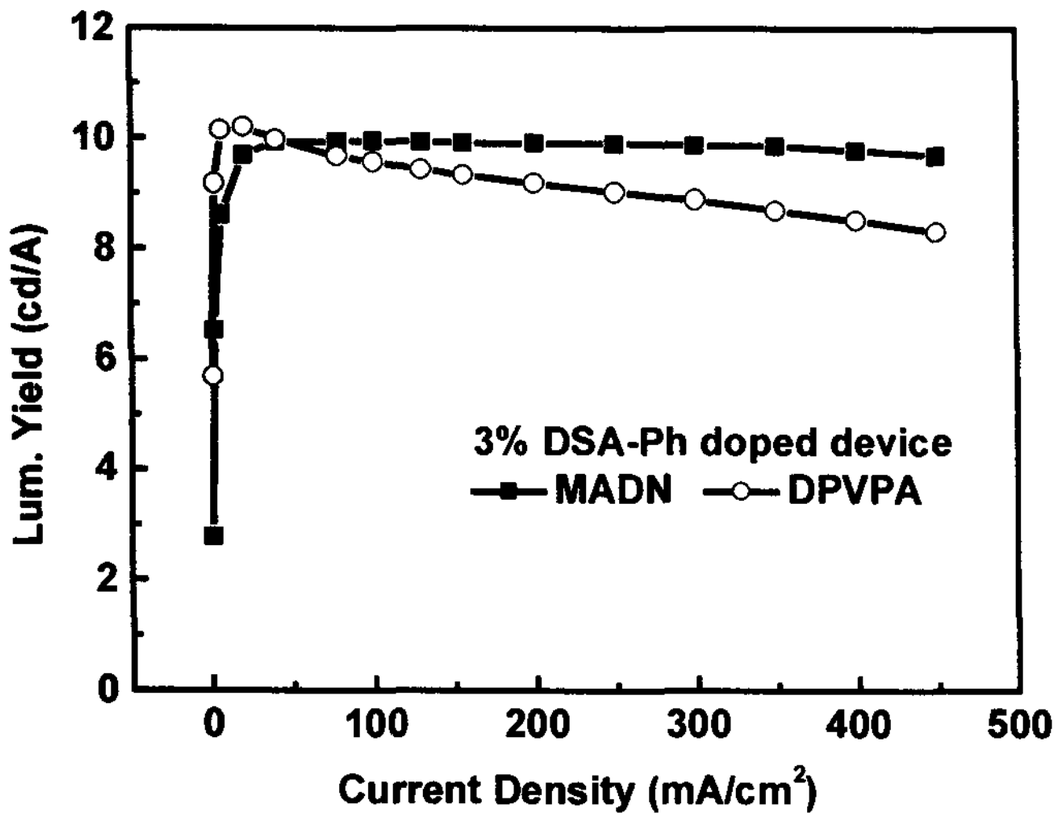
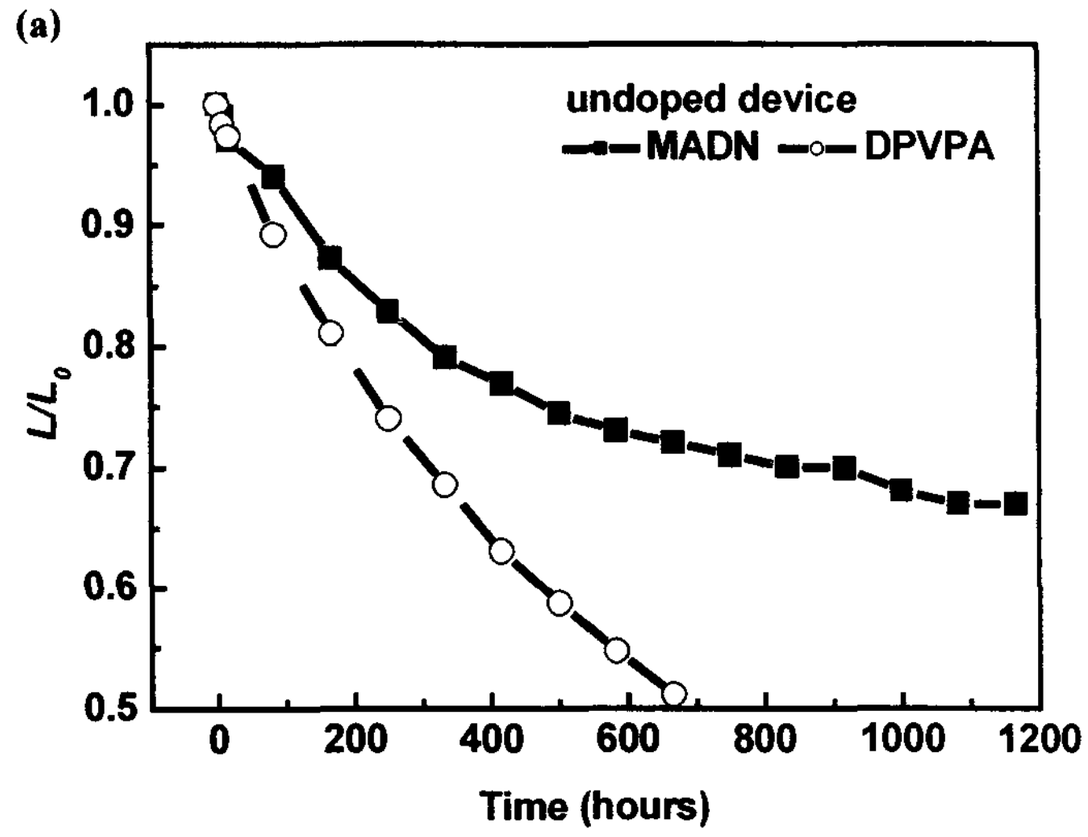


FIG. 4. The dependency of the EL efficiency on the drive current density for the MADN and DPVPA doped devices.

Figure 5(a) shows the device stability of the undoped MADN and DPVPA devices in which the initial brightness (L_0) were 280 and 800 cd/m^2, respectively. After continued dc operation at 20 mA/cm^2 for 700 h, the relative luminance (L/L_0) of undoped DPVPA dropped to 50% while that of undoped MADN decreased only to 70%. By estimation of its extrapolated profile, it is concluded that the half-decay lifetime ($t_{1/2}$) of the undoped MADN and DPVPA are about 2,500 and 700 h, respectively. 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 undoped MADN and DPVPA are projected to be 7,000 and 5,600 h, respectively.

Figure 5(b) shows the device stability of the 3% DSA-Ph doped MADN and DPVPA devices whose initial brightness (L_0) were 1940 and 2040 cd/m^2, respectively. After continued operation for 1000 h, the relative luminance decreased to 0.75 and 0.7, accordingly. By extrapolation, it is estimated that the half-decay lifetime ($t_{1/2}$) of the undoped MADN and DPVPA are about 2,400 and 2,100 h, which are normalized to be 46,000 and 40,000 h, respectively, at L_0 = 100 cd/m^2.



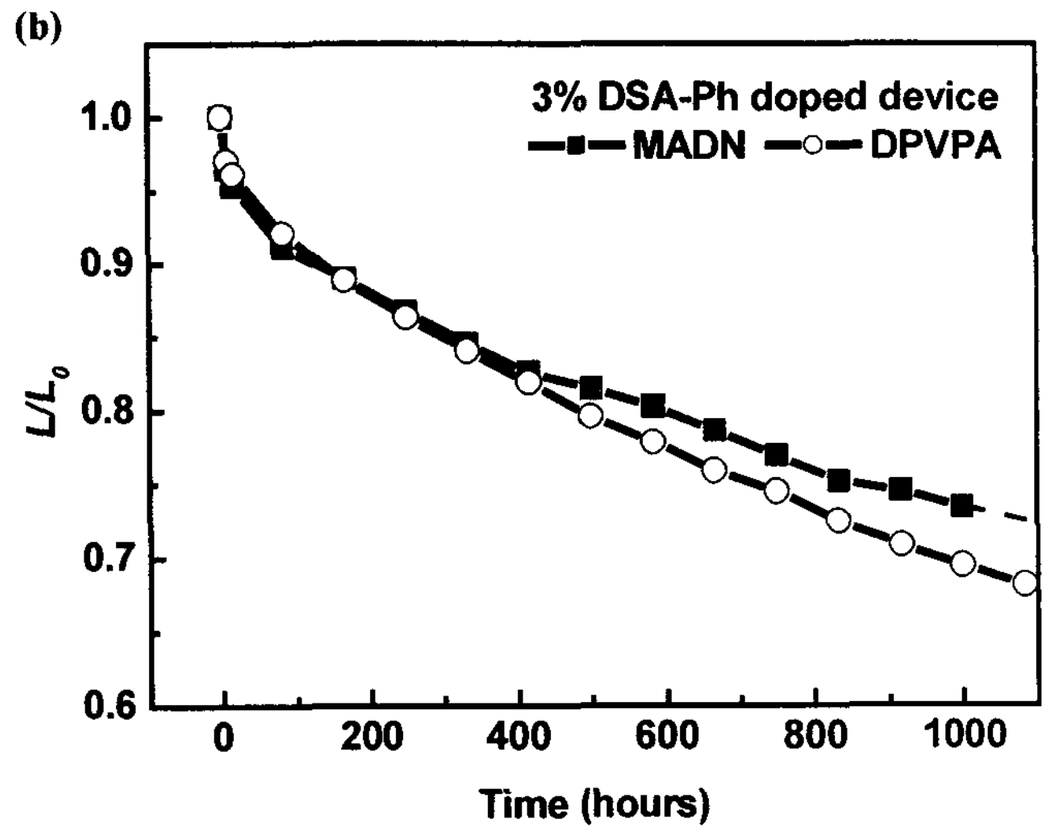


FIG. 5 The device stability for the MADN and DPVPA devices (a) undoped (b) 3% DSA-Ph doped.

4. Conclusion

We show that 2-methyl-9,10-*di*(2-naphthyl)anthracene (MADN) displays good thin-film morphology, deeper blue color as well as longer device stability than that of distyrylarylene (DPVPA) as host material in blue OLEDs. When doped 3% DSA-Ph, MADN achieves an EL efficiency of 9.7 cd/A with a $CIE_{x,y}$ (0.16, 0.32) and a device stability of 46,000 at an initial brightness of 100 cd/m^2. In addition, this new doped blue emitter also is capable of alleviating the high *current induced quenching* problem that are often found in many of today's blue OLEDs.

5. Acknowledgement

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