Efficient deep blue emitters for organic electroluminescent devices

Meng-Huan Ho,[a] Yao-Shan Wu, Shih-Wen Wen, and Teng-Ming Chen
Department of Applied Chemistry, National Chiao Tung University, Hsinshu, Taiwan 300, Republic of China
Chin H. Chen
Display Institute, National Chiao Tung University, Hsinshu, Taiwan 300, Republic of China and Microelectronics and Information Systems Research Center, National Chiao Tung University, Hsinshu, Taiwan 300, Republic of China

Abstract: Highly efficient deep blue organic light emitting devices have been fabricated with a 4-(styryl)biphenyl-core based fluorescent dopant (SK-1) in the wide band gap 2-methyl-9,10-di (1-naphthyl) anthracene (α, α-MADN) host system which achieved an electroluminescence efficiency of 5.0 cd/A and an external quantum efficiency of 4.2% at 20 mA/cm^2 with a saturated blue Commission Internationale de l'Eclairage coordinates of (0.15, 0.14) and a half-decay lifetime of 8000 h at an initial brightness of 100 cd/m^2. The current efficiency and electroluminescent color of SK-1 doped devices have been shown to be essentially immune to drive current density.

In recent years, there has been considerable interest in developing blue organic light-emitting diodes (OLEDs) with high efficiency, deep blue color, and long operational lifetime.[1] Deep blue color is defined here as having a blue electroluminescent emission with a Commission Internationale d'Eclairage (CIEx,y) coordinates of $x \sim 0.15$ and $y < 0.15$. Such an emitter can effectively reduce the power consumption of a full-color OLED (Ref. 2) and also be utilized to generate light of other colors by energy cascade to a suitable emissive dopant.[3]

Unfortunately, literature with full disclosure on deep blue OLED dopant/host material structures is rather rare and sketchy. One notable example, a styrylamine-based dopant BD-3 to produce an electroluminescence (EL) efficiency of 7.2 cd/A and a blue color of (0.14, 0.16) (Ref. 4) was recently presented by Idemitsu Kosan Co. and likewise, Kodak also talked about one of their best deep blue device performances with dopant BK-9 in host BH-3 which achieved an efficiency of 7.4 cd/A and a blue color of (0.14, 0.17)[5] Neither of them disclosed in these presentations any useful structural information that was needed to substantiate their great device performances.

Recently, it was found that an *unsymmetrical* mono(styryl)amine fluorescent dopant, diphenyl-[4-(2-[1,1';4',1'']terphenyl-4-yl-vinyl)-phenyl]-amine (BD-1)upon doping in 2-methyl-9,10-di(2-naphthyl)anthracene (MADN) produced one of the best deep devices reported then of 5.4 cd/A and a CIE$_{x,y}$ of (0.14, 0.13).[6] This optimized efficiency and device stability could only be obtained by incorporating the *composite* hole transporting layer (*c*-HTL) of *N*,*N*’-bis(1-naphthyl)-*N*,*N*’-diphenyl-1,1’-biphenyl-4 ,4’-diamine (NPB):copper phthalocyanin (CuPc)(1:1) to balance the charge carriers,[7] however, which were not readily controlled during fabrication.

Later it was discovered that when BD-1 was doped in the modified wide band gap host of 2-methyl-9,10-di(1- naphthyl)anthracene (α, α-MADN), it could achieve an EL efficiency of 3.3 cd/A with a saturated blue CIE$_{x,y}$ of (0.15, 0.13) without the introduction of *c*-HTL.[8] However, the device efficiency leaves much to be improved and the presence of long wavelength shoulder of these mono (styryl) aminebased emitters which tends to grow with increasing dopant concentration is problematic as it will increase the CIE$_y$ value of the blue devices, leading to an unsatisfactory blue color.[9] This phenomenon can be attributed to the aggregation propensity of these relatively flat dopant molecules at high concentration, which also results in low device efficiency due to concentration quenching.[10] Therefore, how to suppress the molecular aggregation propensity of these blue doped emitters is critical for developing high-efficiency deep blue OLEDs and an adequate approach to molecular engineering is necessary.

In this letter, we report the development of a 4-(styryl)biphenyl-core based deep blue emitter, 4-*N*,*N*’diphenylamino-4’- [(4-*N*’ ,*N*’-diphenylamino)styryl] biphenyl (SK-1) by introducing a particular linkage of aryl group in between the diphenylamino and the styrene moieties, as shown in Fig. 1, which is designed to twist the planar structure of BD-1 and thus alleviate these aforementioned issues related to molecular aggregation.[11] Two types of SK-1 doped blue devices in two different host materials of MADN with lowest unoccupied molecular orbital/highest occupied molecular orbital (LUMO/HOMO) of 2.6/ 5.6 eV (device I) and α, α-MADN with LUMO/HOMO of 2.8/ 5.8 eV (device II) as emitting layers (EMLs) have been fabricated. The basic device structure was indium tin oxide/ CF$_x$ /NPB (50 nm)/EML (40 nm)/tris(8-quinolinolato)aluminum(Alq$_3$) (10 nm)/LiF (1 nm)Al (200 nm), in which CF$_x$, NPB, and Alq$_3$ were used as the hole injection material,12 hole, and electron transport materials, respectively. The optimized doping concentration for SK-1 dopant has been determined to be at 7%.

To investigate the energy transfer between the dopant/host material of SK-1 and MADN, the solid-state emission spectra of various concentrations of SK-1 doped MADN thin films [spin coated with poly(methyl methacrylate) (PMMA),excited with 400 nm uv source which is near the $\lambda_{ex,max}$ of MADN] have been measured, as shown in Fig. 1. The solidstate emission spectra of 5% SK-1 doped MADN feature a main emission peak at 449 nm and a shoulder at 471 nm with a full width at half maximum (FWHM) of 68 nm, we also note that the emission of MADN around 430 nm essentially quenched confirming that the Förster energy transfer from MADN to SK-1 is complete when the dopant concentration reaches 5%. It can also be demonstrated from Fig. 1 that the FWHM of solid-state emission spectra and intensity of long wavelength shoulder were not significantly affected with increasing doping concentration of SK-1 from 5% to 9%.

Detailed EL performances measured at 20 mA/cm^2 are summarized in Table I. Device I shows an

EL efficiency of 4.4 cd/A and an external quantum efficiency (EQE) of 3.5% at 7.0 V with a deep blue CIE$_{x,y}$ coordinates (0.15, 0.15) The SK-1/MADN emitter system shows a near flat EL efficiency versus current density response, as shown in Fig. 2. The EL efficiency is sustained at 4.3 cd/A even at 155 mA/cm^2. It suffers essentially no current-induced quenching, and there is also no EL color shift with respect to varying drive currents as the CIE$_{x,y}$ coordinates only shift from (0.148, 0.156) at 2 mA/cm^2 to (0.145, 0.148) at 155 mA/cm^2 with $\triangle$CIE$_{x,y}$= ±(0.003,0.008). This apparent resistance to color change under various drive current densities suggests that the charge carriers for recombination are well balanced in this blue emitter and both excitation mechanism of charge trapping and Förster energy transfer may be prevalent in the SK-1 doped devices.

The EL spectra of type I devices with various doping concentrations at 20 mA/cm^2 is depicted in the inset of Fig.2, which exhibits one main peak at 448 nm with a shoulder at 472 nm and a FWHM of 60 nm. It is noteworthy that the EL peaks are neither broadened nor enhanced particularly with respect to the intensity of long wavelength shoulder at various SK-1 concentrations of 3%, 5%, 7%, and 9%. As a result, the saturated blue color of these devices is essentially unchanged with CIE$_{x,y}$ coordinates maintained at (0.15, 0.15). Based on these results, we attribute this apparent resistance to color shift to the inserted steric aryl linking group, which effectively prevents the dyes from aggregation at high concentration.

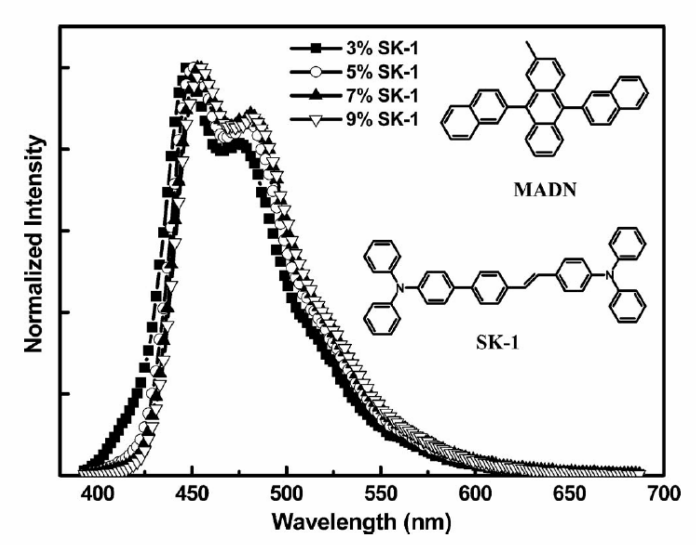


FIG. 1. Solid-state emission spectra of SK-1 doped MADN thin films at various doping concentration and structures of MADN and SK-1.

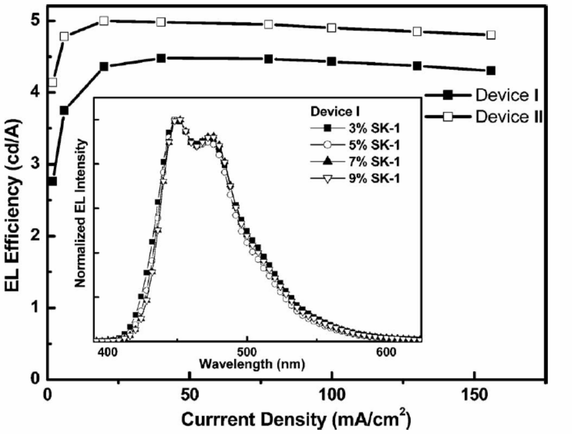
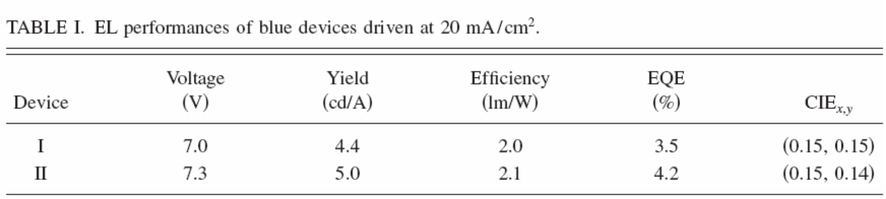


FIG. 2. EL efficiency vs current density characteristics of devices I and II. Inset: EL spectra of device I with various SK-1 doping concentration at 20 mA/cm$^{2.}$

In order to further enhance the efficiency of these deep devices, we turn to the modified blue host material of α，α-MADN (Ref. 8) which has a blueshifted fluorescence emission of about 17 nm with respect to that of MADN, as shown in Fig. 3. It is evident from Fig. 3 that the overlap between the hypsochromic-shifted emission peak of α，α-MADN and the absorption peak of SK-1 is better than that of MADN, which is essential for efficient Förster energy transfer. Figure 3 also depicts the emission spectra of 5% SK-1 doped MADN and α，α-MADN thin films (spin coated with PMMA). The emissive intensity of SK-1/α，α-MADN film is 1.1 times higher than that of SK-1/MADN film confirming that the Förster energy transfer is indeed more efficient between α，α-MADN and SK-1. The EL efficiency of device II was found to boost up to 5.0 cd/A and EQE of 4.2% at 7.3 V with a deep blue $\mathrm{CIE}_{x,y}$ of (0.15, 0.14). This performance is higher than that of device I with SK-1/ MADN system (4.4 cd/A). Furthermore, the low-lying HOMO of α，α-MADN also restrains the hole injection from the hole-transport layer of NPB to EML, which makes the hole-electron recombination more confined in the EML of α，α-MADN device than that of MADN.8We believe that the more balanced carriers for recombination in α，α-MADN device is another reason for the enhanced device efficiency in addition to the more effective Förster energy transfer. DeviceII also shows a near flat EL efficiency versus current density, as shown in Fig. 2, and is resistant to color shift with various doping concentration as well.

TABLE I. EL performances of blue devices driven at 20 mA/cm^2.



Device	Voltage (V)	Yield (cd/A)	Efficiency (lm/W)	EQE (%)	CIE$_{x,y}$
I	7.0	4.4	2.0	3.5	(0.15, 0.15)
II	7.3	5.0	2.1	4.2	(0.15, 0.14)

Figure 4 shows the operational lifetime of these two blue devices at a constant current density of 20 mA/cm^2 monitored in a glovebox under nitrogen atmosphere (H_2O <3 ppm, O_2<3 ppm). The $t_{1/2}$ (the time for the luminance to drop to 50% of initial luminance)and initial luminance(L_0) measured for devices I and II were 800 h at L_0=872 cd/m^2, and 800 h at L_0=1000 cd/m2, respectively. Moreover, the drive voltage of both devices increased only 0.4 V with continuous operation after 600 h. Assuming scalable Coulombic degradation[13] driving at a L_0 value of 100 cd/m^2, the half-lives（t1/2） of devices I (SK-1/MADN) and II (SK-1/α，α-MADN)are projected to be 7000 and 8000 h, respectively.

In summary, we have developed a 4-(styryl) biphenylcore based dopant, SK-1, as an effective emitter for the doped deep blue OLED device. The introduction of steric aryl linkage to SK-1 molecular structure effectively prevents the dyes from aggregation at high doping concentration while maximized device EL efficiency is desired. The current efficiency and CIE$_{x,y}$ color of SK-1 doped devices have been shown to be essentially immune to drive current density. In addition, the deep blue SK-1/α， α-MADN doped emitter with simple device structure can achieve one of the best deep blue EL efficiencies of 5.0 cd/A at 7.3 V with a deep blue CIE$_{x,y}$ color of (0.15, 0.14) and a long operational lifetime.

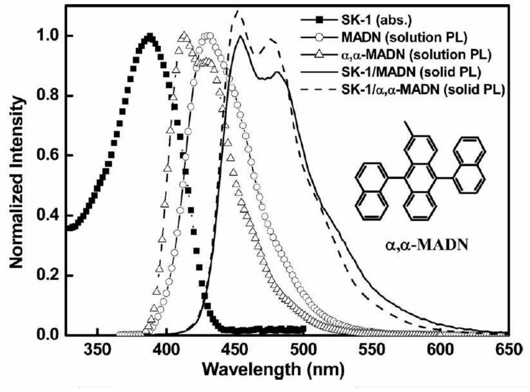


FIG. 3. Absorption and emission spectra of dopant SK-1 and host MADN, α，α-MADN in toluene along with the thin-film solid PL spectra of 5% SK-1 doped MADN and α α-MADN in PMMA and structure of α，α-MADN.

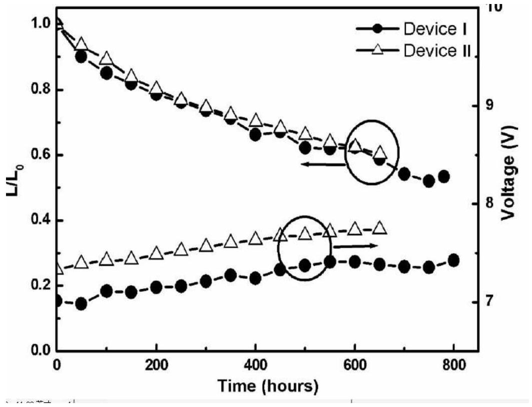


FIG. 4. Device operational stability of devices I and II.

This work was supported by grants from Chunghwa Picture Tubes, Ltd. (CPT) of Taoyuan, Taiwan and National Science Council of Taiwan. The authors also thank e-Ray Optoelectronics Technology Co., Ltd., of Taiwan for generously supplying some of the OLED materials studied in this work.

[1] Y. Kijima, N. Asai, and S. Tamura, Jpn. J. Appl. Phys., Part 1 **38**, 5274 _1999_.

[2] Y. J. Tung, T. Ngo, M. Hack, J. Brown, N. Koide, Y. Nagara, Y. Kato, and H. Ito, Proceedings of the Society for Information Display, Seattle, Washington, 2004 _unpublished_, p. 48.

[3] C. W. Tang, S. A. Van Slyke, and C. H. Chen, J. Appl. Phys. **65**, 3610 _1989_.

[4] T. Arakane, M. Funahashi, H. Kuma, K. Fukuoka, K. Ikada, H. Yamamoto, F. Moriwaki, and C. Hosokawa, Proceedings of the Society for Information Display, San Francisco, California, 2006 _unpublished_, p. 37.

[5] L. S. Liao, K. P. Klubek, M. J. Helber, L. Cosimbescu, and D. L. Comfort, Proceedings of the Society For Information Display, San Francisco, California, 2006 _unpublished_, p. 1197.

[6] M. T. Lee, C. H. Liao, C. H. Tsai, and C. H. Chen, Adv. Mater. _Weinheim, Ger._ **17**, 2493 _2005_.

[7] C. H. Liao, M. T. Lee, C. H. Tsai, and C. H. Chen, Appl. Phys. Lett. **86**, 203507 _2005_.

[8] M. H. Ho, Y. S. Wu, S. W. Wen, M. T. Lee, T. M. Chen, C. H. Chen, K. C. Kwok, S. K. So, K. T. Yeung, and Z. Q. Gao, Appl. Phys. Lett. **89**, 252903 _2006_.

[9] Z. Q. Gao, B. X. Mi, C. H. Chen, K. W. Cheah, Y. K. Cheng, and S. W. Wen, Appl. Phys. Lett. **90**, 123506 _2007_.

[10] C. W. Tang, S. A. Van Slyke, and C. H. Chen, J. Appl. Phys. **65**, 3610 _1989_.

[11] M. H. Ho, Y. S. Wu, S. W. Wen, and C. H. Chen, Proceedings of the Society for Information Display, Long Bench, California, 2007 _unpublished_, p. 1768.

[12] L. S. Hung, L. R. Zheng, and M. G. Mason, Appl. Phys. Lett. **78**, 673 _2001_.

[13] S. A. Van Slyke, C. H. Chen, and C. W. Tang, Appl. Phys. Lett. **69**, 2160 _1996_.