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High-efficiency deep blue host for organic light-emitting devices

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High-efficiency deep blue organic light-emitting devices have been fabricated using asymmetrically substituted 9-(α -naphthyl)-10-(β -naphthyl)-anthracene as blue host material and diphenyl-[4-(2-[1,1';4',1'']terphenyl-4-yl-vinyl)-phenyl]amine as dopant emitter. With an optimized device structure and doping concentration, the deep blue electroluminescent (EL) device achieved an EL efficiency of 4.9 cd/A and an external quantum efficiency of 4.4% at a current density of 20 mA/cm² at saturated blue Commission Internationale de l'Eclairage coordinates of (0.15, 0.13). The deep blue device also has a current efficiency which is invariable with driving conditions ranging from 10 to 100 mA/cm². © 2007 American Institute of Physics. [DOI: 10.1063/1.2715041]

Organic light-emitting diode (OLED) has received much attention due to its potential application in flat panel display and large area illumination light source. Much effort has been devoted to developing materials and device structures to obtain higher efficiency which is part of the need towards commercialization.¹⁻⁴ Among the three principal colors necessary for display applications, blue-emitting materials and devices are particularly in need of improvement in terms of efficiency and color purity than those of the green and red emitters. In recent years, developing deep blue electroluminescence (EL) color with a Commission Internationale de l'Eclairage (CIE_{x,y}) coordinate value of <0.15 has been considered essential⁵ as such emitters can effectively reduce the power consumption of a full-color OLED panel and can also be utilized to generate emission of other colors by energy transfer to a matching emissive dopant.^{6,7}

While high-efficiency green and red emitting colors could be obtained readily by doping in the commonly used host materials, such as tris(8-hydroxyquinolino)aluminum (Alq), a wider band gap host is essential for the efficient generation of blue dopant emission. There were a number of reports on the design and synthesis of dopants that can produce deep blue photoluminescence.⁷ However, because of the considerably blueshifted absorption of these deep blue dopants, better matching host materials with sufficient spectral overlap for efficient Förster energy transfer are needed to facilitate the generation of blue dopant emission with high efficiency as well as deep blue color.⁸ Recently, organic EL devices using anthracene derivatives as host blue emitters have been reported to exhibit very promising performance.⁶⁻⁹ An anthracene-based β , β -isomeric blue host material, 2-methyl-9,10-di(2-naphthyl)anthracene (MADN) with a stable thin-film morphology and a sufficiently wide

band gap, has been reported in 2004.⁶ When doped with a di(styryl)amine-based blue dopant, *p*-bis(*p*-*N*,*N*-diphenylaminostyryl)benzene, it achieved an EL efficiency of 9.7 cd/A with a sky-blue color of (0.16, 0.32) and a long operational lifetime of 46 000 h at an initial brightness of 100cd/m². Nevertheless, the color purity is far from adequate for full-color OLED display application. Despite many reports in display related conferences, reports with full disclosure in materials and devices on deep blue OLEDs remain to be few and far between. One notable example recently was by Idemitsu Kosan, which utilized a styrylamine-based dopant to produce an EL efficiency of 7.0 cd/A and a near deep blue color of (0.14, 0.16).¹⁰ The other was by Canon, which exploited the fluorene-based blue emitter to generate an EL efficiency of 6.0 cd/A with a CIE_{x,y} of (0.15, 0.13).¹¹ It has also been reported that when the OLED device employing a composite hole-transport layer (c-HTL) in a conventional blue OLED architecture with an emitting layer of MADN doped with an *unsymmetrical mono*(styryl)amine fluorescent dopant, diphenyl-[4-(2-[1,1';4',1'']terphenyl-4-yl-vinyl)-phenyl]-amine (BD-1), the device achieved an EL efficiency of 5.4 cd/A at 20 mA/cm² with a saturated blue CIE_{x,y} of (0.14, 0.13) and a normalized operational lifetime of 10 000 h at an initial brightness of 100cd/m².⁷

Although the BD-1 doped MADN emitter with c-HTL can achieve a saturated deep blue color with high efficiency, the fabrication process is complicated with two doped functional organic layers in one device architecture, particularly using the environmentally unfriendly copper phthalocyanine (CuPc). Furthermore the EL efficiency of c-HTL device tends to drop quickly with increasing driving voltage. This is attributed to the hole-trapping dopant of CuPc in c-HTL. The hole-trapping ability of CuPc traps decrease with increasing electric field due to the Poole-Frenkel effect.¹² The density of

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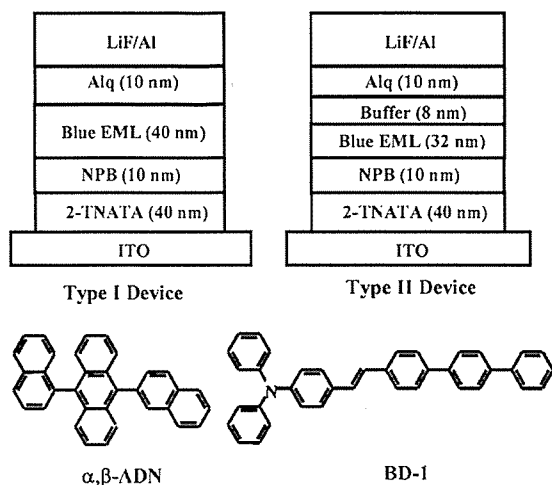


FIG. 1. Chemical structures of blue host and dopant materials and the device architectures.

holes in the c-HTL device tends to increase faster than that of electrons at high electric field which causes an unbalanced hole and electron population. The dropping of efficiency is not favorable for the passive matrix (PM) driving display as PM OLED will need to work under high current density (high driving voltage) and short pulse. Thus, a better approach to make efficient deep blue OLEDs is to have an *undoped* single transport layer and to develop the appropriate matching deep blue host and dopant materials to enhance the Förster energy transfer in the doped emitter.

Here, we report an anthracene-based blue host material (α,β -ADN) in which one of the 2-naphthyl substituents of 9,10-di(2-naphthyl)anthracene (ADN) is replaced with the sterically more demanding 1-(naphthyl) substituent. With a slightly modified conventional blue OLED architecture, we achieved an EL efficiency of 4.9 cd/A and an external quantum efficiency (EQE) of 4.4% at 20 mA/cm² with saturated blue CIE_{x,y} coordinates of (0.15, 0.13). In particular, we were able to obtain deep blue OLED with a near flat current efficiency versus current density response ranging from 10 to 100 mA/cm² in the BD-1/ α,β -ADN guest/host system. This overall EL performance is believed to be among the best that have been reported in the literature for the deep blue OLEDs.

To demonstrate the advantage of α,β -ADN, two types of blue devices (Fig. 1) have been fabricated, where indium tin oxide was used as anode, 4,4',4''-tris[*N*-(2-naphthyl)-*N*-phenyl-amino]-triphenylamine was used as hole injection layer, and *N,N'*-bis-(1-naphthyl)-*N,N'*-diphenyl,1,1'-biphenyl-4,4'-diamine and Alq were used as hole-transport layer (HTL) and electron transport layer (ETL), respectively. LiF (1 nm)/Al (100 nm) was served as cathode. Type I devices are the conventional blue OLED struc-

TABLE I. Type I device performances at the current density of 20 mA/cm².

Device	BD-1 (x%)	V (V)	CE (cd/A)	EQE (%)	CIE _{x,y}
1	0	7.2	2.2	2.0	(0.16, 0.14)
2	1	7.4	3.1	2.9	(0.16, 0.13)
3	3	7.6	4.7	3.7	(0.15, 0.16)
4	5	7.7	5.4	4.2	(0.15, 0.16)
5	8	7.7	6.3	4.8	(0.15, 0.17)

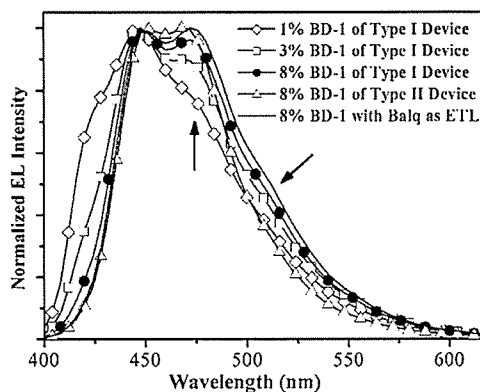


FIG. 2. EL spectra of different BD-1 concentrations in types I and II devices.

ture with an emitting layer (EML) doped with BD-1. Type II devices are BD-1 doped devices with a buffer layer between doped emitting layer and ETL. All devices have an emission area of 0.1 cm² defined by the overlapping of anode and cathode. The device fabrication was completed in one pump down without breaking the vacuum. The chamber vacuum was maintained below 4×10^{-6} Torr during all organic materials and cathode metal deposition. The current-voltage-luminance (*I-V-L*) characteristics of the devices were measured with a computer controlled Keithley 236 source meter and PR650 spectrophotometer in air without device encapsulation. The repeating measurement showed no significant device performance degradation during measurement period.

Table I summarized the performances of the type I devices with various BD-1 doping concentrations in α,β -ADN host which exhibits generally higher efficiency than those using MADN as host. However, we noted that the deep blue color (CIE_y < 0.15) can only be obtained at low BD-1 concentration (~1%). It is obvious that the optimal BD-1 concentration in the α,β -ADN host and in the c-HTL/MADN system is quite different. The optimal BD-1 concentration is as high as 5% which produces a deep blue color with a CIE_{x,y} of (0.14, 0.13) in the c-HTL/MADN system.⁷

Figure 2 shows the normalized EL spectra of type I device with BD-1 doped at concentrations of 1%, 3%, and 8%. It can be seen that the peak at 475 nm grows steadily with dopant concentration increase. Meanwhile, a shoulder peak at 515 nm can be observed when the BD-1 concentration is larger than 3%. This shoulder peak will dramatically increase

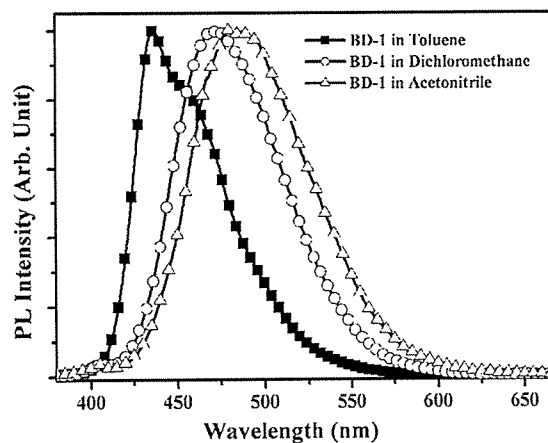


FIG. 3. PL spectra of BD-1 in different solvents.

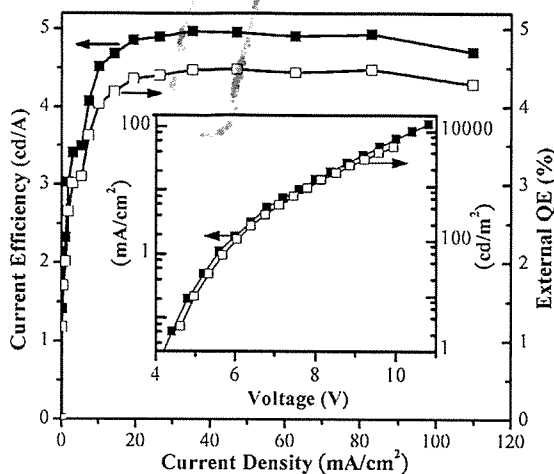


FIG. 4. Current and external quantum efficiency vs current density of type II device with 8% BD-1 doped in α,β -ADN with pure α,β -ADN as buffer layer. Inset: I - V - B curve of the device.

CIE_y value of our OLED device, leading to unsatisfied blue color. To further judge the origination of this shoulder peak, bis(2-methyl-8-quinolinolato) para-phenylphenolato aluminum (peaked at 480 nm) was used to replace Alq (peaked at 520 nm). As shown in Fig. 2, the shoulder peak at 515 nm can still be seen, confirming that the shoulder peak is not originated from Alq emission.

To verify whether the discrepancy in EL performance might be induced by the charge-induced polarization effect of host matrix, the fluorescent emission property of BD-1 in solvents with different polarity was investigated and results are shown in Fig. 3. It can be seen that the PL of BD-1 exhibits a large *bathochromic* shift with increasing solvent polarity. When the solvent polarity¹³ increases from 2.4 (toluene) to 5.8 (acetonitrile), the fluorescent emission wavelength λ_{max} of BD-1 is found to shift from 437 to 485 nm without obvious aggregation. Thus, we believe that the *solvent-induced bathochromic shift* of BD-1 emission is the primary cause for the higher CIE_y value (>0.15) observed in our type I devices as BD-1 doping concentration increases.¹⁴ This device structure has considerable charge injection barriers; therefore, the accumulated charge carriers could build up quite significant dipolar region near the interface of HTL/EML and/or EML/ETL and also introduce additional polarization. Concomitantly, the emission from BD-1 molecules located near this region will be bathochromic shifted. In order to reduce this undesirable polarization effect in the device, we introduced a thin (8 nm) pure α,β -ADN buffer layer (device type II, as shown in Fig. 1) between the doped emission zone and ETL to effectively move the device recombination zone away from the interface. The EL spectrum (in Fig. 2) shows that the shoulder peak located at 515 nm in type I device can be effectively eliminated in type II device and result in the decrease of CIE_y value. The optimal BD-1 doping concentration has increased to about 8% in type II device, as shown in Fig. 4. The device produced a current efficiency of 4.9 cd/A and an EQE of 4.4% at 20 mA/cm² with saturated blue $CIE_{x,y}$ coordinates of (0.15, 0.13). It also

shows a near constant efficiency versus current density response from 10 to >100 mA/cm² as no carrier trap effect is expected to involve in the device operation.

In conclusion, we have developed a modified anthracene derivative as a wide band gap host material for the deep blue OLED device. We find that α,β -ADN is very efficient in Förster energy transfer to the blue dopant (BD-1) which results in significant improvement in EL performance producing one of the best deep blue OLEDs disclosed in the literature. We obtain a deep blue EL device with an EL efficiency of 4.9 cd/A and an external quantum efficiency of 4.4% at 20 mA/cm² with saturated blue $CIE_{x,y}$ coordinates of (0.15, 0.13) as well as an invariable current efficiency with driving conditions ranging from 10 to 100 mA/cm². The high-efficiency deep blue OLED device is achieved by the combination of (1) choosing an appropriate matching blue host material (α,β -ADN) to enable better Förster energy transfer to the BD-1 dopant, (2) preventing the deep blue dopant color from bathochromic shift at high concentration (8%) by alleviating the charge buildup near the EML/HTL interface, and (3) controlling the recombination within the emitter through the insertion of a thin layer of α,β -ADN buffer in-between EML and Alq.

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- ¹C. W. Tang and S. A. Van Slyke, Appl. Phys. Lett. 51, 913 (1987).
- ²R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Bredas, M. Logdlund, and W. R. Salaneck, Nature (London) 397, 121 (1999).
- ³R. J. Tseng, R. C. Chiechi, F. Wudl, and Y. Yang, Appl. Phys. Lett. 88, 093512 (2006).
- ⁴B. W. D'Andrade and S. R. Forrest, Adv. Mater. (Weinheim, Ger.) 16, 1585 (2004).
- ⁵Y. Kijima, N. Asai, and S. Tamura, Jpn. J. Appl. Phys., Part 1 38, 5274 (1999).
- ⁶M. T. Lee, H. H. Chen, C. H. Liao, C. H. Tsai, and C. H. Chen, Appl. Phys. Lett. 85, 3301 (2004).
- ⁷M. T. Lee, C. H. Liao, C. H. Tsai, and C. H. Chen, Adv. Mater. (Weinheim, Ger.) 17, 2493 (2005).
- ⁸M. H. Ho, Y. S. Wu, S. W. Wen, M. T. Lee, T. M. Chne, C. H. Chen, K. C. Kwok, S. K. So, K. T. Yeung, and Z. Q. Gao, Appl. Phys. Lett. 89, 252903 (2006).
- ⁹Y.-H. Kim, D.-C. Shin, S.-H. Kim, C.-H. Ko, H.-S. Yu, Y.-S. Chae, and S.-K. Kwon, Adv. Mater. (Weinheim, Ger.) 13, 1690 (2002).
- ¹⁰T. Arakane, M. Funahashi, H. Kuma, K. Fukuoka, K. Ikada, H. Yamamoto, F. Moriwaki, and C. Hosokawa, SID Int. Symp. Digest Tech. Papers 37, 37 (2006).
- ¹¹A. Saitoh, N. Yamada, M. Yashima, K. Okinaka, A. Senoo, K. Ueno, D. Tanaka, and R. Yashiro, SID Int. Symp. Digest Tech. Papers 35, 150 (2004).
- ¹²P. C. Arnett and N. Klein, J. Appl. Phys. 46, 1399 (1975).
- ¹³C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed. (VCH, Weinheim, 1990), pp. 339–387.
- ¹⁴V. Bulovic, R. Deshpande, M. E. Thompson, and S. R. Forrest, Chem. Phys. Lett. 308, 317 (1999).