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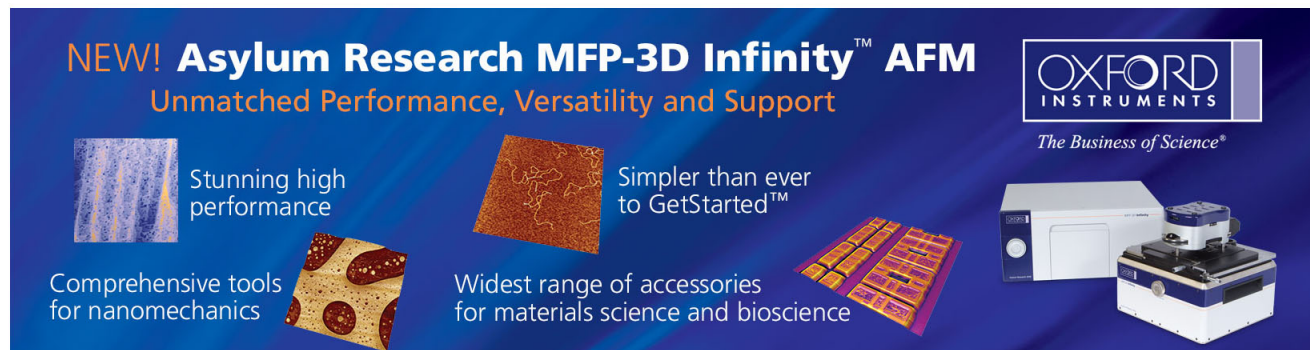
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Highly efficient deep blue organic electroluminescent device based on 1-methyl-9,10-di(1-naphthyl)anthracene

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The authors have developed 2-methyl-9,10-di(1-naphthyl)anthracene (α, α -MADN) as an effective wide band gap host material for Förster energy transfer to the *unsymmetrical* mono(styryl)amine deep blue fluorescent dopant (BD-1). This guest/host emitting system, at the optimal doping concentration of 3%, can also increase the probability of carrier recombination near the hole-transport/emitting layer interface for the blue organic light emitting device which produces electroluminescence efficiencies of 3.3 cd/A and 1.3 lm/W and a deep blue CIE_{x,y} color coordinates of (0.15, 0.13) that are 50% better than those of the traditional β, β -isomeric host (MADN) with the same dopant. © 2006 American Institute of Physics. [DOI: 10.1063/1.2409367]

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 arbitrarily as having a blue electroluminescent emission with a Commission Internationale d'Éclairage (CIE_{x,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

Up until recently, formal reports with full disclosure on deep blue OLED dopant/host materials and devices are rare and sketchy. One notable example recently was by Idemitsu Kosan Co., which utilized a styrylamine-based dopant to produce an electroluminescence (EL) efficiency of 7.0 cd/A and a blue color of (0.14, 0.16).⁴ The other was disclosed by Canon Co., 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).⁵ Recently, it has also been fully disclosed that an anthracene-based blue host material, 2-methyl-9,10-di(2-naphthyl)anthracene⁶ (abbreviated as β, β MADN or MADN) doped with an *unsymmetrical* mono(styryl)amine fluorescent dopant (BD-1), achieved an EL efficiency of 2.2 cd/A at 20 mA/cm² with a saturated blue CIE_{x,y} of (0.15, 0.12) and a normalized operational lifetime of 10 000 h at an initial brightness of 100 cd/m².⁷

Although BD-1 doped MADN emitter could achieve a saturated deep blue color, the device efficiency is still low and inadequate. It is well known that a guest-host doped emitter system can significantly improve device performance in terms of EL efficiency and emissive color.⁶ Therefore, key for developing deep blue OLEDs is not only finding the highly fluorescent deep blue dopant but also the appropriate

matching host material in order to enhance the probability of carrier recombination as well as the efficiency of Förster energy transfer from the host to the dopant molecule.

In this letter, we report the development of an anthracene-based wide band gap host material in which the 2-(naphthyl) substituent of MADN is replaced by the sterically more demanding 1-(naphthyl) substituent. The small *methyl* substituent at C-2 position of the anthracene moiety is preserved with the purpose of disrupting the symmetry of 9,10-di(2-naphthyl)anthracene (ADN) and suppressing its problematic crystallization. We find that BD-1/ α, α -MADN guest/host system can achieve 50% higher EL efficiency of 3.3 cd/A at 20 mA/cm² and a more saturated blue color of CIE_{x,y} (0.15, 0.13) than those of BD-1/MADN system.

To demonstrate the efficacy of α, α -MADN, four blue devices with the structure of indium tin oxide (ITO)/CF_x/N,N'-bis(1-naphthyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB) (50 nm)/emitting layer (EML) (40 nm)/tris(8-quinolinolato)aluminum (Alq₃) (10 nm)/LiF (1 nm)/Al (200 nm) have been fabricated. Devices I and II are standard blue devices with undoped MADN and α, α -MADN as EML, while devices III and IV are blue doped devices with 3% BD-1/MADN and 3% BD-1/ α, α -MADN, respectively. The molecular structures of MADN, α, α -MADN and BD-1 are depicted in Fig. 1. CF_x, NPB, and Alq₃ were used as the hole injection material⁸ and hole and electron transport materials, respectively. For studying the transport phenomenon, two additional carrier-only devices were also fabricated. The electron-only device structure was ITO/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (30 nm)/neat α, α -MADN or MADN (60 nm)/Alq₃ (20 nm)/LiF (1 nm)/Al (200 nm) and the hole-only device structure was ITO/CF_x/NPB (20 nm)/neat α, α -MADN or MADN (60 nm)/NPB (20 nm)/Al (200 nm).

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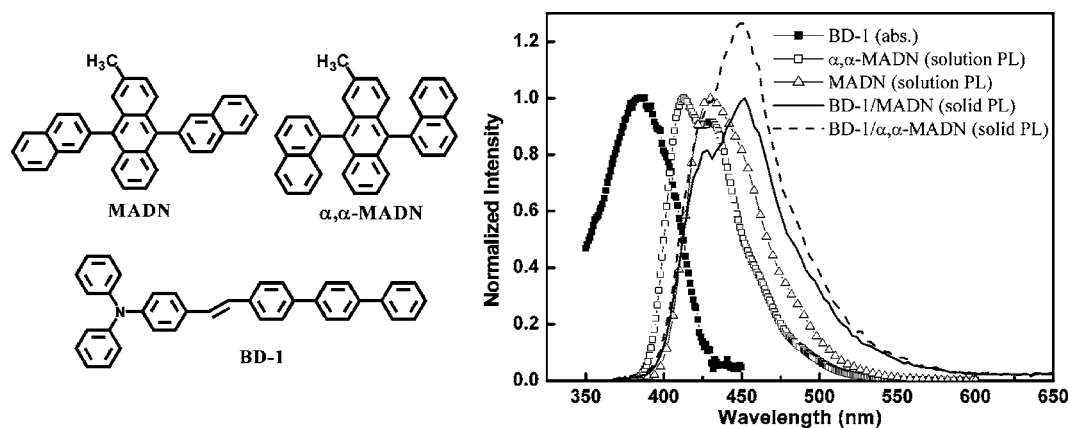


FIG. 1. Structures, absorption, and emission spectra of dopant BD-1 and host MADN, α, α -MADN in toluene along with the thin-film solid PL spectra of BD-1 doped MADN, and α, α -MADN in PMMA.

Figure 1 depicts the absorption spectrum of BD-1 and the solution photoluminescence (PL) spectra of MADN and α, α -MADN in toluene. It is apparent that the spectral overlap between the absorption of BD-1 and emission of MADN is poor and the Förster energy transfer from host to dopant is not expected to be efficient. On the other hand, the fluorescence wavelength λ_{\max} of α, α -MADN is 413 nm, which is blue shifted around 17 nm with respect to that of MADN, albeit the relative fluorescence quantum yield of α, α -MADN is considerably lower to the extent of only 60% of MADN. The principal cause of the *hypsochromic* shift is most likely due to the stronger H atom-H atom repulsions between the 1-(naphthyl) substituent and anthracene moiety of α, α -MADN, which causes the naphthyl group to deconjugate from the anthracene chromophore in the ground state. As a result, the blueshifted emission spectrum of α, α -MADN is found to overlap well with the absorption spectrum of BD-1 that is essential for efficient Förster energy transfer. The emission spectra of 5% BD-1 doped MADN and α, α -MADN thin films [spin coated with polymethylmetacrylate (PMMA)] are also depicted in Fig. 1. We find that the emissive intensity of BD-1/ α, α -MADN film is 1.2 times higher than that of BD-1/MADN film, confirming that the Förster energy transfer is indeed more efficient between α, α -MADN and BD-1.

The charge transporting properties of α, α -MADN and MADN were examined further in the form of amorphous films as functions of electric field and temperature by means

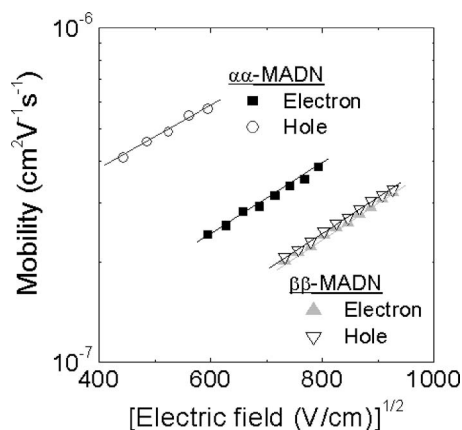


FIG. 2. Field dependent hole and electron mobilities of MADN and α, α -MADN at room temperature.

of time-of-flight technique.^{9,10} Figure 2 depicts the field dependent hole and electron mobility of α, α -MADN versus MADN at room temperature. We find that MADN shows nearly identical hole and electron mobilities [$(2-3) \times 10^{-7} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$] under various field strengths. However, it appears that there is considerable improvement in carrier mobility by changing the substituents attached to anthracene core from 2(β)-naphthyl to 1(α)-naphthyl, especially the hole mobility. The hole and electron mobilities of α, α -MADN are $(3-5) \times 10^{-7}$ and $(2-4) \times 10^{-7} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively, which are all higher than those of MADN.

The detailed EL performances are summarized in Table I. The voltage, luminance yield, power efficiency, external quantum efficiency (EQE), and color coordinates were measured at 20 mA/cm^2 . The EL efficiencies of the undoped α, α -MADN device are only 0.7 cd/A and 0.3 lm/W at 6.7 V with a CIE_{x,y} (0.15, 0.08). But the BD-1 doped α, α -MADN system produced EL efficiencies of 3.3 cd/A and 1.3 lm/W at 6.5 V with a CIE_{x,y} of (0.15, 0.13) that is 1.5 times higher than that of BD-1/MADN system of 2.2 cd/A.

It is interesting to note that α, α -MADN possesses considerably higher carrier mobility than MADN and yet, devices II and IV of the former have a higher applied voltage than devices I and III (see Table I). To explore the underlying physics further, we studied the *J-V* characteristics of the carrier-only devices. The highest occupied molecular orbitals (HOMOs/LUMOs) of α, α -MADN and MADN are 5.8/2.8 and 5.6/2.6 eV, respectively. Figure 3(a) shows *J-V* characteristics of the electron-only devices which reveal that the device of α, α -MADN has a lower applied voltage under high current density (over 40 mA/cm^2). The result can be rationalized by the lower energy barrier (0.1 eV) between the LUMOs of α, α -MADN

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	6.4	1.3	0.6	1.7	(0.15, 0.10)
II	6.7	0.7	0.3	1.0	(0.15, 0.08)
III	6.1	2.2	1.1	2.3	(0.15, 0.12)
IV	6.5	3.3	1.3	3.0	(0.15, 0.13)

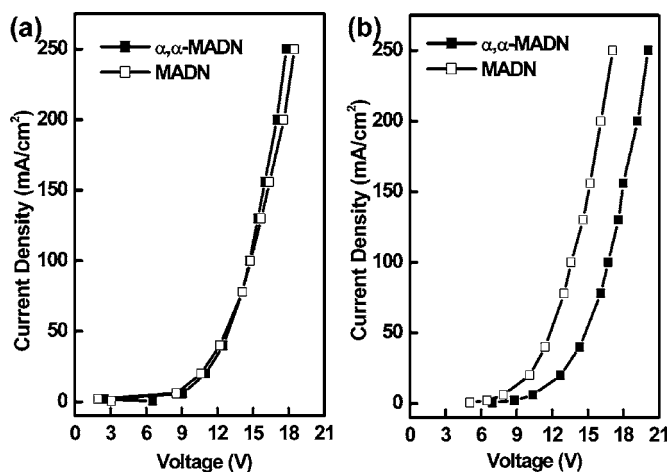


FIG. 3. Current density-voltage (I - V) characteristics of carrier-only devices. (a) Electron-only device and (b) hole-only device.

(2.8 eV) and electron-transporting Alq₃ (2.9 eV), which provides an effective pathway for electron to inject from Alq₃ to α, α -MADN, especially under high current drive conditions. On the contrary, Fig. 3(b) shows that α, α -MADN hole-only device has a higher applied voltage than that of the MADN under the same drive current density. We attribute this to the higher energy barrier (0.4 eV) between the HOMOs of hole-transporting NPB (5.4 eV) and α, α -MADN (5.8 eV), which makes hole injection more difficult from NPB to α, α -MADN. From the J - V characteristics of the carrier-only devices, we conclude that the deeper HOMO of α, α -MADN is the primary reason for causing the high applied voltage of devices II and IV.

Further, in most Alq₃-based OLEDs, the dominant carrier is often the injected hole. With the low-lying HOMO of α, α -MADN which creates a high barrier (0.4 eV) for hole to inject from the hole-transport layer of NPB to the emitter, the probability of carrier recombination near the NPB/ α, α -MADN interface where there will be more hole accumulated would be much increased. This restraint of hole injection can also make the hole-electron recombination more efficient in the emitting layer of α, α -MADN device than that of MADN. We believe that the combined effect of higher carrier mobilities and 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.

Figure 4 shows the operational lifetime of the four blue devices under a constant current density of 20 mA/m² monitored in a dry box. The t_{80} (the time for the luminance to drop to 80% of initial luminance) and initial luminance (L_0) measured for devices I, II, III, and IV were 210 h at $L_0=288$ cd/m², 85 h at $L_0=126$ cd/m², 435 h at $L_0=484$ cd/m², and 350 h at $L_0=660$ cd/m², respectively. It is apparent that the α, α -MADN device stability can be significantly improved with BD-1 doping and can become as stable as the BD-1/MADN device. Assuming scalable Cou-

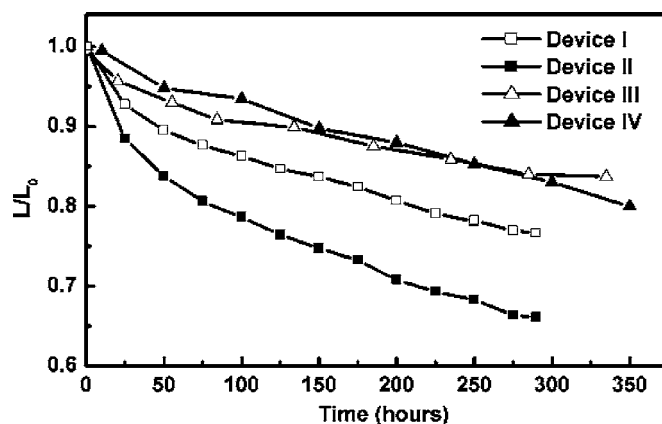


FIG. 4. Device operational stability of the blue devices.

lombic degradation,¹¹ driving at a L_0 value of 100 cd/m², the half-lives ($t_{1/2}$) of devices III (BD-1/MADN) and IV (BD-1/ α, α -MADN) are projected to be 10 000 and 9600 h, respectively.

In summary, we have developed α, α -MADN as an effective wide band gap host material for the doped deep blue OLED. We find that α, α -MADN can be more efficient in Förster energy transfer to the deep blue dopant (BD-1). It can also make the injected carriers for recombination more balanced in the emitting layer which results in significant improvement in EL performance giving rise to blue OLED with EL efficiencies of 3.3 cd/A and 1.3 lm/W and a deep blue CIE_{x,y} color coordinates of (0.15, 0.13).

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