Single-layer organic light-emitting diodes using naphthyl diamine

Tse, S. C.; Tsung, K. K.; So, S. K.

Published in:
Applied Physics Letters

DOI:
10.1063/1.2740110

Published: 01/05/2007

Document Version:
Publisher's PDF, also known as Version of record

Single-layer organic light-emitting diodes using naphthyl diamine

S. C. Tse, K. K. Tsung, and S. K. So[a)]
Department of Physics and Centre for Advanced Luminescence Materials, Hong Kong Baptist University, Kowloon Tong, Hong Kong, China

(Received 18 March 2007; accepted 19 April 2007; published online 21 May 2007)

N,*N*′-diphenyl-*N*,*N*′-bis(1-naphthyl)(1,1′-biphenyl)-4,4′diamine (NPB), a common hole transporter, was employed to fabricate single-layer organic light-emitting diodes (OLEDs). With a quasi-Ohmic anode, NPB device exhibited a bulk-limited hole current in the low-voltage region. Electron injection and light emission were clearly observed for applied voltages exceeding 4 V. In order to confine the recombination zone, intentional doping was applied to the single-layer device. After doping with perylene, the luminance and current efficiency of NPB device increased dramatically. It is expected that more efficient single-layer OLEDs can be achieved by using the doping strategy. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2740110]

Organic light-emitting diodes (OLEDs) are thin, lightweight, and power-efficient solid-state devices, which are highly suitable for applications in portable, full-color displays. Starting with the seminal paper of 1965 that described the discovery of organic luminescence in anthracene,[1] OLEDs technology had an incredible breakthrough in 1987 when Tang and VanSlyke reported that a bilayer organic structure was able to efficiently emit light while running the device at low voltages.[2] As the technology evolves, multilayer structures incorporating carrier injection, transporting, light emitting, and hole blocking layers were introduced to optimize OLED efficiencies and lifetime.[3–5] However, such complicated configurations are industrially unfavorable because the fabrication processes are costly and time consuming. Thus, there are many attempts to fabricate a single-layer device, in which the active organic material is capable of acting simultaneously as the hole transporting, electron transporting, and light-emitting units.[6–10]

To achieve efficient and long-lived single-layer devices, the active materials should satisfy several requirements: (1) desirable thermal stability and morphological properties in solid state, (2) satisfactory mobilities of both electrons and holes, and (3) appropriate energy levels for the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Below, we demonstrate that a single-layer OLED can be fabricated from *N*,*N*′-diphenyl-*N*,*N*′-bis(1-naphthyl)(1,1′-biphenyl)-4,4′diamine (NPB), a well-recognized hole transporter with good film forming and thermal stability. In our previous work, NPB was shown to exhibit an ambipolar transporting ability. From time-of-flight measurements, values of electron and hole mobilities for NPB are $(6-9)\times10^{-4}$ and $(3-6)\times10^{-4}$ cm^2/V s, respectively.[11] The unexpected electron mobility originates from electrons hopping among the naphthyl moieties. In addition, NPB has the appropriate HOMO and LUMO of about 5.4 and 2.4 eV, respectively. Thus, it is expected that NPB can form appreciable charge injection contacts with some common electrodes, such as poly(3,4-ethylenedioxythiophene):polystrenesulphonic acid (PEDOT:PSS), Ca, and Mg:Ag. In order to confine the recombination zone and improve the fluorescence abilities, perylene-doped NPB layer was inserted into single-layer devices. The effect of this intentional doping is discussed.

NPB was purchased from E-ray and was purified once by train zone sublimation. PEDOT:PSS and perylene was obtained from H.C. Starks GmbH and Aldrich, respectively. Their chemical structures are shown in Fig. 1(a). For the undoped NPB single-layer device, the structure was indium tin oxide (ITO)/PEDOT:PSS/NPB(120 nm)/Ca/Ag. Figure 1(b) shows an energy diagram depicting the relevant energy levels for the device.[12] PEDOT:PSS acted as the hole-injecting anode. Ca cathode was used to increase electron injection and was protected by a top layer of Ag. Prior to film

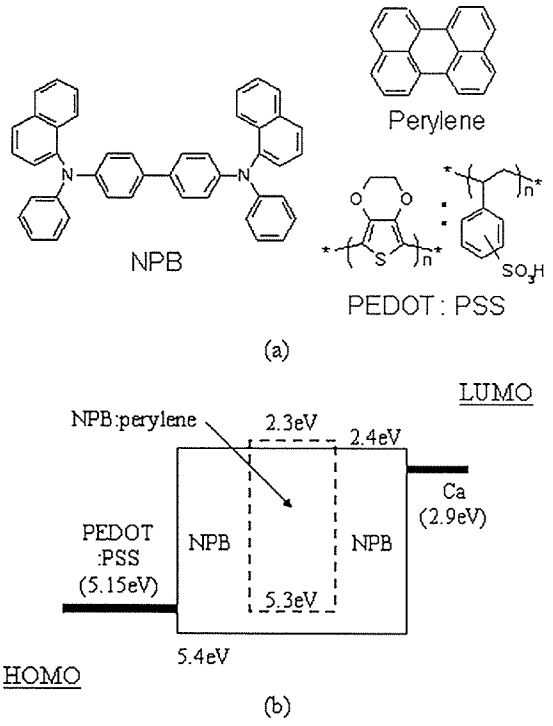

FIG. 1. (a) Chemical structures of NPB, PEDOT:PSS, and perylene. (b) An energy diagram of the undoped and perylene-doped NPB single-layer devices. The dashed rectangle is the doping region, where the LUMO and HOMO of perylene are located at 2.3 and 5.3 eV, respectively.

[a)]Author to whom correspondence should be addressed; electronic mail: skso@hkbu.edu.hk

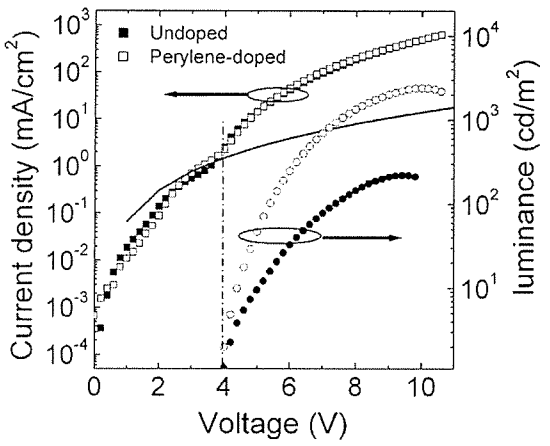

FIG. 2. Current-voltage (*JV*) characteristics and luminance-current (*LJ*) characteristics of NPB devices. The filled (■) and opened (□) symbols represent the undoped and perylene-doped devices, respectively. The solid line is the theoretical hole trap-free space charge-limited current of NPB.

fabrication, ITO substrates were exposed to UV ozone.[13] A 50 nm layer of PEDOT:PSS was spin coated onto ITO for 180 s at 1000 rpm. Afterward, the substrate was annealed in air at 150 °C for 30 min to drive out residual moisture. NPB and Ca/Ag cathode were subsequently evaporated onto PEDOT:PSS to complete device fabrication. All film thicknesses were monitored *in situ* with a quartz crystal sensor and further calibrated by a profilometer. The current-voltage-luminance (*JVL*) characteristics and electroluminescence (EL) measurement were performed with a computer-controlled Keithley Source-Measure Unit (model 236) and Photo Research spectra colorimeter (model 650). All measurements were carried out in ambient atmosphere and at room temperature.

Figure 2 (filled symbols) shows the *JVL* characteristics of the undoped NPB single-layer device. The turn-on voltage is about 4 V and the maximum luminance achieved is 220 cd/m^2. At current density of 80 mA/cm^2, the luminance and the current efficiency were 66 cd/m^2 and 0.1 cd/A, respectively. These results clearly show that NPB has the potential for acting as the active material in single-layer OLEDs.

To further analyze the *JV* characteristic of an undoped NPB device, a theoretical hole current was computed and shown as the solid line in Fig. 2. Here, we assume that NPB is trap-free and has an Ohmic hole injection, so the steady state hole current density should obey the theoretical space-charge-limited current (J_{SCL}). Following the work of Murgatroyd, the J_{SCL} can be approximated by[14]

$$J_{SCL} = \frac{9}{8}\mu_0\varepsilon_0\varepsilon_r \exp(0.89\beta\sqrt{F})\frac{F^2}{d}, \quad (1)$$

where μ_0 is the zero-field mobility, β is the Poole-Frankel (PF) slope, ε_0 is the permittivity in vacuum, ε_r is the dielectric constant ($\varepsilon_r \sim 3$ for organic materials), F is the average electric field, and d is the sample thickness. For NPB, the μ_0 and β are 2.73×10^{-4} cm^2/Vs and 1.32×10^{-3} $(V/cm)^{-1/2}$, respectively, and are obtained from another independent time-of-flight measurement.[15] From Fig. 2, we note that for the applied voltage <4 V, the driving current of the NPB device matches the computed hole current near the vicinity of the EL threshold, which suggests that NPB has an excellent hole injection from PEDOT:PSS. This result is entirely consistent with our previous works, which showed that PEDOT:PSS can form a quasi-Ohmic contact with NPB.[15,16] Thus, the conduction of the NPB device in this regime is mostly hole dominated and bulk limited. At high voltage (>4 V), the *JV* curve of the NPB device acquires a distinctly different shape due to the electron injection from the Ca cathode. The turning point of the *JV* curve is at about 4 V and coincides with the starting voltage of *LV* characteristics, at which the detectable light emission can be observed from the device. Viewed in this manner, for the undoped NPB device, the turning point of the *JV* curve (vertical line in Fig. 2) corresponds to the onset of electron injection from the Ca cathode.

TABLE I. EL performances of undoped and perylene-doped NPB single-layer devices at 80 mA/cm^2.

Devices	Maximum luminance (cd/m^2)	Luminance (cd/m^2)	Current efficiency (cd/A)
Undoped	220 (376 mA/cm^2)	66	0.1
Perylene doped	2400 (490 mA/cm^2)	536	0.7

Besides the electron injection, an undefined recombination zone also limits the performance of the single-layer device. In bilayer structure OLEDs, the recombination zone is easily defined at the hole-transport layer (HTL) and electron-transport layer (ETL) interface. Holes and electrons accumulate at interface and then recombine.[17] For single-layer devices, however, electrons and holes cannot accumulate for the recombination due to the lack of heterointerface. These uncombined electrons and holes become the dark current of the single-layer device. Furthermore, if the electron-hole pair recombines near the metal cathode, exciton quenching will occur at the cathode and will be responsible for lowering the device performance.[18] In order to create an efficient site for the recombination, the single-layer device was intentionally doped in the middle. The doped device structure was ITO/PEDOT:PSS/NPB (40 nm)/NPB:perylene (40 nm)/NPB (40 nm)/Ca/Al, where perylene was doped at 10% concentration by volume. The *JVL* characteristics of the perylene-doped NPB device are shown as the open symbols in Fig. 2. Detailed performances of the undoped and perylene-doped NPB devices are summarized in Table I. Compared to the undoped device, the current efficiency of perylene-doped device was enhanced seven times to about 0.7 cd/m^2 at 80 mA/cm^2, and the maximum luminance also increased to 2400 cd/m^2. Thus, after doping with perylene, the NPB single-layer devices have a notable improvement in the electroluminance performance such as the current efficiency and the luminance. With a view to optimizing device performance, 5% and 20% perylene-doped NPB devices were also constructed. However, both the current efficiency and the electroluminescence spectrum were not sensitive to change in the doping concentration.

Figure 3 shows the EL spectra of the single-layer devices and the absorption spectrum of perylene. Based on the overlapping between the EL spectrum of the undoped device (solid line) and the perylene absorption spectrum (dotted line), Förster energy transfer can be employed to describe the excitation mechanisms of the perylene-doped NPB device. Förster energy transfer is a long range, nonradiative, dipole-

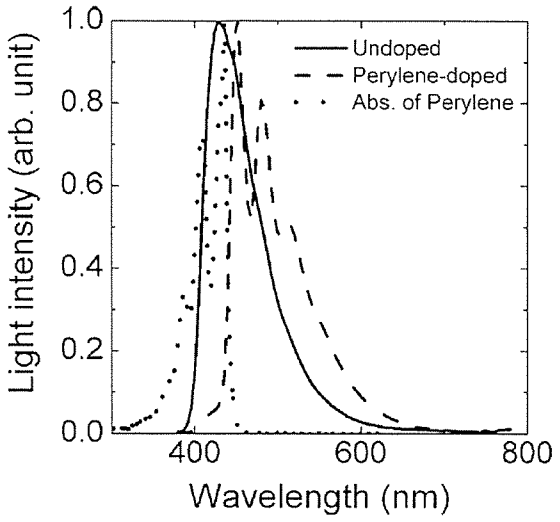

FIG. 3. EL spectra of undoped NPB devices (in solid line) and perylene-doped NPB devices (in dashed line). The dotted line is the absorption spectrum of perylene.

dipole coupling between donor and acceptor molecules, which is often used to explain the energy transfer phenomenon in a doped system.[19,20] For the perylene-doped NPB device, in principle, NPB and perylene can be viewed as donor and acceptor, respectively. Holes and electrons are injected under an external electric field and form excitons in NPB molecules. Förster energy transfer occurs from excited NPB to perylene. Then light will be emitted when the excitons recombine in perylene molecules. The EL spectrum of the perylene-doped NPB device is shown as the dashed line in Fig. 3.

Apart from Förster energy transfer, charge trapping is an alternative approach to describe the excitation mechanism of the perylene-doped NPB device. In this approach, dopants are depicted as traps and provide recombination sites in the doped layer. Thus, the injected electron and hole are trapped and the recombine in the dopant molecule. From Fig. 2, however, the *JV* curves of the undoped and perylene-doped NPB devices are essentially identical. It suggests that the trapping effect does not occur in the perylene-doped device. Hence, for the NPB single-layer devices, the significant improvement by intentional doping can account for the Förster energy transfer between NPB and perylene. As evident from the doped device structure, the recombination zone is confined in the middle of the device.

In conclusion, we demonstrate that NPB, a common hole transporter, can be employed as the host material in single-layer OLEDs. With the ambipolar transporting ability of NPB, the single-layer device attains an appreciable performance. From *JVL* measurement, the NPB device exhibited a bulk-limited hole current in the low-voltage region. Electron injection was clearly observed at about 4 V, which coincides with the onset of light emission. Moreover, perylene was doped into the single-layer device in order to confine the recombination zone. Upon doping, the device performance has a notable improvement and the current efficiencies increase seven times to about 0.7 cd/A. While the number is by no means impressive, this example clearly suggests that the ambipolar material and intentional doping can be applied to simplify OLEDs architecture.

Support of this research from the Research Committee of HKBU under Grant No. FRG/05-06/II-41 and the Research Grant Council of Hong Kong under Grant No. HKBU/2173/04E is gratefully acknowledged.

[1]W. Helfrish and W. G. Schneider, Phys. Rev. Lett. **14**, 229 (1965).
[2]C. W. Tang and S. A. VanSlyke, Appl. Phys. Lett. **51**, 913 (1987).
[3]S. A. VanSlyke, C. H. Chen, and C. W. Tang, Appl. Phys. Lett. **69**, 2160 (1996).
[4]Y. Kijima, N. Asai, and S. I. Tamura, Jpn. J. Appl. Phys., Part 1 **38**, 5274 (1999).
[5]L. S. Hung, C. W. Tang, and M. G. Mason, Appl. Phys. Lett. **70**, 152 (1997).
[6]W. Hu and M. Matsumura, Appl. Phys. Lett. **81**, 806 (2002).
[7]Q. Huang, J. Cui, H. Yan, J. G. C. Veinot, and T. J. Marks, Appl. Phys. Lett. **81**, 3528 (2002).
[8]Y. Gao, L. Wang, D. Zhang, L. Duan, G. Dong, and Y. Qiu, Appl. Phys. Lett. **82**, 155 (2003).
[9]H. F. Wang, L. D. Wang, Z. X. Wu, D. Q. Zhang, J. Qiao, Y. Qui, and X. G. Wang, Appl. Phys. Lett. **88**, 131113 (2006).
[10]P. A. Lane, G. P. Kushto, and Z. H. Kafafi, Appl. Phys. Lett. **90**, 023511 (2007).
[11]S. C. Tse, K. C. Kwok, and S. K. So, Appl. Phys. Lett. **89**, 262102 (2006).
[12]Y. Hamada, H. Kanno, T. Tsujioka, H. Takahashi, and T. Usuki, Appl. Phys. Lett. **75**, 1682 (1999).
[13]W. Song, S. K. So, and L. Cao, Appl. Phys. A: Mater. Sci. Process. **72**, 361 (2001).
[14]P. N. Murgatroyd, J. Phys. D **3**, 151 (1970).
[15]S. C. Tse, S. W. Tsang, and S. K. So, J. Appl. Phys. **100**, 063708 (2006).
[16]S. W. Tsang, S. C. Tse, K. L. Tong, and S. K. So, Org. Electron. **7**, 474 (2006).
[17]C. W. Tang, S. A. VanSlyke, and C. H. Chen, J. Appl. Phys. **65**, 3610 (1989).
[18]A. L. Burin, and M. A. Ratner, J. Phys. Chem. A **104**, 4704 (2000).
[19]V. Bulović, A. Shoustikov, M. A. Baldo, E. Bose, V. G. Kozlov, M. E. Thompson, and S. R. Forrest, Chem. Phys. Lett. **287**, 455 (1998).
[20]H. Mattoussi, H. Murata, C. D. Merritt, Y. Iizumi, J. Kido, and Z. H. Kafafi, J. Appl. Phys. **86**, 2642 (1999).