High efficiency and long lifetime OLED based on a metal-doped electron transport layer

Jiun-Haw Lee [a,*], Meng-Hsiu Wu [a], Chun-Chieh Chao [b], Hung-Lin Chen [b], Man-Kit Leung [b,c]

[a] *Graduate Institute of Electro-Optical Engineering and Department of Electrical Engineering, National Taiwan University, No. 1, Sec. 4, Roosevelt Road, Taipei, Taiwan, Republic of China*
[b] *Department of Chemistry, National Taiwan University, Taipei, Taiwan, Republic of China*
[c] *Institute of Polymer Science and Engineering, National Taiwan University, Taipei, Taiwan, Republic of China*

Abstract

The OLED performance of cesium (Cs) doped 4,4′-bis(5-phenyl-[1,3,4]oxadiazol-2-yl)-2,2′-dinaphthylbiphenyl (bis-OXD), a metal-doped electron transport layer, is reported. Device lifetime increases because: (1) Cs is heavy and difficult to diffuse in an organic matrix, and (2) The host material, bis-OXD, exhibits a high glass-transition temperature (T_g) of 147 °C. The average roughness of the thin film is small hence the leakage current of the corresponding OLED devices is low. By using a silver cathode, an OLED with a 2.59 V reduction in driving voltage, a 47.3% increase in current efficiency, and a 3.14 times enhancement in operation lifetime was demonstrated.
© 2005 Elsevier B.V. All rights reserved.

1. Introduction

Organic light-emitting displays (OLED) have recently attracted much attention because of the advantages of low-power consumption, high brightness, high contrast, and low cost [1,2]. However, high driving voltage and short operation lifetime are major limitations for the current OLED devices in applications as compared to the other competitive display technologies, such as semiconductor light-emitting diodes (LEDs) and liquid crystal displays (LCDs).

In order to break through these limitations, organic materials having high conductivity and good electrical contact with electrodes are desired. Recently, doping techniques, which have been widely used in forming inorganic semiconductors, have been applied for forming organic p- and n-type materials [3]. Although efficient p-type doping is possible for a variety of organic materials, examples based on the n-type doping with high stability are rare [4]. A typical n-type doping electron transport layer (ETL) consists of a low work-function metal doped in an organic material. Co-evaporation of the materials, which is called the metal-doped (MD) technique, is commonly employed for preparing this ETL [5]. Not only the carrier injection is enhanced due to the modification at the ETL/cathode interface, but also the carrier transport is improved due to the incorporation of the metal atoms in ETL [6]. Although lithium was found to be one of the most efficient dopants, it would easily diffuse into the light-emitting layer (EML) and hence, induce the metal ion quenching effect. In a long-term operation, the current efficiency and the lifetime of the devices significantly decrease. 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthrolin (BCP) and 4,7-diphenyl-1,10-phenanthroline (BPhen) are common materials for the host organic materials in MD-ETL. Their molecular structures are shown in Fig. 1. Nevertheless, their low glass-transition temperatures (T_g) of 83 and 62 °C limit the operation lifetime of the devices [7]. Co-evaporating high T_g materials, such as Balq (T_g: 92 °C) with Li:BPhen to form a mixed ETL does increase the operation lifetime. Unfortunately, in the case, the driving voltage increased. There seems to be a tradeoff between operation lifetime and driving voltage in this system.

* Corresponding author. Fax: +886 2 2367 7467.
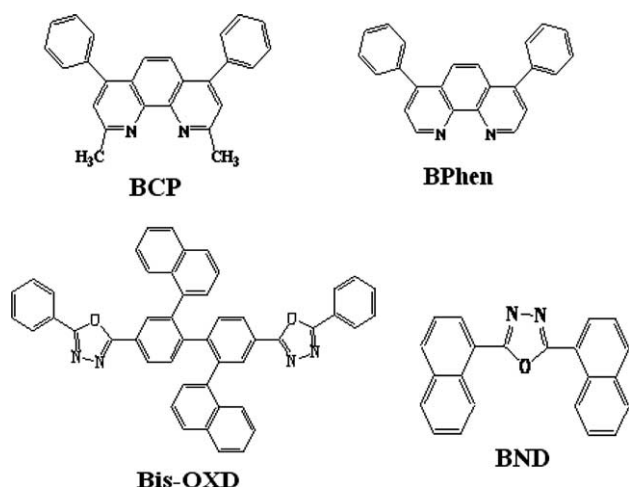 *E-mail address:* jhlee@cc.ee.ntu.edu.tw (J.-H. Lee).

Fig. 1. The chemical structure of BCP, BPhen, BND and bis-OXD.

Herein, we reported the use of cesium (Cs), a heavier alkali atom, as the dopant material in the MD-ETL. Since Cs is much heavier than Li, we expected that the metal–atom diffusion rate would be less. However, the work function of Cs is smaller in comparison with Li. Therefore, an organic material that is compatible with Cs and has high electron mobility is highly desired. In the present work, we adapted 4,4′-bis(5-phenyl-[1,3,4]oxadiazol-2-yl)-2,2′-dinaphthylbiphenyl (bis-OXD), shown in Fig. 1, as the host for the ETL matrix. In addition, 2,5-(binaphth-1-yl)-1,3,4-oxadiazole (BND) was employed as a model for comparison [8].

The family of oxadiazole (OXD) compounds has been extensively used as electron transporting materials [9]. We are interested in developing OLED devices based on this family for several reasons: (1) The coordination-ability of 1,3,4-oxadiazoles, including the oxygen and nitrogen atoms, with Cs should be reasonably good, allowing the Cs atoms to

be dispersed evenly into the organic matrix [10]. (2) The electron mobility in OXD matrix is high [9]. (3) The lowest unoccupied molecular orbital level of OXD is close to the host of our EML, tris-(8-hydroxyquinoline) aluminum (Alq3) [11]. This makes the electron drifting from ETL to EML easier. This may also lead to a decrease in the driving voltage and an increase in the current efficiency.

In our design, we adapted the conjugated bis-oxadiazole derivatives to study. In addition, we intentionally introduced the naphthyl groups on the biphenyl backbone in order to create conformational isomerism. The conformational isomerism between aromatic rings would result in plentiful conformational isomers that reduce the chance of molecular stacking, slow down the nucleation process, and retard the rate of crystalline formation. This would be beneficial for the amorphous thin film formation. Furthermore, introducing rigid side-groups onto the bis-oxadiazole would increase the chance of intermolecular entanglement and a higher T_g would be achieved. In particular, it has been reported that an oxadiazole with naphthyl substituent was found to possess high potential of electron transport [8].

The host material bis-OXD is a newly designed organic material with good thermal stability and high T_g of 147 °C. Careful study revealed that bis-OXD could form an ultra flat thin-film through thermal evaporation and deposition in high vacuum. Fig. 2 shows the atomic force microscope images of BND and bis-OXD thin films. The mean roughness of BND and bis-OXD were found to be 151.03 and 0.113 nm, respectively. As will be shown later, the high mean roughness value of BND results in high leakage current, low current efficiency, and short operation lifetime in an OLED. Although no detailed study about the BND film has been reported in the relevant literature, we tentatively attribute the high roughness of the film surface to the

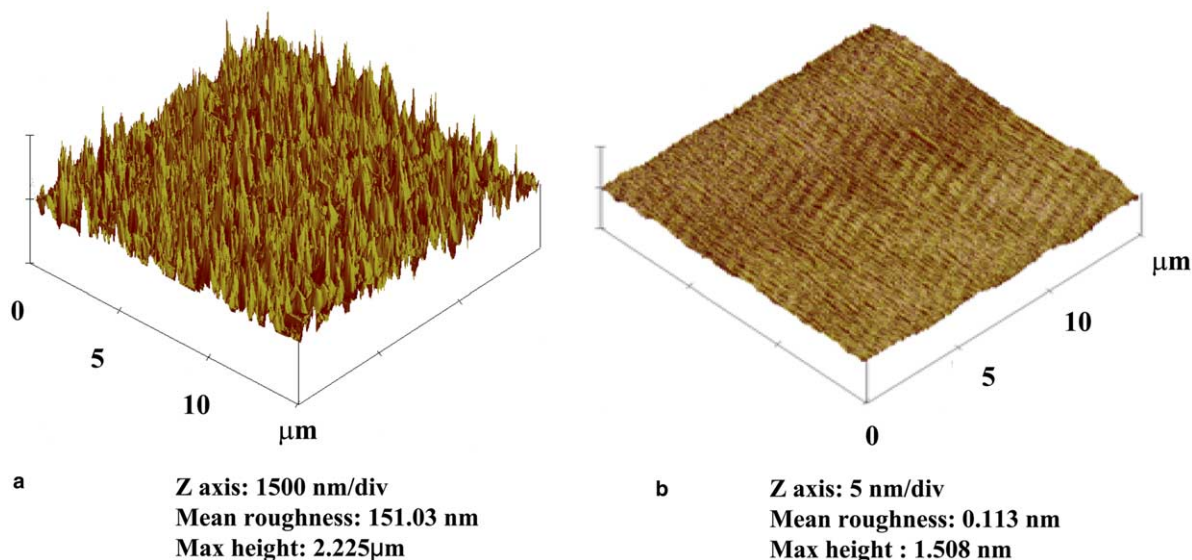| a | Z axis: 1500 nm/div
Mean roughness: 151.03 nm
Max height: 2.225μm | b | Z axis: 5 nm/div
Mean roughness: 0.113 nm
Max height : 1.508 nm |

Fig. 2. AFM images of (a) BND and (b) bis-OXD thin films.

crystallization of the compound. On the other hand, due to the formation of the flat surface, the glassy bis-OXD MD-ETL can form ohmic contact with the cathode materials, including Ag and Al, regardless of the work function. Co-evaporation of Cs and bis-OXD forms a homogeneous organic layer with low resistivity. The driving voltage of the corresponding OLED device was found to be lower in the later experiments. We will present experimental results and related discussions in Section 2 and conclude in Section 3.

2. Results and discussion

In all of the following experiments, we used ITO glass substrates with low sheet resistivity (10 Ohm/sq.) and flat surface roughness ($R_a < 1$ nm). The size of the active region in our test pixel is 0.5×0.5 cm. In our devices, we used N,N'-diphenyl-N,N'-bis(1-napthyl)-1,1'-biphenyl-4,4'-diamine (NPB) as the hole-transport layer (HTL) material, and tris-(8-hydroxyquinoline)aluminum (Alq3) as the EML. In our control device, Alq3 was used as the ETL and LiF of 1.2 nm in thickness was used as the electron injection layer between the ETL and the Al cathode. In our MD-OLEDs, we used Cs as the dopant and BCP, bis-OXD or BND as the host materials of the ETL. The metal-dopant concentration, which is optimized as shown in [12], is 10%, 20% and 50%, respectively in the molar ratio for BCP, bis-OXD and BND. The deposition rate of the organic materials of the ETL is controlled at 0.1 nm/s with different Cs rate. All the organic materials were sublimed before deposition. Since bis-OXD is a novel compound, the thermal properties of bis-OXD were examined by sublimation, thermogravimetric analysis (TGA), and differential scanning calorimetric analysis (DSC). The scanning rates of 10 °C/min were employed in the TGA and DSC analyses. Bis-OXD is stable during sublimation at 245–253 °C under the pressure of 5×10^{-6} Torr without decomposition. On the other hand, the compound shows a 5% weight lost at 438.4 °C in TGA, indicating that the compound would be decomposed at high temperature. The compound shows a glass-transition temperature (T_g) of 147 °C in DSC analysis. The high T_g of bis-OXD benefits for the OLED applications. The resistivity measured for Cs:BCP and Cs:bis-OXD thin films were 9.28×10^4 and 3.24×10^5 Ohm-cm, respectively. The thickness of the Al and Ag cathode were 100 nm. Table 1 illustrates the layer structures and the device performance. After organic and metal deposition, we encapsulated the devices in the glove box with O_2 and H_2O concentrations below 1 ppm. Prior to the lifetime test, devices were characterized with a Keithley 2400 source meter for current–voltage measurement and with a PR-705 photometer for the brightness measurement. In our lifetime test, we fixed the initial luminance at 10 000 cd/m² and supplied a constant current to our devices. The brightness and voltage were recorded with a PR-705 photometer and a Keithley 2400 source meter at different durations.

Current density versus voltage (J–V) and current efficiency versus current density (η–J) comparison among the five devices are shown in Fig. 3a,b, respectively. Device A is the conventional device with the current density and the current efficiency of 0.1 A/cm² and 3.35 cd/A at 9.72 V which is a typical value in such a device. When we change the ETL from Alq3 to Cs:BCP (device B), the driving voltage is reduced by 1.33 V and the current efficiency was increased by 4.79% at a current density of 0.1 A/cm². In an NPB/Alq3 device, holes in NPB exhibit higher mobility than electrons in Alq3 [13]. That means the electric field in ETL is higher than that in HTL. Such a carrier unbalance results in a lower recombination rate and lower current efficiency [14]. Introducing the MD technology in the device design does not only decrease the driving voltage but also improves the electron-hole balance. This explains the higher current efficiency in our MD-OLED. By replacing the Al cathode by an Ag cathode (device C), the driving voltage was further reduced by 0.53 V and the current efficiency increased by 15.4%. Since Ag has a lower optical absorption and higher electrical conductivity than Al, such a replacement could effectively improve device performance. When we changed the host material of the EML from BCP to bis-OXD with an Ag cathode, the driving voltage and the current efficiency reach 4.93 cd/A and 7.32 V, respectively at the same current density. Although the conductivity of Cs:BCP is slightly higher than that of Cs:bis-OXD, the driving voltage was lower in device D than device C. The LUMO energy levels of 1.8, 2.17 and 3.7 eV for BCP, bis-OXD and Alq3 were measured, respectively. The energy gap between BCP/Alq is higher than that of OXD/Alq3, implying that more phonons have to be released when carriers transport from BCP to Alq3 than from OXD to Alq3. This would rationalize the higher driving voltage in device C as compared to device D. Further experiments for proving this assumption are ongoing.

Table 1
Layer structures and device performance of the OLEDs

Device	HTL 55 nm	EML 27.5 nm	ETL 27.5 nm	Cathode 100 nm	Driving voltage (V)	Current efficiency (cd/A)	Half-lifetime (h)
A	NPB	Alq3	Alq3	LiF/Al	9.71	3.35	13.55
B			Cs:BCP	Al	8.39	3.52	NA
C			Cs:BCP	Ag	7.86	4.16	17.25
D			Cs:bis-OXD	Ag	7.32	4.93	42.52
E			Cs:BND	Ag	2.46	0.02	NA

Driving voltage and current efficiency were measured at the current density of 100 mA/cm².
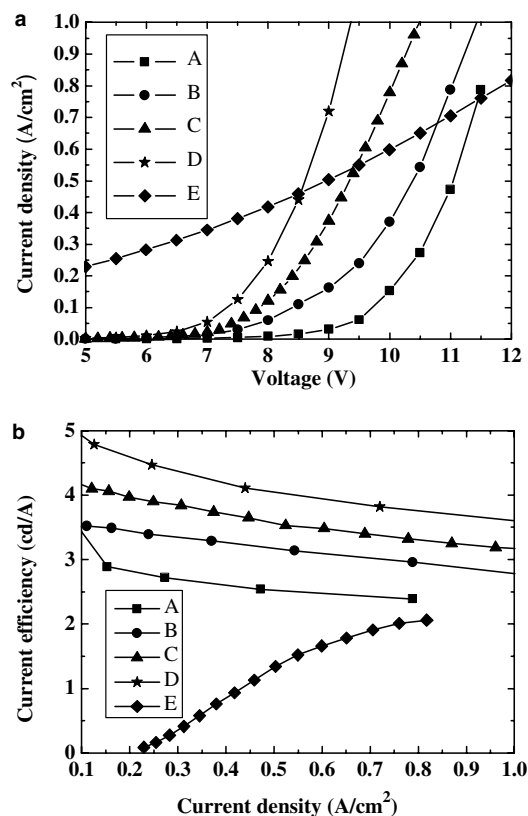
Fig. 3. Comparison of (a) current density versus voltage (b) current efficiency versus current density curves among the five devices.

The *J–V* characteristic of device E is different from other devices. An ultra low turn-on voltage was observed in this case. Extrapolating the *J–V* curve passes the origin which means such a phenomenon may result from the high leakage current of the rough BND thin film surface. The *η–J* curve shows an increasing trend with an increasing current density. However, it is always the lowest among all the samples. These results indicate that the recombination rate is higher under high injection. However, the current at low injection level does not contribute to light emission. We attribute this to a leakage current.

Fig. 4 shows the results of the accelerated operation-lifetime tests of devices A, C and D. One can see that our control device, device A, has the shortest lifetime. The extrapolated half-lifetime under the brightness of 10 000 cd/m^2 is 13.6 h. Device B exhibits a half-lifetime of 24 h, despite the lower T_g of the metal-dopant/host matrix. Two possible reasons may explain this phenomenon. The first is the higher power efficiency of the MD devices which generate less heat during operation. The second is the lower diffusion rate of Cs, which is used as the dopant in the OLED devices. This leads to less quench effect. For device D containing Cs:OXD as the MD-ETL layer, the operation lifetime is as high as 42.5 h. This is 146% and 213% longer than those for the Cs:BCP and control devices, respectively. Although the reasons behind this are unconfirmed, the high T_g characteristics of OXD may play an important role in the high efficiency and the long operation lifetime.
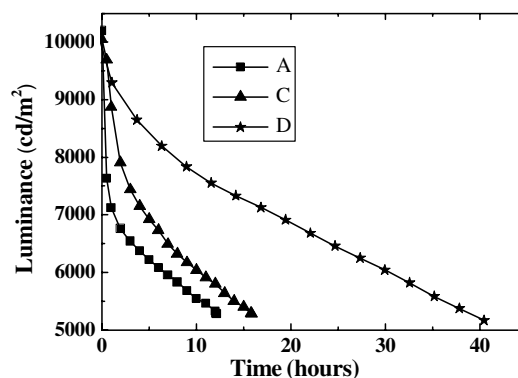

Fig. 4. Accelerated operation-lifetime measurement among devices A, C, and D.

3. Conclusions

In summary, we have shown novel high performance OLED devices based on new MD-ETL and cathode materials. These could effectively decrease the driving voltage of the device and increase the current efficiency and operation lifetime. Ag was used as the cathode electrode to lower the ohmic loss and reduce the optical absorption. We chose Cs as the dopant material in the ETL to decrease the effects of metal ion diffusion, and inhibit the quenching effects in a long-term operation. For devices with MD-ETL, not only the driving voltage was decreased, higher current efficiency was also achieved due to better charge balance. Perhaps, due to the high thermal stability and good energy alignment with EML, the lifetime of the devices based on Cs doped bis-OXD ETL increased.

References

[1] C.W. Tang, S.A. Vanslyke, Appl. Phys. Lett. 51 (1987) 913.
[2] C.W. Tang, S.A. Vanslyke, J. Appl. Phys. 65 (1989) 3610.
[3] J. Huang, M. Pfeiffer, A. Werner, J. Blochwitz, S. Liu, K. Leo, Appl. Phys. Lett. 80 (2002) 139.
[4] S.T. Lee, Z.Q. Gao, L.S. Hung, Appl. Phys. Lett. 75 (1999) 1404.
[5] J. Kido, T. Matsumoto, Appl. Phys. Lett. 73 (1998) 2866.
[6] T. Oyamada, H. Sasabe, C. Adachi, S. Murase, T. Tominaga, C. Maeda, Appl. Phys. Lett. 86 (2005) 033503.
[7] B.W. D'Andrade, S.R. Forrest, A.B. Chwang, Appl. Phys. Lett. 83 (2003) 3858.
[8] H. Tokuhisa, M. Era, T. Tsutsui, S. Saito, Appl. Phys. Lett. 66 (1995) 3433.
[9] S. Oyston, C. Wang, G. Hughes, A.S. Batsanov, I.F. Perepichka, M.R. Bryce, J.H. Ahn, C. Pearson, M.C. Petty, J. Mater. Chem. 15 (2005) 194.
[10] J.F. Wang, G.E. Jabbour, E.A. Mash, J. Anderson, Y. Zhang, P.A. Lee, N.R. Armstrong, N. Peyghambarian, B. Kippelen, Adv. Mater. 11 (1999) 1266.
[11] Y. Kawabe, J. Abe, Appl. Phys. Lett. 81 (2002) 493.
[12] J.H. Lee, M.H. Wu, C.C. Shiau, in: Taiwan Display Conferences, Taipei, Taiwan, June 10–11, 2004.
[13] W. Brütting, S. Berleb, A.G. Mückl, Org. Electron. 2 (2001) 1.
[14] Y. Qiu, Y. Gao, P. Wei, Liduo Wang, Appl. Phys. Lett. 80 (2002) 2628.