Organic Electronics 10 (2009) 1158–1162

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Improving the performance of blue phosphorescent organic light-emitting devices using a composite emitter

Miao-Tsai Chu [a,b], Meng-Ting Lee [a,*], Chin H. Chen [c], Mei-Rurng Tseng [a]

[a] Material and Chemical Research Laboratories, Industrial Technology Research Institute (ITRI), Hsinchu 310, Taiwan
[b] Master Degree Program of Flat Panel Display Technology, National Chiao Tung University, Hsinchu 300, Taiwan
[c] Display Institute, Microelectronics and Information Systems Research Center, National Chiao Tung University, Hsinchu 300, Taiwan

ARTICLE INFO

Article history:
Received 26 April 2009
Received in revised form 6 June 2009
Accepted 6 June 2009
Available online 10 June 2009

PACS:
73.50.Gr
73.61.Ph
78.60.Fi
85.60.Jb

Keywords:
OLED
Phosphorescent
Blue emitter
Carrier transport

ABSTRACT

A composite emitter is constructed by doping a carrier-transporting material into a conventional emitter composing of only host and dopant. The transport of carriers from either hole- or electron-transporting layer into the emitter can be promoted through the carrier-transporting material, in particular, when a wide-band-gap host material is used. A blue phosphorescent OLED based on iridium(III)bis((4,6-difluorophenyl)-pyridinate-N,$C^{2'}$)-picolinate (FIrpic) as dopant in the composite emitter achieved a power efficiency of 20 lm/W and a low driving voltage of 4.2 V at 1000 cd/m^2, whose current efficiency at 20 mA/cm^2 was 2.5 times better than that of device using the conventional emitter.

1. Introduction

Recently, many reports have been disclosed that the efficiency of white organic light-emitting devices (OLEDs) is already superior to that of traditional lighting sources of incandescent bulb and fluorescent lamp [1–9]. These results can mainly be attributed to the progressive development of phosphorescent materials, which utilize both singlet and triplet excitons for generating light emission. Therefore, OLEDs based on phosphorescent emitters can, theoretically, achieve internal quantum efficiency (IQE) up to 100% [10,11].

A blue emitter is indispensable component for generating white light and its device performance is critical to that of white OLEDs. To achieve efficient blue phosphorescent emission, a high triplet excited state (>2.8 eV) is essential in order to prevent the quenching of the dopant emission [12]. However, a high triplet excited state implies a large electrical band gap, i.e., a low-lying highest occupied molecular orbital (HOMO) and/or high-lying lowest occupied molecular orbital (LUMO) level, that will act as energy barriers for the transport of carriers from nearby hole (HTL) or electron-transporting layer (ETL) to emitter, which consequently decrease the probability of carrier recombination and increase the driving voltage. Several organic carbazole-based materials have been proposed to be as blue phosphorescent host [13–16]. Those devices resulted in good quantum efficiency but a relatively high driving voltage, close to 7 V at practical brightness of 1000 cd/m^2, which is due to the energy barriers created between carrier-transporting layers and the host.

Recently, it was reported that blue PHOLEDs operated at practical brightness of 1000 cd/m^2 with a rather low

* Corresponding author.
E-mail address: MTLee@itri.org.tw (M.-T. Lee).

1566-1199/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.orgel.2009.06.005

driving voltage of ~5 V can be achieved by using diphosphine oxide derivatives as host [17–19]. The low driving voltage can be rationalized by the following two reasons. One is the *intrinsic* good electron-transporting ability of diphosphine oxide derivatives, which can be helpful to the transport of electrons in the bulky organic layer. The other contribution comes from the reduction of the energy barrier between diphoshpine oxide derivatives and LiF/Al cathode since these materials have a low LUMO level of 2.9 eV. However, the diphosphine oxide derivatives have a low-lying HOMO level of 6.6 eV, which causes a large energy barrier for the transport of holes from nearby HTL into the host. Consequently, the quantum efficiency of blue PHOLEDs based on diphosphine dioxide derivatives as host was significantly below 100%.

To summarize the development of host material in the previous studies, an appropriate blue phosphorescent host material should not only have a high triplet excited state as well as bipolar transport property, but also a minimum energy barrier between the host and adjacent carrier-transporting material. Unfortunately, up to now, it is not an easy task to find a host material that will satisfy all the above-mentioned requirements. In this paper, we will introduce a composite emitter incorporating a carrier-transporting material into the emitter composed of diphosphine oxide derivatives host and organometallic iridium dopant. The problematic transport of holes from the HTL into diphosphine oxide derivatives host can be alleviated through the adoption of carrier-transporting material, thus the probability of carrier recombination can be increased and the driving voltage can be decreased. Consequently, a blue PHOLED with a power efficiency of 20 lm/W and low driving voltage of 4.2 V at practical brightness of 1000 cd/m^2 is achieved.

2. Experimental

The composite emitter comprises a wide-band-gap host, 2,8-bis(diphenylphosphoryl)dibenzothiophen (PPT) [18], which has a triplet excited state of 3.0 eV, a blue phosphorescent dopant, iridium(III)bis((4,6-difluorophenyl)-pyridinate-N,C$^{2'}$)picolinate (FIrpic), which possessed a triplet excited state of 2.62 eV [2], and a carrier-transporting material, 4,4′,4″-tri(*N*-carbazolyl)triphenylamine (TCTA), which possessed a triplet excited state of 2.76 eV [2] as well as a good hole-transporting ability (1.6×10^{-4} cm^2/Vs at 10^5 V/cm) [The data was measured by time-of-flight method, the detailed results will be reported in elsewhere]. In addition, a electron-blocking layer (EBL), bis[4-(*p*,*p*′-ditolylamino)phenyl]diphenylsilane (DTASi) [20], with high triplet excited state of 2.95 eV and a high-lying LUMO level of 2.2 eV was used to confine all generated exciton in emitter. A high electron mobility material (10^{-4} cm^2/Vs at 10^5 V/cm), 4,7-diphenyl-1,10-phenanthroline (Bphen) [21], and 20% (vol%) cesium carbonation (Cs_2CO_3) doped with Bphen [22] were used as ETL and *n*-ETL, respectively, to achieve low driving voltage. The device architecture used is ITO (150 nm)/NPB (45 nm)/DTASi (15 nm)/composite emitter (15 nm)/Bphen (25 nm)/*n*-ETL (20 nm)/Al (100 nm), where 4,4′-*bis*[*N*-(1-naphthyl)-*N*-phenyl-amino]biphenyl (NPB) is HTL. In order to investigate the effect of doping carrier-transporting material in FIrpic/PPT emitter, the doping concentration of blue dopant was fixed at 15% and the doping concentration of 0%, 10%, and 20% for the carrier-transporting material were tested.

Fig. 1 shows the detailed molecular structures of materials and architecture of device used in this study. All the materials were deposited by thermal evaporation in an UL-

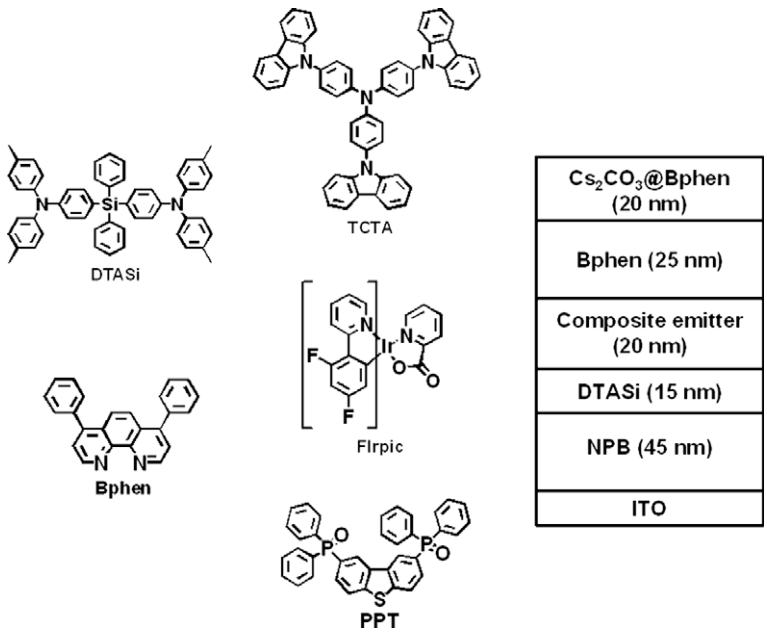

Fig. 1. Molecular structures and device architecture used in the experiment.

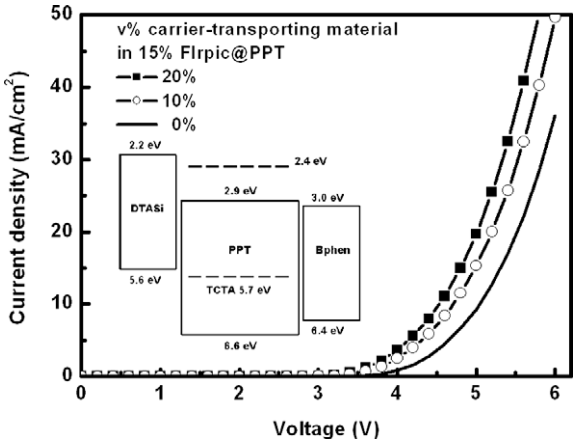

Fig. 2. Current density–voltage (*J–V*) characteristics of blue PHOLEDs as well as the device energy diagram (inset).

VAC Solciet OLED coater at a base vacuum of 10^{-7} Torr. The device performance of luminance yield and EL spectra, $CIE_{x,y}$ color coordinates were measured by a Minolta luminance meter and a Photo Research PR-650 spectrophotometer driven by a programmable dc source, respectively.

3. Results and discussion

Fig. 2 shows the dependence of current density–voltage (*J–V*) characteristics of the blue PHOLEDs on the doping concentration of carrier-transporting material in emitter. Lower driving voltage was observed in the device with doping carrier-transporting material in emitter as compared with that of undoped device. For instance, the driving voltage at current density of 20 mA/cm^2 is 5.0 V for doping 20% carrier-transporting material in the emitter and 5.6 V for the undoped device. The decreased driving voltage can be attributed to the transport of holes from EBL (DTASi) into host (PPT) which was promoted through doping carrier-transporting material (TCTA) in emitter, since TCTA possesses a good hole-transporting ability and a HOMO level (5.7 eV) lying between that of DTASi (5.6 eV) and PPT (6.6 eV). The device energy diagram is shown in the inset of Fig. 2.

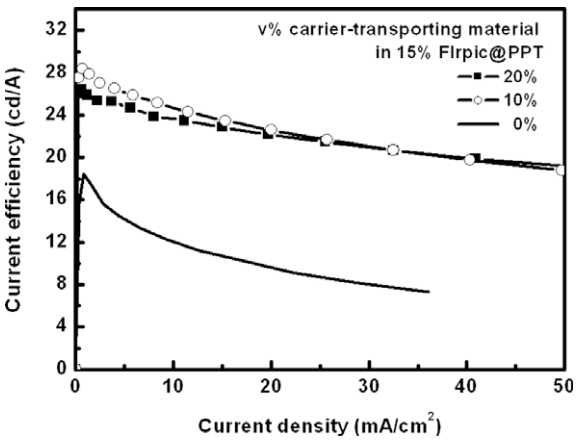

Fig. 3. Current efficiency–current density (*cd/A–J*) characteristics of blue PHOLEDs.

Fig. 3 shows the dependence of current efficiency–current density (*cd/A–J*) characteristics of the blue PHOLEDs on the doping concentration of carrier-transporting material in the emitter. When doping 10% carrier-transporting material in the emitter, the device exhibited a current efficiency of 26.8 cd/A with low driving voltage of 4.2 V ($J \sim 4$ mA/cm^2), which is 2 times higher than that of the undoped device with 12.3 cd/A and 5.0 V ($J \sim 8.2$ mA/cm^2) at a practical brightness of 1000 cd/m^2. The current efficiency sustains as high as 25 cd/A when the doping concentration of carrier-transporting material is increased to 20% in the emitter. We believe the dramatic enhancement in current efficiency when doping carrier-transporting material in the emitter is resulted from the "hole-facilitating" character of carrier-transporting material, which can increase the concentration of holes in the emitter as opposed to that of undoped device. Therefore, the probability of carrier recombination can be increased.

In addition, at current density of 20 mA/cm^2, the device with 10% carrier-transporting material doped in emitter exhibited a current efficiency of 22.6 cd/A, which is 2.5 times higher than that of undoped device with only 9.2 cd/A. This result demonstrates that the problematic efficiency roll-off in blue PHOLEDs can also be suppressed by doping carrier-transporting material in the emitter. For instance, the efficiency roll-off from low (1 mA/cm^2) to high current density (40 mA/cm^2) is 29% and 23% for 10% and 20% carrier-transporting material in the emitter, respectively, while it is nearly 60% for the undoped device. The suppression of efficiency roll-off in blue PHOLEDs when doping carrier-transporting material in the emitter can be attributed to the "hole-facilitating" character of carrier-transporting material, which can reduce the accumulated holes at the EBL (DTASi) and FIrpic/PPT emitter interface to inhibit triplet-polaron quenching. Triplet-polaron quenching has been reported to be one of the major reasons for efficiency roll-off in PHOLEDs [23]. The detailed device performances of these blue PHOLEDs are summarized in Tables 1 and 2.

In order to prove that the transport of holes from EBL (DTASi) into FIrpic/PPT emitter was promoted by doping carrier-transporting material, two additional device architectures were fabricated; one has a pure PPT layer inserted in-between the EBL and emitter while the other has a TCTA:PPT (10:90) composite layer. The detailed device architectures and energy diagram are depicted in Fig. 4. When inserted a pure PPT layer in-between the EBL and FIrpic/PPT emitter, the device exhibited a very low current efficiency (<1 cd/A) and its EL spectrum displayed three dominant peak emissions at 420, 472, and 580 nm as shown in Fig. 5, which were originated from NPB, FIrpic, and the exciplex emission of DTASi/PPT, respectively. This phenomenon can be rationalized by the following mechanism. Firstly, according to the energy diagram, the holes and electrons were accumulated at the EBL/pure PPT interface. Secondly, a portion of the carriers recombined and the others formed the DTASi/PPT exciplex. Thirdly, the excitons diffused to either anode or cathode side across the

Table 1
Device performances of blue PHOLEDs.

Emitter			Voltage (V)	Current efficiency (cd/A)	Power efficiency (lm/W)	EQE (%)	$CIE_{x,y}$	Efficiency roll-off (%)
Host	*v* (%) TCTA	*v* (%) FIrpic	At 1000 cd/m^2, (at 20 mA/cm^2)					From 1 to 40 mA/cm^2
PPT	0	15	5.0 (5.6)	12.3 (9.2)	7.7	5.5	0.18, 0.38	60
	10		4.2 (5.2)	26.8 (22.6)	20	12.1	0.17, 0.36	29
	20		4.2 (5.0)	25 (22.2)	18.7	11.4	0.17, 0.36	23

Table 2
Summary of the characteristics of devices using FIrpic as the blue phosphorescent dopant.

Emitter (Dopant: FIrpic)		Voltage (V)	Current efficiency (cd/A)	Power efficiency (lm/W)	EQE (%)	Reference
Host	Carrier-transporting material	At 1000 cd/m^2				
PPT	TCTA	4.2	26.8	20	12.1	This work
TCZ1	–	6.8	23	10.5	10.2	[13]
CzSi	–	5.0[a]	24[a]	16[a]	12[a]	[14]
SimCP	–	–	–	11.9[b]	14.4[b]	[15]
mCP	–	–	–	8.9[b]	7.5[b]	[16]
MPO12	–	4.8[c]	–	–	9.1[c]	[17]
PO15	–	5.2[c]	–	–	9.8[c]	[18]
DBF	–	5.4[c]	21.2[c]	12.5[c]	8.0[c]	[19]

[a] Reported at 100 cd/m^2.
[b] Reported at maximal value.
[c] Reported at 800 cd/m^2.

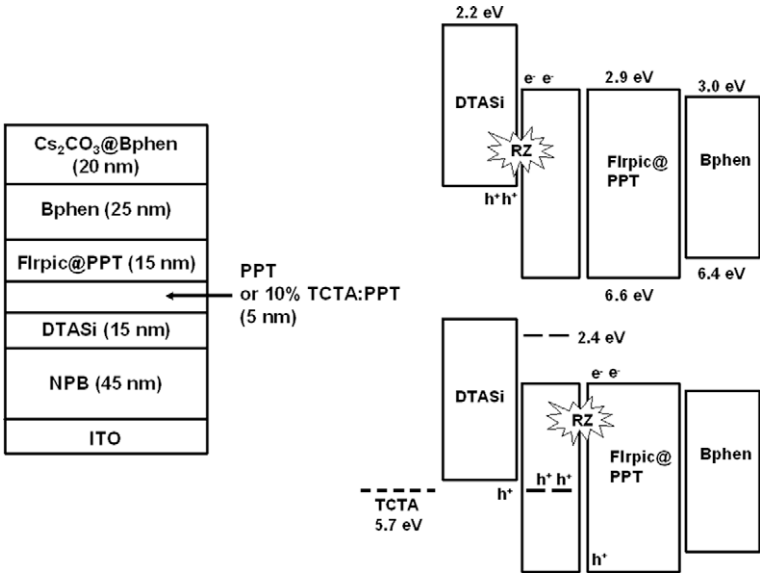

Fig. 4. Device architectures and energy diagram with a pure PPT or TCTA:PPT layer inserted in-between EBL and FIrpic/PPT emitter.

interfacial barriers of DTASi and PPT both of which have high excited state. Finally, the low excited energy of NPB and FIrpic captured the excitons to give the light emission.

On the contrary, when inserted a TCTA:PPT (10:90) composite layer in-between the EBL and FIrpic/PPT emitter, the device with a current efficiency of 11.5 cd/A at a brightness of 1000 cd/m^2 was closed to that of device with whole FIrpic/PPT emitter shown in Fig. 3. And also, the EL spectrum displayed only one dominant peak emission at 472 nm without detecting the emission from the exciplex of DTASi/PPT. This phenomenon further supports the speculation that the transport of holes from the EBL into PPT is promoted by doping carrier-transporting material. Therefore, the holes and electrons can no longer accumulate at EBL/PPT interface and the recombination zone is shifted toward the FIrpic/PPT emitter.

4. Summary

For solid-state lighting application, the low efficiency and the problematic efficiency roll-off are critical issues to be overcome in blue PHOLEDs. Here, we have proposed

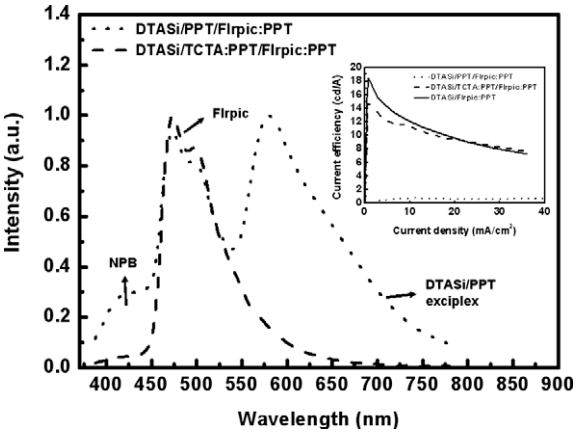

Fig. 5. EL spectra of device with a pure PPT or TCTA:PPT layer inserted in-between EBL and FIrpic/PPT emitter as well as current efficiency–current density (*cd/A–J*) characteristics (inset).

a composite emitter concept and shown that doping a carrier-transporting material in the conventional blue phosphorescent emitter composed of wide-band-gap host and dopant can efficiently facilitate the transport of carriers into the emitter, as well as increase the carrier recombination and reduce carrier accumulation at interface. We showed that this composite blue phosphorescent emitter not only can decrease the driving voltage of device, but also increase the current efficiency as well as suppress the efficiency roll-off problem often encountered at high current density.

Acknowledgment

This work was supported by National Science and Technology Development Fund (Grant No. 8354DL1000) of the National Science Council of Taiwan.

References

[1] B.W. D'Andrade, J. Esler, C. Lin, V. Adamovich, S. Xia, M.S. Weaver, R. Kwong, J.J. Brown, in: Proceedings of the International Display Workshops, Nigata, 2008, p. 143.
[2] S.J. Su, E. Gonmori, H. Sasabe, J. Kido, Adv. Mater. 20 (2008) 4194.
[3] M.T. Lee, J.S. Lin, M.T. Chu, M.R. Tseng, Appl. Phys. Lett. 93 (2008) 13306.
[4] S.H. Eom, Y. Zheng, E. Wrzesniewski, J. Lee, N. Chopra, F. So, J. Xue, Appl. Phys. Lett. 94 (2009) 153303.
[5] T. Nakayama, K. Hiyama, K. Furukawa, H. Ohtani, in: Proceedings of Society for Information Display, Long Beach, CA, 2007, p. 1018.
[6] Y. Sun, S.R. Forrest, Appl. Phys. Lett. 91 (2007) 263503.
[7] G. Schwartz, M. Pfeiffer, S. Reineke, K. Walzer, K. Leo, Adv. Mater. 19 (2007) 3672.
[8] Y. Sun, N.C. Giebink, H. Kanno, B. Ma, M.E. Thompson, S.R. Forrest, Nature 440 (2006) 908.
[9] B.W. D'Andrade, R.J. Holmes, S.R. Forrest, Adv. Mater. 16 (2004) 624.
[10] M.A. Baldo, D.F. O'Brien, Y. You, A. Shoustikov, M.E. Thompson, S.R. Forrest, Nature 395 (1998) 151.
[11] C. Adachi, M.A. Baldo, M.E. Thompson, S.R. Forrest, J. Appl. Phys. 90 (2001) 5048.
[12] S. Tokito, T. Iijima, Y. Suzuri, H. Kita, T. Tsuzuki, F. Sato, Appl. Phys. Lett. 83 (2003) 569.
[13] M.H. Tsai, Y.H. Hong, C.H. Chang, H.C. Su, C.C. Wu, A. Matoliukstyte, J. Simokaitiene, S. Grigalevicius, J.V. Grazulevicius, C.P. Hsu, Adv. Mater. 19 (2007) 862.
[14] M.H. Tsai, H.W. Lin, H.C. Su, T.H. Ke, C.C. Wu, F.C. Fang, Y.L. Liao, K.T. Wong, C.I. Wu, Adv. Mater. 18 (2006) 1216.
[15] S.J. Yeh, W.C. Wu, C.T. Chen, Y.H. Hong, Y. Chi, M.H. Ho, S.F. Hsu, C.H. Chen, Adv. Mater. 17 (2005) 285.
[16] R.J. Homes, S.R. Forrest, Y.J. Tung, R.C. Kwong, J.J. Brown, S. Garon, M.E. Thompson, Appl. Phys. Lett. 82 (2003) 2422.
[17] X. Cai, A.B. Padmaperuma, L.S. Sapochak, P.A. Vecchi, P.E. Burrows, Appl. Phys. Lett. 92 (2008) 083308.
[18] L.S. Sapochak, A.B. Padmaperuma, P.A. Vecchi, X. Cai, P.E. Burrows, Proc. SPIE 6655 (2007) 665506-1.
[19] P.A. Vecchi, A.B. Padmaperuma, H. Qiao, L.S. Sapochak, P.E. Burrows, Org. Lett. 8 (2006) 4211.
[20] N. Ide, T. Komoda, J. Kido, Proc. SPIE 6333 (2006) 63330M-1.
[21] S. Naka, H. Okada, H. Onnagawa, T. Tsutsui, Appl. Phys. Lett. 76 (2000) 197.
[22] T. Hasegawa, S. Miura, T. Moriyama, T. Kimura, I. Takaya, Y. Osata, H. Mizutai, in: Proceedings of the Society for Information Display, Seattle, WA, 2004, p.154.
[23] M.A. Baldo, C. Adachi, S.R. Forrest, Phys. Rev. B 62 (2000) 10967.