Enhanced electroluminescence and reduced efficiency roll-off in electrophosphorescent devices using a very high electron mobility material as emitter host and electron transporter

2009 J. Phys. D: Appl. Phys. 42 065103

(http://iopscience.iop.org/0022-3727/42/6/065103)

J. Phys. D: Appl. Phys. **42** (2009) 065103 (4pp) doi:10.1088/0022-3727/42/6/065103

Enhanced electroluminescence and reduced efficiency roll-off in electrophosphorescent devices using a very high electron mobility material as emitter host and electron transporter

T L Li[1,2], W L Li[1,4], B Chu[1,4], Z S Su[1,2], Y R Chen[1], L L Han[1,2], D Y Zhang[1,2], X Li[1,2], F X Zang[3,4], T C Sum[3] and A C H Huan[3]

[1] Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, People's Republic of China
[2] Graduate School of Chinese Academy of Sciences, Beijing 100039, People's Republic of China
[3] Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, 1 Nanyang Walk, Block 5, Level 3, Singapore 637616, Singapore

E-mail: wllioel@yahoo.com.cn (W L Li), beichu@163.com (B Chu) and fxzang@ntu.edu.sg (F X Zang)

Received 29 September 2008, in final form 1 February 2009
Published 26 February 2009
Online at stacks.iop.org/JPhysD/42/065103

Abstract
We demonstrate markedly improved electroluminescence (EL) intensity and reduced external quantum efficiency (EQE) roll-off of a device which presents two emitting layers of *fac*-tris-(2-phenylpyridine) iridium [Ir(ppy)$_3$] in 4,4′-bis(9-carbazolyl)-2,2′-biphenyl (CBP) and 1,3-bis[2-(2,2′-bipyridine-6-yl)-1,3,4-oxadiazo-5-yl]benzene (Bpy-OXD); 4,7-diphenyl-1,10-phenanthroline/Bpy-OXD layers were used as hole blocking and electron transport layers. The device exhibits a maximum EQE of 15.5% (corresponding to an efficiency of 56.8 cd A^{-1}) at a luminance of 600 cd m^{-2}, which is twice the value (8.2%) of the reference diode using Ir(ppy)$_3$ doped CBP as a single emitting layer; the device still maintained a 6.5% efficiency at a luminance of 70 450 cd m^{-2}. The mechanism of this marked improvement in EL intensity and decrease in the EQE roll-off was also explored in detail.

1. Introduction

Phosphorescent organic light emitting devices (PHOLEDs) using phosphor dye have received considerable attention due to their 100% internal quantum efficiency by harvesting both singlet and triplet excitons [1–3]. A fast reduction in efficiency known as roll-off, however, occurs when the drive current increases. This leads to a much lower luminance and more power consumption that cannot satisfy the need for applications in displays, solid-state lighting, and so on. The efficiency roll-off has been attributed to the long lifetime exciton based triplet–triplet (T–T) and triplet–polaron (T–P) [4, 5] annihilation as well as electric field induced exciton dissociation [6]. Many methods, such as double emitting layers [7, 8] and exciton diffusion layer structures [9], have been used to improve the external quantum efficiency (EQE) and reduce the efficiency roll-off. Recently, Zang *et al* [10] demonstrated slow efficiency roll-off PHOLEDs at a very high drive current with 1,3-bis[2-(2,2′-bipyridine-6-yl)-1,3,4-oxadiazo-5-yl]benzene (Bpy-OXD) and *fac*-tris-(2-phenylpyridine) iridium [Ir(ppy)$_3$] doped 4,4′-bis(9-carbazolyl)-2,2′-biphenyl (CBP) as the electron transporting (ET) and emitting layers. It was explained that the suppression of the T–P quenching rate in the active layer could be the main reason for the reduction in the efficiency roll-off. The EQE and luminance under a drive current density lower than 10 mA cm^{-2}, however, were much

[4] Author to whom any correspondence should be addressed.

lower than those of the traditional device based on $Ir(ppy)_3$ doped CBP with 2,9-dimethyl-4,7-diphenyl-phenanthroline (BCP)/ tris-(8-hydroxyquinoline) aluminium (Alq_3) as HB/ET.

In this paper, we have continued our work based on the findings reported in [10]. This time we focus on the efficiency improvement in the PHOLED at a lower current density as well as a slow efficiency roll-off. We fabricated a new device with *fac*-tris-(2-phenylpyridine) iridium [$Ir(ppy)_3$] doped Bpy-OXD and CBP as two emitting layers (called Ir-Bpy-OXD and Ir-CBP emitter, respectively, hereafter). 4, 7-diphenyl-1, 10-phenanthroline (Bphen)/Bpy-OXD were used as hole blocking (HB)/ET layers. An increase in the charge injection and an expansion of the recombination zone by the introduction of highly ET Bpy-OXD can be expected; more triplet excitons are confined within the two active layers to luminesce with the double emitting structure. As a result, the improved device exhibited a maximum EQE of 15.5% (56.8 cd A^{-1}) at a current density of 1 mA cm^{-2} (600 cd m^{-2}) and the efficiency was still maintained at 6.5% (20.6 cd A^{-1}) at a very high current density of 335 mA cm^{-2} (70 450 cd m^{-2}).

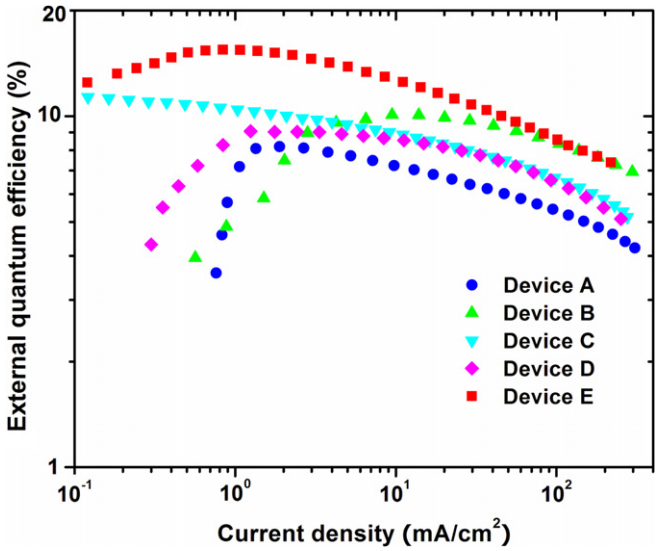

Figure 1. EQE–current density characteristics of PHOLEDs. (This figure is in colour only in the electronic version)

2. Experimental

All materials were commercially purchased (Lumtec, Taiwan) and used without further purification. The PHOLEDs were prepared by thermal evaporation of organic layers on precleaned indium tin oxide (ITO) coated glass substrates in vacuum lower than 3×10^{-4} Pa without vacuum breaking during the deposition of films. ITO substrates with 20 Ω/Sq were cleaned with detergent and organic solvent. They were subsequently treated by O_2 plasma for 30 s at 900 W before being loaded into a vacuum chamber for device fabrication. The brightness–current density–voltage (B–I–V) characteristics of the PHOLEDs were simultaneously measured with a Keithley 2400 source meter and a calibrated TOPCON® luminance colorimeter BM-7 in air without encapsulation. All the made-up devices present an active area of 2×2 mm^2. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies used were obtained from [7, 8, 11, 12, 14], respectively.

Five devices were fabricated with configurations as follows.

Device A. ITO/2-TNATA (10 nm)/NPB (30 nm)/CBP: 6 wt% $Ir(ppy)_3$ (30 nm)/BCP (10 nm)/Alq_3 (30 nm)/ LiF/Al; this device will be considered as the reference device, hereafter.

Device B. ITO/2-TNATA (10 nm)/NPB (30 nm)/TCTA (10 nm)/CBP : 6 wt% $Ir(ppy)_3$ (30 nm)/BCP (10 nm)/Bpy-OXD (30 nm)/LiF/Al; this is the device reported in [10].

Device C. ITO/2-TNATA (10 nm)/NPB (30 nm)/TCTA (10 nm)/CBP : 6 wt% $Ir(ppy)_3$ (30 nm)/Bphen (10 nm)/ Bpy-OXD (30 nm)/LiF/Al.

Device D. ITO/2-TNATA (10 nm)/NPB (30 nm)/TCTA (10 nm)/Bpy-OXD : 6 wt% $Ir(ppy)_3$ (30 nm)/Bphen (10 nm)/Bpy-OXD (30 nm)/LiF/Al.

Device E. ITO/2-TNATA (10 nm)/NPB (30 nm)/ TCTA : 10 nm)/CBP : 6 wt% $Ir(ppy)_3$ (20 nm)/Bpy-OXD: 6 wt% $Ir(ppy)_3$ (10 nm)/Bphen (10 nm)/Bpy-OXD (30 nm)/ LiF/Al.

Here, 2-TNATA is 4, 4′, 4″-tris (*N*-(2-naphthyl)-*N*-phenyl-amino)triphenylamine working as the hole injection material. NPB is *N*, *N*′-bis (1-naphthyl)-*N*, *N*′-diphenyl-1, 1′-biphenyl-4, 4′-diamine functioning as the hole transporting material. TCTA is 4, 4′, 4″-tris (*N*-carbazolyl)-triphenylamine which functions as the electron blocking material for its low electron mobility [8] and also its high triplet energy level is beneficial for confining the triplet excitons within the active layer. BCP is 2, 9-dimethyl-4, 7-diphenyl-phenanthroline and Bphen is 4, 7-diphenyl-1, 10-phenanthroline; they both work as hole or exciton blocking materials.

3. Results and discussions

Figure 1 shows the EQE–current density characteristics of the PHOLEDs and table 1 summarizes their electroluminescence (EL) performances. From them, we can observe that Devices B, C, D and E have better performances than the reference one. Device E exhibits a maximum efficiency of 56.8 cd A^{-1} at a current density of 1 mA cm^{-2}, which is 2.6 and 4 times more than that (21.9 cd A^{-1}) of the reference device and (14.2 cd A^{-1}) of Device B, as well as a slower EQE roll-off than other devices. The efficiencies are still maintained at 24.5 and 22.5 cd A^{-1} for current densities of 200 and 300 mA cm^{-2}. Device C using Bphen as the HB layer shows better EL performance at a lower current density compared with Device B using BCP indicating that it has a higher electron transport ability at a lower current density. We know that the high electron mobility of Bpy-OXD is caused by its strong electronic interactions between adjacent molecules and its co-planar molecular structure [13] with a large π-electron system without any sterically hindered constituents. By comparing the molecule structure of BCP and Bphen (see figure 2), we can find that the difference is that BCP has two sterically hindered methyl moieties, which explains the difference in the electron mobility of Bphen [14] (5×10^{-4} cm^2 V^{-1} s^{-1}) and BCP [15] (6×10^{-7} cm^2 V^{-1} s^{-1}) for three orders of magnitude.

Table 1. Performance of the PHOLEDs.

	Device A	Device B	Device C	Device D	Device E
Maximum efficiency (cd A^{-1})	27.51	35.42	43.18	31.13	56.75
Maximum EQE (photo/electron)	8.18%	10.16%	12.10%	9.09%	15.49%
Efficiency (cd A^{-1}) at 1 mA cm^{-2}	21.93	14.16	36.86	28.42	56.75
EL intensity (cd m^{-2})	205	135	337	228	537
Efficiency (cd A^{-1}) at 20 mA cm^{-2}	21.67	34.46	28.22	27.52	40.60
EL intensity (cd m^{-2})	4249	6941	5503	5400	8365
Efficiency (cd A^{-1}) at 100 mA cm^{-2}	16.51	28.24	21.53	21.08	29.82
EL intensity (cd m^{-2})	15 665	29 378	21 007	21 511	27 396
Efficiency (cd A^{-1}) at 200 mA cm^{-2}	13.65	24.62	18.02	16.77	24.52
EL intensity (cd m^{-2})	27 652	50 642	35 475	32 935	47 292
Efficiency (cd A^{-1}) at 300 mA cm^{-2}	11.64	22.56	14.32	14.20	22.46
EL intensity (cd m^{-2})	35 761	66 898	42 625	40 397	64 480
Maximum current density (mA cm^{-2})	320.29	331.98	322.23	320.33	343.57
Efficiency (cd A^{-1})	11.33	21.94	13.79	13.47	20.60
EL intensity (cd m^{-2})	36 299	72 864	45 625	43 170	70 794

Hence, when Bpy-OXD was deposited onto the BCP or the Bphen layer, electrons injected from the cathode, through the Bpy-OXD layer, are more easily transported through Bphen than through the BCP layer to recombine with holes in the active layer, due to the smaller electron mobility difference between Bpy-OXD and Bphen than that between Bpy-OXD and BCP.

Device D using Ir-Bpy-OXD as the emitter shows better EL performances than Device A although their efficiencies are almost the same at a lower current density, which indicates that Bpy-OXD is a suitable host for the $Ir(ppy)_3$ dopant. In Ir-CBP and Ir-Bpy-OXD emitter based Devices A and D, holes and electrons are the respective dominating charge carriers, which result in unbalanced carrier recombination in those two devices, both devices offering low efficiency at a low current density. However, when Ir-CBP and Ir-Bpy-OXD were used together as emitters, Device E showed top efficiency at a low current density caused by balanced charge carriers in the active layers due to the matched hole mobility [16] of CBP and the electron mobility [13] of Bpy-OXD at the same magnitude of 10^{-3} cm^2 V^{-1} s^{-1}. From the above comparison, the increase in the EL intensity at a lower current and slow efficiency roll-off would be mainly attributed to the use of double emitters and Bphen/Bpy-OXD as HB and ET.

The performance improvement in Device E might be understood in detail as below. Figure 2 shows the schematic energy level diagrams of the devices. We note that there is a hole barrier at the interface between CBP (6.0 eV) and Bpy-OXD (6.6 eV) and no abrupt barriers for electron transport towards the Ir-CBP layer, some holes would accumulate at the interface, which results in more excitons being generated in the Ir-CBP layer at a lower current density. However, at a higher current density, electrons enter the Ir-Bpy-OXD layer via an ET host, slow down by an ambipolar host with lower electron mobility and are likely to recombine before reaching the high barrier to TCTA. Concerning the holes, they can be injected into the Bpy-OXD layer or captured directly by the dopant; the holes gradually slow down and are likely to recombine before reaching the high barrier to the BPhen blocker. So exciton-recombination in the Ir-CBP and Ir-Bpy-OXD layers has self-charge-balancing character [16]. The excitons of the host formed on both sides around the Ir-CBP/Ir-Bpy-OXD interface diffuse, transferring their energy for exciting the dopant; both emitters contribute to the luminance and efficiency and more triplet excitons are confined in the two active layers. This can be supported by the efficiency difference between Device E and Device C or D; that is, the efficiency of Device E is almost the sum of that of Devices C and D at any current density. We can note the differences in the structures of Devices C, D and E; that is, Device E could be considered as the combination of Devices C and D: they have the same Bphen/Bpy-OXD as the HBL/ETL, and the active layer of Device E is actually the addition of that of Devices C and D. In the single emitting layer device, Device C or D cannot offer such a high EQE as observed in Device E. It is believed that more triplet excitons are confined within the active layers of the double emitting layers to improve the EL intensity and efficiency.

4. Summary

In conclusion, high EL intensity and slow EQE roll-off of the double emitting layer device with Bphen/Bpy-OXD as HB/ET were demonstrated with efficiencies of 56.8 cd A^{-1} (600 cd m^{-2}) and 40.6 cd A^{-1} (8365 cd m^{-2}) at 1 mA cm^{-2} and at 20 mA cm^{-2}, respectively. It is still maintained at 20.6 cd A^{-1} with a maximum EL intensity of 70 794 cd m^{-2} at 335 mA cm^{-2}, which is almost 2-fold the reference one. The peak EQE of 15.5% of the double emitting device is almost 2 and 1.5 times that of the reference and the single emitting layer devices, respectively. The use of the oxadiazole derivate with a high electron mobility as the host and the ETL may provide a guide for selecting materials for designing PHOLED devices.

Acknowledgments

This work is supported by the National Natural Science Foundation of China under Grant No 10604054 and in part by a grant (042 101 0014) from the Science and Engineering

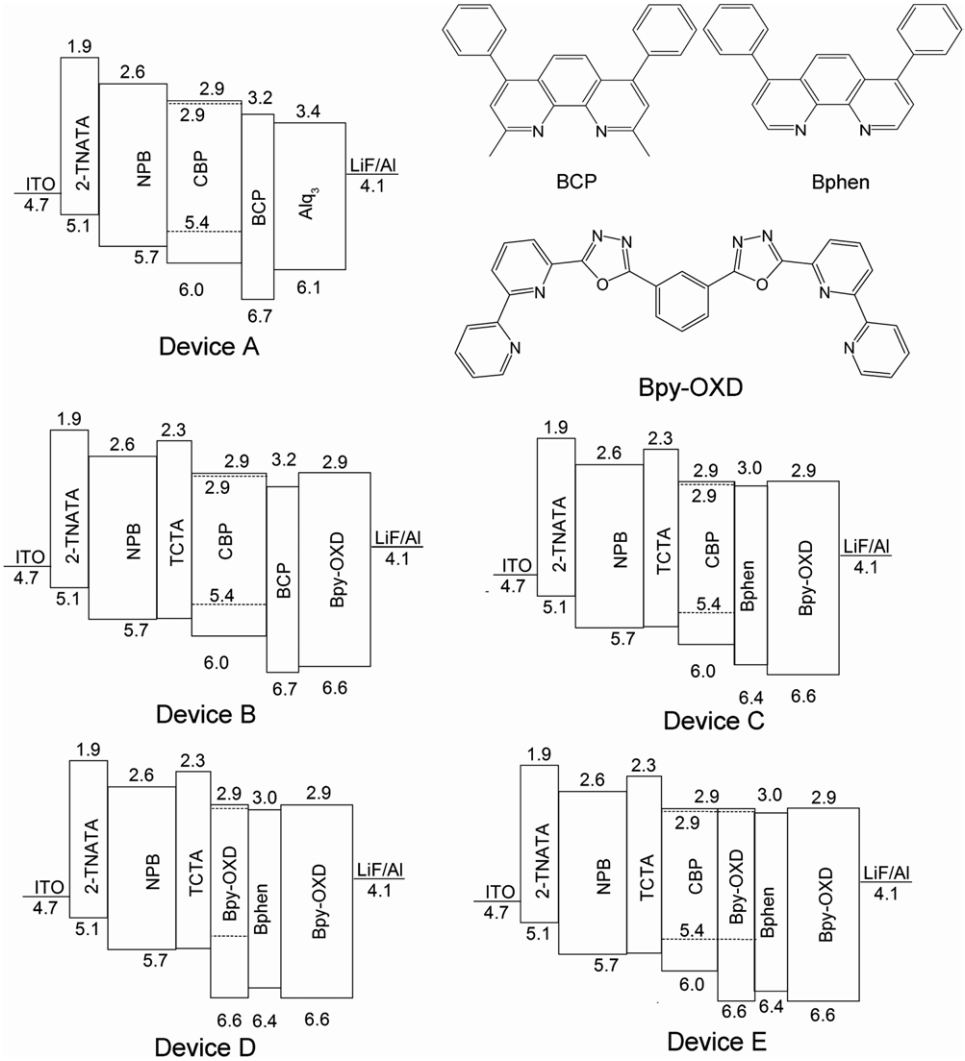

Figure 2. Schematic energy level (eV) diagrams of devices and chemical structures of some materials used.

Research Council (SERC), Agency for Science, Technology and Research (A*STAR), Singapore.

References

[1] Baldo M A, O'Brien D F, You Y, Shoustikov A, Sibley S, Thompson M E and Forrest S R 1998 *Nature (London)* **395** 151

[2] Baldo M A, Lamansky S, Burrows P E, Thompson M E and Forrest S R 1999 *Appl. Phys. Lett.* **75** 4

[3] Adachi C, Baldo M A, Thompson M E and Forrest S R 2001 *Appl J. Phys.* **90** 5048

[4] Bado M A, Adachi C and Forrest S R 2000 *Phys. Rev.* B **62** 10967

[5] Reineke S, Walzer K and Leo K 2007 *Phys. Rev.* B **75** 125328

[6] Kalinowski J, Stampor W, Mezyk J, Cocchi M, Virgili D, Fattori V and Di Marco P 2002 *Phys. Rev.* B **66** 235321

[7] Zhou X *et al* 2002 *Appl. Phys. Lett.* **81** 4070

[8] Kang J-W, Lee S-H, Park H-D, Jeong W-I, Yoo K-M, Park Y-S and Kim J-J 2007 *Appl. Phys. Lett.* **90** 223508

[9] Zhang D Y *et al* 2007 *Appl. Phys. Lett.* **91** 183516

[10] Zang F X, Sum T C, Huan A C H, Li T L and Li W L 2008 *Appl. Phys. Lett.* **93** 023309

[11] Matsushima H, Naka S, Okada H and Onnagawa H 2005 *Curr. Appl. Phys.* **5** 305

[12] Ichikawa M, Kawaguchi T, Kobayashi K, Miki T, Furukawa K, Koyama T and Taniguchi Y 2006 *J. Mater. Chem.* **16** 221

[13] Ichikawa M, Hiramatsu N, Yokoyama N, Miki T, Narita S, Koyama T and Taniguchi Y 2007 *Phys. Status Solidi (RRL)* **1** R37

[14] Naka S, Okada H, Onnagawa H and Tsutsui T 2000 *Appl. Phys. Lett.* **76** 197

[15] Itomo K, Ogawa H and Shirota Y 1998 *Appl. Phys. Lett.* **72** 636

[16] He G F, Pfeiffer M, Leo K, Hofmann M, Birnstock J, Pudzich R and Salbeck J 2004 *Appl. Phys. Lett.* **85** 3911