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

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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
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
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$^{-2}$).

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.

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

Here, 2-TNATA is 4, 4', 4''-tris (N-(2-naphthyl)-N-phenyl-
triphenylnalmine 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)-triphenylnalmine which
functions as the electron blocking material for its low electron
mobility [8] and also its high triplet energy level is benefi-
cial 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.
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. 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 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 almost the sum of that of Devices C and D at any current density. 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/ETL 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 the same at a lower 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 lumiance 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 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.

### Table 1. Performance of the PHOLEDs.

<table>
<thead>
<tr>
<th></th>
<th>Device A</th>
<th>Device B</th>
<th>Device C</th>
<th>Device D</th>
<th>Device E</th>
</tr>
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<tbody>
<tr>
<td>Maximum efficiency (cd A$^{-1}$)</td>
<td>27.51</td>
<td>35.42</td>
<td>43.18</td>
<td>31.13</td>
<td>56.75</td>
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<tr>
<td>Maximum EQE (photo/electron)</td>
<td>8.18%</td>
<td>10.16%</td>
<td>12.10%</td>
<td>9.09%</td>
<td>15.49%</td>
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<tr>
<td>Efficiency (cd A$^{-1}$) at 1 mA cm$^{-2}$</td>
<td>21.93</td>
<td>14.16</td>
<td>36.86</td>
<td>28.42</td>
<td>56.75</td>
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<tr>
<td>EL intensity (cd m$^{-2}$)</td>
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<td>135</td>
<td>337</td>
<td>228</td>
<td>537</td>
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<tr>
<td>Efficiency (cd A$^{-1}$) at 20 mA cm$^{-2}$</td>
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<td>34.46</td>
<td>28.22</td>
<td>27.52</td>
<td>40.60</td>
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<tr>
<td>EL intensity (cd m$^{-2}$)</td>
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<td>6941</td>
<td>5503</td>
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<tr>
<td>Efficiency (cd A$^{-1}$) at 100 mA cm$^{-2}$</td>
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<td>21.53</td>
<td>21.08</td>
<td>29.82</td>
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<tr>
<td>EL intensity (cd m$^{-2}$)</td>
<td>15.665</td>
<td>29.378</td>
<td>21.007</td>
<td>21.511</td>
<td>27.396</td>
</tr>
<tr>
<td>Efficiency (cd A$^{-1}$) at 200 mA cm$^{-2}$</td>
<td>13.65</td>
<td>24.62</td>
<td>18.02</td>
<td>16.77</td>
<td>24.52</td>
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<tr>
<td>EL intensity (cd m$^{-2}$)</td>
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<td>50.642</td>
<td>35.475</td>
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<tr>
<td>Efficiency (cd A$^{-1}$) at 300 mA cm$^{-2}$</td>
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<td>22.56</td>
<td>14.32</td>
<td>14.20</td>
<td>22.46</td>
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<tr>
<td>EL intensity (cd m$^{-2}$)</td>
<td>35.761</td>
<td>66.898</td>
<td>42.625</td>
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<td>64.480</td>
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<tr>
<td>Maximum current density (mA cm$^{-2}$)</td>
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<td>331.98</td>
<td>322.23</td>
<td>320.33</td>
<td>343.57</td>
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<tr>
<td>Efficiency (cd A$^{-1}$)</td>
<td>11.33</td>
<td>21.94</td>
<td>13.79</td>
<td>13.47</td>
<td>20.60</td>
</tr>
<tr>
<td>EL intensity (cd m$^{-2}$)</td>
<td>36.299</td>
<td>72.864</td>
<td>45.625</td>
<td>43.170</td>
<td>70.794</td>
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Figure 2. Schematic energy level (eV) diagrams of devices and chemical structures of some materials used.

References