

Broad band and white phosphorescent polymer light-emitting diodes in multilayer structure

Kai-Chin Tang^a, Shin-Rong Tseng^b, Wei-Shan Li^b, Hsin-Fei Meng^{b,*},
Sheng-Fu Horng^a, Chian-Shu Hsu^c

^a Department of Electrical Engineering, National Tsing Hua University, Hsinchu 300, Taiwan, Republic of China

^b Institute of Physics, National Chiao Tung University, Hsinchu 300, Taiwan, Republic of China

^c Department of Applied Chemistry, National Chiao Tung University, Hsinchu 300, Taiwan, Republic of China

Received 19 November 2007; received in revised form 27 January 2008; accepted 29 January 2008

Available online 28 March 2008

Abstract

Efficient phosphorescent polymer light-emitting diode with poly(vinylcarbazole) (PVK) doped by two or three iridium complexes in single and bilayer structures are studied. With (tris-(2-(4-tolyl)phenyl)pyridine) (Ir(mppy)₃) as the green emitter and (1-phenylisoquinoline)(acetylacetonate) iridium(III) (Ir(piq)₂) as the red emitter the efficiency is as high as 23 cd/A with broad band emission from 500 nm to 720 nm. For white emission a second layer is added with blue emitter ((III) bis[(4, -6-di-fluorophenyl-pyridinato)N,C²] picolinate) (FIRpic) doped in PVK. White light containing three spectral peaks results with efficiency 8.1 cd/A. As the second blue layer is replaced by the fluorescent (poly(9,9-dioctylfluorene)) (PFO) white emission with high color rendering index 86 is achieved. The efficiency is 5.7 cd/A with peak luminance 8900 cd/m². For a given iridium complexes ratio the relative intensity of the green and red emission depends sensitively on the second blue layer.

© 2008 Elsevier B.V. All rights reserved.

Keywords: Phosphorescent; Multilayer; Polymer light-emitting diodes

Organic and polymer light-emitting diodes (OLED/PLED) have attracted great attention for the use in flat panel display and lighting [1,2]. Recently OLED has been demonstrated to reach nearly 100% internal quantum efficiency with the employment of phosphorescent emitters [3]. Due to its low cost solution process, PLED has the potential to be more competitive than OLED in many future applications. One promising way for display application is using white PLED combined with color filters. For this purpose, white light containing three primary colors is essential. Several ways to generate high-efficiency white light in PLED are reported [4,5]. The spectra however usually contains only two peaks and has weak emission in the red, yielding low color rendering index (CRI). The CRI ranges from 0 to 100 and represents how authentic colors look when viewed with the light source. For acceptable illumination sources, it needs to be higher than 80 [6–8]. Ir complex is known to yield very high efficiency as doped into the polymer matrix [9–11]. It is there-

fore desirable to develop efficient white PLED with all three colors resulting from Ir complex emitter. So far high efficiency is reported only for a single color, presumably due to the difficulty to distribute the recombination evenly among the three complexes as their carrier trapping capabilities could be very different. In this work we study PLED with multiple Ir complex doping in single and bilayer structures. Poly(vinylcarbazole) (PVK) blended with electron and hole transport molecules [12–15] is used as the host. It turns out that as the green phosphorescent dye (tris-(2-(4-tolyl)phenyl)pyridine) (Ir(mppy)₃) and red emitter bis(1-phenylisoquinoline)(acetylacetonate) iridium(III) (Ir(piq)₂) are doped together the high efficiency is maintained with current efficiency 23 cd/A and emission spectral extending from 500 nm to 720 nm. As the blue dye (III) bis[(4, -6-di-fluorophenyl-pyridinato)N,C²] picolinate (FIRpic) is added to the same layer there is no blue emission regardless of the concentration, probably due to the much weaker carrier trapping by FIRpic compared with the green and red dyes. In order to obtain white emission a second blue layer is added with either phosphorescent dye FIRpic doped in PVK or fluorescent polymer poly(9,9-dioctylfluorene) (PFO) as the

* Corresponding author. Tel.: +886 5731955.

E-mail address: meng@mail.nctu.edu.tw (H.-F. Meng).

emitter. High color index of 86 and efficiency of 8.1 cd/A are achieved.

We study four kinds of PLED, including a green one based on $\text{Ir}(\text{mppy})_3$ (device I), a yellow broad-band one based on $\text{Ir}(\text{mppy})_3$: $\text{Ir}(\text{piq})_2$ (device II) and two white ones based on $\text{Ir}(\text{mppy})_3$: $\text{Ir}(\text{piq})_2$ / blue (phosphorescent or fluorescent) bilayer structure device III and device IV $\text{Ir}(\text{mppy})_3$ is purchased from American Dye Sources, $\text{Ir}(\text{piq})_2$ and FIrpic are purchased from Luminescence Technology Corporation. $\text{Ir}(\text{mppy})_3$ and $\text{Ir}(\text{piq})_2$ are doped into PVK host blended with N, N' -diphenyl- N, N' -(bis(3-methylphenyl)-[1,1-biphenyl]-4, 4'-diamine) (TPD), and 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD). TPD and PBD are functional materials to enhance carrier transporting ability. FIrpic acts as the blue phosphorescent emitter and is doped into PVK host with 1,3-bis[(4-tert-butylphenyl)-1,3,4-oxadiazolyl]phenylene (OXD-7) to enhance the electron transporting ability [16]. PFO ($M_w = 365,000$, purchased from ADS) is chosen as the blue fluorescent emitter. Poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4-4'-(N -(4-sec-butylphenyl))-diphenylamine)] (TFB, $M_w = 197,000$, purchased from ADS) is used as hole injection layer. The PLED devices were fabricated on glass substrates with patterned indium-tin oxide (ITO) layer. The ITO glass is cleaned in acetone and then exposed to UV-ozone for 20 min. Then 50 nm hole injection layer of poly-(3,4-ethylenedioxy thiophene) doped with poly(styrene sulfonate) (PEDOT: PSS, Baytron P CH 8000) is spin coated and annealed at 100°C for 40 min. TFB dissolved in toluene is spin coated on PEDOT: PSS layer and annealed at 180°C for 40 min to remove the residual solvent, then spin-rinsed by toluene to remove the dissolvable part [17]. Afterwards, the blended emission layer for green light is deposited by spin coating to form a 70 nm thin film for device I then baked for 60 min at 80°C . For device to ensure better solubility of FIrpic and PVK and spin coated directly upon the blended emissive layer to form a 45 nm thin film and followed by annealing at 80°C for 1 h. The high molecular weight PVK ($M_w = 1,100,000$) has poor solubility for toluene solution, so the mutual dissolution is negligible. For white light device IV, PFO is dissolved in toluene and spin coated upon the blending emissive layer to form a 40 nm thin film and then annealed at 120°C for 1 h. All the procedures are performed in air. The CsF (1 nm)/Al (100 nm) cathode for device I, II, IV and CsF (2 nm)/Al (100 nm) for device III are evaporated onto the emissive layer under vacuum at the pressure of 8×10^{-7} Torr. Fig. 1(a) shows the energy profile of the materials use in this work [18–20]. LEP represents light-emitting-polymer which is in general a blend of various materials. The LEP weight blending ratio is PVK:PBD:TPD: $\text{Ir}(\text{mppy})_3 = 61 : 24 : 9 : 6$ for device I, PVK:PBD:TPD: $\text{Ir}(\text{mppy})_3 : \text{Ir}(\text{piq})_2 = 61 : 24 : 9 : 6 : 0.34$ for device II, PVK:PBD:TPD: $\text{Ir}(\text{mppy})_3 : \text{Ir}(\text{piq})_2 = 61 : 24 : 9 : 3 : 12$ for device III and PVK:PBD:TPD: $\text{Ir}(\text{mppy})_3 : \text{Ir}(\text{piq})_2 = 61 : 24 : 9 : 3 : 3$ for device IV. The electron affinity (EA) and ionization potential (IP) of polymer used in this article are shown in Fig. 1(b). The electroluminescent (EL) characteristics of the device are measured with Keithley 2400 and PR650 Spectroscan spectrometer. The CIE coordinates and CRI of the white PLED are calculated with the PR650 soft-

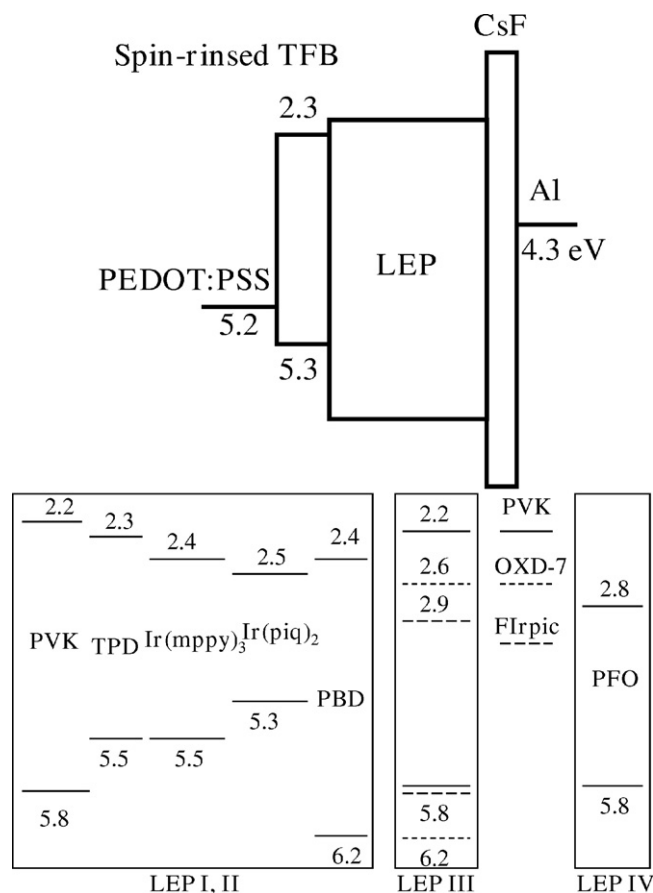


Fig. 1. (a) Schematic energy level diagram of the device. (b) Electron affinity and ionization potential of materials used in this work. Numbers are given in eV.

ware. All the measurements are carried out in ambient air after packaging.

Fig. 2 shows the performance of device I and device II. For green light devices based on $\text{Ir}(\text{mppy})_3$, the current efficiency of the device with spin rinsed TFB layer is 47.9 cd/A with power efficiency of 29.6 lm/W, and the external quantum efficiency (EQE) of 14%, about 20% increase from the device without TFB layer. The current density is also increased, indicating that the TFB layer facilitates the hole injection. The luminance is also enhanced from 2445 cd/m^2 to 7318 cd/m^2 at 10 V. For yellow light device, we dope $\text{Ir}(\text{piq})_2$ together with the $\text{Ir}(\text{mppy})_3$ with the ratio of 1:17.5. The current efficiency is 23 cd/A with power efficiency of 9.8 lm/W and the EQE of 10%, only slightly smaller than that of green $\text{Ir}(\text{mppy})_3$ device (14%). The luminance is 9100 cd/m^2 at 14 V. The current density and luminance decrease relative to the green light device suggesting that $\text{Ir}(\text{piq})_2$ plays as a stronger carrier trap compare with $\text{Ir}(\text{mppy})_3$. As a result, we get yellow light with strong red component by blending little amount of $\text{Ir}(\text{piq})_2$ in $\text{Ir}(\text{mppy})_3$. The inset of Fig. 2 shows the EL spectra of the green light and yellow light devices and the lifetime of the green TFB/ $\text{Ir}(\text{mppy})_3$ device at the constant current mode. The yellow light device are composed of two distinct peaks and the CIE coordinate is (0.40, 0.56). Even though not white, this spectrum is very broad band and covers emission from 500 nm up to 720 nm. This result demonstrates

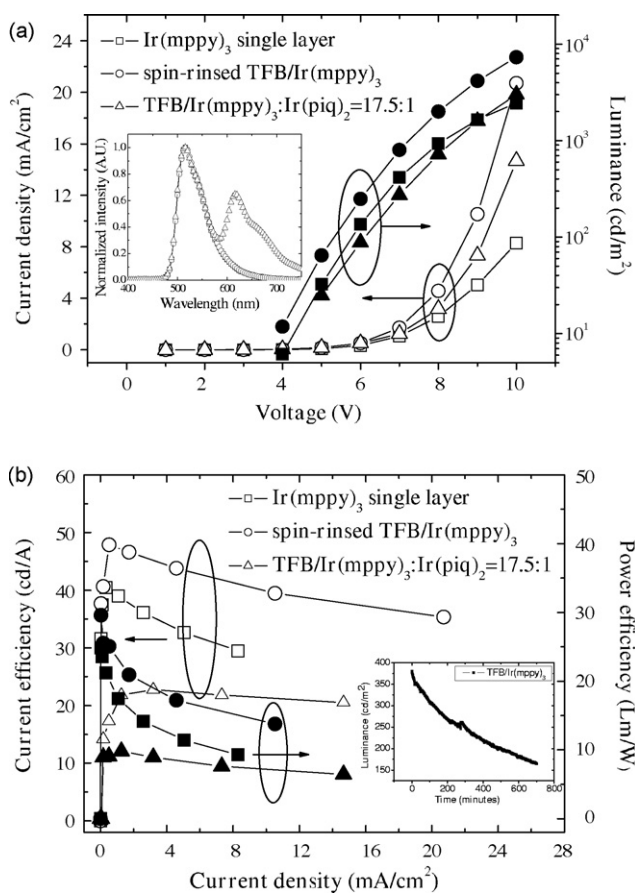


Fig. 2. The performances of PLED including single green emitter and the mixing of the green and red iridium materials: single layer Ir(mppy)₃ blending system (square), spin-rinsed TFB/Ir(mppy)₃ system (circle), spin-rinsed TFB/Ir(mppy)₃:Ir(piq)₂ blending system (triangle). (a) The current density and luminance. Inset is the EL spectrum. Circle is TFB/Ir(mppy)₃, triangle is TFB/Ir(mppy)₃:Ir(piq)₂ = 17.5 : 1. (b) The current efficiency and power efficiency. Inset is the lifetime of green TFB/Ir(mppy)₃ device.

that highly efficient multi-color PLED can be made by properly selecting the combination of Ir complexes.

On the basis green-red emission using Ir complexes, we make white PLED by adding a blue emitter. Two kinds of blue materials are used, one is FIrpic (device III) and the other is PFO (device IV). We first add all three phosphorescent dyes FIrpic, Ir(mppy)₃ and Ir(piq)₂ into the PVK blend host and it turns out that there is no blue emission at all even as the the FIrpic concentration is 20 times higher than the Ir(mppy)₃, in sharp contrast with the above case where a small amount of red dye is enough to cause a large red emission. This implies that the carrier trapping capability of FIrpic is much weaker than the other two dyes. In Fig. 1(b) one sees that the EA (2.9 eV) and IP (5.8 eV) values of FIrpic are both much larger than the green and red dyes. In particular, EA is 0.4 eV and 0.5 eV higher than the red and green dye, respectively. It is also 0.5 eV higher than the electron transport molecule PBD. We suspect that the much deeper molecular level of FIrpic makes it unlikely for an electron to be trapped since a large amount of energy needs to be released. On the other hand, the holes are also not trapped due to the large IP value. The absence of blue emission in the triple Ir blend therefore indi-

cates that in order to have a balanced emission among the three primary colors, the molecular levels of the dyes must be more or less aligned to have an even carrier trapping capability. In order to achieve white light, the blue emission is realized by adding the second blue layer containing FIrpic or fluorescent polymer. Assisted by the poor solubility of high molecular weight PVK in toluene, the blue layer is formed by directly spinning upon the layer. The difference in thickness between the total film and sum of Ir(mppy)₃:Ir(piq)₂ film and PFO film is about 10 nm, indicating that the procedure is feasible for multi-layer structure devices. The performances of white light PLED are shown in Fig. 3. For device III, with FIrpic blended in PVK as the blue layer, the maximum current efficiency is 8.1 cd/A with the corresponding EQE of 4.28% and power efficiency of 3.62 lm/W. The maximum luminance is 4130 cd/m². The CIE coordinates are (0.34, 0.43) at 7 V and (0.32, 0.42) at 10 V. For device IV with pure PFO as the blue layer, the maximum current efficiency is 5.7 cd/A, with the corresponding EQE of 2.1% and power efficiency of 2.2 lm/W. The maximum luminance is 8900 cd/m². The CIE coordinates are (0.34, 0.45) at 7 V and (0.32, 0.42) at 10 V. Fig. 4 shows the spectrum of device III and device IV. The spectrum exhibits three distinct blue, green and red emissions and with the corresponding CRI value of 86 and CIE coordinates of (0.33, 0.44) for device III. Although the CIE coordinate is not pure white (0.33, 0.33), the CRI value is very high for dis-

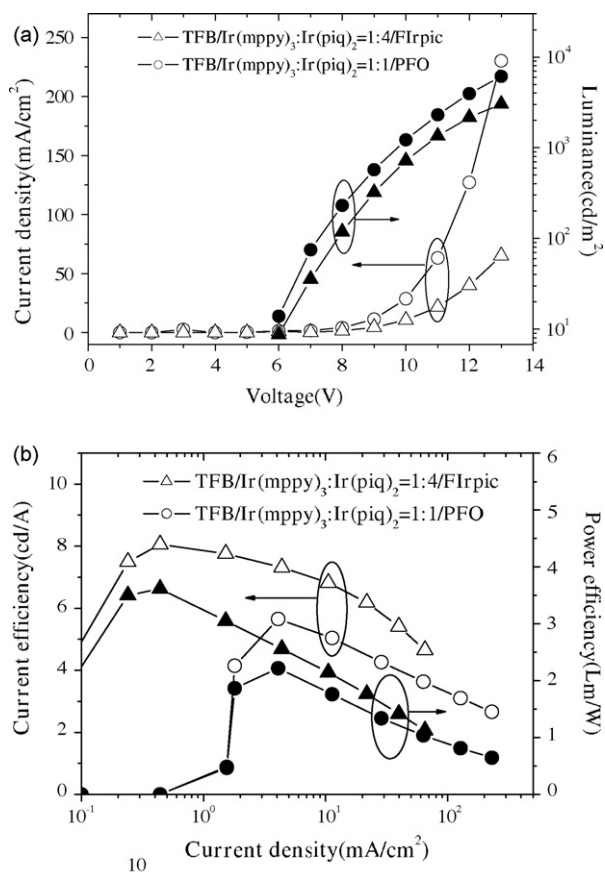


Fig. 3. The performances of white PLED by adding phosphorescent materials (FIrpic, triangle) and fluorescent (PFO, circle). (a) The current density and luminance. (b) The current efficiency and power efficiency.

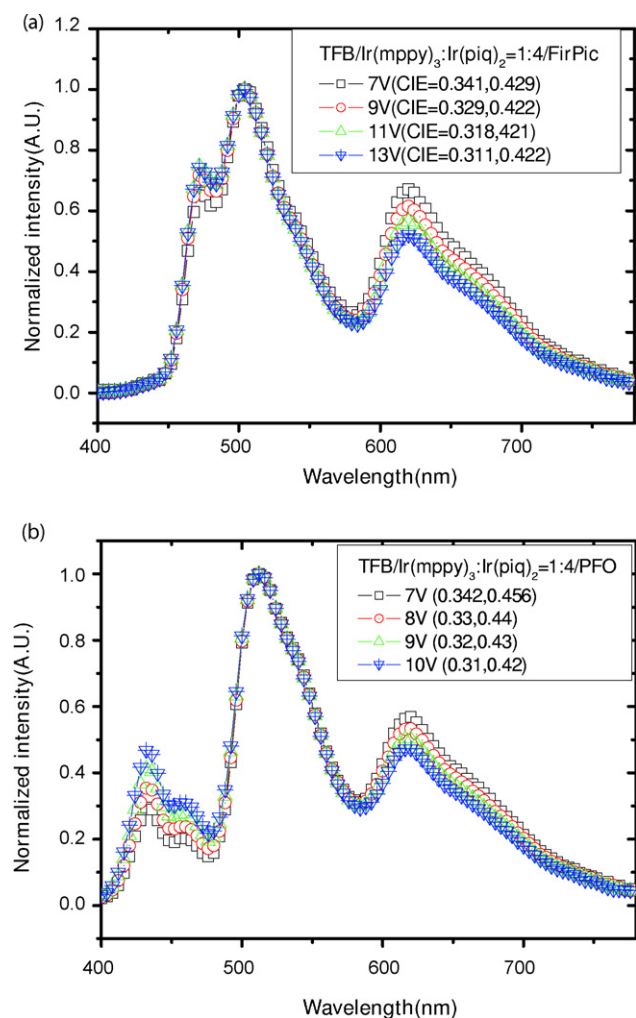


Fig. 4. The EL spectra of white PLED using (a) FIrpic and (b) PFO for the second layer at different voltages.

play application using color filter to separate the three primary colors. The device performances are summarized in Table 1.

One of the remarkable features of the multiple doped phosphorescent PLED is that for a given ratio between Ir(mppy)₃ and Ir(piq)₂ in the first layer, the relative emission intensity of the green and red depends dramatically on the presence and the nature of the second blue layer. For single layer device in order to have the comparable green and red emission as shown in Fig. 2(a), the Ir(mppy)₃ to Ir(piq)₂ dye ratio in the blend is 17.5:1 where the red dye only constitute a small fraction. Surprisingly as the second PFO layer is added, the red ratio

needs to be raised to 1:1 in order to have the balanced emission shown in Fig. 4. Furthermore, as FIrpic doped in PVK blend is used as the second blue layer, the red dye have to be further increased to as much as 1:4 and become the predominant component in the first layer in order to obtain the spectrum in Fig. 4. We believe that this feature indicates that the operation of the device is dominated by the amount of the electron flow into the first layer. Apparently, the relative electron trapping capability of Ir(piq)₂ and Ir(mppy)₃ depends sensitively on the electron current density. As the electron supply is high, Ir(mppy)₃ may become easily saturated and the rest of the electron has to recombine in Ir(piq)₂. This is why we only need a small amount of Ir(piq)₂ for single layer where the electrons are directly injected from the CsF cathode. As the blue layer is inserted between the cathode and the first layer, electrons are blocked in the blue layer with poor electron mobility and the electron current supplied to the first layer become limited. In that case Ir(mppy)₃ can trap electrons as efficiently as Ir(piq)₂, so the red dye needs to be increased. Another reason for this is the red dye is the deepest hole trap in the PVK system and the trapped holes will attract electrons and facilitate electron injection from the cathode. FIrpic doped PVK appears to have poorer electron transport than PFO since even higher red dye is necessary. Further support comes from the dependence of the green-red spectrum on the thickness of the blue layer and the CsF in cathode which modulates the electron flow. CsF is increased from 1 nm to 2 nm for device III for better electron injection.

Above we report PLED with green, green plus red, and green plus red plus blue iridium emitters. It turns out that before the addition of blue emitter FIrpic the efficiency is high and comparable to small molecule OLED: external quantum efficiency of 14% for green, 10% for green plus red. Unfortunately when blue emitter is added the quantum efficiency drops to 4.3% which is even lower than the best fluorescent white PLED. Such reduced efficiency directly results from the low efficiency for PLED with blue emitter only. In Fig. 5 the purely blue PLED with FIrpic emitter shows efficiency up to only 9 cd/A (4%) no matter how we tune the ratio other small molecules including electron and hole transport materials. Neher and co-workers were the first to report high efficiency PLED with green Ir complex, but their blue PLED efficiency is only 5.7% which is close to our result [21]. It is probably because the triplet energy of PVK is not high enough to confine the triplet excitons of blue Ir complex. Indeed the host used for blue Ir OLED is much higher than PVK. Such superior host for PLED seems yet to be discovered. Recently high efficiency is reported for blue Ir PLED by Mathai et al.

Table 1
Performance of PLED in this work

Label	Maximum current efficiency (cd/A)	Maximum EQE (%)	Maximum luminance (cd/m ²)	CRI
Ir(mppy) ₃	40.46 (at 6 V)	11.53 (at 6 V)	2445 (at 10 V)	N/A
TFB/Ir(mppy) ₃ (I)	47.9 (at 6 V)	13.9 (at 6 V)	7318 (at 10 V)	N/A
TFB/Ir(mppy) ₃ :Ir(piq) ₂ (II)	22.8(at 8 V)	9.84 (at 8 V)	3012 (at 10 V)	N/A
TFB/LEP/FIrpic(III)	8.1 (at 7 V)	4.28 (at 7 V)	3026 (at 13 V)	74
TFB/LEP/PFO(IV)	5.7 (at 8 V)	2.1 (at 8 V)	6124 (at 13 V)	86
FIrpic	9 (at 7 V)	4 (at 7 V)	2200 (at 13 V)	N/A

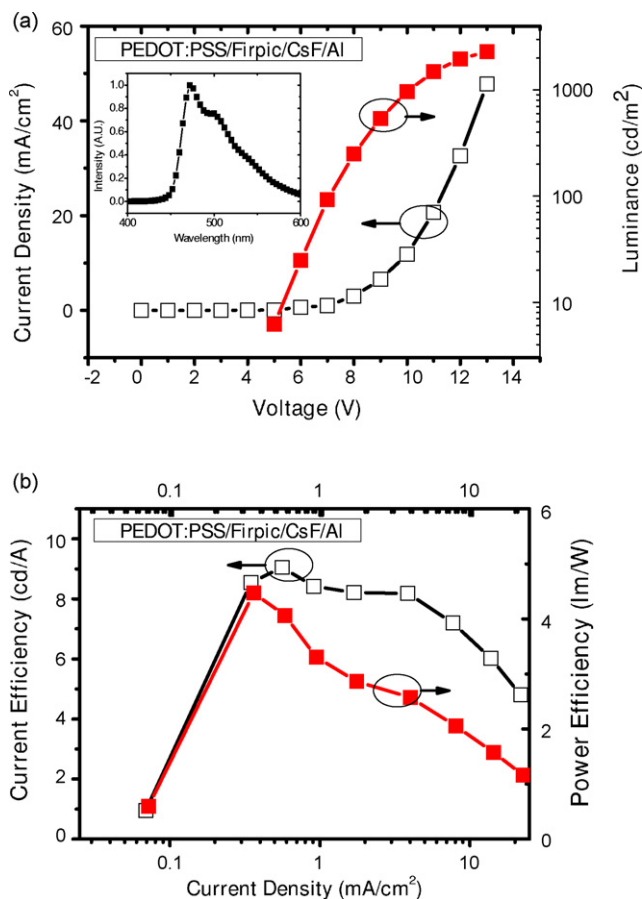


Fig. 5. The performances of blue Firpic PLED. (a) The current density and luminance. (b) The current efficiency and power efficiency.

[16] using the same materials and device structure. The difference in processing conditions between their and our works is not understood so far. Regardless of the problem of the blue emitter, the major result of our work is that very high efficiency yellow emission can be achieved with both green and red dopants. As for white PLED more works are needed to solve the reproducibility of blue PLED efficiency first. Furthermore the stability of the device is not good compared with fluorescent PLED. In fact this is general problem for PLED with PVK host doped with Ir complexes.

In conclusion, we demonstrate simple device structure for multiply Ir complex-doped white light PLED with high color-rendering index by employing green and red iridium dyes in one layer and adding another layer of blue iridium dye blend or fluorescent blue polymer by direct spin coating. Without the

blue layer, the broad band yellow emission reaches 23 cd/A in efficiency. With the blue layer, the white light current efficiency is 8.1 cd/A for the blue Ir dye and 5.7 cd/A for the blue polymer. The CRI reaches as high as 86 with maximum luminance is 8900 cd/m². With the easy solution manufacturing and high CRI value, it is applicable to large-area full color display and lighting.

Acknowledgment

The authors would like to thank Chunghwa Picture Tube LTD. for offering the Student Grant. This work is supported by the National Science Council of Taiwan under grant number NSC 96-2112-M-009-036.

References

- [1] R.H. Friend, R.W. Gymer, A.B. Holmes, J.H. Burroughes, R.N. Marks, C. Taliani, D.D.C. Bradley, D.A.D. Santos, J.L. Bredas, M. Logdlund, W.R. Salaneck, *Nature* 397 (1999) 121.
- [2] S.R. Forrest, B.W.D. Andrade, *Adv. Mater.* 16 (2004) 1587.
- [3] Y. Sun, N.C. Giebink, H. Kanno, B. Ma, M.E. Thompson, S.R. Forrest, *Nature* 440 (2006) 908.
- [4] G. Lei, L. Wang, Y. Qiub, *Appl. Phys. Lett.* 88 (2006) 103508.
- [5] J. Huang, W.J. Hou, J.H. Li, G. Li, Y. Yang, *Appl. Phys. Lett.* 89 (2006) 133509.
- [6] X. Gong, S. Wang, D. Moses, G.C. Bazan, A.J. Heeger, *Adv. Mater.* 17 (2005) 2053.
- [7] X. Niu, L. Ma, B. Yao, J. Ding, G. Tu, Z. Xie, L. Wang, *Appl. Phys. Lett.* 89 (2006) 213508.
- [8] T.H. Kim, H.K. Lee, O.O. Park, B.D. Chin, S.H. Lee, J.K. Kim, *Adv. Fun. Mater.* 16 (2006) 611.
- [9] V. Cleave, G. Yahioğlu, P. Le Barny, R.H. Friend, N. Tessler, *Adv. Mater.* 11 (1999) 285.
- [10] C.L. Lee, K.B. Lee, J.J. Kim, *Appl. Phys. Lett.* 77 (2000) 2280.
- [11] Y. Kawamura, S. Yanagida, S.R. Forrest, *J. Appl. Phys.* 92 (2002) 87.
- [12] S. Lamansky, P.I. Djurovich, F. Abel-Razzaq, S. Garon, D.L. Murphy, M.E. Thompson, *J. Appl. Phys.* 92 (2002) 1570.
- [13] X. Gong, M.R. Robinson, J.C. Ostrowski, D. Moses, G.C. Bazan, A.J. Heeger, *Adv. Mater.* 14 (2002) 581.
- [14] X.H. Yang, D. Neher, D. Hertel, Th.K. Daubler, *Adv. Mater.* 16 (2004) 161.
- [15] X.H. Yang, D. Neher, *Appl. Phys. Lett.* 84 (2004) 2476.
- [16] M.K. Mathai, V.E. Choong, S.A. Choulis, B. Krummacker, F. Sob, *Appl. Phys. Lett.* 88 (2006) 243512.
- [17] S.A. Choulis, V.E. Choong, M.K. Mathai, F. So, *Appl. Phys. Lett.* 87 (2005) 113508.
- [18] D. Kolosov, V. Adamovich, P. Djurovich, M.E. Thompson, C. Adachi, *J. Am. Chem. Soc.* 124 (2002) 9945.
- [19] C.H. Yang, C.C. Tai, I.W. Sun, *J. Mater. Chem.* 14 (2004) 947.
- [20] P. Zacharias, M.C. Gather, M. Rojahn, O. Nuyken, K. Meerholz, *Angew. Chem. Int. Ed.* 46 (2007) 4388.
- [21] X. Yang, D.C. Müller, D. Neher, K. Meerholz, *Adv. Mater.* 18 (2006) 948.