

## Efficient, Color Stable White Organic Light-Emitting Diode Based on High Energy Level Dopant

Young-Seo Park<sup>1</sup>, Dong Min Kang<sup>2</sup>, Jong-Won Park<sup>2</sup>, Soon-Ki Kwon<sup>2</sup>, Jae-Wook Kang<sup>3</sup>, Yun-Hi Kim<sup>4</sup> and Jang-Joo Kim<sup>1</sup>

<sup>1</sup>OLED Center, Department of Materials Science and Engineering, Seoul National University, Seoul 151-744, Korea

TEL:82-2-02-880-9216, e-mail: pys0125@snu.ac.kr

<sup>2</sup>School of Nano & Advanced Materials Engineering, Gyeongsang National University, Jinju, 660-701, Korea

<sup>3</sup>Surface Technology Research Center, Korea Institute of Machinery and Materials (KIMM), Changwon, 641-010, Korea

<sup>4</sup>Department of Chemistry, Gyeongsang National University, Jinju, 660-701, Korea

**Keywords :** white OLED, WOLED, color stability, high energy level dopant

### Abstract

*Efficient, color stable multi-EML WOLED have been fabricated using newly synthesized yellowish green dopant Ir(chpy)<sub>3</sub> or Ir(mchpy)<sub>3</sub>. The devices have high external quantum efficiency of 11.7%, color rendering index of 87, variation of CIE coordinate of (0.02, 0.01) between 10 to 5000 cd/m<sup>2</sup>, and low roll-off in efficiency with increasing brightness*

### 1. Introduction

White organic light-emitting diodes (WOLEDs) attract much attention in recent years due to their potential use in back light unit of flat panel displays, full color display and solid state lighting applications. The applications require WOLEDs possess high efficiency, appropriate color temperature, high color rendering index, and high color stability.<sup>[1]</sup>

Various approaches have been reported to improve the performance up to now, which include doping of several fluorophors or phosphors in a single emitting layer (EML),<sup>[2-7]</sup> synthesis of polymers incorporating different color emitting moieties,<sup>[8-9]</sup> use of excimer or exciplex formed by one or two dopants,<sup>[10,11]</sup> stacked several organic light emitting diodes (OLEDs),<sup>[12-14]</sup> use of microcavity effect from single emission layer,<sup>[15]</sup> down conversion of blue light,<sup>[1,16]</sup> and multi-EML structure doped with different color emitting dopants.<sup>[17-21]</sup> Among them, multi-EML structure has advantages over other architectures in terms of efficiency and color controllability because the recombination current, singlet and triplet energy transfer and performance of each layer can be

controlled by layer thickness, doping concentration and charge blocking layers.

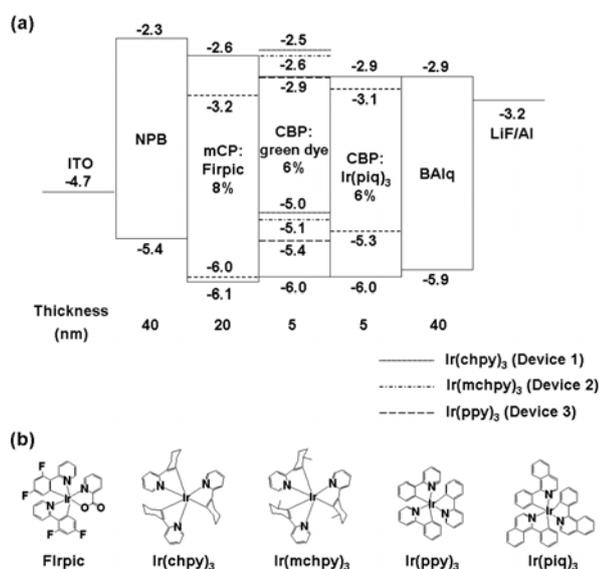
One drawback of the WOLEDs with multi-emissive layers is the color shift with increasing voltage<sup>[18-21]</sup> The color shift is believed to be originated from the shift of recombination zone with increasing voltage and easier formation of high energy excitons at higher voltage.<sup>[5]</sup>

In this paper, we report the fabrication of efficient, color-stable, multi-EML WOLEDs using newly synthesized dopant tris-*fac*-(2-cyclohexenyl)pyridine iridium(III) (Ir(chpy)<sub>3</sub>) or tris-*fac*-[2-(3-methylcyclohex-1-enyl)pyridine] iridium(III) (Ir(mchpy)<sub>3</sub>) which have high energy level compared with host.

### 2. Experimental

The WOLEDs were fabricated by thermal evaporation onto a cleaned glass substrate precoated with indium tin oxide (ITO) without breaking the vacuum. Prior to organic layer deposition, the ITO substrates were exposed to UV-ozone flux for 10 min following degreasing in acetone and isoprophylalcohol. All layers were grown by thermal evaporation at the base pressure of  $< 5 \times 10^{-7}$  Torr. Layers were deposited in following order: hole transporting layer (HTL)/blue EML/green EML/red EML/electron transporting layer (ETL)/cathode. 40-nm-thick N,N'-di(naphthalene-1-yl)-N,N'-diphenylbenzidine (NPB) was used as the HTL and 20-nm-thick N,N'-dicarbazolyl-3,5-benzene (mCP)

doped with 6 wt% iridium(III)bis[(4,6-difluorophenyl)pyridinato-N,C2']picolate (Firpic) as the blue EML. Green EML is 5-nm-thick CBP doped with 6 wt% green dopant. Ir(chpy)<sub>3</sub>, Ir(mchpy)<sub>3</sub>, and *fac* tris(2-phenylpyridine) iridium (Ir(ppy)<sub>3</sub>) were used as the green dopant for device 1, 2, and 3, respectively. 5-nm-thick CBP doped with 6 wt.% tris[1-phenylisoquinolinato-C2,N]iridium(III) (Ir(piq)<sub>3</sub>) was used as the red EML and 40-nm-thick aluminum(III) bis(2-methyl-8-quinolino)4-phenylphenolate (BAIq) was used as the ETL, respectively. Finally, the cathode consisting of a 1-nm-thick LiF and a 100-nm-thick layer of Al were deposited onto the sample surface. Figure 1(a) shows the structures of the devices, and the energy levels of the materials. The molecular structures of the dopants used in this study are shown in Figure 1(b).

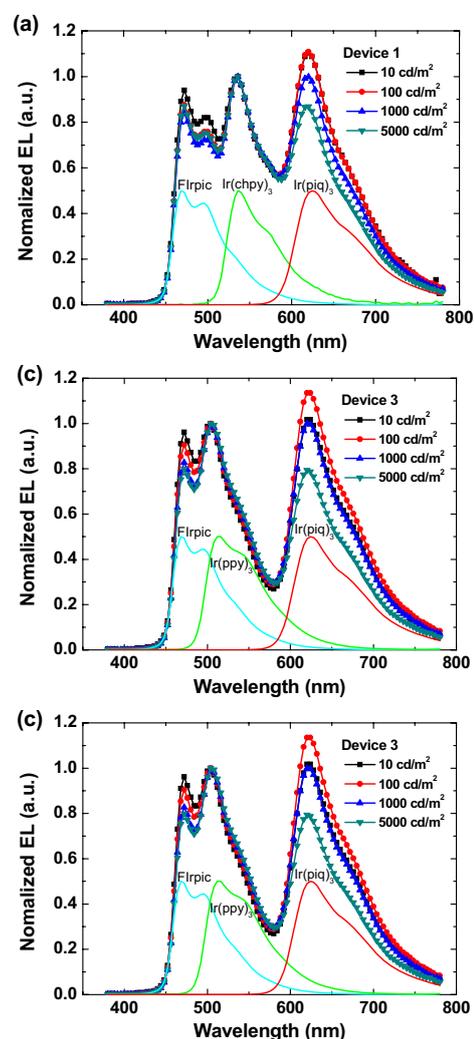


**Fig. 1. (a) Structures of the devices and energy levels of materials. (b) Molecular structures of dopants used in the study.**

Ir(chpy)<sub>3</sub> and Ir(mchpy)<sub>3</sub> were synthesized in Gyeongsang National University. Two ligands, 2-(1-cyclohexenyl)pyridine (chpy) and 2-(3-methyl-1-cyclohexenyl)pyridine (mchpy) were prepared from 2-bromopyridine with cyclohexanone derivatives in two steps. The desired iridium complexes were synthesized according to a modified procedure reported previously.<sup>[22,23]</sup> Bis-cyclometalate Iridium complexes bearing acetylacetonate (acac) as ancillary ligand were synthesized by a conventional two-step reaction from iridium trichloride via Ir(III)- $\mu$ -chloro-bridged dimer complexes. The tris-cyclometalated complexes (Ir(chpy)<sub>3</sub>, Ir(mchpy)<sub>3</sub>) were prepared by

reaction of the ligands with bis-cyclometalated Ir complexes in glycerol. Details of the synthesis of the materials will be described elsewhere.<sup>[24]</sup> All the materials were purified using train sublimation before use.

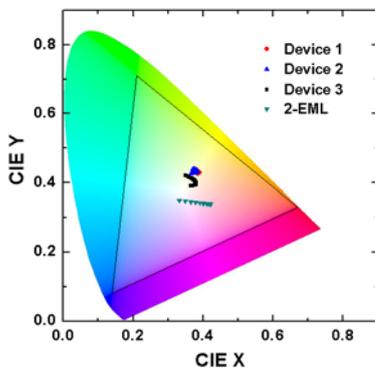
HOMO levels of organic materials are obtained from the cyclic voltammetry measurement, and LUMO levels are calculated from HOMO level and energy gap which is obtained from the edge of the absorption spectra. Current density-voltage-luminescence (J-V-L) characteristics of the WOLEDs were measured simultaneously using a Keithley 2400 programmable source meter and a SpectraScan PR650 (Photo Research). External quantum efficiency was calculated from the spectral luminance



**Fig. 2. EL spectra of (a) device 1, (b) device 2, and (c) device 3 with different luminance. Solid lines are EL spectra of OLEDs with single emitting layer.**

### 3. Results and discussion

Figure 2 displays the electroluminescent (EL) spectra of the WOLEDs at several different luminances of 10, 100, 1000 and 5000  $\text{cd m}^{-2}$ . The EL spectra exhibited the peak wavelengths at 472, 536 and 620 nm in the device 1 and 2. They correspond to the peak wavelengths of the EL spectra of the single color OLEDs using FIrpic, Ir(chpy)<sub>3</sub> (or Ir(mchpy)<sub>3</sub>) and Ir(piq)<sub>3</sub> dopants, respectively. The EL spectra of these WOLEDs covered all wavelengths from 450 nm to 750 nm and were stable as the luminance varied. At 1,000  $\text{cd m}^{-2}$ , CRI and color temperature were calculated to reach 87.94 and 4,246 K for device 1, and 87.27 and 4,316 K, respectively. These high CRI's of the device 1 and 2 are originated from the similar intensity of the three emission peaks and coverage of the whole visible wavelength. In contrast, the EL spectra of the device 3 exhibited the peak wavelength at 472, 508, and 620 nm and very low emission near 580 nm. Therefore the device shows lower CRI of 66.13 at 1,000  $\text{cd m}^{-2}$ . Moreover, the relative intensity of the red peak varied significantly as the luminance increased.

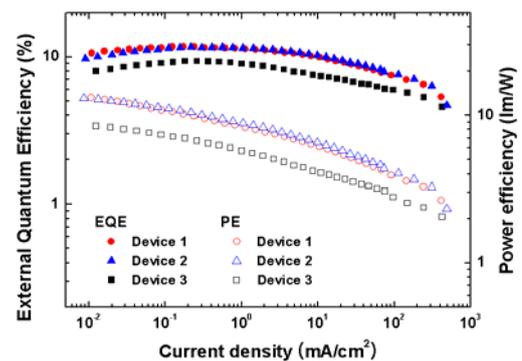


**Fig. 3.** CIE chromaticity coordinates of WOLEDs at luminance ranges of 10~5,000  $\text{cd/m}^2$ . 2-EML device is ITO/NPB (40 nm)/mCP:8%FIrpic (25 nm)/CBP:6%Ir(piq)<sub>3</sub> (5 nm)/BALq (40 nm)/LiF (1 nm)/Al (100 nm)

CIE chromaticity coordinates of the WOLEDs at the luminance range of 10~5000  $\text{cd m}^{-2}$  are displayed in Figure 3. When the luminance changed from 10  $\text{cd m}^{-2}$  to 5,000  $\text{cd m}^{-2}$ , the CIE chromaticity coordinates of the device 1 and 2 changed less than the device 3: CIE X = 0.37 ~ 0.39 and CIE Y = 0.43 ~ 0.44 for the device 1, CIE X = 0.37 ~ 0.38 and CIE Y = 0.43 ~ 0.44 for the device 2, and CIE X = 0.35 ~ 0.38 and CIE Y = 0.39 ~ 0.42 for the device 3.

We interpret the high color stability of the device 1

and 2 based on the energy level difference between the host and the dopant of the green EML. As depicted in Figure 1(a), Ir(chpy)<sub>3</sub> [Ir(mchpy)<sub>3</sub>] has the higher HOMO and LUMO level than that of CBP. Due to the high HOMO levels of the dopants, the dopants act as deep traps of holes. At deep traps, detrapping probability of trapped charges is low and mobility of charge carrier is lowered. On the other hand, the LUMO levels of the dopants are higher than that of the host, so that electrons are scattered at the dopants sites. Then the mean free path of electrons is shortened and the drift velocity of the electrons gets lowered. Mobility of both charge carriers are reduced at the green EML. The reduced electron and hole mobilities by the dopants in the middle green emitting layer somehow lead to the recombination ratio in each layer constant with increasing current. On the contrary Ir(ppy)<sub>3</sub> in CBP host works as a relatively shallower hole trap and doesn't function as an electron scattering center. Therefore, the recombination zone of the device 3 shifted more than the device 1 or 2. This interpretation is further supported by a two-EML device [(ITO/NPB (40 nm)/ mCP:8%FIrpic (25 nm)/CBP:6%Ir(piq)<sub>3</sub> (5 nm)/BALq (40 nm)/LiF (1 nm)/Al (100 nm)] where the middle green EML layer was removed from the device 1 and 2. The two-EML device exhibited large shift of color coordinate as shown in Figure 3. This fact clearly demonstrates that the middle layer functions as the controlling layer preventing the recombination zone shift as well as the yellowish-green EML.



**Fig. 4.** External quantum efficiency and power efficiency of the WOLEDs.

Figure 4 shows external quantum efficiency and power efficiency of the emitted light in the forward direction of the WOLED. The maximum quantum efficiency and luminance efficiency of the WOLEDs were 11.7 % and 22.8  $\text{cd A}^{-1}$  for the device 1, and 11.7 % and 23.4  $\text{cd A}^{-1}$  for the device 2 at the current

density of  $0.2 \text{ mA cm}^{-2}$ , respectively. The efficiency of these devices are higher than that of the device 3 (maximum quantum efficiency of 9.3% and maximum luminance efficiency of  $15.0 \text{ cd A}^{-1}$ ). It implies that the balance between electrons and holes are improved by using the dopants having high energy levels. Moreover the external quantum efficiency of these WOLEDs remained high of 8.1 % in the device 1 and 8.5 % in the device 2 at luminance of  $10,000 \text{ cd m}^{-2}$  and the current density about  $50 \text{ mA cm}^{-2}$ . This low roll-off of efficiency is remarkable in phosphorescent WOLEDs. Maximum power efficiencies were  $13.2 \text{ lm W}^{-1}$  for the device 1 and  $13.0 \text{ lm W}^{-1}$  for the device 2, respectively, which are also much higher than  $8.4 \text{ lm W}^{-1}$  for the device 3.

#### 4. Summary

In summary, efficient and color stable multi-EML phosphorescent WOLED had been presented using newly synthesized  $\text{Ir}(\text{chpy})_3$  and  $\text{Ir}(\text{mchpy})_3$  as yellowish-green dopants. The WOLED exhibited maximum external quantum efficiency of 11.7 % and maximum luminance efficiency of  $23.4 \text{ cd A}^{-1}$ , and maximum power efficiency of  $13.2 \text{ lm W}^{-1}$ , respectively. The roll-off of efficiency was low with external quantum efficiency of 8.5% at  $10,000 \text{ cd m}^{-2}$  ( $\sim 50 \text{ mA cm}^{-2}$ ). The WOLED also exhibited high CRI over 87 and the color temperature of about 4,300 K. Moreover the WOLEDs showed very high color stability (CIE X = 0.37  $\sim$  0.38 and CIE Y = 0.43  $\sim$  0.44 at the luminance ranges of 10  $\sim$  5,000  $\text{cd m}^{-2}$ ). The dopants have higher LUMO and HOMO levels than the host so that the dopants behaves as hole traps and electron scattering centers. As a result the recombination ratio in each EML was maintained constant with increasing voltage to keep the CIE almost constant. The middle green emitting layer also improves the electron and hole balance in the EMLs to improve the device efficiency. According to these characteristics, these WOLEDs have sufficient potential for solid-state lighting applications.

#### 5. References

1. R. Duggal, J. J. Shiang, C. M. Heller, and D. F. Foust, *Appl. Phys. Lett.* 2002, 80, 3470.
2. J. Kido, K. Hongawa, K. Okuyama, and K. Nagai, *Appl. Phys. Lett.* 1994, 64, 815.
3. W. D'Andrade, R. J. Holmes, and S. R. Forrest, *Adv. Mater.* 2004, 16, 624.
4. C. H. Chuen and Y. T. Tao, *Appl. Phys. Lett.* 2002, 81, 4499.
5. Y. Shao and Y. Yang, *Appl. Phys. Lett.* 2005, 86, 073510.
6. J.-H. Jou, Y.-S. Chiu, C.-P. Wang, R.-Y. Wang, and H.-C. Hu, *Appl. Phys. Lett.* 2006, 88, 193501.
7. Y.-H. Niu, M. S. Liu, J.-W. Ka, J. Bardeker, M. T. Zin, R. Schofield, Y. Chi, and A. K.-Y. Jen, *Adv. Mater.* 2007, 19, 300.
8. J. Liu, Q. Zhou, Y. Cheng, Y. Geng, L. Wang, D. Ma, X. Jing, and F. Wang, *Adv. Funct. Mater.* 2006, 16, 957.
9. J. Jiang, Y. Xu, W. Yang, R. Guan, Z. Liu, H. Zhen, and Y. Cao, *Adv. Mater.* 2006, 18, 1769.
10. J. Feng, F. Li, W. Gao, S. Liu, Y. Liu, and Y. Wang, *Appl. Phys. Lett.* 2001, 78, 3947.
11. B. W. D'Andrade, J. Brooks, V. Adamovich, M. E. Tompson, and S. R. Forrest, *Adv. Mater.* 2002, 14, 1032.
12. H. Kanno, R. J. Holmes, Y. Sun, S. Kena-Cohen, and S. R. Forrest, *Adv. Mater.* 2006, 18, 339.
13. F. Guo and D. Ma, *Appl. Phys. Lett.* 2005, 87, 173510.
14. C.-C. Chang, J.-F. Chen, S.-W. Hwang, and C. H. Chen, *Appl. Phys. Lett.* 2005, 87, 253501.
15. T. Shiga, H. Fujikawa, and Y. Taga, *J. Appl. Phys.* 2003, 93, 19.
16. B. C. Krummacker, V.-E. Choong, M. K. Mathai, S. A. Choulis, F. So, F. Jermann, T. Fiedler, and M. Zachau, *Appl. Phys. Lett.* 2006, 88, 113506.
17. Y. Sun, N. C. Giebink, H. Kanno, B. Ma, M. E. Thompson, and S. R. Forrest, *Nature* 2006, 440, 908.
18. C.-H. Kim, and J. Shinar, *Appl. Phys. Lett.* 2002, 80, 2201.
19. K. O. Cheon and J. Shinar, *Appl. Phys. Lett.* 2002, 81, 1738.
20. G. Lei, L. Wang, and Y. Qiu, *Appl. Phys. Lett.* 2006, 88, 103508.
21. X.-M. Yu, H.-S. Kwok, W.-Y. Wong, and G.-J. Zhou, *Chem. Mater.* 2006, 18, 5097.
22. S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, R. Keong, I. Tsyba, M. Bortz, B. Mui, R. Bau, M. E. Thompson, *Inorg. Chem.* 2001, 40, 1704.
23. A. B. Tamayo, B. D. Alleyne, P. I. Djurovich, S. Lamansky, I. Tsyba, N. N. Ho, R. Bau, M. E. Thompson, *J. Am. Chem. Soc.* 2003, 125, 7377.
24. D. M. Kang, J.-W. Kang, J. W. Park, S. O. Jung, S.-H. Lee, H.-D. Park, Y.-H. Kim, S. C. Shin, J.-J. Kim, and S.-K. Kwon, *Adv. Mater.* 2008, 20, 2003.