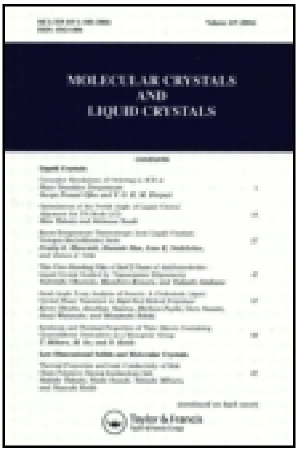

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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To cite this article: Jin Cheol Jeong & Ji Geun Jang (2011): Red Phosphorescent Organic Light-Emitting-Diode with the Doubly Doped Emitter on the Plastic Substrate, Molecular Crystals and Liquid Crystals, 551:1, 1-8

To link to this article: http://dx.doi.org/10.1080/15421406.2011.600104

Mol. Cryst. Liq. Cryst., Vol. 551: pp. 1–8, 2011
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.600104

Red Phosphorescent Organic Light-Emitting-Diode with the Doubly Doped Emitter on the Plastic Substrate

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To obtain a high efficiency flexible deep-red light source, phosphorescent organic light-emitting-diodes with the emitter of bis(10-hydroxy-benzo(h)quinolinato)beryllium [Bebq$_2$] doubly doped with iridium(III)bis(2-phenylquinoline-N,C2′)acetylacetonate [(pq)$_2$Ir(acac)] and RP411 (proprietary red phosphorescent dye) have been fabricated on the polyethylene-2,6-dicarboxylnaph-thalate (PEN) substrates. The device doubly doped with (pq)$_2$Ir(acac) and RP411 in the emitter showed the maximum current efficiency of 22.4 cd/A with current efficiency improvement of 10% under a luminance of 10,000 cd/m^2 compared to that of the device singly doped with RP411. In this device, luminance and current efficiency were found to be 12000 cd/m^2 at an applied voltage of 8 V and 17.3 cd/A under a luminance of 10,000 cd/m^2, respectively. The peak wavelength in the electroluminescent spectral distribution and color coordinates on the Commission Internationale de I'Eclairage (CIE) chart were 623 nm and (0.66, 0.34), respectively.

Keywords Red PhOLED; PEN substrate; flexible; double doping; Bebq$_2$

Introduction

Red organic light-emitting-devices (OLEDs) have been investigated for their applications in a wide variety of fields such as flat panel display, illumination, and medical phototherapeutics [1]. Especially, flexible red OLEDs have attracted considerable attention for the use of ubiquitous environment due to their unique features of light-weight and portability [2,3].

Phosphorescent OLEDs (PhOLEDs) based on phosphorescent dyes generally exhibit the improved electroluminescent characteristics in comparison with fluorescent OLEDs because both of singlets and triplets can be used for light emission. The effect of heavy metal in phosphors like iridium compounds leads to the good intersystem crossing from singlets to triplets and strong phosphorescence even at room temperature [4]. When PhOLEDs are applied to practical devices, however, the quantum efficiency remarkably decreases due to carrier injection loss and triplet-triplet annihilation at high current density [5,6]. Moreover, the triplet excitons have a rather long lifetime so that they may diffuse into adjacent organic layers from the emitter. This effect also results in the decline of luminous efficiency and

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*Corresponding author. E-mail: semicgk@dankook.ac.kr color purity due to relaxation of triplets outside the emitter [7,8]. In order to obtain the good electroluminescent characteristics in a red PhOLED, the electrons injected from cathode should be confined in the emission layer and the diffusion loss of triplets into the adjacent carrier transport layers should not happen. And also, the energy transfer from host to dopant can easily take place.

Conventional red PhOLEDs have a singly doped host-dopant system in the emitter with organic structure of hole transport layer (HTL)/emissive layer (EML)/electron transport layer (ETL) [9,10]. However, it is not easy for a single HTL to fulfill all the requirements of low hole injection barrier, high hole mobility, and high triplet energy. Furthermore, the energy transfer from host to dopant can be poor in a deep-red PhOLED due to large energy difference between energy gap of host and triplet energy of dopant.

To solve these problems of conventional red PhOLEDs, a device with organic structure of HTL1/HTL2/doubly doped EML (DDEML)/ETL is newly proposed in this paper. HTL1 is a hole transport layer which can be also referred as hole injection layer for easy injection of hole from anode, and HTL2 is a layer not only to transport holes into the emitter but also to protect diffusion loss of triplets and confine electrons in the emitter. The highest occupied molecular orbital (HOMO) level of HTL1 should be nearly aligned with the Fermi level of anode (indium-tin-oxide, ITO) to lower the injection barrier height for hole at the interface. The lowest unoccupied molecular orbital (LUMO) level of HTL2 should be as shallow as possible below zero level to confine the electrons injected from cathode in the emitter, and the high triplet energy and good hole mobility are required in this layer as well. The DDEML is an emission region in which the primary dopant emitting deep-red light with a lower triplet energy and the assistant dopant with a higher triplet energy are co- doped in a host. When the energy difference between energy gap of host and triplet energy of the primary dopant is large in the case of deep-red phosphorescent emission, the introduction of assistant dopant with an intermediate triplet energy can be helpful to make the energy transfer from host to the primary dopant easier.

Figure 1 shows the energy diagram of organic layers in the multilayer configuration of the proposed device. The structure shown in Figure 1 was formed on the plastic substrate using N,N′-diphenyl-N,N′-bis-[4-(phenyl-m-tolvlamino)-phenyl]-biphenyl-4,4′-diamine [DNTPD] as the HTL1, 1,1-bis-(di-4-poly-aminophenyl)cyclohexane [TAPC] as

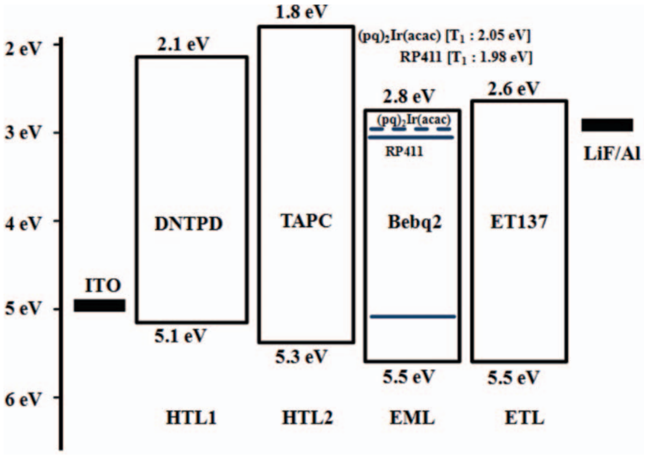

Figure 1. Energy diagram of organic materials in the multilayer configuration.

the HTL2, and Bebq$_2$ doubly doped with assistant dopant of (pq)$_2$Ir(acac) and primary dopant of RP411 as the EML. For comparison, a device with the emitter singly doped with only RP411 in the structure of Fig. 1 was also prepared in the experiments.

Experimental Procedure

The devices were prepared by thermal evaporation of organic and metallic layers onto the ITO-coated PEN substrates in a high vacuum chamber with a base pressure lower than 5×10^{-8} Torr. The sheet resistance of the ITO layer was 15 Ω/sq. Starting substrates were cleaned by acetone and isopropyl alcohol prior to organic thin film deposition. In the formation of HTL, a 500 Å-thick film of DNTPD as the HTL1 was firstly deposited followed by a 300 Å-thick film of TAPC as the HTL2. In the formation of EML, two different depositions were performed according to the doping techniques. A 330 Å-thick film of the emitter consisting of Bebq$_2$ doped with [7% (pq)$_2$Ir(acac) + 3% RP411] (by volume ratio to the host) was formed in the doubly doped device, while Bebq$_2$ doped with 10% RP411 in the singly doped device. Next, a 500 Å-thick film of ET137 which is a proprietary material with a LUMO level of 2.6 eV was deposited as the ETL followed by 10 Å-thick LiF/1200 Å-thick Al bilayer as a cathode.

The electrical properties were investigated using a Polaronix M6100 J-L-V test system (McScience). The optical properties such as luminance, electroluminescence spectra, and CIE color coordinates were evaluated using a CS-1000 spectro-radiometer (Konica Minolta) in a dark condition.

Results and Discussion

As shown in Fig. 1, DNTPD with a HOMO level of 5.1 eV has the low hole injection barrier from an anode of ITO, and the LUMO barrier of about 1 eV at the interface of TAPC and Bebq$_2$ is sufficiently large to confine the electrons injected from cathode in the emitter. The energy gap of Bebq$_2$ is 2.7 eV, and the triplet energies of (pq)$_2$Ir(acac) and RP411 are 2.05 eV and 1.98 eV, respectively. The hole mobility and triplet energy of TAPC are 0.01 cm^2/Vs [11] and 2.87 eV, respectively. TAPC can be used as a good material of HTL2 in the proposed device due to the high carrier mobility and high triplet energy.

In the doubly doped device, the excitons formed from Bebq$_2$ can easily transfer their energies to the triplet states of RP411 via (pq)$_2$Ir(acac). UV-vis absorption and photoluminescence spectra of Bebq$_2$ at 300 °K are shown in Fig. 2. In Fig. 2, the peak wavelength of PL spectra was about 490 nm. UV-vis absorption and photoluminescence spectra of (pq)$_2$Ir(acac) at 300 °K and 77 °K are shown in Fig. 3(a). And also, UV-vis absorption and photoluminescence spectra of RP411 at 300 °K and 77 °K are shown in Fig. 3(b). The triplet energy of an organic material can be obtained from a peak wavelength of photoluminescence spectra measured at 77 °K. Peak wavelengths of photoluminescence spectra at low temperature of (pq)$_2$Ir(acac) and RP411 were 604 nm and 624 nm in Figure 3, respectively. Judging from the wide overlap between photoluminescence spectra of host and UV-vis absorption spectra of dopants with deep-red emission of the primary dopant of RP411, the composition of Bebq$_2$:[(pq)$_2$Ir(acac) + RD411] can be a good host-dopant system as the EML for a new high efficiency deep-red PhOLED.

Current density-voltage-luminance (J-V-L) characteristics of the fabricated devices are shown in Fig. 4. The shapes of luminance-voltage curves are similar to those of current density-voltage curves in Fig. 4 because the fabricated devices are driven by injection of current. Current density and luminance of the doubly doped device were higher than those

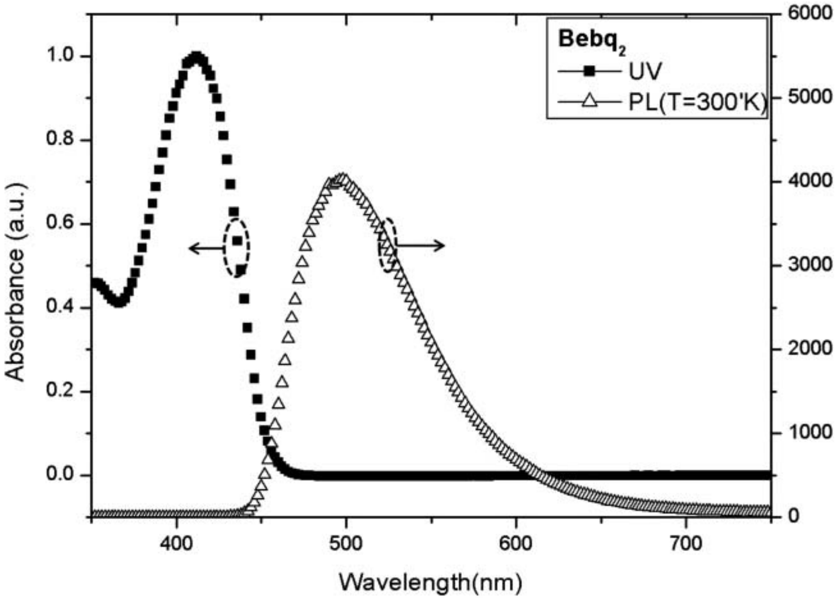

Figure 2. UV-vis absorption and photoluminescence spectra of $Bebq_2$ at 300 °K.

of the singly doped device under the same voltages. Luminous intensities at an applied voltage of 8 V were 12,000 cd/m^2 for the doubly doped device and 6700 cd/m^2 for the singly doped device.

Current efficiency is a convenient parameter to evaluate the electroluminescent characteristics of light emitting devices because it does not greatly depend on the driving voltage. The current efficiency (η) can be calculated by an equation of $\eta = L/J$, if current density-voltage-luminance relationships are known, where L [cd/m^2] and J [A/m^2] are luminance and current density, respectively. Figure 5 represents the current efficiency-luminance curves. Current efficiencies tended to monotonously decrease according to the increase of voltage above a luminance of about 500 cd/m^2. The maximum current efficiency in the doubly doped device was 22.4 cd/A, while 21.5 cd/A in the singly doped device. To our knowledge, the maximum current efficiency of 22.4 cd/A is one of the highest values ever reported in the deep-red PhOLEDs with a central wavelength of more than 620 nm [12,13]. The current efficiencies under a luminance of 10,000 cd/m^2 were 17.3 cd/A for the doubly doped device and 15.8 cd/A for the singly doped device, which resulted in a current efficiency improvement of 10% in the doubly doped device. The doubly doped device also showed the better roll-off characteristics of current efficiency according to the increase of luminance. The overall electroluminescent improvement of the doubly doped device in comparison with the singly doped device is thought to come from the active transfer of energy between $Bebq_2$ and RP411 through the assistant dopant of $(pq)_2Ir(acac)$ with an intermediate energy.

Electroluminescence spectra and CIE color coordinates for the fabricated devices are shown in Figs. 6 and 7. Central wavelengths of electroluminescence spectra were 623 nm for the doubly doped device and 628 nm for the singly doped device as shown in Fig. 6. Considering the peak wavelengths in the photoluminescence spectra of $(pq)_2Ir(acac)$ (604 nm) and RP411 (624 nm), the central wavelength of 623 nm in the electroluminescence spectra of the doubly doped device means that most of light is emitted from triplets

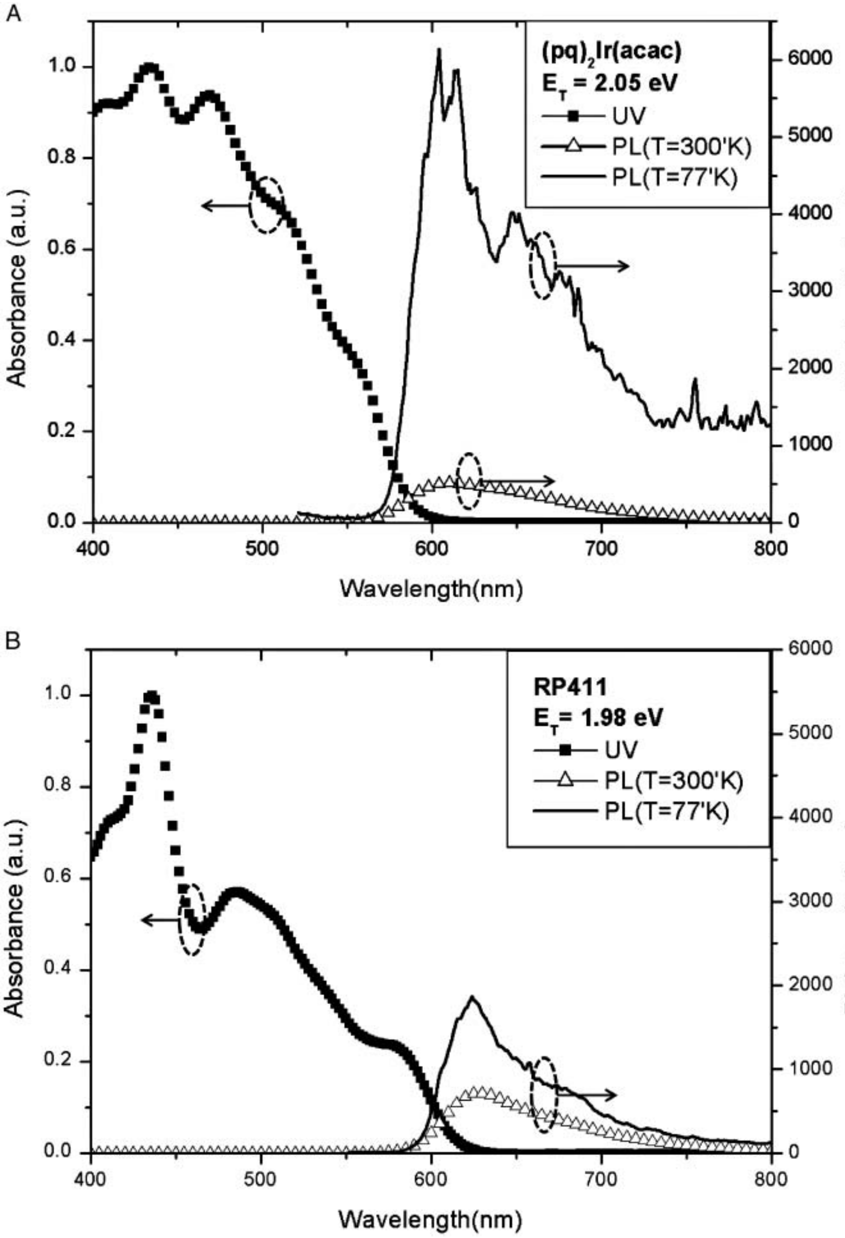

Figure 3. UV-vis absorption and photoluminescence spectra of dopants at 300 °K and 77 °K: (a) $(pq)_2$Ir(acac), (b) RP411.

of RP411 rather than $(pq)_2$Ir(acac). Though the central wavelength of the doubly doped device is shorter by 5 nm than that of the singly doped device, the doubly doped device still gives good deep-red emission with a central wavelength of above 620 nm, showing better characteristics in the luminance and current efficiency than the singly doped one. It is thought that the small reduction of central wavelength in the doubly doped device is due to the partial effect of direct emission from $(pq)_2$Ir(acac). The color coordinates on the CIE

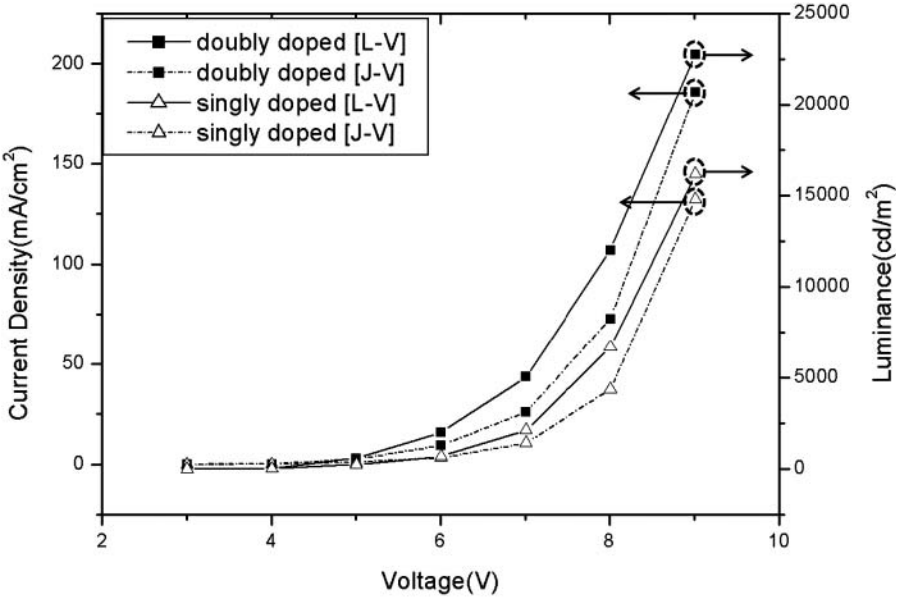

Figure 4. Current density-voltage-luminance characteristics of the doubly doped device (square symbols) and the singly doped device (triangle symbols).

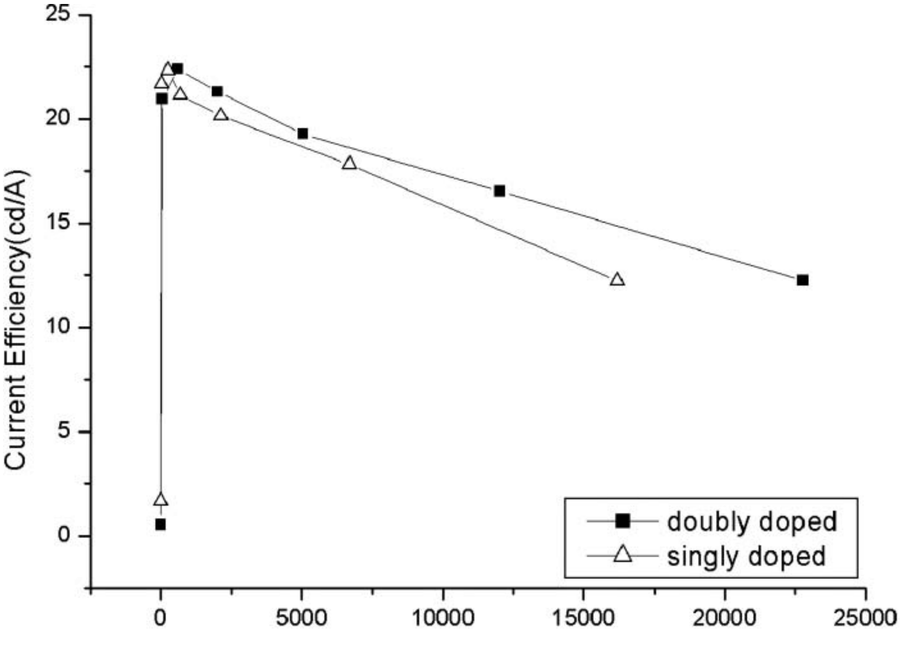

Figure 5. Current efficiency-luminance characteristics of the fabricated devices.

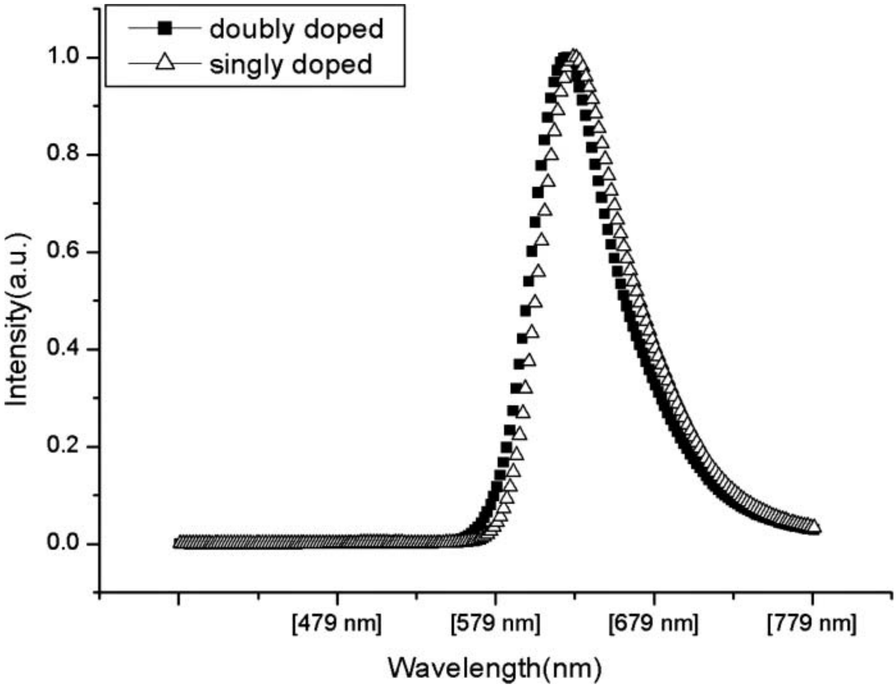

Figure 6. Electroluminescence spectra with deep-red emission.

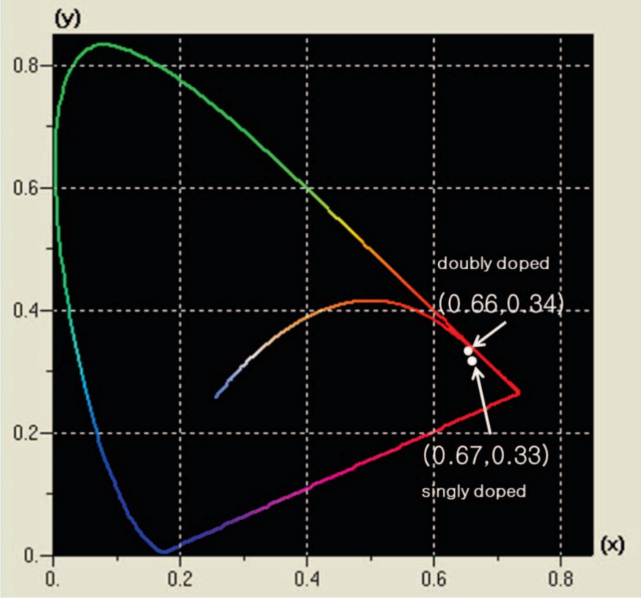

Figure 7. Color coordinates on the CIE chart of the fabricated devices.

chart in Fig. 7 are (0.66, 0.34) for the doubly doped device and (0.67, 0.33) for the singly doped device. The CIE coordinates obtained in the fabricated devices almost coincide with the red standards from the National Television Standards Committee with color purity of more than 90%.

Consequently, the doubly doped device exhibited the good electroluminescent characteristics with deep-red phosphorescent emission even though it was prepared on the PEN substrate. The PEN film has a relative strong resistance to water vapor penetration with a permeability of 2 g/m^2/day for the thickness of 0.1 mm [14]. If the device can be encapsulated well, it will be able to be used as a new high efficiency deep-red light source in a variety of flexible applications.

Conclusions

New high efficiency deep-red PhOLEDs with structure of ITO/DNTPD/TAPC/Bebq$_2$: [(pq)$_2$Ir(acac), RP411]/ET137/LiF/Al on the PEN substrates were fabricated and evaluated.

In this study, two kinds of devices were fabricated in order to investigate the double doping effect in the EML: one has the emitter of Bebq$_2$ doubly doped with (pq)$_2$Ir(acac) and RP411, and the other has the emitter of Bebq$_2$ doped with only RP411.

Though the central wavelength of the doubly doped device was shorter by 5 nm than that of the singly doped one, the doubly doped device showed the current efficiency improvement of 10% under a luminance of 10,000 cd/m^2 compared to the singly doped one. Besides, other electroluminescent characteristics such as luminous intensity and efficiency roll-off were also improved in the doubly doped device compared to the singly doped device.

The well-encapsulated device with organic structure of HTL1/HTL2/DDEML/ETL on a plastic substrate like the doubly doped device in the experiments is expected to be used as a high efficiency deep-red light source in a variety of flexible applications.

References

[1] C. Legnani, C. Vilani, V.L. Calil, H.S. Barud, W.G. Quirino, C.A. Achete, S.J.L. Ribeiro, M. Cremona, *Thin Solid Films*, **517**, 1016, (2008).

[2] H.Y. Low, S.J. Chua, *Materials Letters*, **53**, 227, (2002).

[3] L. Stergios, *Materials Science and Engineering. B*, **152**, 96, (2008).

[4] G. Zhang, H. Guo, Y. Chuai, D. Zou, *Materials Letters*, **59**, 3002, (2005).

[5] M.A. Baldo, C. Adachi, S.R. Forrest, *Phys. Rev. B*, **62**, 10967, (2000).

[6] X.Y. Sun, W.L. Li, M.L. Xu, B. Chu, D.F. Bi, B. Li, Y.W. Hu, Z.Q. Zhang, Z.Z. Hu, *Solid-State Electronics*, **52**, 211, (2008).

[7] J.Y. Lee, *Synthetic Metals*, **157**, 1004, (2007).

[8] S.O. Jung, Y.H. Kim, S.K. Kwon, H.Y. Oh, J.H. Yang, *Organic Electronics*, **8**, 349, (2007).

[9] W.S. Jeon, T.J. Park, K.H. Kim, R. Pode, J. Jang, J.H. Kwon, *Organic Electronics*, **11**, 179, (2010).

[10] Z.Y. Xia, X. Xiao, J.H. Su, C.S. Chang, C.H. Chen, D.L. Li, H. Tian, *Synthetic Metals*, **159**, 1782, (2009).

[11] P.M. Borsenberge, L. Pautmeier, R. Richert, H. Bassler, *J.chem.Phys*, **94**, 12, (1991).

[12] S.O. Jeon, K.S. Yook, C.W. Joo, H.S. Son, S.E. Jang, J.Y. Lee, *Organic Electronics*, **10**, 998, (2009).

[13] C.H. Wu, P.I. Shih, C.F. Shu, Y. Chi, *Appl. Phys. Letters*, **92**, 233303, (2008).

[14] M.C. Choi, Y.K. Kim, C.S. Ha, *Prog. Polym. Sci*, **33**, 581, (2008).