Highly Efficient Simple-Structure Red Phosphorescent OLEDs with an Extremely Low Doping Technology

Woo Sik Jeon[**], **Tae Jin Park**[**], **and Jang Hyuk Kwon**[*]

Abstract

Highly efficient red phosphorescent OLEDs (PHOLEDs) with a simple, organic, triple-layer structure was developed using the narrow-bandgap fluorescent host material bis(10-hydroxybenzo[h] quinolinato)beryllium complex (Bebq$_2$) and the deep-red dopant tris(1-phenylisoquinoline)iridium (Ir(piq)$_3$). The maximum current and power efficiency values of 12.71 cd/A and 16.02 lm/W, respectively, with an extremely low doping technology of 1%, are demonstrated herein. The results reveal a practical, cost-saving host dopant system for the fabrication of highly efficient PHOLEDs involving the simple structure presented herein, with a reduction of expensive Ir dopants.

Keywords: Low doping, energy transfer, phosphorescent OLEDs

1. Introduction

Organic light-emitting diodes (OLEDs) are natural self-emitting devices that have superior properties for diverse display and solid-state lighting applications. High-efficiency phosphorescent OLEDs (PHOLEDs) have generated an intense research interest of late as they have the potential to produce displays and lighting with 100% internal quantum efficiency [1-3]. Some examples of well-known phosphorescent emitters are the iridium (III) and platinum (II) complexes. The iridium (III) complexes have been shown to be the most efficient triplet dopants, employed in highly efficient OLEDs [4, 5]. The doping concentration of these emitters in PHOLEDs is usually very high, about 6-10% weight percentage, compared with about 1% in fluorescent devices. Energy transfer between the host and dopant molecules can occur through either coulombic interactions (long-range interaction) or electron exchange (short-range interaction). The former is called *dipole-dipole* or *Förster-type energy transfer*. Fluorescent devices are

mainly reported to utilize this energy transfer between the host singlet to the dopant singlet. As a result, less than 1% doping is sufficient. The energy transfer from the host triplet to the dopant triplet follows the electron exchange mechanism called "Dexter mechanism." Therefore, a high doping concentration is required in the triplet emitter system. It is well known that the iridium (III) metal complex has a metal-to-ligand charge transfer (MLCT) state. This state has a short (microsecond) lifetime, unlike the general organic triplet state, because of its mixed singlet and triplet characteristics. Therefore, efficient Förster energy transfer from the host singlet and the MLCT state may be possible. The possibility of such Förster energy transfer in PHOLEDs has been reported by Xiong Gong et al. and G. Ramos-Ortiz. et al., based on the solid photoluminescence studies that they conducted, respectively [6, 7]. They reported that the energy transfer in their host dopant system was enough even at a doping condition of below 1%. Real PHOLEDs, however, generally require a doping condition of more than 3% and do not consider the presence of efficient Förster energy transfer in the triplet emitter system. Usually, the host materials in PHOLEDs have a wide bandgap due to the large energy exchange between the singlet and triplet states. Therefore, dopant molecules work as deep trapping sites in such host dopant system. High doping concentrations of over 3% are essential to achieve good carrier movement in PHOLEDs. A narrow-bandgap fluorescent host material, the bis(10-hydroxybenzo[h] quinolinato)beryllium complex

[*] Member, KIDS; [**] Sutdent Member, KIDS
Corresponding author: Jang Hyuk Kwon
Department of Information Display, Kyung Hee University, Dongdaemoon-ku, Seoul 130-701, Republic of Korea
E-mail: jhkwon@khu.ac.kr   **Tel**: +82-2-961-0948

(Bebq$_2$), was recently found. This host molecule has strong fluorescence and small singlet-triplet exchange energy (<0.4 eV). Such narrow-bandgap characteristic is very good for minimizing the charge-trapping issue in the red PHOLEDs. After the application of an orange Ir(phq)$_2$acac dopant in this host, a 1% doping technology and an interesting energy transfer mechanism was reported by these authors [8]. In this study, using this host and a deep-red dopant, tris(1-phenylisoquinoline)iridium (Ir(piq)$_3$), highly efficient deep-red PHOLEDs with an organic triple-layer structure and about 1% doping condition were developed. The energy transfer mechanism was also investigated via fluorescence-quenching studies.

2. Experiment

Red PHOLEDs were fabricated using the organic triple-layer structure ITO/NPB (N,N'-bis(naphthalen-1-yl)-N,N'-bis(phenyl)benzidine) (40 nm)/Bebq$_2$ with the Ir(piq)$_3$ deep-red dopant (30 nm)/Bebq$_2$ (20 nm)/LiF (0.5 nm)/Al (100 nm). The material structures that were used in this study are shown in Fig. 1.

The fabrication of OLED devices began by selecting clean 2.5x2.5-cm glass substrates precoated with a 150-nm indium-tinoxide (ITO) layer and with a sheet resistance of 12 Ohm/□. The ITO glass was cleaned via sonification in isopropylalcohol (IPA) and acetone, then rinsed in deionized water. Finally, it was irradiated in a UV-ozone chamber. All the organic materials were deposited using the vacuum evaporation technique, under ~3.0×10^{-7} Torr pressure. Doping was carried out by co-evaporation from independent sources, and the effusion rates were monitored using a quartz-crystal microbalance. Subsequently, Al with a deposition rate of ~5 Å/s was deposited in a vacuum chamber

without breaking the vacuum, and was used as a cathode. PHOLEDs were fabricated by varying the dopant concentration from 1 to 2%. The current density-voltage (J-V) and luminance-voltage (L-V) data of the PHOLEDs were measured using Keithley SMU 238 and Minolta CS-100A, respectively. The electroluminescence (EL) spectra and CIE color coordinates were obtained using a Photoresearch PR-650 spectroradiometer. The photoluminescence (PL) spectra were measured in thin films using a Jasco FP-6500 spectrofluorometer.

Cyclic-voltammetry experiments were performed using BASi (Bioanalytical Systems, Inc.) analysis equipment (C-3 standard). A platinum wire electrode and 150-nm ITO film on glass were used as counter- and working electrodes, respectively. Silver/silver ion (Ag wire in a 0.1M AgNO$_3$ solution) was used as a reference electrode. The Ag/Ag$^+$ (AgNO$_3$) reference electrode was calibrated at the beginning of the experiments by running cyclic voltammetry on ferrocene as the internal standard. By means of the internal ferrocenium/ferrocene (Fc+/Fe) standard, the potential values were converted to the saturated calomel electrode scale. Experiments were run on the film states of the materials that were used. The films that had been coated with these materials were made on ITO glass through the solution drop coating or thermal-deposition method, and then dried in a vacuum oven at 80°C. A 0.1M Bu$_4$NClO$_4$(tetrabutylammonium perchlorate) electrolyte solution in acetonitrile was used in all the experiments. To confirm the accuracy of the measurements, Alq$_3$ was also measured, and the measured value was compared with the reported results. Alq$_3$ showed a 5.54 eV oxidation potential in the proposed system, which is very similar to the reported value [9]. Solid-state electrochemistry was performed at a scan rate of 150 mV/s, and the starting potential voltage was supplied from 0.5 eV, to reduce the potential damage.
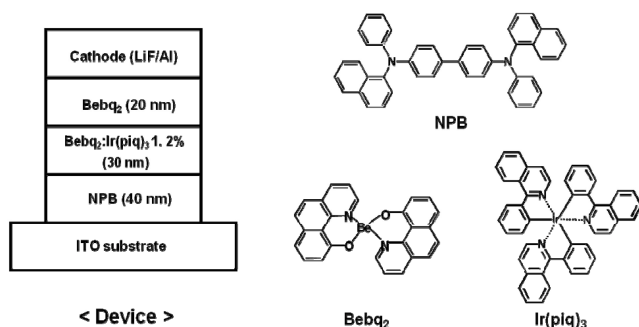
3. Results and Discussion

To determine the HOMO and LUMO energy levels of the organic materials that were used, the optical bandgap was calculated from the absorption spectrum of each material, and cyclic-voltammetry experiments were performed. The ferrocene with 4.8 eV HOMO energy showed an onset oxidation potential at 0 eV in the optimized cyclic-voltammetry system. From the onset voltage of + 0.7 eV oxidation curve, the HOMO energy level of Bebq$_2$ was

Fig. 1. The devices and molecular structures that were used in this study.

estimated to be 5.5 eV. The LUMO energy was found to be 2.8 eV. These values are the same as the previously reported ones [9]. Thus, beryllium complex was found to have a very good LUMO energy level for the easy transfer of electrons from the cathode. It has been reported that the well-known triplet red dopants $Ir(piq)_3$ and $Ir(phq)_2acac$ have HOMO levels of 4.8 eV and 5.1 eV, respectively, as well as triplet energies of 2.2 and 2.4 eV, respectively [10, 11]. According to the measurement values obtained in this study, however, the HOMO energy level of $Ir(piq)_3$ is about 5.1 eV and not 4.8 eV, and its LUMO energy level is 3.1 eV. Therefore, $Ir(piq)_3$ has a triplet energy of about 2.0 eV. The triplet energy of the $Bebq_2$ host was estimated to be 2.2 eV via the triplet sensitization technique, at a low temperature [12]. The triplet phosphorescent dopant of $Ir(phq)_2acac$ was evaluated to have approximately 2.2 eV triplet energy, 5.3 eV HOMO, and 3.1 eV LUMO energy. Both the $Ir(piq)_3$ and $Ir(phq)_2acac$ dopants have triplet energy values that are sufficient for them to receive a triplet energy of the $Bebq_2$ host. Generally, it is well known that characteristics of strong phosphorescences and long triplet lifetimes in organic materials are good for the triplet host. $Bebq_2$, however, has a strong fluorescence emission and shows very good energy transfer characteristics compared to red dopants. This is a very strange phenomenon because strong fluorescent materials show very good host performance. Therefore, Förster energy transfer mechanism from the $Bebq_2$ host to the red dopants was investigated in this study. As shown in Fig. 2, $Ir(piq)_3$ has a higher HOMO energy than $Ir(phq)_2acac$. The hole trapping by the $Ir(piq)_3$ dopant may give rise to phosphorescence emission because of the large energy gap (~0.4 eV) between the HOMO levels of the host and dopant molecules. Such hole-trapping emission mechanism was already reported in these authors' previous papers [13]. In the case of $Ir(phq)_2acac$, as shown Fig. 2(a), the HOMO and LUMO energy gaps are very small (both ~0.2 eV). Moreover, the charge-trapping emission is almost negligible in such host dopant system. As a result, the doping concentration can be minimized, and the device efficiency can be enhanced by reducing the exciton-exciton self-quenching issues.

The efficient Förster energy state from the $Bebq_2$ host to $Ir(phq)_2acac$ and $Ir(piq)_3$ was studied via fluorescent lifetime measurement and quenching experiments in a tetrahydrofuran solution. The Stern-Volmer equation is very good for checking the energy transfer rate. The singlet lifetime of
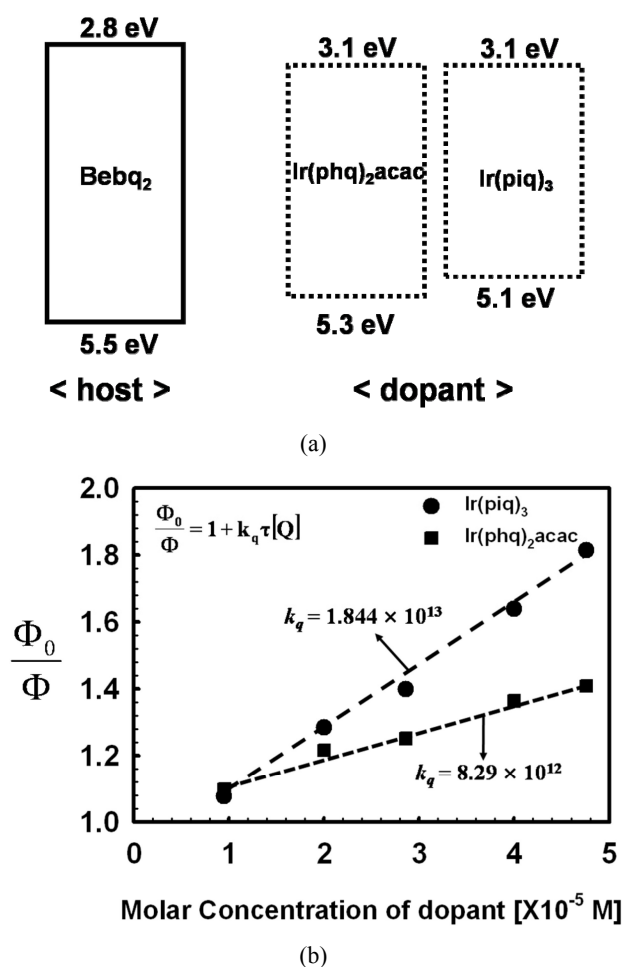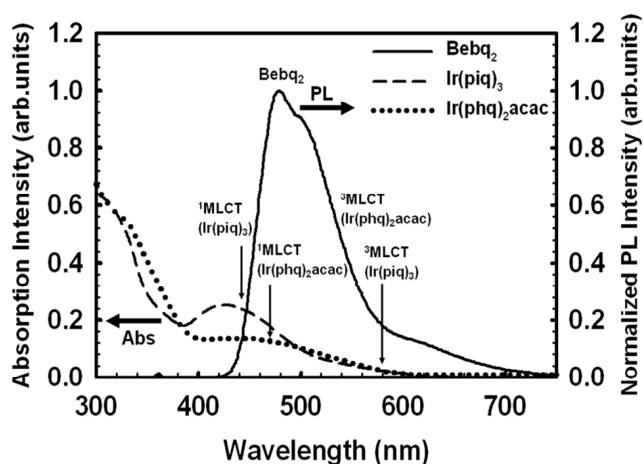

Fig. 2. (a) Energy diagram of the host and dopant materials. (b) Stern-Volmer plot of the $Bebq_2$ fluorescence-quenching by the $Ir(piq)_3$ and $Ir(phq)_2acac$ dopants.

$Bebq_2$ was determined to be 5.0 nsec via time-resolved spectroscopy. In the slope in Fig. 2(b), k_q is 1.8×10^{13} and 8.3×10^{12} $sec^{-1}M^{-1}$, indicating that the energy transfer from the singlet state of the host to the dopant triplet state occurs quantitatively via Förster energy transfer. The energy transfer from the host singlet to the dopant singlet may not be involved in this system because the singlet states of dopants are higher than those the hosts. Furthermore, efficient Förster energy transfer was confirmed via Förster radius measurement. The fluorescent quantum efficiency of $Bebq_2$ is about 0.39, which was determined using the relative PL intensity technique.
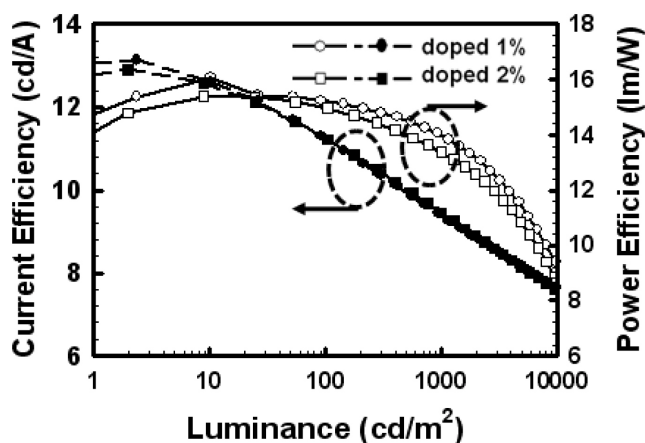
As shown in Fig. 3, the spectrum overlapping between the host emission and the dopant absorption spectra was measured in this study. The MLCT triplet absorptions of the dopants can well overlap with the host emission, indicating good Förster energy transfers. The energy transfer
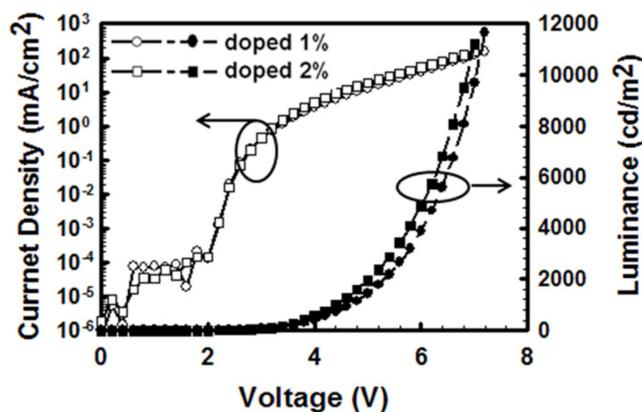
Fig. 3. PL spectrum of Bebq2 and absorption spectrum of Ir(piq)3 and Ir(phq)2acac.

(a)

(b)

Fig. 4. (a) Current-voltage characteristics of red PHOLED 1 and 2. (b) Current and power efficiency characteristics of red PHOLED 1 and 2.

radius was calculated using a Förster energy transfer equation. The radius (R_0) was about 1.3 nm in both dopant cases. These results support efficient Förster energy transfer even though the measurement values are relatively small compared with those in the previous fluorescent-device reports (~3 nm).

In these authors' previous studies, a narrow-bandgap electron-transporting host material for PHOLEDs, Bebq$_2$, with an orange-red dopant of Ir(phq)$_2$acac, was reported [8]. Highly efficient organic, bilayered PHOLEDs with a 1% doping technology were demonstrated in such ideal host-dopant system. When the Ir(piq)$_3$ dopant was used in a Bebq$_2$ host system with the same organic bilayer structure, the doping concentration could not be significantly reduced. This can be attributed to the hole-carrier trappings of the dopant molecules. To overcome such hole trapping, an organic triple-layer structure was designed in this study. The thickness of the emissive layer in the organic bilayer structure was 50 nm, indicating that the emission zone seems to be wide. The charge balance in the organic triple-layer structure is much better, because the emissive layer is only 30 nm thick. The hole-trapping issue may significantly improve in such devices. Therefore, an ITO/NPB (40 nm)/Bebq$_2$: Ir(piq)$_3$ (30 nm)/Bebq$_2$ (20 nm)/LiF (0.5 nm)/Al device structure was employed. To minimize the doping concentration, the concentration of Ir(piq)$_3$ was varied from 2 to 1%. Fig. 4(a) shows the current-voltage characteristics of red PHOLED devices. Red PHOLED 1, with a 1% doping concentration, and red PHOLED 2, with a 2% doping concentration, were made and evaluated. In similar general

charge-trapped devices, J-V improvement was achieved by adding a greater amount of dopants, indicating that hole-carrier trappings existed in the device configuration. The drive voltages required to reach 1000 cd/m^2 are 4.7 V for PHOLED 1 and 4.4 V for PHOLED 2. Fig. 4(b) shows the current and power efficiency performances of red PHOLED 1 and 2. The maximum current and power efficiencies of red PHOLED 1 were found to be 12.71 cd/A and 16.02 lm/W, respectively, and 12.26 cd/A and 15.53 lm/W for red PHOLED 2. At the given constant luminance of 1000 cd/m^2, the current and power efficiency values of red PHOLED 1 were found to be 11.37 cd/A and 7.77 lm/W, respectively, and 10.92 cd/A and 7.79 lm/W for red PHOLED 2. The efficiency was maximized at the 1% doping condition. The color coordinates of these devices were found to be (0.66,

0.33) and (0.67, 0.32) for 1.0 and 2.0%, respectively. Even in the 0.5%-doped device, a good red color was observed. It was found, however, that the 0.5% doping condition shows some host emissions. It is thus concluded that 0.5% doping is not a sufficient condition for the doping concentration.

Interesting and intriguing results regarding the performance of red PHOLEDs with an organic triple-layer structure and 1% doping condition were obtained in this study. The LUMO level of the $Bebq_2$ material (2.8 eV), which is very close to the LUMO level of the LiF cathode (2.9 eV), offers almost no barrier to the electron injection between the emitting layer and the LiF cathode. Furthermore, the excellent electron-transporting property of the $Bebq_2$ material favors the mobility of electrons, which provides a good charge balance in the emitting layer. The HOMO levels of the $Bebq_2$ host and the NPB hole transport layer in the fabricated devices are very close, and the LUMO energy levels of the host and the dopant are almost the same. Therefore, the emission process in PHOLEDs via hole trapping at HOMO are optimized. High-efficiency characteristics are obtained by reducing exciton self-quenching and minimizing the hole-trapping zone.

4. Conclusion

Highly efficient red PHOLEDs with a simple, organic, triple-layer structure and a low (1%) doping condition was demonstrated herein. Efficient Förster energy transfer from the host singlet to the metal-to-ligand charge transfer (MLCT) state of the Ir complex was also realized in phosphorescent devices. This simple structure with a low doping technology is very useful for designing an efficient host-dopant system and for the fabrication of highly efficient PHOLEDs. In addition, this technology is very useful for saving manufacturing costs through a simple structure with reduced expensive Ir dopants.

References

[1] X. Gong, J.C.Ostrowski, D. Moses, G.C. Bazan, and A.J. Heeger, App. Phys. Lett. **81**, 3711 (2002).

[2] T. Tsuzuki, N. Shirasawa, T. Suzuki, and S. Tokito, Adv. Mater. **15**, 1455 (2003).

[3] C. Adachi, M.A. Baldo, S.R. Forrest, and M.E. Thompson, App. Phys. Lett. **77**, 904 (2000).

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

[5] C. Adachi, M.A. Baldo, M.E. Thompson, and S.R. Forrest, J App. Phys. **90**, 5045 (2001).

[6] X. Gong, J.C. Ostrowski, D. Moses, G.C. Bazan, and A.J. Heeger, Adv. Funct. Mater. **13**, 439 (2003).

[7] G. Ramos-Ortiz, Y. Oki, B. Domercq, and Kippelen, Phys. Chem. Chem. Phys. **4**, 4109 (2002).

[8] W. S. Jeon, T. J. Park, S. Y. Kim, R. Pode, , J. Jang, and J. H. Kwon, Organic Electronics **10**, 240 (2009).

[9] S. W. Liu, C. A. Huang, J. H. Lee, K. H. Yang, C. C. Chen, and Y. Chang, Thin Solid Films., **453**, 312 (2004).

[10] B. D. Chin, M. C. Suh, M. H. Kim, S. T. Lee, H. D. Kim, and H. K. Chung, Appl. Phys. Lett., **86**, 133505 (2005).

[11] T.-H. Kim, H. K. Lee, O. O. Park, B. D. Chin, S.-H. Lee, and J. K. Kim, Adv. Funct. Mater., **16**, 611 (2006).

[12] T. Tsuboi , W. S. Jeon , and J. H. Kwon, Optical Materials, in press (2009).

[13] T. J. Park, W. S. Jeon, J. J. Park, S. Y. Kim, Y. K. Lee, J. Jang, R. Pode, and J. H. Kwon, Appl. Phys. Lett. **92**, 113308 (2008).