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Solution Processed Red Phosphorescent Organic Light-Emitting Diodes with Green Phosphorescent Ir Sensitizer

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We fabricated the organic light-emitting diodes (OLEDs) with sensitizer by solution process. The addition of sensitizer into the emission layer improved the device efficiency. 4,4′-N,N′-dicarbazole-biphenyl (CBP), bis(2-phenylquinoline) iridium(III) (acetylacetonate) [Ir(pq)$_2$(acac)], tris(2-phenylpyridine)iridium [Ir(ppy)$_3$] were used as host, red emitting dopant, and sensitizer, respectively. The sensitizer leads to the cascade energy transfer from the host into the red emitting dopant. The doping concentration of sensitizer was varied as 0∼20 wt% and optimized. As a result, the device with 5% Ir(ppy)$_3$ shows the luminous efficiency, power efficiency, and quantum efficiency of 5.1 cd/A, 4.0 lm/W, and 3.0%, respectively. These efficiencies are about 3 times as high as that of device without sensitizer.

Keywords Cascade energy transfer; organic light-emitting diode; sensitizer

1. Introduction

Organic light-emitting diodes (OLEDs) have been widely recognized as a technology for flat-panel displays due to their low-voltage operation, wide-viewing angle, high contrast, and mechanical flexibility [1]. The development of the first organic material emitting visible light in multilayered structure when a bias voltage was applied on the structure by Tang and coworkers [2–3], had stimulated the research in OLEDs and emitting materials [4–5]. In a typical fluorescent OLEDs system, triplet states constitute 75% of electro-generated excited states. These triplet states are generally non-emissive due to their spin-forbidden nature for radiative relaxation to the ground states. Consequently, the maximum internal quantum efficiency of the fluorescent OLEDs is normally limited to 25%. To remove such constraint, efforts have been directed to using electrophosphorescent materials incorporating complexes of

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third-row transition metal elements [6–8]. The strong spin-orbit coupling caused by heavy metal ions in these complexes results in efficient intersystem crossing from the singlet to the triplet excited state. The mixing of the singlet and triplet excited states removes the spin-forbidden nature of the radiative relaxation of the triplet state. Therefore, the phosphorescent OLEDs can theoretically obtain the 100% internal quantum efficiency. However, the phosphorescent OLEDs lead to the Triplet-triplet (T-T) annihilation at the highly applied voltage because the triplet state has the relatively long radiative decay lifetime in general. The occurrence of T-T annihilation decreases the performance of a phosphorescent material, particularly its maximum brightness and luminous efficiency at high currents. Thus, in order to improve the efficiency of phosphorescent OLEDs, this problem must be solved. We have reported that the heteroleptic iridium complexes can suppress the T-T annihilation and improve the device efficiency [9–12]. For example, the ppy ligand of the heteroleptic iridium complex, $Ir(ppy)_2$(dpq-3 F) (ppy = 2-phenylpyridine, dpq-3 F = 2-(3--fluorophenyl)-4-phenylquinoline), were used as sensitizer. The sensitizer ligand extends the space that exciton is formed and leads to the efficient inter-ligand energy transfer (ILET). On the other hand, in this paper, we used the phosphorescent homoleptic iridium complex, $Ir(ppy)_3$, as sensitizer, which suppressed the T-T annihilation of red phosphorescent emitting material, $Ir(pq)_2$(acac). These devices were fabricated by solution process that exhibit promising potentials for the low-cost and large-area flat panel display technology. The solution process is very proper method to fabricate the device with iridium complex, $Ir(ppy)_3$, as sensitizer because the blending of complexes is very easy and simple, while the heteroleptic iridium complexes with sensitizing effect is proper to the thermal evaporation process due to the difficult doping process is unnecessary.

2. Experiments

Indium tin oxide (ITO) coated glass with resistance of 30 Ω/sq was cleaned in an ultrasonic bath by following sequence: in acetone, methanol, diluted water and isopropyl alcohol. Thereafter, pre-cleaned ITO was treated by O_2 plasma with the power conditions of 125 W for 2 min under low vacuum of 2×10^{-2} torr. After the pre-treatment of ITO, We fabricated the devices with a structure of ITO (180 nm)/poly(ethylendioxy thiophene):poly(styrene sulfonic acid) (PEDOT:PSS) (~40 nm)/4,4′-N,-,N′-dicarbazole-biphenyl (CBP): 8 wt% bis(2-phenylquinoline) iridium(III)(acetylacetonate) [$Ir(pq)_2$(acac)]: × wt % tris(2-phenylpyridine)iridium [$Ir(ppy)_3$] (~50 nm)/BPhen (10 nm)/ET137 (30 nm)/lithium quinolate (Liq) (2 nm)/aluminum (Al) (100 nm). PEDOT:PSS, BPhen, and Liq/Al were used as hole transporting layer, hole blocking layer, and cathode, respectively. ET137 is new electron transporting layer supplied from SFC Co., Ltd. [13]. CBP, $Ir(pq)_2$(acac), and $Ir(ppy)_3$ consisting of the emission layer were used as host, red emitting dopant, and sensitizer, respectively, where the concentration of $Ir(ppy)_3$ was varied from 0 wt% to 20 wt%. In order to form the PEDOT:PSS layer on the pre-cleaned ITO, it is spin-coated with 3000 rpm for 60 s and baked at 120°C for 30 min in vacuum oven. The emission layer was also spin-coated from the chloroform (CH_2Cl_2) solution with 0.21 wt% solute. The solution was coated onto the PEDOT:PSS layer at 3000 rpm for 60 s. Then, it was baked at 60°C for 20 min in vacuum oven. The other layers were deposited by thermal evaporation process for the efficient electron injection and transport except for the PEDOT:PSS and emission layers. The device configuration is shown in the Figure 1(a).

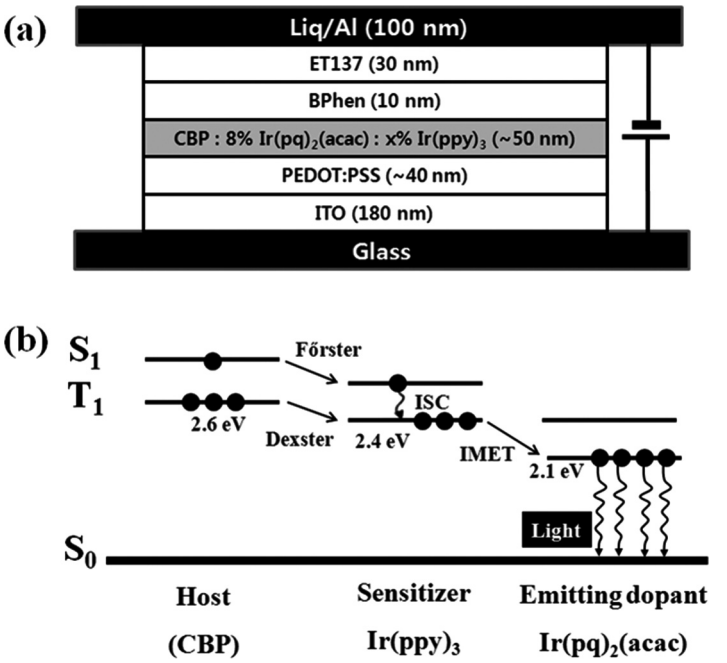

Figure 1. (a) Configuration of the devices fabricated in this study. (b) Emission mechanism of the red OLEDs with sensitizer.

The photoluminescence (PL) spectra and UV-Vis. absorption spectra of the iridium complexes, $Ir(pq)_2(acac)$ and $Ir(ppy)_3$, were measured on a Perkin Elmer LS 50B spectrometer and Hewlett Packard 8425A spectrometer, respectively. The iridium complexes were measured in 10^{-5} M dilute chloroform solution. Moreover, the optical and electrical properties of the devices such as the current density, luminance, luminous efficiency, CIE coordinates and electroluminescence (EL) spectra characteristics were measured with Keithley 237 and CHROMA METER CS-1000 instruments, respectively. All measurements were carried out under ambient conditions at room temperature with the DC voltage bias. The emitting area of device is 3 mm × 3 mm.

3. Results and Discussion

We used the phosphorescent iridium complex, $Ir(ppy)_3$, as sensitizer in red phosphorescent OLEDs. We expected that $Ir(ppy)_3$ leads to the sensitizing effect between the CBP and $Ir(pq)_2(acac)$. It is because the triplet energy level (T_1) of $Ir(ppy)_3$ is higher than T_1 of $Ir(pq)_2(acac)$ as shown in Figure 1(b) and because the energy transfer time from $Ir(ppy)_3$ to $Ir(pq)_2(acac)$ is shorter than the radiative decay lifetime of $Ir(ppy)_3$. It has known that the energy transfer time from a one excited triplet state to the other excited triplet state is within ns time scale, while the radiative decay lifetime of iridium complex is μs time scale. Therefore, we also expected that the device with sensitizer shows the monochromatic luminescent color from $Ir(pq)_2(acac)$. The sensitizing mechanism is shown in Figure 1(b). Firstly, the excitons are formed on the excited state of CBP and the excitons are rather dominantly transferred into the

excited state of $Ir(ppy)_3$ than the excited state of $Ir(pq)_2(acac)$ because the excited state of CBP is closer to the excited state of $Ir(ppy)_3$ than that of $Ir(pq)_2(acac)$. Secondly, the excitons located on the singlet excited state (S_1) of $Ir(ppy)_3$ are transferred into the T_1 of $Ir(ppy)_3$ by inter-system crossing (ISC). Finally, the excitons existed on T_1 of $Ir(ppy)_3$ are transferred into the T_1 of $Ir(pq)_2(acac)$ by the inter-molecular energy transfer (IMET) and then they are decayed with red emission of $Ir(pq)_2(acac)$. The sensitizer can suppress the T-T annihilation occurred at T_1 of emitting iridium complex, $Ir(pq)_2(acac)$, due to this cascade energy transfer and improve the device efficiency. It was proved by analyzing the electrical characteristics of devices with various sensitizer concentration. Figure 2 and the inset of the Figure 2 show the luminance *vs* current density and current density *vs* voltage properties, respectively. The Luminance is changed as $Ir(ppy)_3$ ratio is varied, while the current density flow of all devices is similar regardless of the $Ir(ppy)_3$ ratio. It proves that the addition of $Ir(ppy)_3$ has influence on the emission. The devices with $Ir(ppy)_3$ of 0%, 5%, 10%, 15%, and 20% have the luminance of 2168 mA/cm^2, 2792 mA/cm^2, 4481 mA/cm^2, 3235 mA/cm^2, and 2165 mA/cm^2, respectively, at the applied voltage of 8 V. The luminance of devices with $Ir(ppy)_3$ is higher than that without $Ir(ppy)_3$ at the same current density as shown in Figure 2, except for the device with 20% $Ir(ppy)_3$. This fact reflects that the carriers injected from the electrodes can be transformed into the relatively much more light under the existence of sensitizer. In other words, the cascade energy transfer by sensitizer allows that the excitons are spatially extended and are relatively became free from the T-T annihilation occurred at the excited state of $Ir(pq)_2(acac)$. However, the luminance of device is rather reduced when $Ir(ppy)_3$ is doped more than 10% due to concentration quenching of $Ir(ppy)_3$. It is because that the high doping concentration of sensitizer as well as emitting dopant affects the T-T annihilation of Ir phosphorescence. Therefore, the sensitizing effect is optimized with 10% $Ir(ppy)_3$. The efficiency tendencies of devices are same with luminance tendency of devices and the device with 10% $Ir(ppy)_3$ have the best efficiency. Figure 3, inset of Figure 3, and Figure 4 show the luminous efficiency, power efficiency, and quantum

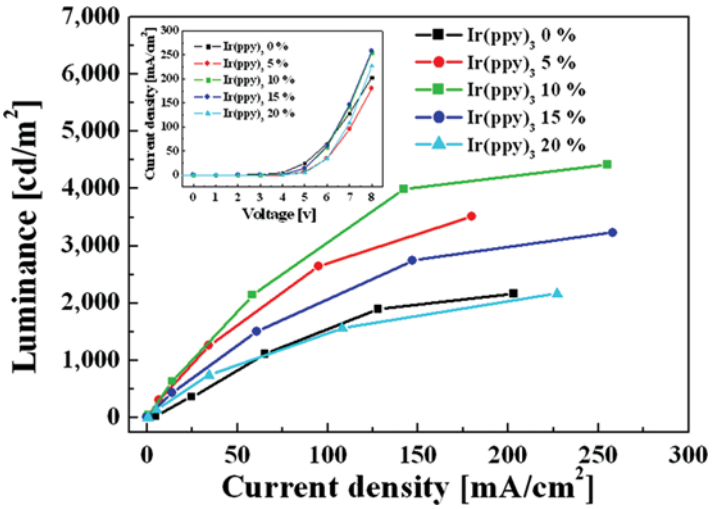

Figure 2. Luminance *vs* current density (inset; current density *vs* voltage) curves of devices with various sensitizer concentration.

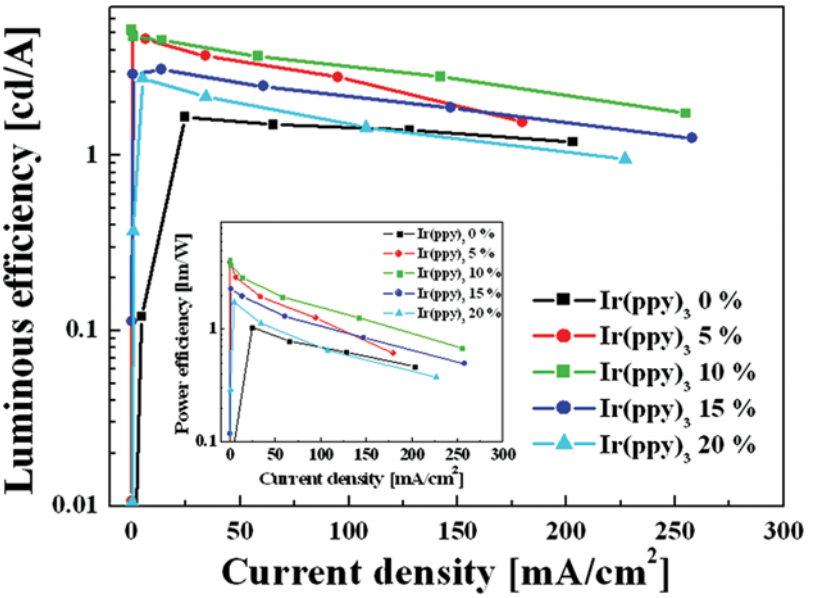

Figure 3. Luminous efficiency (inset; power efficiency) of the devices with various sensitizer concentration as increase of the current density.

efficiency of the devices with various $Ir(ppy)_3$ concentration, respectively, as increase of current density. The devices show the max. luminous efficiency of 1.7 cd/A, 5.1 cd/A, 5.2 cd/A, 3.1 cd/A, and 2.8 cd/A, the max. power efficiency of 1.1 lm/W, 4.0 lm/W, 4.1 lm/W, 2.3 lm/W, and 1.8 lm/W, and the max. quantum efficiency of 1.0%, 3.1%, 3.2%, 1.9%, and 1.7% for the devices with $Ir(ppy)_3$ of 0%, 5%, 10%, 15%, and 20%, respectively. As a result, we could confirm that the device efficiency

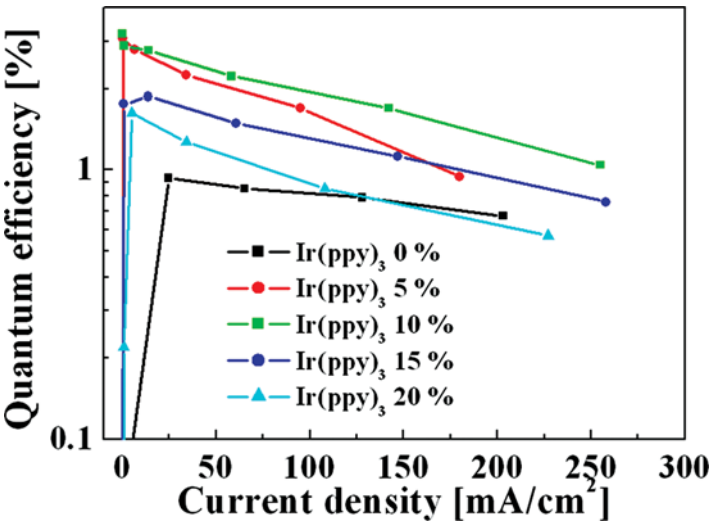

Figure 4. Quantum efficiency of the devices with various sensitizer concentration as increase of the current density.

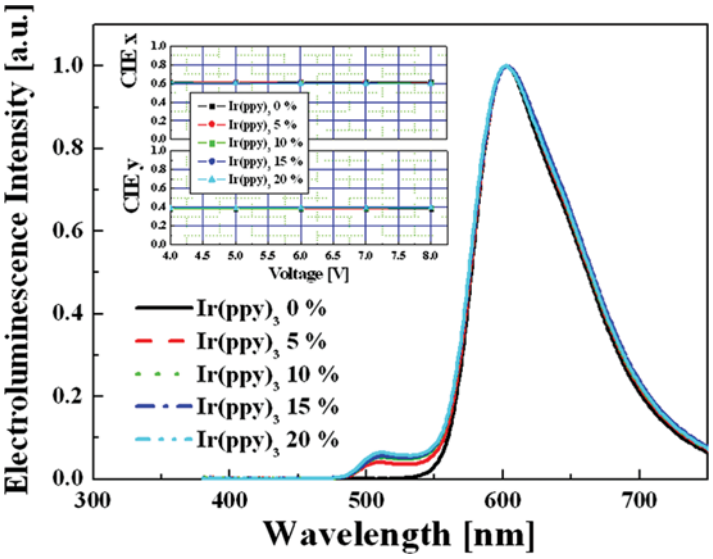

Figure 5. Electroluminescence (EL) spectra (inset; CIE coordinates) of the devices with various sensitizer concentration.

can be improved to about 3 times by using the sensitizer. On the other hand, the electroluminescence (EL) spectra and CIE coordinates of devices are shown in Figure 5 and the inset of Figure 5, respectively. The CIE coordinates of all devices is $(0.60 \pm 0.01,\ 0.38 \pm 0.01)$ regardless of the ratio of $Ir(ppy)_3$ and applied voltage as shown in the inset of Figure 5. Although the devices with $Ir(ppy)_3$ have very weak emission peak at about 510 nm due to $Ir(ppy)_3$, all devices have strong emission peak

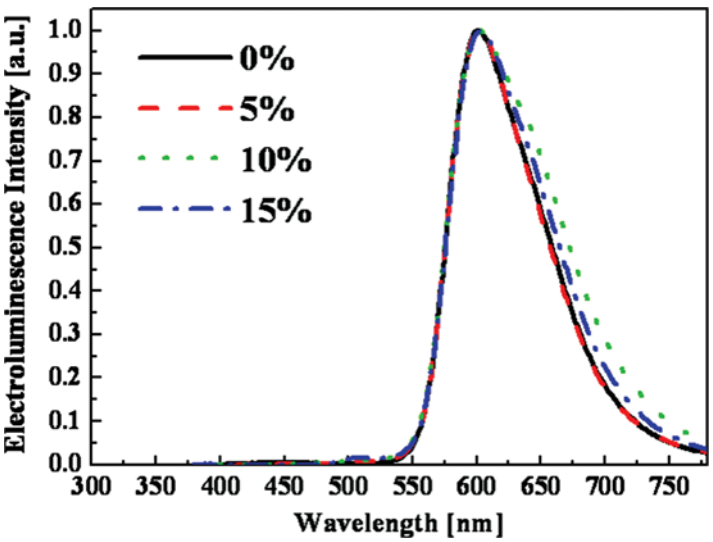

Figure 6. Photoluminescence (PL) spectra of CBP: 8% $Ir(pq)_2(acac)$: ×% $Ir(ppy)_3$ in 10^{-5} M dilute chloroform solution.

at about 605 nm due to $Ir(pq)_2(acac)$ as our expectation. Moreover, Figure 6 shows photoluminescence (PL) spectra of CBP: 8% $Ir(pq)_2(acac)$: × % $Ir(ppy)_3$ in 10^{-5} M dilute chloroform solution. The PL spectra are similar with EL spectra, which proves the strong red emission peaks in EL are due to $Ir(pq)_2(acac)$ and the weak green emission peaks in EL are due to $Ir(ppy)_3$ not exciplex occurred at the interface of device.

4. Conclusions

The red emitting OLEDs with sensitizer, $Ir(ppy)_3$, was fabricated by solution process. As a results, we demonstrated that the sensitizer added into the emission layer improves the device efficiency because the sensitizer allows the cascade energy transfer from the host, CBP, into the red emitting dopant, $Ir(pq)_2(acac)$. The high doping of $Ir(ppy)_3$ leads to the concentration quenching and device are optimized with 10% $Ir(ppy)_3$. The efficiencies of optimized device are about 3 times as high as that of device without sensitizer. We consider that the using phosphorescent sensitizer is very suitable in solution process and these results are helpful to the low-cost and large-area flat panel display technology.

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References

[1] Lee, H. K., Seo, J. H., Kim, J. H., Koo, J. R., Lee, K. H., Yoon, S. S., & Kim, Y. K. (2006). *J. Korean Phys. Soc.*, *49*, 1052.
[2] Tang, C. W., & Van Slyke, S. A. (1987). *Appl. Phys. Lett.*, *51*, 913.
[3] Baldo, M. A., Thompson, M. E., & Forrest, S. R. (2000). *Nature*, *403*, 750.
[4] Lamansky, S., Djurovich, P., Murphy, D., Abdel-Razzaq, F., Kwong, R., Tsyba, I., Bortz, M., Mui, B., Bau, R., & Thompson, M. E. (2001). *Inorg. Chem.*, *40*, 1704.
[5] Lamansky, S., Djurovich, P., Murphy, D., Abdel-Razzaq, F., Lee, H. E., Adachi, C., Burrows, P. E., Forrest, S. R., & Thompson, M. E. (2001). *J. Am. Chem. Soc.*, *123*, 4304.
[6] Baldo, M. A., Thompson, M. E., & Forrest, S. R. (1999). *Pure Appl. Chem.*, *71*, 2095.
[7] Thompson, M. E., Burrows, P. E., & Forrest, S. R. (1999). *Curr. Opin. Solid State Mater. Sci.*, *4*, 369.
[8] Kohler, A., Wilson, J. S., & Friend, R. H. (2002). *Adv. Mater.*, *14*, 701.
[9] Seo, J. H., Lee, S. C., Kim, Y. S., & Kim, Y. K. (2007). *Mol. Cryst. Liq. Cryst.*, *471*, 305.
[10] Seo, J. H., Park, G. Y., Kim, Y. K., & Kim, Y. S. (2007). *Mol. Cryst. Liq. Cryst.*, *471*, 313.
[11] Seo, J. H., Kim, Y. K., & Ha, Y. (2009). *Thin Solid Films*, *517*, 1807.
[12] Seo, J. H., Lee, S. C., Kim, Y. K., & Kim, Y. S. (2009). *Thin Solid Films*, *517*, 4119.
[13] Jung, H. C., Lee, K. H., Seo, J. D., Park, C. G., Bin, J. K., Pi, S. H., & Kim, J. K. (2009). KR Patent No. 10-0747311.