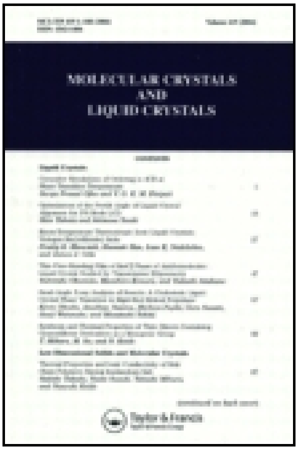

Molecular Crystals and Liquid Crystals

Charge Trapping Effect in Phosphorescent Organic Light-Emitting Diodes

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Charge Trapping Effect in Phosphorescent Organic Light-Emitting Diodes

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Charge trapping in phosphorescent light emitting diodes was investigated by changing doping concentration of phosphorescent emitting material in light emitting layer. In red phosphorescent devices, both hole and electron trapping had the same effect on charge injection, while in green devices hole trapping played a major role in determining charge injection. In blue devices, hole or electron trapping effect was not observed. In addition, the efficiency of red and green devices could be improved by graded doping structure due to high luminance at the same driving voltage.

Keywords: charge trapping; graded doping structure; phosphorescent organic light emitting diodes

INTRODUCTION

There have been many models to explain the charge injection and transport of organic light emitting diodes (OLED). Schottky emission and tunnel or field emission have been suggested as the mechanism for injection limited current flow model [1–3], and space charge limited current flow model, trap limited current flow model, and ohmic contact have been proposed as the mechanism for bulk limited current flow model for OLEDs [4–7]. These models could successfully describe the charge injection and conduction in the devices. For the emission mechanism, charge trapping and energy transfer models have been used to explain the light emission in the doped light emitting layer [5,6,8–10]. Charge trapping model assumes that the dopant acts as a trap site which can capture electron or hole [5,6,10]. The trapped charge is

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ionized and recombine with charge carriers with opposite charge, forming an exciton which can contribute to light emission. In this mechanism charge carriers are directly trapped at dopant site and the dopant is the center for the recombination and emission. The charge trapping mechanism is usually observed when there is a large energy barrier for charge injection from a charge transport layer to a host material. The other model for light emission is energy transfer model, in which light emission from dopant is originated from energy transfer from host to dopant [8,9]. The exciton is formed in the host material and then the exciton is transferred from host to dopant material. The two light emitting mechanisms are different in that exciton formation center is dopant for the charge trapping model and host for the energy transfer model. Both mechanisms contribute to the light emission and compete each other depending on the device structure and energy level of the organic material in the devices.

Based on the mechanism suggested above, several different device structures have been developed to improve the efficiency and lifetime of OLEDs. Graded polymer phosphorescent devices were fabricated by thermal dye diffusion method [11] and a graded mixture of different types of light emitting layer (EML)s was also effective to improve the lifetime of the devices [12].

In this work, light emission mechanism of phosphorescent OLEDs was investigated using graded device structure. The light emission of red, green and blue phosphorescent devices was compared and correlated with energy levels of organic materials. In addition, the efficiency of phosphorescent OLEDs was also correlated with device structures.

EXPERIMENTAL

Standard OLED configuration used in this experiment was ITO (150 nm)/NPB(50 nm)/CBP:dopant(30 nm)/Balq(5 nm)/Alq_3(25 nm)/LiF(1 nm)/Al(200 nm). Four different device structures were fabricated to study charge trapping effect in the emission layer. Figure 1 shows the four different device configurations for this experiment. A standard device has uniform doping concentration over the whole light emitting layer, while device I has high doping concentration near hole transport layer(HTL) and low doping concentration near electron transport layer(ETL). Device II has high doping concentration only at EML-ETL interface, while device III has high doping concentration both at HTL-EML and EML-ETL interface. Same device structures were used for red, green and blue colors except for dopant materials. ITO Glass substrate was a product of Samsung Corning Co. and ITO thickness was 150 nm. N, N′-di(1-naphthyl)-N,N′-diphenylbenzidine(NPB) was

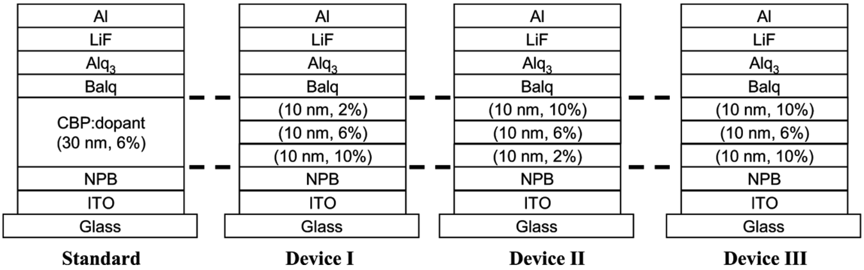


FIGURE 1 Four different device configurations for graded devices

used as a hole injection and hole transport material and light emitting material was a mixture of (4,4′-N,N′-dicarbazole)biphenyl(CBP) and tris(2-phenylpyridine) Iridium($Irppy_3$) for green, tris(1-phenylisoquinolinato) iridium($Irpiq_3$) for red, and bis(2-(4,6-difluorophenyl)pyridyl) iridium picolinate (FIrpic) for blue. Chemical structures of phosphorescent dopant materials are shown in Figure 2. Biphenoxy-bi(8-hydroxy-3-methylquinoline) aluminum(Balq) was a hole blocking material and electron transport material was tris(8-hydroxyquinoline) aluminium (Alq_3). LiF/Al double layer was used as a cathode system. Glass substrates were cleaned with acetone and isopropyl alcohol in an ultrasonic bath for 15 min respectively and were dried at 120°C for 2 hr before use. The ITO glass was exposed to UV-ozone for 10 min for surface treatment and the glass substrate was transferred to evaporation chamber. NPB was evaporated at a thickness of 50 nm as a hole transport layer and CBP:$Irppy_3$ phosphorescent light emitting layer was evaporated at a thickness of 30 nm and doping concentration was 6%. Balq thickness was 5 nm and Alq was formed at a thickness of 25 nm. LiF thickness was 1 nm and Al was evaporated at a thickness

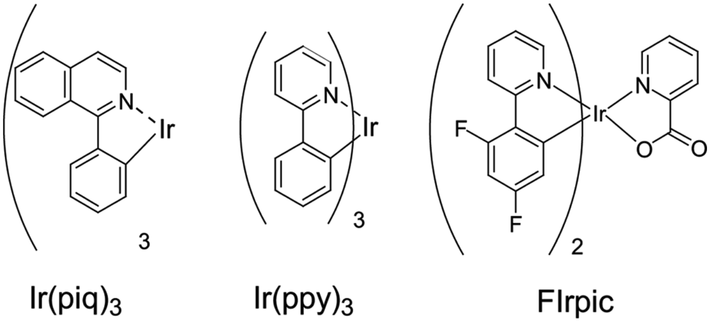


FIGURE 2 Chemical structures of dopant materials

of 200 nm. Organic materials were deposited at a base pressure of 5×10^{-7} Torr at a rate of 1 Å/s. Devices were encapsulated with glass lids after metal deposition. Current density-voltage-luminance (I-V-L) characteristics of the devices were measured with PR 650 spectrometer and energy level of organic materials was measured by surface analyzer (Riken-Keiki AC2).

RESULTS AND DISCUSSION

I-V-L characteristics of the four devices with different device configurations were measured to study the effect of graded doping profile on current injection in phosphorescent OLEDs. Figure 3 shows I-V-L performances of red devices with different doping profile in light emission layer. In red devices, device III which has high doping concentration both at HTL-EML and EML-ETL interfaces showed high luminance and efficiency value compared with other devices. The luminance and efficiency of device I and device II were not changed greatly by doping profile. This behavior can be explained by charge trapping at dopant materials in light-emitting layer. If energy transfer process dominates light emission, there should be little change of luminance depending on doping concentration in light-emitting layer. The high luminance value in device III with high doping concentration both near HTL and ETL indicates that charge is trapped by dopant materials rather than it is transferred to host material. In energy transfer mechanism, doping concentration cannot greatly contribute to charge injection in the device because holes and electrons are injected to host material. The moderate luminance value in device I and device II is due to low charge density in light-emitting layer with low doping concentration. In device I, even though the hole injection to EML is facilitated by charge trapping through highly doped EML, the electron injection to EML is retarded because less charge is trapped by dopant material and the hopping of the electrons between dopant sites is also difficult at low doping concentration. In device II, slow hole injection to EML affects the whole charge flow in the device in spite of efficient electron injection from ETL. In other words, hole and electron trapping mechanisms dominate light emission in red phosphorescent devices. The origin for the hole and electron trapping in red devices can be found in energy level of host and dopant materials. Energy level diagram of the HTL, EML, and ETL materials is summarized in Figure 4. The highest occupied molecular orbital (HOMO) levels of HTL, host, and red dopant materials are 5.5 eV, 5.9 eV, and 5.2 eV respectively. There is an energy barrier of 0.7 eV for the hole injection from HTL to host material, while there is no energy barrier for hole injection to dopant material. Therefore, holes

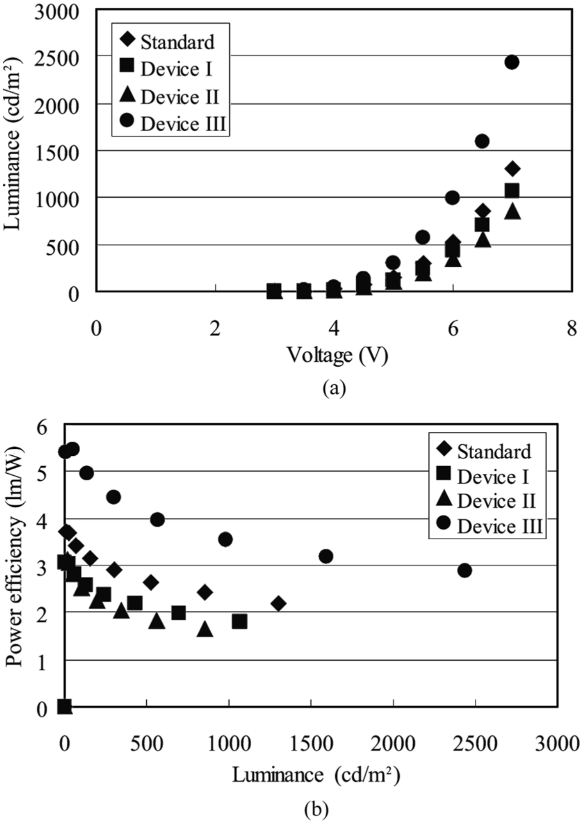


FIGURE 3 Current density-voltage-luminance performances of red phosphorescent devices. (a) Luminance-voltage and (b) power efficiency-luminance.

are directly trapped to dopant materials rather than they are injected to host material because HOMO level of dopant materials is stabilized by 0.7 eV compared with that of host. The same explanation can be applied for electron injection from ETL to EML. The LUMO level difference between host and dopant is 0.6 eV and the energy barrier for electron injection from ETL to host is 0.3 eV, while there is no energy barrier for electron injection from ETL to dopant material. Therefore, the electrons are also directly trapped to dopant sites. The charge trapping effect of the dopant material has also positive effect on device efficiency because driving voltage of OLEDs can be lowered by spatial doping. The power efficiency of the graded devices with high doping concentration at HTL-EML or EML-ETL interface was improved by 50% compared with that of simple device with uniform doping concentration.

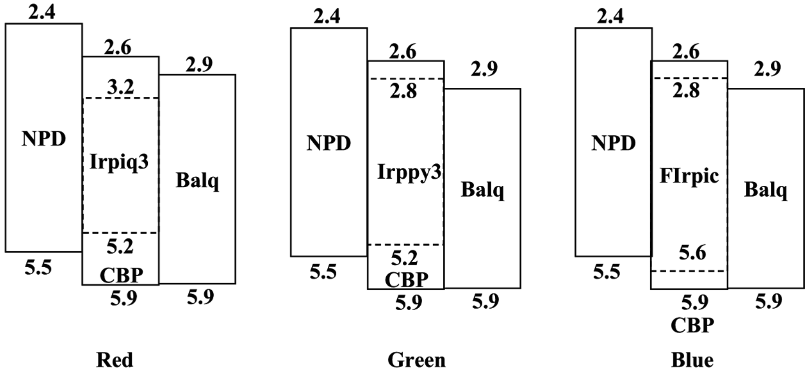
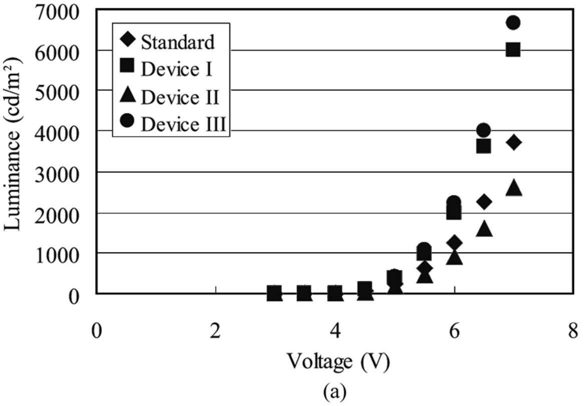


FIGURE 4 Energy level diagram of red, green and blue phosphorescent devices.

Green devices showed different I-V-L characteristics compared with red devices (Fig. 5). Graded devices with high doping concentration at HTL-EML interface showed higher luminance value than conventional devices, but the device with high doping concentration only at EML-ETL interface showed lower luminance value than conventional device. High luminance value in the devices with high doping concentration at HTL-EML interface indicates high hole trapping effect in green phosphorescent devices, while there is no electron trapping effect observed for green devices because there is no luminance increase in the devices with high doping concentration at EML-ETL interface. This behavior is closely related to the HOMO and LUMO level of green dopant materials. HOMO level of $Irppy_3$ is 5.2 eV and the energy gap between CBP and $Irppy_3$ is 0.7 eV, while the LUMO level of $Irppy_3$ is 2.8 eV and energy gap between CBP and $Irppy_3$ is only 0.3 eV. Therefore, holes injected from HTL layer can be trapped to dopant sites due to large energy barrier for hole injection to CBP, while electrons injected from ETL can be transferred to host material due to low energy gap between host and dopant. $Irppy_3$ can act as a deep trap for hole injection, but it cannot capture electrons from ETL. Therefore, device II shows low luminance value because less holes are trapped by dopant material at low doping concentration. Hole injection determines total charge injection in device II. Power efficiency was improved only for the devices with high doping concentration at HTL-EML interface. Device I and device III showed higher efficiency value than standard device by 50% due to efficient charge injection through highly doped EML side.



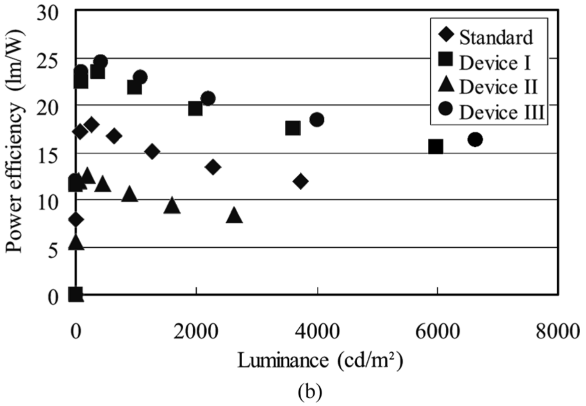
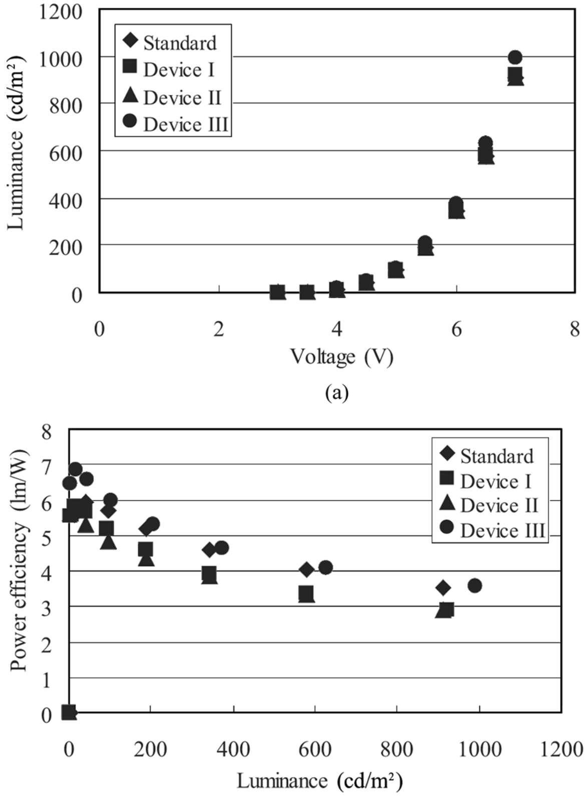


FIGURE 5 Current density-voltage-luminance performances of green phosphorescent devices. (a) Luminance-voltage and (b) power efficiency-luminance.

I-V-L performances of blue phosphorescent devices with FIrpic as the dopant material were also investigated to study the emission mechanism in blue devices. Four devices with different device structures were also fabricated and luminance value and efficiency were compared. I-V-L characteristics of blue devices are shown in Figure 6. Compared with a conventional device, graded devices did not show any difference in luminance and efficiency values. Luminance and efficiency values were almost the same for all devices, indicating that there is little hole and electron trapping effect in blue devices because there is no change of luminance value for the devices with different doping profile. This can be clearly explained by the HOMO and LUMO level of FIrpic and CBP (Fig. 4). In blue devices, the energy gap between CBP and FIrpic is only 0.1 eV and 0.2 eV for



(a)

(b)

FIGURE 6 Current density-voltage-luminance performances of blue phosphorescent devices. (a) Luminance-voltage and (b) power efficiency-luminance.

HOMO and LUMO, which enables charge injection from a charge transport layer to a host material rather than direct charge trapping at dopant sites. Dopant sites can act just as shallow traps for holes ad electrons. Therefore, energy transfer dominates light emission process in blue devices and doping profile do not have any significant influence on light emission. Efficiency value was also not affected greatly by the doping profile.

CONCLUSIONS

In summary, charge trapping dominated the light emission process in red phosphorescent devices, while energy transfer dominated light emission process in blue phosphorescent devices. In green devices, a hole trapping effect was clearly observed, but little electron trapping effect was observed. The graded doping structure had a positive effect on the luminance and efficiency value of red and green devices, while blue devices were not influenced by the doping profile. Therefore, the performances of red and green devices can be improved greatly by using a graded doping structure.

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