

Extremely low doping technology in phosphorescent OLEDs

Woo Sik Jeon¹, Tae Jin Park¹, Sun Young Kim¹,
Ramchandra Pode², Jin Jang¹ and Jang Hyuk Kwon^{1*}

¹Department of Information Display and ²Department of Physics,
Kyung Hee University, Dongdaemoon-gu, Seoul 130-701, Korea

Phone : 02-961-0948, E-mail: jhkwon@khu.ac.kr

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Abstract

We report extremely low doping technology in phosphorescent organic light emitting diodes (PHOLEDs). Highly efficient red PHOLEDs with excellent energy transfer characteristics even under 1 % doping condition have been demonstrated. Results reveal efficient host-dopant system to realize highly efficient PHOLEDs and useful cost saving way by reduction of expensive Ir complex dopants.

1. Introduction

Phosphorescent organic light-emitting devices (PHOLEDs) are acquiring the mainstream position in the field of organic electroluminescence owing to their potential use in solid state lighting, and flat panel displays. High current- and power-efficiencies requirements for these applications are realized in PHOLEDs as phosphorescent materials can harvest both singlet and triplet excitons.[1-3] Well-known phosphorescent emitters are iridium (III) and platinum (II) complexes. Iridium (III) complexes have been shown to be the most efficient triplet dopants employed in highly efficient organic light-emitting devices (OLEDs).[4,5] The doping concentration of these emitters in PHOLEDs is usually very high as about 6~10 wt % (weight percentage) compared with about 1% in fluorescent devices. Energy transfer between host and guest molecules can occur through either coulombic interactions (long range interaction) or electron exchange (short range interaction). The former is due to dipole-dipole interaction, called Förster energy transfer. The emission in fluorescent devices is mainly due to energy transfer between host singlet to dopant singlet due to Förster energy transfer mechanism.[6] As a result, the 1 % doping is

sufficient to achieve maximum emission efficiency. While Dexter mechanism (i.e. electron exchange mechanism) is responsible for the energy transfer from the host triplet to dopant triplet.[7] Therefore, high doping concentration is required in triplet emitter system. It is known that the metal-to-ligand charge-transfer (MLCT) state of iridium (III) metal complex has a short lifetime in micro-second because of singlet and triplet mixing characteristics, unlike to triplet state in general organic materials. Therefore, the efficient Förster energy transfer from host singlet and MLCT state in certain host-guest systems may be possible. However in conventional PHOLEDs, direct charge trapping (both electrons and holes) on the phosphorescent guest molecules appears to be the main operating mechanism and usually requires more than 3% doping condition. Förster energy transfer plays a minor role in achieving high efficiencies in these devices. Most of the reported phosphorescent host materials have a wide band gap (triplet-singlet gap) due to large exchange energy between singlet and triplet states. The phosphorescent dopant molecules act as deep trapping sites. Because of this charge trapping movement in the device, high doping concentration is indispensable in PHOLEDs. Recently, we have reported a narrow band-gap fluorescent host material, bis(10-hydroxybenzo[h] quinolinato) beryllium complex (Bebq₂) for red emitting PHOLEDs.[8] This host molecule has a strong fluorescence and small singlet-triplet exchange energy (< 0.3 eV). We propose that this molecule is an ideal Förster type host and negligible charge trapping issue with Ir(phq)₂acac dopant for phosphorescent emission. Using this host-dopant system, highly efficient red phosphorescent OLEDs under 1 % doping condition have been fabricated. The energy transfer mechanism has been investigated by fluorescence quenching

studies and Förster radius measurement.

2. Experiment

To fabricate OLED devices, a clean glass substrate precoated with a 150-nm ITO layer with a sheet resistance of $10 \sim 12 \Omega/\square$ was used and the substrate size was $2 \text{ cm} \times 2 \text{ cm}$. The patterns of $2 \times 2 \text{ mm}^2$ were formed by photolithography and wet etching processes and used as an anode. The glass substrate was cleaned by sonification in an isopropyl alcohol, acetone, and methanol, rinsed in deionized water, and finally irradiated in a UV-ozone chamber. All organic materials were deposited by the vacuum evaporation technique under a pressure of $\sim 3.0 \times 10^{-7}$ Torr. Doping is carried out by co-evaporation from independent sources and effusion rates were monitored using a quartz crystal microbalance (QCM). Subsequently, Al with a deposition rate of $\sim 5 \text{ \AA/s}$ was deposited in vacuum chamber without breaking the vacuum and used as a cathode. The fabricated simple bilayer PHOLED consists of ITO / DNTPD (40 nm) / Beq₂: Ir(phq)₂acac (50 nm, 1%) / LiF(0.5 nm) / Al(100 nm). PHOLEDs were fabricated by varying dopant concentration from 0.5 to 2%. The current density-voltage (J-V) and luminance-voltage (L-V) data of PHOLEDs were measured with a Keithley SMU 238 and Minolta CS-100A, respectively. Electroluminescence (EL) spectra and CIE color coordinate were obtained using a Photo-research PR-650 spectroradiometer.

3. Results and discussion

Using a narrow band gap electron transporting host material, Beq₂, and tris(1-phenylisoquinoline)iridium (Ir(pi_q)₃) dopant, we have reported simple and high efficiency bi-layered PHOLEDs.[8] The HOMO and LUMO energy levels of Beq₂ are 5.5 eV and 2.8 eV, respectively. The triplet emission energy of Beq₂ host is estimated to be 2.5 eV by molecular modeling. Triplet phosphorescent dopants such as Ir(pi_q)₃ and bis(2-phenylquinoline)(acetylacetonate)iridium (Ir(phq)₂acac) have about 2.2 eV and 2.1 eV triplet emission energy, respectively. Both dopants have reasonable triplet energy values to be received from Beq₂ host. Usually good triplet host materials are considered to have strong phosphorescences with very a long triplet lifetime. However, Beq₂ has a strong fluorescence emission and shows a very good energy

transfer characteristics to red dopants. In addition, this Beq₂ host does not show any phosphorescence peaks even at 77 K. This is very strange phenomena because strong fluorescent material shows very good host performance. Therefore, Förster energy transfer mechanism with this host is investigated.

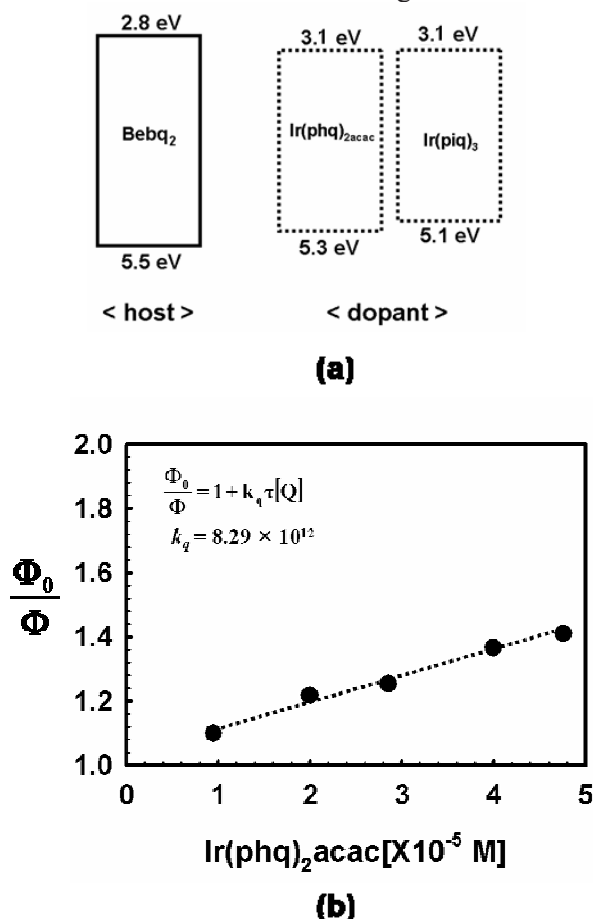


Figure 1. Energy band diagram and Stern-Volmer plot. (a) Energy diagram of host and dopant materials, (b) Stern-Volmer plot on Beq₂ fluorescence quenching by dopant (Ir(phq)₂acac)

As shown in Fig. 1, hole trapping by dopants may arise because the energy gap between host HOMO and dopant HOMO is about 0.4 eV. Recently, the emission by such hole trapping mechanism was already reported by our group.[8] In case of Ir(phq)₂acac, the HOMO energy gap between host and dopant is very small (~ 0.2 eV) and the LUMO energy gap between host and dopant also very small (~ 0.2 eV). The charge trapping emission can be minimized in this host dopant system. The efficient Förster energy transfer from Beq₂ host to Ir(phq)₂acac have been studied by fluorescent lifetime measurement and quenching experiments in THF solution. Stern-Volmer

equation is adequate to check energy transfer rate. The singlet lifetime of Bebq_2 has been measured to be 5.0 ns by time resolved spectroscopy. From the slope of straight line in Fig. 1, k_q was measured as $8 \times 10^{12} \text{ sec}^{-1} \text{ M}^{-1}$, indicating that energy transfer from excited singlet state of the host to dopant triplet occurs quantitatively via Förster energy transfer. Furthermore, the strong spin orbital coupling induced by a transition metal ion displays a narrow energy gap between $^1\text{MLCT}$ and $^3\text{MLCT}$ states (0.3 eV) which opens a path for efficient energy transfer from the singlet to the emitting triplet states. Therefore, two channels for Förster energy transfer from the host singlet to $^1\text{MLCT}$ and $^3\text{MLCT}$ states of iridium complex are available. Overlapping of the host emission and dopant absorption spectra substantiates the hypothesis of efficient Förster energy transfer from the host singlet to guest emitting triplet states via two channels (see Figure. 2). Furthermore, the strong fluorescent quantum efficiency 0.39 of host (Bebq_2) in solution, obtained using relative quantum yield measurement, favors Förster energy transfer.

Förster radius was calculated by using Förster energy transfer equation. The radius (R_0) was about 1.3 nm. This radius value is a little small compared with previous fluorescent reports (~ 3 nm). However, this value is sufficient to support efficient Förster energy transfer.

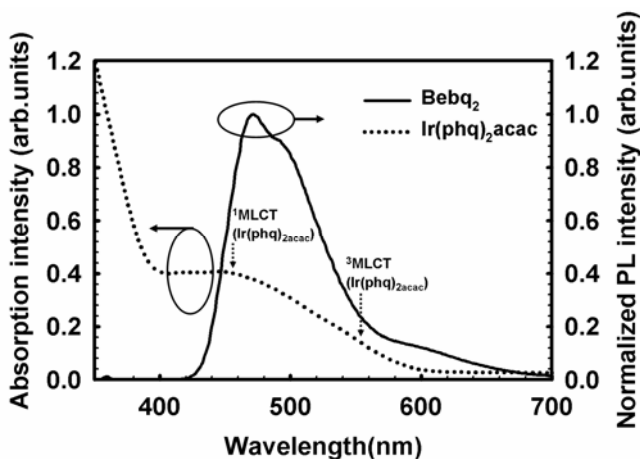


Figure 2. Photoluminescence spectrum of Bebq_2 and absorption spectrum of $\text{Ir}(\text{phq})_2\text{acac}$.

Fig. 3 shows the performance of extremely low doped red PHOLEDs devices fabricated for the energy transfer study. In order to know minimum doping concentration in our host dopant system, the concentration of $\text{Ir}(\text{phq})_2\text{acac}$ was varied from 2 % to

0.5 %. Four devices having 0.5 %, 1 %, 1.5 %, and 2 % doping concentration was made and evaluated.

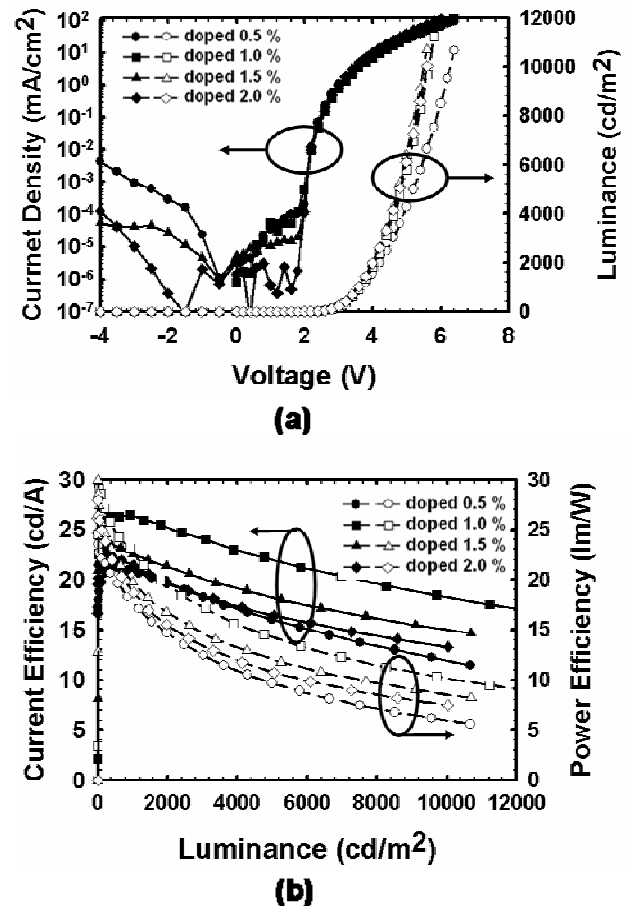


Figure 3. J-V-L and efficiency characteristics of extremely low doped red PHOLEDs. (a) current and luminance vs. voltage characteristics, (b) current and power efficiency vs. luminance characteristics.

The J-V characteristics were saturated over 0.5 % doping condition. No significant improvement in J-V performance by adding more dopant amount is observed, indicating that the charge trapping is not severe in this device. At a given constant luminance of 1000 cd/m^2 , the current efficiency and power efficiency of each device were 20.71 cd/A and 17.12 lm/W, 26.53 cd/A and 23.14 lm/W, 22.61 cd/A and 19.73 lm/W, and 21.45 cd/A and 18.72 lm/W for 0.5, 1.0, 1.5, and 2.0 % $\text{Ir}(\text{phq})_2\text{acac}$, respectively. The efficiency is optimized at 1% doping condition. The color coordinates of these devices are (0.61, 0.38), (0.62, 0.37), (0.62, 0.37), (0.62, 0.37) for 0.5, 1.0, 1.5, and 2.0 % $\text{Ir}(\text{phq})_2\text{acac}$, respectively. Even at 0.5% doped device, a good red color is observed. Slight

emission at 500 nm due to Bebq₂ host along with a dominant dopant peak at 605 nm when the dopant concentration is extremely low (~ 0.5%), suggests no complete energy transfer from Bebq₂ host to Ir(phq)₂acac guest.

4. Summary

We have demonstrated phosphorescent OLEDs with extremely low doping concentration. Efficient Förster energy transfer from host singlet to metal-to-ligand charge-transfer (MLCT) state of Ir complex has been realized in phosphorescent devices. Such a low doping technology is very useful to design efficient host dopant system and to fabricate highly efficient PHOLEDs. In addition, this technology is very useful to save manufacturing cost by reducing expensive Ir dopants.

5. References

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