Deep red electrophosphorescent organic light-emitting diodes based on new iridium complexes

Doowon Gong

Dept. of Information Display, Hongik University, Seoul, Korea Center for Organic Materials and Information Devices, Hongik University, Seoul, Korea *Jun Ho Kim*

Center for Organic Materials and Information Devices, Hongik University, Seoul, Korea Dept. of Electronic Engineering, Hongik University, Seoul, Korea

> *Kum Hee Lee* Dept. of Chemistry, Sungkyunkwan University, Suwon, Korea

> Seung Soo Yoon Dept. of Chemistry, Sungkyunkwan University, Suwon, Korea

Young Kwan Kim Dept. of Information Display, Hongik University, Seoul, Korea Center for Organic Materials and Information Devices, Hongik University, Seoul, Korea Tel: +82-2-320-1646 ; E-mail: ssyoon@skku.edu, kimyk@wow.hongik.ac.kr

Abstract

New iridium complex was synthesized and demonstrated a deep red light emission in organic light-emitting diodes (OLEDs). The maximum luminance of 8320 cd/m2 at 15 V and the luminance efficiency of 2.5 cd/A at 20 mA/cm2 were achieved. The peak wavelength of the electroluminescence was at 626 nm with the CIE coordinates of (0.69, 0.30), and the device also showed a stable color chromaticity with various voltages.

1. Introduction

The efficiency of organic light-emitting diodes (OLEDs) has been dramatically improved by the use of heavy metal phosphorescent emitters [1-5]. Heavy-metal complexes which have strong spin-orbit coupling leads to singlet-triplet state mixing and removes the spin-forbidden nature of the radiative relaxation of the triplet state, result in high efficiency electrophosphorescence in OLEDs at room temperature [6–8]. The holes and electrons recombine to form radiative excited states, or excitons. This electrically generated exciton can be either a singlet or Both theoretical predictions а triplet. and experimental measurements give a singlet/triplet ratio for these excitons of 1 to 3. If only singlet is radiative in fluorescent materials, internal quantum efficiency

 (η_{int}) is limited to 25 %. In contrast, by using high efficiency phosphorescent materials which harvest both singlet and triplet excitons, (η_{int}) can approach 100 %.The iridium complexes developed by Thompson et al.[6] containing the 2-phenyl pyridine type cyclometalated ligands, such as Ir(ppy)₃, have been extensively studied for the fabrication of green LEDs. The strong emission occurring at λ_{max} =514 nm is believed to originate from the triplet manifold containing both the intraligand $\pi - \pi^*$ and the metal-toligand charge transfer (MLCT) characters. It is anticipated that color tuning from green to red can be achieved by lowering the energy gap of either the π - π^* or the MLCT excited states. Ir complexes usually have efficient phosphorescence and short lifetimes, which typically range from 1 to 14 μ s [9]. The shorter exciton lifetime makes Ir complexes more attractive candidates than platinum porphyrins, which usually have about one order of magnitude longer lifetime.

In this study, we synthesized the new red phosphorescent materials derived from iridium 1-(phenyl)isoquinoline (Ir(piq)₂(acac)) and fabricated deep red electrophosphorescent devices with these complexes as red-light emitters.[10,11,12] The RED-1 and the RED-2 molecules were introduced *tert*-buthyl group and phenyl group to Ir(piq)₂(acac), respectively.[13]

2. Experimental

OLEDs using iridium complexes were fabricated by high vacuum (10^{-6} torr) thermal evaporation onto precleaned ITO coated glass substrates. ITO coated glass was cleaned in an ultrasonic bath by regular sequence: in acetone, methanol, distillated water and isopropyl alcohol. Hereafter, pre-cleaned ITO was treated by O₂ plasma treatment whose condition was 2 x 10^{-2} torr and 125 W for 2 min.[14] Figure 1 shows the configuration of the devices. Structure was as follows: ITO 4,4′ -bis[N-(naphthyl)-N-phenyl-amino] biphenyl (NPB) as a hole transport layer / red dye doped in 4,4,N,N' -dicarbazole-biphenyl (CBP) as an emissive layer / bathocuproine (BCP) as an exciton / tris-(8-hydroxyquinoline)aluminum(III) blocker (Alq₃) as an electron transport layer / lithiumquinolate (Liq) as an electron injection layer / Aluminum as a cathode, respectively.[15]



Figure 1. The structure of devices.

All of the optical and electrical properties of OLEDs such as the current density, luminance, luminous efficiency and CIE coordinate characteristics were measured with keithley 236 and CHROMA METER CS-100A, respectively.

3. **Results and Discussion**

Figure 2 show the photophysical properties of these three iridium species. The bands below 350 nm were assigned to the spin-allowed ${}^{1}\pi \rightarrow \pi^{*}$ transition of cyclometalated ligand, and the band around 480 nm can be assigned to spin-allowed ${}^{1}MLCT$. The most surprising feature for these complexes is the strong intensity of the band around 550 nm, which can be assigned to the spin-forbidden ${}^{3}MLCT$ band. This

information indicates an efficient spin-orbit coupling that is prerequisite for phosphorescent emission.



Figure 2. UV abs. and PL spectra of Ir complexes in methylen chloride with 10 μ M.

Figure 3 showed similar characteristics of current density for all red dopants. The highest maximum current density at 15 V was 572 mA/cm² in RED-2 compared with the lowest was 539 mA/cm² in $Ir(piq)_2(acac)$.



Figure 3. The current density-voltage (J-V) characteristics of devices.

However as figure 4 showed, the maximum brightness at 15 V reached 19900 cd/m^2 for Ir(piq)₂(acac), 16000 cd/m^2 for RED-1 and 8320 cd/m^2 for RED-2, respectively.



Figure 4. The luminance-voltage (L-V) characteristics of devices.

The device with 8 % of Ir(piq)₂(acac) in CBP shows the highest EL efficiency.[16] Figure 5 shows the voltage,-current-luminance characteristics of the devices with 8 % Ir complexes. The luminous efficiency-current characteristics of the same devices are also given in Figure 5. The maximum luminance efficiency and the luminance efficiency at 20 mA/cm² reached 7.0 cd/A and 6 cd/A for Ir(piq)₂(acac), 5.6 cd/A and 5 cd/A for RED-1 and 3.1 cd/A and 2.5 cd/A for RED-2, respectively.



Figure 5. The luminous efficiency-current density characteristics.

Figure 6 shows the EL spectra of devices based on these three iridium species at voltage of 12 V.

 $Ir(piq)_2(acac)$ and RED-1 showed similar EL characteristics with the main emission peak at 616 nm, whereas RED-2 exhibits the bathochromatic shift in luminance compared to $Ir(piq)_2(acac)$ and RED-1.[17] The main emission peak of RED-2 was at 626 nm.



Figure 6. EL spectrum of devices at the applied voltage of 12 V.

As shown in Figure 7, the corresponding Commission Internationale de L'Eclairage (CIE) coordinates were (0.67, 0.33) for Ir(piq)₂(acac), (0.67, 0.32) for RED-1 and (0.69, 0.30) for RED-2, respectively.



Figure 7. CIE X and Y coordinate on the devices with the operating voltages.

4. Conclusion

We synthesized a series of red phosphorescent Ir complexes and fabricated OLEDs with these emitters. The characteristics of Ir complex with *tert*-buthyl group (RED-1) were similar to those of $Ir(piq)_2(acac)$, and Ir complex with phenyl group (RED-2) showed the improved color chromaticity. The color chromaticity was affected by several factors as follows. First, highest occupied molecular orbital (HOMO) lever was pull down, according as *tert*-buthyl group was act on electron withdrawing. Second, phenyl group acts on conjugation effect.

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6. References

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