

Color mixing between phosphorescence and fluorescence by incomplete Förster energy transfer

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(Received 19 May 2007 • accepted 13 June 2007)

Abstract—We have successfully showed the color mixing between fluorescence and phosphorescence by the incomplete Förster energy transfer. The emission color from fluorescent Rubrene and phosphorescent Ir(ppy)₃ was found possible to be mixed for a single-layer device doped with both dyes, maintaining the high luminance efficiency of the phosphorescence. We also found out that the Förster energy transfer was very efficient and independent of the applied voltage with no loss of energy during the transfer.

Key words: Phosphorescence, Fluorescence, Screen Printing, Förster Energy Transfer

INTRODUCTION

Polymer light-emitting devices (PLEDs) have attracted much attention due to their applications in display technology [1,2]. Especially, since polymers can be coated easily on large areas by simple low-cost coating processes such as screen printing and gravure printing, it is expected to make them considerably attractive for many applications in the future. Recently, the screen printing technique has been utilized to fabricate the PLEDs successfully [3-6]. However, the wet coating techniques have a disadvantage in that it is difficult to fabricate multi-layer PLEDs. This is for the reason that most PLEDs fabricated by the wet coating techniques are single-emitting-layer devices. To grant the diversity of emitting color with a single-emitting layer, the fluorescent and phosphorescent dopants can be incorporated into a host polymer. However, it has been known that the efficiency of fluorescence should be limited since it only involves singlet relaxation present in about 25% of the total excited-state population. In contrast, phosphorescent materials offer improved light-emission efficiencies as the result of utilizing both singlet and triplet states.

A pioneering work by Baldo et al. [7] has invoked intense research on high-efficiency fluorescent organic light-emitting devices (OLEDs) [8-11] and PLEDs [12] by using a phosphorescent sensitizer. He et al. [12] reported red fluorescence from Nile Red dye sensitized by a phosphorescent dye, PPIr. In their report, the emission efficiency of phosphorescence-sensitized fluorescence was found to be over 6 cd/A, while that of fluorescence without the phosphorescent dye was around 2 cd/A. Their devices are polymer single-emitting-layer devices using a PVK host fabricated by spin coating.

In this study, we report the color mixing between fluorescence and phosphorescence by incomplete Förster energy transfer. We use Rubrene and Ir(ppy)₃ as an orange-emitting fluorescent dye and a green-emitting phosphorescent dye, respectively. The emission efficiency of fluorescence sensitized by phosphorescence is studied to show that the fluorescent and phosphorescent emissions can be

mixed with the same high emission efficiency of phosphorescence.

EXPERIMENTAL

ITO glasses of a nominal sheet resistance of 30 $\Omega/\square$ were ultrasonically cleaned, followed by rinsing with deionized water, trichloroethylene, acetone and methanol. The cleaned ITO glasses were patterned via a standard microlithographic process. HCl (37%, Aldrich) was used as the etchant for the ITO. Poly(3,4-ethylenedioxy thiophene) doped with poly(styrene sulfonate) (PEDOT : PSS) (Baytron P, AI 4083) was spin-coated onto the pre-cleaned patterned ITO glasses, yielding a layer with a thickness of 40 nm. The PEDOT : PSS layer was then baked at 120 °C for 10 minutes. On top of the PEDOT : PSS layer, a single emissive polymer layer was subsequently screen-printed by using a semi-automatic commercial screen printing machine. For the screen printing, a 400 mesh screen composed of stainless steel fabric was used. The viscosity of screen-printing ink was 2.4 cp and the screen printing resulted in a polymer thin film with a thickness of 50 nm. For the polymer film, the host polymer was PVK (poly(9-vinylcarbazole)) of average molecular weight 1,100,000. In order to adjust the viscosity of printing ink, 260 mg of PVK was dissolved in 25 ml of chlorobenzene solvent. Besides the host polymer, small molecular dyes of PBD, α -NPD, Ir(ppy)₃, and Rubrene were found not to change the viscosity noticeably.

We have fabricated four different PLED structures. A single-emitting layer of a control device is composed of a host polymer PVK, an electron transporting PBD, and a hole transporting α -NPD of which the composition is 65%, 26%, and 9%, respectively. The second fluorescent device has the same composition as the control device except the fluorescent Rubrene with 1.5% of the weight of PVK. The third phosphorescent device has the same composition as the control device except the phosphorescent Ir(ppy)₃ with 6.5% of the weight of PVK. The final device is a single-layer device with both 1.5% fluorescent Rubrene and 6.5% phosphorescent Ir(ppy)₃ of the weight of PVK.

The thicknesses were measured by using a KLA Tencor alpha-step. An LiF layer of 0.5 nm and an Al layer of 120 nm thickness

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were deposited on top of the printed polymer layer under 5×10^{-7} torr pressure. Luminance, chromaticity and electroluminescence (EL) spectra of OLEDs were recorded with a Minolta CS100 and Ocean Optics spectrophotometer. The characteristics of current-voltage were measured with a Keithley 2400 source meter. All measurements were carried out at room temperature in air.

RESULTS AND DISCUSSION

In Fig. 1, the control device is the device which does not have a fluorescent or phosphorescent dye. The light emission of the control device could be from blue-emitting constituents, which are α -NPD, NPB, or a host polymer PVK. The maximum intensity and CIE coordinate of the emission are 60 cd/m^2 and (0.19, 0.25) in blue region, respectively. The doping of a fluorescent dye of Rubrene with 1.5% concentration causes a noticeable increase in the emission intensity and the emission color change to the yellow-orange, which corresponds to (0.43, 0.53) in the CIE coordinate. The maximum intensity was measured to be $1,000 \text{ cd/m}^2$. Meanwhile, the doping of a phosphorescent dye of Ir(ppy)_3 with 6.5% concentra-

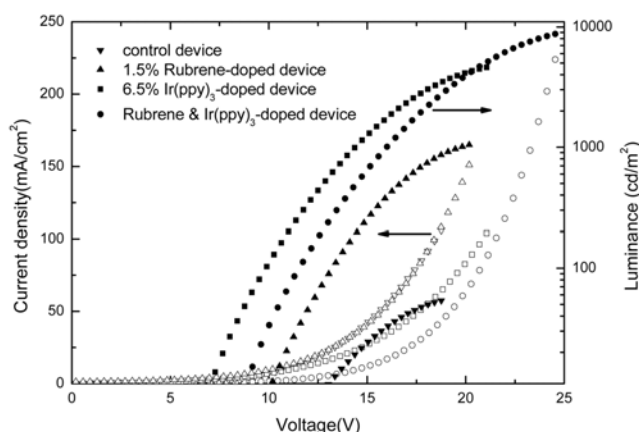


Fig. 1. Current density-voltage-luminance (I-V-L) characteristics for four different electroluminescent devices.

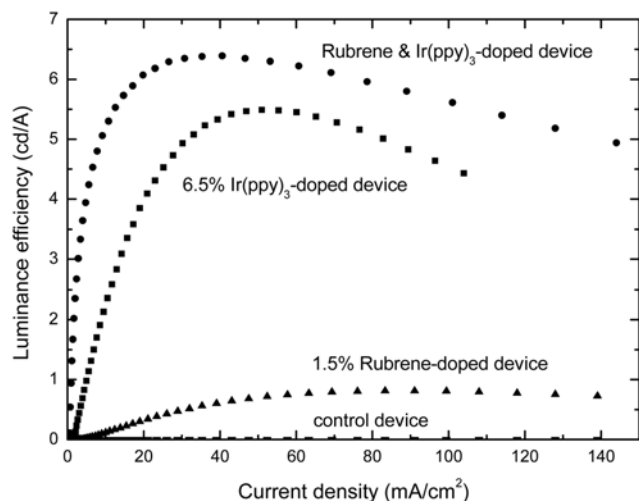


Fig. 2. Luminance efficiency graph with respect to the current voltage for four different electroluminescent devices.

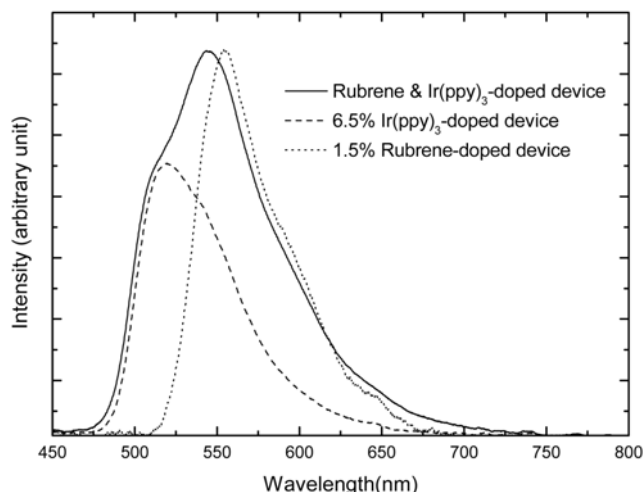


Fig. 3. EL spectra of the three different electroluminescent devices fabricated in this work. Note that the peak intensities of each of the spectra are normalized for comparison.

tion changes the emission color to green, which means the emission is originating from the phosphorescent dye. Since phosphorescence has much higher emission efficiency than fluorescence, the emission efficiency increased significantly to 5.5 cd/A as shown in Fig. 2. The maximum emission intensity was measured to be $5,000 \text{ cd/m}^2$ at an applied voltage of 22 V. When both the fluorescent Rubrene and phosphorescent Ir(ppy)_3 were incorporated in a device, the emission color was found to be mixed with the two dyes as shown in Fig. 3. The maximum luminance intensity was $8,000 \text{ cd/m}^2$ at an applied voltage of 24 V. Even though the less efficient fluorescence was mixed with the phosphorescence, the luminance efficiency turned out to increase to about 6.4 cd/A . It means that the fluorescence from Rubrene dye should be caused by the Förster energy transfer from the phosphorescent dye, Ir(ppy)_3 . Since the emission color was mixed between Rubrene and Ir(ppy)_3 , the CIE coordinate was measured to be (0.35, 0.58) which is in between (0.43, 0.53) a device with Rubrene only and (0.29, 0.63) a device with Ir(ppy)_3 only. Since the Förster energy transfer was incomplete, the EL spectra were mixed between the fluorescence and phosphorescence as shown in Fig. 3. It should be mentioned here that the emission peak from Rubrene in the device with Rubrene and Ir(ppy)_3 -doped device was blue-shifted about 30 nm in wavelength. We consider that it should be caused in the course of the Förster energy transfer. The fluorescent emission from Rubrene in the device doped with Rubrene only was responsible to the direct recombination of holes and electrons transported from the anode and cathodes, respectively. However, since the phosphorescence-sensitized fluorescence from Rubrene occurs via the Förster transfer, the excitation and recombination take place in Rubrene near Ir(ppy)_3 slowly in accordance with the phosphorescence. Even though the device structures were different, the same blue-shift was also observed by Baldo et al. [7].

As shown in Fig. 4, the phosphorescence-sensitized fluorescence was found independent of the applied voltage. Even at low applied voltages, the Förster energy transfer from Ir(ppy)_3 to Rubrene was found efficient. In that the device doped with both the fluorescent and phosphorescent dyes showed higher efficiency than the phos-

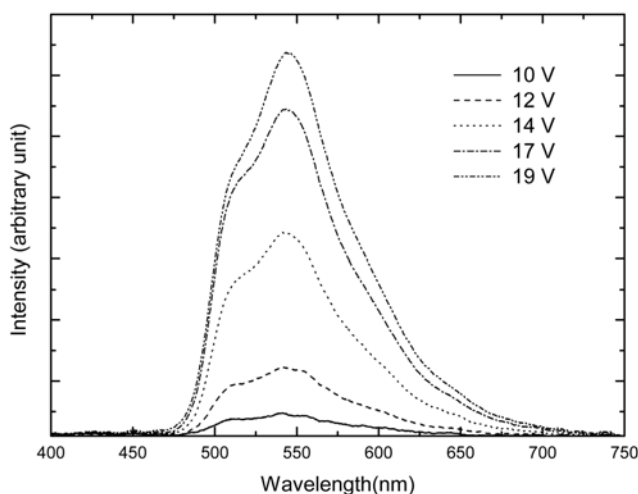


Fig. 4. EL spectra of the device doped with both fluorescent Rubrene and phosphorescent Ir(ppy)₃ at different applied voltages.

phorescent device, we think that the energy transfer is very efficient so that there is no loss in energy.

In summary, we have demonstrated the efficient color mixing of the fluorescence and phosphorescence by the incomplete Förster energy transfer. The luminance efficiency of fluorescent emission was as high as that of phosphorescent emission. It was the proof that the phosphorescent emission energy was efficiently transferred for the fluorescent emission.

CONCLUSIONS

We have successfully showed the color mixing between fluorescence and phosphorescence by the incomplete Förster energy transfer. The emission color from fluorescent Rubrene and phosphorescent Ir(ppy)₃ was found to be mixed for the single-layer device doped with both dyes, maintaining the high luminance efficiency of the phosphorescence. Since the Förster energy transfer was very efficient, the luminance efficiency of phosphorescence-sensitized fluorescence was found as high as that of phosphorescence only. The maximum luminance and luminance intensity of the Ir(ppy)₃-sen-

sitized device was 8,000 cd/m² and 6.4 cd/A, respectively.

ACKNOWLEDGMENTS

This work was supported in part by the 'Local Government Initiated R&D Program (Project No. 2004-0693-100)' of the Korea Ministry of Commerce, Industry and Energy accompanying with the Gyeonggi Province and supported in part by Grant No. (R01-2006-000-10140-0) from the Basic Research Program of the Korea Science & Engineering Foundation. It was also partly supported by the Advanced Materials Process Research Center for IT at Sungkyunkwan University.

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