Tetra-Chromatic White Phosphorescent Organic Light-emitting Diodes with an External Color Tuning Layer

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Abstract

A highly efficient white phosphorescent OLED with a "tetra-chromatic" emission was fabricated by using an external color tuning layer (ECTL) which is composed of a layer of greenish yellow organic dye dispersed in PMMA on the outside of the glass. The ECTL combining with a lower red dopant concentration in the device has been found to improve the efficiency of a conventional WOLED by more than 27%.

1. Introduction

White OLED devices are a prime focus of OLED research for backlight system of full color displays and solid state lightings as extremely thin light sources with large surface areas can be fabricated with this technology. In the future it will be possible to use OLEDs as flexible or transparent light sources. A transparent OLED over a window in a roof would be able to allow natural light in during the day and provide fascinating illumination for the room at night.

The efficiency of OLEDs can be improved by the introduction of phosphorescent dye as guest material in a host material to fabricate the emissive layer, as the so-called electro-phosphorescent OLEDs or PHOLEDs can make use of both singlet and triplet excitons. As a result, these PHOLEDs have been the subject of intense research in recent years due to their high external quantum efficiency and power efficiency.

White light-emitting OLEDs can be generated by many approaches. In most cases, white emission is achieved by using a vertical red-green-blue (RGB) stack with different layers comprising three primary colors or two complementary colors and the output spectrum of such a device is determined by the light emitting components. [1-3] Several different approaches have been taken to generate white light emission, such as white PHOLEDs with a single emissive layer, [4] broad exciplex or excimer emission, [5] and the use of microcavity. [6] A few papers introduced the idea of using a color emitting OLED in combination with a down-conversion layer to produce white OLED. White light-emitting devices based on inorganic blue LED and down-conversion by phosphor which were first published by Schlotter et al. [7] Duggal et al. were the first to implement the idea to the field of OLEDs generating white light by combining a blue OLED with a down-conversion phosphor system. [8] However, the efficiency of this device is limited by the efficiency of the blue OLED. In 2006, the OSRAM Opto Semiconductors, Inc., fabricated a WOLED by using a down conversion system composed of YAG:Ce which has been widely used in most LEDs fabrication systems. This device produced an extraordinary enhancement on device performance, resulting in a white electroluminescence device with luminance efficacy of 25 lm/W and a luminance efficiency reaching 39 cd/A. [9] But this device only shows a $CIE_{x,y}$ of (0.26, 0.40), deviate from the E point on the black body locus. And the spectral composition of the light produced by the conventional two-band white device differs from that of natural white light, particularly in the red region. In this study, we introduced a tetra-chromatic system by adding a green and red emission layer inside the structure, higher efficiencies from the green emissive layer and improved color rendering index is also expected by using this method.

To the best of our knowledge, this paper describes what appears to be one of the first reports on using the down conversion method to produce tetra-chromatic white light in OLED systems.

2. Experimental

Prior to the organic deposition, the ITO coated glass plate was patterned by lithography and then thoroughly cleaned by sonication, oxygen and CF_x plasma treatment, in order to remove the micro particles and further increase the work function of the ITO glass to match the HOMO of the hole transport layer. All of the organic layers were then routinely deposited in a high vacuum chamber with the vacuum of the order of 5×10^{-4} Pa by thermal evaporation using resistively heated tantalum boats. Typically, the rate was controlled at 1.0 Å/s for obtaining smooth layer-layer boundaries. The cathode is then deposited. Finally, the

device is encapsulated in a glove box. The active area of the glowing size is defined as the overlap of the ITO and the cathode electrodes, which is 9 mm^2. The EL emission spectra and the current-voltage-luminance characteristics were measured with a diode array rapid scan system using a Photo Research PR650 spectrophotometer. The $CIE_{x,y}$ were measured by the JETI Spectro-radiometer 1210, and the PL emission spectrum was measured from the photo luminance instrument. These processes were performed right after the encapsulation of the device. In this study, we fabricated two devices. Device **A** is a plain tri-chromatic white phosphorescent OLED. For the ease of fabrication process, the whole multi-emission layer have the same host material CBP throughout, and is composed of a FIrpic doped CBP blue EML, a $Ir(ppy)_3$ doped CBP green EML, and a x % $Ir(piq)_3$ co-doped inside the green emission layer. The CBP layer close to NPB is to prevent the emission of NPB, and the layer between the two emission layers is to restrict the flow of the energy transfer from the blue emission layer to the other layers,[10] which quenches the emission of FIrpic. And also a very thin layer hole blocking material BCP is added. By trapping the excitons, their residence time and recombination probability in the EML were increased, leading to a concomitant increase in OLED efficiency. Device **B** has the same tri-chromatic white phosphorescent OLED but at the light out coupling side we additionally added an external color tuning layer (ECTL) in order to form a tetra-chromatic WOLED. This dye was dissolved in PMMA, and was then applied on the substrate using the doctor blade technique for a thickness of about 7 μm. By applying this thickness, the devices can obtain the same major conversion peak near 544 nm. We controlled the doping concentrations y % of $Ir(ppy)_3$ inside the green emission layer in order to achieve white light.

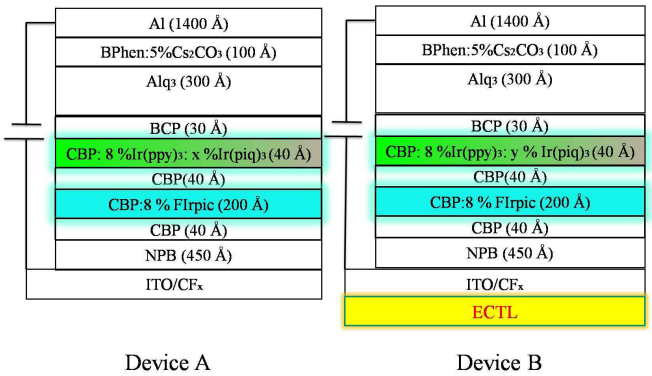

Fig. 1. The Devices

3. Results and discussion

From our results, shown in Fig. **2** and Table **1**, the efficiency of Device **A** drops from 33.5 cd/A for 0.0% concentration to 16.1 cd/A for 2.5% of $Ir(piq)_3$, while the voltage raises from 8.2 V to 9.4 V under 10 mA/cm^2 current density. A doping concentration of at least 2.5% is needed to produce acceptable white emission. This effect shows that although by using a triplet sensitizer which can induce efficient energy transfer from CBP to $Ir(piq)_3$ is necessary to get high performances in $Ir(piq)_3$ devices. [11] The large energy gap between CBP and $Ir(piq)_3$ still results in charge trapping in the red dopant rather than energy transfer from CBP to $Ir(piq)_3$.

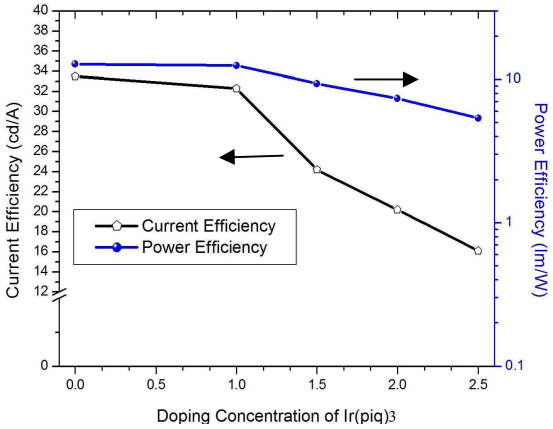

Fig. 2. The efficiencies of Devices A with different $Ir(piq)_3$ concentrations under 10 mA/cm^2

TABLE 1 Performance of Devices A under 10 mA/cm^2

Devices A x (%)	(V)	Current Eff. (cd/A)	Power Eff. (lm/W)	Lum. (nits)	EQE (%)	CIE 1931
0.0	8.2	33.5	12.8	3349	10.6	(0.26, 0.56)
1.0	8.1	32.3	12.5	3225	10.8	(0.27, 0.55)
1.5	8.1	24.2	9.4	2420	9.2	(0.29, 0.52)
2.0	8.5	20.2	7.4	2015	8.3	(0.32, 0.50)
2.5	**9.4**	**16.1**	**5.4**	**1614**	**7.8**	**(0.37, 0.46)**

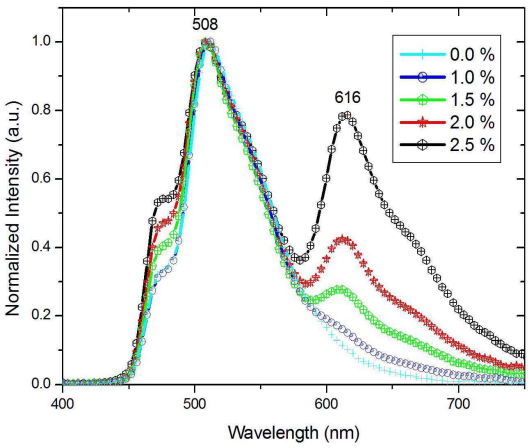

Fig. 3. The EL performances of Devices A.

We exanimate the effect of the doping concentration of the ECTL dye inside polymethylmethacrylate (PMMA) host, which is considered the most transparent thin film material. It is found that the spectrum tends to red-shift at higher doping condition, but the emission peak near 538 nm is nearly not changed. We also estimate that the strongest absorption and emission for the dye is between 0.5wt.% and 1wt.%. We finally chose 1.0wt.% as the concentration for our ECTL.

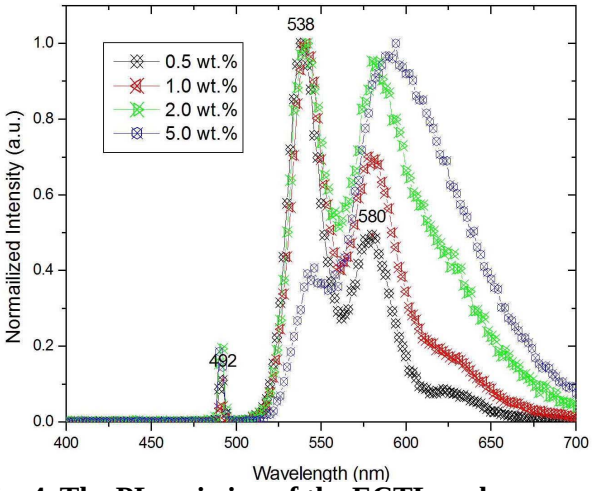

Fig. 4. The PL emission of the ECTL under different concentrations.

Device **B** with contrast to device **A**, only needs a concentration of 2.0% $Ir(piq)_3$ doped inside the green emission layer, thus a higher efficiency and operation device can be fabricated. The two devices showed yellowish-white emission color with CIE positions at (0.36, 0.48) and (0.37, 0.46) respectively. But device **B** showed a much higher power efficiency of 6.6 lm/W compared with device **A** which is about 5.4 lm/W, nearly an increase of 27% under 10 mA/cm^2. Also the original valley of spectrum near 580 nm is alleviated, leading to a four major peaks spectrum at 476, 508, 544 and 612 nm. We believe that after the invention of a more saturated blue material, a device closer to the planckian locus will be produced.

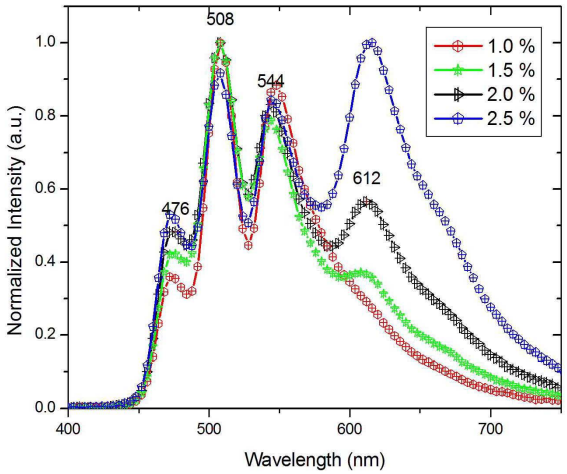

Fig. 5. The EL performances of Devices B.

TABLE 2 Performances of Devices B under 10 mA/cm^2

Devices B y (%)	(V)	Current Eff. (cd/A)	Power Eff. (lm/W)	Lum. (nits)	E Q E (%)	CIE 1931
1.0	8.2	24.5	9.4	2446	8.4	(0.33, 0.52)
1.5	8.2	20.9	8.1	2094	8.0	(0.33, 0.50)
2.0	**8.6**	**18.0**	**6.6**	**1800**	**7.6**	**(0.36, 0.48)**
2.5	9.3	15.4	5.2	1543	7.6	(0.42, 0.45)

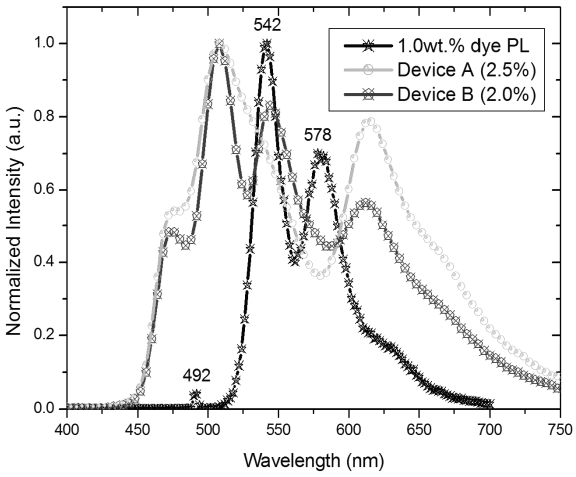

Fig. 6. Comparison of the EL performances for Devices A, B after optimized.

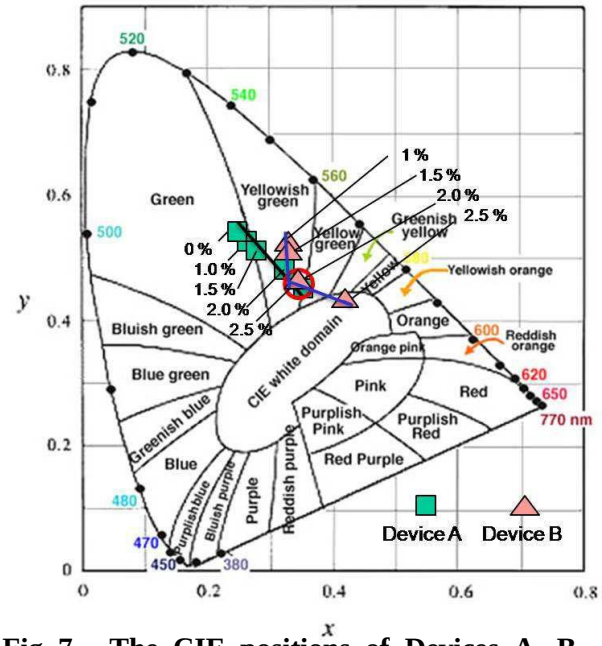

Fig. 7. The CIE positions of Devices A, B.

4. Summary

Down conversion process has already been introduced in OLED devices by using a blue OLED plus a yellow down conversion layer in producing white light, with a few researches reported, but none had reported in forming tetra-chromatic systems and modifying the spectrum and efficiency by this technique. In this work, we improved the efficiency of WOLEDs from 5.4 to 6.6 lm/W by using this technology without moving the $CIE_{x,y}$. We believe that this might be a very convenient method in slightly tuning the device, and the efficiency might be even improved by using a higher quantum efficiency dye and novel dopant materials.

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