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Three White Organic Light-emitting Diodes with Blue-green Fluorescent and Red Phosphorescent Dyes

Ragchaa Galbadrakh[a], Hwan-Seok Bang[b], Heume-Il Baek[**b], and Changhee Lee[*b]**

Abstract

This paper reports that well-balanced white emission with three primary colors can be achieved with a simple white organic light-emitting diode (WOLED) structure of ITO / α-NPD (50 nm) / α-NPD: Btp2Ir(acac) (8 wt%, 6 nm) / α-NPD (5 nm) / BCP (3 nm) / Alq_3: C545T (0.5 wt%, 10 nm) / Alq_3 (40 nm) / LiF (0.5 nm) / Al (100 nm). The external quantum efficiency of the device reached 3.8% at a current density (luminance) of 4.6 mA/cm^2 (310 cd/m^2), and the maximal lum inance of the device reached 19,000 cd/m^2 at 11.5 V. The insignificant blue shift of the emitting color with an increasing current density can be attributed to the narrowing of the exciton formation zone width.

Keywords : white organic light-emitting device, electroluminescence, energy transfer mechanism, guest-host system

1. Introduction

In the last decade, there has been keen interest in white organic light-emitting diodes (WOLEDs) for general-purpose lighting and flat panel display application. The luminous efficiency of WOLEDs already surpasses that of incandescent bulbs [1 and 2], but intense studies are still being conducted to achieve a higher efficiency and color rendering index, a longer lifetime, and a lower fabrication cost.

In principle, all-phosphor-doped WOLED devices can have 100% internal quantum efficiency, but parasitic energy losses are difficult to avoid. For example, a phosphorescent dopant excited via the conductive host introduces exchange energy losses from the singlet-to-triplet intersystem crossing. The new WOLED device concept introduced recently by Sun et al. [3], in which a blue fluorescent dopant exploits in combination with green and red organic phosphor dopants, demonstrates a very high efficiency, with a peak external quantum efficiency (EQE) of 18.7%. In that device's architecture, blue fluorescent dopants harvest all the electrically generated singlet excitons for the blue emission, and phosphorescent dopants harvest the rest of the triplet excitons for the green and red emissions. The use of blue fluorophor instead of blue phosphor eliminates the exchange energy loss, and the longer operational lifetime of blue fluorophores compared with their phosphorescent counterparts allows the achievement of better color stability than all-phosphor-doped WOLEDs.

This paper reports a three-color WOLED with a simple device structure that uses fluorescent and phosphorescent dyes, in which two different methods of energy transfer deliver electrically generated singlet excitons for the green guest and blue host fluorescent emitters, while the rest of the triplet excitons diffuse from the exciton formation zone to the red-phosphor-doped layer. Here, the energy transfer mechanism that governed the light emission from the device structure was focused on, and minor attention was given to device optimization to achieve a precisely balanced efficient white emission. Therefore, the characteristics of the devices will be briefly demonstrated, and some interesting details on the energy transfer mechanism in the host-guest system of the WOLED structure will be mainly discussed.

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[*] Member, KIDS; [**] Student Member, KIDS
Corresponding Author: Changhee Lee
[1]Department of Experimental and Theoretical Physics, School of Physics and Electronics, National University of Mongolia, 46A-337, Ulaanbaatar, Mongolia
[2]School of Electrical Engineering and Computer Science and Inter-University Semiconductor Research Center, Seoul National University, Seoul 151-744, Korea
E-mail : chlee7@snu.ac.kr **Tel** : 02-880-9093 **Fax** : 02-877-6668

2. Experimental methodology

WOLEDs with active emissive areas of 1.4x1.4 mm^2 were fabricated on a glass substrate with a pre-patterned indium tin oxide (ITO) anode via sequential and co-deposition of organic materials and an LiF/Al cathode in the background vacuum of -4x10^{-6} Torr without breaking the vacuum.

Common materials such as 4,4'bis[N-1-naphtyl-N-phenyl-amino] biphenyl (α-NPD) and tris-(8-hydroxyquinoline) aluminium (Alq_3) were used as hole- and electron-transport layers (HTL and ETL), respectively. A hole and exciton blocking layer (HBL) of 2,9-dimethyl, 4,7-diphenyl, 1,10-phenanthroline (BCP), the thickness of which ranged from 1 to 5 nm, was inserted between the HTL and the ETL. The deposition rate for the α-NPD, BCP, and Alq_3 was about 1 Å/s. The red organic phosphorescent dye of bis [2-(2'-benzothienyl) pyridinato-N, *C3'*] (acetylacetonato) iridium (III) [Btp2Ir (acac)] was doped in the HTL with the optimal doping concentration of 8 weight% (wt%), at the rate of 0.08 or 0.16 Å/s. The green fluorescent dye of 10-(2-benzothiazolyl)-2,3,6,7-tetramethyl-H,5H,11H-(1)-benzopyropyrano (6,7-8-i,j) quinolizin-11-one (C545T) was doped in the HTL (Devices A, B, and C) or in the ETL (Devices D, E, F, and G) at the rate of 0.01 Å/s. The C545T doping concentration was about 0.5 wt% in the ETL or the HTL host. The 0.5-nm-thick LiF electron injection layer was deposited at a rate of about 0.1 Å/s, and then the 100-nm-thick aluminium cathode was deposited at the rate of 3-5 Å/s. The evaporating rate and thickness of the growing layers were monitored with the quartz oscillator thickness monitor SQM-160.

Before the ITO-coated glass substrates were loaded into the deposition chamber, they were cleaned in five ultrasonication steps with isopropyl alcohol (10 mins.), de-ionized water (5 mins.), acetone (10 mins.), de-ionized water (5 mins.), and methanol (10 mins.). After the ultrasonication, the substrates were purged with pure nitrogen gas and stored in an oven for more than 1 hour of drying at 120°C. Immediately before the substrates were loaded into the deposition chamber, they were finally UV-ozone-treated for 5 mins. The current-voltage- luminance (IVL) characteristics of the fabricated devices were measured with a Keithley 236 source/measure unit and a Keithley 2000 multimeter. The electroluminescence (EL) intensity was detected through a calibrated silicon photodiode. The EL spectra were measured with an ARC SpectraPro-275 monochromator equipped with a photomultiplier tube. The measurements of the IVL characteristics were carried out in a vacuum.

3. Results and discussion

The EL spectra of the simple OLED device structure of ITO / α-NPD (60 nm) / BCP (0-6 nm) / Alq3 (60 nm) / LiF (0.5 nm) / Al (100 nm) changed from green (Alq_3 emission) to blue (α-NPD emission) when the BCP thickness increased from 0 to 6 nm due to the decrease in the Förster energy transfer [4] from α-NPD to Alq_3, across the BCP {interlayer sequential energy transfer (ISET) mechanism [5]}. Therefore, a white emission was obtained with the three primary colors of red, green, and blue (RGB) by adding a red guest emission to the balanced green-blue emission of the simple device structure. Both the α-NPD and Alq_3 hosts are known as low efficient emitters [6], though. To increase the efficiency of the RGB white emission from this structure, a red phosphorescent Btp2Ir(acac) was doped into the α-NPD and the green fluorescent C545T with a photoluminescence quantum yield of 0.95 [7] into the Alq_3. Even though the Alq_3 doped with C545T is known as a highly efficient green-emitting host-guest system, it was first checked if there were other possible guest-host combinations for high EL efficiency and white light spectra. For this purpose, the following set of test devices was fabricated:

Device A: ITO / α-NPD (50 nm) / α-NPD: Btp2Ir 8 wt%: C545T 0.5 wt% (5 nm) / α-NPD (4 nm) / BCP (5 nm) / Alq_3 (50 nm) / LiF (0.5 nm) / Al (100 nm)

Device B: ITO / α-NPD (50 nm) / α-NPD: Btp2Ir 8 wt% (5 nm) / α-NPD: C545T 0.5 wt% (5 nm) / α-NPD (4 nm) / BCP (5 nm) / Alq_3 (50 nm) / LiF (0.5 nm) / Al (100 nm)

Device C: ITO / α-NPD (50 nm) / α-NPD: C545T 0.5 wt% (5 nm) / α-NPD: Btp2Ir 8 wt% (5 nm) / α-NPD (4 nm) / BCP (5 nm) / Alq_3 (50 nm) / LiF (0.5 nm) / Al (100 nm)

In these devices, the red guest Btp_2Ir(acac) was co-doped (Device A) or sequentially doped (Devices B and C) with the green guest C545T into the HTL host (α-NPD). The thin (4-nm) non-doped spacer layer of α-NPD between the HBL and the doped part of the HTL served as an exciton-formation and blue-emitting layer. The devices in this set contained an equal number of green and red guest molecules, but the intensity of each guest emission in the EL spectra differed markedly, as shown in Fig. 1. The Commission Internationale d'Eclairage 1931 chromaticity coordinates (CIE xy) of the three devices calculated from their EL spectra, as presented in Fig. 1, were distant from the white point of (0.33 and 0.33). The intensity of the green emission was low for Devices A and C but very strong for Device B.

The low green and strong red emissions from the co-doped Device A can be attributed to an efficient cascade energy transfer [8] from the blue host (α-NPD) to the green guest (C545T), and then to the red guest [Btp2Ir(acac)]. In Device B, the red-phosphor-doped layer was located 9 nm away from the HTL/HBL interface, where most of the excitons originated. This distance is too long for both the singlet and triplet excitons to be transferred efficiently from the exciton formation zone (the HTL/HBL interface) to the red-phosphor-doped layer using both Förster energy transfer and exciton diffusion mechanisms, which resulted in the observed low red and strong green emissions. In addition, the green fluorescent C545T-doped layer between α-NPD and the red-phosphor-doped layer filtered out most of the singlet excitons for the green emission, which made the intersystem crossing mechanism [9] unemployed for the triplet emission in the next red-phosphor-doped layer. In Device C, where the red- and green-dye-doped layers were in an order opposite to that in Device B, the red-phosphor-doped layer consumed most of the singlet and triplet excitons transferred from the α-NPD layer near the HTL/HBL interface, since it was located nearest to the α-NPD layer. As a result, the green-fluorescent-dye-doped layer suffered from a shortage of excitons, which resulted in a negligible green emission.

In Device C, the triplet and singlet excitons reached the nearest red-phosphor-doped layer that was used for the red emission. In this case, the energy transfer from the host to the guest was an efficient process. In the co-doped Device A, some of the excitons were utilized at the green fluorescent guest molecules, which were less efficient than their phosphorescent counterparts. As a consequence, the EL efficiency of Device C was higher than that of Device A, as shown in Fig. 2. Device B showed the lowest efficiency, since majority of the triplet excitons non-radiatively decayed before they reached the remote phosphor-doped layer. Since Device B showed fluorescent blue and green emissions, it showed a lower efficiency roll-off than Devices A and C at high current densities, which is typical of phosphorescent OLEDs [10].

As the abovementioned results show, effective guest emission from both C545T and Btp$_2$Ir(acac) is difficult to achieve simultaneously when both dopants are hosted in a single α-NPD layer. The about 3% maximal EQE of Devices A and C indicates, however, that α-NPD may be an effective host for red-phosphor Btp2Ir(acac). A balanced white emission without loss of efficiency due to the cross-quenching of the guests in the abovementioned device structures may be achieved if the guests are doped into

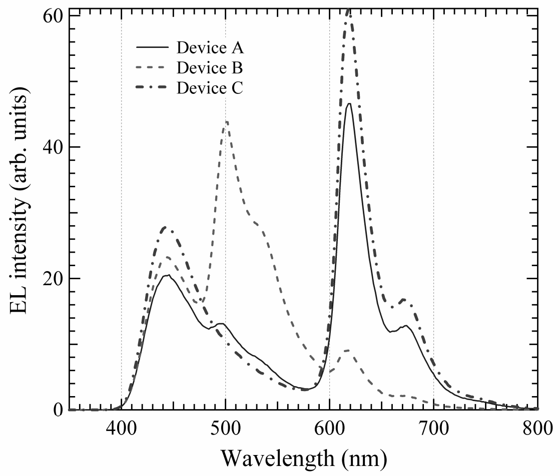

Fig. 1. The EL spectra of Devices A, B, and C at the same current density of 50 mA/cm^2. The chromaticity coordinates CIE xy were calculated as (0.377, 0.248), (0.226, 0.359), and (0.385, 0.219) for Devices A, B, and C, respectively.

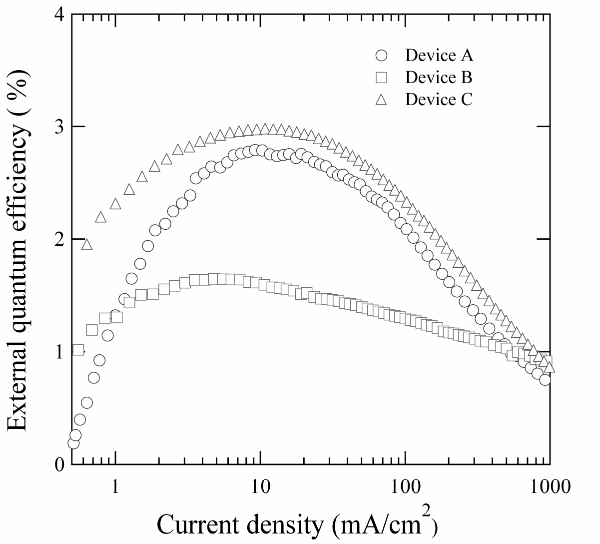

Fig. 2. External quantum efficiencies of Devices A, B, and C as functions of the current density.

separate hosts, as, for example, Btp2Ir(acac) into HTL and C545T into ETL. In this case, the excitation channels for both guests will be separated spatially and the doping concentrations may be adjusted independently to their optimal levels. To verify these possibilities, another set of devices was fabricated in which red-phosphor $Btp_2Ir(acac)$ was doped at 8 wt% into the HTL and green-fluorescent C545T was doped at 0.5 wt% into the ETL. The thicknesses of the doped layers were 6 nm for the HTL and 10 nm for the ETL, and the thickness of the α-NPD spacer layer was 5 nm. An efficient, well-balanced white emission was achieved by setting the thickness of the BCP hole blocking layer at around 3-4 nm.

Fig. 3 (a) shows the device structure and energy level diagram of Devices D, E, F, and G with 1, 2, 3, and 4nm-thick hole blocking BCP layers, respectively. Fig. 3 (b) shows their EL spectra. The EL spectra changed from green to RGB white when the HBL's thickness was increased from 1 to 4 nm. The more-than-4nm-thick HBL deteriorated the RGB white balance to a purple color due to the reduced number of excitons that could be transferred from the HTL to the ETL across the HBL. For example, when the thickness of the HBL was increased to 6 nm, the test device's EL spectra (not shown here) contained only a weak C545T green peak trace and its color became purple mixed with blue (α-NPD) and red [$Btp_2Ir(acac)$]. These results, which are consistent with those of the ISET mechanism, would be effective if the energy transfer distance is not longer than the Förster energy transfer radius [5], which was calculated earlier as 3.47 nm in the case of the α-NPD donor to the C545T acceptor molecule [11].

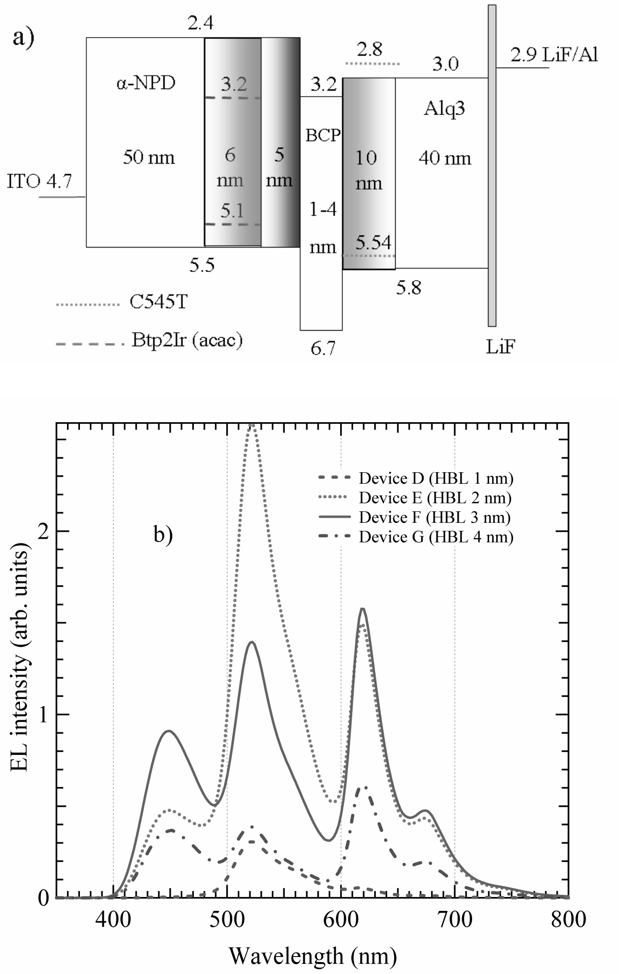

Fig. 3. (a) Proposed energy level diagram of Devices D, E, F, and G, and (b) their EL spectra at a current density of 100 mA/cm^2. The energies are given in the unit of eV. The CIE xy color coordinates were calculated as (0.303, 0.619), (0.334, 0.489), (0.329, 0.353), and (0.334, 0.310) for Devices D, E, F, and G, respectively,

Fig. 4 (a) and (b) shows the CIE xy color coordinates and the EQE of the devices, depending on the HBL thicknesses and the current density. As shown in Fig. 4 (a), another well-manifested phenomenon in this structure is the blue shift of the emission color with an increase in the current density (or luminance). For example, the CIE xy coordinates of Device F shifted from (0.377, 0.371) to (0.329, 0.353) when the current density (luminance) rose from 5 (310) to 100 (4,800) mA/cm^2 (cd/m^2). This behavior is attributed to the narrowing of the recombination zone width with an increasing current density [12]. As the current density rose, the width of the electron and hole recombination zone became narrow and moved towards the α-NPD/BCP interface, so that the exciton energy transfer probability from the α-NPD spacer layer to the red-guest-doped layer decreased. The observed blue shift was practically unnoticeable with the naked eye, since it occurred nearly along the Planckian locus [2], from warmer to colder white. The last figure, Fig. 4 (b), shows that the EQE of the best white Device F reached 3.8% at the current density (luminance) of 4.6 mA/cm^2 (310 cd/m^2). The maximal luminance of Device F reached 19,000 cd/m^2 at 11.5 V.

4. Conclusions

In this paper, it was demonstrated that a well-balanced white emission with three primary colors can be achieved with a simple structure of ITO / α-NPD (50 nm) / α-NPD: Btp2Ir(acac) (8 wt%, 6 nm) / α-NPD (5 nm) / BCP (3 nm) /

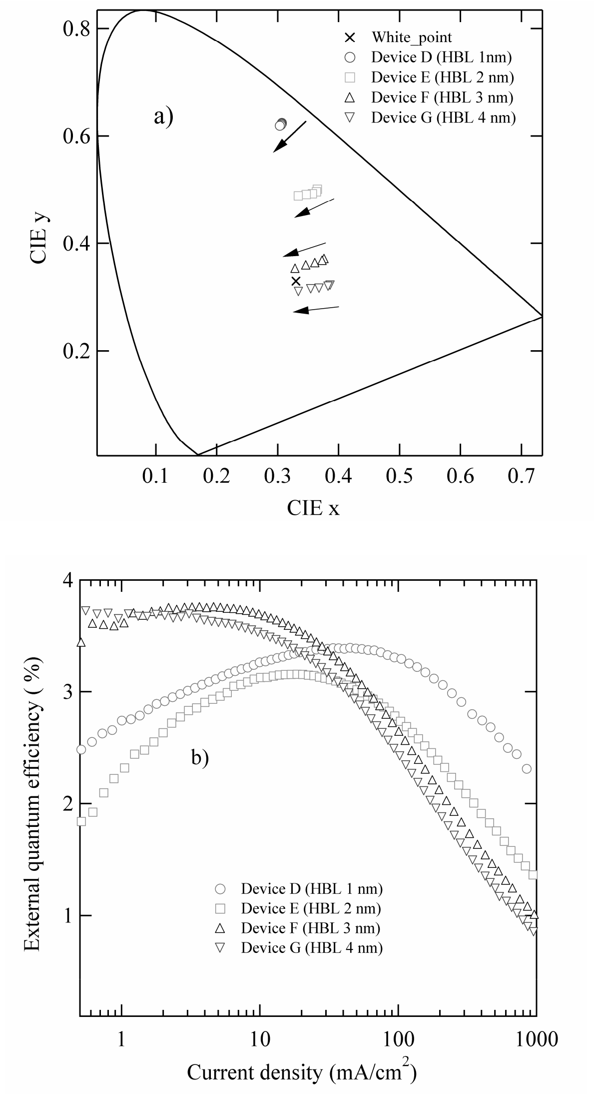

Fig. 4. (a) The CIE xy chromaticity coordinates, and (b) the EQE of Devices D, E, F, and G at different current densities. The arrows indicate the direction of the color shift with an increasing current density from 5 to 100 mA/cm^2.

Alq_3:C545T (0.5 wt%, 10 nm) / Alq_3 (40 nm) / LiF (0.5 nm) / Al (100 nm). Exciton formation and the energy transfer mechanism in the host-guest system of this WOLED structure were discussed. Most of the excitons were generated in the α-NPD spacer layer, near the α-NPD/BCP interface. From the exciton formation zone, triplet excitons immediately diffused to the red-phosphor-Btp2Ir(acac)-doped part of the hole transporting layer, as did some of the singlet excitons used for the α-NPD blue host emission in the spacer layer, but some of them jumped across the BCP hole blocking layer to the Alq_3 electron transport layer, which was doped with green-fluorescent-dye C545T. The external quantum efficiency of the device reached 3.8% at the current density (luminance) of 4.6 mA/cm^2 (310 cd/m^2), and the maximal luminance of the device reached 19,000 cd/m^2 at 11.5 V. The insignificant blue shift of the emitting color with an increasing current density can be attributed to the narrowing of the exciton formation zone width.

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