

White Light Emission Obtained by Direct Color Mixing in Multi-Layer Organic Light-Emitting Devices

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Abstract—Three different structures of multi-layer organic light-emitting devices, which consisted of two emitting layers separated by a carrier blocking layer, were investigated. Since the emitting layers are constructed to emit different colors, the colors emitted from the structures are mixed. It was found that the colors were directly mixed in the structures of this study due to the carrier blocking layer sandwiched by the two emissive layers. The blocking layer splits the carrier recombination zone, and with the emission color is controlled by balancing the split. For the white light the CIE coordinate of (0.30, 0.33) is obtained at an applied voltage of 14 V. The luminance is measured to be 1,000 cd/m² at 14 V with the power efficiency of 0.4 lm/W. For a luminance of 100 cd/m² at 11 V, the CIE coordinate is found to be (0.31, 0.34) and the power efficiency was as high as 0.53 lm/W.

Key words: Organic EL, OLED, OLED, White Light Emission, Recombination Zone Split

INTRODUCTION

Organic light emitting devices (OLEDs) have attracted much attention because of their superior characteristics such as high luminance, wide range of color and wide viewing angle, etc. [Kido et al., 1995; Xie et al., 1999, 2000]. Since the OLEDs were first introduced in 1987, remarkable technological progress has been made in the field, including the recent advent of commercial products using the technology [Rajeswaran et al., 2000]. As the result of the enormous number of previous studies, the optimized structures and materials for OLEDs have been well known and routinely exercised for many studies [Deshpande et al., 1999; Kido et al., 1995]. Among many kinds of OLEDs, white-light-emitting OLEDs have been studied much recently due to their potential applications in the backlights for liquid crystal displays (LCDs) or in other illumination devices. In order for the white OLEDs to be used as backlights in LCDs, the light emission should be bright and have Commission Internationale d'Eclairage (CIE) chromaticity coordinates of (0.33, 0.33). To obtain white emission from OLEDs, different colors should be mixed with proper balances, and there exist a few methods for mixing colors.

The most widely studied method for achieving white emission is to use incomplete energy transfer, in that the light emission comes from both host material and dopant material. The simplest structure using this method has either a single layer that is a polymer host layer doped with red, blue, and green fluorescent dyes or a combination of several electroluminescent polymer blends [Christ et al., 1997; Granström et al., 1996; Kido et al., 1995; Tasch et al., 1997]. However, it is not an easy task to accomplish incomplete energy transfer from the host to the dopant, or carrier trapping at the dopant site, because the concentration of dopants used in the emissive layer should be quite low for the purpose, normally much less than 1 wt%.

Another method to achieve white emission is to control the spatial location of the exciton recombination zone by introducing a carrier blocking layer between the hole transport layer (HTL) and the electron transport layer (ETL). The carrier blocking layer located between two layers emitting different colors blocks electrons or holes supplied from ETL or HTL, respectively, and as a result the spatial location of the carrier recombination zone is changed. In recent years, a few small-molecule-based multi-layer OLEDs have been reported to achieve white emission, using two [Deshpande et al., 1999; Jordan et al., 1996] or three [Kido et al., 1996] different color-emitting layers. It is possible to mix the different colors to generate white emission via controlling the thickness of the blocking layers, because it could change the spatial distribution of carriers across the blocking layers. The use of three different color-emitting layers is somewhat straightforward except for the complexity of the structure. In a study using two different color-emitting layers [Deshpande et al., 1999], the color emission was tuned to white by controlling both the thickness of the blocking layer and the concentration of dopant. In order to achieve white emission, the concentration of dopant should be reduced to 0.6 wt% for balancing the light emissions from both the host and dopant. Therefore, a structure should have been considered that not only uses the carrier blocking layer, but also the incompleteness of energy transfer between the host and the dopant. In this study, however, we report the two-emissive-layer structure that emits white light by direct mixing of pure blue from an emissive layer and orange from a fluorescent-dye dopant in the other emissive layer.

In this work, we report the emission characteristics of multi-layer OLEDs and a method to obtain white light emission. The structure reported in this study does not use the incomplete energy transfer between the host and the dopant, and consequently, the concentration of dopant is not so critical in the device performance unless the concentration is too high to deteriorate the host material properties. The emitted lights from emissive layers could be directly mixed to show a resultant color, and the degree of mixing should be dependent on the level of split of carrier recombination zone by a block-

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ing layer in the middle of the emissive layers. By controlling the thickness of blocking layer, the resultant color could be tuned to white.

EXPERIMENTAL

In order to fabricate the OLEDs in this study, ITO-coated glass substrates were used of which the sheet resistivity was about $15 \Omega/\square$. The ITO substrates were wet-cleaned and wet-etched to form the anode structure of OLED. The wet cleaning method included sonification by de-ionized (DI) water, degreasing by flushing in warm TCE, rinsing in acetone and methanol, and finally rinsing in DI water. On top of the anode a buffer layer of phthalocyanine copper complex (CuPc) was deposited by vacuum sublimation in order to enhance the hole injection from the anode. The 4,4-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl (α -NPD) was used as the blocking layer and also HTL material. The low molecular weight organic materials used in this study were 4,4-bis(2,2-diphenylvinyl)-1,1-biphenyl (DPVBi) as a blue emitting material, [2-methyl-6-[2-(2,3,6,7-tetrahydro-1H,5H-benzoquinolizin-9-ethenyl)-4H-pyran-4-ylidene]propane dinitrile (DCM2) as a red dopant, 5,6,11,12-tetraphenyl-naphthacene (Rubrene) as an orange emitting dopant, and aluminum tris(8-hydroxyquinoline) (Alq_3) as a green emitting material and a host material for the red dopant. All the organic layers were

thermally deposited with an approximate growth rate of $1\text{--}2 \text{ \AA/s}$. For a cathode electrical contact, Al:Li alloy was finally capped over the organic layers which are thermally sublimated in a vacuum less than 10^{-6} torr. The thickness of CuPc, HTL, and ETL was set to 15, 50, and 50 nm, respectively. The thickness of each emissive layer and α -NPD was 15 nm and 4 nm, respectively. Current-voltage characteristics and luminescence intensity were measured with a Keithley 236 measure unit and a silicon photodiode calibrated with a luminance meter (Minolta CS-100). And electroluminescent spectra were measured with a fiber optic spectrometer (S2000). Current-voltage characteristics, luminance intensity and spectra were measured at the same time.

RESULTS AND DISCUSSION

Fig. 1 shows the schematic cross-sections of fabricated OLED structures. The OLED structures represented in Fig. 1(a), (b) and (c) were designated as structures (I), (II), and (III), respectively. The structures (I), (II), and (III) are identical except the combination of

	thickness
Cathode(Al:Li)	100 nm
ETL(Alq_3)	50 nm
Blue(DPVBi)	15 nm
blocking layer(α -NPD)	4 nm
Green(Alq_3)	15 nm
HTL(α -NPD)	50 nm
CuPc	15 nm
Anode(ITO substrate)	

	thickness
Cathode(Al:Li)	100 nm
ETL(Alq_3)	50 nm
Red(Alq_3 : DCM2, 5wt%)	15 nm
blocking layer(α -NPD)	4 nm
Blue(DPVBi)	15 nm
HTL(α -NPD)	50 nm
CuPc	15 nm
Anode(ITO substrate)	

	thickness
Cathode(Al:Li)	100 nm
ETL(Alq_3)	50 nm
Orange(Alq_3 : Rubrene, 5wt%)	15 nm
blocking layer(α -NPD)	2 - 4 nm
Blue(DPVBi)	15 nm
HTL(α -NPD)	50 nm
CuPc	15 nm
Anode(ITO substrate)	

Fig. 1. The schematic cross-sections of fabricated OLED structures; (a) structure (I), (b) structure (II), and (c) structure (III).

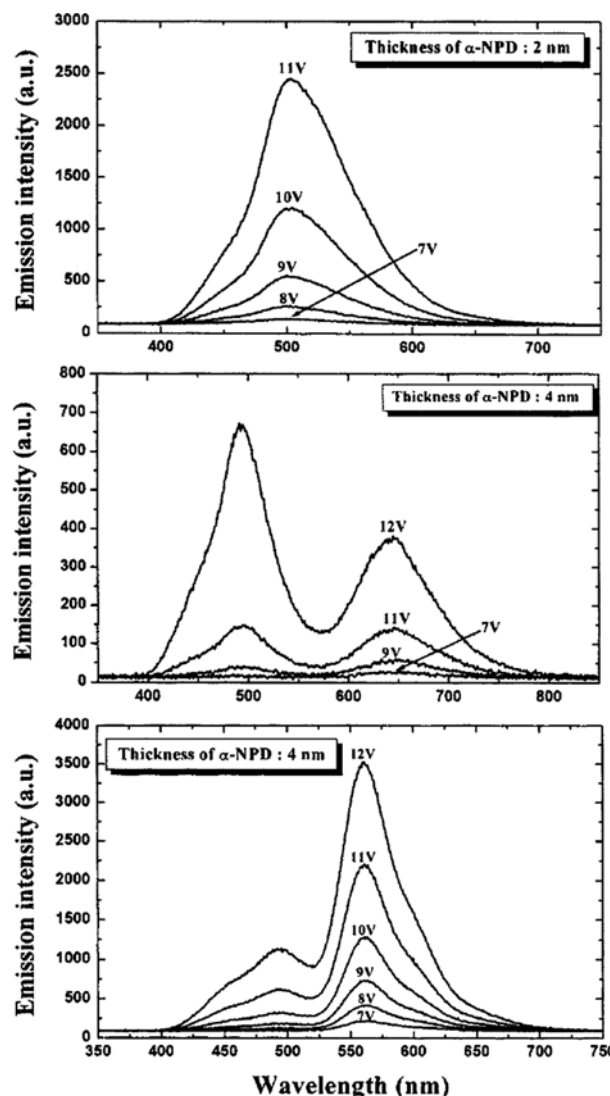


Fig. 2. EL emission spectra at various applied voltages; (a) structure (I), (b) structure (II), and (c) structure (III).

two different emission layers is different. The sequence of color-emitting layers on top of the HTL follows an order of green and blue in structure (I), blue and red in structure (II), and blue and orange in structure (III). The thickness of each emissive layer was set to be 15 nm.

As shown in Fig. 2, the fabricated OLEDs were turned on at around 7 V with the emission color of the second emissive layer from the HTL since electrons would start to be accumulated at the interface between the second emissive layer and blocking layer due to the LUMO level discontinuity at the low voltage. Therefore, the OLED structure (I) emits blue, and structure (II) emits red, while the structure (III) emits orange. As the applied voltage increases, however, the electrons get more energy to jump across the blocking layer to reach the first emissive layer from the HTL. As the result, the emission from the first emissive layer becomes stronger than that from the second layer at the high applied voltage. Even though the shift of emission wavelength by the applied voltage change could not be seen clearly in the EL spectra of structure (I) [Fig. 2(a)], it is obvious from Figs. 2(b) and (c) that the emission from the first emissive layer becomes stronger as the applied voltage increases. In this way, the emission colors from the first and second emissive layers are directly mixed to give the resultant emission color which changes with the applied voltage.

In Fig. 3, the band diagrams of the OLEDs structures (I), (II), and (III) are shown. As expected, the blocking layer of α -NPD has the LUMO and HOMO level discontinuities at both interfaces. Due to the energy level discontinuities introduced by the blocking layer, the electrons and holes are hindered from transporting to the first and second emissive layers. Since the α -NPD has a hole mobility higher than the electron mobility, the electron transport would con-

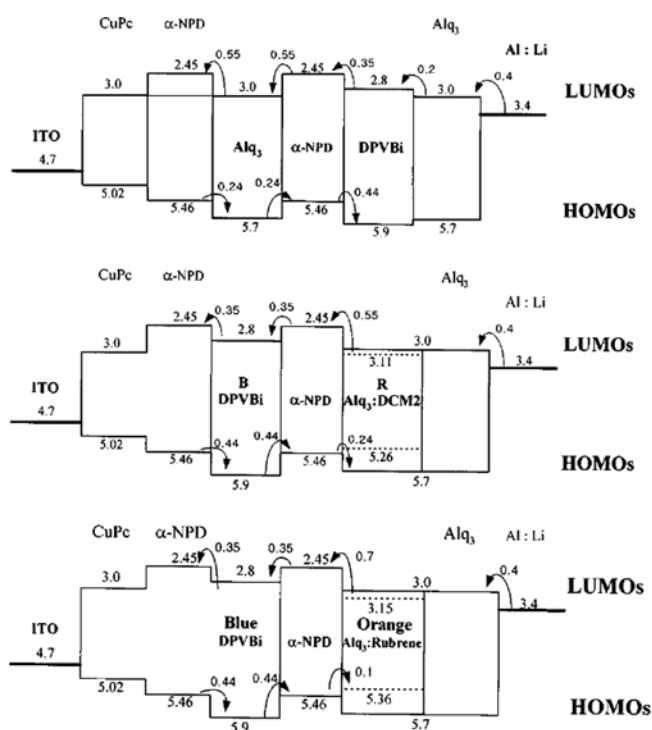


Fig. 3. The estimated energy band diagrams [Bulovic et al., 2000; Kijima et al., 1999]; (a) structure (I), (b) structure (II), and (c) structure (III).

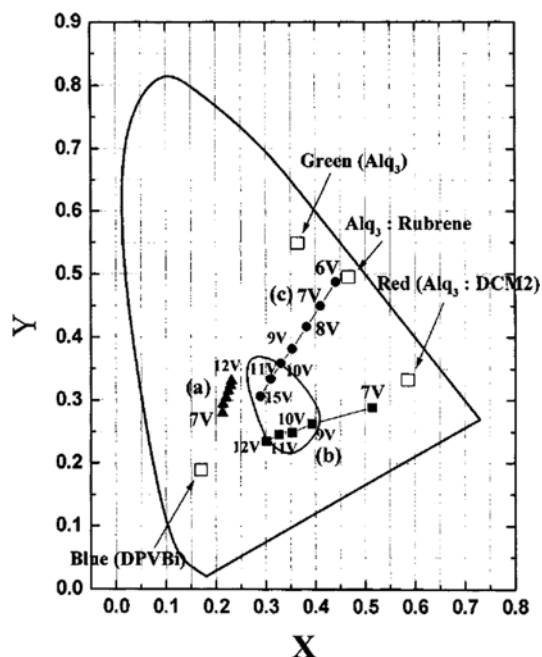


Fig. 4. The CIE chromaticity diagram at various applied voltages; (a) structure (I), (b) structure (II), and (c) structure (III).

trol the hole-electron recombination (i.e., emission). The LUMO level discontinuity at the interface between α -NPD and DPVBi is 0.35 eV in energy, which is much lower than the HOMO level discontinuity at the same interfaces. It means that the electrons should not accumulate much at the interface. For this reason, the change of the emission color is not noticeable in case of the structure (I) as the applied voltage increases.

The CIE color coordinates of the resultant emissions from OLED structures are shown in Fig. 4. In the case of structure (I), the color coordinate shifts from blue color to green color as the applied voltage increases. It should be mentioned here that the coordinates of the resultant emissions at various voltages are right on the connecting line between the coordinates of DPVBi and Alq_3 . It is because the structure (I) is composed of two emissive layers of DPVBi and Alq_3 . From this observation, it could be concluded that the emission colors from two different emissive layers are directly mixed to result in a resultant emission.

In the case of structure (II), a similar behavior is observed except that the shift of the CIE coordinate is much larger when the applied voltage varies. As mentioned earlier, the reason why the shift is larger is due to the larger LUMO energy gap at the interface between the blocking layer and the second emissive layer from HTL. At a voltage range of 9–11 V, the emission color is close to white color (purplish white). The CIE coordinates of the emission colors from the structure (II) are also on the connecting line for the two emissive layers as in the case of structure (I).

In order to obtain the white emission with the CIE coordinate close to (0.33, 0.33), one of the emissive layers should be substituted with an emissive material that emits mixed color of two pure colors among red, green, and blue. The Rubrene-doped Alq_3 is known to emit yellow color, and it was used in structure (III) in which the red emitting DCM2-doped Alq_3 layer was substituted with the Rubrene-doped Alq_3 layer. Structure (III) emits light close to or-

ange at low voltage, which is the color for Rubrene-doped Alq₃, but as the applied voltage increases, the color of light emitted from the structure shifts to blue, which is the color for DPVBi. This behavior is similar to the cases of structures (I) and (II). In this case, however, the CIE coordinate of light moving with the applied voltage passes the white color region which is indicated as a circle in Fig. 4. Similar to the cases of structure (I) and (II), the CIE coordinate of the light emitted from the structure (III) is located on the connected line between the DPVBi blue and Rubrene-doped Alq₃ orange color coordinates. Even though it is not shown in Fig. 4, in case of the device with 2 nm-thick blocking layer, the electroluminescence was first observed at around the coordinate (0.34, 0.34), which corresponded to balanced white emission. As the applied voltage increases, the color coordinate tends to move to the shorter wavelengths. Above 13 V, the luminescence color was found to be almost pure DPVBi blue. At an applied voltage that the white emission occurs, the intensity of light was too low to be used for LCD back-light or other illumination purposes. When the thickness of -NPD blocking layer increases to 4 nm such as shown in Fig. 4, the device begins emitting light of the orange color at low applied voltages. The color coordinate of light out of the device moves to the shorter wavelengths as the applied voltage increases. In this case, the white light that has the CIE coordinate of (0.30, 0.33), is obtained at an applied voltage of 14 V. At this applied voltage, the luminance was measured to be 1,000 cd/m² with the power efficiency of 0.4 lm/W. For a luminance of 100 cd/m², the CIE coordinate was found to be (0.31, 0.34), and the power efficiency was as high as 0.53 lm/W.

SUMMARY

In summary, we reported white-light emission by direct mixing of two different lights from two different emissive regions. Unlike the previous reports related to white-light emission, we did not only utilize only two emissive layers in order to obtain the white light, but also did not utilize the incomplete energy transfer of a doped emissive layer. The color of light emission could be tuned by the applied voltage for obtaining white emission. In this study, we found out that two different colors were directly mixed due to the blocking layer sandwiched by the two emissive layers. The blocking layer acts to split the carrier recombination zone and the emission color can be controlled by balancing the split. The white light that has the CIE coordinate of (0.30, 0.33) is obtained at an applied voltage of 14 V. At the applied voltage, the luminance is measured to be 1,000 cd/m² with the power efficiency of 0.4 lm/W. For a luminance of 100 cd/m², the CIE coordinate is found to be (0.31, 0.34) and the power efficiency was as high as 0.53 lm/W at the applied voltage of 11 V.

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