Spectral broadening in electroluminescence of white organic light-emitting diodes based on complementary colors

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The authors report the optical and electroluminescent (EL) properties of white organic light-emitting diodes (OLEDs) which have two emitters with similar structures: 1, 1, 4, 4-tetraphenyl-1, 3-butadiene and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline have an emission peak of 400 nm around the near ultraviolet, and tris-(8-hydroxyquinoline) aluminum doped with 4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran has an emission peak of 580 nm producing a yellow color. The EL spectra of the white OLED have shown a broadening through visual range from 400 to 780 nm. This spectral broadening is related to an exciplex emission at the organic solid interface. © *2007 American Institute of Physics*.
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Recently, white light emission from organic light-emitting diodes (OLEDs) have received considerable attention because of its potential application in full color displays, backlights, as well as general illuminant light sources.[1] A number of strategies have been reported to produce white OLEDs.[2] Alternative methods to produce full color displays usually use a white emission combined color filter. To obtain white emission from an OLED, two complementary colors or three primary colors from organic active layers to emitting are combined. Most recently, an exciplex formation in organic solid interface was used, to make OLEDs emit white light with spectral tuning.[3–6]

Exciplex formation in OLEDs is an attractive and significant subject from the viewpoint of the scientific application of white emission and spectral tuning. Exciplex formation possibly occurs at the interface between the charge transport layer and the emitting layer for certain combinations of emitting and color. An exciplex formation is an excited state whose wave function straddles two dissimilar molecules, one a net electron donor and the other an acceptor.[7–11] Also, emission color can be tuned by the formation of an exciplex at the organic interface, resulting in spectral broadening of the electroluminescence (EL) of white OLEDs using multilayered organic active layers.

In this letter, we demonstrate a high purity white OLED using exciplex formation between active layers consisting of near ultraviolet and yellow emissions. The OLEDs have two emitters with similar structures: 1, 1, 4, 4-tetraphenyl-1, 3-butadiene (TPD) and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) has an emission peak of 400 nm in the near ultraviolet (N-UV), and tris-(8-hydroxyquinoline) aluminum (Alq_3) doped with concentration (0.1%) of 4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran (DCM1) has an emission peak of 580 nm producing a yellow color. An EL spectrum of the devised white OLED with Commission Internationale de l'Eclairage (CIE) coordinates of (0.33, 0.34) at 1000 cd/cm^2 has shown a range of wavelength from 400 to 780 nm with a full width at half maximum (FWHM) of 184 nm.

Devices with active areas of 10×10 mm^2 were fabricated by thermal evaporator deposition methods. Indium tin oxide with a thickness of 200 nm and a sheet resistance of ~30 $\Omega/\square$ was used as a transparent anode, TPD as a hole transport layer, BCP as a carrier blocking layer, Alq_3 as an electron transport layer, and a yellow light host material and DCM1 as a yellow light dopant material. The structures and energy diagrams of white OLED are shown in Fig. 1. Thicknesses of organic layers and metal layer were controlled by a programmable SID-242 thin film codeposition controller (Sigma Instruments). Current-voltage-luminance characteristics of the OLEDs were measured with a Minolta CS-1000 luminance meter. The EL and photoluminescence (PL) spectra were taken using an Orial MS 125 spectrophotometer.

Figure 2(a) shows the normalized PL of the component materials and shows the normalized EL spectra of the OLED devices [shows inset of Fig. 2(a)]. The PL maximum peaks of BCP, TPD, Alq_3, and Alq_3 doped DCM1 were 380, 405, 528, and 585 nm, respectively. The EL spectra of OLEDs for N-UV and yellow emissions were observed with a maximum peak around 400 nm and shoulder peaks at 500 nm, and a maximum peak at 560 nm with a shoulder peak at 580 nm, respectively. At N-UV, the maximum peak originates from TPD and the shoulder peaks originate from BCP. So, an energy transfer dose from BCP to TPD did not occur in the case of our device. The PL emission of the yellow device was centered at 560 nm with an energy transfer from Alq_3 to DCM1 by Förster transfer.[12] On the chromaticity diagram,

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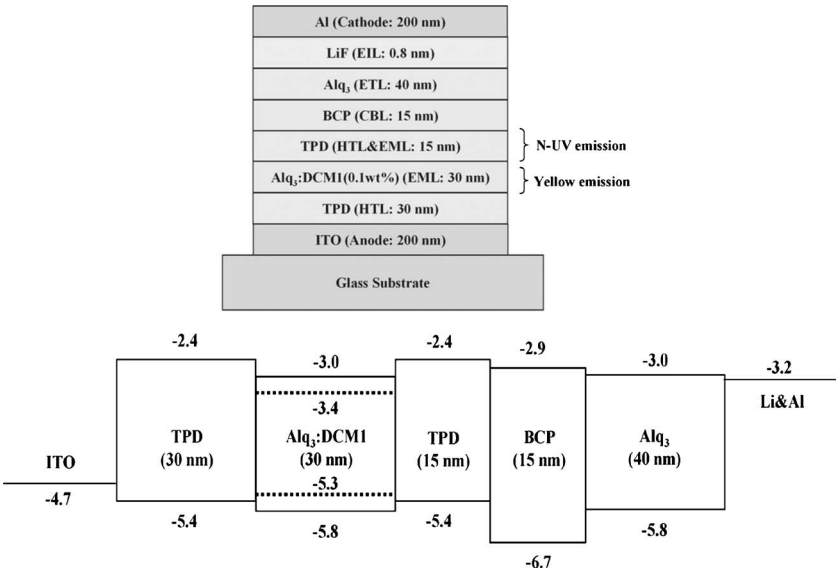

FIG. 1. Structures and energy band diagrams of white device with complementary emitter using the N-UV emission (TPD and BCP layers) and yellow emission (Alq_3 doped DCM1 layer).

the emissions of N-UV and yellow show CIE coordinates at (0.15, 0.07) and (0.48, 0.51) and do not change with applied bias.

In Fig. 2(b), the EL spectra, from the white light device, are shown using complementary color in the emitters. The broadening EL spectra observed the monopeak covering over the visible range from 400 to 780 nm. Note that the FWHM of the EL spectra is 184 nm with the maximum at 515 nm and shoulder peak at 580 nm. A curve fit uses the Gaussian equation and probability distribution function in order to analyze the active data of the EL peak. By this fitting method, two separate peaks are shown at 495 and 576 nm which cover about 65% of the area under EL peak [see inset in Fig. 2(b)]. The peak at 576 nm originates from the yellow emitter which consists of Alq_3 doped DCM1. Another peak at 495 nm, however, does not agree with any of the materials, indicating that it is from other excited species. Therefore, the emission peak around 495 nm results believed that the exciplex or charge transfer complex is due to the interaction between TPD and Alq_3.

To explain the exciplex formation at the interface of the TPD and the Alq_3, we measured the absorbance and PL spectra of TPD/Alq_3, and TPD/Alq_3/TPD on quartz substrate with 50 nm per each layer [see Fig. 3(a)]. TPD clearly has absorption maxima at 316 and 355 nm, and Alq_3 has maxima at 260 and 394 nm. The PL spectrum of TPD and the absorption spectrum of Alq_3 have good overlap, so energy transfer from excited TPD to Alq_3 could be expected. Therefore, they normally interact with each other to form charge-transfer complexes.[13]

The PL peaks of 402, 420, 494, and 524 nm are observed in films of TPD/Alq_3 and TPD/Alq_3/TPD. The 402, 420, and 524 nm are due to TPD and Alq_3; however, the emission peak at 494 nm is quite different from the spectra of pure TPD or Alq_3.

The maximum emission energy of charge transport exciplex emission can be evaluated from an empirical relationship using one-electron oxidation and reduction potentials;[14]

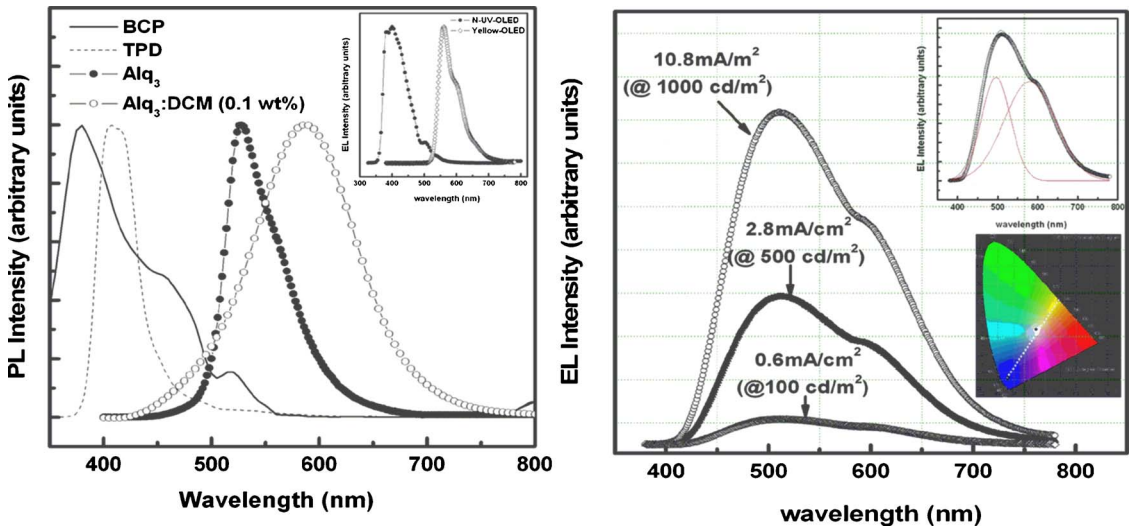

FIG. 2. (Color online) (a) PL spectra of materials to white emission of BCP, TPD, Alq_3, and Alq_3 doped DCM1 (0.1 wt%). The inset is the EL spectra of the near-ultraviolet and yellow devices. (b) EL spectra of white device based on complementary colors as the applied current density. The inset shows the fitted EL spectra using Gaussian equation and probability distribution function and CIE coordinates of near-ultraviolet, yellow, and white devices at 1000 cd/m^2.

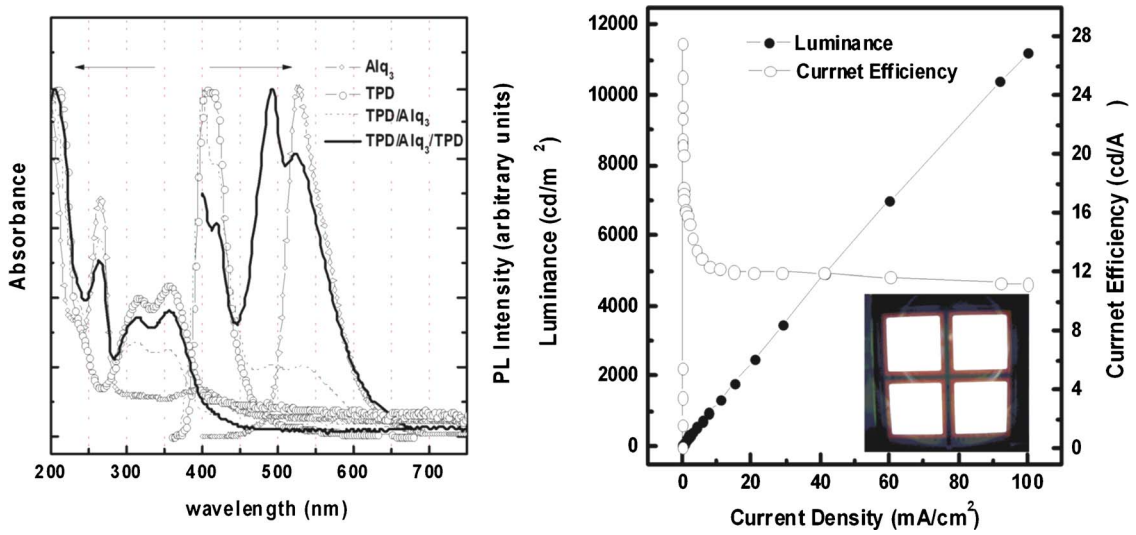

FIG. 3. (Color online) (a) Absorption and photoluminescence spectra of Alq_3, TPD, TPD/Alq_3, and TPD/Alq_3/TPD films. (b) Luminance characteristics (filled circle) and current efficiency characteristics (empty circle) as a function of applied current density for white devices. The inset shows the image of white device at 1000 cd/m^2.

$$h\nu_{ex}(\mathrm{CT}) = E^{ox}(\mathrm{TPD}) - E^{red}(\mathrm{Alq}) - 0.15 \pm 0.1 \text{ eV}$$
$$= (0.35 + 2.30 - 0.15) \pm 0.1 \text{ eV} = 2.5 \pm 0.1 \text{ eV}.$$

The recombination process of an electron-hole pair with the electron located at an Alq_3 and the hole located at a TPD molecule may cause the EL maximum at ≅495 nm, which gives good agreement with experimental spectrum in our devices.

Therefore, we can conclude that the emission peak at 576 nm is attributed to the exciton emission of Alq_3 doped DCM1, and that the emission peak of 494 nm is from the exciplex emission at the solid-state interface of the TPD and the Alq_3 layer. The reasons more increasing the emission peak at 494 nm in TPD/Alq_3/TPD than TPD/Alq_3 interface are related to the coverage of interface at TPD/Alq_3, diffusion property, and bend banding of barrier for carrier injection.[15]

A high luminance of 11 000 cd/m^2 is observed when the device is operated at 100 mA/cm^2 as seen in the luminance and current efficiency characteristics shown in Fig. 3(b). At that driving current density, the voltage is 21 V and the device efficiency is 11.2 cd/A. The CIE coordinate of white OLED was (0.33, 0.34) at 1000 cd/m^2 and it changed to (0.34, 0.40) at 11 000 cd/m^2 as the electric field was increased. Increasing the applied external electrical field will increase the number of carriers injected, which, in turn, enhances the probability of the formation of exciplexes at the interface.[16] For this reason, the emission color can be shifted to green or red. Although a white OLED by exciplex emission is dependent on the applied field, it may seem to fine-tune the emission spectrum.

In summary, we have demonstrated highly fine white OLEDs which use the complementary colors, N-UV and yellow. The EL spectral broadening from the devised white OLED had a FWHM of 184 nm and covered the range of the visible spectrum due to exciplex formation at the TPD/Alq_3 interface. The white device which used a complementary color had a CIE coordinate of (0.33, 0.34) at 1000 cd/m^2 and a current efficiency of 11.2 cd/A at 100 mA/m^2. The color purity of the white OLED shows variation toward green or red emission by increasing the electrical field; however, it may seem that fine-tuning of the emission spectrum can be done by changing the applied field. Hence, the white OLED can be used in applications requiring a white light source, such as a backlight unit or illumination.

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