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## Pure red emission from co-doped organic electroluminescent devices with high brightness

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Organic light emitting diodes (OLED) have been attracted because of their advantages for an emission in wide visible region and for an application to flat-panel display driven at low voltage. In such application, under the existing circumstances, red emitting devices<sup>1.2)</sup> with high brightness and high purity are required. In this paper, we report the emission characteristics of co-doped OLED with two red-emitting dopants.

We used 8-hydroxyquinorine aluminum (Alq<sub>3</sub>) as electron transporting material, N,N'-diphenyl -N,N'-(3-methyl-phenyl) -1,1'-biphenyl -4,4'-diamine (TPD) as hole transporting material, 4-(dicyano methylene) -2-methyl -6-(p-dimethylaminostyryl) -4H-pyran (DCM) as non-emitting dopant, and 5,10,15,20 tetra-phenyl -21H,23H-porphine (TPP) as redemitting dopant.

Ar gas Mg:Ag Alq<sub>3</sub> Alq<sub>3</sub>: TPP : DCM TPD ITO on Glass

Figure 1 shows a schematic of EL device used in our experiment. ITO coated glass substrates were ultrasonicated in several organic solvents and then

Fig. 1 Schematic of the structure of co-doped OLED.

treated in UV ozone cleaning for 10 min. EL devices were fabricated by organic molecular beam deposition (OMBD). The device consists of indium-tin-oxide (ITO) coated glass substrate as anode, vacuum evaporated 40nm-thick TPD as hole transport layer, 50nmthick DCM and TPP doped Alq<sub>3</sub> as an emission layer, 10nm-thick Alq<sub>3</sub> as electron transporting layer, successively, and finished Mg: Ag electrode as cathode. Here, emission layer was fabricated by co-evaporation of DCM and TPP with Alq<sub>3</sub>, and the concentration (mole %) of the dopant materials was estimated by the ratio of the evaporation rate and the molecular weight of each material. After vacuum evaporation, the EL devices were encapsulated by epoxy resin in Ar atmosphere to prevent Mg: Ag electrodes from oxidation. Effective emissive area was  $2\times 2$  [mm<sup>2</sup>], and all of the measurements were conducted under room temperature.



Fig. 2 (a) Current-voltage, and (b) EL intensity-current characteristics co-doped OLED.

Figure 2(a) shows current-voltage (I-V) characteristics of the DCM and TPP co-doped ELdevice. By comparing this result with that of the device consisting of undoped Alq<sub>3</sub> and TPD, we found that the doping of even a small amount of TPP into the Alq<sub>3</sub> emissive layer resulted in the increase of turn-on voltage by about 5 [V]. With increasing DCM concentration in the TPP doped emissive layer, the turn-on voltage decreased to that of the device with undoped  $Alq_3$  and TPD. By doping of a sufficient amount of DCM molecules in the TPP doped emissive layer, the turn-on voltage significantly reduced to that of undoped Alq<sub>3</sub> device.

Figure 2(b) shows EL intensitycurrent (L-I) characteristics of the co-



Fig. 3 EL spectrum of co-doped OLED. Inset shows residual emission from  $Alq_3$  and DCM.

doped EL device. In the device with TPP doped into the  $Alq_3$  emissive layer, EL efficiency was 0.8 [mW/A] at the injection current of 100 [mA/cm<sup>2</sup>]. Adding a small amount of DCM molecules into the TPP doped emissive layer, EL efficiency slightly reduced. However, adding a sufficient amount of DCM molecules into the TPP doped emissive layer led to increase the EL intensity, and the efficiency reached 1.6 [mW/A] at the injection current of 100  $[mA/cm^2]$ , which was twice as much as the device without doping DCM.

Figure 3 shows EL spectrum of the co-doped device when the injection current was 100  $[mA/cm^2]$ . The inset shows the close-up for the emission spectrum from Alq<sub>3</sub> and DCM molecules around 515nm and 600nm, respectively. The emission from Alq<sub>3</sub> reduced drastically by doping of DCM molecules into the TPP doped emissive layer, even with a small amount of DCM molecules. However, the emission from the DCM appeared in the device with high concentration of DCM. As far as the emission from DCM, however, emission intensity was negligibly small compared with that of TPP, and emission wavelength of DCM was close to that of TPP. Therefore, in the device doped with DCM at high concentration, emission was still pure red to naked eye, and the chromaticity coordinates was (0.629, 0.353) at 6 [V], and (0.621, 0.358) at 10 [V], respectively.

From these experimental results, mechanisms for the enhancement of emission intensity are discussed as follows.

In the device doped only TPP into  $Alq_3$  emissive layer, the turn-on voltage increased by about 5 [V], which is shown in Fig. 2(a). It is because the carrier-transporting property in the emissive layer is significantly affected by TPP doping, TPP molecules act as carrier trapping sites to the injected carriers. As a result, carrier recombination was occurred on the TPP molecules, and then formed excitons followed by pure red light emission from the TPP molecules. Such carrier trapping by TPP molecules will cause the increase of turn-on voltage.

In the device doped DCM at low concentration into TPP doped emissive layer, emission process didn't change, that is, carrier trapping process was still dominant. As a result, the turn-on voltage was still remained. On the other hand, in the device doped only DCM into  $Alq_3$  emissive layer, it is generally thought that excitons are formed on  $Alq_3$  molecules, and then the excitonic energy transfers to DCM molecules by Förster energy transfer process. In our experiments, in EL devices including DCM in TPP doped emissive layer, the most part of the emission arose from TPP as is shown in figure 3.

According to these results, in the DCM and TPP co-doped device, emission mechanism from TPP molecules will be interpreted by the following two mechanisms.

In the first mechanism, electrons and holes are injected from the cathode and anode, respectively, to the Alq<sub>3</sub> sites. As a result, excitons are formed on Alq<sub>3</sub> sites, and then excitonic energy is effectively transferred to the DCM sites by Förster energy transfer process. After this process, by taking our experimental results into account, the excitonic energy is interpreted to be transferred from the DCM molecules to the TPP molecules. As discussed above, in the first mechanism, excitons are formed on Alq<sub>3</sub> molecules, and then its energy is transferred to the TPP molecules via DCM molecules. This can be described as two steps energy transfer process.

In the second mechanism, injected electrons are directly trapped on TPP molecules, and then excitons were formed after carrier recombination. As a result, the emission from TPP molecules is obtained. The second mechanism is important in the device doped only TPP into  $Alq_3$  emissive layer, but adding of DCM molecules reduces its contribution. It is because there is obvious change in carrier transporting properties and emission efficiencies in the co-doped device as is shown in figure 2(a) and figure 3.

Thus, at high concentration of DCM, in particularly, we suppose emission mechanism from TPP molecules is dominated comparing with the first mechanism, i.e. two steps energy transfer. Thus, excitonic energy formed on  $Alq_3$  molecules probably transfers to DCM molecules and then to TPP molecules. This two steps energy transfer may help for increasing emission efficiency to its high value. And also turn-on voltage is improved because the contribution of carrier trapping effects is small.

The energy transfer from DCM to TPP molecule cannot be occurred by Förster energy transfer, because the peak wavelength of absorbance spectrum in TPP is around 430nm, and the peak wavelength of fluorescence spectrum in DCM is from 570nm to 630nm depending on DCM concentration, and there is hardly overlap between these spectrum. Nevertheless, in our experiments, adding a sufficient amount of DCM molecules makes emission efficiency improve, that is, two steps energy transfer from Alq<sub>3</sub> to TPP via DCM molecules surely happens. We infer that it is due to another energy transfer process, for instance, based on exciton diffusion for an alignment of energy gap.

In summary, we found that the unique dye doping method to improve emission characteristics, e.g. emission efficiency, purity of emission color, and driving voltage by adding different kind of dopant into the emissive layer. These effects are not specific phenomenon occurred only when TPP and DCM molecule are used, it can be occurred in any combination of dopants. This method is applicable not only to red emitting OLED but also to infrared emitting OLED, and it is powerful method to realize red emitting OLED with high efficiency and high brightness. Moreover, optimized combination of dopant and dopant concentration will further improve emission efficiency.

References

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