

## D-2-4

# Energy Transfer Employing Europium Complex and Blue Phosphorescent Dye and Application for White Organic Light-Emitting Diodes

Yuichi Hino, Hirotake Kajii and Yutaka Ohmori

Osaka University, Center for Advanced Science and Innovation (CASI)  
2-1 Yamada-oka, Suita, Osaka 565-0871, Japan  
Phone: +81-6-6879-4212 E-mail: ohmori@casi.osaka-u.co.jp

## 1. Introduction

Organic light-emitting diodes (OLEDs) have attracted attention because their potential applications for full color and flat panel displays. Among various emitting materials, europium (Eu) complexes show the narrow band emission spectra in the red region[1]. On the other hand, phosphorescent organic light-emitting diodes (PHOLEDs) fabricated using phosphorescent dyes have demonstrated high external quantum efficiencies. Phosphorescence derives from either direct injection into the triplet metal ligand charge transfer state ( $^3\text{MLCT}$ ), or from intersystem crossing (ISO) from the singlet charge transfer state ( $^1\text{MLCT}$ ).

In this study, we discuss the energy transfer between the polymer host, Eu complexes and phosphorescent dyes. We apply for white OLEDs utilizing red and blue emission from the Eu complex and phosphorescent material [2].

## 2. Experimental Procedure

Chemical structures of materials and the device structure are shown in Fig. 1. Organic layers were fabricated by spin-coating onto a glass substrate coated with a patterned indium-tin-oxide (ITO) electrode. First, a PEDOT:PSS hole injection layer was spun over the ITO-coated glass substrate with a 35 nm-thick layer and baked in air at 130 °C for 10 min. We used poly(N-vinylcarbazole) (PVK) as the host and tris (dibenzoylmethane)-mono(4,7-diphenylphenanthroline)europium (III) [ $\text{Eu}(\text{DDP})_3\text{phen}$ ] as the Eu complex. The phosphorescent dopant bis[(4,6-difluorophenyl)pyridinato- N, C2'] (picolinate) iridium(III) (FIrpic) used for blue emission. FIrpic exhibits the emission around 470 nm, so the sharp emission with 612 nm from Eu complex easily confirm because the emission peaks separate each other. The emitting layer which consisted of the polymer and dopants were dissolved in dichloroethane. The weight ratios of  $\text{Eu}(\text{DDP})_3\text{phen}$  is 6 wt% for PVK. In the case of white OLEDs, the weight ratios are 6 and 12 wt% for FIrpic and  $\text{Eu}(\text{DDP})_3\text{phen}$ , respectively. The polymer containing dopants was formed by a spin-coating method into 95 nm-thick layers. The solvent was removed by baking the samples in air at 110 °C for 10 min after spinning. The cathode consisting of CsF/MgAg/Ag, was deposited in vacuum at a base pressure of  $10^{-4}$  Pa. Finally, the device was covered with a glass plate and encapsulated with epoxy resin in an argon gas atmosphere to prevent oxidation of the cathode and the organic layer.

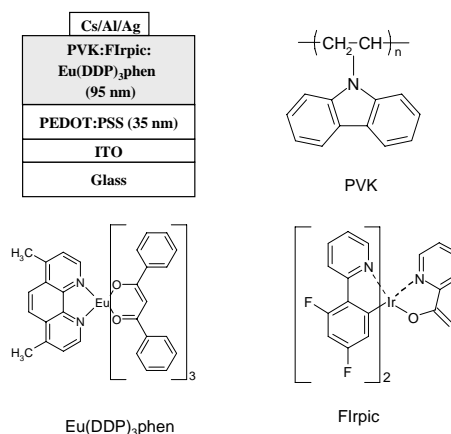


Fig. 1 Device structure and chemical structure employed in this study.

## 3. Result and Discussion

Figure 2 shows the absorption spectrum of FIrpic and  $\text{Eu}(\text{DDP})_3\text{phen}$ , and photoluminescence (PL) spectra of PVK, FIrpic and  $\text{Eu}(\text{DDP})_3\text{phen}$ . The PL spectrum of PVK and the absorption spectrum of  $\text{Eu}(\text{DDP})_3\text{phen}$  overlap around the wavelength of 390 nm. Therefore, the singlet energy transfers from PVK to  $\text{Eu}(\text{DDP})_3\text{phen}$  and that between PVK and  $\text{Eu}(\text{DDP})_3\text{phen}$ , the singlet energy transfer between PVK and FIrpic should occur. In the case of PVK:FIrpic system, the energy transfer process via the metal ligand charge transfer state (MLCT). The excited energy transfers from the single state of PVK to the single metal ligand charge transfer state ( $^1\text{MLCT}$ ), and transfers the triplet metal ligand charge transfer state ( $^3\text{MLCT}$ ) via intersystem crossing (ISC).

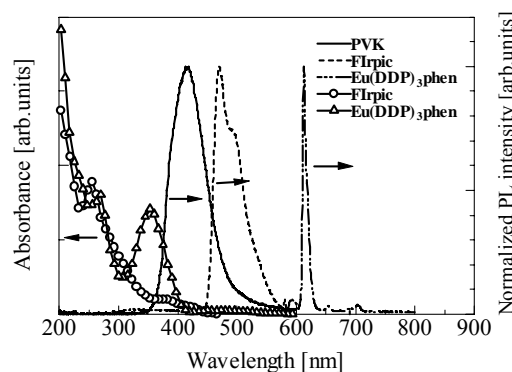


Fig. 2 Absorption and PL spectra of PVK, FIrpic and  $\text{Eu}(\text{DDP})_3\text{phen}$ .

In order to demonstrate the role of the doped  $\text{Eu(DDP)}_3\text{phen}$  on the device characteristics, we fabricated the three devices are as follows: (a) ITO/PEDOT:PSS (35 nm)/PVK: $\text{Eu(DDP)}_3\text{phen}$  (95 nm)/CsF/MgAg/Ag; (b) ITO/PEDOT:PSS (35 nm)/PVK:Firpic: $\text{Eu(DDP)}_3\text{phen}$  (95 nm)/CsF/MgAg/Ag; (c) ITO/PEDOT:PSS (35 nm)/PVK:Firpic (95 nm)/CsF/MgAg/Ag. The concentrations of Firpic and  $\text{Eu(DDP)}_3\text{phen}$  are 6 and 6 wt% for device (a), (c), and device (b) doped with 6 and 12 wt%, respectively. Figure 3 shows the EL spectra for different current density of the device (b). The spectra exhibit the broad emission due to Firpic and the sharp emission with slightly peak due to  $\text{Eu}^{3+}$ , showing that the excited energy transferred from PVK to  $\text{Eu(DDP)}_3\text{phen}$ . In the case of the same weight ratio of 6 wt%-Firpic and 6 wt% $\text{Eu(DDP)}_3\text{phen}$ , the sharp emission due to  $\text{Eu}^{3+}$  was not observed. The emission from  $\text{Eu(DDP)}_3\text{phen}$  and Firpic around 612 and 470 nm increase with increase the current density, respectively. At the low current region, the emission from  $\text{Eu}^{3+}$  are relatively high compared with that of Firpic. For high current region, however, the emission from Firpic increases and  $\text{Eu(DDP)}_3\text{phen}$  emission seems to be saturated from the inset of Fig. 3. The spectrum is composed of the blue emission from Firpic and red emission from  $\text{Eu(DDP)}_3\text{phen}$ . The saturation behavior due to the characteristics of  $\text{Eu}^{3+}$  based emitters when used in doping method such as polymer light-emitting diodes. The reason can be found that the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition characteristics of  $\text{Eu}^{3+}$  which is responsible for the sharp spectra line at 612 nm. The inversion symmetry is broken because the transition of  $4f \rightarrow 4f$  is strictly forbidden in a free  $\text{Eu}^{3+}$  ion and captures electric dipole. These transitions result in a long lifetime of emitters including  $\text{Eu}^{3+}$  [3].

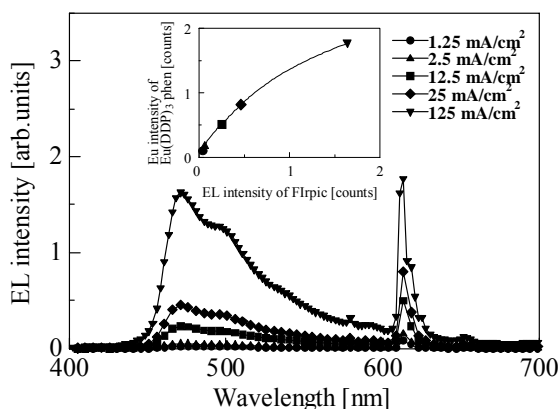


Fig. 3 EL spectra for different current density of the device (b).

Figure 4 shows the CIE coordinates of device (b) and the pure emission of Firpic and  $\text{Eu(DDP)}_3\text{phen}$ . The emission color shift to blue derived from Firpic emission with increasing the current density. Compared with the luminance-voltage characteristics of the device (a) and (c), the luminance of the device (a) decreases at the high voltage region due to the saturation of  $\text{Eu(DDP)}_3\text{phen}$ . The nearly

white emission with the CIE coordinates of (0.31, 0.38) was obtained at the current density of  $0.5 \text{ mA/cm}^2$ . Compared with the typically OLEDs such as fluorescent and phosphorescent materials doped in the host. The doping ratio of red dopants is approximately  $\sim 0.1 \text{ wt\%}$  for the host because the energies tend to transfer red dopants due to the lower energy level than blue and green dopants. Therefore, detailed control of the doping ratio especially in the case of red dopants. Advantages of employing the Eu complexes, however, for white OLEDs are able to dope the dopants at the high concentration (in this study, 12 wt%- $\text{Eu(DDP)}_3\text{phen}$  doped in PVK) because of their high triplet level. It is unnecessary to control the doping ratio of red dopants thoroughly and is possible to obtain the white emission easily.

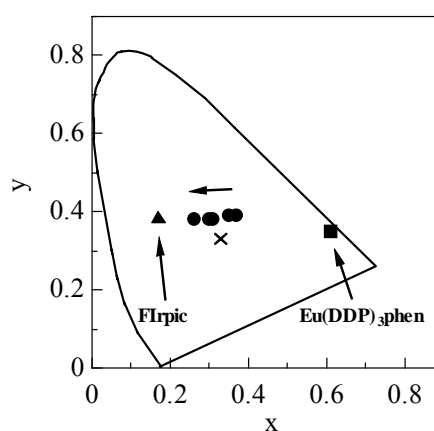


Fig. 4 CIE coordinates of device (b) and the pure emission of Firpic and  $\text{Eu(DDP)}_3\text{phen}$ .

#### 4. Conclusions

We investigated the energy transfer process and demonstrated white OLEDs utilizing the phosphorescent emission of Firpic and the sharp emission spectrum of  $\text{Eu(DDP)}_3\text{phen}$ . The PVK doped with Firpic and  $\text{Eu(DDP)}_3\text{phen}$  device exhibited the nearly white emission with the CIE coordinates of (0.31, 0.38) was obtained. One of the advantages of using Eu complexes for red dopant is, it is easy to control the doping ratio and obtain the white emission because of their high triplet level.

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#### References

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