Red Organic Electroluminescent Devices Based on Novel Furan-Contained Eu Complex as an Emitting Layer

Keizou Okada, Masahiro Uekawa,† Yan-Feng Wang, Tian-Ming Chen, and Tadao Nakaya*
Department of Bioapplied Chemistry, Faculty of Engineering, Osaka City University,
3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585
†*Research & Development Group, Oki Electric Industry Co., Ltd., 550 Higashiasakawa, Hachioji, Tokyo 193-8585*

(Received April 15, 1998; CL-980284)

A novel europium complex, Eu(DFP)$_3$(phen) (DFP=1,3-Di-(2-furyl)-1,3-propanedione, phen=1,10-phenanthroline), was synthesized and used as an emitting material in organic eletroluminescent (EL) devices. The structure of fabricated EL devices is composed of ITO / TPD / Eu(DFP)$_3$(phen) / AlLi(99:1). The double layered EL device emitted red light originating from Eu(DFP)$_3$(phen) with a maximum luminance of 34.3 cd/m^2 at 12 V and 25.7 mA/cm^2.

Organic electroluminescent (EL) devices are expected to be applied to a flat panel full color display. These devices are injection type and show a low driving voltage of less than 10 V. Since Tang and Van Slyke reported the first architecture of the double layered organic EL device,[1] many researchers have developed high performance green organic EL devices with tris(8-hydroxyquinolinate)aluminum (Alq$_3$).[2,3] Moreover, bright blue organic EL devices with distyryl derivatives have been reported by Hosokawa *et al.* [4] Some orange and red organic EL devices utilizing some complexes and/or organic dyes have also been discussed.[3,5] However, a bright red device has not yet been fabricated with high performance.

In order to realize an applicable red EL device, some researchers have investigated the organic EL devices with europium (Eu) complexes as an emitting layer because Eu complexes exhibit sharp red emission.[6-8] Additionally, since Eu complexes emitted at 615 nm via triplet of ligand, the devices emitted using singlet excitations and triplet excitations. From this point of view, it is possible to improve the quantum efficiency of the red light organic EL devices by using Eu complexes. However, there was some problems in the organic EL devices with Eu complexes. Sano and his co-workers overcome the problem of Eu complexes by synthesizing of a new Eu complex which was volatile.[7] They reported that the luminance of the device using the Eu complex as the dopant was higher than that of the device using the complex as the emitting material. However, in the case of device using the complex as the dopant, the problem of the energy transfer from the host material to the complex occurred. Moreover, the luminance of the device using the complex as the emitting material was low because the complex showed a poor carrier transportability and film formability. In this study, the preparation and characterization of a novel Eu complex, and the EL properties of such Eu complex will be discussed.

1,3-di-(2-furyl)-1,3-propanedione (DFP) was synthesized according to the Claizen condensation method.[9] To a solution of 2–acetylfuran in tetrahydrofuran (THF), were added of 2–furancarboxylic acid ethyl ester and of sodium amide. The mixture was stirred at 60 °C for 90 h. The solution was evaporated to a small volume and acidified with hydrochloric acid (HCl) solution. Then, the mixture was extracted with diethyl ether and purified by recrystallization from ethanol to give a pure product as a yellow solid. Elemental analysis of compound DFP: Found: C, 65.01; H, 4.15; O, 31.63%. Calcd for $C_{11}H_8O_4$: C, 64.71; H, 3.95, O, 31.34%. mp 55-58 °C.

(1,10-phenanthroline)-tris-[1,3-di-(2-furyl)-1,3-propanedione] -europium (III) or Eu(DFP)$_3$(phen) was synthesized by the conventional method.[10] To a solution of DFP and of 1,10-phenanthroline (phen) in ethanol which was stirred and neutralized with 1N sodium hydroxide (NaOH) solution, $EuCl_3 \cdot 6H_2O$ aqueous solution, was added by dropwise at room temperature. Then, the mixture was stirred at 60 °C for 1 h. The crude product, which simultaneously precipitated from the solution, was collected by filtration and purified by reprecipitation from hexane to afford the pure complex as a yellow solid. Elemental analysis of Eu complex: Found: C, 57.75; H, 3.48; N, 3.20; O, 20.11%. Calcd for Eu($C_{45}H_{29}N_2O_{12}$): C, 57.40; H, 3.10; N, 2.97; O, 20.39%. mp 127-129 °C. The chemical structure of Eu(DFP)$_3$(phen) is shown in Figure 1.

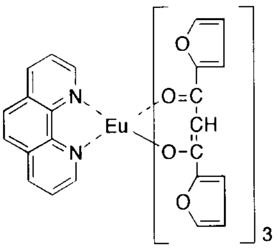

Figure 1. Molecular structure of Eu(DFP)$_3$(phen).

Preparation of EL devices: The double layered EL device was fabricated by using Eu(DFP)$_3$(phen) as an emitting layer (EML) sandwiched beween a hole transporting layer (HTL) and a cathode. The device structure is glass substrate / ITO anode / HTL (*N,N'*–diphenyl–*N,N'*–(3–methylphenyl)–1,1'–biphenyl–4,4'–diamine=TPD) (600 Å) / EML (Eu complex) (600 Å) / a cathode (Al:Li=99:1) (2000 Å). The organic layers and the AlLi top cathode were successively vacuum deposited onto an ITO–coated glass substrate at 3 × 10^{-6} Torr. Indium-tin-oxide (ITO) coated glass substrates were purchased from Matsunami Glass Industry Co., Ltd. Japan. The ITO layers, having a sheet resistance of 10 Ω / square, were etched to form stripes of 2 mm witdth which were used as anodes. The emitting area was 2 × 2 mm^2. Photoluminescent properties were investigated with a SHIMADZU RT-5000 spectrofluorophotometer. The thickness of vacuum-deposited films was measured with an Alpha Step profilometer. Luminance in units of cd/m^2 was measured by a luminance colorimeter TOPCON BN-7 Fast (TOPCON Co. Japan) at a measuring field of 0.2°.

The homogeneous thin film of the complex could be easily formed by vapor deposition method and confirmed by SEM observation. Figure 2 shows the EL spectrum and the photoluminescence (PL) spectrum of Eu(DFP)$_3$(phen) in THF solution. The EL spectrum was recorded when the luminance was 20 cd/m^2 (9.5V, 6.0 mA/cm^2). It can be seen that the Eu complex containing furan groups exhibited a sharp emission peak at 614 nm in THF solution. Moreover, the double layered EL device exhibited a sharp red emission peak at 611 nm due to the $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} ion.[11] The identical two spectra suggested that there was no interaction between the TPD layer and Eu(DFP)$_3$(phen) layer, and indicated that the hole–electron recombination occurred in the Eu(DFP)$_3$(phen) layer.

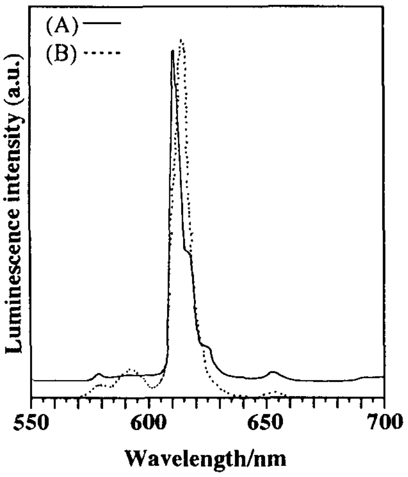

Figure 2. (A) EL spectrum of [ITO / TPD (600 Å) / Eu(DFP)$_3$(phen) (600 Å) / AlLi(2000 Å) device, and (B) PL spectrum of Eu(DFP)$_3$(phen) in THF solution (λ_{ex}=250nm).

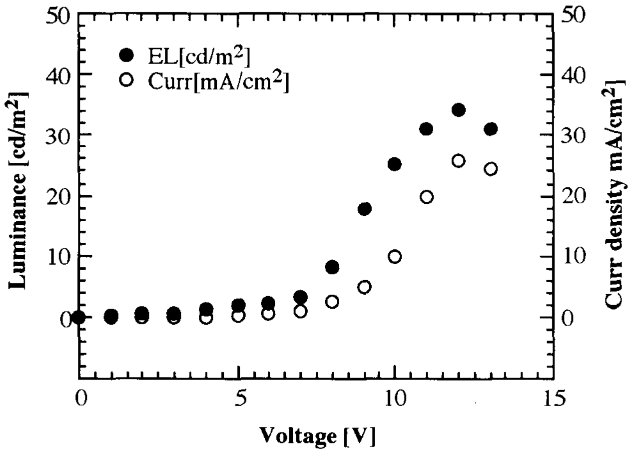

Figure 3. The luminance-current density-voltage characteristics of the double layer type EL device.

The luminance-current density-voltage characteristics of the double layered EL device is shown in Figure 3. It can be found that the Luminance increases with increasing injection current as well as bias voltage. The bright red light with the maximum luminance of 34.3 cd/m^2 was observed at 12 V and 25.7 mA/cm^2 from Eu(DFP)$_3$(phen) device, which was higher than that of the luminance (7 cd/m^2) from Eu(TTA)$_3$(phen) (TTA= thenoyltrifluoroacetone) device.[12] In comparison with the Eu (TTA)$_3$(phen) device which the efficiency was estimated to be 5.76 x 10^{-2} (lm/W), the EL efficiency of Eu(DFP)$_3$(phen) device at the 1.96 x 10^{-2} (lm/W) by the following equation: h (lm/W) = πL[cd/m^2] / vj[W/m^2], where L was the luminance and J was the current density.[13]

In conclusion, a novel volatile Eu complex was synthesized and used to prepare the double layered EL device. A very sharp EL spectral band centered at the wavelength of 611 nm and a bright red light with the maximum luminance of 34.3 cd/m^2 were observed from the prepared organic EL device without any electron transport layer. This is to say that Eu(DFP)$_3$(phen) has a good carrier transportability in the solid state. The further study concerning lifetime will be discussed in the near future and reported elsewhere. We are currently focussed on some other metal complexes to improve the luminous efficiency and obtain different luminescent colors such as yellow and blue.

References and Notes

1 C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.*, **51**, 913 (1987).
2 C. W. Tang, S. A. VanSlyke, and C. H. Chen, *J. Appl. Phys.*, **65**, 3610(1989).
3 C. Adachi, S. Tokito, T. Tsutsui, and S. Saito, *Jpn. J. Appl. Phys.*, **27**, L269 (1988).
4 C. Hosokawa, H. Higashi, H. Nakamura, and T. Kusumoto, *Appl. Phys. Lett.*, **67**, 3853 (1995).
5 J. Kido and J. Endo, *Chem. Lett.*, **1997**, 633.
6 N. Takada, T. Tsutsui, and S. Saito, *Jpn. J. Appl. Phys.*, **33**, 863 (1994).
7 T. Sano, M. Fujita, T. Fujii, Y. Hamada, K. Shibata, and K. Kuroki, *Jpn. J. Appl. Phys.*, **34**, 1883 (1995).
8 J. Kido, H. Hayase, K. Hongawa, K. Nagai, and K. Okuyama, *Appl. Phys. Lett.*, **65**, 2124 (1994).
9 Y. H. Zhou, R. Q. Liu, D. L. Kong, and J. T. Sun, *Macromol. Symp.*, **105**, 223 (1996).
10 L. R. Melby, N. J. Rose, E. Abramson, and J. C. Caris, *J. Am. Chem. Soc.*, **86**, 5117 (1964).
11 R. A. Campos, I. P. Kovalev, Y. Guo, N. Wakili, and T. Skotheim, *J. Appl. Phys.*, **80**, 7144 (1996).
12 T. Sano, M. Fujita, T. Fujii, and Y. Hamada, *Jpn. J. Appl. Phys.*, **34**, 1883 (1995).
13 S. Shioya and A. Ibuki, *Appl. Phys.*, **57**, 935 (1988).