Efficient Red Electroluminescence from New Europium Complex

Mitsuharu Noto, Kazutaka Irie,† and Masanao Era††
R&D Group, Daiden Co. Ltd, Kitashigeyasu, Saga 849-0114
†*Department of Physics, Kurume National College of Technology, Kurume, Fukuoka 830-8555*
††*Department of Chemistry and Applied Chemistry, Faculty of Science and Engineering, Saga University, Saga 840-8502*

(Received December 15, 2000; CL-001123)

Efficient red electroluminescence (EL) was performed in the organic electroluminescent device using emissive layer of a new Eu complex, which has 2,4-dioxopentanedinitrile (1,3-dicyano-1,3-propanedione, DCNP), 1,3-diphenyl-1,3-propanedione (dibenzoylmethane, DBM) and 1,10-phenanthroline (phen) (1:2:1) as ligands, doped into 2-(biphenyl-4-yl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) host; luminance, external quantum efficiency and power efficiency of the EL were 10 cd m^{-2}, 3.5% and 2.0 lm W^{-1} at a current density of 0.17 mA cm^{-2}, and 84 cd m^{-2}, 1.6% and 0.69 lm W^{-1} at 2.9 mA cm^{-2}.

Organic electroluminescent (EL) device has attracted the great interest as display application since the innovative report by C. W. Tang and S. A. VanSlyke.[1] For the attainment of high performance display using organic EL, it is indispensable to develop highly efficient emissive materials in the three primary color (red, green and blue). However, a few highly efficient red emission materials have been reported although a lot of effort has been made in the development of emissive materials.[2–4] The development of red emission materials is one of the key issues for high performance display of organic EL.

Eu complex is a promising candidate for red emission material.[5–7] Its sharp emission due to ^5Dx–^7Fx transition of Eu^{3+} is expected to provide not only high color purity of red EL but higher power efficiency in comparison with that of broad-band emission materials even when their external quantum efficiencies are comparable. In addition, the complex possesses the possibility to attain very high quantum efficiency of EL because the emission is caused through the energy transfer from the triplet excited state of ligand to the excited state of Eu^{3+}; the EL may arise from both singlet and triplet excited states created by recombination of injected charge carriers. However, almost previous works on EL device using Eu complex as emissive material have been reported low external quantum efficiency of less than 1%. In this work, we prepared a new complex Eu(DCNP)$(DBM)_2$phen, and attained efficient red emission in the organic EL device with emissive layer of the Eu complex doped into PBD host.

Molecular structure of the new Eu complex is shown in Figure 1. The Eu complex has 2,4-dioxopentanedinitrile(1,3-dicyano-1,3-propanedione, DCNP), 1,3-diphenyl-1,3-propanedione (dibenzoylmethane, DBM) and 1,10-phenanthroline (1:2:1) as ligands. DCNP was prepared by the Claisen condensation of ethyl cyanoformate and 2-oxopropionitrile.[8] DBM and 1,10-phenanthroline were purchased from Tokyo Kasei Co. Ltd. and used without further purification. Stoichiometric amounts of $EuCl_3 \cdot 6H_2O$ and the ligands were dissolved in ethanol. For precipitation of the Eu complex, pH of the solution was adjusted to be about 6.5 by addition of 1 M HCl solution. The precipitated complex was purified by the recrystallization from ethanol.

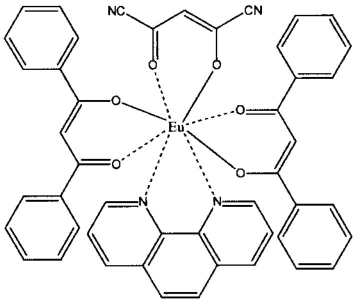

Figure 1. Molecular structure of Eu complex prepared in this study.

In this study, we prepared two types of device structure. One (device 1) consisted of transparent indium-tin-oxide (ITO) anode, a 50-nm thick hole-transport layer of TPD, a 10-nm thick emissive layer of PBD doped with Eu(DCNP)$(DBM)_2$phen, a 25-nm thick electron-transport layer of TAZ, a 30-nm thick electron-injection layer of (Alq), and 10:1 Mg:Ag alloy cathode (200 nm thick). The other (device 2) consisted of ITO, 50-nm thick TPD layer, a 20-nm thick emissive layer of CBP doped with Eu(DCNP)$(DBM)_2$phen, a 15-nm thick hole-blocking layer of BCP, a 30-nm thick Alq layer, and 200-nm thick MgAg cathode, where TPD; *N,N'*-bis(3-methylphenyl)-*N,N'*-diphenylbenzidine, TAZ; 3-(biphenyl-4-yl)-4-phenyl-5-(4-*tert*-butyl)phenyl-1,2,4-triazole, Alq; tris(8-hydroxyquinoline)aluminium; CBP; 4,4'-bis(carbazol-9-yl)biphenyl, BCP; 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline. Doping concentration of Eu(DCNP)$(DBM)_2$phen was 10 wt% in the both devices. All organic layers and MgAg alloy were prepared with vacuum-deposition at a base pressure of about 10^{-6} torr. After the deposition of Eu(DCNP)$(DBM)_2$phen, a small amount of darken residue was observed in the crucible, suggesting that the Eu complex was slightly decomposed during the deposition.

Figure 2 shows EL spectra of the devices at a current density of 0.17 mA cm^{-2}. The EL spectra correspond well to the photoluminescence of the Eu complex; a main sharp peak, which is originated from ^5Dx–^7Fx transition of Eu^{3+}, locates at 615 nm. In addition, the EL spectra are independent of current density even in high current density region of more than 100 mA cm^{-2} while emission from host material was not observed. The results demonstrate that radiative recombination occurred only in Eu^{3+} site. These also suggest that creation of triplet excited states of ligands through energy transfer from host to ligand or carrier-trap of the complex was very efficient, and that excitation of host materials by triplet–triplet annihilation of ligands did not occur even in high current density region. From the spectra, chromaticity coordination of the EL was determined to be x:0.64 and y:0.33, implying the EL is of good red color purity.

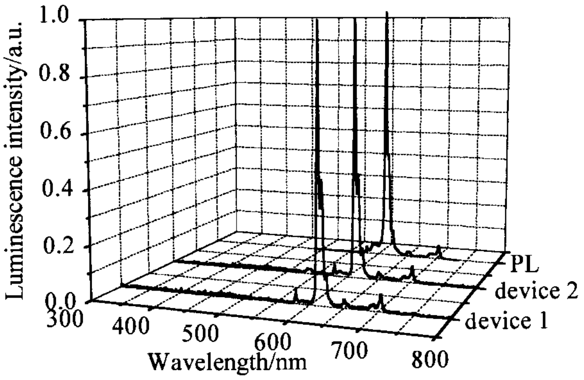

Figure 2. EL spectra of device 1 (ITO/TPD/Eu(DCNP)(DBM)$_2$-phen doped PBD/TAZ/Alq/MgAg), device 2 (ITO/TPD/Eu-(DCNP)(DBM)$_2$phen doped CBP/BCP/Alq/MgAg), and PL spectrum of vacuum-deposited film of Eu(DCNP)(DBM)$_2$phen.

Figure 3 shows the luminance (L) and current density (J) characteristics of the devices. External quantum efficiency η of EL, which was estimated from the L–J characteristics, is also shown in the same figure. Device 1 exhibited very high external quantum efficiency η_{ex} and power efficiency η_{pw}. The η_{ex} and of η_{pw} of device 1 were 3.5% and 2.0 lm W^{-1} at L = 10 cd m^{-2} at J = 0.17 mA cm^{-2}, and 1.6% and 0.69 lm W^{-1} at L = 84 cd m^{-2} at J = 2.9 mA cm^{-2}. To our knowledge, the efficiency values are highest in comparison with those of the EL device using Eu complex which have been reported. As observed in other EL device using Eu complex, however, η_{ex} is decreased with increasing current density. As increasing J to 223 mA cm^{-2}, L reached to 480 cd m^{-2}, and η_{ex} and η_{pw} decreased to 0.12% and 0.034 lm W^{-1}.

Using the Eu complex, Eu(DBM)$_3$phen which has been reported to exhibit a good,[7] for a comparison, we prepared the EL device having the same device-structure with device 1; the η_{ex} of the EL device using Eu(DBM)$_3$phen was about one third that of device 1, η_{ex} = 1.1% at L = 3.2 cd m^{-2} at J = 0.16 mA cm^{-2}. The result suggests that very efficient EL of device 1 is due to the employment of the new Eu complex.

While efficiency of device 2 is about one order of magnitude lower than that of device 1 in relatively low current density region of less than 100 mA cm^{-2}, the efficiency is comparable with that of device 1 in current density region of more 300 mA cm^{-2}. Maximum luminance of device 2 reaches to very high value of 924 cd m^{-2} at a current density of 380 mA cm^{-2}.

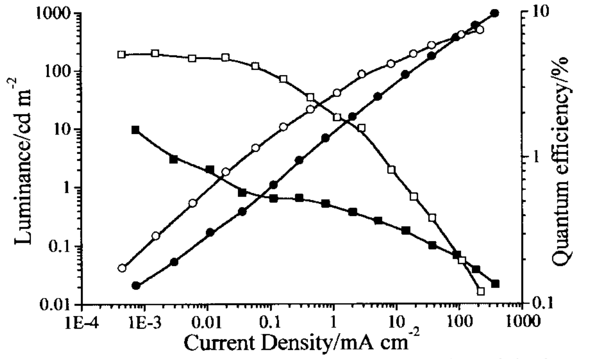

Figure 3. Luminance-current density characteristics of device 1 (open circles) and device 2 (solid circles). Open and solid squares show external quantum efficiencies of device 1 and device 2, respectively.

In this work, we demonstrated that the EL devices using our new Eu complex exhibit very high external quantum efficiency, power efficiency, and maximum luminance in addition to the good red color purity of the EL. This demonstration reveals that our new Eu complex is promising as red emission material. Further investigations on mechanism of the high efficient EL and improvement of the emission efficiency in high current density region are now in progress.

References

1 C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.*, **51**, 1489 (1987).

2 B. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, and S. R. Forrest, *Nature*, **385**, 151 (1998).

3 C. H. Chen, C. W. Tang, J. Shi, and K. P. Klubek, *Macromol. Symp.*, **125**, 49 (1998).

4 T. Shimoda, M. Kimura, S. Miyashita, R. H. Friend, J. H. Burroughes, and C. R. Towns, *SID 99 DIGEST*, **1999**, 372.

5 J. Kido, H. Hayase, K. Hongawa, K. Nagai, and K. Okuyama, *Appl. Phys. Lett.*, **65**, 2124 (1994).

6 C. Adachi, M. A. Baldo, and S. R. Forrest, *J. Appl. Phys.*, **87,** 8049 (2000).

7 C. J. Liang, D. Zhao, Z. R. Hong, D. X. Zhao, X. Y. Liu, W. L. Li, J. B. Peng, J. Q. Yu, C. S. Lee, and S. T. Lee, *Appl. Phys. Lett.*, **76**, 67 (2000).

8 I. Yoshida, Y. Oono, H. Kobayashi, and K. Ueno, *Bull. Chem. Soc. Jpn.*, **45**, 174 (1972).