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# Enhanced electroluminescence of europium(III) complex by terbium(III) substitution in organic light emitting diodes

Dongxu Zhao<sup>a</sup>, Ziruo Hong<sup>a</sup>, Chunjun Liang<sup>a, b</sup>, Dan Zhao<sup>a</sup>, Xingyuan Liu<sup>a</sup>, Wenlian Li<sup>a, b,\*</sup>, C.S. Lee<sup>c</sup>, S.T. Lee<sup>c</sup>

<sup>a</sup>Changchun Institute of Physics, Chinese Academy of Sciences, Changchun, People's Republic of China, 130021 <sup>b</sup>Laboratory of Excited State Processes, Chinese Academy of Sciences, Changchun, People's Republic of China, 130021 <sup>c</sup>Department of Physics and Materials Science, City University of Hong Kong, Hong Kong, China

#### **Abstract**

A binuclear complex  $Tb_{0.5}Eu_{0.5}(aca)_3$ phen was synthesized and used as the emission material. It was found that there is an efficient energy transfer from  $Tb^{3+}$  to  $Eu^{3+}$  in the emitting layer. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Binuclear complex; Organic electroluminescence; Energy transfer

#### 1. Introduction

Organic electroluminescence (OEL) has been extensively studied because of their potential application in flat panel displays since the first two-layer OEL device with high efficiency and luminance was fabricated in 1987 [1–3]. Rare earth (RE) metal complexes have some good characteristics, such as extremely narrow emission bands and high internal quantum efficiencies, which are suitable for use as the emission materials in OEL [4]. Tb<sup>3+</sup> complex was first introduced into OEL devices, and sharp green emission from Tb<sup>3+</sup>ion has been observed [5]. Since then, many RE complexes have been synthesized and used as the emitters in OEL devices successfully [6,7]. However, the luminance of the devices using these RE complexes is relatively low as comparing to Alq<sub>3</sub>.

In order to get brighter OEL, two methods can be applied to the RE complexes besides choosing a suitable device structure: (i) selection of proper ligands, especially adopting a second ligand; (ii) introduction of another metal ion into the complex. The second approach has not been used for OEL applications. In this paper, an OEL device with a Tb<sup>3+</sup> and Eu<sup>3+</sup> binuclear complex as the emitter was fabricated. It was found there was an efficient energy transfer process between the ligands and metal ions when the device was operated at low voltages.

# 2. Experimental

The binuclear complex is  $Tb_{0.5}Eu_{0.5}(aca)_3$ phen. The ligands are acetylacetonato (aca) and monophenanthroline (phen) which have been proven efficient for  $Tb^{3+}$  ion. The device structure (Device I) is shown in Fig. 1. For comparison purpose, another device (Device II) with the same structure except replacing  $Tb_{0.5}Eu_{0.5}(aca)_3$ phen with  $Eu(aca)_3$ phen has also been fabricated. The hole-transporting material is poly(N-vinylcarbazole) (PVK) which was spin-coated on ITO from its chloroform solution. The complex was thermally evaporated on the surface of the PVK film at  $4\times 10^{-5}$  Torr. Finally an aluminum cathode was deposited by thermal evaporation. Spectra presented in this paper were measured using a Hitachi 4000 Spectrometer in air at room temperature.

## 3. Results and discussion

The maximum luminance of the device ITO/PVK/ Tb(aca)<sub>3</sub>phen/Al was found to be 210 cd/m² [8]. The red emission was only a few cd/m² in the device ITO/PVK/ Eu(aca)<sub>3</sub>phen/Al (Device II). When using Tb<sub>0.5</sub>Eu<sub>0.5</sub>(aca)<sub>3</sub>phen as the emitter the red light was much stronger at the same voltage. The EL spectra were obtained at 5 V (Fig. 2a). It was observed that the main emitting peak is at 615 nm which can be attributed to the transition of  $^5D_0 \rightarrow ^7F_2$  of Eu $^{3+}$  ion. The peak at 545 nm from the Tb $^{3+}$  is much lower. The intensity of the red emission at 615 nm in Device I is about ten times as strong as that in Device II.

<sup>\*</sup> Corresponding author.

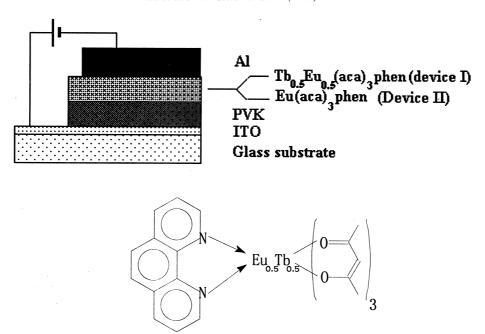


Fig. 1. Configuration of the devices fabricated and the structure of the binuclear complex.

The current-voltage curves of Device I and II are shown in Fig. 3. From the figure it can be seen that these two curves are almost the same. In conclusion, an efficient energy transfer from Tb<sup>3+</sup> to Eu<sup>3+</sup> exists in the complex of Tb<sub>0.5</sub>Eu<sub>0.5</sub>(a-ca)<sub>3</sub>phen. This process has resulted in much enhanced red emission from OEL device made of this binuclear metal complex. So the enhanced red emission in Device I is most likely due to the enhanced energy transfer form Tb<sup>3+</sup> to Eu<sup>3+</sup>.

A probable process of energy transfer is shown in Fig. 4. The holes and electrons are injected into the organic layers from the ITO and the Al layers, respectively. The recombining zone of the hole and electron should be at the Eucomplex layer. Then the energy is transferred to the binuclear complex. This process results in an electron transition from the  $S_0$  states the first singlet  $S_1$  and triplet  $T_1$  excited

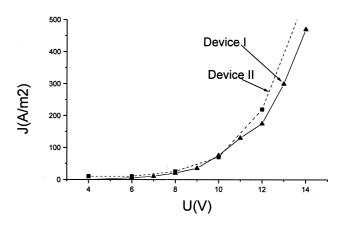


Fig. 3. Current density-voltage characteristic of the two devices.

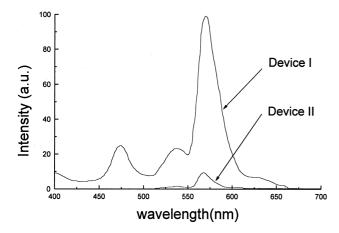


Fig. 2. Electroluminescence spectra at a driving voltage of 5 V.

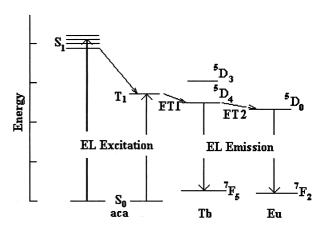


Fig. 4. The energy transfer process.

states at the organic ligand. Several non-radiation relaxation processes can occur:  $S_1 \rightarrow T_1 \rightarrow Tb^{3+} \rightarrow Eu^{3+}$ . Finally, most of the energy is given out by the radiation of  $^5D_0 \rightarrow ^7F_2$  transition of the Eu<sup>3+</sup> ion. So the emission at 615 nm should be much greater than the green emission from  $Tb^{3+}$ . Hence, the red OEL emission of  $Tb_{0.5}Eu_{0.5}(aca)_3$ phen is about one order of magnitude brighter than that of the  $Eu(aca)_3$ phen complex.

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## References

- [1] C.W. Tang, S.A. Van Slyke, Appl. Phys. Lett. 51 (1987) 913.
- [2] T. Tsutsui, E. Aminaka, Y. Hamada, C. Adachi, S. Saito, SPIE Proc. 180 (1988) 1910.
- [3] C. Adachi, T. Tsutsui, S. Saito, Appl. Phys. Lett. 57 (1990) 531.
- [4] J. Kido, H. Hayase, K. Hongawa, K. Nagai, K. Okuyama, Appl. Phys. Lett. 65 (1994) 2124.
- [5] J. Kido, M. Nagai, Y. Ohashi, Chem. Lett. (1990) 657.
- [6] W.L. Li, J.Q. Yu, G. Sun, et al., Synth. Met. 91 (1997) 263.
- [7] L. Liu, W.L. Li, Z.R. Hong, et al., Synth. Met. 91 (1997) 267.
- [8] G. Sun, W.L. Li, et al., J. Chin. Lumi. (in Chinese) 17 (1996) 93.