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White light emitting organic electroluminescent devices using lanthanide dinuclear complexes

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Abstract

Organic electroluminescent devices with $Eu_xTb_{1-x}(aca)_3phen$ dinuclear complex as the emitting layer were fabricated. When the devices are operated under proper voltage the white light can be obtained. It consists of three parts: red from Eu^{3+}, green from Tb^{3+} and blue from TPD (or NPB). © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Organic electroluminescence; White light; Energy transfer; Dinuclear complex; $Eu_xTb_{1-x}(aca)_3phen$

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1. Introduction

Organic light emitting diodes (OLEDs) have attracted considerable interest in these years, because of their potential application in large area flat-panel display [1,2]. Now OLEDs have achieved in full color display covering the visible spectrum from blue to red [3–5]. Differing from other colors, the white emission from OLEDs has some special advantage. It can be used as the backlight of liquid crystal displays, which is as thin as a piece of paper, and the white can also produce full color display using micropattered color filter [6]. There are several devices designed from which the white light has been observed [6–10]. The materials used in these devices include conjugated polymers [11], metal complexes [6,7] and organic dyes [12]. Some spectra of the white light have a broad band covering the whole visible region. In order to achieve maximum efficiency and high color purity, white light should be composed of three discrete peaks in the blue, green and red region. But organic fluorescent dyes and polymers possess broad spectra and are not suitable for this purpose [6]. The rare-earth metal complexes exhibit extremely sharp emission bands in photoluminescent (PL) and electroluminescent (EL) spectra. Kido et al. has used Tb^{3+} and Eu^{3+} complexes to achieve a white device with a multilayer structure [6,7].

In this study, a series of $Eu_xTb_{1-x}(aca)_3phen$ dinuclear complexes are employed as the emitting layer in OLEDs from which the white emission can be observed at an appropriate DC voltage.

2. Experimental

The dinuclear complexes $Eu_xTb_{1-x}(aca)_3phen$ ($x = 0 - 1$) were synthesized in our laboratory. The

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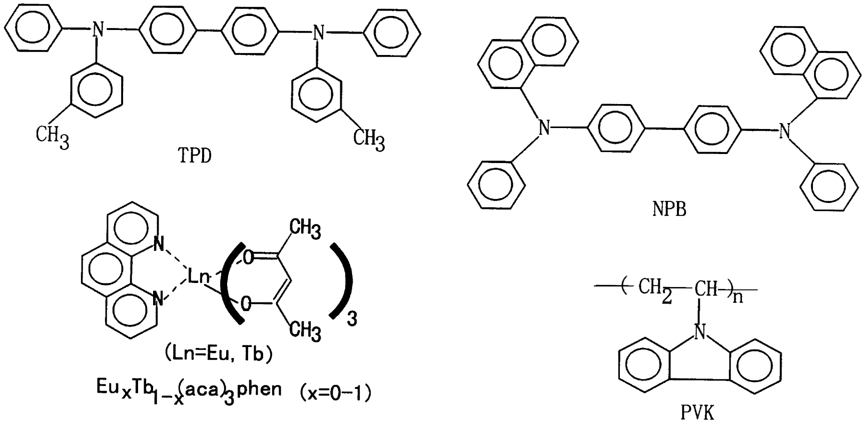

Fig. 1. The molecular structures of the materials used in this work.

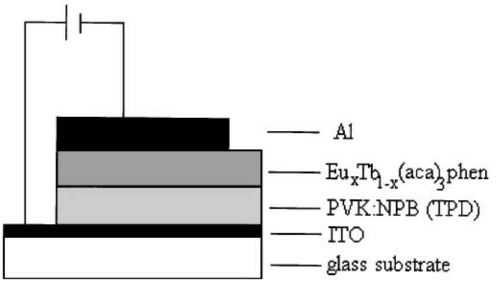

Fig. 2. The device structure used.

detailed method and other properties will be delivered in another article. The molecule structure is shown in Fig. 1. The mole ratios of the Eu^{3+} and Tb^{3+} are 8 : 2, 5 : 5, 2 : 8, 1 : 9, respectively. The Eu^{3+} and Tb^{3+} ions are just in one molecule. These complexes can easily evaporate into film.

The typical structure of the device is shown in Fig. 2. It consists of two active organic layers sandwiched between an electron injecting (aluminum) and a hole injecting contact (indium–tin-oxide, ITO). The poly (*N*-vinylcarbazole) (PVK) doped with tetraphenyldiamine derivative (TPD) or 4,4'-bis[*N*-(1-naphthyl)-*N*-phenylamino]-biphenyl (NPB) was introduced as the first layer by spin-coating from their chloroform solution on an ITO coated glass slide at 2000 rpm. The weight ratio of the PVK and the diamine is 5 : 2. The second layer is one of $Eu_xTb_{1-x}(aca)_3phen$ which was deposited by evaporation at the presser of 5×10^{-5} Torr. The thickness of the first two layers is about 100 and 80 nm, respectively. At last a 150 nm aluminum layer was evaporated at 5×10^{-5} Torr. All sample preparation and handing was carried out in laboratory atmosphere. The active area of the devices was 2×3 mm^2.

The PL and EL properties of the films and devices were determined with the Hitachi 4000 Spectrometer at room temperature in air.

3. Results and discussion

Fig. 3 shows the emission spectrum of $Eu_{0.5}Tb_{0.5}(aca)_3phen$ film evaporated onto glass substrate. There are three main peaks at 615, 595 and 550 nm. The first two bands come from Eu^{3+} ion corresponding to the transition of $^5D_0$–$^7F_2$ and $^5D_0$–$^7F_1$ and the third corresponds to the $^5D_4$–$^7F_5$ electronic transition of Tb^{3+} ion. The peak at 615 nm is much stronger than the others.

The EL spectra based on pure PVK and $Eu_{0.5}Tb_{0.5}(aca)_3phen$ at different voltage is shown in Fig. 4 in which there are two main peaks: one is green at 550 nm which comes from Tb^{3+} ion, the other is red at 616 nm coming from Eu^{3+} ion. When operated at 7 V, the emission intensities of the two peaks are almost the same. When the bias voltage is increased to 10 V, the green emission increases more quickly than the red. Because of scaring of blue light, the color range of the device

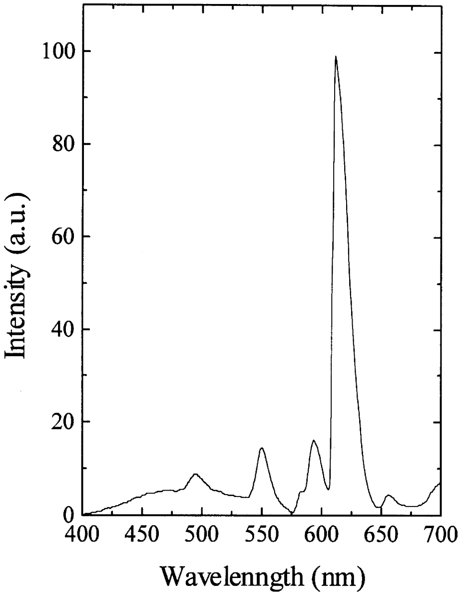

Fig. 3. The PL spectrum of the $Eu_{0.5}Tb_{0.5}(aca)_3phen$ film (Ex = 277 nm).

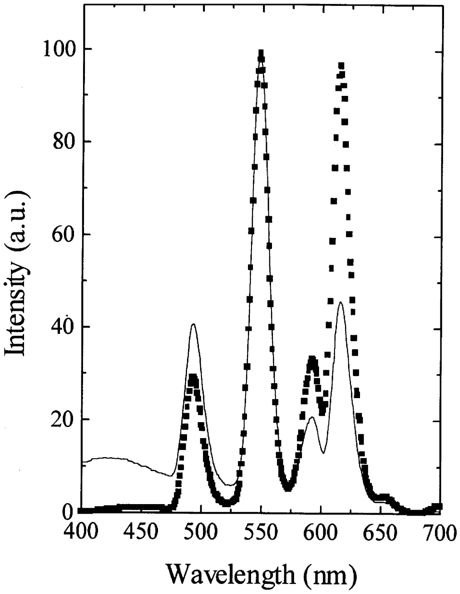

Fig. 4. The EL spectra of the device $ITO/PVK/Eu_{0.5}Tb_{0.5}(aca)_3phen/Al$ at 7 V (- - - -) and 10 V (———).

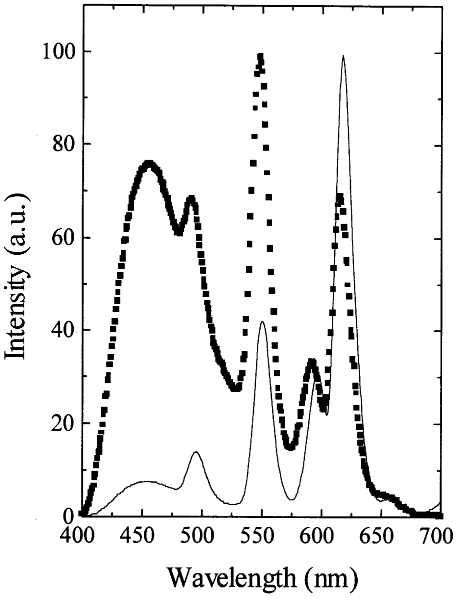

Fig. 5. The EL spectra of the device $ITO/PVK:NPB/Eu_{0.5}Tb_{0.5}(aca)_3phen/Al$ at 6.8V (———) and 10.7V (- - - -).

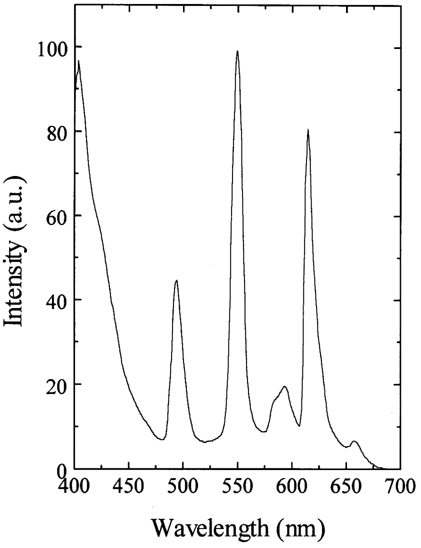

Fig. 6. The EL spectrum of the device $ITO/PVK:TPD/Eu_{0.5}Tb_{0.5}(aca)_3phen/Al$.

is changed from yellow to yellow–green. In order to observe white light, the blue emission is needed besides green and red. So NPB or TPD was doped into the PVK layer. Two kinds of devices were obtained based on them. Device I: $ITO/PVK:NPB/Eu_{0.5}Tb_{0.5}(aca)_3phen/Al$, and Device II: $ITO/PVK:TPD/Eu_{0.5}Tb_{0.5}(aca)_3phen/Al$. The EL spectra are shown in Figs. 5 and 6, respectively. To device I, there are three main peaks at

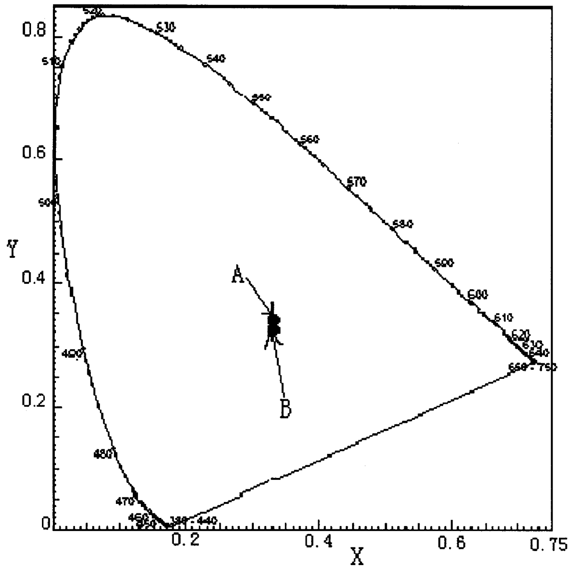

Fig. 7. CIE 1993 x, y chromaticity diagram for (A) ITO/PVK : NPB/ $Eu_{0.5}Tb_{0.5}(aca)_3phen$/Al, (B) ITO/PVK : TPD/ $Eu_{0.5}Tb_{0.5}(aca)_3phen$/Al.

450, 550 and 617 nm which come from NPB, Tb^{3+} and Eu^{3+}, respectively. When the device is driven with a continuous DC mode for a forward bias with ITO at positive, the color of the device is varied from red to white. It is at 10.7 V that the white light appears. The commission Internationale de l'Eclairage (CIE) coordinates of the emitted light at 10.7 V are $X = 0.325$, $Y = 0.337$ (Fig. 7, spot A). The EL spectrum of device II that was measured at 15 V is shown in Fig. 6, which corresponds to CIE coordinates of $X = 0.333$, $Y = 0.332$ (Fig. 7, spot B). It is observed that there is an obvious peak in the blue region at 406 nm that was emitted by TPD. From the spectrum it is also noticed that there is no broad band ranging from 500 to 700 nm which was found in the spectrum of Ref. [6], and was believed that comes from an exciplex formed between TPD and the phenanthroline of $Tb(acac)_3phen$ [6]. The main reason is that since TPD is dispersed in PVK film uniformly, the contact in the interface is mainly between PVK and dinuclear complex. The exciplex cannot be formed.

Although white light can be obtained from both types of devices, the voltage values at which the white emission begins to appear are very different. The performance of device I is better than that of device II, because the white light can be seen at lower voltage.

It is also noticed that differing from the PL spectrum the green emission becomes more and more prominent when the operating bias is higher in EL spectra. It is believed that the recombination of holes and electrons mainly takes place in the dinuclear complex layer at low voltage. So the blue light is very poor, and because there is an efficient energy transfer process from Tb^{3+} to Eu^{3+} the red light emitted from Eu^{3+} ion is brighter than the green. But when the bias is raised the recombination region moves to the interface of the two organic layers. The blue emission is enhanced sharply. Because of the influence of the PVK layer at the interface, the probability of the $^5D_4$–$^7F_5$ electronic transition of Tb^{3+} is increased and the energy transfer efficiency of Tb^{3+} to Eu^{3+} was reduced.

Our devices are of a simple structure and easy to be fabricated, and because there is only one interface where the recombination of electrons and holes may occur, the white light can be observed more conveniently. An exciplex that could lower the quantum efficiency of the device cannot form in our devices.

From the other mole ratio of Eu^{3+} and Tb^{3+} ions in dinuclear complex, such as 2 : 8, the white emission can also be seen. The EL spectrum of the device ITO/PVK : NPB/$Eu_{0.2}Tb_{0.8}(aca)_3phen$/Al is shown in Fig. 8. It was acquired at 6.5 V and the CIE coordinates are $X = 0.328$, $Y = 0.335$.

The dependence of the driving voltage of white emission on the ratio of the Eu^{3+} and Tb^{3+} ions in the dinuclear complex is shown in Fig. 9. It indicates that when the mole ratio of the Tb^{3+} ion is enhanced, the voltage of the appearing white light is lowered. The possible explanation is that although there is an energy transfer process in binuclear complex the opportunity of the electron transition of Tb^{3+} ion is increased when raising the content of the Tb^{3+} ion and the proportion of the green light is enhanced in the EL spectra at low voltage.

In conclusion, the devices of two layers using Eu^{3+} and Tb^{3+} binuclear complexes as the emitter can be developed to achieve the white light, and the

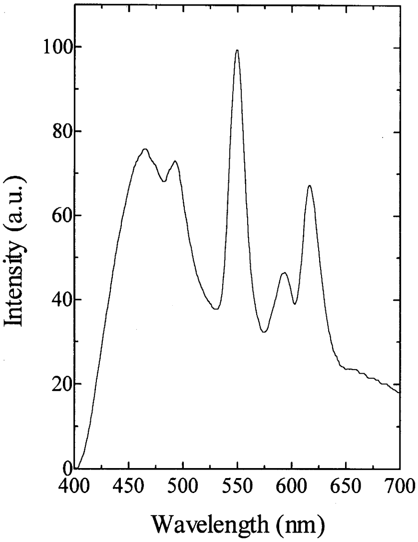

Fig. 8. The EL spectrum of the device ITO/PVK : NPB/ $Eu_{0.2}Tb_{0.8}(aca)_3phen/Al$.

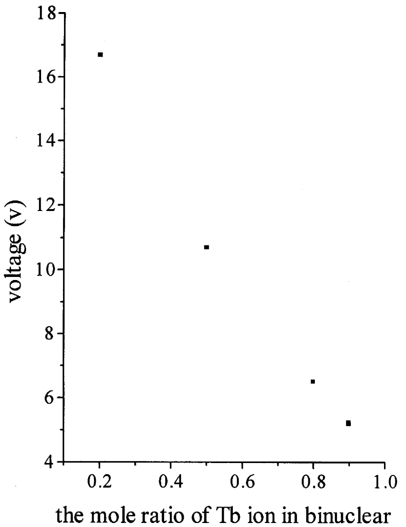

Fig. 9. The origin voltage of the white following the different ratio of the Eu^{3+} and Tb^{3+} ions in dinuclear complexes.

voltage under which the white light appears is verified with the different proportion of Tb^{3+} ion. The white emission is simple to realize in our devices. The use of binuclear complexes with Eu^{3+} and Tb^{3+} in EL device will be interesting for design of new organic EL materials and a new type EL device configuration.

Acknowledgements

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References

[1] C.W. Tang, S.A. Vanslyke, Appl. Phys. Lett. 51 (1987) 913.
[2] C.W. Tang, S.A. Vanslyke, C.H. Chen, J. Appl. Phys. 65 (1989) 3610.
[3] G. Grem, G. Leditzky, B. Ullrich, G. Leising, Adv. Mater. 4 (1992) 36.
[4] N.C. Greenham, S.C. Moratti, D.D.C. Bradley, R.H. Friend, A.B. Holmes, Nature (London) 365 (1993) 628.
[5] Y. Ohmori, M. Uchido, K. Muro, K. Yoshino, Jpn. J. Appl. Phys. Part 2 30 (1991) L1938.
[6] J. Kido, W. Ikeda, M. Kimura, K. Nagai, Jpn. J. Appl. Phys. 35 (1996) L394.
[7] J. Kido, M. Kaimura, K. Nagai, Science 267 (1995) 1332.
[8] R.H. Jordan, A. Dodabalapur, M. Strukelj, T.M. Miller, Appl. Phys. Lett. 68 (1996) 1192.
[9] M. Matsura, H. Tokailin, M.C. Hosokawa, Y. Hironaka, T. Kusumoto, Proc. Asia Display '95, 1995, p. 269.
[10] C.C. Wa, J.C. Sturm, R.A. Register, Appl. Phys. Lett. 69 (1996) 3117.
[11] S. Tasch, E.J.W. List, O. Ekstrom, W. Graupner, G. Leising, Appl. Phys. Lett. 71 (1997) 2883.
[12] J. Kido, K. Hongawa, K. Okuyama, K. Nagai, Appl. Phys. Lett. 64 (1994) 815.