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Infrared electroluminescence of ytterbium complexes in organic light emitting diodes

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Abstract

A comparison of near infrared (IR) emitting properties among Yb^{3+} complexes containing devices was made. Ytterbium $(dibenzoylmethanato)_3$(bathophenanthroline) $[Yb(DBM)_3bath]$ was used as electron-transport and emitting material. *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD) acted as a hole-transport layer. Utilizing a device of trilayer structure ITO/TPD (40 nm)/$Yb(DBM)_3$ bath: TPD (weight ratio approx. 1:1, 40 nm)/$Yb(DBM)_3$ bath (80 nm)/Ag:Mg (150 nm), an intense emission corresponding to the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ electronic transition of the trivalent Yb ion, Yb^{3+}, was observed from the organic electroluminescent device. Current density dependence on drive voltage revealed good electron injection and transport properties of the $Yb(DBM)_3$ bath. The tendency of the efficiencies of IR and visible emissions under different current densities was discussed. A broad band at approximately 580 nm was observed in the EL spectrum, which could be assigned to exciplex emission. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Electroluminscence; Ytterbium complex; Infrared emission

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1. Introductions

After Tang and VanSlyke demonstrated an efficient electroluminescence (EL) device driven by a low dc bias for the first time in 1987 [1], rare earth (RE) complexes have been employed as light emitting materials in the visible range, including bright red light from an Eu complex by Kido et al. [2] and the authors' group [3] and green light from a terbium complex by author's group [4]. However, the progression of RE complexes containing EL devices has not been as great as that of small molecular and polymer systems that are almost competitive in practical applications nowadays. The choice of materials should be the crux to obtain both better efficiency and improved stability of EL devices. Photoluminescence (PL) from RE complexes in the IR range excited by near ultraviolet light has been the subject of several investigations [5,6]. Due to the characteristics of line-like emissions of chelated RE ions, which cover the visible and near infrared spectral range, RE complexes possess widely practical and potential uses. On the other hand, only scant attention was paid to infrared EL, which provided the possibility of light communication and electro-pump lasers [7–9].

The trivalent ytterbium ion with $4f^{13}$-orbital configuration has a unique simple level structure of internal f-electrons differing from other RE elements. There are only two energy levels of 4f electrons in the Yb^{3+} ion: ground state $^2F_{7/2}$ and excited state $^2F_{5/2}$. $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition within f-orbital results in an emission band at approximately 988 nm. In this article, we have demonstrated the very good electron injection ability of the Yb complex and better optical and electrical properties of EL devices based on the Yb complex.

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2. Experimental

Yb complexes were synthesized according to the conventional method [10] and employed as an emitting and electron-transporting material. TPD was used as a hole-transporting layer. Organic thin films and a Mg/Ag (10:1) alloy cathode of EL devices were deposited onto an indium–tin oxide (ITO) glass substrate (100 Ω/□), successively, by thermal evaporation in the same vacuum chamber at 2×10^{-4} Pa without the interruption of a vacuum. The thickness and deposition rate of organic and metallic layers were monitored by a quartz oscillator thickness monitor. The emitting area for a typical device is 3×4 mm^2. Made-up devices were encapsulated in a glove-box with dried nitrogen ambient. IR (700–1800 nm) and visible (400–750 nm) spectra were measured on a Biorad PL-9000FT spectrometer equipped with a liquid-nitrogen-cooled Ge detector and a Hitach-4000 fluorescence spectrophotometer, respectively. The brightness was measured by a 1980A spot photometer.

3. Results and discussion

Selecting acetylacetonato 2-thenoylfluoroacetone DBM as first ligands and 1,10-phenonthroline bathophenonthroline as second ligands, the comparison among these trivalent Yb complexes shows that the Yb(DBM)$_3$ bath possesses both outstanding stability under heat and superior electron injection and transport properties. Other complexes exhibit serious thermal decomposition and poor electric properties. Thus, the main part of our work was focused upon the Yb(DBM)$_3$bath.

As shown in Fig. 1, a typical IR emission spectrum from the trilayer device ITO/TPD (30 nm)/ Yb(DBM)$_3$bath:TPD (weight ratio approx. 1:1, 30 nm)/Yb(DBM)$_3$bath (60 nm)/Ag:Mg (150 nm). A well-defined IR spectral structure in Fig. 1 and current density dependence on drive voltage shown are in Fig. 2, which indicates significant improvement of device performance, although the absolute energy output of IR emissions cannot be conducted yet under our present experimental conditions. By introducing a mixing layer sandwiched between TPD and the Yb(DBM)$_3$bath, the two interfaces formed by three organic layers are blurred and facilitate carrier-injection into the mixing layer in which light emission takes place. This postulation has been verified by our experiment. A large current injection, approximately 400 mA/cm^2, can be reached under a drive voltage of less than 21 V. The integrated intensity of the IR emission band under different current densities is shown in Fig. 3. As shown in Fig. 3, the threshold values of drive voltage and current density for the observation of IR emission are 4.5 V and 1.6 mA/cm^2, respectively; much less than that in Kawamura [8]. Near infrared emission from an EL device with a trilayer structure of ITO/TPD/Yb(DBM)$_3$bath/Alq$_3$/Ag/Mg has been reported by the Yanagida group for the first time [9], whereas the excellent electron injection and transport properties of Yb(DBM)$_3$bath were ignored. A trilayer structure with double heterojunctures in EL devices prevents current injection and increases drive voltage drastically. As a result, IR emission can only be observed when the drive voltage is higher than 15 V, much higher than our device. For our trilayer device with a mixing layer structure, the intensities of IR

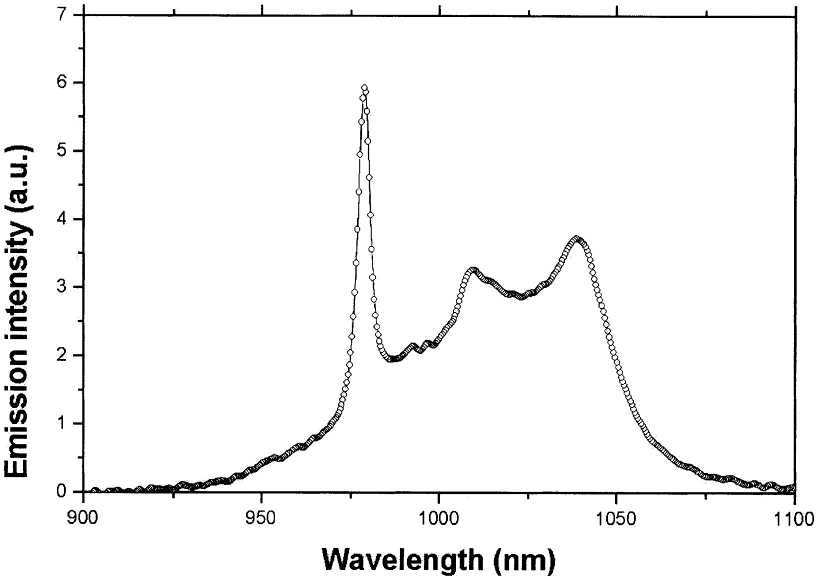

Fig. 1. IR spectrum of trilayer device ITO/TPD (30 nm)/Yb(DBM)$_3$bath:TPD (weight ratio 1:1, 30 nm)/Yb(DBM)$_3$bath (60 nm)/Ag/Mg (150 nm), 8 V, 35 mA/cm^2.

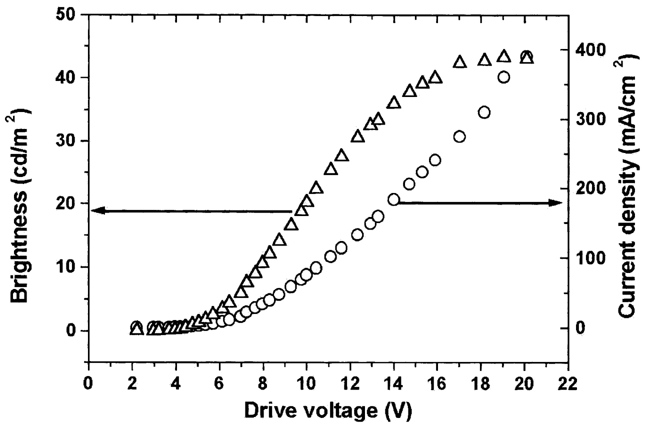

Fig. 2. Brightness (△) and current density (○) of ITO/TPD (30 nm)/Yb(DBM)$_3$bath:TPD (weight ratio approx. 1:1, 30 nm)/Yb(DBM)$_3$bath (60 nm)/Ag/Mg (150 nm) device as a function of drive voltage.

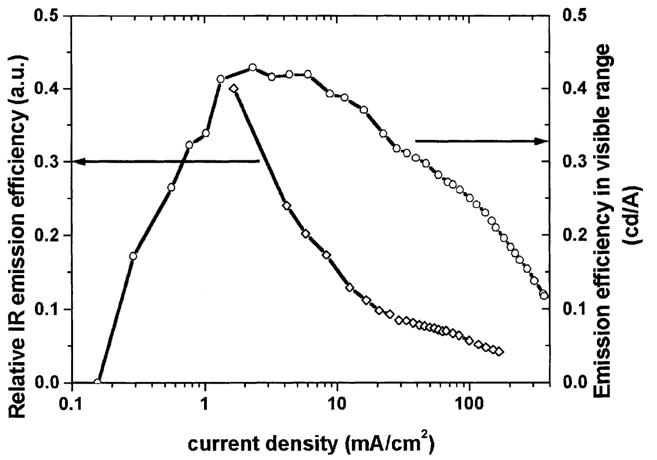

Fig. 4. Efficiency–current density characteristics for both visible (○) and IR (◇) emissions.

emission increase approximately linearly with increasing current densities below and above 80 mA/cm^2, respectively. The decrease of slope in Fig. 3 may be explained by an unrecoverable decay of the device when current density exceeds 80 mA/cm^2.

Although the absolute energy output of IR emissions cannot be measured directly, the ratio of the integrated intensity of IR emission bands to corresponding current density can be regarded as relative efficiency (shown in Fig. 4). Relative efficiency drops down rapidly with increasing current density. This phenomenon is very similar to that observed in the case of the Eu(DBM)$_3$bath in our previous work [3]. It can also be noticed that intensities of visible emission from this trilayer device gradually become saturated when current densities are above 200 mA/cm^2, as shown in Fig. 2. In the Eu(DBM)$_3$bath case, the injected hole played a critical negative role, which brought about an obvious diminishing of efficiency with increasing current density. This explanation should be valid in EL devices based on a Yb(DBM)$_3$bath.

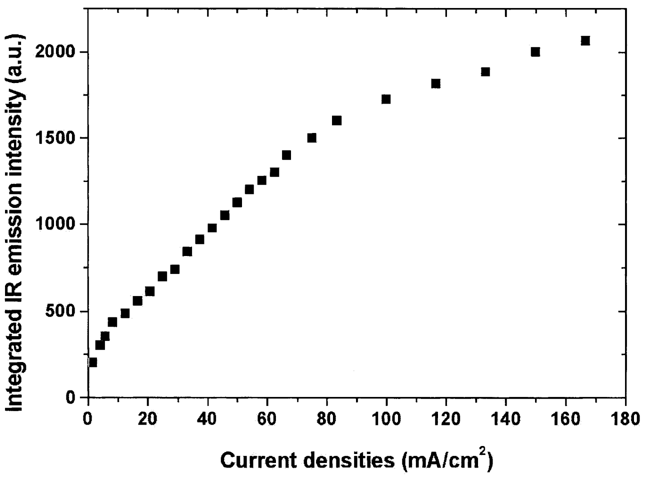

Fig. 3. Dependence of integrated intensity of IR emission from ITO/TPD (30 nm)/Yb(DBM)$_3$bath:TPD (weight ratio approx. 1:1, 30 nm)/Yb(DBM)$_3$bath (60 nm)/Ag/Mg (150 nm) device on current densities (■).

Four discernible peaks at 980, 995, 1010 and 1040 nm over the whole emission band are attributed to the Stark splitting of both $^2F_{7/2}$ and $^2F_{5/2}$. The relative intensity of the three peaks does not change under various drive voltages. In other words, the outline of the IR spectrum is independent to the driving voltage. This indicates that the environment surrounding the Yb^{3+} ion is constant in the EL process.

As we will report elsewhere, a broad band emission at 580 nm, with full width at half maximum (FWHM) at approximately 100 nm in the visible range, emerges. As shown in Fig. 4, the efficiencies of visible emissions increase under current densities below 2.3 mA/cm^2, and decrease under current densities above 2.3 mA/cm^2. Absorption and PL spectra of the Yb(DBM)$_3$bath film show no absorption and emission bands originating from the charge transfer states of Yb^{3+}, and thus the excitation of charge transfer states for EL mechanism is denied [12]. As Meshkova et al. reported [13], the intramolecular energy transfer of Yb complexes in solutions is highly efficient. However, in the case of electric excitation in the solid state, energy transfer seems weak. The large mismatch between the lowest excited triplet state of DBM and the $^2F_{5/2}$ level of the Yb^{3+} ion may result in an inefficient energy transfer which leads to emission from exciplex [11].

A bilayer device of ITO/TPD (40 nm)/Yb(DBM)$_3$bath (60 nm)/Ag/Mg (150 nm) was fabricated. Compared with the trilayer device mentioned above, the endurance of bilayer devices to current beyond 10 mA/cm^2 is weak and the IR emission from it under large current density attenuates even during the span of spectral measurement.

4. Conclusion

In a series of Yb complexes, the Yb(DBM)$_3$bath was chosen to be the IR emission material in EL devices for its excellent electron injection and transport properties of Yb(DBM)$_3$bath according our experiment. Current densities as large as 400 mA/cm^2 can be obtained at approximately 21 V. Threshold values of drive voltage and current density for the observation of IR emission from Yb^{3+} ion were 4.5 V and 1.6 mA/cm^2, respectively. IR emission was obtained under a low drive voltage (below 10 V). EL devices under a low voltage DC bias possess obvious advantages over other excitation resources. Yb complex systems provide an interesting object for both attractive potential applications for IR light resources in the future and for basic research due to its simple energy structure of 4f electrons.

Acknowledgements

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