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Observation of near infrared and enhanced visible emissions from electroluminescent devices with organo samarium(III) complex

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Abstract

Samarium (dibenzoylmethanato)$_3$bathophenanthroline (Sm(DBM)$_3$bath) was employed as an emitting and electron transport layer in organic light emitting diodes (OLEDs), and narrow electroluminescent (EL) emissions of a Sm^{3+} ion were observed in the visible and near infrared (NIR) region, differing from those of the same devices with Eu^{3+}- or Tb^{3+}-complex EL devices with the same structure. The EL emissions of the Sm^{3+}-devices originate from transitions from $^4G_{5/2}$ to the lower respective levels of Sm^{3+} ions. A maximum luminance of 490 $cd\,m^{-2}$ at 15 V and an EL efficiency of 0.6% at 0.17 $mA\,cm^{-2}$ were obtained in the visible region, and the improved efficiency should be attributed to introducing a transitional layer between the N,N′-diphenyl-N,N′-bis(3-methylphenyl)-1,1′-diphenyl-4,4′-diamine (TPD) film and the Sm(DBM)$_3$bath film and the avoidance of interfacial exciplex emission in devices. Sharp emissions of Sm^{3+} ions in the NIR region were also observed under a lower threshold value less than 4.5 V.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The study of organic electroluminescence (EL) has been given much attention recently due to its promise for devices for large-area displays, which are operative at lower drive voltages [1]. Organic small molecules, polymers and some classes of metal complexes are known as EL materials having excellent luminescence properties [2, 3]. Especially, trivalent rare earth (RE^{3+}) complexes are metal-centre luminescent complexes showing characteristic luminescence due to their inner f–f transitions, which give specific sharp emission bands. On the other hand, during the EL excitation process, both the singlet (S_1)- and the triplet (T_1)-excitons would be generated simultaneously, thus RE^{3+} can be excited by intramolecular energy transfer from T_1 of the ligands. So, theoretically, EL internal quantum efficiencies of RE^{3+}-devices are not limited to 1/4 of PL efficiencies and are expected to reach up to 100% [4, 5]. Inner 4f electronic transitions of RE^{3+} ions demonstrate miscellaneous spectroscopic properties, and emissions cover the spectral region from the ultraviolet to the infrared (IR). Considerable EL studies on Eu^{3+}-, Tb^{3+}-, Tm^{3+}- and Dy^{3+}-devices, emitting red, green, blue and white light in the visible range, have been reported by Kido *et al* [5] and by our group [6–9].

In our previous work [10], highly efficient EL devices based on an Eu^{3+}-complex with blurry interface have been

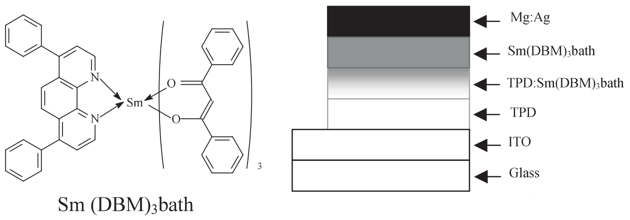

Figure 1. The molecular structure of Sm(DBM)$_3$bath and the structure of a device with a transitional layer.

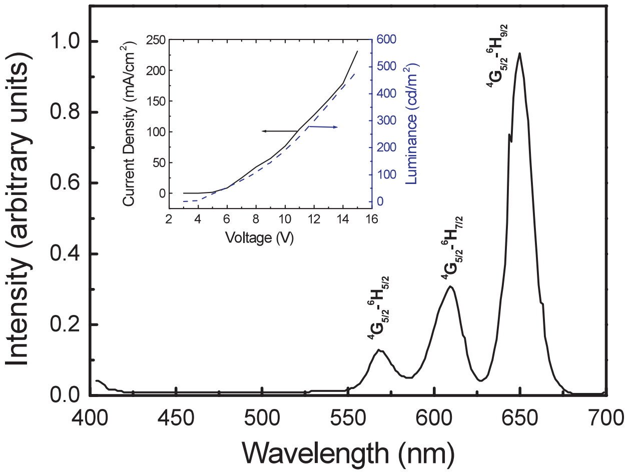

Figure 2. EL spectrum of the device (——) driven by 5 V in the visible region. Inset: luminance–voltage (——) and current density–voltage (- - - -) characteristics of the device.

studied, and an external EL quantum efficiency of 4.6% was obtained, which was much higher than 1/4 of 8% PL efficiency. Recently, IR emissions of Er^{3+}-, Yb^{3+}-, Nd^{3+}-, Tm^{3+}- and Pr^{3+}-EL devices have been reported, which probably have potential applications for optical fibre communication and electro-pump lasers [11–15].

Sm^{3+} ions are often doped in inorganic materials in order to detect IR light or prepare a reddish brown glass [16, 17], and luminescence properties of Sm-complexes in solutions have also been investigated [18, 19]. Recently, EL properties of the Sm^{3+} ion have been reported [20–22]. However, the turn-on voltage was high, up to 10 V and the maximum luminance was only 135 cd m^{-2}, and no NIR-emission from a Sm^{3+} ion was observed, as far as we know. In this paper, we demonstrate a new observation of NIR EL emission and a considerable improvement in an orange EL emission of Sm^{3+} ions in EL devices with a samarium (dibenzoylmethanato)$_3$bathophenanthroline (Sm(DBM)$_3$bath) as an emitter.

2. Experimental

The Sm(DBM)$_3$bath was synthesized in our laboratory according to a traditional method [23], which has been demonstrated to give a good electron-transport material [24]. N,N′-diphenyl-N,N′-bis(3-methylphenyl)-1,1′-diphenyl-4,4′-diamine (TPD) was selected as the hole-transporting material due to its good hole-transporting property [1]. Indium-tin-oxide (ITO) and a Mg : Ag (10 : 1) alloy were used as anode and cathode for the devices, respectively. All thin films were deposited on a precleaned ITO glass substrate with a sheet resistance of 30 Ω/□ by conventional vapour vacuum evaporation at a pressure of 3×10^{-4} Pa and onto areas of 0.15 cm^2. The film thickness was controlled *in vacuo* with a quartz crystal monitor. The EL spectra and the Commission Internationale De L'Eclairage (CIE) colour coordinates of the devices were recorded on a Hitachi MPF-4 fluorescence spectrophotometer. The luminance was measured by a 1980A spot photometer. The IR (700–1500 nm) spectra were obtained on a modified Biorad PL-9000 FT spectrometer equipped with a liquid-nitrogen-cooled Ge detector. All measurements were conducted in ambient atmosphere.

3. Results and discussion

Figure 1 indicates the chemical structure of the Sm(DBM)$_3$bath and the EL device structure. We can see that the Sm-complex was employed as an emitter in a three-layer device, which was fabricated by depositing three layers of organic films successively. This device structure with a transitional layer was different from those either with a graded layer [25] or with two blurry interfaces plus a mixing layer [10]. After the TPD layer had been deposited on precleaned glass substrates with the conducting ITO, the evaporation speed of the TPD molecule was controlled to gradually decrease. At the same time, the deposition ratio of the Sm-complex molecules was gradually increased until the TPD deposition was stopped when this layer thickness reached 30 nm. Then, another single Sm-complex layer was deposited continuously. Figure 2 shows the visible EL spectrum of the device with a structure of ITO/TPD(30 nm)/TPD : Sm(DBM)$_3$bath(30 nm)/Sm(DBM)$_3$ bath(30 nm)/Mg : Ag at 5 V, which is identical to the PL spectrum of a mixing film, (Sm(DBM)$_3$bath : TPD) (1 : 1). The three sharp spectrum bands are composed of characteristic emissions peaked at 567 nm, 609 nm and 649 nm corresponding to $^4G_{5/2}$–$^6H_{5/2}$, $^4G_{5/2}$–$^6H_{7/2}$ and $^4G_{5/2}$–$^6H_{9/2}$ transitions of Sm^{3+} ions, respectively. A pure emission of the Sm^{3+} ion without exciplex emission was clearly observed, differing from EL emissions from a device with Eu- or Tb-complexes [6, 7]. Inset in figure 2 is the voltage–current density and voltage–luminance properties of the EL device. It can be seen that the EL emission threshold bias was lowered to 3 V and a maximum luminance of 490 cd m^{-2} at 15 V has been obtained, which are much better than results reported in [20–22].

For comparison, a device with a simple two-layer structure of ITO/TPD(30 nm)/Sm(DBM)$_3$bath (60 nm)/ Mg : Ag was also constructed, but it showed very low maximum luminance (only 30 cd m^{-2}). Therefore, the significant improvement in the EL performance should be ascribed to an optimized device structure. That is, by introducing a transitional layer between the TPD film and the Sm(DBM)$_3$bath film, the potential barrier at the interface could be erased and a uniform local electric field could be intensively decreased, which benefited carrier injection and transportion into the recombination region, so that emission efficiency can be improved. The CIE colour coordinates of the device with bend structure are $x = 0.623$ and $y = 0.376$, respectively, when driven at 5 V. The electroluminescent main peak of the device at deep red

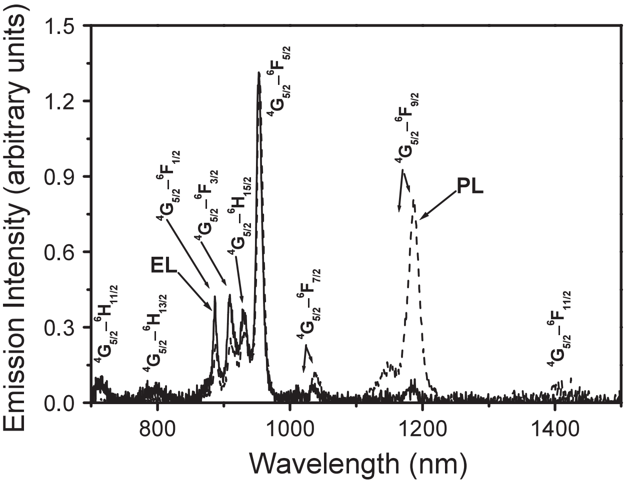

Figure 3. PL spectrum (- - - -) for Sm(DBM)$_3$bath film by exciting at 448 nm and EL spectrum (——) for the device with a transitional layer driven by 4.5 V in the NIR region.

649 nm does not sensitize human eyes because of its longer wavelength; at the same time, there is a peak at 567 nm; thus, the observed colour would still be bright amber (i.e. yellow) in colour. The colour is very valuable for designing a white EL device and for mono-colour display application since it is not tiring to human eyes. An external quantum efficiency (η_{eq}) of 0.6% is obtained at a current density of 0.17 mA cm^{-2} in the visible region.

According to our previous results, EL emissions of devices containing RE-complexes had almost exciplex emissions at about 550 nm accompanying the characteristic narrow-band emissions of RE^{3+} ions [6,7]. However, it is surprisingly found that exciplex emission has not been observed again for either a two-layer device or a three-layer device with a transitional layer, which indicates that there could be different interactions between the TPD and the Sm-complex and between the TPD and the Eu-complex. The triplet energy transfer from the ligand to Sm^{3+} ions was presumed to be more effective probably because there could seemingly be a more optimum distance between the T$_1$ level of the ligand and the resonance level of the Sm^{3+} ion [26]. Even for a simple two-layer device, exciplex emission could not be observed because of a probable completing process between the Sm^{3+} emission resulting from the energy transfer from T$_1$ to the Sm^{3+} ion and the exciplex emission from the interface of the complex/TPD [14]. That is this effect might show that the T$_1$ (20 500 cm^{-1}) [27] matches with the $^4G_{5/2}$ (17 860 cm^{-1}) level of Sm^{3+} ions for the energy transfer so that only the narrow band emissions from the Sm^{3+} could be obtained in the devices. The detailed mechanism has been argued in [28].

A Sm^{3+} ion with 4f^5-orbital configuration has plenty of energy levels, so it is quite possible that there should be many emission bands covering the visible and NIR spectral range. Figure 3 shows the NIR PL spectrum of the Sm(DBM)$_3$bath film excited by 448 nm laser at 49 mW at room temperature. The main NIR emissions peaks at about 887–953 and 1010–1183 nm are clearly observed, though there are also weak NIR peaks at 713–795 and 1406 nm. The energy differences are very small (<3000 cm^{-1}) between $^4F_{3/2}$ and $^4G_{7/2}$, $^4F_{3/2}$ and $^4G_{5/2}$, $^4G_{7/2}$ and $^4G_{5/2}$ levels and non-radioactive relaxation via phonons to the $^4G_{5/2}$ level is rapid. So, it has been considered that electrons of $^4F_{3/2}$ and $^4G_{7/2}$ levels easily relax to the $^4G_{5/2}$ level, and only electronic transitions of the $^4G_{5/2}$ to its lower energy levels can occur.

Four discernible peaks at 1010 nm and 1036 nm, 1148 nm and 1183 nm are suspected to be due to the Stark splitting of $^6F_{7/2}$ and $^6F_{9/2}$, respectively. The other emissions are assigned to the transitions of $^4G_{5/2}$ to $^6H_{11/2}$ (713 nm), $^6H_{13/2}$ (795 nm), $^6F_{1/2}$ (887 nm), $^6F_{3/2}$ (909 nm), $^6H_{15/2}$ (932 nm), $^6F_{5/2}$ (953 nm) and $^6F_{11/2}$ (1406 nm). Figure 3 also displays the EL spectral structure of the device in the NIR region. The threshold bias and the current density of the NIR emissions were less than 4.5 V and 1.27 mA cm^{-2}, respectively; which were much lower than those in other RE complexes [11–14], because a transitional layer introduced between the TPD film and the Sm(DBM)$_3$bath film decreased the injection barrier of carriers at the interface. Comparing the EL and PL spectra, which have been normalized, we find that the NIR emission peaks of PL and EL correspond well to each other. From figure 3, it is noted that relative emission intensities at 1148 and 1183 nm in the PL emission are stronger than those in the EL emission, which may be due to a different excitation mechanism. In the PL process, the Sm^{3+} ion is excited by an 448 nm (22 321 cm^{-1}) laser, it is however, excited by the energy coming from the T$_1$ level (20 500 cm^{-1}) of the ligand in the EL process. The NIR EL emission has a well-defined spectral structure, indicating that emission performances of Sm^{3+} ions were significantly improved by choosing suitable ligands and designing a novel device structure.

4. Conclusion

In conclusion, the EL efficiency of 0.6% at 0.17 mA cm^{-2} in visible range is ascribed to introducing a transitional layer between the TPD film and the Sm(DBM)$_3$bath film and the avoidance of interfacial exciplex emission because of a better match of the T$_1$ level of the ligand with the resonance level ($^4G_{5/2}$) of the Sm^{3+} ion for intramolecular energy transfer in devices. The potential advantages of EL devices based on the Sm-complex are to make an amber display not tiring for human eyes and also to fabricate a white device using it as a yellow component. NIR emissions from Sm^{3+} ions, which were assignable for their electron transitions in an organic EL device, were also observed. At the same time, an NIR EL emission has been realized at such a low voltage in the organic device. The narrow NIR emission of the EL device at a low voltage is very interesting and has potential for applications such as optical fibre communication, electro-pump lasers and so on.

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