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1.4 μm band electroluminescence from organic light-emitting diodes based on thulium complexes

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Near-infrared (NIR) electroluminescence (EL) devices have been fabricated employing thulium complexes as emitting materials. The EL emissions at 1.4 and 0.8 μm were observed from the devices of tris-(dibenzoylmethanato)-mono-(bathophenanthroline or 1,10-phenonthroline) thulium [Tm(DBM)$_3$bath or Tm(DBM)$_3$phen] at room temperature and assigned to $^3F_4$–$^3H_4$ and $^3F_4$–$^3H_6$ transitions of Tm^{3+} ions, respectively. By comparison with the NIR emissions of four Tm complexes with different ligands, it was found that the first ligand played a more important role for the Tm^{3+} ion emissions rather than the second one. In order to meet the requirement of optical communication, both Tm(DBM)$_3$bath and erbium [Er] (DBM)$_3$bath were incorporated into EL devices so that a broadened EL emission band ranging from 1.4 to 1.6 μm was obtained, showing the potential application of Tm complexes for optical communication systems. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1695098]

Recently, optical properties of trivalent thulium doped inorganic materials have been insensitively investigated in order to achieve both photon induced upconversion[1] and near-infrared (NIR) emissions. Especially in the case of 1.4 μm band emission of Tm^{3+} ions, being the potential candidates of broadening amplification band from *C* band (1530–1560 nm) to S^+ band (1450–1480 nm) in optical fiber, Tm^{3+} doped or Tm^{3+}–Er^{3+} co-doped fiber amplifiers[2] have been regarded as one of important components used in wavelength division multiplexing technology.

Rare earth (RE) complexes of NIR emissions, such as trivalent Nd and Er complexes,[3,4] have been introduced into optical telecommunication systems. These complexes that can be dispersed in polymer fiber feature advantages such as low cost, easy fabrication, etc. With the help of resonant energy transfer, RE ions in RE complexes may accept energy from the lowest triplet states of ligands in photoluminescence (PL) and electroluminescence (EL) processes. Theoretically, given the high probability of intersystem crossing from singlets to triplets and high intrinsic luminescence efficiency of RE ions, efficient emissions corresponding to internal $f-f$ transition of RE ions are expected, especially for the EL case in which the spin-independent carrier recombination results in average triplet generation fraction of about 75%. As a result, many efforts were made to achieve efficient RE complex EL emissions from visible[5] to infrared.[6] 1.54 μm emission from silicon-based organic light-emitting diodes using Er complex as an emitter has been reported by Curry *et al.*,[7] demonstrating attractive future of integrating infrared-emitting organolanthanides into silicon-based optoelectronic devices. Further studies upon NIR emissions from trivalent Yb and Pr complexes[8,9] have also been reported. However, in spite of multiple energy levels of Tm^{3+} that may give rise to photon emissions from near ultraviolet to NIR, only few reports were concentrated on the visible emissions of Tm^{3+} ions in organic matrices[10,11] and the NIR EL emissions from thulium complexes have become an attractive subject.

In this letter, we employed four kinds of thulium complexes, i.e. tris-(dibenzoylmethanato)-mono-(bathophenanthroline or 1,10-phenonthroline) thulium [Tm(DBM)$_3$bath or Tm(DBM)$_3$phen] and tris-(acetylacetonato)-mono-(bathophenanthroline or 1,10-phenonthroline) thulium [Tm(AcA)$_3$bath and Tm(AcA)$_3$phen]. Intensive NIR EL emission peaks at 1.4 and 0.8 μm were observed from Tm(DBM)$_3$bath and Tm(DBM)$_3$phen devices. For application purpose of organic optoelectronic devices in optical communication systems, a mixture of Tm(DBM)$_3$bath and Er(DBM)$_3$bath was introduced into the EL device to produce a wide infrared EL emission band ranging from 1.4 to 1.6 μm which match the working window of quartz fiber.

All the RE complexes (molecular structures are shown in Fig. 1) used in this study were synthesized according to the conventional method[12] and employed as the emitting and electron transporting material. N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1$'$-biphenyl-4,4$'$diamine (TPD) was used as hole-transporting material. Organic films and Mg:Ag (10:1) alloy cathode were deposited onto indium-tin oxide (ITO) glass substrate (100 Ω/□) successively by thermal evaporation in vacuum chamber at 2×10^{-4} Pa without breaking vacuum. The evaporating rate was kept at 2–3 Å/s for organic layers and 10 Å/s for alloy cathode, respectively. The made-up devices were encapsulated in a glove-box with dried nitrogen ambient and the active areas were 0.3×0.4 cm^2. NIR (700–1600 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

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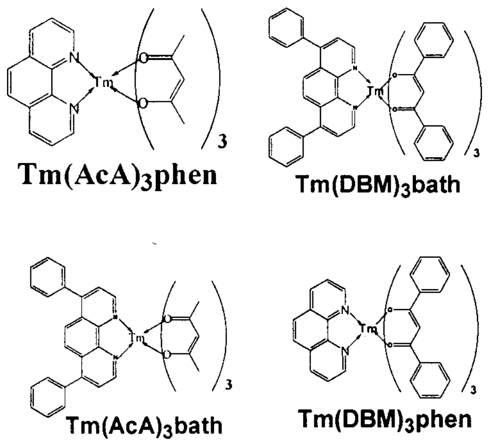

FIG. 1. The chemical structures of Tm complexes with different ligands.

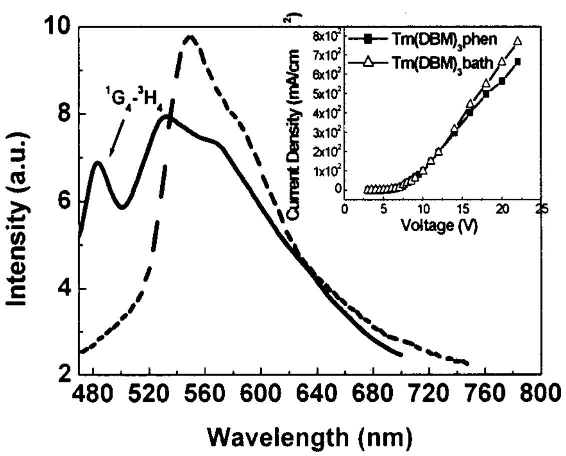

FIG. 3. The visual EL spectra of bilayered devices based Tm(AcA)$_3$bath (solid line) and Tm(DBM)$_3$bath (dash line) at the current density of 150 mA/cm^2.

Hitach-4000 fluorescence spectrophotometer at room temperature, respectively.

The double layered devices ITO/TPD (60 nm)/ Tm complexes (60 nm)/ Mg:Ag (10:1, 150 nm) using the four Tm complexes were fabricated. Assuming that only the first ligands take part in the excitation of central ions during PL and EL processes, energy diagram of the Tm complexes was given in Fig. 2(a). In Fig. 2(b), the devices based on Tm(DBM)$_3$phen and Tm(DBM)$_3$bath exhibited a sharp peak at 0.8 μm (803 nm) and a broad-band emission of 1.4 μm that were ascribed to $^3F_4$–$^3H_6$ and $^3F_4$–$^3H_4$ transitions of Tm^{3+} ions, respectively. In both cases of Tm(DBM)$_3$phen and Tm(DBM)$_3$bath, the intensity ratios between 0.8 and 1.4 μm emissions were almost invariable as increasing current density, implying the constant branching ratio of the $^3F_4$ level under the various electric fields. It was also found that the 1.4 μm band emission consisted of two peaks at 1450 and 1470 nm, which could be ascribed to the Stark splitting of 4f electronic levels. The small difference between EL spectra of Tm(DBM)$_3$phen and Tm(DBM)$_3$bath should be due to the slight change of coordinated field which was caused by the different second ligands.[4] On the other hand, when using AcA as the first ligand, only a weak emission at 0.8 μm was observed in the cases of Tm(AcA)$_3$phen and Tm(AcA)$_3$bath. The NIR emissions are consistent with that in inorganic hosts.[13]

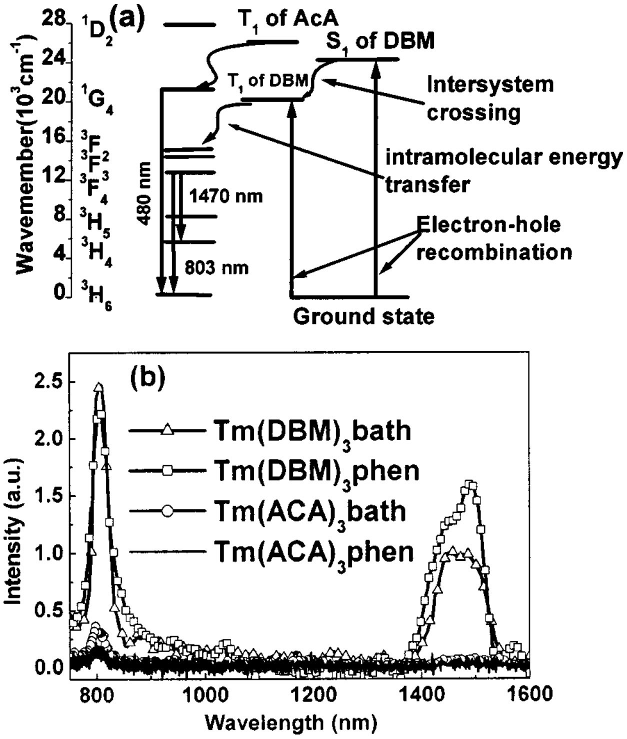

FIG. 2. (a) The energy diagram of Tm complexes; (b) the NIR EL spectrum of four devices using Tm(DBM)$_3$abth, Tm(DBM)$_3$phen, Tm(AcA)$_3$bath, Tm(AcA)$_3$phen as emitter were obtained at 150 mA/cm^2.

The EL visible spectra of Tm(AcA)$_3$bath and Tm(DBM)$_3$bath devices were given for comparison in Fig. 3. The 0.48 μm emission corresponding to the $^1G_4$–$^3H_6$ transition was only observed from the Tm(AcA)$_3$bath device, indicating considerable energy transfer from T_1 of AcA to the $^1G_4$ level. The wide band emissions ranging from 0.5 to 0.7 μm were attributed to the exciplex emissions on the interface of organic materials. We observed similar 0.48 μm emission in the case of Tm(AcA)$_3$phen device and the Tm(DBM)$_3$phen device did not exhibit blue emission as the same as Tm(DBM)$_3$bath.

Basically, intramolecular energy transfer in RE complex molecules is strongly affected by the energy difference between T_1 of donor and 4f electronic levels of RE ion acceptor.[14] In common cases, optimum energy difference favors efficient energy transfer. According to the T_1 position of AcA (25 500 cm^{-1}) as shown in Fig. 2(a), most of the excitation energy may transfer to the $^1G_4$ (21 200 cm^{-1}), which results in the 0.48 μm emission assigned to the transition of $^1G_4$–$^3H_6$ while the three adjacent levels, $^3F_2$, $^3F_3$, and $^3F_4$, are most likely populated through nonradiative decay from the $^1G_4$ level because of the large mismatch of energy levels. The excited electrons on upper $^3F_2$ and $^3F_3$ levels may relax to the $^3F_4$ level easily and then radiatively decay to the lower levels. That is reason for the extremely weak IR emissions from the Tm(AcA)$_3$bath and Tm(AcA)$_3$phen devices. In contrast, in the case of DBM, the T_1 position of DBM is 20 300 cm^{-1} lower than the $^1G_4$ level, resulting in more excited electrons on the $^3F_2$, $^3F_3$, and $^3F_4$ levels and favoring the IR emission from $^3F_4$ level. Weak infrared emissions coincide with pronounced $^1G_4$–$^3H_6$ transition and strong IR emission is accompanied by the absence of emis-

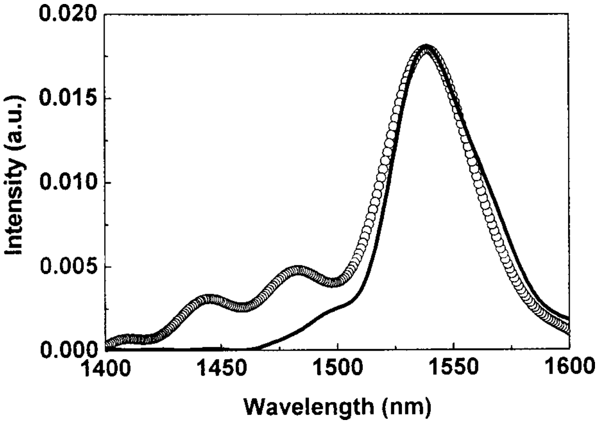

FIG. 4. The typical IR EL spectrum of double layer device employing pure $Er(DBM)_3$bath as an emitter under 12 V with the current density of 200 mA/cm^2 (line). The open circles represented the broad IR emission of device using mixture as active emitter under the same voltage with current density of 180 mA/cm^2.

sion from $^1G_4$. Such a coincidence implies the critical role of match of the energy levels between donor and acceptor in the intramolecular energy transfer processes.

It was also worth considering the effects of the second ligand on the NIR emissions of Tm complexes. However, by comparison with the visible EL spectra of $Tm(DBM)_3$bath and $Tm(AcA)_3$bath, there was no 0.48 μm emission from the device based on $Tm(DBM)_3$bath. Furthermore, due to the weak IR emission of $Tm(AcA)_3$bath, it indicated that the second ligands did not participate in the energy transfer process. In previous reports, introducing neutral second ligands into the RE complexes saturates the coordination of RE ions, reduce the evaporation temperature and prevent the center ions from quenching effects caused by high-frequency vibration bonds.[15,16] On the other hand, the $I-V$ characters of $Tm(DBM)_3$bath and $Tm(DBM)_3$phen were almost the same as shown in the inset of Fig. 3. It indicated that bath and phen could have similar electron transporting abilities. According to our results, it should be noted that an energy-level match between the T_1's of ligands and corresponding emissive levels plays an important role.[17]

The full width at half maximum of 1.4 μm band of Tm $(DBM)_3$bath was estimated to be 98 nm. Further effort to broaden the emitting band was fulfilled by introducing Er complex with same ligands. After optimizing the mixing ratio, a double-layer device TPD (60 nm)/$Tm(DBM)_3$bath:$Er(DBM)_3$bath (60 nm, mass ratio 9:1)/Mg:Ag (10:1, 150 nm) was fabricated. As comparison, control device only using $Er(DBM)_3$bath as the emitting layer was also fabricated. The EL spectra of the two devices were shown in Fig. 4. Control device featured the characteristic EL emission from Er^{3+} ion. Device of mixing layer exhibited emissions ranging from 1.4 to 1.6 μm corresponding to $^3F_4-^3H_4$ transition of Tm^{3+} ions and $^4I_{13/2}-^4I_{15/2}$ transition of Er^{3+} ions. It was noticed that even the mass ratio of $Tm(DBM)_3$bath and $Er(DBM)_3$bath was 9:1, the Er emission was still much stronger than that of Tm. This means that the EL efficiency of IR emission from Tm complexes is not good probably due to the excitation of the $^3F_4$ level by T_1 of DBM is not efficient enough yet. Further improvement of energy transfer efficiency is expected by employing more suitable ligands. The overlapping emission band provided a method of modulating emission by mixing different active organic emitters, which may make contribution to RE doped polymer waveguide[18,19] and organic IR sources in optical communication field.

In summary, NIR emissions from organic EL device based on Tm^{3+} complexes were observed. Emitting peaks at 1.4 and 0.8 μm in EL spectrum were assigned to $^3F_4-^3H_6$ and $^3F_4-^3H_4$ transitions, respectively. Based on the 1.4 μm band emission, a broadband EL emission from 1.4 to 1.6 μm was obtained by introducing a mixture of Tm and Er complexes as an emitter. This will provide prosperous use for electrically pumped amplifier and optical communication in the future.

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