

Spectrally-narrow blue light-emitting organic electroluminescent devices utilizing thulium complexes

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Abstract

Organic electroluminescent (OEL) devices with trivalent thulium (Tm^{3+}) complex ($\text{Tm}(\text{acetylacetonato})_3(\text{monophenanthroline})$ [$\text{Tm}(\text{AcA})_3\text{phen}$]) as an emitting layer were fabricated. Double-layer type cells with a structure of glass substrate/indium–tin oxide (ITO)/poly-(vinylcarbazole) (PVK)/Tm complex/Al exhibit blue luminescence when forward bias dc voltage was applied. Spectrally-narrow OEL emission at 482 nm from Tm^{3+} ion in Tm complex was observed. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Since Tang et al. [1] reported organic light-emitting diodes (OLEDs) using multilayer organic thin films in 1987, much progress has been made in OLEDs by creative researchers all through the world. Organic materials can easily realize variant color emission in visible spectrum (400–700 nm). However, the broad spectral emission of organic dyes results in luminescent colors which are dull and therefore not best suited for actual display applications. The emission spectra usually have spectral bandwidths of 100–200 nm, which require the use of filters to obtain highly monochromatic light. Although a spectrally-narrow emission can be obtained from microcavity structure [2], the fabrication of this kind of devices is rather complicated and inconvenient. In order to solve this problem, rare earth (RE) complexes have been used in OEL devices because they have higher internal quantum efficiencies and narrower band emission compared with organic fluorescent dyes or polymers. Bright red (from Eu complexes) and green (from Tb complexes) light emis-

sions with a full width at half-maximum (FWHM) of 10–20 nm have been observed by Kido et al. [3,4] and our group [5–8] in past a few years. For the purpose of constituting a full-color flat display, a spectrally-narrow blue emitting material for OLEDs is required. However, spectrally-narrow (FWHM < 20 nm) blue light emission from RE ions complexes or other organic materials in common OEL devices has not been achieved until now.

Among RE elements, $4f(^1G_4) \rightarrow 4f(^3H_6)$ electronic transition of Tm^{3+} provides a spectrally-narrow light emission at about 480 nm. The spectroscopic properties of Tm^{3+} ion have mostly been studied in inorganic crystals, glasses [9–12] and, where the luminescence of Tm^{3+} is efficient enough to facilitate the use of these ions as laser media [13]. Blue luminescence of Tm(III) ions in ZnS:Tm^{3+} inorganic thin film electroluminescent (EL) devices (drive voltage ~ 100 V or higher) based on the $4f(^1G_4) \rightarrow 4f(^3H_6)$ transition has also been investigated [14,15]. But to our best knowledge, OEL devices using Tm complexes as an emitter have not yet been studied.

In this paper, our objective is to develop spectrally-narrow (FWHM < 20 nm) blue light OLEDs devices using Tm complexes, although photoluminescence of Tm^{3+} in organic solution or polymer matrices have been observed [16].

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2. Experimental details

In Fig. 1, the cell configuration and the molecular structures of the materials used in this study are given. PVK (40 mg) was dissolved in 5 ml chloroform and the solutions were spin-coated onto ITO substrate to form a hole transport layer (~ 60 nm). $\text{Tm}(\text{AcA})_3\text{phen}$ layer (~ 50 nm) and an aluminum metal electrode (~ 150 nm) were deposited successively under a vacuum of 2×10^{-5} Torr. The emission area was 0.3×0.5 cm². Materials used in this study, PVK and $\text{Tm}(\text{AcA})_3\text{phen}$, were synthesized in our lab according to the conventional methods. Spectra presented in this paper were measured with a Hitachi 4000 Spectrometer in air at room temperature.

The EL spectrum of the OEL devices with a drive voltage of 10 V and the photoluminescent (PL) spectrum under an excitation wavelength at 350 nm are shown in Fig. 2. From Fig. 2, it is clear that the main emitting peak (FWHM ~ 20 nm) of the Tm^{3+} -containing OEL device is a strongly blue emission peaked at 482 nm and a weaker peak (650 nm) is also observed. Fig. 3 shows the continuous dc current vs. voltage (I - V) curve. The emitting intensity of 6.0 cd/m² was achieved when a 16-V forward bias voltage was applied. Both of EL and PL spectra of $\text{Tm}(\text{AcA})_3\text{phen}$ powder shows peaks at 482 nm and 650 nm which agree with the PL spectrum of Tm complex given in [16]. The peaks located at 482 nm and 650 nm correspond to $4f(^1G_4) \rightarrow 4f(^3H_6)$ and $4f(^1G_4) \rightarrow 4f(^3H_4)$ transitions of $\text{Tm}(\text{III})$ ion, respectively.

3. Results and discussion

The mechanism of the blue light emission from Tm^{3+} ion can be divided into three main steps: first, carrier

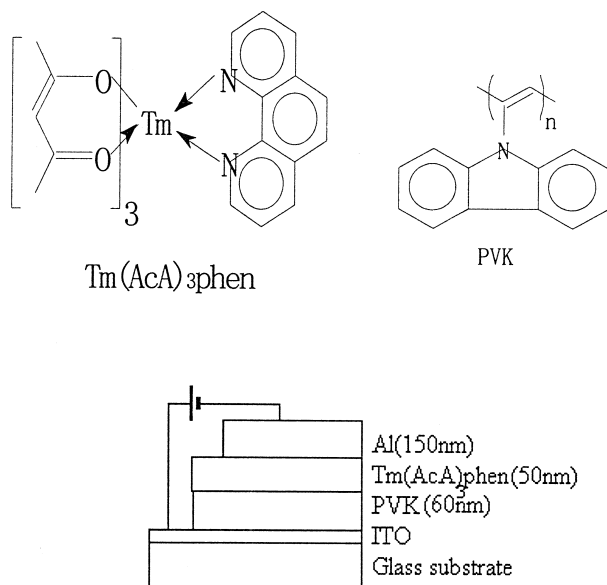


Fig. 1. The chemical structures of materials used and the cell structure.

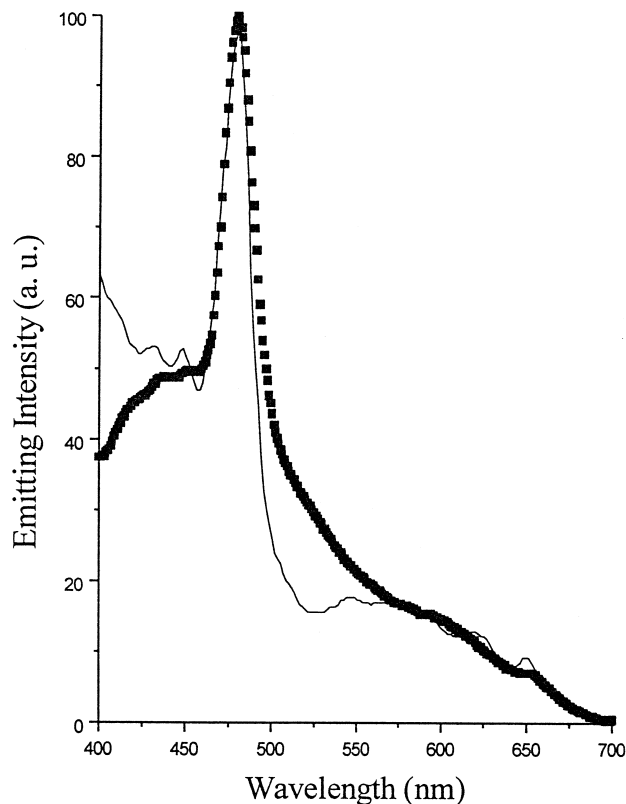


Fig. 2. A—square dot, the EL spectrum of the devices at a drive voltage of 10 V; B—solid line, the PL spectrum of the $\text{Tm}(\text{AcA})_3\text{phen}$ powder (excitation wavelength 350 nm).

recombination occurred at the interface between PVK and Tm complex layers results in generation of excitons and the ligands are excited to the excited triplet (T_1) state. Second, the excited ligands transfer energy to 1G_4 level of Tm^{3+} . At last, $^1G_4 \rightarrow ^3H_6$ transition gives rise to the blue light emission at 482 nm. Excitation of the ligands should be efficient because tris(acetylacetonato)-(mono-phenanthroline)terbium($\text{Tb}(\text{AcA})_3\text{phen}$) shows an intense emission of $\text{Tb}(\text{III})$ ions in device with a structure of ITO/PVK/ $\text{Tb}(\text{AcA})_3\text{phen}$ /Al [5], so the relative weak emission and poor efficiency (~ 0.0074 lm/W at 16 V) may be due to large difference between excited triplet state level ($25\,500\text{ cm}^{-1}$) of the ligand and 1G_4 level ($21\,196\text{ cm}^{-1}$) of Tm^{3+} ion [16]. Symmetry of Tm complexes molecule is also expected to be an important factor affecting the intensity of the $^1G_4 \rightarrow ^3H_6$ transition [17] which involves no change in parity and is strictly forbidden. Choosing more compatible ligands and changing the symmetry of Tm complexes may increase the efficiency of the devices and the EL emission intensity of Tm^{3+} ion in OEL devices.

However, it is also noticed that there is a broad band overlapped with the Tm^{3+} emission peaks. The EL emission spectrum is converted to the x , y chromaticity diagram coordinates of Commission Internationale De L'Eclairage (CIE) as shown in Fig. 4. The broad band may be originated from luminescence of the ligands because of

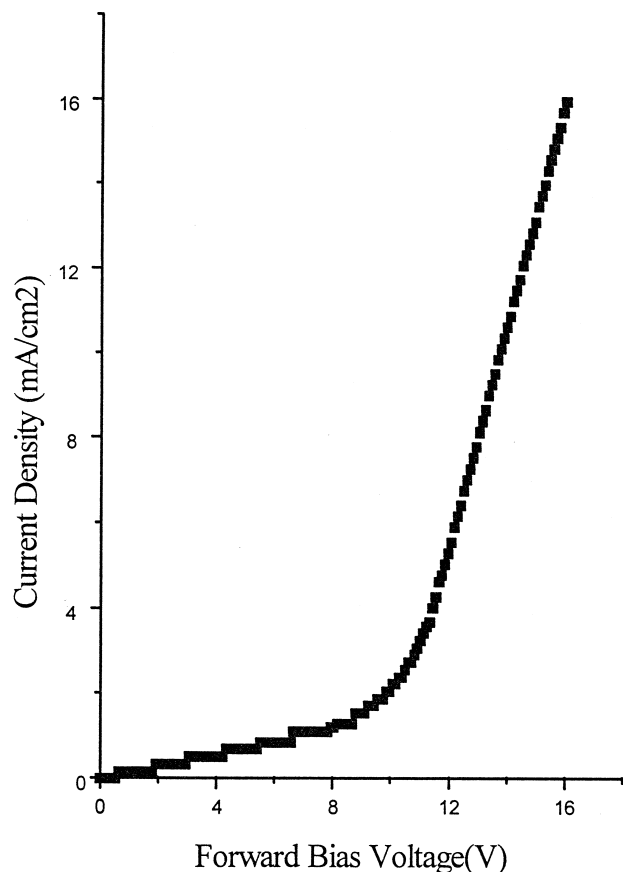


Fig. 3. Current density vs. voltage characteristics of an ITO/PVK/Tm(AcA)₃phen/Al cell.

inefficient energy transfer from ligands to Tm(III) ion. The broad emission band is presumably from the mixed ligands

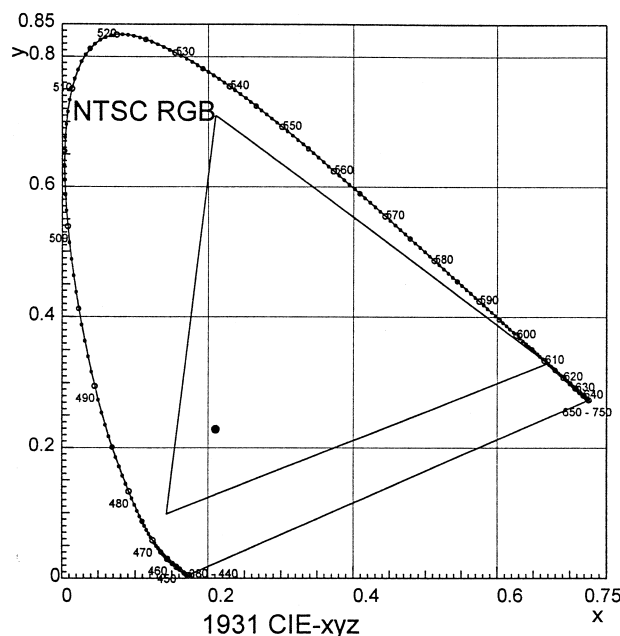


Fig. 4. Solid circle in the CIE x , y chromaticity diagram showing the color of the emitted light.

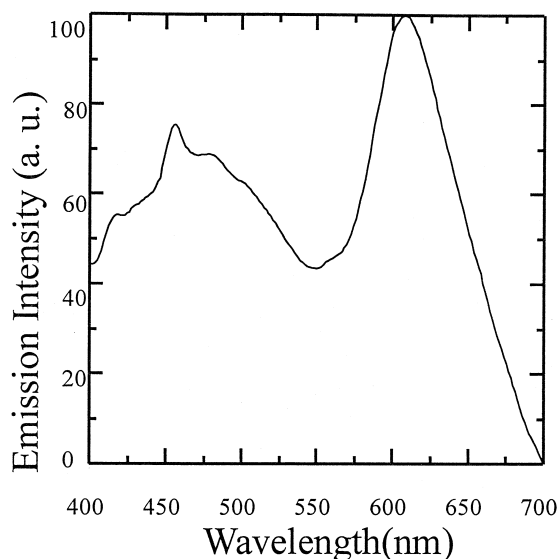


Fig. 5. The EL spectrum of an ITO/PVK/Tm(AcA)₃phen/Al devices at 18 V.

of acetylacetone and *o*-phenanthroline chelated with the central thulium ion. This indicates incomplete energy transfer from the excited ligands to the central Tm(III) ion.

Tm(AcA)₃ was also synthesized to investigate the effects of the second ligand(phenanthroline). In contrast with Tm(AcA)₃phen, Tm(AcA)₃ requires higher temperature for evaporation. The second ligand reduces the polarity of Tm(AcA)₃phen unit and makes it easy to evaporate. The cell with a structure of ITO/PVK (50 nm)/Tm(AcA)₃(50 nm)/Al(150 nm) gave an identical EL spectrum, as shown in Fig. 2, and showed lower current densities and weaker EL emission. This indicates that phenanthroline improves electron-transport ability of the Tm complex.

It is a phenomenon of interest that the emission color was gradually changed from pure blue to orange when a dc forward bias above 18 V was applied and it was an irreversible process. That is, spectrum of the orange light emission shown in Fig. 5 is considerably steady after the conversion has been accomplished. Similar result was also observed when trivalent terbium (Tb³⁺) ion took the place of Tm(III) in the same complex. Using RE(AcA)₃ (RE = Tm or Tb) as a emitter does not bring out the same consequence. It is indicated that the chelated phenanthroline act as a reactant during the change. Thus we can say that the changing of the EL spectrum is presumably due to an electrochemical interaction at the interface between the ligand (phenanthroline) and PVK polymer under a certain current and strong electronic field. We will discuss this result in our following work.

4. Conclusion

Spectrally-narrow blue light emission from OEL devices based on Tm complex at a drive voltage as low as 10

V was obtained. Maximum emitting intensity of the devices under a drive voltage of 16 V attained 6 cd/m². Thulium complexes are believed to be a candidate as blue light-emitting material for actual application. This work provides a promising and convenient way to achieve pure blue light for future full color displays.

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