

Near-infrared Electroluminescence from Ytterbium(III) Complex

Yuichiro Kawamura, Yuji Wada, Mitsunori Iwamuro, Takayuki Kitamura, and Shozo Yanagida*
Material and Life Science, Graduate School of Engineering, Osaka University, Yamada-oka, Suita, Osaka 565-0871

(Received December 8, 1999; CL-991035)

The room temperature near-infrared electroluminescence (EL) was observed from organic EL devices using the ytterbium(III) [Yb(III)] complex as an emitter over 15 V, though there was no spectral overlap between the lowest triplet state of ligand and the emissive level of Yb(III) ion needed for the intramolecular energy transfer. The EL emission with a peak at 985 nm was assigned to the $^2F_{5/2} \rightarrow ^2F_{7/2}$ transition of Yb(III) ion.

Organic electroluminescent (EL) devices have been studied for the next generation flat panel display.¹ Recently, organic EL devices also have attracted attention in the field of optoelectronics as novel, semiconductor LED compatible, light sources for optical fiber communications, because their easy fabrication will enable integration of the signal source with the fiber media at the terminal of local area network. However, only a few reports have described about organic compounds having near-infrared (IR) emission over 800 nm possessing the high transparency through the optical fiber materials and their applications for EL devices.^{2,3}

On the other hand, lanthanide ions such as neodymium(III)[Nd(III)], erbium(III)[Er(III)] and ytterbium(III)[Yb(III)] are known as near-IR emitters having excellent luminescent properties due to the characteristics of the $f-f$ transitions, such as long lifetimes and specific sharp emission bands around 900-1500 nm. Recently, luminescent properties of their complexes have been reported for the possibilities of the application to biosensing materials,⁴ and for the organic fluid laser system, especially Nd(III).⁵ EL devices using terbium(III) and europium(III) complexes have already been designed by Kido et al., that showed pure green and red emission, respectively.^{6,7} An EL device using a Er(III) complex which can be driven at room temperature was also reported.⁸ We have also reported the device using a Nd(III) complex and successfully observed the near-IR EL assigned to the $f-f$ transitions of Nd(III) ion at room temperature.⁹

The Yb(III) ion has thirteen electrons in its $4f$ orbitals and specific two transition levels, the $^2F_{7/2}$ (ground state) and the $^2F_{5/2}$ (excited state). Thus, the pure emission around 980 nm due to the $^2F_{5/2} \rightarrow ^2F_{7/2}$ transition should be obtained. In the case of organic complexes, an absorption band due to the

organic ligand can be used for the excitation of the Yb(III) ion instead of the absorption band of the ion.^{4,10} If the emission from the Yb(III) ion is obtained by not optical, but electrical excitation, the organic Yb(III) EL system will produce a novel pure near-IR light source for the optical fiber communications mentioned above. In this letter, we report the fabrication of an organic EL device using an Yb(III) complex, tris(dibenzoyl-methanato)(monobathophenanthroline)Yb(III)[Yb(DBM)₃bath] as a near-IR emitting material.¹¹

The cell consisted of three layers, i.e., hole transport/emitting/electron transport layers. For the hole and electron transport layers, conventional *N,N'*-diphenyl-*N,N'*-di(*m*-tolyl)benzidine (TPD) and tris(8-quinolinolato)aluminum(III) complex (Alq₃) were used, respectively. All of the organic layers and the cathode were fabricated by vacuum deposition onto a pre-cleaned indium-tin oxide (ITO) coated glass substrate having a sheet resistance of 40 Ω/cm² at 2×10^{-5} Torr. The thicknesses of the TPD, Yb(DBM)₃bath and Alq₃ layers were 500, 250 and 500 Å, respectively, as determined using an oscillating quartz crystal thickness monitor. The cathode was fabricated by codepositing magnesium and silver, resulting in an alloy (Mg:Ag = 10:1) film of 1000 Å thickness. The deposition rates were maintained at 1-2 Å/s for organic materials and 10 Å/s for Mg:Ag. The emitting area of the cell was 0.3 × 0.1 cm². A film for photoluminescence (PL) measurements was also fabricated by vacuum deposition of Yb(DBM)₃bath directly on a glass substrate. EL and PL spectra in the near-IR region were measured at room temperature and ambient conditions using a JASCO SS-25 system with a liquid N₂ cooled Ge photodiode as a detector.

Near-IR emission around 900-1100 nm was observed when the device was operated under dc bias with ITO at positive polarity. The EL spectrum at 19 V is shown in Figure 1(a). The emission band with a peak at 985 nm was assigned to the

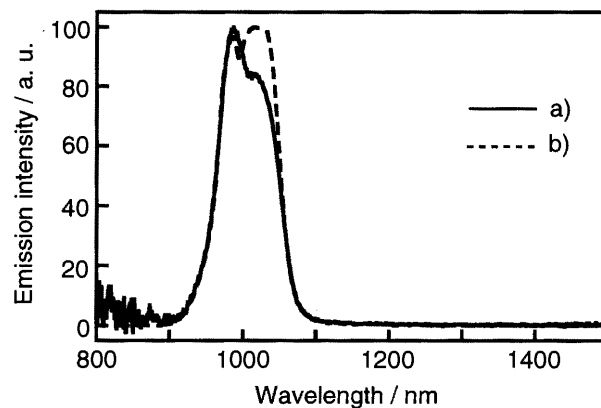
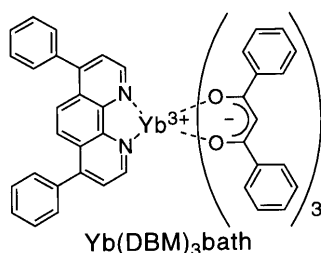


Figure 1. Emission spectra in the near-IR region; (a) EL spectrum of ITO/TPD/Yb(DBM)₃bath/Alq₃/Mg:Ag device at the applied voltage of 19 V, (b) PL spectrum of deposited film of Yb(DBM)₃bath excited by 390 nm.

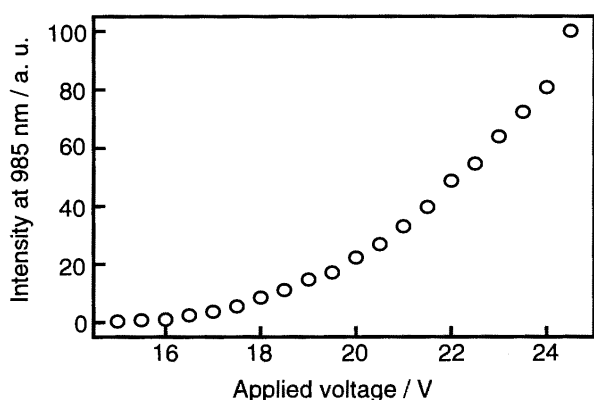


Figure 2. Luminescence-voltage characteristics of ITO/TPD/Yb(DBM)₃bath/Alq₃/Mg:Ag device.

$^2F_{5/2} \rightarrow ^2F_{7/2}$ transition of Yb(III) ion. The PL spectrum of the Yb(DBM)₃bath film excited at 390 nm is also shown in Figure 1(b). The EL peak was slightly different from the PL. The reason for this is not clear at this stage. The full width at half maximum (FWHM) of both emissions was 89 nm. For this FWHM broadening, the emission band seems to consist of multiplexed peaks. The multiplexed peaks should be explained by the Stark splitting of both *f*-orbital levels ($^2F_{5/2}$, $^2F_{7/2}$) of the Yb(III) ion induced by the highly asymmetric ligand field in this complex. Pale green luminescence was also observed from the device, especially at higher voltages. This luminescence was mainly due to the EL of Alq₃ because of poor charge blocking at the interface between Yb(DBM)₃bath and Alq₃.⁹

Figure 2 shows the luminescence-voltage characteristics of the device. The EL threshold value of the applied voltage was approximately 15 V. The luminescence intensity at 985 nm increased with an increase of applied voltage and was not saturated even when the applied voltage reached 24 V. This result shows the possibility of obtaining more intense near-IR emission from the device. The device showed good response for the luminescence-current characteristics as shown in Figure 3, and the EL intensity increased almost linearly with the current density. However, the current density in the device was not very high and the value was 9.7 mA/cm² even at 20 V. This is due to the poor charge injection abilities of the Yb(DBM)₃bath layer.

The PL mechanism of the lanthanide complexes is generally accepted as follows; the ligand absorbs light energy, undergoes intersystem crossing into a triplet state, and then transfers its energy to the ion. So the matching of the lowest triplet level of the ligand and the excited levels of the ion is important for effective sensitized luminescence.¹² For the excitation of the Yb(III) in our case, however, there is no spectral overlap between the lowest triplet state of the ligand (around 20800 cm⁻¹) and the emissive level of Yb(III) ion (at 10150 cm⁻¹). Crosby et al. noted similar results in the early stage,¹⁰ explaining the vibrational interaction in the mechanism of intramolecular energy transfer. Recently, another explanation for the luminescence from Yb(III) complex has been proposed: the electron transfer mechanism between the ligand and the ion.¹³ In the case of our EL, a similar mechanism would be applied for the energy transfer to the ion though the electric excitation source is used.

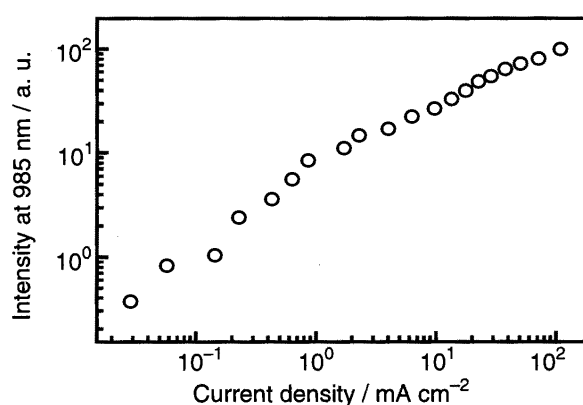


Figure 3. Luminescence-current density characteristics of ITO/TPD/Yb(DBM)₃bath/Alq₃/Mg:Ag device.

In conclusion, an EL device using the Yb(III) complex [Yb(DBM)₃bath] as an emitting center was fabricated, and near-IR EL due to the $^2F_{5/2} \rightarrow ^2F_{7/2}$ transition of Yb(III) ion was successfully observed at room temperature from the device under forward bias. The present results exhibit that Yb(III) complexes are potential materials for the application of the near-IR emitting devices in the field of optoelectronics. To produce more intense and effective EL emission, future research should be conducted with respect to optimizing the balance of the electron and hole injections to the emitting layer, and to suppressing the spectral broadening due to the Stark splitting of the Yb(III) ion. The luminescence mechanism should also be investigated in detail.

The authors thank Dr. Nobuaki Nakashima for discussion, and Dr. Tatsuhiko Yamanaka and the members of Institute of Laser Engineering for help with the spectral measurements in the near-IR region. Y. K. gratefully acknowledges the Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists. This work was partially sponsored by the Asahi Glass Foundation.

References and Notes

- 1 C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.*, **51**, 913 (1987).
- 2 A. Fujii, Y. Ohmori, and K. Yoshino, *IEEE Trans. Electron Devices*, **44**, 1204 (1997).
- 3 D. R. Baigent, P. J. Hamer, R. H. Friend, S. C. Moratti, and A. B. Holmes, *Synth. Met.*, **71**, 2175 (1995).
- 4 M. H. V. Werts, J. W. Hofstraat, F. A. J. Geurts, and J. W. Verhoeven, *Chem. Phys. Lett.*, **276**, 657 (1999).
- 5 M. Iwamuro, T. Adachi, Y. Wada, T. Kitamura, and S. Yanagida, *Chem. Lett.*, **1999**, 539.
- 6 J. Kido, K. Nagai, and Y. Ohashi, *Chem. Lett.*, **1990**, 657.
- 7 J. Kido, H. Hayase, K. Hongawa, K. Nagai, and K. Okuyama, *Appl. Phys. Lett.*, **65**, 2124 (1994).
- 8 R. J. Curry and W. P. Gillin, *Appl. Phys. Lett.*, **75**, 1380 (1999).
- 9 Y. Kawamura, Y. Wada, Y. Hasegawa, M. Iwamuro, T. Kitamura, and S. Yanagida, *Appl. Phys. Lett.*, **74**, 3245 (1999).
- 10 G. A. Crosby and M. Kasha, *Spectrochim. Acta*, **10**, 377 (1958).
- 11 L. R. Melby, N. J. Rose, E. Abramson, and J. C. Caris, *J. Am. Chem. Soc.*, **86**, 5117 (1964); Yellow solid. Identified by elemental analysis.
- 12 G. A. Crosby, R. E. Whan, and R. M. Alire, *J. Phys. Chem.*, **34**, 743 (1961).
- 13 W. D. Horrocks, Jr., J. P. Bolender, W. D. Smith, and R. M. Supkowski, *J. Am. Chem. Soc.*, **119**, 5972 (1997).