Electron mobility of rare earth complexes measured by transient electroluminescence method

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Abstract

Electron mobility of gadolinium/europium (dibenzoylmethanato)$_3$(bathophenanthroline) (Gd/Eu(DBM)$_3$ bath) was measured by transient electroluminescence (EL) method. Although electron mobility of the two complexes were expected to be same, the value of mobility (1.2×10^{-4} cm^2/Vs at electric field of 1 MV/cm) of Eu(DBM)$_3$ bath complex was bigger than that (8×10^{-5} cm^2/Vs at electric field of 1 MV/cm) of Gd(DBM)$_3$ bath complex. It was found to be related to the different luminescent mechanisms of active materials and recombination zones in the devices. According to this, penetration length of hole injected into electron transport layer of Eu(DBM)$_3$ bath was estimated.
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1. Introduction

Rare earth (RE) complexes have been used in the field of organic light emitting diodes (OLEDs) mainly due to their unique narrow-band emissions in visible spectrum and potential high EL quantum efficiency [1,2]. Recently, high electroluminescence (EL) efficiency of Eu [3] and Tb [4] complexes suggested that RE complexes were promising luminescent materials for harvesting both singlet and triplet energies in the case of electrical excitation and hence for breaking the theoretical 5% external quantum efficiency limitation to OLEDs based on fluorescent dyes. Furthermore, because of the abundant energy levels of RE ions,

the electroluminescence (EL) emissions of OLEDs using RE complexes cover a wide spectral range from blue to infrared [5–7], and may be applied in the fields of both display and optical fiber communication.

As the EL performances of RE complexes, such as efficiency and color purity were improved by better complexes [4] and device structures [8], only few papers concentrated on the inside mechanism with respect to the carrier transporting and non-radiative/radiative relaxations [9]. Thus electricity properties of the RE complexes need to be identified at present stage. Detail information is necessary to build a suitable architecture of OLEDs using RE complexes as emitting components, measurement of the electron mobility of RE complexes is of importance. However, there is no report on electron mobility of rare earth complexes yet.

The transient EL method is a powerful tool to obtain the detail information in OLEDs including the measuring of

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electron mobility [10]. This method is based on the superior hole mobility of hole transport materials (HTM) which often is two orders of magnitude larger than electron mobility of electron transport materials (ETM). However, the penetration of hole into ETL through the organic interface therefore results in a recombination zone locating in the ETL. When the injected electrons encounter the holes inside recombination zone, an advanced EL signal will appear and give rise to an imprecise calculation of mobility. This problem does not exist when excited complex (exciplex) emission dominates the EL emission of a bilayered device because exciplex formation and emission only take place at organic interface [11]. Therefore, exciplex emissive materials should be chosen to provide more exact value of electron mobility after the electrons moved throughout the whole ETL. In our previous work [12], $Gd(DBM)_3$ bath is the typical exciplex emissive material due to the mismatch intra-energy transferring between the ligand and Gd^{3+} ions, resulting in that only exciplex emission occurs, when the hole transporting material contacts the Gd^{3+}-complex. Therefore, we chose $Gd(DBM)_3$ bath as the object that will provide more accurate information of electron mobility. Contrarily, self-emission dominant material $Eu(DBM)_3$ bath [6], which mainly shows characteristic red emission of Eu^{3+} ion during EL process, is also chosen to give a comparison with $Gd(DBM)_3$ bath.

In this paper, the electron nobilities of the two RE complexes with same ligands, $Gd(DBM)_3$ bath and $Eu(DBM)_3$ bath, were measured using transient EL method. The electron mobility of $Gd(DBM)_3$ bath is 8×10^{-5} cm^2/Vs at electric field of 1 MV/cm, comparable to classic ETM, such as PBD [13] (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) or ALQ [14]. On the other hand, the electron mobility of $Eu(DBM)_3$ bath at electric field of 1 MV/cm was almost one and a half times than that of $Gd(DBM)_3$ bath and attributed to the hole–electron recombination inside the Eu-complex layer instead of at the organic interface. Furthermore, we estimated the width of recombination zone at various electric fields according to the EL delay times.

2. Experimental details

Two complexes were synthesized using traditional method [15]. TPD that has an hole mobility of $\sim 10^{-3}$ cm^2/Vs [16] was chosen as HTM, and $Gd(DBM)_3$ bath and $Eu(DBM)_3$ bath as ETM. 150 nm thick Mg and Ag alloy with atom rate of 10:1 acted as cathode and indium-tin oxide (ITO) of sheet resistance 30 $\Omega/\square$ as anode. The organic layers and the cathode were deposited on ITO coated glass substrate successively under 1×10^{-4} Pa in one vacuum run. Quartz crystal monitor was used to monitor the deposition thickness and evaporation rate. The thicknesses of HTM and ELM were 50 nm and 60 nm, respectively. The devices based on Gd-complex and Eu-complex were denoted by A and B, respectively. To minimize the capacitive effect, the active area was kept to 1×1 mm^2. The electron affinities (EA) of the RE com-

plexes were measured by a cyclic voltammetry under nitrogen atmosphere, and recorded by EG&G Model 283 potentiostat/galvanostat. The electrolyte was a solution of tetrabutylammonium perchlorate in anhydrous CH_2Cl_2. For the transient EL measurement, a pulse voltage generator, which can provide voltage pulses of the rising and falling time less than 20 ns, was employed as an electrical switch to generate a pulse width of 8 μs. The transient EL responses were obtained and analyzed by a storage oscilloscope (HP 54810) with a 100 consecutive signals averaging. The EL spectra were measured using a Hitachi 4000 fluorescence spectrophotometer.

3. Results and discussion

Two typical double-layered devices A and B employed $Gd(DBM)_3$ bath and $Eu(DBM)_3$ bath as the emitters were fabricated following the device structures: ITO/TPD(50 nm)/RE (DBM)$_3$ bath(60 nm)/Ag:Mg (10:1, 150 nm). Under the same voltage of 5 V, we obtained the different EL spectra including the 560 nm exciplex emission from device A and 612 nm Eu^{3+} ions emission from device B, respectively, which indicated different emission mechanisms between the two devices, as shown in Fig. 1. Based on the EL emissions, the Fig. 2a gives the transient EL behaviors of the device A and B under DC bias of 7 V, it was noted that the delay times (t_ds) were obtained within the range of 100 ns and the ones of device A were longer than those of device B, as shown in Fig. 2b. Assumed a
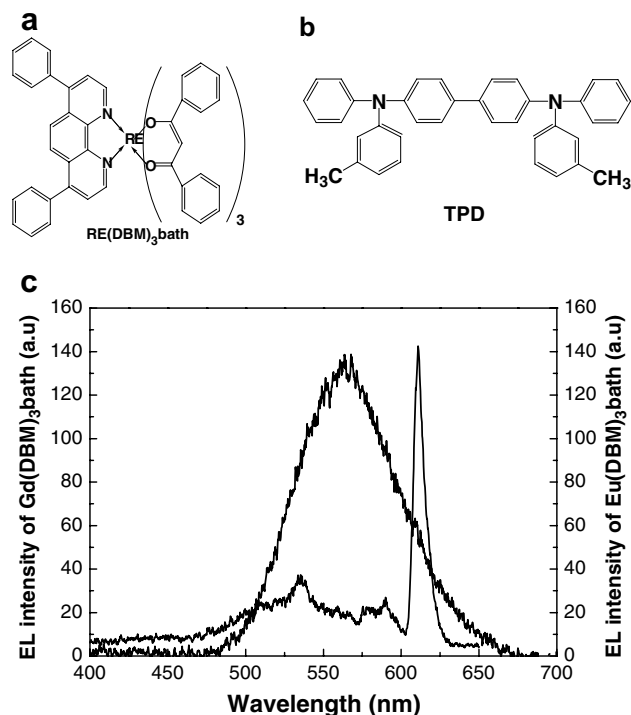

Fig. 1. The chemical structures of RE(DBM)$_3$ bath (RE = Eu or Gd) (a) and TPD (b) and the EL emission of exciplex from device A and Eu ion characteristic EL emission from device B under 5 V forward bias (c).
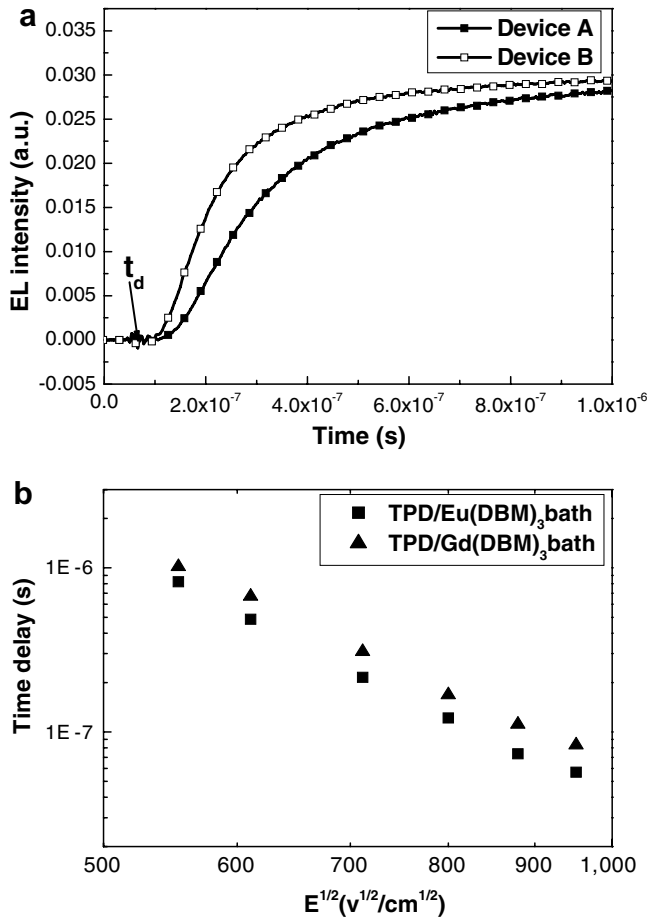
Fig. 2. (a) Transient EL response curves of bilayered TPD/Gd(DBM)$_3$ bath device, 7 V pulse voltages (pulse width 8 μs) were applied on the device. (b) Delay times versus the square root of electric field of transient EL spectra of device A (triangle) and B (square). The line in the figure is merely guide for eye.
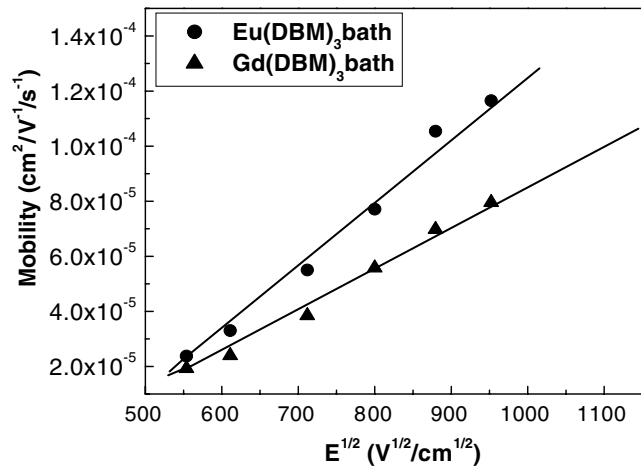

Fig. 3. Electron mobility of Gd(DBM)$_3$ bath (triangle) and Eu(DBM)$_3$ bath (circle) versus square root of electric field.

constant distribution of electric fields throughout organic layers, Fig. 3 illustrate that electron mobility and EL signal delay time of Gd(DBM)$_3$ bath are field dependent. The

calculated mobility of Gd(DBM)$_3$ bath is near to 8×10^{-5} cm^2/Vs at the electric field of 1 MV/cm, showing good electron transporting property of Gd(DBM)$_3$ bath. In addition, the EA level of Gd(DBM)$_3$ bath was 2.8 eV, similar to ALQ [17]. The excellent electron injection and transporting properties of Gd(DBM)$_3$ bath complex was proved. According to the Fig. 2b, the delay times of device B were conformably shorter than those of device A under same electric field, and hence the electron mobility of Eu(DBM)$_3$ bath seemed to be higher than that of Gd-complex. However, it is not necessary the truth that the electrons travel faster in Eu(DBM)$_3$ bath film than Gd(DBM)$_3$ bath. Taking the similar electronic configurations of trivalent Eu^{3+} and Gd^{3+} ions (only one more electron in inner 4f shell of Gd^{3+}) into consideration, the different calculated mobility of Eu(DBM)$_3$ bath and Gd(DBM)$_3$ bath are more likely due to the different luminescent mechanism, rather than the central ions. For device A, the EL emission resulted from recombination at the TPD/Gd(DBM)$_3$ bath interface. In such a case, the travel distance of electron equals to the thickness of ETM layer. However, for the device B, it should be noticed that the holes might diffuse into the ETM layer in both devices, i.e. A and B, recombination in the bulk layer of Eu(DBM)$_3$ bath gave off sharp red emission from Eu^{3+} ion. This means that the transporting distance of electron was shorter than the thickness of Eu(DBM)$_3$ bath film, and as a result a reduced t_d was observed. In such a case, the travel distance of electron equals to the thickness of ETM layer. While for the device B, the recombination in the bulk layer of Eu(DBM)$_3$ bath gave sharp red emission from Eu^{3+} ion. This means that the transporting distance of electron was shorter than the thickness of Eu(DBM)$_3$ bath film, and it will result in the decreasing t_d.

Due to the existence of imine nitrogen(s) (C=N) site [18], the second ligand of the RE complexes, bath (Bphen), is considered as an electron acceptor. Additional experiments were carried out to give the EA values of the first ligand DBM, the second ligand bath, Eu(DBM)$_3$ bath and Gd(DBM)$_3$ bath under the same condition. The result of similar EA values (2.8 eV) of Eu(DBM)$_3$ bath, Gd(DBM)$_3$bath and bath except DBM indicated that the three materials with bath had similar electron-accepting abilities. According to the excellent electron transporting property of bath reported by Naka et al. [19], bath could be the main component affecting the electron transporting property in RE(DBM)$_3$ bath film, and the electron mobility of Eu(DBM)$_3$ bath should be similar as Gd(DBM)$_3$ bath.

Based on the different delayed times, we also estimated the width of recombination zone in the double-layered Eu(DBM)$_3$ bath device. Supposed that both materials have same electron mobility, therefore, the electron mobility was achieved following the formula:

$$\mu = \frac{D_{eA}}{t_{dA}\frac{V-V_i}{D_t}} = \frac{D_{eB}}{t_{dB}\frac{V-V_i}{D_t}}$$

a

2.4 eV

Recombination Zone

2.8 eV

Hole

Mg:Ag 3.7 eV

ITO 4.7 eV

Electron

5.4 eV
TPD

Exciplex emission

5.8 eV
RE(DBM)$_3$bath
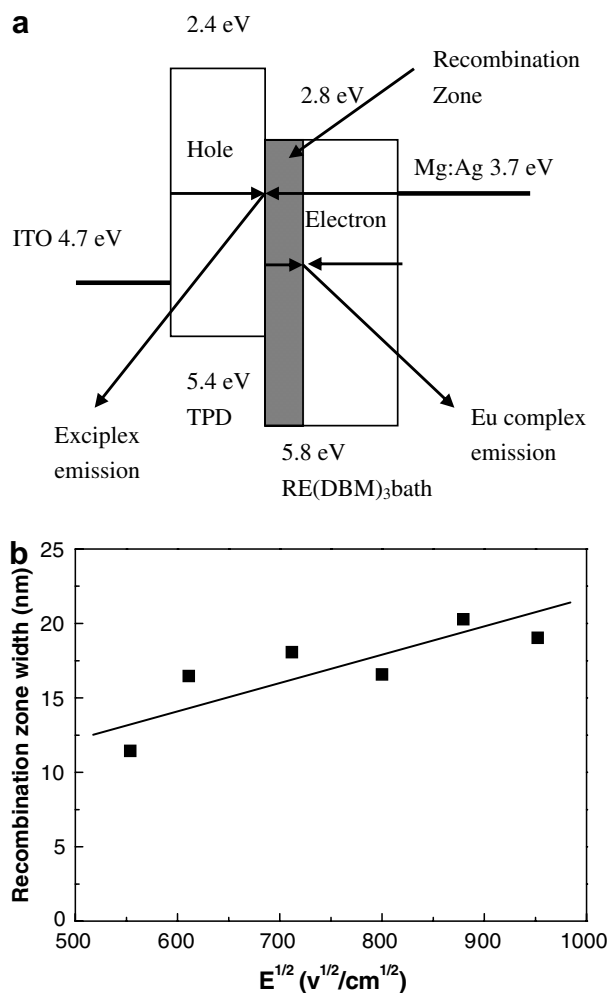
Eu complex emission

b

Fig. 4. (a) The energy diagram of bilayered OLED devices and different emission mechanisms. (b) The width of recombination zone of device B versus square root of electric field. The line is merely a guide to the eye.

Here, D_e is the thickness of the electron transport layer; t_d is the delay time of EL signal; V is the drive voltage; V_i, the voltage distributed on the out circuit; was estimated to be 0.2 V, D_t is the total thickness of organic layers that reach to 110 nm. The constant distribution of electric field E was obtained from the result of $\frac{V-V_i}{D_t}$. The D_{eA} of device A has been known to be 60 nm and unchangeable with the electrical fields because the interface exciplex emission of Gd(DBM)$_3$ bath. Due to the different t_ds of two devices, we can obtain D_{eB} of device B, the real transferring distance of Eu(DBM)$_3$ bath. We also estimate the width of recombination zone of device B by subtracting D_{eB} from the thickness of the electron transport layer 60 nm. As shown in the Fig. 4, we found that the width of the recombination zone was between 12 nm and 20 nm and field dependent, this result is consistent with that of our previous report that reported the width could reached to 12 nm [9]. Moreover, the increased tendency indicated that the penetration distance of holes enlarged as the electronic field increase in Eu(DBM)$_3$ bath film. We also supposed the same recombination zone existing in device A whereas,

unless the excitons in the Gd-complex layer need to diffuse to the organic interface and form exciplex with TPD molecule, it will not luminesce.

4. Conclusions

Electron mobility of two RE complexes, Gd(DBM)$_3$ bath and Eu(DBM)$_3$ bath, were measured using transient EL method. The electron mobility of RE(DBM)$_3$ bath is estimated to be 8×10^{-5} cm^2/Vs at electric field of 1 MV/cm. On the other hand, Gd(DBM)$_3$ bath was ascribed to the difference in EL mechanism, device of Gd-complex emits at interface, while device of Eu-complex in bulk, we also estimate a recombination zone (12 nm $\sim$ 20 nm width) in RE(DBM)$_3$ bath film. Our results showed that the transient EL measurement might not be suitable to measure the mobility of some RE complexes, especially for those containing emitting central ion.

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