

Self-quenching of excited europium ions in $\text{Eu}(\text{DBM})_3$ bath-based organic electroluminescent devices

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2001 J. Phys. D: Appl. Phys. 34 L61

(<http://iopscience.iop.org/0022-3727/34/12/102>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 159.226.165.151

The article was downloaded on 11/09/2012 at 04:49

Please note that [terms and conditions apply](#).

RAPID COMMUNICATION

Self-quenching of excited europium ions in $\text{Eu}(\text{DBM})_3$ bath-based organic electroluminescent devices

C J Liang¹, T C Wong¹, L S Hung¹, S T Lee¹, Z R Hong² and W L Li²

¹ Center of Super-Diamond and Advance Films (COSDAF), and Department of Physics and Materials Science, City University of Hong Kong, Hong Kong, People's Republic of China

² Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun, People's Republic of China

E-mail: cjliang@yahoo.com

Received 12 April 2001

Abstract

Luminance–current characteristics of organic electroluminescent devices based on the europium complex of europium(dibenzoylmethanato)₃ (bathophenanthroline) ($\text{Eu}(\text{DBM})_3$ bath) have been investigated. Transient measurements were carried out to study the decay process of excited Eu^{3+} ions. A comparison of experimental data and theoretical calculation shows that biexcitonic quenching among the excited Eu^{3+} ions is an important channel in their decay process, and this quenching process is a primary cause for our observation of a rapid decrease in quantum efficiency with increasing current density. Extending the recombination zone is found to be beneficial to reducing this defective effect. The mechanism of the quenching process is also discussed.

Earlier photoluminescence (PL) studies have shown that rare-earth complexes are characterized by highly efficient intra-energy conversion from the ligand singlet to the triplet and thence to the excited states of the central rare-earth ions [1, 2]. Thus both singlet and triplet excited states of the ligands could contribute to the final emission of the central rare-earth ions. For this reason rare-earth complexes are anticipated to exhibit high efficiencies in organic electroluminescent devices (OLEDs). The sharp-band emissive rare-earth complexes have been used as emitting material in OLEDs with various configurations [3–7]. An important and common problem is that the devices show significant efficiency decrease with increasing current density [3, 6, 7]. In order to make further improvement, efforts to clarify the physical origin of the efficiency decrease are necessary.

The efficiency decrease with increasing current density is also common in OLEDs using phosphorescent materials [8, 9]. A biexcitonic quenching model proposed by Baldo *et al* [10] was used to analyse the EL response of various phosphorescent guest–host systems as well as a europium-complex doped system. The effects of triplet–triplet annihilation in the guest and host were found to be the primary cause for the efficiency

decrease in these systems. For their low-concentration (2%) europium-complex doped system, no sign of biexcitonic quenching between the excited europium ions was found, since electroluminescent decay of Eu^{3+} ions was monoexponential and independent of excitation intensity.

In this rapid communication, we investigate the efficiency–current characteristics of a simple double-layer europium-complex OLED. Transient measurements were performed to investigate the decay process of excited Eu^{3+} ions. Comparison between the experimental data and the biexcitonic quenching model shows that biexcitonic quenching among the excited Eu^{3+} ions is an important channel in their decay process, and this quenching process is a primary cause for the rapid decrease in quantum efficiency with increasing current density in our devices. We also find that extending the recombination zone is beneficial to reducing this defective effect. The mechanism of the quenching process is also discussed.

The double-layer devices of ITO/TPD(30 nm)/ $\text{Eu}(\text{DBM})_3$ bath(80 nm)/MgAg (device A) and triple-layer devices of ITO/TPD(30 nm)/TPD: $\text{Eu}(\text{DBM})_3$ bath(30 nm)/ $\text{Eu}(\text{DBM})_3$ bath(50 nm)/MgAg (device B) were fabricated by using

conventional vacuum evaporation and by following the procedures described previously [6]. The luminance of the devices was measured with a PR650 SpectraScan. The transient electroluminescence was generated by applying a voltage pulse across the device of interest and recorded by a photomultiplier and an oscilloscope.

For convenience, we first introduce the biexcitonic quenching model in our case. Considering that interaction between two excited Eu^{3+} ions causes a quenching channel in the decay process of the excited Eu^{3+} ions, the process can be described as follows:

$$\frac{dn}{dt} = -\frac{n}{\tau} - \frac{k_q}{2}n^2 + k_f \frac{j}{qd} \quad (1)$$

where n is the concentration of the excited Eu^{3+} ions, τ is the lifetime of the excited ions, k_q is the biexcitonic quenching parameter, j is the current density, q is the electron charge, d is the thickness of the exciton formation zone, and k_f is the possibility for a charge-carrier to form an excited Eu^{3+} ion.

At steady state, the quantum efficiency can be calculated from equation (1):

$$\eta = \eta_0 \frac{j_0}{4j} \left(\sqrt{1 + 8 \frac{j}{j_0}} - 1 \right) \quad (2)$$

where η is the device quantum efficiency, η_0 is the quantum efficiency in the absence of the biexcitonic quenching effect among the excited Eu^{3+} ions, and

$$j_0 = \frac{4dq}{k_q k_f \tau^2} \quad (3)$$

is the characteristic current density at which $\eta = \eta_0/2$. If j_0 were small, the quenching effect would be serious. Thus a large value of j_0 is expected in our devices.

The transient decay process could also be deduced from equation (1). After a pulse excitation, the emission intensity L follows:

$$L(t) = \frac{L(0)}{(1 + K\tau)e^{t/\tau} - K\tau} \quad (4)$$

where $L(0)$ is the initial emission intensity and K is defined by

$$K = \frac{k_q n(0)}{2}. \quad (5)$$

Here $n(0)$ is the initial concentration of the excited Eu^{3+} ions.

Now we can make a comparison between the theory and experiments. Figure 1 shows the efficiency–current characteristics of device A. The experimental data are well fitted with the simulation line based on equation (2), except that at a current density greater than 200 mA cm^{-2} the efficiencies are slightly lower than the calculated values. We believe that, due to the unstable nature [6] of $\text{Eu}(\text{DBM})_3$ bath, the degradation of the europium complex at high current densities may also play a role in the decrease in efficiency, and thus causes the difference between the experimental data and the calculated line. In the computer-assisted simulation, the values $\eta_0 = 1.2\%$ and $j_0 = 2.4 \text{ mA cm}^{-2}$ were used. This means that if the current density is higher than 2.4 mA cm^{-2} the efficiency will be less than half of the initial value.

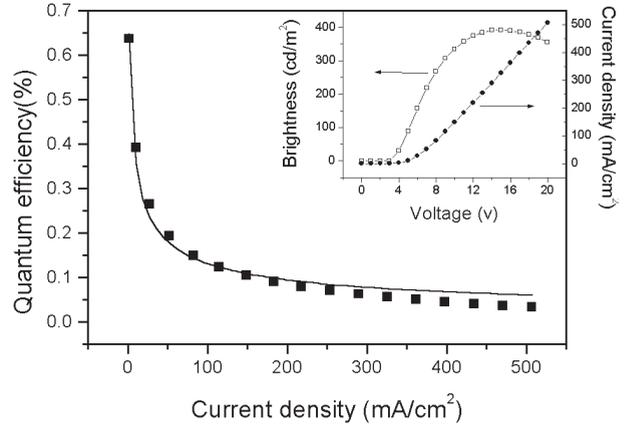


Figure 1. Efficiency–current characteristics of device A: experimental data (full squares) and simulated data (full curve) by using equation (2) with $\eta_0 = 1.2\%$ and $j_0 = 2.4 \text{ mA cm}^{-2}$. The inset shows brightness–current–voltage characteristics of device A.

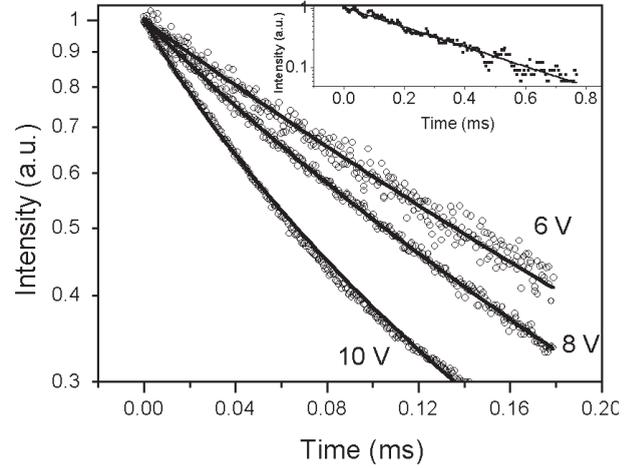


Figure 2. Transient luminescence of device A after the pulse excitations at 6, 8 and 10 V: experimental data (open circles) and fitting curves (full curves) by using equation (4) with $K = 1.7 \times 10^3$, 3.9×10^3 and $9.2 \times 10^3 \text{ s}^{-1}$ for 6, 8 and 10 V, respectively. The fitting curves are normalized at $t = 0$ for comparison. The inset shows the decay time of $\text{Eu}(\text{DBM})_3$ bath characterized by PL measurements.

Figure 2 shows the decay process after excitation with a pulse voltage. The measurement was performed at pulse voltages of 6, 8 and 10 V. The experimental data show that the decay becomes faster with increasing exciting voltages, indicating the presence of a biexcitonic quench process in the Eu complex. It was further found that the measured transient luminescence could not be simply described by a single exponential decay, especially at 10 V, also suggesting a nonlinear term in the decay process. The inset of figure 2 shows PL measurements on the decay time of $\text{Eu}(\text{DBM})_3$ bath. The exponential decay fit on this data gives a lifetime of 0.26 ms. Using this value for τ in equation (4) we successfully fit the decay process as shown in figure 2. The values of K are 1.7×10^3 , 3.9×10^3 and $9.2 \times 10^3 \text{ s}^{-1}$ for 6, 8 and 10 V, respectively. The K values increase with increasing voltages. According to equation (5), this trend is reasonable because a higher voltage pulse would give a higher initial concentration $n(0)$ and thus a larger K .

The above results show that biexcitonic quenching among the excited Eu^{3+} ions indeed plays a significant role in the decay process and it is a primary cause for the decrease in efficiency with increasing current densities. In such a case, j_0 can be used to quantify the quenching effect. A larger j_0 means a weaker influence of the quenching effect. According to equation (3), a simple way to increase j_0 is to raise the thickness of the exciton formation zone (d).

According to our ultraviolet photoelectron and optical absorption measurements the ionization potential (IP) and electron affinity (EA) of $\text{Eu}(\text{DBM})_3\text{bath}$ are about 5.9 eV and 2.9 eV, respectively, which are very close to those of Alq_3 . For that, the following method is proposed to estimate the recombination zone of the double-layer device. EL spectra were taken for different thicknesses of the $\text{Eu}(\text{DBM})_3\text{bath}$ layer in the device ITO/TPD(30 nm)/ $\text{Eu}(\text{DBM})_3\text{bath}/\text{Alq}_3$ (50 nm)/MgAg. If the recombination zone is within the $\text{Eu}(\text{DBM})_3\text{bath}$ layer, there would be no emission from Alq_3 in the EL spectra. Our experiments show that the thickness of the recombination zone in the double-layer device is less than 12 nm. Therefore, one cannot simply raise the thickness of $\text{Eu}(\text{DBM})_3\text{bath}$ to extend the recombination zone in order to improve device performance.

A mixed layer of $\text{Eu}(\text{DBM})_3\text{bath}$ and the hole-transport material was then suggested to extend the emitting zone to more than 30 nm, and thus increase the value of j_0 . The effects on quantum efficiency were confirmed in our experimental data and computer simulation.

Figure 3 shows the efficiency–current characteristics of device B. In the mixed layer, the weight ratio of TPD to $\text{Eu}(\text{DBM})_3\text{bath}$ is approximately 1:3. The experimental data agree well with the calculated line at lower current densities. Again, at a current density higher than 200 mA cm^{-2} , the experimental data are slightly lower than the simulation. The data fitting gives $\eta_0 = 1.7\%$ and $j_0 = 7.6 \text{ mA cm}^{-2}$, where j_0 is more than three times higher than that of the double-layer device. This is one of the reasons for the observed better luminance of device B (shown in the inset of figure 3). In device B, it is expected that the formation zone of excitons extends to the entire mixed layer, thus resulting in a large j_0 value.

It is well known that rare-earth ions have abundant excited state processes. Among these, energy transfer between the excited rare-earth ions has been an important process in the earlier up-conversion luminescence studies [11]. In our case, we suppose the following quenching process (as shown in the inset of figure 4): $\text{E}^* + \text{E}^* \rightarrow \text{E}^{**} + \text{E}$, where E^* represents the emissive excited state $^5\text{D}_0$ of Eu^{3+} ions, E^{**} represents a higher excited state, and E is the ground state. Energy transfer from one E^* to another E^* forms a higher excited state E^{**} , then E^{**} relaxes to a lower energy level. This relaxation process may cause emission from other levels such as $^5\text{D}_1$, since it is another emissive but weak level of Eu^{3+} ions.

Figure 4 shows the different EL spectra of device B at 4 and 10 V. At 4 V the spectrum shows only emission from the $^5\text{D}_0$ level as the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition gives the main emission peak at 613 nm. When increasing the driving voltage two small peaks at 536 nm and 588 nm, which correspond to the $^5\text{D}_1 \rightarrow ^7\text{F}_1$ and $^5\text{D}_1 \rightarrow ^7\text{F}_3$ transitions respectively, gradually appear in the

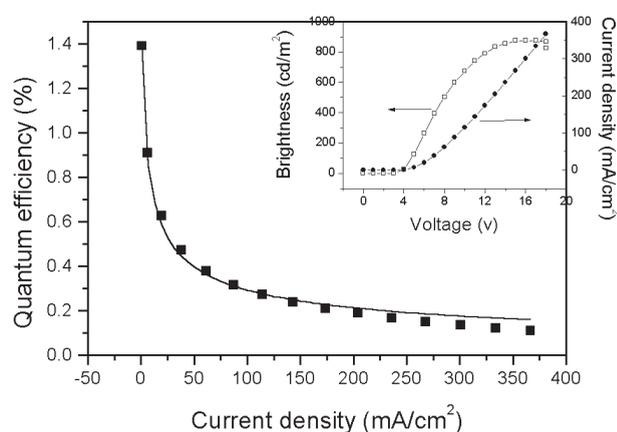


Figure 3. Efficiency–current characteristics of device B: experimental data (full squares) and fitting curves (full curves) by using equation (2) with $\eta_0 = 1.7\%$ and $j_0 = 7.6 \text{ mA cm}^{-2}$. The inset shows brightness–current–voltage characteristics of device B.

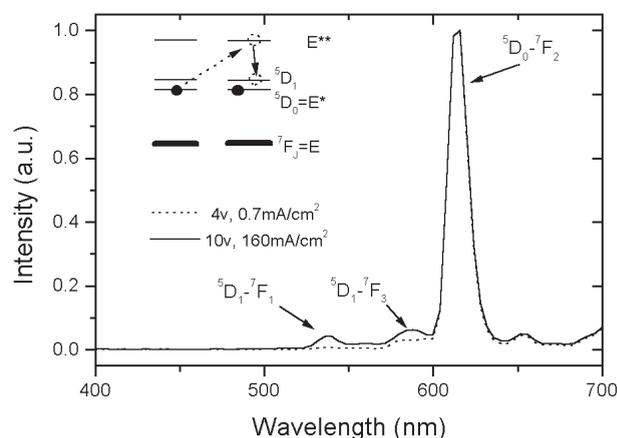


Figure 4. EL spectra of device B at 4 V (dotted curve) and at 10 V (full curve). The spectra are normalized at the peak of 613 nm for comparison. The inset shows the proposed quenching process.

spectra. These peaks are clearly shown in the spectrum at 10 V. These results support our assumption about the biexcitonic quenching process. At high current densities the quenching among the excited Eu^{3+} ions becomes a dominant process. The $^5\text{D}_1$ level is then excited at a high population from relaxation of E^{**} and gives detectable emission.

The possibility for the quenching process to occur may vary with the distance between two neighbouring excited states. This may be a possible reason for the different mechanism supposed by Baldo *et al.* They showed that the quenching effect among the excited Eu^{3+} ions is not important when they doped one europium complex into a host of CBP at a concentration of 2%, and attributed their observations on the decreased efficiency with increasing current densities to the triplet–triplet annihilation of excited CBP molecules [10].

In conclusion, because the excited rare-earth ions possess a very long lifetime the interaction between the ions at their excited states becomes significant. We have shown that the biexcitonic quench among excited Eu^{3+} ions is an important channel in their decay process, and this quenching process is a primary cause for the efficiency decrease when using the Eu complex at a high concentration. Extending the recombination zone is a simple and effective way to ease this defective effect.

Acknowledgments

The authors wish to acknowledge Man Keung FUNG for UPS analysis. The work was supported by a CERG Grant (Project No. 9040495).

References

- [1] Crosby G A, Whan R E and Alire R M 1961 *J. Chem. Phys.* **34** 743
- [2] Crosby G A and Whan R E 1962 *J. Chem. Phys.* **36** 863
- [3] Kido J, Hayase H, Hongawa K, Nagai K and Okuyama K 1994 *Appl. Phys. Lett.* **65** 2124
- [4] Gao X C, Cao H, Huang C and Li B 1998 *Appl. Phys. Lett.* **72** 2217
- [5] Sano T, Fujita M, Fujii T, Hamada Y, Shibata K and Kuroki K 1995 *Japan. J. Appl. Phys.* **34** 1883
- [6] Liang C J, Zhao D, Hong Z R, Zhao D X, Liu X Y, Li W L, Peng J B, Yu J Q, Lee C S and Lee S T 2000 *Appl. Phys. Lett.* **76** 67
- [7] Hu W, Matsumura M, Wang M and Jin L 2000 *Appl. Phys. Lett.* **77** 4271
- [8] Baldo M A, O'Brien D F, You Y, Shoustikov A, Sibley S, Thompson M E and Forrest S R 1998 *Nature* **395** 151
- [9] Baldo M A, Lamansky S, Thompson M E and Forrest S R 1999 *Appl. Phys. Lett.* **75** 4
- [10] Baldo M A, Adachi C and Forrest S R 2000 *Phys. Rev. B* **62** 10967
- [11] Auzel F E 1973 *Proc. IEEE* **61** 758