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Efficient red electroluminescence from organic devices using dye-doped rare earth complexes

Z. R. Hong, C. S. Lee, and S. T. Lee^{a)}

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

W. L. Li

Laboratory of Excited States Processes and Changchun Institute of Optics, Fine Mechanics, and Physics, Chinese Academy of Sciences, 130021, People's Republic of China

S. Y. Liu

National Laboratory of Integrated Optoelectronics, Jilin University, Changchun 130023, People's Republic of China

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Using rare earth complexes with electron-transporting properties as host materials, and 4-(dicyanomethylene)-2-*t*-butyl-6(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTB) as a dopant, bilayer doped electroluminescent (EL) devices with efficient red light emission were fabricated. When a europium complex was adopted, the EL spectrum consisted of emissions from DCJTB and Eu³⁺ ions. At optimal dopant concentration, an EL efficiency of 5.7 cd/A at 0.04 mA/cm² was observed. Although the EL efficiency decreased with an increase in current density, it remained higher than 2.0 cd/A with brightness of 347.0 cd/m² at 5.7 V bias. DCJTB and Eu³⁺ ions collected the energy of singlet and triplet excitons, respectively, and then gave rise to pure red color emission, suggesting a promising way by which to utilize both singlet and triplet excited states in EL devices. © 2003 American Institute of Physics. [DOI: 10.1063/1.1564631]

For organic electroluminescence (EL) devices, the development of high-performance red emission is still much in demand. This is because both blue and green emitting materials and devices that meet the requirements for commercial application are already available. For practical use, high EL efficiency as well as good purity of color are required. So fluorescent¹ and phosphorescent² dyes of red emission have been used as dopants to improve the EL efficiency and color purity.

It is well known that in rare earth (RE) complexes energy is transferred from the triplet state of ligands to the center RE ion, which raises the 4f electron of the ions to excited energy levels. Radiative electronic transitions back to the ground state or to other lower states give off photons. Due to the shielding effect of electrons in the outer shells, inner 4f electronic transitions of the RE ions give rise to a narrow emission band which is insensitive to the chemical environment. The advantages of RE³⁺ complexes for organic EL, such as good color and potential high EL efficiency, were first proposed by Kido *et al.*³ and proven recently.⁴ Europium complexes which exhibit strong photoluminescence (PL) corresponding to the $^5D_0 - ^7F_2$ transition in Eu³⁺ ions are hence promising materials for red EL devices.⁵

RE complexes, in some sense, are intrinsic dopant-matrix systems because the ligands and the center ion can be regarded as the matrix and dopant, respectively. The atomic ratio of ligands to ions is a constant that is determined by the nature of the coordination chemistry. This is beneficial for

efficient internal energy transfer and luminescence.^{6,7} However, only those complexes of suitable chemical structures yield strong light emission from RE ions under a certain excitation condition, since in most cases, the composition of the complexes is fixed. For a common complex, the atomic percentage of RE ions is about ~1% or less. For example, the ratio of Eu³⁺ to other atoms in a tris(theetyltrifluoroacetonate)phenanthroline Eu³⁺ [Eu(TTA)₃phen] complex, a widely used material, is 1:76, and this ratio could be even smaller in other cases. The low concentration of RE ions in complexes together with their relatively long luminescent decay time (typically several hundreds of microseconds) make RE complexes generally not suitable for application as dopants in organic EL devices, although suitable hosts capable of efficient energy transfer to RE complex dopants are available.⁸ One solution to this problem is to utilize RE complexes as the carrier transporting and emitting layer. Another solution is to increase the atomic ratio of RE ions in the complexes, but this often results in concentration quenching of Eu³⁺ luminescence.^{9,10}

Using RE complexes as a host requires that the complexes possess good carrier transporting properties. In such a device, the center ion acts as a dopant and accepts energy from the triplet state of the ligands generated by charge recombination. Compared to using RE complexes as dopants,¹¹ this method may increase the concentration of energy acceptors (the center ions) and avoid the possibility of saturation of energy transfer. Efficient energy transfer should therefore decrease the chance of other emission processes from the host or excited complex (exciplex) that degrade color purity. Unfortunately, even though films of RE complexes have

^{a)}Author to whom correspondence should be addressed; electronic mail: apannale@cityu.edu.hk

been used as emitting layers, other emission components could not be reduced completely.¹²

According to previous studies on the PL properties of RE complex,⁶ RE ions primarily accept the excitation energy of the triplet but not that of the singlet state of the ligands. As a result, 100% efficiency of energy transfer from the ligands to the center ion is only possible when the efficiency of the ligand's internal conversion from singlet to triplet is unity.¹³ Recently, we showed that the exciplex formed in the system of *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-diphenyl-4,4'-diamine (TPD) and a RE complex originated from the interaction between the singlet excited state of ligands and the ground state of the TPD molecule. The exciplex so formed was naturally also in the singlet state. Therefore, one approach by which to gain additional efficiency would be to convert the singlet state of ligands into light emission in EL devices based on the RE complex.

In this letter, we report the use of Eu-tris(dibenzooylmethanato) bathophenanthroline [Eu(DBM)₃ bath]¹⁴ as a host to enhance the EL efficiency of red devices by utilizing energy from both the triplet and singlet excited states. To collect energy from the singlet state and to quench the exciplex emission in the EL device, a well-known red fluorescent dye, 4-(dicyanomethylene)-2-*t*-butyl-6(1,1,7,7-tetramethyljulolidyl-9-enyl)-4*H*-pyran (DCJTB),^{1,15} was used as a dopant in the host of the RE complex. It was found that the RE³⁺ ion and DCJTB acted as an energy acceptor for the triplet and singlet excited states of the ligands of the RE complex, respectively. As a result, exciplex emission was suppressed and EL efficiency was substantially improved.

TPD was used as a hole transporting material. RE(DBM)₃bath (RE=Gd or Eu) was synthesized according to the traditional method.¹⁶ Organic layers and a Mg:Ag (atomic ratio 10:1) alloy cathode were successively deposited on a glass substrate coated with transparent indium-tin oxide (ITO) by vacuum (2×10^{-6} Torr) thermal evaporation in one pump down. ITO glass substrates with a sheet resistance of $100 \Omega/\square$ were precleaned and treated in UV ozone. Bilayer devices with a configuration of ITO/TPD(50 nm)/RE-complex:DCJTB(60 nm)/Mg:Ag (200 nm) were fabricated. The deposition rates for the organic and metal layers were monitored by quartz oscillators and kept at 0.1 and 0.5 nm/s, respectively. The active area of each emitting pixel was 0.1 cm^2 . Current density and brightness versus drive voltage as well as EL spectra were measured with a SpectraScan PR650 spectrophotometer connected to a computer-controlled voltage-current source (Keithley 236).

In the present work, two different RE complexes were used. First, we used Gd(DBM)₃bath as a host and found that it was suitable as a DCJTB dopant. Due to the large energy gap of the Gd³⁺ ion, the organic ligand cannot excite the center Gd³⁺ ion. Thus the Gd complex is ideal for investigating the excited states of coordinating ligands. Previous investigation of the spectral properties of the bilayer ITO/TPD/Gd(DBM)₃bath/Mg:Ag device showed its EL was dominated by exciplex emission.¹⁷ For this device, the maximum EL efficiency was only 0.5 cd/A and it decreased rapidly with an increase in current density. By doping DCJTB into the Gd(DBM)₃bath layer, a strong red emitting peak near 620 nm from DCJTB, identical to that reported by Chen

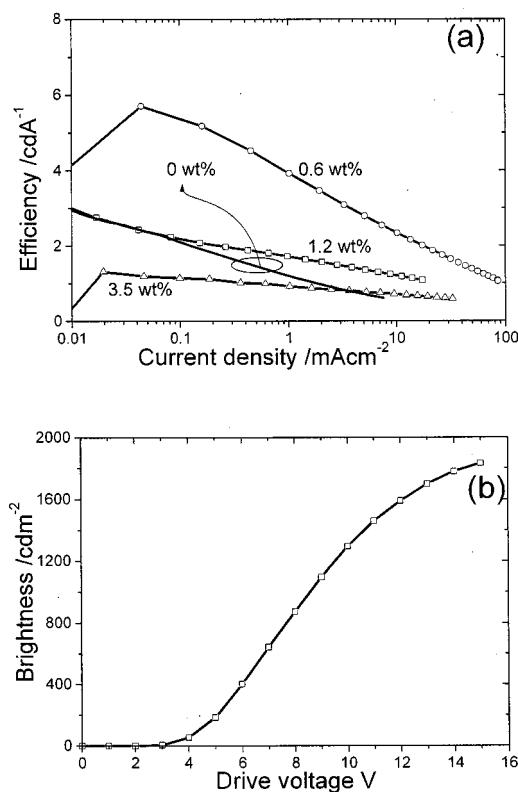


FIG. 1. (a) EL efficiency vs current density curves of DCJTB-doped Eu(DBM)₃bath devices with different doping concentrations: 0 wt % (solid line), 0.6 wt % (line with circles), 1.2 wt % (line with squares), 3.5 wt % (line with triangles). (b) Brightness–voltage curve of TPD/Eu(DBM)₃bath:DCJTB (0.6 wt %).

et al.,¹⁵ was observed. At the same time, exciplex emission was quenched completely. The PL spectrum (not shown here) of the Gd(DBM)₃bath film under 360 nm excitation consists of two peaks. The lowest energy band at 480 nm overlapped the absorption spectrum of DCJTB,¹⁵ suggesting that efficient energy transfer may occur from the singlet of the RE complex to DCJTB molecules. This was confirmed by PL measurement of the DCJTB-doped Gd(DBM)₃bath film, which exhibited only emission from DCJTB. With 1.0% DCJTB dopant, the bilayer TPD/Gd(DBM)₃bath showed a maximum EL efficiency of 2.9 cd/A. These results suggest that using a fluorescent dopant in a RE complex matrix can be an effective means by which to utilize the singlet energy.

When the Eu(DBM)₃bath was used, the EL efficiency was improved further. As expected, the dopant concentration affected the EL efficiency. Similar to the DCJTB-doped tris(8-hydroxyquinoline) aluminum (AlQ) devices,¹⁵ a medium concentration favored EL efficiency. Figure 1 shows the dependence of the EL efficiency on the dopant concentration at different current densities. The EL spectra consisted of emission from both Eu³⁺ and DCJTB. For a dopant concentration of 0.6 wt %, a maximum current efficiency of 5.7 cd/A was obtained. The EL efficiency was sensitive to the injection density and dopant concentration. From Figs. 1 and 2, it is clear that, compared to the undoped TPD/Eu(DBM)₃bath device, the 0.6% DCJTB-doped device exhibited considerably improved EL efficiency even at high current density and showed no exciplex emission. The maximum EL efficiency of the 0.6% DCJTB-doped

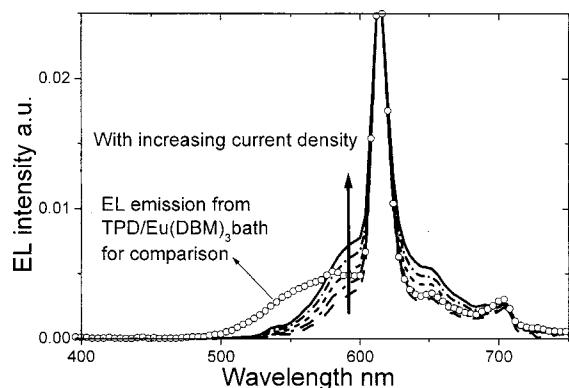


FIG. 2. Evolution of EL spectra of TPD/Eu(DBM)₃bath:DCJTB (0.6 wt %) with an increase in injected current; the line with circles line is an EL spectrum of the undoped TPD/Eu(DBM)₃bath device at 20 mA/cm². This comparison shows that dopant can quench exciplex emission.

Eu(DBM)₃bath device is almost equal to the total efficiency of the undoped TPD/Eu(DBM)₃bath and TPD/Gd(DBM)₃bath:DCJTB (1.0%) devices, suggesting that the excitation energy of the Eu³⁺ ion and DCJTB comes from two different sources. Otherwise, if the excitation processes of Eu³⁺ ion and DCJTB competed with each other, one would not expect the EL efficiency of the TPD/Eu(DBM)₃bath:DCJTB to exceed 3.0 cd/m².

These results show that RE(DBM)₃bath complexes are potentially good hosts for fluorescent dyes, and suggest that using a RE complex as a host may be an attractive approach by which to harvesting both singlet and triplet energy in one EL device.

Increasing the DCJTB concentration in the Eu(DBM)₃bath not only resulted in self-quenching, but also in quenching the Eu³⁺ emission. That is, when the DCJTB concentration reached 3.5%, emission spectra were dominated by DCJTB emission. A reasonable explanation is as follows. In the case of low DCJTB concentration in the Eu(DBM)₃bath, we supposed that recombination of the electron and hole took place in the host molecules. Therefore, the average distance between the excited states of ligands and DCJTB molecules was relatively long, favoring long-distance Förster energy transfer. As a result, most of energy transfer from the ligands to the DCJTB was from singlet to singlet. However, as the concentration increased, Dexter energy transfer may become more dominant. DCJTB molecules were more likely to get energy from ligand triplets and suppressed Eu³⁺ emission. This mechanism may result in a decrease in EL efficiency as observed in this study. However, due to the similar position of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of AlQ and the RE(DBM)₃bath,¹⁰ a charge trapping mechanism could also be responsible for the phenomenon mentioned above.

Another finding of interest was that the use of DCJTB dopant in RE complexes made the devices more stable. The curves of brightness versus time at 5.0 mA/cm² for undoped and 0.6% doped devices (both bare and tested in ambient) are shown in Fig. 3. It is clear that the decay time until half brightness of the doped device was longer than that of the

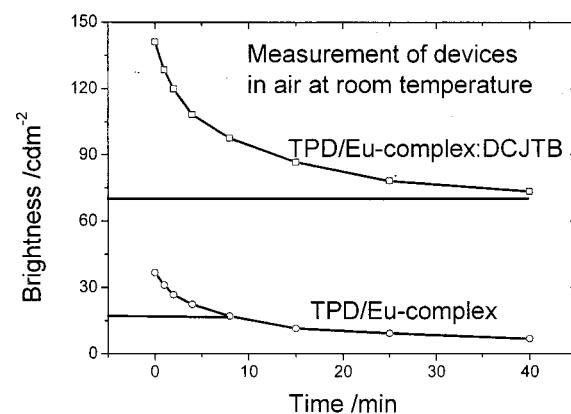


FIG. 3. Brightness decay curves of the TPD/Eu(DBM)₃bath:DCJTB (0.6 wt %) (line with squares) and TPD/Eu(DBM)₃bath (line with circles) at current density of 5.0 mA/cm² in air at room temperature.

undoped one. While RE complex based devices often show sharp pure color emission, they are notorious for their short lifetime.⁴ The present doping method appears to be a viable approach with which to substantially improve the lifetime and efficiency of RE complex-based EL devices while preserving the sharp emission peak.

In conclusion, bilayer red EL devices based on RE complexes of high efficiency were demonstrated. A promising way for achieving high EL efficiency was proposed, that is, using RE complexes as the host and fluorescent dyes as the dopant, both triplet and singlet energy could be converted into light emission.

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