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A mechanistic study of exciplex formation and efficient red light-emitting devices based on rare earth complexes

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Abstract

The mechanisms of exciplex formation between hole-transporting material *N,N′*-diphenyl-*N,N′*-bis(3-methylphenyl)-1,1′-diphenyl-4,4′-diamine (TPD) and electron-transporting materials tris(dibenzoylmethanato)-mono(bathophenanthroline)-rare earth (RE(DBM)$_3$bath) in TPD/RE(DBM)$_3$bath bilayer electroluminescence (EL) devices were studied. The formation process was identified by using fluorescent dye as dopant. It was found that interaction between the excited states of RE(DBM)$_3$bath and the ground state of TPD molecules resulted in the exciplex. The recombination zone of the TPD/RE(DBM)$_3$bath device was proved to be mainly in the RE(DBM)$_3$bath layer near the organic interface. On the other hand, by using dopant as efficient energy acceptor in RE-complex hosts, we found that exciplex emission was quenched thoroughly and efficient red light emission was observed, proving that RE(DBM)$_3$bath may act as an efficient energy donor in EL devices. In the case of Eu^{3+} as the central ion, maximum EL efficiency and highest brightness of red light emission reached 2.6% and 2000 cd/m^2, respectively.

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1. Introduction

When an exciton is formed in a molecule, it is possible for the excited molecule to strongly interact with other adjacent ones. This would lead to the formation of excimer if the two molecules are the same, or exciplex if the two molecules are different. Delocalization of the excited electron in the excimer/exciplex would lead to different electronic states. The new excited state involving two molecules bound together differs significantly from that of the original exciton. Comparing with the exciton on one molecule, the corresponding ground state of the exciplex/excimer is a weak bound state and hence has a very short lifetime, namely extremely unstable. In fact, most of the time, this type of ground states is undetectable. Usually, mainly due to delocalization of the excited electron, the energy of exciplex emission is smaller than that of the intrinsic emission of the constituting molecules of the excimer/exciplex, resulting in red-shift of exciplex emissions. Thus the self-absorption of excimer/exciplex emission is relatively weak. One may easily relate these unique properties to population inversion and lasing action. Therefore, in-depth investigation of the

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luminescent, especially electroluminescence (EL), properties of exciplex is of importance in the pursuit of electrically pumped lasers.

Exciplex formation is a common phenomenon among organic EL devices in previous reports [1–4]. Exciplex emission is usually not efficient except for a few cases [5]. It is generally undesirable in organic EL devices based on rare earth (RE) complexes. EL emission from RE complexes is characterized by narrow bands and potentially high EL efficiency. Thus, exciplex emission from the RE complexes-based EL devices is often harmful to both EL efficiency and color purity [6,7]. To avoid exciplex formation and emission and to convert the energy of exciplex to more efficient emission, it is also important to understand the mechanisms of exciplex formation.

The exciplex formation between hole-transport material *N,N′*-diphenyl-*N,N′*-bis(3-methylphenyl)-1,1′-diphenyl-4,4′-diamine (TPD) and tris(dibenzoylmethanato)-mono(phenanthroline or its derivatives) RE compounds, in which dibenzoylmethanato (DBM) acts as the first ligand and phenanthroline (phen) or bathophenanthroline (bath) as a neutral ligand has been studied [7,8]. A broad and featureless band different from the photoluminescence (PL) band of TPD and $\mathrm{RE(DBM)_3}$bath was observed in TPD/$\mathrm{RE(DBM)_3}$bath double-layer devices. It is of interest to understand the formation mechanisms of the exciplex and to convert the exciplex emission to more efficient emission of the desired wavelength. In this article, the formation process of the exciplex was studied by using fluorescent dopant as a probe. Furthermore, by comparing the EL spectra from devices of different structures, the charge recombination zone was verified to be in the RE-complex layer and near to the organic interface, and the formation position of the exciplex was located. At the same time, EL efficiency was improved due to the dopant, which quenched the exciplex emission thoroughly.

2. Experimental details

RE-complexes used in this study were synthesized as reported in [9]. Other organic materials were purchased from Aldrich. Anode and cathode of the organic EL devices were the indium tin oxide (ITO)-coated glass substrate (100 Ω/□) and Mg:Ag (10:1, 200 nm) alloy, respectively. After cleaning, the ITO substrate was UV ozone treated for 25 min and then loaded into a vacuum chamber. Organic films and Mg:Ag cathode were deposited onto the ITO substrate successively by thermal evaporation during one pump-down. Deposition rate for organic films and alloy cathode was monitored by crystal oscillators and kept at 0.1–0.2 and 0.8–1 nm/s, respectively. Thicknesses of the TPD and the $\mathrm{RE(DBM)_3}$bath layers were 60 and 80 nm for all the EL devices. Active area of typical devices was 0.10 $\mathrm{cm^2}$. Dependence of current density on drive voltage on EL spectra was measured by a Spectrascan PR650 Spectrophotometer connected to a computer-controlled Keithley-236 power resource. PL and absorption spectra were recorded with a Perkin Elmer LS50 fluorescence spectrophotometer and a Hewlett-Packard HP8453 spectrometer, respectively. All measurements were carried out in ambient air at room temperature.

3. Results and discussions

3.1. Mechanism of exciplex formation

$\mathrm{Gd^{3+}}$ and $\mathrm{Eu^{3+}}$ were adopted in this work as the central ions of the $\mathrm{RE(DBM)_3}$bath materials which possess good electron injection and transport properties [7,8]. $\mathrm{Gd^{3+}}$ ion with a stable $\mathrm{4f^7}$ configuration has the largest energy gap among the trivalent rare earth ions. In a $\mathrm{Gd(DBM)_3}$bath molecule, the $\mathrm{Gd^{3+}}$ ion bonds with its four chelated ligands and forms the complex, but cannot be an energy acceptor due to its large energy gap. For $\mathrm{Eu(DBM)_3}$bath, well matched energy levels between $\mathrm{Eu^{3+}}$ ion and excited states of ligands enable efficient energy transfer from the surrounding ligands to the $\mathrm{Eu^{3+}}$ ion and leads to efficient luminescence from $^5\mathrm{D}_0$ level of $\mathrm{Eu^{3+}}$ ion.

It was found that deposited $\mathrm{Gd(DBM)_3}$bath film showed weak luminescence between 400–500 nm under 365 nm UV excitation. By doping 1 wt% of 4-dicyanomethylene-2-methyl-6-(p-di-

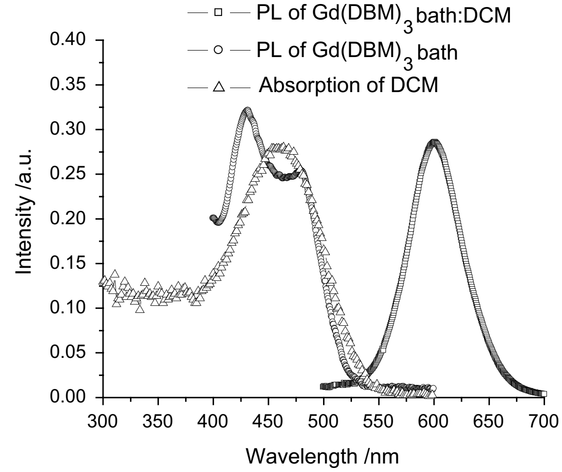

Fig. 1. PL spectra of Gd(DBM)$_3$bath and DCM (1%) doped Gd(DBM)$_3$bath film under 365 nm UV excitation, and absorption of DCM in MeOH solution (10^{-4} M).

methyl-aminostyryl)-4H-pyran (DCM) in this film, strong PL emission from DCM was observed as shown in Fig. 1. The PL efficiency of the doped Gd(DBM)$_3$bath film was estimated to be 23% using an empirical method [10], while the undoped film was only about 1%. The former value is comparable to that of neat ALQ film [11], suggesting efficient host-to-guest energy transfer. So efficient EL emission from the DCM doped RE-complex films is expected. The PL spectrum of undoped Gd(DBM)$_3$bath film and absorption spectrum of DCM in methanol solution are also shown in Fig. 1. According to the spectral overlap, efficient energy transfer from RE(DBM)$_3$bath to DCM is expected. Thus, DCM dopant was used as a probe in subsequent experiments to locate the recombination zone in the TPD/RE(DBM)$_3$bath bilayer devices. EL devices of different structures were fabricated, including (A) TPD (60 nm)/Gd(DBM)$_3$bath (80 nm), (B) TPD (60 nm/Gd(DBM)$_3$bath:DCM (1 wt%, 8 nm)/Gd (DBM)$_3$bath (72 nm), (C) TPD (60 nm)/Gd(DBM)$_3$bath (8 nm)/Gd (DBM)$_3$bath:DCM (1 wt%, 72 nm), (D) TPD (52 nm)/TPD:DCM (1 wt%, 8 nm)/Gd(DBM)$_3$bath(80 nm).

Fig. 2 shows the EL spectra of devices (A), (B), (C) and (D). For the undoped device (A), broadband exciplex emission at 560 nm with a full width at half maximum of about 130 nm was observed and the maximum EL efficiency was merely 0.5 cd/A. With a narrow doped-zone in Gd(DBM)$_3$bath near the TPD/Gd(DBM)$_3$bath interface, device (B) showed red light emission from DCM and no exciplex emission. The red emission could be due to energy transfer from the RE complex to DCM. Taking the energy levels of DCM [12] and RE-complex [13] into account, charge carrier trapping on DCM sites was also a possibility. However, the extinction of exciplex emission in the presence of DCM and PL measurement on DCM-doped Gd(DBM)$_3$bath film convinced the existence of efficient energy transfer. When the doped-zone was 8 nm away from the organic interface, i.e. device (C), the EL shows emission from both the exciplex and DCM. This confirms that exciplex was formed between RE complex and TPD molecules and located exactly at the TPD/Gd(DBM)$_3$bath interface, but not due to the interaction of DBM and bath in the complex. This also shows that a considerable amount of recombination took place inside the Gd(DBM)$_3$bath layer. In the case of neat Gd(DBM)$_3$bath film, this part of excitation energy was wasted due to the weak luminescence of Gd(DBM)$_3$bath complex.

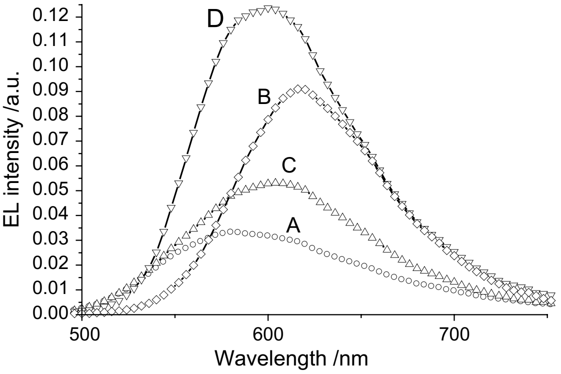

Fig. 2. EL spectra of devices (A) TPD/Gd(DBM)$_3$bath; (B) TPD/Gd(DBM)$_3$bath:DCM (1%, 8 nm)/Gd(DBM)$_3$bath; (C)TPD/Gd(DBM)$_3$bath (8 nm)/Gd(DBM)$_3$bath:DCM (1%); (D) TPD/TPD:DCM (1%, 8 nm)/Gd(DBM)$_3$bath.

The fact that DCM dopant in Gd(DBM)$_3$bath quenched the exciplex emission suggests that it was the excited states of RE(DBM)$_3$bath triggering the exciplex formation. Hence the formation process of exciplex could be defined as follows. Charge recombination took place on the RE(DBM)$_3$bath molecule. Excited RE(DBM)$_3$bath molecule at the organic interface would interact with ground-state TPD molecule to form the exciplex. Because DCM is a fluorescent material, the excitation energy of the RE(DBM)$_3$bath complex which finally leads to EL emission from DCM should be intrinsically a singlet state [14]. So it was the singlet exciton on the RE(DBM)$_3$bath molecule which interacted with the ground state of the TPD molecule and then formed the RE(DBM)$_3$bath-TPD exciplex, although it remains unclear whether the exciplex was in the singlet or the triplet state.

When DCM was doped in the TPD layer, device (D) exhibited emission from both exciplex and DCM. It rules out the possibility that the exciplex acted as an energy donor for DCM, because there would have been no exciplex emission considering the efficient energy transfer from the exciplex to DCM. EL emission from DCM might be due to charge trap of DCM in the TPD layer. In fact, exciton on TPD molecule was hard to form except at high electric field because of its large band-gap and good electron block property [13].

3.2. Efficient red EL emission from DCM-doped RE(DBM)$_3$bath devices

The low EL efficiency observed in the bilayer device (A) can be ascribed to three main reasons. The first one is inferior luminescent ability of the RE(DBM)$_3$bath-TPD exciplex, i.e. non-radiative relaxation dominates the decay processes. The second one is the limitation to exciplex population because the exciplex can only form at the organic interface. The third one is the poor hole block ability of RE(DBM)$_3$bath that led to the percolation of holes inside the film. Even these holes recombined with electrons, it was hard for the exciton to move to the interface and to form exciplex.

To improve the EL efficiency, DCM was doped into the RE(DBM)$_3$bath layer. The EL efficiencies of bilayer devices with different DCM concentrations were shown in Fig. 3. With 0.8 wt% DCM dopant, bilayer device TPD (60 nm)/Gd(DBM)$_3$bath:DCM (80 nm) gave a maximum EL efficiency of 1.4%. As mentioned above, DCM dopant accepted energy from the singlet in RE(DBM)$_3$bath host. Therefore, using DCM as a dopant in RE(DBM)$_3$bath complex can be an effective means to utilize the singlet energy.

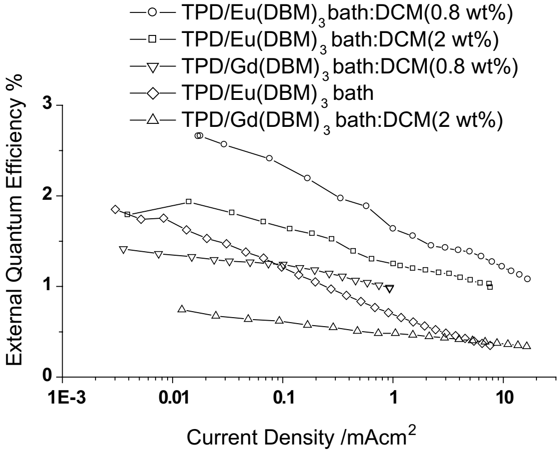

Fig. 3. EL efficiency versus current density curves of EL devices with different DCM concentration.

To improve EL efficiency further, Eu(DBM)$_3$bath was used. As expected, the dopant concentration affected EL efficiency. Fig. 3 shows the dependence of EL efficiency on current densities at different dopant concentrations. For a dopant concentration of 0.8 wt%, a maximum current efficiency of 2.6% was obtained. This device showed the best performance among all in this work. The maximum brightness at a current of 16 mA/cm^2 under 6 V bias exceeded 350 cd/m^2 and the CIE coordinates of red light emission were $x = 0.62$ and $y = 0.37$.

The EL spectra consist of emissions from both Eu^{3+} and DCM as shown in Fig. 4. From Fig. 3, it is clear that, comparing to the undoped TPD/Eu(DBM)$_3$bath device, the 0.8 wt% DCM-doped device exhibited significantly improved EL efficiency even at high current density and showed no exciplex emission. The maximum EL efficiency of the 0.8 wt% DCM-doped Eu(DBM)$_3$bath device is only slightly smaller than the sum of efficiencies of the undoped TPD/Eu(DBM)$_3$bath and 0.8 wt%-doped TPD/Gd(DBM)$_3$bath:DCM devices. This suggests that the excitation energy for Eu^{3+} ion

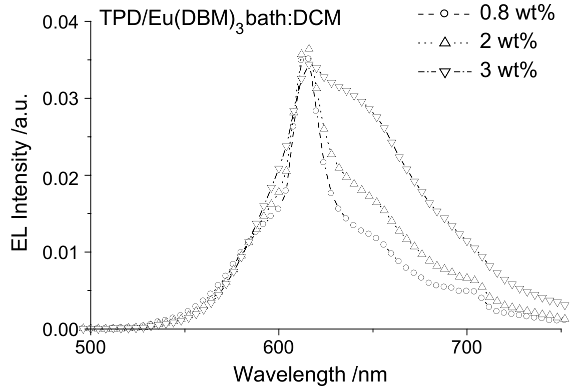

Fig. 4. EL spectra of TPD/Eu(DBM)$_3$bath:DCM device with different DCM concentration.

and DCM comes from two different sources. Otherwise, if the excitation processes of Eu^{3+} ion and DCM competed with each other, one would not expect the EL efficiency of TPD/Eu(DBM)$_3$bath:DCM to be higher than 1.8%. One possible explanation is that the fluorescent dye and the central Eu^{3+} ion accept excitation energy from the singlet and the triplet states in the RE complex matrix, respectively. These results show that the RE(DBM)$_3$bath complexes are potentially good hosts for fluorescent dyes, and suggest that using RE complex as a host may be an attractive approach to harvest both singlet and triplet energy in one EL device.

As shown in Fig. 3, increasing DCM concentration in Eu(DBM)$_3$bath not only resulted in self-quenching, but also in decreased Eu^{3+} emission. That is, when the DCM concentration reached 3 wt%, emission spectra were dominated by DCM emission. A reasonable explanation was given as follows. In the case of low DCM concentration in Eu(DBM)$_3$bath, we suppose that recombination of electron and hole took place on the host molecules. The average distance between the excited states of ligands and DCM molecules was relatively long, favoring the long-distance Förster energy transfer. As a result, most of energy transfer from the ligands to DCM was from singlet to singlet. However, as concentration increased, Dexter energy transfer may become more dominant. DCM molecules were more likely to get energy from ligand's triplets, and suppressed the Eu^{3+} emission [14]. This mechanism may result in decreasing EL efficiency as observed in this study. However, due to the similar positions of HOMO and LUMO of AlQ and RE(DBM)$_3$bath [13], charge trapping mechanism could also be responsible for the phenomenon mentioned above.

4. Conclusions

The formation process of exciplex in the bilayer TPD/RE(DBM)$_3$bath device was clarified by using the DCM dopant as a probe. The RE(DBM)$_3$bath molecules at the organic interface were first excited and then formed the exciplex with the ground state of the TPD molecules. On the other hand, with the help of DCM and Eu^{3+} ion, EL devices of high red light EL efficiency were obtained.

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