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Exciplex emissions in bilayer and doped thin films containing a non-fluorescent gadolinium complex

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Abstract

Bilayer and doped thin films of a non-fluorescent gadolinium complex gadolinium(dibenzoylmethanato)$_3$(bathophenanthroline) [Gd(DBM)$_3$bath] and *N,N′*-diphenyl-*N,N′*bis(3-methylphenyl)-1,1′-diphenyl-4,4′-diamine (TPD) are prepared. The exciplex formation between TPD and Gd(DBM)$_3$bath in doped film is confirmed through the measurement of the emission, excitation and absorption spectra. Exciplex emissions in electroluminescent process and the different electroluminescent spectra in the bilayer and the doped films are observed.

Keywords: Exciplex; Electroluminescence; Photoluminescence; Rare earth complex

1. Introduction

Extensive studies have been made of organic electroluminescence (EL) in view of both academic interest and practical application. Generally, multilayer devices consisting of charge transport and emitting layers exhibit higher performance than single-layer devices because in the multilayer device more balanced charge carriers are confined in the emitting layer. Doping with some high yield fluorescent dyes further enhances the electroluminescent properties of the devices. Hole-transport molecules have the tendency to provide electrons while electron-transport materials have the tendency to accept the one. So when some hole-transport materials and electron-transport materials are combined in an EL device, exciplex formation, which is a transient donor–acceptor complex between an excited state and a ground state, is likely to take place. Exciplex formation between different materials is a subject of interest. Several groups have reported exciplex emission in polymer EL devices [1–3]. For low molecular materials, although no exciplex emission is found in a *N,N′*-diphenyl-*N,N′*bis(3-methylphenyl)-1,1′-diphenyl-4,4′-diamine (TPD) and Alq_3 bilayer EL device, Itano et al. [4] have confirmed exciplex formation between Alq_3 and some hole-transport materials with low ionization potentials.

Rare earth complexes are of interest because rare earth ions show sharp emission bands and some are very suitable for multicolor display [5–7]. However, in addition to the expected sharp emission, a not clearly understood broad band frequently shows in the emission spectra [8,9]. In this paper, we chose a non-fluorescent rare earth complex gadolinium(dibenzoylmethanato)$_3$(bathophenanthroline) [Gd(DBM)$_3$bath] and investigated exciplex formations between this complex and TPD in bilayer and doped thin films through photoluminescence (PL) and EL study.

2. Experimental

Fig. 1 shows the molecular structure of the Gd

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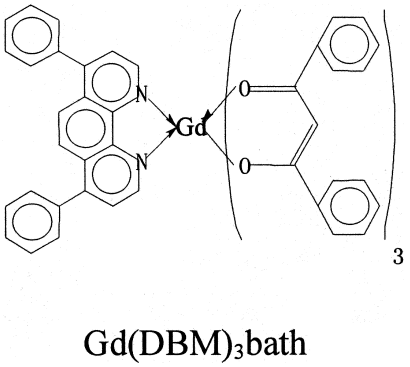

Fig. 1. The molecular structure of $Gd(DBM)_3bath$.

complex. Because of the mismatch of the excited state levels between the ligand and the central Gd^{3+} ions, the possibility of energy transfer from the ligand to the central ions is very low. As a result, $Gd(DBM)_3bath$ has no fluorescence even if it has an absorption peak at 360 nm (see Fig. 3a). From experiments, it is shown that the $Gd(DBM)_3bath$ can be used as an electron-transport layer in EL devices. The well-known material TPD is the hole-transport layer. For the EL devices, all of the organic layers and cathode layer ($Mg_{0.9}Ag_{0.1}$) are deposited by conventional vapor vacuum deposition at a pressure of 10^{-6} torr. The layer thickness is controlled in vacuo with a quartz crystal monitor. The emission area is 10 mm^2. For PL studies, the TPD-doped $Gd(DBM)_3bath$ layer is prepared by spin coating from a toluene solution. PL and EL are measured with a Hitachi 4000 fluorescence spectrophotometer. Absorption spectra are measured with a Shimadzu UV-3000 spectrophotometer.

3. Results and discussion

3.1. Photoluminescence

As shown by the dotted line in Fig. 2, the emission at 404 nm originates from TPD layer when excited by 360 nm wavelength UV light. However, the emission spectra change dramatically when even a small amount of $Gd(DBM)_3bath$ is doped into the TPD layer, i.e. a red-shifted broad band with a peak near 550 nm appears in the spectrum. In Fig. 2, lines 1, 2 and 3 show the spectral change of the $Gd(DBM)_3bath$ doped TPD films with different molar ratios. At the molar ratio of TPD:$Gd(DBM)_3bath$ = 100:1, the 550-nm wavelength band begins to show strong emission, which is comparable with the TPD emission in the PL spectrum. If the content of the $Gd(DBM)_3bath$ is further increased, the relative intensity of the emission from TPD continuously decreases. At the molar ratio of 1:1, the TPD emission totally disappears in the PL spectra.

Fig. 3a shows the absorption spectra of TPD, $Gd(DBM)_3bath$, and TPD:$Gd(DBM)_3bath$ (ratio 1:1)

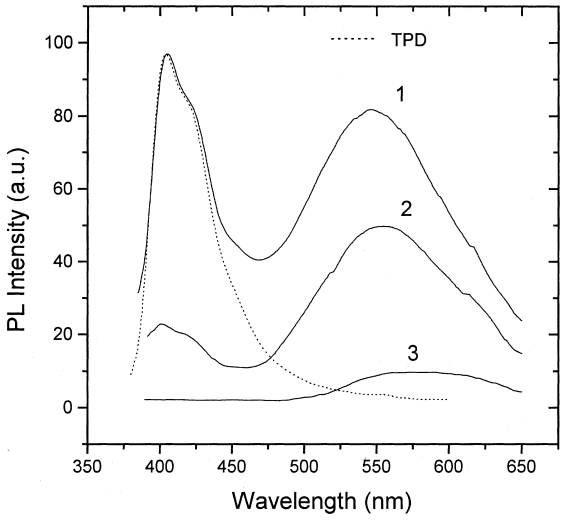

Fig. 2. Photoluminescence spectra of TPD (dotted line) and the TPD:$Gd(DBM)_3bath$ films with different molar ratios: (1) TPD:$Gd(DBM)_3bath$ = 100:1; (2) 10:1; and (3) 1:1.

films. The absorption of the doped layer is the sum of the single TPD layer absorption and the single $Gd(DBM)_3bath$ layer absorption. The excitation spectra of TPD film and $Gd(DBM)_3bath$ doped TPD film with the molar ratio of TPD:$Gd(DBM)_3bath$ = 10:1 are tested with monitoring the emissions at 404 and 550 nm, respectively. As shown in Fig. 3b, the emission from the pure TPD film is stronger than that from the doped layer, but the line shapes of the excitation spectra are very similar. This indicates that the emission of the 550-nm wavelength band comes from the excitation of TPD molecules.

The fact that there are no new absorption and excitation features in the doped film implies that the new

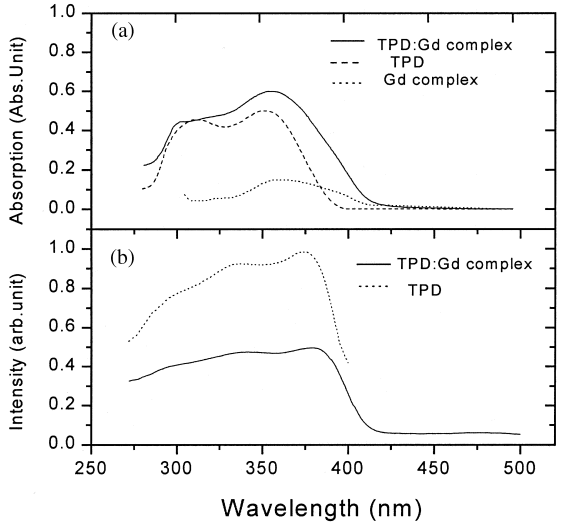

Fig. 3. (a) The absorption spectra of TPD, $Gd(DBM)_3bath$ and TPD:$Gd(DBM)_3bath$ (molar ratio 1:1) films. (b) The excitation spectra of TPD and TPD:$Gd(DBM)_3bath$ films, the excitation spectra are recorded at wavelengths of 404 and 550 nm, respectively.

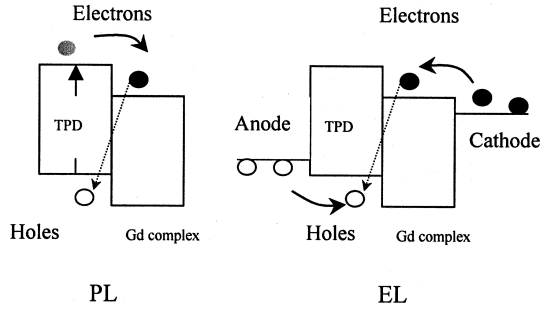

Fig. 4. Sketch showing the different exciplex formation processes in PL and in EL.

emission band originates from an excited state process. Thus, it is concluded that the new emission band is the result of exciplex formation between TPD and $Gd(DBM)_3$bath molecules. When a TPD molecule is excited, the excited electron will transfer to an adjacent $Gd(DBM)_3$bath molecule; thus bound by the Coulomb force, a transient donor–acceptor complex between the excited TPD molecule and the ground state of $Gd(DBM)_3$bath is formed and the new feature should be the exciplex emission.

The exciplex may also form at the interface between the TPD and $Gd(DBM)_3$bath layers when the bilayer film is prepared. But in our experiment, the PL spectrum of TPD (50 nm)/$Gd(DBM)_3$bath (50 nm) bilayer film only shows emission from TPD and the exciplex emissions are not visible. A possible reason may be that the exciplex only forms in a narrow zone at the interface of the organic layers, and compared with the strong emission from the whole TPD layer the exciplex emission is too small to be observed.

3.2. Electroluminescence

In the EL study, the situation is different. For the bilayer EL device ITO/TPD/$Gd(DBM)_3$bath:Mg/Ag, electrons and holes are injected from the cathode and anode, respectively, then through the carrier-transport layers, large numbers of electrons and holes gather at the interface of TPD and $Gd(DBM)_3$bath layers. At this stage, exciplexes are naturally formed by these adjacent electrons and holes. Fig. 4 is a sketch showing the different processes of exciplex formation in PL and in EL.

For the EL study, two devices are fabricated. One is a bilayer device with a structure of ITO/TPD (30 nm)/$Gd(DBM)_3$bath (50 nm) Mg/Ag (Device A). The other includes a doped layer (TPD:$Gd(DBM)_3$bath = 3:1) and has a structure of ITO/TPD (30 nm)/TPD:$Gd(DBM)_3$bath (30 nm)/$Gd(DBM)_3$bath (30 nm): Mg Ag (Device B). Fig. 5 shows the EL spectra of these devices. The EL spectrum of device B at 8 V shows exciplex emission, which is identical with the 550-nm emission band in the former PL study. At a higher voltage of 10 V, the emission from TPD also appears in the spectrum. Device A at 8 V also shows a broad emitting band but has a peak at 470 nm, which corresponds to an 80-nm blue shift from the 550-nm emission band. We believe this band is also due to the exciplex emission. Since exciplexes are transient donor–acceptor complexes and are bound by Coulomb force, the distance between the donor and the acceptor is an important factor that affects the energy state of the exciplex. The farther the distance is, the higher the energy level will be. Thus, the 80-nm blue shift is due to the different average distances between the electrons and the holes in device A and in device B. The inset to Fig. 5 shows that the average distance at the bilayer interface is larger than that in doped layer. From Fig. 5a, we notice that at higher voltage the emission due to TPD appears and dominates the spectrum. This indicates that the recombination area changes at different drive voltages.

4. Conclusions

The non-fluorescent gadolinium complex Gd-$(DBM)_3$bath has electron-transport property and it has the tendency to accept electrons. Thus, exciplex formation between the complex and the hole-transport material TPD is observed in the PL and in EL processes. The exciplex emissions show different features in bilayer and doped films due to different donor–acceptor distances.

From absorption and excitation spectra, we know that exciplex emission has no counterpoint at ground

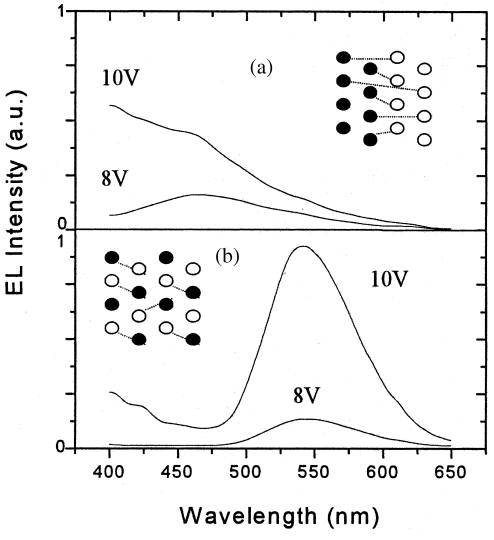

Fig. 5. (a) EL spectra of the bilayer device. (b) EL spectra of the device including a TPD/$Gd(DBM)_3$bath layer. The inset shows the different average donor–acceptor distances at the bilayer interface and in the doped layer.

state and this characteristic could be an advantage for laser study in the films.

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