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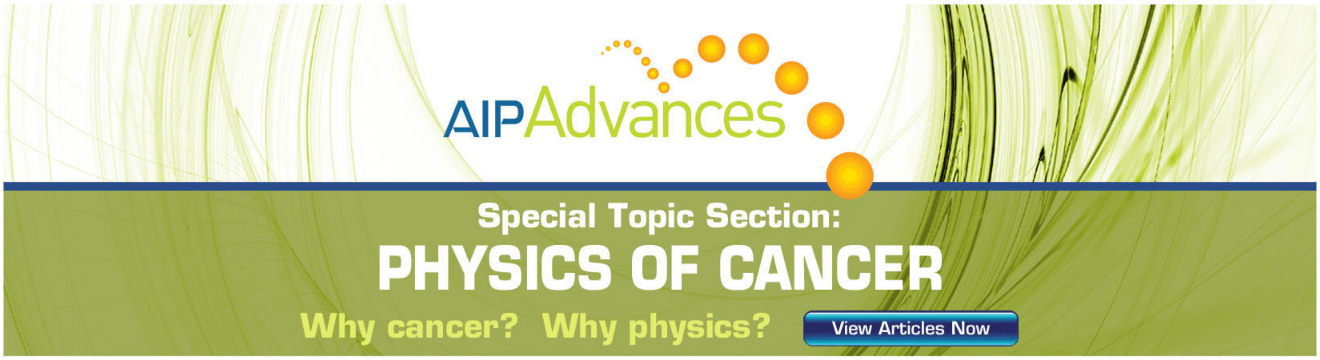

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Effect of exciplex formation on organic light emitting diodes based on rare-earth complex

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An exciplex can be formed due to the charge transfer between the lowest unoccupied molecular orbital (LUMO) of the acceptor and the highest occupied molecular orbital (HOMO) of the donor. By introducing a mixing layer composed of [N,N'-diphenyl-N,N'bis (3-methylphenyl)-1,1′-diphenyl-4,4′-diamine] (TPD) and europium(dibenzoylmethanato)$_3$(bathophenanthroline) [Eu(DBM)$_3$bath] and a graded interface, elimination of light emission from the exciplex and significant luminescence enhancement of trivalent europium ions (Eu^{3+}) in organic light emitting devices have been achieved. The elimination mechanism of exciplex emission based on the concept that an exciplex can be formed between LUMO of the acceptor (Eu complex) and HOMO of donor (TPD) was investigated. To comprehensively understand the mechanism, devices consisting of a Eu(DBM)$_3$bath as the emitting material and the devices using other rare-earth (RE) complex [RE(DBM)$_3$bath] as the emitting material were fabricated with the same device configuration. As a reference, four spin-coated films with the blend composed of TPD and the gadolinium complex [Gd(DBM)$_3$bath] were also fabricated. The electroluminescence (EL) spectra from the devices and photoluminescence spectra from the spin-coating films were fully investigated. The results show that the exciplex was formed by the charge transfer from the donor TPD to the acceptor RE complex, the exciplex state that acted as a transient excited state can be controlled by altering the molecular ratio in the mixing films. The relation of the exciplex formation based on EL devices with the RE complex versus the variety of the RE ions is also discussed by manipulating the energy level of the excited state. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2214223]

INTRODUCTION

Pure red light emission is still a challenge in organic light emitting devices (OLEDs), although many organic compounds with red emission have been investigated.[1–4] Among these materials, trivalent europium (Eu^{3+}) complexes are more interesting. Earlier photoluminescence (PL) studies on rare-earth (RE) complexes showed that light emission by RE^{3+} ions originates from the excitation of ligands.[5,6] Under ultraviolet (UV) excitation, the excited singlet states of the ligand are formed at first, and then relaxation from the lowest excited singlet state (S_1) to triplet states occurs through the intersystem crossing, and finally the central ion is excited by the intramolecular energy transfer from the lowest excited triplet state (T_1) of the ligand. In electroluminescence (EL) with RE^{3+} (abbreviated as "RE-EL" in the following text), both singlet and triplet excitons were formed by electron-hole recombination and their energy should be transferred to RE^{3+} ions; therefore, the EL characteristics embody the light emission from RE^{3+} ions. Theoretically, RE-EL efficiency is not necessarily limited to 25%.[7,8] On the other hand, the sharp emissions of Eu^{3+} ions are very suitable for red primary component of full-color display. However, when studying narrow EL emission band of RE complex in which β-dichetone and phenanthroline and its derivation are, respectively, used as the first and the second ligands in a device structure of ITO/TPD/RE complex/metal, besides sharp EL emission of RE^{3+} ion, a wide band emission that peaked at yellow-green region frequently appeared, presumably due to the exciplex formation.[9,10] When Eu or Tb was used as RE, their complexes were typically europium (dibenzoylmethanato)$_3$(bathophenanthroline) [Eu(DBM)$_3$bath] and terbium (acetylacetonate)$_3$ (monophenanthroline) [Tb(ACAC)$_3$phen], respectively. In this case a wide band emission that appeared besides narrow emissions peaked at red region or green region (for Eu device or for Tb device), thus their color purity could obviously be altered. The wide band emission is due to the exciplex from the interface of the above-mentioned heterostructure devices. A few investigations on emission from exciplex have been carried out in organic EL devices.[11–13] Itano *et al.* have demonstrated that the exciplex was formed at the interface between Alq$_3$ and some hole-transport materials with

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low ionization potentials (IPs) in the EL devices.[11] Our group has used a mixing layer of Eu(DBM)$_3$bath and TPD to successfully fabricate bright and stable red Eu^{3+} devices by eliminating the disturbing emission from the exciplex itself.[9] We also observed that the EL efficiency depends on the molecular ratio in the mixed Eu^{3+} device and there apparently exists an optimal molecular ratio for obtaining a high EL color purity and efficiency.[14]

In this article, the formation of exciplex has been studied by considering the notion that an exciplex was formed through the charge transfer from the donor to the acceptor due to interaction of the donor with acceptor.[15,16] Because pure red EL devices were more difficult to obtain by using common red fluorescent dye due to low color purity of the dyes. Thus as an example, Eu^{3+} devices based on [Eu(DBM)$_3$bath] are especially interesting for studying formation and elimination mechanism of the exciplex.

In order to comprehend the formation of exciplex the PL and EL spectra of Eu devices were compared with those of the device (Gd^{3+} device) having gadolinium complex, [Gd(DBM)$_3$bath], because the ionic radii of Eu^{3+} ion (1.06 Å) and Gd^{3+} ion (1.05 Å) are very similar, and the properties of the two RE complexes with the same ligand should be considered electronically similar. Furthermore, the role of the mixing layer was investigated by examining the PL spectra of the spin-coated films with the mixing layer composed of different molar ratios of TPD to Gd(DBM)$_3$bath. Finally, the energy transfer processes are scrutinized, which can be used to interpret the aforementioned fact that there exists an optimal ratio of TPD to Eu^{3+} complex (a weight ratio being 1:2 by experiment) for obtaining the highest EL efficiency.

EXPERIMENTS

Basic devices A, B, and C with a mixture of TPD:RE(DBM)$_3$bath were fabricated. They consisted of ITO/TPD(30 nm)/TPD:RE(DBM)$_3$bath(30 nm)/RE(DBM)$_3$bath(60 nm)/Mg$_1$:Ag$_{0.1}$. Here indium tin oxide (ITO) was used as an anode. TPD was used as a hole-transport (HT) material. Eu(DBM)$_3$bath was used as an electron transport and emitting material (ET-EM) in devices A and B. As a comparison, Gd(DBM)$_3$bath was used to replace Eu(DBM)$_3$bath in device C. The weight ratios of TPD to RE(DBM)$_3$bath in the mixed layer were 1:1 in device A, 50:1 in device B, and 50:1 in device C, respectively. Eu(DBM)$_3$bath and Gd(DBM)$_3$bath were synthesized without further purification according to the conventional method used in our group, respectively.[15] Figure 1(a) shows the molecular structures of TPD, Eu(DBM)$_3$bath, and Gd(DBM)$_3$bath, while the device configuration is depicted in Fig. 1(b). The organic films in devices A, B, and C were fabricated by successively depositing the organic materials onto clean ITO substrates at 3.0×10^{-4} Pa in vacuum. The cathode of magnesium and silver (Mg$_1$Ag$_{0.1}$) was deposited onto the top organic layer by simultaneously evaporating the two metals from the two separate sources. The film thickness was monitored with an oscillating quartz crystal. The deposition area was about 10 mm^2. To study the properties of the exciplex and the role of the mixture, four TPD and Gd(DBM)$_3$bath mixed films by spin coating were prepared onto quartz substrates from chloroform solution. PL and EL spectra were acquired with a Hitachi-4000 fluorescence spectrometer in ambient temperature.

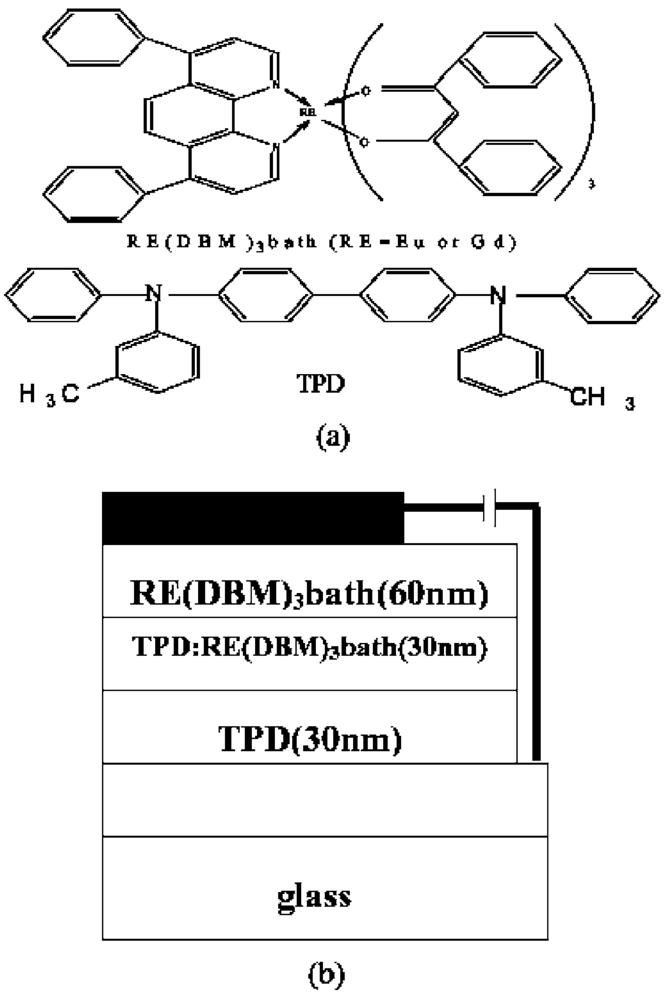

FIG. 1. (a) Molecular structure of the materials used. (b) The configuration of EL devices with a device structure of ITO/TPD (30 nm)/TPD: RE(DBM)$_3$bath (30 nm)/RE(DBM)$_3$bath (60 nm)/Mg1Ag0.1. Device A: RE=Eu and the weight ratio of TPD:Eu(DBM)$_3$bath was 1:1. Device B: RE=Eu and the weight ratio of TPD:Eu(DBM)$_3$bath was 50:1. Device C: RE=Gd and the weight ratio of TPD:Gd(DBM)$_3$bath was 50:1.

RESULTS AND DISCUSSION

EL spectra of devices A, B, and C at a bias of 10 V as well as PL spectrum of TPD film are shown in Fig. 2. In the EL spectra, the band at about 404 nm is due to the emission from TPD, while the red emission at 612 nm is from Eu^{3+} ions. It is well known that the emission from the ligand of Eu(DBM)$_3$bath cannot be so strong at room temperature, so the emission at 450–525 nm is probably from the interfacial exciplex. However, it is generally believed that an exciplex is formed at the interface between HT and ET layers, that is, charge transfer from donor molecule (TPD) to the acceptor molecule [Eu(DBM)$_3$bath] would carry out. In other words, these bands must probably result from the interaction between the excited state of the donor and the ground state of the acceptor,[16,17] the detailed generation mechanism will be

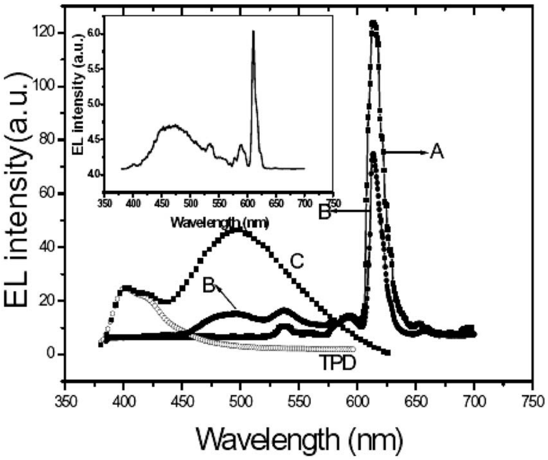

FIG. 2. The EL spectra from devices A, B, and C (labeled by A, B, and C, respectively), and the PL spectrum of TPD (dotted curve). The inset shows the EL spectrum from a device with the exciplex emission peaked at about 471 nm (shorter than 487.8 nm).

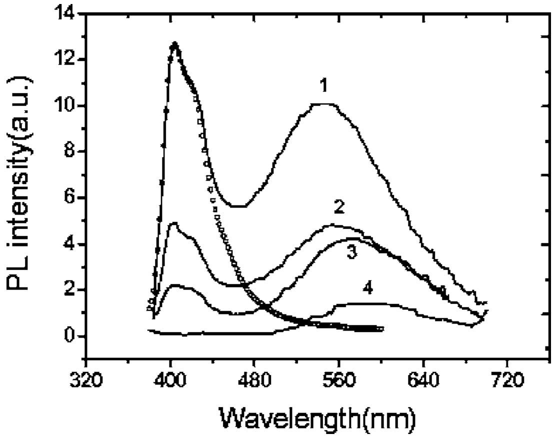

FIG. 3. PL spectra of TPD (dotted curve) and the spin-coated films composed of TPD:Gd$(DBM)_3$bath with different molar ratios of TPD to Gd$(DBM)_3$bath: (1) 100:2, (2) 100:5, (3) 100:10, and (4) 100:100, respectively.

discussed later. The spectral characteristics of device B [exhibited by curve B in Fig. 2, where RE is Eu and the weight ratio of TPD to Eu$(DBM)_3$bath is 50:1] manifest that the exciplex is indeed generated in the mixing layer. According to the aforementioned concept, the exciplex is assumed to be created through the charge transfer between the excited states of TPD molecule (donor) and the ground state of RE-complex molecule (acceptor) in device B. Actively, it should be the ground state of the ligand for the RE complex because $4f$ orbit of RE^{3+} ion is effectively shielded from the influence of the external forces by the overlapping of $5s^2$ and $5p^6$ orbits, so the resonance level of RE^{3+} ion does not contribute to the formation of the exciplex, although the central RE^{3+} ion may affect the emission intensity of the exciplex. Thus its formation should be only related to the ligand properties of the RE complex. To prove this hypothesis, device C with Gd$(DBM)_3$bath to replace Eu$(DBM)_3$bath was constructed because the Gd$(DBM)_3$bath has no fluorescence besides their similar properties of Eu^{3+} with Gd^{3+}, which is convenient to selectively observe the emission from the exciplex. The emission spectrum of device C is plotted with curve C in Fig. 2. Apart from the emission spectrum peak at 404 nm of TPD, there is a band emission peaked at about 498 nm in the spectra, which should be resulted from the exciplex emission. This clearly proves the previous hypothesis that the RE^{3+} ion does not contribute to the exciplex formation, and consequently the formation is primarily associated with the ligand in RE complex acting as acceptor.

In order to further investigate the properties of the exciplex and the role of the mixing layer, four spin-coated mixing films composed of TPD and Gd$(DBM)_3$bath were fabricated. Their PL spectra are shown in Fig. 3, where the dotted line with a peak at 404 nm is due to the PL spectrum of TPD excited by UV light at 360 nm. It is also found that with increasing the content of the Gd complex, the 404 nm emission is gradually decreased, but new emission band at longer wavelength from 540 to 554 nm, to 566 nm, and to 583 nm gradually appeared. However, except the new emission peak with shift in the different contents of the Gd complex, no new peak is again observed, indicating that anyone of these new emission bands is not due to a new species, which is just the characteristic of exciplex emission. In order to further investigate the properties of the exciplex and the role of the mixing layer, four spin-coated mixing films composed of TPD and Gd$(DBM)_3$bath were fabricated. Their PL spectra are shown in Fig. 3, where the dotted line with a peak at 404 nm is due to the PL spectrum of TPD excited by an UV light at 360 nm. It is also found that with increasing the content of the Gd complex, the 404 nm emission is gradually decreased, but new emission band at longer wavelength from 540 to 554 nm, to 566 nm, and to 583 nm gradually appeared. However, except the new emission peak with shift in the different contents of the Gd complex, no new peak is again observed, indicating that anyone of these new emission bands is not due to a new species, which is just the characteristic of exciplex emission. In other words, as the content of Gd complex gradually becomes greater the energy of exciplex state gradually becomes lower. Just as discussed above that because there are similar ionic radii for Eu^{3+} ion (1.06 Å) and Gd^{3+} ion (1.05 Å), the two RE complexes should show electronically similar behavior. So for Eu-complex devices the energy of exciplex E^* would gradually become lower as the Eu-complex content increases in the TPD/Eu-complex mixture. Therefore the molar ratio of TPD to Gd complex was also deemed as that of TPD to Eu complex in the mixture, different molar ratios should confirm the position of different energy levels of the exciplexes. This indicates that E^* level of the exciplex can be controlled by modifying the molar ratio of the two molecules. So it can be speculated that the energy of exciplex emission is not from the T_1 level, but from the lowest excited singlet state (S_1) of the ligand, although T_1 exciton of the Eu complex can also result from carrier recombination. This can also be understood by experiment. If the energy is from the T_1 level, the wavelength corresponding to the peak of the exciplex emission from the devices composed of the mixture of TPD and Eu$(DBM)_3$bath could not be shorter than 487.8 nm, because the T_1 level is at around 20 500 cm^{-1}. However, the exciplex emission with a wavelength shorter than 487.8 nm has been

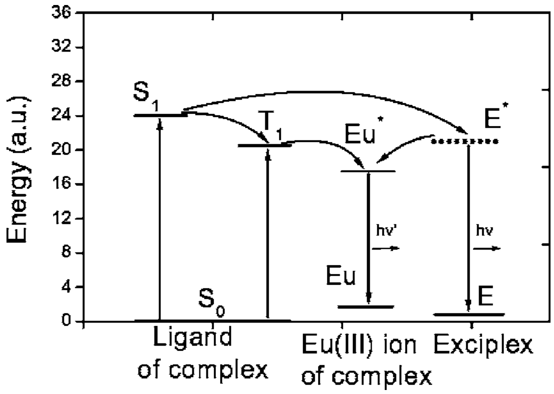

FIG. 4. The excitation and energy transfer processes in EL devices: the short dotted line (E^*) corresponds to the transient level of the exciplex (the peak of the broadband in Fig. 2) and E is the ground state of the exciplex.

experimentally observed, as highlighted by the inset in Fig. 2, where the weight ratio of TPD to Eu(DBM)$_3$bath in the mixture was 100:1. Therefore, it can be concluded that the exciplex in the mixture of TPD and RE complex results from the interaction between the two molecules. Actually, for Eu-complex devices, there are two excited states at the interface between the two molecules, one is the exciplex originated from the interaction between TPD and Eu complex, and the other is the excited Eu-complex itself because Eu^{3+} emission and band emission from exciplex were all observed,[11,12] just as shown by the inset in Fig. 4. In other words, there would be two possible EL pathways: $S_1 \to E^* \xrightarrow{h\nu} E^*$ and $S_1 \to T_1 \to \mathrm{Eu}^* \xrightarrow{h\nu'} \mathrm{Eu}$, where E^* and E, and Eu* and Eu represent the transient excited state and ground state of the exciplex, and the excited state and ground state of Eu^{3+} ion, respectively. Note that the process of $S_1 \to E^* \xrightarrow{h\nu} E$ occurs via the intermolecular energy transfer, whereas the process of $S_1 \to T_1 \to \mathrm{Eu}^* \xrightarrow{h\nu'} \mathrm{Eu}$ takes place via the intramolecular energy transfer. The energy sources of two EL pathways are both from S_1 of the ligand, and consequently an energy competition process appears between the emissions by Eu^{3+} ion and by the exciplex. The content of RE complex is the same in the mixtures of devices C and B, but the central Gd^{3+} ion of RE complex in device C cannot emit. So the light emission intensity by the exciplex is stronger from device C than that from device B. Since the content of Eu complex in the mixture of device A is much more than that in device B, the E^* level greatly decreases and the efficiency of energy transfer from S_1 to E^* becomes low, and the emission intensity of Eu^{3+} ion from device A becomes much stronger than that from device B. According to our previous results compared with double-layer device without mixing layer of TPD/RE(DBM)$_3$bath, the efficiency of the mixing layer device with 1:3 of ratio of TPD/RE(DBM)$_3$bath was increased for 5.5 times at a brightness of 100 cd/m^2, as shown in Table I in Ref. 9. From curve A, the emission of the exciplex completely disappeared. However, when only the central ion, Eu^{3+} ion, is replaced by Er^{3+} ion or Yb^{3+} ion in device A without changing any other conditions, where Er and Yb are erbium and ytterbium, respectively, the emission from the exciplex at about 580 nm reappears.[18,19] As it is known, the resonant levels of Er^{3+} ion and $^4I_{11/2}$, $^4I_{13/2}$, and $^2F_{5/2}$, respectively, are much lower than the $^5D_0$ of Eu^{3+} ion.[20] This implies that Eu^{3+} ion can completely quench the emission from the exciplex. On the contrary, Er^{3+} and Yb^{3+} ions can just partially quench the emission. In other words, only a part of energy E^* is transferred to the excited levels of the central ion. Therefore, the elimination of an exciplex is due to two reasons. First, if the E^* level of the exciplex is decreased by controlling the molecular ratio in the mixture, the efficiency of energy transfer from S_1 to E^* will become small. Second, the excited state levels of the central ion can quench the emission of the exciplex.

In view of the aforementioned discussion on EL spectra of devices A, B, and C, the total energy transfer process is schematically depicted in Fig. 4 in more detail. This can be understood as follows.

It is well known that the singlet exciton (S_1) and triplet exciton (T_1) can simultaneously be formed by carrier recombination under electrical excitation, and energy at S_1 state can transfer to T_1 by the intersystem crossing and then transfer to the central Eu^{3+} ion, and the other part of energy in S_1 state is transferred to the exciplex state. Hence both the exciplex and Eu^{3+} ion are brought about by EL emission. From the previous discussion, it is discerned that if the content of Eu(DBM)$_3$bath in the mixture decreases, the E^* energy will become higher. Then the energy match between S_1 and E^* will become larger. Therefore, the efficiency of $S_1 \to T_1 \to \mathrm{Eu}^*$, the energy transfer from S_1 to E^*, will become larger, whereas the efficiency of $S_1 \to T_1 \to \mathrm{Eu}^*$ will become smaller. In this case, the emission from the exciplex is dominant, as embodied by the EL spectrum of device B. If the E^* state is too close to the S_1 state, the emission intensity from the exciplex is larger than that from Eu^{3+} ion under the increasing bias on the device. Hence, the emitting color will alter under the different biases. Conversely, if E^* state is far away from S_1, the efficiency of $S_1 \to E^*$ will become smaller and the efficiency of $S_1 \to T_1 \to \mathrm{Eu}^*$ will become larger. As a result, the emission from Eu^{3+} ion will become dominant and the emission from the exciplex will become weak. In addition, the excited state levels of Eu^{3+} ion quench the emission from the exciplex. In this case, the device always emits a pure red light under the different biases, as demonstrated by the EL spectrum of device A. If the E^* state is too close to Eu* level, the efficiency of $S_1 \to E^*$ will become too small to detect. Although the efficiency of $E^* \to \mathrm{Eu}^*$ becomes high, it will not enhance the Eu^{3+} ion emission. Furthermore, the E^* state is so close to Eu* level that the energy mismatch between E^* level and Eu* level is too small to prevent a thermal deactivation process.[21] Eventually the emission from Eu^{3+} ion will become weak, though the emission color of the device is solely red. Hence, there is an optimal energy state of E^* (the exciplex state), which is dependent on the molecular ratio in the mixture. It is manifested by the fact that the EL efficiency of the devices largely depends on the molecular ratio in the mixture and there is an optimal ratio [the weight ratio being 1:2 for TPD:Eu(DBM)$_3$bath] for obtaining a high EL efficiency, as will be discussed below.

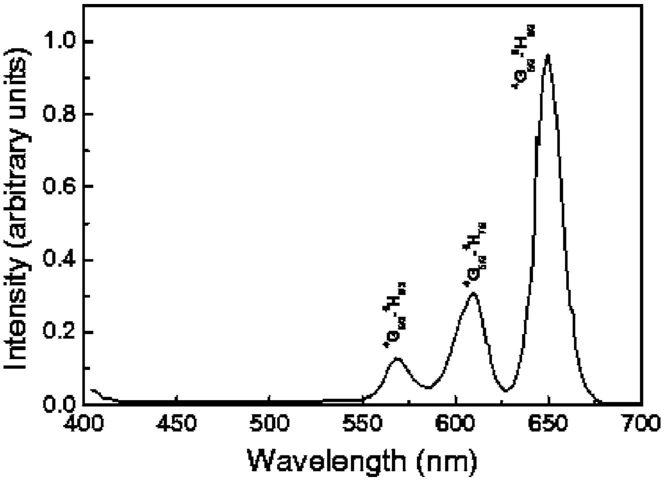

FIG. 5. Visible EL spectrum of Sm device with a structure of ITO/TPD(30 nm)/TPD:Sm(DBM)$_3$bath(30 nm)/Sm(DBM)$_3$bath(30 nm)/Mg:Ag biased at 5 V.

To further verify our model discussed previously, the emission spectra from EL devices with Sm(DBM)$_3$bath (Sm device) have been studied with a device structure similar to that used before, i.e., ITO/TPD/TPD:Sm(DBM)$_3$bath/Sm(DBM)$_3$bath/Mg$_1$:Ag$_{0.1}$, where Sm is samarium, and the weight ratio of TPD to Sm(DBM)$_3$bath is 1:1. It is found that when Sm(DBM)$_3$bath is used as the EM-ET layer, the emission from the exciplex cannot be clearly found in the heterostructure device, while in the mixture device, apart from the absence of the emission from the exciplex, the light emission from Sm^{3+} ion is weaker than that from the heterostructure device, as shown in Fig. 5.[22] Not only in the EL of mixtured Sm device but in the PL spectrum of mixing TPD/Sm-complex film exciplex emission was not determined, which will be discussed in detail elsewhere. When Tb(DBM)$_3$bath (Tb=terbium) is used as the EM-ET layer, the emissions from the exciplex and Tb^{3+} ions are both very weak due to their no matching of Tb^{3+} level and T_1 level of DBM.[6] All the phenomena can be explained by the previously deliberated understanding. In the case of the device composed of Sm(DBM)$_3$bath, the energy level of Sm^{3+} ion ($^4G_{5/2}$ level, about 17 924 cm^{-1}) is slightly higher than the $^5D_0$ level (about 17 500 cm^{-1}) of Eu^{3+} ion, i.e., the mismatch between the $^4G_{5/2}$ level and the T_1 level of the ligand is smaller than that between the $^5D_0$ level and the T_1. Therefore, the efficiency of energy transfer to the central ion Sm^{3+} is higher than that in the case of Eu^{3+} ion. Hence the emission intensity from the exciplex in the device having the mixture composed of Sm complex is too weak to observe, while the emission from the exciplex in the device having the mixture composed of Eu complex is so strong that it affects the emission color of the device. In the mixture device, the E^* level, which becomes small by increasing the content of Sm complex, is so close to the $^4G_{5/2}$ level in comparison with the $^5D_0$ level that it influences the emission from Sm^{3+} ion. Therefore the emission from Sm^{3+} ion in the mixture device becomes weak by comparing with that from the heterostructure device. In the extreme case of Tb(DBM)$_3$bath, the $^5D_4$ level (about 20 400 cm^{-1}) of Tb^{3+} ion is almost as high as the T_1 level (about 20 500 cm^{-1}) of the ligand. Consequently, the energy in T_1 level is nonradioactively consumed by the electron relaxation between T_1 and the $^5D_4$. As a result, the emissions from Tb^{3+} ion and the exciplex are nearly unobservable. The cases of Er complex and Yb complex have been discussed aforetime. The comparison among Er, Yb, Sm, Tb, and Eu complexes explicates that the energy match between the excited levels of the central ion and the T_1 state of the ligand is essential in order to selectively obtain the emission from the central ion and to eliminate the exciplex emission. If the mismatch between the excited levels of the central ion and the triplet state level of the ligand is very large, e.g., in the case of Er(DBM)$_3$bath and Yb(DBM)$_3$bath, it is very likely that the emission from the exciplex is largely eliminated and the emission from the central ion is significantly enhanced by introducing the high content of RE complex in the mixture. If the mismatch is too small, e.g., in the case of Tb(DBM)$_3$bath, the strong emission from the central ion is difficult to obtain, although the emission from the exciplex may be very weak. If the match is appropriate, the emission from the exciplex will be very weak and the emission from the central ion will be very strong. In this case, the mixture device configuration with a low content of RE complex should be desirable, e.g., the case of Sm(DBM)$_3$bath. If the match is not optimal, e.g., in the case of Eu(DBM)$_3$bath, the strong emission from the central ion can also be obtained with the mixture structure having a proper molecular ratio. So it can be concluded that significant enhancement of the red emission of Eu complex would be achieved by adjusting the E^* state through the mixture structure. Also it is anticipated that other RE complexes with different central ions or different ligands would also follow the similar rules as discussed.

CONCLUSIONS

It is demonstrated that the exciplex is formed between the excited state of TPD and the ground state of the RE-complex's ligand, particularly associated with Eu(DBM)$_3$bath. By carefully examining the processes of energy transfer, the transient state of the exciplex E^* has been demonstrated, showing an important role in EL of OLED with RE complexes. The enhancement of red emission from the Eu complex has been observed by introducing a device structure composed of a mixture and by modifying the compositional ratio in the mixture. Therefore, the EL device with bright pure red emission from Eu^{3+} has been designed and achieved.

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