Dependence of charge trapping of fluorescent and phosphorescent dopants in organic light-emitting diodes on the dye species and current density*

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This paper utilizes multilayer organic light-emitting diodes with a thin layer of dye molecules to study the mechanism of charge trapping under different electric regimes. It demonstrates that the carrier trapping was independent of the current density in devices using fluorescent material as the emitting molecule while this process was exactly opposite when phosphorescent material was used. The triplet–triplet annihilation and dissociation of excitons into free charge carriers was considered to contribute to the decrease in phosphorescent emission under high electric fields. Moreover, the fluorescent dye molecule with a lower energy gap and ionized potential than the host emitter was observed to facilitate the carrier trapping mechanism, and it would produce photon emission.

Keywords: organic light-emitting diodes, excitation mechanism, charge trapping, current density
PACC: 7120F, 7280L, 7360P

1. Introduction

Doped emissive layers in organic light-emitting diodes (OLEDs) have been found to be an effective approach to achieving high luminance in addition to their colour selectivity[1,2] and superior stability[3−5] by utilising diverse organic fluorescent or phosphorescent dyes as an emitter.[6−8] It was reported that such doped structures could well confine and control the motion of the charge carrier and molecular excitons inside an emitter layer, resulting in a high electroluminescent (EL) efficiency.[9,10] In the host-guest emitting system, a small number of molecules with very high luminescent efficiency were incorporated into the host material, so energy is transferred from host to guest and then photon emission by means of Förster energy transfer or Dexter energy transfer.[11] In addition to the energy transfer mechanism, the guest molecule also can be excited by carrier trapping,[12] that is, electrons and holes recombine to form Frenkel excitons on the guest emitter directly. For excitons produced by carrier trapping, electrons and holes from the host are sequentially captured by the dye, resulting in exciton formation on the dye and then photon emission due to exciton decay.[13]

However, in one doped OLED with a host-guest system as an emissive layer, it is hard to judge which mechanism dominates exciton formation for different dye molecules. Moreover, the effect of high current density on the charge trapping for different type of dyes, especially for phosphorescent dopants, is infrequently reported.

In this work, we have utilized a kind of multilayer device with a thin layer of dye molecules to study the excitation mechanism of OLEDs under different electric regimes. By measuring the EL spectra of devices with different dye materials, we have investigated the effect of current density on exciton recombination sites for revealing the carrier trapping mechanism.

2. Experimental

The device structure of OLEDs is schematically shown in Fig. 1(a). 4,4'-bis[N-(1-napthyl)-N-phenyl-amino]-biphenyl (α-NPD) was used as a hole transport layer (HTL), with two layers of tris(8-hydroxyquinoline)aluminium (Alq_3) as a light-emitting layer (LML) and an electron transport layer (ETL). Between the Alq_3 layers, there is a thin layer of dye material. The dye materials used in the experiment were fluorescent materials, rubrene, coumarin

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6 and phosphorescent material, Pt(II) octaethylporphine (PtOEP), respectively. The molecular structure of dye materials used in this study was shown in Fig. 1(b). The thickness of α-NPD and Alq_3 were 50 nm and 60 nm, respectively. In addition, a layer of lithium fluoride (LiF) of 0.5 nm was deposited onto ETL to facilitate the electron injection before depositing 200 nm Al as the electron injection layer and cathode. To eliminate the possible energy transfer from the Alq_3 exciton which formed in the interface between HTL and ETL to the dye emitter, we have set the distance of the dye layer adjacent to the interface to be 30 nm, which is longer than the exciton diffusion length of Alq_3.[14]

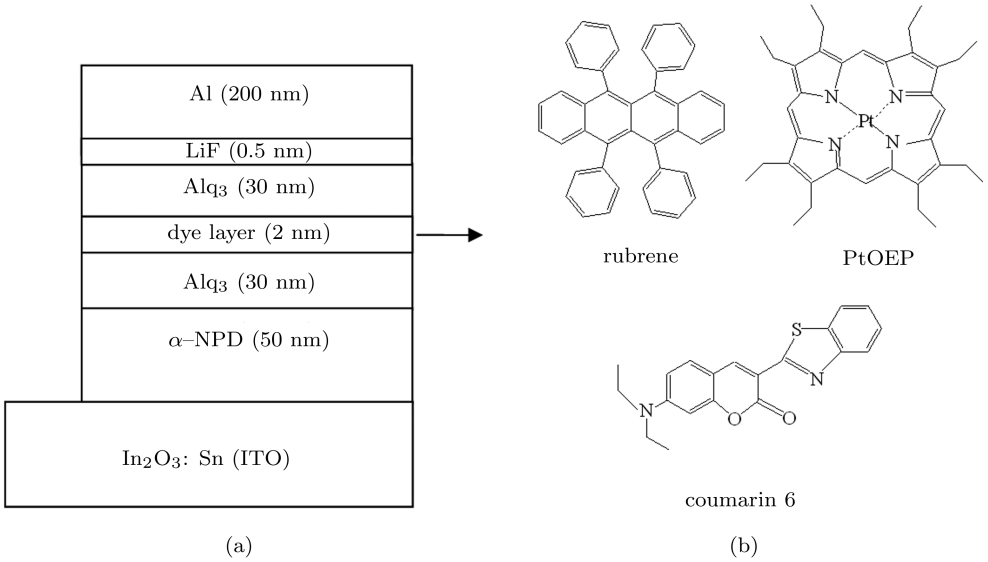


Fig. 1. Device structure (a) and molecular structure of dyes used in the study (b).

The OLEDs were fabricated by using high-vacuum (8×10^{-5} Pa) thermal deposition of organic materials onto the surface of an indium tin oxide (ITO, 15 Ω/sheet, 150 nm) coated glass substrate. The ITO-coated glass was cleaned with detergent solution, distilled water, acetone, then subjected to oxygen plasma treatment for 5 minutes immediately before use. The typical deposition rates of organic materials, LiF, Al, were 0.6, 0.1 and 5.0 Å/s (1 Å = 0.1 nm). For comparison, the device structures used are as follows:

Device A: ITO/α-NPD(50 nm)/ Alq_3 (30 nm)/ rubrene (2 nm) / Alq_3 (30 nm)/LiF(0.5 nm)/Al(200 nm);
Device B: ITO/α-NPD(50 nm)/ Alq_3 (30 nm)/ coumarin 6 (2 nm)/ Alq_3 (30 nm)/LiF(0.5 nm)/Al(200 nm);
Device C: ITO/α-NPD(50 nm)/ Alq_3 (30 nm)/ PtOEP (2 nm) / Alq_3 (30 nm)/LiF(0.5 nm)/Al(200 nm).

For comparison, we have fabricated four reference devices corresponding to each device. One was undoped and the other threes were doped devices, in which LML used a guest-host hybrid system with the following structure: ITO/α-NPD(50 nm)/dye:Alq_3 (30 nm)/ Alq_3 (30 nm)/LiF(0.5 nm)/Al(200 nm). The dopant concentration was 1% and 5% for fluorescent (rubrene and coumarin 6) and phosphorescent dye(PtOEP)-doped OLEDs, respectively.

To investigate the effect of current densities, constant wave and pulsed biases have been applied on devices for measuring the low and high current density, respectively. Pulse width and duration were set to be 1 ms and 100 ms, respectively, using an Agilent pulse generator. In addition, we have employed the spectrophotometer USB 2000 (Ocean Optics Company) to record the EL emission intensity from the pulsed OLEDs.

3. Results and discussion

3.1. Charge trapping of fluorescent dyes

Figures 2(a) and 2(b) showed the EL spectra of devices A and B, respectively. The EL spectra of devices with rubrene and coumarin 6 doped LML are also presented for reference. For device A, as shown in Fig. 2(a), all of the EL spectra curves under differ-

ent current densities from 10.6 mA/cm^2 to 26.8 A/cm^2 were almost consistent. Moreover, the two wavelength regions of EL spectra of device A with a single rubrene layer overlapped the short wavelength region of EL spectra of the undoped device and the long wavelength region of EL spectra of the device with rubrene doped Alq_3 as LML. The peak of EL spectra of device A was located between the peaks of the other two reference EL spectra. This indicated that the light emission of device A was the combination of the EL of Alq_3 and rubrene excitons, which were formed by captured charges in rubrene molecules. Moreover, the ratio of rubrene excitons with respect to Alq_3 excitons was kept unchanged with the increase in the current density.

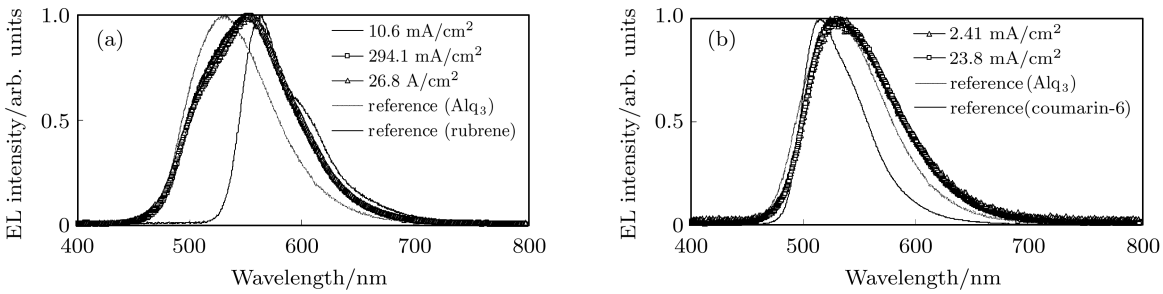


Fig. 2. The EL spectra of devices with rubrene (a) and coumarin 6 (b) under different current densities.

With regard to device B, similar results have been observed in the EL spectra with increasing current density, as shown in Fig. 2(b). However, we found that the EL spectra of device B were identical in shape and the peak (532 nm) to those of Alq_3, revealing that the light emission mainly contributed to Alq_3 excitons rather than coumarin 6. It was observed that the short and long wavelength regions of EL spectra were found to shift 6 nm and 10 nm towards the red zone, and the full width at half maximum of EL spectra for the devices with Alq_3 and coumarin 6 doped Alq_3 as the emissive layer was 86 nm and 60 nm respectively, while that for device B was 90 nm. This phenomenon might be attributed to a small amount of excitons formed on coumarin 6.

Different charge trapping mechanisms could be explained from the energy level diagram of devices A and B, as shown in Figs. 3(a) and 3(b), respectively. The values of optical energy gap (E_g) and ionisation energy (I_p) of rubrene are 2.2 eV and 5.4 eV, respectively. For coumarin 6, the values of E_g and I_p are 2.4 eV and 5.6 eV, respectively. The E_g and I_p of rubrene are less than those of the host molecule Alq_3 (E_g = 2.8 eV, I_p = 5.7 eV), as shown in Fig. 3(a), indicating that rubrene could capture electrons and holes from Alq_3 more easily, so electrons and holes recombined on the rubrene molecule directly followed by photon emission.

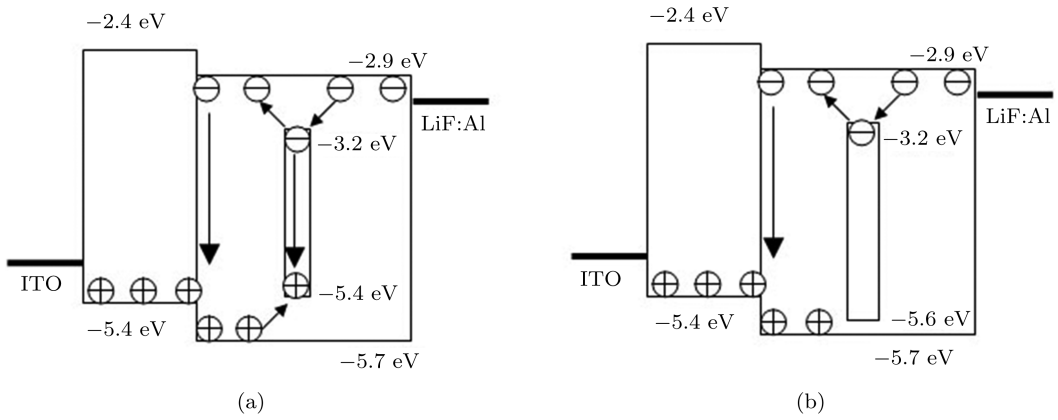


Fig. 3. Energy level diagram of device A (a) and device B (b) showing the mechanism of charge trapping in the devices.

In addition, the excited Alq_3 could not transfer energy to rubrene since the distance of the Alq_3 layer adjacent to the interface was longer than the diffusion length of the Alq_3 exciton, so the exciton of the Alq_3 molecule deactivates to the ground state ultimately with photon emission. Therefore, the emission of device A with rubrene was attributed to both the radiation decay of the singlet excitation of the rubrene molecule and the Alq_3 molecule. On the other hand, the I_p of coumarin 6 ($I_p = 5.6$ eV) is slightly lower than that of Alq_3 ($I_p = 5.7$ eV), as shown in Fig. 3(b). The Frenkel exciton of the dye emitter was at a relatively higher energy state, which made against photon emission.[2,15–17] So the component of the emission from coumarin 6 was found to be low in the EL spectra for device B, as shown in Fig. 2(b). The emission of device B with coumarin 6 was attributed mainly to the radiation decay of the singlet excitation of the Alq_3 molecule. Therefore, we could demonstrate that it was easier for rubrene molecules to capture holes than coumarin 6 due to their different I_p drop from Alq_3 to the molecules in ultra thin film.

3.2. Charge trapping of phosphorescent dyes

An efficient energy transfer from Alq_3 to PtOEP in the doped thin films has been demonstrated.[18] We investigated the charge capture in PtOEP molecules further in this study. Figure 4 shows the EL spectra of device C using PtOEP as a thin layer inserted in the ETL layer. Two peaks of 532 nm and 650 nm appeared when the current density was low, corresponding to the EL emission of the Alq_3 molecule and PtOEP molecule for those reference devices (not shown in Fig. 4). However, with increasing current density, the peak of 650 nm disappeared at 15.0 A/cm^2 and above. This phenomenon was very different from the observation in devices A and B.

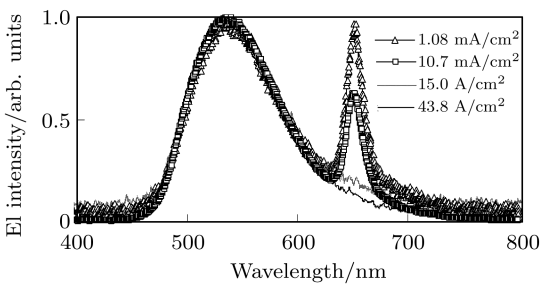


Fig. 4. The EL spectra of the device with PtOEP as a thin emissive layer under different current densities.

We also explained the charge trapping mechanism from the schematic diagram of energy levels of device C under low and high current densities, as shown in Fig. 5. Both the E_g and I_p of PtOEP ($E_g = 2.4$ eV, $I_p = 5.3$ eV)[19] were lower than those of the host molecule Alq_3 ($E_g = 2.8$ eV, $I_p = 5.7$ eV). This indicated that PtOEP could capture electrons and holes, electron–hole pairs recombined on the guest emitter directly and then photon emission. So the emission of device C with PtOEP as a thin layer was attributed not only to the radiation decay of the singlet excitation of the Alq_3 molecule but also to the triplet excitation PtOEP molecule (Fig. 5(a)). However, because the phosphorescent lifetime of PtOEP was very long ($\approx$ 80 μs), the triplet–triplet annihilation occurred at high current density.[20] Moreover, since the lowest unoccupied molecular orbital of PtOEP is very close to that of Alq_3, more electrons can easily migrate through the ultra thin layer of PtOEP and form excitons between the interface α-NPD and Alq_3. In addition, we assume that the dissociation of excitons into free charge carriers under high electric fields might, as shown in Fig. 5(b), leads to the significantly decreasing component of the emission from PtOEP in the EL spectra of device C. These mechanisms might coexist in organic phosphorescent emitters.[21]

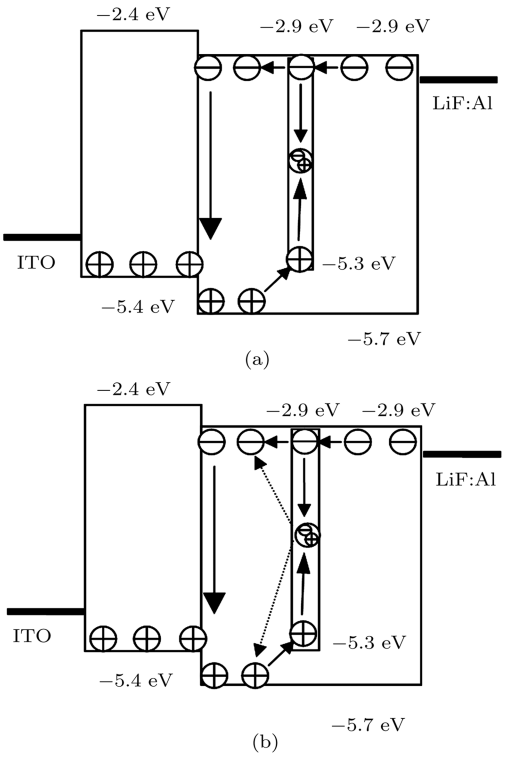


Fig. 5. Schematic diagram of charge trapping and exciton formation of PtOEP under low current density (a) and high current density (b).

3.3. Characteristics of current density and brightness via voltage

The current density (J)–voltage (V) and brightness (B)–voltage (V) characteristics of the OLEDs with the three different species of fluorescent and phosphorescent materials as thin-layer materials in ETL provide supporting evidence that the E_g and I_p affect current and recombination significantly, as shown in Fig. 6.

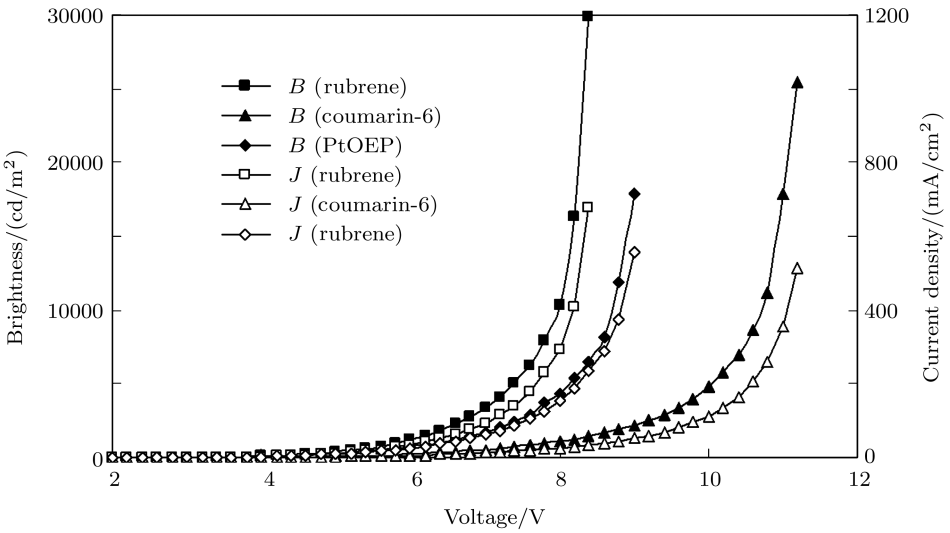


Fig. 6. Luminance– and current density–voltage characteristics of devices A, B, and C which contained rubrene, coumarin 6 and PtOEP thin film in ETL, respectively.

The turn-on voltage at which the luminance was detected was 3.0, 3.2 and 3.0 V for rubrene, coumarin 6 and PtOEP as the thin layer was inserted in ETL, respectively. However, the increase in voltage caused different evolution of the current and luminance by employing different species of fluorescent and phosphorescent thin layer. The current densities were 294.1, 26.2 and 153.6 mA/cm^2, and the corresponding luminance values were 10347.9, 1061.7 and 4297.0 cd/m^2 at 8.0 V for devices A, B and C, respectively. This is because the carrier balance changed as a result of carrier trapping in dye molecules. The higher luminance of device A probably contributed to the excellent carrier capture quality of rubrene.

4. Conclusion

In conclusion, we have demonstrated that the carrier trapping is independent of the current density in devices using fluorescent material as the emitting molecule while this process was exactly the opposite when phosphorescent material was used. The device with rubrene as a thin layer in ETL was found to achieve higher luminance at low voltage. Phosphorescent emission of PtOEP was found to decrease greatly at high current density due to the very close lowest unoccupied molecular orbital level of the PtOEP molecule to the Alq_3 molecule, leading to electron detrapping from PtOEP. The dissociation of excitons and/or triplet–triplet annihilation was attributed to the decrease in phosphorescent emission at high current density too. Furthermore, the florescent dye whose E_g and I_p of the guest emitter was much lower than that of the host emitter, which was observed to facilitate the carrier trapping mechanism, and it would make against photon emission when the Frenkel exciton of the guest emitter was at a relatively higher energy state.

References

[1] Tang C W, Vanslyke S A and Chen C H 1989 *J. Appl. Phys.* **65** 3610

[2] Uchida M, Adachi C, Koyama T and Taniguchi Y 1999 *J. Appl. Phys.* **86** 1680

[3] Sakamoto G, Adachi C, Koyama T, Taniguchi Y, Merritt C D, Murata H and Kafai Z H 1999 *Appl. Phys. Lett.* **75** 766

[4] Sano T, Fujii H, Nishio Y, Hamada Y, Takahashi H and Shibata K 1997 *Synth. Met.* **91** 27

[5] Nie H, Zhang B and Tang X Z 2007 *Chin. Phys.* **16** 730

[6] Burrows P E, Bulovic V, Forrest S R, Sapochak L S, Mccarty D M and Thompson M E 1994 *Appl. Phys. Lett.* **65** 2922

[7] Adachi C, Tsutsui T and Saito S 1990 *Appl. Phys. Lett.* **57** 531

[8] Zhang L J, Hua Y L, Wu X M, Wang Y and Yin S G 2008 *Chin. Phys.* B **17** 3097

[9] Wakimoto T, Yonemoto Y, Funaki J, Tsuchida M, Murayama R, Nakada H, Matsumoto H, Yamamura S and Nomura M 1997 *Synth. Met.* **91** 15

[10] Baldo M A, O'Brien D F, Thompson M E and Forrest S R 1999 *Phys. Rev.* B **60** 14422

[11] Berggren M, Dodabalapur A, Slusher R E and Bao Z 1997 *Nature* **389** 466

[12] Pschenitzka F and Sturm J C 2001 *Appl. Phys. Lett.* **79** 4354

[13] Littman J and Martic P 1992 *J. Appl. Phys.* **72** 3610

[14] Garbuzov D Z, Forrest S R, Tsekoun A G, Burrows P E, Bulović V and Thompson M E 1996 *J. Appl. Phys.* **80** 4644

[15] Suzuki H and Hoshino A 1996 *J. Appl. Phys.* **79** 8816

[16] Lamansky S, Kwong R C, Nugent M, Djurovich P I and Thompson M E 2001 *Org. Electron.* **2** 53

[17] Lamansky S, Djurovich P I, Abdel-Razzaq F, Garon S, Murphy D and Thompson M E 2002 *J. Appl. Phys.* **92** 1570

[18] Wu C H, Liu P Y, Hou L T and Li Y W 2008 *Acta Phys. Sin.* **57** 7317 (in Chinese)

[19] Adachi C, Kwong R C, Djurovich P, Adamovich V, Baldo M C A, Thompson M E and Forrest S R 2001 *Appl. Phys. Lett.* **79** 2082

[20] Baldo M A, Thompson M E and Forrest S R 2000 *Nature* **403** 750

[21] Kalinowski J, Stampor W, Szmytkowski J, Virgili D, Cocchi M, Fattori V and Sabatini C 2006 *Phys. Rev.* B **74** 085316