

## Study on Formation Cross-section of Singlet and Triplet Exciton in Organic Phosphorescent and Fluorescent Material

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In this study, the photoluminescence and electroluminescence device based on PVK [poly-(N-vinylcarbazole)] co-doped by Ir(ppy)<sub>3</sub> [*tris*(2-phenylpyridine)-iridium(III)] and DCJTb (4-(dicyanomethylene)-2-*t*-butyl-6-(1,1,7,7-tetramethyl-julolidyl-9-enyl)-4*H*-pyran) have been fabricated. According to the luminescence process and the changing spectrum of photoluminescence (PL) and electroluminescence (EL), the formation cross-section of singlet and triplet exciton were investigated and the value of the formation cross-section of triplet exciton in Ir(ppy)<sub>3</sub> to that of singlet exciton in DCJTb is 9.

**Key Words:** Formation cross-section, Singlet exciton, Triplet exciton.

### INTRODUCTION

It is generally believed that the electroluminescence efficiency is limited to 25 % of that of photoluminescence based on the statistics of spin multiplicity. It is to say, for recombination of a pair of electron and hole (both spin 1/2), there are four microstates in total, with three triplet states and one singlet state<sup>1-9</sup>. The electroluminescence process of phosphorescent material can utilize both singlet and triplet exciton which can enhance the luminescence efficiency<sup>10,11</sup> and the improved efficiency is relative to larger formation cross-section of triplet exciton.

In order to investigate the formation cross-section of singlet exciton and triplet exciton, the Ir(ppy)<sub>3</sub> and DCJTb co-doped photoluminescence and electroluminescence device with PVK have been studied.

### EXPERIMENTAL

The device ITO/PEDOT:PSS/PVK:Ir(ppy)<sub>3</sub>:DCJTb/BCP (10 nm)/Alq<sub>3</sub> (20 nm)/Al has been fabricated. The ITO glass substrates (the sheet resistance is 50 Ω<sup>-1</sup>) were cleaned with ultrasonic bath in acetone, ethanol and de-ionized water. The PEDOT:PSS [poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)] and PVK: Ir(ppy)<sub>3</sub>: DCJTb were fabricated by spin-coating method with the rotation rate 2000 RPM (rotation/min). The PVK, Ir(ppy)<sub>3</sub> and DCJTb were dissolved in chloroform with the concentration 10, 0.1 and 0.5 mg/mL, respectively. The ratio of PVK to Ir(ppy)<sub>3</sub> and DCJTb was 1:0.2 %:0.1 % in weight. The BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline), Alq<sub>3</sub> (*tris*(8-hydroxy-quinolinato)aluminium) and Al were deposited in a vacuum chamber (the pressure was 10<sup>-6</sup> Torr) by thermal

evaporation method. The typical deposition rate was about 0.03 nm/s. The thickness of layer is controlled by a quartz crystal monitor. The electroluminescence was measured using the fluolog-3 fluorescent spectrometer made by SPEX. The photoluminescence was operated on the quartz substrate. The measurement was carried out at room temperature in ambient atmosphere.

## RESULTS AND DISCUSSION

Fig. 1 is the photoluminescence of PVK:Ir(ppy)<sub>3</sub>:DCJTb and the excitation wavelength is 340 nm. The emission peaks locate at 415, 510 and 565 nm which are from PVK, Ir(ppy)<sub>3</sub> and DCJTb, respectively. The lower doping concentration can make the energy transfer from PVK to Ir(ppy)<sub>3</sub> and DCJTb is not complete, so the PVK emission peak is observed in the Fig. 1. Besides the energy transfer between Ir(ppy)<sub>3</sub> and DCJTb can be neglected.

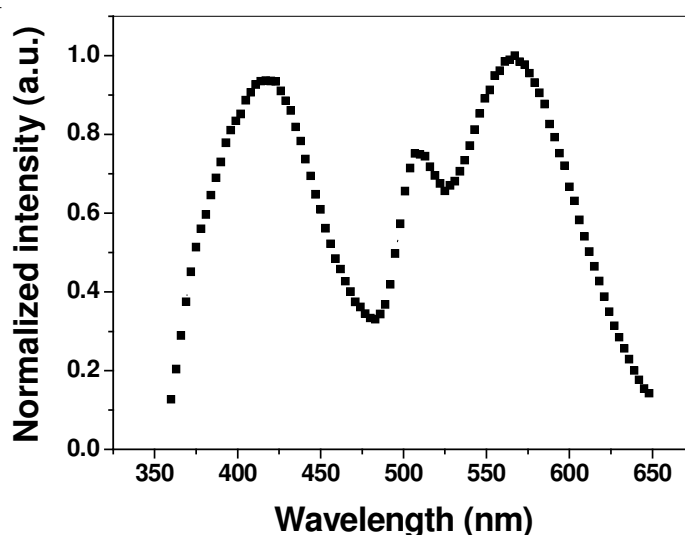


Fig. 1. Photoluminescence spectrum of the device PVK:Ir(ppy)<sub>3</sub>:DCJTb

In photoluminescence, a number  $I$  of excitons are originally all created in the singlet  $S_1$  state and from there they decay radiatively (with a decay rate  $k_{R(S_1)}$ ) or non-radiatively (with a decay rate  $k_{NR(S_1)}$ ) to the singlet ground state  $S_0$  or undergo energy transfer to the triplet (with a rate  $k_{ET(T)}$ ) and to the singlet (with a rate  $k_{ET(S_2)}$ ). Both radiative and non-radiative decay occurs from the triplet state  $T$  and the singlet state  $S_2$  to the ground state  $S_0$ . The process of photoluminescence can be modeled in Fig. 2.

Fig. 3 is the electroluminescence spectrum of device ITO/PEDOT:PSS/PVK:Ir(ppy)<sub>3</sub>:DCJTb/BCP (10 nm)/Alq<sub>3</sub> (20 nm)/Al under 12 V and it has the same luminescence peak with photoluminescence spectrum except the intensity is changed.

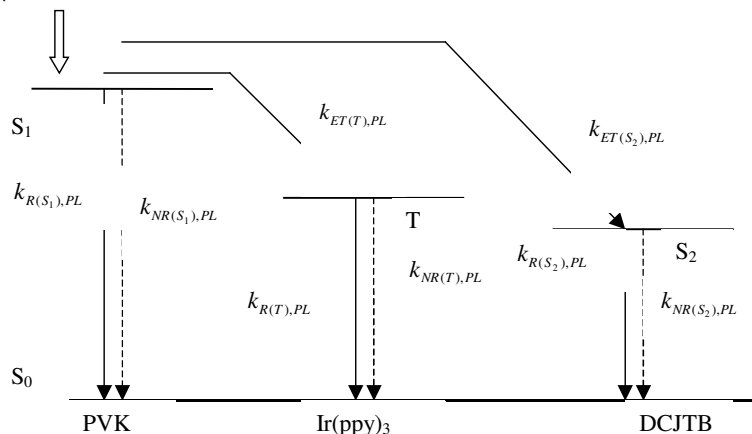


Fig. 2. Emission process of photoluminescence

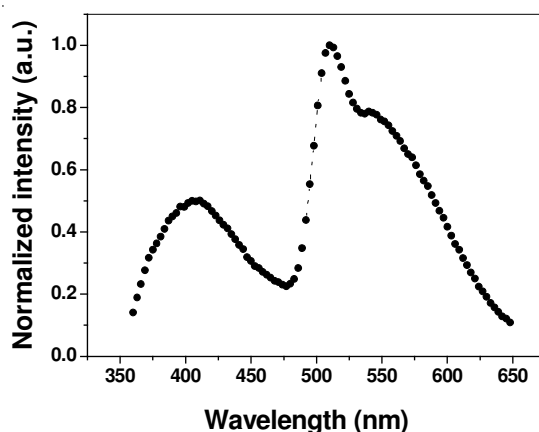


Fig. 3. Electroluminescence spectrum of the device ITO/PEDOT:PSS/PVK:Ir(ppy)<sub>3</sub>:DCJTb/BCP (10 nm)/Alq<sub>3</sub> (20 nm)/Al

As to electroluminescence, the processes are exactly the same as in photoluminescence, with the important exception that it is also possible to create a fraction  $\chi_T$  of triplet excitons and a fraction  $\chi_S$  of singlet excitons directly. Fig. 4 is process of electroluminescence.

Quantum yield for radiative emission of singlet (SR) and triplet (TR) emission and for energy transfer (ET):

$$\Phi_{S_1R} = \frac{k_{R(S_1)}}{k_{R(S_1)} + k_{NR(S_1)} + k_{ET(S_2)} + k_{ET(T)}} \quad (1)$$

$$\Phi_{S_2R} = \frac{k_{R(S_2)}}{k_{R(S_2)} + k_{NR(S_2)}} \quad (2)$$

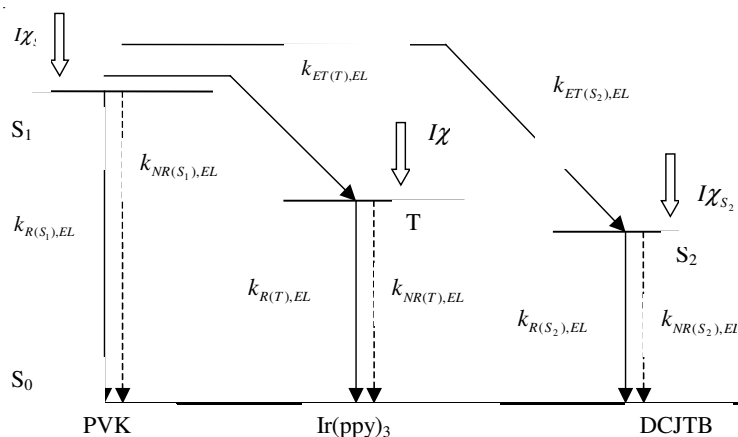


Fig. 4. Emission process of electroluminescence

$$\Phi_{\text{TR}} = \frac{k_{\text{R(T)}}}{k_{\text{R(T)}} + k_{\text{NR(T)}}} \quad (3)$$

$$\Phi_{\text{S}_2\text{ET}} = \frac{k_{\text{ET(S}_2)}}{k_{\text{R(S}_1)} + k_{\text{NR(S}_1)} + k_{\text{ET(S}_2)} + k_{\text{ET(T)}}} \quad (4)$$

$$\Phi_{\text{TET}} = \frac{k_{\text{ET(T)}}}{k_{\text{R(S}_1)} + k_{\text{NR(S}_1)} + k_{\text{ET(S}_2)} + k_{\text{ET(T)}}} \quad (5)$$

The number of photons emitted from the triplet and singlet states are denoted  $N_{\text{T}}$  and  $N_{\text{S}}$ , respectively and the ratio is  $R$ .

For the photoluminescence (PL):

$$N_{\text{S,PL}} = I \cdot \Phi_{\text{S}_1\text{R,PL}} \quad (6)$$

$$N_{\text{S}_2\text{,PL}} = I \cdot \Phi_{\text{S}_2\text{ET,PL}} \cdot \Phi_{\text{S}_2\text{R,PL}} \quad (7)$$

$$N_{\text{T,PL}} = I \cdot \Phi_{\text{TET,PL}} \cdot \Phi_{\text{TR,PL}} \quad (8)$$

$$R_{\text{S}_2/\text{S}_1\text{,PL}} = \frac{\Phi_{\text{S}_2\text{ET,PL}} \cdot \Phi_{\text{S}_2\text{R,PL}}}{\Phi_{\text{S}_1\text{R,PL}}} \quad (9)$$

$$R_{\text{T/S}_1\text{,PL}} = \frac{\Phi_{\text{TET,PL}} \cdot \Phi_{\text{TR,PL}}}{\Phi_{\text{S}_1\text{R,PL}}} \quad (10)$$

For the electroluminescence (EL):

$$N_{\text{S}_1\text{,EL}} = I \cdot \chi_{\text{S}_1} \cdot \Phi_{\text{S}_1\text{R,EL}} \quad (11)$$

$$N_{\text{S}_2\text{,EL}} = I \cdot \chi_{\text{S}_1} \cdot \Phi_{\text{S}_2\text{ET,EL}} \cdot \Phi_{\text{S}_2\text{R,EL}} + I \cdot \chi_{\text{S}_2} \cdot \Phi_{\text{S}_2\text{R,EL}} \quad (12)$$

$$N_{\text{T,EL}} = I \cdot \chi_{\text{S}_1} \cdot \Phi_{\text{TET,EL}} \cdot \Phi_{\text{TR,EL}} + I \cdot \chi_{\text{T}} \cdot \Phi_{\text{TR,EL}} \quad (13)$$

$$R_{\text{S}_2/\text{S}_1\text{,EL}} = \frac{\chi_{\text{S}_1} \cdot \Phi_{\text{S}_2\text{ET,EL}} \cdot \Phi_{\text{S}_2\text{R,EL}} + \chi_{\text{S}_2} \cdot \Phi_{\text{S}_2\text{R,EL}}}{\chi_{\text{S}_1} \cdot \Phi_{\text{S}_1\text{R,EL}}} \quad (14)$$

$$R_{T/s_1,EL} = \frac{\chi_{S_1} \cdot \Phi_{TET,EL} \cdot \Phi_{TR,EL} + \chi_T \cdot \Phi_{TR,EL}}{\chi_{S_1} \cdot \Phi_{S_1,R,EL}} \quad (15)$$

In which

$$I \cdot \chi_{S_1} = kC_{S_1} \cdot \sigma_{S_1} \quad (16)$$

$$I \cdot \chi_{S_2} = kC_{S_2} \cdot \sigma_{S_2} \quad (17)$$

$$I \cdot \chi_T = kC_T \cdot \sigma_T \quad (18)$$

$\sigma$  is formation cross-section of singlet exciton.

According to (9) and (14)

$$\frac{R_{s_2/s_1,PL}}{R_{s_2/s_1,EL}} = \left( \frac{\chi_{S_1} \cdot \Phi_{S_2ET,PL}}{\chi_{S_1} \cdot \Phi_{S_2ET,EL} + \chi_{S_2}} \right) \cdot \left( \frac{\Phi_{S_2R,PL}}{\Phi_{S_2R,EL}} \right) \cdot \left( \frac{\Phi_{S_1R,EL}}{\Phi_{S_1R,PL}} \right) \quad (19)$$

According to (10) and (15)

$$\frac{R_{T/s_1,PL}}{R_{T/s_1,EL}} = \left( \frac{\chi_{S_1} \cdot \Phi_{TET,PL}}{\chi_{S_1} \cdot \Phi_{TET,EL} + \chi_T} \right) \cdot \left( \frac{\Phi_{TR,PL}}{\Phi_{TR,EL}} \right) \cdot \left( \frac{\Phi_{S_1R,EL}}{\Phi_{S_1R,PL}} \right) \quad (20)$$

For the purpose of research convenient, it is assumed both the photoluminescence (PL) and electroluminescence (EL) have the same decay and they have the same energy transfer rate  $K(K \propto C^2)$ ,  $C$  is the Mohr concentration of donor (the molecular weight of DCJTb and Ir(ppy)<sub>3</sub> is 453.63 and 654.82, respectively),  $R$  can be calculated by spectrum integral. So the (19) and (20) can be modified as:

$$\frac{\sigma_T}{\sigma_{S_2}} = \frac{k_{ET(T)}}{k_{ET(S_2)}} \cdot \frac{C_{S_2}}{C_T} \cdot \frac{\frac{R_{s_2/s_1,PL}}{R_{s_2/s_1,EL}} \left( 1 - \frac{R_{T/s_1,PL}}{R_{T/s_1,EL}} \right)}{\frac{R_{T/s_1,PL}}{R_{T/s_1,EL}} \left( 1 - \frac{R_{s_2/s_1,PL}}{R_{s_2/s_1,EL}} \right)} = 9 \quad (21)$$

The value of formation cross section of triplet to that of siglet is 9. If the energy transfer from Ir(ppy)<sub>3</sub> to DCJTb is involved, the value is much large.

### Conclusion

The photoluminescence (PL) and electroluminescence (EL) light-emitting diodes employing N-vinylcarbazole (PVK) doped by phosphorescent material Ir(ppy)<sub>3</sub> and fluorescent material DCJTb were fabricated. According to the changing in the electroluminescence (EL) spectrum and photoluminescence (PL) spectrum, we deduce that the value of formation cross section of triplet to that of siglet is 9.

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## REFERENCES

1. Y. Cao, I.D. Parker, G. Yu, C. Zhang and A.J. Heeger, *Nature*, **397**, 414 (1999).
2. D. Beljonne, A. Ye, Z.G. Shuai and J.L. Bredas, *Adv. Funct. Mater.*, **17**, 684 (2004).
3. M. Wohlgenannt, K. Tandon, S. Mazumdar, S. Ramasesha and Z.V. Vardeny, *Nature*, **409**, 494 (2001).
4. J. Lu, Y.B. Hou, Q.M. Shi, Y.B. Li and H. Jin, *Spectrosc. Spectral Anal.*, **3**, 420 (2007).
5. J.S. Wilson, A.S. Dhoot, A.J.A.B. Seeley, M.S. Khan, A. Kohler and R.H. Friend, *Nature*, **413**, 828 (2001).
6. Z.G. Shuai, D. Beljonne, R.J. Silbey and J.L. Bredas, *Phys. Rev. Lett.*, **84**, 131 (2000).
7. S.W. Yin, L.P. Chen, P.F. Xuan, K.Q. Chen and Z.G. Shuai, *J. Phys. Chem. B*, **108**, 9608 (2004).
8. M.A. Baldo, D.F. O'Brien, M.E. Thompson and S.R. Forrest, *Phys. Rev. B*, **60**, 14422 (1999).
9. L.C. Lin, H.F. Meng, J.T. Shy, S.F. Horng, L.S. Yu, C.H. Chen, H.H. Liaw, C.C. Huang, K.Y. Peng and S.A. Chen, *Phys. Rev. Lett.*, **90**, 036601 (2003).
10. M.N. Kobrak and E.R. Bittner, *Phys. Rev. B*, **62**, 11473 (2000).
11. M.A. Baldo, D.F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M.E. Thompson and S.R. Forrest, *Nature*, **395**, 151 (1998).

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