Electrical and optical characteristics of red organic light-emitting diodes doped with two guest dyes

Feng Li [a,*], Jiuling Lin [b], Jing Feng [a], Gang Cheng [a], Hongyu Liu [a], Shiyong Liu [a], Ligong Zhang [b], Xiufeng Zhang [b], S.T. Lee [c]

[a] *National Laboratory of Integrated Optoelectronics, Jilin University, Changchun 130023, PR China*
[b] *Laboratory of Excited State Processes, Chinese Academy of Sciences, Changchun 130021, PR China*
[c] *Department of Physics and Materials Science, City University of Hong Kong, Kowloon, Hong Kong*

Abstract

We report the red organic light-emitting diodes doped with rubrene and 4-(dicyanomethylene)-2-*t*-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTB). *N,N*′-Diphenyl-*N,N*′-bis(1-naphthyl)-(1,1′-biphenyl)-4,4′-diamine (NPB) and doped tri-(8-hydroxyquinoline)-aluminum (Alq$_3$) are used as hole and electron-transport layers, respectively. The performances of the co-doped diodes are found to be improved compared to only DCJTB doped diodes. We attribute the improvement to rubrene that assists the energy transfer from Alq$_3$ to DCJTB more efficiency. The energy transfer rates from Alq$_3$ to DCJTB, from Alq$_3$ to rubrene, and from rubrene to DCJTB are proximately calculated to be 1.04×10^9, 3.89×10^9, and $2.79 \times 10^9 \, s^{-1}$ according to the fit of the fluorescence decay curves, respectively. It can be seen clearly that the energy transfer rate from Alq$_3$ to DCJTB through rubrene is 2.7 times higher than that from Alq$_3$ to DCJTB directly.
© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Organic light-emitting diodes; Energy transfer; Time-resolved photoluminescence spectra

1. Introduction

Organic light-emitting diodes (OLEDs) have attracted considerable attention over the past decade because they have the potential to achieve low-cost, full-color flat-panel display [1]. The doping method is often used to prevent the concentration quenching in OLEDs [2–4]. One distinctive characteristic of OLEDs is that they can produce various emission colors according to the selection of organic fluorescent or phosphorescent dopants. Red OLEDs are often fabricated by doping a red dopant into the host materials. However, the emission obtained from such a doping system is generally not red but orange. Poor energy transfer from the host to the guest is observed and limits the improvement of red electroluminescence [5]. Recently, some groups report a two-step energy transfer method to increase the emission characteristics of OLEDs [5–8]. Two kinds of guest dyes are doped into the host material, one acts as a sensitizer to assist the energy transfer from the host to the other dye. Hamada et al. report that rubrene is used as an emitting assistant dopant to assist the energy transfer from the Alq$_3$

to the red dopant DCM2 to improve the color purity of red emission [5]. Mori et al. report that the electroluminescence efficiency and luminance of DCM- and Sq-doped OLEDs are two to three times higher than those of only Sq-doped OLEDs [7]. Ohmori et al. report that DCM and TPP are co-doped into Alq$_3$ layer to improve red light emission [8].

In this work, we report electrical and optical characteristics of another co-doped OLEDs. Rubrene and 4-(dicyanomethylene)-2-*t*-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTB) are selected as the sensitizer and the red dopant, respectively. tri-(8-Hydroxyquinoline)aluminum (Alq$_3$) is used as the host due to its excellent stability and charge-transporting ability. It is found that the performances of the DCJTB doped red OLEDs can be improved by doping rubrene as the sensitizer. The energy transfer rate from Alq$_3$ to DCJTB through rubrene is 2.7 times higher than that from Alq$_3$ to DCJTB directly in Alq$_3$:rubrene:DCJTB (100:5:3 weight ratio) thin film.

2. Experiment

For the electrical measurements, OLEDs with the structure of indium–tin-oxide (ITO)/*N,N*′-diphenyl-*N,N*′-bis(1-naphthyl)-(1,1′-biphenyl)-4,4′-diamine (NPB) (50 nm)/Alq$_3$:

rubrene:DCJTB (50 nm)/LiF (0.5 nm)/Al (120 nm) are fabricated by the multiple source organic molecular beam deposition method. In these devices, NPB is used as the hole-transport layer, Alq₃ doped with rubrene and DCJTB as the emissive as well as the electron-transport layer. The sheet resistance of ITO anode is about $120 \, \Omega/\square$. The doping process is carried out by co-evaporation method. The chamber pressure is under 3×10^{-4} Pa. The doping concentration of DCJTB is controlled to 1 and 3% (weight ratio), and that of rubrene to 0, 3, and 5% (weight ratio) relative to the Alq₃ weight. The emitting area is $4 \, \text{mm}^2$. The luminance–current–voltage characteristics, chromaticity coordinates, and electroluminescence (EL) spectra are measured simultaneously by the programmable Keithley model 2400 and PR650 spectrometer.

For the optical measurements, thin films of Alq₃, Alq₃:DCJTB (100:3 weight ratio) and Alq₃:rubrene:DCJTB (100:5:3 weight ratio) have been prepared by spin casting from a chloroform solution on a quartz substrate, respectively. To avoid contamination among different materials, the thermal evaporation method has not been used to prepare these films. Due to the concentration quenching, the photoluminescence (PL) of rubrene and DCJTB thin film are very weak. So, the rubrene and DCJTB chloroform solution are used to measure their PL and absorption spectra. Steady-state absorption and photoluminescence spectra are measured with a RF-5301Pc spectrofluorophotometer, respectively. The picosecond time-correlated single photon counting spectrometer is used to measure the time-resolved PL spectra. A mode-locked Ti:sapphire laser (Spectra Physics, Tsunami) operating at a repetition rate of 82 MHz is pumped by a cw Nd:YVO₄ laser (Spectra Physics, Millennia). The mode-locked Ti:sapphire laser is sent through a BBO double-frequency crystal and then is used as the exciting laser operating at 394 nm. All measurements are carried out at room temperature under ambient atmosphere. Fig. 1 shows the structure of the OLEDs and chemical structures of the organic materials used.

3. Results and discussions

Fig. 2 shows the steady-state PL and absorption spectra of Alq₃, rubrene, and DCJTB, respectively. The spectral overlap between Alq₃ emission and DCJTB absorption spectrum appears to be larger than that between Alq₃ and rubrene. Moreover, the overlap between rubrene emission and DCJTB absorption spectra is small. According to the Förster energy transfer theory, the energy transfer from Alq₃ to DCJTB should be more efficient than that from Alq₃ to DCJTB through rubrene. However, in the following experiments, the energy transfer from Alq₃ to DCJTB through rubrene is demonstrated to be more efficient. This will be explained at the end of this work. Fig. 3 shows the EL spectra of these cells with different concentrations of rubrene and DCJTB. An [x, y] cell is used to express the device doped
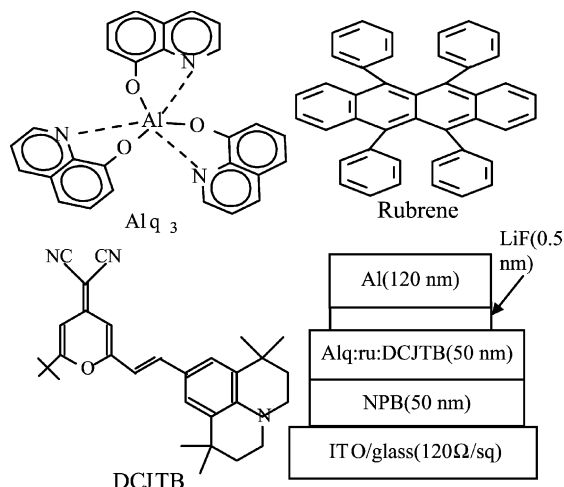

Fig. 1. Structure of OLEDs and chemical structure of the organic materials studied in this work.

with x% DCJTB and y% rubrene. As can be seen, there is an emission of Alq₃ (peak at 516 nm) besides the red emission of DCJTB in [1, 0] and [3, 0] cells, which indicates that the energy transfer from Alq₃ to DCJTB is not complete in the range of the DCJTB concentration tried (1 and 3 wt.%). The emission of Alq₃ disappears and the emission of rubrene (peak at 561 nm) appears in [1, 3] and [1, 5] cells, which indicates that the energy of Alq₃ excitons can be transferred to rubrene and the energy transfer from rubrene to DCJTB is not complete when the concentration of DCJTB is low (1 wt.%). The emissions of Alq₃ and rubrene disappear in [3, 3] and [3, 5] cells, which indicates that the energy transfer from Alq₃ to rubrene and then from rubrene to DCJTB is complete as the concentration of DCJTB increases to 3 wt.%.

The PL spectra of Alq₃:rubrene (100:5 weight ratio) and rubrene:DCJTB (5:3 weight ratio) films are shown in
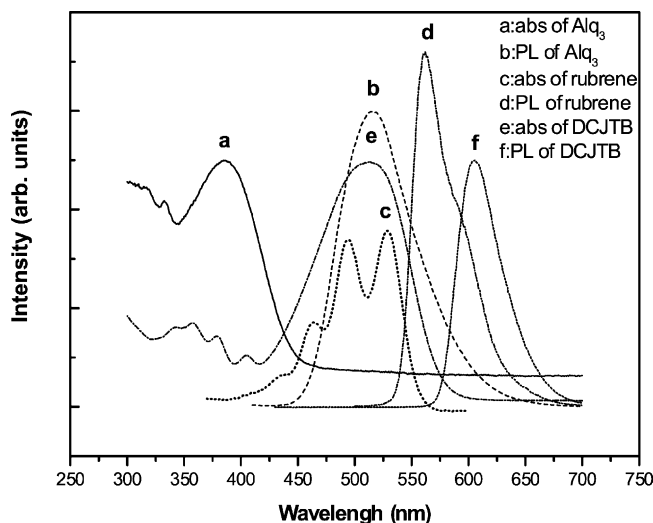

Fig. 2. Absorption of Alq₃ (a) and PL of Alq₃ (b) in thin film, absorption of rubrene (c) and DCJTB (e), PL of rubrene (d) and DCJTB (f) in chloroform solution.
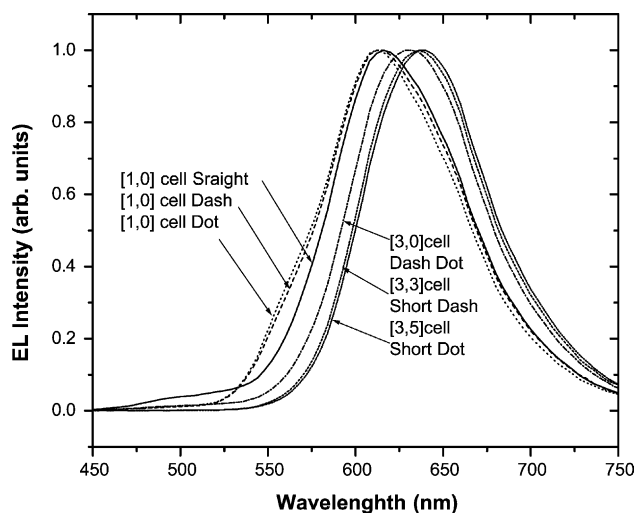
Fig. 3. Electroluminescence spectra of the OLEDs with different concentration of rubrene and DCJTB.


Fig. 4(a) and (b), respectively. The wavelengths of exciting lights are 384 and 494 nm which are located at the absorption peak of Alq3 and rubrene, respectively. It can be seen that there is no the emission of Alq3 and rubrene in the films of Alq3:rubrene (100:5 weight ratio) and rubrene:DCJTB (5:3 weight ratio) films, respectively. Only the emissions of rubrene and DCJTB are observed in the Alq3:rubrene (100:5 weight ratio) and rubrene:DCJTB (5:3 weight ratio) films, respectively. These results indicate that rubrene can efficiently quench the emission of Alq3 in Alq:rubrene (100:5 weight ratio) film. It is similar to DCJTB for quenching the emission of rubrene in rubrene:DCJTB (5:3 weight ratio) film. That is to say the energy really can be transferred from Alq3 to DCJTB through rubrene when the ratios of them are suitable.

Table 1 shows the chromaticity coordinates of these cells at voltages of 6, 12 and 18 V. The [3, 3] and [3, 5] cells exhibit good red color. When the concentration of DCJTB is 3 wt.%, the red purity of co-doped cells is better than that of DCJTB only doped cells.

Figs. 5 and 6 show the luminance-voltage and luminance efficiency–voltage characteristics of these cells, respectively. As can be seen, the luminance and luminance efficiency of
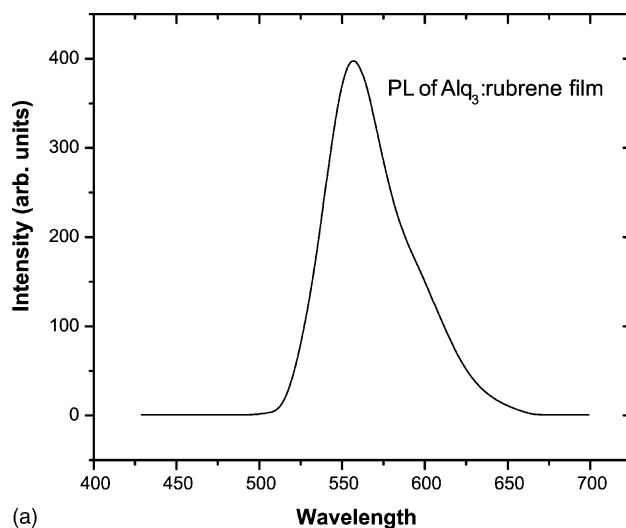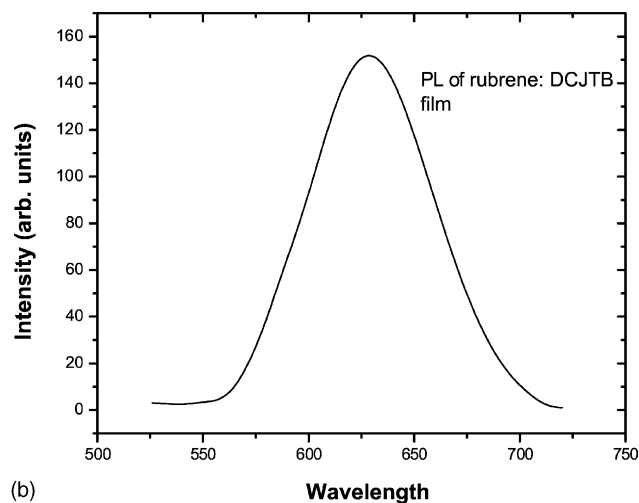
Fig. 4. PL spectra of Alq3:rubrene (100:5 weight ratio) (a) and rubrene:DCJTB (5:3 weight ratio) (b) films, the exciting wavelength are 384 and 494 nm for Alq3:rubrene and rubrene:DCJTB films, respectively.

the co-doped cells are improved compared to the DCJTB only doped cells. The luminance and luminance efficiency of the cells with 3 wt.% DCJTB are lower than those of the cells with 1 wt.% DCJTB. However, the red purity of the cells with 3 wt.% DCJTB is better than those of the cells with

Table 1
The change of chromaticity coordinates in red OLEDs at voltages of 6, 12, and 18 V

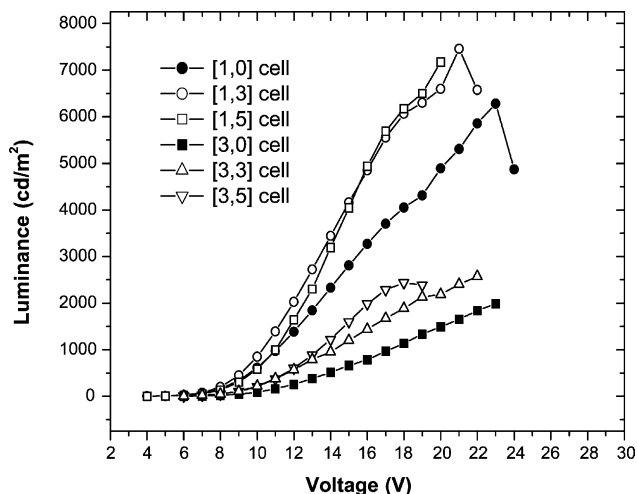| DCJTB (%)	Rubrene (%)	V		
		At 6 V	At 12 V	At 18 V
1	0	$x = 0.63, y = 0.36$	$x = 0.60, y = 0.39$	$x = 0.60, y = 0.39$
	3	$x = 0.62, y = 0.37$	$x = 0.60, y = 0.40$	$x = 0.59, y = 0.40$
	5	$x = 0.61, y = 0.37$	$x = 0.59, y = 0.40$	$x = 0.58, y = 0.41$
3	0	$x = 0.60, y = 0.33$	$x = 0.64, y = 0.36$	$x = 0.63, y = 0.36$
	3	$x = 0.64, y = 0.33$	$x = 0.66, y = 0.34$	$x = 0.65, y = 0.35$
	5	$x = 0.64, y = 0.32$	$x = 0.66, y = 0.34$	$x = 0.64, y = 0.35$

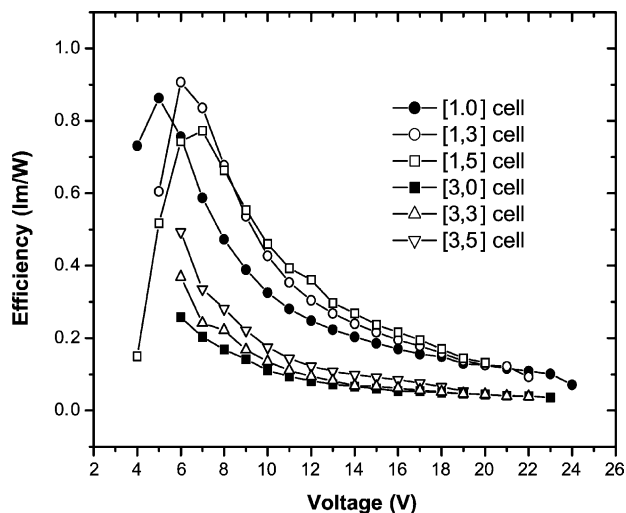Fig. 5. Luminance-voltage characteristics of the OLEDs with different concentration of rubrene and DCJTB.

Fig. 6. Luminous efficiency–voltage characteristics of the OLEDs with different concentration of rubrene and DCJTB.

with 1 wt.%, which are shown in Table 1. In the view of red purity, 3 wt.% concentration of DCJTB should be chosen to fabricate the red OLEDs.

Fig. 7 shows the fluorescence decay curves at the PL peak wavelengths of Alq$_3$ (516 nm) (a), rubrene (561 nm) (b) and DCJTB (610 nm) (c). The decay curves of the PL intensity, $I_{PL}(t)$, are fitted according to

$$I_{PL}(t) = \sum_{i=1}^{n} a_i \exp\left(\frac{-(t - t_0)}{\tau_i}\right) \tag{1}$$

The fitted parameters are shown as Table 2, where the pre-exponential factors a_i are normalized. The averaged decay time $\bar{\tau}$ is calculated as

$$\frac{1}{\bar{\tau}} = \sum_{i=1}^{n} a_i \frac{1}{\tau_i} \tag{2}$$

For the emission from Alq$_3$ shown in Fig. 7(a), the fluorescence decays in Alq$_3$ film, Alq$_3$:DCJTB film, and Alq$_3$:rubrene:DCJTB film are fitted to mono-exponential, bi-exponential, and tri-exponential functions, respectively. The PL intensity decay of Alq$_3$ becomes much faster in Alq$_3$:DCJTB film compared with that in Alq$_3$ film, which indicates there exists an additional deactivating process

besides the intrinsic deactivating process of Alq$_3$ excitons in Alq$_3$:DCJTB film. The process is thought to be the energy transfer from Alq$_3$ to DCJTB. The PL intensity decay of Alq$_3$ in Alq$_3$:rubrene:DCJTB film is faster than that in Alq$_3$:DCJTB film, which indicates there exists another deactivating process in addition to the intrinsic deactivating processes of Alq$_3$ excitons and the energy transfer from Alq$_3$ to DCJTB in Alq$_3$:rubrene:DCJTB film. This process is thought to be the energy transfer from Alq$_3$ to rubrene. The fluorescence lifetime of Alq$_3$ thin film is described as

$$\frac{1}{\tau_{Alq_3}} = K_{FT} + K_{n\text{-}FT} + K_{ISC} \tag{3}$$

where K_{FT} is the rate of the radiation process, $K_{n\text{-}FT}$ is one of radiationless deactivating process, and K_{ISC} is the intersystem crossing process. The fluorescence lifetimes of Alq$_3$ in Alq$_3$:DCJTB film and Alq$_3$:rubrene:DCJTB film are described as

$$\frac{1}{\bar{\tau}'_{Alq_3}} = K_{FT} + K_{n\text{-}FT} + K_{ISC} + K_1 \tag{4}$$

$$\frac{1}{\bar{\tau}''_{Alq_3}} = K_{FT} + K_{n\text{-}FT} + K_{ISC} + K_1 + K_2 \tag{5}$$

Table 2
Time components (T_i) and pre-exponential factors (a_i) from the fit of fluorescence decay curves of Alq$_3$, rubrene, and DCJTB

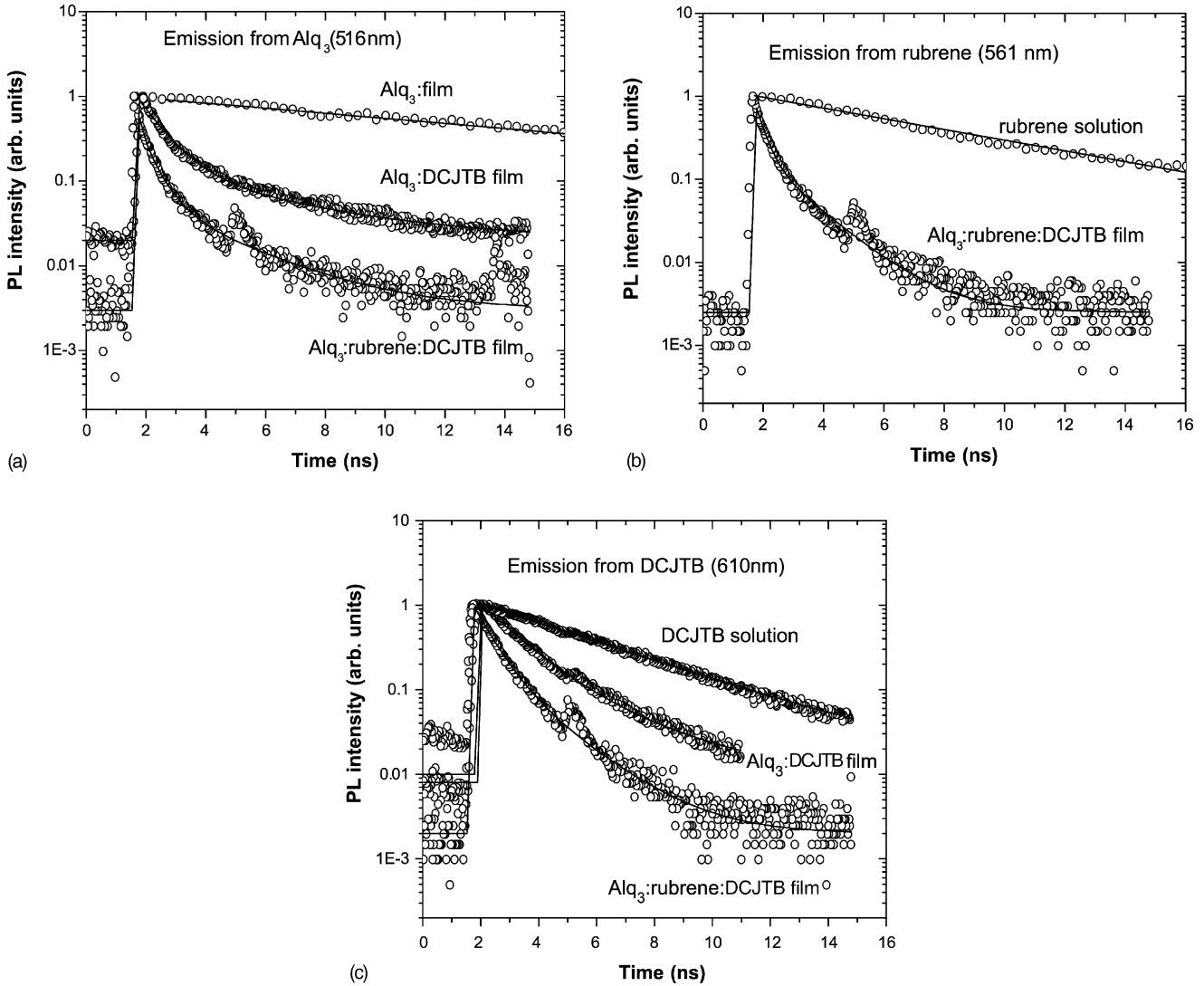|	Alq$_3$				Rubrene			DCJTB		
	τ_1 (a_1) (ns)	τ_2 (a_2) (ns)	τ_3 (a_3) (ns)	$\bar{\tau}$ (ns)	τ_1 (a_1) (ns)	τ_2 (a_2) (ns)	$\bar{\tau}$ (ns)	τ_1 (a_1) (ns)	τ_2 (a_2)	$\bar{\tau}$ (ns)
Film Resolusion	14.50 (100%)				6.71 (100%)			3.82 (100%)		
Alq$_3$:DCJTB film	4.09 (14%)	0.80 (86%)		0.90				3.12 (17%)	1.23 (83%)	1.37
Alq$_3$:rubrene:DCJTB film	2.60 (5%)	0.52 (35%)	0.14 (60%)	0.20	1.41 (19%)	0.29 (81%)	0.34	1.68 (20%)	0.62 (80%)	0.71

Fig. 7. Decay curves of photoluminescence (PL) emission at the PL peak wavelengths of Alq3 (516 nm) (a), rubrene (561 nm) (b) and DCJTB (610 nm) (c).

respectively, where K_1 and K_2 are the rates of energy transfer from Alq3 to DCJTB and from Alq3 to rubrene, respectively. So,

$$K_1 = \frac{1}{\bar{\tau}'_{Alq_3}} - \frac{1}{\tau_{Alq_3}} \qquad (6)$$

$$K_2 = \frac{1}{\bar{\tau}''_{Alq_3}} - \frac{1}{\bar{\tau}'_{Alq_3}} \qquad (7)$$

For the emission from rubrene shown in Fig. 7(b), faster PL intensity decay of rubrene can be observed in the Alq3:rubrene:DCJTB film compared with that in the rubrene chloroform solution, which indicates that there may exist energy transfer from rubrene to DCJTB besides the intrinsic deactivating process of rubrene excitons in Alq3:rubrene:DCJTB film. Similarly, the rates of energy transfer from rubrene to DCJTB, K_3 can be

obtained as

$$K_3 = \frac{1}{\bar{\tau}'_{ru}} - \frac{1}{\tau_{ru}} \qquad (8)$$

where τ_{ru} and $\bar{\tau}'_{ru}$ are the fluorescence lifetimes of rubrene in chloroform solution and Alq3:rubrene:DCJTB film, respectively. It should be noted that the calculations from Eqs. (6)–(8) are proximate results. Only if the donor fluorescence decay is single-exponent, are the results strictly valid. For the emission from DCJTB shown in Fig. 7(c), the PL intensity decays of DCJTB in Alq3:DCJTB and Alq3:rubrene:DCJTB films are faster than that in DCJTB chloroform solution. The faster decay in Alq3:DCJTB and Alq3:rubrene:DCJTB films may be attributed to the interaction of DCJTB excitons [9].

Fig. 8 shows the energy transfer routes and rates among these three materials. It can be seen clearly that the energy transfer rate from Alq3 to DCJTB through rubrene is 2.7
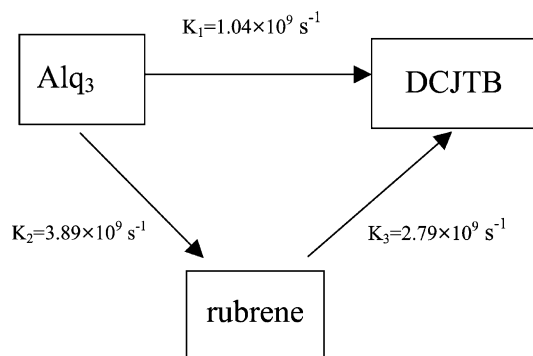
Fig. 8. Sketch of energy transfer routes and rates among Alq$_3$, rubrene, and DCJTB. K_1, K_2, and K_3 are the energy transfer rates from Alq$_3$ to DCJTB, from Alq$_3$ to rubrene, and from rubrene to DCJTB, respectively.

times higher than that from Alq$_3$ to DCJTB directly. So, rubrene is very important to assist the energy transfer from Alq$_3$ to DCJTB.

Judging from the overlap between the emission spectrum of the energy donor and the absorption spectrum of the energy acceptor (Fig. 2), the Förster type energy transfer from Alq$_3$ to DCJTB through rubrene should be less efficient. However, according to the study of the EL, PL, and time-resolved PL spectra in this work, the energy transfer from Alq$_3$ to DCJTB through rubrene is really very efficient. These results indicate that the Förster type energy transfer process is not dominant and there should exist other types of energy transfer processes (such as hopping) that dominate in the energy transfer route from Alq$_3$ to DCJTB through rubrene.

4. Conclusion

In summary, we fabricate the red OLEDs doped with rubrene and DCJTB. The red color purity, luminance and efficiency of the co-doped diodes are found to be improved compared with the DCJTB only doped diodes. We attribute the improvement to rubrene which assist the energy transfer from Alq$_3$ to DCJTB more efficiency. We also use the time-resolved PL spectra to confirm it. The energy transfer rate from Alq$_3$ to DCJTB through rubrene is 2.7 times higher than that from Alq$_3$ to DCJTB directly in Alq$_3$:rubrene:DCJTB (100:5:3 weight ratio) thin film.

References

[1] C.W. Tang, S.A. VanSlyke, Appl. Phys. Lett. 51 (1987) 913.
[2] C.W. Tang, S.A. VanSlyke, C.H. Chen, J. Appl. Phys. 65 (1989) 3610.
[3] H. Suzuki, S. Hoshino, J. Appl. Phys. 79 (1996) 8816.
[4] Y. Hamada, N. Matsusue, H. Kanno, H. Fujii, T. Tsujioka, H. Takahash, Jpn. J. Appl. Phys. 40 (2001) L753.
[5] Y. Hamada, H. Kanno, T. Tsujioka, H. Takahashi, Appl. Phys. Lett. 75 (1999) 1682.
[6] B.W. D'Andrade, M.A. Baldo, C. Adachi, J. Brooks, M.E. Thompson, S.R. Forrest, Appl. Phys. Lett. 79 (2001) 1045.
[7] T. Mori, H.-G. Kim, T. Mizutani, D.-C. Lee, Jpn. J. Appl. Phys. 40 (2001) 5346.
[8] Y. Ohmori, H. Kajii, T. Sawatani, H. Ueta, K. Yoshino, Thin Solid Films 393 (2001) 407.
[9] I. Sokolik, R. Priestley, A.D. Walser, R. Dorsinville, C.W. Tang, Appl. Phys. Lett. 69 (1996) 4168.