Electroluminescence quenching mechanism in Rubrene doped host–guest system*

Yan Guang(闫 光), Zhao Su-Ling(赵谡玲)†, Xu Zheng(徐 征), Zhang Fu-Jun(张福俊), Kong Chao(孔 超), Zhu Hai-Na(朱海娜), Song Dan-Dan(宋丹丹), and Xu Xu-Rong(徐叙瑢)

Key Laboratory of Luminescence and Optical Information (Beijing Jiaotong University), Ministry of Education, Beijing 100044, *China*

Institute of Optoelectronics Technology, Beijing Jiaotong University, Beijing 100044, *China*

(Received 22 July 2009; revised manuscript received 23 October 2009)

In this paper, the electroluminescence quenching mechanism in a 5,6,11,12-tetraphenylnaphthacene (Rubrene) doped host–guest system is studied by utilizing a specially designed organic light-emitting diode with an emission layer consisting of a few periodic host/guest structures. Tris-(8-hydroxyquinoline) aluminium (Alq_3) and Rubrene are used as the host and the guest, respectively. The thickness variation of the guest layer in each period enables the study of the effect of molecule aggregation, and the thickness variation of the host layer suggests a long range quenching mechanism of dipole–dipole interaction. The long range quenching mechanism is a Förster process, and the Förster radius of Rubrene is between 3 and 10 nm.

Keywords: organic light-emitting diode, Förster process, quenching mechanisms
PACC: 7865T, 7860F, 3250F

1. Introduction

Organic light-emitting diodes (OLEDs) have emerged as one of the most promising devices for use in next-generation displays and lighting sources due to their advantages, such as light weight, flexibility, low operating voltage, environmental friendliness, etc. Since the first report on multilayered organic light-emitting diodes based on organic semiconducting films sandwiched between electrodes, given by Tang and van Slyke in 1987,[1] the performance of organic light-emitting diodes has been greatly improved in the past few years. Lots of methods have been reported in the literature to optimise the electroluminescence process in OLEDs, such as balancing the carrier transport and injection,[2−6] confining the excitons,[7] doping the transport[8,9] and emission layers.[10,11]

Molecular dyes doped in the matrix are widely used to tune the colour and improve the efficiency of OLEDs, as the electrical and optical properties can be separately optimised in doping systems. The emission layer is normally formed by a host–guest system in which the host material and a small number of guest molecules are co-evaporated. Most excitons are generated in the host matrix, and then their energy is transferred to guest molecules that give the final emission. The host–guest system minimises the aggregation of guest molecules so as to enable the high quantum yield. In this study, most excitons are generated in tris-(8-hydroxyquinoline)aluminium (Alq_3), and then their energy is transferred to 5,6,11,12-tetraphenylnaphthacene (Rubrene), which gives the final emission.

However, the basic and key issues in this host–guest system, especially quenching mechanisms, needs to be intensively studied. It is generally accepted that in a conventional doping system, concentration quenching occurs because of molecule aggregation.[12] A long range quenching mechanism of dipole–dipole interaction was also reported.[13−15] It is very important to distinguish the quenching mechanisms. In a conventional doping system, only one parameter which is the guest-to-host ratio is allowed to be varied. The effect of molecule aggregation or dipole–

*Project supported by the National Natural Science Foundation of China (Grant Nos. 10974013, 10774013, 10804006 and 60825407), the Research Fund for the Doctoral Program of Higher Education, China (Grant Nos. 20070004024 and 20070004031), the Beijing Science and Technology New Star Program, China (Grant No. 2007A024), and the 111 Project (Grant No. B08002), the Excellent Doctor's Science and Technology Innovation Foundation of Beijing Jiaotong University, China (Grant No. 141049522), and the Research Grants from the Academy of Sciences for the Third World (TWAS).

†Corresponding author. E-mail: slzhao@bjtu.edu.cn

© 2010 Chinese Physical Society and IOP Publishing Ltd

dipole interaction cannot be controlled separately. In the present study, we utilise specially designed OLEDs with an emission layer (EML) consisting of a few periodic structures, which allow two independent parameters to be varied for better control of the device performance. In this way, we distinguish the quenching mechanisms in the Alq_3-Rubrene host–guest system. By comparing the device performances with various guest thicknesses, we find that the concentration quenching may be due to molecule aggregation. By comparing the device performances with various host thicknesses, we find dipole–dipole interaction in the Rubrene doped Alq_3 host–guest system and the Förster radius of Rubrene to be between 3 and 10 nm.

2. Experiment

Here, we employed N, N'-di(naphth-2-yl)-N,N'-diphenyl-benzidine (NPB) as a hole transporting layer, Alq_3 as a host, Rubrene as a guest, 2,9-dimethyl-4, 7-diphenylphenanthroline (BCP) as a hole blocking layer and Alq_3 as an electron transporting layer. A schematic diagram of the device structure and the chemical structures of organic materials in this work are shown in Fig. 1.

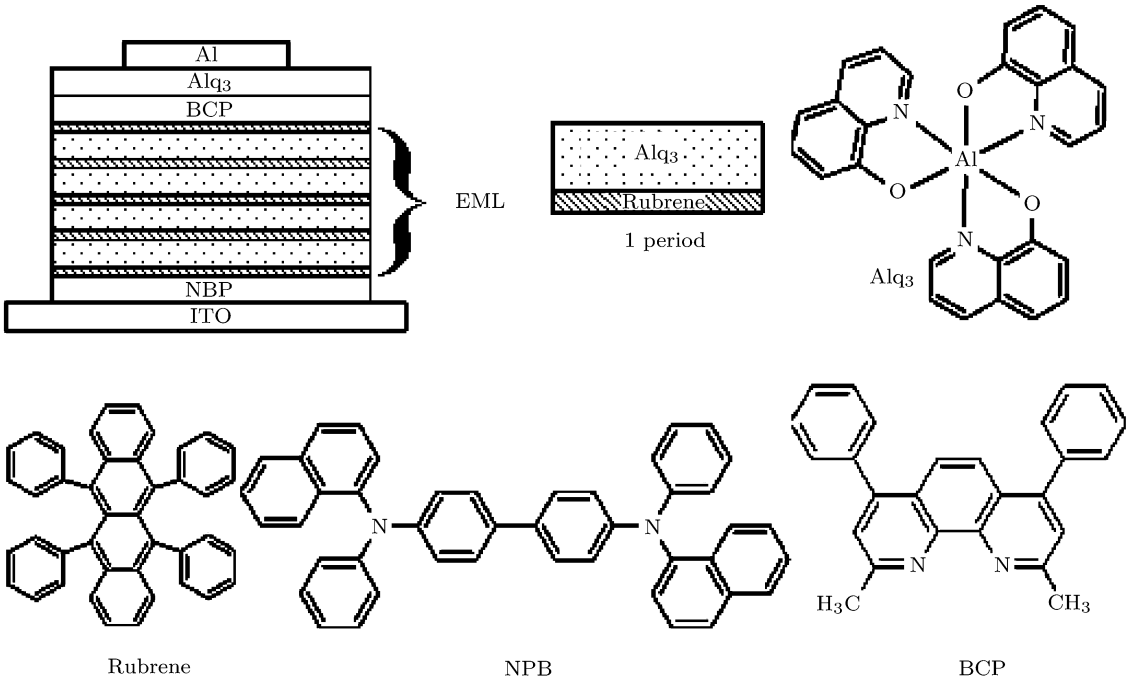


Fig. 1. Schematic diagram of device structure and chemical structures of organic materials used in this work.

Indium tin oxide (ITO)-coated glass substrates each with a sheet resistance of 60 Ω/□ were cleaned in ultrasonic baths containing de-ionised water, ethanol and acetone in sequence. Before deposition, the ITO substrates were treated by oxygen plasma for 5 min. Then the ITO substrates were transferred into the main chamber under high vacuum for the device fabrication. The deposition rate (thickness) was measured by a crystal sensor quartz oscillator combined with a frequency meter. The organic layers were fabricated by thermal evaporation at a rate of about 0.03 nm/s under a high vacuum of 2×10^{-5} Pa. An aluminium (Al) cathode with 100 nm thickness was then deposited through a shadow mask to fabricate eight 0.09-cm^2-square electrodes. The electroluminescence (EL) and photoluminescence (PL) spectra were detected by a charge-coupled device (CCD). The current–voltage–luminance (I–V–L) characteristics of the devices were measured by using a Keithley Source Meter 2410. Absorption spectra of organic films on quartz glass substrates were measured by a Shimadzu UV-3101 PC UV–VIS–NIR spectrophotometer.

3. Results and discussion

3.1. Variation of the thickness of the guest layer

The devices with the structure of ITO/NPB(30 nm)/[Rubrene(x nm)/Alq_3(10 nm)][4 periods]/[Rubrene(x nm)/BCP(12 nm)/Alq_3(18 nm)/Al were fabricated by thermal evaporation without breaking the vacuum. Rubrene thickness x varies from 1, 1.5, to 2, which gives the different guest–host ratios. The total thickness of the emission layer is larger than 20 nm to obtain a good carrier confinement.[12]

Figure 2 shows the curves for current density voltage and luminance versus voltage for devices with various guest thicknesses. Comparing the devices with x=1, 1.5, it can be seen that the current density does not change much, while the luminance drops significantly as the guest thickness increases. This means that Rubrene molecules do trap or block charges, but not significantly enough to influence the current flow in this low guest-to-host ratio. So the decreasing luminance of the device with a thicker guest layer may be attributed to the quenching from the guest molecule aggregation.

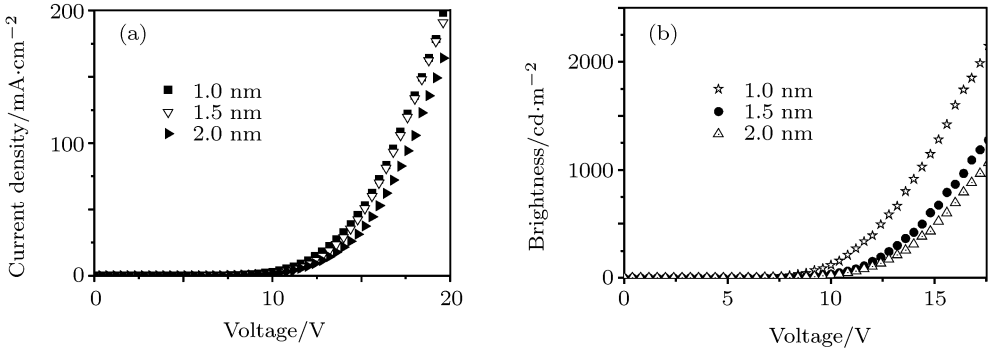


Fig. 2. J–V curves for devices with various Rubrene thicknesses (four periods) (a) and L–V curves for devices with various Rubrene thicknesses (four periods) (b).

Figures 3 (a) and 3(b) show the current efficiency versus current density and the normalised emission spectra of devices with various guest thicknesses, respectively. As the thickness of the guest layer increases, the degree of aggregation increases accordingly, resulting in a reduction in efficiency. It was reported that molecule aggregation led to a significant drop in the efficiency, which was accompanied by a much red-shifted emission spectrum.[12] The efficiency drop and the red-shifted emission spectrum suggest the presence of an aggregate state that is formed when two molecules are positioned close to one another. The aggregate state requires an overlap between two different molecular wave functions; hence, their excited state has a much longer lifetime, i.e. lower quantum yield.[16] As shown in Fig. 3(b), the normalised emission spectra for devices with various Rubrene thicknesses do not vary much except that they are slightly broadened. So we suggest that molecule aggregation is not a main quenching mechanism.

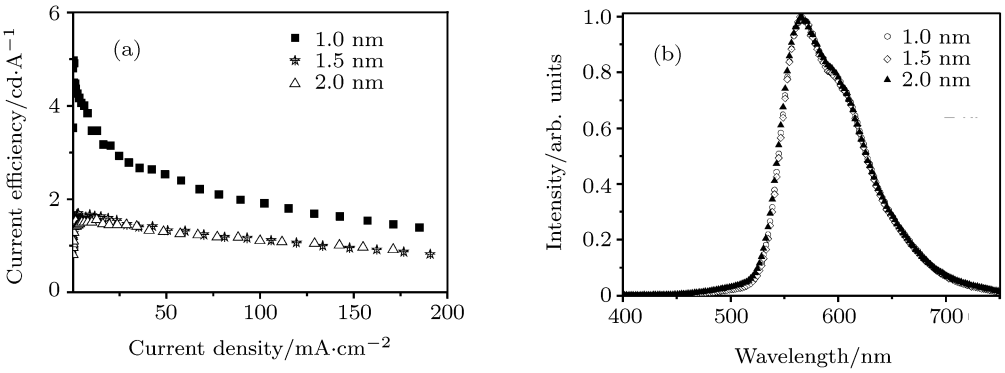


Fig. 3. Current efficiency versus current density for devices with various Rubrene thicknesses (four periods) (a) and normalised emission spectra for devices with various Rubrene thicknesses (b).

3.2. Variation of the thickness of the host layer

To further understand the main quenching mechanism, we carried out another experiment in which the thickness of the host layer was varied. The devices with the structure of ITO/NPB(30 nm)/[Rubrene(1 nm)/Alq_3(y nm)][4 periods]/[Rubrene(1 nm)/BCP(12 nm)/Alq_3(18 nm)/Al, with y being 3, 6. 5, 10, to 13.5, were prepared. Figures 4(a) and 4(b), respectively, show the curves for current density versus voltage and luminance versus voltage for devices with various host thicknesses. It can be seen that the current density and the luminance shift towards high voltages as host thickness increases. This is understandable due to a thicker device structure. The maximum luminance increases with the increase of host thickness for the devices, i.e. when y is 3 and 6.5. But when $y = 10$, the maximum luminance drops. This is attributed to the incomplete energy transfer from Alq_3 to Rubrene.

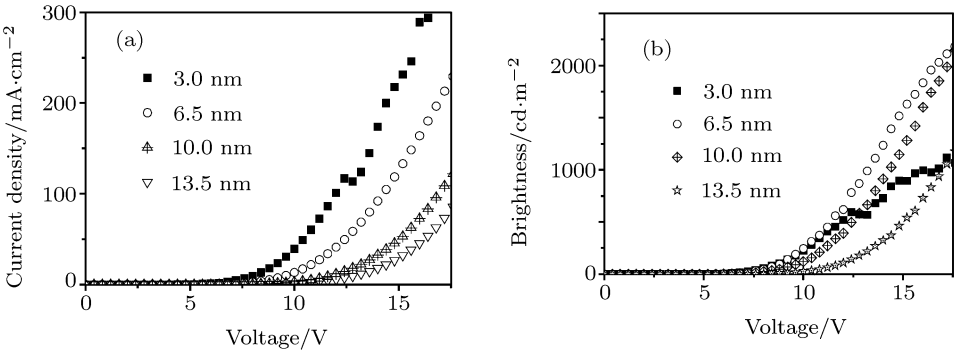


Fig. 4. J–V curves for devices with various Alq_3 thicknesses (four periods) (a), and L–V curves for devices with various Alq_3 thicknesses (four periods) (b).

This can also be proved from the emission spectra as shown in Fig. 5(b) which shows the normalised emission spectra for devices with various Alq_3 thicknesses. The emission of Alq_3 around 530 nm increases as host thickness increases, and there is no red-shifted emission. This means that the energy transfer from Alq_3 to Rubrene is not complete, and there is no increase of aggregate states in number because the emission spectral shape does not change with the increase of host thickness except Alq_3 emission around 530 nm. The non-occurrence of aggregation suggests that the quenching mechanism is involved. But as shown by the curve for current efficiency versus current density for devices with various host thicknesses in Fig. 5(a), it can be seen that the device with a 10 nm Alq_3 layer exhibits a higher current efficiency. The decrease of the current efficiency when the Alq_3 layer turns thicker is attributed to the incomplete energy transfer. However, when Alq_3 thickness increases from 3 to 6.5 nm, the maximum luminance increases significantly. The structures are only different in the Alq_3 thickness that separates the Rubrene molecules. The thinner the Alq_3 layer is, the more intense the interaction between Rubrene molecules will be. Hence, quenching can come only from increasing the interaction between the Rubrene molecules.

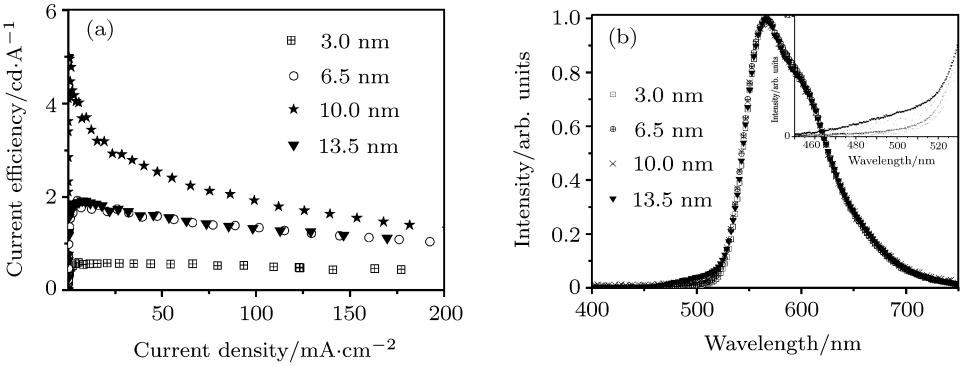


Fig. 5. Current efficiency versus current density for devices with various Alq_3 thicknesses (four periods) (a), and normalised emission spectra for devices with various Alq_3 thicknesses (b).

As shown in Fig. 6, the absorption and the emission spectra of the Rubrene molecule overlap significantly. So the Förster process between Rubrene molecules is the main quenching mechanism. The quenching comes from the dipole–dipole interaction as depicted in the literature.[17] The current efficiency peaks at a thickness of 10 nm for Alq_3, which shows that the Förster radius of Rubrene molecules is between 3 and 10 nm.

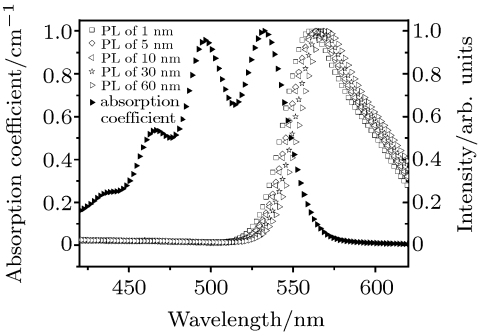


Fig. 6. Absorption coefficient and normalised emission spectra of the Rubrene molecule in thin film.

4. Conclusions

The quenching mechanisms in a Rubrene doped Alq_3 host–guest system are studied. The quenching in thin Rubrene is not mainly due to the occurrence of aggregation state, but it is owing to the presence of intermolecular energy transfer among Rubrene molecules, i.e. by a long-range Förster process between the Rubrene molecules in different layers. The Förster radius of Rubrene molecules is between 3 and 10 nm.

References

[1] Tang C W and van Slyke S A 1987 *Appl. Phys. Lett.* **51** 913

[2] van Slyke S A, Chen C H and Tang C W 1996 *Appl. Phys. Lett.* **69** 2160

[3] Hung L S, Tang C W and Mason M G 1997 *Appl. Phys. Lett.* **70** 152

[4] Li C, Peng J B and Zeng W J 2009 *Acta Phys. Sin.* **58** 1992 (in Chinese)

[5] Zen H Y, Luo C, Zhu D X, Ye H and Wang J P 2008 *Acta Phys. Sin.* **57** 1918 (in Chinese)

[6] Cao G H, Qin D S, Guan M, Cao J S, Zeng Y P and Li J M 2008 *Chin. Phys.* B **17** 1911

[7] D'Andrade B W and Forrest S R 2003 *J. Appl. Phys.* **94** 3101

[8] Pfeiffer M, Forrest S R, Leo K and Thompson M E 2002 *Adv. Mater.* **14** 633

[9] Niu L B and Guan Y X 2009 *Acta Phys. Sin.* **58** 4931 (in Chinese)

[10] Tang C W, van Slyke S A and Chen C H 1989 *J. Appl. Phys.* **65** 3610

[11] Tang X J, Yu J S, Li L, Wang J and Jiang Y D 2008 *Acta Phys. Sin.* **57** 6620 (in Chinese)

[12] Pope M and Swenberg C E 1999 *Electronic Processes in Organic Crystals and Polymers* 2nd ed (Oxford: Oxford University Press) p337

[13] Kawamura Y, Brooks J, Brown J J, Sasabe H and Adachi C 2006 *Phys. Rev. Lett.* **96** 017404

[14] Divayana Y and Sun X W 2007 *Phys. Rev. Lett.* **99** 143003

[15] Ribierre J C, Ruseckas A, Knights K, Staton S V, Cumpstey N, Burn P L and Samuel I D W 2008 *Phys. Rev. Lett.* **100** 017402

[16] Wu T M, Brown D W and Lindenberg K 1993 *Phys. Rev.* B **47** 10122

[17] Divayana Y and Sun X W 2007 *Appl. Phys. Lett.* **90** 203509