Journal of Luminescence 131 (2011) 815–819

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Effect of distance between acceptor and donor on optical properties of composite semiconducting polymer films

Fan Kong [a,*], Jing Liu [a], Xueqin Zhang [a], Yan An [b], Xiaofeng Li [b], Baoping Lin [a], Teng Qiu [c]

[a] School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, People's Republic of China
[b] Institute of Marine Materials and Engineering, Shanghai Maritime University, Shanghai 200135, People's Republic of China
[c] Department of Physics, Southeast University, Nanjing 211189, People's Republic of China

ARTICLE INFO

Article history:
Received 7 September 2010
Received in revised form
28 September 2010
Accepted 6 December 2010
Available online 15 December 2010

Keywords:
Semiconducting polymers
Luminescence
Photophysics
Resonance energy transfer

ABSTRACT

The excitation energy transfer from poly(N-vinylcarbazole) (PVK) to tris(8-hydroxyquinoline) aluminum (Alq_3) in composite films was investigated by adding an inert polymer, poly(methyl methacrylate) (PMMA). The energy transfer efficiency calculated from the photoluminescence (PL) excitation spectra is consistent with that from the time-resolved PL decay data of the composite films. We have found a linear relationship between the two kinds of the distances, which are calculated according to volume density and the Förster theory. Experimental results and analyses provide a facile method to infer the energy transfer efficiency and the distance between the donor and the acceptor molecules in the composite films.

1. Introduction

Organic semiconductors have attracted increasing interest for their application in optoelectronic devices, such as organic light-emitting diodes (OLEDs), solid laser or solar cells [1–3]. For improving the operation properties of the optoelectronic devices, dye doping is an important and facile method [2,4–6]. Resonance energy transfer is a well known phenomenon for organic semiconductor composite films containing donor and acceptor molecules. In organic semiconductors, the interaction energy is much lower than the vibronic bandwidth. For very weak dipole–dipole interaction, the energy transfer efficiency is the inverse sixth power dependence on the distance between the donor and the acceptor based on the Förster theory [7]. Resonance energy transfer is very sensitive to the spectral overlap and the distance between the donor and the acceptor. The spectral overlap can be adjusted by modifying the chemical structures of the acceptor and the donor. Doping concentration and inserting inert spacer have been applied to control energy transfer in semiconducting polymer composite films [8,9]. Polystyrene-poly(4-vinylpyridine) diblock copolymer has been used to form micelle-isolated fluorescent species, and then pure white-light emission from a single-layer film has been realized [10,11]. White-light OLEDs have been prepared with multiple-dye-doped electrospun DNA nanofibers via controlling resonance energy transfer [12]. The energy transfer in a single organic molecule containing a donor segment and an acceptor segment is also affected by molecular conformation, in which large torsion angles restrain the energy transfer processes [13].

Poly(N-vinylcarbazole) (PVK) has been widely applied in OLEDs as a blue light-emitting layer or the donor. Many literatures have proved that the excitation energies in PVK can transfer to organic semiconductors, rare metal complex or quantum dots in composite systems [14–18]. The distance dependence of the energy transfer is contestable in semiconducting polymers. An r^{-2} distance dependence of the energy transfer has been proposed in the two-dimensional layered nanostructures of poly(9,9-dioctylfluorene) derivatives [19]. McGehee and Scully [20] believed that there was an r^{-3} distance dependence of the energy transfer in a donor/acceptor polymer heterojunction and the enhanced exciton harvesting could efficiently improve the photoconversion of organic solar cells [9,20]. Here, PVK and tris(8-hydroxyquinoline) aluminum (Alq_3) are used as the donor and the acceptor, respectively. Poly(methyl methacrylate) (PMMA) is used as a spatially separating spacer to modulate the energy transfer from PVK to Alq_3 in the composite films. Our experimental results indicate that the energy transfer efficiencies in the composite films calculated from time-resolved fluorescence decays are consistent with those from photoluminescence excitation spectra. There is a linear relationship between the two kinds of the distances, which are calculated according to volume density and the Förster theory, respectively. The experimental results infer that the aggregation of the dopant molecules heavily affects the energy transfer efficiency in the

* Corresponding author. Tel.: +86 25 52090624; fax: +86 25 52090622.
E-mail addresses: kongfan@nju.org.cn, kongfan@seu.edu.cn (F. Kong).

0022-2313/$ - see front matter Crown Copyright © 2010 Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.jlumin.2010.12.009

organic semiconductor composite film and also makes the distance dependence of the energy transfer more controversial.

2. Experimental

PVK and PMMA (from Acros Organics) were used as received without purification. The average molecular weights (M_w) of PVK and PMMA were 90,000 and 50,000, respectively. Alq_3 was synthesized in our laboratory and was purified via recrystallization in acetone. PVK and PMMA were dissolved in THF to form the solutions with the concentration of 2 mg/ml. The two kinds of the polymer solutions were blended with different proportions. The weight ratios of PMMA to PVK in the blend polymer solutions were 0%, 25%, 50%, 100%, 200%, 300%, 400% and 500%. Alq_3 was dissolved in THF to form the solution with the concentration of 1 mg/ml. The Alq_3 solution was added into the blend polymer solutions and the weight ratio of Alq_3 to PVK was maintained to be 8%. The blend solutions containing PVK, PMMA and Alq_3 were spin-coated on glass substrates to form composite films. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra of the composite films were obtained by using a FluoroMax-2 fluorescence spectrophotometer. The time-resolved PL decay data were measured on an Edinburgh FLS 920 fluorophotometer equipped with a time correlated single-photon counting (TCSPC) card. All experiments were prepared at room temperature in atmosphere.

3. Results and discussion

Since the absorption spectrum of Alq_3 well overlaps with the emission spectrum of PVK, the effective resonance energy transfer occurs between them in the composite film [21]. Fig. 1 shows the PL spectra of the PVK/Alq_3(8%)/PMMA composite films, in which the weight ratio of Alq_3 to PVK is a constant of 8% and the weight ratio of PMMA to PVK is increased from 0% to 500%. There are two emission bands with the PL peaks at 380 and 500 nm, corresponding to the emissions from PVK and Alq_3, respectively. The inset in Fig. 1 describes the PL intensity at 500 nm relative to that at 380 nm. It can be seen that the relative PL intensity at 500 nm is decreased with increase in the content of PMMA. As the composite films are photoexcited at 320 nm, the emission from Alq_3 mainly originates from resonance energy transfer from PVK since the concentration of Alq_3 is very low [17,21]. So, the relative PL intensity at 500 nm, which is the emission from Alq_3, infers the energy transfer efficiency of the PVK/Alq_3(8%)/PMMA composite films. As the content of PMMA is increased in the composite films, the concentrations of PVK and Alq_3 are decreased, and then the distance between the donor (PVK) and the acceptor (Alq_3) is enlarged. Normally, the energy transfer efficiency heavily depends on the distance between the donor and the acceptor molecules. The decreased PL emission from Alq_3 indicates that the energy transfer efficiency is reduced because the added PMMA makes the donor and the acceptor separated in the composite films.

The effect of the enlarged distance between PVK and Alq_3 on the resonance energy transfer can be elucidated by the PLE spectra of the composite films. Fig. 2 shows the PLE spectra of the composite films measured at the monitoring emission wavelength of 500 nm, which is the emission from Alq_3. There is only one PLE band with a peak at 390 nm in the PLE spectrum of the Alq_3 film, whereas, two PLE bands with peaks at 343 and 390 nm appear in the PLE spectra of the composite films. The 343-nm PLE band is corresponding to the electron transition in PVK and the 390-nm PLE band is connected with the electron transition in Alq_3. The PLE results indicate that the photoexcitation in PVK contributes to the emission from Alq_3 as the composite films are photoexcited at the wavelength of the absorption maximum of PVK. The inset in Fig. 2 shows the PLE intensity at 343 nm relative to that at 390 nm. The relative PLE intensity at 343 nm is obviously decreased as the PMMA content is increased, implying that the resonance energy transfer from PVK to Alq_3 is restrained. The addition of the inert polymer increases the distance between the donor and the acceptor. Thus, the energy transfer efficiency in the composite film is acutely decreased due to the increased distance caused by the inert polymer.

The energy transfer efficiency of the composite films can be proved by the time-resolved PL decays of the PVK/Alq_3(8%)/PMMA composite films obtained by pumping at 343 nm and probing at 405 nm, which are corresponding to the absorption and emission maxim of PVK without the dopant, respectively. The experimental results are shown in Fig. 3. It can be seen that the time-resolved PL

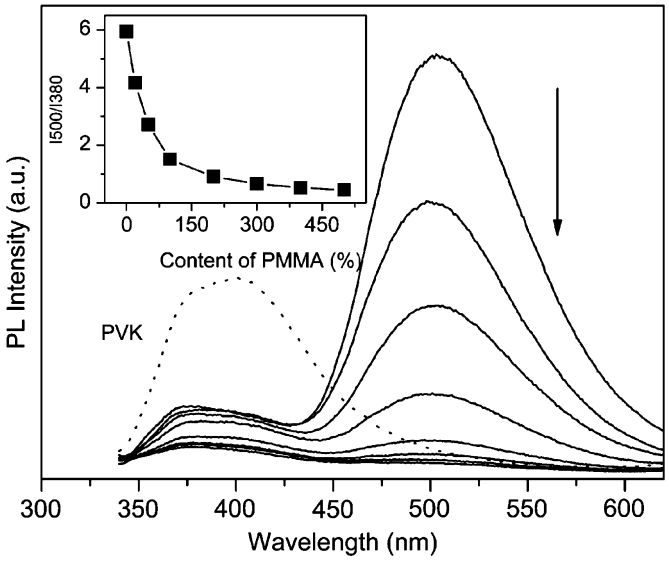

Fig. 1. PL spectra of the PVK film (dotted line) and the PVK/Alq_3(8%)/PMMA composite films (excitation at 320 nm). The weight ratio of PMMA to PVK is increased from 0% to 500% as the arrow shows. The inset is the PL intensity at 500 nm relative to that at 380 nm with increase in the content of PMMA.

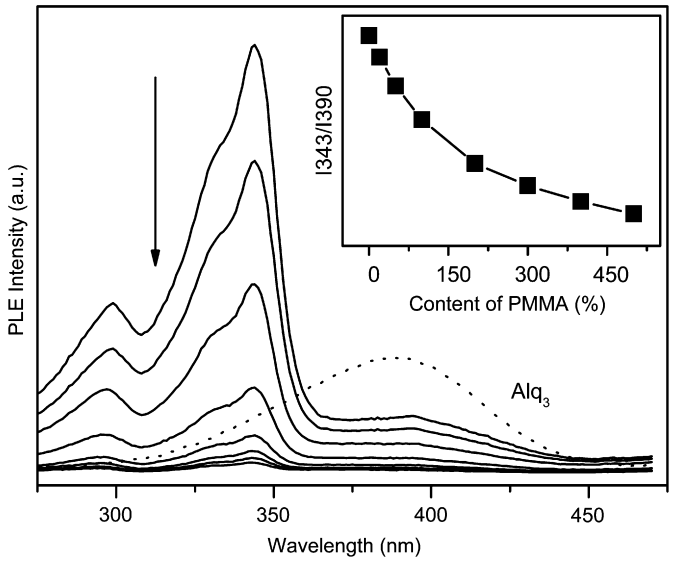

Fig. 2. PLE spectra of the Alq_3 film (dotted line) and the PVK/Alq_3(8%)/PMMA composite films. The weight ratio of PMMA to PVK is increased from 0% to 500% as the arrow shows. The inset is the PLE intensity at 343 nm relative to that at 390 nm with increasing the content of PMMA.