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Photoinduced energy transfer in blend films of hole and electron transport materials

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ABSTRACT

The photoluminescence properties of the blend films consisting of the hole transport and electron transport materials, PVK and Alq_3, are studied by steady-state and time-resolved photoluminescence (PL) spectroscopy. Both the relative intensity and the photoluminescence lifetime are intensively dependent of the weight ratios of PVK and Alq_3. The detailed analysis of experiment data provides clear evidence for a Förster energy transfer from excited PVK, as donor, to Alq_3, as acceptor, based on nonradiative resonant transfer mechanism, and allows the determination of Förster radius and the concentration dependent energy transfer efficiency.

1. Introduction

Since Tang and VanSlyke demonstrated a high-efficiency organic light emitting diodes (OLEDs) consisting of multilayer structures with hole transport layers (HTL) and electron transport layers (ETL) [1,2], OLEDs have been particularly interesting because of their potential applications in new flat-panel display technology. However, the molecular diffusion at organic–organic interfaces cannot be avoided in the OLEDs consisting of multilayer structures, because the OLEDs become hot as a result of Joule heating when an electron current is applied [3]. Therefore, the luminescence properties and mechanism of the blend organic thin films (resembling the diffused layer) become particular interesting. Moreover, mixing the two materials of HTL and ETL as emitting layer can effectively balance charge injection and transport [4], reduce the electric field across the discrete HTL/ETL interface and decrease the probability of Joule heating, thereby increasing the lifetime of the device. However, there are rarely detail report about photoluminescence properties of the blend films of HTL and ETL.

Here, the blend films of poly(*N*-vinylcarbazole) (PVK) and tris(8-hydroxyquinoline)aluminum (Alq_3) was used as the test material. PVK has attracted considerable attention due to its specific electronic properties and photoconductive properties [5]. Containing the positive charge transporting carbazole pendant groups, PVK is now extensively used as the HTL and host material and is one of the most interesting materials in OLEDs [6–9]. Furthermore, Alq_3 is the most widely employed electron transport and emission layer in commercial OLEDs [10].

In this report, we investigate the photoluminescence properties of the blend films of PVK and Alq_3 with various weight ratios by the steady-state and time-resolved PL spectroscopy. It is found that the efficient Förster energy transfer occurs from excited PVK, as donor, to Alq_3, as acceptor, which can enhance the PL quantum efficiency of the blend films. Energy transfer process is of considerable importance because it can affect the dynamics of the excitation in lighting devices. So it is essential to understand the energy transfer mechanism, which may also be important in designing and optimizing the structure [11,12].

2. Experiment

Samples are prepared using commercially available PVK (Express Technology Co., Ltd., $M_w \approx 90{,}000$) and Alq_3 (eLight Co.). PVK and Alq_3 are dissolved in chloroform at the concentration of 10 and 2 mg/ml, respectively, and are mixed in different weight ratios of Alq_3 and PVK. The weight ratios of the Alq_3 and PVK chosen in this work are 1:5, 1:10, 1:50 and 1:100. Then the blend films are prepared by spin-coating at 3000 rpm for 60 s. The thicknesses of the blend films are about 650 nm to 1 μm measured by atomic force microscopy, which utilizes the difference of cantilever deflection in the presence and absence of the blend film between tip and substrate.

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Absorption spectra are measured with SP-723 Vis Spectrophotometer and steady-state PL spectra are recorded on a Varian Cary Eclipse fluorometer employed a xenon lamp for excitation. Time-resolved PL spectra are recorded by a spectrometer (Bruker Optics 250IS/SM) with intensified charge coupled device detector (IStar 740, Andor). The excitation source utilized is the laser pulse of ~110 fs duration generated by Ti: Sapphire regenerative amplifier (Spectra-Physics, Spitfire) with a repetition rate of 83 Hz. Instrument response time is 2 ns by recording the scattered laser light from a ground glass surface. All measurements are carried out at room temperature under ambient atmosphere.

3. Results and discussion

Fig. 1 shows the absorption spectra of Alq_3, PVK, and the blend films with various weight ratios. The weight ratios of Alq_3 and PVK are: (a) pristine Alq_3; (b) 1:5; (c) 1:10; (d) 1:50; (e) 1:100 (Alq_3:PVK); and (f) pristine PVK. PVK shows two electronic absorption maxima at 332 and 345 nm while Alq_3 exhibits the broad absorption bands due to π–π^* transitions around 350–450 nm. The blend films show the absorption peaks corresponding to both Alq_3 and PVK, and their relative intensities are varied depending on the weight fractions of the two materials. The absorption spectra of the blend films show that there is no the inhomogeneous broadening due to blending. Meanwhile, neither distinct phase separation nor layer formation from the observation of an atomic force microscopy (AFM) image is present in the blend films. A large spectral overlap between the PVK emission and the Alq_3 absorption shown in Fig. 2 reveals that efficient excitation energy transfer could take place from the donor PVK molecules to the acceptor Alq_3 molecules. The overlap integral, Ω, is given in wavelength form as [13]:

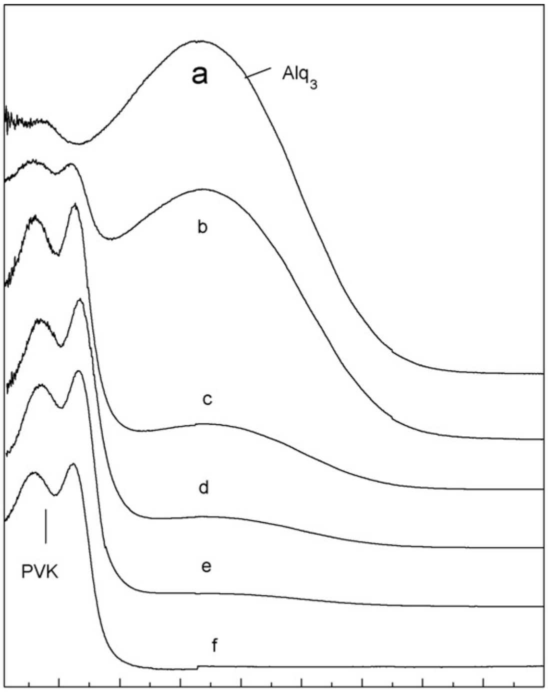

Fig. 1. Absorption spectra of (a) Alq_3, (b)1:5, (c)1:10, (d) 1:50, (e) 1:100 (Alq_3:PVK) blend films, and (f) PVK thin films.

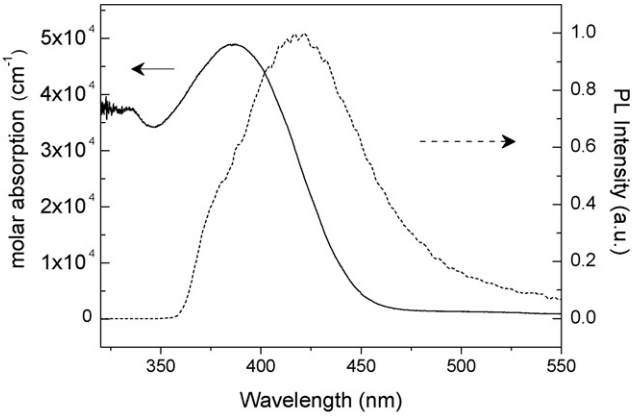

Fig. 2. PL emission spectrum of PVK (dashed line) and molar absorption spectrum $\varepsilon(\lambda)$ of Alq_3 (solid line).

$$\Omega = \int_0^\infty \mathrm{PL}(\lambda)\varepsilon(\lambda)\lambda^4\,d\lambda \tag{1}$$

where λ is the wavelength of light, $\varepsilon(\lambda)$ is the molar absorption spectrum of the acceptor and $\mathrm{PL}(\lambda)$ is the donor fluorescence spectrum normalized on the wavelength scale according to

$$\int_0^\infty \mathrm{PL}(\lambda)\,d\lambda = 1 \tag{2}$$

The overlap integral is determined from isotropic fluorescence emission and absorption spectra of PVK and Alq_3, respectively. $\varepsilon(\lambda)$ (Fig. 2) of solid film sample is determined assuming a homogeneous chromophore concentration and a constant film thickness over the entire sample. The overlap integral, Ω is integrated using Eq. (1) and obtained to be $6.19 \times 10^{-14}\ \mathrm{cm^3\ L\ mol^{-1}}$. Therefore, the Förster radius R_0 is calculated from [14]:

$$R_0^6 = \frac{9000(\ln 10)\kappa^2\Phi_D^0}{128\pi^5 N_A n^4}\Omega \tag{3}$$

to be about 37.7 Å. In our case, $\kappa = 2/3$ is the orientation factor, $n \approx 1.7$ is the average refractive index of the donor PVK [15], and assuming $\Phi_D^0 \approx 1$ is the fluorescence quantum yield of PVK [16]. The value of R_0 is fully consistent with the expected Förster-type transfer (typical Förster radii are between 20 and 50 Å [17]). The relatively large R_0 will result in a much faster energy transfer rate k_{ET} which is proportional to R_0^6 [18].

Fig. 3 shows the steady-state photoluminescence (PL) spectra of the blend films of Alq_3 and PVK with various weight ratios, excited at 350 nm which is strongly absorbed by PVK. The fluorescence peaks at 418 and 508 nm are due to PVK and Alq_3, respectively. If no significant interaction occurs between the PVK and Alq_3 molecules in the blend films, the emission spectra of blend films should be a weighted superposition of the fluorescence peak of the individual components. However, the emission at about 508 nm dominates even at the lowest concentration of Alq_3 (Alq_3:PVK = 1:100) in the blend films. PVK emission at about 418 nm in the blend films is much weaker than the pristine PVK, and as the content of Alq_3 increases, emission from the host molecule PVK decreases. These results suggested that the energy transfer occurred from excited PVK, as donor, to Alq_3, as acceptor. The efficiency of the energy transfer, Ω, can be determined from steady-state by the equation of [19]:

$$\Phi_I = 1 - \frac{I_p}{I_0} \tag{4}$$