

PHOTOCONDUCTIVE PROPERTIES OF PVK:Alq₃ BLEND FILMS STUDIED BY STEADY-STATE AND TIME-RESOLVED TRANSIENT PHOTOCURRENT SPECTRA*

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Abstract The carrier transport properties of the blends of the hole transport material poly(*N*-vinylcarbazole) (PVK) and the electron transport material tris (8-hydroxyquinolinolato) aluminum III (Alq₃) are investigated at room temperature using steady-state and time-resolved transient photocurrent measurements as a function of doping concentration of Alq₃. Due to lower LUMO and higher HOMO energy level of Alq₃ than those of PVK, Alq₃ molecules may act as carrier trap states in PVK films at low concentration. However, at high concentration of Alq₃, phase separation reduces trap states to some extent, which leads to the rise of photocurrent. It is concluded that strong excitation transfer from PVK to Alq₃ does harm to photocurrent, because strong fluorescence effect of Alq₃ inhibits photogeneration of charge carriers. In time-resolved transient photocurrent measurements, it is found that the decay time is obviously shortened because the recombination rate increases and the electron mobility of Alq₃ is higher than the hole mobility of PVK.

Keywords: Steady-State photocurrent; Transient photocurrent; Polymer.

INTRODUCTION

Polymers have been extensively studied for their optoelectronic and electronic properties for device development, including light emitting diodes (LED)^[1] and photovoltaic (PV) cells^[2], *etc.* Especially, the prospect of developing photovoltaic cells using polymers as the active media has attracted significant interest due to polymers' low cost, convenience and mechanical flexibility. It has been known that polymers are low mobility materials, and for disordered organic materials, charge carriers are localized in potential wells formed by single molecules or conjugated molecular segments. Concomitantly, charge transport occurs only *via* carrier hopping within a positionally random and energetically disordered system of localized states^[3,4]. The discovery of efficient charge transfer across a conjugated polymer/fullerene interface paved the way for technological breakthrough in the design of organic photovoltaic devices^[5–10]. Another concept which has been demonstrated is the use of interpenetrating polymer networks for efficient charge carrier separation and transport^[11,12].

Despite the fact that the performance of polymer optoelectronic devices has been improved greatly, the mechanism for charge carrier transport in organic or polymer materials systems remains ambiguous. An analytical model of the equilibrium hopping conductivity in a disordered organic semiconductor at large charge carrier densities has been formulated by Arkhipov *et al.*^[13]. However, the case of low doping or moderate

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doping is also important for application. In present work, doped poly(*N*-vinylcarbazole) (PVK) thin film devices were fabricated. PVK is a well-studied hole transporting material with a band gap of 3.5 eV. Tris (8-hydroxyquinolinolato) aluminum III (Alq_3) was introduced as an electron acceptor and an electron transporting material.

EXPERIMENTAL

The devices studied in this work consist of a single active layer sandwiched between the anode (ITO) and the cathode (Al). The active layer was composed of PVK polymer blended with different concentrations of Alq_3 (5%, 10%, and 20% by weight). The samples were prepared by spin-coating the blend solution in chloroform onto an ITO-coated glass substrate. The Al top electrodes were thermally evaporated through a shadow mask at a typical pressure of 10^{-3} Pa. The blend films were homogeneous with thickness about 70 nm, depending on details of the spin-casting conditions (solution concentration, spin speed, *etc.*). The active area of each test devices was *ca.* 2 mm². All devices have been encapsulated in glove box. The undoped PVK film device also was fabricated in the same process for comparison.

For steady-state photocurrent measurement, electrical data were obtained with a Keithley 2410 Source Measure Unit. The excitation source was a Xe lamp. The light dispersed using a monochromator in the Fluorolog-3 Spectrometer was focused onto the ITO side of the devices. Positive voltage is defined as ITO electrode biased positively. For time-resolved transient photocurrent measurement, the resulting photocurrent was detected with a digital Tektronix oscilloscope (TDS 540D). The samples were illuminated by a YAG Laser of Surelite SSP-2 from the Continuum Company through the ITO electrode. Wave-mode atomic force microscopy (AFM) measurements were carried out on the blend films on substrates coated ITO in order to observe the morphology.

RESULTS AND DISCUSSION

Absorption spectra of PVK: Alq_3 blend films with different concentrations, along with absorption spectrum of undoped PVK, are shown in Fig. 1(a). With the increasing concentration of Alq_3 , the absorption from Alq_3 becomes stronger. Absorption spectrum of blends at each concentration can be fitted to a linear combination of the absorption spectra of the two components, which indicates that ground-state charge transfer (CT) does not occur in the mixture^[14]. Figure 1(b) shows the photoluminescence (PL) spectra for undoped PVK and PVK: Alq_3 blends at three different concentrations with the excitation wavelength of 340 nm. The PL quenching of PVK indicates that efficient energy transfer occurs from PVK to Alq_3 ^[15]. Because of energy transfer, PVK photoluminescence is not visible for concentration above 5%. In later discussion, it is noted that this excitation transfer from PVK to Alq_3 is harmful to the yield of the photocurrent.

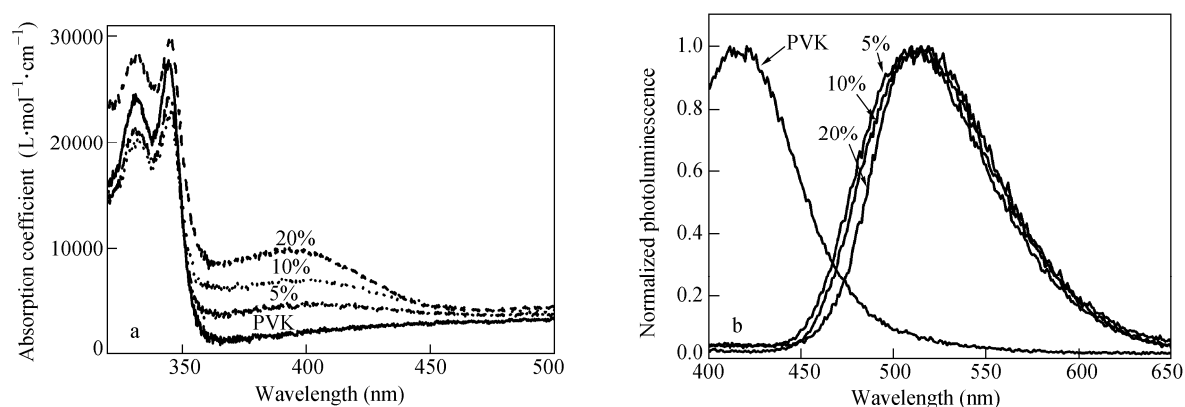


Fig. 1 The absorption spectra (a) and the photoluminescence spectra (b) of the undoped PVK and the blend films of PVK: Alq_3 at the concentrations of 5%, 10% and 20%

Figure 2 shows normalized short-circuit photocurrent response spectra of undoped PVK and blend films at three different concentrations of Alq₃, and the inset presents the changes of the photocurrent peak at 340 nm which is attributed to PVK and the changes of the peak at 390 nm which is attributed to Alq₃. As it is expected, with the increasing concentration of Alq₃, photocurrent around 390 nm becomes stronger, due to the increasing absorption of Alq₃ in blend films (Fig. 1a). However, compared with that of PVK, the photocurrent peak of Alq₃ is much lower. It is not only because the weaker absorption of Alq₃ for the excitation light of 340 nm, but also because Alq₃ has strong fluorescence effect, which competes with photogeneration of charge carrier. Besides, in the blend films, the energy offset between Alq₃ and PVK is not favorable for the transport of charge carriers on Alq₃ (Fig. 3). This point will be discussed later in detail.

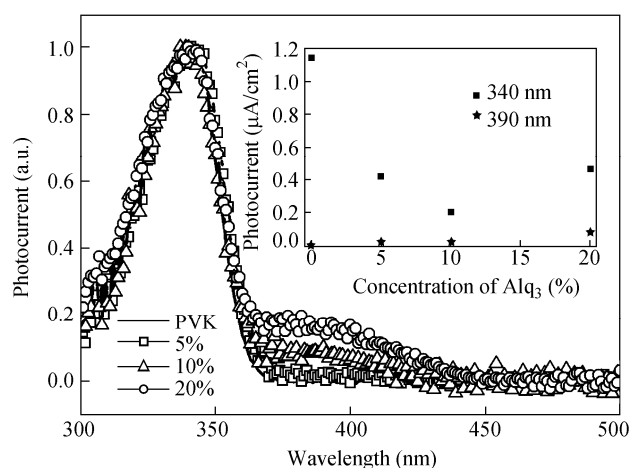


Fig. 2 The steady-state photocurrent spectra of undoped and doped devices. The inset shows the intensity of the peak photocurrent at 340 nm and 390 nm at different concentrations of Alq₃.

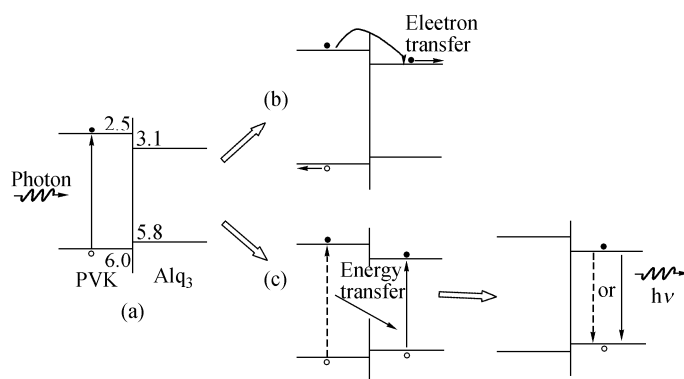


Fig. 3 Steps for energy transfer or charge transfer and transport in PVK:Alq₃ blend films. a) Photogeneration of exciton in PVK upon absorption; b) Electron transfer from PVK to Alq₃, leaving an electron on Alq₃ and a hole on PVK; c) Energy transfer from PVK to Alq₃, followed by non-recombination or recombination on Alq₃ molecules; The process (b) does contribution to photocurrent, but during the transport of electrons and holes, LUMO and HOMO of Alq₃ may act as electron or hole traps for mobile charge carriers; The process (c) competes with (b) and does harm to photocurrent.

For the photocurrent peak at 340 nm which corresponds to the absorption peak of PVK, a sharp decrease occurs at the concentrations of 5% and 10%, while a remarkable increase occurs at 20% Alq₃ concentration. According to the band diagram of the PVK/Alq₃ interface at equilibrium (Fig. 3), the band gap of Alq₃ is narrower than that of PVK, and its lowest unoccupied molecular orbital (LUMO) and the highest occupied

molecular orbital (HOMO) energy levels are located between the LUMO and HOMO of PVK. It is thus to be expected that the Alq₃ will ionize more easily and therefore act as electron and hole traps if it presents in small quantities. Exciton or charge carriers transferred from PVK to Alq₃ *via* energy or charge transfer may be trapped by Alq₃ molecules and localized at the HOMO or LUMO energy level of Alq₃. Due to much small aggregation scales of Alq₃ molecules at low concentrations, it is difficult for charge carriers trapped in localized states to be transported to respective contacts. Eventually these trapped carriers relax back to the ground states *via* recombination or non-recombination on Alq₃ molecules. However, it is energetically favorable for the electron to transfer from PVK to Alq₃ according to energy diagram (Fig. 3), which produces a charge-separated state with an electron on the Alq₃ and a hole on the PVK. When the concentration of Alq₃ is raised up to 20%, the concentration is high enough to form some of phase separation in blend films. Figure 4 illustrates the surface morphology of the film made with a blend of PVK:Alq₃ (20%) as determined by atomic force microscope (AFM) in the wave-mode. According to AFM image, there is a little phase separation. A possibility for the unobvious phase separation is suggested: both PVK and Alq₃ are the organic materials, the phase separation may not be as distinct as that between the organic and inorganic materials. If both PVK and Alq₃ are present at the top surface of the film, they are intimately mixed^[16].

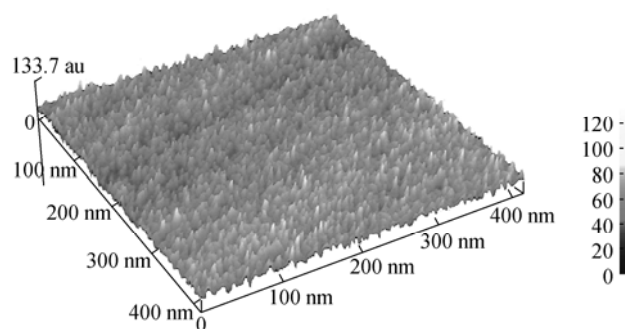


Fig. 4 Wavemode AFM image of a blend of PVK and Alq₃ (with the Alq₃ concentration of 20%) spin-coated on the ITO-glass. The lateral scale is about 400 nm × 400 nm.

Phase separation can provide pathways for charge carrier transport to the electrodes^[12, 17]. Therefore, phase separation raises the photocurrent peak at 340 nm of the blend film at 20% Alq₃ concentration. Figure 3 illustrates the processes for energy transfer or charge transfer and transport in PVK:Alq₃ blend films. After absorption in PVK, the motion of charge carriers can be classified into two processes. The first is shown in Fig. 3(b), in which an electron transfers from PVK to Alq₃ and a hole remains on PVK. Then, a built-in potential drives hole and electron to respective contacts. During the transportation of hole and electron, trap states formed by the LUMO and HOMO energy level of Alq₃ molecules may reduce the photocurrent. The second process is another possible way for the reduction of photocurrent as shown in Fig. 3(c). Bound hole-electron pairs transferred to Alq₃ *via* energy transfer mostly recombine instead of dissociating into free charge carriers, due to strong fluorescence effect of Alq₃ and unfavorable energy offset for the dissociation of excitons on Alq₃. The dissociation of excitons on Alq₃ at the interface between PVK and Alq₃ is not available because of the interface barrier for electron and hole transfer from Alq₃ to PVK. However, once the concentration of Alq₃ is high enough to form phase separation, *i.e.*, electron transition can occur within some clusters, the process (c) is inhibited and the number of trap states declines. The photocurrent attributed to PVK therefore goes up. Generally, an enhancement of the photocurrent in a photocell can be attributed to the improved photogeneration of free charges and/or transportation of charge carriers^[18]. In the PVK:Alq₃ system, energy transfer caused by doping Alq₃ in PVK inhibits the photogeneration of charge carriers, and the reduced trap states by the aggregation of Alq₃ at a high concentration, therefore, explain the enhancement of the photocurrent.

Due to transient measurements offering an avenue for obtaining the desired information about the motion of charge carrier, further research was carried out in the transient photocurrent measurements for 4 photocells, ITO/PVK:Alq₃ (5%, 10%, and 20%)/Al and ITO/PVK/Al. The wavelength of laser light is 355 nm and the pulse width duration of the light is about 4.7 ns. Figure 5 shows time-resolved transient photocurrent responses with reverse polarity (−2 V). With the reverse polarity, the injection current can be neglected. For thin-film devices (the thickness < 100 nm), it is assumed that the external electric field applied is considered as a constant in the whole active layer. Thus, the effect of external electric field is neglected. The time-resolved transient photocurrent follows a extended exponential decay as: $I(t) = I_0 \exp[-(t/\tau)^\gamma]$, in which τ is defined as the decay time of the photocurrent. Inset in Fig. 5 shows the fit to a extended exponential model. In our experiments, all of the values of γ for 4 samples are fitted as 0.66, and the relevant τ are listed in Table 1.

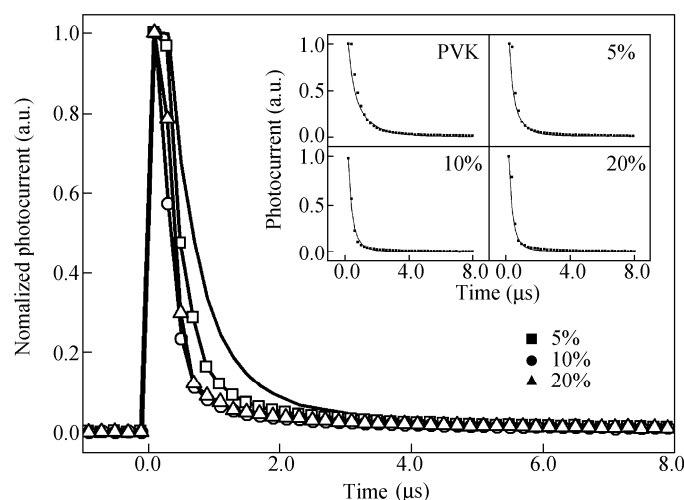


Fig. 5 Transient photocurrent of undoped and doped PVK devices using $\lambda = 355$ nm, 4 ns pulsed laser
The inset shows the fit to a stretched exponential model.

Table 1. The fitted value of decay time τ for 4 photocells, ITO/PVK:Alq₃ (5%, 10% and 20%)/Al and ITO/PVK/Al

	Undoped PVK	5%	10%	20%
τ (μ s)	0.45	0.25	0.16	0.18

The decay of the photocurrent is determined by the photogeneration rate (Fig. 3b) and recombination rate of charge carriers (Fig. 3c). Increasing photogeneration rate can enhance the photocurrent, while increasing recombination rate can reduce it. In lower concentration range, due to the excitation transfer and the strong fluorescence effect of Alq₃, with the increasing concentration of Alq₃, the trapped excitons or charge carriers increase, which leads to the rise of recombination rate on Alq₃ molecules. Therefore, the decay of photocurrent is strengthened at the concentrations of 5% and 10%. At the high Alq₃ concentration of 20%, however, the decay rate reduces since phase separation inhibits the recombination on Alq₃ and enhances the photogeneration on PVK. In fact, the slight increase of the decay of the photocurrent mismatches the obvious enhancement of photocurrent at the concentration of 20%. It is because there is another factor which determines the decay time of average photocurrent. It is the drift mobility of mobile charge carriers. Depending upon properties of PVK:Alq₃, the photocurrent can be carried by hole and/or electron^[3]. With the increasing concentration of Alq₃, the photocurrent in the photocell begins to be partly carried by electrons. The hole mobility in PVK deduced from the time of flight by several groups^[19–21] is between 10^{-7} and 10^{-6} cm²V⁻¹s⁻¹. The electron mobility of Alq₃ is between 10^{-6} – 10^{-5} cm²V⁻¹s⁻¹ against its hole mobility of 10^{-8} cm²V⁻¹s⁻¹^[22–24]. Due to higher electron mobility of Alq₃ than hole mobility of PVK, the increasing concentration of Alq₃ leads to the rise of the average carrier

velocity and the decrease of the decay time of the photocurrent. In lower concentration range, since pathways in Alq₃ still does not occur, electron mobility has little effect on the decay of photocurrent. Once phase separation forms pathways at high concentrations, electron mobility in Alq₃ will function in blend films. Therefore, the decay of the photocurrent becomes weaker.

CONCLUSIONS

The charge carrier transport properties of blends of PVK and Alq₃ at the different concentrations of 5%, 10% and 20% have been investigated by steady-state and time-resolved transient photocurrent measurements. As a good electron-transporting organic material, the energy level of Alq₃ can match that of PVK to form an interface for exciton dissociation. However, the lower LUMO and the higher HOMO of Alq₃ than those of PVK allow Alq₃ to act as trap states in the PVK film in lower concentration range, which leads to the decline of the photocurrent. However, at high concentration, phase separation can reduce trap states and inhibit recombination of electron-hole pairs on Alq₃. Therefore, for composite systems, the concentration threshold of dopant is one of important factors which determine the photocurrent. Besides, the excitation transfer from PVK to Alq₃ does harm to the photocurrent of the blend film systems due to strong fluorescence effect of Alq₃. Accordingly, the fluorescence effect of electron-transporting dopants must be of a serious consideration.

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