Evidence of Photocarrier Generation via the Singlet and Triplet States in a Poly(*N*-vinylcarbazole) Film

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A significant wavelength dependence of the excitation light was observed in the magnetic field effects (MFE) on the photocarrier generation of a benzene-1,2,4,5-tetracarbonitrile-doped poly(*N*-vinylcarbazole) film. The excitation of the carbazole induces positive MFEs, indicating an enhancement of the photoconductivity originating from the charge separation through the triplet exciton. In contrast, a singlet spin state governs the photocarrier generation in the case of the charge transfer band excitation, because negative MFEs are induced.

Electron spin is a subject of study that is attracting interest in the modern technology of organic electronics. It is recognized, for example, that the triplet state plays an important role in the efficient emission from electro-luminescent materials.[1] Also, there has been a renewal of interest in the spin effect in photoconductors.[2] Recently, using time-resolved electron spin resonance (TRESR)[3] and magnetic field effect (MFE)[4] experiments, we have studied the carrier generation mechanism of electron acceptor-doped poly(*N*-vinylcarbazole) (PVCz) thin films. It has been concluded that the photocarrier is generated by stepwise short-range hole hops. Based on a one-dimensional lattice model, in which the hole hops among the nearest carbazole (Cz) sites while holding the electron spin angular momentum, it is pointed out that the external magnetic field can more effectively influence the dynamics of short distance electron–hole (e–h) pairs than the electric field.[5] This property reminds us that the magnetic field interacting with the spins of e–h pairs may effectively control the photoconductivity in aromatic polymer films. Hence, to clarify the influence of the initial spin dynamics on the magneto-photoconductivity, we have investigated the excitation wavelength (λ_{ex}) dependence of MFE on the photocarrier generation yield of a benzene-1,2,4,5-tetracarbonitrile (BTCN)-doped PVCz film.

A 2.2 mol % BTCN-doped film sample with a thickness of 13 μm was prepared using a cast method. The film sample was inserted between a transparent anode of Indium Tin Oxide (ITO) and a semitransparent cathode of Au for the measurements of the photocarrier generation yield at room temperature. Details of the sample preparation and the measurement system have been described in a previous paper.[4b] Lasers with a half-width-at-half-maximum (HWHM) of 1.6 ns (Continuum, SL-OPO, $\lambda_{ex} = 420$–690 nm) and with an HWHM of 4.3 ns (Continuum, ML-II, $\lambda_{ex} = 355$ and 532 nm) were used as the pulse light source. The light with a density of 5–8 $\times 10^{14}$ photons/pulse/cm^2 was perpendicularly led on the film plane from the ITO electrode side. This irradiation condition was approximated to a uniform excitation along the applied electric field of 6.1×10^4 V/cm.

Figure 1a shows the optical absorption spectrum of the BTCN-doped PVCz film. The absorption band from 310 to 360 nm is attributed to the first absorption band to a singlet exciton of the carbazoles (Cz) at the side chains. The broad band observed in the region longer than 380 nm is assigned to the charge-transfer (CT) complex between BTCN and the neighboring Cz, in which the charges are partly separated.[6] Irradiation by laser light with $\lambda_{ex} \geq 650$ nm did not induce significant signals owing to the hole transportation. The photocharge signals were observed by excitation with $\lambda_{ex} < 650$ nm (Figure 1b). In the photocharge signals, there are a fast rising component formed at an early time and an almost flat component.[7] The fast rising component is proportional to the positive charge quantity due to the holes that have escaped from the recombination of the geminate e–h pair, and captured in trap sites or blocked at the cathode. Therefore, the value of the photocharge signal at 16 ns is regarded as the relative number of photocarriers. The photocharge signal increased in intensity with the decrease in λ_{ex}. The relative quantum yield of the photocarrier estimated from the observed photocharge signal and the absorbed photon numbers are shown in Figure 1c. The photocarrier generation yield is almost independent of λ_{ex} within the CT-band, but it slightly increases with UV irradiation, in which the Cz side chains are excited. The present results seem to suggest that the photocarrier generation efficiency depends on the electronic excited state rather than the vibrational energy, the so-called excess

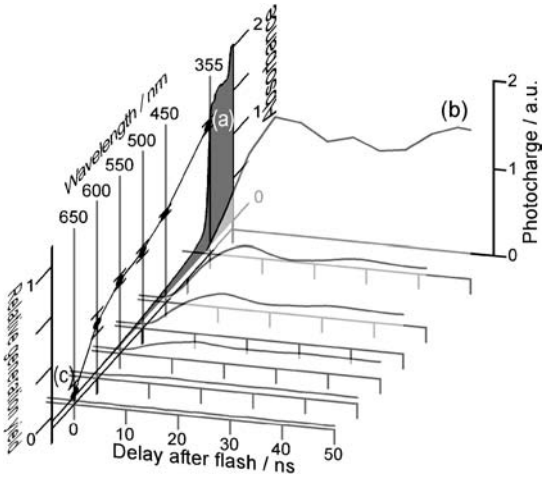


Figure 1. (a) Absorption spectrum, (b) time profiles of photoinduced charge signals, and (c) wavelength dependence of the relative photocarrier generation yield for the BTCN-doped PVCz film observed at a magnetic field of 0.00 mT at room temperature.

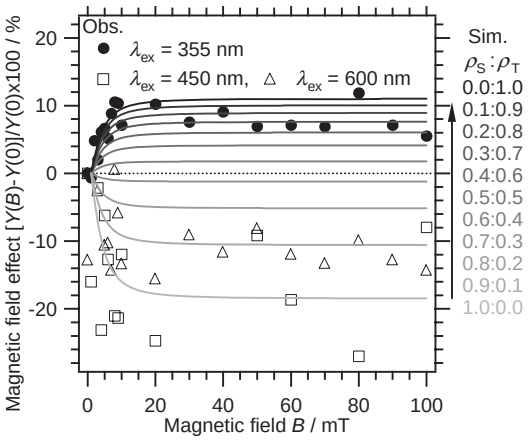
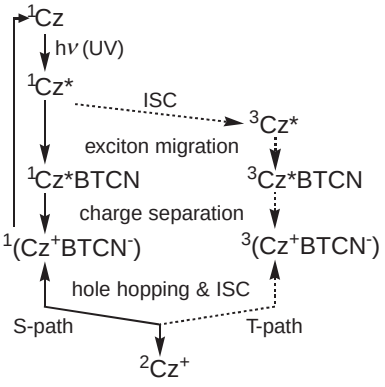


Figure 2. Excitation wavelength dependence of MFEs on the photocarrier generation yield of the BTCN-doped PVCz film. Simulations were obtained using the SLE equations for the one-dimensional lattice model that consisted of eleven e–h pair sites with the recombination and hopping rate constants of 2.0×10^8 and $4.5 \times 10^8\ s^{-1}$, respectively, and a series of exchange coupling constants of $|J_1| = 1 \times 10^{12}$, $|J_{2-11}| < 1 \times 10^8$ rad/s.

thermal energy.

The photocarrier generation yield was also affected by the magnetic field. In Figure 2, the typical MFE on the photocarrier generation yield is depicted. The generation yield steeply changed in the low field range and was saturated above 10 mT. Such behavior of the MFE arises from the hyperfine mechanism of the e–h pairs having a relatively long separation distance. The negative MFE was observed when λ_{ex} was within the CT-band, meaning a decrease in the photocarrier yield by the magnetic field, although they were slightly scattered. On the other hand, the Cz-excitation resulted in an increased photocarrier yield. The observed negative and positive MFEs prove the photocarrier generation from the singlet and triplet states, respectively. The singlet-generation of the photocarrier in the CT-excitation is reasonable, because the CT-excitation produces a hole ($^2Cz^+$) via a contact e–h pair ($^1(Cz^+BTCN^-)$) directly produced from the singlet CT complex ($^1(Cz^{\delta+}BTCN^{\delta-})$). During the Cz-excitation, the existence of both singlet- and triplet-born e–h pairs was confirmed by TRESR measurements. Therefore, it is concluded that the Cz-excitation includes two pathways which are the S- and T-paths indicated by the solid and dashed arrows in the Scheme 1, respectively.



Scheme 1.

The singlet exciton of Cz ($^1Cz^*$) not only migrates among the Cz groups, but also alters the spin multiplicity to the triplet within the lifetime of $^1Cz^*$.[8] The triplet exciton ($^3Cz^*$) can also travel among the Cz groups.[9] Because the $^1Cz^*$ and $^3Cz^*$ have energies higher than the contact e–h pairs (Cz^+BTCN^-), the encountering of excitons with BTCN ($^{1,3}Cz^*BTCN$) may cause a charge separation and produce a contact $^{1,3}(Cz^+BTCN^-)$. Finally, $^{1,3}(Cz^+BTCN^-)$ generates $^2Cz^+$ by stepwise hole hops. It should be noted that the charge recombination takes place on the way of the S-path, which is the origin for the spin effect on the photocarrier generation yield. The magnetic field affects the intersystem crossing (ISC) rate between the distant singlet and triplet e–h pairs. Because the magnetic field depresses the ISC in the distant e–h pairs, the MFE for the S-path shows a decrease in the $^2Cz^+$ yield, which is the same as the CT-excitation. On the other hand, the reduction of the ISC from the distant e–h pairs in the T-path enhances the $^2Cz^+$ yield.

For the sake of a quantitative estimation of the contribution of the S- and T-paths in the observed MFEs, we performed simulations for the e–h pair dynamics based on the spin conservative hole hops in the one-dimensional lattice model using the Stochastic–Liouville equations (SLE). The calculated curve for the pure S-path reproduced the negative MFE observed in the CT-excitation. MFEs considering both contributions of the S- and T-paths were calculated and the increase in the T-path contribution increased the positive effect. The simulations with the T-path contribution of more than 50% fit well with the observe MFE.

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