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Extrinsic Carrier Photogeneration in Poly(*N*-vinylcarbazole) Films Doped with Dimethyl Terephthalate

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Based upon the previously reported experimental results that the exciplex fluorescence of poly(*N*-vinylcarbazole) films doped with dimethyl terephthalate is partly quenched by an electric field, a model is proposed for the extrinsic carrier photogeneration mechanism. Interaction between a migrating singlet exciton and an electron acceptor ("encounter complex") produces an electron-hole ion pair having a rather large separation through a charge-transfer process between the components and a thermalization process of the excess energy. This ion pair dissociates into free carriers with Onsager's probability of escaping the geminate recombination which gives a "relaxed fluorescent exciplex state". The field dependence of the initial separation of the ion pair is also discussed.

Poly(*N*-vinylcarbazole) (PVCz) films exhibit only excimer fluorescence, while PVCz films doped with dimethyl terephthalate (DMTP), a weak electron acceptor, give a broad exciplex fluorescence. In the previous letter,[1] we reported that this exciplex fluorescence is partly quenched by applying an electric field in the solid film state, and suggested that this quenching is due to a field-assisted thermal dissociation of the exciplex into free carriers:

$$D^* + A \longrightarrow (D^+\cdots A^-)^* \longrightarrow D^+ + A^-, \qquad (1)$$

where D and A represent donor (PVCz) and acceptor (DMTP) molecules, respectively.

The possibility of such extrinsic carrier photogeneration process in PVCz–DMTP system had been proposed by Okamoto *et al.*[2] from their observation that the exciplex formation in PVCz films doped with DMTP enhanced the photocurrent in the lowest π-π^* absorption region.

Our observation of the quenching of exciplex fluorescence by an electric field provided direct evidence for the above-mentioned exciplex mechanism in the extrinsic photogeneration of carriers, and also is believed more generally to provide an insight into the mechanism of an extrinsic photogeneration in organic molecular crystals. In the previous paper, however, no explanation was presented for the observed quadratic field-dependence of the fluorescence decrement. In the present paper, we present a mechanism of the field-assisted thermal dissociation of an exciplex, by which the observed field-dependence of the fluorescence decrement will be successfully explained.

Mechanism

The mechanism represented by process (1) assumes the formation of exciplex state and its dissociation into free ions (carriers). Nothing is known hitherto concerning the dissociation process of an exciplex in the solid state. We have, however, some informations in the dissociation process of an exciplex in solution.[3–5]

According to the recent time-resolved spectroscopic investigations of the photoionization processes of DA systems, it is believed that (a) when an excited donor (acceptor) molecule approaches to an acceptor (donor) molecule, the interaction occurs at comparatively large distance resulting in a formation of so-called "encounter complex"; (b) this state converts immediately into "charge transfer state" (ionic state) by a rapid electron transfer; (c) this ionic state is a "nonrelaxed exciplex" with respect to the orientation of the solvent molecules; (d) this state relaxes into the ordinary "fluorescent relaxed exciplex state" being assisted by reorientation of the solvent molecules which liberates polarization energy; (e) in favorable cases, this relaxation process accompanies emission of exciplex fluorescence of somewhat shorter wavelength, main part of the exciplex fluorescence being, however, from the relaxed state; (f) if solvent polarity is large enough, dissociation of relaxed and/or nonrelaxed exciplex state into solvated ions becomes possible.

In our present PVCz–DMTP system in a film, however, the lowering of the ionization or dissociation energy by solvent orientation is impossible. From a simple estimation of the energy relation, the fluorescent relaxed exciplex state, in which D^+ and A^- are separated only about 3—4 Å, is found to be so tightly bound by

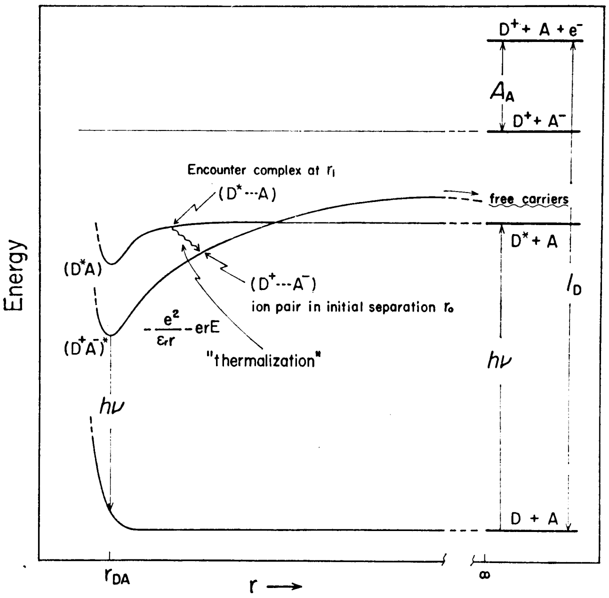
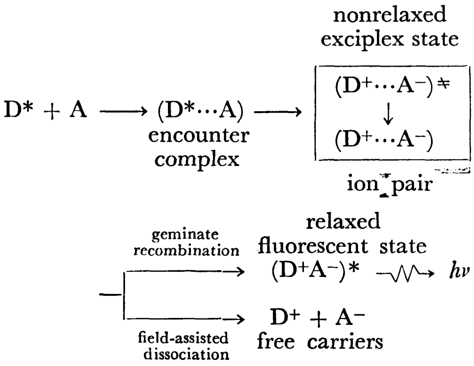


Fig. 1. Schematic energy diagram for the extrinsic photogeneration in DMTP–PVCz exciplex system. The abscissa indicates the separation of donor (D) from acceptor molecule (A), and an asterisk represents the excited state.

Coulombic force that its dissociation into free ions is impossible by the external field in the present experimental range. It is thus certain that any mechanism which involves the field-assisted thermal dissociation from the fluorescent relaxed exciplex state must be excluded in explaining our present results.

Photogeneration of an Ion Pair

Taking into account that (i) the singlet excited state of PVCz migrates effectively through the carbazole chromophores along the polymer chain,[6] and (ii) the major carrier is a hole, D^+, in a DMTP doped PVCz film as well as in a PVCz film, we propose that an electron-hole pair (ion pair), to which an external electric field is effective in assisting its dissociation, is not the relaxed fluorescent exciplex state, $(D^+A^-)^*$, but the one which is produced from the "*encounter complex*," $(D^*\cdots A)$, between a migrating singlet excition, D^*, and an electron acceptor, A, through a charge-transfer process between the components and a thermalization process of the excess energy. This mechanism is summarized in the following scheme and is depicted schematically in Fig. 1.



(2)

The "*nonrelaxed exciplex state*" named here is the one which is produced from an encounter complex through a rapid electron transfer at somewhat larger separation between the components in an encounter complex than in relaxed fluorescent exciplex state. Such a nonrelaxed exciplex state has the excess kinetic energy, and undergoes a thermalization of the excess energy to give an electron-hole ion pair at a separation r_0. This process is possible since the carbazole chromophores locate around an acceptor in high concentration and D^+ is mobile from molecule to molecule in the neighborhood of A^-. An electron-hole pair thus produced will either recombine geminately to give a "*relaxed fluorescent exciplex state*," or dissociate into free carriers being assisted by an external electric field. The field-assisted dissociation process will be treated in the next section.

Dissociation Process of an Ion Pair

As mentioned above, our model shown by Scheme (2) involves a field-assisted dissociation process of an ion pair state. To this process we have attempted to apply Onsager's theory[7] which predicts the field dependent probability of the dissociation of an ion pair into free ions.

Since this dissociation process is competing with geminate recombination into the relaxed fluorescent exciplex state in our case, we obtain the expression that predicts the ratio of the decrement of the exciplex fluorescence by an electric field to its zero field intensity, $\Delta F/F$, as follows:

$$\begin{aligned}\frac{\Delta F}{F} &= \frac{F(0)-F(E)}{F(0)} \\ &= \frac{\eta\phi[1-P(0)]-\eta\phi[1-P(E)]}{\eta\phi[1-P(0)]} \\ &= \frac{P(E)-P(0)}{1-P(0)},\end{aligned} \tag{3}$$

where $F(E)$ is the exciplex fluorescence intensity in a field E, ϕ the quantum yield of the electron-hole pairs (field-independent), η the fluorescence quantum efficiency from the relaxed exciplex state, and $P(E)$ the efficiency as a function of E that an electron-hole pair will escape geminate recombination. Using the notation introduced by Geacintov and Pope[8] according to Onsager's theory, this efficiency will be expressed as,

$$\begin{aligned}P(E) &= \int g(r)f(r,\theta,E)\mathrm{d}\tau \\ g(r) &= (4\pi r_0^2)^{-1}\delta(r-r_0) \\ f(r,\theta,E) &= (\exp(-2q/r))\exp(-\beta r(1+\cos\theta)) \\ &\quad\times\sum_{\substack{0 \\ m,n}}^{\infty}\frac{(2q)^m\beta^{m+n}r^n(1+\cos\theta)^{m+n}}{m!(m+n)!}\end{aligned} \tag{4}$$

Here r_0 is the initial separation of electron and hole; θ, the orientation of the ion pair relative to the field direction; $q=e^2/2\varepsilon_r kT$; $\beta=eE/2kT$; e, electronic charge; ε_r, relative permittivity; kT, the thermal energy.

In Fig. 2 are shown the calculated curves $[P(E)-P(0)]/[1-P(0)]$ for various initial separations r_0 with $\varepsilon_r=3.0$ and $T=300$ K, together with the experimental data of $\Delta F/F$. Fitting of the experimental data with the theoretical curves gives approximately $r_0=26-30$ Å, although some discrepancies can be seen from a single r_0 value. This discrepancy will be discussed later. This r_0 value is in good agreement with the values obtained from the photocurrent measurements, *i.e.*, $r_0=35$ Å for 2,4,7-trinitro-9-fluorenone (TNF)-PVCz system by Melz[9] and $r_0=30$ Å for acid doped PVCz film by Pfister and Williams.[10]

Thus the quadratic field dependence in the decrement of the exciplex fluorescence is successfully explained on the basis of Onsager's model.

Field Dependence of Initial Separation of an Ion Pair

The deviation of experimental results from the prediction based upon Onsager's theory for the single r_0 value, was also pointed out by Melz[9] in his analyses of the carrier photogeneration from photocurrent measurements in TNF–PVCz films. However, any explanations have not yet been presented for this point.

We have attempted to explain this deviation with

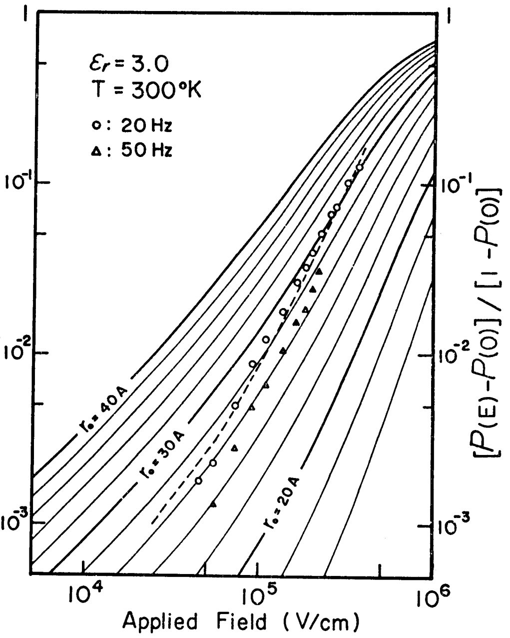


Fig. 2. Field dependence of fluorescence decrement in a 0.5 mol% DMTP doped PVCz film (12 μm thick) with square-wave applied voltage at 20 Hz (○) and 50 Hz (△), and theoretical prediction curves by Onsager's theory for an isotropic initial distribution of electron-hole pairs at various separations; $\varepsilon_r = 3.0$, $T = 300$ K; A dashed line represents the prediction curve including the field dependence of the initial separation r_0.

the idea that the initial separation r_0 of the ion pair produced through the thermalization from nonrelaxed exciplex state might be field dependent.

The thermalization process from nonrelaxed exciplex state at the distance r_i is considered to involve the separation process of an electron-hole pair dissipating the excess kinetic energy by phonon emission as is assumed in Knights-Davis' model.[11] The distance r_i means the separation between a migrating excited donor and an acceptor at which the electron exchange interaction occurs. In our model, the thermalization begins to occur from this point r_i, but not from $r=0$ as in the case of the autoionization in an anthracene crystal. Therefore, the separation of the ion pair will be given by

$$r_0 - r_i = \sqrt{Dt}, \tag{5}$$

where D is the diffusion coefficient, t the thermalization time, and r_0 the separation at the end of the thermalization, respectively. In the present case, the diffusion process involves only D^+, because D^+ is mobile from chromophore to chromophore while A^- is localized on an acceptor molecule.

The excess kinetic energy to be dissipated is taken to be equal to the energy difference between the singlet excition energy level (ε_{D^*}) and the Coulomb potential energy at r_0:

$$\varepsilon_{\text{excess}} = \varepsilon_{D^*} + \frac{e^2}{\varepsilon_r r_0} + e r_0 E, \tag{6}$$

Using the same treatment as described by Knights and Davis,[11] the time to be necessary to dissipate this energy is given by

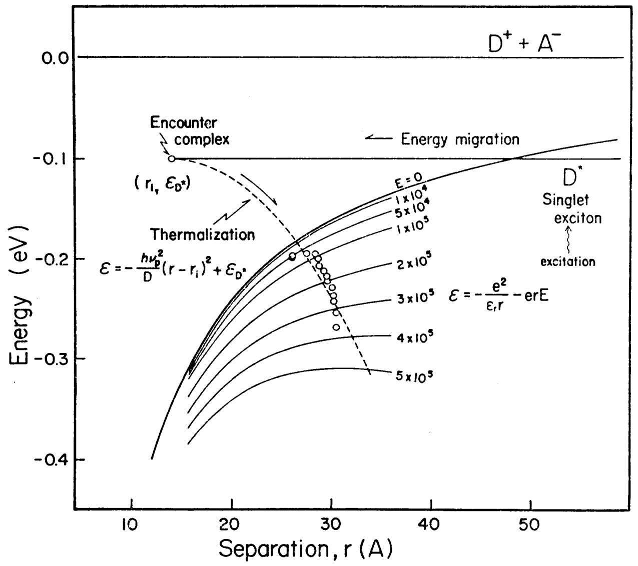


Fig. 3. Schematic representation for field dependence of the initial separations read from Fig. 2 (data at 20 Hz) plotted on the Coulomb potential curves for the corresponding field strengths.

$$t = \frac{\varepsilon_{\text{excess}}}{h\nu_p^2}, \tag{7}$$

where ν_p is a phonon frequency.

From Eqs. 5—7, we obtain the following equation for r_0 to be satisfied:

$$\frac{(r_0 - r_i)^2}{D} = \frac{\varepsilon_{D^*} + \dfrac{e^2}{\varepsilon_r r_0} + e r_0 E}{h\nu_p^2}. \tag{8}$$

Hence,

$$-\frac{h\nu_p^2}{D}(r_0 - r_i)^2 + \varepsilon_{D^*} = -\frac{e^2}{\varepsilon_r r_0} - e r_0 E. \tag{9}$$

The electron-hole initial separation r_0 at the end of the thermalization process, therefore, should be given as a crossing point of the following two curves in the energy diagram.

$$\varepsilon_1 = -\frac{h\nu_p^2}{D}(r - r_i)^2 + \varepsilon_{D^*}, \tag{10}$$

$$\varepsilon_2 = -\frac{e^2}{\varepsilon_r r} - erE. \tag{11}$$

Equation 10 represents the variation of the ion pair separation during the thermalization, which is given by a quadratic function of r with a curvature $h\nu_p^2/D$ and an apex at (r_i, ε_{D^*}). This equation is inherent to the system chosen. On the other hand, the Coulomb potential curve represented by Eq. 11 at an electric field E is field dependent. Thus, the crossing point, *i.e.*, the initial separation r_0 is field dependent.

In Fig. 3 the open circles represent the initial separations obtained from the experimental data (data at 20 Hz in Fig. 2) plotted on the Coulomb potential curves for the corresponding field strengths. Data points seem to trace something like a quadratic curve.

The thermalization curve is drawn so as to give a good fit by assuming ε_{D^*} to be 0.1 eV ($\Delta\varepsilon$) below the ($D^+ + A^-$) level and $r_i = 14$ Å, taking into account that the electron exchange interaction in the triplet-triplet energy transfer occurs at the distance of ~15 Å between donor and acceptor molecules.[12)] The value 0.1 eV for $\Delta\varepsilon$ gives the electron affinity (A_e) of DMTP to be about 1.0 eV, since the ionization potential (I_p) of PVCz in solid film would be about 4.7 eV[13)] and the energy of the singlet exciton (E_{D^*}) of PVCz is estimated to be 3.55 eV from the fluorescence measurements (*i.e.*, $\Delta\varepsilon = I_p - A_e - E_{D^*}$). The value $A_e \sim 1.0$ eV seems to be fairly reasonable from our experience, although unfortunately we have no exact value at present.

Thus, we developed an expression to the field dependence of the initial separation of ion pair, and also showed that it gave a good fit with the experimental data. In Fig. 2 is shown also a prediction curve (dashed line) of the fluorescence quenching including the field dependence of the initial separation of ion pair given by the dashed curve in Fig. 3. As can be seen, the field dependence of the initial separation successfully explains the deviation of the experimental data from a single curve calculated on the basis of Onsager's theory as well as the quadratic field-dependence of fluorescence quenching.

We have developed a mechanism of the extrinsic carrier photogeneration due to a field-assisted thermal dissociation of an exciplex into free carriers. The ion pair which undergoes the dissociation with the assistance of an electric field, is produced through the electron transfer process and the thermalization process from an encounter complex between a migrating singlet exciton and an acceptor. The deviation of the experimental data from Onsager's theory can be explained taking into accout that the initial separation of the ion pair should be field dependent. We believe that the present model for the extrinsic carrier photogeneration would be applicable not only to the present DMTP–PVCz system, but also to organic molecular crystals. Experimental works on the temperature effect and the frequency dependence are now in progress.

Note added in proof. Slightly observed frequency dependence of $\Delta F/F$ values has turned out to be an instrumental artifact due to unexpected partial damage of a load resistance. With a correct resistance, no frequency dependence is observed and the correct values of $\Delta F/F$ are obtained as multiplied by 0.15 for each value at 20 Hz reported.

Since, however, among the curves predicted from the Onsager's theory shown in Fig. 2 the quadratic field-dependence is best reproduced in the case of $r_0 \cong 16$ Å for the initial separation of the ion pair,[9)] we must slide down a prediction curve for $r_0 = 26$ Å so as to fit with the corrected values of $\Delta F/F$. Such shifting indicates the presence of a direct leak process from the nonrelaxed exciplex state $(D^+ \cdots A^-)^*$ to the relaxed fluorescent state $(D^+A^-)^*$ not through the ion pair state in Eq. 2.

Thus, in more general form Eq. 3 should be corrected as follows:

$$\frac{\Delta F}{F} = \frac{\eta\phi[1-P(0)] - \eta\phi[1-P(E)]}{\eta\phi[1-P(0)] + \eta(1-\phi)} = \frac{\phi[P(E)-P(0)]}{1-\phi P(0)} \tag{3$'$}$$

According to Eq. 3′ the fitting of the corrected values of $\Delta F/F$ with the theoretical curve for $r_0 = 26$ Å gives $\phi \cong 0.3$. Even in this case, however, some deviation from the prediction curve for the single $r_0 = 26$ Å value does exist. This deviation can be explained as well by the field-dependent initial separation of r_0 as described in the text.

The detailed analysis based upon the corrected experimental data will be published in this journal as soon as possible.

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