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Quenching of Exciplex and Charge-Transfer Complex Fluorescence of Poly(*N*-vinylcarbazole) - Benzanthrone System

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Summary: When benzanthrone (Bt), a weak electron acceptor, is doped into poly(*N*-vinylcarbazole) (PVCz) solution or film, an excited carbazole chromophore (D*) interacts with Bt to form a new exciplex state, which gives a broad fluorescence band (λ_{max} = 440 nm) in solution and a new state, which gives broad fluorescence (λ_{max} = 550 nm) in the film. In order to elucidate the origin of these new states, we have studied the results of experiments for absorption, concentration dependence of the excimer and exciplex fluorescence quenching, both in solution and in the film, and electric field-induced fluorescence quenching in the film. Taking into account that (i) the new state formation in the PVCz film containing small amounts of Bt enhances the photocurrent in the absorption region, where the photon energy is insufficient to excite polymer molecules directly into the conduction state, (ii) the 550 nm fluorescence of the PVCz - Bt system in film is only partly quenched by electric field, (iii) the appearance of structureless tail in the fluorescence excitation spectrum, the charge transfer interaction model of the PVCz - Bt system in film is proposed.

Keywords: exciplex; fluorescence; photo-carrier generation; poly(*N*-vinylcarbazole)

Introduction

The problem of charge carrier photogeneration in organic semiconductors has been of great importance and interest in the fields of electrophotographic science and solar energy conversion technology. The fact that poly(*N*-vinylcarbazole) (PVCz) is one of the few photoconducting polymers with a very long carrier range[1], which makes it useful in electrophotography application, has stimulated great interest in its electrical and optical properties[2]. The carbazole side groups generally determine the properties, with the polymer chain configuration simply determining the relative position of the side groups. The emission

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properties, energy transfer, and the carrier generation mechanism in this polymer have been studied.

Although the absorption of light in the near UV region of the spectrum is associated with an electronic transition in the monomer chromophore, the fluorescence in thin film samples of PVCz has been associated with emission from the two excimer-like emitting sites[3-6]. No monomer emission can be seen[4]. The broad emission at the longer wavelength (λ_{max} = 415 nm) is assigned to the sandwich-like excimer fluorescence and the broad emission in the shorter-wavelength region (λ_{max} = 380 nm) to the second excimer fluorescence[4-9]. The excimers occur in the samples only at special sites, where the side groups are favourably aligned.

When benzanthrone (Bt), a weak electron acceptor, is doped in a poly(*N*-vinylcarbazole) solution or film, an excited carbazole chromophore (D*) interacts with Bt to form a new exciplex state, which gives a broad fluorescence band (λ_{max} = 440 nm) in solution and a new state, which gives broad fluorescence (λ_{max} = 550 nm) in the film.

In order to elucidate the origin of these states, we have studied the results of experiments for absorption, concentration dependence of the excimer and exciplex fluorescence quenching, both in solution and in the film, and electric field-induced fluorescence quenching. Taking into account that (i) the new state formation in the PVCz film containing small amounts of Bt molecules enhances the photocurrent in the absorption region, where the photon energy is insufficient to excite the polymer molecules directly to the conduction state, (ii) the 550 nm fluorescence of the PVCz - Bt system in the film is only partly quenched by electric field, (iii) the appearance of a structureless tail in the fluorescence excitation spectrum, the C-T interaction model of PVCz - Bt system in film and the symmetric structure of this state is proposed.

Experiment

A. Materials

The required PVCz obtained by radiation polymerisation and commercially available Bt were dissolved in benzene and precipitated out with methanol several times. No interfering emission from the solvents (benzene and cyclohexanone) could be detected under the experimental conditions used here. The dilute polymer solutions (typically 10^{-2} - 10^{-3} M in monomer units) were deoxygenated prior to the study by purging with purified argon gas. The solvent-cast PVCz film (≈ 15 μm thick) containing a known amount of Bt on a NESA quartz plate was equipped with evaporated gold electrodes on the surface. All absorption spectra were recorded on a Specord UV.

B. Instrumentation and measurements

UV absorption spectra were recorded with a Unicam SP-500 spectrophotometer.

Photostationary emission and emission excitation spectra were recorded on a SF-1 Cobrabid spectrophotometer and corrected for photoresponse. Emission was viewed at about 45° to the exciting light in front of the samples.

Quenching of fluorescence measurements was carried out as shown in Figure 1. The square-wave voltage (20 – 1000 Hz) up to 220 V was applied to the samples and the modulated fluorescence was detected with a lock-in amplifier. The excitation wavelength, 360 nm was chosen to excite the bulk of the sample.

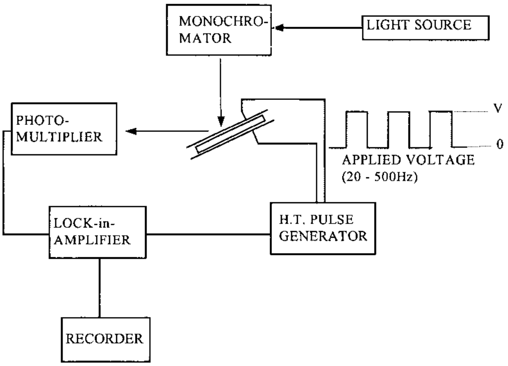


Figure 1. Schematic diagram of the instrumentation for fluorescence measurements in the presence of electric field.

Results and Discussion

In the pioneering work[10] Klöpffer determined the dominant mechanism for energy transfer to be the exciton diffusion. In this case the excitons are electronic excited states of the carbazole chromophores, which hop randomly from one side group to another on either the same or different polymer chains with the excimer sites. As the singlet exciton in PVCz covers many carbazole groups during its lifetime, a fairly high exciplex-forming efficiency can be expected for the π-π* excitation.

In the π-π* absorption region, re-excitation of the trapped carriers by excitons may operate, and, simultaneously, the field-assisted dissociation of the exciplex formed from an excited carbazole group and an electron-accepting compound in the ground state should also be considered.

It is known[8,11] that interaction between PVCz and Bt molecules enhances the photocurrent in the lowest π-π* absorption region of PVCz and we have suggested the following extrinsic carrier photogeneration process, i.e., the field-assisted thermal dissociation of an exciplex into free carriers:

$$D^* + A \rightarrow (D^+ \ldots . A^-)^* \longrightarrow D^+ + A^- \qquad (1)$$

and then

$$A^- + D \xrightarrow{\text{thermalization}} D^- + A \qquad (2)$$

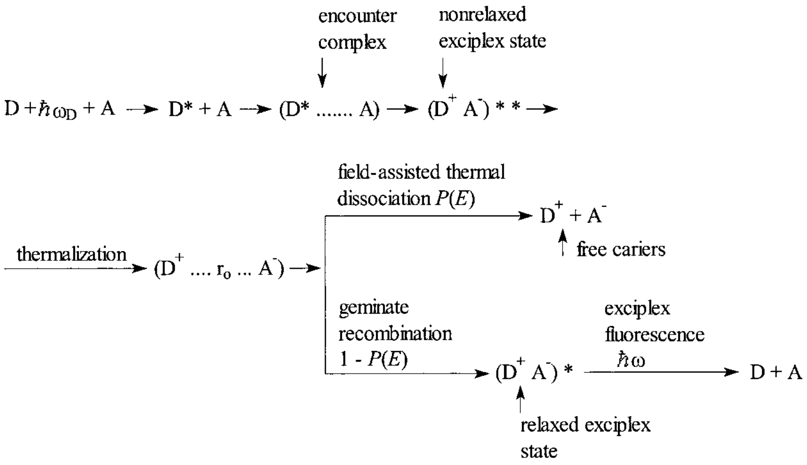
$$A^- + D^* \xrightarrow{\text{singlet exciton}} D^- + A \qquad (3)$$

where D and A represent an electron donor (PVCz) and acceptor (Bt) molecules in the ground state, respectively; D*, a singlet exciton in the PVCz film; A^- an immobile anion; D^+ and D^- are ion radicals of PVCz mobile and an immobile charge carrier, respectively. Equation (1) shows the ionisation of an exciplex into a mobile carrier ion in a film. Equations (2) and (3) show the excitation of an electron donor (A^- in this case) thermally or by a singlet exciton.

It is usually difficult for an exciplex to dissociate into free ions in a film with a low permittivity. This dissociation, however, may be possible under conditions, which reduce the energy required for the separation of an ion pair, for example under a strong electric field. Now we show that the 550 nm fluorescence decreased by applying the square-wave voltage. The decrement of this fluorescence $\Delta F = F(0) - F(E)$ dependent on the field strength and the ratio of the decrement to the total fluorescence intensity at 550 nm increases at the applied voltage 220 V.

In order to explain our results, we have attempted to compare these results with Onsager's theory, which predicts the probability, as a function of the field E, that an electron-hole pair produced at distance r_0 will escape geminate recombination.

Next, we consider that the electron-hole pair is assumed to be produced from nonrelaxed encounter exciplex state ($D^{\delta+} \ldots A^{\delta-}$) by thermalization (Yokoyama's model[12]), as shown in Scheme 1:



Scheme 1

If we assume Scheme 1 for the present case, the expression for the fluorescence decrement $\Delta F/F$ - using the Onsager formula[13] for the dissociation probability of an ion pair $P(E)$ at the initial separation r_0 is

$$\frac{\Delta F}{F}=\frac{F(0)-F(E)}{F(0)}=\frac{\eta\phi(1-P(0))-\eta\phi(1-P(E))}{\eta\phi(1-P(0))}=\frac{P(E)-P(0)}{1-P(0)} \tag{4}$$

where $F(E)$is the exciplex fluorescence intensity in field E; ϕ the quantum yield of the thermalized electron-hole pair; η the fluorescence quantum efficiency from the relaxed state; $P(E)$ the dissociation probability. The dissociation probability is given by the equation

$$\begin{aligned} &P(E)=\int g(r)f(r,\theta,E)\,\mathrm{d}\tau \\ &g(r)=(4\pi r_0^2)^{-1}\delta(r-r_0) \\ &f(r,\theta,E)=\exp(-2q/r)\exp[-\beta r(1+\cos\theta)]\sum_{m,n=0}^{\infty}\frac{(2q)^m\beta^{m+n}r^n(1+\cos\theta)^{m+n}}{m!(m+n)!} \end{aligned} \tag{5}$$

where r_0 is the initial separation of the thermalized electron and hole, θ is the orientation of ion pair relative to the field direction, $q = e^2/2\varepsilon_0 kT$; $\beta = eE/2kT$; e is electron charge, ε_r is relative permittivity; and kT is the thermal energy.

In Figure 2 are shown the calculated curves $[P(E) - P(0)]/[1 - P(0)]$ for various initial separation r_0 with $\varepsilon_r = 3.0$ and $T = 300$ K, together with the experimental data of $\Delta F/F$ (black points).

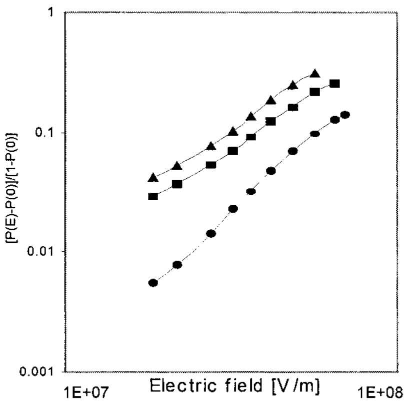


Figure 2. Calculated curves $[P(E) - P(0)]/[1 - P(0)]$ for various initial separation r_0 with $\varepsilon_r = 3.0$ and $T = 300$ K together with the experimental data for $\Delta F/F(0)$ (black points). $\Delta F/F(0)$ - the fluorescence decrement, r_0 = 22 Å (PVCz-DMTP)* exciplex, r_0 = 28 Å (PVCz-Bt) system, r_0 = 30 Å ($PVCz^+$-$4CNB^-$) C-T complex.

The experimental data of $\Delta F/F$ are well reproduced by the theoretical curve for the initial separation of the ion pair, r_0 = 28 Å. The r_0 value of 28 Å is between the value 30 Å obtained for (PVCz-4CNB) C-T complex and 22 Å obtained for (PVCz-DMTP) exciplex by Yokoyama et al.[12] (4CNB – tetracyanobenzene, DMTP – dimethyl terephthalate).

These results, showing emission due to the exciton-doped molecule interaction, not only provide a strong support for mechanism of the photocarrier generation via an exciplex and C-T complex in PVCz but may also provide an insight into the detailed processes in the currently accepted mechanism of the extrinsic photocarrier generation in organic molecular crystals.

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