

SHORT COMMUNICATION

Charge Carrier Photogeneration in the CT Complex Sensitization of Photoconducting Polymers

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In a previous short communication,¹ we reported that the charge-transfer (CT) fluorescence in a poly(*N*-vinylcarbazole) (PVCz) film doped with 1,2,4,5-tetracyanobenzene (4CNB), is quenched by applying electric fields, and this quenching is attributed to the carrier photogeneration due to the field-assisted thermal dissociation of an ion pair of initial interionic separation $r_0 = 30 \text{ \AA}$, competing with the fluorescent recombination process. It was also reported that this ion pair state is probably produced from a certain "nonrelaxed" excited state of the CT complex having excess energy.¹⁻³

In the present short communication, we wish to

report a solution to the most important problem of the nature of the "nonrelaxed" excited state as a precursor of an ion pair, on the basis of a detailed analysis of the excitation wavelength dependence of the field-induced CT fluorescence quenching.

When 4CNB is doped in a PVCz film, a CT absorption band appears at around 470 nm, and by exciting this CT absorption band or the lowest $\pi-\pi^*$ absorption of carbazole (Cz) chromophores, the CT fluorescence is observable at around 620 nm in a solid film.

Figure 1 shows the excitation wavelength dependence of the fluorescence quenching by applying

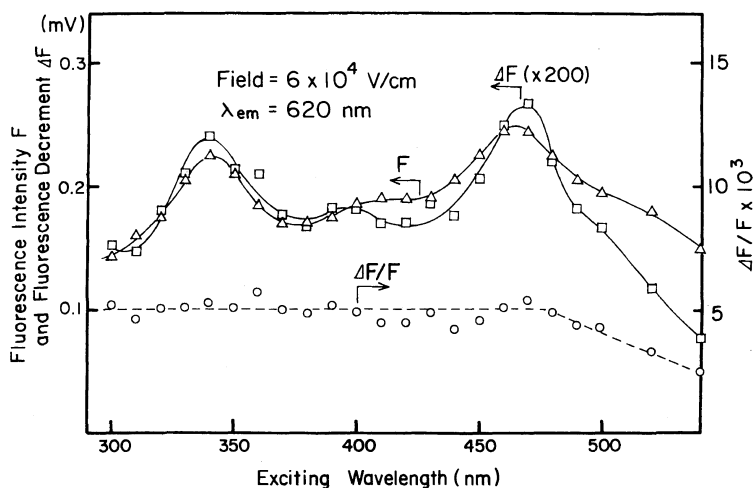


Figure 1. Excitation wavelength dependence of CT fluorescence intensity, F , field-induced fluorescence decrement, ΔF , and their ratio, $\Delta F/F$. Field: $6 \times 10^4 \text{ V cm}^{-1}$. Monitored at 620 nm.

an electric field. The total fluorescence intensity, F , without a field and the field-induced decrement, ΔF , of 620 nm CT fluorescence change with the exciting wavelength, but their ratio, $\Delta F/F$ does remain almost constant irrespective of the excitation wavelengths, *i.e.*, both excitation of Cz chromophore in 350 nm and direct excitation of CT absorption band

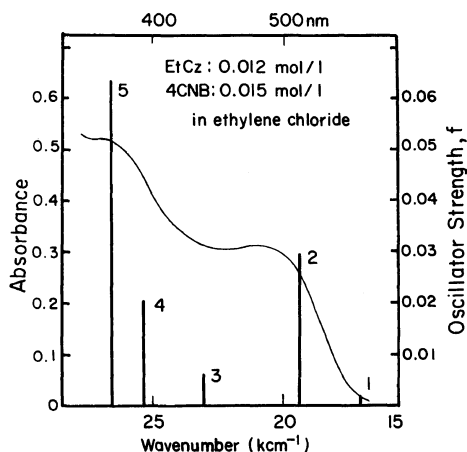


Figure 2. Absorption spectrum of EtCz-4CNB system in an ethylene dichloride solution and the results of SCF-CI calculation. Solid rods represent the calculated oscillator strength for each transition.

in 475 nm. This means that an ion pair having the same initial separation r_0 value (30 \AA)¹ is obtained regardless of the initial input photon energy. This fact strongly suggests that a thermalized 30 \AA ion pair is produced from the same precursor, *i.e.*, from the same “nonrelaxed” excited state of the CT complex.

Figure 2 shows the absorption spectrum of the CT complex of 4CNB and *N*-ethylcarbazole (EtCz), a model compound of PVCz, in solution. The solid rods in the figure represent the oscillator strength of each transition based on the results of the SCF-CI calculations of the present Cz-4CNB complex,⁴ which show good correspondence with the observed spectrum. The transition “2” which evidently corresponds to the observed strong absorption band of around 470 nm, is not a transition from the CT ground state to the first excited CT state, which appears in the lower energy side with small oscillator strength, but a transition to the second excited CT state. The configuration of this 470 nm transition is attributed to an electron transfer from the second highest occupied orbital of Cz chromophore to the lowest unoccupied orbital of 4CNB molecule.

Thus, we can understand the carrier photogeneration process for the present PVCz-4CNB CT complex sensitization system as in the energy dia-

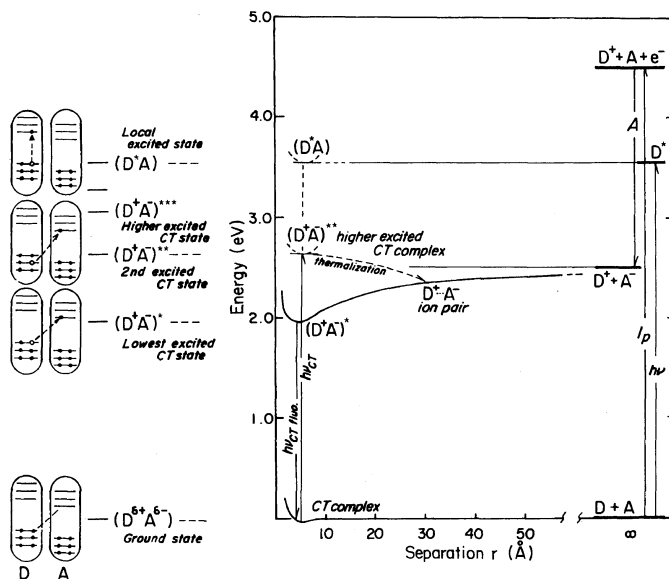
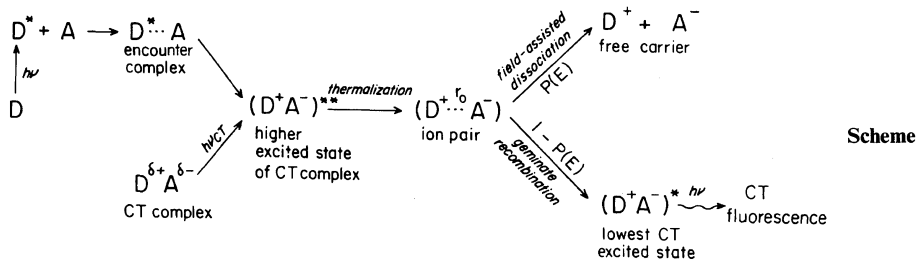


Figure 3. Energy diagram in PVCz-4CNB system and main configuration of each excited state of the CT complex.

CT Complex Sensitization in Carrier Photogeneration



gram shown in Figure 3. Here, the bandgap energy of PVCz film is assumed to be 4.6 eV^5 and the electron affinity of 4CNB, 2.0 eV^6 . The abscissa indicates the separation of a donor (D, Cz) chromophore from an electron accepting molecule (A).

The loose ion pair of the initial separation $r_0 = 30 \text{ \AA}$ on the coulombic potential curve of D^+ and A^- , is considered to be produced through thermalization from the "nonrelaxed" higher excited CT state (the second excited state in the present case), not from the lowest CT excited fluorescent CT state. This model is supported by the fact that $\Delta F/F$ decreases on excitation within the CT band by a lower energy photon beyond 480 nm , as shown in Figure 1.

In the case of the excitation of Cz chromophore, the excited state of Cz migrates and approaches the acceptor molecule, and these interact with each other to undergo an internal conversion into the second excited CT state. The excitation of the CT complex at around 470 nm arises directly the second excited CT state.

As a general mechanism for extrinsic carrier photogeneration which combines both exciplex and CT complex sensitized systems, the following

detailed scheme can be introduced.

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