Direct Observation of a Distant Ion Pair Generated in a Photoconductive Poly(*N*-vinylcarbazole) Film with Dopant**

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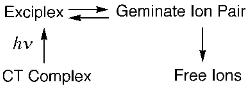
Poly(*N*-vinylcarbazole) (PVCz) has received much attention as an organic photoconductor, since the PVCz film is one of the best functional materials for photodetection systems, electrophotographic imaging, etc.[1] Over the past few decades, a considerable number of studies on the PVCz film have been made to clarify the photoconduction mechanism in the amorphous organic solid state.[2] A simplified mechanism for the carrier generation prior to the carrier transport is proposed for the photoexcitation of charge-transfer (CT) complexes in acceptor-doped films in which the CT complexation takes place efficiently. The geminate ion pair is a key intermediate in the generation of the free ions (Scheme 1).



Scheme 1. Carrier generation process.

The interionic distance (r_0) of the ion pair was reported to be around 20–30 Å on the basis of the external electric field effects on the steady-state fluorescence from the exciplex[3] and on the generation yield of the carriers (free ions).[4] On the other hand, the dichroism relaxation measurements using picosecond optical spectroscopy gave a negative response to the presence of the hypothetical distant ion pair developed during a cooling process of the exciplex.[5] In the present study, we detected a spin-correlated radical pair (SCRP) and determined the distance between the transient pair radicals in 1,2,4,5-tetracyanobenzene (TCNB)-doped PVCz film[6] by using time-resolved electron paramagnetic resonance (EPR) spectroscopy.[7]

The spin-polarized EPR spectrum was clearly observed, as shown in Figure 1 a, when the CT complex in the PVCz film was selectively excited by the laser-pulse irradiation at 532 nm. The spectral phase is enhanced absorption (A) in the low-field half and emission (E) in the high-field half. It is noteworthy that the signals are detected over a relatively wide region of more than 8 mT. The spectrum intensity decreased exponentially with the delay time after the laser flash, in keeping the same broad spectral shape with the A/E pattern during the decay. To assign the observed transient paramagnetic species, we measured separately the conventional steady-state EPR spectra for the TCNB anion[8] and the PVCz cation[9] in rigid glassy solvents (Figure 1 b). Both free ions showed EPR signals at the magnetic field corresponding to $g = 2.0028$, but the spectral widths were quite different from each other, mainly because of the difference of the hyperfine interactions. The central field of the time-resolved EPR spectrum for the TCNB-doped PVCz film is also in agreement with $g = 2.0028$, which indicates that the transient species are associated with the $TCNB^-$ and $PVCz^+$ radicals. However, the spectral width of the transient signal in the film is much broader than that of the component free ions, the signals of which are broadened only by intramolecular interactions such as the anisotropic Zeeman and the hyperfine interactions. The broadness of the time-resolved EPR spectrum implies that the transient signal is attributed to the ion pair ($TCNB^- \cdots PVCz^+$) rather than to the free ions, because the intermolecular magnetic interactions of the exchange and dipolar interactions between $TCNB^-$ and $PVCz^+$ can make the EPR spectrum broader.

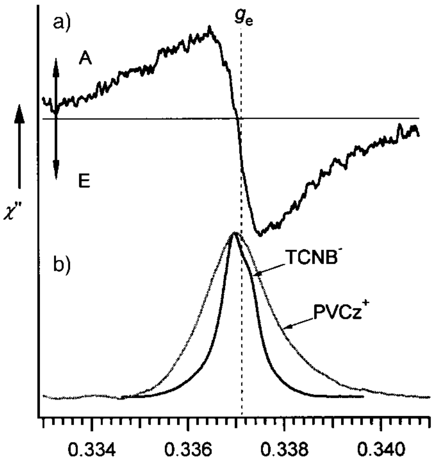


Figure 1. a) Time-resolved EPR spectrum of TCNB-doped PVCz film observed at 500 ns after the pulse excitation at the CT band at room temperature. b) Continuous wave (Cw)-EPR spectra obtained by numerical integration of the first-derivative signals of $PVCz^+$ in concentrated H_2SO_4 and $TCNB^-$ in MTHF at 8 K recorded using a lock-in detection.

The intensity of the time-resolved EPR signal increases with the incident power of the laser excitation. A plot of the EPR intensity versus the laser power is given in Figure 2. The linear laser-power dependence with a unit of slope indicates that the observed ion pair is created through a one-photon process.

The time-profiles of the EPR signal always showed an exponential decay with a time constant of about 1.0 μs, even when the laser power was varied. The exponential behavior, that is, first-order kinetics, supports the fact that the observed decay of the ion pair under zero external electric field represents recombination within a geminate pair rather than a free pair, because the free-pair recombination should obey second-order kinetics.[10] Furthermore, the decay constant of the ion pair is comparable to the apparent time constant estimated from the exciplex fluorescence decay in the micro-

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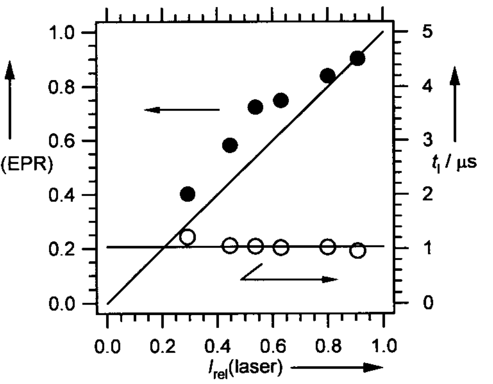

Figure 2. Laser power dependencies of the intensity and the decay constant of the transient EPR signal from the ion pair of PVCz$^+$ and TCNB$^-$; ● = EPR intensity (I_{rel}(EPR)), ○ = lifetime (t_l).

second region. The agreement of the decay kinetic constants strongly suggests that the transient EPR signal arises from the geminate ion pair.

The irradiation with a linearly polarized light preferentially excites the CT complexes such that their transition moment in the CT band is along the polarized direction of light. Hence, the linearly polarized light enables an angle-selection experiment in the randomly oriented film sample to be performed. Since the EPR spectrum is broadened by the large anisotropy because of the spin dipolar interaction (see below), the shape of the EPR spectrum may be distorted by the angle-selection experiment,[11] as long as the ion pair holds the initial orientation of the CT complex. However, excitation with the polarized light did not have any influences on the spectral shape. No effect of the angle-selection experiments could be interpreted in terms of the loss of memory of the initial orientation in the ion pair because of a charge migration. Therefore, it is suggested that the ion pair giving the spin-polarized EPR spectrum is a distant ion pair generated after the successive hole transfers from the exciplex, which occur in random directions and on the nanosecond time scale.[5]

The multiplet spin polarization in the ion pair can be understood by the polarization mechanism of SCRP in which a coherent spin singlet–triplet interconversion takes place within the ion pair.[12] The spin Hamiltonian for a pair consisting of radicals A and B ($\mathscr{H}_{RP}$) can be written in angular frequency units [Eq. (1)].

$$\begin{aligned}\mathscr{H}_{RP} \;=\; & \omega_A S_{Az} + \omega_B S_{Bz} - J_{SS}(\boldsymbol{S}_A \boldsymbol{S}_B - 1/2) \\ & + D_{SS}(\cos^2\theta - 1/3)(3S_{Az}S_{Bz} - \boldsymbol{S}_A \boldsymbol{S}_B)\end{aligned} \tag{1}$$

ω_A and ω_B are determined by the Zeeman and hyperfine interactions within the individual radicals. J_{SS} and D_{SS} are the coupling constants for the exchange and dipolar interactions between the radicals, respectively. θ is the angle between the vector connecting the two radicals and the magnetic field. The coherent spin interconversion is induced by the difference between ω_A and ω_B. The SCRP born from the singlet exciplex under a magnetic field has the four sublevels of the electron spins shown in Figure 3a. The transitions from $|2\rangle$ and $|3\rangle$ to $|1\rangle$ offer the absorptive EPR signals. The emissive signals arise from the transitions from $|2\rangle$ and $|3\rangle$ to $|4\rangle$. The typical spectra calculated on the SCRP model[13] are shown in Figure 3b. The spectral shape depends very much on both J_{SS} and D_{SS}. The simulation using the constants around $J_{SS} = -22 \pm 2$ MHz and $D_{SS} = -140 \pm 20$ MHz reproduced well the A/E-polarized broad spectrum observed for the distant ion pair between PVCz$^+$ and TCNB$^-$.

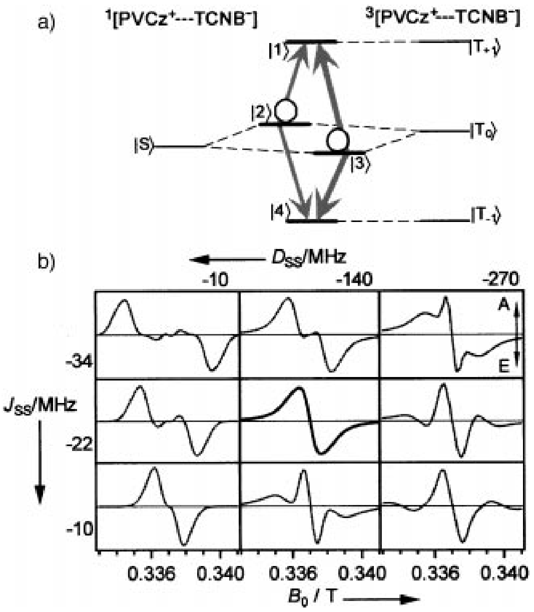

Figure 3. a) Energies of the four spin sublevels in a singlet-born SCRP model having a negative J_{SS}. Circles on the spin sublevels and arrows among the sublevels indicate the populations and the EPR transitions, respectively. b) Simulation spectra calculated by using various values as the intermolecular coupling constants of J_{SS} and D_{SS} on the SCRP model for the distant ion pair consisting of PVCz$^+$ and TCNB$^-$.

The magnitude of the dipolar interaction is proportional to r^{-3}, where r is the separation between the electron spins. The obtained D_{SS} value of the distant ion pair is reduced to $r_0 = 8.3 \pm 0.4$ Å within a point dipole approximation,[14] which is much shorter than the values acquired in the static measurements of the electric field quenching.[4] The analysis based on the Onsager model,[15] in which the polymer matrix is regarded as an isotropic dielectric medium, has been adopted for the electric field quenching experiments. This model has offered understandable physical interpretation of the carrier generation. The assumption for the isotropic continuum, however, seems to be not sensitive on the local scale in the organic solid state. To ignore the molecular structure of the polymer may lead to an overestimate of r_0. Taking into account the dichroism memory of up to several nanoseconds,[5] the distant ion pair may be generated by the stepwise hole hopping rather than by an electron jump of around 8 Å during thermalization of a hot exciplex. The decay rate of the distant ion pair seems to be mainly determined by an endothermic activation step in the process back to the exciplex rather than by the hole hopping, since the EPR signal decayed without any change in the spectral shape.

In conclusion, the present study demonstrated that the distant geminate ion pair separated by ~8 Å with the lifetime of 1 µs exists at the carrier generation in the photoconductive TCNB-doped PVCz film. The presence of the distant ion pair suggests stable trap site for the hole, the position of which is not far from the acceptor. The slow recombination of the geminate ion pair with the relatively short distance would be related to the trap-site structure or some sorts of reorganizations because of the charge shift in the PVCz film.

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[6] PVCz with the mean unit number of around 5.7×10^3 (Aldrich) was purified before use by reprecipitation with toluene and water. TCNB (Tokyokasei), recrystallized from EtOH, was employed as a dopant. The PVCz films containing 3 mol% of TCNB and with a thickness of a few μm were prepared on quartz plates by a spin-coating technique.

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[9] $PVCz^+$ was prepared by the oxidation of PVCz dissolved in conc. H_2SO_4 at room temperature.

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[13] The spectra for $PVCz^+$ and $TCNB^-$ were approximated by the normalized Gaussian functions having $g_{av} = 2.0028$, $\Delta\omega_{hfi} = 41.0$ MHz and $g_{av} = 2.0028$, $\Delta\omega_{hfi} = 21.2$ MHz, respectively. g_{av} corresponds to the central position and $\Delta\omega_{hfi}$ means the full-width-at-half-maximum in the Gaussian.

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C–S Bond Cleavage and C–C Coupling in Cyclopentadienylchromium Complexes To Give the First Dithiooxamide-Bridged and Doubly Dithiocarbamate-Bridged Double Cubanes: $[Cp_6Cr_8S_8\{(C(S)NEt_2)_2\}]$ and $[Cp_6Cr_8S_8(S_2CNEt_2)_2]$**

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There have been extensive studies on the use of the dithiocarbamate ligand in a variety of bonding modes for stabilizing a wide range of oxidation states in coordination compounds of main-group and transition metals.[1] Although generally unreactive in the majority of its complexes, this ligand can undergo C–S bond cleavage, a phenomenon first observed in a Mo complex in 1972 and becoming increasingly common in the last two decades.[2] In most cases, the cleaved S atom takes on a distinctly different coordination role in the complex, except where it is abstracted by an S acceptor such as PEt_3.[2c] For example, the cleaved S atom can assume a bridging mode (M-S-M),[2a,b,f, 3] form an M=S bond,[2d,g] or interact with a neighboring ligand (e.g., the M≡C bond of a coordinated alkyne).[2e] Cleavage of both C–S bonds of the ligand was reported for reactions with $[Ru_3(CO)_{12}]$[2h] and $[Mo_2(\mu\text{-}O_2CMe)_4]$.[3] Other reactions of the dithiocarbamate ligand include oxidative addition of a C–S bond to alkynes[4] and coupling reactions with coordinated alkyne,[2c, 5] alkylidene,[6] vinylidene/allenylidene,[7] and cyanide[8] ligands. Most of these studies involved Mo and W complexes, except for a few examples containing Cu,[4d] Nb and Ta,[2g] and Ru.[2h, 7] In the course of our investigations on the reactivity of $[\{CpCr(CO)_3\}_2]$ ($Cp = \eta^5\text{-}C_5H_5$) towards the E–E bonds of organic substrates such as diphenyl dichalcogenides Ph_2E_2 (E = S, Se, Te),[9] and bis(diphenylthiophosphinyl)disulfane $[Ph_2P(S)S]_2$,[10] we studied reactions with tetraalkylthiuram disulfides $[R_2NC(S)S]_2$, and here we report the first organochromium complexes containing dithiocarbamate and dithiooxamide ligands.

The instantaneous reaction of $[\{CpCr(CO)_3\}_2]$ with one molar equivalent of tetraethylthiuram disulfide $[Et_2NC(S)S]_2$ in toluene at ambient temperature gave a dark red solution, which upon concentration yielded air-stable deep red crystals of $[CpCr(CO)_2(S_2CNEt_2)]$ (**1**) in 87% yield. A similar reaction at 90°C for 2 h gave a dark brown mixture, from which were obtained, in order of elution from a silica gel column, the following compounds: $[\{CpCr(CO)_2\}_2S]$ (**7**) as a dark green solid (ca. 1% yield), (**1**) (22% yield), $[CpCr(CO)_2(SCNEt_2)]$ (**2**) as a dark red crystalline solid (11% yield), $[Cp_4Cr_4S_4]$ (**3**) as a dark solid (22% yield), $[Cp_6Cr_8S_8\{(C(S)NEt_2)_2\}]$ (**4**) as a brown solid (6.8% yield),

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