

Long-Range Jump versus Stepwise Hops: Magnetic Field Effects on the Charge-Transfer Fluorescence from Photoconductive Polymer Films

Fuyuki Ito, Tadaaki Ikoma, Kimio Akiyama, Yasuhiro Kobori, and Shozo Tero-Kubota*

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan

Received November 22, 2002; E-mail: tero@tagen.tohoku.ac.jp

Aromatic vinyl polymers such as poly(*N*-vinylcarbazole) (PVCz) have received much attention as an organic photoconductor,¹ and the acceptor-doped PVCz film has actually been utilized in photocopy machines. For carrier generation in organic photoconductors, geminate ion pairs (IPs) play an important role. Many models have been proposed for the carrier generation,^{2–5} but there is no united view so far. The point at issue is the mechanism of the initial separation between the negative and positive ions, which correspond to electrons and holes, respectively. It seems that the electric field dependence of the charge recombination yield and the escape probability are understood by the long-range jump of the hole based on the Onsager theory.^{2,3} The estimated interionic distance (r_0) of the separated IP ranges from 0.7 to 3.0 nm and depends on the models. Ultrafast hole dynamics directly detected by optical spectroscopic studies has been interpreted by both a long-range jump and stepwise hops of the hole.^{4,5} Recently, on the other hand, we confirmed the distant IP by time-resolved electron paramagnetic resonance,⁶ but the generation mechanism of the distant IP is not totally clear yet. Therefore, to clarify the primary process in the photoconductive organic amorphous solid, we have studied the magnetic field effect (MFE) on the charge-transfer (CT) fluorescence of a PVCz film in which 1,2,4,5-tetracyanobenzene was doped as an acceptor (A).⁷ The MFE experiment is one of the most powerful techniques to understand the radical IP dynamics.

The inset in Figure 1 shows the time-integrated fluorescence spectra detected by a pulse laser irradiation with a wavelength (λ) of 532 nm corresponding to the selective excitation of the CT complex.⁸ The observed fluorescence spectrum with a peak at 620 nm is assigned to the emission from the excited CT complex that can be regarded as the contact IP.^{2c,4} Thus, the CT fluorescence is accompanied by a charge recombination between the acceptor anion (A^-) and the hole. The CT fluorescence decayed with the apparent time constant of 9 ns. It can be considered that the total intensity almost reflects the recombination yield of the geminate pairs rather than the free pairs, the so-called cage product yield.⁸ When the external magnetic field (B) of 10 mT was applied, the CT fluorescence increased in intensity by 12%. The enhancement in the geminate recombination yield by the external magnetic field means that the radical IP was created from the singlet CT state.

Figure 1 shows the magnetic field dependence of the CT fluorescence intensity ($I(B)$) observed at $\lambda = 620$ nm. The MFE is defined by $R(B) = [I(B) - I(0)]/I(0)$. In the low field range of less than 10 mT, the CT fluorescence intensity steeply increases with increasing B . The MFE decreases around 30 mT and then increases above 50 mT. The MFE become nearly constant ($R(B) \approx 0.10$) in the high field range of more than 80 mT. A similar MFE was also observed by monitoring the CT fluorescence at $600 \text{ nm} < \lambda < 720 \text{ nm}$. From the MFE observed in the low field, the $B_{1/2}$ value at which the MFE reaches one-half of the maximum was estimated to be 3 mT. This value is comparable to the mean value of the

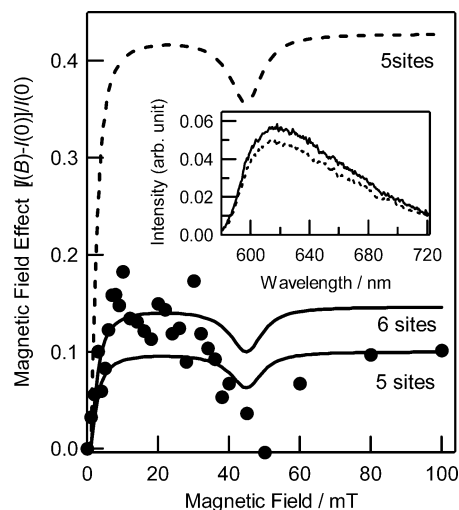
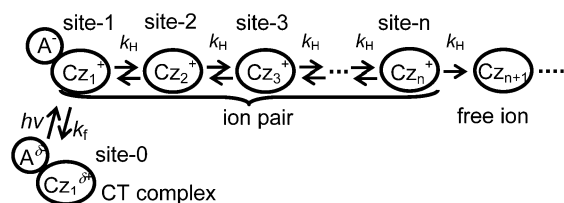


Figure 1. Magnetic field effect on the CT fluorescence of TCNB-doped PVCz films plotted as a function of magnetic field. The closed circles indicate experimental data. The solid and broken lines are SLE simulation as based on the stepwise hops and the long-range jump, respectively. Inset: CT fluorescence spectra measured in the absence (dashed line) and presence (solid line) of the external magnetic field ($B = 10$ mT). The spectra were observed by CT excitation with $\lambda = 620$ nm.

hyperfine interactions¹⁰ for A^- and $PVCz^+$ (~ 2.4 mT). Hence, the MFE observed in the low field is ascribable to the hyperfine mechanism (HFM),⁹ which arises from the distant IPs rather than the contact IPs. On the other hand, the dip in MFE around 46 mT is interpreted in terms of the level-crossing mechanism (LCM),⁹ which is caused by the radical IP having an exchange interaction ($|J|$) of 23 mT ($4 \times 10^9 \text{ rad}\cdot\text{s}^{-1}$). This $|J|$ value is greater than that of the distant IP ($\sim 0 \text{ rad}\cdot\text{s}^{-1}$) with $r_0 \geq 1 \text{ nm}$,⁹ but it is much smaller than a reasonable value for the contact IP ($\geq 10^{12} \text{ rad}\cdot\text{s}^{-1}$) reported in the literature.¹¹ Because PVCz prefers a helical structure in which the nearest neighboring Cz molecules are partially overlapped with a face-to-face arrangement,¹² we can set the intermolecular separation at 0.3–0.4 nm. From the estimated $|J|$ value, therefore, the radical IPs giving the MFE due to the LCM might have an r_0 value in the range of 0.4–0.9 nm.

To quantitatively analyze the radical IP dynamics, we performed the simulation of the observed MFE on the CT fluorescence on the basis of the stochastic Liouville equation (SLE).^{13,14} We adopted a model of the spin-conservative stepwise hole hops (Scheme 1) for the radical IP dynamics.

It is assumed that the hole hops to the nearest carbazole (Cz) units with a same rate constant of k_H and that the recombination occurs only from the contact IP (site-1) by a rate constant of k_f . It should be noted that the hopping and recombination processes maintain the spin multiplicity. On the other hand, the spin state of the radical IP evolves with the time according to the spin

Scheme 1. Radical IP Dynamics on the Stepwise Hole Hops

Hamiltonian ($\hat{H}(n)$) consisting of the exchange (J_n), hyperfine (A), and Zeeman ($g\mu_B B S$) interactions as described below.

$$\hat{H}(n) = -J_n \left(\frac{1}{2} + 2\hat{S}_{1z}\hat{S}_{2z} \right) + \sum_{ij} A_{ij} \hat{S}_i \hat{S}_j + \sum_i g_i \mu_B B \hat{S}_{iz} \quad (1)$$

The notations have their usual meanings. When we take into account n sites of the radical IPs, the SLE for their dynamics is expressed using the density matrixes ($\rho(n,t)$):

$$\begin{cases} \dot{\rho}(0,t) = k_f \rho(1)_{ss} \\ \dot{\rho}(1,t) = -i[\hat{H}(1), \rho(1)] - k_H \rho(1) + k_H \rho(2) - k_f \rho_{ss}(1) \\ \dot{\rho}(2,t) = -i[\hat{H}(2), \rho(2)] + k_H \rho(1) - 2k_H \rho(2) + k_H \rho(3) \\ \vdots \\ \dot{\rho}(n,t) = -i[\hat{H}(n), \rho(n)] + k_H \rho(n-1) - 2k_H \rho(n) \end{cases} \quad (2)$$

Because the site-0 corresponds to the ground CT state, $\rho(0,t)$ has only a singlet character. We took the initial condition of $\rho(1,0)_{ss} = 1$ because of the singlet CT excitation. The simultaneous SLE could be numerically solved after the Laplace transformation (Supporting Information). As a consequence, the MFE on the CT fluorescence was calculated from $\rho(0,\infty)$, which is equivalent to a quantum yield for the recombination,¹³ as a function of B .

The r_0 -dependence of the exchange interaction is approximated by an exponential function of $J(r_0) = J_0 \exp(-\alpha r_0)$. The $|J|$ value for each IP was estimated using the parameters of $J_0 = 1 \times 10^{12}$ rad·s⁻¹ and $\alpha = 1.7 \times 10^{-10}$ m⁻¹. The experimental values for the recombination rate constant ($k_f = 4.7 \times 10^7$ s⁻¹) and hyperfine coupling constant ($A = 1.4 \times 10^8$ rad·s⁻¹) were adapted for the calculation (Supporting Information). If we consider the first three IPs from site-1 to site-3 as having the hopping rate constant of $k_H = 4.5 \times 10^8$ s⁻¹, the SLE calculated an MFE curve showing a sharp rise and dip due to the HFM and LCM in the low and middle field regions, respectively. However, the maximum MFE calculated with the three sites only occurs at $R(B) = 0.008$. This value is very small as compared with the observed one. Therefore, we added some distant IPs as the hopping sites into the calculation. These distant IP sites have a negligible J . The MFE significantly increased with the number of radical IP sites. The calculation using five or six radical IP sites well reproduced the observed MFE as shown in Figure 1. The MFEs were also very sensitive to the hopping rate (Supporting Information).¹⁵

To examine the effect of the long-range hole jump during the initial stage, we calculated the MFE on the recombination yield of a model in which the hole dynamics begins from site- n instead of site-1. The calculated curve using five sites is depicted in Figure 1 (broken line). HFM-MFE dramatically increased because of the extension of the effective time that a hole stays in the distant IP sites until the recombination. The depth due to the LCM was comparable to that of the stepwise hopping model, because it is

also necessary, even in the long-range jumping model, for a hole to undergo a close IP to recombine. The long-range jumping model could not sufficiently simulate the experimental results.

The MFEs on the geminate recombination yield indicated that the spin-conservative stepwise hole hops among the nearest Cz units. The r_0 distances for the site-5 and -6 are estimated to be about 2 nm from the conformation of the PVCz wire. The r_0 for the distant IP with the longest separation corresponds to the boundary distance (r_b) used to distinguish the hole being able to recombine from the positively charged carriers. When the holes hop out of the r_b radius from the A⁻ center, they behave as free ions. It is noteworthy that the boundary distance determined by the stepwise hopping model almost agrees with the interionic distance estimated on the basis of the Onsager theory. The agreement of these distances means that the Onsager analysis may be a good approximation only for the critical distance, which is long enough for the hole to escape from the attractive Coulomb interaction due to the anion, even in amorphous organic solids.

Acknowledgment. T.I. thanks Prof. H. Miyasaka, Prof. M. Tachiya, and Prof. N. Ohta for their stimulating discussion and valuable comments. This research was financially supported by the REIMEI Research Resources of JAERI, Izumi Science & Technology Foundation, Showa Shell Sekiyu Foundation for Promotion of Environmental Research, and the Kyoza Ogura Fund for Young Scientists.

Supporting Information Available: Details of the SLE simulation procedure and the k_H dependence on the MFEs (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Peason, J. M.; Stolka, M. *Poly(N-vinylcarbazole)*; Gordon and Breach: New York, 1981. (b) Mort, J.; Pai, D. M. *Photoconductivity and Related Phenomena*; Elsevier: Amsterdam, 1976; Chapters 7, 8, 10, 11. (c) Mort, J.; Pfister, G. In *Electronic Properties of Polymers*; Mort, J., Pfister, G., Eds.; Wiley-Interscience: New York, 1982; Chapter 6.
- (2) (a) Melz, P. J. *J. Chem. Phys.* **1972**, *57*, 1694. (b) Yokoyama, M.; Endo, Y.; Matsubara, A.; Mikawa, H. *J. Chem. Phys.* **1981**, *75*, 3006. (c) Yokoyama, M.; Shimokihara, S.; Matsubara, A.; Mikawa, H. *J. Chem. Phys.* **1982**, *76*, 724. (d) Okamoto, K.; Itaya, A. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1626. (e) Wang, Y.; West, R.; Yuan, C. *J. Am. Chem. Soc.* **1993**, *115*, 3844.
- (3) Noolandi, J.; Hong, K. M. *J. Chem. Phys.* **1979**, *70*, 3230.
- (4) (a) Miyasaka, H.; Moriyama, T.; Kotani, S.; Muneyasu, R.; Itaya, A. *Chem. Phys. Lett.* **1994**, *225*, 315. (b) Miyasaka, H.; Moriyama, T.; Ide, T.; Itaya, A. *Chem. Phys. Lett.* **1998**, *292*, 339.
- (5) (a) Ruseckas, A.; Gulbinas, V.; Sundström, V.; Undzenas, A.; Valkunas, L. *J. Phys. Chem. B* **1998**, *102*, 7365. (b) Abramavicius, D.; Gulbinas, V.; Ruseckas, A.; Undzenas, A.; Valkunas, L. *J. Chem. Phys.* **1999**, *111*, 5611.
- (6) Ikoma, T.; Nakai, M.; Akiyama, K.; Tero-Kubota, S.; Ishii, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 3234.
- (7) PVCz with the mean unit number of around 5.7×10^3 (Aldrich) was purified before use by reprecipitation with toluene and EtOH. TCNB (Tokyo Kasei) recrystallized from EtOH was employed. TCNB-doped (3 mol %) PVCz films with a thickness of 5 μ m were prepared by a spin coat method.
- (8) Fluorescence spectra were measured by using a multichannel analyzer (Princeton Instruments IRY-700). A nanosecond Nd:YAG laser (Spectra-Physics INDI-40-20, 20 Hz) was utilized as an excitation light. The fluctuation of fluorescence intensity resulting from the power stagger of the excitation light was corrected by monitoring every shot from the laser used. The experimental maximum error is estimated to be $\pm 5\%$.
- (9) (a) Hayashi, H. In *Dynamic Spin Chemistry*; Nagakura, S.; Hayashi, H., Azumi, T., Eds.; Kodansha: Tokyo, 1998; Chapter 2. (b) Steiner, U. E.; Ulrich, T. *Chem. Rev.* **1989**, *89*, 51.
- (10) Weller, A.; Nolting, F.; Staerk, H. *Chem. Phys. Lett.* **1983**, *96*, 24.
- (11) Shkrob, I. A. *Chem. Phys. Lett.* **1997**, *264*, 417.
- (12) Okamoto, K.; Yamada, M.; Itaya, A.; Kimura, T.; Kusabayashi, S. *Macromolecules* **1976**, *9*, 645.
- (13) Busmann, H.-G.; Steark, H.; Weller, A. *J. Chem. Phys.* **1989**, *91*, 4098.
- (14) Kobori, Y.; Akiyama, K.; Tero-Kubota, S. *J. Chem. Phys.* **2000**, *113*, 465.
- (15) Staerk, H.; Treichel, R.; Weller, A. *Chem. Phys. Lett.* **1983**, *96*, 28.

JA0294430