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Effects of electric field and magnetic field on photoinduced electron transfer between *N*-ethylcarbazole and dimethyl terephthalate in a polymer film

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Introduction

Photoinduced electron transfer processes (PIET), which involve the formation of radical-ion pairs, are significantly affected by both electric and magnetic fields [1,2]. Magnetic field effect basically interplays between the spin dynamics and diffusion dynamics. By diffusion, the donor and acceptor of radical-ions can be separated to an optimum distance where the exchange interaction is very small and the singlet and triplet states become degenerate. The application of an external magnetic field removes the degeneracy of the triplet states and reduces the intersystem crossing, resulting in an increase in the population of the initial spin state. The present work addresses the investigation of the magnetic field effect on fluorescence spectrum and electrofluorescence (E-F) spectrum (electric field-induced-change in fluorescence intensity as a function of wavelength) in an electron donor and acceptor pairs of *N*-ethylcarbazole (ECZ) and dimethyl terephthalate (DMTP) in PMMA polymer films, at various donor-acceptor concentration ratios.

Experimental method

Fluorescence of a mixture of ECZ and DMTP in a PMMA film was measured with the simultaneous application of electric and magnetic fields at room temperature under vacuum conditions [3]. During the measurement of E-F spectra, a static magnetic field (H) whose strength was measured with a Bell 640 incremental Gaussmeter, was applied. The sample installed in a vacuum cell and placed between the pole pieces of an electromagnet NS was excited by a UV light from a 500W xenon lamp dispersed with monochromator. Emission which propagates perpendicular to the direction of applied magnetic field was dispersed by a monochromator and detected by a photomultiplier.

Results and discussion

Fluorescence of a mixture of ECZ and DMTP doped in a PMMA film under the simultaneous application of electric and magnetic fields are shown in Figure 1, where the concentrations of ECZ and DMTP were 10 and 1mol%, respectively. The spectra were observed with an electric field strength of 0.8 MVcm^{-1} both at zero magnetic field and in the presence of the magnetic field of 0.9 kG. Plots of $\{\Delta I_F (H=0.9 \text{ kG}) - \Delta I_F (H=0)\}$ are also shown in Figure 1(c). Here, $\Delta I_F (H)$ represents the field-induced change in fluorescence intensity at H . A noticeable magnetic field effect was not observed both for LE fluorescence and for exciplex fluorescence in a PMMA film, and a significant magnetic field effect was observed only for ΔI_F . The

magnitude of the electric field-induced quenching becomes smaller with increasing H and saturates at high fields. The strength of magnetic field where the change in ΔI_F of exciplex fluorescence and LE fluorescence become one-half of the saturated value was ~ 60 G, indicating that the nuclear hyperfine coupling plays a significant role in the magnetic field effect on the electric field on fluorescence.

The origin of the magnetic field effect is regarded as the field dependent spin conversion, and the initial step of PIET which produces the singlet state of radical-ion pairs is unaffected by H . By applying electric fields, dissociative radical-ion pairs having a relatively long D-A distance, which are different from the radical-ion directly produced by PIET, may be generated through the hopping migration of hole and/or electron. In such radical-ion pairs, the exchange interaction may be so small that the intersystem crossing from the singlet to the triplet states is influenced by a magnetic field very efficiently.

The magnitude of electric field-induced quenching of the LE fluorescence becomes smaller in the presence of H since the population of the LE fluorescence state produced by the back electron transfer becomes larger.

When ECZ concentration was 1 mol% and DMTP concentration was 10 mol%, no evidence of magnetic field effect was observed for electric-field-induced fluorescence. This probably comes from the large exchange interaction of the ion pairs because of the large energy gap between the singlet and triplet state of the radical-ion pair.

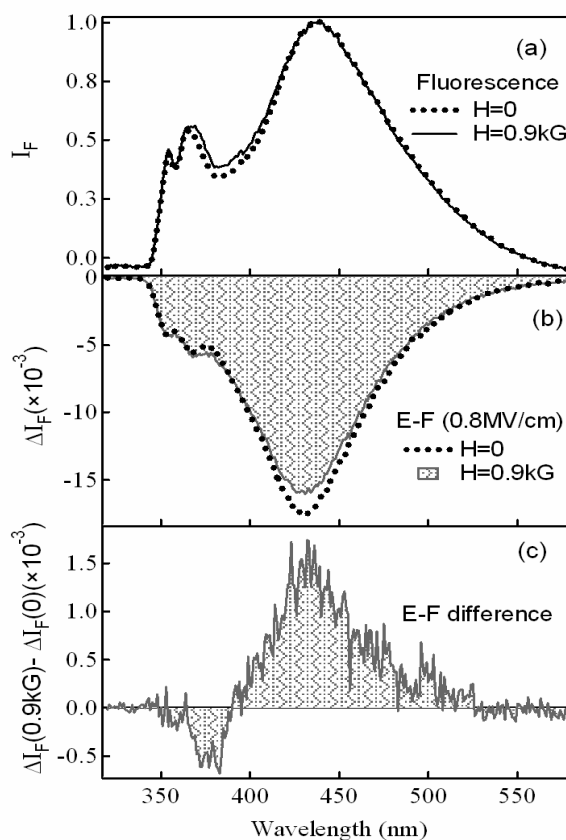


Fig.1.(a) Fluorescence spectra in a mixture of ECZ 10 mol% and DMTP 1 mol% in a PMMA film observed at zero magnetic fields (dotted line) and at 0.9 kG (solid line) and (b) E-F spectra at zero magnetic field (dotted line) and 0.9 kG (shaded line) (c) The difference of the E-F spectra

1. N. Ohta, Bull. Chem. Soc. Jpn. 75 (2002) 1637.
2. S. Nagakura, H. Hyasi, T. Azumi, Dynamic Spin Chemistry; Kodansha-John Wiley & Sons Tokyo, 1998.
3. M. Mizoguchi, N. Ohta, Chem. Phys. Lett. 372 (2003) 66.
4. T. Yoshizawa, M. Mizoguchi, T. Iimori, T. Nakabayashi, N. Ohta, Chem. Phys. 324 (2006) 26.