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MAGNETIC FIELD EFFECT ON THE EXCIPLEX FLUORESCENCE OF POLY-N-VINYLCARBAZOLE

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Magnetic fields were found to increase the prompt exciplex fluorescences in intensity in poly-N-vinylcarbazole films doped with dimethylterephthalate and N,N,N',N'-tetramethyl-p-phenylenediamine by up to 2 % at 500 G. This effect was independent of the intensity and the wavelength of the exciting light, the emission-wavelength, and applied electric fields, although slightly dependent on temperature. This effect was not observed for the exciplex fluorescences in solution.

Recently, Frankevich et al. have found that the prompt fluorescence of exciplexes on the surface of finely-divided rubrene crystals is significantly quenched by weak magnetic fields.$^{1)}$ However, the nature of the acceptor, in the exciplexes is not yet well understood. Poly-N-vinylcarbazole (PVCz) films doped with dimethylterephthalate (DMTP) and N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) show the exciplex fluorescences, the peak of which appears at about 20600 cm^{-1} and 20800 cm^{-1}, respectively (see Fig. 2(a) presented below).$^{2)}$ The carbazole chromophore behaves as a donor in the DMTP-doped system and as an acceptor in the TMPD-doped one. In the present study, we found that these prompt exciplex fluorescences were enhanced by weak magnetic fields. This is the first example of magnetic field effect on well-established exciplex fluorescences.

The PVCz was prepared by radical polymerization and purified by repeated reprecipitations ($\overline{DP} = 600$). The DMTP and TMPD were purified by repeated recrystallization. Thin films of about 9μ in thickness were casted on nesa-coated quartz plates from a solution of PVCz in benzene containing a certain amount of the dopant, upon which semitransparent gold electrodes were evaporated, if necessary. A film thus prepared was set in a cryostat mounted between the poles of an electromagnet and was excited by a light monochromated from a stabilized 500 W xenon lamp. The emission passed to a 1P28 photomultiplier through a light guide and appropriate filters. The photomultiplier current was measured with a Takedariken 8651 differential electrometer. The value of the current at zero magnetic field was compensated and only the variation of the current was fed into a recorder. Small current changes up to 0.2 % could be detected by means of this preliminary measuring system. The results presented below were obtained for the arrangement of the magnetic field vector perpendicular to the film at 0.1 - 0.2 torr.

The prompt excimer fluorescence of undoped PVCz films was not affected by magnetic fields up to 4000 G at all. However, the prompt exciplex fluorescences of PVCz films doped with DMTP and TMPD were enhanced in intensity by magnetic fields. The ratio of this increment to the total prompt fluorescence intensity ($\Delta F/F$) increased monotonically with an increase in magnetic field H and reached a saturation at about 400 G, as is shown in Fig. 1. The $\Delta F/F$ reached a half value of the saturation at about 100 G. The deta presented below were obtained for the saturated values.

The $\Delta F/F$ was independent both of the wavelength (280 - 360 nm) and of the intensity (10^{13-14} photons/cm^2 s) of the exciting light. The $\Delta F/F$ apparently depended on the emission-wavelength, as is shown in Fig. 2. In both doped systems, the $\Delta F/F$ for 400 nm was about 0.6 times as large as for 450 - 600 nm. This is because the excimer fluorescence is superimposed considerably on the exciplex fluorescence in the wavelength region shorter than 400 nm even in heavily-doped PVCz films. For instance, in a PVCz film doped with 3.3 mol% DMTP, the ratio of the exciplex fluorescence to the total one was about 0.55 at 400 nm, and then the ratio of ΔF to the exciplex fluorescence intensity was evaluated to be about 2.1 % at 400 nm, being equal to the $\Delta F/F$ value for 450 - 600 nm (1.9 %) within the experimental error. Therefore, the magnitude of the magnetic field effect on the exciplex fluorescence is safely considered to be independent of the emission-wavelength; it is about 2.0 % and 1.1 % at 25 °C for the DMTP and TMPD doped systems, respectively.

The $\Delta F/F$ depended slightly on temperature, as is shown in Fig. 3. With an increase in temperature, the F value decreased slightly and the $\Delta F/F$ increased, resulting in an activation energy of about 0.04 eV.

The electric field quenching of the exciplex fluorescence of PVCz films doped with DMTP, which has been recently reported by Yokoyama et al.,3) was also observed in the present study. However, the ratio of $\Delta F/F$ due to the magnetic fields was independent of applied electric fields up to ±35000 V/cm. This suggests that

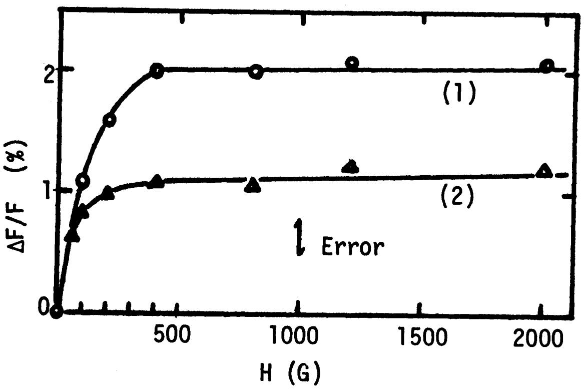

Fig. 1. Magnetic field dependence of relative increase in the exciplex fluorescence of PVCz films doped with (1) 3.3 mol% DMTP and (2) 4.3 mol% TMPD; λ_{ex}= 330 nm, λ_{em}= 500 nm, at 25 °C.

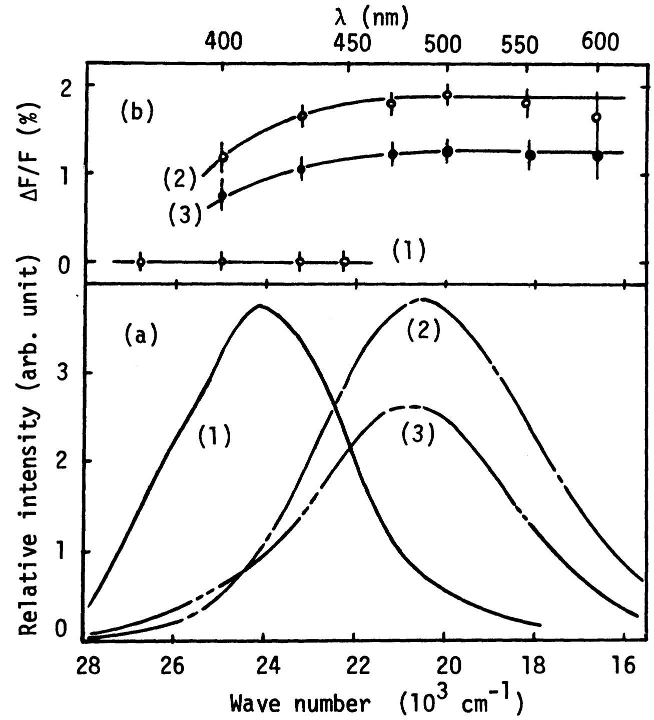

Fig. 2. (a) Fluorescence spectra and (b) emission-wavelength dependence of ΔF/F; λ_{ex}= 330 nm, 2000 G, 25 °C.

(1) undoped PVCz film

(2) PVCz film doped with 3.3 mol% DMTP

(3) PVCz film doped with 4.3 mol% TMPD

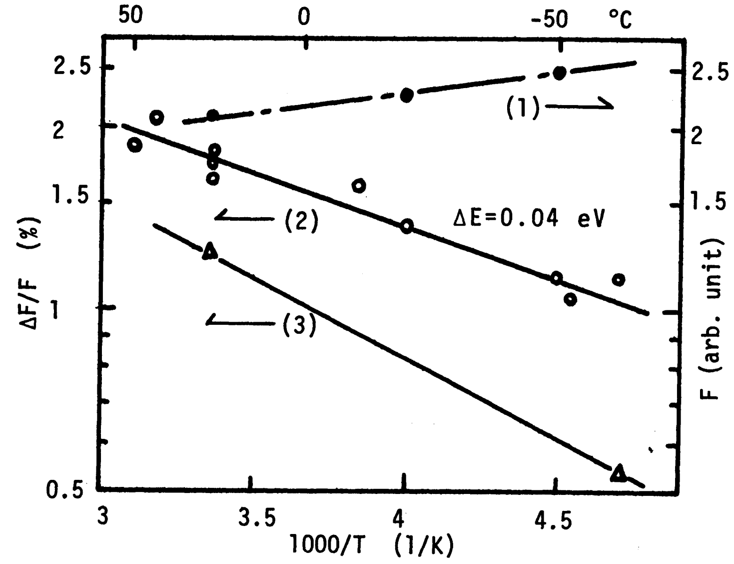

Fig. 3. Temperature dependence of F and ΔF/F in PVCz films doped with 3.3 mol% DMTP (1 and 2) and 4.3 mol% TMPD (3); λ_{ex}=330 nm, λ_{em}=500 nm, 2000G, 25 °C.

magnetic and electric fields affect independently the exciplex fluorescence.

It should be noted that the above-mentioned magnetic field effect has a positive sense, as is opposite to the case of the prompt exciplex fluorescence of finely-divided rubrene crystals.1) This positive magnetic field effect is, therefore, not explained by a mechanism that the rate of the intersystem crossing between the singlet and the triplet exciplex states increases with an increase in magnetic field on an assumption that there may be some difference in the Zeeman energies of the exciplex components (namely, the cation and anion radicals).1) On the other hand, Groff et al. have found the decrease in the dye-sensitized delayed fluorescence in dye-adsorbed anthracene crystals by weak magnetic fields, and explained this phenomenon in terms of reduction in the rate of the intersystem crossing by weak magnetic fields, assuming nearly equal g factors of the cation and anion radicals; the unsymmetrical hyperfine interaction term of the spin hamiltonian, that enables the intersystem crossing to occur, becomes less imortant than the symmetrical Zeeman term with an increase in magnetic field.4) We have recently found the positive magnetic field effect on the photoconductivity of PVCz films both undoped and doped with DMTP, and explained this according to the mechanism proposed by Groff et al..5) The same mechanism may be applicable to the present magnetic field effect on the prompt exciplex fluorescences of these doped PVCz films.

The exciplex fluorescences of these donor-acceptor systems were also observed in N_2-saturated benzene solution at room temperature. However, the exciplex fluorescences in solution were not affected by magnetic fields up to 4000 G at all. It should be noted that the magnetic field effect on the exciplex fluorescences was observed in solid film but not in solution. This is because the unsymmetrical hyperfine interaction of the cation and anion radicals, which enables the singlet-triplet transition to appear at low fields, disappears due to the rapid molecular rotation in solution.

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