Electric-Field-Induced Quenching of Fluorescence of Tetraphenylporphyrin in a PMMA Polymer Film

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Fluorescence of tetraphenylporphyrin (TPP) doped in a polymer film is quenched by an electric field. Field-induced enhancement of the internal conversion from S_1 to the ground state is considered to be accelerated by a molecular association. Electroabsorption spectra and electrofluorescence spectra also show that change in molecular polarizability following excitation increases by a molecular association of TPP.

External electric field dependence of absorption and emission spectra gives an information about the field effects on photophysical and photochemical processes, besides the information of the difference in electronic property between the ground state and the electronically excited state. In fact, a primary process of the photoinduced electron transfer or excimer formation process was found to be affected significantly by an electric field (***F***), based on the measurements of the electrofluorescence spectra.[1–3]

In the present letter, external electric field effects both on absorption spectra and on fluorescence spectra have been examined for tetraphenylporphyrin, which is one of the typical porphyrin derivatives,[4] in a poly(methyl methacrylate) (PMMA) polymer film. Based on the results, both the field effects on excitation dynamics and the difference in electronic property between the ground state and the excited state have been discussed.

Free-base tetraphenylporphyrin (Jyunsei Chemicals), hereafter denoted by TPP, was used without any further purification. TPP dissolved in benzene solution of PMMA was poured onto an ITO coated quartz plate with a spin-coating method. Following a drying in a vacuum, a semitransparent aluminum (Al) film was deposited on the polymer film. A thickness of polymer films, typically ~0.4 µm, was determined using a thickness measurement system (NanoSpec/AFT model M3000, Nanometrics Inc.). The concentration of TPP is defined as the one relative to the monomer unit of PMMA.

All the optical measurements were carried out at room temperature under vacuum conditions. Electrofluorescence spectra (plots of the field-induced change in $I_F(\lambda)$, i.e., $\Delta I_F(\lambda)$ as a function of wavelength (λ)) were measured using electric field modulation spectroscopy.[1–3] Here, $I_F(\lambda)$ is the fluorescence intensity at λ. Electroabsorption spectra (plots of the field-induced change in absorbance, $\Delta A(\lambda)$, as a function of λ) were also obtained with the method mentioned previously.[5,6] Hereafter, electroabsorption spectra and electrofluorescence spectra are abbreviated as E-A and E-F spectra, respectively.

Absorption spectra of TPP doped in a PMMA polymer film show the so-called Soret band with a peak at 23974 cm^{-1} and the weak bands at 19450, 18276, 16845 and 15476 cm^{-1} at 0.1 mol%, which are assigned as the $Q_Y(1,0)$, $Q_Y(0,0)$, $Q_X(1,0)$ and $Q_X(0,0)$ bands, respectively (see Figure 1).[7] E-A spectrum of each band of TPP is very similar in shape to the first derivative of the absorption spectrum, indicating the so-called Stark shift induced by a change in molecular polarizability ($\Delta\alpha$) following photoexcitation.[8,9] Actually, the E-A spectra could be simulated by a linear combination between the absorption spectrum and its first derivative spectrum for each band. The magnitude of $\Delta\alpha$ for excitation at each band was determined from the first derivative part of the E-A spectra.[5,6] The results are shown in Table 1.

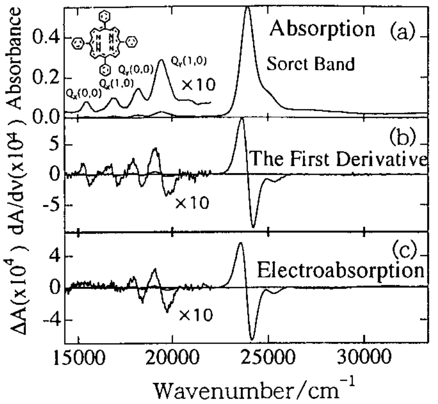

Figure 1. (a) Absorption spectrum of TPP in a PMMA polymer film at a concentration of 1.0 mol%; (b) the first derivative of the absorption spectrum; (c) E-A spectrum obtained with a field strength of 0.75 MVcm^{-1}. In every case, the view extended by a factor of 10 is shown in the region of the Q_X and Q_Y bands.

Table 1. The magnitude of $\Delta\alpha$ following excitation into each band of TPP doped in a PMMA polymer film at different concentrations in the units of $4\pi\varepsilon_0 Å^3$.

	0.10 mol%	0.25 mol%	1.0 mol%	2.0 mol%
Soret band	17 ± 2	26 ± 2	-[a]	-[a]
Q_Y band	17 ± 2	26 ± 2	29 ± 2	33 ± 2
Q_X band	4 ± 1	4 ± 1	6 ± 1	6 ± 1

[a]The absorption intensity was too large to determine the value of $\Delta\alpha$.

The magnitudes of $\Delta\alpha$ at the Soret band and at the Q_Y bands are nearly the same, but both are much larger than the values at the Q_X bands. Further, $\Delta\alpha$ increases with an increase of the TPP concentration. Note that the $Q_X(0,0)$ and $Q_X(1,0)$ bands as well as $Q_Y(0,0)$ and $Q_Y(1,0)$ bands give essentially the same value of $\Delta\alpha$. The absorption peak both of the Soret band and of the Q bands slightly shifts to lower wavenumber as the TPP concen-

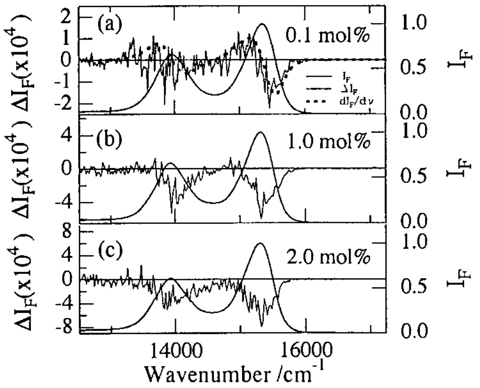

Figure 2. Fluorescence spectra of TPP (solid line) and E-F spectra (thin solid line) observed with a field strength of 0.75 MVcm^{-1} at a concentration of 0.1, 1.0 and 2.0 mol%, respectively, in a PMMA polymer film (from top to bottom). The first derivative of the fluorescence spectrum is also shown in (a) by a dotted line.

tration increases. Note that the peaks of the Soret, $Q_Y(0,0)$ and $Q_X(0,0)$ bands at 2.0 mol% are 23917, 18226 and 15440 cm^{-1}, respectively. The increase of $\Delta\alpha$ with increasing the TPP concentration probably results from a molecular association of TPP at high concentrations.

E-F spectra of TPP in a PMMA film observed with a field strength of 0.75 MVcm^{-1} are shown in Figure 2, together with the fluorescence spectra. Note that ΔI_F as well as ΔA is proportional to the square of the applied field strength in every case. These spectra were obtained with the excitation wavelength where ΔA is negligibly small. Fluorescence spectra also show a red-shift, as the TPP concentration increases; two strong peaks at 15360 and 13960 cm^{-1} at 0.1 mol% are shifted to 15290 and 13928 cm^{-1}, respectively, at 2.0 mol%.

The E-F spectra could be simulated by a combination between the fluorescence spectrum and its first derivative spectrum in every case. The former indicates that the fluorescence quantum yield (Φ_F) is reduced by $\boldsymbol{F}$, while the first derivative part shows the Stark shift induced by $\Delta\alpha$ between the emitting state and the ground state. The emitting state of the TPP fluorescence is regarded as the $Q_X(0,0)$ band. In fact, the magnitude of $\Delta\alpha$ evaluated from the first derivative part of the E-F spectra is essentially the same as the one determined from the E-A spectra of the Q_X bands.

As the concentration increases, the value of $\Delta I_F/I_F$ in the intermediate region between two fluorescence peaks becomes smaller (see Figure 2), indicating that field-induced decrease in Φ_F, i.e., $\Delta\Phi_F$, relative to Φ_F becomes larger with an increase of the TPP concentration. The magnitude of $\Delta I_F/I_F$, which is regarded as $\Delta\Phi_F/\Phi_F$, is evaluated from the simulated spectra at 0.75 MVcm^{-1} and plotted in Figure 3, as a function of the TPP concentration. Field-induced quenching of fluorescence probably results from a field-induced acceleration of the nonradiative process at the emitting state. Furthermore, the fact that $\Delta\Phi_F/\Phi_F$ increases with an increase of the TPP concentration suggests that the nonradiative process which is affected by $\boldsymbol{F}$ is strongly related to intermolecular interactions.

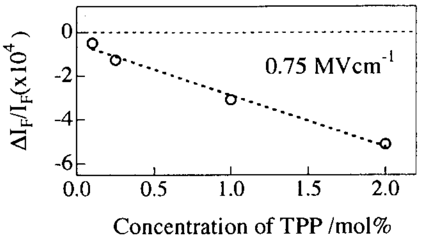

Figure 3. Plots of $\Delta I_F/I_F$ with a field strength of 0.75 MVcm^{-1} as a function of the TPP concentration.

Fluorescence lifetime, radiative lifetime, intersystem crossing and internal conversion life times of TPP were reported to be 14.7 ns, 134 ns, 22 ns and 77 ns, respectively.[10,11] The field-induced increase of the nonradiative rate may be attributed to an increase of the internal conversion rate from S_1 to S_0, rather than the increase of the intersystem crossing from S_1 to the triplet state or the decrease of the radiative decay rate. With the above-mentioned lifetimes, the magnitude of the field-induced change both in fluorescence decay rate and in internal conversion rate is roughly estimated to be 6×10^5 s^{-1} with a field strength of 1.0 MVcm^{-1} at 2.0 mol%. The concentration dependence of $\Delta\Phi_F$ well corresponds to that of $\Delta\alpha$. Therefore, it is considered that the field-induced increase of the internal conversion rate is enhanced by a molecular association.

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