# Delayed Fluorescence of Zinc Porphyrin in Poly(vinyl alcohol) Film

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The delayed fluorescence was observed at room temperature with tetrakis(4-sulfophenyl)porphinatozinc ($ZnTPPS_4$) dyed on poly(vinyl alcohol) (PVA) film. In the film, the T-T annihilation is prohibited since any two molecules in the excited triplet can not encounter during their lifetime. Three types of luminescence emission were observed; fluorescence ($S_1 \rightarrow S_0$), phosphorescence ($T_1 \rightarrow S_0$) and delayed fluorescence ($T_1 \rightsquigarrow S_1 \rightarrow S_0$). The delayed fluorescence can be detected only at elevated temperatures where thermal activation from the lowest excited triplet can repopulate the lowest excited singlet.

The lifetimes of phosphorescence of (2,3,7,8,12,13,17,18-octaethylporphinato)zinc (10 ms)[1] and (5,10,15,20-tetraphenylporphinato)zinc (0.3 ms)[2] have been measured in toluene solution at ambient temperature. Upon low density excitation by a laser, encounters of the long-lived excited metalloporphyrin molecule in the lowest triplet state with another molecule in the ground state result in the formation of an ion-pair in solution ($^3P^* + P \rightarrow P^+ + P^-$). Upon high density excitation, however, the triplet-triplet annihilation is the path of the ion-pair formation.[1-4]

Since the initial population of the excited singlet state is dissipated in a short period after excitation, a delayed fluorescence is observed only when the lowest excited singlet state is repopulated. The triplet-triplet annihilation results in a population of the lowest singlet state. However, competitive to the bimolecular processes, the lowest excited singlet can be repopulated by a thermal activation of the long-lived excited molecule in the lowest triplet state at elevated temperatures. The delayed fluorescence by this mechanism has been reported on Pd porphyrins in liquid methyl methacrylate.[5] In the present work, the delayed fluorescence was studied with water-soluble zinc porphyrin dyed on the poly(vinyl alcohol) (PVA) film, in which any two excited porphyrin molecules can not encounter during their lifetime.

## Experimental

Water-soluble tetrakis(4-sulfophenyl)porphin ($H_2TPPS_4$) was prepared by the method given elsewhere.[6] The sulfonation of all four phenyls of $H_2TPP$ was confirmed by thin-layer chromatography using silica gel. Tetrasodium[tetrakis(4-sulfonatophenyl)porphinato]zinc ($ZnTPPS_4$) was prepared by refluxing $H_2TPPS_4$ and zinc perchlorate in an aqueous solution. $ZnTPPS_4$ thus obtained was purified by recrystallization from methanol and acetone. The counter ion of the sulfonates was converted to sodium by use of a cation-exchange resin column. Anal. Calcd for $ZnTPPS_4Na_4(H_2O)_3$: C, 46.35; H, 2.65; N, 4.91. Found: C, 46.24; H, 2.66; N, 4.78. $CuTPPS_4$ was also prepared by the similar method.

PVA films of 0.2 mm thickness were prepared by spontaneous evaporation of an aqueous solution of PVA (degree of polymerization: 1400) on a glass plate at ambient temperature during 10 days and then the films were heated at 80—90 °C for 1 h. The PVA film was sufficiently swelled in water before use and then dipped in an aqueous solution of the water-soluble porphyrin at 45 °C. After dried under dry nitrogen at ambient temperature, the film was used for measurements.

Luminescence emission and excitation spectra were recorded on a Hitachi fluorescence spectrophotometer model MPF-2A, equipped with a Hamamatsu Photonics photomultiplier R928. A component of the emission with a decay lifetime longer than 1 ms was detected through a rotating chopper which can cut the short-lived fluorescence. The decay lifetime of phosphorescence was measured on the Hitachi MPF-2A spectrophotometer equipped with its phosphorescence measuring attachment. The output from the instrument was AD converted and accumulated on a Kawasaki Electronica M-50E transient memory with its averager model TMC-400. The decay profile obtained from the data accumulated for 512 or 1024 times was analyzed on a Commodore CBM3032 microcomputer interfaced to the transient memory.

The sample film in a quartz tube was placed in a quartz Dewar vessel for emission measurements. Measurements were carried out at several temperatures obtained during elevation of the temperature in the vessel after the Dry Ice disappeared in Dry Ice-methanol mixture. The temperature of the film was measured by a thermocouple placed in the sample tube and regulated within an error less than 2 °C. Similar measurements were achieved also at temperatures obtained during cooling of hot water in the vessel.

Absorption spectra were measured on a Shimadzu recording spectrophotometer model MPS-50 and ESR spectra were taken on a JEOL-ME-3X spectrometer.

## Results and Discussion

Absorption spectra of $ZnTPPS_4$ in PVA films conform to those observed with $ZnTPPS_4$ in methanol. A typical concentration of $ZnTPPS_4$ in the films used for the measurements was $10^{-4}$ M. ESR measurements were carried out on the PVA films dyed with $CuTPPS_4$ in the similar concentrations. The ESR spectra indicate that no appreciable interaction is present between copper porphyrin molecules in the film. In the medium, the molecules are isolated and in random orientation without forming dye aggregates such as dimer.

The ESR spectra of $CuTPPS_4$ in PVA film are in good agreement with those of magnetically diluted CuTPP in polycrystalline. Thus the effect of rotational and diffusional Brownian motions of the molecules in the

PVA film can be disregarded.[6)]

ZnTPPS$_4$ in PVA film exhibits both phosphorescence (13000 cm$^{-1}$) and fluorescence (15000—16500 cm$^{-1}$) emission at ambient temperature, while only fluorescence is observed with ZnTPPS$_4$ in degassed water or methanol media. In the film, the rate of nonradiative process of the excited porphyrin in the lowest triplet state is decreased since the diffusional encounter processes are prohibited. In fact, paramagnetic metalloporphyrins CuTPPS$_4$ as well as VOTPPS$_4$ in the PVA film exhibit a strong phosphorescence even at room temperature.

The emission spectra were observed as shown in Fig. 1, where the component luminescence of decay lifetime shorter than 1 ms was cut by use of the phosphoroscope. Not only the phosphorescence at 13000 cm$^{-1}$ but also the luminescence at 15000—16500 cm$^{-1}$ were observed. The latter showed an identical spectral profile to that of the fluorescence but decayed with a lifetime which comformed to that of the phosphorescence.

Since the migration of molecules is prohibited in the film, the emission should be ascribed to the E(eosin)-type delayed fluorescence.[7)] Repopulation of the lowest excited singlet is attributed to the thermal activation of the long-lived excited porphyrin in its lowest triplet. The thermal activation is possible only at elevated temperatures. In fact, the intensity of the delayed fluorescence decreases with lowering of temperature and is actually not detectable at temperatures below −20 °C.

The rate constants of intramolecular processes between three levels including the ground state (S$_0$), the lowest excited singlet and triplet (S$_1$, T$_1$) are defined as in Fig. 2. The ratio of the yields of delayed fluorescence and phosphorescence is given by

$$\phi_{\mathrm{df}}/\phi_{\mathrm{p}} = k_{-3} \times \frac{1}{k_{\mathrm{p}}} \times \phi_{\mathrm{f}}, \tag{1}$$

where $\phi_{\mathrm{f}}$ stands for the yield of fluorescence. Since an equilibrium is established between S$_1$ and T$_1$ and thus

$$k_{-3}/k_3 = \frac{1}{3}\exp\{-\Delta E_{\mathrm{ST}}/kT\}, \tag{2}$$

the Eq. 1 is rewritten as follows:

$$\phi_{\mathrm{df}}/\phi_{\mathrm{p}} = \frac{1}{3}\phi_{\mathrm{f}}\frac{k_3}{k_{\mathrm{p}}}\exp\{-\Delta E_{\mathrm{ST}}/kT\} \tag{3}$$

where $\Delta E_{\mathrm{ST}}$ is an energy gap between S$_1$ and T$_1$, 1/3, the ratio of the degeneracies of S$_1$ and T$_1$, $k$, Boltzmann constant and $T$, temperature. Provided that the ratio of the observed emission intensities is proportional to $\phi_{\mathrm{df}}/\phi_{\mathrm{p}}$,

$$\begin{aligned}&\ln\,[I_{\mathrm{df}}(660\,\mathrm{nm})/I_{\mathrm{p}}(780\,\mathrm{nm})]\\&\quad = -\Delta E_{\mathrm{ST}}/kT + \ln\!\left(\mathrm{const}\times\frac{1}{3}\frac{k_3}{k_{\mathrm{p}}}\right).\end{aligned} \tag{4}$$

If $k_{\mathrm{p}}$, $k_3$, and $\phi_{\mathrm{f}}$ are temperature independent, a linear relation between $\ln[I_{\mathrm{df}}(660\,\mathrm{nm})/I_{\mathrm{p}}(780\,\mathrm{nm})]$ and $1/T$ is expected. The plots of $\ln[I_{\mathrm{df}}(660\,\mathrm{nm})/I_{\mathrm{p}}(780\,\mathrm{nm})]$ against $1/T$ result in a straight line as shown in Fig. 3. From the slope of the straight line, $\Delta E_{\mathrm{ST}}$ was estimated as $3.5\times10^3$ cm$^{-1}$ which was in good ageement with a gap between the observed fluorescence and phosphorescence maxima ($3.9\times10^3$ cm$^{-1}$). If the minima of the excited singlet and triplet surfaces are shifted, the observed gap of phosphorescence and fluorescence peaks must be greater than the actual gap between S$_1$ and T$_1$. If $k_{-3}$ is thermal in origin, rather than bimolecular, the excited states S$_1$ and T$_1$ will decay as

$$\begin{aligned}S_1 &= c_1\exp(-\alpha t) + c_2\exp(-\beta t)\\ T_1 &= c_3\exp(-\alpha t) + c_4\exp(-\beta t)\end{aligned} \tag{5}$$

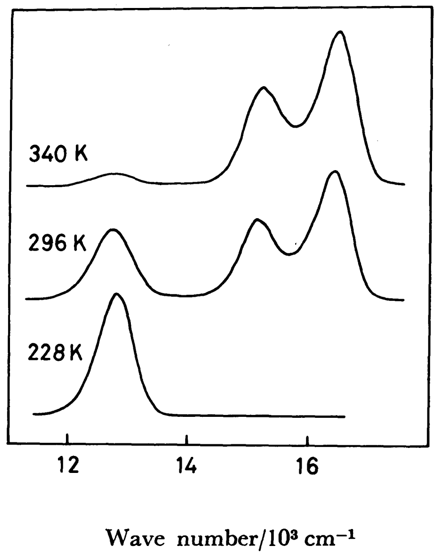

Fig. 1. Phosphorescence and delayed fluorescence of ZnTPPS$_4$ in PVA film at various temperatures.

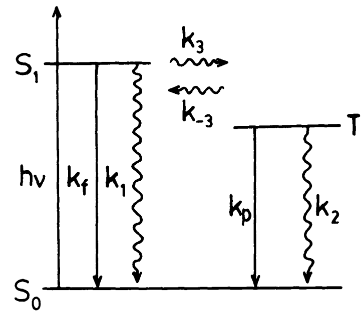

Fig. 2. Energy level diagram and the rate constants of intramolecular processes.
S$_1$ and T$_1$ stand for the lowest excited singlet and triplet states and S$_0$, the ground state.
⟶: radiative and ⇝: nonradiative processes.

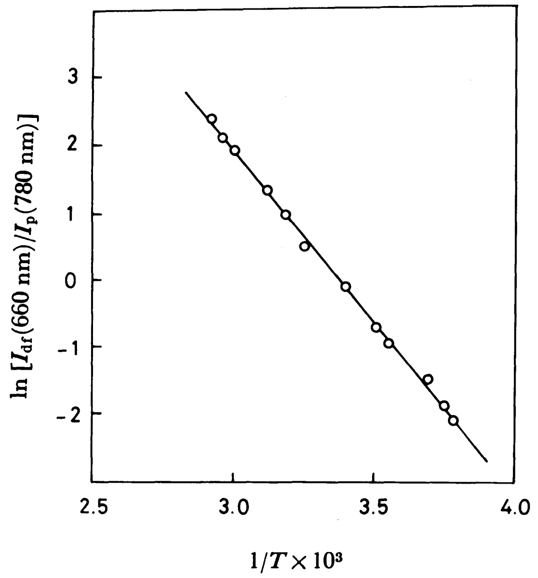

Fig. 3. Temperature dependence of ln [$I_{df}$(660 nm)/$I_p$(780 nm)].
$I_{df}$(660 nm) is the intensity of delayed fluorescence at 660 nm and $I_p$(780 nm), the intensity of phosphorescence at 780 nm.

where

$$\begin{pmatrix}\alpha\\ \beta\end{pmatrix}=\frac{1}{2}\{(A+B)\pm\sqrt{(A-B)^2+4k_3k_{-3}}\} \tag{6}$$

and

$$A\equiv k_f+k_1+k_3,$$
$$B\equiv k_2+k_p+k_{-3}. \tag{7}$$

The faster component of decay ($\alpha > A = k_f + k_1 + k_3$) determines the lifetime of fluorescence. On the other hand, the slower component of decay determines the lifetimes of delayed fluorescence and phosphorescence which are approximated as

$$\beta = 1/\tau_p = 1/\tau_{df} = k_2 + k_p + k_{-3}(1-\phi_t) \tag{8}$$

where it is assumed that $k_{-3} \ll k_3$, $k_2 + k_f$, and $\phi_t$ stands for the yield of $T_1$ state. In fact, the observed decay curves in the ms time scale were of single exponential and yielded an identical lifetime regardless of the monitoring wavelengths, delayed fluorescence at 660 nm and phosphorescence at 780 nm, respectively. However the lifetime varies with temperature. Figure 4 shows the plots of the inverse lifetime of phosphorescence $1/\tau_p$ against temperature. It is noted that the lifetime is almost constant from liquid nitrogen temperature up to −20 °C but it decreases with elevation of temperature only above −10 °C. The delayed fluorescence can be detected above −10 °C where the lifetime of phosphorescence decreases. This indicates that $k_p + k_2$ of ZnTPPS$_4$ in PVA film increases only to a lesser extent with temperature but $k_{-3}$, the rate constant of activation in the thermal equilibrium between $S_1$ and $T_1$, is sufficiently increased with temperature only at elevated temperatures.

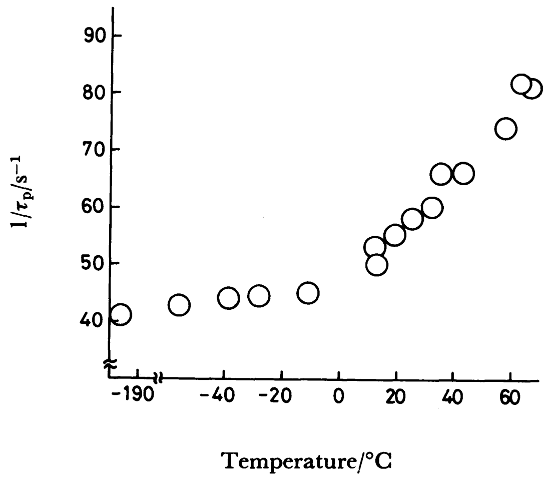

Fig. 4. Plots of the inverse phosphorescence lifetime versus temperature.

In fluid solution, the radiationless transition of the long-lived excited molecules is accelerated by a variety of diffusion-controlled bimolecular processes and thus the rate constant of nonradiative deactivation is sizable and heavily temperature dependent. Since the excited molecules cannot appreciably migrate during their lifetime in the polymer, the diffusion-controlled bimolecular mechanisms cannot play an important role in the relaxation of excited molecules.

In the present work, the metalloporphyrins fixed in the polymer film are isolated from the counterparts and this made it possible to study the intramolecular relaxation processes of excited metalloporphyrin in its lowest triplet by analysis of the temperature dependence of phosphorescence and delayed fluorescence.

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