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Electron transfer quenching of S_2 state fluorescence of Zn-tetraphenylporphyrin

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Abstract

Fluorescence quenching of the second excited (S_2) state of zinctetraphenylporphyrin (ZnTPP) with dichloromethane has been studied by steady state as well as time-resolved spectroscopy. Effective intermolecular electron transfer from the S_2 state of ZnTPP to dichloromethane was observed. The fluorescence decay of the S_2 state of ZnTPP was measured using a fluorescence up-conversion method and the rate constant of the electron transfer in neat dichloromethane was determined to be 1.0×10^{12} M^{-1} s^{-1}.

1. Introduction

The natural porphyrins provide key materials for photosynthesis, respiration and electron transport, and so play a crucial role in all living systems [1]. Thus, they provide great interest and are objects of broad investigations [2,3].

Free base porphyrins and metalloporphyrins, both in general, have a relatively large energy gap between the first (S_1) and the second (S_2) excited singlet states (usually quoted in the literature as Q and Soret bands, respectively). The Soret band is a strongly allowed transition and it is expected to be a very fast radiative transition to the ground state. However, in the free base porphyrins and metallooctaethylporphyrins the Soret band fluorescence has not been observed. The main reason is that the $S_1 \leftarrow S_2$ internal conversion occurs extremely rapidly. Contrary to that, in metallotetrabenzporphyrins (TBP) and metallotetraphenylporphyrins (TPP) the fluorescence from the Soret band was reported [4,5]. The fluorescence quantum yields and the lifetimes were estimated to be in the order of 10^{-3}–10^{-4} and 2.4–3 ps, respectively [4,6]. However, a direct measurement of the fluorescence decay, to our knowledge, is not yet provided.

Additionally, it is expected that the probability of electron transfer from the second excited state of the ZnTPP to the environment becomes higher than that from S_1. Hence, in the case of solvents with high electron affinity the S_2 fluorescence can be quenched via an intermolecular electron transfer process. Moreover, it may be expected that the intermolecular

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electron transfer can produce a photochemical hole burning (PHB) of the absorption spectra of $S_2 \leftarrow S_0$. Previously, Moerner and co-workers [7] reported two-step laser excitation of meso-tetra-*p*-tolyl(tetrabenzoporphyrinato)zinc and its magnesium derivative to their higher triplet state T_n with the presence of halomethane such as chloroform in poly(methyl metachrylate) (PMMA) film at 1.4 K which led to PHB of their absorption spectra attributable to electron transfer from T_n state to halomethane.

In this Letter the Soret band fluorescence decay of ZnTPP in acetonitrile (CH_3CN) and dichloromethane (CH_2Cl_2) using femtosecond time-resolved fluorescence up-conversion technique is reported. Fluorescence quenching in CH_2Cl_2 due to the intermolecular electron transfer process has been observed and discussed. The effect of excitation wavelength on the electron transfer between ZnTPP and CH_2Cl_2 was examined.

2. Experimental

The steady state absorption spectra were measured on Shimadzu UV-260 and Jasco Ubest55 spectrometers. Fluorescence spectra were measured on Hitachi 850E and F-400 spectrofluorimeters. The photoirradiation was performed by an excimer pumped dye laser (Lambda Physik LPX-100/FL-3002, 2 Hz, 4 mJ per pulse) at different wavelengths. EPR experiments were carried out with JEOL JES-ME spectrometer.

The time-resolved fluorescence decay was measured using a fluorescence up-conversion apparatus. The principles of this technique and main specifications are briefly discussed below. The fluorescence from the sample and a portion of the fundamental laser pulse are mixed in a thin non-linear optical crystal to generate light at the sum frequency. Intensity of this signal is proportional to the fluorescence and the time resolution of the measurement is limited only by the laser pulse width. Ar-ion laser pumped $Ti^{3+}:Al_2O_3$ laser was used as a light source (Tsunami, Spectra Physics). The wavelength of the system was held at 820 nm (fwhm = 300 fs, 82 MHz, 450 mW). The second harmonic was generated in 0.8 mm BBO crystal and was focused onto the sample. The resulting fluorescence and the residual laser fundamental are focused in a 0.8 mm BBO type I crystal to create the up-converted signal at the sum frequency. After passing an appropriate filter and a grating monochromator, it is detected with photon counting system (Hamamatsu C1230, photomultiplier type R464-02). The fluorescence decay curve is obtained by varying the optical path of the delay stage for the fundamental beam. As an instrument response function a cross-correlation signal between fundamental and its second harmonic was used.

Picosecond transient absorption spectra were measured by using a dye laser system pumped by a second harmonic of a mode locked Nd^{3+}:YAG laser (Quantel, Picochrome YG-503 C/PTL-10). The laser was operated at 10 Hz and the signal was accumulated for 30 shots. The sample was excited with a second harmonic of the pyridine dye laser (340 nm). The time resolution was about 10 ps. The details of this system were described elsewhere [8].

ZnTPP was prepared by the methods reported elsewhere [9]. The solvents were purified by distillation in the presence of calcium hydride. The sample solutions were deoxygenated by irrigating with a dried nitrogen gas stream before measurement. All measurements were performed at 20°C.

3. Results and discussion

3.1. Steady state dichroism

ZnTPP was irradiated in deaerated dichloromethane solution (4 ml) at ambient temperature with a pulsed laser at several wavelengths. The concentration of ZnTPP was made to show an absorbance of nearly unity at excitation wavelength. The excitation of ZnTPP (4.5×10^{-4} M) at the longer absorption tail of the Q band (600 nm) did not lead to any change of the absorption spectrum. However, excitation of the Soret band of ZnTPP (3.2×10^{-6} M) at 425 nm reduced rapidly the Q-band absorption of ZnTPP as depicted in Fig. 1. The irradiation of ZnTPP in acetonitrile, toluene and benzene at 425 nm did not change at all the absorption spectrum even after prolonged irradiation during 60 min. The irradiation of ZnTPP in 1,1,2,2-tetrachloroethane resulted in nearly the same spectral change as in

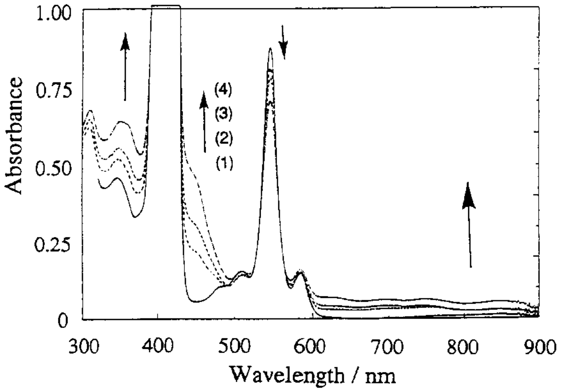

Fig. 1. The change of the absorption spectra of ZnTPP in CH_2Cl_2 by irradiation of the laser pulses at 425 nm: (1) before irradiation, (2) after 70 shots, (3) after 100 shots, (4) after 172 shots.

dichloromethane. The absorptions were grown around 450 nm and at longer wavelengths from 600 nm which correspond to production of the radical cation of ZnTPP ($ZnTPP^+$) [10]. The absorbance at 650 nm was linearly increased with the irradiation at 425 nm and the quantum yield for the disappearance of ZnTPP was determined to be about 10^{-3}. The examination of EPR for the solution of ZnTPP/CH_2Cl_2 irradiated at 425 nm showed signals ($g = 2.0027$) with nine hyperfine splitting separated by 1.6 G (Fig. 2), which is surely assigned to $ZnTPP^+$ [10]. The observed long lifetime of $ZnTPP^+$ may be explained due to the dissociation reaction of the carbon–halogen bond in the anion radical of haloalkanes [11]. However, no EPR signal was detected for the ZnTPP/CH_2Cl_2 solution irradiated at 600 nm and for ZnTPP/CH_3CN solution in general. The integrated intensity of the EPR signal was almost linearly increased with the number of pulses with nearly the same slope as the plots of the absorbance at 650 nm. These observations show that the fluorescence behaviour of ZnTPP in CH_2Cl_2 and in CH_3CN should be different and for this reason fluorescence measurements were carried out.

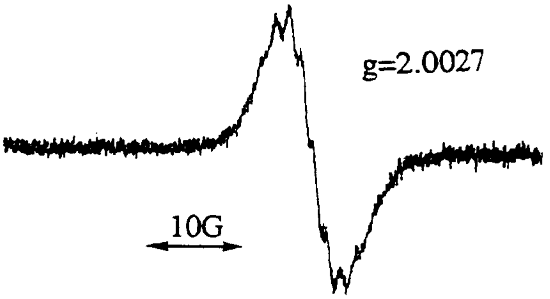

Fig. 2. EPR signal observed after 5 min irradiation (600 pulses) of 425 nm light on ZnTPP in CH_2Cl_2.

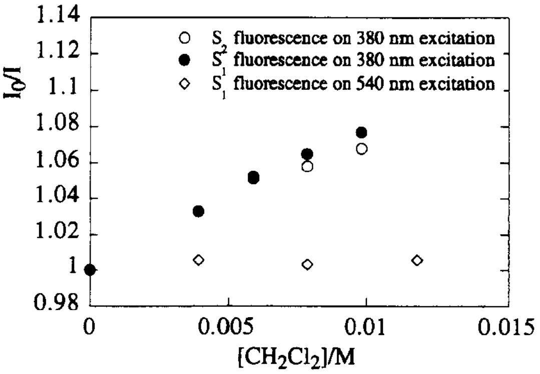

Fig. 3. Stern–Volmer plots of ZnTPP fluorescence in CH_3CN by adding CH_2Cl_2.

The quenching of fluorescence of ZnTPP from the S_2 and S_1 states by dichloromethane was examined by varying concentration of dichloromethane in acetonitrile solution. Fig. 3 shows the results of the Stern–Volmer plots, where I_0 and I denote the fluorescence intensity in the absence and the presence of dichloromethane. At 540 nm excitation the resulting S_1 fluorescence is practically not quenched by CH_2Cl_2. However, at 380 nm excitation, the fluorescence from S_2 and S_1 was quenched by CH_2Cl_2 with nearly the same Stern–Volmer quenching constant $k_{SV} = 7$ M^{-1} for S_2 quenching and 8 M^{-1} for S_1 quenching.

Now, if we take the lifetime of the S_2 state to be about 3 ps [4,6], the quenching rate constant k_q of S_2 by dichloromethane can be estimated as larger than 3×10^{12} M^{-1} s^{-1}. The above findings confirm our expectation, that ZnTPP fluorescence in CH_2Cl_2 is effectively quenched due to the intermolecular electron transfer process with the femtosecond time constant. Therefore, direct measurements of ZnTPP fluorescence decays in CH_2Cl_2 and CH_3CN were performed.

3.2. *Time-resolved measurements*

The absorption maximum of the Soret band of ZnTPP is located at around 418 nm in CH_2Cl_2 and slightly (142 cm^{-1}) bathochromic shifted to 420.5 nm in CH_3CN. The Stokes shift is in both solutions only about 390 cm^{-1}. This behaviour makes the time-resolved fluorescence measurements extremely difficult, because: (1) in the case of the shorter excitation wavelengths (< 405 nm) the strong Raman lines of the solution overlapped with the fluorescence, (2) the excitation wavelength cannot be set at the band edge (around 428 nm) which makes the time or spectral separation of pump and fluorescence lights impossible. However, if the excitation wavelength is chosen around 410 nm, the weak fluorescence is not spectral overlapped by the Raman scattered light and the cross-correlation signal between fundamental and residual second harmonic, passed through the sample cell, can be separated from the fluorescence up-converted signal in the time, because of the strong dispersion effect in the sample. The results of the up-conversion measurements of ZnTPP are plotted in Fig. 4 for CH_2Cl_2 (a) and CH_3CN (b) solutions, respectively. While the excitation (410 nm) and the fluorescence (around 425 nm) are close to each other, and the phase matching condition in the BBO crystal is not very tight, parallel to the fluorescence up-converted signal a cross-correlation signal will be generated. The peaks at 0 delay times in Fig. 4 are the scattering of the cross-correlation signal between fundamental and residual second harmonic. The slow rise and the time shift of the up-converted fluorescence are due to the strong dispersion and re-absorption effects in the 2 mm sample cell. Including these effects the results could be fitted within the experimental error with the single exponential function using the modified deconvolution formula

$$F(t) = \text{const.} \int_0^d \exp[-\alpha' x - \alpha(d-x)] \times \int_{-\infty}^{+\infty} \exp\left[-\left(t' - \frac{x}{c}\Delta n\right)/\tau\right] \times f\left(t - t' + \frac{x}{c}\Delta n\right) \mathrm{d}x\, \mathrm{d}t',$$

where α and α' are the absorption and reabsorption coefficients at excitation and emission wavelengths, respectively. τ is the fluorescence lifetime, Δn is the difference of the refractive index at excitation and emission wavelengths, c is the light velocity, d is the sample thickness and the function f is the system response function.

The lifetimes were determined to be 3.5 and 0.75 ps in CH_3CN and CH_2Cl_2, respectively. The result in CH_3CN agrees well with the earlier reported value of 3 ps estimated by fluorescence polarization

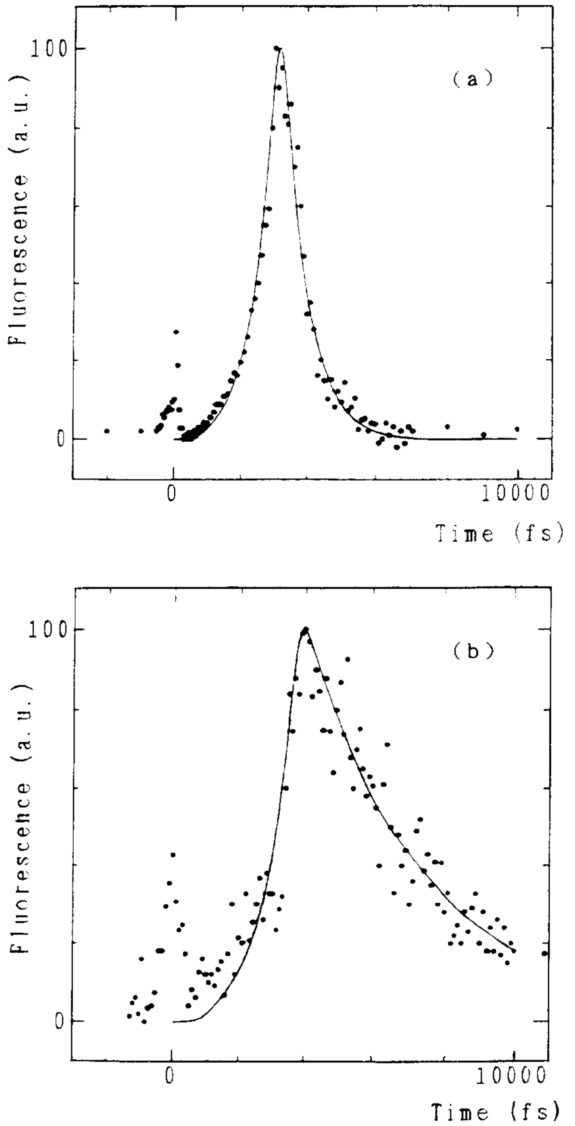

Fig. 4. The S_2 fluorescence decay curves of ZnTPP. (a) In CH_2Cl_2 observed at 425 nm. The single exponential fit with 0.75 ps time constant, including the dispersion and reabsorption effects, is also given by a solid line. (b) In CH_3CN observed at 428 nm. The single exponential fit with 3.5 ps is also given by a solid line. The peaks at 0 fs are the scattering of the cross-correlation signal.

method [6]. However, the fluorescence is strongly quenched in CH_2Cl_2. This strong quenching cannot be explained by the much more rapid intersystem crossing process. According to the theory of radiationless transitions [12], the rate constant of the intersystem crossing is determined by the electronic matrix element and the energy gap between two electronic states involved in the radiationless transition process. Both quantities, however, are for ZnTPP in CH_2Cl_2 and CH_3CN nearly equal. On the other hand, because of the larger electron affinity of CH_2Cl_2 (about −1.8 eV versus SCE), the intermolecular electron transfer process between the second excited state of ZnTPP and CH_2Cl_2 molecules, in agreement with steady state observations, is a relevant explanation for the observed quenching. The electron transfer rate constant was estimated to be about 1.0×10^{12} M^{-1} s^{-1} and the quantum yield of ZnTPP cation to be about 0.79, under the assumption that the fluorescence lifetime of ZnTPP in CH_3CN relates to the lifetime without electron transfer quenching.

In order to verify the transient building of ZnTPP cation in CH_2Cl_2 solution, picosecond transient absorption measurements were carried out. We have compared the transient absorption spectra of ZnTPP in CH_2Cl_2 and CH_3CN solvents. Both samples were prepared with the same absorbances at the excitation wavelength (340 nm) and irradiated by the same laser intensity. The resulting spectra immediately after excitation are given in Fig. 5. The spectrum in CH_3CN, for comparison, was shifted about 8 nm to the shorter wavelengths.

The transient spectrum in CH_3CN immediately after excitation shows the well-known spectral structure of $S_n \leftarrow S_1$ for metalloporphyrins [13] (Fig. 5a). The deeps in the spectrum are resulted due to the bleaching (550 and 585 nm) and the induced emission (650 nm) of the Q band. Contrary to this, the absorption shape of the ZnTPP in CH_2Cl_2 (Fig. 5b) is different from that in CH_3CN (especially in the longer wavelength region (550–900 nm)). This spectral difference can be easily understood if one takes into consideration that in CH_2Cl_2 solution the transient spectrum was resulted due to the overlap of $S_n \leftarrow S_1$ and ZnTPP cation spectra whereas in CH_3CN solution only the $S_n \leftarrow S_1$ spectrum has been risen. The ZnTPP cation spectrum (Fig. 5c) was obtained by subtracting spectrum (a) with appropriate coefficient from the overlapped spectrum (b): (c) = (b) − (1 − 0.79) × (a). The coefficient used was determined as a remaining portion of S_1 molecules estimated from the S_2 fluorescence lifetime in CH_2Cl_2. The difference absorption spectrum of ZnTPP cation was reproduced by using the absorption coefficients of the cation [1] and the ground state as shown in Fig. 5d. Comparison of the spectra (c) and (d) shows a qualitative agreement. The relative intensities of the bands, however, differ from each other. The reason for this difference could be the uncertainty of the absorption coefficients in the solvents used in the experiments.

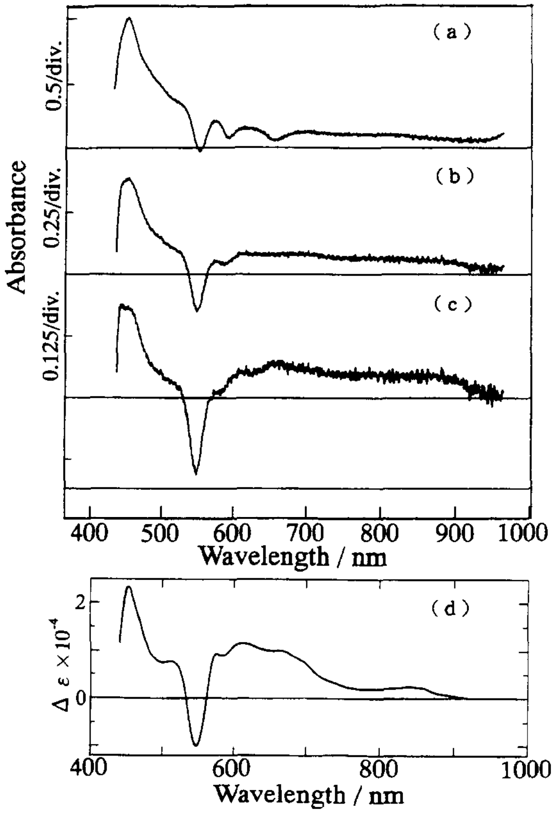

Fig. 5. Picosecond time-resolved absorption spectra immediately after excitation at 340 nm: (a) ZnTPP in CH_3CN, (b) ZnTPP in CH_2Cl_2, (c) remaining spectrum of ZnTPP in CH_2Cl_2 subtracted from the contribution of the estimated $S_n \leftarrow S_1$ spectrum; (b) $-0.21 \times$(a), (d) difference spectrum of ZnTPP cation reproduced by using the absorption coefficients given in Ref. [1].

The decay of the cation band of ZnTPP could not be detected until 6 ns after excitation, while the rise of the $T_n \leftarrow T_1$ absorption band followed by the decay of $S_n \leftarrow S_1$ band was observed. This may indicate that the dissociation reaction of the anion, $CH_2Cl_2^- \rightarrow \cdot CH_2Cl + Cl^-$, proceeds rapidly in the exciting laser pulse.

The efficient quenching of S_2 by CH_2Cl_2 during such a short lifetime shows that the quenching occurs by CH_2Cl_2 molecules surrounding a S_2 molecule according to the Perrin model

$$\ln(I_0/I) = VN_A[CH_2Cl_2],$$

where N_A is the Avogadro number and V is the quenching volume related to the quenching radius R by $V = \frac{4}{3}R^3$. This plot gives $R = 15$ Å which means CH_2Cl_2 molecules located in a sphere of 15 Å radius surrounding a S_2 molecule can effectively quench the S_2 molecule. Since the porphyrin skeleton has a radius of nearly 6.5 Å and the C–Cl distance is 1.8 Å, CH_2Cl_2 molecules in close proximity of ZnTPP efficiently quench the S_2 state.

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