

Kinetics for acid-dissociation of tetraphenylporphinetetrasulfonate in the ground state measured by laser photolysis relaxation method

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Transient absorption spectra (TAS) for tetraphenylporphinetetrasulfonate (tpps^{4-}) and its diprotonated form ($\text{H}_2\text{tpps}^{2-}$; protonated at the two N-atoms of the porphyrin-ring) after laser photolysis (532 nm, pulse width 6 ns) showed the generation of their respective triplet states in aqueous solutions. From the analysis of TAS for tpps^{4-} and $\text{H}_2\text{tpps}^{2-}$ at pH 2.05 and 7.41 (I , 0.01; 25 °C), molar absorption coefficients of tpps^{4-} and $\text{H}_2\text{tpps}^{2-}$ in their triplet states were obtained. On the other hand, as the triplet tpps^{4-} was deactivated, $\text{H}_2\text{tpps}^{2-}$ in the triplet state was generated through the protonation of the triplet tpps^{4-} in the pH range of 5.0–6.0 (I , 0.01; 25 °C). This indicated that the triplet tpps^{4-} was more basic than the ground state. As $\text{H}_2\text{tpps}^{2-}$ in the triplet state was deactivated, an excess amount of $\text{H}_2\text{tpps}^{2-}$ in the ground state was successively generated. The excess $\text{H}_2\text{tpps}^{2-}$ faded to attain the acid-dissociation equilibrium in the ground state again. The total decay curves were successfully fitted to triple-exponential decay functions, and the rate constant for acid-dissociation of $\text{H}_2\text{tpps}^{2-}$ in the ground state was determined as $(3.3 \pm 0.4) \times 10^5 \text{ s}^{-1}$, independent of pH. From this value and the acid-dissociation constants of $\text{H}_2\text{tpps}^{2-}$, the overall acid-dissociation kinetics of tpps^{4-} was proposed.

Introduction

Metalloporphyrins have been widely investigated in chemical, biological, technological and medical fields, and many reports include the complexation kinetics of hydrophilic and hydrophobic porphyrins in homogeneous^{1–5} and heterogeneous systems.^{6–8} It is thought that the slow metalation of porphyrins is caused by a slow deformation of porphyrin-ring occurring before the metalation.^{1,2} Recently, spectra of a novel sitting-atop (SAT) complex of tetraphenylporphine with Cu(II) have been reported in acetonitrile,⁹ which is postulated to be an intermediate of complexation.^{5,10,11} Furthermore, some super-molecules including porphyrins have now been extensively studied.^{12,13} Acid-dissociation is one of the fundamental properties of porphyrins, and its equilibria were investigated for many porphyrins.¹⁴ Its kinetics were, however, studied for only a few kinds of porphyrins by a laser-induced temperature-jump (T-jump) relaxation method.^{15,16} The slow deformation of porphyrin-ring was involved in the process of acid-dissociation of an aqueous porphyrin,¹⁵ and thus the mechanism of acid-dissociation of other porphyrins is also important from the viewpoint of the investigation of complexation kinetics.^{1,2}

Porphyrins are also known to show various photophysical and photochemical phenomena, for example, fluorescence, phosphorescence, electron or charge transfer,^{17–19} and photodecomposition.^{20,21} Recently reactions of photo-induced ligand substitution have been studied for various metalloporphyrins, for example, chromium, iron, and cobalt complexes, so far.^{22–24} The photo-induced relaxation method has a high potential to measure more rapid reactions, such as ns- through to μs -level reactions,^{22–24} than the conventional T-jump relaxation method.

The acid-dissociation constants, $\text{p}K_{\text{a},1}$ and $\text{p}K_{\text{a},2}$, of the conjugated acid (protonated at N-atoms of the porphyrin-ring) of 5,10,15,20-tetraphenylporphinetetrasulfonate (tpps^{4-}) were

reported as 4.60 ± 0.01 and 5.17 ± 0.01 , respectively, at 0.01 M ionic strength at 25 °C,¹⁴ but no reports appeared for the kinetics of its acid-dissociation. In the present study, we measure the acid-dissociation kinetics of tpps^{4-} in the ground state by laser photolysis relaxation method for the first time.

Experimental

Samples

Tpss^{4-} , 2-(*N*-morpholino)ethanesulfonic acid (MES, $\text{p}K_{\text{a}} = 6.15$) and *N*-cyclohexyl-2-hydroxy-3-aminopropane-1-sulfonic acid (CAPSO, $\text{p}K_{\text{a}} = 10.0$) were purchased from Dojindo Lab. (Kumamoto, Japan). Water was distilled and purified with an ion-exchange system (Milli-Q Sp. Toc., Millipore). Other reagents were of analytical reagent grade. The concentrations of tpps^{4-} and the buffer, MES or CAPSO, in aqueous solutions were 3×10^{-6} – 3×10^{-5} M and 1×10^{-3} M, respectively. In order to prevent the aggregation of tpps^{4-} ,²⁵ a lower ionic strength of 0.01 M was employed, which was adjusted with HCl and NaCl. The pH was adjusted to 2.0–7.4.

Measurements

Laser photolysis was carried out with an Nd:YAG laser (Sur-elite I-10, Continuum; repetition, 10 Hz) equipped with a second harmonic (532 nm) generator. The laser pulse width and power were about 6 ns and 18 mJ pulse⁻¹, respectively. The transients were monitored by a detection system (TSP-601, Unisoku, Osaka, Japan). The intensity of an analyzing light beam from a continuous xenon lamp (L2195, 150 W, Hamamatsu Photonics) passing through a sample cell at a right angle of the laser light was measured by a photomultiplier (R2949, Hamamatsu Photonics) attached to a monochromator (slit width, 8 nm). The output of the photomultiplier was connected

to a digital oscilloscope (TDS-320, SONY Tektronix), which was triggered by a split laser light. Transients obtained with 50 to 100 laser shots were averaged for each measurement. The time constants, τ , for the decay of transient species were obtained by applying the non-linear least-squares method to an absorbance change at each wavelength after laser irradiation. The transients were measured in the wavelength range of 350–700 nm in a 10 nm step.

In order to control the concentration of dissolved oxygen, the partial pressure of oxygen, $P(\text{O}_2)$, in gas phase was changed. A mixture of known volume of O_2 and N_2 gases was shaken for 1 min with solutions in a sealed cell three times.

The pH value of the solution after laser irradiation was measured with a pH meter. The temperature of the cell was maintained at $25.0 \pm 0.1^\circ\text{C}$ by the circulation of thermostated water.

Results and discussion

Generation of triplet tpps^{4-} or $\text{H}_2\text{tpps}^{2-}$ by laser photolysis

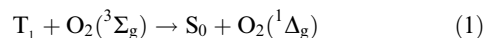
Transient absorption spectrum (TAS) for tpps^{4-} in aerated aqueous solution (pH 7.41) at time $t = 1.5 \mu\text{s}$ after laser irradiation ($t = 0$) is shown in Fig. 1. The valley at 410 nm and the peak at 440 nm correspond to the decrement of the ground state and the generation of transient species, respectively. The absorbance changes in the range of 400–480 nm were successfully fitted to a single-exponential function and the same τ value was obtained. The τ value for the decay of the transient species in aerated aqueous solutions was $1.82 \pm 0.03 \mu\text{s}$ ($n = 7$, $n = \text{data number}$), which corresponded to a rate constant of $(5.49 \pm 0.08) \times 10^5 \text{ s}^{-1}$ for deactivation.

TAS for $\text{H}_2\text{tpps}^{2-}$ in aerated aqueous solution (pH 2.05) at $t = 1.5 \mu\text{s}$ after laser irradiation is also shown in Fig. 1. The valley at 430 nm and the peak at 510 nm correspond to the decrement of the ground state and the generation of transient species, respectively. Fitting the absorbance changes in the range of 420–540 nm to a single-exponential function resulted in the same τ value. Its value for the decay of the transient species in aerated aqueous solutions was obtained as $1.72 \pm 0.02 \mu\text{s}$ ($n = 10$), which corresponded to a rate constant of $(5.81 \pm 0.08) \times 10^5 \text{ s}^{-1}$ for deactivation.

In both cases, an absorbance change at each wavelength (350–700 nm) was close to zero over 9 μs after the photolysis, and this means neither photo-decomposition nor transient species of longer time constant.

$P(\text{O}_2)$ was varied in the range of 0.2–1.0 atm ($(0.2\text{--}1.0) \times 10^5 \text{ Pa}$), and τ values for the decay of the transient species for tpps^{4-} and $\text{H}_2\text{tpps}^{2-}$ were measured. A linear relationship between τ^{-1} and $P(\text{O}_2)$ was obtained. The intercept of the rela-

tionship was close to zero, meaning that the quenching by oxygen molecule was almost the only deactivating process of these transient species. By using Henry's law, the oxygen concentrations in water were calculated and the quenching constants, k_q by O_2 were obtained as $(2.07 \pm 0.03) \times 10^9$ and $(2.19 \pm 0.03) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ for tpps^{4-} and $\text{H}_2\text{tpps}^{2-}$, respectively. These values are in good agreement with the rate constants for diffusion-controlled reactions between common organic compounds in the triplet states and oxygen molecule, $(1\text{--}3) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$.^{26,27} It is known that photolysis of porphyrins leads to the generation of their triplet species T_1 and that the triplet porphyrins are quenched by $\text{O}_2(^3\Sigma_g)$ as:^{28–30}



The rate constant for intrinsic monomolecular decay and the T–T absorption maximum of triplet 5,10,15,20-tetraphenylporphyrine (tpp) in cyclohexane were reported as $1.6 \times 10^3 \text{ s}^{-1}$ and 440 nm, respectively.³¹ k_q by $\text{O}_2(^3\Sigma_g)$ and the maximum of TAS for triplet $\text{H}_2\text{tpp}^{2+}$ in toluene were $1.69 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ and about 500 nm, respectively.³² Bonnet *et al.* reported that k_q for triplet tpps^{4-} by $\text{O}_2(^3\Sigma_g)$ in an aqueous solution was $1.8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$.³³ These facts support that the transient species observed for tpps^{4-} and $\text{H}_2\text{tpps}^{2-}$ in the present study are their respective triplet species.

We considered the possibility of radical generation, since Bonnet *et al.* reported that a radical for tpps^{4-} showing a time constant of 0.37 ms was generated at pH 7.4 by 347 nm-laser irradiation and that the maximum of TAS for the radical was about 450 nm.³³ We did not observe any transient species showing such a long decay constant for 532 nm-laser irradiation. However, we observed that another transient species showing a long time constant (about 0.3 ms) was generated by 355 nm-laser irradiation (with a third harmonic generator) and that the maximum of TAS for the transient species was about 440–450 nm. This observation means that there is at least one path for the radical generation through levels no lower than the second excited singlet level (S_2 ; Soret band, 413 nm) of tpps^{4-} in aqueous solutions.

Absorption spectra of tpps^{4-} and $\text{H}_2\text{tpps}^{2-}$ in their triplet states

In the following sections, the concentrations of tpps^{4-} in the ground state, $\text{H}_2\text{tpps}^{2-}$ in the ground state, tpps^{4-} in the triplet state and $\text{H}_2\text{tpps}^{2-}$ in the triplet state at t after laser irradiation ($t = 0$) are abbreviated to $C_{\text{GP}}(t)$, $C_{\text{GH}}(t)$, $C_{\text{TP}}(t)$, and $C_{\text{TH}}(t)$, respectively, for convenience. Since no decompositions of tpps^{4-} nor $\text{H}_2\text{tpps}^{2-}$ occur by the 532 nm-laser irradiation, the following eqns. (2) and (3) are valid for any time, t , under the neutral (pH 7.41) and acidic (pH 2.05) conditions, respectively:

$$\delta C_{\text{GP}}(t) + \delta C_{\text{TP}}(t) = 0 \quad (2)$$

$$\delta C_{\text{GH}}(t) + \delta C_{\text{TH}}(t) = 0 \quad (3)$$

where $\delta C_{\text{GP}}(t) = C_{\text{GP}}(t) - C_{\text{GP,eq}}$, $\delta C_{\text{GH}}(t) = C_{\text{GH}}(t) - C_{\text{GH,eq}}$, $\delta C_{\text{TP}}(t) = C_{\text{TP}}(t)$, $\delta C_{\text{TH}}(t) = C_{\text{TH}}(t)$, and the subscript eq means the concentration at the acid-dissociation equilibrium, that is, the concentration before the laser irradiation. The lifetimes of tpps^{4-} and $\text{H}_2\text{tpps}^{2-}$ in the excited singlet state (S_1) were found as 11.9 ns and 5.0 ns, respectively, by time-resolved fluorescence measurement. Since they are much shorter than the time range discussed here, the amounts in the S_1 states are ignored in a time scale of μs .

Initial absorbance, $A(\lambda, \text{eq})$, of tpps^{4-} (GP) at wavelength λ before laser irradiation can be written as:

$$A(\lambda, \text{eq}) = \varepsilon_{\text{GP}}(\lambda) b C_{\text{GP,eq}} \quad (4)$$

where $\varepsilon(\lambda)$ is the molar absorption coefficient at λ , and b is the cell path length (1.00 cm in this case). For the TAS for tpps^{4-}

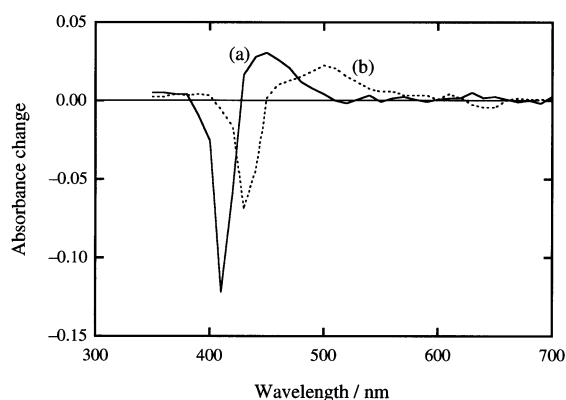


Fig. 1 Transient spectra at 1.5 μs after 532 nm-laser irradiation, averaged for 50 laser shots in aerated aqueous solutions. (a) tpps^{4-} , $3.0 \times 10^{-6} \text{ M}$; pH, 7.41. (b), $\text{H}_2\text{tpps}^{2-}$, $3.0 \times 10^{-6} \text{ M}$; pH, 2.05.

at pH 7.41, absorbance changes, $\Delta A(\lambda, t)$, at λ and t can be expressed as:

$$\begin{aligned} A(\lambda, t) &= \varepsilon_{\text{GP}}(\lambda)bC_{\text{GP}}(t) + \varepsilon_{\text{TP}}(\lambda)bC_{\text{TP}}(t), \\ \Delta A(\lambda, t) &\equiv A(\lambda, t) - A(\lambda, \text{eq}) \\ &= \varepsilon_{\text{GP}}(\lambda)b\delta C_{\text{GP}}(t) + \varepsilon_{\text{TP}}(\lambda)b\delta C_{\text{TP}}(t) \\ &= (\varepsilon_{\text{TP}}(\lambda) - \varepsilon_{\text{GP}}(\lambda))b\delta C_{\text{TP}}(t) \end{aligned} \quad (5)$$

$\varepsilon_{\text{GP}}(\lambda)$ and $\Delta A(\lambda, t)$ are measurable for every λ , but $\varepsilon_{\text{TP}}(\lambda)$ can not be directly obtained only from these data because of the unknown term of $\delta C_{\text{TP}}(t)$. The $\varepsilon(\lambda)$ values of triplet state are frequently determined by experiments of energy transfer to another acceptor or complete conversion method.^{33,34} In fact, $\varepsilon(\lambda)$ values of tpps^{4-} in the triplet state were already reported using 347 nm laser lights by complete conversion method.³³

The purpose of this study is to clarify the acid-dissociation kinetics of tpps^{4-} in the ground state and not in the triplet state, and thus detailed studies on the triplet state were not carried out. We propose a simpler and more conventional method to estimate $\varepsilon(\lambda)$ of triplet species with the following assumption for a set of λ_1 , λ_2 , and λ_3 ($\lambda_1 < \lambda_2 < \lambda_3$, $\lambda_2 - \lambda_1 = \lambda_3 - \lambda_2$):

$$\varepsilon_{\text{TP}}(\lambda_2) \approx \frac{1}{2} \{ \varepsilon_{\text{TP}}(\lambda_1) + \varepsilon_{\text{TP}}(\lambda_3) \} \quad (6)$$

In order to confirm the analysis, two sets of wavelength were selected: 420, 430, 440 nm and 430, 440, 450 nm. Fig. 2(a) reveals the molar absorption coefficients of triplet tpps^{4-} , which were obtained with $\Delta A(\lambda, 1.5 \mu\text{s})$ at pH 7.41. As shown in this figure, the results for different sets of wavelength are in good agreement with each other and the data at other times gave similar $\varepsilon_{\text{TP}}(\lambda)$ values. The validity of eqn. (6) is obvious in the figure. Furthermore, partial $\varepsilon(\lambda)$ values of triplet tpps^{4-} obtained by complete conversion method³³ agreed well with ours in the longer wavelength range of 460–680 nm. These

facts show that the analysis is reasonable. The triplet tpps^{4-} has a broad absorption at about 450 nm with $\varepsilon_{\text{TP}} \approx 8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$.

As for $\text{H}_2\text{tpps}^{2-}$, relations similar to eqns. (4)–(6) are valid by adopting GH and TH instead of GP and TP, respectively. In this case, three sets of wavelength were selected, that is, 410, 420, 430 nm, 440, 450, 460 nm (not shown) and 500, 520, 540 nm. Fig. 2(b) shows $\varepsilon(\lambda)$ values of triplet $\text{H}_2\text{tpps}^{2-}$, which were calculated with $\Delta A(\lambda, 1.5 \mu\text{s})$ at pH 2.05. The results for different sets of wavelength and different times (not shown) agree well again, and the relationship of eqn. (6) is also valid. The triplet $\text{H}_2\text{tpps}^{2-}$ has two absorption maxima at about 440 and 500 nm with $\varepsilon_{\text{TH}} \approx (8\text{--}11) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. There have been no reports on the absorption spectrum of triplet $\text{H}_2\text{tpps}^{2-}$ according to our knowledge.

Shift of acid-dissociation equilibrium in the ground state

The absorbance changes after the laser photolysis in the pH range of 5.0–6.0 were complicated. For instance, Fig. 3 shows the absorbance changes at 430 and 440 nm at pH 5.11 and 5.77. It is obvious that the each absorbance change can not be fitted to a single-exponential function, implying that some transient species other than the triplet were generated. Since almost all the triplet species are deactivated at $t = 10 \mu\text{s}$ after photolysis, the other transient species can be clarified from the TAS observed at this time. Fig. 4 shows the TAS at $t = 10 \mu\text{s}$ at pH 5.11 and 6.02, as well as the difference spectrum between $\text{H}_2\text{tpps}^{2-}$ and tpps^{4-} in their ground states. These three spectra are quite similar to each other. Therefore, it could be thought that excess $\text{H}_2\text{tpps}^{2-}$ in the ground state was generated in the course of the deactivation.

It is probable that the protonation of tpps^{4-} occurs through either the S_1 or T_1 . Each process is discussed from the viewpoint of protonation rate. The rate constant for the diffusion-controlled reaction (k_{diff}) for the reaction between two ionic species i and j can be expressed as ($k_{\text{diff}} = 4\pi N_A a_{ij}(D_i + D_j)\Phi_{ij}$),³⁵ where N_A is the Avogadro's number, a_{ij} the distance of the closest approach of the reacting species, D the diffusion coefficient, and Φ_{ij} a function depending upon the interaction potential for the pair of i and j . The k_{diff} for the pair of tpps^{4-} and H^+ was estimated as $2.0 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ with $(D_{\text{H}^+} + D_{\text{tpps}^{4-}}) \approx D_{\text{H}^+} = 9.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at 25°C ,¹⁵ $a_{ij} 4.0 \times 10^{-10} \text{ m}$,¹⁵ and Φ_{ij} calculated as 7.2.³⁶ Therefore, if the protonation proceeds as the diffusion-controlled reaction, the protonation will take 0.5–50 μs at pH 5–7, which can be calculated as $(k_{\text{diff}} [\text{H}^+])^{-1}$. The lifetime of $\text{S}_1(\text{tpps}^{4-})$ (11.9 ns) is too short and thus the protonation of

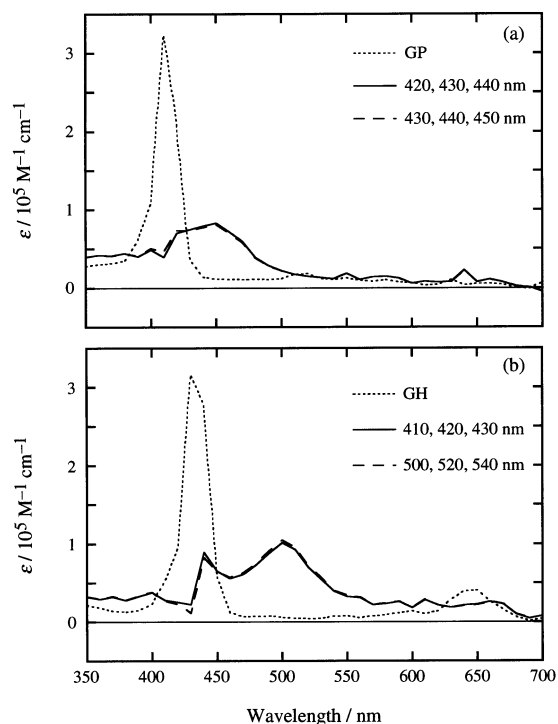


Fig. 2 Molar absorption coefficients (ε) of tppts^{4-} and $\text{H}_2\text{tppts}^{2-}$ in the ground and triplet states. Slit width, 8 nm. (a) tppts^{4-} in the ground state (dotted line) and in the triplet state (the other lines). Sets of wavelength for calculation: 420, 430, 440 nm for solid line, 430, 440, 450 nm for broken line. (b) $\text{H}_2\text{tppts}^{2-}$ in the ground state (dotted line) and in the triplet state (the other lines). Sets of wavelength: 410, 420, 430 nm for solid line, 500, 520, 540 nm for broken line.

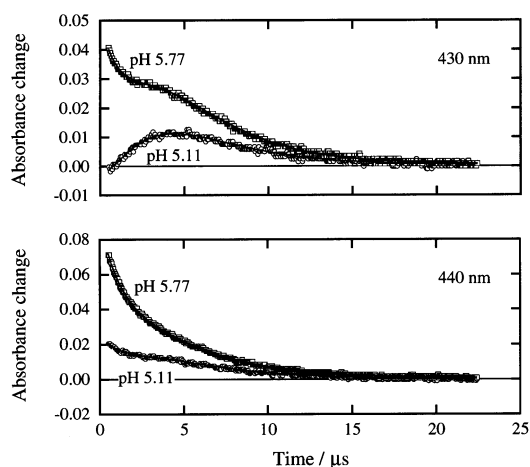


Fig. 3 The change of absorbance at 430 and 440 nm after 532 nm-laser irradiation at $t = 0$ in aerated aqueous solutions. tppts^{4-} , $3.0 \times 10^{-6} \text{ M}$; ○ pH 5.11; □, pH 5.77. Fifty shots were averaged.

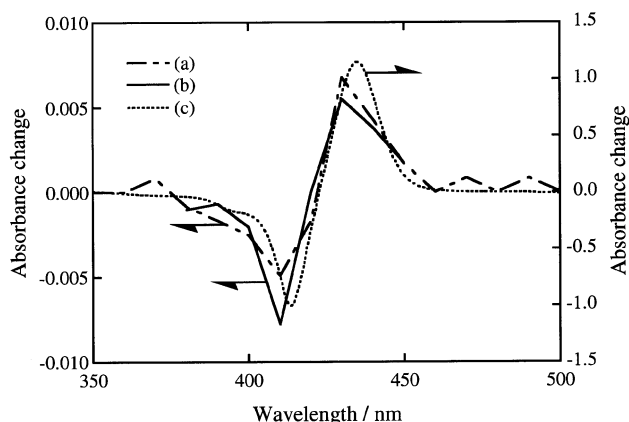


Fig. 4 (a,b) Transient spectra of tpps^{4-} at 10 μs after laser irradiation averaged for 50 laser shots in aerated aqueous solutions, and (c) the difference spectrum between $\text{H}_2\text{tpps}^{2-}$ and tpps^{4-} in their ground states. tpps^{4-} or $\text{H}_2\text{tpps}^{2-}$, 3.0×10^{-6} M. (a) pH 5.11, (b) pH 6.02.

S_1 hardly occurs within the lifetime. The lifetime of $\text{T}_1(\text{tpps}^{4-})$ (1.82 μs in aerated aqueous solution) is comparable to the calculated time for the protonation, and moreover the signal magnitude of the slow transient species decreased with an increase in $P(\text{O}_2)$. These facts mean that $\text{H}_2\text{tpps}^{2-}$ in the ground state was generated by the protonation of triplet tpps^{4-} and its deactivation. This implies that tpps^{4-} in the triplet state possesses higher basicity than that in the ground state.

The charge densities at nitrogen atoms of 21*H*,23*H*-porphine (the porphyrin that possesses no substituent groups) in the ground and triplet states were calculated with a CAChe-MOPAC computer program on Macintosh.³⁷ Their values were obtained as -0.163 for both $-\text{N}=\text{}$ atoms of porphine in the ground state, whereas -0.189 and -0.190 in the triplet state. This result supports the above observations. Quinoline, one of the heterocyclic amines, is known to show higher basicity in the triplet state than that in the ground state ($\text{p}K_{\text{a}}$ values of the conjugated acid in the ground and triplet states are 5.1 and 6.0, respectively).³⁸

The overall scheme for activation, deactivation and acid-dissociation is shown in Fig. 5. As mentioned above, the k_3 and k_4 values in aerated aqueous solutions were determined as $5.81 \times 10^5 \text{ s}^{-1}$ and $5.49 \times 10^5 \text{ s}^{-1}$, respectively. k'_1 , k'_{-1} and k'_5 are apparent rate constants that may depend on H^+ concentration. Detailed discussion is given in the following sections.

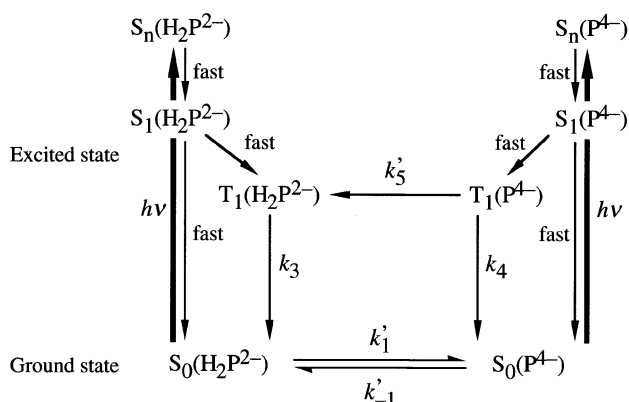


Fig. 5 A schematic illustration of the activation by laser irradiation, deactivation and acid-dissociation processes of tpps^{4-} . S and T represent singlet and triplet states, respectively, and tpps^{4-} is abbreviated to P. k'_1 , k'_{-1} , and k'_5 are apparent rate constants (see text).

Analysis of the decay curves

Since no decomposition of tpps^{4-} nor $\text{H}_2\text{tpps}^{2-}$ occurs by the 532 nm-laser irradiation, the next equation is valid for any pH and any t in the time scale of μs .

$$\delta C_{\text{GP}}(t) + \delta C_{\text{GH}}(t) + \delta C_{\text{TP}}(t) + \delta C_{\text{TH}}(t) = 0 \quad (7)$$

As shown in the above section, the protonation occurs not for $\text{S}_1(\text{tpps}^{4-})$ but for $\text{T}_1(\text{tpps}^{4-})$. In other words, $\text{T}_1(\text{tpps}^{4-})$ and $\text{T}_1(\text{H}_2\text{tpps}^{2-})$ are generated from their respective singlets, $\text{S}_1(\text{tpps}^{4-})$ and $\text{S}_1(\text{H}_2\text{tpps}^{2-})$ at the time $t = 0 \mu\text{s}$. This led to:

$$-\delta C_{\text{GP}}(0) \approx \delta C_{\text{TP}}(0), -\delta C_{\text{GH}}(0) \approx \delta C_{\text{TH}}(0) \quad (8)$$

when all the excited singlets were just deactivated. From the scheme shown in Fig. 5, $\delta C_{\text{TP}}(t)$ is expressed as:

$$\frac{d\delta C_{\text{TP}}(t)}{dt} = -(k_4 + k'_5)\delta C_{\text{TP}}(t) \quad (9)$$

This led to:

$$\delta C_{\text{TP}}(t) = \delta C_{\text{TP}}(0) \exp(-k'_6 t) \quad (10)$$

where $k'_6 = k_4 + k'_5$. As for $\delta C_{\text{TH}}(t)$,

$$\frac{d\delta C_{\text{TH}}(t)}{dt} = k'_5 \delta C_{\text{TP}}(t) - k_3 \delta C_{\text{TH}}(t) \quad (11)$$

From eqns. (10) and (11),

$$\begin{aligned} \delta C_{\text{TH}}(t) = & (\delta C_{\text{TH}}(0) + \frac{k'_5 \delta C_{\text{TP}}(0)}{k'_6 - k_3}) \exp(-k_3 t) \\ & - \frac{k'_5 \delta C_{\text{TP}}(0)}{k'_6 - k_3} \exp(-k'_6 t) \end{aligned} \quad (12)$$

$\delta C_{\text{GH}}(t)$ was expressed as:

$$\begin{aligned} \frac{d(C_{\text{GH,eq}} + \delta C_{\text{GH}}(t))}{dt} = & k_3 \delta C_{\text{TH}}(t) + k'_{-1}(C_{\text{GP,eq}} + \delta C_{\text{GP}}(t)) \\ & - k'_1(C_{\text{GH,eq}} + \delta C_{\text{GH}}(t)) \end{aligned} \quad (13)$$

By substituting $k'_{-1}C_{\text{GP,eq}} = k'_1C_{\text{GH,eq}}$ and eqn. (7),

$$\begin{aligned} \frac{d\delta C_{\text{GH}}(t)}{dt} = & -(k'_1 + k'_{-1})\delta C_{\text{GH}}(t) - k'_{-1}\delta C_{\text{TP}}(t) \\ & + (k_3 - k'_{-1})\delta C_{\text{TH}}(t) \end{aligned} \quad (14)$$

was obtained. From this differential equation and eqns. (10) and (12), $\delta C_{\text{GH}}(t)$ can be expressed as:

$$\begin{aligned} \delta C_{\text{GH}}(t) = & \frac{k_3 - k'_{-1}}{k'_7 - k_3} (\delta C_{\text{TH}}(0) + \frac{k'_5 \delta C_{\text{TP}}(0)}{k'_6 - k_3}) \exp(-k_3 t) \\ & - \frac{\delta C_{\text{TP}}(0)}{k'_7 - k'_6} \left\{ \frac{k'_5(k_3 - k'_{-1})}{k'_6 - k_3} + k'_{-1} \right\} \exp(-k'_6 t) \\ & + \left[\frac{\delta C_{\text{TP}}(0)}{k'_7 - k'_6} \left\{ k'_{-1} + \frac{k'_5(k_3 - k'_{-1})}{k'_7 - k_3} \right\} - \frac{k'_1}{k'_7 - k_3} \delta C_{\text{TH}}(0) \right] \\ & \times \exp(-k'_7 t) \end{aligned} \quad (15)$$

where $k'_7 = k'_1 + k'_{-1}$. Finally $\delta C_{\text{GP}}(t)$ was obtained from eqns. (7), (10), (12) and (15) as:

$$\begin{aligned} \delta C_{\text{GP}}(t) = & -\delta C_{\text{GH}}(t) - \delta C_{\text{TP}}(t) - \delta C_{\text{TH}}(t) \\ = & \frac{k'_{-1} - k'_7}{k'_7 - k_3} (\delta C_{\text{TH}}(0) + \frac{k'_5 \delta C_{\text{TP}}(0)}{k'_6 - k_3}) \exp(-k_3 t) \\ & - \delta C_{\text{TP}}(0) \left[1 - \frac{k'_5}{k'_6 - k_3} - \frac{1}{k'_7 - k'_6} \left\{ \frac{k'_5(k_3 - k'_{-1})}{k'_6 - k_3} + k'_{-1} \right\} \right] \\ & \times \exp(-k'_6 t) \\ & - \left[\frac{\delta C_{\text{TP}}(0)}{k'_7 - k'_6} \left\{ k'_{-1} + \frac{k'_5(k_3 - k'_{-1})}{k'_7 - k_3} \right\} - \frac{k'_1}{k'_7 - k_3} \delta C_{\text{TH}}(0) \right] \\ & \times \exp(-k'_7 t) \end{aligned} \quad (16)$$

Again, k'_6 and k'_7 are the apparent rate constants, which may be functions of the H^+ concentration.

As shown in Figs. 2a and b, $T_1(H_2tpps^{2-})$ had largest absorption at 510 nm among the four species. Therefore the absorbance change at this wavelength and time t , $\Delta A(510 \text{ nm}, t)$, was expressed as $\Delta A(510 \text{ nm}, t) \approx \varepsilon_{TH}(510 \text{ nm})b \delta C_{TH}(t)$. assuming $k'_6 \approx k_4$, that is, $k_4 \gg k'_5$, the absorbance change at 510 nm was analyzed as a double-exponential function according to eqn. (12), where the two rate constants k_3 and $k'_6 (= k_4)$ were fixed to $5.81 \times 10^5 \text{ s}^{-1}$ and $5.49 \times 10^5 \text{ s}^{-1}$, respectively. k'_5 were obtained as 2×10^4 and $5 \times 10^3 \text{ s}^{-1}$ at pH 5.11 and 6.00, respectively, with the pre-exponential factors of $\exp(-k'_6 t)$ and $\delta C_{TP}(0)$; $\delta C_{TP}(0)$ was calculated by eqn. (8) and the concentration of $tpps^{4-}$ in the ground state at equilibrium, $C_{GP,eq}$, before laser irradiation. Clearly $k_4 \gg k'_5$. Similar calculations for the other pH showed that k'_5 depended on pH as was expected and that the relation $k_4 \gg k'_5$ was valid for $pH \geq 5$. In the following, k_4 is equated to k'_6 in the pH range of 5.0–6.0.

Larger absorbance changes were observed in the wavelength range of 430–460 nm due to the large absorptivity of $S_0(H_2tpps^{2-})$ (GH) and $T_1(tpps^{4-})$ (TP), as shown in Fig. 2. $\delta C_{GH}(t)$ was expressed as a triple-exponential function as eqn. (15), whereas $\delta C_{TP}(t)$ was a single-exponential function as eqn. (10). The other species showed smaller absorption in this wavelength region, but their concentration changes possessed the same rate constants, k_3 , $k'_6 (= k_4)$ and $k'_7 (= k'_1 + k'_{-1})$, as shown in eqns. (12) and (16). As the result, the observed absorbance changes can be expressed as triple-exponential functions by taking proper contributions of the species into account. In fact, absorbance changes observed in the wavelength range of 430–460 nm were successfully fitted to the triple-exponential function. By fixing the k_3 and k'_6 values, k'_7 was obtained by the non-linear least-squares method as a function of pH. The lines in Fig. 3 display the fitting curves calculated with the obtained parameters. Since they agreed with the observed points well, the present analysis of the data was proved.

Plots of the observed $k'_7 (= k'_1 + k'_{-1})$ values against pH are shown in Fig. 6, in which the values are independent of pH. Since some amines catalyze acid-dissociation,³⁹ an experiment was carried out without the buffer MES. The k'_7 value without MES agrees with those with MES, meaning that MES had no effects of on k'_7 . In the case of the higher O_2 concentration ($P(O_2) = 0.78 \text{ atm}$), the magnitude of the transient species of the slow decay was quite small and thus the deviation is relatively larger in Fig. 6, but its value is in good agreement with those obtained in aerated aqueous solutions. The average

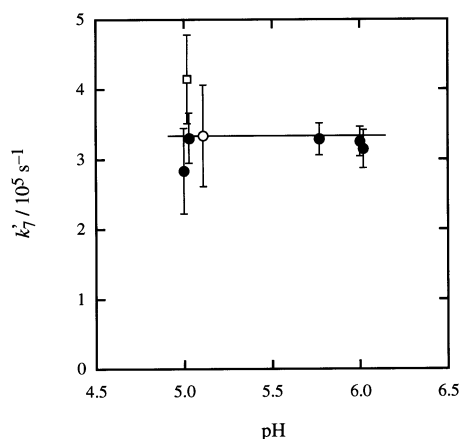
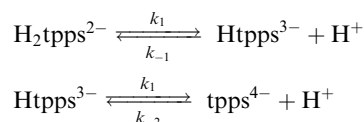


Fig. 6 The pH dependence of the rate constant k'_7 for the acid-dissociation of H_2tpps^{2-} . Bars mean the standard deviation. \circ , without MES; others, containing $1.0 \times 10^{-3} \text{ M}$ MES. \square , $P(O_2) = 0.78 \text{ atm}$ ($0.79 \times 10^5 \text{ Pa}$); others, aerated.

value of k'_7 was obtained as $(3.3 \pm 0.4) \times 10^5 \text{ s}^{-1}$ ($n = 7$) in the pH range of 5.0–6.0.

Rate constants for the acid-dissociation of $tpps^{4-}$ in the ground state

The intrinsic acid-dissociation rate constants for $tpps^{4-}$ in the ground state can be expressed as:



The apparent k'_7 can be expressed using these intrinsic rate constants as $(k_1 k_2 + k_{-1} k_{-2} [H^+]^2) / (k_{-1} [H^+] + k_2)$.¹⁶ Since the obtained k'_7 is independent of pH, $k_1 k_2 \gg k_{-1} k_{-2} [H^+]^2$, $k_2 \gg k_{-1} [H^+]$, and thus k'_7 corresponds to k_1 . In other words, the rate-determining step for the conversion from H_2tpps^{2-} to $tpps^{4-}$ is the process of the dissociation of one proton from H_2tpps^{2-} . The k_{-1} value can be calculated as $(1.3 \pm 0.1) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ from $k_1 (= k'_7)$ and $K_{a,1}$ values. The k_{diff} for the pair of $Htpps^{3-}$ and H^+ was estimated as $1.5 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$.³⁶ The k_{-1} value is somewhat less than the calculated k_{diff} , but is in good agreement with rate constants for the protonation of other amines, for example, $2.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for trimethylamine at 25°C .³⁵ In order to satisfy the observed condition that $k_2 \gg k_{-1} [H^+]$ in the pH range ≥ 5 , k_2 must be larger than $1 \times 10^6 \text{ s}^{-1}$. With $K_{a,2}$ values, k_{-2} should be larger than $1.5 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$. This value is comparable to k_{diff} for the pair of $tpps^{4-}$ and H^+ species ($2.0 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$). As the result, it is suggested that the protonations of $tpps^{4-}$ and $Htpps^{3-}$ almost proceed by the diffusion-controlled reaction, and that the deformation process is not involved in the protonation of $tpps^{4-}$ and $Htpps^{3-}$, unlike $tmpyp^{4+}$ (5,10,15,20-tetra (*N*-methylpyridinium-4-yl)porphine).¹⁵

The rate-determining step for the acid-dissociation of the conjugated acid of tpp, H_2tpp^{2+} , in a dimethylsulfoxide–water mixture was also the process of dissociation of one proton from H_2tpp^{2+} .¹⁶ Therefore, the monoprotonated species, $Htpps^{3-}$ and Htp^{1+} , were not observable. On the other hand, the rate-determining step for the acid-dissociation of H_2tmpyp^{6+} in aqueous solutions was the process of dissociation of one proton from $Htmpyp^{5+}$.¹⁵ The reason for the difference in the rate-determining step is not clear in this stage, but it may be related to electric charge and substituent groups.

Pasternack *et al.* obtained the rate constant for acid-dissociation for $tmpyp^{4+}$ as $4.6 \times 10^7 \text{ s}^{-1}$ by the laser-induced T-jump method.¹⁵ The $pK_{a,1}$ and $pK_{a,2}$ values of the conjugated acid of $tmpyp^{4+}$ are 0.7 and 1.8 at 25°C , respectively. Since the basicity of $tpps^{4-}$ is higher than that of $tmpyp^{4+}$, it is reasonable that the acid-dissociation of H_2tmpyp^{6+} is faster than H_2tpps^{2-} .

Deformation of porphyrin-ring has been suggested as the rate-determining step in the complexation mechanism for $tpps^{4-}$, but the present study is inconsistent with these mechanisms. As mentioned above, the SAT complex was generated in the presence of metal ions.⁹ In the case of tpp or $tpps^{4-}$, the step assumed as the deformation may correspond to the generation of a SAT complex. More detailed studies on the acid-dissociation kinetics for porphyrins should be carried out.

Conclusion

The 532 nm-laser irradiation to $tpps^{4-}$ or H_2tpps^{2-} in aqueous solutions generated each excited singlet state and then each triplet state. The basicity of triplet $tpps^{4-}$ was found to be higher than that in the ground state, similar to the other heterocyclic amines. As a result, excess H_2tpps^{2-} in the ground state was

generated by the protonation of triplet tpps^{4-} in the pH range of 5.0–6.0.

The rate constants for the acid-dissociation of tpps^{4-} in the ground state, k_1 , k_{-1} , k_2 , k_{-2} , in eqn. (17) were obtained as $(3.3 \pm 0.4) \times 10^5 \text{ s}^{-1}$, $(1.3 \pm 0.1) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, $\geq 1 \times 10^6 \text{ s}^{-1}$, $\geq 1.5 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$, respectively. The protonation of tpps^{4-} (k_{-2}) is as fast as the diffusion-controlled reaction, and that of Htpps^{3-} (k_{-1}) is almost the diffusion-controlled reaction. Unlike tmpyp^{4+} , the process of the protonation of tpps^{4-} includes no deformation process of the porphyrin ring.

Laser photolysis has a high potential to investigate the kinetics of acid-dissociation of porphyrins as well as their ligand substitution. Also, the kinetic studies on the acid-dissociation of porphyrins would be essential to elucidate the mechanism of the metalation of porphyrin included in enzyme.

References

- 1 D. K. Lavalley, *Coord. Chem. Rev.*, 1985, **61**, 55.
- 2 J. Turay and P. Hambright, *Inorg. Chem.*, 1980, **19**, 562.
- 3 P. Hambright, *Coord. Chem. Rev.*, 1971, **6**, 247, and references therein.
- 4 P. Bhyrappa, M. Nethaji and V. Krishnan, *Chem. Lett.*, 1993, 869.
- 5 L. R. Robinson and P. Hambright, *Inorg. Chim. Acta*, 1991, **185**, 17.
- 6 S. Tsukahara and N. Suzuki, *Inorg. Chim. Acta*, 1996, **245**, 105.
- 7 W. J. Horvath and C. W. Huie, *Talanta*, 1992, **39**, 487.
- 8 O. Herrmann, S. H. Mehdi and A. Corsini, *Can. J. Chem.*, 1978, **56**, 1084.
- 9 Y. Inada, Y. Sugimoto, Y. Nakano and S. Funahashi, *Chem. Lett.*, 1996, 881.
- 10 M. Tabata and M. Tanaka, *Trends Anal. Chem.*, 1991, **10**, 128.
- 11 S. Funahashi, Y. Yamaguchi and M. Tanaka, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 204.
- 12 V. Marvaud, A. Vidal-Ferran, S. J. Webb and J. K. M. Sanders, *J. Chem. Soc., Dalton Trans.*, 1997, 985.
- 13 C. M. Drain and J.-M. Lehn, *J. Chem. Soc., Chem. Comm.*, 1994, 2313.
- 14 R. Okumura, T. Hinoue and H. Watarai, *Anal. Sci.*, 1996, **12**, 393.
- 15 R. F. Pasternack, N. Sutin and D. H. Turner, *J. Am. Chem. Soc.*, 1976, **98**, 1908.
- 16 F. Hibbert and K. P. P. Hunte, *J. Chem. Soc., Chem. Commun.*, 1975, 728.
- 17 K. Susumu, H. Segawa and T. Shimidzu, *Chem. Lett.*, 1995, 929.
- 18 J. T. Groves, G. D. Fate and J. Lahiri, *J. Am. Chem. Soc.*, 1994, **116**, 5477.
- 19 J.-P. Collin, A. Harriman, V. Heitz, F. Odobel and J.-P. Sauvage, *J. Am. Chem. Soc.*, 1994, **116**, 5679.
- 20 S. Igarashi, T. Aihara and T. Yotsuyanagi, *Anal. Chim. Acta*, 1996, **323**, 63.
- 21 K. M. Smith, S. B. Brown, R. F. Troxler and J.-J. Lai, *Photochem. Photobiol.*, 1982, **36**, 147.
- 22 M. Inamo, M. Hoshino, K. Nakajima, S. Aizawa and S. Funahashi, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 2293.
- 23 M. Hoshino, K. Ozawa, H. Seki and P. C. Ford, *J. Am. Chem. Soc.*, 1993, **115**, 9568.
- 24 M. Hoshino, S. Arai, M. Yamaji and Y. Hama, *J. Phys. Chem.*, 1986, **90**, 2109.
- 25 D. L. Akins, H.-R. Zhu and C. Guo, *J. Phys. Chem.*, 1996, **100**, 5420.
- 26 O. L. J. Gijzeman, F. Kaufman and G. Porter, *J. Chem. Soc., Faraday Trans. 2*, 1973, **69**, 708.
- 27 A. Garner and F. Wilkinson, *Chem. Phys. Lett.*, 1977, **45**, 432.
- 28 J. Feitelson and D. Mauzerall, *J. Phys. Chem.*, 1996, **100**, 7698.
- 29 C. Tanielian and C. Wolff, *J. Phys. Chem.*, 1995, **99**, 9825.
- 30 R. Bonnett, *Chem. Soc. Rev.*, 1995, 19, and references therein.
- 31 K. Kikuchi, in *JOEM Handbook 1 Triplet-triplet Absorption Spectra*, Bunshin, Tokyo, 1989.
- 32 S. Tsukahara and H. Watarai, *Langmuir*, 1998, **14**, 7072.
- 33 R. Bonnet, R. J. Ridge, E. J. Land, R. S. Sinclair, D. Tait and T. G. Truscott, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 127.
- 34 M. Koizumi, S. Kato, N. Mataga, T. Matsuura and Y. Usui, in *Photosensitized Reactions*, Kagaku-Dojin Publishing Co., Inc., Kyoto, 1978.
- 35 M. Eigen, W. Kruse, G. Maass and L. De. Maeyer, *Prog. React. Kinet.*, 1964, **2**, 285.
- 36 $\Phi_{ij} = [\phi_{ij}(a_{ij})] / \{\exp[\phi_{ij}(a_{ij})] - 1\}$ and $\phi_{ij}(a_{ij}) = (z_i z_j e^2) / (4\pi\epsilon_0 \epsilon a_{ij} k T)$, where z is valency, e elementary charge, ϵ_0 permittivity of vacuum, ϵ specific permittivity of medium, k Boltzmann constant, T absolute temperature.³⁵ For a pair of -4 and $+1$ in water, $\phi_{ij}(a_{ij})$ and Φ_{ij} are -7.14 and 7.15 , respectively. For a pair of -3 and $+1$, $\phi_{ij}(a_{ij}) = -5.37$ and $\Phi_{ij} = 5.40$.
- 37 Molecular orbitals were calculated by PM3, MOPAC Version 94.10 in CAChe, Version 3.7, CAChe Scientific, 1994.
- 38 G. Jackson and G. Porter, *Proc. R. Soc. London, Ser. A*, 1961, **260**, 13.
- 39 H. Watarai and N. Suzuki, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 2778.