

EVIDENCE FOR STACKING OF CATIONIC PORPHYRIN IN AQUEOUS SOLUTION

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The dilute aqueous solutions (2×10^{-7} - 1×10^{-5} mol dm⁻³) of 5,10,15,20-tetrakis(4-N-methylpyridyl)porphine (TMPyP) showed a broad fluorescence emission band, which was split into two bands with increasing temperature and/or further dilution. These results as well as the effects of additives on the fluorescence spectrum indicated that TMPyP molecules stack in water.

It has been known that certain anionic porphyrins such as 5-phenyl-10,15,20-tris(p-sulfonatophenyl)porphine (TPPS₃) and 5,10,15,20-tetrakis(p-carboxyphenyl)porphine (TCPP) tend to form dimer in water. Pasternack et al. have studied aggregation phenomena of water-soluble porphyrins by means of absorption spectroscopy and temperature-jump method.¹⁾ They found the deviation from Beer's law for TPPS₃ and TCPP in water containing inorganic salt, but not for a cationic porphyrin, 5,10,15,20-tetrakis(4-N-methylpyridyl)porphine (TMPyP). They concluded that the anionic porphyrins dimerize in water while the cationic one exists in the monomer form. No attention has been paid for stacking of the cationic porphyrins except for a μ -oxo dimer of Fe(III) complex of TMPyP²⁾ in spite of their wide use as the catalysts for light-energy conversion.³⁾

The present study deals with the stacking of TMPyP in water. Since the absorption spectroscopy can not be applied for a highly diluted system, we studied it by means of fluorescence spectroscopy. The paper demonstrates that TMPyP molecules in the ground states stack strongly in water even if the concentration of TMPyP is below 10^{-7} mol dm⁻³.

The tetra(p-toluenesulfonate) and tetrachloride salts of TMPyP were prepared and used in this study. Since no difference was observed between these two porphyrins, the results obtained for the tetra(p-toluenesulfonate) salt are shown in the following. All experiments were carried out in aerobic aqueous solutions without inorganic salt.

Figure 1 shows the fluorescence spectra of TMPyP in water as a function of TMPyP concentration. A broad fluorescence emission band was observed at around 650-700 nm and no difference in the shape of the spectrum was detected in the concentration range from 2×10^{-7} to 1×10^{-5} mol dm⁻³. The spectral change occurred when TMPyP was diluted to 1×10^{-8} mol dm⁻³. The fluorescence spectrum

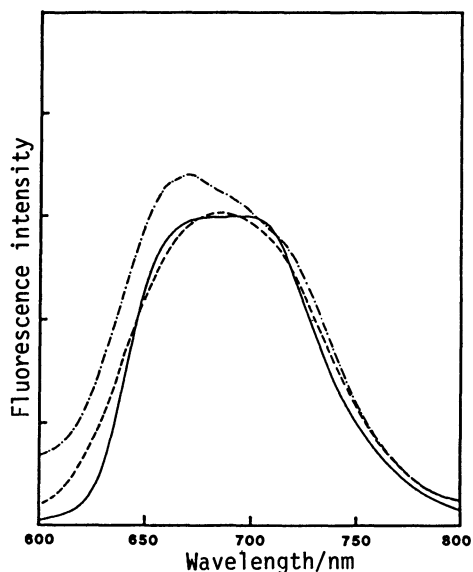


Fig. 1. Fluorescence spectra of TMPyP in water as a function of TMPyP concentration at 25 °C. TMPyP was excited at 420 nm and the fluorescence intensities are arbitrary units.

— : 2×10^{-7} – 1×10^{-5} mol dm⁻³,
 --- : 4×10^{-8} mol dm⁻³,
 - · - : 1×10^{-8} mol dm⁻³.

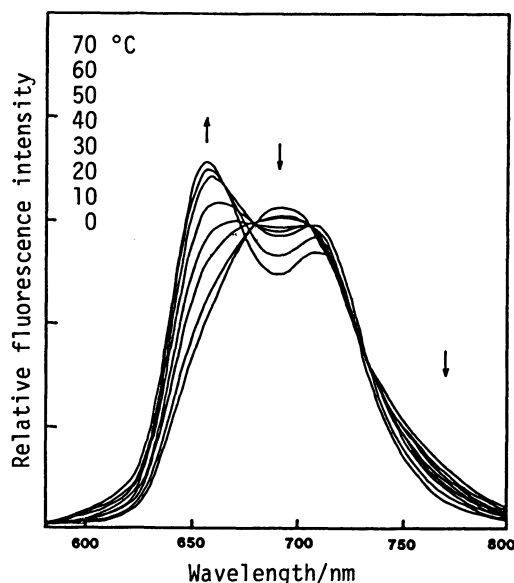


Fig. 2. Fluorescence spectra of TMPyP (1×10^{-6} mol dm⁻³) in water as a function of temperature.

of 1×10^{-8} mol dm⁻³ TMPyP seems to consist of two bands.

The fluorescence spectrum of TMPyP (1×10^{-6} mol dm⁻³) in water changed progressively with varying temperature (Fig. 2). At 0 °C, a fluorescence maximum (λ_{\max}^F) was observed at 692 nm, which was split into two bands with increasing temperature. Up to 50 °C, the isoemissive points were observed at 679, 704, and 735 nm. Above 50 °C, the isoemissive point shifted to 665 nm. TMPyP at 70 °C showed two fluorescence bands centered at 657 and 709 nm which is similar to those of 5,10,15,20-tetrakis(p-sulfonatophenyl)porphine (TPPS₄, $\lambda_{\max}^F = 645$ and 700 nm) in the monomer form.^{3d)} The absorption spectrum of TMPyP also changed with increasing temperature (Fig. 3). With increasing temperature, the optical densities of $Q_y(0-1)$ and $Q_x(0-1)$ bands decreased and $Q_x(0-1)$ and $Q_x(0-0)$ bands shifted to longer wavelengths. Since TMPyP is a symmetric porphyrin, the etio-type absorption spectrum is expected. As Fig. 3 shows, however, the extinction coefficient of the $Q_y(0-0)$ band was smaller than that of the $Q_x(0-1)$ band.

These fluorescence and absorption spectral data show clearly that there are two forms for TMPyP in water; i.e., the monomer and aggregate forms. The split fluorescence bands should be ascribed to the monomer of TMPyP. Judging from the fluorescence lifetime of TMPyP (vide infra) and the concentration of TMPyP (10^{-5} – 10^{-8} mol dm⁻³), the dimer formation in the excited singlet state can be neglected.

The aggregates of TMPyP in water were destroyed upon addition of methanol and/or sodium dodecyl sulfate (SDS) micelles. Figure 4 shows the effect of added methanol on the TMPyP fluorescence. The monomer bands appeared and their

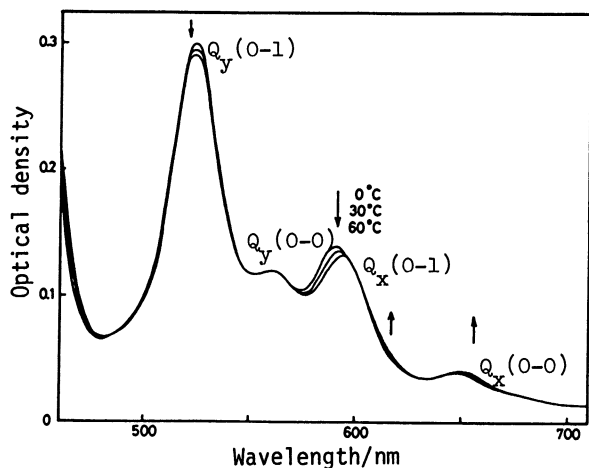


Fig. 3. Absorption spectral change of TMPyP (2×10^{-5} mol dm^{-3}) in water as a function of temperature.

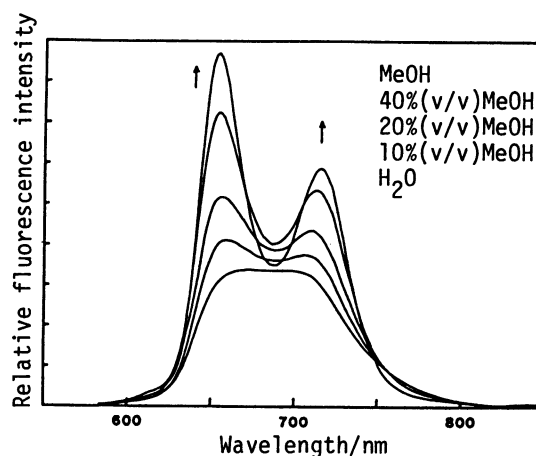


Fig. 4. Effect of methanol on the fluorescence spectrum of TMPyP (1×10^{-6} mol dm^{-3}) in water at 25 °C.

fluorescence intensities increased upon addition of increasing amounts of methanol. TMPyP in methanol has the fluorescence maxima at 654 and 715 nm. The fluorescence lifetime of TMPyP (1×10^{-5} mol dm^{-3}) in methanol ($\tau_F = 7.2$ ns) was larger than that in water (4.1 ns). These results can be interpreted as that the rate of the radiationless decay of the aggregate of TMPyP in the excited singlet state is larger than that of the monomer, resulting in the decrease of the fluorescence yield and the fluorescence lifetime of the aggregated TMPyP. Addition of methanol also caused the change in the absorption spectrum of TMPyP. The characteristic changes are the increase of the extinction coefficient of the $Q_y(0-0)$ band, the red shift of the Q_x bands, and sharpening the each band. The absorption spectrum of TMPyP in methanol can be regarded as the etio type. Solvation of the porphyrin ring by methanol may cause the destruction of the TMPyP aggregates.

The cationic porphyrin binds electrostatically with the negatively charged surfaces of the SDS micelles. In the SDS micellar solution, TMPyP is presumed to exist in the monomer form. Indeed, the monomer fluorescence bands of TMPyP (1×10^{-6} mol dm^{-3}) were observed at 656 and 714 nm in the 0.1 mol dm^{-3} SDS solution and their intensities were ca. 2 times larger than those in methanol. The fluorescence lifetime in the SDS micellar solution was 9.6 ns which is close to the lifetime of TPPS₃ in the monomer form ($\tau_F = 9.2-10.2$ ns).⁴⁾

All of the results obtained by means of fluorescence spectroscopy indicates that TMPyP molecules in water stack each other. Judging from the results of the absorption spectroscopy, Pasternack et al. have concluded that TMPyP does not stack in water.¹⁾ Indeed, no absorption spectral change was observed for TMPyP in the concentration range from 1×10^{-5} to 1×10^{-3} mol dm^{-3} . This should be ascribed to that only aggregate form exists under these conditions. The present study suggests that the monomer-aggregate equilibrium can be detected when the absorption spectrum is measured for TMPyP below 10^{-8} mol dm^{-3} . In the case of an anionic porphyrin, TPPS₃, the self aggregation of the porphyrin is affected

greatly by ionic strength of the solution.^{1,4)} We checked the effect of the ionic strength on the fluorescence spectrum of TMPyP (1×10^{-6} mol dm⁻³) using 0.1 mol dm⁻³ NaCl at 25 °C. The shape of the fluorescence spectrum of TMPyP in water did not change upon addition of NaCl while the fluorescence intensity increased slightly. This result also suggests that no appreciable amount of the TMPyP monomer exist under these conditions. Because of the technical difficulty, we could not determine the equilibrium constant for the TMPyP aggregation in the present study.

It has been known that several cationic dyes, such as methylene blue, cyanines, proflavin, acridine orange, and thionine, aggregate spontaneously in water.⁵⁾ Dewey et al. have assumed that the electrostatic repulsion between proflavin molecules is reduced by delocalization of the positive charge over the ring system.^{5e)} This assumption is supported by the fact that the anionic porphyrin, TPPS₄, does not stack in water^{3d)} while TMPyP does. The negative charges on the sulfonate groups tend to be localized, which causes the electrostatic repulsion between TPPS₄ molecules. It is assumed that the porphyrin ring is not hydrated because of its hydrophobic property. The porphyrin rings may, therefore, face each other via hydrophobic and/or van der Waals interactions.

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