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Complexation of Zn-TPPS$_3$ by Ethyl Viologen and its Role in Photoredox Processes

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Photochemical redox systems have been developed for the purpose of solar energy utilization. The systems containing a photosensitizer, an electron donor and an electron carrier have been used to evolve hydrogen from water when a suitable catalyst is present. Metalloporphyrins, as photosensitizers, have been employed extensively in these studies [1, 2]. Recently the formation of complexes between metallo-porphyrins and methyl viologen has been reported [3–5], but the role of the complex formation in photoredox reactions has not yet been clarified. In this letter we describe the complex formation between zinc-meso-tetraphenylporphyrintrisulfonic acid (Zn-TPPS$_3$) and ethyl viologen, and discuss its role in photoredox processes.

Experimental

All the chemicals, obtained from Wako Pure Chemical Co., were of the highest available purity. Zn-TPPS$_3$ was synthesized by refluxing TPPS$_3$ and zinc acetate (molar ratio 1:10) in methonl for 2 h. The sample solution consisted of photosensitizer, ethyl viologen, and mercaptoethanol (RSH) and was deaerated by repeated freeze–pump–thaw cycles. A typical experiment was performed as follows, under anaerobic conditions. To 8.33×10^{-8} *M* of Zn-TPPS$_3$ and 1.26×10^{-4} *M* of ethyl viologen, 0.21 *M* of RSH was added. The volume of the mixture was adjusted to 6.0 ml with 0.02 *M* of Tris-HCl buffer (pH 7.0). In the photolysis with continuous irradiation the sample in a Pyrex cell with a magnetic stirrer was irradiated with light from a 200 W tungsten lamp (from a slide projector). Light of wavelength less than 390 nm was cut off by a Toshiba L-39 filter.

Results and Discussion

When an aqueous solution containing Zn-TPPS$_3$, ethyl viologen, and RSH was irradiated the growth of the cation radical of ethyl viologen (EtV$^+$), which has characteristic absorption bands at 395 and 605 nm, was observed. The formation rate of EtV$^+$ increased with ethyl viologen concentration and then decreased through a maximum as shown in Fig. 1. This abnormal phenomenon may imply the complexation of Zn-TPPS$_3$ by ethyl viologen. When Zn-TPPS$_3$ was mixed with ethyl viologen, the characteristic Soret absorption band (418 nm) decreased with increase in ethyl viologen concentration and a new spectrum appeared, which has a characteristic absorption band at 425 nm through isosbestic point at 422 nm (Fig. 2).

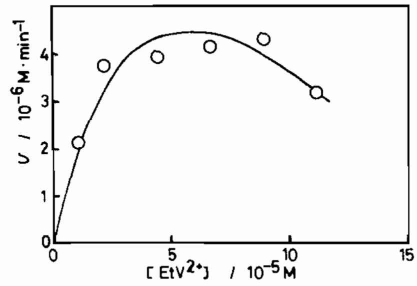

Fig. 1. Dependence of reduction rate on EtV^{2+} concentration.

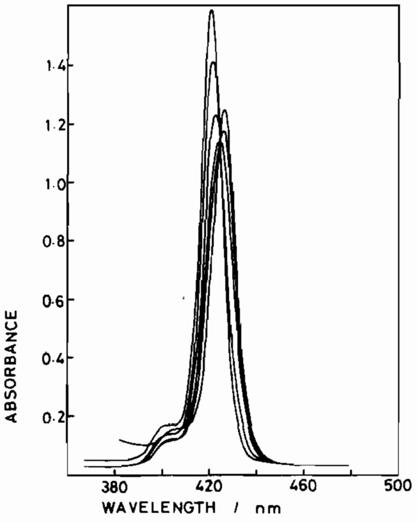

Fig. 2. Spectral change of Zn-TPPS$_3$ upon the addition of ethyl viologen.

If the complex is formed by the following reaction,

$$\text{Zn-TPPS}_3 + \text{EtV}^{2+} \overset{K_1}{\rightleftarrows} [\text{Zn-TPPS}_3\text{EtV}^{2+}]$$

the equilibrium constant, K$_1$, is expressed by

$$K_1 = \frac{[\text{complex}]}{[\text{Zn-TPPS}_3][\text{EtV}^{2+}]}$$

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This equation is rewritten as follows by using the initial Zn-TPPS$_3$ concentration, [Zn-TPPS$_3$]$_0$.

$$\frac{[\text{Zn-TPPS}_3]_0}{[\text{complex}]} = 1 + \frac{1}{K_1[\text{EtV}^{2+}]}$$

As the complex concentration is calculated from the absorbance of the complex, the relation between $[\text{complex}]^{-1}$ and $[\text{EtV}^{2+}]^{-1}$ can be plotted as shown in Fig. 3. The good linear relation between $[\text{complex}]^{-1}$ and $[\text{EtV}^{2+}]^{-1}$ shows the formation of 1:1 complex of Zn-TPPS$_3$ and ethyl viologen.

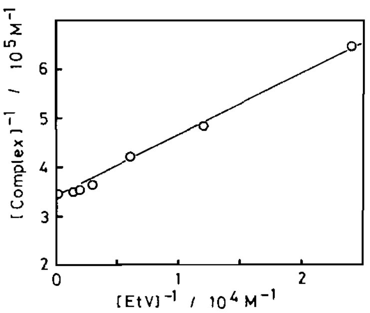

Fig. 3. Relation between $[\text{complex}]^{-1}$ and $[\text{EtV}^{2+}]^{-1}$.

If the complex is not effective for ethyl viologen photoreduction and only free Zn-TPPS$_3$ is effective for this reaction, the decrease of the photoreduction rate at the higher ethyl viologen concentration can be explained.

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References

1 J. R. Darwent, P. Douglas, A. Harriman, G. Porter, and M.-C. Richoux, *Coord. Chem. Rev.*, *44*, 83 (1982) and the references therein.
2 A. B. P. Lever, B. S. Ramaswamy, and S. Licoccia, *J. Photochem.*, *19*, 173 (1982) and the references therein.
3 J. A. Shelnutt, *J. Am. Chem. Soc.*, *103*, 4275 (1981).
4 M. Rougee, T. Ebbesen, F. Ghetti, and R. V. Bensasson, *J. Phys. Chem.*, *86*, 4404 (1982).
5 I. Okura, S. Aono, M. Takeuchi, and S. Kusunoki, *Bull. Chem. Soc. Jpn.*, *55*, 3637 (1982).