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Photoinduced Hydrogen Evolution with Viologen Linked Porphyrin in a Micellar System

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Synopsis. Viologen linked porphyrins, $ZnP(C_nV)_4$, with various methylene chain lengths (n=2—5) between the porphyrin and the viologen have been synthesized. These compounds were applied to photoinduced hydrogen evolution in a system containing NADPH-$ZnP(C_nV)_4$-hydrogenase under steady state irradiation. On the addition of surfactant to the system, a remarkable rate increase of hydrogen evolution was observed in the case of $ZnP(C_5V)_4$.

Photoinduced hydrogen evolution systems containing an electron donor, a photosensitizer, an electron carrier, and a catalyst have been studied extensively. As photosensitizers metallo-porphyrins have been widely used and methyl viologen has been a popular electron carrier. Recently we synthesized viologen linked water-soluble zinc porphyrins and found that they took part as both a photosensitizer and an electron carrier in the same molecule for photoinduced hydrogen evolution.[1,2] To improve the rate of photoinduced hydrogen evolution, effective charge separation between the photoexcited sensitizer and the quencher is needed. As electrostatic field, such as a micellar surface, has been widely applied to separate the charges effectively.[3] Only in a few of the micellar systems, however, has the hydrogen evolution been studied. In this paper we describe the effect of micelles on the photoinduced hydrogen evolution in a system containing NADPH, $ZnP(C_nV)_4$ and hydrogenase.

Experimental

The structure of the viologen linked water soluble zinc porphyrins, $ZnP(C_nV)_4$, is illustrated in Fig. 1. These compounds were synthesized as described elsewhere.[1,2] Hydrogenase was obtained from Desulfovibrio vulgaris (Miyazaki type, IAM 12604) and purified by Yagi's method.[4] The concentration of hydrogenase is not known, but 1.48×10^{-6} mol of hydrogen was generated by the following reaction system: hydrogenase (0.5 cm^3)-$Na_2S_2O_4$ (5.7×10^{-3} mol dm^{-3})-methylviologen (4.1×10^{-5} mol dm^{-3}) in 5.0 cm^3 of 0.02 mol dm^{-3} Tris-HCl buffer (pH 7.0) at 30 °C for 10 min.

Laser flash photolysis was carried out by using a Nd-YAG laser, model DCR-2A-10 from Quanta-Ray Inc., generating the second harmonic (532 nm). Pulses of 10 ns duration, energy of 200 mJ per pulse, and a repetion rate 10 Hz were used for excitation of the sample solution throughout this study. The light beam, after passage through a sample cell, was collimated into the entrance slit of a monochromator (model BM 50/50 from B & M Spectronik Co.). The output signal from the photomultiplier (Hamamatsu Photonics, R 446) attached to the slit of the monochromator was displayed

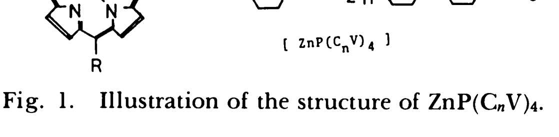

Fig. 1. Illustration of the structure of $ZnP(C_nV)_4$.

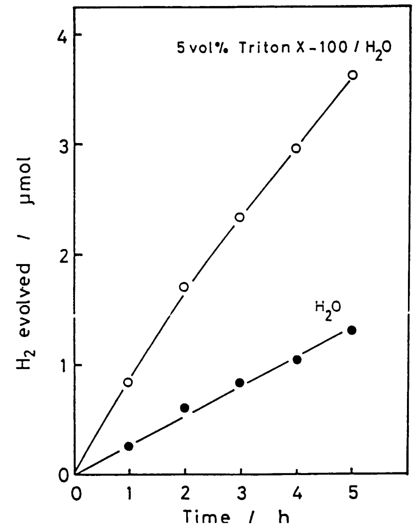

Fig. 2. Time dependence of hydrogen evolution. Sample solution (6.5 cm^3) containing $ZnP(C_5V)_4$ (2.0×10^{-6} mol dm^{-3}), NADPH (1.0×10^{-3} mol dm^{-3}) and hydrogenase (0.5 cm^3) was irradiated at 30°C.

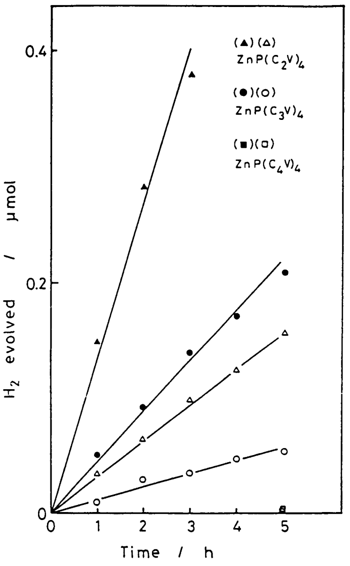

Fig. 3. Time dependence of hydrogen evolution. Sample solution (6.5 cm^3) containing $ZnP(C_nV)_4$ (2.0×10^{-6} mol dm^{-3}), NADPH (1.0×10^{-3} mol dm^{-3}) and hydrogenase (0.5 cm^3) was irradiated at 30°C. (△), (○), (□): 5 vol% Triton X-100/H_2O. (▲), (●), (■): H_2O.

Table 1. Lifetimes of Excited Triplet State of $ZnP(C_nV)_4$

Solvent	$ZnP(C_2V)_4$	$ZnP(C_3V)_4$	$ZnP(C_4V)_4$	$ZnP(C_5V)_4$
H_2O τ_T/s	190	510	640	470
10% Triton X-100 τ_T/s	150	400	890	2000

on a Hitachi oscilloscope, model V-1050F.

For steady state irradiation a 200 W tungsten lamp was used as a light source. The light of wavelength less than 390 nm was removed by a Toshiba L-39 filter.

Photoinduced hydrogen evolution was carried out with $ZnP(C_nV)_4$ with n=2—5 under steady state irradiation at 30 °C. A sample solution containing nicotineamide-adenine dinucleotide phosphate (reduced form, NADPH), $ZnP(C_nV)_4$, hydrogenase and Triton X-100 was deaerated by repeated freeze-pump-thaw cycles.

Results and Discussion

When an aqueous solution containing $ZnP(C_nV)_4$, NADPH and hydrogenase was irradiated, hydrogen evolution was observed as added in Figs. 2 and 3. When surfactant, Triton X-100, was added to the above three component system, remarkable increase of hydrogen evolution rate was observed in the case of $ZnP(C_nV)_4$. On the contrary, the hydrogen evolution rates decreased in the cases of $ZnP(C_2V)_4$ and $ZnP(C_3V)_4$.

The photoexcited lifetimes of these compounds in the presence and in the absence of Triton X-100 were investigated by using laser flash photolysis technique (Table 1). The triplet lifetime of viologen linked porphyrin, $ZnP(C_5V)_4$, increased in the case of the system showing a rise of hydrogen evolution rate by the addition of Triton X-100. On the contrary the triplet lifetimes of $ZnP(C_2V)_4$ and $ZnP(C_3V)_4$ slightly decreased in the case of the systems showing a decrease of hydrogen evolution rate with Triton X-100.

The fact that hydrogen evolution rate increases in the case of $ZnP(C_5V)_4$ in spite of the increase of the triplet state lifetime indicates that the intramolecular quenching between the photoexcited porphyrin and viologen occurs only with difficulty. Accordingly, the reductive quenching of the photoexcited triplet state of porphyrin by NADPH will be predominant, and the following reaction mechanism is proposed.

$$^3P^*\text{-}V + D \longrightarrow P^-\text{-}V + D^+$$
$$P^-\text{-}V \longrightarrow P\text{-}V^-$$

At the first stage of the reaction the photoexcited triplet state ($^3P^*$-V) is reductively quenched by NADPH (D) and the reduced form of porphyrin (P^--V) is formed after which the electron transfers from the porphyrin to the viologen.

The cause of the remarkable increase of hydrogen evolution rate in micelles in the case of $ZnP(C_5V)_4$ has not been clarified completely. As the absorption spectrum of $ZnP(C_5V)_4$ in water is broad, there are some intra- or inter-molecular interactions. When the surfactant, Triton X-100, was added to the system, a sharp absorption spectrum of $ZnP(C_5V)_4$ was obtained. The result indicates that the intra- or inter-molecular interactions disappear and that the suppression of the interaction extends the lifetime of the excited $ZnP(C_5V)_4$ in the micelles.

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