Photoinduced Hydrogen Evolution with Vilogen-linked Water-soluble Zinc Porphyrins in a Micellar System

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Viologen-linked porphyrins, Zn-$PC_3(C_nV)$, with various methylene chain lengths (n = 3–5) between the porphyrin and the viologen have been synthesized. These compounds were applied to photoinduced hydrogen evolution in a system containing NADPH–Zn-$PC_3(C_nV)$–hydrogenase under steady-state irradiation. On the addition of surfactant to the system, a remarkable rate increase in hydrogen evolution was observed.

Photoinduced hydrogen evolution systems containing an electron donor, a photosensitizer, an electron carrier and a catalyst have been studied extensively [1–3]. Metallo-porphyrins have been widely used as photosensitizers 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 [4–6]. To improve the rate of photoinduced hydrogen evolution, effective charge separation between the photoexcited sensitizer and the quencher is needed. An electrostatic field, such as a micellar surface, has been widely applied to separate the charges effectively [7]. 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, Zn-$PC_3(C_nV)$ and hydrogenase.

Experimental

The structure of the viologen-linked water-soluble zinc porphyrins, Zn-$PC_3(C_nV)$, is illustrated in Fig. 1. These compounds were synthesized as follows. The starting material, 4-pyridyl-4′,4″,4‴-tri(ethylcarboxyphenyl)porphyrin (H_2PyTECPP), was synthesized according to the method described in the literature [8]. By-products were removed by Rousseau and Dolphin's method [9]. H_2PyTECPP was then quaternized with an excess amount of α,ω-dibromoalkane at 130 °C to obtain 4-methylpyridyl-4′,4″,4‴-tri(ethylcarboxyphenyl)porphyrin bromide (H_2MPyTECPPBr). After hydroxylation of H_2MPyTECPPBr by excess NaOH in ethanol, zinc porphyrins with a methylene chain (Zn-$PC_3(C_nBr)$, n = 3–5, Fig. 1) were synthesized by the addition of zinc acetate (*ca.* 10-fold excess). The porphyrin (Zn-$PC_3(C_nBr)$, n = 3–5) and a 100-fold molar excess amount of *N*-methyl-4,4′-bipyridyl iodide were refluxed in DMF, and the product was extracted with CH_3Cl, and then washed with water to remove excess *N*-methyl-4,4′-bipyridyl iodide. Excess porphyrins were removed by column chromatography (Biorad, Biobeads SX-2, 60 × 3 cm).

Hydrogenase was obtained from *Desulfovibrio vulgaris* (Miyazaki type, IAM 12604) and purified by Yagi's method [10]. The concentration of hydrogenase was 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})–methyl viologen (4.1×10^{-5} mol

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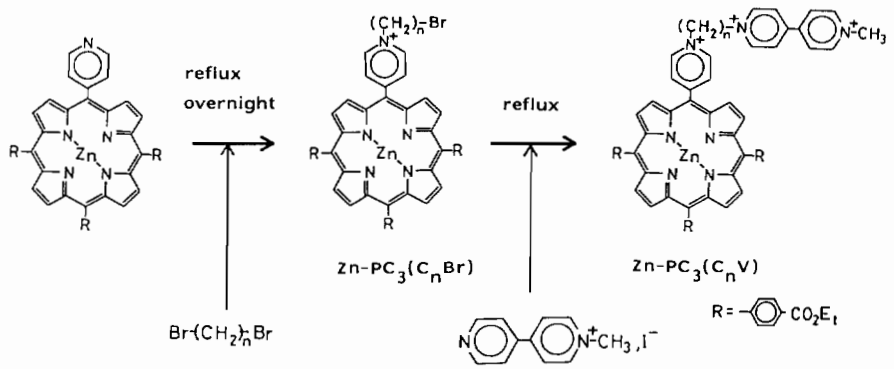

Fig. 1. Illustration of the structure of Zn-$PC_3(C_nV)$.

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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 the method described elsewhere [6]. Emission lifetimes were measured by a Horiba NAES-550. 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 under steady-state irradiation at 30 °C. A sample solution containing nicotineamide–adenine dinucleotide phosphate (reduced form, NADPH), Zn-$PC_3(C_nV)$, hydrogenase and a surfactant (Triton X-100) was deaerated by repeated freeze–pump–thaw cycles.

Results and Discussion

When an aqueous solution containing Zn-$PC_3(C_nV)$, NADPH and hydrogenase was irradiated, hydrogen evolution was observed. A typical time-dependence of hydrogen evolution in the case of Zn-$PC_3(C_3V)$ is shown by closed circles in Fig. 2. When a surfactant, Triton X-100, was added to the above three-component system, a remarkable increase in hydrogen evolution rate was observed, as shown by triangles in Fig. 2.

The lifetimes of the photoexcited triplet state of Zn-$PC_3(C_nV)$ were measured by laser flash photolysis. The T–T absorption decay obeyed first-order kinetics. From the slopes of their first-order plots, the lifetimes of the triplet state of these compounds were obtained; e.g., 286 μs for Zn-$PC_3(C_3V)$ and 295 μs for Zn-$PC_3(C_3Br)$. There were no remarkable differences in the triplet lifetimes between viologen-linked porphyrin (Zn-$PC_3(C_3V)$) and the porphyrin without viologen (Zn-$PC_3(C_3Br)$), indicating that the triplet states of these compounds are not quenched by the linked viologen.

The fluorescence spectra of Zn-$PC_3(C_nV)$ and Zn-$PC_3(C_nBr)$ were measured. The relative fluorescence intensities (obtained by integrating the spectra) of Zn-$PC_3(C_nV)$ are low compared with the zinc porphyrin Zn-$PC_3(C_nBr)$ without viologen.

From the above results, the photoexcited triplet state of Zn-$PC_3(C_nV)$ is not quenched by linked viologen, but the singlet state may be quenched by viologen linked with a porphyrin ring.

Fluorescence decays of these compounds were also measured. The fluorescence decay profile consists of two components with first-order decay; shorter lifetimes (τ_s) and longer lifetimes (τ_l) are shown in Table 1. Though there were no remarkable differences in the lifetimes in the presence and in the absence of the surfactant Triton X-100, the component of the shorter lifetime increased in the presence of Triton X-100. The photoexcited singlet state with the shorter lifetime may play an important role in the photoinduced hydrogen evolution.

The study of the reaction mechanism is now being investigated.

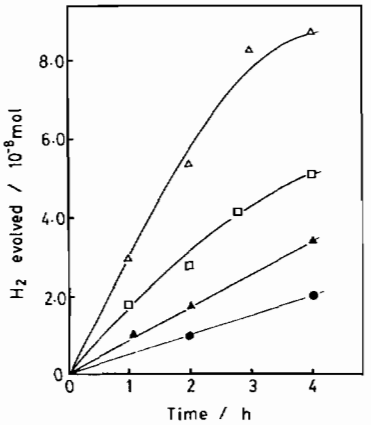

Fig. 2. Time-dependence of hydrogen evolution. Sample solution (6.0 cm^3) containing Zn-$PC_3(C_nV)$ (2.0×10^{-6} mol dm^{-3}), NADPH (1.0×10^{-3} mol dm^{-3}) and hydrogenase (0.5 cm^3) was irradiated at 30 °C in 5 vol% Triton X-100/H_2O (△, □, ▲) and in H_2O (●) (△ and ●, Zn-$PC_3(C_3V)$; □, Zn-$PC_3(C_4V)$; ▲, Zn-$PC_3(C_5V)$).

TABLE 1. Analysis of Fluorescence Decay Profiles of Zn-$PC_3(C_3V)$

Solvent	τ_s (ns)	%	τ_l (ns)	%
Triton X-100 (5 vol%)	1.41	78.3	5.75	21.7
Water	1.50	68.8	7.47	31.2

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References

1 J. R. Darwent, P. Douglas, A. Harriman, G. Porter and M.-C. Richoux, *Coord. Chem. Rev., 44* (1982) 83, and refs. therein.
2 J. Kiwi, K. Kalyanasundaram and M. Gratzel, *Struct. Bonding (Berlin), 49* (1982) 37, and refs. therein.
3 I. Okura, *Coord. Chem. Rev., 68* (1985) 53, and refs. therein.
4 I. Okura, S. Aono and N. Kaji, *J. Chem. Soc., Chem. Commun.*, (1986) 170.

5 N. Kaji, S. Aono and I. Okura, *J. Mol. Catal., 36* (1986) 201.
6 I. Okura, N. Kaji, S. Aono and T. Nishisaka, *Bull. Chem. Soc. Jpn., 60* (1987) 1243.
7 (a) N. J. Turro, M. Gratzel and A. M. Braun, *Angew. Chem., Int. Ed. Engl., 19* (1980) 675; (b) K. Kano, K. Takuma, T. Ikeda, M. Nakajima, Y. Tsutsui and T. Matsuo, *Photochem. Photobiol., 27* (1978) 695; (c) J. R. Escabi-Perez, F. Nome and J. H. Fendler, *J. Am. Chem. Soc., 99* (1977) 7794; (d) U. Lachish, M. Ottolenghi and J. Rabani, *J. Am. Chem. Soc., 99* (1977) 8062.
8 C. Franco and C. McLendon, *Inorg. Chem., 23* (1984) 2370.
9 K. Rousseau and D. Dolphin, *Tetrahedron Lett.*, (1984) 4251.
10 T. Yagi, *J. Biochem., 68* (1970) 649.