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Ichiro Okura^a; Yuichi Kinumi^a; Naruhiko Kaji^a; Shigetoshi Aono^a

^a Department of Bioengineering, Tokyo Institute of Technology, Tokyo, Japan

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PHOTOINDUCED HYDROGEN EVOLUTION WITH VIOLOGEN-LINKED PORPHYRINS

ICHIRO OKURA,* YUICHI KINUMI, NARUHIKO KAJI, and SHIGETOSHI AONO

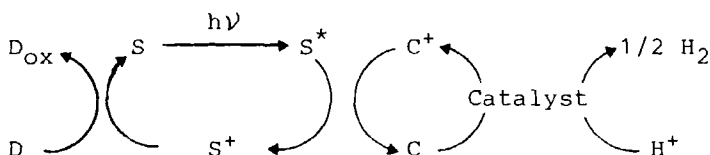
Department of Bioengineering
Tokyo Institute of Technology
Ookayama, Meguro-ku, Tokyo 152, Japan

ABSTRACT

Viologen-linked water-soluble porphyrins with different methylene chain lengths between porphyrin and viologen were synthesized. These compounds were applied to photoinduced hydrogen evolution in a system containing NADPH, viologen-linked porphyrin, and hydrogenase under steady-state irradiation.

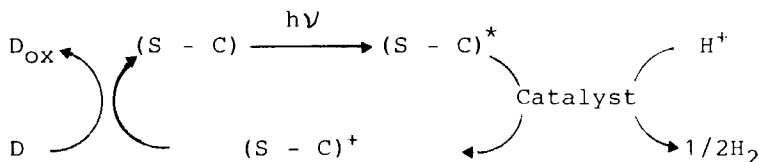
INTRODUCTION

Photoinduced hydrogen evolution systems containing an electron donor (D), a photosensitizer (S), an electron carrier (C), and a catalyst have been studied extensively [1-3]:



*To whom correspondence should be addressed.

Metallo-porphyrins have been widely used as photosensitizers, and methyl viologen has been a popular electron carrier. In this work, viologen-linked water-soluble zinc porphyrins (S-C) were synthesized, which may act as both photosensitizer and electron carrier in the same molecule; these compounds were applied to photoinduced hydrogen evolution as shown in the following scheme:



Viologen was connected to porphyrin with methylene chains. Information about electron transfer along the methylene chain is important to clarify the electron-transfer mechanism in macromolecular metal complexes.

EXPERIMENTAL

All materials were of analytical grade or the highest grade available.

The structures of viologen-linked water-soluble zinc porphyrins are shown in Fig. 1. $\text{ZnP}(\text{C}_n\text{V})_4$ containing four methyl viologen groups is cationic, and ZnPC_nV containing a methyl viologen group and three carboxyl groups is anionic. These compounds were synthesized as shown in Fig. 2.

In the case of cationic porphyrins, $\text{ZnP}(\text{C}_n\text{V})_4$, the starting material, zinc 5,10,15,20-tetra(4-pyridyl)-porphyrin (Zn-TMPyP), was synthesized accord-

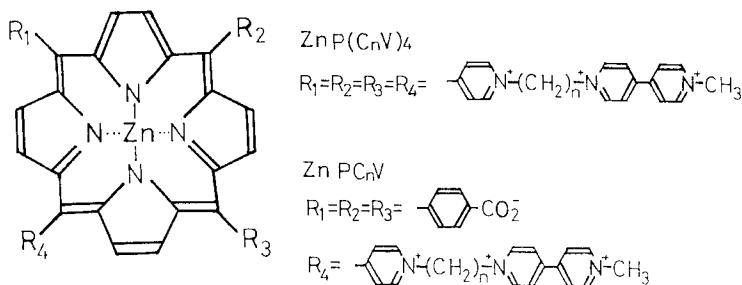


FIG. 1. Structure of viologen-linked porphyrins, $\text{ZnP}(\text{C}_n\text{V})_4$.

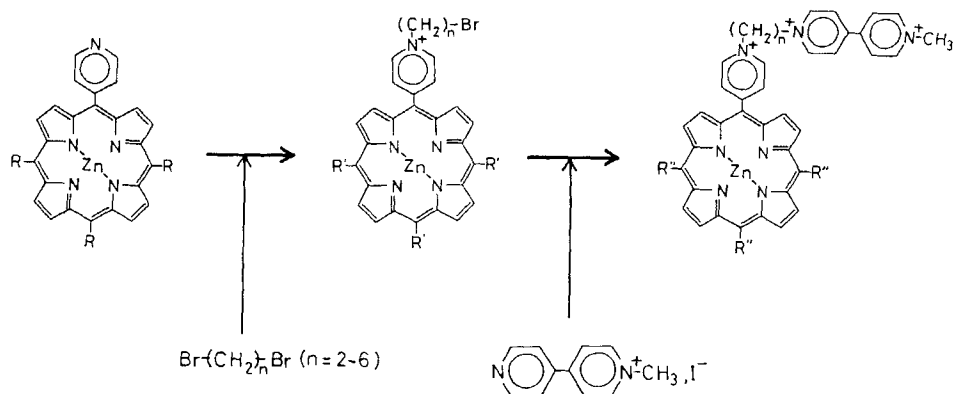


FIG. 2. Synthesis of viologen-linked porphyrins.

ing to methods described in the literature [4, 5]. Zn-TMPyP was then quaternized with an excess of α,ω -dibromoalkane at 130°C . The quaternized porphyrin and a 100 to 200-fold molar excess of 1-methyl-4,4'-bipyridin-1-ium iodide was refluxed in methanol, and the precipitate was filtered off and washed with methanol.

In the case of anionic porphyrin, ZnPC_nV, the starting material, 5-(4-pyridyl)-10,15,20-tri(ethylcarboxyphenyl)porphyrin (PyTEP) was synthesized according to the literature [4, 5]. PyTEP was then quaternized with an excess of α,ω -dibromoalkane at 130°C . The quaternized porphyrin and a 100 to 200-fold molar excess of 1-methyl-4,4'-bipyridin-1-ium iodide was refluxed in methanol to yield the viologen-linked porphyrin. Then it was hydroxidized with NaOH in ethanol and refluxed with zinc acetate to obtain viologen-linked zinc porphyrins.

Hydrogenase was obtained from *Desulfovibrio vulgaris* (Miyazaki type, IAM 12604) and purified by Yagi's method [6]. Its concentration was not known, but 1.48×10^{-6} mol of hydrogen was generated by the following reaction system: hydrogenase (0.5 cm^3) methylviologen ($4.1 \times 10^{-5} \text{ mol/dm}^3$), $\text{Na}_2\text{S}_2\text{O}_4$ ($5.7 \times 10^{-3} \text{ mol/dm}^3$) in 5.0 cm^3 of 0.02 mol/dm^3 Tris-HCl buffer (pH 7.0) at 30°C for 10 min.

Conventional laser flash photolysis was carried out by using a Nd-YAG laser, Model DCR-2A-10 from Quanta-Ray Inc. This generated second-harmonic (532 nm) pulses of 10-ns duration with an energy of 200 mJ/pulse; a repetition rate of 10 Hz was used for the excitation of sample solutions

throughout this study. The light beam, after passing 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 a photomultiplier (Hamamatsu Photonics 446) attached to the slit of the monochromator was displayed on a Hitachi oscilloscope, Model V-1050F.

The absorption spectrum of the $\text{ZnP}(\text{C}_n\text{V})_4$ and NADPH was deaerated by repeated freeze-pump-thaw cycles and then irradiated.

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

Photoinduced hydrogen evolution was carried out with viologen-linked porphyrin under steady-state irradiation at 30°C. A sample solution containing nicotinamide-adenine dinucleotide phosphate (reduced form, NADPH), viologen-linked porphyrin, and hydrogenase was deaerated by repeated freeze-pump-thaw cycles.

RESULTS AND DISCUSSION

Photoreduction of Viologen

When a sample solution containing viologen-linked porphyrin and NADPH was irradiated, growth of the reduced form of viologen was observed. Figure 3 shows an example when $\text{ZnP}(\text{C}_5\text{V})_4$ was used. Since the absorption coefficient of $\text{ZnP}(\text{C}_5\text{V})_4$ was not known, its concentration was determined by using the absorption coefficient of ZnTMPyP ($\epsilon_{\text{max}} = 1.8 \times 10^5 \text{ mol/dm}^3 \text{ cm}^{-1}$ at 438 nm). The concentration of the reduced form of viologen increased with the irradiation time and tended to reach a constant value.

Regarding the exposure of the sample solution to air, the absorption band with $\lambda_{\text{max}} = 600 \text{ nm}$ disappeared, confirming the formation of reduced viologen. The intensity of the absorption with $\lambda_{\text{max}} = 460 \text{ nm}$, due to the Soret band of the porphyrin, decreased upon irradiation. Owing to the exposure to air, the spectrum returned to the original shape to some extent as shown by the dotted line, but did not completely return to the original shape. This fact indicates that the reduced form of the porphyrin was formed by the irradiation and that an irreversible species was formed at the same time due to the irradiation. The reduced form of the porphyrin may be formed by the reductive quenching of the photoexcited porphyrin by NADPH.

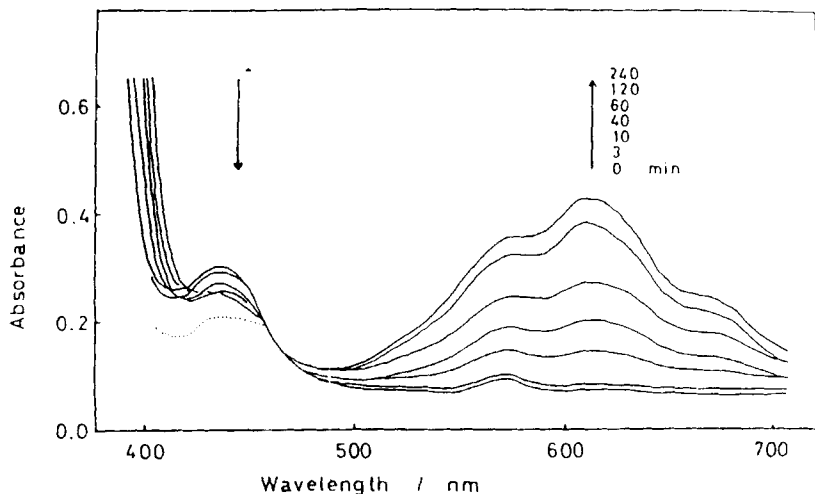


FIG. 3. Absorption spectrum of the $\text{ZnP}(\text{C}_5\text{V})_4$ -NADPH system. Sample solution containing $\text{ZnP}(\text{C}_5\text{V})_4$ (2.0×10^{-6} mol/L) and NADPH (1.0 mmol/L) was irradiated at 30°C .

Photoinduced Hydrogen Evolution

Upon irradiation of the sample solution, hydrogen was generated; the time dependence of the amount of hydrogen evolved is shown in Figs. 4 and 5. Thus, it is apparent that every compound, $\text{ZnP}(\text{C}_n\text{V})_4$ ($n = 2-5$) and ZnPC_nV ($n = 4-6$), participates as both photosensitizer and electron carrier in the same molecule. Since the hydrogen evolved almost linearly with irradiation time, irreversible deactivation of the porphyrin is depressed in these systems. When an intramolecular electron transfer from porphyrin to viologen takes place, the electron can move from the reduced viologen to the catalyst hydrogenase. As shown in Figs. 4 and 5, the hydrogen evolution rate strongly depends on the methylene chain length, n , of viologen-linked porphyrins. In the case of $\text{ZnP}(\text{C}_n\text{V})_4$, within a certain range ($n = 2-4$), the hydrogen evolution rate decreases with increasing chain length. Electron transfer from the porphyrin to viologen may be more difficult when the methylene chain becomes longer. In the case of $\text{ZnP}(\text{C}_5\text{V})_4$, however, a higher evolution rate was observed. The turnover number of hydrogen evolved against $\text{ZnP}(\text{C}_5\text{V})_4$ was 86/h. The

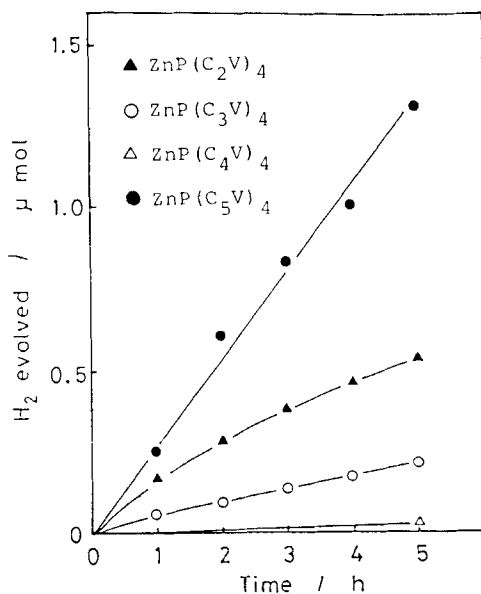


FIG. 4. Time dependence of amount of hydrogen evolved. Sample solution containing $\text{ZnP}(\text{C}_n\text{V})_4$ ($2.0 \mu\text{mol/L}$), NADPH (1.0 mmol/L), and hydrogenase (0.5 cm^3) was irradiated at 30°C .

activity was at most two times more active than that of an individual component system containing ZnTMPyP, methylviologen, NADPH, and hydrogenase. As the chain length is sufficiently long in this case, the porphyrin ring may possibly come close enough to viologen by a conformational change of the molecule so that the electron can transfer directly from the porphyrin ring to viologen.

Laser Flash Photolysis

Figure 6 shows oscilloscope traces of photoexcited $\text{ZnP}(\text{C}_n\text{V})_4$ monitored at 500 nm after a laser flash. From these figures the lifetimes of the triplet state of these compounds were obtained (Table 1). There were no remarkable differences between $\text{ZnP}(\text{C}_n)_4$ and $\text{ZnP}(\text{C}_n\text{V})_4$, except for $n = 4$, indicating that the triplet states of these compounds are not quenched by the linked viologen. Table 2 shows the lifetimes of the triplet state of $\text{ZnP}\text{C}_n\text{V}$. There were no differences among them and the value was almost the same as that

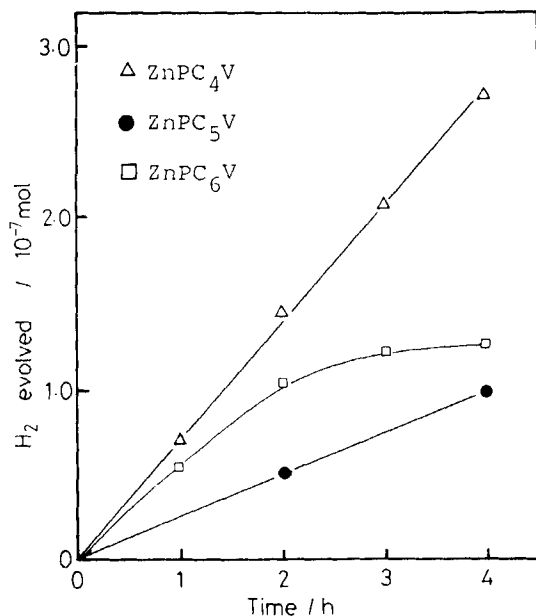


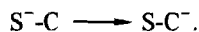
FIG. 5. Time dependence of amount of hydrogen evolved. Sample solution containing ZnPC_nV ($2.0 \mu\text{mol/L}$ for $n = 4$ and 6 , $20 \mu\text{mol/L}$ for $n = 5$), NADPH (1.0 mmol/L), and hydrogenase (0.5 cm^3) was irradiated at 30°C .

of viologen-free zinc porphyrin (ZnPM). In the case of ZnPC_nV also, triplet states are not quenched by the linked viologen. When different laser powers are applied, the concentration of the photoexcited species may change. The lifetimes of the triplet state were independent of the laser power, indicating that the triplet state is not quenched by another molecule in the ground state; that is, intermolecular quenching is negligible under these reaction conditions. Strong dependence of the hydrogen evolution rate on the methylene chain length, as shown in Figs. 4 and 5, also supports the intramolecular reaction.

From the above results the following reaction mechanism is proposed:



and



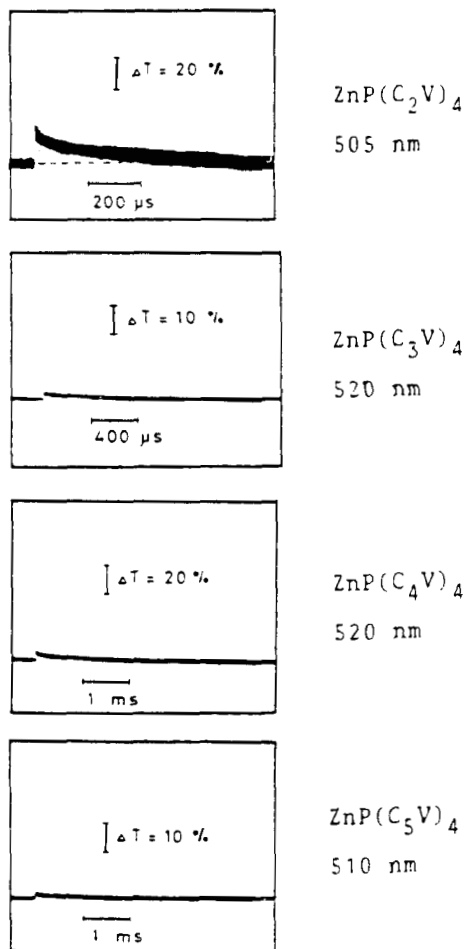


FIG. 6. Typical oscillograms for T-T absorption of $\text{ZnP}(\text{C}_n\text{V})_4$.

During the first stage of the reaction, the photoexcited triplet state (${}^3\text{S}^*\text{-C}$) is reductively quenched by NADPH and a reduced form of porphyrin (S^-C) is formed; then, the electron transfers from the porphyrin to viologen. This reaction mechanism is based on the fact that both intramolecular and intermolecular quenching of the photoexcited triplet state of the porphyrin did not occur, and that reductive quenching by NADPH is predominant.

TABLE 1. Lifetimes of Excited Triplet State of $\text{ZnP}(\text{C}_n\text{V})_4$

	$\tau, \mu\text{s}$		$\tau, \mu\text{s}$
$\text{ZnP}(\text{C}_2)_4$	140	$\text{ZnP}(\text{C}_2\text{V})_4$	190
$\text{ZnP}(\text{C}_3)_4$	530	$\text{ZnP}(\text{C}_3\text{V})_4$	510
$\text{ZnP}(\text{C}_4)_4$	230	$\text{ZnP}(\text{C}_4\text{V})_4$	610
$\text{ZnP}(\text{C}_5)_5$	330	$\text{ZnP}(\text{C}_5\text{V})_4$	470

TABLE 2. Lifetimes of Excited Triplet State of ZnPC_nV

	ZnPM	ZnPC_3V	ZnPC_4V	ZnPC_5V	ZnPC_6V
$\tau, \mu\text{s}$	240	280	290	200	240

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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] J. Kiwi, K. Kalyanasundaram, and M. Gratzel, *Struct. Bonding (Berlin)*, **49**, 37 (1982) and the references therein.
- [3] I. Okura, *Coord. Chem. Rev.*, **68**, 53 (1985) and the references therein.
- [4] A. D. Adler, *J. Org. Chem.*, **32**, 476 (1967).
- [5] A. Harriman, G. Porter, and P. Walters, *J. Chem. Soc., Faraday Trans. 1*, **79**, 1335 (1983).
- [6] T. Yagi, *J. Biochem.*, **68**, 649 (1970).

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