Photoinduced Hydrogen Evolution with Viologen-Linked Zinc Porphyrins

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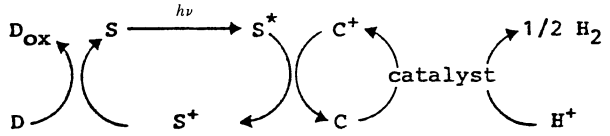
Viologen-linked water-soluble zinc porphyrins with different methylene chain lengths between porphyrin and viologen, Zn-PC$_3$(C$_n$V) (n=2—6), were both synthesized and characterized. The lifetimes of the photoexcited triplet states of these compounds were almost the same as those of zinc porphyrins without linked viologen. The fluorescence decay profiles, however, comprised two components with first-order decay (shorter and longer lifetimes) indicating the existence of two conformations: complexed and extended conformers. In the complexed conformer, photoexcited singlet state is quenched by linked viologen. These compounds were applied to photoinduced hydrogen evolution in a system containing NADPH, Zn-PC$_3$(C$_n$V), and hydrogenase under steady state irradiation. Upon irradiation of the sample solution hydrogen was generated, indicating that all of the compounds, Zn-PC$_3$(C$_n$V) (n=2—6), can be substrates of the enzyme hydrogenase, and that every compound participates as both a photosensitizer and an electron carrier in the same molecule.

Over the past decade much attention has been given to systems capable of using solar energy. The most attractive reaction to convert solar energy into chemical energy is the photodecomposition of water into hydrogen and oxygen. Various attempts have been made to develop suitable redox systems for the photochemical utilization of solar energy. Recent work has shown that the following three component systems containing a photosensitizer, an electron donor, and an electron acceptor can be used to evolve hydrogen when a suitable catalyst is present.[1-3]

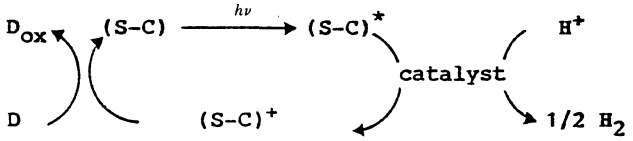


Here, D, S, and C are an electron donor, a photosensitizer, and an electron carrier, respectively.

The described reactions are quite general and have been demonstrated for a wide range of photosensitizers and electron carriers.[4-15]

Metallo-porphyrins have been widely used as photosensitizers, and methyl viologen has been a popular electron carrier. For a catalyst, an enzyme, hydrogenase, or colloidal platinum is widely used; any of these can catalyze the reduction of protons in the presence of suitable electron-donating agents, such as reduced methyl viologen.

In this reaction charge separation between a photoexcited sensitizer and an electron carrier is one of the most important steps. In order to improve this system viologen-linked water-soluble zinc porphyrins (S-C) were synthesized. In the viologen-linked porphyrins, the viologen moiety is close to the porphyrin ring and the photoexcited porphyrin is easily quenched, compared with the non-linked porphyrin and viologen system. Since these compounds possibly act as both a photosensitizer and an electron carrier in the same molecule, they were applied to photoinduced hydrogen evolution, as shown in the following scheme:



We previously reported the synthesis and characterization of four viologen-linked tetra-pyridyl porphyrins and photoinduced hydrogen evolution with these porphyrins.[16,17] In this study different types of viologen-linked porphyrins and one viologen-linked mono-pyridyl porphyrin, were both synthesized and characterized.

Some types of quinone bonded porphyrins have been synthesized as model compounds of chlorophyll.[18-20] Very efficient quenching of photoexcited chlorophyll occurs via the singlet state. It has been found that the photoexcited singlet state of some of these compounds are quenched by bonded quinone. Regarding viologen-linked porphyrins, photoexcited singlet-state quenching was also measured; the reaction mechanism is discussed.

Experimental

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

Hydrogenase was obtained from Desulfovibrio vulgaris (Miyazaki type, IAM 12604) and purified by Yagi's method.[21] Though its concentration is not known, 1.48×10^{-6} mol of hydrogen was generated by the following reaction system; hydrogenase (0.5 ml)-methyl viologen (4.1×10^{-5} mol dm^{-3})-$Na_2S_2O_4$ (5.7×10^{-3} mol dm^{-3}) in 1.0 ml of 0.02 mol dm^{-3} Tris-HCl buffer (pH 7.0) at 30 °C for 10 min.

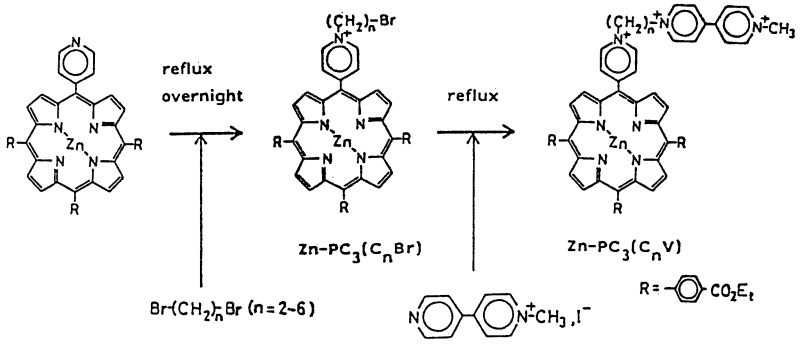


Fig. 1. Structure of viologen-linked zinc-porphyrins and their synthetic route.

Preparation of Viologen-Linked Porphyrins. The preparation route of viologen-linked water-soluble zinc porphyrins is shown in Fig. 1. The starting material, 5-(4-pyridyl)-10,15,20-tetrakis(4-ethoxycarboxyphenyl)porphyrin, was synthesized according to methods described in the literature.[22] By-products were removed by Dolphin's method.[23] The starting material, 5-(4-pyridyl)-10,15,20-tetrakis(4-ethoxycarboxyphenyl)porphyrin, was then quaternized with an excess amount of α,ω-dibromoalkane at 130 °C to obtain 5-[1-(ω-bromoalkyl)-4-pyridino]-10,15,20-tris(ethoxycarboxylphenyl)porphyrin bromide. After hydrolysis of 5-[1-(ω-bromoalkyl)-4-pyridino]-10,15,20-tris(ethoxycarboxylphenyl)porphyrin bromide by excess NaOH in ethanol, zinc-porphyrins with methylene chain (Zn-$PC_3(C_nBr)$, n=2—6, Fig. 1) was synthesized by the addition of zinc acetate (ca. 10 fold molar excess). The porphyrin (Zn-$PC_3(C_nBr)$, n=2—6) and a 100-fold molar excess amount of 1-methyl-4,4′-bipyridinium iodide was refluxed in DMF; the product was extracted with CH_3Cl and then washed with water to remove excess 1-methyl-4,4′-bipyridinium iodide. Excess porphyrins were removed by column chromatography (Biorad, Biobeads SX-2, 60×3 cm). Thus-prepared viologen-linked zinc porphyrins were used for photochemical experiments.

Optical Measurements. The luminescence intensity (an integration along the luminescence spectrum between 570 nm and 750 nm) was measured using a Hitachi-850 spectrometer. The excitation wavelength was 550 nm. The lifetime of luminescence was measured using a Horiba NAES-550.

Conventional laser flash photolysis was carried out by using an Nd-YAG laser (model DCR-2A-10 from Quanta-Ray Inc). This laser generated second-harmonic (532 nm) pulses of 10 ns duration with an energy of 200 mJ per pulse; a repetion 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-1050 F).

Method of Photoinduced Hydrogen Evolution. Photoinduced hydrogen evolution was carried out under steady state irradiation at 30 °C. A sample solution containing nicotinamide-adenine dinucleotide phosphate (reduced form, NADPH), Zn-$PC_3(C_nV)$, hydrogenase and surfactant, Triton X-100 (if included), was deaerated by repeated freeze-pump-thaw cycles. As a light source, a-200 W tungsten lamp was used. Light of wavelength less than 390 nm was removed by a Toshiba L-39 filter. Evolved hydrogen gas was analyzed by gas chromatography (column: active carbon, 2 m; column temp.: 40 °C, carrier gas: nitrogen).

Results and Discussion

Characterization of Zn-$PC_3(C_nV)$. Table 1 shows the peak wavelengths of the electronic spectra of Zn-$PC_3(C_nV)$ and Zn-$PC_3(C_nBr)$. Though the electronic spectra of Zn-$PC_3(C_nV)$ are similar to those of Zn-$PC_3(C_nBr)$, the absorption peak wavelength of Zn-$PC_3(C_nV)$ in the Soret region shifts to longer wavelength, indicating a slight interaction between the central metal ion and the viologen connected at the end of the methylene chain.

Figure 2 shows typical oscilloscope traces of photoexcited Zn-$PC_3(C_nV)$ and Zn-$PC_3(C_nBr)$ monitored at 470 nm after a laser flash. The decay obeyed first-order kinetics. From the slopes of the first-order plots the lifetimes of the triplet state of these compounds were obtained (Table 2). There were no remarkable differences in the triplet lifetimes between Zn-$PC_3(C_nV)$ and Zn-$PC_3(C_nBr)$, 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 also measured. A typical fluorescence

Table 1. Peak Wavelength of Various Porphyrins

	Soret Band/nm	Q Band/nm	
Zn-$PC_3(C_2Br)$	422.0	557.4	597.6
Zn-$PC_3(C_2V)$	423.2	560.8	603.0
Zn-$PC_3(C_3Br)$	422.8	521.0[a]	558.4 599.4
Zn-$PC_3(C_3V)$	422.0	521.0[a]	558.6 599.0
Zn-$PC_3(C_4Br)$	422.0	557.0	598.0
Zn-$PC_3(C_4V)$	423.0	559.2	601.0
Zn-$PC_3(C_5Br)$	423.2	558.8	600.6
Zn-$PC_3(C_5V)$	423.0	559.8	601.0
Zn-$PC_3(C_6Br)$	423.2	521.0[a]	559.4 604.2
Zn-$PC_3(C_6V)$	423.6	562.2	601.8

a) Weak peak.

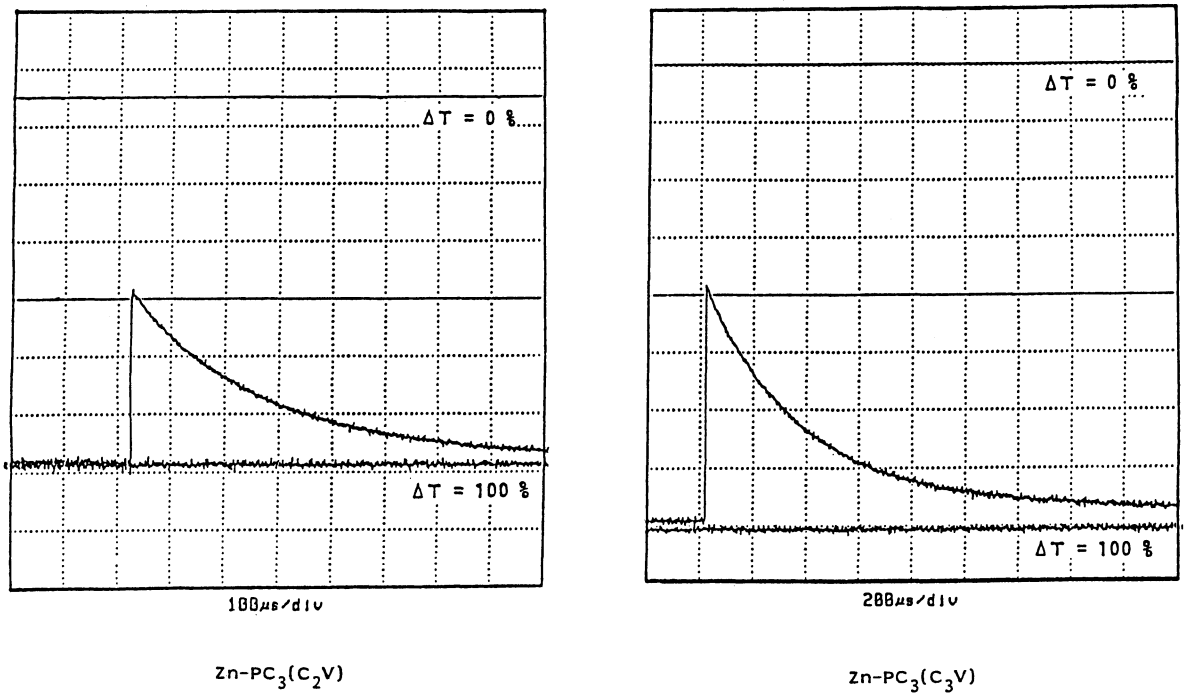


Fig. 2. Typical oscilloscope traces for T-T absorption of Zn-$PC_3(C_nV)$ observed at 470 nm.

Table 2. Lifetimes of Excited Triplet State of Zn-$PC_3(C_nBr)$ and Zn-$PC_3(C_nV)$

	Lifetime/10^{-6} s		Lifetime/10^{-6} s
Zn-$PC_3(C_2Br)$	237	Zn-$PC_3(C_2V)$	200
Zn-$PC_3(C_3Br)$	295	Zn-$PC_3(C_3V)$	286
Zn-$PC_3(C_4Br)$	290	Zn-$PC_3(C_4V)$	203
Zn-$PC_3(C_5Br)$	205	Zn-$PC_3(C_5V)$	322
Zn-$PC_3(C_6Br)$	240	Zn-$PC_3(C_6V)$	200

spectrum of Zn-$PC_3(C_2V)$ is shown in Fig. 3. The relative fluorescence intensity obtained by integrating the spectra are shown in Table 3. The relative fluorescence intensity of Zn-$PC_3(C_nV)$ (n=2—4) are low compared with zinc porphyrin (Zn-$PC_3(CH_3)$) without linked viologen, showing that the singlet state is quenched by viologen linked with a porphyrin ring.

A typical fluorescence decay profile of Zn-$PC_3(C_nV)$ is shown in Fig. 4. The fluorescence lifetimes are summarized in Table 4. In the case of Zn-$PC_3(CH_3)$, the fluorescence decay obeyed first-order kinetics. In the case of viologen-linked porphyrins, however, the fluorescence decay profiles consist of two components with first-order decay; a shorter lifetime (τ_s) and a longer lifetime (τ_l), as shown in Table 4. Both life-

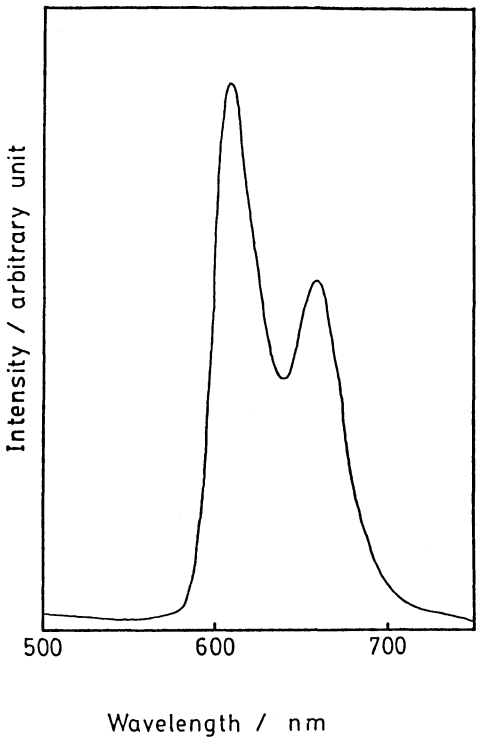


Fig. 3. Fluorescence spectrum of Zn-$PC_3(C_2V)$.

Table 3. Relative Emission Intensity of Zn-$PC_3(CH_3)$ and Zn-$PC_3(C_nV)$

Relative Intensity	Zn-$PC_3(CH_3)$	Zn-$PC_3(C_2V)$	Zn-$PC_3(C_3V)$
	100	56	56
Relative Intensity	Zn-$PC_3(C_4V)$	Zn-$PC_3(C_5V)$	Zn-$PC_3(C_6V)$
	52	77	76

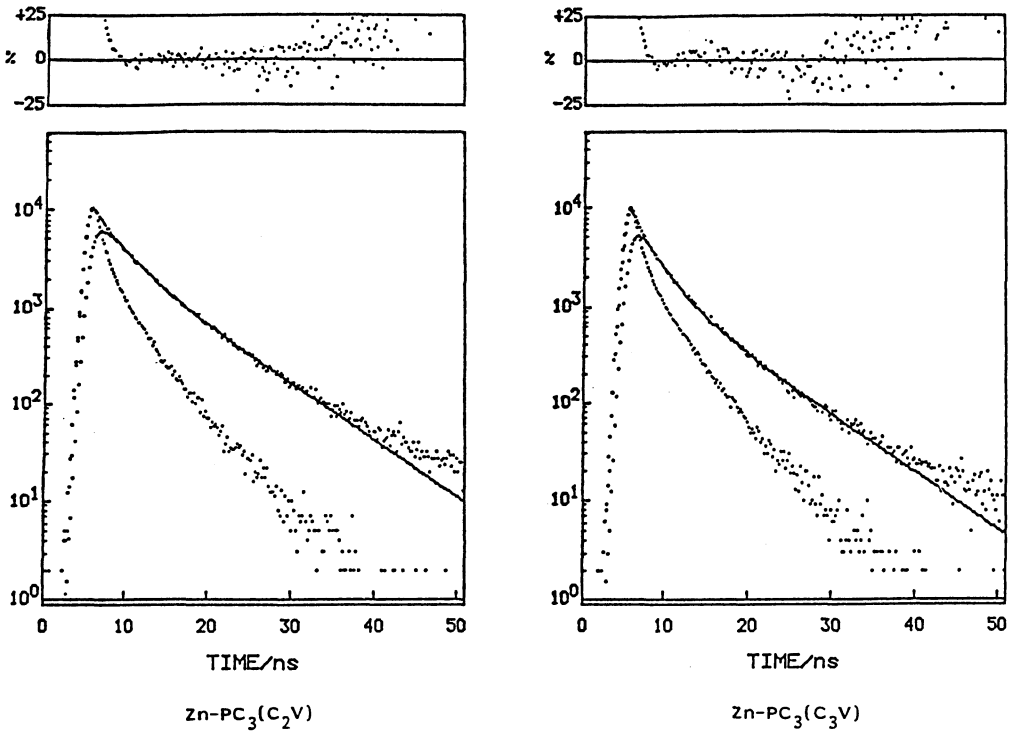


Fig. 4. Fluorescence decay profiles of Zn-PC$_3$(C$_n$V).

Table 4. Analysis of Fluorescence Decay Profiles of Zn-PC$_3$(C$_n$V)

	τ_s/ns	A_s/%	τ_l/ns	A_l/%
Zn-PC$_3$(CH$_3$)			6.76	100
Zn-PC$_3$(C$_2$V)	2.01	54.8	7.52	45.2
Zn-PC$_3$(C$_3$V)	1.50	68.8	7.47	31.2
Zn-PC$_3$(C$_4$V)	2.05	60.7	7.93	39.3
Zn-PC$_3$(C$_5$V)	2.17	64.0	8.09	36.0
Zn-PC$_3$(C$_6$V)	1.88	74.4	8.20	25.6

Table 5. Photoinduced Hydrogen Evolution with NADPH-Zn-PC$_3$(C$_n$V)-Hydrogenase System (See text for reaction conditions)

	Reaction time /h	Hydrogen evolved /10^{-8} mol
Zn-PC$_3$(C$_2$V)	4	0.8
Zn-PC$_3$(C$_3$V)	2	1.0
Zn-PC$_3$(C$_3$V)	4	1.9
Zn-PC$_3$(C$_4$V)	4	1.6
Zn-PC$_3$(C$_5$V)	4	0.8
Zn-PC$_3$(C$_6$V)	4	1.4

times hardly depend on the methylene chain length. The longer fluorescence lifetimes of the viologen-linked porphyrins are almost the same as that of the porphyrin without viologen (Zn-PC$_3$(CH$_3$)).

In the case of quinone-bonded porphyrins, there exists two conformers; complexed and extended conformers.[24] Though the quinone comes close to the porphyrin ring in a complexed conformer, the quinone is extended from the porphyrin ring in an extended conformer. Though the photoexcited singlet state is quenched by quinone in complexed conformer, no quenching reaction occurs in an extended conformer.

In the case of viologen-linked porphyrins there may also be two conformations; a complexed conformer (viologen comes close to the porphyrin ring) and an extended conformer (viologen is extended from the porphyrin ring). In the case of the complexed conformer, the photoexcited singlet state of the porphyrin is quenched by the linked viologen by an intramolecular reaction, as shown in the following scheme:

$$\text{P-V} \xrightarrow{h\nu} {}^1\text{P*-V}$$
$${}^1\text{P*-V} \longrightarrow \text{P-V} + (h\nu)$$
$${}^1\text{P*-V} \longrightarrow \text{P}^+\text{-V}^-$$
$$\text{P}^+\text{-V}^- \longrightarrow \text{P-V}.$$

Here P-V is a viologen-linked porphyrin and P^+-V^- is the charge-separated species.

On the other hand, no quenching reaction occurs in an extended conformer.

Photoinduced Hydrogen Evolution with Zn-PC$_3$(C$_n$V). Photoinduced hydrogen evolution was carried out under steady state irradiation at 30 °C. Upon irradiation of the sample solution hydrogen was generated; the amount of hydrogen evolved is shown in Table 5. It is apparent that all compounds Zn-PC$_3$(C$_n$V) (n=2—6) can be substrates of the enzyme hydrogenase, and that every compound thus participates as both a photosensitizer and an electron carrier in the same molecule. The hydrogen evolution rate strongly depended on the methylene chain length; a

lower hydrogen evolution rate was observed in the case of Zn-$PC_3(C_2V)$. An intramolecular electron transfer from porphyrin to viologen along the methylene chain may hardly take place. When the methylene chain length is sufficiently long ($n>3$), the porphyrin ring possibly comes close enough to viologen, so that an electron easily transfers directly from the porphyrin ring to viologen. A trace amount of hydrogen was observed when an individual component system conatining Zn-$PC_3(CH_3)$, methyl viologen, NADPH, and hydrogenase was used, confirming that the linked viologen of Zn-$PC_3(C_nV)$ serves as an electron carrier.

The lifetimes of the viologen-linked porphyrins (Zn-$PC_3(C_nV)$, n=2—6) were almost the same as those of the porphyrins without viologen (Zn-$PC_3(C_n)$, n=2—6), and also independent of methylene chain length (Table 2). From the above results it can be said that the triplet state of the porphyrin was not quenched by the linked viologen. The hydrogen evolution rate, however, strongly depended on the methylene chain length. In this reaction, the photoexcited singlet state of porphyrin is quenched by the linked viologen.

Photoinduced Hydrogen Evolution in Micellar System. The effect of a surfactant for photoinduced hydrogen evolution was studied, since the conformation of Zn-$PC_3(C_nV)$ may be influenced by the environment. The effect of a surfactant was studied. When a surfactant (Triton X-100) was added to a system containing Zn-$PC_3(C_nV)$, NADPH, and hydrogenase, and then irradiated, a remarkable increase in the hydrogen evolution rate was observed, as shown in Fig. 5.

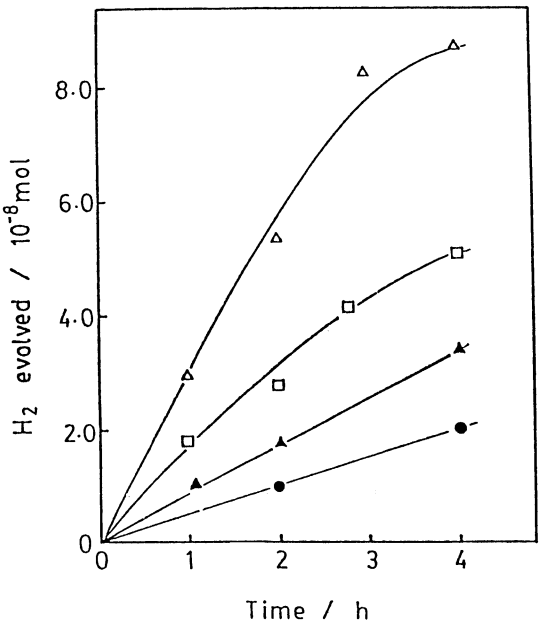


Fig. 5. Time depencence of hydrogen evolution. Sample solution (6.0 cm^3) containing Zn-$PC_3(C_nV)$ (2.0×10^{-6} mol dm^{-3}) NADPH (1.0×10^{-3} mol dm^{-3}) and hydrogenase (0.5 cm^3) was irradiated at 30 °C in 5.0 vol% Triton X-100/H_2O (△, □, ▲) and in H_2O (●). △ and ●: Zn-$PC_3(C_3V)$, □: Zn-$PC_3(C_4V)$, ▲: Zn-$PC_3(C_5V)$.

Table 6. Analysis of Fluorescence Decay Profiles of Zn-$PC_3(C_3V)$

Solvent	τ_s/ns	%	τ_1/ns	%
Triton X-100 (5 vol%)	1.41	78.3	5.75	21.7
Water	1.50	68.8	7.47	31.2

In the presence of Triton X-100, the fluorescence decay profile comprised two components with first-order decay: shorter lifetime and longer lifetime (Table 6). Though there were no remarkable differences in the lifetimes in the presence and in the absence of a surfactant (Triton X-100), the ratio of the shorter-lifetime component increased in the presence of Triton X-100. The photoexcited singlet state with the shorter lifetime may play an important role for photoinduced hydrogen evolution, and rate increase in the presence of Triton X-100 may be caused by an increase in the component with the shorter lifetime.

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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) M. Kirch, J.-M. Lehn, and J. P. Sauvage, *Helv. Chim. Acta*, **62**, 1345 (1979).

5) A. Harriman, "Energy Resources through Photochemistry and Catalysis," Academic Press, New York (1983).

6) J.-M. Lehn and J. P. Sauvage, *Nouv. J. Chim.*, **1**, 449 (1977).

7) K. Kalyanasundaram, J. Kiwi, and M. Gratzel, *Helv. Chim. Acta*, **61**, 2720 (1978).

8) A. Moradpour, E. Amouyal, P. Keller, and H. Kagan, *Nouv. J. Chim.*, **2**, 547 (1978).

9) D. Miller and G. McLendon, *Inorg. Chem.*, **20**, 950 (1981).

10) I. Okura and N. Kim-Thuan, *J. Mol. Catal.*, **5**, 311 (1979).

11) I. Okura and N. Kim-Thuan, *J. Chem. Soc., Chem. Comm.*, **1980**, 84.

12) I. Okura, M. Takeuchi, and N. Kim-Thuan, *Photochem. Photobiol.*, **33**, 413 (1981).

13) G. McLendon and D. S. Miller, *J. Chem. Soc., Chem. Comm.*, **1980**, 553.

14) K. Kalyanasundaram and M. Gratzel, *Helv. Chim.*

Acta, **63**, 478 (1980).
15) A. I. Krasna, *Photochem. Photobiol.,* **29**, 267 (1979).
16) I. Okura, N. Kaji, S. Aono, and T. Nishisaka, *Bull. Chem. Soc. Jpn.,* **60**, 1243 (1987).
17) S. Aono, N. Kaji, and I. Okura, *J. Chem. Soc., Chem. Commun.,* **1986**, 170.
18) S. Ishitani, N. Kuwata, Y. Sakata, S. Misumi, M. Migita, T. Okada, and N. Mataga, *Tetrahedron Lett.,* **22**, 209 (1981).
19) G. Blondeel, D. Dekeukeleire, A. Harriman, and L. R. Milgrom, *Chem. Phys. Lett.,* **118**, 77 (1985).
20) T. A. Moor, D. Gust, P. Mathis, J. C. Mialocq, C. Chachaty, R. V. Bensasson, E. J. Land, D. Doizi, P. A. Liddel, W. R. Lehman, G. A. Nemeth, and A. L. Moor, *Nature,* **307**, 630 (1984).
21) T. Yagi, *J. Biochem.,* **68**, 694 (1970).
22) C. Franco and C. McLendon, *Inorg. Chem.,* **23**, 2370 (1984).
23) C. Rosseau and D. Dolphin, *Tetrahedron Lett.,* 4251 (1984).
24) A. Siemiarczuk, A. R. McIntosh, Te-Hu. Ho, M. J. Stillman, K. J. Roach, A. C. Weedon, J. R. Bolton, and J. S. Connolly, *J. Am. Chem. Soc.,* **105**, 7224 (1983).