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Photoinduced hydrogen evolution using water soluble viologen-linked trisulfonatophenylporphyrins ($TPPSC_nV$) with hydrogenase

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Abstract

A series of water soluble viologen-linked trisulfonatophenylporphyrins with different methylene chain lengths ($n = 3–6$) between porphyrin and viologen, $TPPSC_nV$, were synthesized and were characterized. The intramolecular electron transfer rate constants from the porphyrin moiety of $TPPSC_nV$ to viologen were measured by using fluorescence lifetime and laser flash photolysis. The photoexcited singlet state of the porphyrin was quenched by the bonded viologen. These compounds were applied to photoinduced hydrogen evolution in the system containing nicotinamide-adenine dinucleotide phosphate (reduced form NADPH), $TPPSC_nV$ and hydrogenase under steady state irradiation. © 1997 Elsevier Science B.V.

Keywords: Photoinduced hydrogen evolution; Viologen-linked trisulfonatophenylporphyrin; Hydrogenase; Intramolecular electron transfer

1. Introduction

Photoinduced hydrogen evolution systems consisting of an electron donor (D), a photosensitizer (S), an electron carrier (C) and a catalyst have been used extensively for conversion of solar energy into chemical energy [1–4] (Scheme 1).

In this reaction, charge separation between a photoexcited sensitizer and an electron carrier is one of the important steps. To improve this system some viologen linked porphyrins have been synthesized [5–8]. In the viologen linked porphyrins, the photoexcited singlet state and the triplet state of porphyrin are easily quenched by the bonded viologen, compared with the viologen free porphyrin. As viologen linked porphyrins can act as both a photosensitizer and an electron carrier in the same molecule, these compounds were applied to photoinduced hydrogen evolution. As we reported previously, water soluble viologen-linked cationic porphyrins were synthesized and applied to photoinduced hydrogen evolution [9]. However, the reductive quenching reaction and degradation of zinc porphyrin occurred by using viologen-linked cationic porphyrin. On the other hand, the oxidative quenching reaction and no degradation of porphyrin occurred by using anionic porphyrins. Thus, viologen-linked anionic por-

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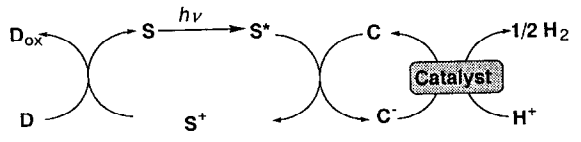


Scheme 1. Photoinduced hydrogen evolution system.

phyrins are attractive to improve the above photoinduced hydrogen evolution system. However, water soluble viologen-linked anionic porphyrins have not been synthesized yet.

In this study, a series of water soluble viologen-linked anionic porphyrins with different methylene chain lengths ($n = 3$–6) between trisulfonatophenylporphyrin and viologen, TPPSC$_n$V were synthesized and were characterized by using UV-vis absorption spectra and fluorescence emission spectra. The quenching processes of the photoexcited singlet and triplet states of the porphyrin moiety of TPPSC$_n$V by the bonded viologen were measured by using fluorescence lifetime and laser flash photolysis. These compounds were applied to photoinduced hydrogen evolution in a system containing NADPH, TPPSC$_n$V and hydrogenase under steady state irradiation.

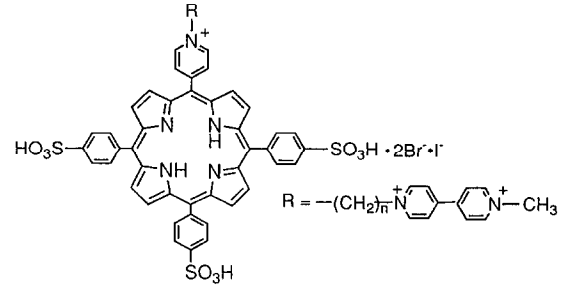
2. Experimental

2.1. Synthesis of water soluble viologen-linked trisulfonatophenylporphyrins (TPPSC$_n$V)

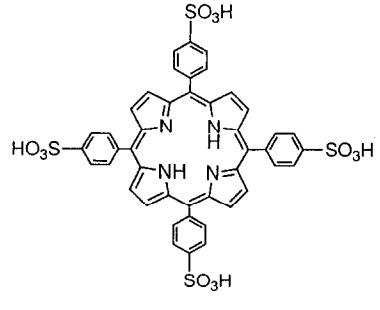
The structures of water soluble viologen-linked trisulfonatophenylporphyrins (TPPSC$_n$V) are shown in Fig. 1. TPPSC$_n$V were prepared by the method reported previously [10]. The starting material, 5-(4-pyridyl)-10,15,20-triphenylporphyrin (PyTP), was synthesized according to the method described in the literature [11]. TPPSC$_n$V was prepared as follows. PyTP was quaternized with an excess amount of α,ω-dibromoalkane (BrC$_n$Br) ($n = 3$–6) in toluene at 110°C for 48 h to obtain 5-(4-bromoalkylpyridinium)-10,15,20-triphenylporphyrin (TPPC$_n$Br). TPPC$_n$Br and an excess amount of 1-methyl-4,4′-bipyridinium were refluxed in dimethylformamide (DMF) for 96 h to obtain viologen linked-porphyrin (TPPC$_n$V). The solvent was removed by vacuum pump. After washing with water and chloroform to remove unreacted 1-methyl-4,4′-bipyridinium and TPPC$_n$Br. A purple precipitate was collected by suction filtration. TPPC$_n$V was refluxed with 20 ml of conc. H_2SO_4 for 4 h. After dilution with double-volume of water, the solution was added to acetone and then a green precipitate was collected by suction filtration and washed with acetone. The molecular structures of the synthesized compounds were characterized by ^{1}H-NMR (Varian GEMINI-200) [10].

2.2. Purification of hydrogenase

Hydrogenase from *Desulfovibrio vulgaris* (Miyazaki) was purified according to Yagi's method [12]. The hydrogenase concentration is not known, but it has the ability to release 0.7



TPPSC$_n$V
n = 3 - 6



TPPS

Fig. 1. Structures of TPPSC$_n$V and TPPS.

μmol of hydrogen in the reaction system of 10 μl hydrogenase, 1.2×10^{-5} mol of methyl viologen and 7.7×10^{-5} mol sodium dithionite in 5.0 ml of 50 mmol dm^{-3} Tris–HCl buffer (pH 7.4) at 30°C for 10 min. One unit of hydrogenase activity was defined to release 1.0 μmol of hydrogen per min.

2.3. Spectroscopic measurements

2.3.1. Absorption spectra

Absorption spectra of $TPPSC_nV$ were recorded using Hitachi U-2000 spectrometer. The molar coefficients were determined by using the value of tetraphenylporphyrin tetrasulfonate (TPPS).

2.3.2. Fluorescence emission spectra

Fluorescence emission spectra of $TPPSC_nV$ were measured using Hitachi F-4010 spectrometer. The excitation wavelength was 421 nm. In these experiments the absorbance at 421 nm was kept constant (0.2) for all the sample solutions.

2.3.3. Fluorescence lifetime

Fluorescence lifetime measurements were carried out by using time-correlated single-photon-counting (Horiba NAES-500 spectrometer) at 25°C.

2.3.4. Laser flash photolysis

Laser flash photolysis was carried out by using Nd-YAG laser (Spectra Physics Quanta Ray DCR-3) with second harmonic light with 532 nm (pulse width 10 ns) at room temperature. Xenon arc lamp was used as a monitoring light beam. The transient spectra were stored in storage oscilloscope (SONY-Tektronix 11401).

2.4. Photoinduced hydrogen evolution under steady state irradiation

In photolysis under steady state irradiation, the sample solution in a Pyrex cell with magnetic stirrer was irradiated with a 200 W tungsten lamp (Philips KP-8) at 30°C. Light of wavelengths less than 390 nm was removed by Toshiba L-39 filter. The sample solution containing NADPH (2.0×10^{-3} mol dm^{-3}), $TPPSC_nV$ (2.5×10^{-6} mol dm^{-3}) and hydrogenase (0.35 unit) in 4.0 ml of 25 mmol dm^{-3} Tris– HCl (pH 7.4) was deaerated by repeated freeze–pump–thaw cycles and the evolved hydrogen was detected by gas chromatography (Shimadzu GC-14B, detector: TCD, column: active carbon).

3. Results and discussion

3.1. Absorption spectra of $TPPSC_nV$

Fig. 2 shows a typical absorption spectra of $TPPSC_3V$ and TPPS. The shape of the absorption spectrum of $TPPSC_3V$ is similar to that of viologen free porphyrin TPPS, indicating no electronic interaction between the porphyrin and the bonded viologen at the ground state.

3.2. Fluorescence spectra of $TPPSC_nV$

The photoexcited singlet states of porphyrin moiety of $TPPSC_nV$ were investigated from

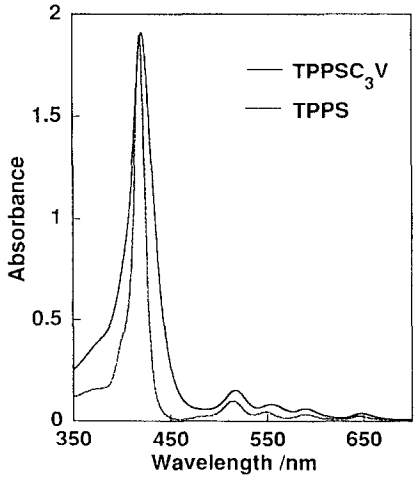


Fig. 2. Absorption spectra of $TPPSC_3V$ and TPPS in water containing 1% Triton X-100.

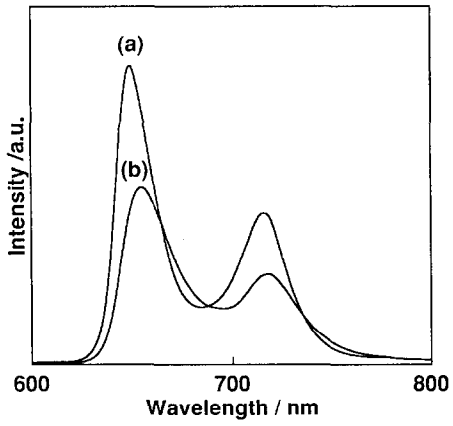


Fig. 3. Fluorescence spectra of TPPS (a) and $TPPSC_3V$ (b) in water containing 1% Triton X-100. The excitation wavelength was 421 nm.

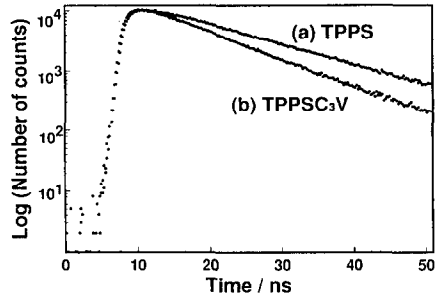


Fig. 4. Fluorescence decay curve of TPPS (a) and $TPPSC_3V$ (b) in water containing 1% Triton X-100. The absorbance at the excitation wavelength (350 nm) was kept at 1.0 for all the sample solutions.

emission spectra. Fig. 3 shows the typical fluorescence spectra of $TPPSC_3V$ and TPPS. Relative fluorescence intensities are summarized in Table 1. These values were obtained by integrating the emission spectra between 600 and 800 nm. The shape of the fluorescence spectrum of $TPPSC_3V$ was the same as that of TPPS, but the fluorescence intensity of $TPPSC_3V$ was lower than that of TPPS, indicating that the photoexcited singlet state of the porphyrin was quenched by the bonded viologen. The quenching of fluorescence of the porphyrin moiety of $TPPSC_nV$ occurred by intramolecular electron transfer between the photoexcited singlet state of the porphyrin and the bonded viologen, because of no electronic interaction between the porphyrin moiety and the bonded viologen at the ground state and no absorption overlap of the porphyrin and the oxidized form of viologen in the visible region.

3.3. Fluorescence lifetimes and electron transfer rate constants

Typical fluorescence decay profiles of $TPPSC_3V$ and TPPS are shown in Fig. 4. The fluorescence decay of TPPS consisted of a single component and the fluorescence lifetime was 12.7 ns. On the other hand, the fluorescence decay of $TPPSC_3V$ also consisted of a single components and fluorescence lifetimes was 9.1 ns. For the other $TPPSC_nV$, the fluorescence decay and the fluorescence lifetimes of $TPPSC_nV$ also consisted of single components as shown in Table 2. The fluorescence lifetime of $TPPSC_nV$ was lower than that of TPPS, indicating that the photoexcited singlet state of the porphyrin was quenched by the bonded viologen.

From the fluorescence lifetimes in Table 2, intramolecular electron transfer rate constants (k_{et}) were estimated by the following equation:

$$k_{et} = 1/\tau_{flu} - 1/\tau_{TPPS}$$

The results are shown in Table 3. The intra-

Table 1
Relative fluorescence intensities of TPPS and $TPPSC_nV$

Compound	I/I_0
TPPS	1
$TPPSC_3V$	0.58
$TPPSC_4V$	0.70
$TPPSC_5V$	0.56
$TPPSC_6V$	0.62

Excitation wavelength: 421 nm.

Table 2
Fluorescence lifetimes of TPPS and $TPPSC_nV$

Compound	τ_{flu} (ns)
TPPS	12.7
$TPPSC_3V$	9.10
$TPPSC_4V$	10.4
$TPPSC_5V$	10.0
$TPPSC_6V$	10.1

Excitation wavelength: 350 nm.

Table 3
Rate constant of intramolecular electron transfer in $TPPSC_nV$

Compound	k_{et} (10^7 s^{-1})
$TPPSC_3V$	3.1
$TPPSC_4V$	1.7
$TPPSC_5V$	1.7
$TPPSC_6V$	1.7

Table 4
Lifetime of photoexcited triplet state of TPPS and $TPPSC_nV$

Compound	τ_{trip} (μs)
TPPS	476
$TPPSC_3V$	403
$TPPSC_4V$	300
$TPPSC_5V$	300
$TPPSC_6V$	429

Excitation wavelength: 532 nm.

molecular electron transfer rate in $TPPSC_3V$ is very rapid compared with other $TPPSC_nV$. In $TPPSC_3V$, the distance between the porphyrin moiety and the bonded viologen is short and the electron transfer from the photoexcited singlet state of the porphyrin to the bonded viologen occurs easily.

3.4. Photoexcited triplet state of $TPPSC_nV$

The electron transfer from the photoexcited triplet state of porphyrin moiety to the bonded viologen was studied by using laser flash photolysis. Fig. 5 shows a typical decay of photoexcited triplet state of porphyrin moiety of $TPPSC_3V$ and TPPS monitored at 470 nm of the maximum absorption of the photoexcited triplet state of the porphyrin moiety. The lifetime of photoexcited triplet state of porphyrin moiety of $TPPSC_nV$ and TPPS are summarized in Table 4. Both the decay of $TPPSC_3V$ and TPPS obeyed first-order kinetics and the lifetime of the photoexcited triplet state was 403 and 476 μs, respectively. In every case of $TPPSC_nV$, the lifetimes of the photoexcited triplet state of the porphyrin moiety were almost the same compared with TPPS, indicating that the photoexcited triplet state of the porphyrin moiety was

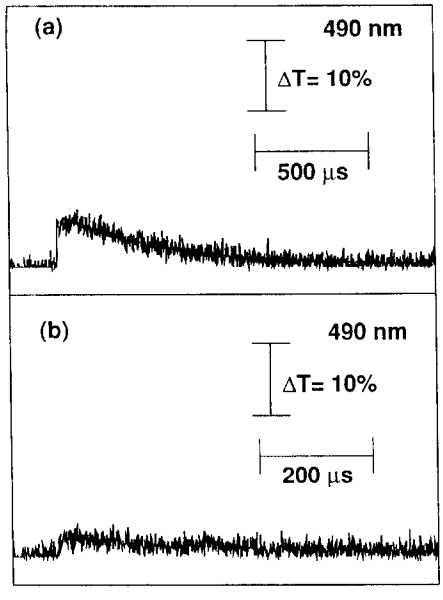


Fig. 5. Decay of the photoexcited triplet state of TPPS (a) and $TPPSC_3V$ (b) monitored at 470 nm. The absorbance at the excitation wavelength (532 nm) was kept to be 0.2 for all the sample solutions. ΔT in this figure is the transmittance of the photoexcited triplet state of the porphyrin moiety.

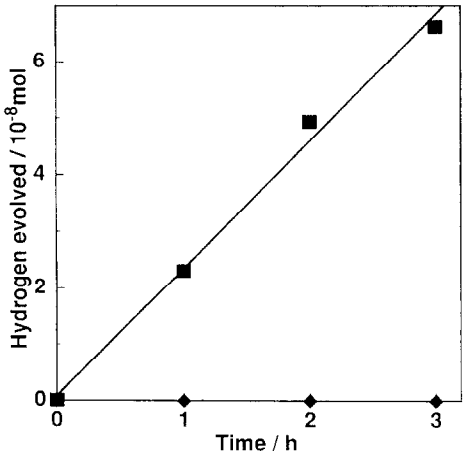


Fig. 6. Time dependence of hydrogen evolution under steady state irradiation. The sample solution consisting of NADPH (2.0×10^{-3} mol dm^{-3}), $TPPSC_6V$ (2.5×10^{-6} mol dm^{-3}) and hydrogenase (0.35 unit) in 4.0 ml of 25 mmol dm^{-3} Tris–HCl (pH 7.4) containing 1% Triton X-100 (■). (◆) NADPH (2.0×10^{-3} mol dm^{-3}), TPPS (2.5×10^{-6} mol dm^{-3}), methylviologen (2.5×10^{-6} mol dm^{-3}) and hydrogenase (0.35 unit) in 4.0 ml of 25 mmol dm^{-3} Tris–HCl (pH 7.4) containing 1% Triton X-100.

not quenched by the bonded viologen. And, no increase of the absorbance at 605 nm, which is the characteristic absorption band of the reduced viologen, was observed. This result shows that the intramolecular electron transfer via the photoexcited triplet state of porphyrin moiety did not occur in $TPPSC_nV$.

3.5. Photoinduced hydrogen evolution with hydrogenase

When the sample solution containing NADPH, $TPPSC_nV$ and hydrogenase was irradiated, the time dependence of hydrogen evolution was observed as shown in Fig. 6. By using $TPPSC_nV$, except for $TPPSC_6V$, no hydrogen evolution was observed. In the case of $TPPSC_6V$ (■), a higher hydrogen evolution rate was observed than that of an individual component system (♦) consisting of TPPS, NADPH, methylviologen and hydrogenase. By using $TPPSC_6V$, the effective photoinduced hydrogen evolution system was accomplished compared with an individual component system. As there was no degradation of the porphyrin moiety by irradiation in $TPPSC_6V$, the photoinduced hydrogen evolution may occur via the photoexcited singlet state of the porphyrin moiety of $TPPSC_6V$.

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