

Hydrogen evolution using photoinduced electron transfer in water soluble bisviologen-linked cationic zinc porphyrin

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Abstract

Water soluble bisviologen-linked cationic zinc porphyrin ($\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$) and butylviologen-linked zinc porphyrin ($\text{ZnP}(\text{C}_4\text{VC}_4)_4$) were synthesized and characterized. The intramolecular electron transfer rate constants from the zinc porphyrin moiety to viologens were measured by fluorescence lifetime and laser flash photolysis. In the case of $\text{ZnP}(\text{C}_4\text{VC}_4)_4$, the photoexcited singlet state and the triplet state of the porphyrin were quenched by the bonded butylviologen. For $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$, on the other hand, only the photoexcited singlet state of the porphyrin was quenched by the bonded viologens. These compounds were applied to photoinduced hydrogen evolution in the system containing nicotinamide adenine dinucleotide phosphate (reduced form NADPH), $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$ or $\text{ZnP}(\text{C}_4\text{VC}_4)_4$ and hydrogenase under steady state irradiation. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Photoinduced hydrogen evolution using four component system consisting of an electron donor, a photosensitizer, an electron carrier and a catalyst have been used extensively for conversion of light energy into chemical energy [1–4]. In this system, charge separation between a photoexcited sensitizer and an electron carrier is one of the important stages. The photosensitizer-acceptor covalently linked systems mainly consist of porphyrin as a photosensitizer and

quinone, pyromellitimide, fullerene or viologen as an electron acceptor [5–29]. Among these compounds, as the porphyrin absorbs visible light and the photoexcited porphyrin can reduce the viologen and the reduction potential of viologen is sufficiently negative to reduce water into hydrogen, viologen-linked porphyrins have the possibility to be the chemical devices to utilize solar energy into chemical energy. To attain the effective photoinduced hydrogen evolution system, some viologen-linked zinc porphyrins have been synthesized [21–31]. 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. The ef-

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fective photoinduced electron transfer and charge separation can occur in these compounds. Among viologen-linked porphyrins, bisviologen-linked zinc porphyrins [26–31], two different viologens are connected covalently, are suitable compounds for establishment of the effective photoinduced hydrogen evolution system, because photoinduced two-step electron transfer of the photoexcited porphyrin to the bonded viologens can occur and the back electron transfer from the reduced viologen to the porphyrin is suppressed.

In this work, water soluble bisviologen-linked cationic zinc porphyrin ($\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$) (two viologens, butylviologen and 1-benzyl-1'-butylviologen, are connected with zinc tetra(4-pyridyl)porphyrin via a methylene chain ($-(\text{CH}_2)_4-$) and butylviologen-linked cationic zinc porphyrin ($\text{ZnP}(\text{C}_4\text{VC}_4)_4$) were synthesized and characterized by UV-Vis absorption spectra and fluorescence emission spectra. The quenching processes of photoexcited singlet and triplet states of the porphyrin moiety of viologen-linked cationic zinc porphyrins by the bonded viologens were measured by fluorescence lifetime and laser flash photolysis. These compounds were applied to photoinduced hydrogen evolution in a system containing nicotinamide adenine dinucleotide phosphate reduced form (NADPH) and hydrogenase under steady state irradiation.

2. Experimental

2.1. Materials

5,10,15,20-Tetra(4-pyridyl)porphyrin (TPyP) was obtained from Aldrich Chemical. Benzyl bromide, 1-bromobutane, 1,4-dibromobutane, ammonium hexafluorophosphate, tetraethylammonium bromide and tetraethylammonium chloride were obtained from Kanto Chemicals. 4,4'-Bypiridinium was obtained from Tokyo Chemical Industry. NADPH was obtained from

Boehringer Mannheim. All the reagents used were analytical or highest grade available.

2.1.1. Synthesis of $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$

The structure of $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$ is shown in Fig. 1. These compounds were prepared by the method reported previously [29–31]. Bisviologen was prepared as follows. 1-Benzyl-1'-(*n*-4-bromobut-1-yl)-4,4'-bipyridinium (C_4V_B) and a 100-fold molar excess of 4,4'-bipyridine were refluxed in acetonitrile (MeCN) to obtain 1-benzyl-1'-[*n*-4-[1-(4,4'-bipyridinium)]but-1-yl]-4,4'-bipyridinium (BpyC_4V_B). BpyC_4V_B was then quaternized with a 100-fold excess of 1,4-dibromobutane in MeCN to obtain bisviologen: 1-Benzyl-1'-[*n*-4-[1-(*n*-4-bromobut-1-yl)-4,4'-bi-

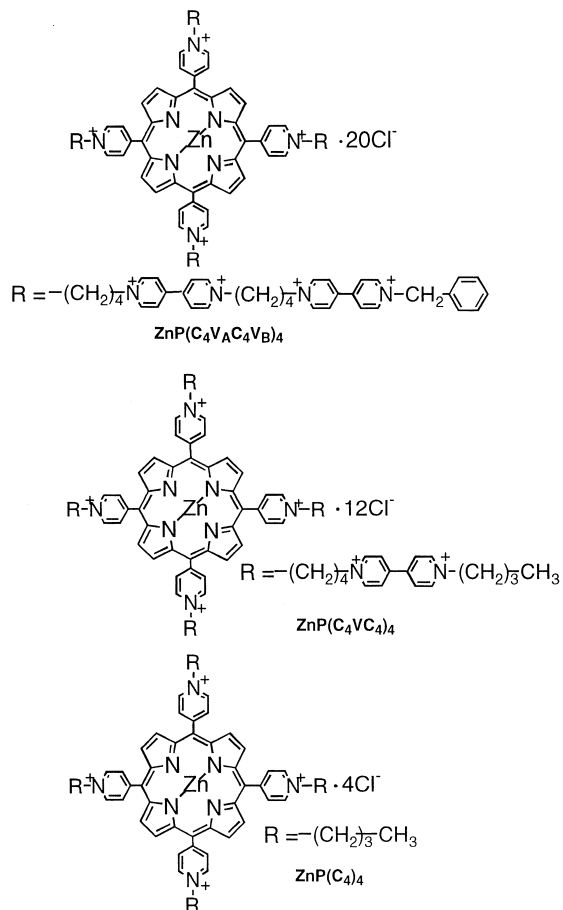


Fig. 1. Structures of $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$, $\text{ZnP}(\text{C}_4\text{VC}_4)_4$ and $\text{ZnP}(\text{C}_4)_4$.

pyridinium)]but-1-yl]-4,4'-bipyridinium ($C_4V_A-C_4V_B$). TPyP and an excess of $C_4V_A C_4V_B$ were refluxed in dimethylformamide (DMF) for 72 h without light. The solvent was removed by evaporation and the product was dissolved in water. The desired product was purified by gel column chromatography (Sephadex LH-20) without light. The molecular structures of the synthesized compounds were characterized by 1H -NMR (Varian GEMINI-200) [29].

Fig. 1 also shows the structures of butylviologen-linked zinc porphyrin ($ZnP(C_4VC_4)_4$) and viologen-free zinc porphyrin ($ZnP(C_4)_4$) as reference compounds. These compounds were prepared by the methods described in the literature [29].

2.2. Spectroscopic measurements

2.2.1. Absorption spectra measurements

The absorption spectra of $ZnP(C_4V_A C_4V_B)_4$, $ZnP(C_4VC_4)_4$ and $ZnP(C_4)_4$ were measured in water using a Hitachi U-2000 spectrometer. The molar absorption coefficients of $ZnP(C_4V_A C_4V_B)_4$, $ZnP(C_4VC_4)_4$ and $ZnP(C_4)_4$ were estimated using the molar absorption coefficient of 5,10,15,20-tetrakis(*N*-methylpyridinium-4-yl) zinc porphyrin ($ZnTMPyP$).

2.2.2. Fluorescence emission spectra measurements

The fluorescence spectra of $ZnP(C_4V_A C_4V_B)_4$, $ZnP(C_4VC_4)_4$ and $ZnP(C_4)_4$ were measured in water at room temperature using a Hitachi F-4000 fluorescence spectrometer. The absorbance at the excitation wavelength was kept constant to be 0.2 for all the sample solutions in these experiments.

2.2.3. Fluorescence lifetime measurements

Fluorescence lifetime measurements were carried out by time-correlated single-photon-counting (Horiba NAES-500 spectrometer) at 25°C. The fluorescence lifetimes were obtained by deconvoluting the fluorescence decay curves

against the profiles of excitation lamp decay at the excitation wavelength.

2.2.4. Laser flash photolysis

Laser flash photolysis was carried out by Nd-YAG laser (Model DCR-3 from Spectra Physics Quanta Ray) with second harmonic light with 532 nm (pulse width ca. 10 ns and a repetition of rate of 10 Hz were used for excitation of the sample solution throughout this study) at room temperature. Xenon arc lamp was used as a monitoring light beam. The light beam, after passing through the sample cell, was collimated into the entrance slit of a monochromator (Model 1410 from Applied Photophysics). The output signal from a photomultiplier (Model 1445 from Applied Photophysics) attached to the slit of the monochromator was displayed on a digitizing oscilloscope (Model 11401 from SONY-Tektronix) and were averaged over 128 flashes.

2.3. Steady state irradiation

The sample solution in a Pyrex cell with a magnetic stirrer was irradiated with 200 W tungsten lamp (Philips KP-8) at 30°C. The light of wavelength less than 390 nm was removed by a Toshiba L-39 filter.

For the photoreduction of the bonded bisviologen or butylviologen in $ZnP(C_4V_A C_4V_B)_4$ or $ZnP(C_4VC_4)_4$, the sample solution consisting of NADPH and $ZnP(C_4V_A C_4V_B)_4$ or $ZnP(C_4VC_4)_4$ was deaerated by repeated freeze–pump–thaw cycles for 5 times. The photoreduction of the bonded viologens was determined by visible spectra at 605 nm. The absorption spectra were measured by a Hitachi U-2000 spectrometer.

For hydrogen evolution with hydrogenase, the sample solution consisting of NADPH, $ZnP(C_4VC_4)_4$ or $ZnP(C_4V_A C_4V_B)_4$ and hydrogenase was deaerated by repeated freeze–pump–thaw cycles for 5 times and argon gas was introduced. The evolved hydrogen was detected by gas chromatography (Shimadzu GC-14B, detector: TCD, column: active carbon).

2.4. Purification of hydrogenase

Hydrogenase from *Desulfovibrio vulgaris* (Miyazaki) was purified according to Yagi's method [32]. The hydrogenase concentration is not known, but it has the ability to release 0.7 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 as release 1.0 μmol of hydrogen per min.

2.5. Electrochemical measurement

Redox potentials were determined by cyclic voltammetry (Hokuto Denko Potentiostat/Galvanostat HA-310, Function Generation HB-111, Reken Denshi X-Y recorder). All measurements were carried out under Ar in solutions 0.2 mol dm^{-3} of KCl and 25 mmol dm^{-3} Tris-HCl (pH = 7.4) at a carbon working electrode. A Pt was used as a counter electrode. All potentials are relative to Ag/AgCl electrode as the reference.

3. Results and discussion

3.1. Absorption spectra of $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$, $\text{ZnP}(\text{C}_4\text{VC}_4)_4$ and $\text{ZnP}(\text{C}_4)_4$

The absorption spectra of $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$, $\text{ZnP}(\text{C}_4\text{VC}_4)_4$ and $\text{ZnP}(\text{C}_4)_4$ are shown in Fig.

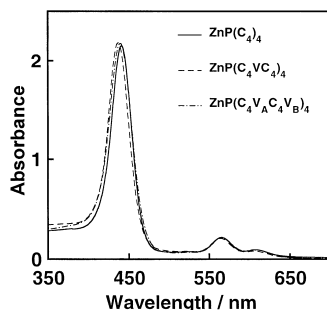


Fig. 2. Absorption spectra of $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$, $\text{ZnP}(\text{C}_4\text{VC}_4)_4$ and $\text{ZnP}(\text{C}_4)_4$.

Table 1

Wavelength of absorption maxima of $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$, $\text{ZnP}(\text{C}_4\text{VC}_4)_4$ and $\text{ZnP}(\text{C}_4)_4$

Compound	Soret band (nm)	Q band (nm)	
$\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$	437 (180000) ^a	565 (17916)	608 (7667)
$\text{ZnP}(\text{C}_4\text{VC}_4)_4$	436 (180000)	564 (17333)	606 (7350)
$\text{ZnP}(\text{C}_4)_4$	438 (180000)	564 (17500)	607 (7700)

^aAbsorption coefficient ($\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$) given in parentheses.

2. The wavelength of absorption maxima and the absorption coefficients of $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$, $\text{ZnP}(\text{C}_4\text{VC}_4)_4$ and $\text{ZnP}(\text{C}_4)_4$ are listed in Table 1. The spectra of $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$ and $\text{ZnP}(\text{C}_4\text{VC}_4)_4$ are similar to that of $\text{ZnP}(\text{C}_4)_4$, indicating no electronic interaction between the zinc porphyrin and the bonded viologens at the ground state.

3.2. Redox potentials of $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$, $\text{ZnP}(\text{C}_4\text{VC}_4)_4$ and $\text{ZnP}(\text{C}_4)_4$

The energy levels of $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$, $\text{ZnP}(\text{C}_4\text{VC}_4)_4$ and $\text{ZnP}(\text{C}_4)_4$ were investigated from the electrochemical measurements. The results are summarized in Table 2. This table shows the energy level of transient states of these compounds relative to the ground state in water. The energies of the first excited singlet state of zinc porphyrin were calculated from the average frequencies of the longest wavelength of absorption maxima and the shortest wavelength of emission maxima. The energies of the charge separated states ($\text{ZnP}^+(\text{C}_4\text{V}_A^-\text{C}_4\text{V}_B)_4$ and $\text{ZnP}^+(\text{C}_4\text{V}_A\text{C}_4\text{V}_B^-)_4$) were estimated from the first oxidation potential of $\text{ZnP}(\text{C}_4)_4$ and the first reduction potential of butylviologen and C_4V_B . Butylviologen was used as the adjacent viologen to zinc porphyrin, and C_4V_B was used as the remote viologen to zinc porphyrin. These values were determined from cyclic voltammetric measurements. No correction from coulombic effect was attempted. As shown in Table 2, the first excited state of the zinc porphyrin lies at 1.99 eV above the ground state, and the $\text{ZnP}^+(\text{C}_4\text{V}_A^-\text{C}_4\text{V}_B)_4$ and $\text{ZnP}^+(\text{C}_4\text{V}_A\text{C}_4\text{V}_B^-)_4$

Table 2

Energies of the first excited singlet state and charge separated state of $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$ and $\text{ZnP}(\text{C}_4\text{VC}_4)_4$

Compound	^1P (eV) ^a	$E(\text{ZnP}^+(\text{C}_4\text{V}^-\text{C}_4)_4)$ (eV) ^b	$E(\text{ZnP}^+(\text{C}_4\text{V}_A^-\text{C}_4\text{V}_B)_4)$ (eV) ^b	$E(\text{ZnP}^+(\text{C}_4\text{V}_A\text{C}_4\text{V}_B^-)_4)$ (eV) ^b
$\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$	1.99		1.65	1.53
$\text{ZnP}(\text{C}_4\text{VC}_4)_4$	1.99	1.65		

^a ^1P is the energy of the first excited singlet state taken as the mean of the frequencies of the longest wavelength of the absorption maxima and the shortest wavelength of the emission maxima.

^bCalculated from the results of cyclic voltammetric measurements.

charge separated states lie at 1.65 and 1.53 eV, respectively. From the energy gap in Table 2, the first excited singlet state of zinc porphyrin can reduce the bonded viologens.

3.3. Fluorescence emission spectra of $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$, $\text{ZnP}(\text{C}_4\text{VC}_4)_4$ and $\text{ZnP}(\text{C}_4)_4$

The photoexcited singlet states of $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$, $\text{ZnP}(\text{C}_4\text{VC}_4)_4$ and $\text{ZnP}(\text{C}_4)_4$ were studied using the fluorescence emission spectra. The fluorescence spectra of $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$, $\text{ZnP}(\text{C}_4\text{VC}_4)_4$ and $\text{ZnP}(\text{C}_4)_4$ are shown in Fig. 3. Relative fluorescence intensities are listed in Table 3. These values were obtained by the integration of the emission spectra of $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$ and $\text{ZnP}(\text{C}_4\text{VC}_4)_4$ relative to $\text{ZnP}(\text{C}_4)_4$. The peak wavelength of the Soret band of $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$ and $\text{ZnP}(\text{C}_4\text{VC}_4)_4$ was used as the excitation wavelength. The absorbance at the excitation wavelength was kept constant to be 0.2 for all the sample solutions in these experiments. The shape of the fluores-

cence spectra of $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$ and $\text{ZnP}(\text{C}_4\text{VC}_4)_4$ are the same as that of $\text{ZnP}(\text{C}_4)_4$. However, the fluorescence intensities of $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$ and $\text{ZnP}(\text{C}_4\text{VC}_4)_4$ are lower than that of $\text{ZnP}(\text{C}_4)_4$. These results indicate that the photoexcited singlet state of porphyrin is quenched by the bonded viologens due to intramolecular electron transfer and no electronic interaction occurs between the porphyrin and the bonded viologens in the photoexcited singlet state. The fluorescence of $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$ is quenched by the bonded viologens more efficiently than that of $\text{ZnP}(\text{C}_4\text{VC}_4)_4$. This result is suggested that effective photoinduced intramolecular electron transfer occurred in $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$.

3.4. Fluorescence lifetimes of $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$, $\text{ZnP}(\text{C}_4\text{VC}_4)_4$ and $\text{ZnP}(\text{C}_4)_4$ and electron transfer rate constants

Typical fluorescence decay profiles of $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$, $\text{ZnP}(\text{C}_4\text{VC}_4)_4$ and $\text{ZnP}(\text{C}_4)_4$ are shown in Fig. 4. The fluorescence decay of $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$ consisted of two components of lifetimes and the lifetimes were 1.4 ns and 4.7 ns, respectively. The decay of butylviologen-linked zinc porphyrins ($\text{ZnP}(\text{C}_4\text{VC}_4)_4$), also

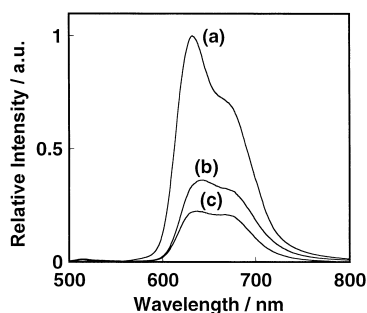


Fig. 3. Fluorescence emission spectra of $\text{ZnP}(\text{C}_4)_4$ (a), $\text{ZnP}(\text{C}_4\text{VC}_4)_4$ (b) and $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$ (c). Excitation wavelength was 438 nm.

Table 3

Relative fluorescence intensities of $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$, $\text{ZnP}(\text{C}_4\text{VC}_4)_4$ and $\text{ZnP}(\text{C}_4)_4$

Compound	I/I_0
$\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$	0.29
$\text{ZnP}(\text{C}_4\text{VC}_4)_4$	0.33
$\text{ZnP}(\text{C}_4)_4$	1

Excitation wavelength was 438 nm.

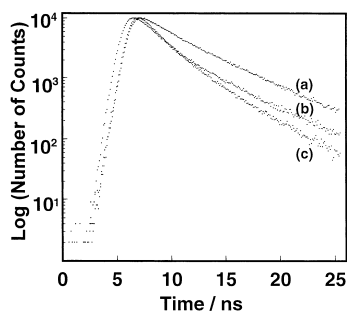


Fig. 4. Typical fluorescence decays of $\text{ZnP}(\text{C}_4\text{V}_\text{A}\text{C}_4\text{V}_\text{B})_4$ (a), $\text{ZnP}(\text{C}_4)_4$ (b) and $\text{ZnP}(\text{C}_4\text{VC}_4)_4$ (c). Excitation wavelength was 350 nm. Monitoring wavelength was more than 540 nm.

consisted of two components. On the other hand, the decay of $\text{ZnP}(\text{C}_4)_4$ consisted of single component and the lifetime was 1.7 ns. Fluorescence lifetimes of these compounds are listed in Table 4. The reason of two components of lifetime was explained as follows. In the case of $\text{ZnP}(\text{C}_4\text{V}_\text{A}\text{C}_4\text{V}_\text{B})_4$, there may be two conformers. A shorter component (τ_s) was attributed to the intramolecular electron transfer reaction (complexed conformer) and a longer component (τ_l) was not attributed to the electron transfer (extended conformer). In quinone-linked porphyrins, two conformers, complexed and extended conformer, are proposed [33]. These results indicate the photoexcited intermolecular electron transfers through the photoexcited singlet state of $\text{ZnP}(\text{C}_4\text{V}_\text{A}\text{C}_4\text{V}_\text{B})_4$. From the fluorescence lifetimes in Table 4, the electron transfer rate (k_{et}) was estimated by the following equation:

$$k_{\text{et}} = 1/\tau_s - 1/\tau_l$$

The results are shown in Table 5. For $\text{ZnP}(\text{C}_4\text{V}_\text{A}\text{C}_4\text{V}_\text{B})_4$, the reaction rate constant of

Table 4
Fluorescence lifetime of $\text{ZnP}(\text{C}_4\text{V}_\text{A}\text{C}_4\text{V}_\text{B})_4$, $\text{ZnP}(\text{C}_4\text{VC}_4)_4$ and $\text{ZnP}(\text{C}_4)_4$

Compound	τ_s / ns (A_1 / %)	τ_l / ns (A_2 / %)
$\text{ZnP}(\text{C}_4\text{V}_\text{A}\text{C}_4\text{V}_\text{B})_4$	1.4 (71.0)	4.7 (19.0)
$\text{ZnP}(\text{C}_4\text{VC}_4)_4$	0.9 (92.0)	3.9 (8.0)
$\text{ZnP}(\text{C}_4)_4$	1.7	

Excitation wavelength was 350 nm.

Table 5

Intramolecular electron transfer rate constant via the photoexcited singlet state, k_{et} , in $\text{ZnP}(\text{C}_4\text{V}_\text{A}\text{C}_4\text{V}_\text{B})_4$ and $\text{ZnP}(\text{C}_4\text{VC}_4)_4$

Compound	k_{et} / s^{-1}
$\text{ZnP}(\text{C}_4\text{V}_\text{A}\text{C}_4\text{V}_\text{B})_4$	5.0×10^8
$\text{ZnP}(\text{C}_4\text{VC}_4)_4$	8.5×10^8

the photoexcited intramolecular electron transfer via the photoexcited singlet state of zinc porphyrins was estimated to be $5.0 \times 10^8 \text{ s}^{-1}$. For $\text{ZnP}(\text{C}_4\text{VC}_4)_4$, on the other hand, the reaction rate constant was $8.5 \times 10^8 \text{ s}^{-1}$, which is similar in the case of $\text{ZnP}(\text{C}_4\text{V}_\text{A}\text{C}_4\text{V}_\text{B})_4$. This result indicates that the effective photoinduced intramolecular electron transfer occurred in these compounds.

3.5. Photoexcited triplet state of $\text{ZnP}(\text{C}_4\text{V}_\text{A}\text{C}_4\text{V}_\text{B})_4$, $\text{ZnP}(\text{C}_4\text{VC}_4)_4$ and $\text{ZnP}(\text{C}_4)_4$

The electron transfer from the photoexcited triplet state of the porphyrin to the bonded viologens was studied using laser flash photolysis. Fig. 5 shows the decay of the transient states of the porphyrin. The decay of the photoexcited triplet state of $\text{ZnP}(\text{C}_4)_4$, as shown in Fig. 5(a), obeyed first-order kinetics, and the lifetime of photoexcited triplet state of $\text{ZnP}(\text{C}_4)_4$ was 1.2 ms. For $\text{ZnP}(\text{C}_4\text{VC}_4)_4$, the decay of the photo-excited triplet state of porphyrin of $\text{ZnP}(\text{C}_4\text{VC}_4)_4$ was shown in Fig. 5(b) and obeyed first-order kinetics. The lifetime of photoexcited triplet state of porphyrin of $\text{ZnP}(\text{C}_4\text{VC}_4)_4$ was 9.5 μs . The lifetime became shorter than that of $\text{ZnP}(\text{C}_4)_4$, indicating that the photoexcited triplet state of the porphyrin of $\text{ZnP}(\text{C}_4\text{VC}_4)_4$ was quenched by the bonded viologens. However, no increase of absorbance at 605 nm due to formation of the reduced viologens was observed. This result indicates that the back electron transfer reaction occurs very rapidly compared with the forward electron transfer reaction. For $\text{ZnP}(\text{C}_4\text{V}_\text{A}\text{C}_4\text{V}_\text{B})_4$, the decay of the photoexcited triplet state of the porphyrin of $\text{ZnP}(\text{C}_4\text{V}_\text{A}\text{C}_4\text{V}_\text{B})_4$ was shown in Fig.

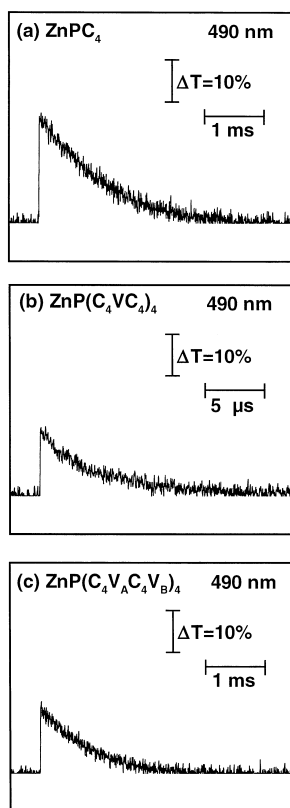


Fig. 5. Typical decays of the photoexcited triplet state of $\text{ZnP}(\text{C}_4)_4$ (a), $\text{ZnP}(\text{C}_4\text{VC}_4)_4$ (b) and $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$ (c) after laser flash photolysis monitored at 490 nm. Excitation wavelength was 532 nm.

5(c) and obeyed first-order kinetics. The lifetime of photoexcited triplet state of the porphyrin of $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$ was 0.89 ms. The lifetime of photoexcited triplet state of $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$, $\text{ZnP}(\text{C}_4\text{VC}_4)_4$ and $\text{ZnP}(\text{C}_4)_4$ are summarized in Table 6. This value is almost the same as that of $\text{ZnP}(\text{C}_4)_4$, indicating no intramolecular electron transfer occurred via the photoexcited triplet state of the porphyrin.

Table 6

Lifetime of the photoexcited triplet state of $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$, $\text{ZnP}(\text{C}_4\text{VC}_4)_4$ and $\text{ZnP}(\text{C}_4)_4$

Compound	$\tau_{\text{trip}} / \mu\text{s}$
$\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$	890
$\text{ZnP}(\text{C}_4\text{VC}_4)_4$	9.5
$\text{ZnP}(\text{C}_4)_4$	1300

Excitation wavelength was 532 nm.

3.6. Photoreduction of the bonded viologens in $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$ and $\text{ZnP}(\text{C}_4\text{VC}_4)_4$

When the sample solution containing NADPH and $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$ or $\text{ZnP}(\text{C}_4\text{VC}_4)_4$ was irradiated, the spectrum of $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$ or $\text{ZnP}(\text{C}_4\text{VC}_4)_4$ changed with time. The time dependence of the change of absorbance at 605 nm is shown in Fig. 6. The change of absorption at 605 nm is due to the reduced viologens and the absorption spectrum intensity with 438 nm is due to the Soret band of the porphyrin decreased by the irradiation. This result indicates that the reduced form of the porphyrin may be formed by the reductive quenching of the photoexcited triplet state of the porphyrin by NADPH and then the bonded viologens are reduced.

3.7. Photoinduced hydrogen evolution with hydrogenase

When the sample solution consisting of NADPH, $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$ or $\text{ZnP}(\text{C}_4\text{VC}_4)_4$ and hydrogenase was irradiated, hydrogen evolution was observed as shown in Fig. 7. $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$ and $\text{ZnP}(\text{C}_4\text{VC}_4)_4$ took part as a photosensitizer and an electron carrier in the same molecule and can be substrate of the hydrogenase. This result indicates that the hydrogen

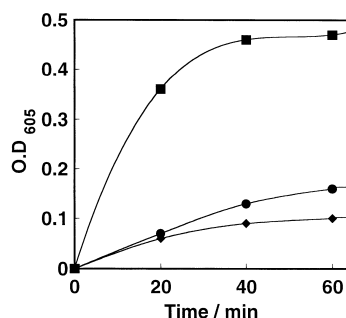


Fig. 6. Time dependence of spectra change of $\text{ZnP}(\text{C}_4\text{VC}_4)_4$ (●) and $\text{ZnP}(\text{C}_4\text{V}_A\text{C}_4\text{V}_B)_4$ (■) under steady state irradiation monitored at 605 nm. $[\text{NADPH}] = 2.0 \text{ mmol dm}^{-3}$, $[\text{viologen-linked zinc porphyrin}] = 2.5 \text{ } \mu\text{mol dm}^{-3}$. ♦: $\text{ZnP}(\text{C}_4)_4$ and butylviologen ($[\text{NADPH}] = 2.0 \text{ mmol dm}^{-3}$, $[\text{ZnP}(\text{C}_4)_4] = 2.5 \text{ } \mu\text{mol dm}^{-3}$ and $[\text{MV}^{2+}] = 10 \text{ mmol dm}^{-3}$).

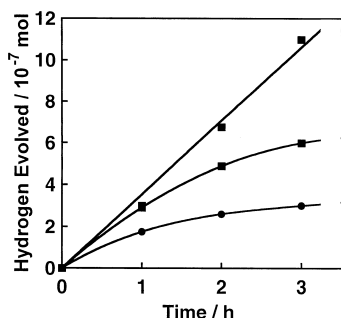


Fig. 7. Time course of photoinduced hydrogen evolved using $\text{ZnP}(\text{C}_4\text{VC}_4)_4$ (●) and $\text{ZnP}(\text{C}_4\text{VA C}_4\text{VB})_4$ (■) under steady state irradiation. $[\text{NADPH}] = 2.0 \text{ mmol dm}^{-3}$, $[\text{viologen-linked zinc porphyrin}] = 2.5 \text{ } \mu\text{mol dm}^{-3}$ and $\text{H}_2\text{ase} = 0.35 \text{ unit}$. ◆: $\text{ZnP}(\text{C}_4)_4$ and butylviologen ($[\text{NADPH}] = 2.0 \text{ mmol dm}^{-3}$, $[\text{ZnP}(\text{C}_4)_4] = 2.5 \text{ } \mu\text{mol dm}^{-3}$, $[\text{MV}^{2+}] = 10 \text{ mmol dm}^{-3}$ and $\text{H}_2\text{ase} = 0.35 \text{ unit}$).

evolution is caused by the electron transfer from the reduced viologens to hydrogenase by the effective electron transfer from photoexcited zinc porphyrin to the bonded viologens and the suppression of back electron transfer from the reduced viologens to zinc porphyrin.

3.8. Mechanism of photoinduced hydrogen evolution

At the first stage of the photoreduction, the photoexcited triplet state of the porphyrin is reductively quenched by the electron donor in the case of cationic porphyrin. When viologen linked cationic zinc porphyrins were irradiated in the presence of NADPH, the absorption spectrum intensity with 438 nm due to Soret band of the porphyrin decreased. From the fluorescence lifetime decay measurements, the electron transfer from the photoexcited singlet state of porphyrin to the bonded viologens was very rapid. These results indicate no photoinduced hydrogen evolution occurs via the photoexcited singlet state of porphyrin. This result indicates that the reduced form of the porphyrin may be formed by the reductive quenching of the photoexcited triplet state of the porphyrin by NADPH. Hydrogen evolution proceeded via the photoexcited triplet state of viologen-linked cationic zinc porphyrins as the same reason of

$\text{ZnP}(\text{C}_n\text{V})_4$ as described in previous report [34]. The proposed mechanism is as follows.

In the first step, the photoexcited singlet state of $\text{ZnP}(\text{C}_4\text{VA C}_4\text{VB})_4$ is formed by the irradiation. Then the photoexcited triplet state of $\text{ZnP}(\text{C}_4\text{VA C}_4\text{VB})_4$ is formed by intercrossing reaction in the second step. In the third, the porphyrin moiety is reduced by quenching of photoexcited triplet state with NADPH. In the fourth, the electron transfer from reduced porphyrin moiety to the bonded butylviologen occurred and butylviologen was reduced. Finally, the electron transfer from the reduced butylviologen to benzylviologen occurred and hydrogen evolved by electron transfer from reduced benzylviologen to hydrogenase.

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