  Bull. Chem. Soc. Jpn., 60, 1243—1247 (1987)

Photoredox Properties of Viologen Linked Porphyrins

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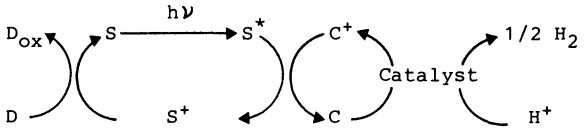
(Received September 13, 1986)

Viologen linked water-soluble porphyrins ($ZnP(C_nV)_4$) with different methylene chain lengths (n=2—5) between porphyrin and viologen were synthesized. These compounds were applied to photoinduced hydrogen evolution in a system containing NADPH-$ZnP(C_nV)_4$-hydrogenase under steady state irradiation.

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]



As photosensitizers metallo-porphyrins have been widely used and methyl viologen has been a popular electron carrier. In this work, viologen linked water-soluble zinc porphyrins were synthesized which may act as both a photosensitizer and an electron carrier in the same molecule; these compounds were applied to photoinduced hydrogen evolution.

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. These compounds were synthesized as follows. The starting material, zinc 5,10,15,20-tetra(4-pyridyl)porphyrin (Zn-TMPyP), was synthesized

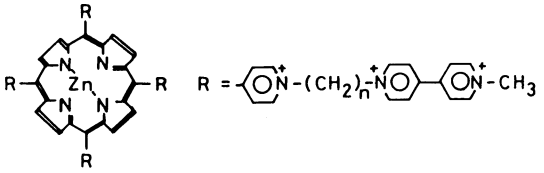


Fig. 1. Structure of viologen linked porphyrins, $ZnP(C_nV)_4$.

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

Hydrogenase was obtained from Desulfovibrio vulgaris (Miyazaki type, IAM 12604) and purified by Yagi's method.[6] Its concentration is not known, but 1.48×10^{-6} mol of hydrogen was generated by the following reaction system: hydrogenase (0.5 cm^3)-methyl viologen (4.1×10^{-5} mol dm^{-3})-$Na_2S_2O_4$ (5.7×10^{-3} 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.

Electronic and fluorescence spectra were recorded on Shimadzu MPS-5000 and Hitachi model 850 instruments, respectively.

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 per 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.

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 $ZnP(C_nV)_4$ with n=2—5 under steady state irradiation at 30 °C. A sample solution containing nicotinamide-adenine dinucleotide phosphate (reduced form, NADPH), ZnP-

Table 1. Peak Wavelength of Various Porphyrins

	Soret band/nm		Q band/nm		
ZnTMPyP	438	565	607		
H_2TMPyP	423	516	552	581	627
$ZnP(C_2)_4$*	440	523	537	647	
$ZnP(C_2V)_4$	445	573	625		
$ZnP(C_3)_4$*	433	523	573	647	
$ZnP(C_3V)_4$	442	572			
$ZnP(C_4)_4$*	423	522	563	590	647
$ZnP(C_4V)_4$	436	571			
$ZnP(C_5)_4$*	428	523	593	645	
$ZnP(C_5V)_4$	432	568			

* $ZnP(C_n)_4$ (n=2—5): 5,10,15,20-tetrakis[1-(2-bromoalkyl)pyridinio]porphyrin tetrabromide.

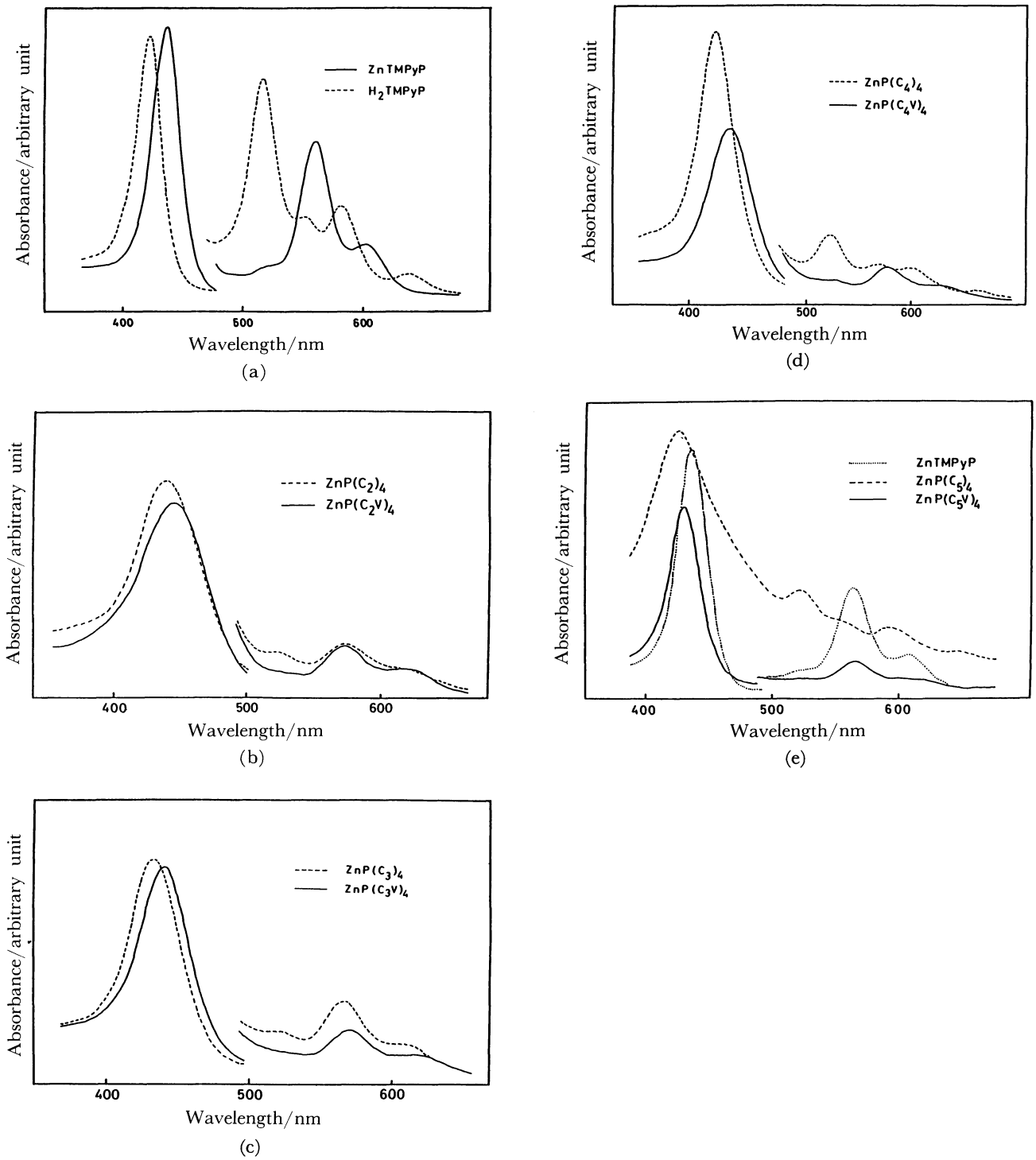


Fig. 2. Absorption spectra of various porphyrins dissolved in water.
(a): ZnTMPyP and H_2TMPyP, (b): ZnP(C_2V)$_4$ and ZnP(C_2)$_4$, (c): ZnP(C_3V)$_4$ and ZnP(C_3)$_4$, (d): ZnP-(C_4V)$_4$ and ZnP(C_4)$_4$, (e): ZnP(C_5V)$_4$ and ZnP(C_5)$_4$.

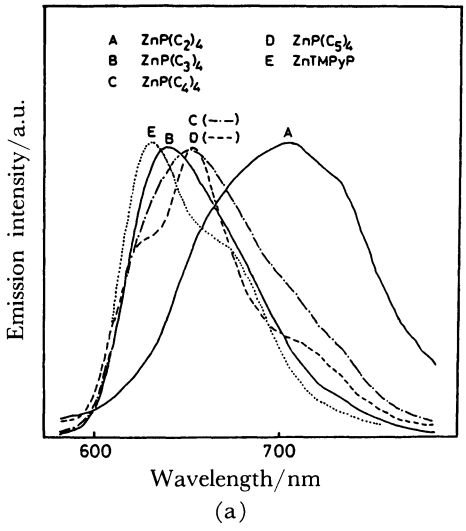
(C_nV)$_4$, and hydrogenase was deaerated by repeated freeze-pump-thaw cycles.

Results and Discussion

Electronic Spectra of ZnP(C_n)$_4$ and ZnP(C_nV)$_4$. The electronic spectra of the compounds are shown in Fig. 2 (a)—(e) and Table 1. Though ZnP(C_n)$_4$ contain metal ions, the Q band spectra of ZnP(C_n)$_4$ (n=2—5) (shown by dotted lines in Figs. 2 (b)—(e)) are similar to the absorption spectrum of metal-free H_2TMPyP (shown in Fig. 2 (a)). The electrons in the porphyrin ring may be significantly influenced by an interaction between the central metal ion and halogen ions connected at the end of the methylene chain.

Table 2. Relative Emission Intensity of $ZnP(C_n)_4$ and $ZnP(C_nV)_4$

	ZnTMPyP	$ZnP(C_2)_4$	$ZnP(C_3)_4$	$ZnP(C_4)_4$	$ZnP(C_5)_4$
Relative intensity	100	32	79	49	44
		$ZnP(C_2V)_4$	$ZnP(C_3V)_4$	$ZnP(C_4V)_4$	$ZnP(C_5V)_4$
Relative intensity		25	35	32	44



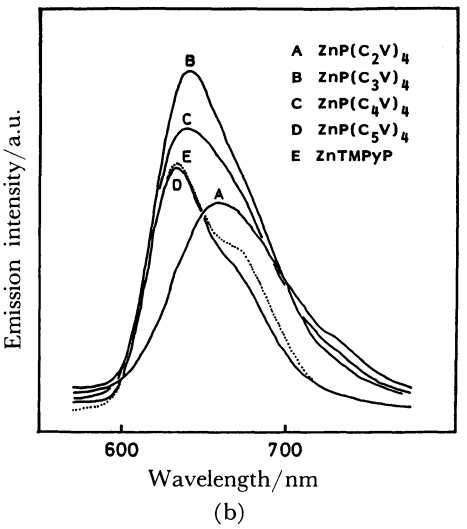


Fig. 3. Fluorescence spectra of various porphyrins. (a): $ZnP(C_n)_4$, (b): $ZnP(C_nV)_4$.

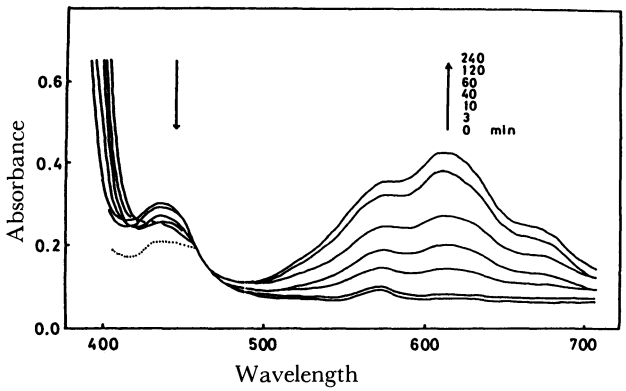


Fig. 4. Absorption spectrum of $ZnP(C_5V)_4$-NADPH system. Sample solution containing $ZnP(C_5V)_4$ (2.0×10^{-6} mol dm^{-3}) and NADPH (1.0×10^{-3} mol dm^{-3}) was irradiated at 30 °C.

The electronic spectra of $ZnP(C_nV)_4$ (shown by solid lines in Figs. 2 (b)—(e)) are similar to the spectrum of ZnTMPyP (Fig. 2 (a)) rather than that of $ZnP(C_n)_4$, showing a smaller interaction between the central metal ion and the viologen connected at the end of the methylene chain. However, there are some interactions between the porphyrin ring and viologen as the absorption spectra of $ZnP(C_nV)_4$ in the Soret region shifts to longer wavelengths.

Fluorescence Spectra $ZnP(C_n)_4$ and $ZnP(C_nV)_4$. The fluorescence spectra of $ZnP(C_n)_4$ and $ZnP(C_nV)_4$ are shown in Figs. 3 (a) and (b). The fluorescence spectra of $ZnP(C_2)_4$ and $ZnP(C_2V)_4$ are broad and the peak wavelengths are at longer wavelengths compared with the other porphyrins shown in Fig. 3. The relative fluorescence intensity obtained by integrating the spectra are shown in Table 2. The relative fluorescence intensity of $ZnP(C_nV)_4$ (n=2—4) are low compared with $ZnP(C_n)_4$. The excited singlet state of the porphyrin with viologen may be quenched by viologen linked with a porphyrin ring.

Photoreduction of Viologen. When a sample solution containing viologen linked porphyrin and NADPH was irradiated, the growth of the reduced form of viologen was observed. Figure 4 shows an example when $ZnP(C_5V)_4$ was used. Since the absorption coefficient of $ZnP(C_5V)_4$ was not known, its concentration was determined by using the absorption coefficient of ZnTMPyP. 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, an absorption spectrum with λ_{max}=600 nm disappeared, confirming the formation of reduced viologen. The absorption spectrum intensity with λ_{max}=460 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, 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.

Photoinduced Hydrogen Evolution. Upon irradia-

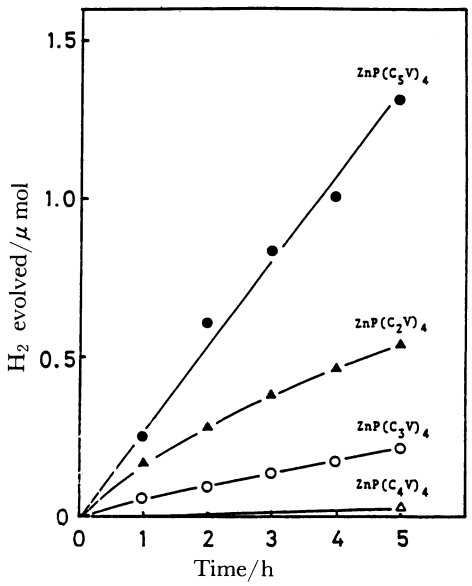


Fig. 5. Time dependence of amount of hydrogen evolved. Sample solution containing $ZnP(C_nV)_4$ (2.0×10^{-6} mol dm^{-3}), NADPH (1.0×10^{-3} mol dm^{-3}) and hydrogenase (0.5 cm^3) was irradiated at 30°C.

tion of the sample solution, hydrogen was generated; the time dependence of the amount of hydrogen evolved is shown in Fig. 5. The concentrations of $ZnP(C_nV)_4$ (n=2—5) were determined by using the absorption coefficient of ZnTMPyP. Thus, it is apparent that every compound, $ZnP(C_nV)_4$ (n=2—5), participates as both a photosensitizer and as an electron carrier in the same molecule. Since the hydrogen evolved almost linearly with irradiation time, an 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 Fig. 5, the hydrogen evolution rate strongly depends on the methylene chain length (n) of $ZnP(C_nV)_4$. Within a certain range (n=2—4), the hydrogen evolution rate decreases with increasing chain length. In the case of $ZnP(C_5V)_4$, however, a higher hydrogen evolution rate was observed. The turnover number of hydrogen evolved against $ZnP(C_5V)_4$ was 86 per hour. The activity was at most two-times more active than that of an individual component system containing ZnTMPyP, methyl viologen, 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 $ZnP(C_nV)_4$ monitored at 500 nm after a laser flash. From these figures the lifetimes of the triplet state of these compounds were obtained (Table 3). There were no remarkable difference between $ZnP(C_n)_4$ and $ZnP(C_nV)_4$, indicating that

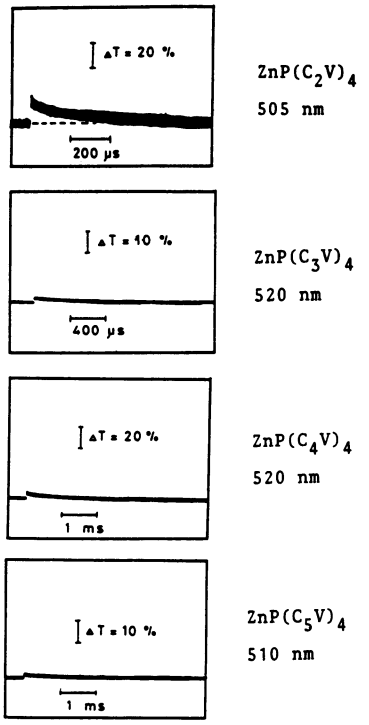


Fig. 6. Typical oscillograms for T-T absorption of $ZnP(C_nV)_4$.

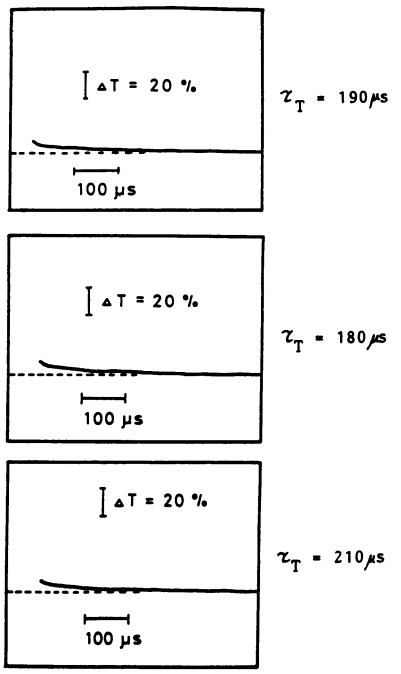


Fig. 7. Typical oscillograms for T-T absorption of $ZnP(C_2V)_4$. laser power (a): 80 mJ pulse^{-1}, (b): 60 mJ pulse^{-1}, (c): 50 mJ pulse^{-1}.

Table 3. Lifetimes of Excited Triplet State of $ZnP(C_n)_4$ and $ZnP(C_nV)_4$

	τ_T/μs		τ_T/μs
$ZnP(C_2)_4$	140	$ZnP(C_2V)_4$	190
$ZnP(C_3)_4$	530	$ZnP(C_3V)_4$	510
$ZnP(C_4)_4$	230	$ZnP(C_4V)_4$	640
$ZnP(C_5)_4$	330	$ZnP(C_5V)_4$	470

the triplet states of these compounds are not quenched by the linked viologen.

Figure 7 shows typical oscillograms for T-T absorption of $ZnP(C_2V)_4$ with different laser powers. Though the intensity of the T-T absorption depends on the laser power, 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.

From the above results the following reaction mechanism is proposed:

$$^3P^*\text{-}V + D \longrightarrow P^-\text{-}V + D^+,$$

and

$$P^-\text{-}V \longrightarrow P\text{-}V^-.$$

During the first stage of the reaction, the photoexcited triplet state ($^3P^*$-V) is reductively quenched by NADPH and a reduced form of porphyrin (P^--V) 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 the reductive quenching by NADPH is predominant.

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