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Synthesis and characterization of water soluble viologen linked zinc porphyrins

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Abstract

A series of water soluble viologen linked zinc porphyrins ($ZnP(C_nV)_4$, $n = 3$–6) were synthesized. Four viologens are connected with the zinc porphyrin via a methylene chain ($-(CH_2)_n-$: $n = 3$–6) in these compounds. The photochemical and electrochemical properties of $ZnP(C_nV)_4$ were measured and the quenching process of the photoexcited porphyrin by the binding viologen was discussed.

Keywords: Viologen; Viologen linked zinc porphyrins; Photosynthesis

1. Introduction

To understand the primary process in photosynthesis and to establish the systems for solar energy conversion and storage, photoinduced intramolecular electron transfer in donor–photosensitizer–acceptor systems have been studied extensively [1–8]. In mimicking the photoreaction center, the donor–photosensitizer–acceptor covalently linked molecules mainly consisting of triethylamine as a donor, porphyrin as a photosensitizer and quinone, pyromellitimide or viologen as an acceptor, were synthesized. In these compounds, photoinduced intramolecular electron transfer between porphyrin and the acceptor takes place via the photoexcited singlet state of the porphyrin site. Kinetic studies of the charge separation and the charge recombination steps have been studied by using laser flash photolysis. These steps depend on the redox potentials of the donor and the acceptor, the distance between the donor and acceptor, and the nature of the linkage [9–17]. Among these donor–photosensitizer–acceptor compounds, viologen linked porphyrins are potentially good chemical devices to change the solar energy into chemical energy, because the porphyrins have a maximum absorption at visible region, the photoexcited porphyrin can reduce the viologen and the reduction potential of viologen is sufficiently negative to reduce water into hydrogen.

Four component systems, consisting of an electron donor, a photosensitizer, an electron carrier and a catalyst, have been widely used in photoinduced hydrogen evolution systems for converting solar energy to chemical energy [18–20]. In these systems, porphyrins and viologens are often used as a photosensitizer and an electron carrier, respectively. As viologen linked porphyrins serve as a photosensitizer and an electron carrier in the same molecule and the photoexcited singlet state of the porphyrin reduces the binding viologen efficiently, these molecules are attractive to develop the above four component systems. To accomplish simpler redox systems for solar energy conversion, viologen linked porphyrins with longer lifetimes of the charge separated states are desired. Earlier, we reported the preliminary study of the photoinduced hydrogen evolution system using synthetic water soluble four viologen linked zinc-porphyrins [21]; in this article we hope to describe the photochemical and electrochemical properties of a series of water soluble viologen linked zinc porphyrins.

2. Experimental details

2.1. Synthesis

All reagents were of analytical or of the highest grade available. The synthesis route of viologen linked zinc porphyrins are shown in Scheme 1, and the structures are shown in Fig. 1.

2.1.1. Zinc tetrakis-(4-pyridyl)-porphyrin (ZnTPyP)

ZnTPyP was synthesized from tetrakis-(4-pyridyl)-porphyrin (TPyP) as a starting material according to the literature [21]. TPyP was obtained from Aldrich Chemical Co.

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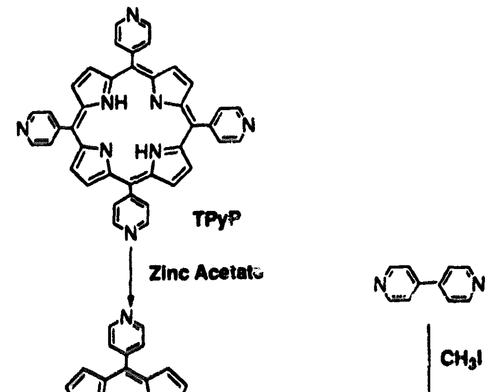


Scheme 1.

TPyP (1.2×10^{-3} mol) and zinc acetate (1.6×10^{-2} mol) were dissolved in 200 ml of acetic acid and heated to reflux at 80 °C for 3 h. The solvent was removed by evaporation. A purple precipitate was collected and washed with water and then with chloroform and dried under a vacuum overnight to yield the desired product.

2.1.2. *1-Methyl-4,4'-bipyridinium (VCH$_3$)*

4,4'-Bipyridine (0.16 mol) and methyl iodide (0.18 mol) were dissolved in 400 ml of acetone and stirred at room temperature for 24 h. A yellow precipitate was collected by suction filtration and washed with acetone. The desired product was recrystallized from ethanol (EtOH) and water and dried under vacuum overnight. Proton nuclear magnetic resonance (^{1}H-NMR) in D$_2$O: δ (ppm) 4.3–4.5 (s, 3H), 7.7–7.8 (m, 2H), 8.2–8.3 (m, 2H), 8.5–8.6 (m, 2H), 8.8–8.9 (m, 2H).

2.1.3. *1-Bromoalkyl-1'-methyl-4,4'-bipyridinium (BrC$_n$VCH$_3$)*

VCH$_3$I$^-$ (1.0 g, 3.4×10^{-4} mol) was dissolved in 150 ml of acetonitrile (MeCN), treated with excess α,ω-dibromoalkane (BrC$_n$Br: n = 3–6) (0.13 mol) and heated to reflux for 24 h. A yellow precipitate was collected by suction filtration, washed with MeCN and dried under a vacuum overnight. The product was recrystallized from EtOH and then dissolved in water and a solution of ammonium hexafluorophosphate (NH$_4$PF$_6$) was added to replace the counter-anion with PF$_6^-$. The white PF$_6^-$ salt was collected by suction filtration, washed with water and dried under a vacuum overnight. The PF$_6^-$ salt dissolved in MeCN and tetraethylammonium chloride ((C$_2$H$_5$)$_4$NCl) was added to replace the counter-anion with Cl$^-$. The white Cl$^-$ salt was collected by suction filtration, washed with water and dried under a vacuum overnight. ^{1}H-NMR in D$_2$O: δ (ppm) BrC$_3$VCH$_3$: 2.55 (quint, 2H), 3.45 (t, 2H), 4.3–4.5 (s, 3H), 4.90 (t, 2H), 8.4–8.6 (m, 2H), 8.9–9.0 (m, 2H), 9.0–9.1 (m, 2H). BrC$_4$VCH$_3$: 1.86 (quint, 2H), 2.14 (quint, 2H), 3.45 (t, 2H), 4.3–4.5 (s, 3H), 4.65 (t, 2H), 8.4–8.6 (m, 2H), 8.9–9.0 (m, 2H), 9.0–9.1 (m, 2H). BrC$_5$VCH$_3$: 1.43 (quint, 2H), 1.82 (quint, 2H), 2.01 (quint, 2H), 3.60 (t, 2H), 4.3–4.5 (s, 3H), 4.64 (t, 2H), 8.4–8.6 (m, 2H), 8.9–9.0 (m, 2H), 9.0–9.1 (m, 2H). BrC$_6$VCH$_3$: 1.2–1.4 (quint, 4H), 1.64 (quint, 2H), 1.95 (quint, 2H), 3.11 (t, 2H), 4.3–4.5 (s, 3H), 4.60 (t, 2H), 8.4–8.6 (m, 2H), 8.9–9.0 (m, 2H), 9.0–9.1 (m, 2H).

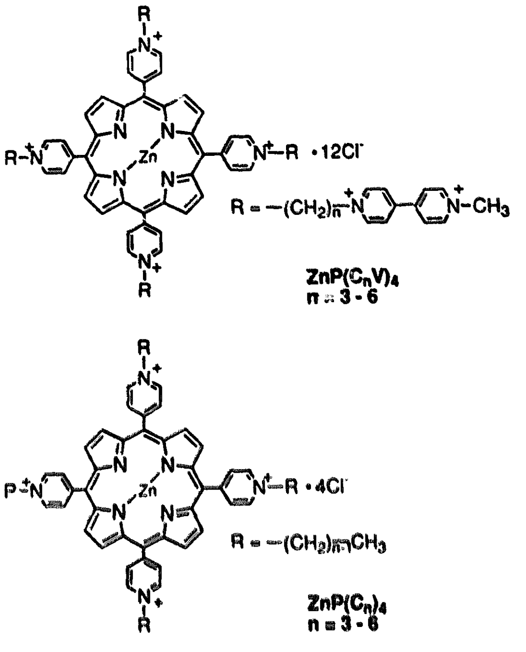


Fig. 1. Structures of viologen linked porphyrin (ZnP(C$_n$V)$_4$.

2.1.4. *Viologen-linked zinc porphyrin (ZnP(C$_n$V)$_4$)*

ZnTPyP (2.9×10^{-4} mol) and BrC$_n$VCH$_3$2Cl$^-$ (5.5×10^{-3} mol) were dissolved in 150 ml of dimethylformamide (DMF) and heated to reflux for 48 h without light. The solvent was removed using a vacuum pump and dissolved in water. The desired product was obtained by column chromatography (Sephadex LH-20 column, eluted with water). ^{1}H NMR in dimethylsulfoxide-d_6 (DMSO-d_6): δ (ppm) ZnP(C$_3$V)$_4$: 3.02 (quint, 8H), 4.4–4.6 (s, 12H), 4.85 (t, 8H), 5.10 (t, 8H), 8.7–9.2 (m, 36H), 9.3–9.6 (m, 20H).

$ZnP(C_4V)_4$: 2.01 (quint, 16H), 4.16 (t, 8H), 4.4–4.6 (s, 12H), 4.74 (t, 8H), 8.7–9.2 (m, 36H), 9.3–9.6 (m, 20H). $ZnP(C_5V)_4$: 1.71 (quint, 8H), 2.07 (quint, 8H), 2.26 (quint, 8H), 4.4–4.6 (s, 12H), 4.70 (t, 8H), 4.83 (t, 8H), 8.7–9.2 (m, 36H), 9.3–9.6 (m, 20H). $ZnP(C_6V)_4$: 1.45 (quint, 16H), 1.80 (quint, 8H), 2.01 (quint, 8H), 4.4–4.6 (s, 12H), 4.70 (t, 16H), 8.7–9.2 (m, 36H), 9.3–9.6 (m, 20H).

2.1.5. *Viologen-free zinc porphyrin ($ZnP(C_n)_4$)*

ZnTPyP (0.2 g, 2.9×10^{-4} mol) and α-bromoalkane (BrC_n: $n = 3–6$) (0.20 mol) were dissolved in 150 ml of dimethylformamide (DMF) and heated to reflux for 48 h without light. The solvent was removed using a vacuum pump and dissolved in water. The desired product was obtained by column chromatography (Sephadex LH-20 column, eluted with water). ^{1}H-NMR in DMSO-d_6: δ (ppm) $ZnP(C_3)_4$: 1.25 (s, 12H), 2.34 (quint, 8H), 4.95 (t, 8H), 9.0–9.3 (m, 16H), 9.5–9.7 (m, 8H). $ZnP(C_4)_4$: 1.25 (s, 12H), 1.74 (quint, 8H), 2.28 (quint, 8H), 4.95 (t, 8H), 9.0–9.3 (m, 16H), 9.5–9.7 (m, 8H). $ZnP(C_5)_4$: 1.05 (s, 12H), 1.43–1.70 (quint, 16H), 2.30 (quint, 8H), 4.95 (t, 8H), 8.9–9.2 (m, 16H), 9.5–9.7 (m, 8H). $ZnP(C_6)_4$: 1.00 (s, 12H), 1.45 (quint, 8H), 1.66 (quint, 8H), 2.29 (quint, 8H), 4.95 (t, 8H), 8.9–9.2 (m, 16H), 9.5–9.7 (m, 8H).

2.2. *Spectroscopic measurements*

For ^{1}H-NMR measurement, the PF_6^- salt of $ZnP(C_nV)_4$ were used. In the case of photochemical and electrochemical experiments, the Cl^- salt of $ZnP(C_nV)_4$ were used.

^{1}H-NMR spectra were recorded on a Varian GEMINI-200. The chemical shifts were referenced to the solvent peak calibrated against tetramethylsilane (TMS).

The absorption spectra of viologen-linked porphyrin ($ZnP(C_nV)_4$) and viologen-free porphyrin ($ZnP(C_n)_4$) were measured in water using a Hitachi U-2000 spectrometer. The absorption coefficients of $ZnP(C_nV)_4$ and $ZnP(C_n)_4$ were estimated using the absorption coefficient of zinc-5, 10, 15, 20-tetrakis(N-methylpyridinium-4yl) porphyrin (ZnTMPyP).

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

2.3. *Electrochemical measurements*

The redox potentials were determined by cyclic voltammetry (Hokuto Denko Potentiostat/Galvanostat HA-301, Function Generation HB-111, Riken Densho X-Y recorder). All measurements were carried out under Ar in solutions containing 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 the Ag/AgCl electrode used as the reference.

3. Results and discussion

3.1. *Preparation of $ZnP(C_nV)_4$*

The preparation route of $ZnP(C_nV)_4$ is shown in Scheme 1. The chemical structures of the synthesized compounds

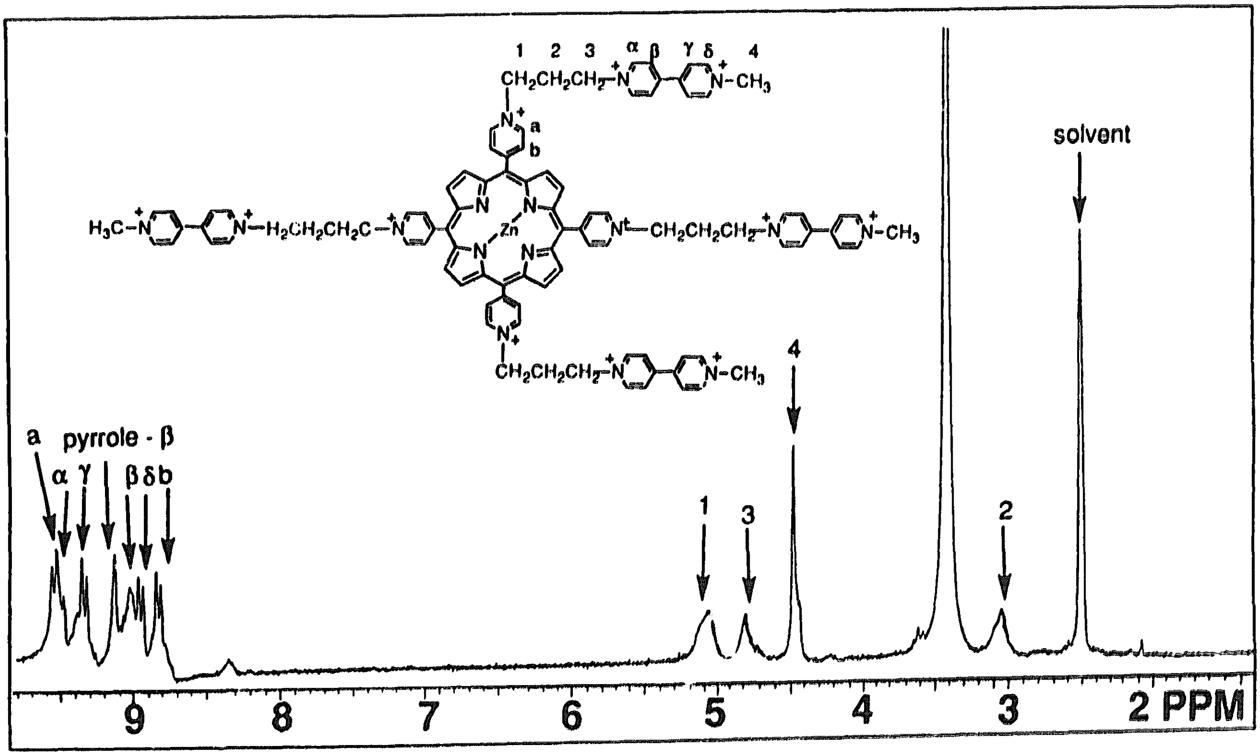


Fig. 2. ^{1}H-NMR spectrum (200 MHz) of $ZnP(C_3V)_4$ in DMSO-d_6. The signal assignment is shown in the figure.

were characterized by ^{1}H-NMR. The ^{1}H-NMR spectrum of $ZnP(C_3V)_4$ is shown in Fig. 2. The signal assignment is also indicated in the figure, as an example.

3.2. Absorption spectra of $ZnP(C_nV)_4$

The wavelength of the absorption maxima and the absorption coefficients of $ZnP(C_nV)_4$ and $ZnP(C_n)_4$ are listed in Table 1. As an example, the absorption spectrum of $ZnP(C_3V)_4$ is shown in Fig. 3. The spectrum of $ZnP(C_nV)_4$ is similar to that of $ZnP(C_n)_4$ or a mixture of $ZnP(C_n)_4$ and C_nVCH_3, indicating no electronic interaction between the porphyrin site and the binding viologen in the ground state.

3.3. Electrochemical property of $ZnP(C_nV)_4$

The energy levels of $ZnP(C_nV)_4$ were studied by electrochemical measurements. The results are listed in Table 2. The energies of the first excited singlet states of the $ZnP(C_nV)_4$ were calculated from the average values of the frequencies with the longest wavelength for absorption maxima and the shortest wavelength for fluorescence emission maxima. The energies of the charge separated states of ZnP^+–V^- were estimated from the first oxidation potential of $ZnP(C_n)_4$ and the first reduction potential of C_nVCH_3 by using cyclic voltammetric measurements. Each energy level is listed in Table 3. No correction for coulombic effects was attempted.

Table 1
Wavelength of absorption maxima of $ZnP(C_nV)_4$ and $ZnP(C_n)_4$

$ZnP(C_3V)_4$	438 (180000) [a]	566 (17500)	610 (7700)
$ZnP(C_3)_4$	437 (180000)	564 (16700)	608 (7900)
$ZnP(C_4V)_4$	438 (180000)	564 (18300)	608 (7800)
$ZnP(C_4)_4$	438 (180000)	564 (17500)	607 (7700)
$ZnP(C_5V)_4$	438 (180000)	565 (16700)	607 (6300)
$ZnP(C_5)_4$	438 (180000)	564 (15900)	606 (5500)
$ZnP(C_6V)_4$	438 (180000)	566 (16700)	607 (6300)
$ZnP(C_6)_4$	436 (180000)	564 (16700)	607 (6800)

[a] Absorption coefficient (M^{-1} cm^{-1}) given in parentheses.

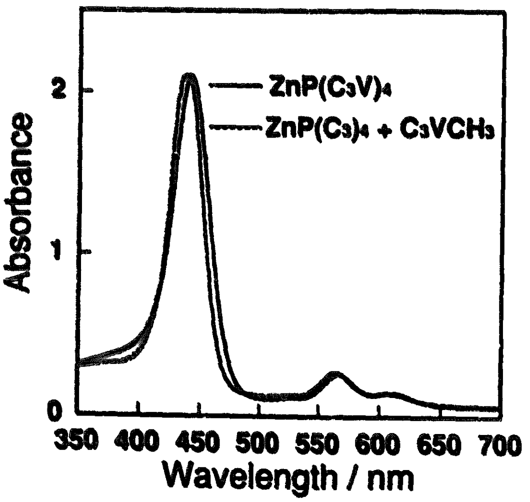


Fig. 3. Absorption spectra of $ZnP(C_3V)_4$ and $ZnP(C_3)_4$ in water.

Table 2
The first excited singlet state energies of $ZnP(C_n)_4$ and redox potentials (vs. Ag/AgCl) for $ZnP(C_n)_4$ and C_nVCH_3

Compound	^1P (eV) [a]	E_0^1 (V) [b]	E_r^1 (V) [c]
$ZnP(C_3)_4$	1.99	0.958	
$ZnP(C_4)_4$	1.99	0.958	
$ZnP(C_5)_4$	1.99	0.958	
$ZnP(C_6)_4$	1.99	0.058	
C_3VCH_3			−0.662
C_4VCH_3			−0.673
C_5VCH_3			−0.682
C_6VCH_3			−0.691

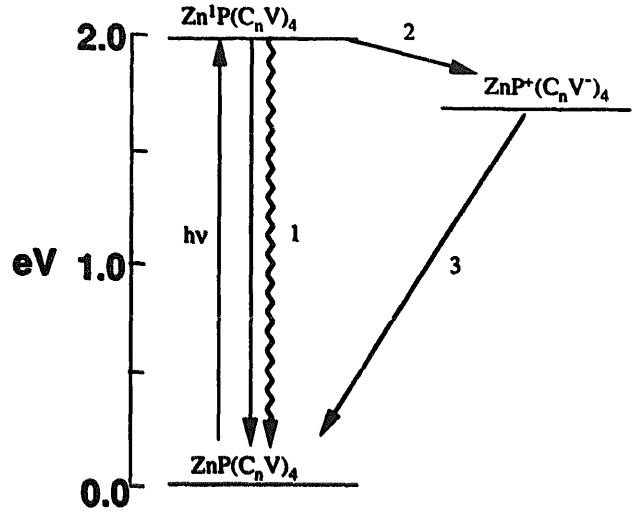
[a] ^1P is the energy of the first excited singlet state taken as the average value of the frequencies of the longest wavelength of the absorption maxima and the shortest wavelength of the fluorescence emission maxima.
[b] E_0^1 is the first oxidation potential.
[c] E_r^1 is the first reduction potential.

Table 3
Energies of the first excited singlet state and charge separated state

Compound	^1P (eV) [a]	$E(P^+V^-)$ (eV) [b]
$ZnP(C_3V)_4$	1.99	1.62
$ZnP(C_4V)_4$	1.99	1.63
$ZnP(C_5V)_4$	1.99	1.64
$ZnP(C_6V)_4$	1.99	1.65

[a] ^1P is the energy of the first excited singlet state taken as the average value of the frequencies of the longest wavelength of the absorption maxima and the shortest wavelength of the fluorescence emission maxima.
[b] Calculated from the value of electrochemical measurement (see Table 3).

Scheme 2 shows the energy levels for the transient states of $ZnP(C_nV)_4$ from Table 2. The first excited singlet state for each $ZnP(C_nV)_4$ lies at 1.99 eV above the ground state and the charge separated state ZnP^+–V^- lies at 1.62–1.65 eV, respectively. The first excited singlet state of the porphyrin site can reduce the binding viologen from the energy gap obtained from Table 2. The electron transfer pathways are considered as shown in Scheme 2. Steps 1, 2 and 3 represent the non-radiative and the radiative process, the electron transfer process and the charge recombination process, respectively. The energy difference between the first excited singlet state of porphyrin site and the charge separated state is 0.34–0.37 eV.



Scheme 2.

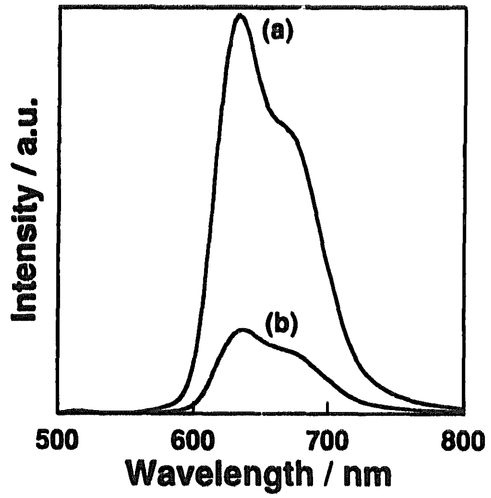


Fig. 4. Fluorescence spectra of (a) $ZnP(C_3)_4$ and (b) $ZnP(C_3V)_4$ in water.

3.4. Fluorescence spectra of $ZnP(C_nV)_4$

The photoexcited singlet state of $ZnP(C_nV)_4$ were studied using the fluorescence emission spectra. As an example, the fluorescence spectrum of $ZnP(C_3V)_4$ is shown in Fig. 4. The relative fluorescence intensities are listed in Table 4. These values were obtained by the integration of the emission spectra of $ZnP(C_nV)_4$ relative to $ZnP(C_n)_4$. The peak wavelength of the Soret band of $ZnP(C_nV)_4$ was used as the excitation wavelength. The absorbance at the excitation wavelength was kept constant at 0.2 for all sample solutions in these experiments. For all $ZnP(C_nV)_4$, the shape of the fluorescence spectrum of $ZnP(C_nV)_4$ are the same as that of $ZnP(C_n)_4$. However, the fluorescence intensity of $ZnP(C_nV)_4$ is lower than that of $ZnP(C_n)_4$. These results indicate that the photoexcited singlet state of the porphyrin site is quenched by the binding viologen due to an intramolecular electron transfer and no electronic interaction occurs between the porphyrin site and the binding viologen in the photoexcited singlet state. The fluorescence of $ZnP(C_3V)_4$ is quenched by binding viologen more efficiently than other $ZnP(C_nV)_4$.

Table 4
Relative fluorescence intensities of $ZnP(C_nV)_4$ and $ZnP(C_n)_4$

Compound	I/I_0
$ZnP(C_3)_4$	1
$ZnP(C_3V)_4$	0.20
$ZnP(C_4)_4$	1
$ZnP(C_4V)_4$	0.65
$ZnP(C_5)_4$	1
$ZnP(C_5V)_4$	0.73
$ZnP(C_6)_4$	1
$ZnP(C_6V)_4$	0.60

Excitation wavelength: 438 nm.

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