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# Preparation and characterization of water-soluble viologen-linked zinc porphyrin and bisviologen-linked zinc porphyrin

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#### Abstract

Water-soluble viologen-linked zinc porphyrin  $(ZnP(C_4V C_4)_4)$  and bisviologen-linked zinc porphyrin  $(ZnP(C_4V_A C_4V_B)_4)$  were synthesized. In  $ZnP(C_4V_A C_4V_B)_4$ , two viologens (butylviologen and 1-benzyl-1'-butylviologen) are connected with the tetrakis-(4-pyridyl)-zinc porphyrin via a methylene chain  $(-(CH_2)_4-)$ , so as to produce a gradient of redox potential in the molecule. The photochemical and electrochemical properties of  $ZnP(C_4V_A C_4V_B)_4$  and  $ZnP(C_4V C_4)_4$  were investigated by using the absorption spectra, the fluorescence spectra and the cyclic voltammetric measurement. The photoexcited triplet state of the porphyrin of  $ZnP(C_4V_B)_4$  and  $ZnP(C_4V C_4)_4$ was studied by using a laser flash photolysis. In the case of  $ZnP(C_4V_A C_4V_B)_4$ , the photoexcited triplet state of the porphyrin was not quenched by the bonded viologen. On the other hand, for the  $ZnP(C_4V C_4)_4$ , the photoexcited triplet state of the porphyrin was quenched by the bonded viologen. @ 1998 Elsevier Science S.A.

Keywords: Zinc complexes; Porphyrin complexes; Water soluble bisviologen complexes; Electron transfer

# 1. Introduction

Photoinduced intramolecular electron transfer in donorphotosensitizer-acceptor systems has been studied extensively to understand the primary process in photosynthesis and to establish the systems for solar energy conversion and storage [1-8]. 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 to mimic the photoreaction center. In these compounds, photoinduced intramolecular electron transfer between porphyrin and acceptor takes place via photoexcited singlet state of the porphyrin. Kinetic studies of the charge separation and charge recombination steps have been studied by using laser flash photolysis. These steps strongly 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 sound to be a good chemical devices to change solar energy into chemical energy, for the porphyrins have maximum absorption in the visible region. the photoexcited porphyrin can reduce the viologen and the reduction potential of the viologen is sufficiently negative to reduce water to hydrogen. As viologen-linked porphyrins serve as photosensitizer and electron carrier in the same molccule, the photoexcited singlet state of the porphyrin reduces the bonded viologen efficiently. Thus, viologen-linked porphyrins are attractive to develop the previous photoinduced hydrogen evolution systems [18-21] consisting of an electron donor, a photosensitizer, an electron carrier and a catalyst. To accomplish simpler redox systems for solar energy conversion, viologen-linked porphyrins with longer lifetimes of the charge-separated states are desired. We have reported the preliminary study of the photoinduced hydrogen evolution system using synthetic water-soluble four viologenlinked zinc porphyrins and the photochemical and electrochemical properties of a series of water-soluble viologen-linked zinc porphyrins [22-24]. To attain the high yield of photoinduced hydrogen evolution, the long-lived chargeseparated species are desired. The long-lived charge-separated state was accomplished by the multi-step electron transfer in a photosensitizer and some different acceptorlinked molecules [11-14,25-27]. In this paper we hope to describe the preparation and photochemical and electrochemical characterization of the water-soluble bisviologen-linked zinc porphyrin as shown in Fig. 1  $(ZnP(C_4V_AC_4V_B)_4)$ . Two different viologens (butylviologen and 1-benzyl-1'-butylviologen) are connected to the zinc porphyrin, so that pho-

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Fig. 1. Structure of bisviologen-linked zinc porphyrin and burylviologen linked zinc porphyrin

toinduced two-step electron transfer can occur to yield the long-lived charge-separated species.

## 2. Experimental

## 2.1. Synthesis

All the reagents used were analytical or highest grade available. The synthesis route and structures of viologen-linked zine porphyrin and bisviologen-linked zine porphyrin are shown in Scheme 1 and Fig. 1, respectively.

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

ZnTPyP was synthesized from tetrakis-(4-pyridy1)-porphyrin (TPyP) as a starting material according to the literature [21]. TPyP was obtained from Aldrich Chem. Co. TPyP ( $1.2 \times 10^{-3}$  mol) and zine acetate ( $1.6 \times 10^{-2}$  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 vacuum overnight to yield the desired product.

# 2.1.2. I-Benzyl-4,4'-bipyridinium (V<sub>B</sub>)

4.4'-Bipyridine (0.16 mol) and benzyl bromide (0.15 mol) were dissolved in 400 ml of acetone and stirred at room temperature for 24 h. A white 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 magneti= resonance (<sup>1</sup>H NMR) in D<sub>2</sub>O:  $\delta$  (ppm) 5.7 (s, 2H).<sup>7</sup>.3-7.5 (m, 5H), 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-Benzyl-1'-(n-4-bromobut-1-yl)-4,4'-bipyridinium (BrC<sub>4</sub>V<sub>n</sub>)

I-Benzyl-4-4'-bipyridinium bromide  $(3.1 \times 10^{-4} \text{ mol})$ was dissolved in 150 ml of acetonitrile (MeCN), treated with excess 1,4-dibromobutane (0.16 mol) and heated to reflux for 24 h. A bright yellow precipitate was collected by suction filtration, washed with MeCN and dried under vacuum overnight. The product was recrystallized from EtOH and then dissolved in water and a solution of ammonium hexafluorophosphate (NH<sub>4</sub>PF<sub>6</sub>) was added to replace the counter-anion with  $PF_0^-$ . The white  $PF_0^-$  salt was collected by suction filtration, washed with water and dried under vacuum overnight. <sup>1</sup>H NMR in dimethylsulfoxide- $d_0^-$  (DMSO- $d_0^-$ ):  $\delta^-$ (ppm) 1.85 (quint, 2H), 2.12 (quint, 2H), 3.60 (t, 2H), 4.72 (t, 2H), 5.92 (s, 2H), 7.4–7.7 (m, 5H), 8.3–8.4 (m, 2H), 8.7–8.8 (m, 4H), 8.4–8.6 (m, 2H).

# 2.1.4. 1-Benzyl-1'-[n-4-[1-(4,4'-bipyridinium)]but-1-yl]-4,4'-bipyridinium (BpyC<sub>4</sub>V<sub>B</sub>)

 $C_4V_B PF_6^-$  (1.5×10<sup>-3</sup> mol) was dissolved in 150 ml of MeCN, treated with excess 4,4'-bipyridine (0.14 mol) and heated to reflux for 12 h. After cooling the solution to room temperature, tetraethylammonium bromide ([Et<sub>4</sub>N]Br)– MeCN solution was added to replace the counter-anion with Br<sup>-</sup>. The yellow precipitate was collected by suction filtration, washed with MeCN. The product (Br salt) was recrystallized from EtOH and MeOH and then dissolved in water and solution of NH<sub>4</sub>PF<sub>6</sub> was added to replace the counteranion with PF<sub>6</sub><sup>-</sup>. The white PF<sub>6</sub><sup>-</sup> salt was collected by suction filtration, washed with water and dried under vacuum overnight to yield BpyC<sub>4</sub>V<sub>B</sub> 3PF<sub>6</sub>. <sup>1</sup>H NMR in DMSO-d<sub>6</sub>: 5 (ppm) 1.9-2.2 (m, 4H), 4.6-4.8 (m, 4H), 5.94 (s, 2H), 7.4-7.7 (m, 5H), 8.0-8.1 (m, 2H), 8.6-9.0 (m, 8H), 9.1-9.6 (m, 6H).

# 2.1.5. 1-Benzyl-1'-[n-4-[1'-(n-4-bromobut-1-yl)-4,4'bipyridinium[but-1-yl]-4,4'-bipyridinium(C<sub>4</sub>V<sub>A</sub> C<sub>4</sub>V<sub>B</sub>)

**BpyC**<sub>4</sub>V<sub>B</sub> 3PF<sub>6</sub> (1.8×10<sup>-3</sup> mol) was dissolved in 250 ml of MeCN, treated with excess 1,4-dibromobutane (0.16 moi) and heated to reflux for 24 h. After cooling the solution to room temperature, [Et<sub>4</sub>N]Br-MeCN solution was added to replace the counter-anion with Br<sup>-</sup>. The yellow precipitate was collected by suction filtration, washed with MeCN. The product (Br<sup>-</sup> salt) was recrystallized from EtOH and MeOH and dried under vacuum overnight to yield  $C_4V_AC_4V_B$  4Br<sup>-, 4</sup>H NMR in D<sub>2</sub>O:  $\delta$  (ppm) 1.85 (quint, 2H), 2.0-2.3 (m, 6H), 3.42 (t, 2H), 4.6-4.8 (m, 6H), 5.81 (s, 2H), 7.42 (m, 5H), 8.3-8.5 (m, 8H), 8.9-9.1 (m, 8H).

## 2.1.6. 1-(n-Butyl)-4,4'-bipyridinium (C<sub>4</sub>V)

4,4'-Eipyridine (0.16 mol) and 1-bromobutane (0.15 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 EtOH and water and dried under vacuum overnight. <sup>1</sup>H NMR in D<sub>2</sub>O:  $\delta$  (ppm) 0.85 (s, 3H), 1.25 (quint, 2H), 1.90 (quint, 2H), 4.55 (t, 2H), 7.7–7.8 (m, 2H), 8.2–8.3 (m, 2H), 8.6–8.7 (m, 2H), 8.8–8.9 (m, 2H).

# 2.1.7. 1-Bromobutyl-1'(n-butyl)-4,4'-bipyridinium (BrC<sub>4</sub>VC<sub>4</sub>)

 $C_4V$  I (3.4×10<sup>-4</sup> mol) was dissolved in 150 ml of MeCN, treated with excess 1,4-dibromobutane (0.13 mol) and heated to reflux for 24 h. A yellow precipitate was collected by suction filtration, washed with MeCN and dried

under vacuum overnight. The product was recrystallized from EtOH and then dissolved in water and a solution of  $NH_4PF_6$ 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 vacuum overnight. The  $PF_6^-$  salt dissolved in MeCN and [Et<sub>4</sub>N]Cl<sup>--</sup> was added to replace the counter-anion with Cl<sup>--</sup>. The white Cl<sup>--</sup> salt was collected by suction filtration, washed with water and dried under vacuum overnight. <sup>1</sup>H NMR in D<sub>2</sub>O:  $\delta$  (ppm): 0.85 (s, 3H), 1.25 (quint, 2H), 1.89 (quint, 4H), 2.14 (quint, 2H), 3.45 (t, 2H), 4.6-4.7 (m, 4H), 8.3-8.5 (m, 4H), 9.0-9.1 (m, 4H).

# 2.1.8. Bisviologen-linked zinc porphyrin $(ZnP(C_4V_A C_4V_B)_4)$

ZnTPyP ( $2.9 \times 10^{-4}$  mol) and  $C_4V_AC_4V_B$  4Br ( $5.5 \times 10^{-3}$  mol) were dissolved in 150 ml of dimethylformamide (DMF)-MeOH (1:1) and heated to reflux for 72 h. The solvent was removed by vacuum pump and dissolved in water. The desired product was obtained by column chromatography (Sephadex LH-20 column 40×3 cm, eluted with w tter). <sup>1</sup>H NMR in DMSO- $d_6$ :  $\delta$ (ppm): 1.9–2.3 (m, 32H), 4 6–4.9 (m, 32H), 5.99 (s, 8H), 8.1–8.2 (m, 20H), 8.7–9.2 (m, 44H), 9.3–9.7 (m, 36H).

# 2.1.9. Butylviologen-linked zinc porphyrin $(ZnP(C_4VC_4)_4)$

ZnTPyP (2.9×10<sup>-4</sup> mol) and BrC<sub>4</sub>VC<sub>4</sub> 2Br (5.5×10<sup>-3</sup> mol) were dissolved in 150 ml of DMF and heated to reflux for 72 h. The solvent was removed by vacuum pump and dissolved in water. The desired product was obtained by column chromatography (Sephadex LH-20 column 40×3 cm, eluted with water). <sup>1</sup>H NMR in DMSO- $d_6$ :  $\delta$  (ppm): 1.00 (s, 12H), 1.39 (quint, 8H), 1.9–2.2 (quint, 16H), 2.41 (m, 8H), 4.6–4.8 (m, 16H), 4.99 (t, 8H), 8.7–9.2 (m, 28H) 9.3–9.6 (m, 20H).

# 2.1.10. Viologen-free zinc porphyrin (ZnP(C4).)

ZnTPyP ( $2.9 \times 10^{-4}$  mol) and 1-bromobutane (BrC<sub>4</sub>) (0.20 mol) were dissolved in 150 ml of DMF and heated to reflux for 48 h. The solvent was removed by vacuum pump and dissolved in water. The desired product was obtained by column chromatography (Sephadex LH-20 column, eluted with water). <sup>1</sup>H NMR in DMSO- $d_6$ :  $\delta$  (ppm) ZnP(C<sub>4</sub>)<sub>4</sub>: 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).

#### 2.2. Spectroscopic measurements

For <sup>1</sup>H NMR measurement, the PF<sub>6</sub> salts of  $ZnP(C_4V_A C_4V_B)_4$ ,  $ZnP(C_4V C_4)_4$  and  $ZnP(C_4)_4$  were used. In the case of photochemical and electrochemical experiments, the Cl salts of  $ZnP(C_4V_A C_4V_B)_4$ ,  $ZnP(C_4V C_4)_4$  and  $ZnP(C_4)_4$  were used.

<sup>1</sup>H NMR spectra were recorded on a Varian GEMINI-200. Chemical shifts were referenced to the solvent peak calibrated against tetramethylsilane (TMS).

The absorption spectra of  $ZnP(C_4V_A C_4V_B)_4$ ,  $ZnP(C_4V C_4)_4$  and  $ZnP(C_4)_4$  were measured in water using a Hitachi

U-2000 spectrometer. The absorption coefficients of  $ZnP(C_4V_A C_4V_B)_4$ ,  $ZnP(C_4V C_4)_4$  and  $ZnP(C_4)_4$  were estimated using the absorption coefficient of zinc-5,10,15,20-tetrakis(*N*-methylpyridinium-4yl) porphyrin (ZnTMPyP).

The fluorescence spectra of  $ZnP(C_4V_A \ C_4V_B)_4$ ,  $ZnP(C_4V \ C_4)_4$  and  $ZnP(C_4)_4$  were measured in water at room temperature using a Hitachi F-4000 spectrometer. The absorbance at the excitation wavelength was kept constant to be 0.2 for all the sample solutions in these experiments.

# 2.3. Electrochemical measurements

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 of  $0.2 \text{ mol dm}^{-3}$  KCl and 25 mmol dm<sup>-3</sup> 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.

#### 2.4. Laser flash photolysis

Laser flash photolysis was carried out by using an 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).

#### 3. Results and discussion

# 3.1. Preparation of $ZnP(C_4V_A C_4V_B)_4$ and $ZnP(C_4V C_4)_4$

The preparation method of  $ZnP(C_4V_A \ C_4V_B)_4$  and  $ZnP(C_4V C_4)_4$  is shown in Scheme 1. The structures of all synthesized compounds were characterized by <sup>1</sup>H NMR. The <sup>1</sup>H NMR spectra of ZnP( $C_4V_A C_4V_B$ )<sub>4</sub> and ZnP( $C_4V C_4$ )<sub>4</sub> is shown in Fig. 2 and the signal assignment is given in the spectra.

# 3.2. Absorption spectra of $ZnP(C_4V_A C_4V_B)_4$ , $ZnP(C_4V C_4)_4$ and $ZnP(C_{4})_{4}$

The wavelength of absorption maxima and the absorption coefficients of  $ZnP(C_4V_A C_4V_B)_4$ ,  $ZnP(C_4V C_4)_4$  and  $ZnP(C_4)_4$  are listed in Table 1. The spectra of  $ZnP(C_4V_A)$  $C_4V_B$ )<sub>4</sub> and  $ZnP(C_4V C_4)_4$  are similar to that of  $ZnP(C_4)_4$ .

Table 1 Wavelength of absorption maxima of  $ZnP(C_4V_A|C_4V_B)_4$ .  $ZnP(C_4V|C_4)_4$ and ZnP(C<sub>4</sub>)<sub>4</sub>

Compound	Soret band (nm)	Q band (nm)	
$ZnP(C_4V_A C_4V_B)_4$	437 (180000) *	565 (17916)	608 (7667)
$ZnP(C_4V C_4)_4$	436 (180000)	564 (17333)	606 (3750)
$ZnP(C_4)_4$	438 (180000)	565 (17500)	607 (7700)

\* Absorption coefficient (M<sup>-1</sup> cm<sup>-1</sup>) given in parentheses

indicating no electronic interaction between the zinc porphyrin site and the bonded viologen at the ground state.

# 3.3. Electrochemical property of $ZnP(C_4V_A C_4V_B)_{4}$ $ZnP(C_4V C_4)_4$ and $ZnP(C_4)_4$

The energy levels of  $ZnP(C_4V_A C_4V_B)_4$  and  $ZnP(C_4V$  $C_4$ )<sub>4</sub> were studied by electrochemical measurements. The results are listed in Table 2. The energies of the first excited singlet states of the  $ZnP(C_4V_A C_4V_B)_4$  or  $ZnP(C_4V C_4)_4$ were calculated from the average value of the frequencies of the longest wavelength of absorption maxima and the shortest wavelength of fluorescence emission maxima. The redox potentials were determined from cyclic voltammetric measurements. The energies of charge-separated states of  $ZnP^{+}(C_4V_A^{-}C_4V_B)_4$ ,  $ZnP^{+}(C_4V_A^{-}C_4V_B^{-})_4$  and  $ZnP^{+}(C_4V_B^{-})_4$  $C_4$ )<sub>4</sub> were estimated from the first oxidation potential of  $ZnP(C_4)_4$  and the first reduction potential of butylviologen and C<sub>4</sub>V<sub>B</sub>. Each energy level is listed in Table 3. No correction for Coulomb effects was attempted because of no interaction between each chromphore at the ground state.

For  $ZnP(C_4V_AC_4V_B)_4$ , the first excited singlet state of the zinc porphyrin lies at 1.99 eV above the ground state and the  $ZnP^+(C_4V_A^- C_4V_B)_4$  and  $ZnP^+(C_4V_A^- C_4V_B^-)_4$  chargeseparated states lie at 1.65 and 1.52 eV, respectively.

For  $ZnP(C_4VC_4)_4$ , the first excited singlet state of the zinc porphyrin lies at 1.99 eV above the ground state and the ZnP \*  $(C_4 V C_4^-)_4$  charge-separated states lie at 1.65 eV. Scheme 2 shows the energy levels of transient states of  $ZnP(C_4V_A)$  $(C_4 V_B)_4$  and  $ZnP(C_4 V C_4)_4$  from Table 2. The electron transfer pathways are considered as shown in Scheme 2. Step 1

Table 2

The first excited singlet state energies of  $ZnP(C_4)_4$  and redox potentials (vs Ag/AgCl) for ZnP( $C_4$ )<sub>4</sub>, butylviologen and  $C_4V_B$ 

Compound	'P (eV) *	$E_0^1$ (V) <sup>b</sup>	$E_{r}^{1}(V)^{v}$	
			AND ALLER A LINE AND ALLER AND ALL AND A	
$ZnP(C_{4})_{4}$	1.99	0.958		
Butylviologen			0.710	
C <sub>4</sub> V <sub>B</sub>			0.591	
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\* 'P 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.

<sup>b</sup>  $E_0^1$  is the first oxidation potential.

 $^{\circ}E_{t}^{1}$  is the first reduction potential

Table 3

Table 3		
Energies of the first excited sing	let state and the charge-separated state of $ZnP(C_4V_A)$	$(C_4V_B)_4$ and $ZnP(C_4V_C_4)_4$

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Compound	'P (eV) *	$E (ZnP^+(C_4V^-C_4)_4) (eV)^{b}$	$E (\operatorname{ZnP}^+(\operatorname{C}_4\operatorname{V}_{\operatorname{A}}\operatorname{C}_4\operatorname{V}_{\operatorname{B}})_4) (\operatorname{eV})^{\operatorname{h}}$	$E \left( \operatorname{ZnP}^{+} \left( \operatorname{C}_{4} \operatorname{V}_{A} \operatorname{C}_{4} \operatorname{V}_{B} \right)_{4} \right) \left( \operatorname{eV} \right)^{+}$
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$ZnP(C_4V_A C_4V_B)_4$	1.99		1.65	1.53
ZnP(C <sub>4</sub> V C <sub>4</sub> ) <sub>4</sub>	1.99	1.65		

\* P 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.

<sup>b</sup> Calculated from the results of cyclic voltammetric measurements



represents non-radiative and radiative processes. Steps 2, 3 and 5 represent electron transfer processes and steps 4 and 6 represent charge recombination processes, respectively. In the case of  $ZnP(C_4V_A C_4V_B)_4$  the energy difference between the first excited singlet state of porphyrin and each chargeseparated state is 0.34 and 0.45 eV.

# 3.4. Fluorescence spectra of $ZnP(C_4V_A C_4V_B)_4$ , $ZnP-(C_4V C_4)_4$ and $ZnP(C_4)_4$

The photoexcited singlet states of  $ZnP(C_1V_A C_4V_B)_4$ ,  $ZnP(C_4V C_4)_4$  and  $ZnP(C_4)_4$  were studied using the fluorescence emission spectra. The fluorescence spectra of  $ZnP(C_4V_AC_4V_B)_4$ ,  $ZnP(C_4VC_4)_4$  and  $ZnP(C_4)_4$  are shown in Fig. 3. Relative fluorescence intensities are listed in Table 4. These values were obtained by the integration of the emission spectra of  $ZnP(C_4V_A C_4V_B)_4$  and  $ZnP(C_4V C_4)_4$ relative to  $ZnP(C_4)_4$ . The peak wavelength of the Soret band of  $ZnP(C_4V_A C_4V_B)_4$ ,  $ZnP(C_4V C_4)_4$  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 fluorescence spectra of  $ZnP(C_4V_A C_4V_B)_4$  and  $ZnP(C_4V C_4)_4$  are the same as that of  $ZnP(C_4)_4$ . However, the fluorescence intensities of  $ZnP(C_4V_A C_4V_B)_4$  and  $ZnP(C_4V C_4)_4$  are lower than that of  $ZnP(C_4)_4$ . These results indicate that the photoexcited singlet state of porphyrin is quenched by the bonded viologen due to intramolecular electron transfer and no electronic interaction occurs between the porphyrin and the bonded viologen



Fig. 3. Fluorescence spectra of (a)  $ZnP(C_4)_a$ , (b)  $ZnP(C_4V C_4)_a$  and (c)  $ZnP(C_4V_A C_4V_B)_a$  in water. The excitation wavelength was 438 nm.

Table 4
Relative fluorescence intensities of $ZnP(C_4V_A C_4V_B)_4$ and $ZnP(C_4V C_4)_5$

Compound	1/10	
$ZnP(C_4V_A C_4V_B)_4$ $ZnP(C_4V C_4)_4$	0.29 0.33	

 $I_0$  is the value of fluorescence intensity of viologen-free zinc porphyrin  $\text{ZnP}(C_4)_4$ .

in the photoexcited singlet state. The fluorescence of  $ZnP(C_4V_A C_4V_B)_4$  is quenched by the bonded viologen more efficiently than that of  $ZnP(C_4V C_4)_4$ .

# 3.5. Triplet state of $ZnP(C_4V_A C_4V_B)_4$ , $ZnP(C_4V C_4)_4$ and $ZnP(C_4)_4$

The electron transfer from the photoexcited triplet state of the porphyrin to the bonded viologen was studied using laser flash photolysis. Fig. 4 shows the decay of the transient states of the porphyrin. The decay of the photoexcited triplet state of  $ZnP(C_4)_4$ , as shown in Fig. 4(a), obeyed first-order kinetics, and the lifetime of photoexcited triplet state of  $ZnP(C_4)_4$ was 1.2 ms. For the  $ZnP(C_4V C_4)_4$ , the decay of the photoexcited triplet state of porphyrin of  $ZnP(C_4V C_4)_4$  was shown in Fig. 4(b) and obeyed first-order kinetics. The lifetime of photoexcited triplet state of porphyrin of  $ZnP(C4V C_4)_4$  was shown in Fig. 4(b) and obeyed first-order kinetics. The lifetime of photoexcited triplet state of porphyrin of  $ZnP(C4V C_4)_4$  was  $9.5 \ \mu$ s. The lifetime became shorter than that of  $ZnP(C_4)_4$ , indicating that the photoexcited triplet state of the



Fig. 4. Typical decay of the photoexcited triplet state monitored at 490 nm after laser flash. The absorbance at the excitation wavelength (532 nm) was kept to be 0.2 for all the sample solutions.

porphyrin of  $ZnP(C_4V C_4)_4$  was quenched by the bonded viologen. However, no increase of absorbance at 605 nm due to formation of the reduced viologen was observed. This result indicates that the back electron transfer reaction occurs very rapidly compared with the forward electron transfer reaction. For  $ZnP(C_4V_A C_4V_B)_4$ , the decay of the photoexcited triplet state of the porphyrin of  $ZnP(C_4V_A C_4V_B)_4$  is shown in Fig. 4(c) and obeyed first-order kinetics. The lifetime of photoexcited triplet state of the porphyrin of  $ZnP(C_4V_A C_4V_B)_4$  was 0.89 ms. This value is almost the same as that of  $ZnP(C_4)_4$ , indicating no intramolecular electron transfer occurred via the photoexcited triplet state of the porphyrin. This result indicates the quenching reaction occurred via the photoexcited singlet state of the porphyrin site of  $ZnP(C_4V_A C_4V_B)_4$ .

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