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Preparation and characterization of water soluble viologen-linked trisulfonatophenylporphyrin ($TPPSC_nV$)

Yutaka Amao, Tomohiro Hiraishi, Ichiro Okura *

Department of Bioengineering, Tokyo Institute of Technology, Nagatsuta-cho 4259, Midori-ku, Yokohama 226, Japan

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Abstract

A series of water soluble viologen-linked trisulfonatophenylporphyrins ($TPPSC_nV$; $n = 3–6$) were synthesized. Viologen is connected with the trisulfonatophenylporphyrin via a methylene chain ($-(CH_2)_n-$: $n = 3–6$) in these compounds. The photochemical and electrochemical properties of $TPPSC_nV$ were investigated by using the absorption spectra, the fluorescence spectra and the cyclic voltammetric measurement. The photoexcited singlet state of the porphyrin moiety of $TPPSC_nV$ was quenched by the bonded viologen. © 1997 Elsevier Science B.V.

Keywords: Viologen-linked trisulfonatophenylporphyrin; Photoexcited electron transfer

1. Introduction

Photoinduced intramolecular electron transfer in donor–photosensitizer–acceptor systems have 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 seem to be good chemical devices for changing solar energy into chemical energy, because the porphyrins have maximum absorption at the visible region, the photoexcited porphyrin can reduce viologen and the reduction potential of viologen is sufficiently negative to reduce water into hydrogen. As viologen linked porphyrins serve as a photosensitizer and electron carrier in the same molecule, viologen linked porphyrins are attrac-

* Corresponding author.

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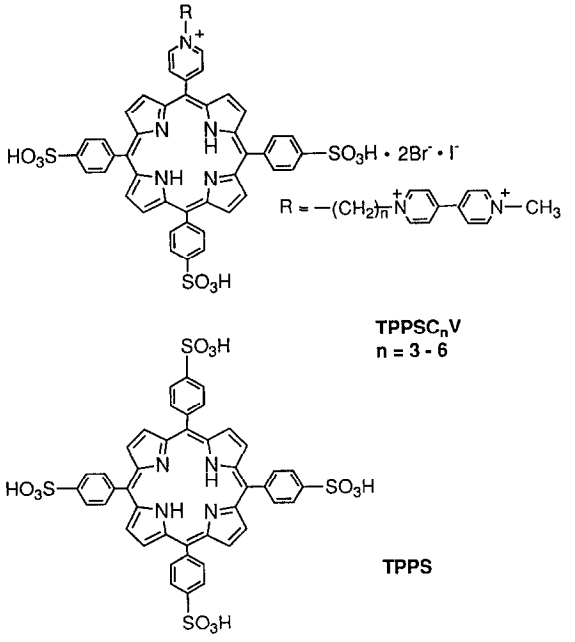


Fig. 1. Structure of water soluble viologen linked trisulfoporphyrin (TPPSC$_n$V).

tive in developing the previous photoinduced hydrogen evolution systems [18–21] consisting of an electron donor, a photosensitizer, an electron carrier and a catalyst. A photoinduced hydrogen evolution system using synthetic water soluble four viologen linked-cationic zinc porphyrins and the photochemical and electrochemical properties of a series of water soluble viologen linked cationic zinc porphyrins have been reported [22–24]. In the cationic zinc porphyrin system, however, the reductive quenching reaction and degradation of zinc porphyrin by irradiation occurred. To attain a high yield of photoinduced hydrogen evolution, a photo-stable photosensitizer and effective electron carrier are desired. Though anionic porphyrin, tetraphenylporphyrin tetrasulfonate (TPPS), is a highly active photosensitizer for the photoinduced hydrogen evolution system, viologen linked TPPS has not yet been synthesized. In this paper we hope to describe the preparation and photochemical and electrochemical characterization of the water soluble viologen linked trisulfonatophenylporphyrin (TPPSC$_n$V) as shown in Fig. 1.

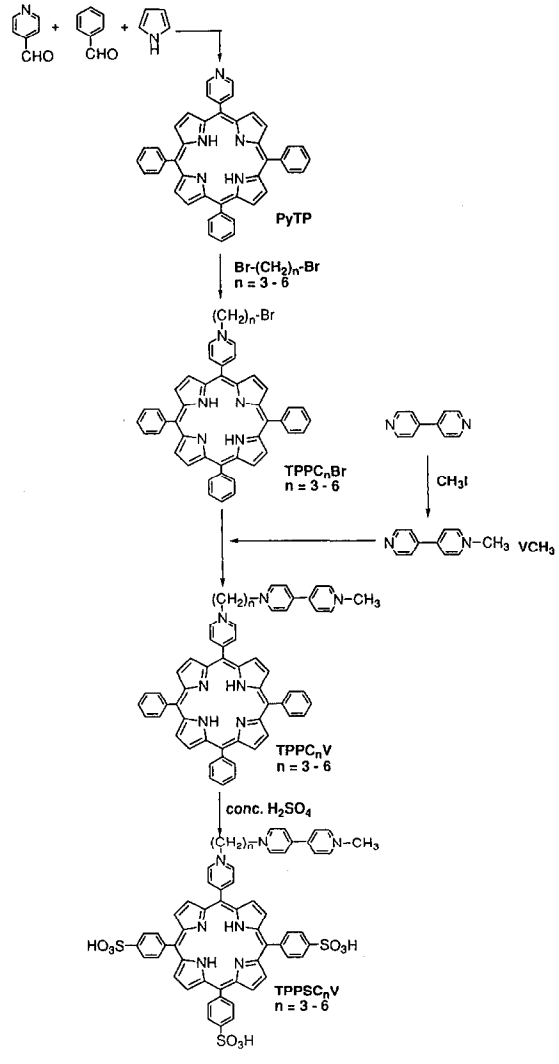
2. Experimental details

2.1. Synthesis

All the reagents used were analytical grade or the highest grade available. The synthesis route and structure of water soluble viologen-linked trisulfonatophenylporphyrin are shown in Scheme 1 and Fig. 1, respectively.

2.1.1. 5-(4-pyridyl)-10,15,20-triphenylporphyrin (PyTP)

The starting material, PyTP was synthesized according to the literature [25]. Pyridine-4-al-



Scheme 1.

dehyde (3.7×10^{-2} mol) and benzaldehyde (0.108 mol) were added into 500 ml of boiling propionic acid and then pyrrol (0.149 mol) was added and was refluxed for 1 h at 165°C. Metallic purple precipitate was collected by suction filtration and washed with methanol and dried under vacuum overnight. The crude product obtained was purified by the column chromatography (100–200 mesh of silica gel: 60×5 cm, eluted: chloroform). The desired product, PyTP, was eluted as a second fraction and dried by evaporation. Purple precipitate was collected and washed with water and then with methanol and dried under vacuum overnight to yield the desired product. Proton nuclear magnetic resonance (^{1}H-NMR) in $CDCl_3$: δ(ppm) −2.9– −2.7 (m, 2H), 7.7–7.8 (m, 9H), 8.1–8.3 (m, 8H), 8.7–9.1 (m, 10H).

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. ^{1}H-NMR in D_2O: 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. 5-(Bromoalkyl-4-pyridyl)-10,15,20-triphenylporphyrin ($TPPC_nBr$)

PyTP (2.9×10^{-4} mol) and α,ω-dibromoalkane (BrC_nBr; $n = 3$–6) (0.20 mol) were dissolved in 100 ml of toluene and heated to reflux for 48 h. After cooling the solution, purple precipitate was collected by suction filtration and washed by toluene and dried under vacuum overnight. ^{1}H-NMR in DMSO-d_6: δ(ppm): $TPPC_3Br$: −2.9– −2.7 (m, 2H), 2.90 (quint, 2H), 3.9 (t, 2H), 5.05 (t, 2H), 7.8–7.9 (m, 9H), 8.2–8.4 (m, 6H), 8.8–9.2 (m, 16H), 9.6–9.7 (m, 2H); $TPPC_4Br$: −2.9– −2.7 (m, 2H), 2.12 (quint, 2H), 2.45 (quint, 2H), 3.90 (t, 2H), 5.05 (t, 2H), 7.8–7.9 (m, 9H), 8.2–8.4 (m, 6H), 8.8–9.2 (m, 10H), 9.6–9.7 (m, 2H); $TPPC_5Br$: −2.9– −2.7 (m, 2H), 1.43 (quint, 2H), 1.85 (quint, 2H), 2.24 (quint, 2H), 2.44 (quint, 2H), 5.05 (t, 2H), 7.8–7.9 (m, 9H), 8.2–8.4 (m, 6H), 8.8–9.2 (m, 10H), 9.6–9.7 (m, 2H); $TPPC_6Br$: −2.9– −2.7 (m, 2H), 1.6–1.8 (quint, 4H), 2.00 (quint, 2H), 2.24 (quint, 2H), 3.75 (t, 2H), 5.05 (t, 2H), 7.8–7.9 (m, 9H), 8.2–8.4 (m, 6H), 8.8–9.2 (m, 10H), 9.6–9.7 (m, 2H).

2.1.4. Viologen-linked porphyrin ($TPPC_nV$)

$TPPC_nBr$ (2.9×10^{-4} mol) and VCH_3 (5.5×10^{-3} mol) were dissolved in 100 ml of dimethylformamide (DMF) and heated to reflux for 48 h. The solvent was removed by a vacuum pump and washed with water to remove excess VCH_3 and then washed with chloroform to remove excess $TPPC_nBr$. A purple precipitate was collected by suction filtration and dried under vacuum overnight. ^{1}H-NMR in DMSO-d_6: δ(ppm): $TPPC_3V$: −2.9– −2.7 (m, 2H), 3.10 (quint, 2H), 4.4–4.6 (s, 3H), 5.15 (t, 4H), 7.8–7.9 (m, 9H), 8.2–8.4 (m, 6H), 8.8–9.2 (m, 16H), 9.3–9.4 (m, 2H), 9.6–9.7 (m, 2H); $TPPC_4V$: −2.9– −2.7 (m, 2H), 2.42 (quint, 4H), 4.4–4.6 (s, 3H), 4.96 (t, 2H), 5.10 (t, 2H), 7.8–7.9 (m, 9H), 8.2–8.4 (m, 6H), 8.8–9.2 (m, 16H), 9.3–9.4 (m, 2H), 9.6–9.7 (m, 2H); $TPPC_5V$: −2.9– −2.7 (m, 2H), 1.85 (quint, 2H), 2.24 (quint, 2H), 2.44 (quint, 2H), 4.4–4.6 (s, 3H), 4.96 (t, 2H), 5.10 (t, 2H), 7.8–7.9 (m, 9H), 8.2–8.4 (m, 6H), 8.8–9.2 (m, 16H), 9.3–9.4 (m, 2H), 9.6–9.7 (m, 2H); $TPPC_6V$: −2.9– −2.7 (m, 2H), 1.84 (quint, 4H), 2.24 (quint, 2H), 2.44 (quint, 2H), 4.4–4.6 (s, 3H), 4.96 (t, 2H), 5.10 (t, 2H), 7.8–7.9 (m, 9H), 8.2–8.4 (m, 6H), 8.8–9.2 (m, 16H), 9.3–9.4 (m, 2H), 9.6–9.7 (m, 2H).

2.1.5. Water soluble viologen-linked trisulfonatophenylporphyrin ($TPPSC_nV$)

The sulfonation of $TPPC_nV$ was carried out according to the literature [26]. $TPPC_nV$ (2.9×10^{-3} mol) was dissolved in 20 ml of conc. H_2SO_4 and heated to reflux for 4 h and then the

reaction mixture was stirred at room temperature for 48 h. The reaction mixture was diluted with double volume of water and then excess acetone was added to the reaction mixture and green precipitate was collected by suction filtration and dried under vacuum overnight. ^{1}H-NMR in DMSO-d_6: δ(ppm): TPPSC$_3$V: −2.9–−2.7 (m, 2H), 3.10 (quint, 2H), 4.4–4.6 (s, 3H), 5.15 (t, 4H), 7.8–7.9 (m, 6H), 8.2–8.4 (m, 6H), 8.8–9.2 (m, 16H), 9.3–9.4 (m, 2H), 9.6–9.7 (m, 2H); TPPSC$_4$V: −2.9–−2.7 (m, 2H), 2.42 (quint, 4H), 4.4–4.6 (s, 3H), 4.96 (t, 2H), 5.10 (t, 2H), 7.8–7.9 (m, 6H), 8.2–8.4 (m, 6H), 8.8–9.2 (m, 16H), 9.3–9.4 (m, 2H), 9.6–9.7 (m, 2H); TPPSC$_5$V: −2.9–−2.7 (m, 2H), 1.85 (quint, 2H), 2.24 (quint, 2H), 2.44 (quint, 2H), 4.4–4.6 (s, 3H), 4.96 (t, 2H), 5.10 (t, 2H), 7.8–7.9 (m, 6H), 8.2–8.4 (m, 6H), 8.8–9.2 (m, 16H), 9.3–9.4 (m, 2H), 9.6–9.7 (m, 2H); TPPSC$_6$V: −2.9–−2.7 (m, 2H), 1.84 (quint, 4H), 2.24 (quint, 2H), 2.44 (quint, 2H), 4.4–4.6 (s, 3H), 4.96 (t, 2H), 5.10 (t, 2H), 7.8–7.9 (m, 6H), 8.2–8.4 (m, 6H), 8.8–9.2 (m, 16H), 9.3–9.4 (m, 2H), 9.6–9.7 (m, 2H).

2.2. Spectroscopic measurements

^{1}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 tetraphenylporphyrin tetrasulfonate (TPPS) and TPPSC$_n$V were measured in water using a Hitachi U-2000 spectrometer.

The fluorescence spectra of TPPS and TPPSC$_n$V were measured in water at room temperature using a Hitachi F-4000 spectrometer. The absorbance at the excitation wavelength was kept constant to be 0.4 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 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. Preparation of TPPSC$_n$V

The preparation method of TPPSC$_n$V is shown in Scheme 1. The structures of all synthesized compounds were characterized by ^{1}H-NMR. The ^{1}H-NMR spectra of TPPSC$_n$V is shown in Fig. 2 and the signal assignment is given in the spectra.

3.2. Absorption spectra of TPPS and TPPSC$_n$V

TPPSC$_n$V formed aggregates in water and the aggregates of TPPSC$_n$V were not photoactive. The measurements of absorption spectra of TPPS and TPPSC$_n$V were carried out in the presence of Triton X-100. The absorption spectra of TPPS and TPPSC$_n$V are shown in Fig. 3. The wavelength of absorption maxima of TPPS and TPPSC$_n$V are listed in Table 1. The spectra of TPPSC$_n$V are similar to that of TPPS, indicating no electronic interaction between the porphyrin site and the bonded viologen at the ground state.

3.3. Electrochemical property of TPPS and TPPSC$_n$V

The energy levels of TPPSC$_n$V were studied by electrochemical measurements. The results are listed in Table 2. The energies of the first excited singlet states of TPPSC$_n$V were calculated from the average value of the frequencies of the longest wavelength of absorption maxima

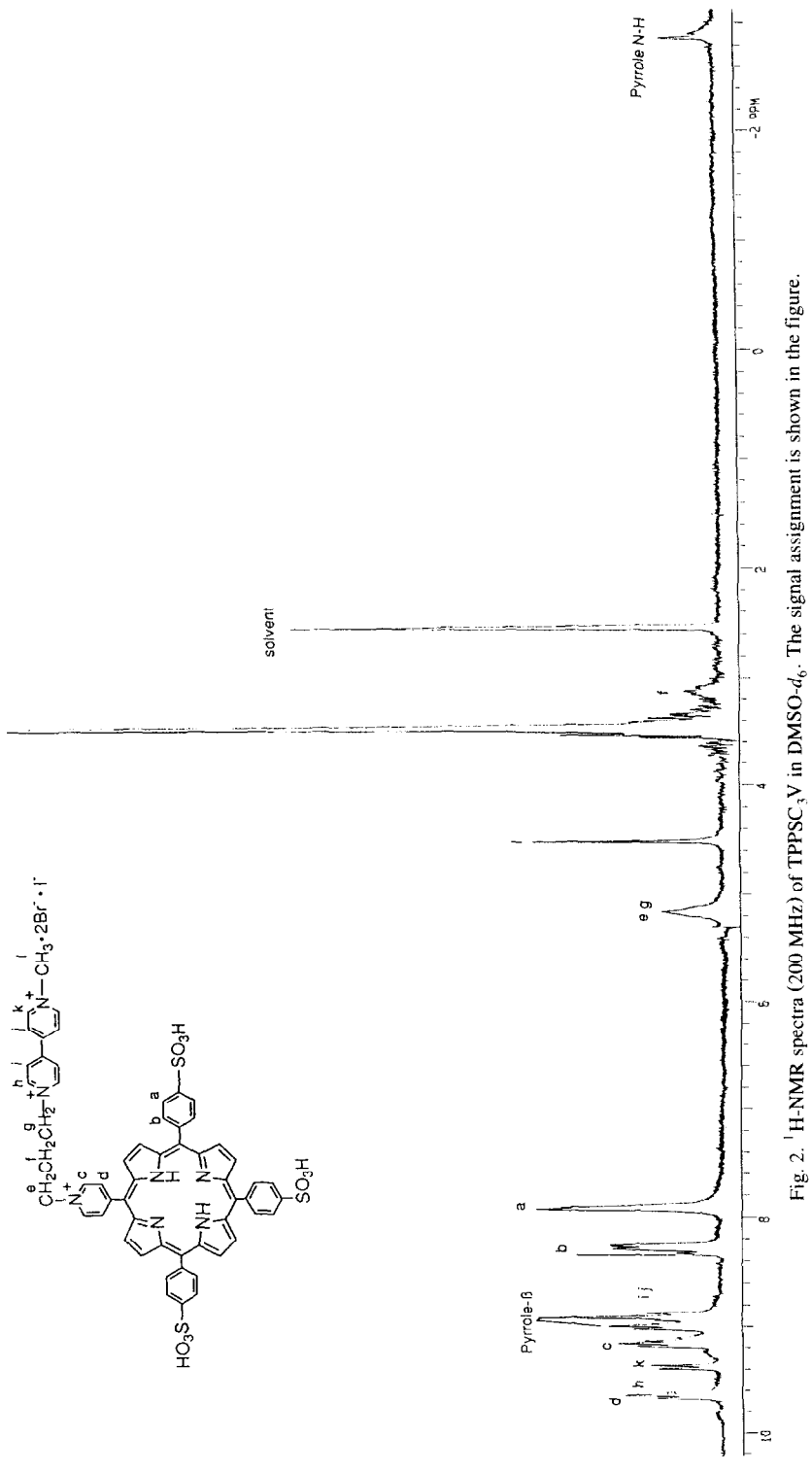


Fig. 2. ^{1}H-NMR spectra (200 MHz) of TPPSC$_3$V in DMSO-d_6. The signal assignment is shown in the figure.

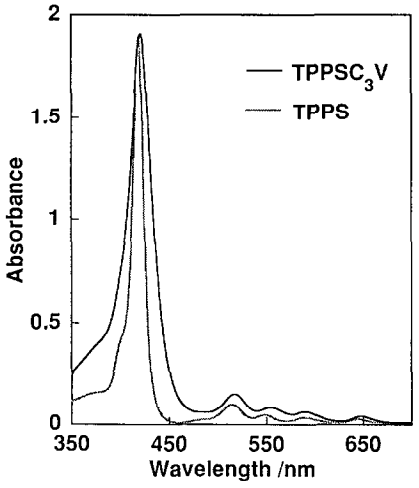


Fig. 3. Absorption spectra of (a) TPPS and (b) $TPPSC_3V$ in water containing 1% Triton X-100.

and the shortest wavelength of fluorescence emission maxima. The redox potentials were determined from cyclic voltammetric measurements. The energies of charge separated states of $TPPS^+C_nV^-$ were estimated from the first oxidation potential of TPPS and the first reduction potential of C_nVCH_3. 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 $TPPSC_nV$, the first excited singlet state of the porphyrin lies at 1.92 eV above the ground state and the $TPPS^+C_nV^-$ charge separated state lie at 1.76–1.79 eV.

Scheme 2 shows the energy levels of transient states of $TPPSC_nV$ from Table 2. The electron transfer pathways are considered as shown in Scheme 2. Step 1 represents non-radiative and radiative processes. Step 2 represents electron transfer processes and Step 3 represents charge recombination processes, respectively.

Table 1
Wavelength of absorption maxima of TPPS and $TPPSC_nV$

Compound	Soret band (nm)		Q band (nm)		
TPPS	419	515	549	589	644
$TPPSC_3V$	421	517	555	590	648
$TPPSC_4V$	422	518	555	591	649
$TPPSC_5V$	421	519	556	591	647
$TPPSC_6V$	422	518	555	591	648

Table 2
The first excited singlet state energies of TPPS and redact potentials (versus Ag/AgCl) for TPPS and C_nVCH_3

Compound	^1P (eV) [a]	E_o^1 (V) [b]	E_r^1 (V) [c]
TPPS	1.92	1.10	
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_o^1 is the first oxidation potential.
[c] E_r^1 is the first reduction potential.

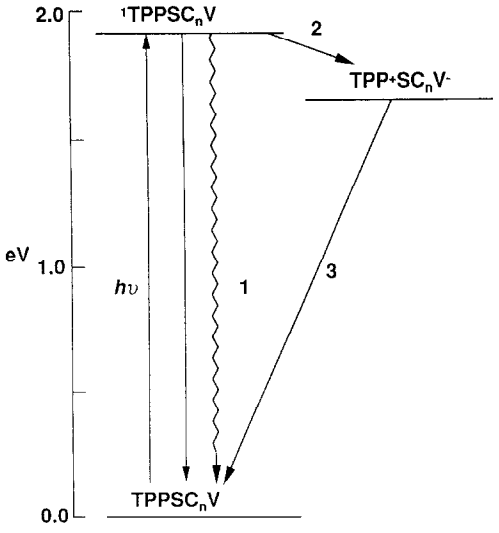
3.4. Fluorescence spectra of TPPS and $TPPSC_nV$

$TPPSC_nV$ formed aggregates in water and the aggregates of $TPPSC_nV$ were not emitted fluorescence. The measurements of fluorescence emission spectra of TPPS and $TPPSC_nV$ were carried out in the presence of Triton X-100. The fluorescence spectra of TPPS and $TPPSC_nV$ are shown in Fig. 4. Relative fluorescence intensities are listed in Table 4. These values were

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

Compound	^1P (eV) [a]	$E(P^+ V^-)$ (eV) [b]
$TPPSC_3V$	1.92	1.76
$TPPSC_4V$	1.92	1.77
$TPPSC_5V$	1.92	1.78
$TPPSC_6V$	1.92	1.79

[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 2).



Scheme 2.

obtained by the integration of the emission spectra of TPPSC$_n$V relative to TPPS. The peak wavelength of the Soret band of TPPSC$_n$V was used as the excitation wavelength. The shape of the fluorescence spectra of TPPSC$_n$V are the same as that of TPPS. However, the fluorescence intensities of TPPSC$_n$V are lower than that of TPPS. 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 in the photoexcited singlet state.

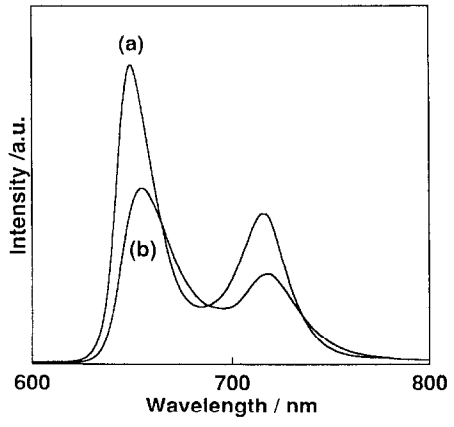


Fig. 4. Fluorescence spectra of (a) TPPS and (b) TPPSC$_3$V in water containing 1% Triton X-100. The excitation wavelength was 421 nm.

Table 4
Relative fluorescence intensities of TPPS and TPPSC$_n$V

Compound	I/I_0
TPPS	1
TPPSC$_3$V	0.58
TPPSC$_4$V	0.70
TPPSC$_5$V	0.56
TPPSC$_6$V	0.62

Excitation wavelength: 421 nm.

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