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Effect of methylene chain length on electron transfer and photocurrent generation using viologen-linked porphyrin monolayer modified ITO electrode

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Abstract

The increase of the electron transfer yield from the photoexcited porphyrin to viologen was achieved by forming a Langmuir–Blodgett (LB) film of viologen-linked porphyrin. Four kinds of porphyrin covalently linked to viologen (BuPC$_n$V: $n = 3,4,5,8$) by methylene chain, in which the center-to-center distance between porphyrin and viologen is less than 1.7 nm, were synthesized, and the molecularly oriented films of BuPC$_n$V ($n = 3,4,5,8$) were prepared on indium tin oxide (ITO) electrodes using an LB technique. The effect of methylene chain length both on the quenching of the fluorescence from porphyrin by viologen and on the photocurrent generation was investigated. The fluorescence quenching by viologen increased with the decrease of the methylene chain length, showing that the electron transfer from the photoexcited porphyrin to viologen is easy to take place when the distance between porphyrin and viologen is shorter. Furthermore, the fluorescence was quenched more efficiently by viologen in the LB film compared with a methanol solution, indicating that the fluorescence is quenched both by the bonded viologen and by the neighboring viologen in the LB film of BuPC$_n$V ($n = 3,4,5$). Under visible light irradiation, a cathodic photocurrent was generated, which increased with the decrease of the methylene chain length owing to the increase of the electron transfer yield from the photoexcited porphyrin to viologen. The orientation of BuPC$_n$V ($n = 3,4,5,8$) molecules on the ITO electrode was investigated by the effect of bias voltage and dioxygen concentration on the photocurrent. It was shown that the porphyrin moieties are attached to the surface of the ITO electrode and that the photocurrent is ascribable to the photoinduced charge separation in the BuPC$_n$V ($n = 3,4,5$) molecules. © Elsevier Science S.A.

Keywords: Porphyrin; Viologen; Langmuir–Blodgett film; ITO electrode; Electron transfer; Photocurrent; Distance

1. Introduction

Photoinduced electron transfer reaction takes place with high quantum yield in the natural photosynthetic reaction center. One approach to an artificial photosynthesis and to mimicking the natural process is to employ cofactors related to those found in the reaction center by using covalent linkages rather than protein matrixes as an organizing principle. Several chromophores covalently linked to acceptors such as quinones or viologens were synthesized to investigate photoinduced electron transfer reactions and the lifetimes of the charge separated species [1–13]. Viologen, which is reduced by a photoexcited chromophore such as porphyrin derivatives or ruthenium complexes and whose reduced form is able to reduce protons to hydrogen in the presence of catalyst (e.g., colloidal platinum or hydrogenase), is an important electron mediator for a photoenergy conversion system [14,15]. Various porphyrins covalently linked to viologens have been synthesized to develop suitable redox systems for photochemical utilization of solar energy [8–13]. One of the authors [16] studied the distance between an artificial chromophore and an acceptor within which photoinduced electron transfer takes place, and reported that electron transfer can occur from the photoexcited tris(2,2′-bipyridine)ruthenium (II) (Ru(bpy)$_3^{2+}$) to 1,1′-dimethyl-4,4′-bipyridinium (methylviologen: MV^{2+}) when the distance between them is less than 1.4 nm in the absence of electron pathway molecules. It is suggested that, to realize a photoelectric conversion using electrodes modified with viologen-linked porphyrins, the distance between porphyrin and viologen should be kept within less than 1.4 nm for the electron transfer. Moreover, these molecules need to realize a directed electron flow. By

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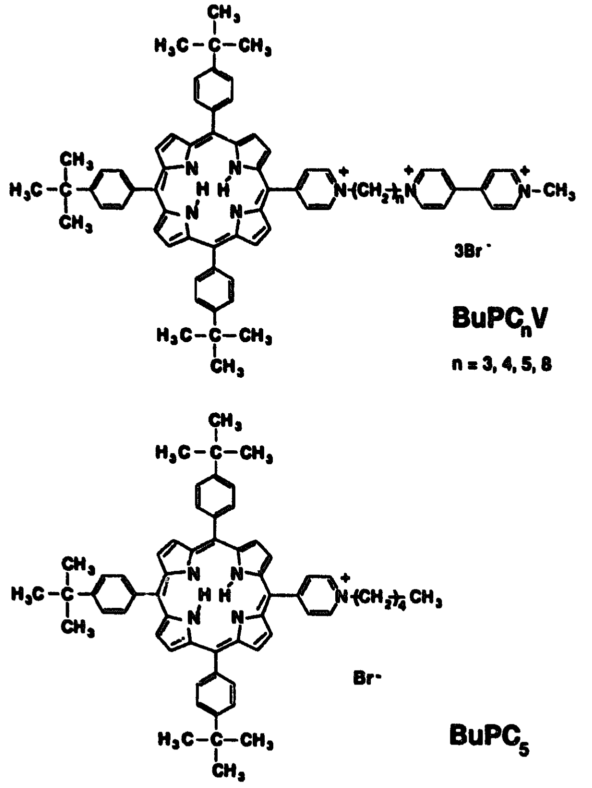
using a Langmuir–Blodgett (LB) technique, it seems easy to obtain a molecularly oriented film of viologen-linked porphyrin and to realize a directed electron flow. Fujihira et al. [17–19] realized a directed electron flow using a gold electrode modified with LB films consisting of a pyrene chromophore, a viologen acceptor and a ferrocene donor by controlling the redox sequence of the three compounds by an LB technique. In addition, they attempted to increase the photocurrent generation using a gold electrode modified with an LB film of triad (ferrocene–pyrene–viologen) for which the charge recombination of the charge separated species is considered to be retarded [17–19]. Cao et al. [10] also attempted to increase the photocurrent generation using a tin oxide electrode modified with an LB film of triad. As another method to increase the photocurrent generation using an electrode modified with an LB film of viologen-linked porphyrin, it is suggested that the electron transfer yield from the photoexcited porphyrin to the viologen should increase. In a homogenous system, one of the authors [11] reported that the electron transfer yield from the photoexcited singlet state porphyrin moiety to the bonded viologen increased when the distance between the porphyrin and the bonded viologen became closer.

In the present work, we attempted to increase the electron transfer yield from the photoexcited singlet state porphyrin to the viologen by changing the distance between the porphyrin and the bonded viologen. Various porphyrins covalently linked to viologen by methylene chain (BuPC$_n$V; $n = 3,4,5,8$) as shown in Fig. 1 were synthesized. The center-to-center distance between the porphyrin moiety and the bonded viologen of BuPC$_3$V, BuPC$_4$V, BuPC$_5$V and BuPC$_8$V was about 1.28 nm, 1.38 nm, 1.44 nm and 1.70 nm, respectively. The molecularly oriented films of BuPC$_n$V were prepared on indium tin oxide (ITO) electrodes using an LB technique and the effect of the distance between the porphyrin and the viologen in an LB film both on the electron transfer yield and on photocurrent generation was investigated. In addition, the characteristics of photocurrent were studied to show the orientation of BuPC$_n$V molecules on an ITO electrode.



BuPC$_n$V

BuPC$_5$

Fig. 1. Structures of viologen-linked porphyrin and alkylporphyrin.

2. Experimental details

2.1. *Synthesis*

All reagents were of either analytical grade or the highest grade available. The structures of viologen-linked porphyrins (BuPC$_n$V: $n = 3,4,5,8$) and viologen free porphyrin (BuPC$_5$) used as a reference compound are shown in Fig. 1.

2.1.1. *Viologen-linked porphyrins (BuPC$_n$V)*

The starting material, 5-(4-pyridyl)-10,15,20-tritert-butylphenylporphyrin (PyTBuP), was synthesized and the byproducts were removed as described in the literature [20,21]. PyTBuP and a 100-fold molar excess of 1-methyl-1′-bromoalkylbipyridinium were refluxed in a toluene and methanol mixed solution (1:1 v/v) for 48 h in the dark. The solvent was removed by evaporation and the solid was washed with water and toluene to remove unreacted 1-methyl-1′-bromoalkylbipyridinium and PyTBuP. The residual solid was purified by a column chromatography (Sephadex LH-20 column, eluted with methanol) in the dark to separate viologen-linked porphyrins. The molecular structures of these synthesized compounds were confirmed by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy (JEOL Model EX 270). Chemical shifts were referenced to the solvent peak, which was calibrated against tetramethylsilane.

For BuPC$_8$V: ^{1}H NMR (270 MHz, CD$_3$CN) δ (ppm) −2.8 (s, 2H), 1.6 (s, 27H), 1.4–1.7 (m, 8H), 2.0–2.1 (m, 2H), 2.2–2.3 (m, 2H), 4.4 (s, 3H), 4.6 (t, 2H), 4.8 (t, 2H), 7.8 (d, 6H), 8.2 (d, 6H), 8.3 (d, 2H), 8.4 (d, 2H), 8.7–8.8 (dd, 4H), 8.8–8.9 (m, 8H), 9.0 (d, 2H), 9.1 (d, 2H).

For BuPC$_5$V: ^{1}H NMR (270 MHz, CD$_3$CN) δ (ppm) −2.8 (s, 2H), 1.6 (s, 27H), 1.6–1.7 (m, 2H), 2.1–2.2 (m, 2H), 2.3–2.4 (m, 2H), 4.3 (s, 3H), 4.7 (t, 2H), 4.8 (t, 2H), 7.8 (d, 6H), 8.2 (d, 6H), 8.3 (d, 2H), 8.4 (d, 2H), 8.7 (d, 2H), 8.7–8.8 (m, 6H), 8.8 (d, 2H), 8.9 (dd, 4H) 9.1 (d, 2H).

For BuPC$_4$V: ^{1}H NMR (270 MHz, CD$_3$CN) δ (ppm) −2.8 (s, 2H), 1.6 (s, 27H), 2.3–2.5 (m, 4H), 4.3 (s, 3H), 4.9 (t, 2H), 5.0 (t, 2H), 7.8 (d, 6H), 8.2 (d, 6H), 8.4 (d, 2H), 8.5 (d, 2H), 8.8–8.9 (m, 10H), 9.0 (d, 2H), 9.1 (d, 2H) 9.2 (d, 2H).

For BuPC$_3$V: ^{1}H NMR (270 MHz, CD$_3$CN) δ (ppm) −2.8 (s, 2H), 1.6 (s, 27H), 3.0 (m, 2H), 4.4 (s, 3H), 4.9

(t, 2H), 5.0 (t, 2H), 7.8 (d, 6H), 8.2 (d, 6H), 8.4 (d, 2H), 8.5 (d, 2H), 8.8–8.9 (m, 8H), 8.9 (d, 2H), 9.0 (d, 2H) 9.1 (dd, 4H).

2.1.2. *Viologen-free porphyrin ($BuPC_5$)*

PyTBuP and a 100-fold molar excess of 1-bromopentane were stirred at 100 °C in toluene for 24 h and the produced precipitate was washed with toluene to remove unreacted PyTBuP and 1-bromopentane.

For $BuPC_5$: ^1H NMR (270 MHz, CD_3CN) δ (ppm) -2.8 (s, 2H), 1.1 (t, 3H), 1.5–1.7 (m, 4H), 1.6 (s, 27H), 2.3–2.4 (m, 2H), 4.8 (t, 2H), 7.8 (d, 6H), 8.7 (d, 2H), 8.8 (m, 6H), 8.9 (d, 2H), 9.0 (d, 2H).

2.2. *Characterization of the compounds*

The absorption spectra of $BuPC_nV$ and $BuPC_5$ were measured in methanol solutions at room temperature using a spectrophotometer (Shimadzu Model UV-3101PC). The fluorescence emission spectra of $BuPC_nV$ and $BuPC_5$ were measured in methanol solutions at room temperature using a fluorescence spectrophotometer (Hitachi Model F-4010). In these experiments the absorbance at the excitation wavelength was kept constant for all the sample solutions. The lifetime of the photoexcited triplet states of $BuPC_nV$ and $BuPC_5$ were measured in methanol solutions at room temperature by a conventional laser flash photolysis. These experiments were carried out by using an Nd:YAG laser (Model DCR-3 from Quanta Ray Inc.) as excitation source. The excitation wavelength of 532 nm, a pulse duration of 10 ns and a repetition rate of 10 Hz were used for the excitation of the sample solution. The light beam, after passing through the sample cell, was collimated into the entrance slit of the monochromator (model 1410 from Applied Photophysics Co., Ltd.). The output signal from a photomultiplier (Model 1445 from Applied Photophysics Co., Ltd.) attached to the slit of the monochromator was displayed on a digitizing oscilloscope (Model 11401 from SONY-Tektronix) and averaged over 64–128 flashes. Sample solutions were adjusted to posses the absorbance of 0.2 at 532 nm and deaerated by repeated freeze–pump–thaw cycles (four times) to remove dissolved dioxygen.

2.3. *Preparation of LB films*

The spreading solvent for the LB film preparation was a benzene and methanol mixed solution (9:1 v/v); they were purchased from Wako Pure Chemical Industries. All materials were of either analytical grade or the highest grade available. Distilled water was deionized by passing through a Yamato water purification system. The electrolyte for the electrochemical experiment was $NaClO_4$, which was obtained from Wako Pure Chemical Industries. ITO optical transparent substrates (resistivity 10 Ω/□) were purchased from Geomatic Co. Ltd.

Monolayers of $BuPC_nV$ and $BuPC_5$ were obtained by spreading a benzene and methanol mixed solution (9:1 v/v) of these compounds (1.0×10^{-4} M) onto an aqueous subphase at 20 °C. Surface pressure–area isotherms and the automated deposition of the LB films on the ITO substrates were measured with a Langmuir trough equipped with an electronic microbalance and a glass Wilhelmy plate (Kyowa Kaimenkagaku Co.). Each monomolecular layer of $BuPC_nV$ and $BuPC_5$ was deposited on an ITO substrate under a constant surface pressure at 10 mN m^{-1}.

All the LB film modified ITO electrodes were prepared by layering a single monolayer of $BuPC_nV$ or $BuPC_5$ on a precleaned ITO substrate (effective surface area 2.0 cm^2).

2.4. *Characterization of LB films*

2.4.1. *Spectroscopic measurements*

The absorption and fluorescence emission spectra of the ITO electrodes modified with the LB films were measured at room temperature using a spectrophotometer (Shimadzu Model UV-3101PC) and a fluorescence spectrophotometer (Hitachi Model F-4010).

2.4.2. *Photoelectrochemical measurements*

The apparatus for the photoelectrochemical studies was composed of an electrochemical analyzer (Model BAS-100B) from Bioanalytical Systems and a xenon arc lamp from Spectra Energy. The incident light was obtained through a Toshiba LH-39 filter and a monochromator (Model GM252, also from Spectra Energy). The monochromatic light intensity was measured with a radiometer (model MS-801) from Eko Instruments trading Co. Ltd.. The intensity of the monochromatic light was 0.60 ± 0.05 mW cm^{-2}. Especially, the monochromatic light at 450 nm was arranged as 0.63 ± 0.01 mW cm^{-2}. Photocurrents were measured in a time-base mode under both ambient and nitrogen conditions; for the latter nitrogen was purged for 120 min before measurement. The dissolved oxygen was measured with a dissolved oxygen meter (model ND-10) from Nagashima Co. Ltd.. The photoelectrochemical cell was made of Pyrex and consisted of an ITO working electrode modified by a monolayer of $BuPC_nV$ or $BuPC_5$, a platinum wire (Pt) counter, and a silver wire (Ag) reference electrode. An aqueous $NaClO_4$ (0.1 M) was used as a supporting electrolyte solution.

3. Results and discussion

3.1. *Absorption spectra of $BuPC_nV$*

The wavelengths of the absorption maxima of $BuPC_nV$ and $BuPC_5$ in methanol are shown in Table 1. The absorption spectra of $BuPC_nV$ are similar to that of $BuPC_5$, indicating the absence of any ground-state electronic interaction between the porphyrin ring and the bonded viologen in meth-

Table 1
Wavelength of absorption maxima of $BuPC_nV$ and $BuPC_5$ in methanol and center to center distance between porphyrin moiety and viologen moiety of $BuPC_nV$ molecules

	Wavelength (nm)					Center-to-center distance (nm)
$BuPC_5$	418	518	558	591	649	
$BuPC_8V$	418	518	557	591	649	1.70±0.12
$BuPC_5V$	418	518	558	591	649	1.44±0.10
$BuPC_4V$	418	518	558	591	649	1.38±0.10
$BuPC_3V$	419	518	559	590	650	1.28±0.09

anol solution. Table 1 also summarizes the center-to-center distance between the porphyrin moiety and the bonded viologen in $BuPC_nV$ molecules. The distances are calculated using a molecular model of time average solution conformation [22].

3.2. Fluorescence emission spectra of $BuPC_nV$

The photoexcited singlet states of porphyrins were investigated using the fluorescence emission spectra. Table 2 shows the peak wavelengths and the relative intensities of the fluorescence emission of $BuPC_nV$ and $BuPC_5$ in methanol. The shapes of the fluorescence emission spectra of $BuPC_nV$ and $BuPC_5$ in methanol were the same as that of porphyrin monomer [10,23]. These intensities were obtained by integration of the emission spectra of $BuPC_nV$ relative to $BuPC_5$. In these experiments the concentration of the sample solution was adjusted to about 8×10^{-7} M in order to keep the absorbance at the excited wavelength (518 nm) constant for all the sample solutions. In the case of such low concentrations, fluorescence quenching can take place only intramolecularly but not intermolecularly. Although the shapes of the fluorescence emission spectra of $BuPC_nV$ are the same as that of $BuPC_5$, the fluorescence intensities of $BuPC_nV$ are lower than that of $BuPC_5$, indicating that the photoexcited singlet state of porphyrin is quenched by the bonded viologen owing to intramolecular electron transfer [8–13] and that no electronic interaction takes place between the porphyrin ring and the bonded viologen in the photoexcited singlet state. In addition, the fluorescence quenching by the bonded viologen increased when the methylene chain length became shorter, showing that photoinduced intramolecular electron transfer from the photoexcited singlet state of porphyrin to the bonded viologen takes place more easily when the distance between porphyrin and viologen is shorter.

Table 2
Wavelength of fluorescence maxima and relative fluorescence intensities of $BuPC_nV$ and $BuPC_5$ in methanol

	Wavelength (nm)		I/I_0
$BuPC_5$	660	723	1.000
$BuPC_8V$	660	723	0.945
$BuPC_5V$	660	723	0.540
$BuPC_4V$	660	723	0.494
$BuPC_3V$	655	718	0.326

3.3. Lifetimes of triplet state of $BuPC_nV$

The intramolecular electron transfer from the photoexcited triplet state of porphyrin to the bonded viologen was studied in methanol solutions using laser flash photolysis. The difference transient spectra of $BuPC_nV$ and $BuPC_5$ (data not shown) were attributed to the T–T absorption of the photoexcited triplet state of $BuPC_5$. The decay of the T–T absorption of $BuPC_nV$ and $BuPC_5$ at 470 nm obeyed first-order kinetics, and the lifetimes of the photoexcited triplet state of $BuPC_3V$, $BuPC_4V$, $BuPC_5V$, $BuPC_8V$ and $BuPC_5$ were 81 μs, 88 μs, 91 μs, 86 μs and 83 μs, respectively, showing almost no quenching of the photoexcited triplet state porphyrin by the bonded viologen. No absorption due to the reduced viologen of $BuPC_nV$ at 600 nm was observed (data not shown). These results indicate that electron transfer from the photoexcited triplet porphyrin to the bonded viologen does not take place.

3.4. Surface pressure–area isotherms

The surface pressure–area isotherms of the monolayer of $BuPC_nV$ and $BuPC_5$ are shown in Fig. 2. They formed stable monolayers on a distilled water subphase. The limiting areas per molecule of $BuPC_3V$, $BuPC_4V$, $BuPC_5V$, $BuPC_8V$ and $BuPC_5$ were about 1.04 nm^2, 1.03 nm^2, 1.12 nm^2, 1.26 nm^2 and 0.828 nm^2, respectively, indicating that $BuPC_nV$ and $BuPC_5$ molecules were almost vertically oriented on a water subphase.

3.5. LB film deposition

The floating monolayers of BuPCnV and BuPC5 could be transferred to ITO substrates using LB technique. The film transfer ratios of $BuPC_nV$ and $BuPC_5$ onto ITO substrates were almost 1.0, indicating that the molecular orientation of the LB films of $BuPC_nV$ and $BuPC_5$ on the ITO substrates must be the same as the ones on the water subphase and must be vertical.

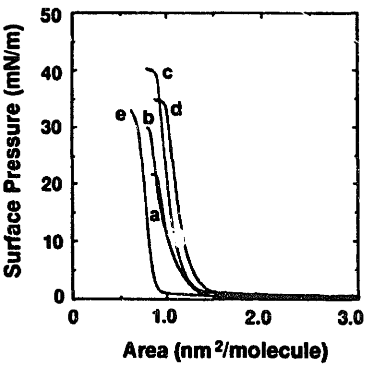


Fig. 2. Surface pressure–area isotherms of monolayers of $BuPC_3V$ (curve a), $BuPC_4V$ (curve b), $BuPC_5V$ (curve c), $BuPC_8V$ (curve d) and $BuPC_5$ (curve e) on an aqueous subphase at 20 °C.

Table 3
Wavelength of absorption maxima of $BuPC_nV$ and $BuPC_5$ in LB films

	Wavelength (nm)				
$BuPC_5$	446	520	559	594	651
$BuPC_8V$	446	520	558	593	650
$BuPC_5V$	446	520	559	593	651
$BuPC_4V$	446	520	559	593	650
$BuPC_3V$	447	520	559	593	650

3.6. *Absorption spectra of ITO electrodes modified with LB films*

The visible absorption spectra of the ITO electrodes modified with the LB films of $BuPC_nV$ ($n = 3,4,5,8$) were similar to that of $BuPC_5$ (Table 3), indicating the absence of any ground-state electronic interaction between the porphyrin ring and the bonded viologen or the neighboring viologen in the LB films. However, the absorption spectra of the LB films are red-shifted comparing with those in a methanol solution (Table 1). The effect could be interpreted in terms of an increase in the delocalization of the π orbital of the porphyrin by forming the LB film [24].

3.7. *Fluorescence emission spectra of ITO electrodes modified with LB films*

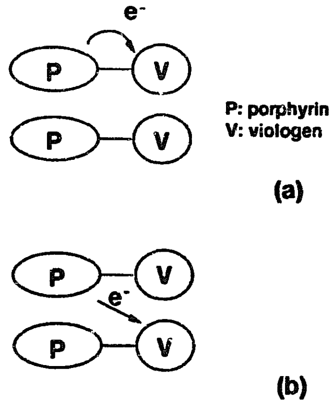
Table 4 shows the peak wavelengths and the relative fluorescence emission intensities of the ITO electrode modified with the LB film of $BuPC_nV$ or $BuPC_5$ excited at 520 nm. The fluorescence intensities are normalized by the absorbance at 520 nm. The shapes of the fluorescence emission spectra of the LB film of $BuPC_nV$ electrodes are the same as that of $BuPC_5$, showing that no electronic interaction exists between the singlet porphyrin and the bonded viologen as well as the neighboring viologen. In addition, the shapes of the fluorescence emission spectra of these LB films (data not shown) were the same as that of porphyrin monomer [10,23].

The relative fluorescence intensity of $BuPC_nV$ ($n = 3,4,5$) was smaller compared with that of $BuPC_5$, indicating that each photoexcited singlet porphyrin is quenched by the bonded viologen or by the neighboring viologen most probably due to electron transfer from the photoexcited porphyrin to the viologen. The fluorescence quenching by the viologen increased when the methylene chain length became shorter, showing that the electron transfer from the photoexcited singlet porphyrin to the viologen is easy to take place when the distance between the porphyrin and the viologen is shorter. On the other hand, no quenching of the fluorescence from the porphyrin by the viologen was observed in the LB film of $BuPC_8V$, indicating that the center-to-center distance between the porphyrin and the bonded viologen as well as the neighboring viologen is not close enough for the electron transfer to take place.

In the case of the LB films of $BuPC_nV$ ($n=3,4,5$), the fluorescence from porphyrin was quenched more efficiently compared with the case in methanol (Table 2), indicating that the fluorescence from the porphyrin of the $BuPC_nV$ ($n=3,4,5$) films is quenched not only by the bonded viologen but also by the neighboring viologen. Especially, the fluorescence of the LB films of $BuPC_4V$ and $BuPC_3V$ was strongly quenched compared with the case in methanol, since the distance between the porphyrin and the neighboring viologen as well as the bonded viologen is closer and the electron transfer from the porphyrin moiety to the neighboring viologen can take place more easily. It is advantageous for the increase of the electron transfer yield to form an LB film of the viologen-linked porphyrin because both the electron transfer from the porphyrin to the bonded viologen (Scheme 1(a)) as well as to the neighboring viologen (Scheme 1(b)) become possible. The effect of the methylene chain length on the electron transfer yield is expected to affect photocurrent generation as described below.

Table 4
Wavelength of fluorescence maxima and relative fluorescence intensities of $BuPC_nV$ and $BuPC_5$ in LB film

	Wavelength (nm)		I/I_0
$BuPC_5$	658	719	1.000
$BuPC_8V$	658	720	1.010
$BuPC_5V$	657	719	0.515
$BuPC_4V$	658	719	0.408
$BuPC_3V$	657	720	0.220



Scheme 1. Electron transfer process in LB film.

3.8. *Photocurrent generation at ITO electrodes modified with LB films*

Cathodic photocurrents were observed when the ITO electrodes modified with the LB films of $BuPC_nV$ and $BuPC_5$ were illuminated by visible light at 0.0 mV (vs. Ag) under both ambient and nitrogen conditions. Fig. 3 shows the action spectra of the cathodic photocurrents under nitrogen and the absorption spectrum of the ITO electrode modified with the LB film of $BuPC_3V$. The action spectra coincide with the absorption spectra of porphyrin in $BuPC_nV$ (Table 3), showing that the photoexcitation of the porphyrin moieties is

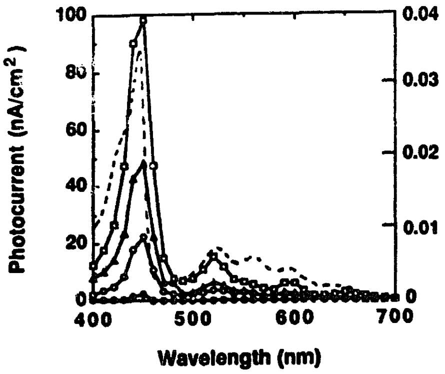


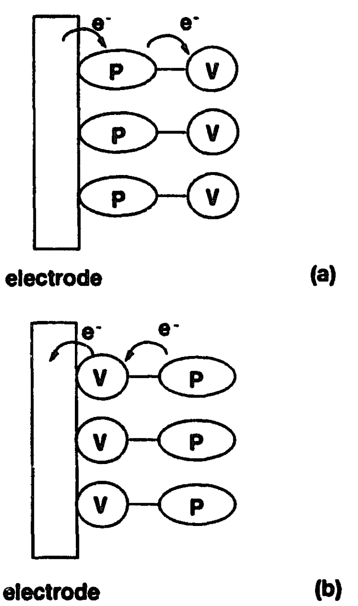
Fig. 3. The photocurrent action spectra of ITO electrodes modified with the LB film of viologen-linked porphyrins at 0.0 V (vs. Ag) under nitrogen atmosphere: □, $BuPC_3V$; △, $BuPC_4V$; ○, $BuPC_5V$; ●, $BuPC_8V$; - - -, absorption spectrum of the ITO electrode modified with the LB film of $BuPC_3V$.

responsible for the photocurrent generation. The photocurrents of the ITO electrodes modified with the LB films of $BuPC_nV$ ($n=3,4,5$) were remarkably larger than that of the electrode modified with the LB film of $BuPC_8V$, indicating that the photocurrent is due to the photoinduced electron transfer from the photoexcited porphyrin to the bonded or the neighboring viologen. The values of photocurrent increased when the methylene chain length became shorter. In the case of $BuPC_3V$, photocurrent was 98 nA cm^{-2} at 450 nm, whose yield defined as the number of electrons flowing per the number of incident photons (not absorbed photons) was 0.043%. The photocurrent should be dependent both on the electron transfer yield and the charge recombination one. Charge recombination also relates with the electron transfer reaction between the viologen-linked porphyrin and the electrode as well as the electrolyte. It is unable to explain the relationship between the absolute value of the photocurrent and the fluorescence quenching ratio. However, it seems to be sure that the increase of photocurrent is due to the increase of the electron transfer yield from the photoexcited singlet porphyrin to the viologen with the decrease of the methylene chain length. On the other hand, the photocurrent of $BuPC_8V$ (2.1 nA cm^{-2} at 450 nm) was almost the same as that of $BuPC_5$, indicating that the photoinduced electron transfer from the porphyrin to the viologen could not take place in the LB film of $BuPC_8V$ since the center-to-center distance between the porphyrin and the bonded viologen as well as the neighboring viologen is too large for the electron transfer. The small cathodic photocurrent (2.0 nA cm^{-2} at 450 nm) observed in the $BuPC_5$ can be attributed to the trace residual dioxygen which is the electron acceptor [25]. Under ambient conditions for which the concentration of the dissolved O_2 was 5.7×10^{-4} M, the photocurrent of $BuPC_5$ was increased to 21 nA cm^{-2}.

3.9. Orientation of $BuPC_nV$ molecules on the ITO electrode

The observation of the cathodic photocurrents indicates that electrons flow from the electrode through the LB film of $BuPC_nV$ to the electrolyte solution. This result shows the orientation of $BuPC_nV$ molecules on the ITO electrode. When the porphyrin moieties of $BuPC_nV$ are attached to the surface of the ITO electrode, cathodic photocurrent must be generated according to the Scheme 2(a). If the viologen moieties are attached to the surface of the ITO electrode, anodic photocurrent must be generated according to the Scheme 2(b). Since cathodic photocurrents were observed, the porphyrin moieties must be attached to the surface of the ITO electrode.

To confirm the orientation of the $BuPC_nV$ molecules on the ITO electrode, the effect of bias voltage was investigated. When the porphyrin moieties are attached to the surface of the ITO electrode, cathodic photocurrent must increase as the negative bias of the electrode increases. On the contrary, when the viologen moieties are attached to the electrode, cathodic photocurrent must decrease as the negative bias of the electrode increases. In fact, cathodic photocurrents increased as the negative bias of the electrode increased (Fig. 4). These results also indicate that the porphyrin moieties are attached to the surface of the ITO electrode as the Scheme 2(a). As the positive bias of the electrode increased,



Scheme 2. Mechanism of photocurrent generation.

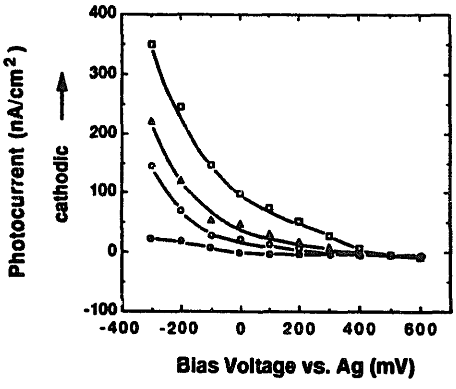


Fig. 4. Effect of bias voltage on the photocurrent generation at ITO electrodes modified with the LB film of viologen-linked porphyrins under nitrogen atmosphere: □, $BuPC_3V$; △, $BuPC_4V$; ○, $BuPC_5V$; ●, $BuPC_8V$.

anodic photocurrents for which the molecular orientation as the Scheme 2(b) is responsible, was generated and saturated about 8 nA cm^{-2}. However, the saturated value of the anodic photocurrent was very small compared with the cathodic photocurrent, indicating that the BuPC$_n$V molecules are well oriented on the ITO electrode as the Scheme 2(a).

The effect of dioxygen (O_2) on the photocurrent was investigated. Under ambient conditions, the cathodic photocurrent of BuPC$_3$V, BuPC$_4$V, BuPC$_5$V and BuPC$_8$V increased to 270 nA cm^{-2} (98 nA cm^{-2} under nitrogen), 243 nA cm^{-2} (48 nA cm^{-2} under nitrogen), 198 nA cm^{-2} (24 nA cm^{-2} under nitrogen) and 25 nA cm^{-2} (2.1 nA cm^{-2} under nitrogen) at 450 nm, respectively. The degree of the photocurrent increase in the LB films of BuPC$_n$V ($n=3,4,5$) was remarkable compared with that of BuPC$_5$, whose photocurrent increased only to 21 nA cm^{-2} from 2 nA cm^{-2}. It is well known that the reduced form of viologen (V^+) is oxidized by O_2 efficiently according to the reaction

$$V^+ + O_2 \rightarrow V^{2+} + O_2^- \qquad (1)$$

In the case of the BuPC$_n$V ($n=3,4,5$) (P–V^{2+}), photoinduced electron transfer from the singlet porphyrin to the viologen takes place to result in the charge separated species ($^+$P–V$^+$). A photocurrent is generated when the electron transfer takes place between the charge separated species and both the ITO electrode (Ed) and the electrolyte (El) (reaction (2a)).

$$\begin{aligned}&P\text{–}V^{2+} \rightarrow {}^+P\text{–}V^+ \rightarrow P\text{–}V^+ - Ed(e^-),\\ &\text{or } {}^+P\text{–}V^{2+} + El(e^-) \rightarrow P\text{–}V^{2+} - Ed(e^-) + El(e^-) \qquad (2a)\end{aligned}$$

$$P\text{–}V^{2+} \rightarrow {}^+P\text{–}V^+ \rightarrow P\text{–}V^{2+} \qquad (2b)$$

$$\begin{aligned}&P\text{–}V^{2+} \rightarrow {}^+P\text{–}V^+ + O_2 \rightarrow {}^+P\text{–}V^{2+} + O_2^-\\ &\qquad \rightarrow P\text{–}V^{2+} + O_2^- - Ed(e^-) \qquad (2c)\end{aligned}$$

However, when charge recombination occurs (reaction (2b)), no photocurrent is generated. Under ambient conditions, the cathodic photocurrent of the electrodes modified with the LB film of BuPC$_n$V ($n=3,4,5$) increased markedly compared with that under nitrogen, since the recombination of the charge separated species of BuPC$_n$V ($n=3,4,5$) molecules is retarded by O_2 oxidation (reaction (2c)). In the case of the LB film of BuPC$_5$ (P), O_2 cannot quench the photoexcited singlet state of porphyrin (^{1*}P) but in its triplet state (^{3*}P) as a result of the energy transfer (reaction (3a)) or the electron transfer (reaction (3b)). When the quenching by O_2 takes place by electron transfer according to reaction (3b), the cathodic photocurrent should increase.

$$P \rightarrow {}^{1*}P \rightarrow {}^{3*}P + O_2 \rightarrow P + {}^{1*}O_2 \qquad (3a)$$

$${}^{3*}P + O_2 \rightarrow {}^+P + O^{-2} \rightarrow P + O_2^- - Ed(e^-) \qquad (3b)$$

Actually, O_2 was not so effective for the increase of the cathodic photocurrent by the LB film of BuPC$_5$, which is because the electron transfer (3b) is competitive with the energy transfer (3a). In the case of BuPC$_n$V, the triplet state of porphyrin can also be quenched by O_2, however, its effect on the photocurrent increase seems small due to the same reason as the case of BuPC$_5$. The effect of O_2 on the photocurrent of BuPC$_8$V was almost the same as the case of BuPC$_5$, indicating that the charge separated species ($^+$P–V$^+$) is not generated in the LB film of BuPC$_8$V because of the large center-to-center distance between the porphyrin and the viologen.

The results of the O_2 effect also indicate that the orientation of BuPC$_n$V ($n=3,4,5$) molecules on ITO electrodes can be depicted as in Scheme 2(a) and the photocurrent generation at the electrodes modified with the LB films of BuPC$_n$V ($n=3,4,5$) is attributable to the photoinduced charge separation in the BuPC$_n$V ($n=3,4,5$) molecules.

4. Conclusions

The electron transfer yield from the photoexcited singlet porphyrin to the viologen could be increased by forming an LB film of viologen-linked porphyrin (BuPC$_n$V; $n=3,4,5$), probably by adding the electron transfer process from the porphyrin to the neighboring viologen (Scheme 1(b)) to the process from the porphyrin to the bonded viologen (Scheme 1(a)). Especially, the electron transfer yield increased remarkably with the decrease of the methylene chain length. Cathodic photocurrent was generated at the BuPC$_n$V ($n=3,4,5$) LB film coated ITO electrode induced by the electron transfer from the photoexcited porphyrin to the viologen. This shows that the porphyrin moiety is attached on the ITO surface. The photocurrent increased with the decrease of the methylene chain length owing to the increase of the electron transfer yield from the photoexcited porphyrin to the viologen. The enhancing effect of O_2 on the cathodic photocurrent also showed that the porphyrin moiety is attached on the electrode surface and that the photocurrent is induced by the electron transfer from the porphyrin to the viologen. Similar results were obtained in methanol and in LB films when chloride was used as a counter-ion instead of bromide, indicating that bromide does not play a role as a quencher of the photoexcited porphyrin.

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