ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 126 (1999) 91–97

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.nl/locate/jphotochem

Hydrogen evolution photoinduced by using platinum-loaded Langmuir–Blodgett films of viologen-linked porphyrin

Hideyuki Hosono *

Frontier Technology Research Institute, Tokyo Gas Company Limited, 1-7-7, Suehiro-Cho, Yokohama 230, Japan

Received 1 March 1999; received in revised form 19 April 1999; accepted 12 May 1999

Abstract

Viologen-linked porphyrin and viologen-free porphyrin were synthesized and the platinum(Pt)-loaded Langmuir–Blodgett (LB) films were prepared. Steady photoinduced hydrogen evolution was observed using both Pt-loaded LB films under steady-state irradiation in the presence of ethylenediaminetetraacetic acid (EDTA) as a sacrificial electron donor. The rate of hydrogen production using viologen-linked porphyrin was larger than that using viologen-free porphyrin. Besides, hydrogen evolution was continued using viologen-linked porphyrin for much longer period compared with using viologen-free porphyrin. The mechanism of hydrogen production was investigated. Three paths to hydrogen production existed in the case of viologen-linked porphyrin. On the other hand, one path existed in the case of viologen-free porphyrin. ©1999 Elsevier Science S.A. All rights reserved.

Keywords: Porphyrin; Viologen; Langmuir–Blodgett film; Platinum; Hydrogen

1. Introduction

Over the last few decades, many studies of biomimetic photoenergy conversion have been attempted in order to attain artificial photosynthesis. To investigate the dynamics of the photoinduced electron transfer at a photosynthetic reaction centre, many organic model compounds were synthesized [1–13]. Among them there were viologen-linked porphyrins which have been synthesized and investigated with the aim of carrying out electron transfer from the photoexcited porphyrin to the bonded viologen efficiently [10–13]. Several studies with respect to photoelectric conversion were reported using electrodes modified with the Langmuir–Blodgett (LB) film of viologen-linked porphyrin to realize a directed electron flow as a photosynthetic reaction centre [14–18]. Reduced form of viologen is well-known to be able to reduce protons in the presence of catalyst such as platinum, leading to H_2 production [19–23]. However, photoreduction of protons to H_2 has never been successful using an LB film of viologen-linked porphyrin in combination with a catalyst. Recently, the author and co-workers have succeeded in producing hydrogen by photoreduction of a proton using an LB film of a viologen-linked porphyrin and catalyst in the presence of ethylenediaminetetraacetic acid (EDTA) as a sacrificial electron donor [24].

In the present work, viologen-linked porphyrin and viologen-free porphyrin shown in Fig. 1 were synthesized and the platinum(Pt)-loaded LB films were prepared. Using these LB films, the photoinduced hydrogen evolution was attempted, and the mechanism of hydrogen production was investigated.

2. Experimental details

2.1. Synthesis

All reagents were of either analytical grade or the highest grade available. The structures of the viologen-linked porphyrin ($BuPC_5V$) and viologen free porphyrin ($BuPC_5$, reference compound) are shown in Fig. 1. For the preparation of $BuPC_5V$ the starting material, 5-(4-pyridyl)-10,15,20-tritert-butylphenylporphyrin (PyTBuP), was synthesized and the byproducts were removed as described in the literatures [25,26]. 1-Methyl-1′-bromopentylbipyridinium was synthesized according to the literatures [10–12] using 4,4′-bipyridyl, methyl iodide and 1,5-dibromopentane. PyTBuP and a 100-fold molar excess of 1-methyl-1′-bromopen-

---

* Tel.: +81-45-505-8817; fax: +81-45-505-8821
E-mail address: hd_hoso@tokyo-gas.co.jp (H. Hosono)

PII: S1010-6030(99)00111-2

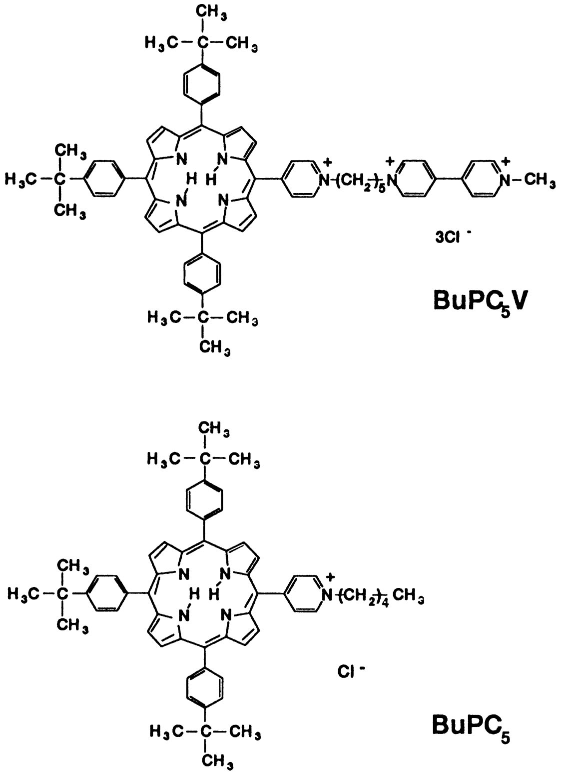

Fig. 1. Molecular structures of the viologen-linked porphyrin and alkylporphyrin.

tylbipyridinium were refluxed in a toluene and methanol mixed solution (1 : 1 v/v) for 48 h in the dark to obtain BuPC$_5$V. The solvent was removed by evaporation and the solid was washed with water and toluene to remove unreacted 1-methyl-1′-bromopentylbipyridinium 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 porphyrin.

For the preparation of 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.

The molecular structures of the synthesized viologen-linked porphyrin and viologen-free porphyrin were confirmed by proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy (JEOL Model EX 270). The compounds were dissolved in ($^2H_3$) acetonitrile (the concentrations being ca. 1.0×10^{-2} mol dm^{-3}) to measure the NMR spectra. Chemical shifts were referenced to the residual solvent peak, which in turn was calibrated against tetramethylsilane.

BuPC$_5$V: ^{1}H-NMR (270 MHz, CD_3CN) 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).

BuPC$_5$: ^{1}H-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

2.2.1. Spectroscopic measurements

The absorption spectra of BuPC$_5$V and BuPC$_5$ were measured in methanol solutions at room temperature using a spectrophotometer (Shimadzu Model UV-3101PC). The fluorescence emission spectra of BuPC$_5$V and BuPC$_5$ were measured in methanol solutions at room temperature using a fluorescence spectrophotometer (Hitachi Model F-4010). The absorbance at the excitation wavelength was kept constant for all the sample solutions. The lifetimes of the photoexcited triplet states of BuPC$_5$V and BuPC$_5$ were measured in methanol solutions at room temperature by a conventional laser flash photolysis with an Nd : YAG laser (Model DCR-3 from Quanta Ray) as an 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). The output signal from a photomultiplier (Model 1445 from Applied Photophysics) 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 have an absorbance of 0.2 at 532 nm and deaerated by repeated freeze-pump-thaw cycles (four times) to remove dissolved dioxygen.

2.2.2. Electrochemical measurements

Redox potentials were determined by cyclic voltammetry (CV) using an electrochemical analyzer(Bioanalytical Systems, Model BAS100B). All measurements were carried out under nitrogen atmosphere in DMSO solutions containing $(C_2H_5)_4NClO_4$ (0.1 mol dm^{-3}) as supporting electrolyte. The electrochemical cell consisted of a platinum (Pt) wire working electrode, a Pt wire counter, and a silver wire (Ag) reference electrode. The concentration of BuPC$_5$V and BuPC$_5$ in DMSO solution was about 5.0×10^{-4} mol dm^{-3}. The concentration of 1-methyl-1′-pentylbipyridinium (V^{2+}) in DMSO solution was 2.0×10^{-3} mol dm^{-3}.

2.3. Preparation of films

2.3.1. Metal-free LB films

The spreading solvent for the LB film preparation was a benzene and methanol mixed solution (9 : 1 v/v); the chemicals 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. Glass plates (70 mm × 50 mm × 0.1 mm) were purchased from Matsunami Glass.

Monolayers of $BuPC_5V$ and $BuPC_5$ were obtained by spreading a benzene and methanol mixed solution (9 : 1 v/v) of these compounds (1.0×10^{-4} mol dm^{-3}) onto an aqueous subphase at 20°C. Surface pressure versus area isotherms and the automated deposition of the LB films on the glass plates were measured with a Langmuir trough equipped with an electronic microbalance and a glass Wilhelmy plate (Kyowa Kaimenkagaku). Each monomolecular layer of $BuPC_5V$ and $BuPC_5$ was deposited on a glass plate under a constant surface pressure at 10 mN m^{-1}. All glass plates modified with the LB films were prepared by layering a single monolayer of $BuPC_5V$ or $BuPC_5$ on precleaned glass plate (165 cm^2).

2.3.2. Platinum-loaded LB films

Pt-loaded LB films were prepared by dipping the metal-free LB films of $BuPC_5V$ or $BuPC_5$ (165 cm^2) into argon-purged aqueous solutions (5 ml) containing 0.1 mol dm^{-3} EDTA and 1.0×10^{-3} mol dm^{-3} H_2PtCl_6, and irradiated for 72 h with visible light ($720 > \lambda$ (nm) > 390) via a Toshiba L-39 filter using a 15 W fluorescence lamp as the illumination source. Negatively charged $PtCl_6{}^{2-}$ is assumed to be incorporated in the LB films of the positively charged porphyrin moiety and viologen moiety and is reduced to Pt by photoreduction [27]. The Pt particles thus produced are fixed in the LB films. The amount of Pt fixed in the LB films were about 0.1 mg. No change of the absorption spectra of both films was observed after platinization (data not shown), so the molecular structure of of $BuPC_5V$ or $BuPC_5$ was maintained. Pt-loaded LB films were washed with distilled water prior to photoinduced hydrogen evolution experiments.

2.3.3. Metal-free cast films

Each cast film of $BuPC_5V$ and $BuPC_5$ was prepared as follows. 0.9 ml of the methanol solution containing 2.0×10^{-4} mol dm^{-3} $BuPC_5V$ or $BuPC_5$ was cast on the glass plate (165 cm^2), and dried up under room temperature. The amount of $BuPC_5V$ in the cast film is about three times as much as that in the LB film.

2.4. Characterization of films

2.4.1. Spectroscopic measurements

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

2.4.2. Photoinduced hydrogen evolution

Each glass plate modified with the metal-free LB and cast films, or Pt-loaded LB films of $BuPC_5V$ and $BuPC_5$ was dipped into an argon-purged aqueous solution containing 1.0×10^{-1} mol dm^{-3} EDTA, and irradiated by visible light ($720 > \lambda$ (nm) >390) obtained through a Toshiba LH-39 filter using a 15 W fluorescence lamp (Mitsubishi Electric Osram, N color) as a light source. The light intensity at the surface of the LB and cast films was 2.8 mW cm^{-2} and the irradiated area was 165 cm^2. Hydrogen was analysed by gas chromatography with molecular seives 5A column and argon carrier gas.

3. Results and discussion

3.1. Absorption and fluorescence emission spectra in methanol

There was virtually no difference in the absorption spectra of $BuPC_5V$ and $BuPC_5$, indicating the absence of any ground-state electronic interaction between the porphyrin ring and the bonded viologen in methanol solution.

The photoexcited singlet states of porphyrins were investigated using fluorescence emission spectroscopy. The concentration of the sample solution was adjusted to ca. 8×10^{-7} mol dm^{-3} in order to keep the absorbance at the excited wavelength (418 nm) constant for all the sample solutions. At such low concentrations, fluorescence quenching can only take place intramolecularly. The shapes of the spectra were the same as for porphyrin monomer [17,28]. The intensity was obtained by integration of the emission spectrum of $BuPC_5V$ relative to $BuPC_5$. Although the shape of the fluorescence emission spectrum of $BuPC_5V$ is the same as that of $BuPC_5$, the fluorescence intensity of $BuPC_5V$ is lower than that of $BuPC_5$, indicating that the photoexcited singlet state of porphyrin is quenched by the bonded viologen by 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.

3.2. Lifetimes of triplet state

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 $BuPC_5V$ and $BuPC_5$ (data not shown) were attributed to the T–T absorption of the photoexcited triplet state of porphyrin. The decay of the T–T absorption at 470 nm obeyed first-order kinetics and the lifetimes of the photoexcited triplet state of $BuPC_5V$ and $BuPC_5$ were 91 and 83 μs, respectively. No quenching of the photoexcited triplet state porphyrin by the bonded viologen was observed. Besides, no transient absorption owing to the viologen radical cation (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 in $BuPC_5V$ molecule.

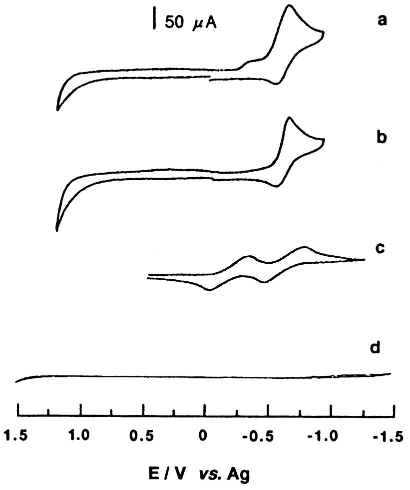

Fig. 2. Cyclic voltammograms of (a) $BuPC_5V$, (b) $BuPC_5$, (c) V^{2+} and (d) no sample at a scan rate of $100\,mV\,s^{-1}$ in DMSO solutions containing $0.1\,mol\,dm^{-3}$ $(C_2H_5)_4NClO_4$ electrolyte.

Table 1
Redox potentials of $BuPC_5V$, $BuPC_5$ and viologen in DMSO

	Redox potentials (V vs. Ag)			
	BuP^+/BuP	V^{2+}/V^+	BuP/BuP^-	V^+/V^0
$BuPC_5$	1.20		0.58	
$BuPC_5V^{2+}$	1.20	−0.18	0.58	
V^{2+}		−0.18		−0.60

3.3. Redox potentials

Fig. 2 shows cyclic voltammograms of $BuPC_5V$, $BuPC_5$ and viologen (1-methyl-1′-pentylbipyridinium; V^{2+}) in DMSO solutions. The redox potentials were estimated as the average of anodic and cathodic peak potentials of the cyclic voltammograms when the reversible waves were observed. Viologen has two reversible waves and the redox potentials are −0.18 and −0.60 V versus Ag corresponding to $E(V^{2+}/V^+)$ and and $E(V^+/ V^0)$, respectively (Fig. 2 (c)). $BuPC_5$ shows one reduction wave at −0.58V versus Ag corresponding to the formation of the one electron reduced porphyrin (BuP^+) (Fig. 2 (b)). $BuPC_5$ shows a reversible wave and two irreversible waves (Fig. 2 (a)). The reversible wave at −0.58V and the irreversible wave around +1.20V (Fig. 2 (a)) coincide with those of BuP (Fig. 2 (b)). Besides, another irreversible wave at −0.18V (Fig. 2 (a)) coincides with the reduction wave of V^{2+} to V^+ (Fig. 2 (c)). So the cyclic voltammogram of $BuPC_5V$ consists of the sum of the cyclic voltammogram of porphyrin and that of viologen. The redox potentials of these compounds are summarized in Table 1. Each redox potential of the viologen and the porphyrin moieties of $BuPC_5V$ is the same as that of viologen (1-methyl-1′-pentylbipyridinium) and $BuPC_5$, respectively, indicating that the bond between porphyrin and viologen does not affect each redox potential. Fig. 2 (d) shows the cyclic voltammogram of the DMSO contained supporting electrolyte only as a blank measurement.

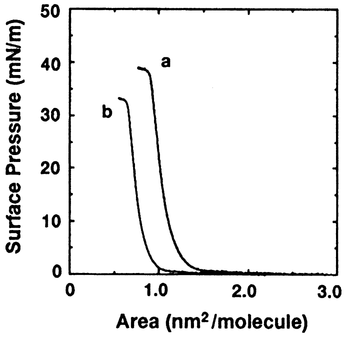

Fig. 3. Surface pressure–area isotherms of monolayers of (a) $BuPC_5V$ and (b) $BuPC_5$ on an aqueous subphase at 20°C.

Table 2
Wavelength of absorption maxima of $BuPC_5V$ and $BuPC_5$ in LB films

	Wavelength (nm)				
$BuPC_5$	446	520	559	594	651
$BuPC_5V$	446	520	559	593	651

3.4. Surface pressure–area isotherms

The surface pressure versus area isotherms of the monolayer of $BuPC_5V$ and $BuPC_5$ are shown in Fig. 3. They formed stable monolayers on a distilled water subphase. The limiting areas per molecule of $BuPC_5V$ and $BuPC_5$ were about 1.12 and $0.828\,nm^2$ per molecule, respectively, indicating that these molecules are almost vertically oriented on a water subphase.

3.5. LB film deposition

The floating monolayers of $BuPC_5V$ and $BuPC_5$ could be transferred to glass plates using the LB technique. The film transfer ratio is defined as A_l/A_s, where A_s is the area of the substrate coated with a monolayer, and A_l is the decrease in area occupied by that monolayer at the air/water interface at constant pressure. The film transfer ratios of $BuPC_5V$ and $BuPC_5$ onto the glass plates were ca. 1.0, indicating that the molecular orientation of the LB films of $BuPC_5V$ and $BuPC_5$ on the glass plates must be vertical.

3.6. Absorption and fluorescence emission spectra of LB films

The absorption spectrum of the glass plate modified with the LB film of $BuPC_5V$ was similar to that of $BuPC_5$ (Table 2), indicating the absence of any ground-state electronic interaction between the porphyrin ring and the bonded viologen in the LB film. However, the absorption spectra of the LB films of $BuPC_5V$ and $BuPC_5$ are red-shifted compared with those in methanol solutions (data not shown). The

Table 3
Wavelength of fluorescence maxima and relative fluorescence intensities of $BuPC_5V$ and $BuPC_5$ in LB film

	Wavelength (nm)		I/I_0
$BuPC_5$	658	719	1.000
$BuPC_5V$	657	719	0.525

effect could be interpreted in terms of any ground-state electronic interaction between porphyrin molecules by forming the LB film. Table 3 summarizes the peak wavelengths and the relative fluorescence emission intensities of the glass plates modified with the LB films of $BuPC_5V$ and $BuPC_5$ excited at 446 nm. The fluorescence intensities are normalized by the absorbance at 446 nm. The shape of the fluorescence emission spectrum of the LB film of $BuPC_5V$ are the same as that of $BuPC_5$, indicating the absence of any electronic interaction between the photoexcited singlet porphyrin and the bonded viologen in the LB film. In addition, the shapes of the fluorescence emission spectra of the LB films (data not shown) were the same as that of porphyrin monomer [17,28].

The relative fluorescence intensity of $BuPC_5V$ was smaller compared with that of $BuPC_5$, indicating that the photoexcited singlet porphyrin of $BuPC_5V$ is quenched by the bonded viologen by intramolecular electron transfer in the LB film [8–13].

3.7. Photoinduced hydrogen evolution using metal-free LB and cast films

No hydrogen evolution was observed using the metal-free LB films of $BuPC_5V$ and $BuPC_5$ after 72 h irradiation. After 0.5 h irradiation, the colour of the LB film of $BuPC_5V$ turned from brown to blue. And then, the blue colour became lighter by degrees and $BuPC_5V$ degraded after 72 h irradiation. On the other hand, the colour of the LB film of $BuPC_5$ turned from brown to green after 0.5 h irradiation. The green colour also became lighter and $BuPC_5$ degraded after 72 h irradiation. In the case of the cast films of $BuPC_5V$ and $BuPC_5$, no hydrogen was also evolved and the similar change of the colour was observed, respectively. To get some information about the blue coloured $BuPC_5V$ and the green coloured $BuPC_5$, the changes of the absorption spectra of $BuPC_5V$ (BuP-V^{2+}) and $BuPC_5$ (BuP) were measured. Fig. 4 shows the absorption spectra of the cast film of $BuPC_5$ before (Fig. 4 (a); the brown coloured $BuPC_5$)and after (Fig. 4 (b); the green coloured $BuPC_5$) 0.5 h irradiation in the presence of 0.1 mol dm^{-3} EDTA under argon atmosphere. When oxygen was purged after 0.5 h irradiation, the absorption spectrum was recovered to that before irradiation (data not shown). The changes of the colour between brown and green were reversible. This shows that the green coloured $BuPC_5$ does not belong to the products by the degradation but to the reduced form of $BuPC_5$ (BuP^-) which is produced owing to the reductive quenching of the photoexcited $BuPC_5$ by EDTA [19,29]. The fluorescence emission spectrum of the cast film of $BuPC_5$ dipped into argon-purged distilled water was measured in the absence and presence of EDTA. As the result, no quenching of the fluorescence emission of $BuPC_5$ by EDTA was observed, indicating that the photoexcited singlet state of porphyrin (^{1*}BuP) is not quenched by EDTA (reaction (1)). This shows that the reductive quenching of the photoexcited $BuPC_5$ by EDTA takes place via the triplet state of porphyrin (^{3*}BuP) (reaction (2)) [19,29].

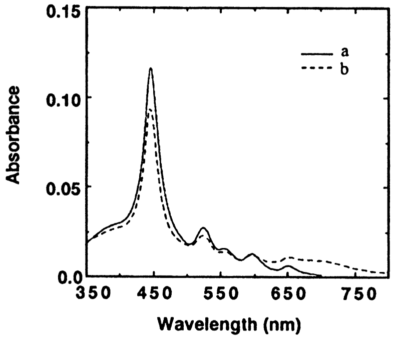

Fig. 4. The changes of the UV–VIS absorption spectra of the cast film of $BuPC_5$ on the glass plate (a) before and (b) after 0.5 h irradiation in an agron-purged aqueous solution containing 0.1 mol dm^{-3} EDTA.

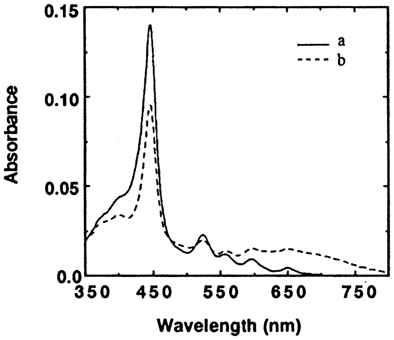

Fig. 5. The changes of the UV–VIS absorption spectra of the cast film of $BuPC_5V$ on the glass plate (a) before and (b) after 0.5 h irradiation in an agron-purged aqueous solution containing 0.1 mol dm^{-3} EDTA.

$$\mathrm{BuP} \xrightarrow{h\nu} {}^{1*}\mathrm{BuP} + \mathrm{EDTA} - \times \rightarrow \mathrm{BuP}^- + \mathrm{EDTA}_{\mathrm{ox}} \qquad (1)$$

$$\mathrm{BuP} \xrightarrow{h\nu} {}^{1*}\mathrm{BuP} \xrightarrow{\mathrm{isc}} {}^{3*}\mathrm{BuP} + \mathrm{EDTA} \rightarrow \mathrm{BuP}^- + \mathrm{EDTA}_{\mathrm{ox}} \qquad (2)$$

Fig. 5 shows the absorption spectra of the cast film of $BuPC_5V$ before (Fig. 5 (a); the brown coloured $BuPC_5V$) and after (Fig. 5 (b); the blue coloured $BuPC_5V$) 0.5 h irradiation. When oxygen was purged after 0.5 h irradiation, the absorption spectrum was recovered to that before irradiation (data not shown). The absorption spectrum (Fig. 5 (b)) is the sum of the absorption spectrum of the reduced form of porphyrin moiety and that of the reduced form of viologen moiety of $BuPC_5V$. In other words, the absorption spectrum (Fig. 5 (b)) belongs to BuP-V^+. At first, BuP-V^+ is produced. There are two processes of BuP-V^+ formation (reactions (3) and (4)). The intramolecular electron transfer takes place from the photoexcited singlet porphyrin to the bonded viologen (reaction (3)), since the fluorescence emission of porphyrin is quenched by the bonded viologen. Judging from the redox potentials of porphyrin and viologen (Table 1), the electron transfer is seemed to take place from the reduced form of porphyrin to the bonded viologen (reaction (4)). And then, the reduced form of porphyrin is produced owing to the reductive quenching by EDTA (reaction (5)).

$$\mathrm{BuP-V^{2+}\xrightarrow{h\nu}{}^{1*}BuP-V^{2+} \rightarrow BuP^{+}-V^{+}+EDTA \rightarrow BuP-V^{+}+EDTA_{ox}} \quad (3)$$

$$\mathrm{BuP-V^{2+}\xrightarrow{h\nu}{}^{1*}BuP-V^{2+}\xrightarrow{isc}{}^{3*}BuP-V^{2+}+EDTA \rightarrow BuP^{-}-V^{2+}+EDTA_{ox} \rightarrow BuP-V^{+}} \quad (4)$$

$$\mathrm{BuP-V^{+}\xrightarrow{h\nu}{}^{1*}BuP-V^{+}\xrightarrow{isc}{}^{3*}BuP-V^{+}+EDTA \rightarrow BuP^{-}-V^{+}+EDTA_{ox}} \quad (5)$$

Anyway, no hydrogen was produced in the absence of Pt and the reduced form of porphyrin was so unstable as to degrade less than 72 h irradiation.

3.8. *Photoinduced hydrogen evolution using Pt-loaded LB films*

Hydrogen was evolved using the Pt-loaded LB films of $\mathrm{BuPC_5V}$ and $\mathrm{BuPC_5}$. The colour of the Pt-loaded LB films of $\mathrm{BuPC_5V}$ and $\mathrm{BuPC_5}$ was not changed and maintained brown. This shows that the reduced forms of $\mathrm{BuPC_5V}$ and $\mathrm{BuPC_5}$ were not accumulated in the case of the Pt-loaded LB films. It is well known that Pt play a role as a catalyst which transfer electrons from the reduced forms of viologen ($\mathrm{V^+}$) to protons, and hydrogen was evolved (reactions (6) and (8)) [19]. However, even in the absence of viologen, hydrogen was produced using the Pt-loaded LB film of $\mathrm{BuPC_5}$, indicating that Pt also plays a role transferring electrons from the reduced forms of porphyrin to protons (reaction (7)). Fig. 6 shows the relationship between the irradiation time and the turnover number of porphyrin molecules for hydrogen production in the presence of EDTA in the aqueous phase. After 714 h irradiation, the turnover number of the $\mathrm{BuPC_5V}$ molecules attained 575. At this time, the colour of the Pt-loaded LB film of $\mathrm{BuPC_5V}$ maintained brown, but became lighter a little. On the other hand, the turnover number of the $\mathrm{BuPC_5}$ molecules attained 62 and then hydrogen evolution was stopped after 234 h irradiation. At this time, the colour of the Pt-loaded LB film of $\mathrm{BuPC_5}$ almost disappeared and $\mathrm{BuPC_5}$ degraded. The reduced form of porphyrin was unstable. However, the Pt-loaded LB film of $\mathrm{BuPC_5}$ became more stable comparing to the metal-free LB film which degraded less than 72 h irradiation. Since the reduced form of porphyrin ($\mathrm{BuP^-}$) was quenched by protons in the presence of Pt (reaction (7)), the degradation of porphyrin was repressed. In the case of the Pt-loaded $\mathrm{BuPC_5V}$, the reduced form of porphyrin ($\mathrm{BuP\text{-}V^{2+}}$) can be quenched by not only protons (reaction (9)) but also the bonded viologen via the electron transfer (reaction (4)). Besides, the production of $\mathrm{BuP\text{-}V^{2+}}$ was repressed, since $\mathrm{BuP^{+}\text{-}V^{+}}$ was produced competitively by the intramolecular electron transfer from the photoexcited singlet porphyrin to the bonded viologen (reaction (3)). As the result, the degradation of $\mathrm{BuPC_5V}$ was more repressed comparing to $\mathrm{BuPC_5}$, and hydrogen was evolved stably for a long period.

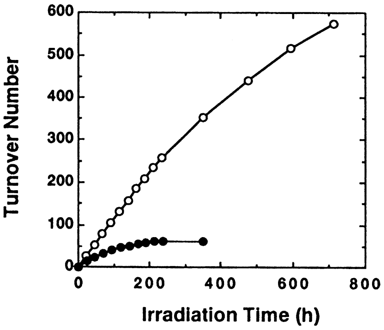

Fig. 6. Relationship between irradiation time and the turnover number of porphyrin molecules for hydrogen production when the glass plates modified with the LB films of $\mathrm{BuPC_5V}$ and $\mathrm{BuPC_5}$ were used to photoinduce the LB films of $\mathrm{BuPC_5V}$ and $\mathrm{BuPC_5}$ were used to photoinduced hydrogen evolution in an argon-purged aqueous solution containing 0.1 mol dm^{-3} EDTA: ○ $\mathrm{BuPC_5V}$, ● $\mathrm{BuPC_5}$.

$$\mathrm{V^{+}+H^{+}\xrightarrow{Pt}V^{2+}+\tfrac{1}{2}H_2} \quad (6)$$

$$\mathrm{BuP^{-}+H^{+}\xrightarrow{Pt}BuP+\tfrac{1}{2}H_2} \quad (7)$$

$$\mathrm{BuP-V^{+}+H^{+}\xrightarrow{Pt}BuP-V^{2+}+\tfrac{1}{2}H_2} \quad (8)$$

$$\mathrm{BuP^{-}-V^{2+}+H^{+}\xrightarrow{Pt}BuP-V^{2+}+\tfrac{1}{2}H_2} \quad (9)$$

The mechanism of hydrogen evolution using the Pt-loaded LB films of $\mathrm{BuPC_5}$ and $\mathrm{BuPC_5V}$ is shown as Schemes 1 and 2, respectively. In the case of $\mathrm{BuPC_5}$, one path to hydrogen production exists. On the other hand, three paths exist in the case of $\mathrm{BuPC_5V}$, so the initial rate of hydrogen production using $\mathrm{BuPC_5V}$(the turnover number frequency was 1.17 h^{-1}) was larger than that using $\mathrm{BuPC_5}$ (the turnover number frequency was 0.51 h^{-1}).

$$\mathrm{BuP\xrightarrow{h\nu}{}^{1*}BuP\xrightarrow{isc}{}^{3*}BuP\xrightarrow{+EDTA}BuP^{-}\xrightarrow{+H^{+},Pt}BuP+\tfrac{1}{2}H_2}$$

Scheme 1.

$$\mathrm{BuP-V^{2+}\xrightarrow{h\nu}{}^{1*}BuP-V^{2+}\rightarrow BuP^{+}-V^{+}\xrightarrow{+EDTA}BuP-V^{+}\xrightarrow{+H^{+},Pt}BuP-V^{2+}+\tfrac{1}{2}H_2}$$

$$\mathrm{BuP-V^{2+}\xrightarrow{h\nu}{}^{1*}BuP-V^{2+}\xrightarrow{isc}{}^{3*}BuP-V^{2+}\xrightarrow{+EDTA}BuP^{-}-V^{2+}\xrightarrow{+H^{+},Pt}BuP-V^{2+}+\tfrac{1}{2}H_2}$$

$$\mathrm{BuP-V^{2+}\xrightarrow{h\nu}{}^{1*}BuP-V^{2+}\xrightarrow{isc}{}^{3*}BuP-V^{2+}\xrightarrow{+EDTA}BuP^{-}-V^{2+}\rightarrow BuP-V^{+}\xrightarrow{+H^{+},Pt}BuP-V^{2+}+\tfrac{1}{2}H_2}$$

Scheme 2.

4. Conclusions

In the case of viologen-linked porphyrin, the reduced form of porphyrin is quenched by not only protons but also the bonded viologen. Besides, the production of the reduced porphyrin is repressed by the formation of the oxidized porphyrin owing to the intramolecular electron transfer via the photoexcited singlet porphryin. As the result, steady photoinduced hydrogen evolution is observed stably using the Pt-loaded LB film of viologen-linked porphyrin, since the degradation via the reduced form of porphyrin is repressed.

References

[1] S. Nishitani, N. Kurata, Y. Sakata, S. Misumi, J. Am. Chem. Soc. 105 (1983) 7771.
[2] B.A. Leland, A.D. Joran, P.M. Felker, J.J. Hopfield, A.H. Zewail, P.B. Dervan, J. Phys. Chem. 89 (1985) 5571.
[3] M.R. Wasielewski, M.P. Niemczyk, W.A. Svec, E.B. Pewitt, J. Am. Chem. Soc. 107 (1985) 5562.
[4] J.A. Schmidt, A.R. McIntosh, A.C. Weedon, J.R. Bolton, J.S. Connolly, J.K. Hurley, M.R. Wasielewski, J. Am. Chem. Soc. 110 (1988) 1733.
[5] M.R. Wasielewski, M.P. Niemczyk, D.G. Johnson, W.A. Svec, D.W. Minsek, Tetrahedron 45 (1989) 4785.
[6] D. Gust, T.A. Moore, A.L. Moore, D. Barrett, L.O. Harding, L.R. Makings, P.A. Liddell, F.C. DeSchryver, M. Van der Auweraer, R.V. Bensasson, M. Rougee, J. Am. Chem. Soc. 110 (1988) 321.
[7] S.J. Lee, J.M. DeGraziano, A.N. Macpherson, E.J. Shin, P.K. Kerrigan, G.R. Seely, A.L. Moore, T.A. Moore, D. Gust, Chem. Phys. 176 (1993) 321.
[8] G. Blondeel, D.D. Keukeleire, A. Harriman, L.R. Milgrom, Chem. Phys. Lett. 118 (1985) 77.
[9] J.D. Batteas, A. Harriman, Y. Kanda, N. Mataga, A.K. Nowak, J. Am. Chem. Soc. 112 (1990) 126.
[10] S. Noda, H. Hosono, I. Okura, Y. Yamamoto, Y. Inoue, J. Chem. Soc. Faraday Trans. 86 (1990) 811.
[11] I. Okura, H. Hosono, Inorg. Chim. Acta 189 (1991) 145.
[12] I. Okura, H. Hosono, J. Phys. Chem. 96 (1992) 4466.
[13] J. Hirota, I. Okura, J. Phys. Chem. 97 (1993) 6867.
[14] M. Fujihira, K. Nishiyama, H. Yamada, Thin Solid Films 132 (1985) 77.
[15] M. Fujihira, H. Yamada, Thin Solid Films 160 (1988) 125.
[16] M. Sakomura, M. Fujihira, Thin Solid Films 243 (1994) 616.
[17] Y. Cao, B.W. Zhang, W.Y. Qian, X.D. Wang, J.W. Bai, X.R. Xiao, J.G. Jia, J.W. Xu, Solar Energy Materials and Solar Cells 38 (1995) 139.
[18] H. Hosono, M. Kaneko, J. Photochem. Photobiol. A: Chem. 107 (1997) 63.
[19] A. Harriman, G. Porter, M.C. Richoux, J. Chem. Soc., Faraday Trans. 2 77 (1981) 833.
[20] A. Harriman, G. Porter, M.C. Richoux, J. Chem. Soc., Faraday Trans. 2 77 (1981) 1939.
[21] A. Harriman, M.C. Richoux, J. Photochem. 15 (1981) 335.
[22] I. Okura, N.K. Thuan, J. Chem. Soc., Faraday Trans. 1 76 (1980) 2209.
[23] I. Okura, S. Kusunoki, Inorg. Chim. Acta 54 (1981) 249.
[24] H. Hosono, T. Tani, I. Uemura, J. C. S. Chemical Communications 16 (1996) 1893.
[25] C. Franco, C. McLendon, Inorg. Chem. 23 (1984) 2370.
[26] K. Rosseau, D. Dolphin, Tetrahedron Lett. (1984) 4251.
[27] J.M. Lehn, J.P. Sauvage, Nouv. J. Chem. 1 (1977) 449.
[28] D.L. Akins, S. Ozcelik, H.R. Zhu, C. Guo, J. Phys. Chem. 100 (1996) 14390.
[29] K. Kalyanasundaram, J.A. Shelnutt, M. Graetel, Inorg. Chem. 27 (1988) 2820.