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Conformation-dependent photoinduced hydrogen evolution with Co(II)tetraphenylporphyrin–poly(L-glutamate) complex

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Abstract

Hydrogen production was performed under visible-light and combined UV/visible-light irradiation by using a system consisting of cobalt(II)tetraphenylporphyrin (CoTPP), methylviologen (MV^{2+}), ethylenediaminetetraacetic acid disodium salt and Pt-loaded poly(L-glutamate) (Poly(Glu)) in aqueous decylammonium chloride (DeAC) solution. CoTPP was solubilized in hydrophobic clusters of DeAC induced by its cooperative binding to Poly(Glu). About 0.15 and 3.5 μmol of hydrogen gas were obtained after irradiation for 3 h using visible-light and combined UV/visible-light, respectively. The rate of hydrogen evolution depended on the change in the conformation of Poly(Glu) induced by the cooperative binding with DeAC. An electron was transferred from CoTPP to MV^{2+} in the Poly(Glu)–DeAC complex system via the singlet state, finally resulting in the hydrogen evolution.

Keywords: Cobalt(II)tetraphenylporphyrin; Conformation dependence; Hydrogen production; Platinum colloid; Poly(L-glutamate); Cooperative binding

1. Introduction

Divalent cobalt forms numerous complexes of various stereo chemical types and Co(II)porphyrins can exist as four-, five-, and six-coordinate species. The nature of the axial coordination of cobalt in macrocyclic ligands has been extensively studied in order to understand the structure and functions of vitamin B_{12} synthetic oxygen carriers [1]. It has also been shown in a series of recent investigations that cobalt porphyrin molecules modified by attachment of ruthenium or osmium complexes to the periphery of the porphyrin ring exhibit the high catalytic activity for the electroreduction of O_2 directly to H_2O [2]. Co(II)tetraphenylporphyrin (CoTPP) has been used for the selective oxidation of aldehydes in organic solvents [3]. It is used for the selective oxidation of organic substrate owing to its molecular oxygen activating function [1,3]. It is also used as a catalyst in the reduction of cycloalkenes with diazo groups and in the reduction of carbon dioxide [4,5]. The photocatalytic application of CoTPP has not been reported in aqueous solution. However, a number of artificial photosynthetic systems have been reported on the hydrogen production, composed of four main components: a photosensitizer (chlorophyll a or zinctetraphenylporphyrin), an electron acceptor or relay, an electron donor and a platinum catalyst for the reduction of protons [6–9]. In such systems the electron transfer has been carried out by the use of lipid vesicles, micelle systems [9] and microemulsions [10].

CoTPP like any other metalloporphyrins has suitable properties for the conversion of solar energy owing to its absorption of ultraviolet (UV)/visible-light for the Soret band in the 380–450 nm and the red band in the 500–600 nm regions [1,11]. It is also very stable compared to the natural porphyrins, i.e., chlorophylls. However, this porphyrin has not been used as a photosensitizer in energy conversion systems owing to its insolubility in water and its aggregation in aqueous surfactant solutions below critical micelle concentrations. We selected this compound due to its numerous catalytic applications in organic solvents and also due to its high stability compared to the natural porphyrins. Preliminary hydrogen evolution experiments have been carried out using CoTPP, as the photosensitizer, solubilized in poly(L-glutamate) (Poly(Glu))–decylammonium chloride (DeAC) systems in which we observed conformation dependence of the rate of hydrogen evolution [12]. These

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preliminary results prompted us to investigate this system in more detail.

We therefore present here the detailed photoinduced hydrogen evolution reaction using CoTPP in Poly(L-Glu)–DeAC systems. Spectroscopic methods such as circular dichroism (CD), absorption, fluorescence emission and fluorescence lifetime spectroscopy were used to characterize the reaction medium composed basically of CoTPP solubilized in the Poly(Glu)–DeAC complex in the presence of methylviologen (MV^{2+}). Hydrogen production was carried out with CoTPP as a photosensitizer, methylviologen (MV^{2+}) as an electron acceptor, ethylenediaminetetraacetic acid disodium salt ($EDTA^{2-}$) as a sacrificial reagent and platinum colloid as a catalyst for the reduction of protons to hydrogen gas. The platinum colloid was loaded on an anionic polypeptide, Poly(Glu). This polypeptide not only stabilizes the platinum colloid but interacts electrostatically with cationic decylammonium chloride surfactant to form a polypeptide–surfactant complex. Some CoTPP is then solubilized in the polypeptide–surfactant complex solution by its hydrophobic interaction with the alkyl chains of DeAC, whereas some remain in the bulk solution as aggregates.

The effect of DeAC on the rate of hydrogen evolution was evaluated and related to the circular dichroism (CD) spectra of Poly(Glu) in aqueous DeAC solution. The effect of $EDTA^{2-}$ and MV^{2+} on the rate of hydrogen evolution was studied. The effect of MV^{2+} on the fluorescence intensity as well as the fluorescence lifetime of CoTPP was also investigated. An increase in the rate of hydrogen evolution occurred around the concentration of DeAC at which a conformational change in Poly(Glu) was indicated from CD spectra. About 0.15 and 3.5 μmol of hydrogen gas were evolved after 3 h of visible-light irradiation as well as combined UV/visible-light.

2. Experimental

2.1. Reagents

Cobalt(II)tetraphenylporphyrin (CoTPP) (Wako, 99%), methylviologen (MV^{2+}) (Sigma, 99%), hydrogen hexachloroplatinate(IV) hexahydrate ($H_2PtCl_6.6H_20$) (Wako, 98.5%) and sodium borohydride ($NaBH_4$) (Wako, 99%) were used as received. Poly(L-glutamate) (Peptide Institute, molecular weight: 8000) was dissolved in 0.06 M ($1\,M = 1\,mol\,dm^{-3}$) NaOH and dialyzed against redistilled water. The concentration of Poly(Glu) was determined by colloid titration with standard potassium poly(vinyl sulfate) solution [13]. Decylammonium chloride was prepared by titration of decylamine (Nacalai Tesque, 99%) with hydrochloric acid [14,15]. The resultant salt formed was recrystallized twice from ethanol and washed with ethyl ether. The other chemicals were analytical grade or the highest grade available. Laboratory deionized water was distilled twice and used throughout the experiment.

2.2. Spectroscopic characterization

Circular dichroism (CD) spectra were measured (190–650 nm range) with a JASCO J-720 spectropolarimeter and digitized data were transferred to a microcomputer and processed. Absorption and steady state fluorescence spectra (excitation wavelength: 420 nm) were recorded on a Shimadzu MPS-2000 spectrophotometer and Shimadzu RF-5000 spectrofluorophotometer, respectively. Fluorescence lifetime measurements were carried out using a Horiba NAES-1100 time-correlated spectrofluorometer. Fluorescence lifetimes were analyzed by deconvoluting the fluorescence decay curves by computer against the profile of the excitation lamp. After deconvolution, the fluorescence lifetimes (τ) were obtained by using Eq. (1),

$$I(t) = A \exp\left(\frac{-t}{\tau}\right) \quad (1)$$

where A is a pre-exponential factor.

2.3. Methods

The platinum colloid was prepared by reduction of hexachloroplatinate (IV) ions with sodium borohydride in aqueous Poly(Glu) solution in a mole ratio of 1:6:40. The presence of reduced platinum particles was confirmed by the disappearance of the 250 nm band attributed to platinum (IV) ions in the absorption spectrum [16]. For hydrogen evolution, a 10-cm^3 sample solution consisting of CoTPP (1×10^{-5} M), $EDTA^{2-}$ and MV^{2+} was placed in a Schlenk tube (30 cm^3). The concentration of Pt-colloid and that of the polypeptide were kept constant at 2.5×10^{-6} M and 1×10^{-4} M, respectively, throughout the experiment. The pH was not controlled, but was found to be about 6.5. The Schlenk tube was sealed with a silicone rubber septum. Ar gas was bubbled into the solution for 3 h after 2-min sonication to remove oxygen gas in the solution. The photoirradiation was carried out for 4 h under Ar atmosphere and magnetic stirring. The light source was provided by a 500 W xenon lamp and filtered through a water cell and an L-42 filter ($\lambda >$ ca. 400 nm). The reaction was also carried out in the absence of the filter. Gas sampling was performed at a constant time interval, usually 1 h, through a silicone septum using a 1 cm^3 gas syringe. The gas produced by photoirradiation was quantitatively analyzed by using a Shimadzu GC-8A gas chromatograph (detector: TCD, column packing: MS 5 Å, carrier gas: Ar). All measurements were carried out at room temperature (about 25 °C).

3. Results and discussion

3.1. Spectroscopic characterization

CD spectroscopy has been shown to be a useful instrumental technique in the characterization of random-coil, α-helix and β-sheet structures of polypeptides [17]. To investigate the effect of Poly(Glu) on the overall rate of hydrogen production, the CD spectra of Poly(Glu) was measured first in the presence of increasing concentrations of DeAC and later in the additional presence of CoTPP in the 190–250 nm region. The CD spectra of CoTPP were also measured for the same sample but in the Soret and Q-band region (400–650): we did not observe any induced CD. We also measured the CD spectra of solutions of Poly(Glu)

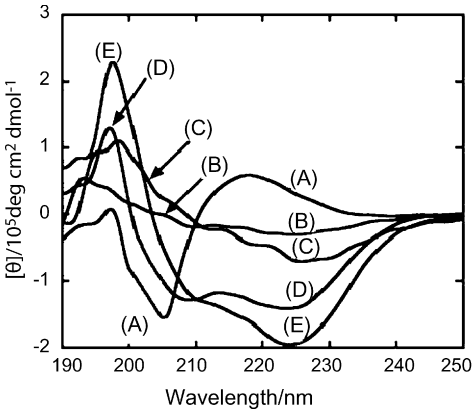

Fig. 1. [DeAC] dependence of CD spectra of CoTPP–Poly(Glu) systems in aqueous DeAC solutions. [DeAC]: (A) 0, (B) 0.2, (C) 0.3, (D) 0.4 and (E) 0.6 mM.

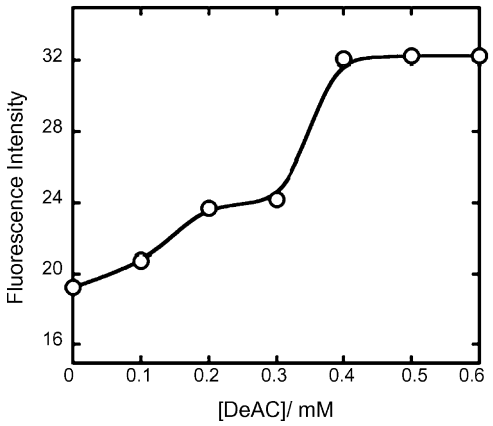

Fig. 2. Effect of [DeAC] on the fluorescence intensity of CoTPP in Poly(Glu)–DeAC aqueous solution.

in the presence of increasing concentrations of MV^{2+}: in this case no distinct induced CD was observed upon the addition of MV^{2+} to a solution of Poly(Glu) only (data not shown).

Fig. 1 shows the CD spectra of Poly(Glu) in aqueous DeAC solutions in the presence of CoTPP. The spectra vary from a spectrum characteristic of a random-coil (with a small positive band at 217 nm and a negative shoulder band around 200 nm, Fig. 1(A)) to a typical α-helix spectrum which has a double minimum at 209 and 222 nm (Fig. 1(D)). The spectral pattern in Fig. 1(A) is similar to that of a random-coil Poly(Glu) but with a weak interaction between Poly(Glu) and CoTPP in solution. This interaction may split the random-coiled Poly(Glu) band which usually occurs at 196 nm [14] into a strong negative band around 205 nm and a shoulder around 200 nm, respectively. Upon addition of DeAC to the Poly(Glu)–CoTPP solution (Fig. 1(D)), a strong electrostatic attraction occurs between the anionic Poly(Glu)–CoTPP between the anionic Poly(Glu) and cationic DeAC to form the Poly(Glu)–DeAC complex. This interaction is called the cooperative binding because it occurs at [DeAC] much lower than its critical micelle concentration (cmc = 67 mM) [18]. The cooperative binding induces the conformation change of Poly(Glu) from the random-coil to the α-helix. A similar interaction has been reported for Poly(Glu) in aqueous DeAC solutions as well as for other ionic polypeptides in aqueous surfactant ions of opposite charges [19–22]. The cooperative binding of surfactant ions to polypeptide ions of opposite charges arises from both the electrostatic attraction between the charged polypeptide and the oppositely charged surfactant and also the hydrophobic interaction between the bound surfactant ions which induce the formation of a micelle-like surfactant cluster [23]. The origin of another strong negative band at 205 nm in Fig. 1(A) is not clear at present, but might be due to an induced CD of CoTPP. The hydrophobic interaction created around the Poly(Glu) is anticipated to solubilize hydrophobic CoTPP.

The absorption spectra of CoTPP were measured in Poly(Glu)–DeAC complexes. It consists of a broad Soret band (with a maximum absorbance at 400 nm and a shoulder at 420 nm) and a weak Q-band around 530 nm. The broad absorption band of CoTPP is characteristic of mixtures containing both aggregated and monomeric porphyrin molecules [24]. The fluorescence spectrum of CoTPP in an aqueous Poly(Glu) solution (excited at 420 nm) gave a symmetrical peak around 620 nm. The fluorescence emission intensity observed is characteristic of monomeric porphyrin molecules. It is generally known that aggregated porphyrin molecules do not emit fluorescence or have very weak fluorescence intensities [25]. Upon addition of DeAC, the fluorescence emission intensity increases with increasing concentration of DeAC as shown in Fig. 2. Similar results have been reported for Chl in poly(L-glutamate, L-tyrosine)–cetyltrimetylammonium chloride systems [26].

A gradual increase in fluorescence lifetime was also observed upon addition of DeAC to a CoTPP–Poly(Glu) solution. For example, the fluorescence decay of CoTPP in the Poly(Glu)–DeAC complex ([DeAC] = 0.4 mM) showed a single component with a lifetime of 11.3 ns which is longer than that of a homogenous CoTPP/benzene solution (9.4 ns). The increase in fluorescence emission intensity and also the longer lifetime of CoTPP in the Poly(Glu)–DeAC complex occurs around the concentration of DeAC at which a conformation change is indicated from the CD spectra. These increase suggest the equilibrium between the aggregated porphyrin and monomeric species. Hence, CoTPP aggregates are gradually converted to the monomeric species as they are incorporated in the hydrophobic micelle-like clusters induced around the polypeptide.

To investigate the electron transfer reaction from CoTPP to MV^{2+} in the Poly(Glu)–DeAC complexes, we carried out fluorescence quenching experiments in the absence and presence of MV^{2+}. As a control experiment, the fluorescence intensity of CoTPP in the presence of MV^{2+} was measured in another polypeptide–surfactant complex, made up of poly(L-lysine) and sodium dodecylsulfate (vide infra). Fig. 3 shows the Stern–Volmer plots for the quenching of the fluorescence intensity of CoTPP by MV^{2+} in the Poly(Glu)–DeAC complex. The Stern–Volmer equation is given by Eq. (2).

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + K_{SV}[MV^{2+}] \quad (2)$$

Here I_0, I, τ_0, and τ denote the fluorescence intensities and fluorescence lifetimes of CoTPP in the absence and presence

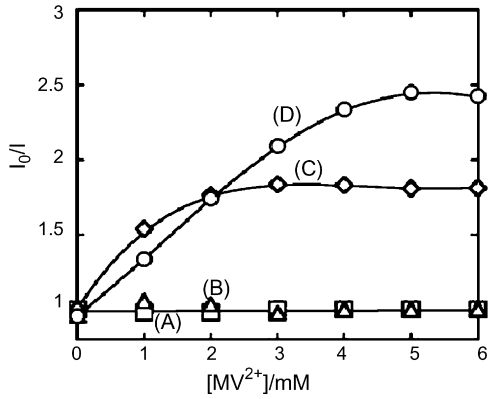

Fig. 3. Stern–Volmer type plots for the quenching of fluorescence intensity of CoTPP by MV^{2+} in the Poly(Glu)–DeAC system. [DeAC]: (A) 0, (B) 0.2, (C) 0.4 and (D) 0.6 mM.

of MV^{2+}, respectively. K_{SV} is the Stern–Volmer constant and $[MV^{2+}]$ is the quencher (MV^{2+}) concentration. The fluorescence intensity as well as the fluorescence lifetime of CoTPP was quenched by MV^{2+}, in the present system. In Fig. 3, we show plots of fluorescence intensity ratio (I_0/I), at varying concentrations of DeAC. We can see in Fig. 3 that the fluorescence quenching of CoTPP by MV^{2+} increases with increasing concentration of DeAC. Also the curves show the downward curvature at higher concentrations of MV^{2+}. The downward curves in Fig. 3 may be ascribed to protected quenching in which one portion of CoTPP is accessible to the quenching while the other is not [27–30]. The detailed mechanism is under study.

Solubilization of CoTPP into the hydrophobic clusters of DeAC also leads to the enhancement of the electron transfer, since the fluorescence quenching increased with increasing [DeAC] (Fig. 3). The quenched fluorescence intensity as well as the lifetime suggests that an electron is transferred from CoTPP to MV^{2+}, probably through the singlet excited state. The electrostatic attraction between the side-chain group ($–COO^-$) of Poly(Glu) and divalent MV^{2+} may results in the partial solubilization of MV^{2+} into the polypeptide–surfactant complex from the aqueous bulk phase. This interaction is weak since MV^{2+} alone did not induce a conformation change of Poly(Glu) from the CD studies of solutions containing Poly(Glu) and MV^{2+} only (data not shown). Hence, MV^{2+} and DeAC may compete for the –COO– group of Poly(Glu). This situation was also confirmed by the observation that the fluorescence quenching by MV^{2+} occurred when CoTPP was solubilized in Poly(Glu)–DeAC complexes in the presence of MV^{2+}, whereas no fluorescence quenching by MV^{2+} occurred when similar experiments were carried out in a complex formed between a cationic polypeptide, poly(L-lysine), and an anionic surfactant, sodium dodecylsufate, due to the repulsion between the side-chain charge ($–NH_3^+$) of poly(L-lysine) and MV^{2+}. The above juxtaposition may accounts for the downward curves and the electron transfer from CoTPP to MV^{2+}.

Generally, electron transfer from a porphyrin molecule to an electron acceptor molecule occurs via the triplet state [6,10]. However, in molecular assemblies such as the present system, Zn(II)porphine derivative/liposome systems,

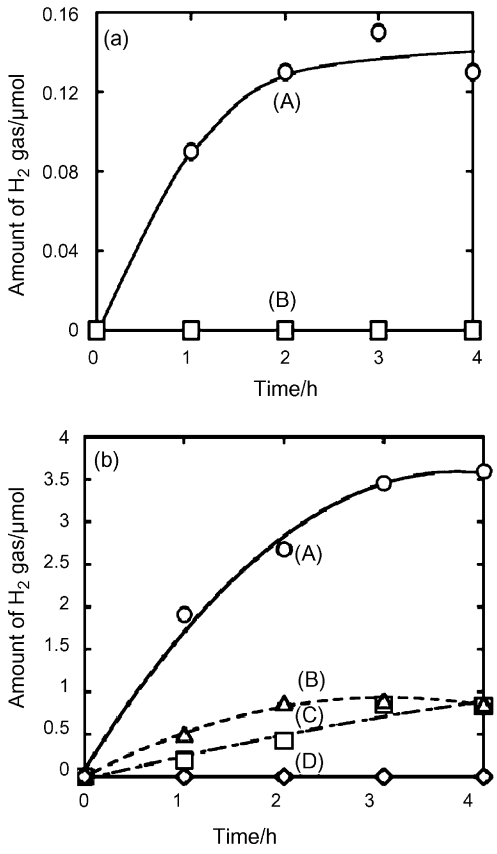

Fig. 4. Time course for hydrogen production under (a) visible and (b) UV/visible-light irradiation. CoTPP (1×10^{-5} M), Pt (2.5×10^{-6} M), MV^{2+} (2.5 mM), $EDTA^{2-}$ (10 mM), DeAC (0.4 mM) and Poly(Glu) (0.1 mM). (a) (A) All components and (B) absence of any of the components. (b) (A) All components, (B) without Pt-colloid, (C) without Poly(Glu) and (D) without $EDTA^{2-}$, CoTPP or MV^{2+}.

porphyrin/polymer systems and porphyrin–viologen systems as well as the photosynthetic system in nature, the electron donor and acceptor are close enough to each other so that photoinduced electron transfer can take place via the short-lived singlet excited state [6,10,31–35]. Since the singlet state is quenched in the present system, therefore, we suspect a similar situation in which MV^{2+} is closer to CoTPP in the polypeptide–surfactant complex, leading to the electron transfer from CoTPP to MV^{2+} (via the singlet and/or the triplet state) to form the methylviologen radical ($MV^{\bullet+}$). In turn a methylviologen cation radical transfers an electron to Pt protected by the Poly(Glu)–DeAC complex. The Pt then reduces hydrogen ions to give H_2 gas.

3.2. Photoinduced hydrogen evolution

Photoinduced hydrogen evolution was performed using a reaction mixture consisting of CoTPP (1×10^{-5} M), Pt-loaded Poly(Glu), MV^{2+} and EDTA (10 mM). Fig. 4 shows the time course for hydrogen evolution when the sample was irradiated with (a) visible and (b) UV/visible-light, respectively. The amount of hydrogen gas evolved initially increases with time and then becomes nearly constant. As can be seen in Fig. 3(C and D), the fluorescence quenching, i.e., the quenching due to

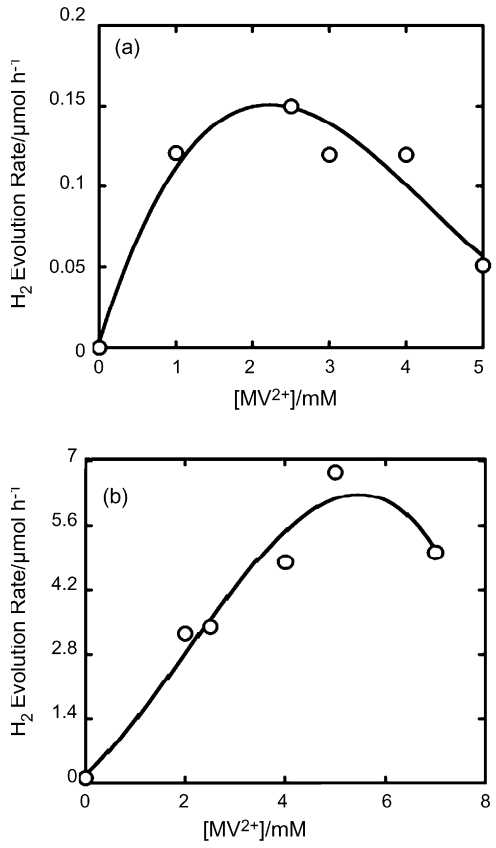

Fig. 5. Effect of $[MV^{2+}]$ on the rate of hydrogen production under visible-light irradiation. (a) Visible and (b) UV/visible-light irradiation. CoTPP (1×10^{-5} M), Pt (2.5×10^{-6} M), $EDTA^{2-}$ (1×10^{-2} M), DeAC (0.4×10^{-3} M) and Poly(Glu) (0.1×10^{-3} M).

the electron transfer from CoTPP to MV^{2+}, reaches the plateau. This may be responsible for the saturated hydrogen evolution (Fig. 4). Hydrogen gas was not evolved in the absence of either of CoTPP, MV^{2+} or $EDTA^{2-}$ upon irradiation under visible-light as well as UV/visible-light (Figs. 4 and 5), suggesting that these three components are essential for the production of hydrogen in this system and the possible route for electron transfer is via oxidative quenching by MV^{2+}. About 0.15 and 3.5 μmol of hydrogen gas was obtained after irradiation for 3 h using visible as well as combined UV/visible-light. The amount of hydrogen gas produced is larger when the sample was irradiated with UV/visible than when irradiated with visible-light ($\lambda >$ ca. 400 nm) only. Under visible-light irradiation, hydrogen gas was produced only when all the components were present (Fig. 4(a)), whereas under UV/visible-light irradiation, a little amount of hydrogen gas was produced even in the absence of Pt-colloid alone or in the absence of Poly(Glu) alone (Fig. 4(b)).

The $[MV^{2+}]$ dependence of the rate of hydrogen evolution in the presence of 4×10^{-4} M DeAC, 1×10^{-5} M CoTPP, 1×10^{-2} M $EDTA^{2-}$ and Pt-Poly(Glu) is shown in Fig. 5. The rate of hydrogen evolution increases until about 2.5 mM (using visible-light) (Fig. 5(a)) and about 5 mM (using UV/visible-light) (Fig. 5(b)) and then it decreases through the maximum value. The increase in the rate of hydrogen evolution at lower concentrations of MV^{2+} is in correlation with that MV^{2+} is closer to CoTPP in the polypeptide–surfactant complex, leading to the effective electron transfer probably via the short-lived singlet state. However, at higher concentrations of MV^{2+} (Fig. 5), the rate of hydrogen evolution decreases. The decrease in the hydrogen gas formation rate at higher MV^{2+} concentrations could be interpreted by the following reasons. A possible side reaction such as the hydrogenation of MV^{2+} in the presence of Pt-colloid may occur. Also the blue color of reduced $MV^{\bullet+}$ can acts as an inner filter and competes with the porphyrin for absorption of the incident light [6]. Finally the decrease in the rate of hydrogen production could also be caused by the formation of complex species such as CoTPP–MV^{2+} in the ground state, which is not photoreactive, since they do not yield photoredox products [27,36]. Although the first two factors can also account for the decreased rate of hydrogen evolution, we think that the dominant factor is the formation of ground state complex species such as CoTPP–MV^{2+}. Since MV^{2+} is partially incorporated in the Poly(Glu)–DeAC complex probably by bonding to the side chain (–COO^- group) of Poly(Glu), increase in the concentration of MV^{2+} might lead to an additional bonding to CoTPP complicating the electron transfer process. Charge transfer complexes have also been reported to be formed between electron donors (such as pyrene and porphyrins) and the electron acceptor, MV^{2+} [28,37]. Increase in the $[MV^{2+}]$ could also lead to ground-state charge transfer complexes between $EDTA^{2-}$ and MV^{2+} which have been reported to occur in alkaline and slightly acidic media [29,38,39]. The formation of ground state complexes (MV^{2+}–EDTA and/or CoTPP–MV^{2+}) complicates charge separation and hence decreases the rate of hydrogen production. Similar model systems for the study of hydrogen evolution, but in the absence of a polypeptide–surfactant complex, have been reported. Such model systems consist of zinc tetrakis(*N*-methylpyridium-4-aryl)porphyrin, $EDTA^{2-}$, MV^{2+} and Pt-colloid, and also zinc tetraphenylporphyrintetrasulfonate, MV^{2+}, triethanolamine and hydrogenase catalyst [6,10,40].

In Fig. 6, we show the $[EDTA^{2-}]$ dependence on the rate of hydrogen evolution. Hydrogen gas was not produced in the absence of $EDTA^{2-}$. Below 3 mM $EDTA^{2-}$ hydrogen gas was not evolved under visible-light irradiation. On the other hand, irradiating the sample solution with UV/visible-light resulted in trace amount of hydrogen gas below 3 mM $EDTA^{2-}$. Above 3 mM $EDTA^{2-}$, the rate of hydrogen evolution increases with increasing concentration of $EDTA^{2-}$. Hence in this system hydrogen gas was evolved only in excess of $EDTA^{2-}$ compared with the concentration of CoTPP. This observation may suggest that $EDTA^{2-}$ is not incorporated into the Poly(Glu)–DeAC complex, but is located at the interphase between the bulk phase and the complex phase as well as in the bulk phase. $EDTA^{2-}$ at the interphase serves as a sacrificial electron donor to the oxidized CoTPP.

The effect of [DeAC] on the rate of hydrogen evolution is shown in Fig. 7. An increase in the rate of hydrogen evolution is observed mostly at [DeAC] above 0.3 mM under visible as well as UV/visible-light irradiation. The results can be associated with the effect of [DeAC] on the CD spectra of Poly(Glu) (Fig. 1) and on the fluorescence intensity of CoTPP (Fig. 2). This remarkable increase in the rate of hydrogen gas observed above 0.3 mM

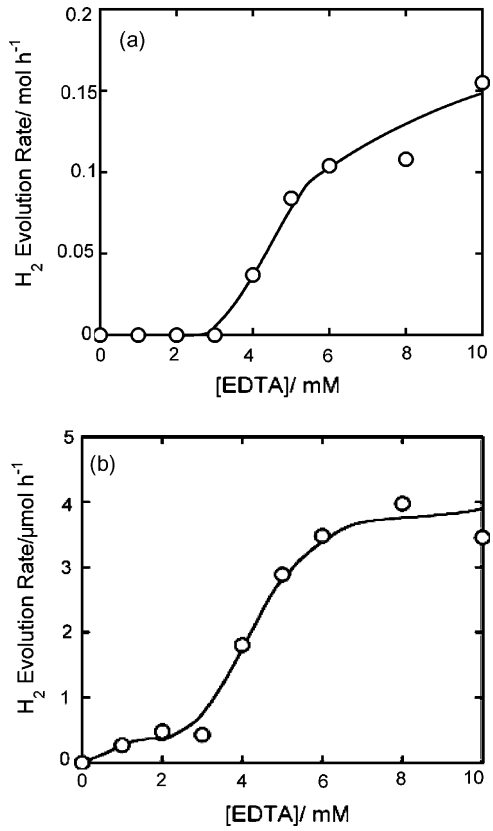

Fig. 6. Effect of $[EDTA^{2-}]$ on the rate of hydrogen production (a) visible and (b) UV/visible-light irradiation. CoTPP (1×10^{-5}), Pt (2.5×10^{-6}), Poly(Glu) (0.1×10^{-3} M) and MV^{2+}: (a) 2.5×10^{-3} M and (b) 5×10^{-3} M.

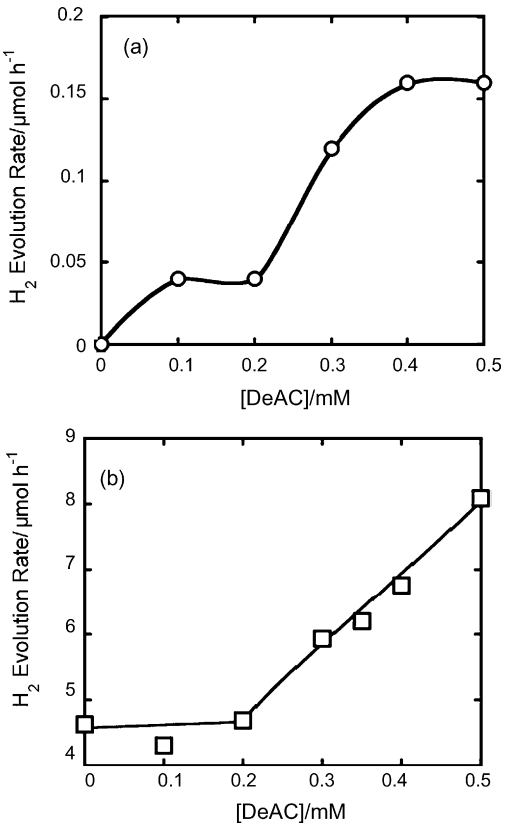

Fig. 7. Effect of [DeAC] on the rate of hydrogen production under (a) visible and (b) UV/visible-light irradiation. CoTPP (1×10^{-5}), Pt (2.5×10^{-6}), $EDTA^{2-}$ (1×10^{-2} M), Poly(Glu) (0.1×10^{-3} M) and MV^{2+}: (a) 2.5×10^{-3} M and (b) 5×10^{-3} M.

DeAC (Fig. 7) can be ascribed to two possible reasons: the electrostatic repulsion between cationic DeAC and reduced $MV^{\bullet+}$ and also the change in the conformation of Poly(Glu) from the random-coil to the α-helix. The former reason may be ruled out because in this system the concentration of DeAC (0–0.5 mM) is much lower than its cmc (67 mM) and the cooperative binding between the Poly(Glu) and DeAC is the dominant force in solution [14]. The increase in the rate of hydrogen evolution corresponds to [DeAC] at which a change in the conformation of Poly(Glu) was indicated from the CD spectra (Fig. 1). This fact strongly suggests that the rate of hydrogen production in this system depends on the change in the conformation of the

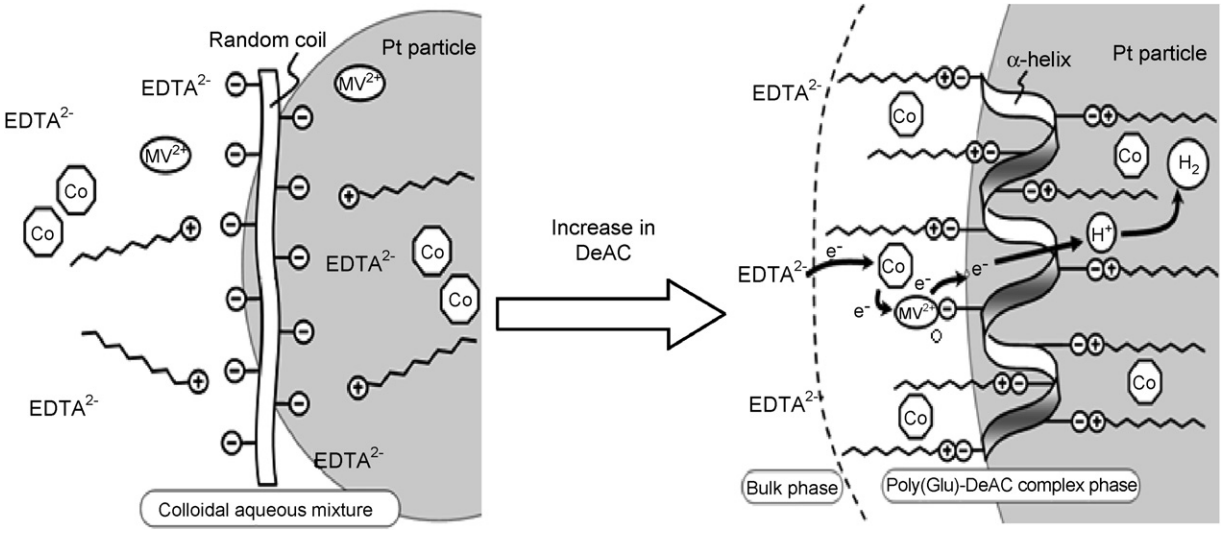

Fig. 8. Schematic representation depicting the probable mode of solubilization of CoTPP in the Poly(Glu)–DeAC complex and the hydrogen production reaction in the complex system.

polypeptide used. Therefore, the latter reason may be responsible for the observed increase (Fig. 7). The ordered structure of Poly(Glu) induced at higher concentrations of DeAC may contribute to a directional forward electron transfer. This may suppress back electron transfer and lead to an increase in the rate of hydrogen production.

Fig. 8 summarizes the plausible mode of solubilization of CoTPP in the complex and the reactions leading to the production of hydrogen gas. Initially we have a mixture containing random-coiled Poly(Glu) to which Pt is loaded and also insoluble CoTPP in an aqueous solution containing both MV^{2+} and excess $EDTA^{2-}$ in the presence of lower [DeAC]. In the presence of higher [DeAC], however, the cooperative binding of DeAC (above 0.3 mM) to Pt-loaded Poly(Glu) occurs. This leads to the solubilization of CoTPP in the micelle-like clusters of DeAC and the change in conformation of the Poly(Glu) from the random-coil to the α-helix. The interaction of MV^{2+} with the side chain group ($–COO^-$) of Poly(Glu) brings MV^{2+} closer to CoTPP. This closeness results in the electron transfer and the formation of the methylviologen radical. This radical transfers the electron to Pt-colloid which in turn is used to produce hydrogen gas. The conformational change of Poly(Glu) might also enhance the separation of charged species formed and leads to the increases of the hydrogen production. Excess $EDTA^{2-}$ found at the interphase between the bulk phase and the polypeptide–surfactant complex phase donates electrons to the oxidized CoTPP and thus CoTPP is regenerated.

4. Conclusion

CoTPP is solubilized in the hydrophobic clusters induced in the Poly(Glu)–DeAC complexes. The solubilized CoTPP can serve as a photosensitizer for the production of hydrogen. The presence of polypeptide–surfactant complexes enhances the rate of hydrogen production by solubilizing the photosensitizer and possibly enhancing the separation of charged species. The rate of hydrogen evolution is markedly dependent on the conformational change of Poly(Glu). It is important to use low [MV^{2+}] to avoid the formation of ground-state complexes that have a serious implication for the full understanding of typical water photoreduction systems.

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