# POLYMER VIOLOGEN AS A STABILIZING AGENT OF COLLOIDAL PLATINUM FOR PHOTOINDUCED ELECTRON TRANSFER REACTIONS

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## Summary

Photoinduced electron transfer and hydrogen evolution were investigated using colloidal platinum stabilized by viologen-pendant Nylon ($Pt-PV^{2+}$). From laser flash photolysis experiments, the $Pt-PV^{2+}$ was found to accept directly an electron from excited $ZnTMPyP^{4+}$, and the reverse electron transfer was retarded by the positive charge of the protecting polymer, while no net electron transfer was observed for colloidal platinum stabilized by poly(vinyl alcohol) ($Pt-PVA$). The rate of hydrogen evolution was measured via steady-state irradiation experiments in the presence of a sacrificial electron donor. The quantum yield of hydrogen production with a $Pt-PV^{2+}$ catalyst was higher than that with $Pt-PVA$ by a factor of 7 and reached 0.38.

## 1. Introduction

Of the large amount of research on the photochemical conversion of solar energy, hydrogen production by visible light in homogeneous solution is one of the major topics [1 - 11]. A typical artificial hydrogen generation system consists of a photosensitizer, electron mediator, sacrificial electron donor and catalyst such as colloidal platinum [6 - 11] or hydrogenase [12]. In order to increase the efficiency of hydrogen production, the separation of the photoinduced electron–hole pair is the most important factor. In the case of the colloidal platinum catalyst, several kinds of stabilizing agents, such as poly(vinyl alcohol) (PVA) and poly(ethylene glycol) and surfactants were used [6 - 11]. Matsuo and coworkers reported that polystyrene-based polymer viologen could be used as a protective agent and that the efficiency of hydrogen evolution in steady-state irradiation experiments increased [9]. By using a polymer viologen with a similar structure, Lee *et al.* [11] reported that the hydrogen production efficiency decreased contrary to the result reported by Matsuo. While they employed tris(bipyridyl)ruthenium (Ru-$(bpy)_3{}^{2+}$) as a photosensitizer, zinc porphyrin (zinc 5,10,15,20-tetra(*p-N-*

methylpyridyl)porphyrin, ZnTMPyP$^{4+}$) was also reported to be useful. The excited state of the zinc porphyrin has a long lifetime, and thus this seems a convenient compound for the study of photoinduced electron transfer reactions [4].

Recently we have synthesized a new type of polymer viologen (PV$^{2+}$) from aqueous Nylon and reported some results for the polymer as an electron relay in the system, with ZnTMPyP$^{4+}$ as a photosensitizer [13]. Compared with methyl viologen (MV$^{2+}$), the electron transfer efficiency from photosensitizer to viologen was improved for the polymer viologen [13]. The polymer viologen was also useful as a matrix polymer to immobilize hydrogenase [14]. In the present paper we report a study on the utility of this polymer viologen as a stabilizing agent for colloidal platinum. The kinetic analysis of the electron transfer process was investigated by the method of laser flash photolysis. The catalytic activity of platinum colloids stabilized by PV$^{2+}$ and PVA was tested by steady-state irradiation in the presence of triethanolamine (TEOA) as a sacrificial electron donor and MV$^{2+}$ as an electron mediator.

## 2. Experimental details

The PV$^{2+}$ used in the present study was prepared by the quaternization of the dimethylamino groups of aqueous Nylon (AQN; poly[imino(2-dimethylamino-1-oxo-hexamethylene)] from Toray Industries, Inc.) by 4-iodobutylmethyl viologen. The PV$^{2+}$ containing 5% and 25% pendant viologen are abbreviated as PV(5)$^{2+}$ and PV(25)$^{2+}$ respectively. The details for the synthesis of the viologen-pendant polymer have been described in a previous paper [13]. ZnTMPyP$^{4+}$ was synthesized using literature methods [15, 16].

Colloidal platinum was prepared by the method reported by Grätzel and coworkers [6]. The platinum colloid made by citrate reduction of H$_2$PtCl$_6$ followed by ion exchange was stabilized on the addition of the protective agent. The concentration of colloidal platinum was calculated by assuming that the reagent was completely transformed into colloidal metal. The weight of stabilizing agent used was twice that of the platinum. For comparison, PVA (No. 2040 of Kuraray Co. Ltd.) was employed instead of PV(5)$^{2+}$, PV(25)$^{2+}$ or AQN.

Laser flash photolysis was performed by means of a conventional laser system constructed with a DL-1200VXH laser head (Phase R Co. Ltd.). The 440 nm excitation light was obtained by lasing Coumarin 120 dye solution at an energy of about 2 mJ cm$^{-2}$ (pulse)$^{-1}$ and a duration time of 0.5 $\mu$s. For the measurement of transient absorption, a 150 W xenon lamp, a 200 mm monochromator (Ritsu Applied Optics) and a TCH-1000S transient digital memory (Riken Denshi) were used. The steady-state irradiation experiment was performed with 3 ml argon-bubbled sample solution, employing a 300 W tungsten lamp and a 440 nm interference filter of 10 nm

bandwidth. The flux of the incident light was measured by using a ferri-oxalate actinometer [17]. The amount of hydrogen produced was measured using argon as a carrier gas by means of a gas chromatograph equipped with a column containing a 5A molecular sieve, and a thermal-conductivity detector.

## 3. Results and discussion

### 3.1. Reaction of the triplet excited state of ZnTMPyP$^{4+}$

The reaction of excited ZnTMPyP$^{4+}$ with MV$^{2+}$ is well characterized as an electron transfer from the triplet state of ZnTMPyP$^{4+}$ (*ZnTMPyP$^{4+}$) to MV$^{2+}$ [16, 18].

$$*\text{ZnTMPyP}^{4+} + \text{MV}^{2+} \xrightarrow{k_q} \text{ZnTMPyP}^{5+} + \text{MV}^{\overset{+}{\cdot}} \tag{1}$$
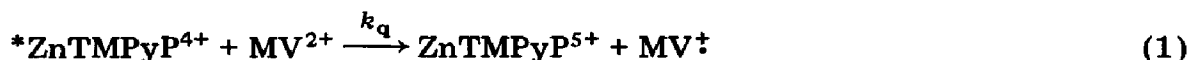
The deactivation rate of *ZnTMPyP$^{4+}$ was measured by the decay of the 470 nm triplet–triplet absorption band. The decay profiles in the presence of 0.1 - 1.0 mM MV$^{2+}$ were represented by exponential curves. The bi-molecular quenching rate constant was calculated to be $k_q = 2.9 \times 10^7$ M$^{-1}$ s$^{-1}$ at pH 6.9 and ionic strength $\mu = 0.1$ M, which is consistent with the value reported in ref. 18. The electron transfer reaction was confirmed by observing the growing absorbance of MV$^{\overset{+}{\cdot}}$ at 600 nm and of ZnTMPyP$^{5+}$ and MV$^{\overset{+}{\cdot}}$ at 397 nm.

The reaction of *ZnTMPyP$^{4+}$ with colloidal platinum was also moni-tored. The decay profile was exponential and was analysed by using pseudo-first-order reaction kinetics. The increase in the decay rate is shown in Table 1. In the case of Pt–PVA, growth of the 397 nm absorption of ZnTMPyP$^{5+}$ was not observed, indicating that net electron transfer does not occur. That is, *ZnTMPyP$^{4+}$ is quenched by the reaction

$$*\text{ZnTMPyP}^{4+} + \text{Pt–PVA} \xrightarrow{k_q} \text{ZnTMPyP}^{4+} + \text{Pt–PVA} \tag{2}$$
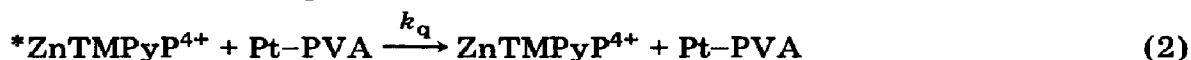
When the colloidal platinum was stabilized by polymer viologen the value of $k_q$ was greater than that for Pt–PVA and the 600 nm absorption

TABLE 1

Decay rate $k_q$[Pt] for the triplet state of ZnTMPyP$^{4+}$ with colloidal platinum

| Colloidal platinum | $k_q$[Pt] ($\times 10^3$ s$^{-1}$) |
|---|---|
| Pt–PVA | 0.85 |
| Pt–PV(5)$^{2+}$ | 4.6 |
| Pt–PV(25)$^{2+}$ | 5.7 |

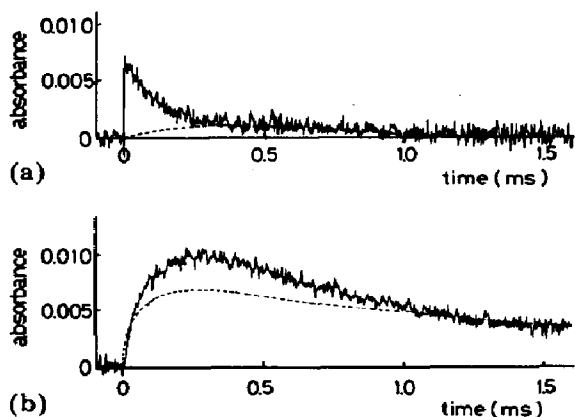[ZnTMPyP$^{4+}$] = 5.7 $\mu$M; [MV$^{2+}$] = 1 mM; [colloidal Pt] = 0.13 mM; ionic strength, 0.05 M; pH, 6.9.

Fig. 1. Time profiles for absorption of transient species appearing in the laser-excited solution of ZnTMPyP$^{4+}$ and Pt–PV(5)$^{2+}$. (a) Measured at 600 nm: — — —, calculated by subtraction of the contribution of *ZnTMPyP$^{4+}$, showing the transient absorption of PV(5)$^{+}_{\bullet}$. (b) Measured at 397 nm: — — —, contribution of ZnTMPyP$^{5+}$.

for PV$^{+}_{\bullet}$ was observed to grow as shown in Fig. 1(a). This observation indicates that the electron transfers from *ZnTMPyP$^{4+}$ to the viologen group of the stabilizing agent:

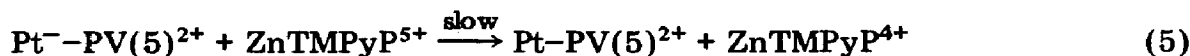$$\text{*ZnTMPyP}^{4+} + \text{Pt–PV}^{2+} \longrightarrow \text{ZnTMPyP}^{5+} + \text{Pt–PV}^{+}_{\bullet} \qquad (3)$$

While the absorbance at 600 nm disappears about 1.5 ms after the flash, the transient absorption at 397 nm (Fig. 1(b)) remains. In the cases of ZnTMPyP$^{4+}$–PV$^{2+}$ and ZnTMPyP$^{4+}$–MV$^{2+}$–Pt–PV$^{2+}$, the absorption at 600 nm showed a growth and decay similar to that at 397 nm.

These transient absorptions observed for the ZnTMPyP$^{4+}$–Pt–PV$^{2+}$ system may be analysed into contributions from three chemical species, i.e. *ZnTMPyP$^{4+}$, ZnTMPyP$^{5+}$ and PV$^{+}_{\bullet}$. The difference $\Delta\epsilon$(*ZnTMPyP)$^{4+}$ between the molar extinction coefficients ($\Delta\epsilon$(*ZnTMPyP$^{4+}$) = $\epsilon$(*ZnTMPyP$^{4+}$) − $\epsilon$(ZnTMPyP$^{4+}$)) was estimated from the measurement of the transient spectrum and was calibrated with the values reported for wavelengths longer than 640 nm [19]. The value of $\Delta\epsilon$(ZnTMPyP$^{5+}$) (i.e. $\epsilon$(ZnTMPyP$^{5+}$) − $\epsilon$(ZnTMPyP$^{4+}$)) was estimated from the spectrum reported in ref. 20. The molar extinction coefficient of PV(5)$^{+}_{\bullet}$ was measured by reduction with Na$_2$S$_2$O$_4$. Thus the values obtained for the 600 nm absorption were $\Delta\epsilon$(*ZnTMPyP$^{4+}$) = 2400 ± 1000 M$^{-1}$ cm$^{-1}$, $\Delta\epsilon$(ZnTMPyP$^{5+}$) = 200 ± 500 M$^{-1}$ cm$^{-1}$ and $\epsilon$(PV$^{+}_{\bullet}$) = (1.0 ± 0.2) × 10$^4$ M$^{-1}$ cm$^{-1}$. Therefore, the observed transient absorption at 600 nm is considered to consist of *ZnTMPyP$^{4+}$ and PV$^{+}_{\bullet}$. The value of $\Delta\epsilon$(*ZnTMPyP$^{4+}$) at 470 nm was (4.6 ± 0.5) × 10$^4$ M$^{-1}$ cm$^{-1}$ and predominates over $\epsilon$(PV$^{+}_{\bullet}$) ($\epsilon$(PV$^{+}_{\bullet}$) = 1800 M$^{-1}$ cm$^{-1}$). Therefore, from the decay profile at 470 nm, the concentration of the triplet states can be calculated as a function of the time after the flash. Thus the time profile of PV$^{+}_{\bullet}$ absorption at 600 nm was obtained by subtracting the contribution of *ZnTMPyP$^{4+}$ from the decay profile at 600 nm and this is shown by the broken line in Fig. 1(a).

The values of the molar extinction coefficient at 397 nm were $\Delta\epsilon(\text{*Zn-TMPyP}^{4+}) = -400 \pm 1000$ $\text{M}^{-1}$ $\text{cm}^{-1}$, $\Delta\epsilon(\text{ZnTMPyP}^{5+}) = 7000 \pm 2000$ $\text{M}^{-1}$ $\text{cm}^{-1}$ and $\epsilon(\text{PV}^{+}) = (3.1 \pm 0.5) \times 10^{4}$. By using these values and the concentrations of $\text{*ZnTMPyP}^{4+}$ and $\text{PV}^{+}$ obtained above the contribution of ZnTMPyP$^{5+}$ to the 397 nm absorbance was calculated and is plotted in Fig. 1(b). For example, from Figs. 1(a) and 1(b), at 0.3 ms after the flash the concentrations of ZnTMPyP$^{5+}$ and PV(5)$^{+}$ were $(1.0 \pm 0.4) \times 10^{-6}$ M and $(8 \pm 3) \times 10^{-8}$ M respectively. Here, the initial concentration of $\text{*ZnTMPyP}^{4+}$ was also calculated to be $(2.7 \pm 1.4) \times 10^{-6}$ M from Fig. 1(a).

These observations clearly show that the electron transfer reaction (4) from PV(5)$^{+}$ to colloidal platinum occurs very efficiently and that the transferred electron remains on the platinum without recombination with ZnTMPyP$^{5+}$ (reaction (5)):

$$\text{Pt--PV(5)}^{+} \xrightarrow{\text{rapid}} \text{Pt}^{-}\text{--PV(5)}^{2+} \tag{4}$$

$$\text{Pt}^{-}\text{--PV(5)}^{2+} + \text{ZnTMPyP}^{5+} \xrightarrow{\text{slow}} \text{Pt--PV(5)}^{2+} + \text{ZnTMPyP}^{4+} \tag{5}$$

This experimental evidence for slow electron transfer is explained by the influence of positive charges in the stabilizing polymer. In other words, when colloidal platinum is stabilized by cationic polymer viologen, the charge separation from illuminated ZnTMPyP$^{4+}$ is greatly improved. An effect similar to that of PV(5)$^{2+}$ was observed for colloidal platinum stabilized by PV(25)$^{2+}$.

## 3.2. Reactions with reduced $MV^{2+}$

Colloidal platinum was usually used with an electron mediator such as MV$^{2+}$. Therefore, we tested the utility of Pt--PV$^{2+}$ in the reactions with reduced methyl viologen (MV$^{+}$) formed by electron transfer from flash-excited ZnTMPyP$^{4+}$ as stated above. When colloidal platinum was absent from the solution, the decay of MV$^{+}$ observed at 600 nm followed second-order kinetics. This decay corresponds to reverse electron transfer from MV$^{+}$ to oxidized porphyrin.

$$\text{MV}^{+} + \text{ZnTMPyP}^{5+} \xrightarrow{k_{r}} \text{MV}^{2+} + \text{ZnTMPyP}^{4+} \tag{6}$$

From the kinetic plot, the rate constant $k_{r}$ was determined to be $1.6 \times 10^{9}$ $\text{M}^{-1}$ $\text{s}^{-1}$, which agrees with the value of $1.34 \times 10^{9}$ $\text{M}^{-1}$ $\text{s}^{-1}$ reported in ref. 21.

On the addition of Pt--PVA the decay became rapid, indicating that electron transfer occurs from MV$^{+}$ to colloidal platinum. As had been reported by Harriman et al. [20], the second-order kinetic plots for MV$^{+}$ did not lie on a single straight line. Although the decay with colloidal platinum is expressed by rather complicated reaction kinetics [20], the apparent second-order rate constant is given in Table 2. The rate constants were

TABLE 2

Apparent rate constant $k_r$ for the bleaching of MV$\overset{+}{\cdot}$ measured at 600 nm and 397 nm in laser flash experiments

| Solute | $k_r$ ($\times 10^9$ M$^{-1}$ s$^{-1}$) | |
|---|---|---|
| | 600 nm | 397 nm |
| ZnTMPyP$^{4+}$ + MV$^{2+}$ | 1.6 | 1.6 |
| ZnTMPyP$^{4+}$ + MV$^{2+}$ + Pt–PVA | 3.3[a], 7.9[b] | 3.6[a], 8.3[b] |
| ZnTMPyP$^{4+}$ + MV$^{2+}$ + Pt–PV(5)$^{2+}$ | 2.1 | 2.2 |

[ZnTMPyP$^{4+}$] = 4.7 $\mu$M; [MV$^{2+}$] = 1 mM; [colloidal Pt] = 0.13 mM.
[a]Obtained from the initial decay.
[b]Obtained from the decay after 0.7 ms.

also determined from the decay of the 397 nm absorbance and these are listed in Table 2. Since the absorption at 397 nm has contributions from both ZnTMPyP$^{5+}$ and MV$\overset{+}{\cdot}$ as mentioned above, the agreement between the rate constants measured at the two wavelengths means that ZnTMPyP$^{5+}$ decays simultaneously with MV$\overset{+}{\cdot}$. This observation agrees with the reported result that electrons transferred to colloidal platinum disappear by rapid reaction with ZnTMPyP$^{5+}$ [20].

For the reaction with Pt–PV$^{2+}$, the decay profile of MV$\overset{+}{\cdot}$ was expressed by second-order kinetics. The reaction rate constant was not very much greater than that of MV$^{2+}$ alone, indicating that the electron transfer from MV$\overset{+}{\cdot}$ to Pt–PV$^{2+}$ occurs less easily than for the case of Pt–PVA. This difference in efficiency for the electron transfer is explained by the cationic nature of the protecting polymer as has been pointed out for colloidal platinum stabilized by cationic polysoap [6] or cationic surfactants [20].

## 3.3. Hydrogen production with a sacrificial electron donor

The catalytic activities of three kinds of colloidal platinum (Pt–PVA, Pt–AQN and Pt–PV(5)$^{2+}$) were compared. In each colloidal solution Zn-TMPyP$^{4+}$, MV$^{2+}$ and TEOA were added as a photosensitizer, an electron mediator and a sacrificial reagent respectively. The amount of hydrogen produced increased linearly for several hours at least.

Figure 2 shows the pH dependence of the quantum yield. At high pH the quantum yield decreases because of the shift of the redox potential $E(H^+/\frac{1}{2}H_2)$. The decrease in the quantum yield at acidic pHs is explained by the reaction of MV$\overset{+}{\cdot}$ with oxidized TEOA [5]. The pH profile shows a rather narrower maximum than that reported for the Ru(bpy)$_3^{2+}$–MV$^{2+}$–ethylenediaminetetraacetic acid system [22]. However, the maximum pH value of 5.0 is almost the same as that reported in ref. 22.

The rates of hydrogen evolution and the quantum yields are given in Table 3. The higher activity of Pt–PV(5)$^{2+}$ compared with Pt–AQN is not explained by the increase in total viologen concentration, because the concentration of pendant viologen in the protective polymer was less than

TABLE 3

Reaction rate $v$ and quantum yield $\Phi(\frac{1}{2}H_2)$ for the production of hydrogen, obtained from steady-state irradiation experiments

| Catalyst | [Colloidal Pt] ($\mu$M) | pH | $v$ ($\mu$mol h$^{-1}$) | $\Phi(\frac{1}{2}H_2)$ |
|---|---|---|---|---|
| Pt–PVA | 12 | 5.5 | 0.22 | 0.016 |
| Pt–AQN | 12 | 5.0 | 0.68 | 0.050 |
| Pt–PV(5)$^{2+}$ | 12 | 5.0 | 1.65 | 0.12 |
| Pt–PV(5)$^{2+}$ | 29 | 5.0 | 5.1 | 0.38 |

Irradiation with a 300 W tungsten lamp through a 440 nm bandpass filter; volume of sample solution, 3 ml; [ZnTMPyP$^{4+}$] = 4.3 $\mu$M; [MV$^{2+}$] = 4.3 mM; [TEOA] = 34 mM.
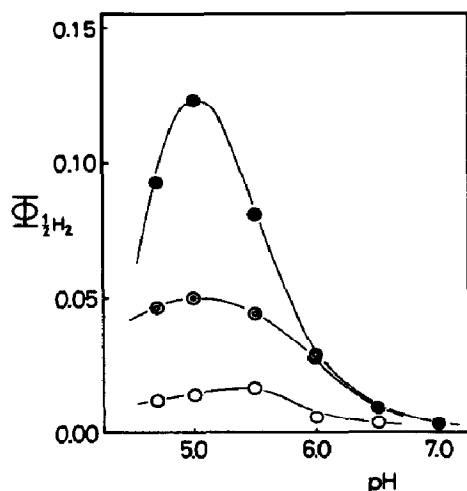


Fig. 2. pH dependence of the quantum yield for hydrogen evolution: ○, Pt–PVA, ◉, Pt–AQN; ●, Pt–PV(5)$^{2+}$; 4.3 $\mu$M ZnTMPyP$^{4+}$, 4.3 mM MV$^{2+}$, 34 mM TEOA and 12 $\mu$M colloidal platinum were contained in 0.04 M acetate or phosphate buffer.

1 $\mu$M. The catalytic activity of Pt–PV(5)$^{2+}$ is higher than that of Pt–PVA by a factor of 7. The quantum yield for hydrogen production was found to increase with the amount of colloidal platinum, as has been already reported [7]. When 29 $\mu$M Pt–PV(5)$^{2+}$ were used the quantum yield reached 0.38. This value is comparable with 0.3 reported by Harriman et al. as a maximum value obtained for the initial irradiation [18]. This characteristic of Pt–PV(5)$^{2+}$ is consistent with the result from laser flash experiments: the electrons transferred to colloidal platinum are attracted by the positive charges on the viologen group of the stabilizing polymer, while the forward electron transfer from MV$^{\ddagger}$ to Pt–PV$^{2+}$ is retarded by the positive charges. In contrast to the case of Pt–PV$^{2+}$, the forward electron transfer from MV$^{\ddagger}$ to Pt–PVA is rapid, but net electron transfer was not observed because of a rapid back electron transfer [20].

Judging from the results of both the laser flash and the steady-state experiments, it may be concluded that the efficiency of the hydrogen

production is controlled by the attraction of the electrons to the colloidal platinum. For this reason, polymer-viologen-stabilized colloidal platinum is found to be useful in the catalysis of photoinduced production of hydrogen from water.

## Acknowledgment

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