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Photoinduced hydrogen generation from water-insoluble polymer photosensitizer films

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Photoinduced hydrogen generation from functional polymer films with photosensitizing ability, in which ruthenium(II) complexes are coordinated to imidazolyl residues on partially quaternized poly(1-vinylimidazole) (RuQPIm), have been investigated in aqueous solution. This system consists of RuQPIm free-standing films having various degrees of quaternization, electron relays such as 1,1′-dimethyl-4,4′-bipyridinium (MV^{2+}) and 1,1′-dioctyl-4,4′-bipyridinium (C_8V^{2+}) dications, the sacrificial donor triethanolamine (TEOA), and bis(2,2′-bipyridine)platinum(II) ($[Pt(bpy)_2]^{2+}$) as a catalyst. In MV^{2+}, hydrogen generation was observed with light irradiation ($\lambda > 440$ nm) under an argon atmosphere. The maximum volume of hydrogen generated decreased with increasing degree of quaternization. This was attributed to a decrease in the efficiency of photosensitized charge separation induced by increasing electrostatic repulsion, being supported by the fact that the volume of hydrogen generated was increased by the addition of sodium chloride (NaCl). For C_8V^{2+} the volume of hydrogen generated was smaller than that for MV^{2+}, although the efficiency of charge separation was highly larger than that for MV^{2+}. Since the C_8V^{2+} species interacted with the polymer film through hydrophobic interaction, the $C_8\dot{V}^+$ species formed by electron transfer from the photoexcited ruthenium(II) complex to C_8V^{2+} hardly diffused into the bulk, leading to inhibition of the reaction between $C_8\dot{V}^+$ and the positively charged platinum catalyst. Therefore, it was clear that the diffusion of viologen radical species into the bulk is an important factor for the hydrogen generation reaction. Further, it was found that these polymer films have excellent stability for the present reaction. © 1997 Elsevier Science Ltd. All rights reserved.

(**Keywords: photoinduced hydrogen generation; polymer photosensitizer; polymer-bound ruthenium(II) complex**)

INTRODUCTION

In the photosynthesis of green plants, sunlight energy is effectively converted into chemical and electrochemical energies[1]. Of late there has been considerable interest in research to mimic the natural photosynthesis process[2,3] and many attempts to construct artificially the photosynthesis of green plants. In relation to such artificial photosynthesis systems, many photoinduced hydrogen-generation systems have been investigated[4-9].

Many photosensitizers such as metalloporphyrins[7,9], metallophthalocyanines[10] and tris(2,2′-diimine)ruthenium(II) complexes have been used in photosensitized charge separation systems and have attracted much attention for application to solar energy conversion[11,12]. In particular, tris(2,2′-bipyridine)ruthenium(II), $[Ru(bpy)_3]^{2+}$, has been widely employed as a photocatalyst for water cleavage and as a photosensitizer in many hydrogen-generation systems[13-16].

Macromolecular ruthenium(II) complexes with poly(4-vinylpyridine) and poly(1-vinylimidazole) as polymer ligands have been investigated, and application to polymer catalysts, photosensitizers and molecular diodes has been proposed[17-19]. However, there are few reports on the application of these photosensitizers to photoinduced hydrogen generation. Recently, we have reported the photosensitizing abilities of new ruthenium(II)-complex-containing polymers such as partially quaternized poly(1-vinylimidazole)-bound ruthenium(II) complexes (RuQPIm) in methanol[20,21]. These investigations indicated that the RuQPIms are excellent photosensitizers and that the sensitizing ability is readily varied by changing the primary structure of the polymer backbone, via the degree of quaternization, and the length of alkyl side chains on the polymer backbone. Furthermore, it was found that these metallopolymers are readily prepared as water-insoluble polymer films that also have photosensitizing abilities[22].

A typical scheme for photoinduced hydrogen generation is illustrated in *Scheme 1*, where P and *P are photosensitizers in their ground and photoexcited states, A is an electron relay (electron acceptor), Cat is a catalyst such as platinum or gold, and D is a sacrificial donor. The key photochemically-driven step is oxidation of the photoexcited sensitizer, which is accomplished by electron transfer to A which acts as an electron relay, usually in the presence of a catalyst. The singly oxidized sensitizer is then scavenged to its original neutral state by a sacrificial electron donor, which is an irreversible electron donor. The radical anion produced upon oxidation of the sensitizer transfers an electron to water in the presence of a catalyst, thus producing hydrogen. In this paper, new hydrogen-generation systems with water-insoluble polymer-bound ruthenium(II) complex films as photosensitizers were investigated in aqueous solution.

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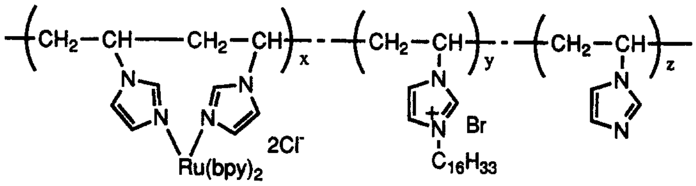
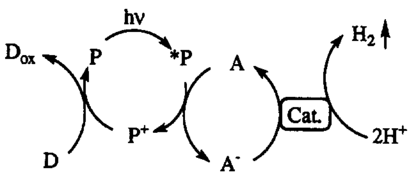


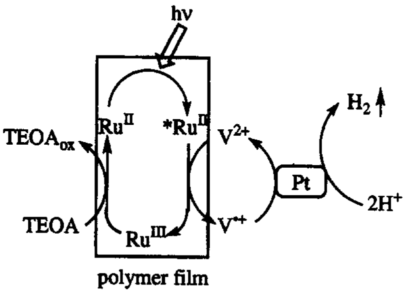
Figure 1 Chemical structure of RuQPIm

Table 1 Degree of coordination and quaternization and thickness of films

Metallopolymer	*x*	*y*	*z*
RuQPIm-19	0.0033	0.1915	0.8052
RuQPIm-25	0.0033	0.2531	0.7436
RuQPIm-38	0.0033	0.3821	0.6146
RuQPIm-44	0.0033	0.4404	0.5563



Scheme 1



Scheme 2

EXPERIMENTAL

Materials

All reagents such as 4,4′-bipyridine, 2,2′-bipyridine and alkyl bromide (commercially available guaranteed reagents) were used without further purification. 2,2′-Azobisisobutyronitrile was purified by recrystallization from methanol at 30°C. 1,1′-Dimethyl-4,4′-bipyridinium chloride was purchased from TCI Co., Ltd and recrystallized from methanol. 1,1′-Dioctyl-4,4′-bipyridinium bromide was prepared by refluxing 4,4′-bipyridine and 1-bromooctane in dimethylformamide (DMF) for 8 h and purified by recrystallization from methanol. Characterization was carried out by means of Fourier transfrom infra-red (*FT*i.r.) and ^{1}H nuclear magnetic resonance (n.m.r.) spectroscopies and elemental analysis. Poly(1-vinylimidazole) (PIm) was prepared by a free-radical polymerization of freshly distilled 1-vinylimidazole with 2,2′-azobisisobutyronitrile as initiator at 60°C in EtOH for 10 h and purified by reprecipitation from methanol into acetone. The average molecular weight of PIm determined by viscosity measurement was about 100 000. PIm-bound ruthenium(II) complexes were synthesized according to the literature[18].

Partially quaternized PIm-bound ruthenium(II) complexes (RuQPIm) were prepared by a method described elsewhere[20]. Polymer films were prepared by the casting method. A methanol solution of RuQPIm (10–15 wt%) was cast on a glass plate, and allowed to stand in the desiccator for 1 week. The polymer film was taken off the glass plate, washed with water and acetone, and dried at room temperature over calcium chloride. The thickness of these polymer films was 0.18 ± 0.02 mm.

Measurements

Ultraviolet–visible (u.v.–vis.) spectra were recorded on a Jasco UVIDEC-505 spectrophotometer. Luminescence spectra of the photoexcited RuQPIm were recorded on a Hitachi 650-10 S fluorescence spectrophotometer.

The hydrogen generation was performed at 25°C under an argon atmosphere. A test tube (10 cm^3) containing RuQPIm free-standing film ([Ru(II)] = 2×10^{-5} mol), viologen (5.0×10^{-3} mol dm^{-3}), triethanolamine (TEOA) (0.1 mol dm^{-3}) and bis(2,2′-bipyridine)platinum(II) ($[\mathrm{Pt(bpy)_2}]^{2+}$) ($1.0 \times 10^{-3}$ mol dm^{-3}) was irradiated with a 300 W slide projector (Elmo Co., Ltd, S-300) equipped with a u.v. cut-off filter ($\lambda > 440$ nm). The amount of hydrogen generated was detected by using a GC-9A Shimazu Gas Chromatograph and monitored as a function of irradiation time. Experimental errors were within ± 0.05.

RESULTS AND DISCUSSION

Chemical structure of RuQPIm is shown in *Figure 1*, and the degree of coordination of ruthenium(II) complexes and the degree of quaternization are summarized in *Table 1*.

When applying the present work to *Scheme 1*, P is polymer-bound ruthenium(II) complex film, A is alkylviologen such as 1,1′-dimethyl-4,4′-bipyridinium (MV^{2+}) or 1,1′-dioctyl-4,4′-bipyridinium ($\mathrm{C_8V}^{2+}$), D is TEOA, and Cat is $[\mathrm{Pt(bpy)_2}]^{2+}$, as shown in *Scheme 2*.

Furthermore, *Scheme 2* can be expressed by equations (1)–(6):

$$\mathrm{Ru^{II}QPIm} \xrightarrow{h\nu} {}^{*}\mathrm{Ru^{II}QPIm} \tag{1}$$

$$ {}^{*}\mathrm{Ru^{II}QPIm} \rightarrow \mathrm{Ru^{II}QPIm} + h\nu' + \Delta \tag{2}$$

$$ {}^{*}\mathrm{Ru^{II}QPIm} + \mathrm{V^{2+}} \rightarrow \mathrm{Ru^{III}QPIm} + \mathrm{V^{+}} \tag{3}$$

$$\mathrm{Ru^{III}QPIm} + \mathrm{V^{+}} \rightarrow \mathrm{Ru^{II}QPIm} + \mathrm{V^{2+}} \tag{4}$$

$$\mathrm{Ru^{III}QPIm} + \mathrm{TEOA} \rightarrow \mathrm{Ru^{II}QPIm} + \mathrm{TEOAox} \tag{5}$$

$$n\mathrm{Pt} + \mathrm{V^{+}} + \mathrm{H^{+}} \rightarrow 1/2\mathrm{H_2}\uparrow + n\mathrm{Pt} + \mathrm{V^{2+}} \tag{6}$$

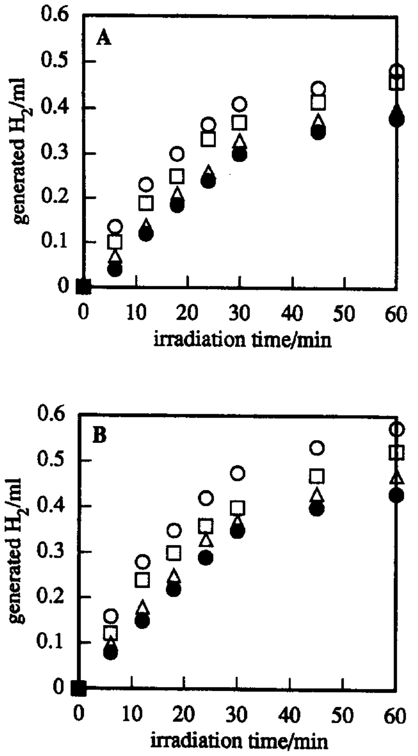


Figure 2 Hydrogen generation with light irradiation to aqueous solution containing RuQPIm free-standing film, 5.0 × 10^{-3} mol dm^{-3} MV^{2+}, 0.1 mol dm^{-3} TEOA and 3.0 × 10^{-3} mol dm^{-3} platinum catalyst for RuQPIm-14 (○), RuQPIm-25 (□), RuQPIm-38 (△) and RuQPIm-44 (●): (A) [NaCl] = 0 mol dm^{-3}, (B) [NaCl] = 1 mol dm^{-3}

Table 2 Maximum volume of hydrogen generated for RuQPIm/viologen/TEOA/Pt catalyst systems

Polymer	Generated hydrogen (cm^3)^a			
	NaCl = 0 mol dm^{-3}		NaCl = 1 mol dm^{-3}	
	MV^{2+}	C$_8$V^{2+}	MV^{2+}	C$_8$V^{2+}
RuQPIm-14	0.521	0.017	0.633	≈ 0
RuQPIm-25	0.483	0.011	0.556	≈ 0
RuQPIm-38	0.418	0.006	0.507	≈ 0
RuQPIm-44	0.395	0.002	0.476	≈ 0

^{a}After irradiation for 120 minutes

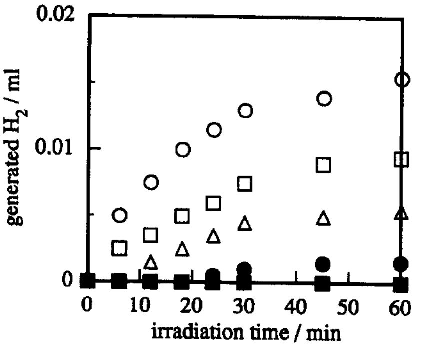


Figure 3 Hydrogen generation with light irradiation to aqueous solution containing RuQPIm free-standing film, 5.0 × 10^{-3} mol dm^{-3} C$_8$V^{2+}, 0.1 mol dm^{-3} TEOA and 3.0 × 10^{-3} mol dm^{-3} platinum catalyst for RuQPIm-14 (○), RuQPIm-25 (□), RuQPIm-38 (△), RuQPIm-44 (●) and RuQPIm-25 at 1 mol dm^{-3} NaCl (■)

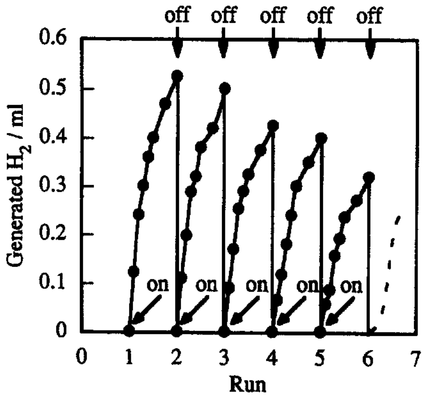


Figure 4 Hydrogen generation on repeated light on and off run for RuQPIm-25 film/MV^{2+}/TEOA/Pt catalyst. Irradiation time in one cycle is 60 min

where V^{2+} and $\dot{V}^{+}$ represent alkylviologens MV^{2+} and C$_8$V^{2+} and their radicals, respectively.

Figure 2 shows the relationship between the volume of hydrogen generated and irradiation time for RuQPIm/MV^{2+}/TEOA/[Pt(bpy)$_2$]$^{2+}$ systems. In all systems, the volume of hydrogen generated upon irradiation saturated after 120 min. The maximum volume of hydrogen generated is summarized in *Table 2*. The maximum volume of hydrogen decreased with increasing degree of quaternization. This result is attributed to a decrease in the efficiency of charge separation. As described in our previous work[22], the efficiency of photosensitized charge separation is affected by electrostatic effects and steric hindrance. The MV^{2+} species approach the film surface through the π–π interaction between the heteroaromatic moieties of MV^{2+} and the imidazolyl residue on the polymer backbone. The enhancement of degree of quaternization, which corresponds to an increase in positive charge density and number of alkyl side chains, causes an increase in the electrostatic repulsion and steric hindrance for reaction between MV^{2+} species and ruthenium(II) complex residues, leading to a decrease in the efficiency of charge separation. As shown in *Figure 2B*, the volume of hydrogen generated was increased by addition of 1 mol dm^{-3} NaCl. Since the addition of NaCl causes an increase in π–π interaction and a decrease in electrostatic repulsion, the diffusion of MV^{2+} species into the surface of the polymer film is accelerated. Therefore, the efficiency of charge separation increases and the volume of hydrogen generated increases.

Figure 3 shows hydrogen generation with light irradiation for RuQPIm film/C$_8$V^{2+}/TEOA/[Pt(bpy)$_2$]$^{2+}$. With light irradiation, only slight hydrogen generation was found for a low degree of quaternization, while hydrogen generation was barely observed for a high degree of quaternization. Furthermore, in the presence of 1 mol dm^{-3} NaCl, hydrogen generation was not observed in all systems. The volume of hydrogen generated was much smaller than that the presence of MV^{2+}. In our previous work[22], the efficiency of charge separation for the RuQPIm film/C$_8$V^{2+} system was greater than that for the corresponding MV^{2+} system; particularly, the efficiency of charge separation for the C$_8$V^{2+} system was significantly increased by the addition of 1 mol dm^{-3} NaCl. The result led us to conclude that this may be attributed to a stronger driving force for diffusion of the C$_8$V^{2+} species into the surface of the polymer film than for the MV^{2+} species. As mentioned above, the MV^{2+} species diffuse into the polymer film through π–π

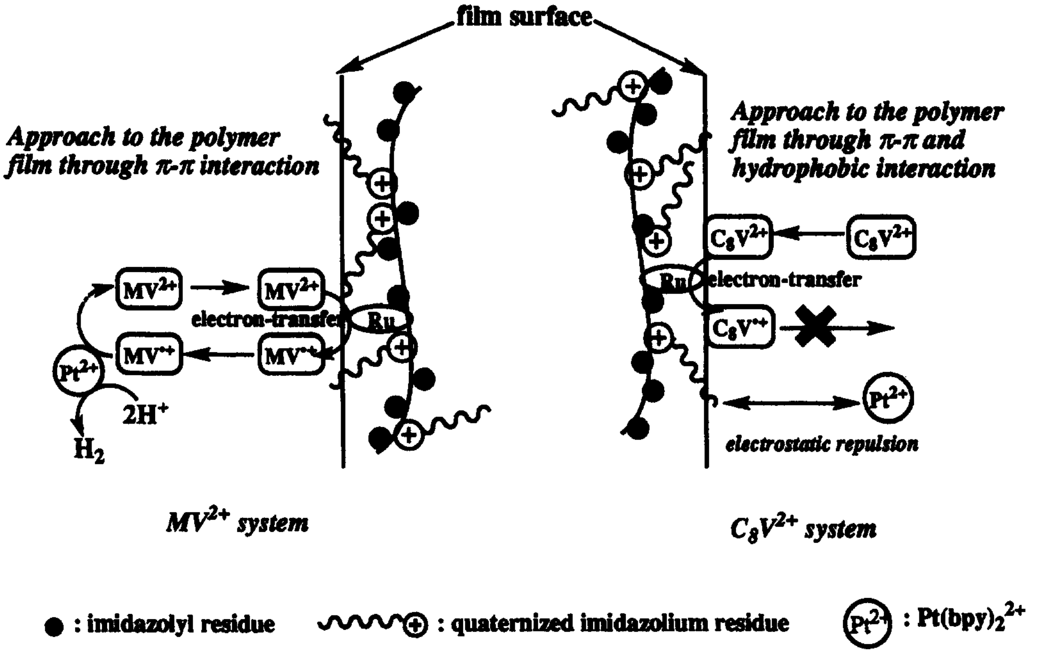


Figure 5 Illustration of tentative reaction mechanism for hydrogen generation

interaction. On the other hand, the driving force for the diffusion of C_8V^{2+} species into the polymer film is hydrophobic interaction of alkyl groups in the C_8V^{2+} as well as $\pi-\pi$ interaction: namely, the diffusion of C_8V^{2+} species is accelerated by two interactions. Consequently, the efficiency of charge separation for the C_8V^{2+} system becomes large. As regards hydrogen production, however, the volume of hydrogen generated for the C_8V^{2+} system is very small. This is due to hydrophobic interaction with the polymer film. The C_8V^+ species are formed by electron transfer from the photoexcited ruthenium(II) complex residues to C_8V^{2+} species which diffuse into the surface of the polymer film by $\pi-\pi$ and hydrophobic interactions. These interactions, particularly the hydrophobic interaction, inhibit diffusion of the radical species into the bulk solution: most of the radical species remain adsorbed to the polymer film. The electrostatic repulsion restricts the diffusion of positively charged platinum catalyst into the film surface, and the hydrophobic interaction restricts the reaction between viologen radical and platinum catalyst according to equation (6), which leads to a low efficiency of hydrogen production.

Figure 4 shows hydrogen generation during repeated light on and off runs for the RuQPIm-25/MV^{2+}/TEOA/$[Pt(bpy)_2]^{2+}$ system. With repeated switching of light on and off, the volume of hydrogen generated upon light irradiation for 60 min decreased and no hydrogen generation was observed at the 25th run. U.v.–vis. absorption and luminescence spectra of the RuQPIm-25 film after the 25th run are almost identical to those before the measurements*, indicating that the RuQPIm-25 film rarely breaks during light irradiation and reaction. Considering this fact, the decrease in the volume of hydrogen generated with repetitive irradiation is caused by inactivation of the platinum complex. In fact, hydrogen generation is observed again when platinum catalyst is added to the solution after 25 runs. Further, it is found that the RuQPIm-25 film is an excellent photosensitizer that can be used for more than 200 cycles†.

CONCLUSION

We have reported new hydrogen-generation systems using polymer photosensitizers containing partially quaternized poly(1-vinylimidazole)-bound ruthenium(II) complex (RuQPIm) films. Hydrogen generation was observed with light irradiation to aqueous solutions containing RuQPIm free-standing film as a photosensitizer, MV^{2+} or C_8V^{2+} as electron relays (acceptors), TEOA as sacrificial donor, and platinum(II) catalyst. The volume of hydrogen generated decreased with increasing degree of quaternization. This is caused by a decrease in the efficiency of charge separation. The increase in degree of quaternization brings about an increase in the positive charge density on the surface of the polymer film, which is the reaction field, and the number of alkyl side chains on the polymer backbone, indicating the enhancement of electrostatic repulsion and steric hindrance. Such effects decrease the efficiency of charge separation, consequently leading to a decrease in the volume of generated hydrogen. Compared with MV^{2+} systems, the volume of hydrogen generated for C_8V^{2+} systems was very small, although the efficiency of charge separation was large. The fact can be explained by interaction of C_8V^{2+} species with the polymer film as shown in *Figure 5*. For MV^{2+} systems, the MV^{2+} species diffuse from the bulk solution into the surface of the polymer film, and the MV^+ species, which are formed by electron transfer from the photoexcited ruthenium(II) complex to MV^{2+}, diffuse readily into the bulk. By contrast, the diffusion of C_8V^+ species into the bulk is restricted since the viologen radical species adsorb on the polymer film through hydrophobic interaction. The reaction between

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*The spectra change slightly after 25 runs: the absorbance and luminescence intensity decrease by about 2%

†The absorbance and luminescence intensity of the RuQPIm film used for 200 cycles decreased by about 9%

viologen radical species and positively charged platinum catalyst corresponding to equation (6) would mainly take place in the bulk due to the electrostatic repulsion between the polymer film surface and platinum catalyst. The $M\dot{V}^+$ species, which diffuse into the bulk, react readily with platinum catalyst, while reaction of the $C_8\dot{V}^+$ species, which hardly diffuse into the bulk due to hydrophobic interaction, with platinum catalyst is restricted, leading to a low volume of generated hydrogen. These results indicate that the volume of hydrogen generated barely depends on the efficiency of charge separation: namely, high efficiency of charge separation does not necessarily bring about efficient hydrogen generation. Further, it is noteworthy that the hydrophobic interaction plays as acceleration effect for photosensitized charge separation, while it plays as decelation effect for the hydrogen-generation reaction.

The volume of hydrogen generated during repeated light on and off runs decreased gradually, and then hydrogen generation ceased to be observed in the 25th repeat run. This is attributed to inactivation of the platinum catalyst; in fact, hydrogen generation was observed again by irradiating the solution after an addition of platinum catalyst after the 25th run. The RuQPIm films kept their photosensitizing ability even after 200 cycles. Furthermore, u.v.–vis. absorption and luminescence spectra measurements showed that the absorbance and luminescence intensity of the RuQPIm films after use for 200 cycles decreased by only about 9%, compared with the values before measurements. Therefore, it is clear that the RuQPIm films have an excellent stability for the photochemical reactions.

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