

Hydrogen generation using water-insoluble polymer-bound ruthenium(ii) complexes

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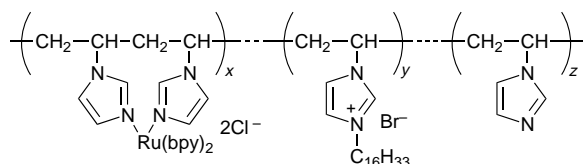
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Water-insoluble free-standing films of partially quaternized poly(1-vinylimidazole)-bound ruthenium(ii) complexes are prepared, and photoinduced hydrogen generation is observed with light irradiation ($\lambda > 440$ nm) of aqueous solutions containing the polymer-bound ruthenium(ii) complex film, methyl viologen, triethanolamine and bis(2,2'-bipyridine)platinum(ii).

Tris(2,2'-diimine)ruthenium(ii) complexes have attracted much attention as photosensitizers for application to solar-energy conversion.¹⁻³ In particular, tris(2,2'-bipyridine)ruthenium(ii), [Ru(bpy)₃]²⁺, has been widely employed as a photocatalyst for water cleavage and used as a photosensitizer in many hydrogen generation systems.⁴⁻⁷ Metallopolymers, in which ruthenium(ii) complexes are coordinated to poly(4-vinylpyridine) and poly(1-vinylimidazole), have been investigated, and applications to polymer catalysts, photosensitizers, and molecular diodes have been proposed.⁸⁻¹⁰ However, there are no reports on the application of these photosensitizers to photoinduced hydrogen generation.

Recently, we have reported the preparation of partially quaternized poly(1-vinylimidazole)-bound ruthenium(ii) complexes [Ru(QPIm)] and their films, and luminescence quenching and photosensitized charge separation using Ru(QPIm)s as photosensitizers.¹¹⁻¹³ These results indicated that Ru(QPIm)s and their films are sufficiently capable of utilization as photosensitizers. In this work, hydrogen generation using Ru(QPIm)s as photosensitizers was investigated in methanol-water and water.

The polymer photosensitizers were prepared according to the literature¹¹ and the structures were confirmed by ¹H NMR and absorption spectroscopies (Fig. 1). The polymer films were prepared by casting from methanol solution, and the measured thicknesses were 0.182 mm for C₁₆RuQPIm-25 and 0.184 mm for C₁₆RuQPIm-44. 1,1'-Dimethyl-4,4'-bipyridinium (MV²⁺) and 1,1'-dioctyl-4,4'-bipyridinium (C₈V²⁺) were used as acceptors. Triethanolamine (TEA) was used as a sacrificial donor and bis(2,2'-bipyridine)platinum(ii) [Pt(bpy)₂]²⁺ was used as the catalyst for hydrogen evolution, respectively. Hydrogen generation was performed at 25 °C with light irradiation by a 300 W



Polymers	x	y	z
C ₁₆ RuQPIm-25	0.0033	0.2531	0.7436
C ₁₆ RuQPIm-44	0.0033	0.4404	0.5563

Fig. 1 Chemical structure of Ru(QPIm)

slide projector under an argon atmosphere. Light with $\lambda < 440$ nm was cut off by a Toshiba Y-44 filter.

Fig. 2 shows the relationship between hydrogen generation and irradiation time for Ru(QPIm)s in methanol-water (9:1 v/v) and RuQPIm films in aqueous solution.

The amount of generated hydrogen for C₁₆RuQPIm-25 was larger than that for C₁₆RuQPIm-44. This is attributed to electrostatic repulsion between viologen species and quaternized imidazolium residues and steric hindrance of alkyl side-chains.

Compared with MV²⁺ systems, hydrogen generation for C₈V²⁺ systems was lower. We have already reported that viologens with long alkyl groups show van der Waals interactions with alkyl side-chains on the polymer backbone.^{11,12} After electron transfer from the photoexcited ruthenium(ii) complex to MV²⁺ in the polymer domain, the MV^{•+} species formed quickly diffuse into the bulk solution and readily react with the Pt catalyst. However, the C₈V^{•+} species barely diffuse into the bulk solution due to interaction with the polymer, leading to the inhibition of reaction with the positively charged Pt catalyst; consequently, hydrogen generation decreases.

In Ru(QPIm) film systems, 0.46 and 0.36 ml of hydrogen was evolved for C₁₆RuQPIm-25/MV²⁺ and C₁₆RuQPIm-44/MV²⁺, respectively, while hydrogen evolution was scarcely observed in the C₈V²⁺ systems. During light irradiation, the colour of reaction solution and polymer film do not change, indicating that the MV^{•+} species formed react rapidly with the platinum catalyst. For C₈V²⁺ systems, however, the colour of the polymer film changes from orange to deep blue (but the solution is

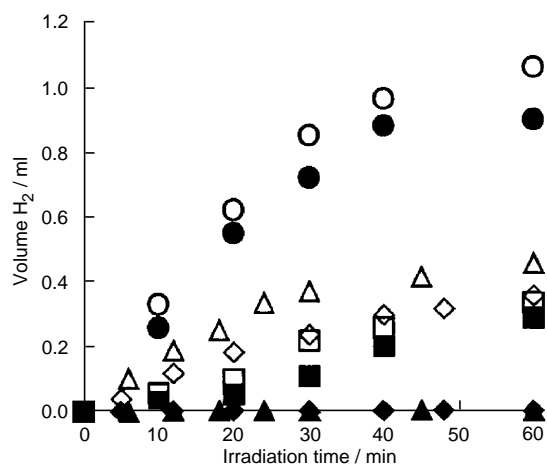


Fig. 2 Hydrogen generation upon light irradiation of methanol-water (9:1 v/v) containing 5.0×10^{-5} mol dm⁻³ Ru(QPIm), 5.0×10^{-3} mol dm⁻³ viologen, 0.1 mol dm⁻³ TEOA, and 3.0×10^{-3} mol dm⁻³ platinum catalyst for C₁₆RuQPIm-25/MV²⁺ (○), C₁₆RuQPIm-44/MV²⁺ (□), C₁₆RuQPIm-25/C₈V²⁺ (●), C₁₆RuQPIm-44/C₈V²⁺ (■), C₁₆RuQPIm-25film/MV²⁺ (△), C₁₆RuQPIm-44film/MV²⁺ (◇), C₁₆RuQPIm-25film/C₈V²⁺ (▲) and C₁₆RuQPIm-44film/C₈V²⁺ (◆)

unchanged), which indicates that a charge separation reaction occurs and the C_8V^{+} species scarcely react with the platinum catalyst. In a previous paper,¹³ we reported that C_8V^{2+} species are adsorbed on the surface of the polymer film and only adsorbed C_8V^{2+} species react with photoexcited ruthenium(ii) complexes. Considering this fact, the present results can be explained as follows. After electron transfer from the photoexcited ruthenium(ii) complex to the MV^{2+} species on the surface of the polymer, the MV^{+} species formed diffuse into the bulk solution and react with the platinum catalyst, leading to hydrogen generation. On the other hand, C_8V^{2+} species are adsorbed on the surface of the polymer film and the charge separation takes place only on the film surface. Therefore, no evolution of hydrogen is observed since the adsorbed C_8V^{+} species do not react with the positively charged platinum catalyst. Quantum yields for H_2 formation are summarized in Table 1.

Table 1 Maximum amount of generated hydrogen and quantum yields for hydrogen generation for solution and film systems

	H_2^a/ml	$\phi(H_2)$
In MeOH–H ₂ O		
$C_{16}RuQPIIm-25/MV^{2+}$	1.01	0.026
$C_{16}RuQPIIm-25/C_8V^{2+}$	0.34	0.025
$C_{16}RuQPIIm-44/MV^{2+}$	0.91	0.022
$C_{16}RuQPIIm-44/C_8V^{2+}$	0.29	0.018
In aqueous solution (film)		
$C_{16}RuQPIIm-25/MV^{2+}$	0.46	0.015
$C_{16}RuQPIIm-25/C_8V^{2+}$	0.36	0.014
$C_{16}RuQPIIm-44/MV^{2+}$	< 0.01	< 0.001
$C_{16}RuQPIIm-44/C_8V^{2+}$	< 0.01	< 0.001

^a Irradiation for 1 h.

The present results demonstrate that partially quaternized poly(1-vinylimidazole)-bound ruthenium(ii) complex films can be used for a photoinduced hydrogen generation reaction as new polymer-solid photosensitizers. Furthermore, it is found that the high efficiency of charge separation does not necessarily bring about high efficiency of hydrogen generation in the present systems. A detailed investigation on the hydrogen generation is now in progress in our laboratory.

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