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Photoinduced Charge Separation at Solid–Liquid Interface Utilizing Polymer Pendant $Ru(bpy)_3Cl_2$ Complex

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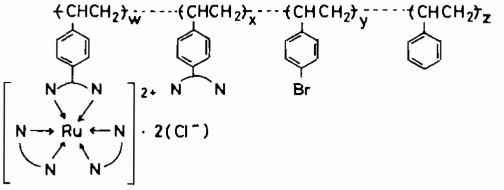
Tris(2,2′-bipyridyl)ruthenium(II) complex (Ru(bpy)$_3$) is attracting much attention as a photocatalyst for decomposing water by solar irradiation [1–3]. In order to construct an efficient solar energy conversion system, utilization of heterogeneous reaction is required, since a photochemical reaction in a homogeneous solution usually results in back electron transfer which consumed the acquired energy. The use of photochemical reaction at solid-liquid interface is one of the promising approaches to this subject, however, there have been but few works concerning it [4].

The present authors have recently reported the preparation of polymer pendant Ru(bpy)$_3$ complex in order to use it in photoenergy conversion [5]. It was achieved by thus utilizing the polymer pendant Ru(bpy)$_3$ to reduce methyl viologen (1,1′-dimethyl-4,4′-dipyridinium dichloride; MV^{2+}) photochemically at solid–liquid interface and to evolve hydrogen gas as a model for water photolysis. Photocatalytic activity of the polymer pendant Ru(bpy)$_3$ in a homogeneous solution as well as its application to photoinduced charge separation at solid–liquid interface will be described in this paper.

Polystyrene (PSt) pendant Ru(bpy)$_3$ (abbreviated as PSt-bpy-Ru) was prepared by the procedure reported [5]. The average composition of the PSt-bpy-Ru used in Table I is as follows:



(1)

w = 0.004, x = 0.047, y = 0.266, z = 0.683

where N⌒N denotes 2,2′-bipyridyl group.

This polymer complex showed photocatalytic activity in the reduction of MV^{2+} with the reducing agent, EDTA or triethanolamine (TEOA), in a homogeneous solution of DMF/H_2O as shown in Table I. Lower activity of the polymer pendant complex than monomeric Ru(bpy)$_3$ (about one fourth) under the same condition might be due to steric hindrance caused by the polymer chain.

By utilizing the polymer pendant Ru(bpy)$_3$ complex photoinduced charge separation at solid-liquid interface was achieved. A finely mixed powder (75.2 mg) of PSt-bpy-Ru having the composition, w = 0.039, x = 0.011, y = 0.212 and z = 0.738 in eqn. (1), and EDTA (Ru gion/EDTA mol = $1/10^3$) was suspended in a 10^{-2} *M* MV^{2+}/methyl alcohol solution (2 ml), and the suspension was irradiated with a halogen lamp (12V, 100W) through UV and IR cutoff filters under argon at 30 °C. The light intensity at the illuminated cell surface was 80.7 mW/cm^2. The color of the liquid turned to blue induced by the irradiation. In order to measure the visible spectrum of the solution, a new reaction mixture was allowed to stand till the suspension settled, and thereafter the precipitated solid–liquid interface was irradiated. Photoinduced formation of $MV^{\ddagger}$ in the liquid phase was confirmed by the characteristic absorptions at 396 and 607 nms in the visible spectrum of the solution. The initial rate of $MV^{\ddagger}$ formation was 1.47×10^{-6} *M*/min, which is comparable to that in the homogeneous solution under the same irradiation conditions shown in Table I, although the exact comparison is impossible because of the interfacial reaction of the polymer

TABLE I. Photocatalytic Activity of PSt-bpy-Ru in the Photoreduction of MV^{2+} in a Homogeneous Solution (DMF/H_2O). Ru: 4×10^{-5} gion/l, irradiated with visible light (400–800 nm) under argon at 30 °C.

Complex	Reducing agent	(*M*)	MV^{2+} (*M*)	Solvent DMF/H_2O (v/v)	Initial rate ($MV^{\ddagger}$ *M*/min)
PSt-bpy-Ru	EDTA	1.00×10^{-3}	2×10^{-3}	4/1	1.53×10^{-6}
Ru(bpy)$_3$	EDTA	1.00×10^{-3}	2×10^{-3}	4/1	6.31×10^{-6}
PSt-bpy-Ru	TEOA	7.54×10^{-1}	1×10^{-3}	8/1	2.85×10^{-5}

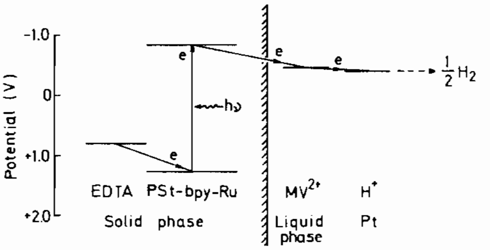


Fig. 1. Photoinduced charge separation at solid–liquid (methyl alcohol) interface.

system. It was confirmed by the visible spectrum that the polymeric Ru complex is retained in the solid phase. A blank experiment using the mixture of PSt pendant bipyridyl (starting polymeric ligand [5] for preparation of PSt-bpy-Ru) and EDTA did not give $M^{\ddagger}$ at all. Photoreduction of MV^{2+} did not occur also in the system where solid PSt-bpy-Ru is present in the aqueous solution of MV^{2+} and EDTA. These results indicate that photoinduced electron transfer from the solid phase to the liquid phase sensitized by Ru complex in solid phase occurs in the [EDTA-PST-bpy-Ru] solid–[MV^{2+}/MeOH] liquid heterogeneous system. The presence of 10% 1 *N* HCl and platinum black plate in the methyl alcohol phase caused generation of hydrogen gas due to reduction of H^+ by $MV^{\ddagger}$.

Such a photochemical charge separation at solid–liquid interface and successive hydrogen gas evolution at platinum black placed in liquid phase can be schematically illustrated in Fig. 1. In this figure the reduction potential of EDTA is estimated to be about 0.8 V according to Sakata *et al.* [6]. The free energy acquired by this photochemical reaction is estimated to be about 56 kcal/mol EDTA consumed. Thus, charge separation at solid–liquid interface and separation of the products, *i.e.* oxidized compound of EDTA and hydrogen gas, in each phase were realized by utilizing polymer pendant $Ru(bpy)_3$ complex.

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