Photoelectrochemical Behaviour of Ruthenium(II) Complex Layers at a Platinum Electrode immobilized by the Common-ion Effect in Aqueous Electrolyte Solution

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The photoelectrochemical behaviour of multi-molecular layers of $Ru(bipy)_3(BPh_4)_2$, where bipy = 2,2′-bipyridine, immobilized on a platinum electrode by the common-ion effect was studied under potentiostatic conditions in an aqueous electrolyte solution with no added redox agents. Upon illumination, anodic photocurrents were generally observed, the quantum efficiency being 3.5×10^{-4} at 480 nm with an applied potential of +150 mV (saturated calomel electrode). The effects of applied potential, light intensity, and pH were also examined. During each experiment, the surface layer stabilized by the common-ion effect was sufficiently stable to obtain reproducible data. The results are interpreted in terms of the reaction of a photo-generated ruthenium(III) complex with OH^- ions.

Several different methods for immobilizing chemical species on various electrode surfaces, including chemical modification using covalent bonding and strong adsorption, have been developed.[1] In the present study, the so-called common-ion effect has been used to immobilize charged species on an electrode surface. The method involves precipitation of a charged species using appropriate large counter ions such as tetraphenylborate in aqueous solution, followed by dissolution of the precipitate in an appropriate organic solvent and injection onto a platinum electrode. After evaporation of the organic solvent, multi-molecular layers of the complex are formed. The coated electrode is then immersed in an aqueous solution containing excess of an electrolyte having a common counter ion. Due to the common-ion effect, the solubility of the surface layer is further decreased so that the electrode thus modified has sufficient stability for examination of its characteristics.

This simple technique was used here in a photoelectrochemical study of a ruthenium(II) complex immobilized on a platinum electrode. Photoelectrochemical studies of $[Ru(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridine) have previously been carried out.[2–7] Kobayashi *et al.*[2] obtained a cathodic photocurrent from dissolved $[Ru(bipy)_3]^{2+}$ along with oxidizing scavengers at an SnO_2 electrode. Memming and co-workers [3,4] studied both dissolved and monolayer-coated $[Ru(bipy)_3]^{2+}$ complexes on SnO_2 electrodes and obtained anodic photocurrents in both cases. In the latter case a stearyl surfactant derivative of $[Ru(bipy)_3]^{2+}$ was employed to make a stable surface monolayer. However, to our knowledge, no study has been reported on multi-molecular layers of this ruthenium(II) complex on metal electrodes where photocurrents are expected to be observed.[8–10]

Experimental

In order to immobilize $[Ru(bipy)_3]^{2+}$ on a platinum electrode, tetraphenylborate was chosen as counter ion. The resulting complex is far less soluble for example than $[Ru(bipy)_3][ClO_4]_2$ in aqueous solution. 1×10^{15} Molecules were generally deposited on a clean polished platinum electrode (0.2 cm^2 in area) by allowing 10 μl of a 5×10^{-4} mol dm^{-3} solution in acetonitrile to evaporate on the surface of the electrode. In order to prevent the dissolution of the multi-molecular layers from the platinum surface, 0.1 mol dm^{-3} $NaBPh_4$ was used as a supporting electrolyte. As a result of the common-ion effect of BPh_4^- between the solid and solution phases the surface solid membrane of $Ru(bipy)_3(BPh_4)_2$ was stable after 12 h duration in the dark.

Sample solutions were exhaustively degassed by argon bubbling. The reference electrode was a saturated calomel electrode (s.c.e.) with an agar–KCl salt bridge. A platinum coil was used as the auxiliary electrode. Photocurrents were measured with a Hokuto(Tokyo) model HA-501 potentiostat and a model TR-8651 electrometer (Takeda Riken Co., Tokyo). The light source was a 500-W xenon lamp. The photocurrent spectra were measured with model L line filters (Koshin Optics Co., Kanagawa, Japan) each having a band width of 10 nm. The spectral distribution of the light source and the actual light intensities on the electrode surface were determined with a model S-642 silicon photocell calibrated at Hamamatsu TV Co. (Shizuoka, Japan).

A focused light beam from a 500-W xenon lamp was applied to the electrode surface through a quartz window underneath. The steady photocurrent I_p was defined as $I_p = I_l - I_d$, where I_l is the observed photocurrent after the transient (see Figure 1) and I_d the dark current in the absence of light, the latter being generally one order of magnitude smaller than the former. The direction of I_p in the present study was always *anodic*.

Results and Discussion

Photocurrent vs. *Time*.—Because the photodecomposition of water catalyzed by $[Ru(bipy)_3]^{2+}$ is well known,[11] the present photoelectrochemical study was performed in aqueous electrolyte with no added redox reagents. Figure 1 shows a characteristic photocurrent–time curve for a $Ru(bipy)_3(BPh_4)_2$-coated electrode in 0.1 mol dm^{-3} $NaBPh_4$ aqueous solution with no added redox systems. The overall shape of the curve is divided reproducibly into three different regions; (*i*) initial stage where some transient behaviour exists; (*ii*) steady photocurrent; and (*iii*) decay of steady current. The turn-over (ratio of number of electrons transferred to that of molecules deposited on the Pt electrode) in 1 h is greater than 10, indicating that the origin of the observed photocurrent is photocatalytic as expected, rather than due to a simple photodecomposition of the membrane. However, it seems reasonable to conclude that the decay of the steady photocurrent after *ca.* 90 min is due to photochemical inactivation of the surface layer rather than to simple physical desorption. In fact, desorption of the surface layer became appreciable upon continuous light illumination over 2—3 h and the colour of the surface layer changed from light orange to light brown. As stated in the Experimental section, the membrane layer was physically stable on a plati-

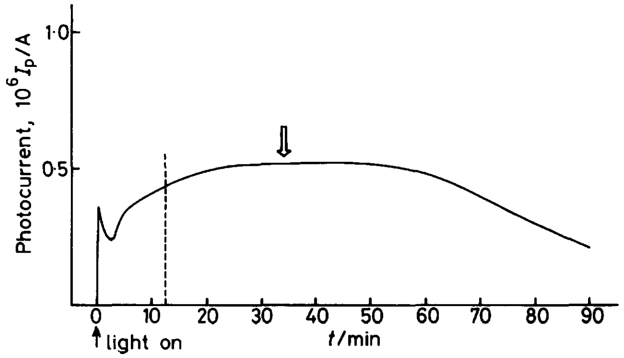

Figure 1. Typical photocurrent–time behaviour of a Ru(bipy)$_3$(BPh$_4$)$_2$-coated platinum electrode in 0.1 mol dm^{-3} NaBPh$_4$ aqueous solution, pH 11.9; applied potential, 0 V (s.c.e.); turn-over *ca.* 10. The arrow indicates the region of the steady photocurrent as described in text. Non-monochromatic light from a xenon lamp was focused on the electrode through u.v. and i.r. cut-off filters. The photocurrent, I_p in A per 0.2 cm^2, is the observed value at the electrode with a surface area of 0.2 cm^2. The same is also true for Figures 3—5

num electrode in 0.1 mol dm^{-3} NaBPh$_4$ aqueous solution for >12 h in the absence of light. When the same electrode was used again after dipping it in a similar solution for 12 h in the dark, the photocurrent observed was reproducible within 15% with respect to the first run. However, when NaClO$_4$ of the same concentration was used as supporting electrolyte, the photocurrent decayed by 20% in 30 min due to dissolution of the surface layer.

Photocurrent Spectra.—As shown in Figure 2, the patterns of the photocurrent spectra differ slightly depending upon the experimental conditions. Under three-electrode potentiostatic conditions a single peak at 480 nm was observed, but under two-electrode short-circuit conditions another absorption tail at 520 nm appeared as a shoulder on the band at 475 nm. The main peaks at around 470—480 nm in Figure 2 are probably due to light absorption by [Ru(bipy)$_3$]$^{2+}$, since the spectral distribution is close to that of the charge-transfer (c.t.) absorption spectrum ($\lambda_{\text{max.}}$ = 457 nm in acetonitrile). The small shift of the photocurrent spectra from the absorption spectrum may be caused by weak interactions between complex molecules in the solid phase on the platinum electrode. The weak peak at 520 nm in Figure 2(*b*) may be assigned to a direct singlet–triplet ($S_0 \rightarrow T_1$) transition, in agreement with Demas and Crosby,[12] and Gleria and Memming.[3] Demas and Crosby [12] found that the intersystem-crossing efficiency from the ^{1}c.t. state to the ^{3}c.t. state was almost unity. Therefore, it is assumed here, in agreement with Gleria and Memming,[3] that the electron transfer to the platinum electrode occurs also *via* the triplet state according to equations (1)—(3),

$$[\text{Ru(bipy)}_3]^{2+} \xrightarrow[470\text{–}480\ \text{nm}]{h\nu} [\text{Ru(bipy)}_3]^{2+}\ (^1\text{c.t., excitation process}) \quad (1)$$

$$[\text{Ru(bipy)}_3]^{2+}(^1\text{c.t.}) \longrightarrow [\text{Ru(bipy)}_3]^{2+}\ (^3\text{c.t., intersystem crossing}) \quad (2)$$

$$[\text{Ru(bipy)}_3]^{2+}(^3\text{c.t.}) \longrightarrow [\text{Ru(bipy)}_3]^{3+} + e^-\ (\text{charge transfer}) \quad (3)$$

$$[\text{Ru(bipy)}_3]^{2+} \xrightarrow[520\ \text{nm}]{h\nu} [\text{Ru(bipy)}_3]^{2+}\ (^3\text{c.t., direct } S_0 \rightarrow T_1 \text{ excitation}) \quad (4)$$

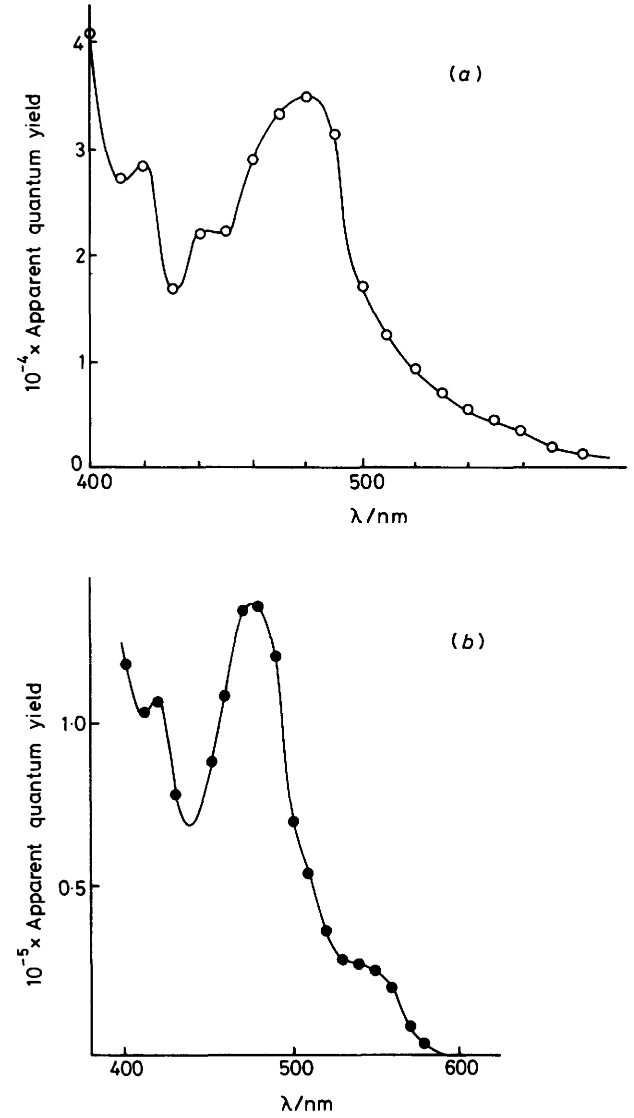

Figure 2. Photocurrent spectra, given as apparent quantum efficiency *vs.* wavelength, for a Ru(bipy)$_3$(BPh$_4$)$_2$-coated platinum electrode. (*a*) Potentiostated at +150 mV (s.c.e.), 0.1 mol dm^{-3} NaBPh$_4$, pH 12.2; u.v. and i.r. cut-off filters were used. (*b*) Two-electrode short-circuit conditions; Ru(bipy)$_3$(BPh$_4$)$_2$-coated platinum electrode in 0.1 mol dm^{-3} NaBPh$_4$ (pH 9) as the working electrode and a platinum wire in 0.1 mol dm^{-3} tetraethylammonium perchlorate (pH 2) as the counter electrode. Other experimental conditions as in (*a*)

or instead of (1) and (2), equation (4). The reason why the peak at 520 nm appeared under short-circuit conditions and not under the three-electrode potentiostatic condition is not known at present.

As shown in Figure 2, typical apparent quantum efficiencies for the incident light in the present system are 3.5 × 10^{-4} under three-electrode potentiostatic conditions with an applied potential of +150 mV (s.c.e.) on the substrate platinum electrode and 1.5 × 10^{-5} under short-circuit conditions at the respective main peaks. These values and therefore the observed photocurrents were dependent upon the applied potential, pH of the electrolyte solution, and the thickness of the membrane layer as mentioned later.

Among the [Ru(bipy)$_3$]$^{2+}$ molecules in the membrane, those

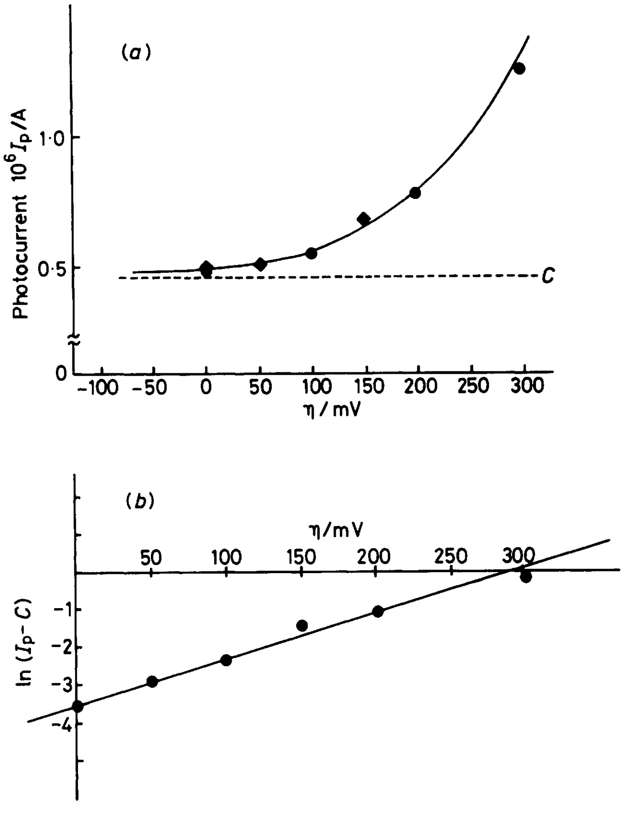

Figure 3. Dependence of photocurrent on applied potentials: (*a*) applied potential (s.c.e.) *vs.* anodic photocurrent (◆ and ● from two separate experiments); (*b*) $\ln(I_p - C)$ as a function of applied potential η ($C = 0.46 \times 10^{-6}$)

in the innermost layer in direct contact with the platinum electrode do not contribute to the photocurrent. The reason is that, even if the complex in this layer is photoexcited, rapid quenching of excited states by free electrons in the metal and a reversible and simultaneous exchange of electrons *via* the metal–ruthenium(II) complex interface occurs. Since 1×10^{15} molecules of $Ru(bipy)_3(BPh_4)_2$ were generally deposited on the platinum electrode (0.2 cm^2) in the present case, the thickness of the film was calculated from crystallographic data [13,14] to be 120 molecular layers. Indeed, with decreasing thickness of this surface layer, the observed photocurrent decreased for example by 40% at 32 molecular layers, by 70% at 16 molecular layers, and finally disappeared. This result excludes a mechanism of electron transfer *via* a platinum oxide layer (supposedly semiconductive) by photosensitization.

By comparing our results with those of Memming and coworkers [3,4] it is concluded that in the present system the charge separation (generation) and charge transfer take place in the bulk multimolecular layers of the ruthenium(II) complex, whereas the ruthenium(II) complex monolayer behaves as a photosensitizer on a SnO_2 semiconductor electrode in the previous case.

Applied Potential Dependence.—Figure 3 demonstrates the dependence of photocurrent on applied potential at the platinum substrate electrode. A Butler-type exponential relation holds for I_p *vs.* η, the applied potential where i_0, k,

$$I_p = i_0 \exp(k\eta) + C \qquad (5)$$

and C are constants; k may be written as $\alpha nF/RT$ and i_0 and C are the potential-independent terms of the photocurrent. The relation (5) indicates that the rate-determining step for the reaction is a c.t. step; probably, after the electron is excited, the process in which the electron hops to the platinum electrode across the membrane [see equation (3)] is potential dependent.

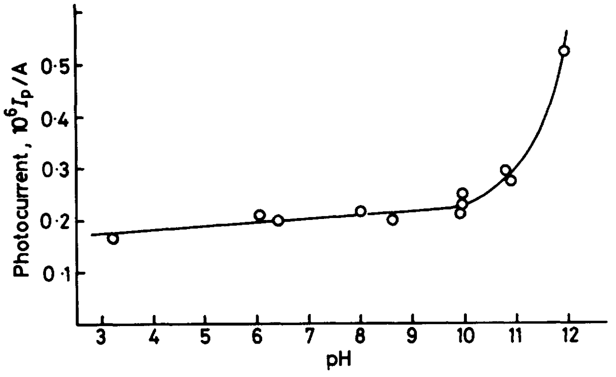

Figure 4. pH dependence of photocurrent. Experimental conditions as in Figure 1 except that the pH was changed with dilute NaOH or $HClO_4$

pH *Dependence.*—Figure 4 demonstrates the pH dependence of the anodic photocurrent. As expected, with increasing pH, the photocurrent increased anodically as a result of the reaction of OH^- ion with photogenerated $[Ru(bipy)_3]^{3+}$ ions [equation (6)].

$$[Ru(bipy)_3]^{3+} + OH^- \longrightarrow [Ru(bipy)_3]^{2+} + \tfrac{1}{4}O_2 + \tfrac{1}{2}H_2O \qquad (6)$$

The regeneration by OH^- ion of $[Ru(bipy)_3]^{2+}$ from $[Ru(bipy)_3]^{3+}$ in homogeneous solution was reported to be kinetically rather complex and the yield of the reaction was less than 100% (depending upon pH).[11] In basic solution an intermediate species involving nucleophilic attack by OH^- on the bound bipyridine ring was proposed.[11] Therefore, it is assumed that the same is true for the reaction of $[Ru(bipy)_3]^{3+}$ photogenerated in the solid matrix of $Ru(bipy)_3(BPh_4)_2$ on the platinum electrode. This is partly supported by the fact that desorption of the surface layer became appreciable upon continuous light illumination for 2—3 h and the colour of the surface layer was changed from light orange to light brown under the experimental conditions of Figure 1 as mentioned earlier.

In order to examine the possibility of hydrogen evolution as in the Honda–Fujishima cell [15] at a dark platinum counter electrode (in 0.1 mol dm^{-3} tetraethylammonium perchlorate, pH varied) short circuited with illuminated $Ru(bipy)_3(BPh_4)_2$–Pt(0.1 mol dm^{-3} $NaBPh_4$), the photocurrent was also measured as a function of the pH of the solution contacting the counter platinum electrode which is separated from the illuminated cell by a glass frit. It was found that the photocurrent increased by 50% on decreasing the pH from 5.95 to 2.30. At first this result seemed to imply the possibility of hydrogen evolution at the counter electrode. However, addition of methylviologen (1,1′-dimethyl-4,4′-bipyridinium) to the solution contacting the platinum counter electrode did not noticeably change the photocurrent. In the same cell assembly without methylviologen, the maximum photopotential was measured to be 475 mV at pH 5.95.

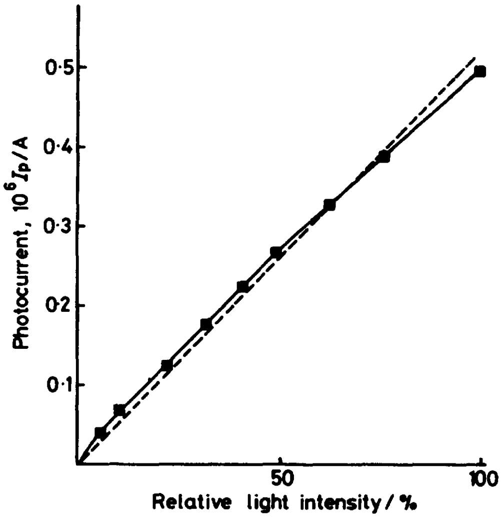

Figure 5. Dependence of photocurrent on relative light intensity. Applied potential, 0 V (s.c.e.); pH 11.9; supporting electrolyte, 0.1 mol dm^{-3} NaBPh$_4$. (■), Experimental; (– – – –), theoretical

Light Intensity.—A two-photon process such as that in equation (7) was also expected to contribute to the present

$$[\mathrm{Ru(bipy)_3}]^{2+} \xrightarrow{h\nu} [\mathrm{Ru(bipy)_3}]^{2+}(^3\mathrm{c.t.}) \xrightarrow{h\nu} [\mathrm{Ru(bipy)_3}]^{3+} + e^- \text{ (charge transfer)} \quad (7)$$

photovoltaic effect. In homogeneous solution, Meisel *et al.*[16] proposed a biphotonic process for the $[\mathrm{Ru(bipy)_3}]^{2+}$ system [equations (8) and (9)]. In the present study, however, the

$$[\mathrm{Ru(bipy)_3}]^{2+} \xrightarrow{h\nu} [\mathrm{Ru(bipy)_3}]^{2+}(^3\mathrm{c.t.}) \xrightarrow{h\nu} [\mathrm{Ru(bipy)_3}]^{3+} + e^- \text{(aq)} \quad (8)$$

$$e^-\text{(aq)} + [\mathrm{Ru(bipy)_3}]^{2+} \longrightarrow [\mathrm{Ru(bipy)_3}]^{+} \quad (9)$$

dependence of the photocurrent on light intensity was almost perfectly linear (see Figure 5) indicating that the observed photoelectrochemical reaction is a one-photon process at least up to the photon flux employed here.

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