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Multistep photocatalytic reduction of dioxygen by immobilized $[Ru(bpy)_3]^{2+}$ in Nafion and cellulose matrices and macrocyclic cobalt(III) complexes

J. Premkumar and R. Ramaraj *

School of Chemistry, Madurai Kamaraj University, Madurai-625 021, India

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The ruthenium(II) complex $[Ru(bpy)_3]^{2+}$, incorporated into Nafion (Nf) and cellulose (CL) matrices was used for the photosensitized reduction of macrocyclic cobalt(III) complexes. Photocatalytic reduction of oxygen (O_2) to hydrogen peroxide (H_2O_2) was carried out by the reaction of the photoproduced cobalt(II) complex. The photoproduced $[Ru(bpy)_3]^{3+}$ complex was reduced by the sacrificial electron donor triethanolamine. High turnover numbers of $[Ru(bpy)_3]^{2+}$ at the membrane were observed. The multistep one-electron photoreduction of O_2 to H_2O_2 in the Nf/$[Ru(bpy)_3]^{2+}$ and CL/$[Ru(bpy)_3]^{2+}$ systems was realized using macrocyclic cobalt(III) complexes as catalyst.

Introduction

The difficulty in creating non-biological model systems to realize multielectron reduction processes lies in the requirement to couple the multistep one-electron reactions of the redox molecules.[1,2] One way of achieving this is the design of a catalyst system in a solid phase or in a membrane system.[3,4] Attempts to construct model systems have been made by using microheterogeneous reaction environments such as micelles, bilayers, *etc.*[5–7] On the other hand, macroheterogeneous membrane systems (solid–solution interface) have not been exploited extensively.[3–8] When the reactant molecules are incorporated into the membrane systems the electron transfer reactions can be accelerated.[8–14]

The photocatalyst, tris(2,2′-bipyridine)ruthenium(II), $[Ru(bpy)_3]^{2+}$, has been one of the most extensively studied sensitizer molecules in solar energy conversion systems in the last two decades.[3–8,14–18] The quenching of the excited state of $[Ru(bpy)_3]^{2+}$ incorporated into cation-exchange resin,[19] Sephadex-sp and Nafion[11] by various metal ions has been reported and is found to be non-homogeneous in these environments.[11,19] The apparent increase in the quenching efficiency was attributed to the high local concentrations of the $[Ru(bpy)_3]^{2+}$ and the quencher in the microheterogeneous domain of the membrane. The use of Nafion (Nf)[20] and cellulose (CL)[21] matrices in the construction of solid phase photoredox systems using $[Ru(bpy)_3]^{2+}$ and MV^{2+} (methyl viologen; 1,1′-dimethyl-4,4′-bipyridinium) has been recognized in the field of solar energy conversion.[11,21–25] However, the catalytic activity of macrocyclic cobalt(III) complexes[26] has not been fully exploited in photocatalytic systems.[27] Such complexes are efficient catalysts for dioxygen reduction.[26] The interesting feature of this metal complex is that the O_2 reacts with the cobalt(II) complex forming an adduct and undergoes further reduction. We have made an attempt[28] to use membrane systems such as Nafion and cellulose to carry out the photoinduced multistep one-electron transfer reactions. Here we report the multistep photocatalytic reduction of O_2 to H_2O_2 using $[Ru(bpy)_3]^{2+}$ incorporated into Nafion and cellulose membrane systems and cobalt(III) complexes.

Experimental

The complex $[Ru(bpy)_3]Cl_2{\cdot}6H_2O$ was prepared according to the literature method.[29] Macrocyclic cobalt(III) complexes, $[Co(cyclam)(H_2O)_2][ClO_4]_3$ and $[Co(teta)(H_2O)_2][ClO_4]_3$ where cyclam = 1,4,8,11-tetraazacyclotetradecane and teta = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, were prepared by using reported procedures.[26,30,31] The Nafion membrane obtained from Aldrich (type 125, equivalent weight 1100, thickness *ca.* 0.13 mm) was pretreated prior to use by boiling in concentrated nitric acid for about 10–20 min.[32] Cellulose paper (Toyo Rosho Chemical Company) was used as received. The $[Ru(bpy)_3]^{2+}$ incorporated Nf and CL matrices were prepared by dipping the 1 cm^2 Nafion (Nf) or cellulose (CL) membrane in a solution containing a known concentration of $[Ru(bpy)_3]^{2+}$. The $[Ru(bpy)_3]^{2+}$ complex was irreversibly adsorbed under the conditions employed. The $[Ru(bpy)_3]^{2+}$ adsorbed Nf and CL membranes {Nf/$[Ru(bpy)_3]^{2+}$ and CL/$[Ru(bpy)_3]^{2+}$} were washed with distilled water and dried at room temperature in the dark. The $[Co(teta)(H_2O)_2]^{3+}$ complex adsorbed into Nf and CL matrices was prepared by dipping the membranes in an acetonitrile solution containing a known concentration of $[Co(teta)(H_2O)_2]^{3+}$. The films were washed and dipped in an aqueous solution containing a known concentration of $[Ru(bpy)_3]^{2+}$ and then washed with distilled water {Nf/$[Co(teta)(H_2O)_2]^{3+}$/$[Ru(bpy)_3]^{2+}$ and CL/$[Co(teta)(H_2O)_2]^{3+}$/$[Ru(bpy)_3]^{2+}$}. The amounts of $[Ru(bpy)_3]^{2+}$ and $[Co(teta)(H_2O)_2]^{3+}$ complex incorporated into the Nf and CL matrices were determined spectrophotometrically by measuring the absorbances of $[Ru(bpy)_3]^{2+}$ in solution before and after dipping the membranes.

The resulting membranes were dipped in a glass cell containing known concentrations of triethanolamine (TEA) and $HClO_4$ at 25 °C and illuminated with a 500 W tungsten–halogen lamp using UV and IR filters. The distance from the center of the lamp to the surface of the cell was 45 cm. A procedure typical of kinetic experiments for the formation of H_2O_2 was used and the amount of H_2O_2 estimated using titrimetry and spectrophotometry methods.[33,34] Pure grade nitrogen and oxygen gases were used for deaeration and oxygenation purposes. To maintain the oxygen concentration during the photolysis experiment, O_2 was continuously bubbled through the experimental solution. The surface morphology of the $[Ru(bpy)_3]^{2+}$ and $[Co(teta)(H_2O)_2]^{3+}$ treated Nf and CL membranes was analysed by a scanning electron microscope (Hitachi S-450). The absorption spectral measurements were carried out by using a JASCO 7800 UV/VIS spectrophotometer. The emission and excited state quenching studies were carried out by using a Hitachi F-4500 spectrofluorometer.

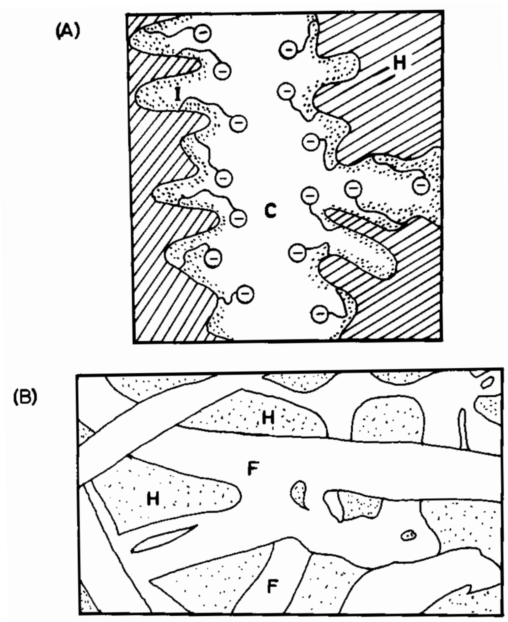


Fig. 1 (A) Schematic structure of the Nf membrane: H = hydrophobic fluorocarbon region, C = hydrophilic ionic cluster region, I = interfacial region, − = SO_3^- group of the Nf polymer. (B) Schematic structure of the CL membrane: H = hydrophilic region and F = fibres.

Experiments were repeated several times and reproducible results obtained.

Results and discussion

The amount of $[Ru(bpy)_3]^{2+}$ incorporated into the Nf membrane was almost an order of magnitude higher when compared to that into the CL matrix under the same experimental conditions. The cationic $[Ru(bpy)_3]^{2+}$ complex resides mainly in the interfacial hydrophilic region of the Nf and CL matrices (Fig. 1). The CL matrix largely consists of a hydrophilic region and fibres and the $[Ru(bpy)_3]^{2+}$ complex mainly occupies the hydrophilic region.[21] The electrostatic interaction between the $[Ru(bpy)_3]^{2+}$ and SO_3^- groups and the hydrophobic interaction of the metal complex with the interfacial region of the Nf membrane are responsible for the adsorption of the higher amount of $[Ru(bpy)_3]^{2+}$ complex in the Nf membrane[23] than in the CL matrix. The absorption and emission spectra of the $[Ru(bpy)_3]^{2+}$ complex and the absorption spectra of the cobalt(III) complex incorporated in the Nf and CL membranes are very similar to those obtained for the metal complexes in solution. This observation indicates that the Nf and CL membranes do not affect the spectral characteristics of the incorporated metal complexes.[11,23] The absorption spectrum of $[Ru(bpy)_3]^{2+}$ in Nafion was not affected by the presence of cobalt(III) complexes or TEA. The scanning electron micrographs of Nf, Nf/$[Ru(bpy)_3]^{2+}$, CL and CL/$[Ru(bpy)_3]^{2+}$ membranes clearly show the adsorption of the metal complex in the membrane. Numerous dark spots on the Nf and CL membranes showing the adsorption of the metal complex were observed.

Two major strategies are being considered in the design of potential membrane devices for the photocatalytic reduction of O_2 using a suitable photocatalyst and electron relay. The first approach involves the photosensitizer alone immobilized in the Nf and CL matrices and the electron relay molecule solubilized in solution. In the second both the sensitizer and electron relay molecules are immobilized in the membranes.

The Nf/$[Ru(bpy)_3]^{2+}$ or CL/$[Ru(bpy)_3]^{2+}$ matrix dipped in a solution containing oxygenated 0.52 mM $[Co(cyclam)(H_2O)_2]^{3+}$, 0.1 M $HClO_4$ and 0.1 M TEA was irradiated for different time intervals and the observed yields of H_2O_2 are shown in Fig. 2. The corresponding turnover numbers (TONs) of $[Ru(bpy)_3]^{2+}$ are also shown, calculated by (2 × moles of H_2O_2)/moles of $[Ru(bpy)_3]^{2+}$. In all the systems, H_2O_2 was observed only in the case of oxygenated solutions containing TEA and cobalt(III) complex. It was not observed in the absence of complex or in the dark; a small amount was found in the absence of TEA. The solid {Nf/$[Co(teta)(H_2O)_2]^{3+}$/$[Ru(bpy)_3]^{2+}$}–solution (O_2) system was also used for the photocatalytic reduction of O_2. In this both the sensitizer and the catalyst molecules are immobilized in the solid phase. The Nf/$[Co(teta)(H_2O)_2]^{3+}$/$[Ru(bpy)_3]^{2+}$ or CL/$[Co(teta)(H_2O)_2]^{3+}$/$[Ru(bpy)_3]^{2+}$ membrane was dipped in an oxygenated aqueous acidic solution containing 0.1 M $HClO_4$ and 0.1 M TEA and then irradiated with visible light. The observed yields of H_2O_2 at these membranes with different irradiation times are shown in Fig. 3. The corresponding TONs of $[Ru(bpy)_3]^{2+}$ are also shown. In the absence of any one of the reaction components in the solid–solution photoredox system the formation of H_2O_2 was not observed. The results were reproducible and the membranes very stable over extended periods. A negligible amount of H_2O_2 was observed when a homogeneous solution containing the photoredox system {$[Ru(bpy)_3]^{2+}$–$[Co(cyclam)(H_2O)_2]^{3+}$ or $[Co(teta)(H_2O)_2]^{3+}$} was irradiated. At longer irradiation times the amount of H_2O_2 almost reached a maximum. As the formed H_2O_2 undergoes decomposition, its concentration remains constant as shown in Figs. 2 and 3. However, when the membrane was washed and reused in the experiment very similar results were observed. At longer irradiation time the build-up of H_2O_2 may lead to decomposition of H_2O_2 by the $[Ru(bpy)_3]^{3+}$ complex or surface catalysed decomposition of H_2O_2 or other side reactions.

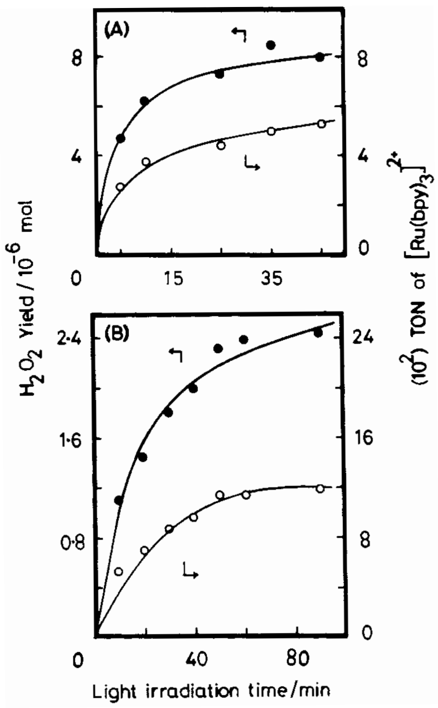


Fig. 2 Yields of H_2O_2 and the corresponding TONs of $[Ru(bpy)_3]^{2+}$ observed at different irradiation times in an oxygenated solution containing 0.52 mM $[Co(cyclam)(H_2O)_2]^{3+}$, 0.1 M $HClO_4$ and 0.1 M TEA for (A) Nf/$[Ru(bpy)_3]^{2+}$ and (B) CL/$[Ru(bpy)_3]^{2+}$. Amounts of $[Ru(bpy)_3]^{2+}$ in the Nf and CL membranes are 3.34×10^{-8} and 4.11×10^{-9} mol respectively and $I_0 = 6.52 \times 10^3$ W cm^{-2}.

In the membrane systems, the excited state electron transfer quenching between $[Ru(bpy)_3]^{2+}$ and cobalt(III) complexes produces $[Ru(bpy)_3]^{3+}$ and cobalt(II) complex. The latter reacts with O_2 to produce Co^{III}–O_2H in acidic solution. Macrocyclic cobalt(II) complexes are known to react with O_2 to form Co^{III}–O_2H in acidic solution.[26,27] This hydroperoxo complex quenches the excited state $[Ru(bpy)_3]^{2+}$ and produces cobalt(II) complex

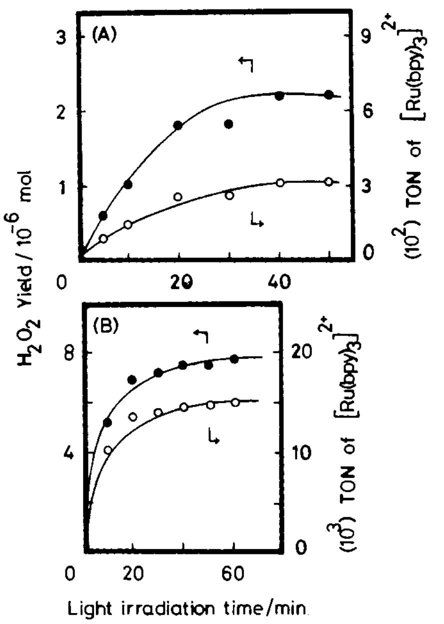
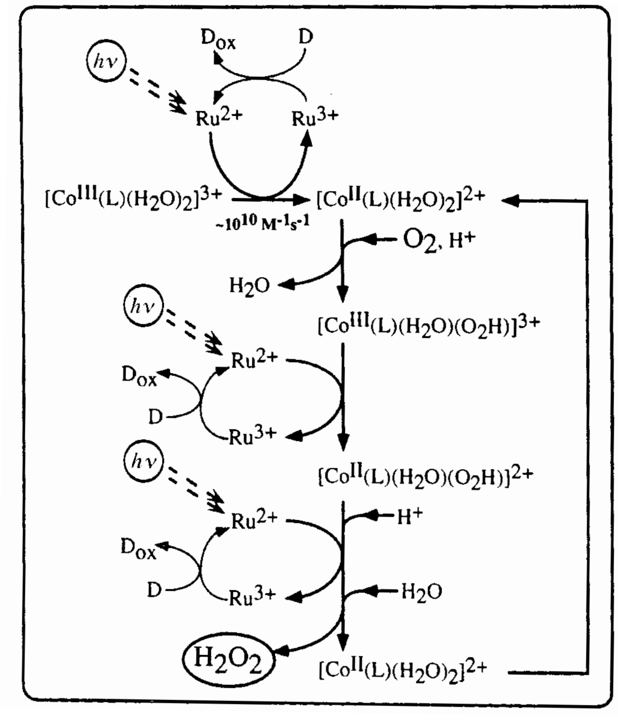


Fig. 3 Yields of H_2O_2 and the corresponding TONs of $[Ru(bpy)_3]^{2+}$ observed at different irradiation times in an oxygenated solution containing 0.1 M $HClO_4$ and 0.1 M TEA. (A) Nf/$[Co(teta)(H_2O)_2]^{3+}$/$[Ru(bpy)_3]^{2+}$ and (B) CL/$[Co(teta)(H_2O)_2]^{3+}$/$[Ru(bpy)_3]^{2+}$. Amount of $[Co(teta)(H_2O)_2]^{3+}$ in Nf, 1.47×10^{-6} mol and in CL, 7.37×10^{-8} mol. Amounts of $[Ru(bpy)_3]^{2+}$ in Nf and CL membranes are 1.40×10^{-8} and 1.02×10^{-9} mol respectively and $I_0 = 6.52 \times 10^3$ W cm^{-2}.



Scheme 1 Photocatalytic reduction of dioxygen at Nafion and cellulose membranes containing $[Ru(bpy)_3]^{2+}$ and macrocyclic cobalt(III) complex. $[Co(cyclam)(H_2O)_2]^{3+}$ or $[Co(teta)(H_2O)_2]^{3+}$, $Ru^{2+} = [Ru(bpy)_3]^{2+}$, L = cyclam or teta and D = TEA.

and H_2O_2 (Scheme 1). The excited state electron transfer quenching rate constant for the $[Ru(bpy)_3]^{2+}$–Co^{III} photoredox systems in the Nf membrane was determined as $\approx 10^{10}$ M^{-1} s^{-1} using the photoelectrochemical method.[14] In a photoelectrocatalytic reduction of O_2 the photoproduced Co^{III}–O_2H complex undergoes one-electron reduction at a potential of 0.1 V(SCE) to produce cobalt(II) complex and H_2O_2.[27] This observation clearly shows that the energetics of the Co^{III}–O_2H complex is sufficient to quench the excited state $[Ru(bpy)_3]^{2+}$ complex in the presence of a sacrificial electron donor. Since the reduction potential of $[Co^{III}–O_2^-]$ is more positive than that of the cobalt(III) complex itself,[27,35] the Co^{III}–O_2H complex will quench the excited state $*[Ru(bpy)_3]^{2+}$ complex to form Co^{II}–O_2H. This hydroperoxo complex, Co^{II}–O_2H is reduced at more negative potentials $\approx$0.0 V(SCE) to yield cobalt(II) complex and H_2O_2.[26,27] This means that the protonated Co^{II}–O_2H complex oxidatively quenches the excited state $[Ru(bpy)_3]^{2+}$ complex to produce Co^{II} and H_2O_2. In the presence of TEA, the photoproduced $[Ru(bpy)_3]^{3+}$ complex was efficiently reduced to $[Ru(bpy)_3]^{2+}$. The $[Ru(bpy)_3]^{3+}$ was also reduced by water[36] and the reduction found to be efficient in the adsorbed site.

The $[Co(cyclam)(H_2O)_2]^{3+}$ complex is soluble in water and reversibly adsorbs on the Nf and CL matrices. The $[Co(teta)(H_2O)_2]^{3+}$ complex is soluble only in aqueous acetonitrile solution and irreversibly adsorbs on the Nf and CL matrices. Exploiting this property we have constructed two different photocatalytic membrane systems, *viz.* (i) solid $\{[Ru(bpy)_3]^{2+}\}$–solution$\{[Co(cyclam)(H_2O)_2]^{3+}, O_2$, TEA and $HClO_4\}$ and solid$\{[Ru(bpy)_3]^{2+}, [Co(teta)(H_2O)_2]^{3+}\}$–solution($O_2$, TEA and $HClO_4$) systems. The complex $[Co(cyclam)(H_2O)_2]^{3+}$, reversibily diffuses into the hydrophilic ionic cluster region of the membranes and the photoinduced electron transfer reaction occurs between the $[Ru(bpy)_3]^{2+}$ and cobalt(III) complexes in the membrane. In the case of $[Co(teta)(H_2O)_2]^{3+}$ the photoinduced electron transfer occurs in the solid state leading to the formation of $[Ru(bpy)_3]^{3+}$ and cobalt(II) complex. In the static quenching process the back electron transfer process competes with the reaction of $[Ru(bpy)_3]^{3+}$ with TEA. The $[Co(cyclam)(H_2O)_2]^{3+}$ complex resides in the cluster region, diffuses in the hydrophilic channels of the membranes and reacts with O_2 to form the Co^{III}–O_2H complex. The results are best interpreted by a mechanism in which the back electron transfer reaction between $[Ru(bpy)_3]^{3+}$ and cobalt(II) complexes is prevented by the reaction of $[Ru(bpy)_3]^{3+}$ with the electron donor TEA. The reaction between $*[Ru(bpy)_3]^{2+}$ and cobalt(III) complexes in the membranes may be explained by eqns. (1)–(6), where the

$$[Ru^{2+}]_a\{[Co^{3+}]_m[TEA]_n\}_s \xrightarrow[k_1]{h\nu} [{*}Ru^{2+}]_a\{[Co^{3+}]_m[TEA]_n\}_s \quad (1)$$

$$[{*}Ru^{2+}]_a\{[Co^{3+}]_m[TEA]_n\}_s \xrightarrow{k_2} [Ru^{2+}]_a\{[Co^{3+}]_m[TEA]_n\}_s + h\nu' \quad (2)$$

$$[{*}Ru^{2+}]_a\{[Co^{3+}]_m[TEA]_n\}_s \xrightarrow{k_3} [Ru^{2+}]_{a-1}[Ru^{3+}]\{[Co^{3+}]_{m-1}[Co^{2+}][TEA]_n\}_s \quad (3)$$

$$[Ru^{2+}]_{a-1}[Ru^{3+}]\{[Co^{3+}]_{m-1}[Co^{2+}][TEA]_n\}_s \xrightarrow{k_4} [Ru^{2+}]_a\{[Co^{3+}]_m[TEA]_n\}_s \quad (4)$$

$$[Ru^{2+}]_{a-1}[Ru^{3+}]\{[Co^{3+}]_{m-1}[Co^{2+}][TEA]_n\}_s \xrightarrow{k_5} [Ru^{2+}]_a\{[Co^{3+}]_{m-1}[Co^{2+}][TEA]_{n-1}[TEA]_{ox1}\}_s \quad (5)$$

$$[Ru^{2+}]_a\{[Co^{3+}]_{m-1}[Co^{2+}][TEA]_{n-1}[TEA]_{ox1}\}_s \xrightarrow{H^+} [Ru^{2+}]_a\{[H^+][Co^{3+}]_{m-1}[TEA]_{n-1}[TEA]_{ox1}\}_s + [Co^{2+}]_s \quad (6)$$

chemical species given in square brackets with subscript '*a*' represents the irreversibly adsorbed $[Ru(bpy)_3]^{2+}$ (Ru^{2+}) in the Nf or CL membrane and '*s*' represents the cobalt(III) complex $\{[Co(cyclam)(H_2O)_2]^{3+}\}$ and the TEA present in the solution and in contact with Ru^{2+}. The subscripts '*m*' and '*n*' represent the numbers of cobalt(III) complex and TEA, Ru^{2+}, $*Ru^{2+}$, Ru^{3+} and Co^{3+} represent $[Ru(bpy)_3]^{2+}$, $*[Ru(bpy)_3]^{2+}$, $[Ru(bpy)_3]^{3+}$, and $[Co(cyclam)(H_2O)_2]^{3+}$ respectively and $(TEA)_{ox}$ is the oxidized species of TEA. The reduction reaction of Ru^{3+} by TEA [eqn. (5)] competes with the back electron transfer reaction (4). Eqn. (6) represents the ion-exchange equilibrium of Co^{II} and H^+ present in the solution.

The Co^{2+} complex reduces one molecule of O_2 and forms an adduct $Co^{III}–O_2H$. This complex is further reduced in two steps to produce Co^{II} and H_2O_2. The photoproduced $[Ru(bpy)_3]^{3+}$ is reduced to $[Ru(bpy)_3]^{2+}$ by TEA. Considering the input light energy in addition to the input energy of the sacrificial electron donor TEA the formation efficiency of H_2O_2 comes to 14%. The formation of H_2O_2 depends on the concentration of cobalt(III) complex and the intensity of the incident light (I_0). The yields of H_2O_2 obtained in the Nf/$[Ru(bpy)_3]^{2+}$ and CL/$[Ru(bpy)_3]^{2+}$ systems using different concentrations of $[Co(cyclam)(H_2O)_2]^{3+}$ complex in 0.1 M $HClO_4$ and 0.1 M TEA at a light irradiation time of 15 min are shown in Fig. 4 and the corresponding TONs of $[Ru(bpy)_3]^{2+}$ are also shown. For the above systems linear plots were observed.

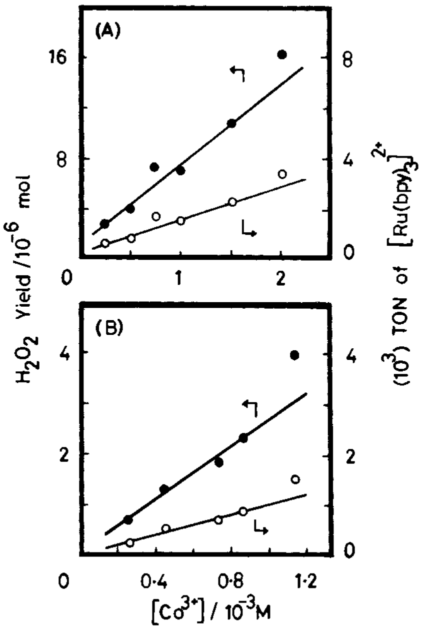


Fig. 4 Yields of H_2O_2 and the corresponding TONs of $[Ru(bpy)_3]^{2+}$ observed at different concentrations of $[Co(cyclam)(H_2O)_2]^{3+}$ in an oxygenated solution containing 0.1 M $HClO_4$ and 0.1 M TEA. (A) Nf/$[Ru(bpy)_3]^{2+}$ and (B) CL/$[Ru(bpy)_3]^{2+}$. Light irradiation time = 15 min. Amounts of $[Ru(bpy)_3]^{2+}$ in Nf and CL membranes are 0.95×10^{-8} and 5.31×10^{-9} mol respectively and $I_0 = 6.52 \times 10^3$ W cm^{-2}.

The amount of $[Ru(bpy)_3]^{2+}$ adsorbed in the CL membrane was found to influence the yield of H_2O_2 produced [Figs. 5(a) and 6(a)]. An increase in the concentration of $[Ru(bpy)_3]^{2+}$ in the CL membrane increased the yield of H_2O_2 and the corresponding TON of $[Ru(bpy)_3]^{2+}$. The TON of $[Ru(bpy)_3]^{2+}$ first increased and then decreased at higher concentrations of $[Ru(bpy)_3]^{2+}$ [Figs. 5(b) and 6(b)]. This may be due to the self quenching of the excited state $[Ru(bpy)_3]^{2+}$ complex and the possible back electron transfer reaction at higher local concentrations of $[Ru(bpy)_3]^{2+}$ in the membrane and the light filtering effect at the membrane surface. Very similar results were also observed at the Nf membrane.

The quenching of the excited state $[Ru(bpy)_3]^{2+}$ in the Nf membrane by $[Co(cyclam)(H_2O)_2]^{3+}$ was studied (Fig. 7). In sharp contrast to the quenching of M^{n+} ions,[11,15] the Stern–Volmer plot strongly deviates from linearity. The non-homogeneous behavior was observed in repeated experiments with different amounts of $[Ru(bpy)_3]^{2+}$. A similar observation has been reported for the quenching of excited state $[Ru(bpy)_3]^{2+}$ in a Nf membrane by MV^{2+}.[11] The positively charged $[Ru(bpy)_3]^{2+}$ complex is quantitatively adsorbed on the Nf and CL matrices and appropriate absorption spectral changes could be studied. The quencher ions $[Co(cyclam)(H_2O)_2]^{3+}$ are free to diffuse inside the hydrophilic cluster region in which they happen to reside at the time of excitation and thereby encounter the excited $[Ru(bpy)_3]^{2+}$ complex. This behavior resembles the features observed for the quenching of solubilized sensitizer molecules in micellar systems by quencher molecules confined to the micelle–water interface.[7,37,38]

The probable photoinduced electron transfer quenching mechanism leading to the formation of H_2O_2 in the Nf/$[Ru(bpy)_3]^{2+}$ and CL/$[Ru(bpy)_3]^{2+}$ systems dipped in a solution containing cobalt(III) complex, TEA and $HClO_4$ can be suggested as follows.

$$[Ru^{2+}]_a\{[Co^{3+}]_m[TEA]_n\}_s \xrightarrow{h\nu} [Ru^{2+}]_a\{[Co^{3+}]_{m-1}[Co^{2+}][TEA]_{n-1}[TEA]_{ox1}\}_s$$

$$[Ru^{2+}]_a\{[Co^{3+}]_{m-1}[Co^{2+}][TEA]_{n-1}[TEA]_{ox1}\}_s \xrightarrow{O_2,\ H^+} [Ru^{2+}]_a\{[Co^{3+}]_{m-1}[Co(O_2H)]^{3+}[TEA]_{n-1}[TEA]_{ox1}\}_s$$

$$[Ru^{2+}]_a\{[Co^{3+}]_{m-1}[Co(O_2H)]^{3+}[TEA]_{n-1}[TEA]_{ox1}\}_s \xrightarrow{h\nu}$$

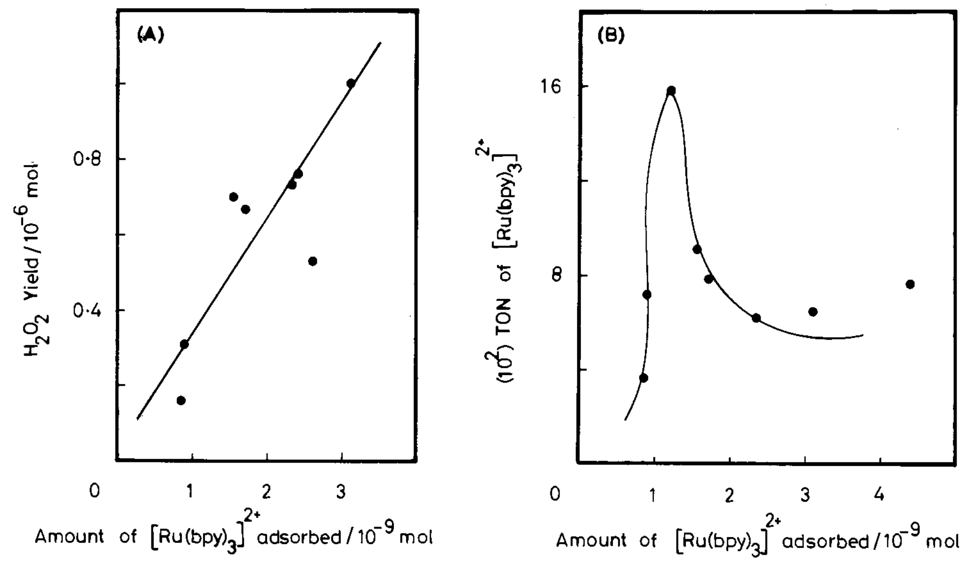


Fig. 5 The H_2O_2 yield (A) and TON of $[Ru(bpy)_3]^{2+}$ (B) observed for a CL/$[Ru(bpy)_3]^{2+}$ membrane dipped in an oxygenated solution containing 0.15 mM $[Co(cyclam)(H_2O)_2]^{3+}$, 0.1 M $HClO_4$ and 0.1 M TEA. Light irradiation time = 15 min and $I_0 = 6.52 \times 10^3$ W cm^{-2}.

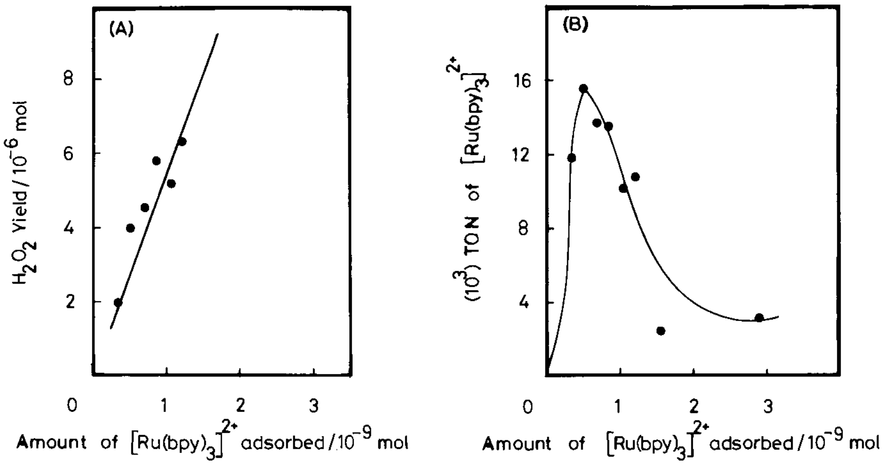


Fig. 6 The H_2O_2 yield (A) and TON of $[Ru(bpy)_3]^{2+}$ (B) observed for CL/$[Co(teta)(H_2O)_2]^{3+}$/$[Ru(bpy)_3]^{2+}$ system dipped in an oxygenated solution containing 0.1 M $HClO_4$ and 0.1 M TEA. Light irradiation time = 15 min. Amount of $[Co(teta)(H_2O)_2]^{3+}$ in the CL matrix is 7.37×10^{-6} mol and $I_0 = 6.52 \times 10^3$ W cm^{-2}.

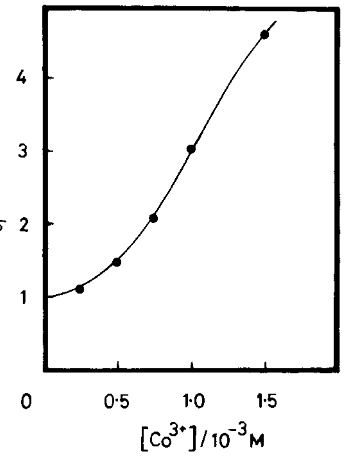


Fig. 7 Stern–Volmer plot obtained for the quenching of excited state Nf/$[Ru(bpy)_3]^{2+}$ by $[Co(cyclam)(H_2O)_2]^{3+}$ in 0.1 M $HClO_4$ and 0.1 M TEA. Excitation wavelength = 453 nm and emission wavelength = 600 nm.

$$[Ru^{2+}]_{a-1}[Ru^{3+}]\{[Co^{3+}]_{m-1}[Co(O_2H)]^{2+}[TEA]_{n-1}[TEA]_{ox1}\}_s$$

$$[Ru^{2+}]_{a-1}[Ru^{3+}]\{[Co^{3+}]_{m-1}[Co(O_2H)]^{2+}[TEA]_{n-1} \longrightarrow$$

$$[TEA]_{ox1}\}_s[Ru^{2+}]_a\{[Co^{3+}]_{m-1}[Co(O_2H)]^{2+}[TEA]_{n-2}[TEA]_{ox2}\}_s$$

$$[Ru^{2+}]_a\{[Co^{3+}]_{m-1}[Co(O_2H)]^{2+}[TEA]_{n-2}[TEA]_{ox2}\}_s \xrightarrow[H^+]{h\nu}$$

$$[Ru^{2+}]_a\{[Co^{3+}]_{m-1}[Co^{2+}][TEA]_{n-3}[TEA]_{ox3}\}_s + \{H_2O_2\}_s$$

In the present photoredox system $\{[Ru(bpy)_3]^{2+}–Co^{III}\}$ the importance of the Nf and CL membranes is: (i) the immobilization of the positively charged metal complexes in a dispersed state in the membrane, (ii) the imposition of a microheterogeneous environment on the reacting molecules and (iii) the presence of a large hydrophilic solvated cluster network connecting channels in the membrane. The advantage of the solid-phase $[Ru(bpy)_3]^{2+}–Co^{III}$ photoredox system is that the reactivity and the disproportionation of O_2^- ions[39] are suppressed by the formation of the $Co^{III}–O_2H$ complex. The multistep one-electron transfer process occurs efficiently in the membrane rather than in a homogeneous solution. Thus the present work demonstrates the importance of the immobilization of catalytic molecules in a membrane to a realize multielectron reduction process by a series of single step one-electron transfer reactions (Scheme 1).

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