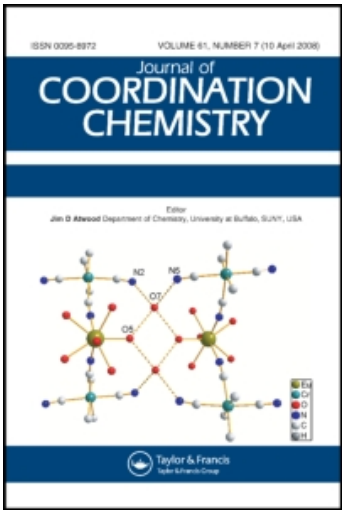


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# ELECTRON-TRANSFER ACROSS INTERFACES BETWEEN WATER AND HYDROPHOBIC REGION AS CATALYZED BY PHOTOEXCITED AMPHIPATHIC RUTHENIUM COMPLEX

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# ELECTRON-TRANSFER ACROSS INTERFACES BETWEEN WATER AND HYDROPHOBIC REGION AS CATALYZED BY PHOTOEXCITED AMPHIPATHIC RUTHENIUM COMPLEX[1]

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An amphipathic ruthenium complex in the photoactivated state was found to serve as a good catalyst for electron-transfer across the interface between water and hydrophobic interior of micelles or liposomes. The reaction proceeded via oxidative quenching of the photoexcited complex by methylviologen homologues, if EDTA was used as the final electron source (reducing agent). Reductive quenching was observed, however, when either NTA (in CTAC system) or triethylamine (in loposome system) was the electron source of the reaction under similar conditions. The mechanism was discussed and the possible application to the energy conversion process was suggested.



## INTRODUCTION

Photoinduced redox reactions of tris(2,2′-bipyridine)-ruthenium(II) and the analogues have been investigated in detail, since they were suggested to be possible catalysts for photochemical cleavage of water into hydrogen and oxygen molecules.[2] Among various studies, photochemical behaviors of several amphipathic polypyridine complexes have been noticed to possess promising characteristics.[3] On the other hand, laser flash photolysis studies on the photoinduced ionization and electron-transfer reactions of aromatic compounds in micellar systems have revealed that charge-separations of the photoproduced ion pairs are facilitated by the electric charge at the micellar surface.[4] The polarity gradient at the hydrophobic bilayer of a synthetic vesicle has also been reported to aid the charge separation.[5] The present authors have then studied photoinduced redox reactions of an amphipathic derivative of tris(2,2′-bipyridine)ruthenium(II) (abbreviated to $Ru(bpy)_3^{2+}$) at the micellar surface and proved that photoreductions of methylviologen homologues smoothly proceeded via the reduced ruthenium complex in the presence of mild reducing agents such as DMA (*N,N*-dimethylaniline).[6] Fendler and his associates have also reported that the charge separation of the photo-produced ion pair, $RuC_{18}(bpy)_3^+$ and *N*-methylphenothiazine cation radical ($MPTH^{\cdot+}$), is prompted by electrostatic repulsion between $MPTH^{\cdot+}$ and positively charged outer surface of dioctadecyl dimethylammonium chloride vesicles.[7]

In the present experiment, photoinduced redox reactions of amphipathic ruthenium complex in micellar systems were investigated by the use of hydrophilic reducing agents, EDTA and NTA (nitrilotriacetate), rather than the above mentioned hydrophobic compounds (DMA and MPTH).

In addition, photoinduced electron-transport across phospholipid liposome wall has been shown to be useful for separating photoproduced redox pairs.[8] Therefore, photoinduced redox reactions of the ruthenium complex in liposomal system were also studied in detail as described here.

## EXPERIMENTAL

The amphipathic ruthenium complex used in this experiment is (*N,N*′-di(dodecyl-2,2′-bipyridine-4,4′-dicarboxamide)-bis(2,2′-bipyridine)ruthenium(II)$^{2+}$ (abbreviated to $RuC_{12}B^{2+}$). The complex was obtained by the reaction between bis(2,2′-bipyridine)Ru(II) dichloride and separately prepared *N,N*′-di(dodecyl-2,2′-bipyridine-4,4′-dicarboxamide under reflux in ethanol solution.[9] The pertinent analytical data are in agreement with the expected formura including two water molecules (Found: C, 55.09%; H, 6.30%; N, 9.22%. Calcd. for $C_{56}H_{76}N_8O_{12}Cl_2Ru$: C, 54.89%; H, 6.26%; N, 9.15%). An amphipathic homologue of

methylviologen ($MV^{2+}$) was also prepared by the reaction between dodecyl bromide and 4,4′-bipyridine to obtain dodecylviologen (1,1′-dodecyl-4,4′-bipyridinium$^{2+}$, denoted by $C_{12}V^{2+}$). As to the rest of the materials, extra pure grade chemicals were purchased and further purification was carried out before use, if it was required. In addition to $MV^{2+}$ and $C_{12}V^{2+}$, AQαS (9,10-anthraquinone-1-sulfonate), vitamin $K_1$ and $K_3$ were used as the electron acceptors, while the following chemicals were chosen as the reducing agents: EDTA,[10] NTA (trisodium nitrilotriacetate), and TEA (triethyl amine).[11] Micellar solutions were prepared by the sonication of aqueous solutions containing appropriate amounts of surfactant above cmc: SDS (sodium dodecylsulfate, $1 \times 10^{-2}$ M), CTAC (cetyltrimethylammonium chloride, $1 \times 10^{-2}$ M), and Triton X-100 (nonionic surfactant, 1% (v/v)). Liposome solutions were prepared by the sonication of dispersed dipalmitoyl phosphatidylcholine (DPPC, $1 \times 10^{-3}$ M) in aqueous solutions according to the standard procedures.

In the case of micellar systems, an aqueous solution containing $RuC_{12}B^{2+}$, reducing agent, substrate and appropriate amounts of surfactants was degassed by repeated freeze-pump-thaw cycles and irradiated by light with wavelength above 450 nm. Reduction of the substrates such as $MV^{2+}$, $C_{12}V^{2+}$ and AQαS was followed by the difference absorptions. The sample for liposomal systems was prepared in essentially the same manner except for the deaerating process, which consists of repeated cycles (ca. 20 times) of degassing-argon flush-degassing at the room temperature. The quenching constants were obtained by the ordinary Stern–Volmer plot of the luminescence intensity of the photoexcited $RuC_{12}B^{2+}$ at relatively small quencher concentrations. The reduction of the electron acceptors such as viologen homologues and quinones was followed by measuring the increase in the difference absorption due to the reduced product. Flash photolysis was carried out as described in the previous paper.[6]

## RESULTS AND DISCUSSIONS

### *Photochemical Behaviors of Amphipathic Ruthenium Complex at the Micellar Surface*

In aqueous methanol solutions (methanol : water = 1 : 1 (v/v), the luminescence of photoexcited $RuC_{12}B^{2+}$ was quenched by NTA with a rate constant ($k_q = 3 \times 10^8$ $M^{-1}s^{-1}$) much less than diffusion controlled rates. No quenching was observed, however, if NTA was replaced by EDTA. A nearly threefold increase in the quenching efficiency was observed when CTAC micellar solutions of NTA were utilized. It is apparent that the enrichment of NTA anions to the positively charged surface of CTAC micelles is in favor of the quenching process. Due to the close resemblance in the molecular structure between NTA and EDTA, one may easily suggest that photoexcited $RuC_{12}B^{2+}$ is reduced by NTA ion. The above observed difference in the quenching experiments should be expected, if NTA is somewhat stronger reductant than EDTA. Unfortunately, the direct evidences for the formation of $RuC_{12}B^{+}$ could not be obtained by flash photolysis technique. The reason may be that the annihilation of the photo-produced geminate ion-pair takes place with an extremely rapid rate when the ion-pairs bear opposite charges. As a consequence, the quantum yield for the surviving $RuC_{12}B^{+}$ becomes so small to be detected by flash photolysis technique. A good supporting evidence for the formation of $RuC_{12}B^{+}$ was obtained, however, by the chemical reactions as described below.

Sensitized photoreductions of AQαS ($1 \times 10^{-4}$ M) in CTAC ($1 \times 10^{-2}$ M) solutions served as the best chemical probe to testify the above suggested quenching mechanisms. The amphipathic ruthenium complex, $RuC_{12}B^{2+}$ ($2 \times 10^{-5}$ M), was solubilized into the micellar solution and served as the sensitizer. The photoreduction of AQαS easily took place in the system containing NTA ($1 \times 10^{-3}$ M) as the reducing agent, while no reaction was observed if NTA was replaced by EDTA ($1 \times 10^{-3}$ M). This result is in good agreement with the above discussed quenching behaviors. The following analyses in details indicate that the reaction in NTA system proceeds via reductive quenching of the photoexcited $RuC_{12}B^{2+}$, while the reaction in EDTA system requires oxidative quenching.

The present authors have previously shown that the sensitized reduction of AQαS by EDTA smoothly proceeds via photooxidation of $Ru(bpy)_3^{2+}$ only in the presence of electron-transfer mediator such as $MV^{2+}$ and benzylviologen.[12] Essentially the same phenomena were observed with micellar systems. The luminescence from photoexcited $RuC_{12}B^{2+}$ was efficiently quenched by AQαS ($1 \times 10^{-4}$ M) in the CTAC system, but no photoreduction of AQαS was observed as stated above. In the presence of $MV^{2+}$, the photoreduction proceeds with a rate, which is approximately 10% of that observed with $Ru(bpy)_3^{2+}$-$MV^{2+}$-AQαS-EDTA system under similar conditions. When an amphipathic mediator ($C_{12}V^{2+}$)

TABLE I
Comparison between quenching rate constants for viologens and relative quantum yields of reduced products $V^{\ddagger}$ and $AQ\alpha SH_2$) in various systems

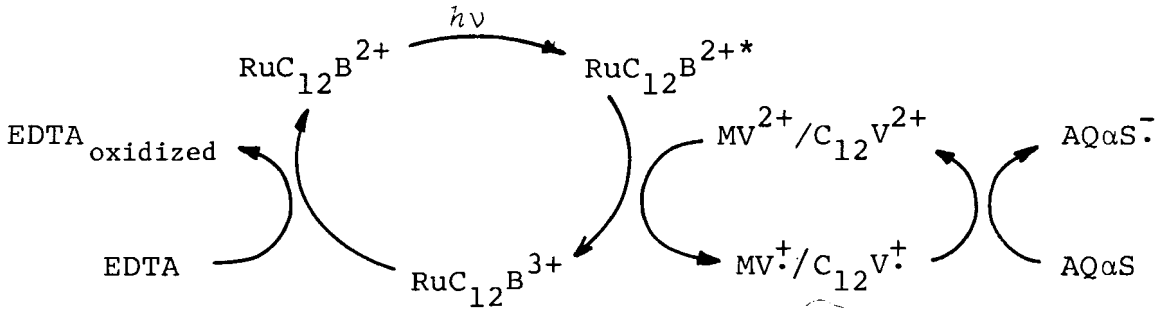
| System | $k_q$-value for viologen ion[a] | Relative quantum | |
|---|---|---|---|
| | | $V^{\ddagger}$ | $AQ\alpha SH_2$ |
| $Ru(bpy)_3^{2+}/MV^{2+}$/ water | $2 \times 10^8$ $M^{-1}s^{-1}$ | 100 | 100 |
| $RuC_{12}B^{2+}/MV^{2+}$/ CTAC | $3 \times 10^6$ | 10 | 10 |
| $RuC_{12}B^{2+}/C_{12}V^{2+}$/ CTAC | $1 \times 10^{10}$ | 210 | 210 |

[a]The quenching experiments were carried out under the following conditions: [Ru(II) complex] = $1 \times 10^{-5}$ M at 20°C.
[b]The values were obtained with solutions containing the following material: [EDTA] = $10^{-3}$ M, [Ru(II) complex] = $2 \times 10^{-5}$ M, [viologen ion] = $5 \times 10^{-4}$ M, and [AQαS] = $10^{-4}$ M.

was used in place of hydrophilic $MV^{2+}$, an approximately twentyfold increase in the reduction rate of AQαS was observed. Further insight into the reaction mechanism may be obtained by comparing the quenching rate constant and the efficiency of sensitized reductions. The quenching rate constants for various systems investigated in this experiment are summarized in Table I. In the same Table, are shown the relative yields of the reduced form of viologen homologue and AQαS. The relative yields of $AQ\alpha SH_2$, hydroquinone corresponding to AQαS, are in good agreement with the yields of viologen cation radicals obtained in the absence of AQαS. The $k_q$-value for $MV^{2+}$ in $RuC_{12}B^{2+}$/CTAC system is only 2% of that in $Ru(bpy)_3^{2+}$/water system. This observation is easily understood as due to the coulombic repulsion between the positive charges of CTAC micellar surface and the approaching $MV^{2+}$. The relative yield of $MV^{\ddagger}$ in CTAC system, on the other hand, is 10% of that in non-micellar system. In other words, the yield of $MV^{\ddagger}$ in CTAC system is somewhat better than that expected from the $k_q$-value. It is strongly suggested that the separation of the geminate ion pair, $RuC_{12}B^{3+}$ and $MV^{\ddagger}$, is facilitated by the coulombic repulsion between the leaving $MV^{\ddagger}$ and positive charges at the micellar surface. The quenching efficiency in $RuC_{12}B^{2+}$/-$C_{12}V^{2+}$/CTAC system is much more improved in comparison with that in $RuC_{12}B^{2+}/MV^{2+}$/CTAC system at least by two reasons: (1) $C_{12}V^{2+}$ is confined to micellar surface, so that the effective concentration around $RuC_{12}B^{2+}$ should be appreciably higher than the case of $MV^{2+}$, and (2) the positive charges at the CTAC micellar surface do not extend any effect on the mutual approach between $RuC_{12}B^{2+}$ and $C_{12}V^{2+}$ as far as they stay on the same micell. In spite of this large increase in $k_q$-value (by a factor of $10^4$), relative yields of $V^{\ddagger}$ and $AS\alpha SH_2$ in $RuC_{12}B^{2+}/C_{12}V^{2+}$/-CTAC system is only twenty times higher than those in $RuC_{12}B^{2+}/MV^{2+}$/CTAC system. The separation between the geminate ion pair, $RuC_{12}B^{3+}$ and $C_{12}V^{\ddagger}$, may be hindered because $C_{12}V^{\ddagger}$ cannot easily leave the micellar surface. In any event, the catalytic reduction of AQαS by EDTA in the bulk water proceeds via oxidative quenching of the photoexcited amphipathic ruthenium complex by viologen homologues at the micellar surface (Scheme I).

The reduction of substrates incorporated into the core of CTAC micelles was also catalyzed by photoexcited $RuC_{12}B^{2+}$, when an amphipathic mediator ($C_{12}V^{2+}$) was used in place of hydrophilic $MV^{2+}$. For example, reduction of vitamin $K_1$ (or $K_3$) was accelerated by a factor of five, in the presence of $C_{12}V^{2+}$ ($1 \times 10^{-4}$ M), in comparison with the rate obtained in the absence of $C_{12}V^{2+}$. The luminescence from photoexcited $RuC_{12}B^{2+}$ was quenched by vitamin $K_1$ ($k_q = 2 \times 10^{10}$ $M^{-1}s^{-1}$) to almost the

SCHEME I



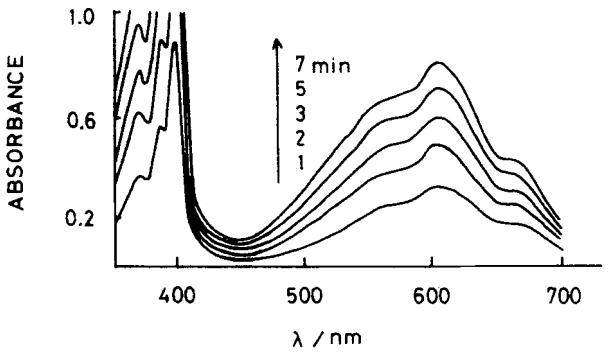



FIGURE 1 The growth of $C_{12}V^{+\cdot}$ along the irradiation ($\lambda > 450$ nm) of an aqueous solution containing the following materials: $RuC_{12}B^{2+}$ ($2 \times 10^{-5}$ M), $C_{12}V^{2+}$ ($5 \times 10^{-4}$ M), EDTA ($1 \times 10^{-3}$ M), and CTAC ($1 \times 10^{-2}$ M).

same extent as that obtained with $C_{12}V^{2+}$ ($k_q = 1 \times 10^{10}$ $M^{-1}s^{-1}$). All of these data indicate that the reduction of quinones by EDTA also proceed via photooxidation of $RuC_{12}B^{2+}$ in the presence of $MV^{2+}$-homologues as the mediator as shown in Scheme I. The reaction scheme was verified by observing the growth of characteristic absorption due to the reduced form of $C_{12}V^{2+}$ under the irradiation of a CTAC solution containing $RuC_{12}B^{2+}$ and EDTA (Figure 1). In the presence of vitamin $K_1$, the absorption due to $C_{12}V^{+}$ does not grow. It appears that photoexcited $RuC_{12}B^{2+}$ is quenched by the quinones via oxidative processes but back electron-transfer takes place before the geminate ion-pair is separated. In the case where the electron acceptor is either $MV^{2+}$ or the homologue, the photoproduced ion-pairs bear positive charges and the coulombic repulsion between the geminate ion-pair helps the charge separation. Some fractions of $MV^{+\cdot}$ (or the homologue) may successfully escape the recombination cage and deliver the electron to quinone molecules away from the oxidized ruthenium complex. In the meantime, EDTA reduced the oxidized ruthenium complex back to $RuC_{12}B^{2+}$, and the reduced quinones start accumulating.

The photoreduction of AQαS in the NTA-CTAC system is fairly rapid: the reaction rate is approximately fifty times larger than that of $MV^{2+}$-mediated photoreduction in EDTA-CTAC system under similar condition. In this case, the reaction pathway via the oxidative quenching of photoexcited $RuC_{12}B^{2+}$ should be clearly disregarded on the basis of the above arguments. An alternative pathway is the reduction of the photoexcited ruthenium complex by NTA. In good agreement with this suggestion, the luminescence from the photoexcited $RuC_{12}B^{2+}$ is actually quenched by NTA. Then, an attempt was made to compare the relative quantum yield for the reduction of AQαS and the quenching efficiency of the luminescence from the photoexcited ruthenium complex in various micellar solutions as summarized in Table II.

The small quantum yield of $AQ\alpha S^{-\cdot}$ in Triton X-100 micelles is in good agreement with the fact that the quenching efficiency of the luminescence from the photoexcited $RuC_{12}B^{2+}$ is only 2% of that in the CTAC system under the same condition. Essentially the same results were also obtained with the aqueous methanol solutions. It may be that the effective concentrations of NTA in the microenvironment surrounding the ruthenium complex in these two systems are approximately one twenty-fifth of that at the surface of CTAC micelles.

In the case of SDS system, the charge of negative head groups at the micellar surface extends strong repulsion against approaching anions such as NTA and AQαS. This is a really unfavorable situation for the formation of $AQ\alpha S^{-\cdot}$, as well as for reductive quenching of the luminescence. The data in Table II are exactly as expected. On the basis of these observations the sensitized reduction of AQαS in the presence of NTA is concluded to proceed via

SCHEME II

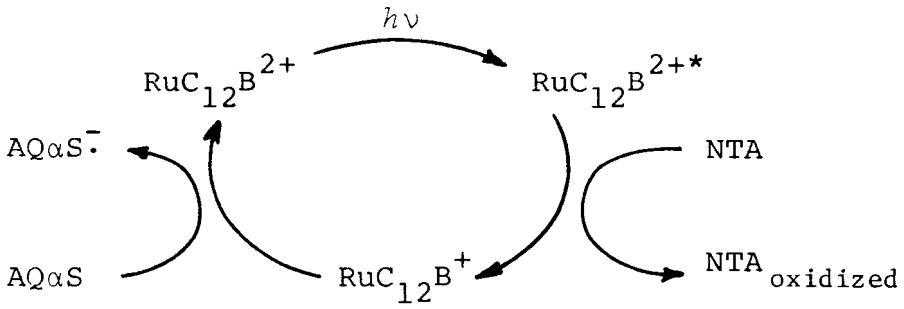


TABLE II
Relationship between relative quantum yield for the formation of AQαS$^-$ and quenching effeciency of luminescence in $RuC_{12}B^{2+}$-NTA system in various micellar solutions[a]

| Surfactant | Relative quantum yield of AQαS$^-$ | Relative quenching efficiency |
|---|---|---|
| CTAC (0.01 M) | 100 | 100 |
| Triton X-100 (1% (v/v)) | 2 | 2 |
| SDA (0.01 M) | 0 | 0 |
| None (aqueous methanol 50% (v/v)) | 2 | 4 |

[a]An aqueous solution containing $RuC_{12}B^{2+}$ ($2 \times 10^{-5}$ M), NTA ($1 \times 10^{-3}$ M), AQαS ($1 \times 10^{-4}$ M) and appropriate amounts of surfactants was irradiated.

formation of $RuC_{12}B^+$ at the micellar surface as shown in Scheme II.

*Photoelectron-transfer Across Liposomal Interface as Catalyzed by Amphipathic Ruthenium Complex*

Simulation of photosynthesis by pure chemical means has been pointed out to afford one of the most promising techniques for solar energy conversion.[8a] Along this line, Calvin and his associates, studied photosensitized electron transport across lipid vesicle walls incorporating amphipathic ruthenium complex and partly succeeded in up-energy conversion of photon into redox potentials.[8b] Similar results were also reported by Sudo and Toda, who used liposome containing methylene blue.[8d] Phospholipid liposomes have thus been proved to be a very useful system which mimics the thylakoid membranes in chloroplast.

In comparison with the above described micellar systems, several new characteristics are expected to affect the redox reactions at the interface between liposomal interior and aqueous phase:

1) The electric field at the liposome interface, where zwitterionic head groups of phospholipid are lined up, should be appreciably different from that as provided by monopolar head groups of micellar systems.

2) The microviscosity of the liposomal interior is much higher than that of micelles.

3) Liposomes possess two interfaces, which are separated by an extremely thin (ca. 50 Å) bilayer of aliphatic chain of phospholipid.

In the present experiments, photoinduced redox reactions of $RuC_{12}B^{2+}$ were studied step by step. Quenching behaviors of photoexcited $RuC_{12}B^{2+}$ were investigated at first. To be a surprise, the luminescence from the photoexcited $RuC_{12}B^{2+}$ could not be quenched at all by $MV^{2+}$ at the concentration of $2 \times 10^{-2}$ M, which means that the $k_q$-value must be much less than $10^7$ $M^{-1}s^{-1}$. In addition, the luminescence was not quenched either by NTA ($1 \times 10^{-2}$ M). The later behavior is close to that in SDS system rather than to that at CTAC micellar surface as shown in Table II. It is quite likely that the zwitterionic head groups of phospholipid set up a microscopic fence around the ionic moiety of $RuC_{12}B^{2+}$ so that the above two quenchers ($MV^{2+}$ and TEA) in the aqueous phase experience large difficulty in approaching the photoexcited reaction center. The luminescence from the photoexcited $RuC_{12}B^{2+}$ was quenched by $C_{12}V^{2+}$, the amphipathic homologue of $MV^{2+}$, in the liposomal system in an efficiency better ($k_q = 1 \times 10^{11}$ $M^{-1}s^{-1}$) than that in CTAC micellar solutions ($k_q = 1 \times 10^{10}$ $M^{-1}s^{-1}$) under similar conditions. At the cincentrations of $RuC_{12}B^{2+}$ ($2 \times 10^{-5}$ M) and CTAC (0.01 M) used in the present experiments, the average number of $RuC_{12}B^{2+}$ in a micell (aggregation number, 60) is only an order of $10^{-1}$. Then, majority of $C_{12}V^{2+}$ molecules are in the unoccupied micelles and they do not have much chance to meet photoexcited $RuC_{12}B^{2+}$ within the life time (0.57 μs). In the case of DPPC liposomes, on the other hand, at least several molecules of $RuC_{12}B^{2+}$ will be found in each liposome, which consists of approximately 2600 DPPC molecules so that all of $C_{12}V^{2+}$ become useful quencher. Thus, the compartmentalization (or partition) effect of the relevant species will account for the large fraction of the increase in the quenching constant on going from CTAC micelles to DPPC liposomes.

In the presence of EDTA, together with $RuC_{12}B^{2+}$ and $C_{12}V^{2+}$, the sensitized reduction of $C_{12}V^{2+}$ smoothly proceeded as shown in Figure 2. In contrast to the case of micellar solutions, however, the absorption bands due to the dimer form of $C_{12}V^{+}$[13] were as strong as those due to the monomer. In addition to the partition effect, the increased microviscosity in the liposomal system may favor the dimer formation. In any event, the relative quantum yield for the formation of $C_{12}V^{+}$ in liposomal system is approximately 10% of that in the CTAC system. Taking into account of the increased $k_q$-value, one should conclude that the charge-separation of the initially formed ion-pair is much more strongly

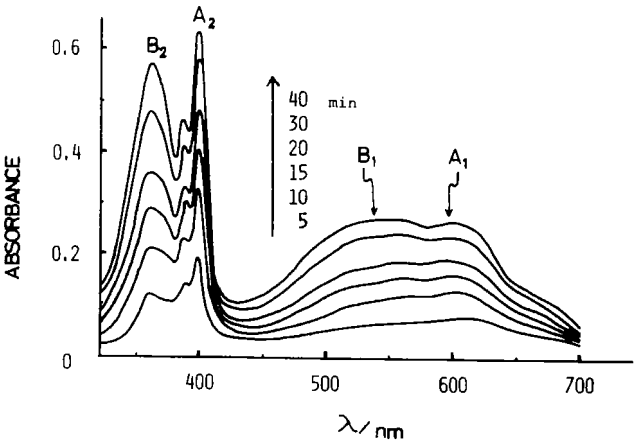



FIGURE 2 Photoindiced reduction of $C_{12}V^{2+}$ as catalyzed by $RuC_{12}B^{2+}$ in the liposomal solutions of EDTA. The characteristic absorptions due to the monomer and the dimer of $C_{12}V^{+}$ are indicated by A and B, respectively. The reaction conditions are the same as those in the caption of Figure 1 except that CTAC is replaced by DPPC ($1 \times 10^{-3}$ M).

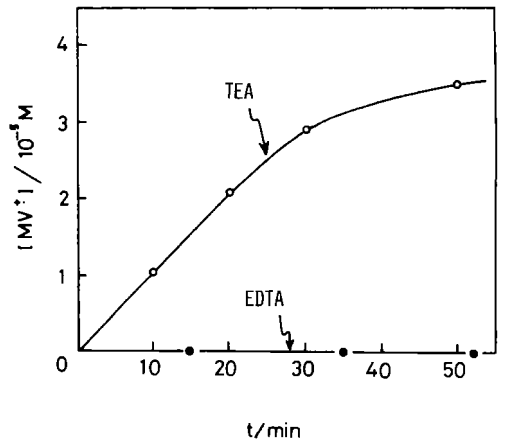



FIGURE 4 Formation of $MV^{+}$ along the irradiation of $RuC_{12}B^{2+}$ ($1 \times 10^{-4}$ M) incorporated into DPPC liposomes in the presence of TEA ($1 \times 10^{-2}$ M). The data with EDTA ($1 \times 10^{-3}$ M) practically coincide with the abscissa. $[MV^{2+}] = 5 \times 10^{-4}$ M.

hindered in the liposomal interface due to the large viscosity than in CTAC system. The initial product was identified with $C_{12}V^{+}$ monomer by the flash photolysis technique (Figure 3), even in the presence of hydrophobic electron-acceptor such as vitamin $K_1$ and $K_3$. The transient absorption decays within a few ms, and the dihydroxynaphthalene derivatives of vitamin $K_1$ (or $K_3$) are accumulated as the final product, which are detected in the usual steady irradiation of the liposomal solutions. Thus, the electron transfer from EDTA in the aqueous phase to vitamin $K_1$ (or $K_3$) in the liposome wall is achieved

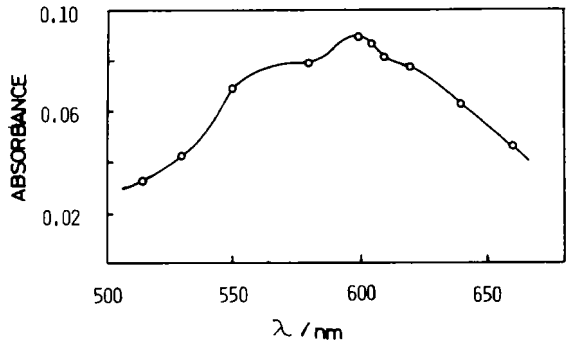



FIGURE 3 Transient absorption spectrum at 1 msec after the flash-photolysis of DPPC liposome solution containing $RuC_{12}B^{2+}$ ($2 \times 10^{-5}$ M), $C_{12}V^{2+}$ ($1 \times 10^{-4}$ M), vitamin $K_1$ ($2 \times 10^{-4}$ M), EDTA ($1 \times 10^{-3}$ M) and NaCl ($1 \times 10^{-1}$ M). The concentration of DPPC was $10^{-3}$ M and the solution was adjusted to pH 7 with buffer.

by oxidative quenching of $*RuC_{12}B^{2+}$ at the liposomal interface.

The reductive quenching of the photoexcited $RuC_{12}B^{2+}$ could be achieved by various reducing agents such as N,N-dimethylaniline (DMA)[6], phenothiazine[14], triethanolamine[15], and triethylamine (TEA)[11]. Since, the above described oxidative quenching of $*RuC_{12}B^{2+}$ clearly indicated that prompt back-electron transfer took place in the photo-produced ion pair at the liposome interface, TEA was chosen as the reducing agent in the present experiment so that irreversible reductive quenching of $*RuC_{12}B^{2+}$ could be achieved.[11] An example is shown in Figure 4, where the formation of $MV^{+}$ along the irradiation was followed by the use of liposomal solutions containing TEA ($1 \times 10^{-2}$ M). As previously pointed out, $MV^{2+}$ in the aqueous phase does not quench $*RuC_{12}B^{2+}$. As a consequence, reduction of $MV^{2+}$ did not proceed as expected if TEA was replaced by EDTA (Figure 4). Thus, it is clear that electron transfer from TEA in the liposome wall to $MV^{2+}$ in the aqueous phase proceeds via reductive quenching of $*RuC_{12}B^{2+}$ at the liposomal interface.

In short, both the oxidative-and reductive quenching processes of the amphipathic ruthenium complex, were verified to take place at the interface between bulk water and liposomal interior. If the reaction center of these two processes are located at the different interfaces of the liposome, two-photon activated electron-transport across the liposome wall can be constructed as shown in Figure 5. Calvin and

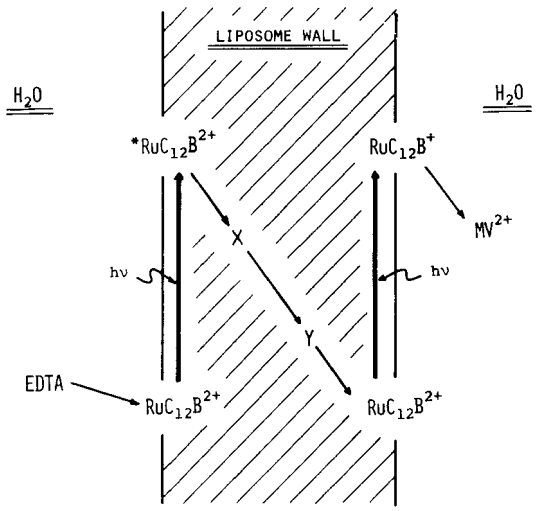



FIGURE 5 A schematic presentation of a man-made electron-transport system activated by the use of two photons.

his associates actually reported that they have succeeded in photoactivated electron transport across the liposome wall by the use of amphipathic ruthenium complex and viologen derivatives.[8b] An electron exchange mechanism was proposed to explain the rate constant of electron transport across the liposome walls.[8c] However, no clear cut explanation has been given to account for the electron-transfer from liposomal interior to the $MV^{2+}$ in the aqueous phase. The present experiment proved that $MV^{2+}$ does not quench photoexcited $RuC_{12}B^{2+}$ at the liposomal interface. No electron-transfer from $C_{12}V^{\ddagger}$ to $MV^{2+}$ could be detected either in the liposomal system.[16] The reduction of $MV^{2+}$ in the bulk water smoothly proceeded only if photoreduced amphipathic ruthenium complex was produced at the liposomal interface. On the basis of these observations, it is quite conceivable that the photosensitized electron transport reported by Calvin and his associates proceeded via two-photon mechanism as indicated in Figure 5. All of the above-discussed data clearly indicate that the most difficult part of photoinduced electron-transport is the remarkable drawback due to back electron-transfer. The two-photon activated electron-transport will become a practical mean for solar energy conversion, if one succeeds in preparing efficient mediateors (*X* and *Y*) which are not much accompanied with back electron-transfer.

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