Pure & Appl. Chem., Vol.54, No.9, pp.1693-1703, 1982.
Printed in Great Britain.

0033-4545/82/091693-11$03.00/0
Pergamon Press Ltd.

PHOTOINDUCED ELECTRON-TRANSFER REACTIONS IN MEMBRANE AND POLYMER SYSTEMS FOR SOLAR ENERGY CONVERSION

Taku Matsuo

Department of Organic Synthesis, Kyushu University 36, Fukuoka 812, Japan

Abstract - Suppression of reverse electron-transfer between a pair of redox species, as obtained in photoinduced electron-transfer reaction, is achieved by the aid of various biomembrane-model systems in aqueous solutions. Longer life-times of the redox pairs can be attained in micellar systems, if they are either generated in electric fields of the micelles or separately trapped in a different microenvironment for each component. Molecular bilayers afford a better model system, where a pair of different photoredox reaction centers can be installed at the front- and back walls of the membrane. A concerted two-step activation of electron-transport across the membrane is achieved by the use of the reaction centers in combination with electron-relay systems. Electron-relay systems in membranes and polymers further provide an excellent method to increase the probability of survival for the photo-generated redox pair. Aligned viologen units on various molecular assemblies, for example, are capable of transporting electrons even in competition with intramolecular reverse electron-transfer.

INTRODUCTION

In order to achieve photochemical conversion and storage of solar energy, a number of attempts have been made to mimic the processes involved in the photosynthesis by the use of completely artificial systems. One of the most important problems encountered in those studies is how to control the competition between reverse electron-transfer and separation of the primary redox pairs as generated on the photoexcitation of various sensitizers. In homogeneous solutions, the probability of survival for the primary redox pairs is mainly determined by the cage-escape yield of each component. The charge separation of the primary redox pair has been facilitated, to some extent, by the use of molecular assemblies such as surfactant micelles and molecular bilayers in aqueous solutions (Ref. 1~3). In the present study, characteristics of several biomembrane model systems will be discussed in terms of the charge separation processes involved in the photoinduced electron-transfer reactions in highly organized systems. The charge separation process can be controlled in two different manners depending on the types of electron-transport system: (1) molecular diffusion of an electron mediator, and (2) electron migrations (or hopping) in organized molecular assemblies.

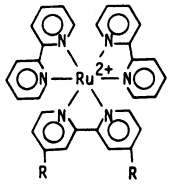
EFFECTS OF MICROENVIRONMENT AS OBSERVED IN MICELLAR SYSTEMS

Surfactant micelles provide the simplest model system for biomembranes, which play key roles in bioenergetics as observed in the photosynthesis. The primary redox pairs, the direct product of the photoinduced electron-transfer, are easily annihilated via reverse electron-transfer as far as the pair of redox species remain closely located. The life time of the redox pair may be considerably extended, however, if the redox species are generated in electric fields or trapped in different microenvironments. Typical examples of the micellar effects on the fates of the primary redox pair will be discussed here.

Redox pair generation in bulk aqueous phase

Remarkable effects of cetyltrimethylammonium chloride (CTAC) micelles on retarding the reverse electron-transfer between photooxidized tris(2,2'-bipyridine)ruthenium(II) ion, abbreviated to Ru(bpy)(2+), and reduced N-tetradecyl-N'-methylviologen (C14MV(2+)) have been ascribed to the solubilization of C14MV(+) into micelles due to the increased hydrophobicity upon reduction and electrostatic repulsion between oxidized Ru(bpy)(2+) and the micellar surface (Ref. 4). Coulombic repulsion has also been reported to be responsible for the increase in the photoreduction rate of zwitterionic propylviologen sulfonate (PS(2-)V(2+)) as sensitized by Ru(bpy)(2+) in the presence of negatively charged colloidal particles

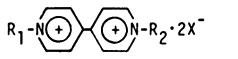
(Ref. 5). On the basis of this information, it may be expected that the charge separation of the primary redox pair generated in the bulk aqueous phase will also be assisted by the aid of electric field associated with ionic molecular assemblies such as surfactant micelles and molecular bilayers. Results of a critical examination of the electric field effects will be discussed below. The investigated reaction is the photoinduced electron-transfer from Ru(bpy)(2+) to PS(2-)V(2+), which revealed that the presence of either CTAC micelles or didodecylammonium bromide (2C12NB) bilayers remarkably facilitate charge separation of the primary ion pairs in the aqueous solutions (Ref. 6).



Ru(bpy)(2+):R=H

RuC12B(2+):R=CNC$_{12}$H$_{25}$ (H, O)

(1)



2MV(2+):R_1=R_2=CH_3, X=Cl

PS(2-)V(2+):R_1=R_2=$(CH_2)_3SO^-$

(2)

Photoreduction of PS(2-)V(2+), as sensitized by Ru(bpy)(2+), smoothly proceeds in the presence of triethanolamine (TEOA) as a sacrificing agent. The reverse electron-transfer in this system is in competition with reduction of photooxidized Ru(bpy)(2+) by TEOA, which also determines the amount of photoreduced PS(2-)V(2+). The yield of primary ion pair, on the other hand, may be estimated from the Ru(bpy)(2+)-luminescence quenching efficiency (Eq). Then, it is possible to evaluate the relative probability of survival (Prel) by the use of Eq-value and the relative quantum yield (ϕrel) of reduced PS(2-)V(2+): ϕ rel = Eq x Prel. The ϕrel-values are normalized to that of Ru(bpy)(2+)-2MV(2+) system as shown in Table 1.

TABLE 1. Photoreduction of viologen sensitized by tris(2,2'-bipyridine)-ruthenium complex in aqueous solutions

System No.	Viologen	Electron donor	Surfactant	ϕrel	Eq(%)	Prel
1	2MV(2+)	TEOA	none	100	5.7	17.5
2	PS(2-)V(2+)	TEOA	none	130	13.8	9.4
3	PS(2-)V(2+)	TEOA	CTAC	324	12.3	26.3
4	PS(2-)V(2+)	TEOA	2C12NB	324	13.4	24.2

[Ru(bpy)(2+)] = 2.0 x 10^{-5} M, [2MV(2+)] , [PS(2-)V(2+)] = 5.0 x 10^{-4} M, [TEOA] = 10^{-3} M, and [CTAC], [2C12NB] = 10^{-2} M

On the addidion of CTAC (System 3 in Table 1), the photoreduction rate of PS(2-)V(2+) remarkably increased. The ϕrel-value varies with the concentration of CTAC as shown in Fig. 1.

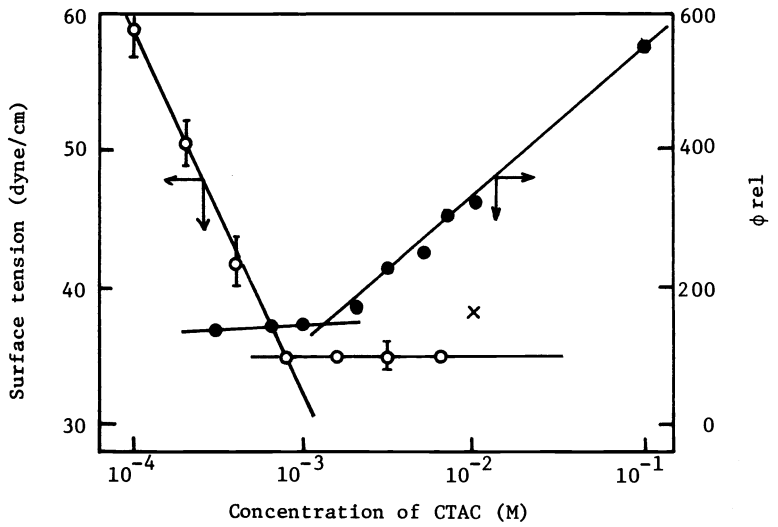


Fig. 1. Effects of CTAC concentration on ϕrel and surface tension.

The ϕrel-value sharply rises with CTAC concentration above CMC, while non-micellar forming tetraethylammonium chloride causes only a small increase of ϕrel as indicated by a cross mark in Fig. 1. On the basis of these results, it is strongly suggested that the increase in the Prel-value in System 3 is caused by the electrostatic field around the CTAC micelles.

The addition of bilayer-forming cationic surfactant (2C12NB; Ref. 7) caused almost the same increase in ϕrel as CTAC (Table 1, System 4). Because the Eq-values are hardly affected by the addition of either CTAC or 2C12NB, it is clear that PS(2-)V(2+) molecules are free from the surfactant micelles or the molecular bilayers before the reduction. When one-electron reduction of PS(2-)V(2+) molecules occurs, they bear negative net charges and are expected to be driven along the electrostatic field of micelles or bilayers until they are trapped by positively charged interface between the bulk water and the molecular assemblies.

Transient absorptions obtained with ns-laser photolysis clearly indicates that the above suggested enrichment of reduced PS(2-)V(2+) starts immediately after the formation of the primary redox pair. In the absence of CTAC micelles, the absorption due to the photoreduced PS(2-)V(2+) almost completely decays away within 160 μs, while approximately one third of the ion radicals still survive at 400 μs after the photolysis in the 10 mM CTAC solution. It is apparent that photoreduced PS(2-)V(2+) is captured by electrostatic field of CTAC micelles before the primary redox pair annihilates. Since photooxidized Ru(bpy)(2+) is repelled by the positively charged micellar surface, the desorption of the trapped PS(2-)V($\dot{+}$) is required for the reverse electron-transfer to take place. The life-time of the charge-separated state is considered to be long enough for TEOA to reduce the photooxidized Ru(bpy)(2+). As a consequence, the corresponding amounts of trapped PS(2-)V($\dot{+}$) will survive the reverse electron-transfer so that both Prel and ϕrel increase with the concentration of CTAC micelles.

Redox pair generation at the micellar surface

Recent studies on photoexcitation of the charge-transfer system, pyrene-N,N'-dimethylaniline (DMA), revealed that efficient electron transfer and subsequent ion separation occur when the reactants are located on strongly charged surface and move relatively freely (Ref. 8). The same applies to the photoreduction of an amphipathic derivative of Ru(bpy)(2+), RuC12B(2+) as shown by structural formula (1), by DMA in micellar system (Ref. 9). Flash photolysis studies of RuC12B(2+)-DMA system indicates that the decay of the photoreduced RuC12B(2+) strongly depends on the nature of microenvironments surrounding the primary redox pair as shown in Fig. 2.

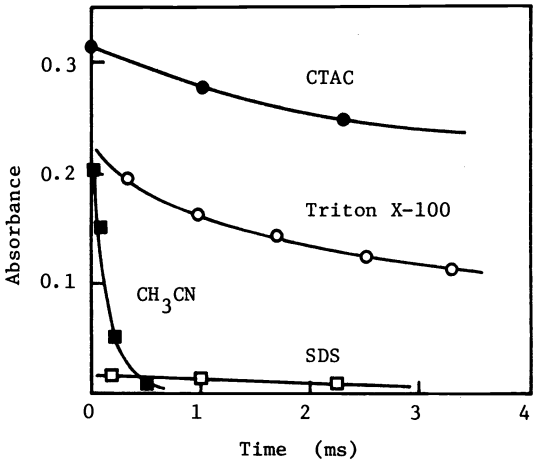


Fig. 2. The decay curves of RuC12B(+)-absorption (515 nm) in various environments.

In the CTAC micellar solution, the decay of photoreduced RuC12B(2+) is considerably retarded as expected from the Coulombic repulsion between the photooxidized DMA and the micellar surface. The extremely low yield of RuC12B(+) in SDS micellar system can be easily explained as due to quick annihilation of the primary redox pair, which are more or less immobilized at the negatively charged micellar surface. It is rather surprising that the decay rate in a nonionic surfactant system (Triton X-100) is not very far from that in CTAC system. Since the primary redox pair bears the same charge, Coulombic repulsion between the components will aid the charge separation at the initial step and the free DMA cation, thus produced, may find shelter in micellar compartment from reverse electron-transfer.

Redox pair generation in the inner core of the micelles

Electric fields associated with micelles are also capable of assisting the charge separation of the redox pair generated in the micellar interior (Ref. 10). When 1,2,4,5-tetracyanobenzene (TCNB) molecules are solubilized into the micelles of ammonium amphiphiles with para-substituted benzene ring, charge-transfer absorptions are observed. The photoinduced charge separation of the TCNB complex is detected by flash photolysis. The TCNB anion radicals disappear according to second-order reaction kinetics, and the relative rate constant ($k' = k/\varepsilon$) strongly depends on the location of the benzene ring as shown in Fig. 3.

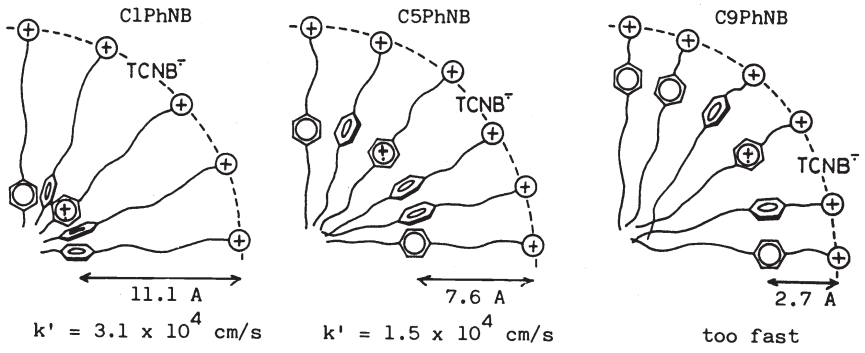


Fig. 3. Schematic presentation of photoinduced charge separation of TCNB complex in micellar systems with benzene ring, and the relative rate constants for the decay of TCNB anion.

The intensity of transient absorption due to TCNB anion is almost the same between C1PhNB and C5PhNB systems, while no transients were detected in C9PhNB micelles. In relatively viscous micellar interior, most of the TCNB anion will disappear by the geminate recombination reaction with para-substituted benzene cation radicals. Some of the anion radicals which escaped the cage reaction will be attracted by the positively charged micellar surface and be trapped near the interface between the micelle and bulk water. In the case of C9PhNB, the distance between TCNB anion and the donor cation radical may not be large enough to retard the reverse electron-transfer.

In short, micellar systems afford useful microenvironments for the charge separation of the primary redox pair. The charge separation yield is mainly determined by the rate of molecular diffusion, since geminate recombination in the cage is in competition with the micellar effects.

ELECTRON TRANSPORT ACROSS BILAYER MEMBRANES

Molecular bilayers afford a better model system for biomembranes. Two types of bilayer membranes are available at present. One is phospholipid membranes as schematically shown in Fig. 4a, and the other is synthetic bilayer membranes as in Fig. 4b.

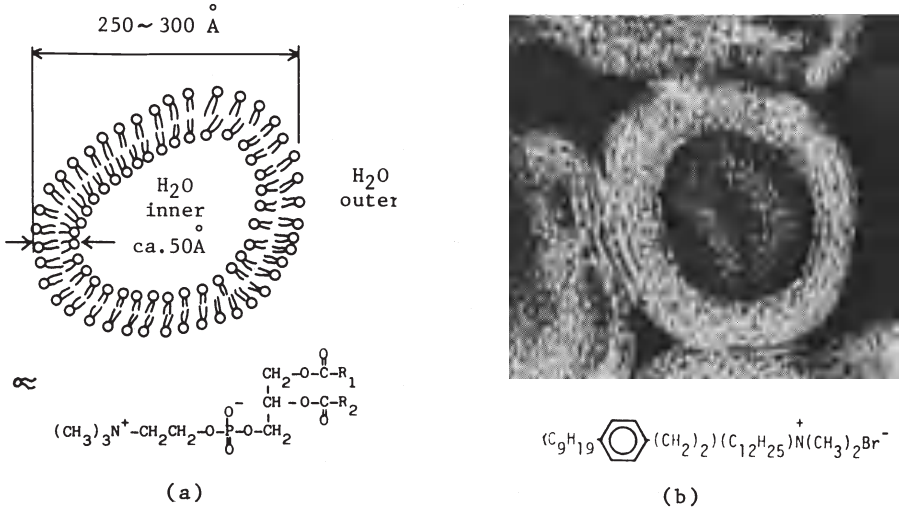


Fig. 4. Structures of phospholipid vesicles (a), and synthetic bilayer membranes(b).

Photosensitized electron-transport across phospholipid vesicle walls has been reported by Calvin and his associates (Ref. 11), while electron-transfer across a synthetic bilayer membrane has also been discussed by Fendler (Ref. 12). In both of these studies, direct electron-transfer across the membrane wall has been suggested. Since reaction rates in this mechanism are not necessarily rapid, attempts have been made to enhance the electron-transport across the membrane wall by the use of electron mediators as described here.

Two-step photoactivation of electron-transport across the membrane

The most remarkable features of bilayer membrane is the fact that a pair of photosensitized redox systems may be separately activated at the two surfaces of the membrane. In analogy to the Z-scheme of photosynthesis, the pair of photoredox systems may be linked by the use of electron-transport systems so that large redox potentials are accumulated across the membrane wall. One of the simplest systems may be constructed by the use of vesicles incorporating an amphipathic zinc porphinato complex (ZnP) as the sensitizer as shown in Fig. 5 (Ref. 13).

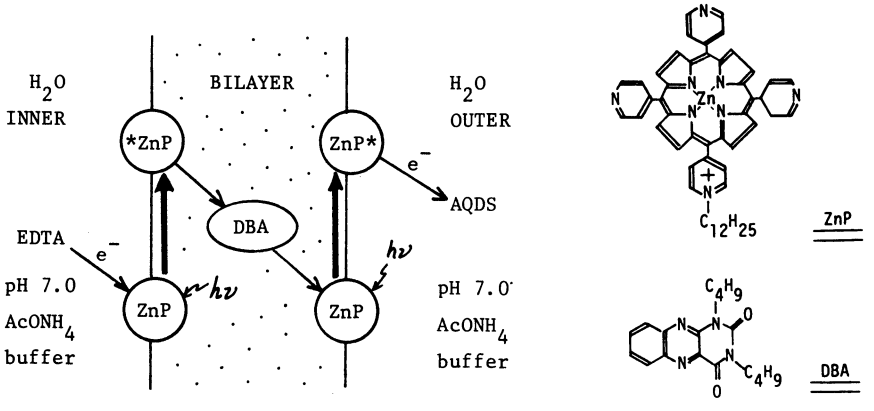


Fig. 5. Schematic diagram for two-step activation of electron-transport across vesicle wall.

The single-walled liposomes or vesicles are prepared by sonicating dipalmitoyl-D,L-α-phosphatidylcholine (DPPC) dispersion in buffered aqueous solutions. The water pool inside the vesicle contains EDTA, while disodium 9,10-anthraquinone-2,6-disulfonate (AQDS) is added to the outer aqueous phase. The photosensitized reduction of AQDS smoothly proceeds in the presence of appropriate electron-mediators such as 1,3-dibutylalloxazine (DBA) and 1,3-didodecylalloxazine (DDA). Remarkable enhancements of the AQDS reduction rate are observed with these electron mediators: DBA system, 5.2×10^{-5} ; DDA system, 2.7×10^{-5}; and without mediator, 0.81×10^{-5} M/min. Only small effect is observed however with vitamin K_1, which has frequently been used as the electron mediator in various membrane systems. The relative rate of electron-transport across the vesicle wall appears to be strongly affected by the redox potential of the electron mediator, as well as its mobility (Ref. 14). The rate of direct electron-transfer from the mediator to AQDS may be estimated by the use of 3,6-diamino-10-methylacridinium chloride (acriflavin, AF) as a sensitizer trapped in the inner water pool. The photoexcited AF is reduced by EDTA and delivers the electron to electron mediators in the membrane. The rate of AQDS reduction in this mechanism is estimated to be less than one percent of that in the ZnP-sensitized reduction under the corresponding conditions. Thus, it is clear that the photoexcitation of ZnP at the outer surface plays very important roles in the electron-transport across the membrane. In addition, flash photolysis shows that photooxidation of ZnP by AQDS is a very efficient process. On the basis of these facts, it is suggested that the electron-transport across the membrane proceeds via two-step activation of ZnP, one at the inner- and the other at the outer surface of the vesicle:

$$ZnP^*_{outer} + AQDS \longrightarrow ZnP^+_{outer} + AQDS^- \quad (1)$$

$$ZnP^*_{inner} + DBA \longrightarrow ZnP^+_{inner} + DBA^- \quad (2)$$

The final electron source is EDTA at the inner water pool. The reduction rate of AQDS at the outer surface, in this reaction, is regulated by the rate of electron supply at the inner surface, which depends on the efficiency of charge separation between the photo-oxidized ZnP and photoreduced electron mediators in turn. This is one of the most essential problems for all types of electron-transport across bilayer membranes. Several studies on this problem will be then discussed in the next section.

Photoinduced electron-transfer and charge separation at the surface of bilayer membranes

Photoinduced electron-transfer between amphipathic ruthenium complex (RuC12B(2+), cf. structural formula (1)) and DMA in synthetic bilayer membranes and phospholipid liposomes will be discussed at first (Ref. 15). Photoinduced electron-transfer from DMA to RuC12B(2+) and the reverse electron-transfer is confirmed by the transient absorption spectra due to RuC12B(+). In a synthetic bilayer system, dihexadecyldimethylammonium bromide (2C16NB), the decay curves beyond 1 ms after the photolysis follows the second order reaction kinetics with rate constants, k. The decay of RuC12B(+) in liposome systems (DPPC and DMPC) is somewhat faster than in a 2C16NB bilayer system and appears to consist of two different components. The second order reaction rate constants obtained in the initial and later regions are shown in Table 2.

TABLE 2. The second order rate constant, k, for the reverse electron-transfer reaction between RuC12B(+) and DMA(+) in a synthetic bilayer and phospholipid liposome systems.

System	$k(M^{-1})$		Temperature (°C)
	First decay	Second decay	
2C16NB (1×10^{-3} M)	2.3×10^{7}	none	17
	3.3×10^{7}	none	25
	7.1×10^{7}	none	50
DPPC (1×10^{-3} M)	1.7×10^{8}	8.8×10^{6}	25
DMPC (1×10^{-3} M)	9.8×10^{7}	1.2×10^{7}	13
	9.8×10^{7}	9.1×10^{6}	25
	1.3×10^{8}	1.2×10^{7}	50
CTAC (1×10^{-2} M)	2.6×10^{7}		
Triton X-100 (1%(v/v))	1.5×10^{8}		
Acetonitrile	7.8×10^{9}		

Zwitterionic phospholipid liposomes with no net surface charges show k-values comparable to that observed in a nonionic Triton X-100 micellar system. On the other hand, the k-values for positively charged 2C16NB bilayer in the room temperatures are very close to that for CTAC system. The transient absorptions under discussions are due to the photogenerated redox pairs, which escaped from the cage surrounding the site of generation. Then, the rate of reverse electron-transfer depends almost solely on the diffusion of once-separated DMA(+) to re-encounter with RuC12B(+), as it is obvious from the fact that k-values in bilayer systems are very close to those for micellar system with the same net charges. The cage-escaped DMA(+) ions are thus suggested to be repelled into bulk aqueous phase in these systems.

The diffusion processes in bilayer membrane systems are expected to be affected by the phase transition. In agreement with this expectation, the k-value for 2C16NB system considerably increase at the temperature above Tc (28°C). In the case of DMPC liposomes, however, the k-values are hardly affected by the phase transition (23.9°C). It may be that the microenvironment around head groups of RuC12B(2+) solubilized in liposomes would hardly change upon the phase transition. On the other hand, not only the aligned long alkyl chains but the head groups also appear to begin molecular motions with considerable amplitude near and above Tc in synthetic bilayers. In connection with the temperature effect on the k-value in bilayer system, an interesting behavior is observed with N-butylphenothiazine-RuC12B(2+) in 2C16NB (Ref. 16). In this system, the k-value decreases at the temperature above Tc. This is in good contrast with the above discussed behavior of DMA-RuC12B(2+) system. It should be pointed out that DMA(+) is water soluble, while N-butylphenothiazine cation (BPTZ(+)) is soluble to hydrophobic region of the molecular assemblies. The peculiar temperature dependence of BPTZ system is likely caused by the diffusion of BPTZ(+) into the hydrophobic region, but not to the bulk water, of the molecular assemblies.

If either an electron donor or acceptor stays in the hydrophobic region of bilayer membranes, the relatively large viscosity in the microenvironment becomes a serious problem for the charge separation of the primary redox pair. The examples will be found in the photoreduction of viologen derivatives as sensitized by RuC12B(2+) in various systems (Ref. 17). Dodecylviologen (1,1'-didodecyl-4,4'-bipyridinium ion, denoted by 2C12V(2+)) is used as the amphipathic electron acceptor together with EDTA as a sacrificing reductant. The quenching rate constants and the relative quantum yields (ϕrel) of the reduced viologen ions are summarized in Table 3.

TABLE 3. Comparison between quenching rate constants for viologens and relative quantum yields of reduced viologens (V(+)) in various systems

System	kq($M^{-1}s^{-1}$)	ϕrel of V(+)
Ru(bpy)(2+)/2MV(2+)/water	2×10^{8}	100
RuC12B(2+)/2MV(2+)/CTAC micelle	3×10^{6}	10
RuC12B(2+)/2C12V(2+)/CTAC micelle	1×10^{10}	210
RuC12B(2+)/2C12V(2+)/DPPC bilayer membrane	1×10^{11}	20

The quenching rate constants (kq) are obtained from Stern-Volmer plots by the use of oridinary bulk concentration for the viologen ions. Since 2C12V(2+) molecules are enriched to the surface of micelle or bilayer membrane, the microscopic concentration in these molecular assemblies must be much higher than the bulk concentrations. Then, the kq-values in Table 3 must be taken as an apparent quenching constant. For a given concentration of viologen ion however, the kq-values may be used as a good measure for quenching of ruthenium complexes in the above four systems. The data in Table 3 clearly indicate that the relative quantum yields of reduced 2C12V(2+) in micelle and bilayer membrane systems are surprisingly small in comparison with the increase in the quenching efficiency. The primary redox pairs generated in these systems must be quickly annihilated before the components are separated by molecular diffusion. The situation is particularly serious in the highly viscous bilayer membranes.

In short, bilayer membranes are found to be a good model systems for photosynthetic biomembranes. However, the charge separation of the primary redox pair via molecular diffusions are not favored in viscous environments of these systems.

ENHANCEMENT OF CHARGE SEPARATION BY THE USE OF ELECTRON-TRANSFER IN MEMBRANE AND POLYMER SYSTEMS

The major fraction of photogenerated primary redox pairs will be lost in viscous environments of man-made molecular assemblies such as membrane or polymer systems, as far as the charge separation depends on the molecular diffusion. One of the possible means to get around the difficulties will be provided if one succeeds in transporting the photoliberated electron alone, as in the case of chloroplasts, without disturbing the molecular alignments. Spectroscopic studies, as well as photochemical investigations, proved that the charge separation is certainly assisted by the use of aligned electron acceptors in self-organized systems.

Electron migration in the micellar systems and polymer chains

N-hexadecyl-N'-ethylviologen (C16EV(2+)), an amphipathic homologue of 2MV(2+), affords a micellar system, where the viologen units are aligned along the surface as shown in Fig. 6.

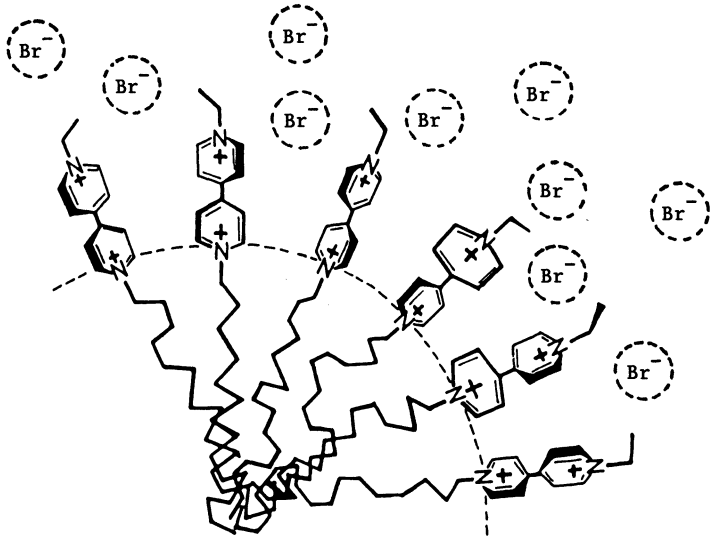


Fig. 6. Schematic illustration of C16EV(2+) micelles.

The proposed micellar structure is supported by proton NMR and electronic absorption spectroscopies (Ref. 18). ESR spectroscopy also affords data in favor of the micellar structure in Fig. 6. Photochemically generated C16EV(+) ion radical shows hyperfine structures similar to those of well-known methylviologen ion radical, if a small number of C16EV(2+) molecules are incorporated into CTAC micelles. The ESR signal is very sensitive to the mole fraction of C16EV(2+) in the CTAC-C16EV(2+) mixed micelles. The hyperfine structures of the spectra show appreciable broadening with increasing mole fraction of C16EV(2+), and a single line signal without hyperfine structure is observed above 30% (Fig. 7).

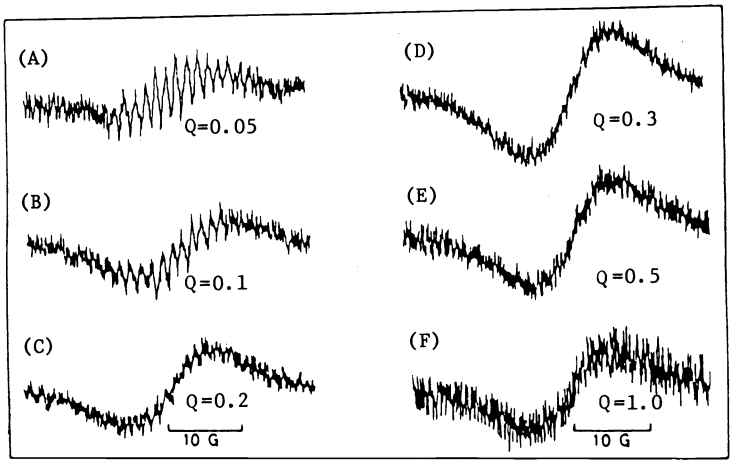
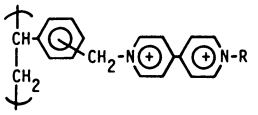


Fig. 7. ESR spectra of C16EV(+) in CTAC-C16EV(2+) mixed-micellar system under various mole fractions (Q) of C16EV(2+).

The line-broadening is due to the presence of electron exchange between C16EV(2+) and C16EV(+) on the micellar surface. On the basis of kinetic arguments on the concentration dependence of the line width as shown in Fig. 7, the rate constant for the exchange reaction is estimated to be approximately 5×10^9 $M^{-1}s^{-1}$. Thus the photoliberated electron in the C16EV(2+) micelles are concluded to migrate on the micellar surface with ease.

The electron migration is also observed with aligned viologen units in polymer chains (Ref. 19). The polymer with pendant viologen units can be prepared by polymerization of N-vinylbenzyl-N'-n-propyl-4,4'-bipyridinium bromide chloride (abbreviated to VBPRB). The viologen polymer will be denoted by PV(2+)PR as shown below (structural formula (3)). Copolymerization of N-vinylbenzyl-N'-n-hexadecyl-4,4'-bipyridinium bromide chloride (abbreviated to VBHDB) and VBPRB affords a polysoap-type viologen polymer PSV(2+)HD, which consists of 75% VBPRB and 25% VBHDB.



PV(2+)PR:R=C_3H_7

PSV(2+)HD:R=C_3H_7(75%), $C_{16}H_{33}$(25%)

(3)

On the photoreduction of PV(2+)PR, as sensitized by Ru(bpy)(2+) in the presence of EDTA, the observed electronic absorption spectra coincide with that of viologen cation radical dimers even if the concentration of the reduced viologen units is extremely low. The PSV(2+)HD-RuC12B(2+) system also shows the spectrum of viologen cation radical dimers from the very early stage of irradiation. The same radical dimers are observed by the irradiation of solid PV(2+)PR film where molecular motions of polymer chains are assumed to be frozen. This result excludes the possiblity of the dimer formation by a bending mechanism of polymer chains. In addition, the spectrum of viologen cation radical monomers alone is observed during irradiation, if the contents of pendant viologen units are as low as 1%. These results strongly indicate that the photoinjected electron migrates along the polymer chain until it is trapped as radical dimers in the polymer systems with pendant viologen groups in adjacent positions.

Another piece of evidence is obtained from ESR spectra. The ESR spectrum of PV(2+)PR radical is a broad singlet without the characteristic hyperfine structures for viologen cation radicals. The line width of component lines is estimated to be approximately 2 G by comparison with simulated ESR spectra. The component line width of 2 G is too broad for polymer radicals in solutions. The line broadening is most likely caused by the electron

exchange mechanism, although contributions of restricted molecular motions are not completely excluded. Thus, it will be possible to transport electrons along the polymer chains to an appropriate electron sink with a high efficiency. Photosensitized generation of dihydrogen in aqueous solutions actually proceeds by the use of the above polymer viologen and colloidal platinum as the electron mediator and the electron sink, respectively.

On the basis of the above observations, several attempts have been made to enhance charge separation of the primary redox pairs by the use of immobilized electron-transport systems. One of the systems uses aligned amphipathic viologen molecules either on CTAC micelles or on bilayer molecular membranes of didodecyldimethylammonium bromide (2C12NB) (Ref. 20). When the above discussed amphipathic viologen C16EV(2+) and RuC12B(2+) are incorporated into the molecular assemblies, photochemical behaviors of the system strongly depend on the ratio between C16EV(2+) and the host surfactant molecules. The quenching of luminescence from the excited RuC12B(2+) smoothly increase with the mole fraction (Q) of C16EV(2+) in both CTAC micelles and 2C12NB bilayer systems in almost the same manner. The Q-dependence of the relative quantum yield for RuC12B(2+)-sensitized reduction of C16EV(2+) in CTAC micelles is entirely different from that for 2C12NB bilayer systems as shown in Fig. 8.

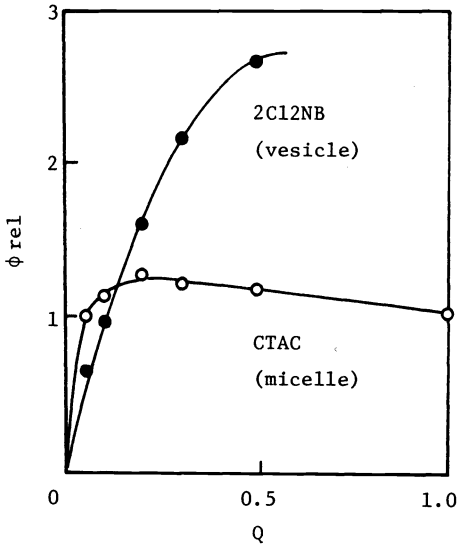


Fig. 8. Relative quantum yield of C16EV(+) formation, as sensitized by RuC12B(2+) in the presence of EDTA, in micellar and bilayer systems.

It is clear that the bilayer system is superior to the micellar system in the region above Q = 0.2. The probability of survival (Prel) for C16EV(+) may be evaluated form the φrel and the efficiency of luminescence quenching (Eq), if it is granted that the yield of primary redox pair is proportional to Eq-values in the investigated Q region as discussed in the beginning of this paper. The Prel-values for 2C12NB sharply rises in the region above Q = 0.2, while slow but steady decrease is observed with Prel in CTAC system.

The ESR signal of C16EV(+) also depends on the Q-values. In the case of 2C12NB system, the spectra shows appreciable broadening until Q = 0.2, where it becomes a broad singlet. Then, the signal gradually becomes sharper with increasing Q-values. The data indicate that the photoliberated electron is shared by a considerable number of C16EV(2+) molecules in 2C12NB system. The electron may easily migrate from the vicinity of RuC12B(3+) to a distance, where the reverse electron-transfer would not easily take place. Electron migration at the surface of bilayer system is thus concluded to enhance the charge separation of the primary redox pair as schematically shown in Fig. 9.

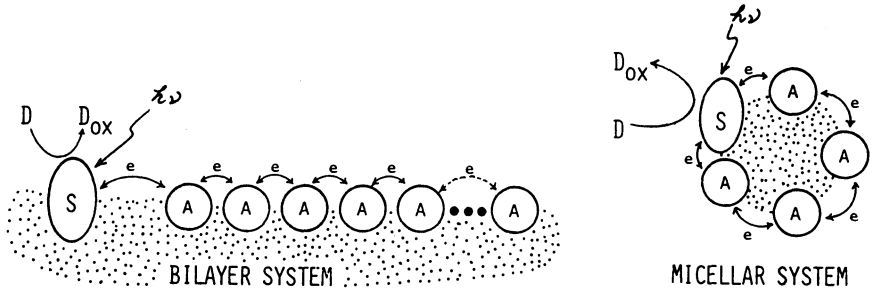
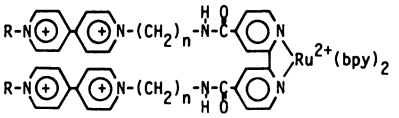


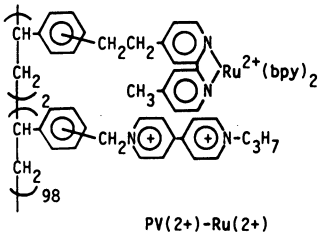
Fig. 9. Schematic illustration for the charge separation of photoliberated electron by the electron migration. S; RuC12B(2+), A; C16EV(2+), and D; EDTA.

Electron migrations in biomembrane model systems are also capable of even competing with intramolecular reverse electron-transfer process (Ref. 21). If an electron acceptor and a sensitizer are covalently bonded to each other, intramolecular electron-transfer quenching of the photoexcited state becomes very efficient as it has been verified in several linked-porphyrins (Refs. 22～24). The same type of efficient quenching is observed with the luminescence from ruthenium complex units in the following linked polypyridine ruthenium-(II) complexes:



2C3V(2+)C2Ru(2+):R=C_3H_7, n=2
2C16V(2+)C2Ru(2+):R=$C_{16}H_{33}$, n=2
2C16V(2+)C6Ru(2+):R=$C_{16}H_{33}$, n=6

(4)



PV(2+)-Ru(2+)

(5)

When the luminescence from the ruthenium complexes of similar structure without the viologen unit is used as a reference, the quenching in the linked complexes (structural formula (4)) is estimated to exceed 84%. No luminescence is observed at all with the polymer system of the structural formula (5).

Photosensitized reduction of the viologen units in the above linked system (4) proceeds in the presence of EDTA, but the efficiency is extremely low. In the case of 2C3V(2+)C2Ru(2+), an example of the water-soluble linked polypyridine complexes, 95% of the luminescence is quenched, but the quantum yield of the photoreduced viologen is only 2% of that for Ru(bpy)(2+)-2MV(2+) standard system. Since the luminescence quenching efficiency in the standard system is 51%, it is clear that the probability of survival for the primary redox pair in the linked complex is extremely small. Analogously, the relative quantum yield of the photoreduced viologen units in 2C16V(2+)C2Ru(2+), amphipathic linked complex, is very small if the complex is in an isolated state on the surface of CTAC micelles.

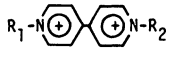
The quantum yields of photoreduced viologen units remarkably increase, when the linked polypyridine ruthenium(II) complexes are used in combination with the electron-relay systems of aligned viologen units on various molecular assemblies such as micelles, molecular bilayers, and polymers as shown in Table 4.

Table 4. Relative quantum yields (ϕrel) of photoreduced viologen units on the photoexcitation of linked polypyridine ruthenium(II) complexes in combination with the electron-relay systems of aligned viologens on molecular assemblies

System No.	Photoredox system	ϕrel
1	Ru(bpy)(2+), 2MV(2+)[a]	100
2	2C3V(2+)C2Ru(2+)	2
3	2C16V(2+)C2Ru(2+)/CTAC	1
4	2C16V(2+)C2Ru(2+)/(CTAC + 2C12V(2+))[a]	5
5	2C16V(2+)C2Ru(2+)	35
6	2C16V(2+)C2Ru(2+)/PSV(2+)HD[a]	25
7	PV(2+)-Ru(2+)	55
8	2C16V(2+)C6Ru(2+)/2C16AmC2V(2+)E	67
9	2C16V(2+)C6Ru(2+)/(2C12NB + C16EV(2+))	135

[Ru(2+) unit] = 2 x 10^{-5} M, [CTAC] = 1 x 10^{-2} M, [2C12NB] = 7 x 10^{-3} M, and [EDTA] = 1 x 10^{-3} M. [a][viologen unit] = 1 x 10^{-3} M.

The photoliberated electron is apparently transferred to the electron-relay system via the viologen units in the linked polypyridine ruthenium(II) complex, and the succeeding electron migration in the molecular assemblies retards the reverse electron-transfer. In the meantime, EDTA reduces the photooxidized ruthenium complex so that the reduced viologen unit on the molecular assembly survives the reoxidation by the reverse electron-transfer. The best result is obtained, here again, by the use of 2C12NB bilayer system incorporating the amphipathic viologen molecule C16EV(2+). A self-assembling system of amphipathic viologen derivative with two long alkyl chain (2C16AmC2V(2+)E, structural formula (6)) gives the second best result. It may be worth to notice that the linked complex with long alkyl chain on the viologen unit also behaves as a self-assembling surfactant in the aqueous solution. The molecular assembly of the amphipathic linked complex has aligned



2C12V(2+):$R_1=R_2=C_{12}H_{25}$
C16EV(2+):$R_1=C_{16}H_{33}$, $R_2=C_2H_5$
2C16AmC2V(2+):$R_1=(CH_2)_2-\underset{O}{C}N(C_{16}H_{33})_2$, $R_2=C_2H_5$

(6)

viologen units on the surface. The unexpectedly large difference between Systems No. 3 and No. 5 may be thus ascribed to the presence of electron migration in the latter system. The electron migration in polymer systems also certainly helps to raise the ϕrel-values as shown in Systems No. 6 and No. 7. The effects are rather small, however, in comparison with those of bilayer systems. The situation will be considerably improved if sterochemically regulated polymer system is used as an electron relay system.

In conclusion, it is possible to assist charge separation of the primary redox pair by the use of immobilized electron transport systems on molecular assemblies. Construction of highly organized molecular assemblies such as bilayers and polymer systems will provide useful devices for the solar energy conversion.

Acknowledgement-This work was partly supported by Grant in Aid of Scientific Research of the Ministry of Education, Science and Culture, Japan (Project No. 56040056) and by the Mitsubishi Foundation.

REFERENCES

1. M. Calvin, Acc. Chem. Res., 11, 369-374 (1978).
2. J. H. Fendler, Acc. Chem. Res., 13, 7-13 (1980).
3. M. Grätzel, Acc. Chem. Res., 14, 376-384 (1981).
4. P.-A. Brugger and M. Grätzel, J. Am. Chem. Soc., 102, 2461-2463 (1980).
5. I. Willner, J.W. Otvos and M. Calvin, J. Am. Chem. Soc., 103, 3203-3205 (1981).
6. T. Nagamura, T. Kurihara and T. Matsuo, J. Phys. Chem., submitted for publication.
7. T. Kunitake and Y. Okahata, J. Am. Chem. Soc., 99, 3860-3861 (1977).
8. S.S. Atik and J.K. Thomas, J. Am. Chem. Soc., 103, 3550-3555 (1981).
9. Y. Tsutsui, K. Takuma, T. Nishijima and T. Matsuo, Chem. Lett., 617-620 (1979).
10. T. Nagamura, T. Kurihara and T. Matsuo, J. Phys. Chem., 86, (1982). in press.
11. W.E. Ford, J.W. Otvos and M. Calvin, Proc. Natl. Acad. Sci. USA, 76, 3590-3593 (1979).
12. M.S. Tunuli and J.H. Fendler, J. Am. Chem. Soc., 103, 2507-2513 (1981).
13. T. Matsuo, K. Itoh, K. Takuma, K. Hashimoto and T. Nagamura, Chem. Lett., 1009-1012 (1980).
14. K. Kano, T. Yamaguchi and T. Matsuo, J. Phys. Chem., 84, 72-76 (1980).
15. T. Nagamura, K. Takuma, Y. Tsutsui and T. Matsuo, Chem. Lett., 503-506 (1980).
16. T. Takayanagi, T. Nagamura and T. Matsuo, Ber. Bunsenges. Phys. Chem., 84, 1125-1129 (1980).
17. T. Matsuo, K. Takuma, Y. Tsutsui and T. Nishijima, J. Coord. Chem., 10, 187-193 (1980).
18. K. Takuma, T. Sakamoto, T. Nagamura and T. Matsuo, J. Phys. Chem., 85, 619-621 (1981).
19. T. Nishijima, T. Nagamura and T. Matsuo, J. Polym. Sci., Polym. Lett. Ed., 19, 65-73 (1981).
20. K. Takuma, T. Sakamoto and T. Matsuo, Chem. Lett., 815-818 (1981).
21. T. Matsuo, T. Sakamoto, K. Takuma, K. Sakura and T. Ohsako, J. Phys. Chem., 85, 1277-1279 (1981).
22. I. Tabushi, N. Koga and M. Yanagita, Tetrahedron Lett., No. 3, 257-260 (1979).
23. T.-F. Ho, A.R. McIntosh and J.R. Bolton, Nature, 286, 254-256 (1980).
24. M. Migita, T. Okada, N. Mataga, S. Nishitani, N. Kurata, Y. Sakata and S. Misumi, Chem. Phys. Lett., 84, 263-266 (1981).