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A NOVEL PHOTO-INDUCED CHARGE SEPARATION BY THE USE OF ELECTRON MIGRATION ON THE MAN-MADE MOLECULAR ASSEMBLIES[1)]

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Electron exchanges between amphipathic viologens lead to electron migration along the surface of a molecular bilayer system, which affords efficient means for photo-induced charge separation (PICS) as sensitized by an amphipathic derivative of tris(2,2'-bipyridine)ruthenium(II) complex.

One of the most important problems for artificial photosynthesis is how to achieve PICS between the photo-oxidized sensitizer (S^+) and reduced acceptor (A^-) in competition with back electron-transfer (Eq. 2) just after the primary electron transfer (Eq. 1):

$$S^* + A \longrightarrow S^+ + A^- \quad (1)$$

$$S^+ + A^- \longrightarrow S + A \quad (2)$$

Coulombic repulsions between charged micellar surfaces and photoproduced molecular ions have been proved to be useful for PICS by the present authors,[2-4)] as well as by other groups.[5,6)] Incoporation of a photo-reduced amphipathic viologen derivative into micelles has also been successfully used for PICS by Grätzel and his associates.[7)] All of these PICS reguire molecular diffusion of photoproduced ion pairs.

A completely new PICS was achieved by the use of electron migration on the surface of man-made molecular assemblies, and the results will be described here.

The presence of electron migration along polymer chain with pendant viologen units was suggested on the basis of spectroscopic and photochemical evidences.[8)] ESR studies confirmed that electron migration also takes place on the hexadecyltrimethylammonium chloride (CTAC) micellar surface where 1-ethyl-1'-hexadecyl-4,4'-bipyridinium ($C_{16}C_2V^{2+}$) ions are incorporated.[9)] In the present paper, $C_{16}C_2V^{2+}$ was incorporated into bilayer membrane of didodecyldimethylammonium bromide ($2C_{12}NB$) which has been reported to afford multilayered liposomes.[10)] ESR spectroscopic studies were carried out, and the results were compared with charge separation efficiency for the photo-sensitized reduction of $C_{16}C_2V^{2+}$.

For the ESR studies, $C_{16}C_2V^{+\cdot}$ was photochemically generated in sample solutions, which contained (N,N'-didodecyl-2,2'-bipyridine-4,4'-dicarboxamide)-bis(2,2'-bipyridine)ruthenium(II) ($RuC_{12}B^{2+}$, 2×10^{-5} M, sensitizer), disodium ethylenediaminetetraacetate (EDTA, 1×10^{-3} M, reductant) together with appropriate surfactants ($[2C_{12}NB] + [C_{16}C_2V^{2+}] = 1 \times 10^{-2}$ M) in various molar ratios. The samples were degassed and irradiated with a collimated beam (>375 nm) from 500 W high-pressure mercury lamp. The photoreaction proceeds via oxidative quenching of $*RuC_{12}B^{2+}$, as

in the case of $Ru(bpy)_3^{2+}$-methylviologen-EDTA system,[11] and the irradiation was continued until $C_{16}C_2V^{+\cdot}$ concentration reached ca. 1×10^{-4} M.

$$RuC_{12}B^{2+} \xrightarrow{h\nu} {}^*RuC_{12}B^{2+} \quad (3)$$

$${}^*RuC_{12}B^{2+} \xrightarrow{k_4} RuC_{12}B^{2+} + h\nu' \text{ (luminescence)} \quad (4)$$

$${}^*RuC_{12}B^{2+} \xrightarrow{k_5} RuC_{12}B^{2+} + \Delta \text{ (heat)} \quad (5)$$

$${}^*RuC_{12}B^{2+} + C_{16}C_2V^{2+} \xrightarrow{k_6} RuC_{12}B^{3+} + C_{16}C_2V^{+\cdot} \quad (6)$$

$$RuC_{12}B^{3+} + C_{16}C_2V^{+\cdot} \xrightarrow{k_7} RuC_{12}B^{2+} + C_{16}C_2V^{2+} \quad (7)$$

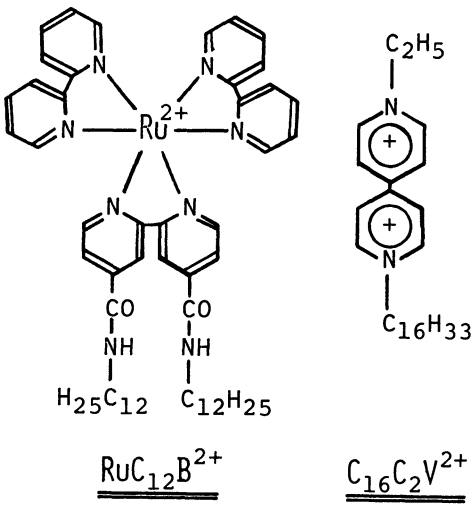
$$RuC_{12}B^{3+} + EDTA \xrightarrow{k_8} RuC_{12}B^{2+} + EDTA_{ox} \quad (8)$$

The irradiated samples showed characteristic ESR spectra of $C_{16}C_2V^{+\cdot}$,[12] which varied with the molar ratio of $C_{16}C_2V^{2+}$ ($q = [C_{16}C_2V^{2+}]/([C_{16}C_2V^{2+}] + [2C_{12}NB])$).

a) Region A ($q \leqq 0.2$); The hyperfine structure of the spectra showed appreciable broadening with increasing the q-value, and reached a broad singlet without hyperfine structures at $q = 0.2$.

b) Region B ($0.5 \geqq q \geqq 0.3$); The singlet ESR signal gradually became a much sharper single line in comparison with that at $q = 0.2$.

The sharp singlet was observed, for the first time, with reduced viologen units. These data indicate that electron migration in the bilayer membrane system is much faster than that in the micellar system (apparent rate constant of electron exchange between $C_{16}C_2V^{2+}$ was 5×10^9 $M^{-1}s^{-1}$).[9]



$RuC_{12}B^{2+}$ $C_{16}C_2V^{2+}$

In order to study charge separation processes involved in the photo-sensitized reduction of $C_{16}C_2V^{2+}$, the quenching of luminescence from ${}^*RuC_{12}B^{2+}$ was studied at first. The quenching efficiency is defined as $E(Q) = (I_0 - I)/I_0$, where I_0 and I are the luminescence intensity in the absence and in the presence of $C_{16}C_2V^{2+}$, respectively. Then, relative quantum yields (Φ_{rel}) for the $RuC_{12}B^{2+}$-sensitized reduction of $C_{16}C_2V^{2+}$, in the presence of EDTA, were determined by measuring the growth of absorption (λ_{max} = 603 nm) due to $C_{16}C_2V^{+\cdot}$ as usual. The Φ_{rel}-values were normalized to that $q = 0.05$ as a standard. Since the quenching of ${}^*RuC_{12}B^{2+}$ proceeds via an electron transfer process (Eq. 6), the E(Q)-value also represents the primary yield of $RuC_{12}B^{3+}$-$C_{16}C_2V^{+\cdot}$ ion pair just after the photoexcitation. Some fractions of the primarily produced $C_{16}C_2V^{+\cdot}$ will be lost due to the back-electron transfer process (Eq. 7). Then, the probability of survival for $C_{16}C_2V^{+\cdot}$ may be defined as an apparent charge separation efficiency (E(CS)) of the primary ion pair. The E(CS)-value is controlled by the removal of $RuC_{12}B^{3+}$ from the system (Eq. 8) in competition with the back-electron transfer (Eq. 7) as shown by the following equations:

$$\Phi_{rel} = \text{constant} \times E(Q) \times E(CS) \quad (9)$$

$$E(Q) = \frac{k_6[C_{16}C_2V^{2+}]}{k_4 + k_5 + k_6[C_{16}C_2V^{2+}]} \quad (10)$$

$$E(CS) = \frac{k_8[EDTA]}{k_7[C_{16}C_2V^{+\cdot}] + k_8[EDTA]} \quad (11)$$

The luminescence intensity of $*RuC_{12}B^{2+}$ was measured at various molar ratio between $C_{16}C_2V^{2+}$ and CTAC (or $2C_{12}NB$), and the obtained E(Q)-values are summarized in Fig. 1. Fig. 2 shows relative quantum yield (Φ_{rel}) of $C_{16}C_2V^{+\cdot}$ under the same condition for E(Q) measurements. The E(Q)- and Φ_{rel}-values afford the relative charge separation efficiency ($E(CS)_{rel}$), which is normalized at q = 0.05, as shown in Fig. 3. It is strongly emphasized that the value of $E(CS)_{rel}$ in the bilayer membrane system increased with the q-value, while an opposite trend was observed with the micellar system.

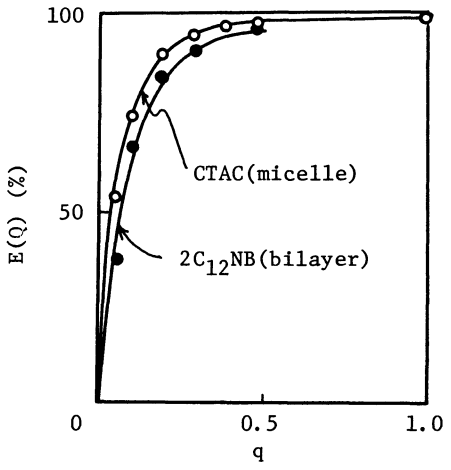


Fig. 1 Quenching of $*RuC_{12}B^{2+}$ by $C_{16}C_2V^{2+}$ in micellar and bilayer systems of surfactants (Sur). $q = [C_{16}C_2V^{2+}] / ([C_{16}C_2V^{2+}] + [Sur])$, $[C_{16}C_2V^{2+}]+[Sur]=1\times10^{-2}M$, $[RuC_{12}B^{2+}]=2\times10^{-5}M$.

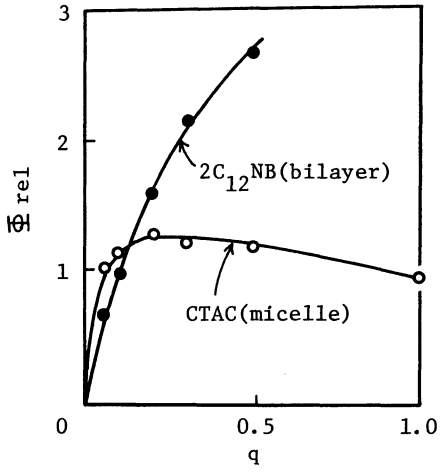


Fig. 2 Relative quantum yield of $C_{16}C_2V^{+\cdot}$ formation in micellar and bilayer systems. $[RuC_{12}B^{2+}] = 2\times10^{-5}$ M, $[EDTA] = 1\times10^{-3}$ M.

The extraordinary narrow ESR signal at large q-values strongly indicates that the photoliberated electron is shared by a considerably large number of $C_{16}C_2V^{2+}$ molecules.[13] In other words, the rate of electron exchange, as well as the migration sites, increases with the relative abundance of $C_{16}C_2V^{2+}$ in the bilayer membrane. In addition, it should be noticed that $2C_{12}NB$ affords a considerably large molecular assembly: aggregation number is a few thousands and the diameter is close to 10^3 Å.[10]

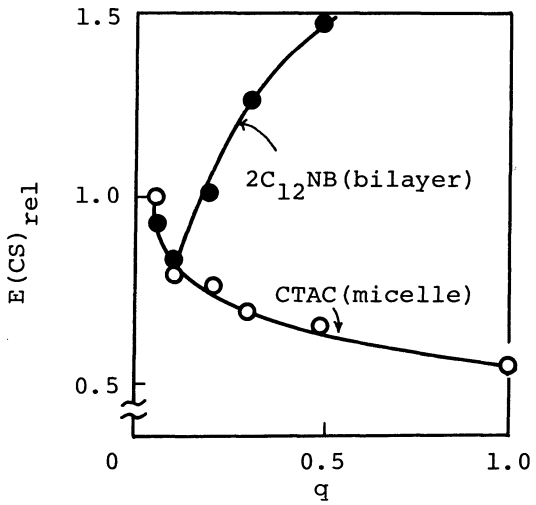


Fig. 3 Relative charge separation efficiency. The conditions are same as given in the caption for Fig. 2.

Then, the photoliberated electron may easily migrate from the vicinity of $RuC_{12}B^{3+}$ to a distance, where back-electron transfer would not quickly take place. Electron migration at the surface of bilayer membrane is thus concluded to enhance PICS as schematically shown in Fig. 4.

It is not clear, however, why the E(CS)-value decrease at large q-values in micellar system. One of the important factors may be that the size of CTAC micelle is relatively small: aggregation number is 62 and the diameter is approximately 20 Å.[14] As a consequence, the photoliberated electron may be easily recaptured by $RuC_{12}B^{3+}$. Further details of the microscopic structures of micelles are required to clarify the mechanism.

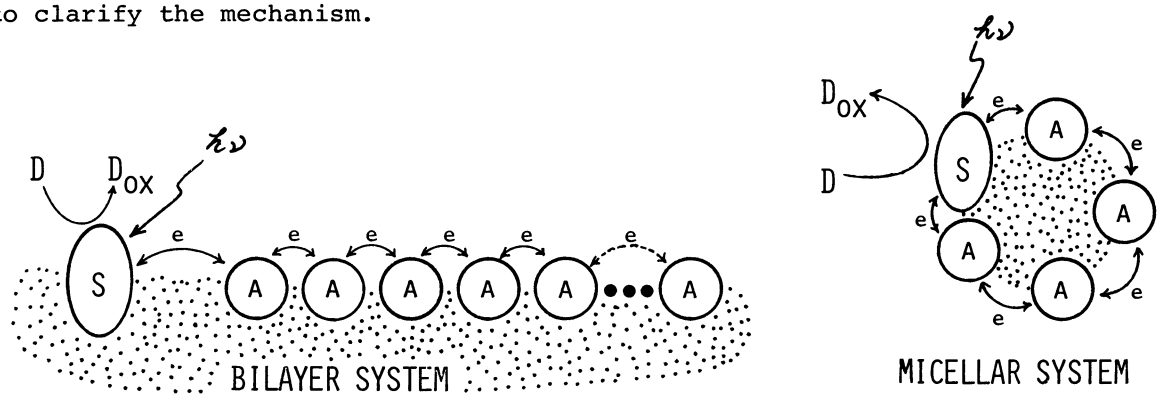


Fig. 4 Schematic illustration for the charge separation of photoliberated electron by the electron migration. S; $RuC_{12}B^{2+}$, A; $C_{16}C_2V^{2+}$, and D; EDTA.

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1) Contribution No. 634 from the Department of Organic Synthesis, Faculty of Engineering, Kyushu University.

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12) The detail will be published elsewhere as a full paper.

13) The line width of ESR signal at q = 0.5 is narrower than that at q = 0.2 by $\sqrt{25}$, which indicates that the photoliberated electron is delocalized over 25 $C_{16}C_2V^{2+}$ molecules.

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