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THE COMPETITION BETWEEN INTER- AND INTRAMOLECULAR ELECTRON-TRANSFER PROCESS INVOLVING POLYPYRIDINERUTHENIUM(II) COMPLEXES WITH LINKED VIOLOGEN UNITS IN SURFACTANT-TYPE VIOLOGEN ASSEMBLIES[1)]

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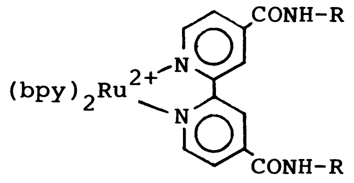
Polypyridineruthenium(II) complex with linked viologen units was synthesized as the model of man-made photoreaction center. Luminescence quenching of the ruthenium complex by a surfactant-type viologen in micellar or bilayer membrane systems was resolved into inter- and intramolecular processes and it became apparent that the photoinduced charge separation in intramolecular process was more efficient than that in intermolecular process.

A number of attempts have been made to build an efficient solar energy conversion system by the use of tris(2,2'-bipyridine)ruthenium(II) ($Ru(bpy)_3^{2+}$) and its derivartives in combination with various viologen homologues.[2-4)] The indispensable requirements for this system are an effective electron-transfer from the photoexcited ruthenium complex to the viologen (η) and a large probability of survivals (Fr) for the photogenerated primary ion pairs against the reverse electron-transfer. The former requirement is fulfilled in the systems where the viologen units are bound to the ruthenium complex moiety, as in the case of polypyridineruthenium complexes with linked viologen units, in spite of the presence of coulombic repulsion. In these systems, however, Fr-values are usually very small because of the dominant back electron-transfer. The back electron-transfer may be suppressed to some extents by the aid of various intermolecular interactions such as coulombic repulsion or selective compartmentalization into micelles, bilayer membranes, polymers and so on.[5-10)] In these systems, the Fr-values entirely depend on the rate of molecular diffusion. Novel methods to increase the Fr-values were recently developed by the use of electron-exchange between aligned viologen groups on various molecular assemblies.[11-14)]

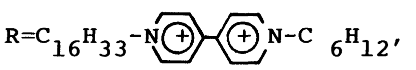
In order to increase η-values, a new polypyridineruthenium(II) complex with linked viologen units across an appropriate spacer chain was prepared and incorporated into organized molecular assemblies with aligned viologen to improve the Fr-values in the present investigation. The spacer chain between the rutheniumcomplex- and viologen moieties contained six methylene- and an amide groups, as shown by the structural formula 2, so that the reverse electron-transfer process was suppressed in comparison with the case of shorter spacer chains.[13)] A ruthenium complex without viologen units ($RuC_{12}B^{2+}$, 1) served as a reference. Either CTAC micellar or bilayer membrane ($2C_{16}NB$, 5) system was used to provide molecular assemblies which incorporated the ruthenium complex and a surfactant-type viologen molecule ($C_{16}C_2V^{2+}$, 3).

The quenching of luminescence from the ruthenium complex, as well as the ruthenium complex-sensitized reduction of viologen, was studied under various molar ratios (f) of 3 to the host surfactant (4 or 5) as shown by eq (1) as described before.[14] The luminescence intensity of 1 in the absence of 3 was used as a reference (I_0) for the quenching experiments.

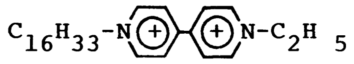
$$f = [C_{16}C_2V^{2+}]/([C_{16}C_2V^{2+}] + [\text{host surfactant}]) \qquad (1)$$



1 R=$C_{12}H_{25}$,

2 R=

where **bpy** stands for 2,2'-bipyridine unit.

3 

4 $(C_{16}H_{33})_2N^+(CH_3)_2Br^-$

Abbreviation of structural formulae

Ruthenium complex	Viologen	Surfactant
1 $RuC_{12}B^{2+}$	3 $C_{16}C_2V^{2+}$	4 CTAC
2 $2C_{16}V^{2+}C_6Ru^{2+}$		5 $2C_{16}NB$

The investigated photosystems

System No.	Ruthenium complex	Viologen	Surfactant
I	1	3	4 micelle
II	2	3	4 micelle
III	1	3	5 bilayer
IV	2	3	5 bilayer

The rate of reduction of viologen was obtained with degassed sample containing ruthenium complex (2×10^{-5}M), 3 ($0\sim1 \times 10^{-2}$M), surfactant ($1\sim0 \times 10^{-2}$M), and EDTA (1×10^{-3}M). The samples were irradiated (λ>420nm) and viologen cation radical concentrations were determined from absorption spectra (radical monomer;ε_{603nm}=10500 $M^{-1}cm^{-1}$ and radical dimer;ε_{535nm}=6910$M^{-1}cm^{-1}$)[13] at various irradiation time. The relative quantum yields (ϕ_{rel}) for the formation of viologen cation radicals were evaluated from the rate of formation at the very beginning of the irradiation by taking $Ru(bpy)_3^{2+}$ - methyl viologen system as a reference (ϕ_{rel}=100%).

More than 80 percent of the luminescence from the ruthenium complex moiety of 2 was quenched when the complex was incorporated into CTAC micelle without 3 (f=0). This quenching efficiency (Eq) may be taken as a measure of intramolecular quenching in the isolated complex on the micellar surface. The Eq-value for system II increased with f, as shown in Fig.1 (Curve B), due to the contribution of intermolecular quenching process. The simple intermolecular quenching was also responsible for quenching in system I (Curve A). The concentration effects of 3 on the luminescence quenching in system II was analayzed by the use of simple Stern-Volmer plot, under an assumption that the rate of intramolecular quenching in 2 could be taken as constant throughout the investigated f-values. The results are summarized in Fig.1, where the Eq-value for system II (Curve B) is resolved into intramolecular (Curve C) and intermolecular processes (Curve D). Essentially the same behaviors were observed with system IV in the region below f=0.5. The Eq-value started from 80.2 percent (at f=0) and reached 93.1 percent (at f=0.5), which could be divided into intramolecular (30.2 percent) and intermolecular contributions (62.9 percent). No experiment was carried out above f=0.5 because the system gradually approached micellar solution.

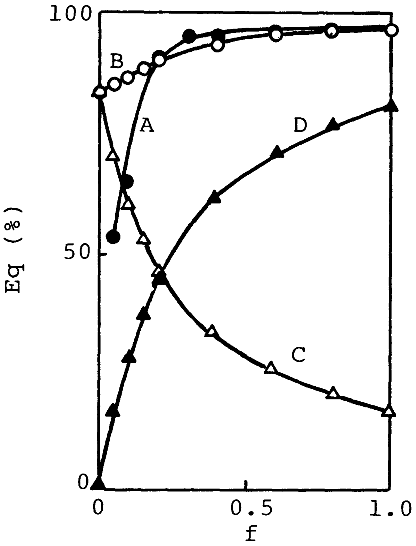


Fig.1 Luminescence quenching efficiencies of ruthenium complexes by 3 in micellar system. Intermolecular quenching of 1 (A) and total quenching (B), intra- (C), intermolecular (D) quenching efficiencies of 2.

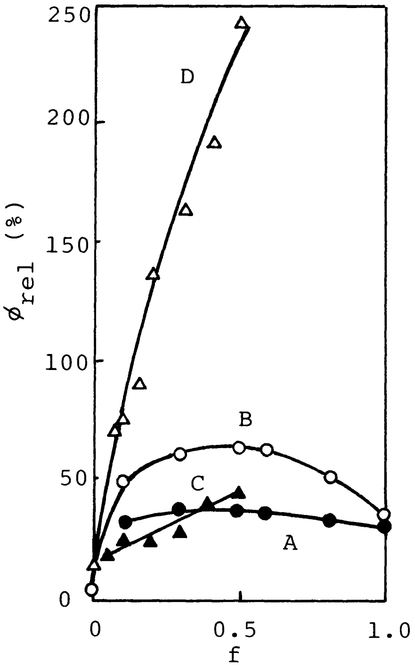
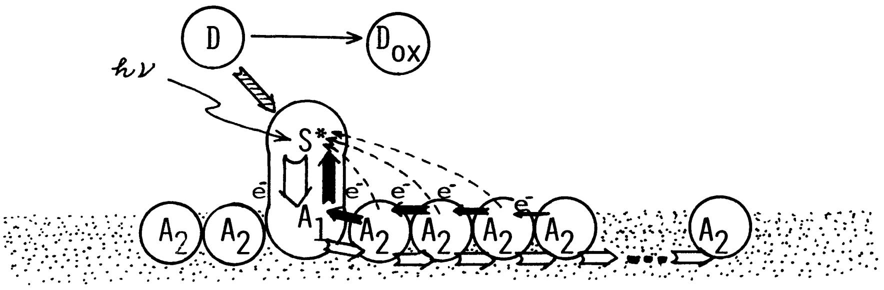


Fig.2 Dependence of relative quantum yields (ϕ_{rel}) on f-values in system I (A), II (B), III (C) and IV (D).

The relative quantum yields of viologen cation radicals (ϕ_{rel}) are summarized in Fig.2. The ϕ_{rel}-value is determined by the quantum yield of photogenerated primary ion pairs (η) and probability of survivals of primary ion pairs (Fr). Since η is proportional to Eq-value,[15] the ϕ_{rel}-value may be given by eq (2).

$$\phi_{rel} = \text{const.} \times \text{Eq} \times \text{Fr} \qquad (2)$$

In the micellar system, the ϕ_{rel}-values for system II are larger than that for system I in the region between f=0.2 and 0.8 (Curves A and B in Fig.2), in spite of the fact that the Eq-values are hardly different each other (Curves A and B in Fig. 1). In the neighborhood of f=1, the ϕ_{rel}-value for system II approaches to that for system I, as the intermolecular quenching becomes dominant in system II. Then, the increment of ϕ_{rel}-values for system II, as compared with system I, in the region between f=0.2 and 0.8 may be ascribed to the contribution of the intramolecular process. It may be reasonable to assume that Fr-value for the intermolecular process is not much different between system I and II. By the use of Eq-values in Fig. 1, ϕ_{rel}-value attributed to intermolecular process in system II at f=0.5 is estimated to be approximately two thirds of that for system I. Taking into consideration of the contribution of intramolecular quenching process (Fig.1, Curve C) and relationship between ϕ_{rel} and Fr (eq.(2)), one obtains Fr-value for the intramolecular process which is 3-4 times larger than that for intermolecular process in the neighborhood of f=0.5. The difference between 1 and 2 becomes enomous in the bilayer system (Curves C and D in Fig.2). The Fr-value for intramolecular process is larger than that for intermolecular process by at least one order of magnitude. The photoinjected electron between the secondary acceptors (A_2) may be easily removed from the photoreaction center ($S-A_1$) by the electron-echange as shown in the following scheme:



Schematic presentation of forward and backward electron-transfers in system II or IV.

This difference between micelle and bilayer system was also observed with photoreduction of viologen or spectroscopic studies in other ruthenium-viologen systems.[12-14] The electron-exchange is apparently aided by the highly ordered molecular alignment in bilayer systems[16] and Fr-values for the intramolecular photoelectron-transfer process will be accordingly increased.

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