Tris buffer described (containing ethanol and EDTA).

Quantitative Thin-Layer Chromatography. After qualitative thin-layer chromatographic analysis was made (iodine detection), silica gel containing adsorbed lipid was removed from appropriate zones and analyzed directly for phosphorus content. Procedures used were similar to those previously described,[37] except a larger volume of magnesium nitrate solution (ca. 0.20 mL) was employed, and the derivatized mixture was filtered to remove silica gel prior to UV analysis.

Vesicle Polymerization. Typically, 7 μL of 30% H_2O_2 (20 equiv) was added to a 1.0-mL dispersion of **1a** containing 2.0 mg of lipid, and the resulting dispersion was heated under a nitrogen atmosphere for 3 h at 40 °C. Thin-layer chromatography showed a single spot at the origin (iodine). The dispersion was then dialyzed against 100 mL of doubly distilled water for 18 h at room temperature in order to remove excess hydrogen peroxide. Quantitative analysis for thiol content indicated that ca. 5% of the thiol groups remained.

Vesicle Depolymerization. Typically, a 1.0 mL of polymerized dispersion of **1a** (2.0 mg of lipid) that had been dialyzed to remove excess hydrogen peroxide was purged with a stream of nitrogen and mixed with 60 mg (0.388 mmol) of dithiothreitol. The resulting dispersion was purged with nitrogen for 5 min and heated in a water bath for 1.5 h at 50 °C. Qualitative analysis by TLC indicated substantial regeneration of **1a**; R_f = 0.22, solvent C, positive thiol test. Quantitative phosphorus

analysis revealed a 63% yield of regenerated **1a**.

Freeze-Fracture Electron Microscopy. Samples of sonicated and polymerized dispersions of **1a** (20 mg/mL) were frozen in liquid nitrogen, fractured with etching by using a Balzer apparatus, and replicated with Pt/C by using standard procedures.[38] Glycerol (5%) was added to prevent freeze damage. Electron micrographs of freeze-fractured samples were obtained by using a Philips 201 instrument.

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Electron-Relay Chain Mechanism in the Sensitized Photoisomerization of Stilbazole Salts in Aqueous Anionic Micelles

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Abstract: Cis to trans isomerization of *N*-methyl-4-(β-styryl)pyridinium halide (4-MSPX, X = I or Cl) via electron-transfer sensitization by Ru(bpy)$_3^{2+}$ has been studied for some micellar systems under the illumination of 468 ± 5 nm light. Efficiencies for the isomerization ($\phi_{c\rightarrow t}$) were markedly enhanced on addition of anionic surfactants; e.g., the quantum yields in the presence of sodium dodecylsulfate (SDS) reached the maximum value of 64 ± 2, which is about 100-fold as much as those without SDS. The value is comparable to the aggregation number, N_A, of the SDS micelle, involving the pyridinium ions equal to SDS molecules. Similar agreement between N_A and $\phi_{c\rightarrow t}$ values was observed with micelles of other anionic surfactants $CH_3(CH_2)_nOSO_3Na$ ($n = 9, 11, 13$). It is postulated that an electron-relay chain mechanism is operative on the anionic micellar surface for the sensitized isomerization of pyridinium ions attached electrostatically. The line-width measurements of ^{23}Na NMR indicated that 4-MSP ion effectively substitutes the Na$^+$ ion adsorbed on SDS micelles. An overwhelming high adsorptivity of 4-MSP ion on anionic micelles over Na$^+$ ion was also evidenced by effects of various added salts in the reaction mixture.

An efficient electron transfer between donor D* and acceptor A (eq 1) in micellar systems is the subject of recent interest. The

$$D^* + A \rightarrow D^+ + A^- \qquad (1)$$

$$D^+ + A^- \rightarrow D + A \qquad (2)$$
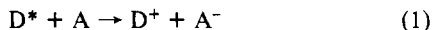
heterogeneous electrostatic field formed by surfactant molecules is considered to retard the back transfer of an electron once generated (eq 2), enhancing the efficiency of net charge separation.[1] Thus, much attention has been focused on redox reactions utilizing anionic micellar systems in relation to solar energy storage.[2] Interaction of a hydrated electron with surfactant-solubilized benzene, for example, showed significant micellar effects;[3] the electron addition to the benzene molecule was retarded by sodium dodecyl sulfate (SDS) but enhanced by the cetyltrimethylammonium bromide (CTAB) micelle. The two opposite effects suggest that the penetration of e_{aq}^- into the micelle interior

of solubilized benzene is hindered by the negatively charged SDS micellar surface but enhanced by cationic CTAB micelle.[4]

As an alternative effect of micellar systems, anionic micelles are expected to force cationic substrates to aggregate on its negatively charged surface. There are few studies forcused on the reactions of substrates adsorbed on micellar surfaces. Electron

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transfer between an electron donor and an acceptor adsorbed electrostatically on the micellar surface is an interesting but unsettled area in relation to many electron transport phenomena, e.g., photosynthesis and solar energy storage.

We wish to report here our findings that aggregation of a positively charged electron acceptor on anionic micelles may lead to a highly efficient chain reaction initiated by an electron transfer from the excited donor molecule. Thus, $Ru(bpy)_3^{2+}$-sensitized isomerization of cis-N-methyl-4-(β-styryl)pyridinium halide (cis-4-MSPX; X = Cl or I) takes place quite efficiently in the presence of anionic surfactants with the quantum yields as high as 50–100. The high efficiency is probably based on an electron-relay chain isomerization of cis-4-MSPX aggregates on the anionic micelles. This is, to our knowledge, the first example of chemical reactions of aggregates on micelles by an electron-relay chain mechanism.

Experimental Section

Materials. Tris(2,2'-bipyridine)ruthenium dichloride $[Ru(bpy)_3]^{2+}$ $(Cl^-)_2$,[5] zinc tetraphenylporphyrin (Zn(TPP)),[6] zinc tetrasodiotetrakis-(p-sulfophenyl)porphyrin (Zn(TPP)S),[7] and zinc tetrakis(4-N-methyl-pyridinium)porphyrin tetraiodide[8] were prepared according to the literature. The complexes prepared were satisfactorily pure (UV and NMR spectroscopically) and dried at 100 °C for 1 h prior to use. cis-N-methyl-4-(β-styryl)pyridinium chloride (cis-4-MSPX, X = Cl) was prepared by the halogen ion exchange of cis-N-methyl-4-(β-styryl)-pyridinium iodide (cis-4-MSPX, X = I)[9] through a column packed with ion-exchange resin (Amberlite IRA-400, Rohm & Haas Co.). cis- and trans-N-methyl-3-(β-styryl)pyridinium iodides (cis- and trans-3-MSPX, X = I) were obtained by the methylation of cis- and trans-3-β-stilba-zoles,[10] respectively, with MeI in refluxing benzene. The cis and trans isomers melt and decomose at 133–137 and 222–224 °C, respectively. The content of the iodide ion was determined after the oxidation with 3% aqueous H_2O_2 followed by the extraction of iodine with $CHCl_3$ (λ_{max} 535 nm).[11] The results showed that ~97% of the iodide ion was substituted for chloride ion in the case of the exchange of the counterion of cis-4-MSP ion.

Sodium decyl sulfate (SDeS) and tetradecyl sulfate (STS) were prepared by the reaction of the corresponding alcohols with chlorosulfonic acid followed by neutralization with aqueous NaOH.[12] The crude sulfates were purified by extraction of the organic impurities with refluxing n-hexane and recrystallization from H_2O. Sodium dodecyl sulfate(SDS) was of commercial extra pure grade (Tokyo Kasei Co.) and dried under vacuum before use.

Apparatus. Absorption spectra were recorded on a Hitachi ultraviolet spectrophotometer (Model 124). Proton NMR spectra were done on a Hitachi R-24B NMR spectrometer using dimethyl-d_6 sulfoxide or $CDCl_3$ containing TMS. ^{23}Na NMR spectra were taken on a Varian FT-80A NMR spectrometer (21.039 MHz) at 30 ± 0.5 °C. The line widths at half-height were read directly from the spectral chart. The reference used as a 0.02 M aqueous solution of NaI. Luminescence spectra were recorded on a Hitachi 650-10 fluorescence spectrophotometer in appropriate solutions. Reduction potentials were taken on a Yanagimoto P 1100 polarographic analyzer. Electrochemical analyses were performed using a mercury electrode in acetonitrile containing 10^{-3} M substrates and 0.05 M tetraethylammonium perchlorate (TEAP) as an electrolyte. HPLC analyses were made on a Jasco Twinkle HPLC instrument equipped with a UV detector (345 nm). The HPLC analysis was done using an ODS column (Fine Sil C_{18}-10; Jasco) and a mixture of 0.1 M aqueous NaCl and MeOH (1:4) as an eluent. Cmc's were determined by a Shimadzu du Nouy type tensiometer.

Irradiation. Continuous illumination experiments were carried out in the same cell of a fluorescence spectrophotometer equipped with a 150-W xenon lamp and a monochromator.

In a typical run, an aqueous solution (3 mL) of $Ru(bpy)_3^{2+}$ sensitizer (3.1 × 10^{-5} M), cis-4-MSPI (0.01 M), and SDS (8.5 × 10^{-3} M) was transferred into a 1 × 1 cm glass cuvette equipped with a serum stopper, deaerated by flushing with oxygen-free argon, and irradiated continuously
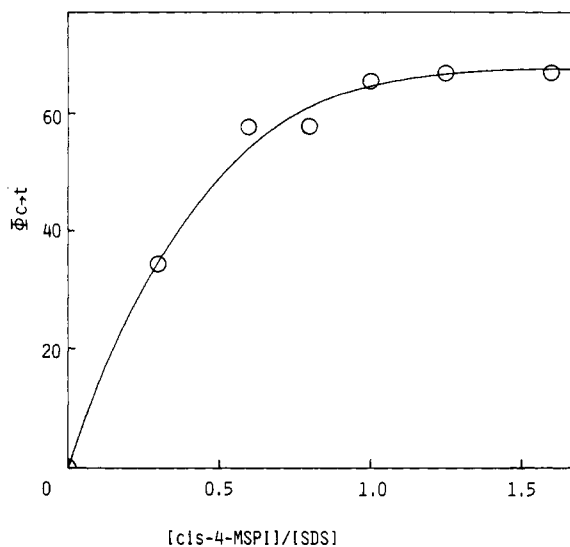
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Figure 1. Effect of molar ratios of cis-4-MSPI/SDS on the quantum yields ($\phi_{c \to t}$) of the photoisomerization of cis-4-MSPI in water at 20 ± 2 °C: $[Ru(bpy)_3^{2+}]$, 8.6 × 10^{-5} M; [SDS], 6.0 mM; irradiated at 468 ± 5 nm.

at 468 ± 5 nm. The formation of trans-4-MSPI was monitored by HPLC analysis of an aliquot taken at appropriate time intervals.

The quantum yields were determined by potassium ferrioxalate actinometry.[13] The incident photoflux amounts to 9.5 × 10^{-7} einsteins/L min.

Results and Discussion

We have already shown that the photochemical cis-to-trans isomerization of N-methyl-4-(β-styryl)pyridinium halide (4-MSPX) is induced via a one-electron reduction by visible-light sensitizers.[9] Irradiations of cis-4-MSPI in the presence of $Ru(bpy)_3^{2+}$ or tetraphenylporphyrin complexes result in the predominant formation of the trans isomer ($\gtrsim89\%$) at the photostationary state (pss). The rate constants for the quenching of the fluorescence of the sensitizers by various MSPI's are correlated with their reduction potentials, showing that the excited dyes initiate the isomerization by an electron transfer to cis-4-MSPI as depicted in eq 3.[9] The isomerization is quite in contrast to

cis-4-MSP ion

PR

$$(3)$$

trans-4-MSP ion
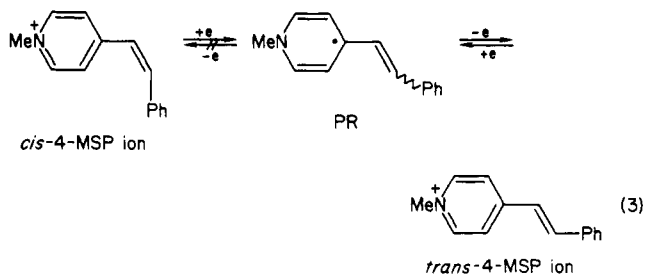
ordinary triplet-sensitized isomerizations leading to cis-rich mixtures. The trans-predominant photoequilibria of MSP ions reflect the almost exclusive formation of the more stable trans isomer from the pyridinyl radical intermediate (PR).

Cis-to-Trans Isomerization to cis-4-MSPI by $Ru(bpy)_3^{2+*}$ in Micellar Solutions. The quantum yields for the photochemical isomerization of cis-4-MSPI sensitized by $Ru(bpy)_3^{2+}$ were remarkably enhanced by the addition of sodium dodecyl sulfate (SDS) in comparison to those in homogeneous aqueous solutions. Mostly, the isomerization was carried out under argon in aqueous solutions containing 6–10 mM SDS, the critical micelle concentration (cmc) of which was quite below 0.0081 M. Figure 1 shows that the efficiency for the isomerization increased steadily with the increasing ratios of [cis-4-MSPI] to [SDS] and reaches to a limiting value of 64 ± 2 at the ratio around 1.0. Similarly, the

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Photoisomerization of Stilbazole

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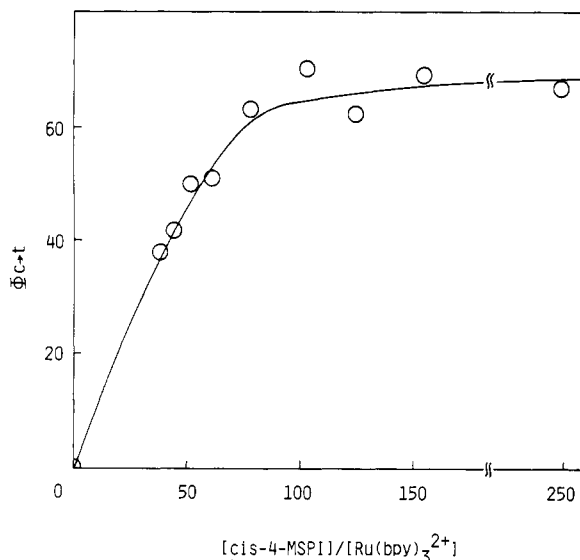**Figure 2.** Effect of cis-4-MSPX/Ru(bpy)$_3^{2+}$ on the quantum yields ($\phi_{c \to t}$) of the photoisomerization of cis-4-MSPI in water at 20 ± 2 °C: [Ru(bpy)$_3^{2+}$], 8.6 × 10^{-5} M; [SDS] = [cis-4-MSPI]; irradiated at 468 ± 5 nm.

Table I. Limiting Quantum Yields ($\Phi_{c \to t}$)$_{max}$ for the Isomerization of cis-4-MSPI in Various Surfactant Systems[a]

surfactant	($\Phi_{c \to t}$)$_{max}$	aggregation no.[b]	
		$N_A{}^0$	N_A
	0.58 ± 0.03		
sodium dodecyl sulfate (SDS)	64 ± 2 (63)[c]	62[d]	70[e]
sodium decyl sulfate (SDeS)	49 ± 1	50[d]	60[e]
sodium tetradecyl sulfate (STS)	86 ± 4	82[e]	
SDS microemulsion[f]	98 ± 9	100[g]	113[e]
dodecyltrimethylammonium bromide (DTAB)	0.73 ± 0.05	50[d]	

[a] Conditions: [Ru(bpy)$_3^{2+}$], 7.7 × 10^{-6} to 9.7 × 10^{-5} M; [surfactant], 1.8–6.0 mM; [cis-4-MSPI], 2.0–7.2 mM. Irradiation was carried out under argon with light at 468 ± 5 nm at 20 ± 2 °C. [b] $N_A{}^0$ and N_A mean aggregation numbers determined in the absence of and in the presence of 0.01 M benzyltrimethylammonium bromide (BTAB). The N_A values represent more accurately the true aggregation numbers in the presence of cis-4-MSPI. [c] Using cis-4-MSPX (X = Cl) instead of cis-4-MSPI. [d] Reference 16a. [e] Calculated by a luminescence probe.[19] [f] A mixture of SDS (10 mM), amyl alcohol (61 mM), and dodecane (16 mM) in water. [g] Reference 16b.

effect of molar ratios of [cis-4-MSPI]/[Ru(bpy)$_3^{2+}$] on the efficiency resulted in the same limiting quantum yield when the ratios were larger than around 70 (Figure 2). Thus, the optimum reaction system to attain the maximum quantum yield appears to consist of ca. 70 molecules of cis-4-MSPI and SDS per one molecule of Ru(bpy)$_3^{2+}$.

The sensitized isomerization was enhanced by anionic micelles more than 100 times as compared to that in the homogeneous aqueous solution. In the micellar reactions, no effect of counterion, X$^-$, in cis-4-MSPX was observed; the $\phi_{c \to t}$ value for cis-4-MSPCl was identical with that of cis-4-MSPI (Table I). In contrast to the acceleration by anionic micelles, cationic micelles such as DTAB (dodecyltrimethylammonium bromide) had little effect on the isomerization. These results clearly suggest that the electrostatic anionic field is essential for the dramatic enhancement of the quantum yields.

Quenching of Luminescence of Ru(bpy)$_3^{2+*}$ with cis-4-MSPI in Micellar Solutions. The effect of SDS micelles on the luminescence of Ru(bpy)$_3^{2+*}$ is noteworthy. The luminescence quenching constants (i.e., $k_q \tau$) by cis-4-MSPI as determined from the Stern–Volmer plots were maximum at the SDS/Ru^{2+} ratio

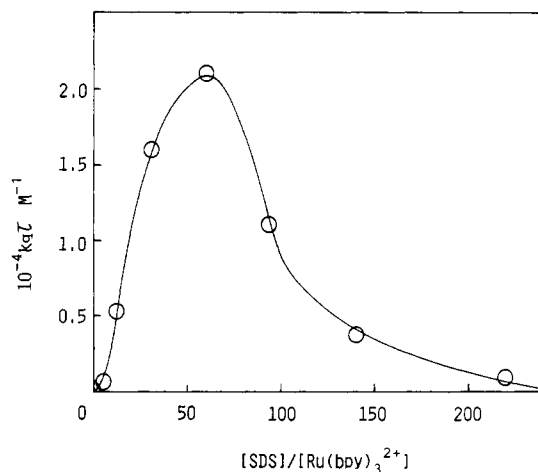**Figure 3.** Effect of molar ratios of SDS/Ru(bpy)$_3^{2+}$ on the fluorescence quenching of Ru(bpy)$_3^{2+*}$ by cis-4-MSPI at 20 ● 2 °C: [Ru(bpy)$_3^{2+}$], 3.2 × 10^{-5} M; [SDS], 0–7.0 mM; τ, lifetime of Ru(bpy)$_3^{2+*}$. The $k_q \tau$ values were determined by the Stern–Volmer plots with [cis-4-MSPI] = 0–2.0 mM. Open circles were obtained from the slopes of the linear relationship between I_0/I and [cis-MSPX].

of ca. 63 (Figure 3). Namely, the quenching was the most efficient when just one molecule of the Ru^{2+} complex was attached to each SDS micelle. The lower $k_q \tau$ values at SDS/Ru^{2+} < 60 reflect the bimolecular quenching of Ru^{2+*} with ground-state Ru^{2+} since one micelle involves several molecules of Ru^{2+} ions under these conditions. In general, deactivation of Ru^{2+*} may be expressed as in eq 4. The third term in eq 4 is noted to play an

$$-d[\text{Ru}^{2+*}]/dt =$$
$$k_1[\text{Ru}^{2+*}] + k_2[\text{Ru}^{2+*}]^2 + k_3[\text{Ru}^{2+*}][\text{Ru}^{2+}] \quad (4)$$

important role for the deactivation in case of weak and steady-state illumination.[14]

Above the SDS/Ru^{2+} ratio of 60, the apparent quenching by cis-4-MSPI decreased by the increasing ratio. This is responsible for the net decrease of cis-4-MSPI molecules per one molecule of the Ru^{2+} complex, since the number of micelles involving only cis-4-MSPI but not Ru^{2+} molecules increases. Thus, the quenching studies lead to the same conclusion that the most efficient sensitization consists of one molecule of Ru^{2+} per an anionic micelle.

Effects of Anionic Micelles of CH$_3$(CH$_2$)$_n$OSO$_3$Na (n = 9, 11, and 13) on the Isomerization. The above results on the SDS micelle suggest that the optimum quantum yield can be obtained when an anionic micelle contains one Ru^{2+} complex and cis-4-MSPI molecules approximately equal to the aggregation number ($N_A{}^0$), where $N_A{}^0$ denotes the number of surfactant molecules for a micelle without any additives. Similar results were obtained with other anionic micelles and a microemulsion system for the Ru^{2+}-sensitized isomerization of cis-4-MSPI. As shown in Table I, the resulting quantum yields for the isomerization are in good agreement with the reported $N_A{}^0$ values[15,16] of corresponding anionic surfactants. The detailed discussion about $\phi_{c \to t}$ and $N_A{}^0$'s will be given later in mechanistic considerations. Cationic micelles (e.g., DTAB) did not show any accelerating effect.

Effects of Added Salts on the Isomerization. It is known that added salts tend to increase the aggregation number of SDS and to decrease the cmc.[17,18] In the present photoisomerization of cis-4-MSPI, the addition of salts to the SDS micellar solution is expected to exert a significant effect. Sodium chloride, benzyltrimethylammonium bromide (BTAB), and tetramethyl-

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(15) These aggregation numbers, $N_A{}^0$, are the reported ones in the absence of the additives.[16]
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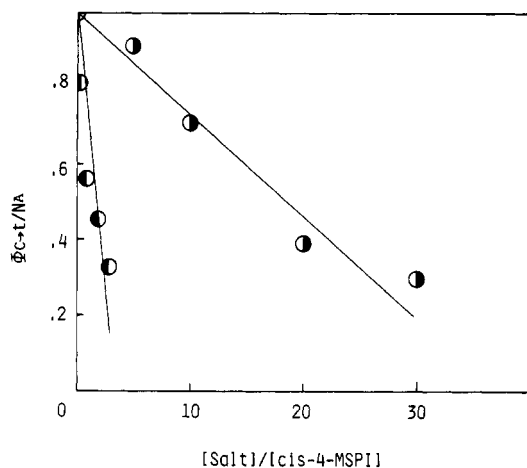(17) Mysels, K. J.; Princen, L. H. *J. Phys. Chem.* **1959**, *63*, 1696.
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Table II. Effect of Added Salts on Quantum Yields and N_A and SDS[a]

[salt]$_{added}$, M	$\Phi_{c \rightarrow t}$	N_A[b]
0	64	62
NaCl		
0.05	62	68
0.10	53	75
0.20	34	87
0.30	30	101
BTAB[c]		
0.005	51	63
0.010	39	70
0.020	33	71
0.030	25	75
TAB[d]		
0.030	59	
0.10	38	72

[a] Conditions: [Ru(bpy)$_3$$^{2+}$], 3.1×10^{-5} M; [SDS], 8.5 mM. Irradiation, 468 ± 5 nm under argon at 20 ± 2 °C. [b] Aggregation numbers in the presence of salts as measured by the method of Turro et al. (ref 19). [c] Benzyltrimethylammonium bromide. [d] Tetramethylammonium bromide.
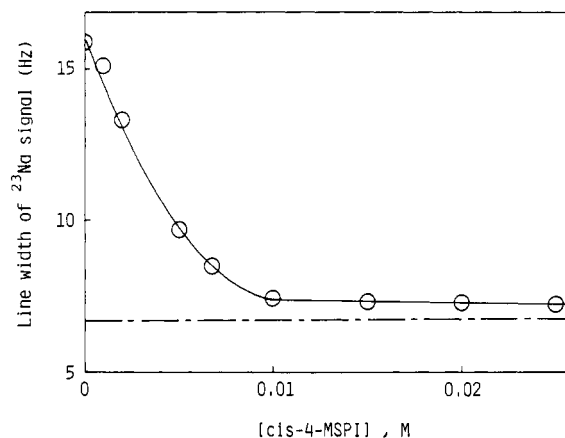

Figure 4. Dependence of quantum yields ($\phi_{c \rightarrow t}$) on added salts for the isomerization of *cis*-4-MSPI: (◑) for addition of NaCl; (◐) for benzyltrimethylammonium bromide (BTAB). The reaction conditions are identical with those in Table II.

ammonium bromide (TAB) were examined. Table II summarizes the $\phi_{c \rightarrow t}$ values together with the aggregation numbers (N_A) of SDS in the presence of the salts which were measured according to the procedure of Turro et al.[19]

All the salts examined retarded the isomerization significantly. The least soluble BTAB retarded the reaction 10 times as efficiently as NaCl or TAB, implying that BTAB tends to adsorb most effectively on the anionic micellar surface of SDS and hence decrease the adsorption sites available for *cis*-4-MSPI. Thus, 0.3 M NaCl increased the $N_A{}^0$ values of SDS almost twice but, at the same time, reduce the $\phi_{c \rightarrow t}$ value to a half when 0.01 M *cis*-4-MSPI was used. In other words, the adsorption equilibrium constant for the *cis*-4-MSP ion appears to be 20 times as high as that for the sodium cation.

Interestingly, a hydrophobic, i.e., less soluble, BTAB cation is more susceptible to absorption to the SDS micelle. It is clearly shown in Figure 4 that the hydrophobic salt adsorbs on the micellar surface effectively, and its adsorption constant is approximately the same with *cis*-4-MSPI. It is reasonable that cationic ions of similar hydrophobic groups possess the adsorption constants of the same order.

NMR Study of ^{23}Na Ion in Aqueous SDS. It is apparent in Figure 4 that the sodium ion adsorbs to the SDS micelle 20 times less effectively than *cis*-4-MSPX. It is then expected that the

(19) Turro, N. J.; Yekta, A. *J. Am. Chem. Soc.* **1978**, *100*, 5951.

Figure 5. Effect of *cis*-4-MSPI on the line widths of ^{23}Na NMR spectra in 0.02 M SDS solution at 30 ± 0.5 °C.

Table III. Electron Transfer Efficiency from Excited Ru(bpy)$_3$$^{2+}$ to Acceptor[a]

acceptor	solvent	$\Phi_{c \rightarrow t}$	% trans at pss	ΔG,[b] kcal/mol	remarks
cis-4-MSPI	H_2O	0.58	89	−8.6	c
cis-4-MSPI	SDS/H_2O	66	98	(−8.6)	d
trans-4-MSPI	H_2O		89	−8.6	
cis-3-MSPI	H_2O	0.047		−5.3	d
cis-3-MSPI	SDS/H_2O	3.1	45	(−5.3)	d
cis-stilbene	CH_3CN		5	+17.5	e

[a] Conditions: [Ru(bpy)$_3$$^{2+}$], 3.2×10^{-5} M; [olefin], 4.1 mM; [SDS], 8.5 mM. Irradiation at 468 ± 5 nm under argon at 20 ± 2 °C. [b] The free-energy change in the electron-transfer process between excited Ru(bpy)$_3$$^{2+}$ and acceptor. [c] Electron-transfer-induced isomerization is operative (ref 9). [d] The present work. [e] Energy-transfer-induced isomerization is operative (ref 26).

sodium ion would be easily detached on addition of *cis*-4-MSPX. This could most directly be measured by ^{23}Na NMR relaxation. Since the ^{23}Na nucleus possesses an electric quadrupole Q, its relaxation rates are governed by the coupling between Q and the electric field gradient at the nucleus. The latter should be quite small for the free Na$^+$ and substantial when the ion is paired to the counteranion. Therefore, the slow and fast relaxation rates would mean the free and ion-paired Na$^+$'s, respectively.[20] Figure 5 shows the dependency of the observed line widths of the ^{23}Na NMR signal on the concentration of *cis*-4-MSPX in the presence of SDS. Under extreme narrowing conditions, the line width represents the apparent rate (R_{obsd}) which is the average relaxation rate of free (R_f) and adsorbed ions (R_m) as indicated by eq 5.[20]

$$R_{obsd} = R_f \frac{(1 - \beta)c_t + \beta c_{cmc}}{c_t} + R_m \beta \frac{c_t - c_{cmc}}{c_t} \quad (5)$$

Here, c_t and c_{cmc} denote the total concentration and cmc of SDS, respectively, and β means the degree of adsorption on the micelle. The results in Figure 5 clearly indicate that the addition of *cis*-4-MSPX promotes the release of adsorbed sodium ion, implying the concurrent adsorption of *cis*-4-MSP pyridinium ion. In other words, the β value of Na$^+$ was steadily decreased by the addition of *cis*-4-MSPX[21] and was estimated to be 3.8% at the *cis*-4-MSPX/SDS ratio of 0.5, which is significantly lowered compared to the reported β value of 73% in the absence of *cis*-4-MSPX.[22-24]

The adsorbed sodium ion appears to be substituted almost completely with the pyridinium ion at the *cis*-4-MSP$^+$/Na$^+$ ratio of 0.5. The ^{23}Na study supports the above-mentioned micelle

(20) (a) Laszlo, P. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 254. (b) Gustavsson, H.; Lindman, B. *J. Am. Chem. Soc.* **1975**, *97*, 3923.

(21) The cmc of SDS in the presence of 4.1 mM *cis*-4-MSPI was measured to be 9.1×10^{-5} M.

(22) Estimations of the micellar charge have been reported by several workers.[23] The β values are scattered between 0.22 and 0.36, among which $\beta = 0.27$ has been assessed to be the most reliable by Nishikido.[24]

(23) Koshinuma, M.; Sasaki, T. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2755.

(24) Nishikido, N. *J. Colloid Interface Sci.* **1983**, *92*, 588.

model, consisting of one Ru^{2+} complex and selectively adsorbed 4-MSP cation on the anionic micelle.

Electron-Transfer Isomerization of Various Olefins. In Table III are summarized the Ru^{2+}-sensitized cis–trans isomerization of various olefins. The SDS micellar system revealed the remarkable, enhancing effect on the quantum yields for the isomerization of MSPI's. Thus, the $\phi_{c \to t}$ for the Ru^{2+}-sensitized isomerization of *cis*-4-MSPX in aqueous solution increased more than 100-fold by addition of SDS.
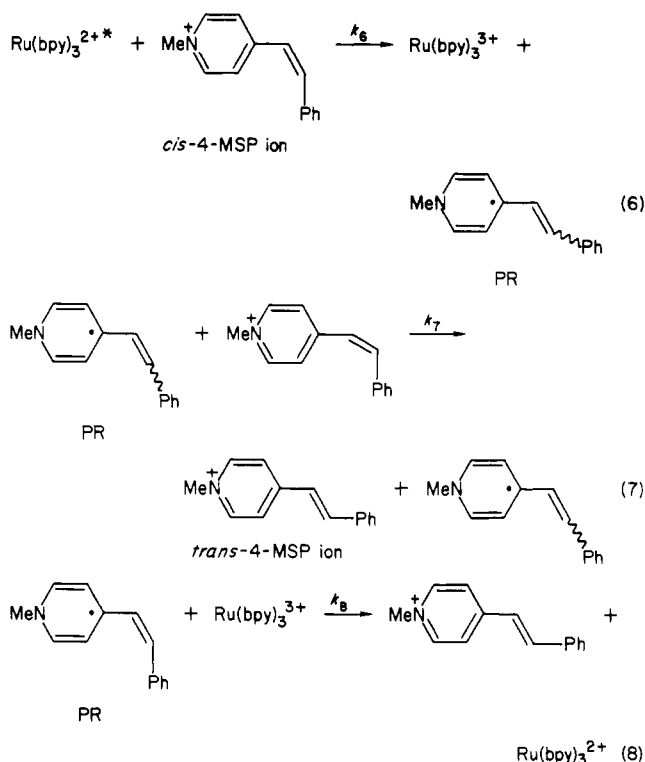
Excited ruthenium complexes can induce the isomerization of olefins via an excited triplet sensitization and/or one-electron-transfer mechanisms. Sensitization by triplet energy transfer can induce isomerizations from both isomers (trans and cis), while one-electron-induced isomerizations lead to irreversible cis-to-trans isomerizations as a diagnostic index.[9] Hence, the %trans at the pss would be close to 100% if only the electron-induced isomerization is operative. For the Ru^{2+}-sensitization in homogeneous aqueous solution, the high trans/cis ratio of 8.1 (i.e., %trans ~89%) at the pss indicates an almost but not exclusive occurrence of the electron-transfer mechanism. Interestingly, the %trans further increased to >98% at the pss in the SDS micellar solution, implying the electron-transfer chain isomerization on micellar surface and the negligibly small contribution of triplet sensitization.

An enhancement (ca. 60-fold) of the $\phi_{c \to t}$ value by SDS was also observed for the 3-styryl analogue (*cis*-3-MSPI). The electron transfer from Ru^{2+}* is expected to be diffusion-controlled judging from the exothermic free-energy change (i.e., negative ΔG value) for *cis*-3- and -4-MSPX. The approximately 10-fold lower quantum yields for *cis*-3-MSPI as compared with the *cis*-4-isomer suggest the less efficient isomerization by the one-electron transfer. The less efficient and lower %trans of 45% at the pss for *cis*-3-MSPX may reflect the lower exothermicity.[25] It is understandable that the efficiency for electron transfer to the 3-isomer is less favorable on account of the lower exothermicity than that to the 4-isomer, while the triplet energy transfer from Ru^{2+}* to MSPX is of similar efficiency between the 3- and 4-isomers because of the same E_T value of ca. 50 kcal/mol.[9] That is, the Ru^{2+}*-sensitized isomerization of *cis*-3-MSPX is implicated to take place, even in the SDS micellar system, via the triplet sensitization to a considerable extent. The isomerization of *cis*-stilbene via the electron-transfer mechanism is unfavorable because of the larger positive ΔG value; in fact, the %trans was only 5% at the pss as shown in Table III.[26]
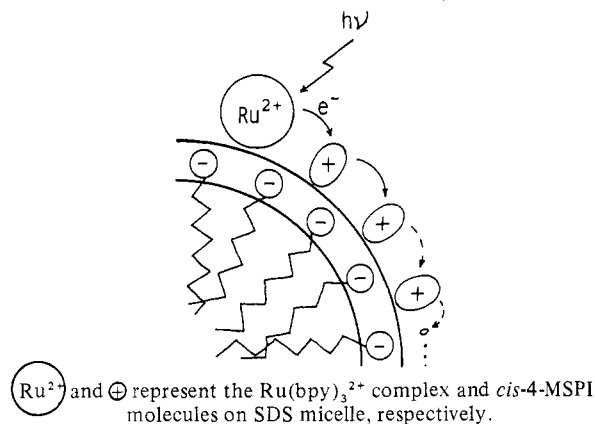
cis-3- and -4-MSPX may be photoisomerized by direct irradiation at 285 ± 10 nm, but the efficiency (i.e., $\phi_{c \to t}$) could not be enhanced by addition of SDS. This fact rules out the occurrence of the triplet energy induced chain isomerization of the stilbazole salts adsorbed on the SDS micellar surface. We have already shown that zinc tetraphenylporphyrin (Zn(TPP)) sensitizes the isomerization of stilbazoles by a one-electron transfer.[9] When negatively charged Zn(TPP)S was used for the present sensitization, the accelerating effect of the SDS micelle (3–8 mM SDS) was very low, i.e., by factors of 1.5–2. The result is easily understood since the coulombic repulsion does not allow Zn(TPP)S to adsorb on the anionic SDS micellar surface.

Electron-Relay Chain Mechanism. All the above results indicate that it is essential for the efficient electron transfer between D* and A to come in contact with each other on the same micellar surface. A possibility that the present high quantum yields might be originated on intermicellar electron-exchange processes could not be substantiated on the basis of almost constant $\phi_{c \to t}$ values in the high concentration range of [*cis*-MSPX] as shown in Figure 2. The electron-relay chain reaction as depicted in Scheme I is

(25) Another reason for the lower efficiency is probably the lower delocalization of the electron in the PR radical having the meta substitution.

(26) Wrighton, M.; Markham, J. *J. Phys. Chem.* **1973**, *77*, 3042.

Scheme I

Scheme II. Schematic Picture for Electron-Relay Chain Reaction

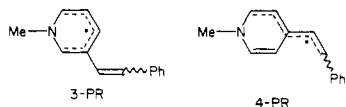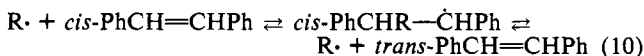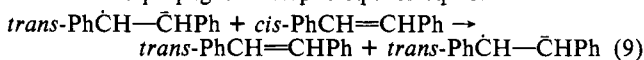(Ru^{2+}) and ⊕ represent the Ru(bpy)$_3$$^{2+}$ complex and *cis*-4-MSPI molecules on SDS micelle, respectively.

proposed for such a high quantum yield.

The correlation of $[\phi_{c \to t}]_{max}$ with N_A clearly indicates that the adsorbed Ru^{2+} complex in the photoexcited state transfers an electron to the *cis*-4-MSPX molecule on the anionic micelle surface and that the resulting pyridinyl radical (PR) relays the electron to a neighboring *cis*-4-MSPX molecule without decaying by back transfer to the oxidized donor, Ru(bpy)$_3$$^{3+}$. The schematic representation for the electron relay is drawn in Scheme II.

The data in Table I show that the limiting quantum yields are somewhat smaller than the aggregation numbers, N_A, which were determined in the presence of 0.01 M BTAB. BTAB was chosen since it has an adsorptivity to SDS micelle quite similar to MSPX. The ratios of the quantum yield to N_A were calculated to be 91%, 82%, and 89% for SDS, SDeS, and SDS microemulsion systems, respectively. About 10% of the anionic sites has to be vacant for the anionic micelles being dissolvable in aqueous solutions. This is reasonable since the micelles should precipitate out if all the anionic sites are neutralized. The quantum yields in Table I seem to be in agreement with the aggregation number N_A^0 in the absence of the additives. The coincidence is probably due to the cancellation of the increase in the aggregation number by 10% vacancy of the anionic sites in the micelle. The ratio of the surfactant anion to the MSP ion may independently be estimated by using extramicellar luminescent probes.[27] In fact, preliminary

results indicate the adsorption of 0.9 MSP ion–molecules per one SDS molecule at 0.01 M SDS, which is nicely coincident with the ratio of $\phi_{c\rightarrow t}$ to N_A for the SDS micellar solution.

The amazing point is that the back electron transfer (k_8) from the PR radical to the Ru^{3+} complex does not compete with the electron migration (k_7) to the *cis*-4-MSP ion, resulting in the almost complete isomerization of the *cis*-4-MSP ions on a micelle. A rough estimate[28] suggests that in order to cause such a complete isomerization, the k_7 value should be $\gtrsim 1000$ times as high as that of k_8. The extremely high rate ratio of $k_7/k_8 \gtrsim 1000$ may be rationalized partly by the more negative reduction potential $(Ru^{2+}/Ru^{3+} = -1.32$ V vs. SCE)[29] in comparison to *cis*- or *trans*-4-MSPX $(E_{1/2} = -1.01$ V vs. SCE). We suppose that the high rate ratio is principally caused by the different existing sites between the MSP ion and the Ru^{2+} complex. That is, the hydrophobic styryl group of the MSP ion and the PR would be directed to and dissolved in the interior of the SDS micelle since the MSP ion and the PR are both rather hydrophobic in contrast to the very hydrophilic Ru^{2+} complex. In fact, it has been reported that the driving force for solubilization of the hydrophobic cation is largely attributed to the decrease or elimination of the hydrocarbon–water interface.[27,30] Hence, there is very low probability for the PR radical in the interior to contact with the Ru^{3+} ion on the anionic surface, thus lowering the rate of back electron transfer (i.e., k_8). In addition, the concentration effect of the bound MSP ions in the interior would be an another promoting effect for the isomerization.[31,32] Similar concentration effects in the homogeneous solution were observed in the radiolytic isomerization of stilbene.[33]

It has been noted that the radiolysis of stilbene gives rise to the cis–trans chain isomerization.[33] At higher stilbene concentrations the stationary state becomes trans-preodminant; i.e., $G_{c\rightarrow t}$ increases and may exceed 200 at a 0.6 M concentration in benzene. The results were explained on the basis of an anionic chain reaction in which the propagation step is eq 9 or eq 10.

trans-PhĊH—C̄HPh + *cis*-PhCH=CHPh →
$$\text{*trans*-PhCH=CHPh} + \text{*trans*-PhĊH—C̄HPh} \quad (9)$$

R· + *cis*-PhCH=CHPh ⇌ *cis*-PhCHR—ĊHPh ⇌
$$\text{R·} + \text{*trans*-PhCH=CHPh} \quad (10)$$

The present isomerization of *cis*-4-MSPX aggregates on the micellar surface is comparable with the radiolytic isomerization of stilbene in homogeneous solution. A similar electron-relay chain mechanism induces the high quantum efficiency in these reactions. However, the present reaction is essentially different from the radiolytic isomerization in some points. Firstly, *cis*-4-MSPX aggregates on the micellar surface do not undergo such a chain reaction by direct irradiation in the absence of redox sensitizers. Secondly, the chain isomerization is effective at much lower concentrations (e.g., several millimolar) of *cis*-4-MSPX. Thirdly, the maximum quantum yields can be controlled by the kinds of surfactants used.

This remarkably efficient cis–trans isomerization is to our knowledge the first electron-relay chain reaction on a controlled charged surface. The chain propagation step involves only one reaction sequence, an electron-relay between the pyridinyl radical (PR) and *cis*-MSPX (eq 7). This is very interesting since ordinary electron-transfer chain reactions consist of donors and acceptors of different redox potentials.[34] The present results indicate that the adsorbed Ru^{2+*} causes the isomerization of almost all the molecules of *cis*-4-MSPX attached on the micelle, and the redox relay isomerization should take place much faster than the dissociation of the micelle.[35,36]

Here, it should be noted that a photoliberated electron is believed to delocalize over 25 molecules of *N*-ethyl-*N'*-hexadecyl-4,4'-bipyridinium ion $(C_{16}C_2V^{2+})$ along the bilayer surface consisting of the $C_{16}C_2V^{2+}$ and an amphipathic Ru^{2+} complex.[37] The electron delocalization was inferred from the line sharpening of the ESR signal of $C_{16}C_2V^{+\cdot}$ with increasing $[C_{16}C_2V^{2+}]$.[37] A similar fast electron migration is also feasible in a system involving aligned units in polymer chains.[38] The electron-relay mechanism suggested so far by these physical and spectroscopic means has now been demonstrated chemically by the highly efficient isomerization of *cis*-4-MSPX on the anionic micelle.

Further investigations are in progress in other systems such as vesicle or molecular bilayer which will show similar effects.

(27) We are grateful to a referee for the suggestion. Bonilha, J. B. S.; Foreman, T. K.; Whitten, D. G. *J. Am. Chem. Soc.* **1982**, *104*, 4215.

(28) A factor of over 1000 for the rate ratio of k_7/k_8 should be assumed to complete the isomerization of adsorbed 4-MSP ions via the electron-relay chain mechanism.

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(31) Local concentration of the *cis*-MSP ion bound to a SDS micelle may be estimated to be as high as ca. 2.5 M by assuming that ca. 60 molecules of *cis*-4-MSP ions are included in the spherical-shaped SDS micelle, its volume being reported to be 4×10^4 Å^3.[32]

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(35) The rate constant for the dissociation of SDS micelle is reported to be 3.5×10^{-1} M^{-1}.[36]

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