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Light-Initiated Electron Transfer in Functional Surfactant Assemblies. 1. Micelles with Transition Metal Counterions

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Abstract: The photoinduced reduction of cupric ions by organic donors (D) was studied in functional surfactant assemblies in which the Cu^{2+} ions constitute the counterion atmosphere of the micelle. The donors employed were *N*-methylphenothiazine (MPTH) and *N,N'*-dimethyl-5,11-dihydroindolo[3,2-*b*]carbazole (DI). Laser photolysis, steady-state illumination, and fluorescence techniques were used to investigate the photoredox processes. The transfer of an electron from the excited donor inside the micelle to the counterion occurs so rapidly that it cannot be resolved kinetically by nanosecond laser techniques. In the case of DI, the reactive excited state was found to be the first excited singlet state whose lifetime in the Cu^{2+} micelles is 1.2×10^{-9} s. The cuprous ion formed in the photoredox process escapes from the micelle into the bulk solution before back transfer of electrons to D^+ can occur. There it may be used for a second redox reaction with a negative ion or a zwitterion. In such a system, the back reaction between reduced acceptor ion and oxidized donor is prevented by the micellar surface potential allowing for storage of light energy. The dynamics of excited-state interaction with micellar counterions was investigated also in aggregates with Co^{2+} and Ni^{2+} counterion atmospheres, respectively.

Introduction

In the photoredox reaction

$$A + D \underset{\Delta}{\overset{h\nu}{\rightleftarrows}} A^- + D^+ \qquad (1)$$

a large fraction of the incident light energy may be initially converted into chemical energy. The practical application of such a system is hampered by the fact that back reaction occurs rapidly. Thereby the chemical potential available in the radical ion pair $A^- \cdots D^+$ is degraded thermally. A promising approach to overcome this problem is to employ charged surfactant aggregates such as micelles or vesicles in aqueous solution as a reaction medium. Hitherto the role of these assemblies has been[1] (1) to solubilize hydrophobic photoactive species in their interior; (2) to provide an ultrathin electrostatic barrier, i.e., the electrical double layer surrounding the surfactant aggregate, through which kinetic control of the forward and backward reaction in eq 1 becomes feasible.[2]

Recently, light-induced charge separation has been investigated in our laboratory with systems where the micellar assembly itself serves as a functional unit, i.e., the electron donor and/or acceptor in the photoredox reaction are a part of the surfactant molecules constituting the micelle.

The simplest kind of such a "functionalized surfactant" is one where the counterion is a participant in the redox reaction. Cooperative effects obtained with such a system are reported in this paper.

Experimental Section

N-Methylphenothiazine was synthesized by the method of Normant and Curigny.[3] The crude, pink-colored crystals were recrystallized several times from argon-saturated ethanol until no impurity could be detected by thin layer chromatography (solvent hexane–acetone (3:1); visualization, photooxidation and/or thermal oxidation by a mixture of 0.2% H_2PtCl_6 and 1% KI in H_2O). One obtains colorless needles, mp 99.5 °C (lit. 100 °C[4]). The chromophore *N,N'*-dimethyl-5,11-dihydroindolo[3,2-*b*]carbazole (DI) was a generous gift of Professor S. Hünig from the University of Würzburg, West Germany, and was used as supplied.

The transition metal ion lauryl sulfates, $Cu(LS)_2$, $Ni(LS)_2$, and $Co(LS)_2$, were synthesized according to a procedure described previously.[5a] The cmc value of these surfactants is 1.2×10^{-3} M and the micellar aggregation number around 95.[5b] Deionized water was dis-

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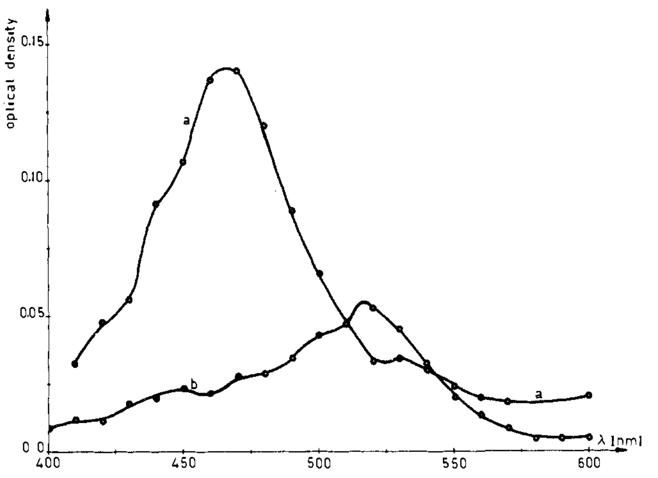

Figure 1. Absorption spectra immediately after the laser pulse. (a) 1×10^{-4} M MPTH in 5×10^{-2} M NaLS; (b) 1×10^{-4} M MPTH in 2×10^{-2} M $Cu(LS)_2$.

tilled from alkaline permanganate and subsequently twice from a quartz still. All other compounds were analytical reagent grade. The samples were deoxygenated by flushing with highly purified argon.

Laser photolysis experiments were carried out with a frequency doubled JK 2000 ruby laser. The 347.1-nm pulse had a duration of 15 ns and a maximum energy of 300 mJ. Transient spectra were detected by kinetic spectroscopy.[6]

Results and Discussion

In this report photoredox reactions will be analyzed that involve the reduction of a transition metal ion M^{n+} by an excited organic donor D*:

$$D^* + M^{n+} \rightarrow D^+ + M^{(n-1)+} \quad (2)$$

Most of the experiments were carried out using *N*-methylphenothiazine as photoactive species. This donor exhibits several properties that are suitable for mechanistic studies in surfactant aggregates. The reactive excited state, the triplet ($MPTH^T$), is a powerful reductant; hence electron transfer to metal ions with relatively negative redox potential can be studied. The donor cation radical ($MPTH^+$) is extremely stable in anionic micellar solution. This is due to the fact that no deprotonation can occur as is the case for phenothiazine.[1c] The absorption spectra of $MPTH^T$ and $MPTH^+$ are well separated, which alleviates the kinetic analysis. Finally, MPTH fulfills the requirement of being very hydrophobic and thus in micellar solution will be associated almost exclusively with the surfactant aggregates.

A. Reduction of Cupric Ion. In the following section we shall compare results obtained from laser photolysis studies of MPTH in NaLS and $Cu(LS)_2$ micellar solutions.

In these two systems the amphiphilic anions forming the micellar body are identical while the counterions differ and are constituted by Na^+ and Cu^{2+} ions, respectively. Figure 1 shows absorption spectra present immediately after the laser pulse. Curve a was obtained from micelles with a Na^+ counterion atmosphere. On the basis of quenching experiments, it is readily identified with the MPTH triplet spectrum. Like in the case of phenothiazine, the absorption maximum is located at 465 nm.[1c]

MPTH in NaLS micellar solution exhibits a weak fluorescence for which the spectrum is displayed in Figure 2, curve a. The emission maximum is located at 450 nm and the quantum yield obtained from comparison with a quinine sulfate standard is ca. 3×10^{-2}. As will be shown below, the primary photophysical events in the Na^+ surfactant solution lead to the formation of triplet states with practically unit quantum efficiency. The triplet energy derived from energy transfer experiments is 2.64 eV[7a] and hence close to that determined for unsubstituted phenothiazine.[7b] Their subsequent deactivation via T-T annihilation is retarded considerably[8,9] leading to triplet lifetimes greater than 1 ms.

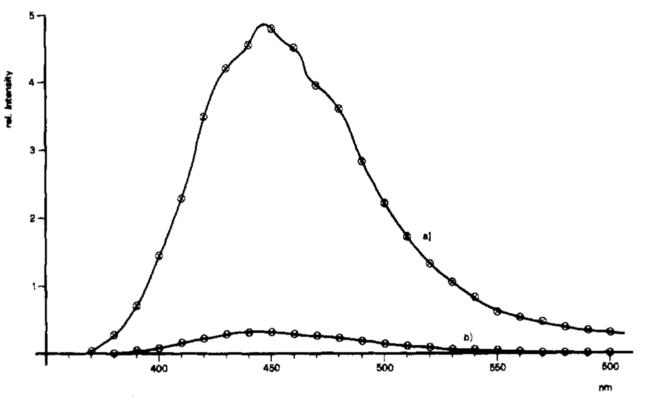

Figure 2. Fluorescence emission of MPTH in NaLS and $Cu(LS)_2$ solutions. (a) 5×10^{-5} M MPTH in 5×10^{-2} M NaLS; (b) 5×10^{-5} M MPTH in 2×10^{-2} M $Cu(LS)_2$.

$$\begin{tikzcd}
\text{MPTH} \arrow[r, "347.1\text{ nm}"] & \text{MPTH }(S_1) \arrow[r, "\text{isc}"] \arrow[d] & \text{MPTH }(T_1) \arrow[r] & \text{MPTH} \\
& \text{MPTH} + h\nu & &
\end{tikzcd} \quad (3)$$

At high laser intensities (>50 mJ/pulse), a biphotonic photoionization of MPTH was found to occur in competition with reaction 3. These conditions were therefore avoided in the present study.

Returning now to Figure 1, one notices a striking change in the laser photolysis results when micelles are considered where the Na^+ counterions have been replaced by Cu^{2+} (curve b). The end of pulse spectrum here is readily identified with that of $MPTH^+$ cation radicals whose absorption spectrum has been reported in the literature.[10] This indicates oxidative quenching of MPTH excited states by Cu^{2+} ions:

$$MPTH + Cu^{2+} \xrightarrow{h\nu} Cu^+ + MPTH^+ \quad (4)$$

As the electron transfer is completed already within the 15-ns duration of the laser pulse, it must occur at an extremely rapid rate. The fluorescence results displayed in Figure 2 further corroborate this finding. Introduction of Cu^{2+} as a counterion reduces the fluorescence intensity by a factor of 16. As the excited singlet state lifetime of MPTH is only about 10^{-9} s, the quenching process must occur within a fraction of a nanosecond. Two ways of interaction of Cu^{2+} ions with the $MPTH\text{-}S_1$ state can be envisaged. The first comprises direct electron transfer from the singlet state to Cu^{2+}, the second Cu^{2+} enhancement of intersystem crossing and subsequent oxidation of the MPTH triplet states.

In order to test whether $MPTH^T$ is capable of reducing Cu^{2+}, laser photolysis experiments were carried out in homogeneous solution, i.e., a mixture of ethanol/water (1/2 v/v). The experimental results indicate the formation of $MPTH^T$ by the laser pulse. In the presence of Cu^{2+} ions (3×10^{-4} to 5×10^{-3} M), the triplet is oxidized according to the equation

$$MPTH^T + Cu^{2+} \rightarrow Cu^+ + MPTH^+ \quad (5)$$

The rate of $MPTH^T$ decay was measured at a series of Cu^{2+} concentrations under conditions where $[MPTH^T] \ll [Cu^{2+}]$. A linear relation was found between the observed rate constant of triplet deactivation and the Cu^{2+} concentration. A Stern-

Table I. Experimental Conditions Employed in the Determination of the MPTH Triplet Yield

solution	solution absorbance at 347.1 nm	laser energy, quanta/pulse	concn of quanta absorbed, M	concn of triplets produced, M	ϕ_T
pyrene (4.4×10^{-5} M)	0.110	4.23×10^{15}	3.17×10^{-6}	8.88×10^{-7}	0.28
in 0.05 M NaLS		1.90×10^{15}	1.41×10^{-6}	3.94×10^{-7}	
MPTH (1.0×10^{-4} M)	0.110	4.23×10^{15}	3.17×10^{-6}	3.29	1.04
in 0.05 M NaLS		1.90×10^{15}	1.41×10^{-6}	1.43	1.02

Volmer plot of the data yields

$$k_5 = (1.0 \pm 0.1) \times 10^9\ \mathrm{M^{-1}\,s^{-1}}$$

These experiments establish that electron transfer from $\mathrm{MPTH^T}$ to $\mathrm{Cu^{2+}}$ can occur at a rate that is slightly below the diffusion-controlled limit.

From the data obtained in homogeneous solutions, it may be inferred that the reductant of $\mathrm{Cu^{2+}}$ ions in the micellar aggregates is also the MPTH triplet. Still, in view of the very rapid nature of the electron transfer process in the latter system, it cannot be excluded that S_1 states participate at least partially in the reduction. Laser experiments with subnanosecond time scale resolution are required to resolve this question umambiguously.

In order to quantitatively assess the yield of $\mathrm{Cu^{2+}}$ reduction, it is necessary to first determine the quantum yield of triplet formation (ϕ_T) and the extinction coefficient of $\mathrm{MPTH^T}$ (ϵ_{465} ($\mathrm{MPTH^T}$)) as well as that of the cation radical (ϵ_{516} ($\mathrm{MPTH^+}$)) at the wavelength of their respective absorption maxima.

The parameter ϵ_{465} ($\mathrm{MPTH^T}$) was obtained by using the method of triplet energy transfer which has been described previously.[11] Naphthalene (N), whose lowest triplet state energy is 2.64 eV, was selected as an energy acceptor. Since the statistics of probe distribution complicate the analysis of triplet energy transfer in micellar systems, the laser photolysis experiments were carried out in hexane solution. The 347.1-nm light pulse produces first MPTH triplets which subsequently transfer the excitation energy to naphthalene according to the equation

$$\mathrm{MPTH^T + N \rightarrow N^T + MPTH} \qquad (6)$$

The concentrations of naphthalene employed were sufficiently high to ensure quantitative conversion of $\mathrm{MPTH^T}$ into $\mathrm{N^T}$. Using for $\epsilon_{413}(\mathrm{N^T})$ the literature value $2.45 \times 10^4\ \mathrm{M^{-1}\,cm^{-1}}$ one obtains

$$\epsilon_{465}(\mathrm{MPTH^T}) = (2.30 \pm 0.03) \times 10^4\ \mathrm{M^{-1}\,cm^{-1}}$$

A careful comparison of the $\mathrm{MPTH^T}$ spectra in hexane and NaLS micelles revealed no difference in the spectral features as well as the position of the absorption maximum. Hence, it appears safe to consider this extinction coefficient to be valid also for the micellar system.

The quantum yield of $\mathrm{MPTH^T}$ formation was determined by comparison with a standard chromophore. Pyrene was chosen as a suitable reference substance since its triplet extinction coefficient[11] (ϵ_{412} $3.04 \times 10^4\ \mathrm{M^{-1}\,cm^{-1}}$) and quantum yield[12] ($\phi_T = 0.28$) have been ascertained previously. The procedure employed consisted in the preparation of two micellar NaLS solutions containing pyrene and MPTH, respectively. Their concentrations were adjusted to give identical optical densities at 347.1 nm. If the laser intensity is kept constant, the relative concentration of triplets produced in these two samples corresponds to the ratio of triplet yields. This method[23] gives the value

$$\phi_T(\mathrm{MPTH}) = 1.04 \pm 0.04$$

This result indicates that the exclusive channel of photophysical events following MPTH excitation is triplet formation in agreement with the mechanism formulated in eq 3. It explains also why MPTH does not display any fluorescence in solution.

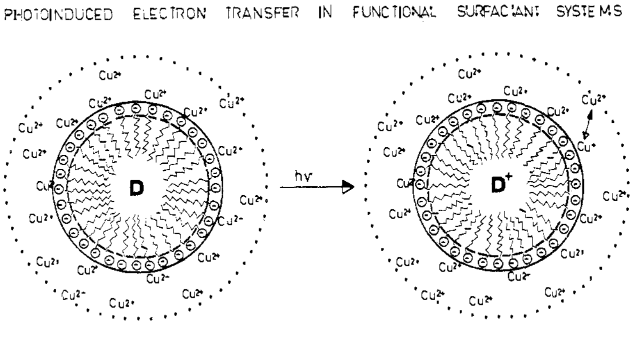

Figure 3. Schematic illustration of an electron transfer reaction in $\mathrm{Cu(LS)_2}$ micellar solution.

The extinction coefficient $\epsilon_{516}(\mathrm{MPTH^+})$, finally, was determined via quantitative oxidation of MPTH to $\mathrm{MPTH^+}$ by ferricyanide:

$$\mathrm{MPTH + [Fe(CN)_6]^{3-} \rightarrow MPTH^+ + [Fe(CN)_6]^{4-}} \qquad (7)$$

As the standard redox potential E_0 ($\mathrm{MPTH^+/MPTH}$) is 0.86 V[13] whereas E_0 ($\mathrm{[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}}$) is only 0.36 V, reaction 7 is endoergic by 0.5 eV and hence cannot occur spontaneously. It may, however, be initiated in $\mathrm{Cu(LS)_2}$ micellar solution via the aforementioned light-induced electron transfer to $\mathrm{Cu^{2+}}$ ions. The sequence of events is indicated schematically in Figure 3. First, $\mathrm{Cu^{2+}}$ receives an electron from excited MPTH. The monovalent ion subsequently escapes into the bulk solution where in turn it reduces $\mathrm{[Fe(CN)_6]^{3-}}$. The approach of $\mathrm{[Fe(CN)_6]^{4-}}$ to $\mathrm{MPTH^+}$, which remains associated with the original micelle, is impaired by the negative micellar surface potential. In Figure 4 are presented experimental data obtained with several MPTH concentrations. Illumination of a $\mathrm{MPTH(Cu(LS)_2)}$ solution containing $\mathrm{[Fe(CN)_6]^{3-}}$ results in the rapid appearance of the $\mathrm{MPTH^+}$ absorption spectrum. This effect is demonstrated in the upper part of the figure. The $\mathrm{MPTH^+}$ produced in such a way is relatively stable, the 516-nm absorption diminishing only by about 20% within a 24-h period. (Faster spectral changes occur in the wavelength region between 350 and 450 nm. They are attributed[14] to a partial transfer of $\mathrm{CN^-}$ ligands from $\mathrm{[Fe(CN)_6]^{3-}}$ to $\mathrm{Cu^{2+}}$ under formation of ($\mathrm{Cu(CN)_4{}^{2-}}$). The optical density change at 516 nm induced by $\mathrm{[Fe(CN)_6]^{3-}}$ increases linearly with the MPTH concentration as is apparent from inspection of the lower part of Figure 4. This implies that MPTH in the presence of light is stoichiometrically titratable with ferricyanide. From the slope of the straight line one obtains

$$\epsilon_{516}(\mathrm{MPTH^+}) = (9.18 \pm 0.04) \times 10^3\ \mathrm{M^{-1}\,cm^{-1}}$$

With the knowledge of these parameters, it is now possible to determine the quantum yield of $\mathrm{MPTH^+}$ formation in

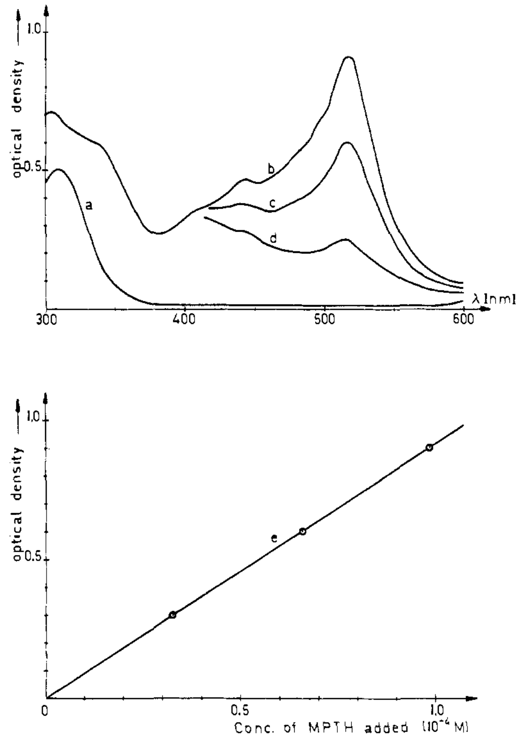

Figure 4. Absorption spectral change induced by addition of $Fe[(CN)_6]^{3-}$ solution to MPTH-$Cu(LS)_2$ micellar solution and determination of the extinction coefficient of MPTH cation. (a) 1×10^{-4} M MPTH in 2×10^{-2} M $Cu(LS)_2$; (b), (c), (d) 0.99×10^{-4}, 0.66×10^{-4}, 0.33×10^{-4} M MPTH in 2×10^{-2} M $Cu(LS)_2$ 5 min after mixing with 2.8×10^{-4} M[$Fe(CN)_6]^{3-}$ solution, respectively; (e) optical density at 516 nm extrapolated to time zero.

$Cu(LS)_2$ micelles. The procedure employed consisted in the solubilization of identical amounts of MPTH in NaLS and $Cu(LS)_2$ micellar solutions. The solutions were exposed to laser radiation of constant intensity and the $MPTH^+$ as well as $MPTH^T$ concentrations produced were determined.

From the ratio of these concentrations, one derives

$$\phi(MPTH^+) = 0.93 \pm 0.04$$

which indicates that electronic excitation of MPTH in $Cu(LS)_2$ aggregates leads to exclusive formation of cation radicals. This astonishing result must be attributed to a pronounced micellar enhancement of the rate of reaction 5. It is of course a consequence of the fact that within such a functional unit of a surfactant aggregate, regions with extremely high local concentrations of Cu^{2+} prevail. (Theoretical estimates[15] predict the counterion concentration in the micellar Stern layer to be between 3 and 6 M.) The significance of this functional organization will become evident also in the subsequent paragraph where the back reaction of Cu^+ and $MPTH^+$ is considered.

B. Electron Transfer from Cu^+ to $MPTH^+$. The reversible nature of photoredox reactions was already referred to above. In the specific case of the Cu^{2+}/MPTH system the back transfer of electron

$$Cu^+ + MPTH^+ \rightarrow Cu^{2+} + MPTH \qquad (8)$$

is associated with a gain in standard free energy of 0.7 eV and can therefore occur spontaneously and at a high rate.

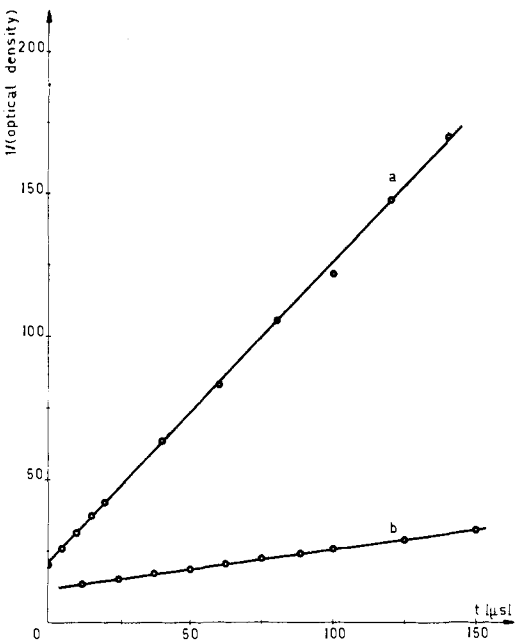

Figure 5. Kinetics of MPTH cation decay in $Cu(LS)_2$ micellar and in ethanol-water (1/2 v/v) mixed solvent solutions. (a) 1×10^{-4} M MPTH in 2×10^{-2} M $Cu(LS)_2$; (b) 3×10^{-4} M MPTH in 5×10^{-3} M $CuSO_4$.

This expectation is confirmed by the experimental results presented in Figure 5. The kinetic analysis was performed by recording the decay of the 516-nm absorption of $MPTH^+$ under conditions of various initial $MPTH^+$ concentrations. The figure shows two representative plots of the reciprocal absorption vs. time observed in homogeneous and micellar solutions, respectively. In both cases, the $MPTH^+$ decay strictly follows a second-order rate law. From the evaluation of these data, one obtains

$$k_8(H_2O/EtOH;\ \text{ionic strength} = 2.0 \times 10^{-2}\ M) = (1.3 \pm 0.1) \times 10^9\ M^{-1}\ s^{-1}$$

$$k_8(Cu(LS)_2) = (9.3 \pm 1) \times 10^9\ M^{-1}\ s^{-1}$$

The observation that reaction 8 in the surfactant system obeys second-order kinetics deserves further attention. It is instructive to consider in this context again Figure 3. The electron transfer from MPTH excited states to Cu^{2+} results in the formation of $Cu^+/MPTH^+$ pairs that are initially associated with their host micelles. If the subsequent back reaction occurred via an intramicellar process, it should obey first-order kinetics since it involves an ensemble of reactant pairs which are associated with isolated surfactant aggregates. The fact that the $MPTH^+$ decay follows a second-order rate law indicates that a different mechanism is operative here. It implies that Cu^+ escapes from its native micelle before the back transfer of an electron can occur. An efficient escape route is provided by the exchange with one of the Cu^{2+} ions present in high local concentration in the Gouy-Chapman layer. By mere electrostatic arguments the latter ion is $\exp(-e\psi/kT)$ more likely to be absorbed on the micellar surface than Cu^+. (With a typical value of $\psi = -79$ mV[16] for the surface potential, this factor becomes as large as 22.) Once in the aqueous bulk phase, Cu^+ will undergo random diffusion until it encounters a micelle with $MPTH^+$ association where back transfer of electron can take place.[24] Such a model is consistent with the second-order character of reaction 8 in $Cu(LS)_2$ solutions.

It remains to explain why in the micellar system the value for k_8 is higher than in homogeneous solution. A decisive factor which has to be taken into consideration is the influence of the ionic strength on the rate of reaction. In the case of a reaction between ions of identical charge, the rate increases with increasing ionic strength owing to electrostatic screening. The anionic head groups into which $MPTH^+$ is embedded exert a pronounced screening effect rendering the approach of Cu^+ ions easier than in homogeneous solutions.

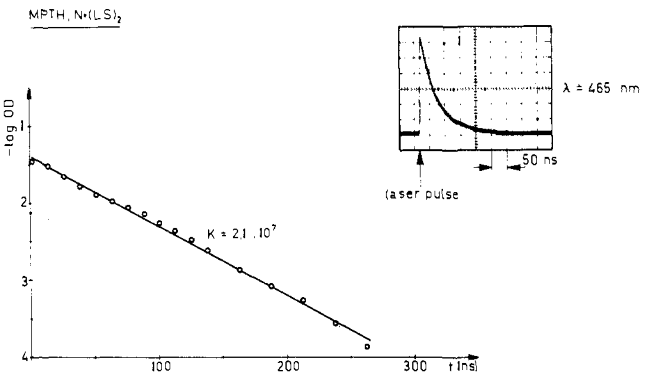

Figure 6. Kinetics of MPTH triplet decay in $Ni(LS)_2$ micellar solution; 1×10^{-4} M MPTH in 2×10^{-2} M $Ni(LS)_2$. Insert: oscilloscope trace showing $MPTH^T$ decay at the same condition as above.

C. MPTH Triplet Deactivation in Micelles with Co^{2+} and Ni^{2+} Counterions. The ions Co^{2+} and Ni^{2+} are heavy atom perturbers which are known to increase the rate of radiationless triplet deactivation for a number of organic molecules.[17] The triplet state of MPTH is also quenched by these ions owing to the reaction

$$MPTH^T + M^{2+} \rightarrow MPTH + M^{2+} \qquad (9)$$

In homogeneous solution, i.e., a solvent mixture of ethanol/water (1/2 v/v), one obtains the rate constants

$$k_9(Ni^{2+}) = (7.7 \pm 0.1) \times 10^6\ M^{-1}\ s^{-1}$$

$$k_9(Co^{2+}) = (1.4 \pm 0.1) \times 10^7\ M^{-1}\ s^{-1}$$

A drastic increase in the quenching rate is observed when MPTH is solubilized in lauryl sulfate micelles containing Ni^{2+} or Co^{2+} counterion atmospheres. Figure 6 shows laser photolysis data obtained with $Ni(LS)_2$ micellar solutions. As shown by the inserted oscillogram, the 465-nm absorption disappears here within a time period of less than 1 μs. No $MPTH^+$ formation was associated with the triplet decay implying that eq 9 correctly describes the pathway of quenching. The deactivation follows first-order kinetics and a semilogarithmic plot of the transient optical density vs. time yields

$$k_9(Ni^{2+}) = (2.1 \pm 0.1) \times 10^7\ s^{-1}$$

$$k_9(Co^{2+}) = (4.2 \pm 0.1) \times 10^7\ s^{-1}$$

The deactivation of $MPTH^T$ in the surfactant systems may be divided into two parts consisting of the diffusion of the excited probe toward the surface followed by the actual quenching event at the site of the ionic perturbers. The question may be asked whether the triplet deactivation time observed in the surfactant systems corresponds to the average time needed for the probe to cross the distance from the interior to the surface region of the micelle. A comparison of the relative quenching efficiency k_9 (Co^{2+}/Ni^{2+}) observed in homogeneous and micellar solution reveals that this ratio is two in both systems. Thus, the different reactivity of Co^{2+} and Ni^{2+} ions toward $MPTH^T$ found in homogeneous solution is maintained in the micelles. This excludes the possibility that $MPTH^T$ in the latter system is quenched on the first encounter with the Ni^{2+} or Co^{2+} counterion atmosphere.[25] Hence, the $MPTH^T$ lifetime cannot be regarded as the mean time for diffusion from the site of solubilization to the surface. Conversely, the very fast nature of the triplet deactivation observed in the $Co(LS)_2$ and $Ni(LS)_2$ systems suggests that the solubilization site of MPTH is located very close to the micelle-water interface where a high local quencher concentration is present.

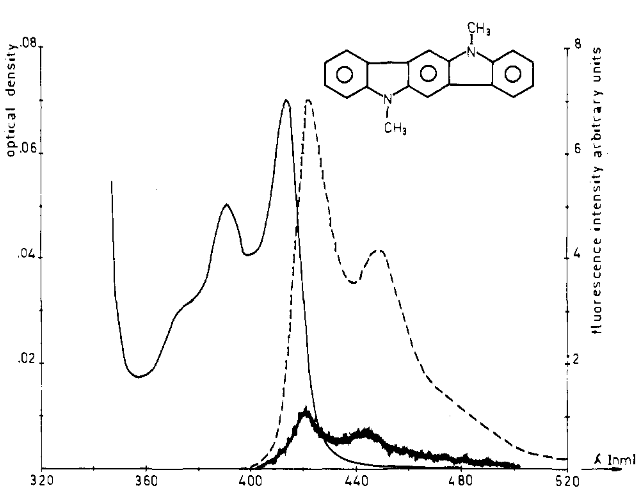

Figure 7. Absorption spectra immediately after the laser pulse. (a) 3.7×10^{-5} M DI in 0.2 M NaLS; (b) 5.1×10^{-5} M DI in 0.1 M $Cu(LS)_2$.

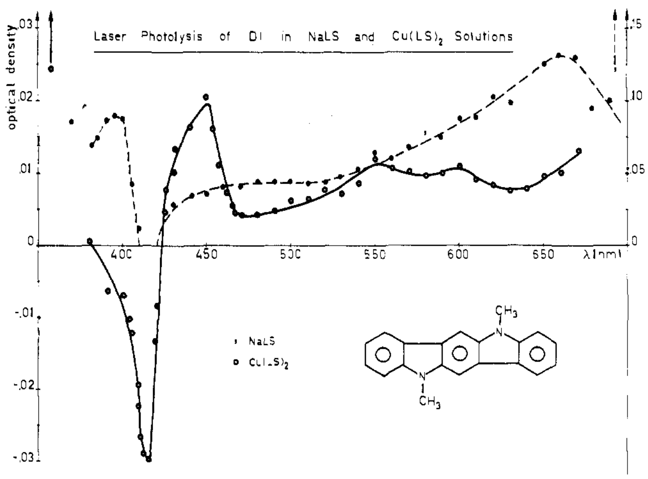

Figure 8. Absorption and fluorescence spectra of DI. (a) 1.2×10^{-5} M DI in ethanol; (b) fluorescence emission of DI in NaLS and $Cu(LS)_2$ solutions, respectively, at the same condition as (a) and (b) in Figure 7.

D. Cu^{2+} Reduction by a Novel Donor System. Although MPTH is an excellent probe to study some principal features of light-induced redox reactions in micellar solutions, its absorption as well as redox behavior makes it less suitable to act as a sensitizer in an energy conversion system. Presently, we are exploring a number of other chromophores whose properties appear more satisfactory from this point of view. A promising candidate which will now be dealt with briefly is *N,N'*-dimethyl-5,11-dihydroindolo[3,2-*b*]carbazole[18] (DI). The absorption spectrum of an aqueous micellar solution of DI is shown in Figure 7. When dissolved in NaLS micelles, DI displays an intense fluorescence whose spectrum is also included in the figure. The fluorescence lifetime τ_0 measured by laser techniques is 144 ns. In competition with the emission, intersystem crossing occurs leading to the formation of triplet states (DI^T). The absorption spectrum of DI^T obtained a few hundred nanoseconds after laser excitation is presented in Figure 8. Thus, the primary photochemical events occurring in this system may be summarized as

$$\begin{tikzcd} \mathrm{DI} \arrow[r, "h\nu"] & \mathrm{DI}\,(S_1) \arrow[r, "\mathrm{isc}"] \arrow[d, "h\nu'"] & \mathrm{DI}^T \arrow[dl] \\ & \mathrm{DI} & \end{tikzcd} \qquad (10)$$

A remarkable change is introduced in these photoevents when Na^+ ions are replaced by a Cu^{2+} counterion atmosphere. Under these conditions, the fluorescence of DI is almost entirely quenched (Figure 7). Moreover, the transient absorption spectra obtained after the laser pulse has changed as shown in Figure 8. The new spectra is identical with that published for DI^+ cation radicals.[19] This unequivocally shows that the excited singlet state of DI is quenched during the laser pulse under formation of cation radicals:

$$DI + Cu^{2+} \xrightarrow{h\nu} DI^+ + Cu^+ \qquad (11)$$

Although DI is a much weaker donor than MPTH ($E_0\,(D^+/D) = +1.1$ V[19]), the electron transfer reaction occurs with a yield of 100% and at an extremely rapid rate. From the ratio of the fluorescence intensity $I_0/I = 113$ observed in NaLS and $Cu(LS)_2$ solutions, respectively, and $\tau_0 = 144$ ns, one derives for the lifetime of $DI(S_1)$ in the $Cu(LS)_2$ aggregates the value $\tau = 1.2 \times 10^{-9}$ s.

It is instructive to consider the distance which the excited state can cross during this interval. The expression for the mean square displacement obtained from diffusion theory is

$$\sqrt{\bar{x}^2} = \frac{kT\tau}{3\pi\eta r} \qquad (12)$$

If we insert in this equation a value for the microviscosity of $\eta = 30$ cP,[20] an effective radius of DI of 3 Å and the observed fluorescence liftime of 1.2 ns, we obtain $\sqrt{\bar{x}^2} \simeq 2$ Å. Therefore, it must be concluded that during the excited state lifetime DI virtually does not change its position in the micelle. In other words, the system is static in this time domain. The oxidative quenching exerted by Cu^{2+} ions must then be interpreted as a static effect. The question remains open whether this is caused by the fact that DI is located in the vicinity of the micellar Stern layer where a high local Cu^{2+} ion concentration prevails or, alternatively, whether the electron can be transferred at a high rate over distances comparable to the micellar radius. The reaction radius for an electron transfer process can exceed 10 Å and thus be much larger than a collisional cross section.[21] These effects have been interpreted in terms of a tunneling transition of the electron.[1c,7a,21,22]

Similar to the results obtained with MPTH in $Cu(LS)_2$ micellar solution, the back transfer of electrons from Cu^+ to DI^+ ion, i.e., the reverse of reaction 11, was found to obey second-order kinetics. The rate constant obtained for this process from the kinetic evaluation is $k = (1.85 \pm 0.18) \times 10^9$ $M^{-1}\,s^{-1}$.

Conclusions

Two important cooperative effects have been discovered in the course of this investigation. The first concerns the rate of the photoinduced reduction of bivalent metal ions by organic donor species. This reaction was accelerated drastically by introducing the metal ion as the micellar counterion. As a consequence, the electron transfer can occur already from the excited singlet state of the donor instead of the triplet state. Thus, a larger fraction of the light energy initially absorbed becomes available for the redox process.

The second cooperative effect exhibited by the functional micellar unit concerns the back transfer from the reduced metal ion to the donor cation. In the case of a bivalent metal ion surfactant, this intramicellar reaction is considerably slower than the exchange with counterions present in the Gouy–Chapman layer. This allows the reduced metal ion to escape from its native micelle into the bulk solution. There, it may be used for a redox reaction with a negative ion or zwitterion. The advantage of this second redox process is that the reduced metal ion is converted into a reduced negative ion. The back reaction of the latter with the donor cation radical is prevented by the micellar surface potential. Hence, such a system is successful in storing a large fraction of the light energy originally converted into chemical energy during the photoredox process.

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(25) It is assumed that the local Ni^{2+} and Co^{2+} concentrations in the surface region are the same.