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Drastic Fluorescence Enhancement and Photochemical Stabilization of Cyanine Dyes through Micellar Systems

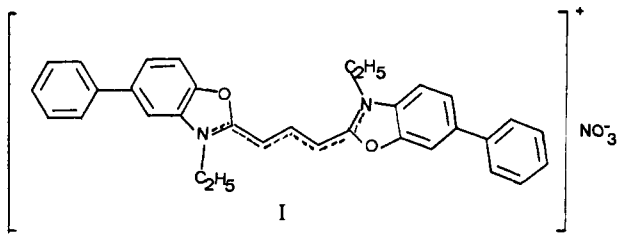
Sir:

Cyanine dyes play an important role as sensitizers in photographic processes.[1] Also, they have been widely employed as model chromophores in monolayer assemblies.[2] A common behavior found with this class of molecules is their photochemical instability. Conformational changes occurring after excitation along the polymethine chain was found to precede the degradation process.[3] These structural fluctuations account also for the relatively low fluorescence yield observed for a variety of cyanine dyes. In fact, by decreasing the flexibility of these molecules through chemical rigidization, high fluorescence yields and photostability may be obtained.[4]

In the present communication, micellar effects on the fluorescence behavior and photostability of the cyanine dye I will be examined. It will be shown that, by suitable choice of the micellar system, drastic enhancements of the emission intensity and stability of this dye can be achieved.

Fluorescence spectra were run on a Hitachi Perkin-Elmer MPF-44A spectrofluorimeter which is equipped with a corrected spectra unit. The instrument displays true fluorescence spectra, the measured quantity being photon flux per unit wavelength interval. The emission quantum yields were obtained by comparison with the standard quinine sulfate. Emission lifetimes were obtained using PRA single-photon counter.

The cyanine dye I was of high purity (elemental analysis,



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thin-layer chromatography). Sodium lauryl sulfate (NaLS), Merck, "for tenside investigation", was purified by repeated recrystallization from diethyl ether and water. The purified product was used to synthesize magnesium lauryl sulfate [$Mg(LS)_2$] and cadmium lauryl sulfate [$Cd(LS)_2$], whereby a previously described procedure[5] was followed. Deionized water was distilled from permanganate and subsequently twice from a quartz still.

Figure 1 displays the absorption and fluorescence spectrum of the cyanine dye I (10^{-6} M) in water and aqueous micellar

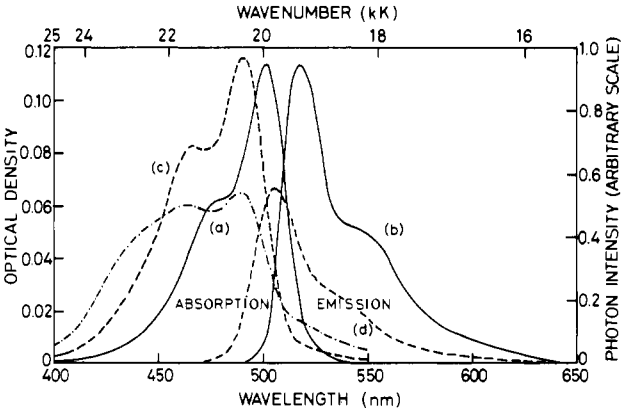

Figure 1. (a) Absorption spectrum of a solution of 10^{-6} M cyanine I in 10^{-2} M aqueous NaLS and (b) fluorescence spectrum of the same solution at an exciting wavelength of 480 nm. (c) Absorption spectrum of a 10^{-6} M cyanine I in water, and (d) fluorescence spectrum of the same at 480 nm excitation (scale is ten times the scale of b). (e) Absorption spectrum of a solution of 10^{-6} M cyanine I in water after 12 h.

solution. The optical phenomena in water were found to be time dependent. With freshly prepared solutions the spectra indicated by the dashed lines c and d were obtained. The absorption curve displays here a maximum at 484 and a shoulder at 465 nm, while the emission peak is located at 506 nm. The intensity of the principal absorption decreases with time, a broad shoulder appearing at ~440 nm. Concomitantly, the intensity of the fluorescence decreases. These observations are attributed to the effect of dye aggregation, the absorptions at 484, 465, and 440 nm being assigned to monomer, dimer, and H aggregates, respectively.

Addition of micellar NaLS to the aqueous solution induces drastic changes in the behavior of the cyanine dye. Time-dependent phenomena are no longer observed, the absorption and emission curves indicated by the solid lines in Figure 1 remaining unchanged over a period of days or weeks. The absorption band in the micellar solution shows essentially the same characteristic as the monomer dye, as observed in methanol. This is indicative of no chromophore aggregation in the former medium. The emission maximum is located at 517 nm which is red shifted by 11 nm with respect to water and 7 nm with respect to methanol. From these observations it may be inferred that the cyanine is predominantly associated with the surfactant aggregates. Attractive electrostatic and hydrophobic interactions occurring between the dye and the anionic micelle make such an association particularly favorable.

Apart from preventing dye association, the micellar aggregates also strongly enhance the fluorescence emission of the cyanine dye. Emission quantum yields obtained in several micellar and homogeneous phases are listed in Table I. Comparison of the ϕ_F values in NaLS solution with those in methanol and water indicates a fivefold enhancement in the former case and at least a fifteenfold one in the latter. Parallel with the augmentation of the quantum yield goes an increase in the excited-state lifetime. τ_F values in NaLS and methanol are 1.2 ± 0.2 and 0.5 ± 0.5 ns as determined by single-photon counting technique. This indicates that the decreased quantum yield in methanol is caused by an increase in the rate of radiationless relaxation processes and not to a change of the radiative rate constant.

This inhibition of the radiationless decay by the micellar aggregates may be rationalized in terms of a rigidization of the cyanine dye by the local environment encountered in the micelle. Compound I has hydrophobic and polar groups and hence is expected to be solubilized in the palisade layer of the aggregate. A common behavior found with such a type of molecules is that the polar groups tend to be directed toward the

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Table I. Fluorescence Parameters for the Cyanine Dye I in Methanol and Surfactant Micelles

medium	ϕ_F	λ_{max}, nm	η^{25}, cP	ϵ^a
methanol	0.09	510	0.547	32.6
NaLS-water	0.45	517	±30	
$Mg(LS)_2$-water	0.54	518		
$Cd(LS)_2$-water	~0.7	518		
water	~0.03	506	0.89	78.5
glycerol	0.82	514	954	42.5

[a] Dielectric constant.

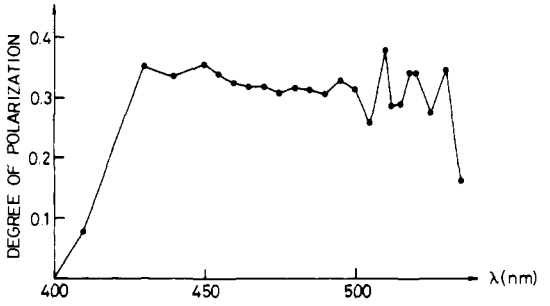

Figure 2. Polarization spectrum of a solution of 10^{-6} M cyanine in 10^{-2} M aqueous NaLS.

surface region, the rest protruding into the micellar interior. Internal molecular motion of the cyanine will be controlled by the local microviscosity which is significantly higher in the surfactant assembly than in methanol.[6] Thus, conformational changes along the polymethine chain leading to radiationless deactivation are retarded and the fluorescence quantum yield is increased. This is corroborated by the high ϕ_F (= 0.82) found for I in a high viscosity medium like glycerol (η^{25} = 954 cP). Furthermore, the nature of the counterion affects the fluorescence behavior (Table I). The replacement of the sodium counterion by either Mg^{2+} or Cd^{2+} ions induces a further increase in the quantum yield. The effect of Mg^{2+} or Cd^{2+} is to contract adjacent head groups of the monomer surfactant units which leads to further immobilization of the dye by an effective increase in viscosity.[6]

A direct means to investigate the rotational motion of excited states is provided by fluorescence polarization measurements. The degree of polarization is defined as[7]

$$p = (I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp}) \quad (1)$$

where $I_{\parallel}$ and $I_{\perp}$ refer to the emission intensity measured with parallel and crossed polarizers, respectively, and corrected for instrumental artifacts. Figure 2 shows a polarization spectrum of I in NaLS micellar solution. The value of p varies between 0.3 and 0.4 for most of the excitation wavelengths in the first absorption band. The degree of polarization is related to the rotational correlation time τ_R. If the absorption and emission oscillators are parallel, as is the case when the dye is excited in the last absorption band, then[7]

$$\tau_R = 6\tau_F[(1/p_0 - 1/3)/(1/p - 1/p_0)] \quad (2)$$

where τ_F is the fluorescence lifetime and p_0 the degree of polarization measured in an extremely viscous medium. The theoretical upper limit for p_0 is 0.5, and this was indeed observed for I in glycerol. The values obtained in NaLS and methanolic solution are 0.31 and 0.25, respectively. Inserting in eq 2 τ_F(NaLS) = 1.2 and τ_F(MeOH) = 0.24 ns, one calculates τ_R(NaLS) = 1.0×10^{-8} and τ_R(MeOH) = 1.2×10^{-9} s indicating that the rate of rotation is almost one order of magnitude slower in the micellar than in the alcoholic solution. It is concluded that the lifetime of the excited cyanine as well as the fluorescence yield are unequivocally related to the *viscosity* and *not the polarity* present in the local environment of the cyanine dye.

Further studies showed that the nonradiative deactivation of the cyanine S_1 state, which is so effectively blocked in the micellar medium, corresponds in fact to those processes leading to the destruction of the dye. The enhancement of cyanine fluorescence through aqueous micellar systems goes parallel with a remarkable increase of the photostability of the dye. Thus, while irradiation of I in aqueous solution with a 450-W Xe lamp through a 400-nm cut-off filter results in a complete depletion of the dye within 0.5 h, no fading at all could be detected after 24-h irradiation in NaLS micellar solution. Moreover, the micellar cyanine solution is also resistant toward high-intensity laser irradiation. After exposure of such a solution to 50–100 pulses of a 347.1-nm ruby laser (pulse width 20 ns, energy per pulse 250 mJ), no significant alterations of the absorption spectrum could be observed. From the combined effects of fluorescence enhancement and prevention of dye fading exerted by the micellar aggregates, a variety of practical applications may be envisaged. For example, the use of these systems in photographic processes or as dye laser components appears feasible.

The above-described effects have been qualitatively confirmed with a variety of cyanine dyes and merocyanines containing different heterocycles. Surfactants, other than NaLS, $Mg(LS)_2$, and $Cd(LS)_2$, have also been successfully used.

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Models of Siroheme and Sirohydrochlorin. π Cation Radicals of Iron(II) Isobacteriochlorin

Sir:

We here report the preparation of the first synthetic iron complex of the isobacteriochlorin family and demonstrate the existence of π cation radicals of this heme.

The presence of an iron-isobacteriochlorin prosthetic group (siroheme) in two redox enzymes which catalyze the six-electron reductions of sulfite to sulfide (sulfite reductase) and of nitrite to ammonia (nitrite reductase) has recently been elucidated in conjunction with related vitamin B_{12} biosynthetic studies.[2-4] Siroheme has been shown to be the site of interaction between substrate and the electron transport chain, but the mechanism by which siroheme plays this unique role in these multielectron redox enzymes is unknown. Because of the

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