

# Drastic Photo-stabilization of 4,4'-Diaminostilbene 2,2'-Disulfonates in Micellar Solutions

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Drastic photo-stabilization of 4,4'-diaminostilbene 2,2'-disulfonate fluorescent dyes, DAS-1, DAS-2, and DAS-3, was found in the micellar CPC solution over the cmc. However, the addition of CTAB, SDS, and B-35 to the aqueous solutions of the dyes had no effect on stabilization. The results were interpreted in terms of highly efficient energy transfer *via* exciplex from the excited fluorescent dye molecule to the pyridinium ion moiety in CPC.

## Introduction

Diaminostilbene sulfonate dyes (DAS) play an important role as fluorescent whitening agents in industrial finishing processes. A common behavior found with this class of molecules is their photochemical instability. *Trans-cis* isomerization<sup>1-4</sup> around carbon-carbon double bond during irradiation was found to be main route for disappearance of the fluorescence in addition to oxidative cleavage reactions<sup>4</sup>, or possible dimerizations to cyclobutane occurring at higher concentrations of the dyes<sup>5</sup>. In particular, photo-equilibrium of DAS lies to *cis*-form over 95%<sup>2</sup>. However, there seems no report about prevention of the undesirable photo-reaction as far as we know, despite of its intrinsic interest and practical importance.

In the present report, micellar effect on the photo-stabilization of some 4,4'-diaminostilbene 2,2'-disulfonates, DAS-1, DAS-2, and DAS-3 will be examined. It will be described that drastic photo-stabilization of the fluorescent dyes can be achieved by suitable choice of the micellar systems.

## Experimentals

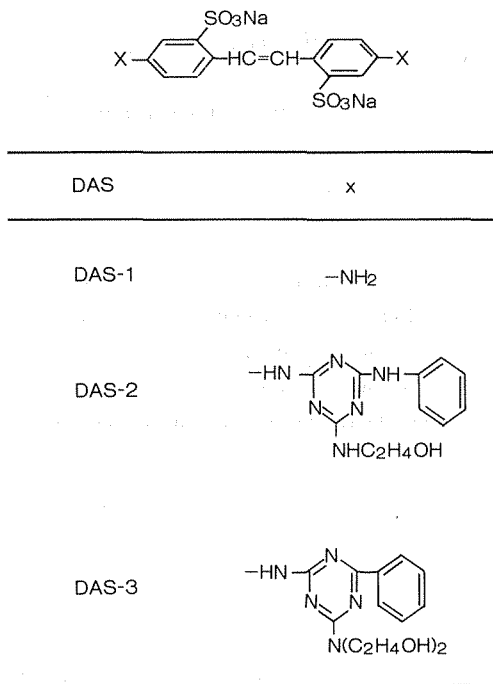
*Materials.* The DAS-1, DAS-2, and DAS-3 were purified according to the previous report<sup>6</sup>. The

surfactants used here were the following; hexadecylpyridinium chloride (CPC) and hexadecyltrimethylammonium bromide (CTAB) as cationic surfactants, sodium dodecyl sulfate (SDS) and sodium dodecylbenzene sulfonate (SBS) as anionic surfactants, and poly(oxyethylene) (23)-1-dodecanol (B-35) as a non-ionic surfactant, whereby a previously described procedure for purifications<sup>6</sup> was followed.

*Irradiation of Dye Solution.* Irradiation of sample solutions of the fluorescent dyes ( $5 \times 10^{-5}$  mol·dm<sup>-3</sup>) in a 1 cm-length of quartz cell from two conventional fluorescent lamps (18W. National Electric Co.) as a light source at a distance of 15 cm was carried out at 25°C air-conditioned. The absorption spectra were recorded on a Shimadzu UV-240 spectrometer at appropriate intervals. All measurements and procedures were performed in the dark.

*Recovery of Fluorescence from CPC-DAS Solution.* To DAS-1 solution ( $10^{-5}$  mol·dm<sup>-3</sup>) containing CPC ( $5 \times 10^{-3}$  mol·dm<sup>-3</sup>) were added various concentrations ( $0-10^{-2}$  mol·dm<sup>-3</sup>) of SBS or freshly prepared ammonium cobalt thiocyanate<sup>7</sup>. The flocculated mixtures were stirred and filtered when necessary. The fluorescent intensity of the filtrate was measured at excitation maximum 340 nm and emission maximum 442 nm. Fluorescent spectra were obtained by a Hitachi 650-10S fluorescent spectrometer.

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### Results and Discussion

Figure 1 displays the absorption spectrum of *trans*-DAS-3 during irradiation in water and aqueous CPC solution. The optical phenomena in water were found to be as time-dependent due to *trans*-*cis* isomerization as reported in the literatures<sup>1-4</sup>. However, addition of micellar CPC at concentrations of  $10^{-4}$  mol · dm<sup>-3</sup> (Fig. 1(b)) and  $10^{-2}$  mol dm<sup>-3</sup> (Fig. 1(c)) over the cmc to the aqueous solution induces drastic changes in the photochemical behavior of the fluorescent dyes. As seen in Fig. 1(c), time-dependent phenomena as represented in Fig. 1(a) are no longer observed, the absorption curve remaining unchanged by irradiation over a period of days. The absorption band in the micellar solution shows essentially the same characteristic as in water, except for the strong absorption observed at 270 nm due to pyridinium salt. The drastic photo-stabilization in the CPC solution was observed quite similarly when the other fluorescent

dyes (DAS-1 and DAS-2) were employed. However, other surfactant micelles, CTAB, SDS, and B-35, caused no stabilization.

What is the cause of photo-stabilization by CPC? DAS has hydrophobic and polar groups and hence is expected to be solubilized in the Stern layer of the cationic micelle. A common behavior found with such a type of molecule is that the polar groups tend to be directed toward the micelle surface region, the rest protruding into micellar interior<sup>8</sup>. However, the findings that cationic CTAB, anionic SDS, and non-ionic B-35 micelles are never attributable to the photo-stabilization of the dyes employed, indicate that the drastic photo-stabilization in the CPC micelle as described above can be explained only neither in terms of ionic characters of the micelles nor of changes in the surrounding polarity due to solubilization into the micelles. Presumably, highly efficient energy transfer from the electron-rich excited dye molecule to the electron-poor pyridinium ion should be responsible for the photo-stability in the CPC micellar solution, which can be closely connected with the disappearance of the fluorescence as reported previously<sup>6</sup>.

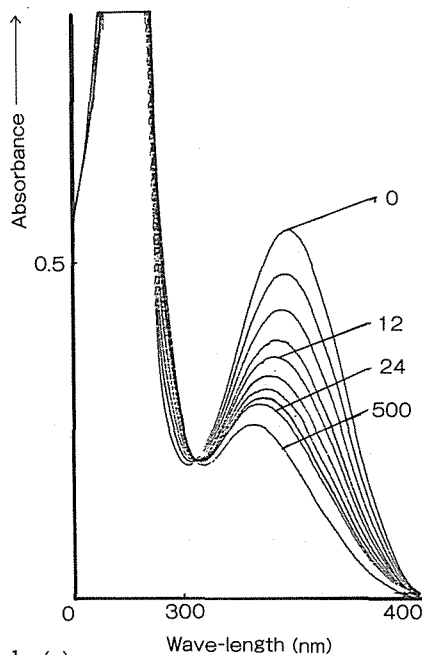


Fig. 1 (a)

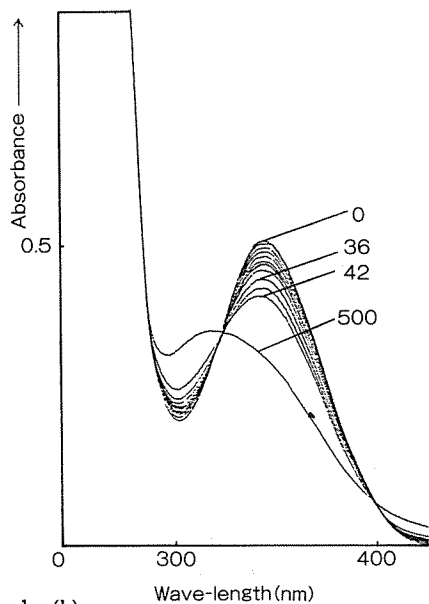


Fig. 1 (b)

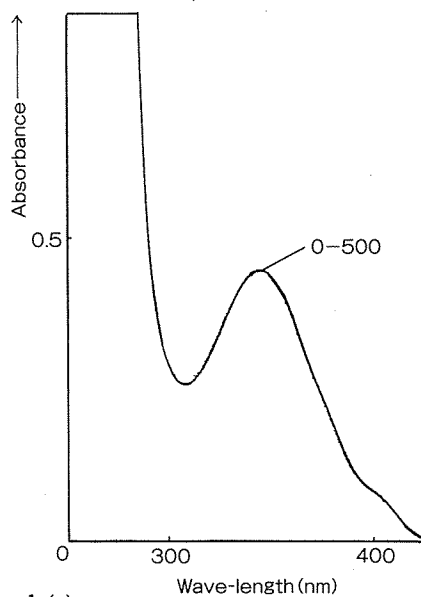


Fig. 1 (c)

Fig. 1 Photochemical Behavior of DAS-3 on Absorption Spectra. Numerals denote irradiation Time (min).

(a) in the absence of surfactant

(b) in the presence of CPC ( $1 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ )

(c) in the presence of CPC ( $1 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$ )

Furthermore, the measurements of fluorescent lifetime of DAS-1 in CPC solution showed two types of excited singlet states, intrinsic singlet state and long-lived singlet state. The latter is probably due to an exciplex of DAS-CPC. These data of fluorescent lifetime will be discussed in detail in the following paper. Furthermore, inevitable proximity of the dye and the pyridinium salt at their counterionic moieties in the CPC micelles and resultant profitable overlapping of  $\pi$ -electron of both relating species should be favorable, in particular, for the energy transfer process<sup>9</sup>.

Although it was found that CPC had a great ability to prevent the isomerization of DAS as described above, the addition of CPC caused totally quenching of their fluorescence<sup>6</sup>, unfortunately. Therefore, for the purpose of practical use the removal of CPC from the solution is essential. Some attempts to remove CPC as precipitates were

carried out; the gradual addition of SBS or ammonium cobalt thiocyanate into the CPC-DAS solution. These results were shown in Fig 2. As expected, DAS completely regained original fluorescence intensity from non-fluorescence properties.

Further investigations on photo-stabilization of fluorescent whitening agents are in progress.

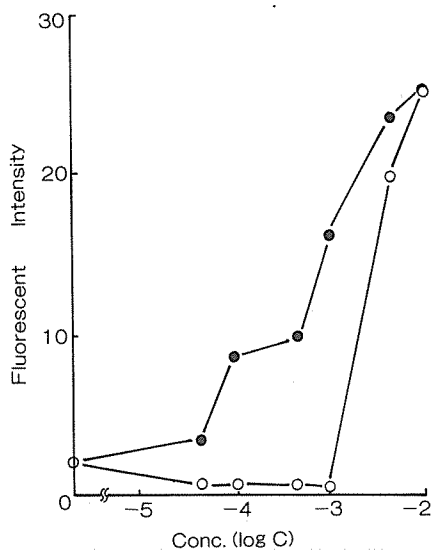


Fig. 2 Recovery of fluorescence of DAS-1 by precipitation agents.

○; SBS ●; (NH<sub>4</sub>)<sub>2</sub> [Co(SCN)<sub>6</sub>]

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(1989年9月21日受理)