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LETTERS

Photophysical Properties of 3,3′-Diethylthiacarbocyanine Iodide in Binary Mixtures

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The photophysics of 3,3′-diethylthiacarbocyanine iodide (DTCI) in liquid mixtures of dimethyl sulfoxide (DMSO) with toluene was studied by means of steady-state and time-resolved optical spectroscopy. By variation of the diminution of the volume fraction of DMSO, the solvation shell around a DTCI species significantly decreases the quantum efficiency of its photoisomerization. The character of the fluorescence decay, observed upon excitation at 570 nm, also changes. For DMSO volume fractions larger than 14 vol %, a single-exponential function with a lifetime of about 300 ps is found; in the range from 14−8 vol % of DMSO, biexponential functions with time components of 200 and 500 ps are observed, and when the DMSO volume fraction decreases from 8 to 1.6 vol %, the fluorescence decay is again single exponential (lifetimes 500−700 ps). These findings will be explained in terms of the Rullière model by assuming a fast equilibrium between electronically excited trans and cis isomers of DTCI.

Introduction

For many years, considerable effort has been undertaken for the study of the photophysical properties of cyanine dyes. This interest was mainly provoked by many uses of these compounds in technology, e.g., photography industry, laser technology, etc. (for a recent review, see ref 1). Nevertheless, despite the numerous publications on the subject, the number of studies of the influence of preferential solvation on relaxation of the excited cyanine dye in binary mixtures is actually small.[2]

In binary mixtures, a solvent composition in the near vicinity of a solute molecule can differ from that in the bulk provided the solute interacts differently with each of the solvent components. The production of such microheterogeneity is called preferential solvation.[3] It is well-known that preferential solvation might strongly affect physicochemical processes involving charged particles or species with a large dipolar moment, e.g., ions or ion pairs. Because cyanine dyes in solution usually exist in such forms, one might expect that preferential solvation in binary mixtures could affect photophysical behavior of dyes, especially in the case of nonpolar-component-rich mixtures. It is worth noting that the use of binary mixtures for enhancement solubility of dyes is a widespread practice but a possible microheterogeneity of solution is usually not taken into account.

The purpose of this work is to demonstrate that preferential solvation in binary mixtures actually can influence relaxation mechanisms of excited cyanine dyes. As a typical example, the dye 3,3′-diethylthiacarbocyanine iodide (DTCI), whose chemical structure is shown in Figure 1, was used in toluene/DMSO mixtures, i.e., the binary system that had already been studied recently by means of optical spectroscopy.[4−6]

Experimental Section

The used solvents of spectroscopic grade (Uvasol, Merk) were toluene, whose dielectric constant was $\epsilon = 2.4$ and viscosity was $\eta = 0.55$ cP, and dimethyl sulfoxide (DMSO), with $\epsilon =$

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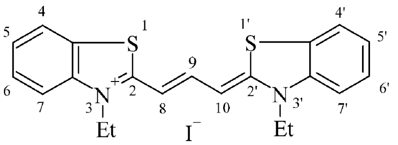

Figure 1. Structural formula of 3,3′-diethylthiacarbocyanine iodide (DTCI).

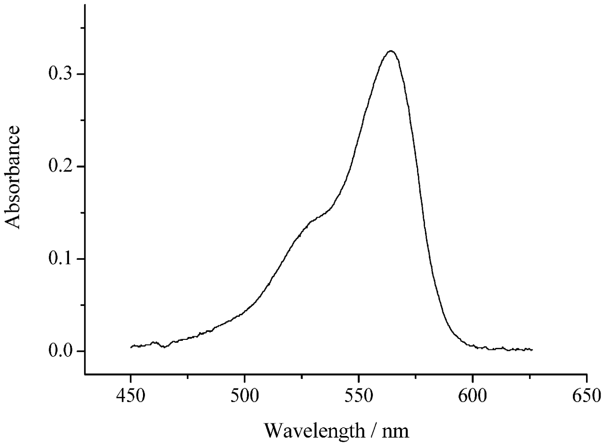

Figure 2. Absorption spectra of DTCI solution in neat DMSO.

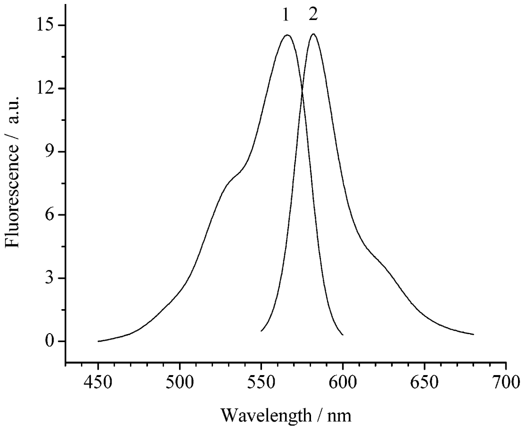

Figure 3. Excitation (1) and fluorescence (2) spectra of DTCI solution in neat DMSO.

49, $\eta = 1.98$ cP.[7] The dye, 3,3′-diethylthiacarbocyanine iodide, was purchased from Fluka and used without further purification. Steady-state fluorescence emission and excitation spectra were recorded by a Fluorolog-3 spectrofluorometer (Jobin Yvon-Spex, France) and corrected according to manufactor specifications. Absorption spectra were measured by a Cary 5E spectrophotometer. The conventional time-correlated single-photon counting technique was also used for lifetime measurements by a Fluotime 200 fluorometer comprising a PDL800-B unit with a PLS-600 diode head (PicoQuant, Germany) as a source of exciting light. Fitting of data obtained was made with a FluoFit software (PicoQuant). The concentration of the dye was about 2×10^{-6} M. All measurements were carried out at room temperature with freshly prepared samples.

Results and Discussion

When the DMSO volume fraction diminishes in toluene/DMSO mixtures down to 1.6 vol %, the absorption peak of DTCI solution (at 564 nm in neat DMSO, see Figure 2) slightly (~15 nm) shifts to the longer wavelengths and the fluorescence peak (at 581 nm in neat DMSO, see Figure 3) has a shift of about 10 nm to longer wavelengths. As seen in Figure 3, the fluorescence−excitation spectrum, obtained under the same conditions, seems fairly close to a corresponding absorption spectrum (Figure 2). However, one can compare the absorption and fluorescence−excitation spectra in a more quantitative fashion, using the concept generally outlined by Parker.[8]

The fluorescence−excitation spectrum is defined as the dependence of fluorescence intensity I, detected at a given wavelength, upon wavelengths of exciting light λ. In dilute solutions it is

$$I \approx 2.3\varphi I_0[\epsilon(\lambda)cl] \qquad (1)$$

Here, φ is the fluorescence quantum yield independent of excitation wavelengths, I_0 is the intensity of exciting light, $\epsilon(\lambda)$ is the molar extinction coefficient, c is the fluorofore concentration and l is the optical depth. If I_0 is corrected to its dependence upon exciting light wavelengths and nonradiative processes are negligible, the fluorescence−excitation spectrum is a replica of the absorption spectrum.[8] By definition, the latter is $\mathrm{Abs}(\lambda) \equiv \epsilon(\lambda)cl$, the optical density or absorbance that is directly recorded by a spectrophotometer. In other words, a properly scaling excitation spectra should coincide with the corresponding absorption spectrum, provided nonradiative processes are negligible. Therefore, deviation from the absorption profile indicates the existence of a nonradiative channel of relaxation.

By taking into account nonradiative processes in a more precise manner, and rearranging the extinction coefficient as follows

$$\epsilon(\lambda) = \epsilon^{\mathrm{f}}(\lambda) + \epsilon^{\mathrm{nr}}(\lambda) \qquad (2)$$

where $\epsilon^{\mathrm{f}}(\lambda)$ is the cross section of the fluorescent excited state and $\epsilon^{\mathrm{nr}}(\lambda)$ is the cross section of the excited state, which relaxes nonradiatively, we have by definition

$$\mathrm{Abs}(\lambda) = [\epsilon^{\mathrm{f}}(\lambda) + \epsilon^{\mathrm{nr}}(\lambda)]cl \qquad (3)$$

and

$$I \approx 2.3\varphi I_0[\epsilon^{\mathrm{f}}(\lambda)]cl \qquad (4)$$

Further, subtracting from eq 3 a properly scaled eq 4, one can obtain

$$\mathrm{Act}(\lambda) \equiv \epsilon^{\mathrm{nr}}(\lambda)cl \qquad (5)$$

which is a measure of the efficiency of nonradiative processes as a function of excitation wavelengths and can be called the action spectrum of nonradiative relaxation. Therefore, the total optical density can be expanded into a fluorescent term and a nonradiative term. In practice, to do so, one should find a scaling factor independent of wavelengths so that the excitation-spectrum profile will be as close as possible to the absorption-spectrum curve but *never exceed the latter* (just because $\epsilon^{\mathrm{nr}}(\lambda) \geq 0$ for any wavelengths). Assuming the Rullière model for the special case of cyanine-dye isomerization (see below), $\epsilon^{\mathrm{nr}}(\lambda) \ll \epsilon^{\mathrm{f}}(\lambda)$ for the long wavelength tail of the absorption band of cyanine dyes.

Figure 4 shows the action spectra as obtained by the above-defined procedure for various toluene/DMSO mixtures. The radiationless quantum efficiency q can be estimated from these spectra as a ratio of the area under the action-spectrum curves to that of the corresponding absorption spectra (see Table 1). As the volume fraction of DMSO diminishes from 14 to 1.6 vol %, it monotonically decreases from $q \approx 0.33$ to $q = 0.06$.

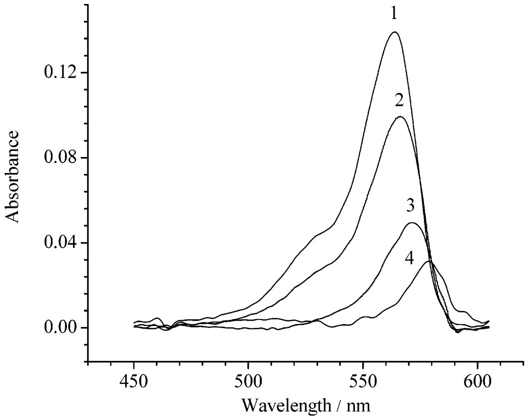

Figure 4. Action spectra of DTCI solutions in toluene/DMSO mixtures: neat DMSO (1), 12 vol % DMSO (2), 8 vol % DMSO (3), 1.6 vol % DMSO (4).

TABLE 1: Nonradiative Quantum Efficiency *q* for Various Volume Fractions of DMSO/Toluene Mixtures

DMSO, vol %	q
100	0.34
20	0.33
14	0.33
12	0.25
8	0.10
3.2	0.06
1.6	0.06

TABLE 2: Fluorescence Lifetimes τ_i for Various Volume Fractions of DMSO in Mixtures with Toluene (Excitation Wavelength 570 nm; Emission Recorded at 585 nm)

DMSO, vol %	τ_1, ps	τ_2, ps
100	299	
20	295	
17	335	
14	284	452
12	236	419
8	178	497
6	507	
3.2	629	
1.6	684	

The time-resolved fluorescence measurements also confirm that preferential solvation affects the photophysical behavior of carbocyanine dyes. It has been found that upon excitation in a 570 nm spectral band, the fluorescence-decay dynamics recorded at 585 nm depends on the mixture composition. For neat DMSO and polar mixtures, the decay can be fitted to a single exponent with a lifetime component of about 300 ps; for toluene-rich mixtures (volume fraction of DMSO is less than 6 vol %), a longer component from 500 to 700 ps is found. Between (from 6 to about 14 vol % of DMSO), fluorescence decays fit well to a biexponential function with components of about 200 and 500 ps (see Table 2).

We will rationalize the above findings on the basis of the Rullière scheme,[9] which is simple and physically meaningful and usually in good agreement with experimental and theoretical studies on photoisomerization[10−13] (see Figure 5). In this model, the reaction coordinate is the twisting angle. It is assumed that in the S_0 ground state there is an energy barrier at $\theta = 90^\circ$ (assuming about 1 eV for the transition from the trans to cis form). This maximum corresponds to a minimum in the S_1, the intermediate twisted state, which can be reached via a small barrier (less than 0.2 eV in MeOH[10]) upon rotation of a bond of the polymethine chain after exciting from the S_0. The twisted state can nonradiatively decay rapidly (the dashed arrow) to the ground state, producing either the initial trans form or an unstable cis isomer. The lifetime of the latter with respect to the transition to the trans state is on the microsecond time scale or even slower.[11]

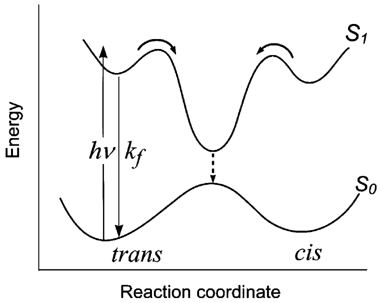

Figure 5. Schematic energy diagrams describing cyanine-dye isomerization (explanation, see text).

As the binary-mixture composition varies, the solvation shell (i.e., the microcluster) around DTCI molecules changes. In toluene-rich mixtures, such a DMSO microcluster becomes smaller.[5,6] The interface tension pressure inside it increases and the viscosity of the dye's microenvironment might also increase. This results in diminishing the probability of trans−cis isomerization. In terms of the Rullière model, preferential solvation affects the profile of the potential energy hypersurface (PES) of the excited singlet state, as can be indicated by the variation of the quantum efficiency q and the fluorescence lifetimes.

Because k_f, the fluorescence rate constant, is about 3×10^8 s^{-1} in MeOH,[11] in the framework of the Rullière model the measured fluorescence lifetime is determined by isomerization, which is known to be the main channel of nonradiative relaxation of cyanine-dye solution.[10] Under the experimental conditions used, the excitation is so weak that a steady-state population of the cis form state is absolutely negligible. With this in mind, one can see that the Rullière model readily predicts a single-exponential fluorescence decay, which is determined by the barrier separating the excited trans form from the funnel. This occurs for small and large volume fractions of DMSO (see Table 2).

However, the existence of two time components found for intermediate volume fractions of DMSO indicates that more than one electronically excited conformer of DTCI is involved in the relaxation processes. The cis side of the S_1 potential well (Figure 5) might be populated via excited vibrational states from the Franck−Condon region in a barrierless fashion. So a very rapid equilibrium (less than 1 ps) can be established between trans and cis isomers that further relax through the funnel of the dye PES. Because the DTCI cis isomer is supposed to have negligible quantum yield of fluorescence at room temperature,[10] we observed emission only from the trans isomer excited state. The cis isomer relaxes via its own barriers, which might be different from that of trans isomer,[10] so that the second long component in the fluorescence decays appears. It is worth noting that Sahyan and Blair[14] have recently considered the necessity of introducing a rapid equilibrium between isomers of cyanine dyes.

In conclusion, preferential solvation of thiacarbocyanine dyes in binary mixtures, whose components strongly differ in dielectric properties, could affect the potential energy hypersurface of singlet excited states. It leads to a significant diminution of isomerization efficiency in mixtures with a small fraction of the polar component and to changes in fluorescence dynamics.

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