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PHOTONICS

Triplet States of 3,3'-Alkylsubstituted Thiacarbocyanine Dimers and Dimeric Complexes with Cucurbit[8]uril in Water

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Abstract—Alkylsubstituted thiacarbocyanines (3,3'-diethylthiacarbocyanine, **D1**, and 3,3'-disulfopropylthiacarbocyanine, **D2**), existing in water as monomers and dimers, manifest the ability to transition to the triplet state. The spectrum of triplet-triplet (T–T) absorption of the D2 dimers is shifted in the range higher than 590 nm by 20 nm to the red in comparison with the T–T spectrum of monomers. The D1 dimers in the presence of cucurbit[8]uril form a dimeric complex with two bands in the differential absorption spectrum. The band at 550 nm belongs to the triplet-triplet absorption of the dimeric complexes, and the band in the range of 620–700 nm is the result of charge transfer in the triplet state. The rate constants of deactivation for these triplet states coincide.

Keywords: thiacarbocyanines, cucurbit[8]uril, dimers, dimeric complexes, triplet states, laser pulse photolysis

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Photonics of the polymethine dyes is a subject of a large variety studies because of their wide use in the laser technique [1, 2], as spectral sensitizers for registration of information [3], and in other fields. A specific feature of polymethine dyes is their ability to aggregation and in particular to formation of dimers as supramolecular systems. One of the peculiarities of polymethine dyes is a low quantum yield of intersystem crossing to the triplet state [4–6], which increases distinctly upon dimerization [7–9] and in the presence of electrolytes [10].

It is well-known that polymethine dyes in particular thiazolinocarbo-, indocarbo-, and indodicarbocyanine dyes form 1 : 1 host-guest complexes with cavitands, cucurbit[7]uril among them [11–13]. Recently, we have shown that 3,3'-diethylthiacatbocyanine and 3,3'-diethyl-5,5'-dichloro-9-ethylthiacarbocyanine in water in the presence of cucurbit[7]uril manifest thermally activated delayed fluorescence [14, 15]. The presence of delayed fluorescence indicates the formation of a triplet state, which is confirmed by the measurements of triplet–triplet absorption by pulse photolysis. As follows from the spectrum of the ground state and the triplet–triplet absorption spectrum, 3,3'-diethylthiacarbocyanine iodide forms dimers in the presence of cucurbit[7]uril [16]. For cucurbit[8]uril (**CB8**) with a larger cavitand cavity than that for cucurbit[7]uril, the formation of 2 : 1 and 2 : 2 host–guest complexes is possible as shown for thiazole orange [17].

In this paper, we present the results of the spectral and kinetic study of aqueous solutions of monomers and dimers of alkylated thiacarbocyanines D1 and D2 in the triplet state in the absence of CB8 and of the dimeric complexes of D1 with cucurbit[8]uril under pulse laser excitation.

EXPERIMENTAL

The alkylthiacarbocyanines (3,3'-diethylcarbocyanine cation, D1, and 3,3'-disulfopropylthiacarbocyanine anion, D2) were synthesized at the Institute of Organic Chemistry, National Academy of Sciences of Ukraine. Cucurbit[8]uril (CB8) from Aldrich was used. Difference triplet–triplet absorption spectra (difference between the triplet–triplet A_{T-T} and singlet–singlet A_{S-S} absorbances of the dyes ($\Delta A = A_{T-T} - A_{S-S}$)) were recorded on a nanosecond laser photolysis setup described elsewhere [12]. The ground state (singlet–singlet) absorption spectra of thiacarbocyanines were recorded on an Agilent 8454 spectrophotometer. Water purified with a Direct–Q3 Millipore system was used. In some experiments, methanol (Aldrich) was used without additional purification. All measurements were carried out in oxygen-free solutions at room temperature.

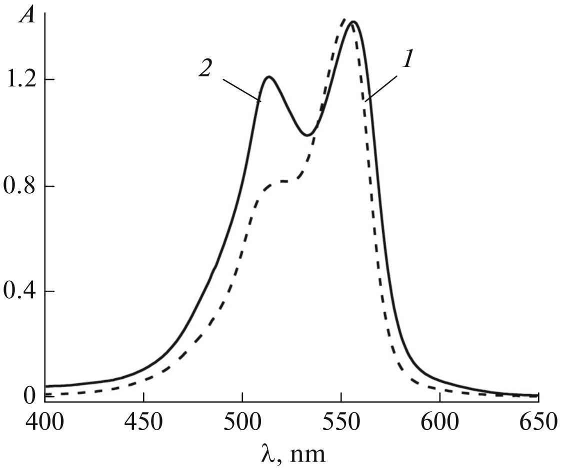

Fig. 1. Absorption spectra of (*1*) D1 and (*2*) D2 in water.

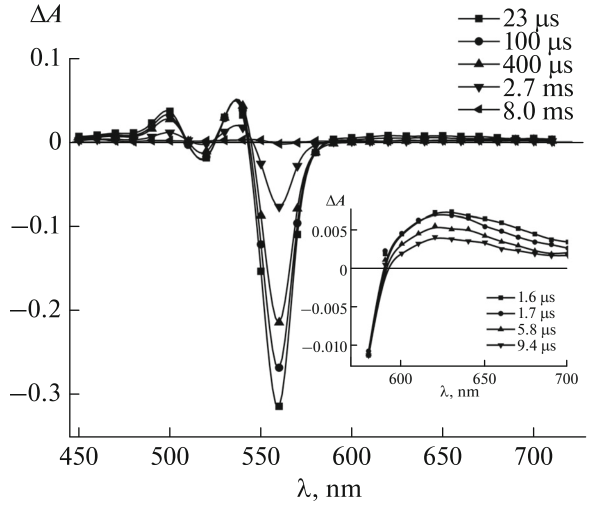

Fig. 2. Time-resolved difference absorption spectra of D1 in water (2×10^{-5} mol L^{-1}). Inset: difference spectra of triplet–triplet absorption. Frames: the times of measurements of the spectra after the laser pulse.

RESULTS AND DISCUSSION

Spectral and kinetic measurements were carried out in two experimental series. In the first series, the measurements were carried out with aqueous solutions of the dye in the absence of CB8. In the second series, the measurements were carried out with aqueous solutions of D1 in the presence of CB8, which forms dimeric complexes between oppositely charged D1 and CB8. As follows from the absorption spectra, there is no complex formation between likely charged D2 and CB8.

The following results were obtained in the first series. The D1 and D2 molecules in water form an equilibrium mixture of monomers and dimers. The absorption spectra of D1 and D2 consist of two bands (Fig. 1). The short-wavelength band at 514–517 nm is due to the dye dimers, and the band at 553–557 nm belongs to monomers, with the absorbance of the D2 dimers being higher than that of the D1 dimers. The concentration of the dimers can be increase by increasing the initial concentration of the dyes in solution [18]. However, in the case of strong absorption ($A_{532} > 2$) at the laser emission wavelength (532 nm) in the spectral time-resolved measurements, the irradiation of the solution by a laser pulse passing through the cell will be nonuniform, thereby resulting in errors in the measurements of difference spectra. Therefore, the measurements were carried out with solutions having an absorbance of $A_{532} = 1.2–1.5$.

Unlike D1, D2 having a higher solubility in water than D1 is characterized by a higher concentration of the dimers, which explains the choice of D2. The ratio of the dimer to monomer absorbance is $\alpha = 0.86$ for D2 indicating the higher amount of the dimers in comparison with D1 ($\alpha = 0.55$, Fig. 1).

The pulse irradiation of oxygen-free solutions of D1 and D2 were carried out. The time-resolved difference absorption spectra of D1 measured using direct laser excitation of the solution are given in Fig. 2.

In the spectra depicted in Fig. 2, both positive (500, 535, and 630 nm) and negative (520 and 560 nm) maximums are observed. As shown earlier with the use of lamp flash photolysis [4, 5], the initial *trans*-isomer of the dye monomer in alcohol solutions of D1converts to the *cis*-isomer by the action of a light pulse with a duration of 5×10^{-5} s. The positive maximums at 500 and 535 nm observed in this study under the laser excitation of the aqueous solution of D1 are due to the absorption of the monomer *cis*-isomer generated in the *trans–cis* photoisomerization. The back *cis* → *trans* thermal transition occurs with a rate constant of $k_{cis \to trans} = 2.3 \times 10^3$ s^{-1}.

In addition to the *trans–cis* photoisomerization, we observed earlier the triplet–triplet absorption of the D1 monomers with a maximum at 610 nm in *n*-butanol in sensitized lamp pulse excitation of the dye. In this study, we observed the appearance of D1 triplet–triplet absorption under direct laser excitation of the aqueous solutions. Positive changes in ΔA with a maximum at 630–660 nm in the case of excitation of D1 (Fig. 2) are caused by populating the triplet level of both the monomers and dimers. Negative changes in ΔA in the range of 514–517 nm are caused by both depleting the *trans*-isomer level as a result of the *trans* → *cis* transition in the monomers and populating the triplet level of the monomers and dimers.

The laser excitation of D2 in the aqueous solution is also characterized by the presence of both positive peaks at 500, 540, and 650 nm and negative peaks at 514 and 560 nm in the difference spectrum (not shown). Similarly to D1, the positive maximums at

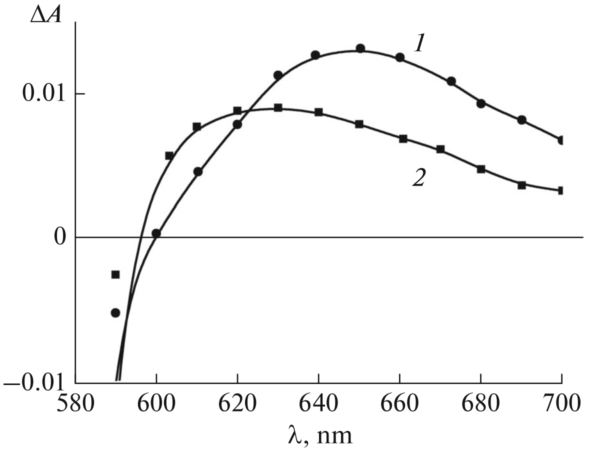

Fig. 3. Time-resolved triplet–triplet absorption spectra of D2 in (*1*) water and (*2*) 30 vol % MeOH, measured 2 μs after the laser pulse.

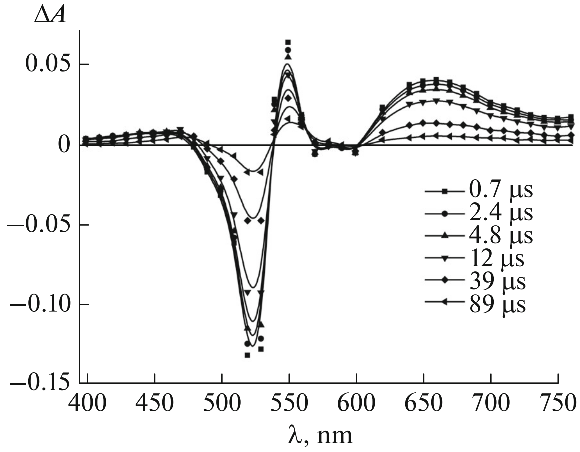

Fig. 4. Time-resolved difference absorption spectra of dimeric complex of D1 with CB8 (1×10^{-5} mol L^{-1}). Frame: the times of measurements of the spectra after the laser pulse.

500 and 540 nm are due to the D2 *cis*-isomer generated in the *trans–cis* photoisomerization. The negative peaks are caused by depleting the D2 monomers level of the *trans*-isomer and populating the triplet level of the monomers and dimers. Moreover, there is a bathochromic shift in the triplet–triplet absorption maximum by 20 nm in the D2 difference spectrum relative to that for D1. Thus, the changes in the absorption spectrum of D2 are caused by the *trans–cis* photoisomerization and population of the triplet level of both the monomers and dimers.

To reveal the contribution of the dye monomers and dimers to the triplet–triplet absorption spectrum in the range above 590 nm, experiments with water–methanol solutions of D2 containing 1, 3, 10, and 30 vol % methanol were carried out. Spectral time-resolved measurements show that the maximum in the triplet–triplet absorption spectrum hypsochromically shifts from 650 to 630 nm with an increase in the methanol content from 1 to 30% in the water–alcohol mixture (Fig. 3). Thus, triplet–triplet absorption spectrum of the dimer is shifted to the longer wavelengths in comparison with the monomer triplet–triplet absorption spectrum.

The results obtained in the second experimental series are presented in Fig. 4. Recently, we have shown that a band with λ_{max} = 525 nm due to the dimeric complex is observed in the spectrum of ground-state D1 in the presence of CB8 [19]. In the laser excitation of oxygen-free aqueous solution of the complex, the absorbance at 525 nm decays, and a relatively narrow band at 550 nm and a broad structureless band in the range of 620–700 nm with a maximum at ~665 nm appear (Fig. 4).

The decay kinetics of the absorbance at 550 and 650 nm obeys exponential law with a rate constant of $k = 1.2 \times 10^3$ s^{-1}, which is the rate constant for the deactivation of the lowest triplet state of the dimer. The lifetime depends on the presence of dissolved oxygen and decreases to several microseconds after admission of air into the cell, a behavior that is typical of dye triplet molecules in water.

To account for the origin of the two bands in the difference absorption spectrum of D1 dimers in the presence of CB8, we consider two models. According to the first model, the participation of not only initial *trans*-isomers, but also *cis*-isomers formed in the photoisomerization was proposed. The absorption of a light quantum by the *trans*-isomer molecule in the dimer first results in the formation of an excited singlet state of the *trans*-isomer with subsequent intersystem crossing to the triplet state competing with *trans* → *cis* isomerization. Thus, the formation of the *trans–trans* dimers in the triplet state and *trans–cis* dimers in the ground state occurs with relatively high probability. If so, one of the bands in the difference absorption spectrum of the dimer could be attributed to the triplet–triplet transition in the *trans–trans* dimers and the other band could be assigned to the singlet–singlet transition in the *trans–cis* dimers. However, the two bands are of the triplet origin, which manifests itself in the disappearance of the triplet–triplet transition with the same rate constant after air admission into the irradiated cell. Thus, the explanation of the origin of one of the bands by the generation of the *trans–cis* isomers does not seem to be true. The results obtained for the covalently bound *trans*-monomers of indocarbocyanines (bis-dyes) are additional confirmation for the assignment of the two bands to the absorption of the *trans–trans* dimers [24, 25]. Two bands were also observed in the difference the triplet–triplet absorption spectrum for bis-dyes, but the formation of a *cis*-isomer in the *trans* → *cis* photoisomerization is practically impossible for bis-dyes because of steric hindrance due to their cyclic structure.

The second model proposed for the explanation of the appearance of the two bands in the difference spectrum is based on the possibility of population by a laser pulse of both the triplet level of the dimeric complex and the dimeric complex with charge transfer in the triplet state. Earlier, it has been assumed that the two bands in the difference triplet–triplet absorption spectrum of the covalently bound indocarbocyanine dimers are the result of triplet level splitting [24, 25]. However, according to the theory of triplet excitons of aromatic molecular crystals, the value of the matrix element of the exchange coupling of the triplet states for aromatic molecules at low distances is ~10 cm^{-1} [20–22]. This value is significantly lower than that observed in the study (~3000 cm^{-1}). Thus, the observed bands in the triplet–triplet absorption spectrum of the dimers cannot result from the splitting of the triplet level.

According to the theory of triplet excitons for aromatic molecular crystals, there is a possibility for the formation of triplet states in crystals with intermolecular charge transfer [20–22]. It should be taken into account that the probability of an optical transition to these states decreases with an increase in the distance between the interacting fragments and, in such systems, the corresponding bands will broaden as a results of the interaction of the charge-transfer states with surrounding molecules. Thus, the band at 550 nm is due to the triplet–triplet absorption of dimeric complexes and is characterized by low broadening and exchange coupling. The band at 620–700 nm can be due to the triplet–triplet absorption of the dimeric complexes with prevalence of configurations with charge transfer between the moieties. The substantial band broadening is a result of dipole–dipole interaction of the dimer with molecules of the medium.

Note that the presence of two bands in the triplet–triplet absorption spectra is observed not only for dimeric complexes of cationic polymethine dyes with CB8, but also for the dimers of anionic polymethine dyes in water [23].

Thus, the D1 and D2 dimers formed in pure water solutions are capable to intersystem crossing to triplet state with a higher efficiency in comparison with polymethine monomers. The formation of dimeric dye complexes with cucurbit[8]urils facilitates the population of their triplet level. The triplet–triplet absorption spectrum of the dimers and dimeric complexes is characterized by the presence of two bands, unlike that for the monomers exhibiting one band.

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