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Photosensitized processes in dicarbocyanine dyes induced by energy transfer: delayed fluorescence, *trans* → *cis* isomerization and electron transfer

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Abstract

The triplet-induced photoprocesses of 3,3′-diethylthiadicarbocyanine (**1**), 3,3′-diethyloxadicarbocyanine (**2**), its methyl (**3**), ethyl (**4**) and phenyl (**5**) derivatives as well as of 1,1′,3,3,3′,3′-hexamethylindodicarbocyanine (**6**) and its chlorine (**7**), bromine (**8**) and methyl (**9**) derivatives were studied in deoxygenated acetonitrile upon anthracene-sensitized excitation by conventional and ns-flash photolysis. The emission is attributed to the sensitized (mixed) type rather than E- or P-type delayed fluorescence. The triplet state of the dyes, radicals and a *cis* isomer with absorption maxima at 650–1000, 450–500 and 620–695 nm, respectively, were spectroscopically and kinetically distinguished. The *trans* → *cis* photoisomerization can be initiated by both triplet (mostly) and singlet states of the dyes. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Dicarbocyanine dyes; Sensitization; Triplet state; Photoisomerization; Delayed fluorescence

1. Introduction

Cyanine dyes have been intensively studied by various photophysical and photochemical means [1–37]. They are important compounds and widely applied, e.g. in conventional silver halide and non-conventional information recording [20]. A major deactivation route of 3,3′-diethylthiadicarbocyanine (**1**) and 3,3′-diethyloxadicarbocyanine (**2**) is the *trans* → *cis* photoisomerization which occurs via singlet states [1–10,22]. **2** is one of the most frequently studied synthetic dyes of all and its iodode is the “so-called” DODCI [1–19]. Detailed studies of the fluorescence properties of **2** in methanol and ethylene glycol have recently been reported [17,18].

Sterically non-hindered cyanine dyes generally show a relatively weak fluorescence and a quantum yield of intersystem crossing (Φ_{isc}) which is negligibly small [19]. Specific covalently linked bis-dyes, however, reveal a markedly enhanced Φ_{isc} [34–37]. A restriction of the flexibility of these cyanine dimers has a strong reducing influence on the quantum yield of *trans* → *cis* photoisomerization ($\Phi_{t\rightarrow c}$) and, therefore, an enhancement of Φ_{isc} and the quantum yield of fluorescence (Φ_{f}) [36].

In a recent study of 1,1′,3,3,3′,3′-hexamethylindodicarbocyanine (**6**) and several derivatives we found that $\Phi_{t\rightarrow c}$ depends significantly on the medium and *meso* substituent, e.g. chlorine, bromine and methyl groups. $\Phi_{t\rightarrow c}$ is substantial (up to 0.2) in ethanol at 24°C and decreases with decreasing temperature, whereas Φ_{f} markedly increases, approaching 0.7–0.9 at −196°C [37]. In addition, delayed fluorescence was observed as long as oxygen was rigorously excluded. The mixed type of delayed fluorescence has been established earlier for 3,3′-diethylthiacarbocyanine dyes [19,25].

In this paper, we present results concerning the triplet-induced processes obtained with dyes of the type thiadicarbocyanine (**1**), oxadicarbocyanine (**2**) and indodicarbocyanine (**6**). Dicarbocyanine dyes exhibit *cis* isomer and triplet state absorbance which are both positioned at a longer wavelength with respect to that of *trans*-band. This is in contrast to monocarbocyanine dyes, where the *cis* isomer absorbs at shorter wavelengths than the *trans* isomer [19] and makes it possible to observe the kinetics of formation of the *cis* isomer upon intermolecular triplet energy transfer. Since Φ_{isc} of the dicarbocyanines is low (<0.01)

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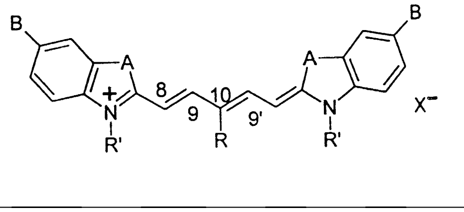
[1] we used anthracene-sensitized excitation to yield the triplet state of the dicarbocyanines which is the precursor of delayed fluorescence and two competing reactions, *trans* → *cis* isomerization and electron transfer.



Dye	A	B	R	R′	X^-
1	S	H	H	Et	I^-
2	O	H	H	Et	ClO_4^-
3	O	H	Me	Et	I^-
4	O	H	Et	Et	I^-
5	O	C_6H_5	H	Et	I^-
6	CMe_2	H	H	Me	I^-
7	CMe_2	H	Cl	Bu	ClO_4^-
8	CMe_2	H	Br	Bu	ClO_4^-
9	CMe_2	H	Me	Me	ClO_4^-

2. Experimental

The compounds, which are mostly all-*trans* isomers, have been synthesized according to methods described elsewhere [38] or were the same as in previous work (**6**) [37]. The counter ions are iodide for **1**, **3–6** and perchlorate for **2**, **7–9**. The identity was checked by absorption spectroscopy and elementary analysis. Anthracene (Aldrich) was recrystallized and acetonitrile was Uvasol quality. The dye concentration was varied in the 0.1–100 μM range. The absorption spectra were recorded on spectrophotometers (Shimadzu UV-3100 and HP 8453) and the steady-state fluorescence spectra on a spectrofluorometer (Shimadzu RF-500).

Transient absorption measurements were carried out by means of either 15 μs (half-peak width) or 20 ns flash photolysis (pathlength: 20 and 1.0 cm quartz cells, respectively). For conventional flash photolysis (energy ≤ 150 J) at room temperature cut-off filters were used [36]; i.e. only the main band was excited, and for anthracene-sensitized excitation the visible part was cut-off by filters. Other experiments were performed with $\lambda_{exc} = 354$ nm from a Nd-laser and the set-up was essentially the same as used previously [37].

Several other possible energy donors (ketones or naphthalene) and polar solvents (e.g. ethanol) were checked using $\lambda_{exc} = 354$ nm (or 308 nm from an excimer laser [37]) with the aim to initiate delayed fluorescence. Where prompt fluorescence was too large, trace amounts of oxygen, which always gave rise to disappearence of the delayed fluorescence, was used as criterium. In order to keep the dye concentration and the prompt fluorescence as low as possible, we used the anthracene/acetonitrile system where self-quenching and T–T annihilation of the donor triplet as competing processes and direct excitation of the acceptor molecule are minimized.

Simulation of kinetics of formation and decay of triplet and delayed fluorescence for E-, P- and mixed types was carried out as follows. The rate constant of formation of the triplet state of the dye is taken as $k_1 = 6 \times 10^9\,M^{-1}\,s^{-1}$. The formation of the two radicals is $k_4 = 3 \times 10^9\,M^{-1}\,s^{-1}$ and those which are also identical for the three cases are: $k_6 = k_7 = 1 \times 10^{10}\,s^{-1}$, $k_8 = 1 \times 10^4\,s^{-1}$ and $k_9 = 1 \times 10^2\,s^{-1}$. The rate constants of formation of the $^{1*}A_t{}^+$ state used for computer simulation of kinetics for E-type reaction (5), P-type reaction (3) and mixed (sensitized) type reaction (2) are $k_5 = 1 \times 10^3\,s^{-1}$, $k_3 = 3 \times 10^9\,M^{-1}\,s^{-1}$ and $k_2 = 6 \times 10^9\,M^{-1}\,s^{-1}$, respectively (otherwise zero).

3. Results

3.1. Triplet state of the dicarbocyanine dyes

Upon excitation of anthracene in argon-saturated acetonitrile at room temperature the anthracene triplet state appears concomitant with the laser pulse. In the presence of a dicarbocyanine dye, an increase of transient absorption was observed which matches the decay of the donor triplet state at 420 nm. The absorption of the triplet state of **2** has T–T maxima at $\lambda_{TT} = 648$, 855 and 968 nm (Fig. 1) and the maxima of all dyes examined are collected in Table 1. For **2** in ethanol, a molar absorption coefficient of $\varepsilon_{700} = 2.5 \times 10^5\,cm^{-1}\,M^{-1}$ has been reported [1]. The kinetics of formation and decay of the triplet state of **2** at 660 nm are shown in Fig. 1, inset. The rise time of T–T absorption decreases with the dye concentration (not shown). The absorption signal increases with increasing [dye] and approaches a plateau value (Fig. 2). For diluted solutions (<1 μM) the kinetics can be fitted by first-order triplet decay with rate constants in the range $k_T = (0.7–16) \times 10^3\,s^{-1}$ (Table 1). At higher dye concentrations a second-order component

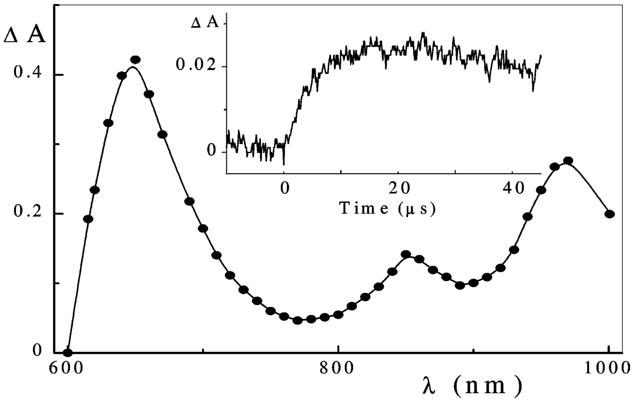


Fig. 1. T–T absorption spectra of **2** (0.5 μM) in argon-saturated acetonitrile upon anthracene-sensitized excitation by the 15 μs flash; inset: kinetics for **2** (10 μM) at 660 nm, $\lambda_{exc} = 354$ nm.

Table 1
T–T absorption maxima, rate constant for triplet decay and maxima and rate constant of delayed fluorescence of dicarbocyanine dyes[a]

Dye	λ_{TT} (nm)	k_T ($\times 10^3$, s^{-1})[b]	λ_f (nm)[c]	k_f ($\times 10^5$, s^{-1})[d]
1	703, 976	1.2	670	2.2
2	648, 855, 968	0.74	600	1.3
3	670, 970	13	605	1.7
4	680, 970	16	605	1.9
5	690, 880	13	625	1.1
6	700, 800, 855, 960	0.67	660	1.0
7	710, >1000	2.4	660	2.7
8	690	0.78	660	3.9
9	700, 870, 970	1.3	655	1.0

[a] Obtained by anthracene-sensitized excitation in argon-saturated solution at room temperature.

[b] Using [dye] = 0.5–1 μM and 15 μs flash.

[c] Similar values using either conditions given in footnote "b" or [dye] = 10 μM, λ_{exc} = 354 nm.

[d] Using $A = 1.8$ for anthracene at 354 nm and [dye] = 9–11 μM.

contributes to the overall decay kinetics. The triplet state of the dyes was also observed at lower temperatures, albeit with a smaller rate constant, e.g. $k_T = 1.2 \times 10^5\ s^{-1}$ for **4** (30 μM) at −34°C with respect to $k_T = 2.5 \times 10^5\ s^{-1}$ at 25°C. The rate constant of triplet decay decreases on decreasing temperature. For **3** (10 μM), where $k_T = 1.6 \times 10^5\ s^{-1}$ at 25°C, the activation energy and the pre-exponential factor are 7.8 kJ mol^{-1} and $3.8 \times 10^6\ s^{-1}$, respectively.

3.2. Delayed fluorescence

A long-lived emission, which was observed for anthracene-sensitized excitation of **2** in acetonitrile (in the absence of the analyzing light beam), is assigned to delayed fluorescence. The spectrum with maximum at λ_f = 600 nm is identical to that of the prompt fluorescence (Fig. 3). All nine dicarbocyanine dyes exhibit both prompt and delayed fluorescence with similar or identical spectra, the fluorescence maxima are collected in Table 1. An example of the kinetics of delayed fluorescence (observed at 610 nm, where no re-absorption takes place) is shown for **2** in Fig. 3, inset. The rate constant for decay increases with [dye] and the values are $k_f = (1–4) \times 10^5\ s^{-1}$ for a concentration of 10 μM (Table 1).

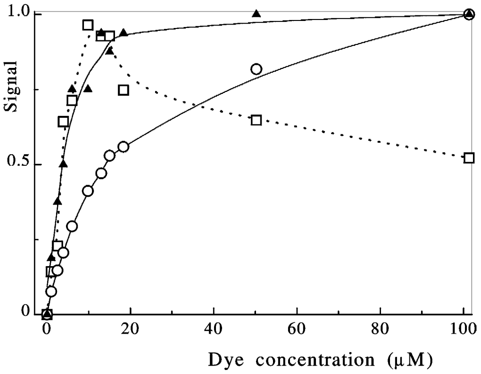


Fig. 2. Dependence of the normalized signals with increasing [**2**] in argon-saturated acetonitrile in the presence of anthracene for: T–T absorption at 660 nm (○), the S_f value of delayed fluorescence (□) and transient absorption at 620 nm due to the *cis* isomer ((▲), at 0.3 ms after the 354 nm pulse).

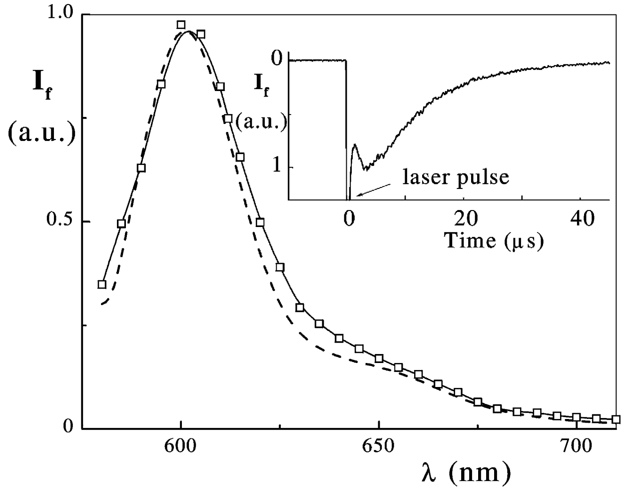


Fig. 3. Spectra of prompt and delayed fluorescence (broken and full lines, respectively) of **2** (1 μM) in argon-saturated acetonitrile in the presence of anthracene, 15 μs flash, λ_{exc} = 580 and 300–400 nm, respectively; inset: kinetics of delayed fluorescence of **2** (10 μM) at 610 nm, λ_{exc} = 354 nm.

The time of reaching the maximum fluorescence intensity (t_{max}) is shorter than that of triplet absorption (see insets of Figs. 1 and 3). The t_{max} value as well as the inverse rate constant for delayed fluorescence decay ($1/k_f$) depend on the dye concentration, decreasing with increasing [dye]. The rate constant for the build-up of the T–T absorption signal correlates with the k_f value. The area (S_f), which was taken as a measure of the quantum yield of delayed fluorescence, increases with increasing [dye], reaches a maximum and then decreases (Fig. 2). Trace amounts of oxygen give rise to the disappearence of both the delayed fluorescence and T–T absorption of the dyes, due to quenching of the anthracene triplet. The delayed fluorescence was also observed at lower temperatures, where t_{max} is prolonged, e.g. from 2 μs for **3** at 25°C to ca. 6 μs at −34°C.

3.3. cis-Dicarbocyanines isomer

A *cis* isomer was observed for the anthracene/**3** system at 25°C, its absorption spectrum with maximum at λ_{cis} = 630 nm is similar to that observed upon direct excitation into the main band of the dye (Fig. 4). The similarity of the absorption spectra of the *cis* isomer upon direct and anthracene-sensitized excitation was found in all cases. For **2** in ethanol $\Phi_{t\to c} = 0.08$ and the molar absorption coefficient is $\varepsilon_{620} = 1.8 \times 10^5\ cm^{-1}\ M^{-1}$ [1]. The rate constant for decay of the *cis* isomer under sensitized and direct excitation ($k^{sens}_{c\to t}$ and $k_{c\to t}$, respectively) are the same

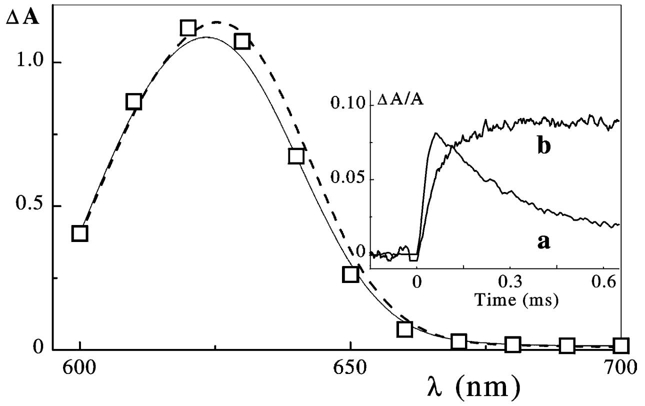


Fig. 4. Absorption spectra of the *cis* isomer of **3** (1 μM) in argon-saturated acetonitrile upon direct and anthracene-sensitized excitation 0.5 ms after the 15 μs flash (broken and full lines, respectively); insets: kinetics of (a) triplet decay at 670 nm and (b) *cis* isomer build-up at 615 nm.

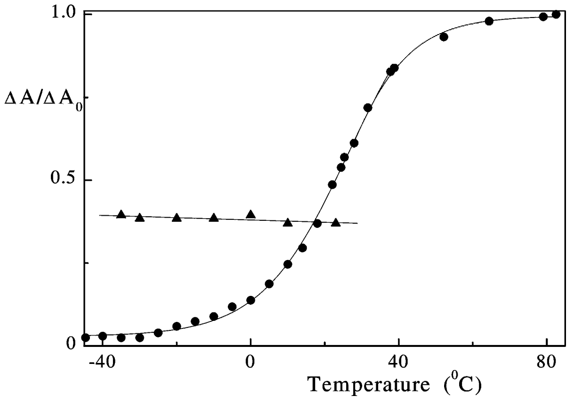


Fig. 5. Temperature dependence of the relative yield of the *cis* isomer (●) and radicals (▲) of **3** (10 μM) in argon-saturated acetonitrile in the presence of anthracene (observed at 630 and 460 nm, respectively, and normalized for the *cis* signal ΔA_0 at 85°C), $\lambda_{exc} = 354$ nm.

within experimental error. The values are $(0.2–1.2) \times 10^3$ s^{-1} (Table 2). For **2** various $k_{c\to t}$ values are known from the literature [3,7,9,12–14]. The absorption of the *cis* isomer of **2** at $\lambda_{cis} = 620$ nm (after triplet decay) increases with increasing [**2**] and reaches a plateau (Fig. 2). The slope of this dependence, however, is steeper than that in the case of T–T absorption.

The yield of the *cis* isomer of **3**, observed after decay of the dye triplet (e.g. at 0.1 ms after the pulse), strongly decreases with decreasing temperature, approaching a value above zero. The change between 80 and −40°C is ca. 50-fold (Fig. 5). In contrast, the yield of the *cis* isomer upon direct excitation of the dye changes only by ca. 50%. Moreover, the area and the lifetime of the delayed fluorescence as well as the T–T absorption signal (e.g. at 15 μs) are almost constant between 25 and −40°C and similar results were obtained for **2** and **4**.

3.4. Dicarbocyanines radicals

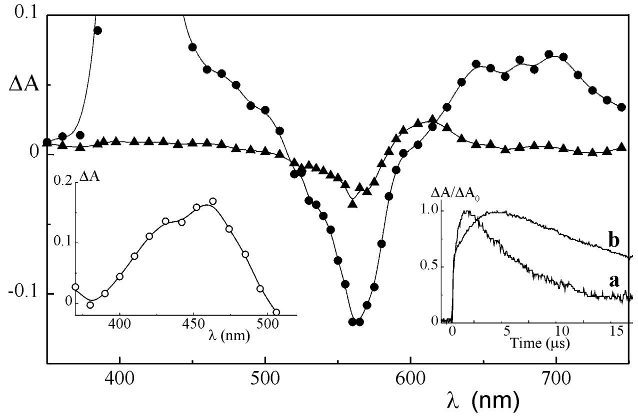


Fig. 6. Transient absorption spectra of **4** (10 μM) in argon-saturated acetonitrile upon anthracene-sensitized excitation at 2 μs (●) and 20–50 μs (▲) after the 354 nm pulse; insets — right: kinetics of (a) triplet decay at 670 nm and (b) partial build-up and decay of the radicals at 450 nm, left: spectrum for [**4**] = 60 μM at 10 μs.

On anthracene-sensitized excitation we also observed transients absorbing in the 350–500 nm range, which are absent on direct excitation of the dyes. An example with maximum at 460 nm is shown for **4** (Fig. 6). We assign these species to a neutral radical and a dication radical, resulting from electron transfer between two triplet states of the dye molecules [5,39]. Similar spectra of radicals with respective maximum at 480, 450, 460, 470, 500 and 510 nm were recorded for **1–3**, **5**, **8** and **9**, respectively. The yield of radicals was found to be essentially independent of temperature (Fig. 5).

Table 2
Absorption maximum and rate constants for decay of the *cis* isomer of the dicarbocyanine dyes under direct and anthracene-sensitized excitation[a]

Dye	λ_{cis} (nm)	$k_{c\to t}$ ($\times 10^3$, s^{-1})	$k^{\mathrm{sens}}_{c\to t}$ ($\times 10^3$, s^{-1})
1	695	0.88	0.9
2	620	0.33	0.32
3	630	0.78	0.8
4	630	1.2	1.1
5	630	0.4	0.35
8	680	0.24	0.2
9	685	1.1	0.98

[a] At ca. 20°C, [dye] = 1 μM (15 μs flash).

4. Discussion

4.1. Reaction scheme

A model is presented which describes the photophysical and photochemical features of the dicarbocyanine dyes under examination. All reactions are initiated by population of the donor triplet (^{3*}D) and energy transfer to the acceptor molecule, which is present as cation and (mostly) in the *trans* form (A_t^+). The triplet state of the dye ($^{3*}A_t^+$) is generated via reaction (1) and energy transfer competes successfully with self-quenching and T–T annihilation of the donor triplet.

$$^{3*}D + A_t^+ \rightarrow D + {}^{3*}A_t^+ \qquad (1)$$

$$^{3*}D + {}^{3*}A_t^+ \rightarrow D + {}^{1*}A_t^+ \qquad (2)$$

$$^{3*}A_t^+ + {}^{3*}A_t^+ \rightarrow {}^{1*}A_t^+ + A_t^+ \qquad (3)$$

$$^{3*}A_t^+ + {}^{3*}A_t^+ \rightarrow A^{\bullet} + A^{2+\bullet} \qquad (4)$$

$$^{3*}A_t^+ \rightarrow {}^{1*}A_t^+ \qquad (5)$$

$$^{1*}A_t^+ \rightarrow A_t^+ + h\nu_f \qquad (6)$$

$$^{1*}A_t^+ \rightarrow A_c^+ \qquad (7)$$

$$^{3*}A_t^+ \rightarrow A_c^+ \qquad (8)$$

$$A_c^+ \rightarrow A_t^+ \qquad (9)$$

The excited singlet state ($^{1*}A_t^+$) can be created via reactions (2), (3) and (5), which lead to delayed fluorescence, reaction (6). Moreover, two radicals may be formed via electron transfer, reaction (4). A_c^+ in reactions (7) and (8) refers to the *cis* isomer as photoproduct after rotation about one of the three C–C bonds of the polymethine chain in the singlet or triplet state, respectively. Eventually, the *cis* isomer converts thermally back via reaction (9).

4.2. Types of delayed fluorescence

The delayed fluorescence, originating from reactions (5), (3) and (2), is denoted as E-type, P-type and mixed (sensitized) type, respectively (rate constants: k_5, k_3 and k_2) [40]. As follows from computer simulation for the E-type delayed fluorescence of **2**, the rise times for fluorescence and T–T absorption are the same as the respective lifetimes (Fig. 7a). For the P-type delayed fluorescence, the rise times are also the same, but the fluorescence lifetime is about two times shorter than the triplet lifetime. In contrast, for the mixed type delayed fluorescence the rise time for fluorescence is shorter than that for T–T absorption and the decay is much longer (Fig. 7b). The time of reaching the maximum fluorescence intensity is $t_{max} < 5\,\mu s$, i.e. much shorter than the calculated values of ca. 40 μs for E- and P-types.

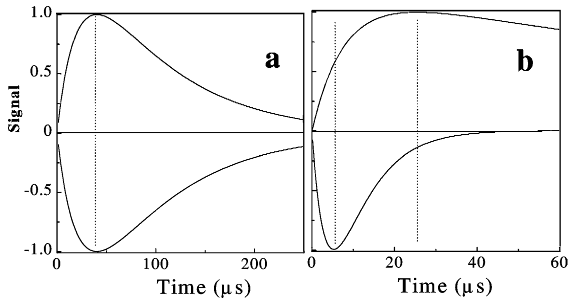


Fig. 7. Simulation of kinetics of formation and decay of the triplet (upper) and delayed fluorescence (lower) of **2** for (a) E- and (b) mixed types using $k_5 = 1 \times 10^3\,s^{-1}$ and $k_2 = 6 \times 10^9\,M^{-1}\,s^{-1}$, respectively; and $k_1 = 6 \times 10^9\,M^{-1}\,s^{-1}$, $k_4 = 3 \times 10^9\,M^{-1}\,s^{-1}$, $k_6 = k_7 = 1 \times 10^{10}\,s^{-1}$, $k_8 = 1 \times 10^4\,s^{-1}$ and $k_9 = 1 \times 10^2\,s^{-1}$.

The delayed fluorescence (inset of Fig. 3) is in accordance with the mixed type and in contradiction to E- and P-types. Therefore, the experimentally found delayed fluorescence is attributed to the mixed type, where also the fluorescence lifetime is equal to the rise time for T–T absorption (insets of Figs. 1 and 3). Other evidence for the mixed type delayed fluorescence under our conditions comes from the concentration dependence of the area S_f (Fig. 2). For E- and P-type, the S_f value should steadily increase with increasing [dye] (calculations not shown). However, for the mixed type a maximum of S_f appears which depends on the lifetime of $^{3*}D$ and the rate constant k_1 for energy transfer. Moreover, a contribution of the P-type delayed fluorescence is unlikely since T–T annihilation via reaction (3) is less efficient for cationic dyes due to Coulomb repulsive forces. Since a delayed fluorescence was also monitored at lower temperatures, e.g. at −34°C, its assignment to E-type is rather unlikely due to a negligibly small rate constant k_5. An S_1–T_1 gap of ca. $6000\,cm^{-1}$ can be expected for **2** [18]. Longer t_{max} values of reaching the maximum intensity at lower temperatures are the result of smaller k_1 and k_2 values (1).

Delayed fluorescence (without definition of the type) has been mentioned for **6–8** [37] and a weak delayed fluorescence of a carbocyanine dye at −196°C, originating from a trace impurity, has been reported [42]. While delayed fluorescence of the mixed type has already been detected for phenazine and thiazine dyes at room temperature [41], this is, to our knowledge, the first report for dicarbocyanine dyes.

4.3. Precursor of the cis isomer

trans → *cis* photoisomerization of cyanine dyes and in particular of carbocyanines has been the subject of numerous publications [1–10,19]. Upon direct excitation of these dyes the *cis* absorption band was observed in degassed or air-saturated solutions. In contrast to dicarbocyanines [19], the *cis*-carbocyanine peak is positioned at shorter wavelengths with respect to that of the *trans* principal band. Upon sensitized excitation of carbocyanines, besides the T–T absorption located at longer wavelengths [19], only reversible bleaching was detected in the spectral region of the *cis* isomer absorbance. The bleaching, originating from population of the triplet level of the dye, could mask the *cis* isomer formation. This would lead to the conclusion that *trans* isomer is formed only via the excited singlet state. For dicarbocyanine dyes this is not the case and we could observe the triplet and the *cis* isomer upon sensitized excitation. It follows from Fig. 4 that the latter kinetics match those of the triplet decay. Thus, the dye triplets are involved in *trans* → *cis* photoisomerization.

One of the possible reasons for the slow kinetics of the *cis* isomer formation is a relatively high energy barrier

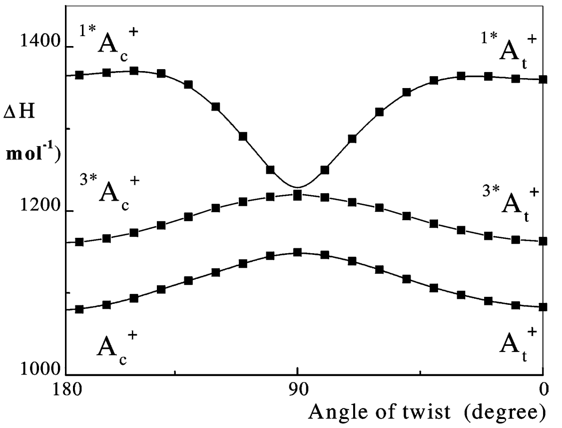


Fig. 8. Potential energy surface of **3** in the ground and excited singlet states (at the restricted Hartree–Fock, RHF level) and in the triplet state (at the unrestricted UHF level) using the PM3 semi-empirical SCF MO method as complemented in the HyperChem program.

in passing from the *trans* triplet to the *cis* isomer. This assumption was confirmed by calculations of the potential energy surface in the ground, excited singlet and triplet states of dye **3** (Fig. 8). The potential energy surface in the triplet state, in contrast to the excited singlet state, has a maximum at a twisting angle of 90°. A similar curve has been reported for polymethines [6]. The *trans* → *cis* isomerization of the dicarbocyanines in the triplet state (Fig. 8) should occur adiabatically, involving the *cis* triplet state as precursor of the *cis* ground state. However, only the *trans* triplet and no *cis* triplet state could be detected. Alternatively, the potential energy surface in the triplet state may resemble that of the excited singlet state, which has a maximum at a twisting angle between 0° and 90°, but a much higher barrier. The presence of the energy barrier in the route from the *trans* to the *cis* triplet state leads to a strong temperature dependence of the *cis* yield (Fig. 5). The *cis* concentration changes less strongly below 0°C than above. Under the low temperature conditions the triplet route (8) does not contribute and isomerization occurs only via the excited singlet state (7) in agreement with the temperature dependence upon direct excitation.

Further evidence, excluding isomerization via the excited singlet state as major route at ambient temperature, follows from the dependence of the yield of the *cis* isomer on [dye]. This plot should be similar to that of the fluorescence behavior (Fig. 2) and should contain no maximum. If the isomerization only occurs via the triplet reaction (8), then the yield of the *cis* isomer should show a steep increase vs. [dye] approaching a plateau. The slope should be the same as that of the triplet yield. The experimental curve of the *cis* isomer (Fig. 2) resembles that of the triplet, but the slope is steeper. From this we conclude that at a lower [dye] ($<10\,\mu$M) both pathways take place, whereas at high [dye] the *cis* isomer is mostly formed via the triplet pathway (8). Thus the *trans* → *cis* photoisomerization at ambient temperature occurs mostly via the triplet state. The minor pathway of the photoreaction via the excited singlet state implies that the triplet state plays a role as precursor in the reaction of the excited singlet state. The activation energy of $8\,\mathrm{kJ\,mol^{-1}}$ observed for **3** is probably due to intersystem crossing and self-quenching rather than rotation about one of the three C–C bonds of the polymethine chain in the triplet state.

4.4. Radicals

The most common mechanism of photochemical formation of radicals of organic dyes is electron transfer. Radicals are formed by interaction of two molecules in the triplet state or one in the triplet and one in the ground state [43]. The former electron transfer process is known for thiacarbocyanine dyes [19]. For **8** and another dicarbocyanine dyes with a structure similar to **7** and triphenylbutyl borate as counter ion for both dyes in non-polar solvents, radicals have been formed upon direct excitation [23]. Thereby, the electron is transferred in the ion pair from the counter ion to the excited singlet state. Similar absorption spectra in the 350–500 nm range were now registered upon anthracene-sensitized excitation in acetonitrile (Fig. 6). We, therefore, assign these transients to a semi-reduced ($A^{\bullet}$) and a semi-oxidized ($A^{2+\bullet}$) radical according to reaction (4). This is in agreement with the spectra derived from one electron oxidation and reduction [39].

The triplet state of the dye is the origin of two competing reactions, *trans* → *cis* isomerization and electron transfer. For **4**, the ratio of absorbances at 680, 630 and 460 nm is 5:2:1 (Fig. 6), reflecting the ratio of yields of triplet, *cis* isomer and radicals. Comparable contributions were also found for other dyes. Electron transfer is predominant at lower temperatures since the triplet route (8) is completely blocked and the amount of *cis* isomer via the excited singlet state (7) is small (Fig. 5). On the other hand, *trans* → *cis* isomerization is the main deactivation pathway at ambient temperatures.

4.5. Effects of structure

The observed features of the triplet state, *cis* isomer and radicals vary only moderately without a conveivable trend (Tables 1 and 2) when the sulfur in position A is replaced by oxygen or the CMe_2 group as well as when substituents are introduced in positions R and R′ for oxadicarbocyanines and indodicarbocyanines. The most pronounced difference is the enhancement of the k_T values for the methyl, ethyl and phenyl derivatives of **2** (Table 1). On the other hand, *meso* substituents in **6** have pronounced effects on $\Phi_{t\rightarrow c}$ at 24°C and Φ_f at −196°C under conditions of direct excitation [37].

Most dicarbocyanine dyes are present in the all-*trans* configuration [11,14,44]. From calculations at the restricted Hartree–Fock (RHF) level (PM3 semi-empirical SCF MO method as implemented in the HyperChem program) it follows that the heat of formation is smallest for the TTTTTT ground state of **1–6** and **9**, and the CTTCTT and TTCCTT ground state of **7** and **8**, respectively. The next less stable isomer refers to rotation about the C_9–C_{10} bond in the polymethine chain for the former cases, in agreement with the literature for **2** [14], and about the $C_{9'}$–C_{10} bond in the latter two cases. The instability of the ground state of the *cis* isomer is due to an energy level of 14 and 154 $\mathrm{kJ\,mol^{-1}}$ above that of the all-*trans* configuration for **1** and **2**, respectively [8,27].

5. Conclusions

The thia-, oxa- and indodicarbocyanine dyes examined exhibit *trans* → *cis* isomerization and formation of dye radicals upon anthracene-sensitized excitation in deoxygenated acetonitrile due to energy transfer from the anthracene triplet to the cationic dye. Formation of the *cis* isomer occurs via the triplet state of the dicarbocyanine dye as the major isomerization pathway and via the excited singlet state of the dye as minor pathway. The excited singlet state is mainly populated via T–T heteroannihilation and observable by mixed type delayed fluorescence. Dicarbocyanine radicals are proposed to be produced by electron transfer between two dye molecules in the triplet state. Since *trans* → *cis* isomerization via the triplet state, in contrast to radical formation, is essentially a thermally activated process, the yield of *cis* isomer can be strongly diminished by lowering of the temperature. The formation of the *cis* isomer via the triplet state proceeds in the microsecond time domain, in contrast to photoisomerization occurring via the excited singlet state within a few picosecond.

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