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Photophysical and aggregation properties of a long-chain squarylium indocyanine dye

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Abstract

The photophysical properties of a long-chain squarilium indocyanine dye, bis[(1-octadecyl-3,3-dimethylindol-2-ylidene)methyl]-squaraine (SQI1), were studied in various solvents and in normal and reverse micelles. The dependence of these properties on different solvent parameters is compared with the literature data on other squaraines. The absorption and fluorescence maxima of SQI1 and similar heterocyclic squarilium cyanines exhibit a good linear correlation with the Lorentz–Lorenz function. The rate of nonradiative deactivation of the SQI1 fluorescent state increases with the solvent polarity, but the viscosity effect is very small. A reversible photoisomerization process leading to the formation of a transient photoisomer with a long-wavelength absorption band was detected in SQI1. The lifetime of the photoisomer varies within a wide range, depending on the solvent polarity. SQI1 forms nonfluorescent aggregates in aqueous medium, which dissociate into monomeric molecules upon addition of TX100 above the critical micelle concentration. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Squarylium cyanine; Absorption and fluorescence spectra; Nonradiative deactivation; Aggregation

1. Introduction

Squaraine dyes have received considerable attention mainly due to their various applications, in particular, as photosensitizers in photoelectrochemical and imaging systems [1–5], second harmonic generation [6–8], probes for polarity and water content in a medium [9–11], and chemosensors [12–15]. In this respect, many studies have been directed to the photophysics of substituted bis(4-aminophenyl)squaraines and bis(4-hydroxyphenyl)squaraines, both in homogeneous solution and in heterogeneous systems of micelles and Langmuir–Blodgett films [16–20]. In dioxane/water mixtures and aerosol-OT (AOT) reverse micelles hydrogen bonding in the excited state is responsible for the large increase in the nonradiative processes of bis[4-(dimethylamino)phenyl]squaraine, and nonnegligible solute–solvent polar interactions were detected in a variety of polar solvents [9–11]. Another important group of squaraine dyes, squarylium cyanines, contain the central squarylium unit incorporated in the polymethine chain. This group of squaraines, while studied in less detail than the former ones, were shown to be promising when used as probes in a biological application; namely, indolenine derivatives (squarylium indocyanine dyes; SQI), which display the highest photostability, were suitable for use in labeling proteins [21]. Nevertheless, their photophysical behavior in various media remained poorly investigated. Recent studies of photophysical properties of bis(4-dimethylaminophenyl)squaraine, bis[4-(monoaza-15-crown-5-ether) phenyl]squaraine [22], bis[(1,3,3-trimethylindol-2-ylidene) methyl]squaraine, and bis(cyclopentylamino)squaraine [23] over a wide range of temperatures (from 300 down to 113 K) have disclosed the mechanism of nonradiative deactivation of the squaraine fluorescent state and have shown the importance of a temperature-dependent intramolecular nonradiative decay process which quenches fluorescence of the squaraines. For the first three squaraines, this process is induced by solvent polarity leading to an increase in the dipole moment of the solute (intramolecular charge transfer), and possibly involves twisting relaxation of the squaraine molecule [22,23].

We extended the photophysical investigation of squarylium cyanines to a long-chain squarylium indocyanine dye, bis-[(1-octadecyl-3,3-dimethylindol-2-ylidene)methyl]squaraine (SQI1), which was studied in homogeneous media (using a wide set of solvents including viscous ones and a polymer matrix) as well as in nonionic micelles of Triton X-100 (TX100) and AOT reverse micelles. The ability of the dye

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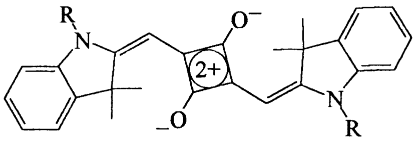
to form aggregates and the possibility of photoisomerization in the course of its nonradiative deactivation were also studied. The photophysical data obtained were correlated with the solvent parameters (functions of dielectric constant and refractive index, empirical solvation parameters) together with the literature data available on the photophysics of other squaraines.



SQI

R = $C_{18}H_{37}$ (SQI1), C_6H_{13} (SQI2), CH_3 (SQI3), C_2H_5 (SQI4).

2. Materials

SQI1 was obtained from the dye collection of the Laboratory of Photosensitization (Institute of Biochemical Physics, Russian Academy of Sciences); its purity was checked by thin layer chromatography. All solvents used were of spectroscopic grade. Sodium dodecylsulfate, sodium bis(2-ethylhexyl)sulfosuccinate (AOT), polyoxyethylene 23 lauryl ether (Brij 35) were purchased from Sigma, TX100 from Merck, and silicon elastomer E 301 (polymer $(CH_3)_3SiO-[(CH_3)_2SiO]_nSi(CH_3)_3$, where $n = 15\,000–35\,000$) (SE301) from Ferak (Germany); they were used as received.

3. Sample preparation

A solution of SQI1 in SE301 was prepared by dissolving SE301 in chloroform containing SQI1 and subsequent evaporation of chloroform upon warming the solution. For preparation of SQI1 solutions in isooctane/AOT/water reverse micelles, a binary stock solution of SQI1 ($\sim 1 \times 10^{-6}$ mol l^{-1}) and AOT (0.1 mol l^{-1}) in isooctane was used. Solutions with different w_0 (w_0 = [water]/[AOT]) were prepared by adding appropriate amounts of doubly distilled water, using calibrated micropipets, to the stock solution. The solutions were agitated for 4–5 min to achieve a homogeneous ternary mixture. The samples were incubated for 12–18 h at room temperature before carrying out any measurements. SQI1 solutions containing TX100 were kept at room temperature at least 24 h before measurements.

4. Methods

Absorption spectra were recorded with a JASCO V-560 UV–VIS absorption spectrophotometer at room temperature. Steady-state emission measurements were made on a Perkin-Elmer LS 50B spectrofluorimeter with the sample holder thermostated at 298 K. Corrected fluorescence spectra were obtained using the correction file provided by the manufacturer. Fluorescence quantum yields ($\Phi_{\rm fl}$) were measured at 298 K using rhodamine 101 in ethanol ($\Phi_{\rm fl} = 0.92$ [24]) as a standard, after applying necessary corrections for the refractive index of the solvent. Dye concentrations were usually below 1×10^{-6} mol l^{-1} in order to keep the optical density below 0.1. The error in the estimation of $\Phi_{\rm fl}$ is ±10%. Fluorescence lifetimes ($\tau_{\rm fl}$) were determined with a PTI LS-1 time correlated single photon counting instrument described earlier [25]. The temperature dependence of fluorescence decays was measured in the temperature range 285–310 K (for *tert*-BuOH solutions 299–315 K). Flash photolysis experiments were performed at room temperature using a conventional flash photolysis instrument with xenon lamp photoexcitation (flash duration $\tau_{1/2} \sim 7$ μs, energy 50 J [26]). Glass cutoff filters were used to select the appropriate excitation region ($\lambda > 590$ nm).

5. Results and discussion

5.1. Squarylium cyanine dye in homogeneous solutions

5.1.1. Solvent effects on absorption and fluorescence spectra of squarylium cyanine

Table 1 contains a summary of the photophysical parameters of SQI1 in various solvents and Fig. 1 contains its representative absorption and fluorescence spectra. As for its homologue SQI3 [23], the fluorescence of SQI1 is the mirror image of the absorption and exhibits small Stokes shifts, the fluorescence excitation spectra closely follow the absorption spectra, and the band widths at half maximum are around 600 cm^{-1}. Fluorescence quantum yields for SQI1 are markedly higher than those for SQI3 (e.g. in toluene 0.58 and 0.38, respectively), apparently, due to the presence of bulky substituents ($C_{18}H_{37}$) in the SQI1 molecule, which hinder the nonradiative decay. SQI1 is well soluble in both polar and nonpolar solvents except water and polyhydric alcohols (the solubility in ethylene glycol is low and sufficient only for measurements of the fluorescence and excitation spectra); there were no concentration effects in these solvents on the shape of the spectra within the range 10^{-8}–10^{-5} mol l^{-1}. A linear correlation is observed between the wavenumbers of the absorption or fluorescence maxima ($\nu_{\rm abs}^{\rm max}$ and $\nu_{\rm fl}^{\rm max}$, respectively) and the Bayliss function $f(n^2) = (n^2 - 1)/(2n^2 + 1)$ of the solvent refractive index n: $\nu_{\rm abs}^{\rm max} = 16\,819\,{\rm cm}^{-1} - [5624\,{\rm cm}^{-1} f(n^2)]$ and $\nu_{\rm fl}^{\rm max} = 16\,550\,{\rm cm}^{-1} - [5591\,{\rm cm}^{-1} f(n^2)]$, with the correlation coefficients $r = 0.889$ and 0.785, respectively. A linear correlation is also observed between $\nu_{\rm abs}^{\rm max}$ or $\nu_{\rm fl}^{\rm max}$ of SQI1 and the Lorentz–Lorenz function $\phi(n^2) = (n^2 - 1)/(n^2 + 2)$: $\nu_{\rm abs(fl)}^{\rm max} = 16\,567\,(16\,302)\,{\rm cm}^{-1} - [3484\,(3471)\,{\rm cm}^{-1}\,\phi(n^2)]$, $r = 0.894$ (0.793) (Fig. 2a). The analogous correlation has been found recently for $\nu_{\rm abs}^{\rm max}$ of SQI2 [27]. Similar correlations can be obtained using the literature data for the squaraine SQI3 [23] as well as for squarilium cyanines

Table 1
Photophysical properties of SQI1 in homogeneous media and TX100 micelles

Solvent	ε[a]	n[b]	η[c] (cP)	λ_{abs}^{max}[d] (nm)	λ_{fl}^{max}[e] (nm)	ν_{00}[f] (cm^{-1})	$\Delta\nu_s$[g] (cm^{-1})	$\Delta\nu_{abs}^{1/2}$[h] (cm^{-1})	τ_{fl} (ns)	Φ_{fl}	k_{fl}[i] $\times 10^{-8}$ (s^{-1})	k_{nr}[j] $\times 10^{-8}$ (s^{-1})	$E_{a(nr)}$[k] (kJ mol^{-1})
Heptane	1.92	1.3876	0.418	635.5	644	15 632	208	571	1.67	0.45	2.67	3.32	21.8
Isooctane	1.94	1.3915	0.504	635	643.5	15 644	208	547	1.81	0.49	2.70	2.83	23.8
Cyclohexane	2.02	1.4262	0.98	637.5	647	15 571	230	555	1.84	0.48	2.64	2.80	25.3
CCl_4	2.24	1.4601	0.969	640	650.5	15 499	252	587	2.03	0.65	3.22	1.70	29.2
Toluene	2.38	1.4961	0.587	642.5	653	15 439	250	573	1.77	0.58	3.28	2.37	19.9
Dioxane	2.21	1.4224	1.439	639.5	652	15 487	300	601	1.65	0.49	2.96	3.10	23.7
CS_2	2.64	1.628	0.363	654	666	15 153	276	586	1.92	0.69	3.59	1.61	23.0
$CHCl_3$	4.81	1.4459	0.58	636.5	647	15 583	255	594	1.53	0.42	2.78	3.76	12.6
C_6H_5Cl	5.71	1.5248	0.799	644	653.5	15 415	226	585	1.74	0.50	2.89	2.86	16.1
Ethyl acetate	6.02	1.3723	0.455	635.5	646	15 608	256	602	1.2	0.28	2.37	5.97	16.3
Triacetin	7.11	1.43	16.2	639	650	15 517	265	624	2.24	0.44	1.96	2.50	12.8
n-Decanol	8.1	1.437	11.9	637	646	15 589	219	576	2.3	0.69	3.02	1.33	16.6
CH_2Cl_2	8.93	1.4242	0.449	637.5	649	15 547	278	614	1.06	0.27	2.55	6.89	12.7
o-$C_6H_4Cl_2$	9.93	1.5515	1.32	645.5	657.5	15 350	283	592	1.92	0.57	2.95	2.26	17.2
tert-BuOH	12.5	1.3877	3.316	632.5	643.5	15 675	270	592	1.9	0.49	2.57	2.69	27.2
n-Hexanol	13.3	1.4178	4.87	636	647	15 590	267	576	2.25	0.51	2.26	2.19	20.1
EtOH	24.6	1.3614	1.078	632.5	643.5	15 675	270	628	0.78	0.15	1.92	11.0	17.9
MeOH	33.6	1.3288	0.551	630	641	15 737	272	632	0.48	0.054	1.9	18.9	–
DMF	36.7	1.4305	0.924	642	654.5	15 428	297	624	0.95	0.21	2.25	8.31	14.8
MeCN	37.5	1.3442	0.345	634	647	15 614	317	655	0.49	0.061	1.9	18.5	–
Ethylene glycol	37.7	1.4318	26.09	639	649	15 529	241	–	–	–	–	–	–
DMSO	46.7	1.477	1.996	645	658	15 351	306	655	1.15	0.23	2.01	6.72	16.8
TX100 (neat)		1.490	1000 [41]	642.5	653.5	15 433	262	599	2.5	0.72	2.87	1.13	9.8
SE301 (polymer)		1.4062		635.5	647	15 596	280	566	2.2	0.55	2.48	2.06	24.7
TX100 (micelles)[l]				641.5	651	15 475	227.5	627	2.81	0.50	1.79	1.77	–

[a] Dielectric constant.

[b] Refractive index.

[c] Viscosity.

[d] Wavelength of the absorption maximum.

[e] Wavelength of the fluorescence maximum.

[f] Energy of the 0–0 transition.

[g] Stokes shift.

[h] Absorption band width at half maximum.

[i] Rate constant of radiative deactivation of S_1 state (298 K).

[j] Rate constant of nonradiative deactivation of S_1 state (298 K).

[k] Apparent activation energy of nonradiative deactivation of S_1 state calculated from the slope of the dependence $\ln k_{nr} = \ln k_{nr,0} - E_{a(nr)}/RT$.

[l] $[TX100] = 4.33 \times 10^{-2}\ mol\ l^{-1}$ in water.

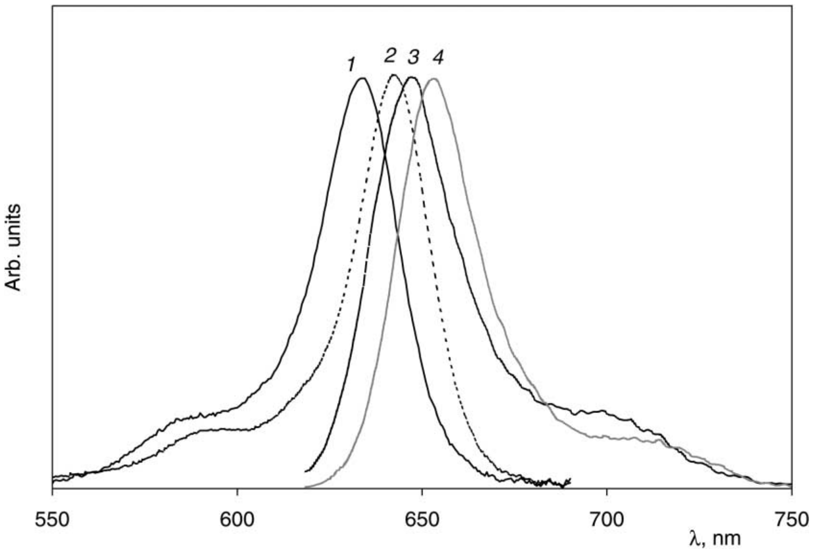


Fig. 1. Absorption (1, 2) and fluorescence (3, 4) spectra of SQI1 in MeCN (1, 3) and toluene (2, 4).

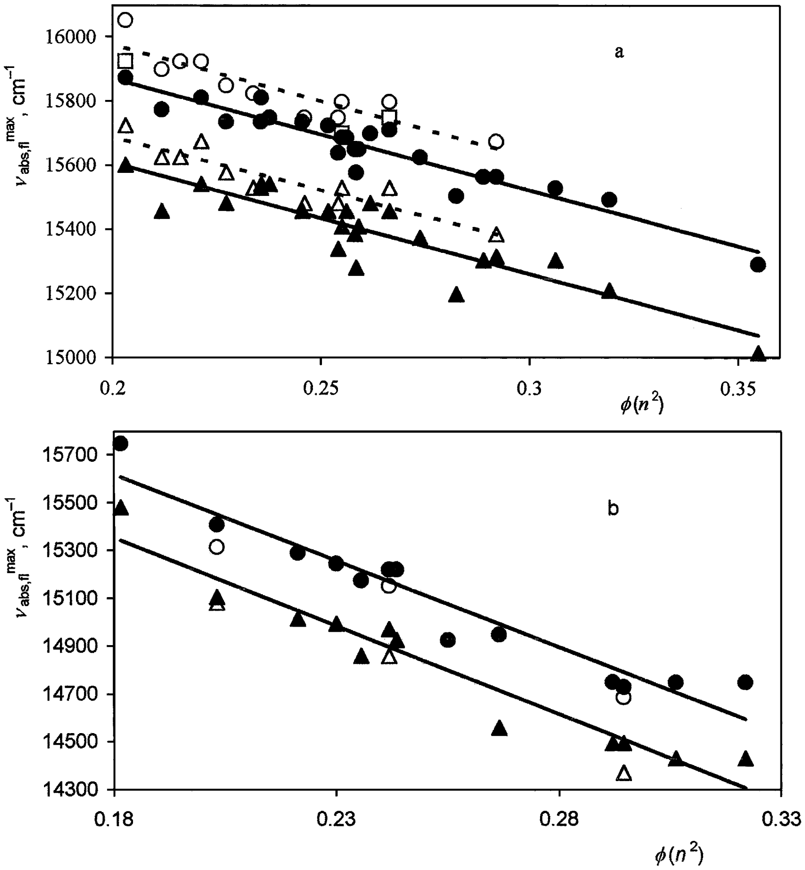
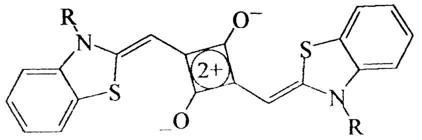


Fig. 2. Plots ν_{abs}^{max} and ν_{fl}^{max} vs. $\phi(n^2)$ and their linear trendlines. (a) Data for SQI1 (filled circles and triangles, solid lines; this work), SQI3 (open circles and triangles, dashed lines; taken from [23]) and SQI4 (open squares; taken from [21]). (b) Data for SQT1 (filled circles and triangles, solid lines; taken from [21,28]) and SQT4 (open circles and triangles; taken from [28]).

with benzothiazole terminal heterocycles SQT1–SQT3 [21,28,29].



where R = C_2H_5 (SQT1), 4-$CH_2C_6H_4COOH$ (SQT2), CH_2COOH (SQT3), $C_{18}H_{37}$ (SQT4) (see Fig. 2a). It should be noted that the correlation between λ_{abs}^{max} (or ν_{abs}^{max}) and Kamlet–Taft's solvation parameter π^* made for SQT1 in [28] can be greatly improved by taking $\phi(n^2)$ or $f(n^2)$ instead of π^*: in this case a linear plot can be obtained for all points considered (even including two additional points for SQT1 taken from [21]), with $r = 0.924$. Correlations between the absorption (fluorescence) maxima, ν_{00} ($\nu_{00} = (\nu_{abs}^{max} + \nu_{fl}^{max})/2$) or Stokes shift of SQI1 and any other polarity function peculiar to dipole–dipole interactions, $f(\varepsilon)$, $f(\varepsilon) - f(n^2)$, or $\phi(\varepsilon) - \phi(n^2)(f(\varepsilon) = (\varepsilon - 1)/(2\varepsilon + 1), \phi(\varepsilon) = (\varepsilon - 1)/(\varepsilon + 2))$, where ε is the dielectric constant of the solvent, or specific solvation (Dimroth–Reichardt's E_T (30), Kamlet–Taft's π^*) are poor ($r < 0.3$). A linear dependence of ν_{abs}^{max} and ν_{fl}^{max} on $\phi(n^2)$ can result from dispersive interactions between a nonpolar solute molecule and a solvent [27,30]; in particular, the position of the absorption maximum of a nonpolar solute in nonpolar medium obeys well the Bakhshiev equation [30,31].

$$\nu_{abs}^{max} = \nu_0 - p\phi(n^2) \qquad (1)$$

where $p = 3II'\Delta\alpha/[2(I + I')a_r^3]$, I and I' are the ionization energies of the solute and solvent molecules, $\Delta\alpha$ the polarizbility difference between the excited and the ground states of the solute, and a_r the Onsager cavity radius. The spectral behavior of SQI and SQT in different solvents is in accordance with the centrosymmetric conformation of their molecules, for which the dipole moment in the ground (μ_0) and the excited state vanish. Solute quadrupole–solvent dipole interactions are probably of minor importance for SQI1, because they should cause the spectral shifts governed by the function $\phi(\varepsilon) - \phi(n^2)$ [27]. The trend of the ν_{abs}^{max} and ν_{fl}^{max} decrease with rising $\phi(n^2)$ results from higher polarizability of the squaraine excited state compared with the ground state and lowering its relative energy at the expense of the dispersive interaction with a solvent. In accordance with the model of Baur and Nicol for spectral shifts of a nonpolar solute in both polar and nonpolar solvents [32,33], linear regressions $\nu^{\max}_{\text{abs(fl)}} = \nu_{0,\text{abs(fl)}} + A_{\text{abs(fl)}} f(n^2) + B_{\text{abs(fl)}} \psi(\varepsilon, n^2)$, where $B_{\text{abs(fl)}}$ characterizes the solvent Stark effect and $\psi(\varepsilon, n^2) = (\varepsilon - n^2)(2\varepsilon + n^2)/\varepsilon(n^2 + 2)^2$, were obtained for SQI1 and SQI3 with fair reliability: $\nu^{\max}_{\text{abs(fl)}} = 16\,918\ (16\,738)\,\text{cm}^{-1} - [6018\ (6334)\,\text{cm}^{-1}\ f(n^2)] - [12\ (22)\,\text{cm}^{-1}\ \psi(\varepsilon, n^2)]$, $r = 0.914$ (0.861). Small values of B compared with A show insignificant contribution from the Stark effect of polar solvents to the spectral shifts in comparison to the effect of dispersive interactions.

The Bayliss–Ooshika–McRae theory of solvent effects [34,35] gives for the solvent shifts the relationship $\nu^{\max}_{\text{abs(fl)}} = \nu_{0,\text{abs(fl)}} + a_{\text{abs(fl)}} f(n^2) + b_{\text{abs(fl)}}[\phi(\varepsilon) - \phi(n^2)] + c_{\text{abs(fl)}}[\phi(\varepsilon) - \phi(n^2)]^2$, where $a_{\text{abs(fl)}}$ is a function, in particular, of the energy and polarizability of the ground and excited states of the solute, and $b_{\text{abs(fl)}}$ and $c_{\text{abs(fl)}}$ characterize the linear and quadratic Stark effect, respectively, on absorption and fluorescence spectra. Its application to SQI1 leads to good linear fits, in which $\nu_{0,\text{abs(fl)}} = 16\,915$ $(16\,762)\,\text{cm}^{-1}$, $a_{\text{abs(fl)}} = -6116\ (-6549)\,\text{cm}^{-1}$, $b_{\text{abs(fl)}} = 284\ (324)\,\text{cm}^{-1}$, $c_{\text{abs(fl)}} = -486\ (-650)\,\text{cm}^{-1}$, $r_{\text{abs(fl)}} = 0.921\ (0.857)$. Small values of $b_{\text{abs(fl)}}$ as compared with the absolute values of $a_{\text{abs(fl)}}$ show that at least the linear Stark effect is insignificant.

For substituted bis(4-aminophenyl)squaraines (SQA), the correlations between $\nu^{\max}_{\text{abs(fl)}}$ and $\phi(n^2)$ or $f(n^2)$, as well as the Baur–Nicol linear regressions, in series of neat solvents are bad ($r < 0.7$; the data were taken from [10,22,36,37]). This could be, in particular, due to the effect of hydrogen-bonding interactions of excited SQA with solvent molecules, which are not taken into account in n values for bulk solvents. Indeed, hydrogen-bonding solvation of bis(4-dimethylaminophenyl)squaraine (SQA1) by alcohols shifts its absorption and fluorescence maxima to the red side out of the linear plots $\nu^{\max}_{\text{abs(fl)}}$ versus Taft's solvation parameter π^*, which are observed for SQA1 in aprotic solvents with good reliability [10]. Nevertheless, a good linear relationship occurs between $\nu^{\max}_{\text{abs(fl)}}$ of SQA1 and the Lippert parameter $\Delta f = f(\varepsilon) - f(n^2)$ in dioxane–water solvent mixtures due to a hydrogen-bonding interaction of SQA1 with water [9]. Good multilinear regressions ($r = 0.93$) were obtained for SQA1 in terms of the Bayliss–Ooshika–McRae theory, which were explained by quadrupole–dipole solute–solvent interactions [10].

Unlike SQA, hydrogen bonding with protic solvents has apparently a minor effect on the spectra of SQI and SQT. This is reflected in the fact that the points for protic and aprotic solvents belong to the common linear plots $\nu^{\max}_{\text{abs(fl)}}$ versus $\phi(n^2)$.

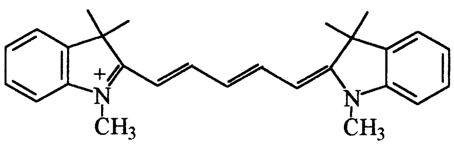
5.1.2. Nonradiative deactivation of SQI1

The fluorescence quantum yields and lifetimes for SQI1 in different solvents at 298 K are summarized in Table 1. The rate constants of radiative and nonradiative deactivation from the fluorescent state of SQI1 (k_{fl} and k_{nr}, respectively) were obtained using the standard relationships $k_{\text{fl}} = \Phi_{\text{fl}}/\tau_{\text{fl}}$ and $k_{\text{nr}} = 1/\tau_{\text{fl}} - k_{\text{fl}}$; apparent activation energies of the nonradiative deactivation ($E_{\text{a(nr)}}$) were calculated using fluorescence decay measurements at different temperatures, from the slope of the dependence $\ln k_{\text{nr}} = \ln k_{\text{nr},0} - E_{\text{a(nr)}}/RT$ (Table 1). As for SQI3 and SQA1 [22,23], the fluorescence quantum yield and lifetime for SQI1 decrease sharply in polar solvents. The value of Φ_{fl} is determined by both k_{fl} and k_{nr} ($\Phi_{\text{fl}} = k_{\text{fl}}/(k_{\text{fl}} + k_{\text{nr}})$); however, the changes of k_{fl} are relatively small throughout the solvents investigated (from 1.9×10^8 to $3.6 \times 10^8\,\text{s}^{-1}$), whereas, k_{nr} is strongly dependent on the nature of the solvent (varies from 1.1×10^8 to $1.9 \times 10^9\,\text{s}^{-1}$). Therefore, the decisive factor determining the behavior of Φ_{fl} with changing the solvent (at least at high k_{nr}) is the variation of k_{nr}.

Plotting k_{nr} against any solvent polarity parameter (e.g. the Lippert parameter Δf or the Pekar factor $C = 1/n^2 - 1/\varepsilon$) shows similarity in polarity induced nonradiative deactivation of the squaraines SQI1, SQI3 [23], SQA1 [11,22], and bis[4-(monoaza-15-crown-5-ether)phenyl]squaraine [22] (SQA2) (Fig. 3). For all four dyes, the nonradiative processes are accelerated approximately at $\Delta f > 0.25$ (or $C > 0.45$); for SQI3 and SQA1, a very steep rise of k_{nr} is observed, whereas, the squaraines SQI1 and SQA2 exhibit a moderate increase of k_{nr}. On the other hand, in the low polarity region ($\Delta f < 0.25$ or $C < 0.45$), the values of k_{nr} are relatively small and scattered (scattering of the corresponding points of Fig. 3 shows that factors other than polarity affect k_{nr} in this region). This is consistent with the mechanism of squaraine fluorescence quenching in polar solvents established earlier [22,23] as the temperature-dependent nonradiative decay induced by solvent polarity and connected with intramolecular charge transfer and twisting relaxation. The more moderate quenching for SQI1 and SQA2 in comparison to the enhanced process for SQI3 and SQA1 could be explained by the presence of bulky side groups in SQI1 (long chains $C_{18}H_{37}$) and SQA2 (crown-ether macrocycles) involved in the intramolecular twisting motion, which could slow down the motion.

5.1.3. Photoisomerization

Upon flash photolysis of SQI1 with photoexcitation at its long-wavelength band, formation of a transient species is observed, which reversibly returns to the parent dye with following the exponential law and exhibits no effect of the presence of atmospheric oxygen (Fig. 4). By analogy with 1,3,3,1′,3′,3′-hexamethylindodicarbocyanine (HIDC)



which has the electronic structure equivalent to that of SQI [23] and undergoes *trans–cis*-photoisomerization from

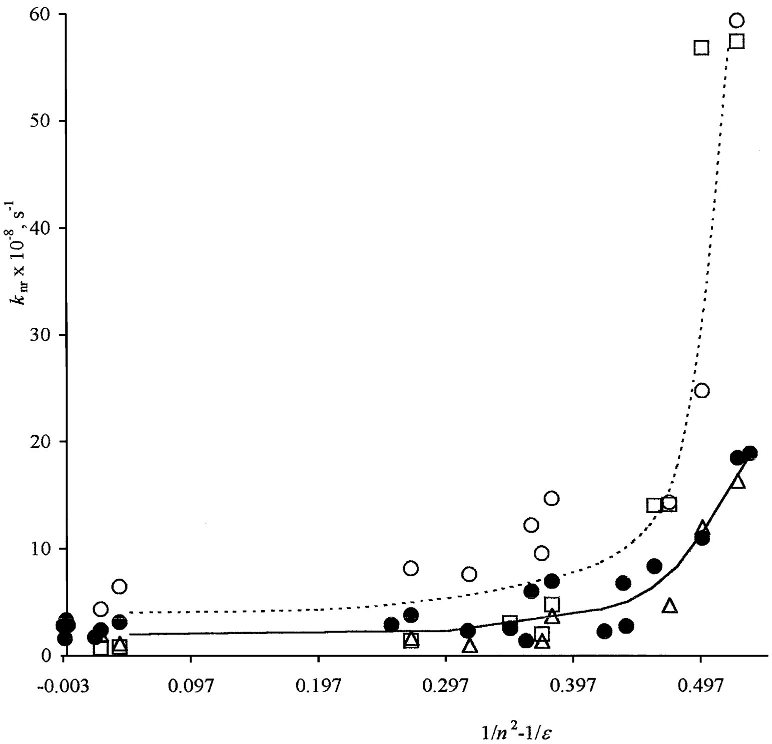


Fig. 3. Rate constant of nonradiative deactivation k_{nr} for SQI1 (filled circles; this work), SQI3 (open circles) [23], SQA1 (open squares) [11,22] and SQA2 (open triangles) [22] as a function of the solvent polarity parameter (Pekar factor) $C = 1/n^2 - 1/\varepsilon$.

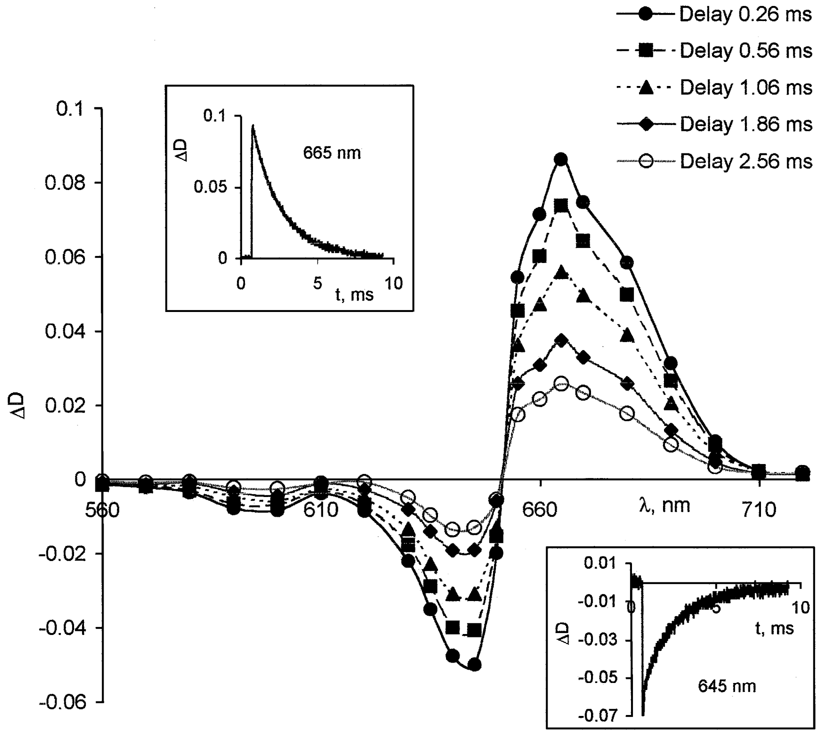
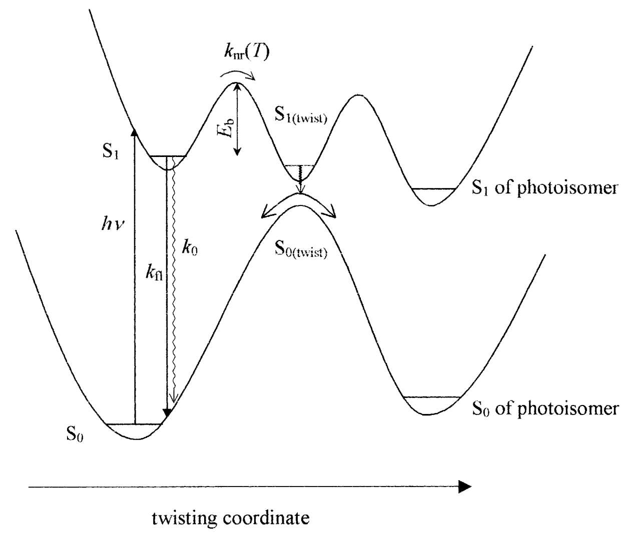


Fig. 4. Difference absorption spectra of the SQI1 photoisomer (in toluene) obtained by flash photolysis, with different delays after flash. Insets: decay kinetics of the photoisomer (recovery to the parent dye) at different wavelengths.

the S_1 state giving a *cis*-photoisomer [38,39], we assume that such photoisomerization occurs for SQI1 and proceeds around one of its free polymethine bonds with formation of a similar transient photoisomer. As can be seen in Fig. 4, its absorption spectrum (difference absorption maximum at 665 nm in toluene) is shifted to the red side with respect to the band of the parent squarylium indocyanine (bleaching maximum at 643 nm in toluene). The similar spectroscopic behavior is exhibited by the photoisomer of HIDC [38,39]. As the photoisomerization is connected with the twisting motion and the twisting about the free bond adjacent to the terminal heteroresidue of SQI was shown to be the most energetically favorable [23], we may reasonably suppose that the photoisomerization occurs around this bond. The lifetime of the photoisomer strongly depends on the solvent polarity and varies (at room temperature) from microseconds (in acetonitrile and methanol) up to hundreds of milliseconds (in alkanes). The efficiency of the intersystem crossing to the SQI1 triplet manifold was found to be very small, hence the $S_1 \rightarrow T$ deactivation channel may be neglected.

The photophysical processes in SQI molecule may be sketched by Scheme 1 analogous to Rullière's model for cyanine dyes [40]. Here, we suppose that $k_{nr}(T)$ corresponds to crossing the potential barrier E_b with formation of the twisted state, from which the fast nonradiative deactivation occurs giving the parent squaraine and its photoisomer in the ground states, and k_0 is the barrierless internal conversion $S_1 \rightarrow S_0$ via transition to vibronic sublevels of the ground state ($k_{nr} = k_0 + k_{nr}(T)$). Polar solvents decrease the potential barrier E_b, because its crossing is connected with growing dipole moment of the squaraine (intramolecular charge transfer) [22,23]. This is reflected in the rise of k_{nr} in high polarity solvents.

The effect of viscosity on k_{nr} is determined by the influence of η on the deactivation channels involving molecular motions. Since the viscous alcohols used in this work to check the viscosity effect are not too polar (TX100, *n*-decanol, *n*-hexanol and *tert*-butanol have $C < 0.45$), the enhanced nonradiative deactivation peculiar to polar solvents does not occur there. Whereas in nonviscous solvents (at $\ln(1/\eta) > -1$) a correlation between η and k_{nr} or $E_{a(nr)}$ is absent, in alcohols with high η ($\ln(1/\eta) < -1$) a very small trend of a decrease in k_{nr} and $E_{a(nr)}$ with growing η is observed, and the lowest k_{nr} and $E_{a(nr)}$ are reached in the most viscous solvent studied, TX100.



Scheme 1. Schematic presentation of photophysical processes in SQI molecules.

A polymer matrix (SE301) would be expected to restrict the molecular motion in SQI1, which could strongly affect the photophysical properties of the squaraine (decrease k_{nr} and $E_{a(nr)}$ and increase Φ_{fl} and τ_{fl}). The values of ν_{abs}^{max} and ν_{fl}^{max} of SQI1 in SE301 obey well the plots $\nu_{abs(fl)}^{max}$ versus $\phi(n^2)$ presented in Fig. 2a. At the same time, in spite of very high viscosity of SE301 (>10^5 cP [41]), the values of Φ_{fl}, τ_{fl}, k_{nr}, and $E_{a(nr)}$ in the polymer matrix are typical for nonviscous weakly polar solvents (in particular, alkanes, see Table 1). Therefore, we may infer that SQI1 molecules in the SE301 matrix do not sense the medium viscosity and have sufficient space for molecular motions leading to nonradiative deactivation.

5.2. SQI1 in heterogeneous media

5.2.1. Aggregation and deaggregation of SQI1

As mentioned above, SQI1 is insoluble in water. Upon addition of increasing amounts of water to solutions of SQI1 in methanol, dioxane, or other solvent miscible with water, aggregates of SQI1 are formed, which is revealed in the absorption spectra as broadening of the absorption band at the expense of a rise of relative intensity of the short-wavelength shoulder at 600 nm and of the long-wavelength part of the spectrum (>630 nm). The relative absorbance of the aggregates grows also with concentration of the dye (Fig. 5). Fluorescence of the dye simultaneously vanishes, showing that the aggregates are nonfluorescent.

The effect of additives of TX100 and other surfactants on the aggregates was studied in the dioxane/water mixture (1:1000 in volume). The aggregates were previously formed by addition of water (1000 parts) to a concentrated solution of SQI1 in dioxane (one part). Addition of TX100 at concentrations below the critical micelle concentration (CMC $= 2.7 \times 10^{-4}$ mol l^{-1} [42]) has a minor effect on the absorption spectra and fluorescent properties of the system: at [TX100] $< 10^{-4}$ mol l^{-1}, there is no fluorescence; in the premicellar region ($(1.7–2.5) \times 10^{-4}$ mol l^{-1}), the fluorescence appears and slightly increases, showing appearance of very small amounts of the monomeric dye associated with premicellar aggregates of TX100 as a result of slight decomposition of SQI1 aggregates (see inset (a) in Fig. 6). TX100 at concentrations above CMC causes decomposition of a major part of the dye aggregates into the monomer, which is exhibited as growing of the narrow absorption band of the monomeric dye and a steep rise of its fluorescence

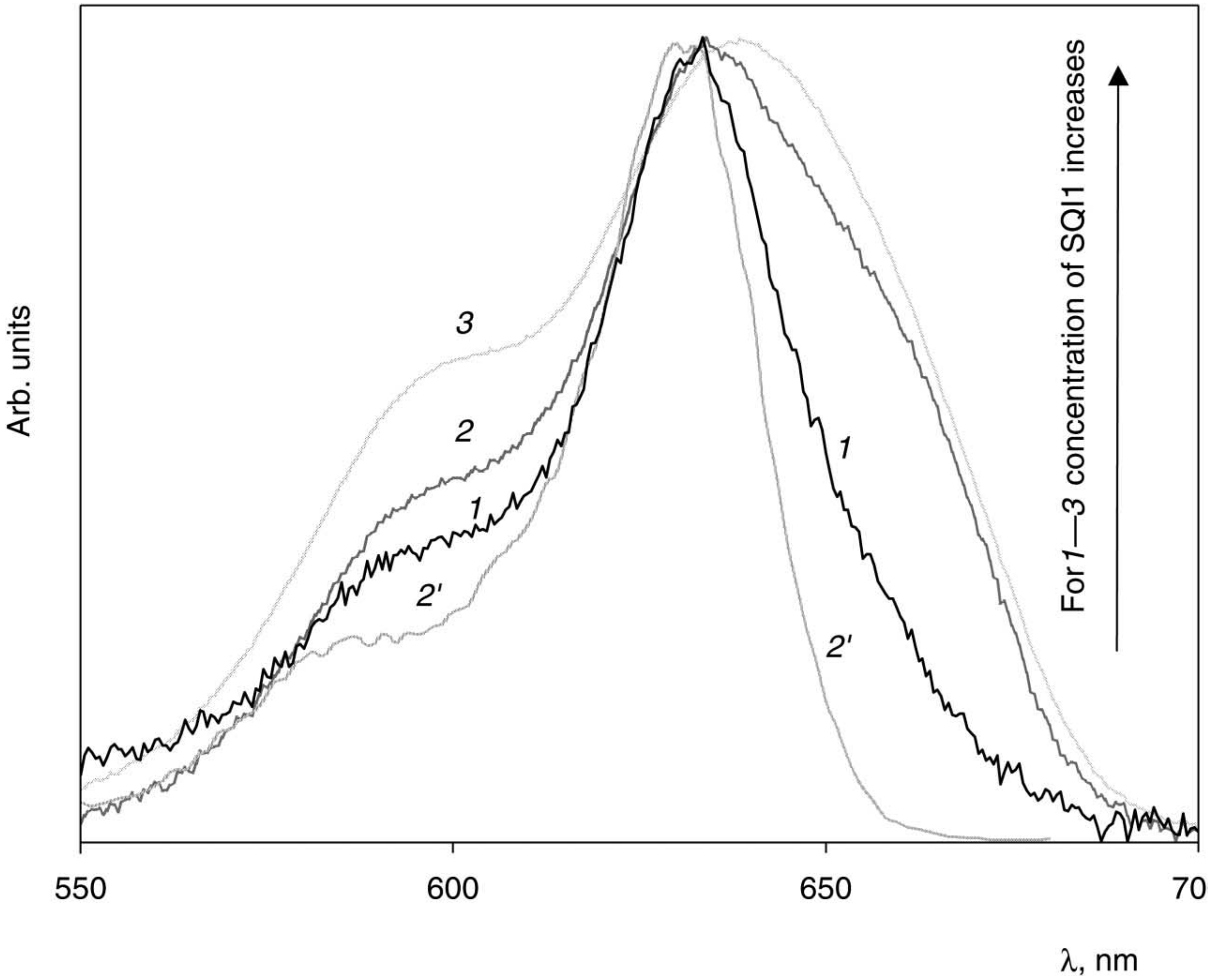


Fig. 5. Normalized absorption spectra of SQI1 (1–3) in MeOH/H_2O (5:2 v/v) solvent mixture as a function of dye concentration; 2′ is the fluorescence excitation spectrum of the solution having the absorption spectrum 2.

(Fig. 6 and inset (b)). Almost complete decomposition of the aggregates occurs at [TX100] $> 10^{-3}$ mol l^{-1}, and in the concentration range [TX100] $= 10^{-3}$–10^{-1} mol l^{-1} only moderate increase of the dye fluorescence is observed. Since SQI1 is insoluble in water, molecules of the monomeric dye are apparently associated with TX100 micelles, which protect them from aggregation. As can be seen in Table 1, the maxima of the absorption and fluorescence spectra of SQI1 in TX100 micelles are similar to those in neat TX100 (with a slight hypsochromic shift); the value of k_{nr} in TX100 micelles is also similar to that in neat TX100. This means that monomeric SQI1 molecules do not feel the presence of water in the micelles. At [TX100] $> 10^{-3}$ mol l^{-1}, the micelles are of the cylindrical type [43], which leads to stronger shielding of the extended dye molecules from the influence of water.

Addition of sodium dodecylsulfate, cetyltrimethylammonium chloride, AOT, or Brij 35 to the solution of SQI1 aggregates does not lead to deaggregation of the dye. The specific deaggregation effect of TX100 may be explained by the presence of phenyl groups in its structure (such groups are absent in other surfactants studied).

5.2.2. *SQI1 in isooctane/AOT/water reverse micelles*

Since SQI1 is insoluble in water and well soluble in isooctane, it can be present in the isooctane phase and at the isooctane/water interface, but not in the water phase. The fluorescence decay of the dye in the micelles with $w_0 = 0$ is nonexponential with a main decay component $\tau_{fl} = 2.5$ ns and a minor contribution of a short-lived component <0.5 ns. Increasing w_0 from 0 to 10 decreases Φ_{fl} (from 0.59 to 0.44), τ_{fl} (from 2.5 to 1.9 ns) and the contribution of the short-lived decay component. At $w_0 > 10$, all photophysical parameters of SQI1 remain essentially constant and are similar to those in neat isooctane. The nonexponential decay of SQI1 fluorescence points to a distribution of the dye molecules between different regions in the micelles, more hydrophilic (in the interface close to the water pool) and more hydrophobic (the hydrophobic domain of the interface and the isooctane phase). The short-lived component apparently

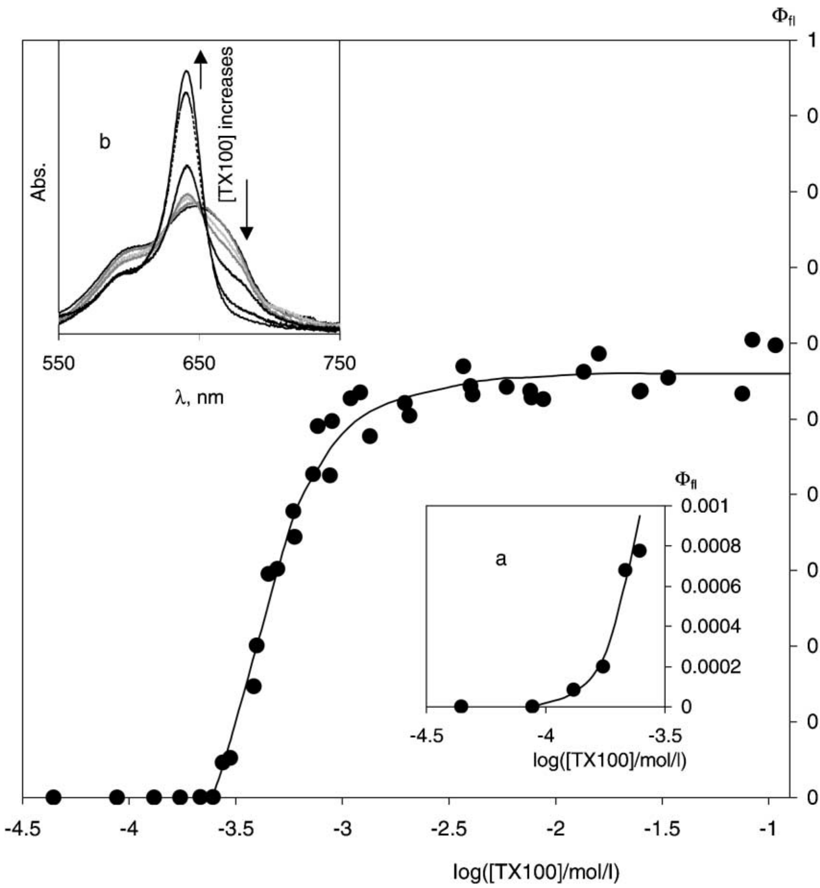


Fig. 6. Dependence of SQI1 fluorescence quantum yield ($\lambda_{ex} = 595$ nm) in dioxane/H_2O (1:1000) mixture on concentration of added TX100. Inset: (a) the same at low [TX100]; (b) absorption spectra of SQI1 in dioxane/H_2O (1:1000) mixture in the presence of different concentrations of TX100.

belongs to dye molecules present in the hydrophilic region, where quenching of the SQI1 excited state by water molecules is operative [11]. The enhancement of hydrophilicity of the interface with growing w_0 causes more molecules of hydrophobic SQI1 to move from the hydrophilic region of the interface to the hydrophobic domain and the isooctane phase. At high w_0, the most part of dye molecules is probably present in the isooctane phase, which is reflected in the similarity of λ_{abs}^{max}, λ_{fl}^{max} (635 and 643 nm, respectively), τ_{fl} (1.9 ns) and Φ_{fl} (0.44) to those in isooctane (see Table 1).

6. Concluding remarks

The study of photophysical characteristics of the squarylium indocyanine dye SQI1 in a wide set of solvents together with the analysis of the literature data on other squaraines shows the similarity in the spectral and photophysical behavior of squaraines having various structures (bis(cyclopentylamino)squaraine should be left aside, because it has no extended π-electronic system, its $S_0 \rightarrow S_1$ transition is strongly forbidden and buried under the absorption spectrum, which is located in the UV region [23]). Because, they all have the centrosymmetric conformation, their absorption and fluorescence maxima exhibit a trend of a linear correlation with the Lorentz–Lorenz function $\phi(n^2)$. This feature is inherent in the dispersive interactions of the nonpolar dye molecule with a solvent and is a consequence of a centrosymmetric conformation of squaraines.

The second common feature of squarylium cyanines is the action of the efficient deactivation channel for their fluorescent state in polar solvents, which involves intramolecular charge transfer in the excited state and twisting around free bonds. Comparison of the photophysical behavior of squarylium cyanines and classical cyanine cations shows that introducing the squaraine unit into the polymethine chain of cyanines changes their electronic structure (along with creating some steric effect) leading to intramolecular charge transfer from the donor side groups to the acceptor squaraine unit. The charge transfer is enhanced in the excited twisted state, giving rise to the solvent polarity induced nonradiative decay. Unlike squaraines, the intramolecular charge transfer is much less peculiar to cyanines (it appears only in the vicinity of 90° twisting on the excited state potential surface of isomerization [44]), and viscosity of the medium is a decisive factor determining the rate of their nonradiative decay [45,46]. Nevertheless, a photoisomerization process similar to that of cyanines was found for a squarylium indocyanine as a channel of the nonradiative deactivation of the S_1 state. The lifetime of the transient photoisomer of SQI1 strongly depends on solvent polarity, which could result from variation of the potential barrier for the thermal back isomerization in different solvents. Such photoisomerization should also occur for squarylium cyanines with other side heterocycles (however, it is impossible for bis(4-aminophenyl)squaraines and bis(4-hydroxyphenyl)squaraines, because of mirror symmetry of their molecules). In this respect, similarity in the photophysical behavior of squarylium cyanines and merocyanines can be shown: the intramolecular charge transfer and a strong increase in the nonradiative rate with solvent polarity take place in both cases [46].

The presence of long-chain hydrocarbon substituents imparts to SQI1 the ability for strong aggregation in aqueous solutions and the tendency to associate with micelles. The photophysical study of SQI1 in micelles (both normal and reverse) shows this molecule to be suitable as a probe for the refractive index (using the effect of n on the absorption and fluorescence spectra) and polarity (using their effects on the fluorescence lifetime and k_{nr}) of different regions of heterogeneous media. Taking into account high photochemical stability of squarilium indocyanines [21], SQI1 can find a practical application, e.g. in studies of polymers and biomacromolecules (we showed this in a study of the SE301 polymer matrix). The variable lifetime of the SQI1 photoisomer, which strongly depends on polarity of the medium, gives the additional benefit of using SQI1 as an indicator of solvent polarity.

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