

Photophysics of symmetrical biscyanines and their aggregations in solutions

V.I. Yuzhakov, K.G. Blinova, A.A. Ishchenko, L.V. Levshin,
S.V. Patsaeva, and A.V. Pekhota

M.V. Lomonosov Moscow State University

Received October 7, 2001

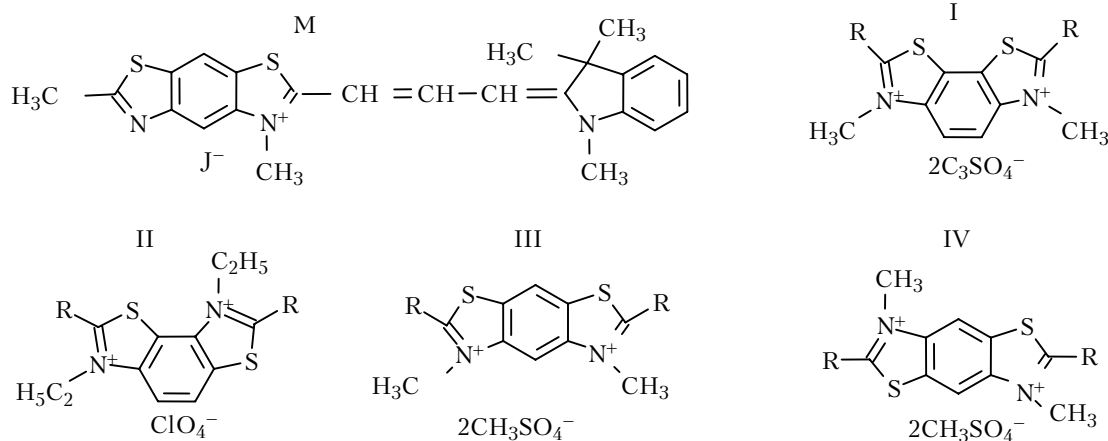
Photophysical processes and molecular aggregation of four biscyanine and parent dye solutions are investigated. The interaction energy of chromophores and the dipole transition moments of biscyanine dyes are calculated; the fluorescence lifetime and the quantum yield of the intersystem crossing are determined using the technique of nonlinear fluorimetry. Some conclusions are drawn on the causes of hypsochromic shift of the luminescence band of biscyanine dyes in polymer films under laser excitation.

Polymethine dyes (PD) are widely used as photosensitizing dyes, passive gates and active media of lasers, fluorescent probes, and new information carriers.^{1,2} A particular attention is paid to PD with two chromophores, because the intramolecular energy transfer from one chromophore to another makes them to efficiently re-emit this energy with a large "red" shift.² Cyanine dyes in the case of their aggregation also may prove to be excellent converters of light energy. However, the effect of the PD molecular structure (in particular, mutual arrangement of chromophores of biscyanine dyes) on the efficiency of the processes of their association, as well as on their luminescent properties, is not sufficiently studied by now.

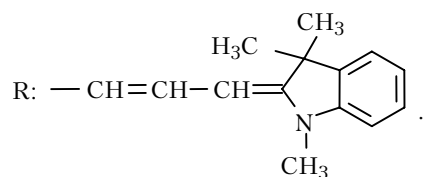
One more open problem is the study of nonlinear effects arising at the excitation of PD fluorescence by laser radiation. This problem is important, because practical applications of these dyes are based on the interaction of their molecules with the intense light fields.

This paper is devoted to the spectroscopic study of photoprocesses and molecular association in solutions of polymethine dyes – bifluorophores.

We have studied the aqueous and ethanol solutions, as well as polymer matrices (of polyvinyl alcohol) for the four chemically bonded dimers (I–IV) and the corresponding monomer dye (M):



where



These biscyanine dyes are synthesized based on isomeric dimethylbenzobistiazols and include two equivalent polymethine chromophores. According to data of X-ray structure analysis, the angle between the directions of chromophores in biscyanines I–IV is, respectively, 90, 126, 145, and 180° (Ref. 3).

We have studied solutions of biscyanines with the concentration from $7 \cdot 10^{-7}$ to $3 \cdot 10^{-3}$ mol/l. Absorption spectra of dye solutions were recorded with an Ultraspec 2000 (Pharmacia Biotech) spectrophotometer, and the spectra of fluorescence and fluorescence excitation were measured with a Jobin Yvon 3CS spectrofluorimeter. The ethanol solutions of biscyanine dyes were studied by the method of nonlinear fluorimetry based on the effect of fluorescence saturation. The effect of saturation of fluorescence of complex organic compounds at high-power laser excitation consists essentially in depletion of the ground state of molecules or, in other words, in the medium clearing-up, which manifests itself in the nonlinear dependence of fluorescence intensity on the excitation power. In Refs. 4–6, the approach was developed for using the emission spectra of organic compounds recorded under conditions of fluorescence saturation to determine the spectral-luminescent characteristics of these compounds. Application of this method is described thoroughly in Refs. 7 and 8; therefore, here we give only the basics needed for consideration of the obtained results.

The fluorescent parameter Φ is the ratio of the number of photons of dye fluorescence to the number of photons of solvent Raman scattering, which are emitted by the solution under study after excitation by a laser pulse: $\Phi = N_{fl}/N_{RS}$. The curve of fluorescence excitation is the dependence of the value reciprocal to the fluorescent parameter on the flux density of exciting radiation ρ . The degree of deviation of the dependence $\Phi^{-1}(\rho)$ from the non-saturated value is usually characterized by the factor of fluorescence saturation $\Gamma(\rho) = \Phi_0/\Phi(\rho)$, where $\Phi_0 = \lim_{\rho \rightarrow 0} \Phi(\rho)$. The dependence $\Gamma(\rho)$ is determined by the following spectral-luminescent parameters of an organic dye: absorption cross section at the excitation wavelength σ , lifetime in the excited state τ , and the quantum yield of the intersystem crossing ϕ_T . The theory of nonlinear fluorimetry allows one of these parameters to be found, if two others are known. In this paper, we used the method of nonlinear fluorimetry to determine the quantum yield ϕ_T of the intersystem crossing into the triplet state of biscyanine dyes. The absorption cross section at the dye excitation wavelength was determined from the absorption spectra, and the lifetime in the excited state was estimated from the kinetics of the fluorescence decay.

The absorption spectra of ethanol solutions of biscyanine dyes I–IV and the parent dye M are depicted in Fig. 1.

The absorption spectra of bis-dyes have bands shifted hypsochromically and bathochromically with

respect to the absorption band of the parent dye. The splitting of the absorption spectra of dyes containing two chromophores is explained based on the exciton theory.⁹ The interaction of chromophores in biscyanine leads to splitting of the dye excited state into two sublevels.

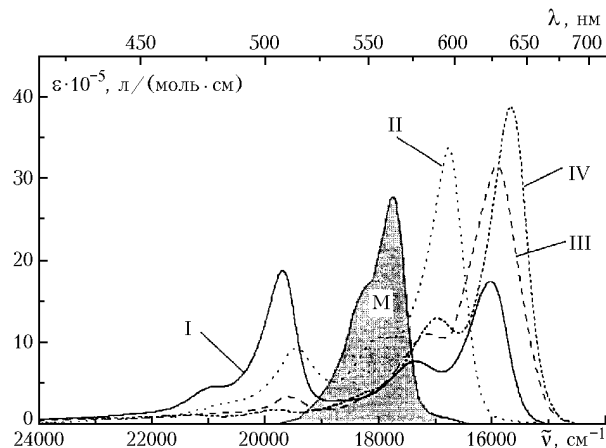


Fig. 1. Absorption spectra of biscyanines I–IV and the parent dye M in ethanol ($C \sim 10^{-6}$ M).

The selection rules for the allowed transitions in the system of energy levels of the molecule depend on the mutual arrangement of chromophores.¹⁰ If chromophores of the molecule are arranged at 90° angles to each other (biscyanine I), then the transitions to the upper and lower sublevels of the split excited states are equiprobable. If the angle between chromophores is 180°, as in biscyanine IV, then the transition to the upper level is forbidden, and only one band is observed in the absorption spectrum. This band is located on the longwave side from the absorption band of the parent dye. At the point dipole-dipole approximation of the exciton theory, the energy of chromophore interaction ΔE is described by the equation:

$$\Delta E = 2\mu^2 (\cos\alpha + 3 \cos\theta_1 \cos\theta_2) / r^3, \quad (1)$$

where μ is the dipole moment of the transition in the monomer molecule; α is the angle between the chromophores; θ_1 and θ_2 are the angles between the chromophores and the line passing through their centers; r is the distance between the chromophores. The ratio of the moments of shortwave and longwave transitions is connected with the angle between the chromophores by the following equation:

$$\frac{|\mu_{SW}|}{|\mu_{LW}|} = \frac{1 + \cos\alpha}{1 - \cos\alpha}. \quad (2)$$

The transition dipole moments μ were determined from the absorption spectra of dyes I–IV and M, and the energies of the chromophore interaction ΔE_{calc} and the angles α_{calc} between the chromophores were calculated by Eqs. (1) and (2) (see Table 1). To determine the angles entering into Eq. (1) and the distances between chromophores of biscyanine

molecules, these molecules were modeled in the SYBYL Program,¹¹ which allows one to determine the energetically most efficient spatial conformations of the molecules with the allowance for the solvent and the temperature.

Table 1. Characteristics of dyes I–IV and M (see the text for comments)

	μ , D		$\Delta E_{\text{exp}} \times 10^{-20}$, J	α_{calc} , deg	r , Å	$\Delta E_{\text{calc}} \times 10^{-20}$, J
	SW	LW				
M	13.15		–	–	–	–
I	11.44	12.77	7.29	95	8.95	7.28
II	3.80	14.73	5.17	126	8.50	9.88
III	1.69	16.87	7.37	145	9.60	7.30
IV	0.02	17.76	8.02	176	9.45	8.01

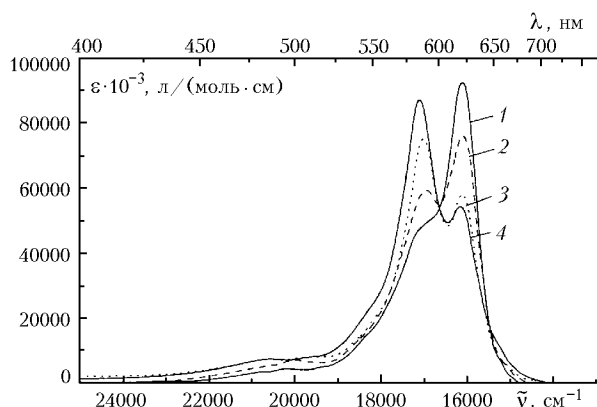


Fig. 2. Concentration dependence of aqueous solution of biscyanine III: $C = 1.0 \cdot 10^{-6}$ (1), $4.5 \cdot 10^{-6}$ (2), $4.5 \cdot 10^{-5}$ (3), and $4.5 \cdot 10^{-4}$ M (4).

For dyes I, III, and IV, a close agreement was achieved between the calculated values of the

interaction energy ΔE_{calc} and the experimentally observed splitting of the absorption spectra of dye solutions ΔE_{exp} . For all biscyanines, the angles between chromophores α_{calc} calculated by Eq. (2) agree with the data of X-ray structure analysis of these dyes.

As the concentration of aqueous solutions and polymer films of biscyanine and parent dyes increases, H-association of molecules is observed. This type of association can be attributed to appearance of a new band in the dye absorption spectra. This new band is located on the shortwave side of the absorption band of a diluted solution. The concentration dependence of the absorption spectra of the aqueous solution of biscyanine III is presented as an example in Fig. 2. It was found that the association of biscyanine dyes is more efficient than the H-association of the parent dye, and the larger is the angle between the chromophores, the easier is the association.

Addition of inorganic salts (NaCl or KCl) to the concentrated aqueous solutions of the parent dyes prevented from the process of H-association and stimulated J -aggregation. The latter type of the association leads to appearance of an intense and relatively narrow band in the longwave region of the absorption spectrum of dye solution. The absorption spectra of aqueous solutions of the dye M including 20 mM NaCl are depicted in Fig. 3 as functions of the dye concentration. For J -aggregation in solution, the degree of association n (i.e., the number of molecules in the composition of the J -aggregation) was determined. It was found that in the aqueous solution of the parent dye in the presence of an inorganic salt, the complex association occurs and the number of molecules in the association is $n = 4$.

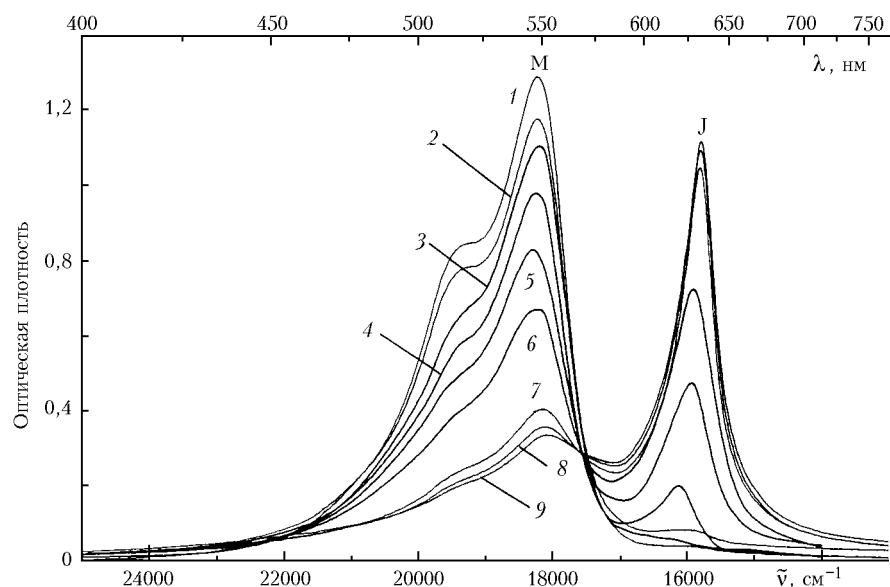


Fig. 3. Concentration dependence of absorption spectra of aqueous solution of the parent dye containing 20 mM NaCl: $C = 6 \cdot 10^{-7}$ (1), $5 \cdot 10^{-6}$ (2), $9 \cdot 10^{-6}$ (3), $1 \cdot 10^{-5}$ (4), $2 \cdot 10^{-5}$ (5), $3 \cdot 10^{-5}$ (6), $7 \cdot 10^{-5}$ (7), $8 \cdot 10^{-5}$ (8), and $1 \cdot 10^{-4}$ mole/l (9).

To study dyes by the method of nonlinear fluorimetry, the FEMTA copper-vapor laser was used as a source of pulsed excitation. Under the exposure of biscyanine solutions to laser radiation with the wavelength $\lambda_{\text{las}} = 511$ nm, absorption occurs mostly in the shortwave band. Because of the fast nonradiative relaxation from the upper to the lower sublevel of the split excited state of biscyanine dyes, only one fluorescence band is observed in the emission spectra, and this band is shifted bathochromatically with respect to the longwave absorption band. To determine the quantum yields of the IR biscyanine dyes by the method of nonlinear fluorimetry, we have studied the dependence of the emission spectra on the excitation power. Figure 4 depicts the emission spectra of biscyanine I at different flux density of the exciting radiation ρ . The saturation of fluorescence manifests itself in the change of the intensity ratio between the dye fluorescence bands (band A) and solvent Raman scattering band (B) at the increasing excitation power.

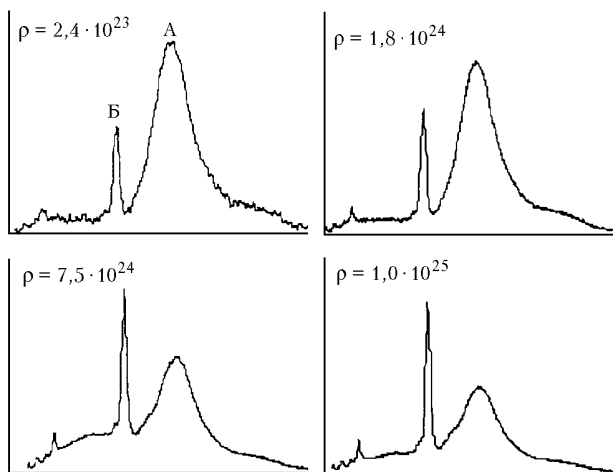


Fig. 4. Emission spectra of biscyanine I solutions in ethanol at different flux density of the exciting radiation ρ [$\text{cm}^{-2} \cdot \text{s}^{-1}$].

Table 2. Spectral-luminescent characteristics of I–IV and M dyes

	$\lambda_{\text{max}}^{\text{ab}}$, nm	$\lambda_{\text{max}}^{\text{fl}}$, nm	ΔE , cm^{-1}	$\sigma_{511} \cdot 10^{-16}$, cm^2	Φ_{T}	τ , ns
M	554	583		0.78	–	1.0
I	509. 626	643	3672	2.40	0.03	1.1
II	516. 596	612	2601	1.45	<0.01	0.6
III	510. 629	650	3710	0.56	0.08	1.3
IV	508. 639	658	4036	0.17	0.27	1.2

The spectral-luminescent characteristics of the studied dyes are given in Table 2. It was found that the probability Φ_{T} of transition of the biscyanine molecule into the triplet state is directly proportional to the energy of interaction between its chromophores. This dependence can be explained by the fact that as the interaction between the chromophores increases, the splitting of the excited singlet state increases, and, consequently, the energy difference between the singlet

sublevel and the triplet level becomes larger, thus leading to an increase in the IR conversion probability.

For the first time, we have studied the emission spectra of biscyanines incorporated into a polymer matrix under pulsed laser excitation. It was found that the dye fluorescence band shifts toward shorter waves by 10–12 nm as we pass from lamp to laser excitation. In our opinion, the shift of the fluorescence peak is explained by the peculiarity in saturation of fluorescence of dye molecules included in a rigid matrix. This peculiarity is connected with an inhomogeneous configuration broadening of the electronic levels of the biscyanine molecules. Fluorescence of molecules interacting with the ambient medium with a different force is saturated to different degree: the transitions having the largest absorption cross section and the longest lifetime of the excited state are saturated in the first turn, and this leads to the observed hypsochromic shift of the fluorescence band in the saturation mode.

The experimental studies suggested the following conclusions on the photophysical processes and molecular association in solutions of the biscyanine dyes. The spatial structure of molecules of polymethine dyes with two chromophores determines the efficiency of their interaction and thus affects considerably the spectral-luminescent properties of the dyes, as well as their capability to form molecular aggregations. The stronger the interaction between the chromophores determined by their mutual arrangement in biscyanine, the more probable is the intersystem crossing. The larger the angle between the directions of the chromophores in a molecule, the more efficient is the association of biscyanine dyes in aqueous solution and in the polymer film. The presence of an inorganic salt in the aqueous solution of the parent dye leads to a complex *J*-aggregation.

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