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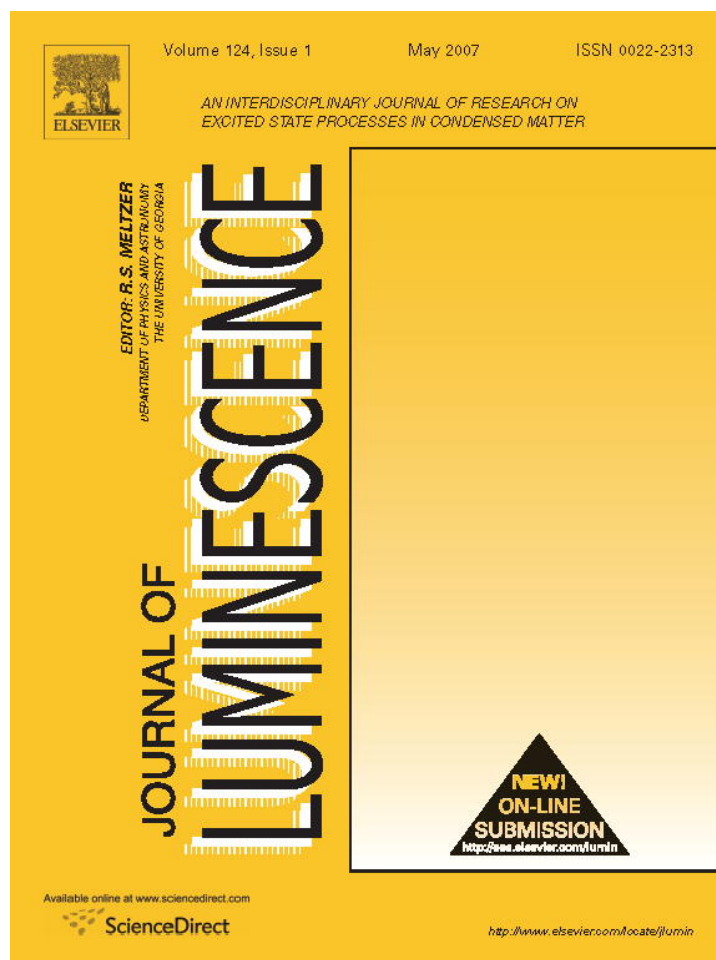


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# Fluorescence and solvatochromism of a merocyanine dye with a high quadratic polarizability in solutions and polymer films

Stanislav L. Bondarev<sup>a,\*</sup>, Sergei A. Tikhomirov<sup>a</sup>, Valeri N. Knyukshto<sup>a</sup>, Alexander A. Turban<sup>a</sup>, Alexander A. Ishchenko<sup>b</sup>, Andrey V. Kulinich<sup>b</sup>, Isabelle Ledoux<sup>c</sup>

<sup>a</sup>*Institute of Molecular and Atomic Physics, National Academy of Sciences of Belarus, Nezalezhnasti av. 70, Minsk 220072, Belarus*

<sup>b</sup>*Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Kiev 02094, Ukraine*

<sup>c</sup>*Laboratoire de Photonique Quantique et Moléculaire—Ecole Normale Supérieure de Cachan—61 avenue du président Wilson 94235 Cachan, France*

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## Abstract

The influence of medium polarity on the spectroscopic and photophysical properties of 2-[(2*E*,4*E*)-6-(1,3,3-trimethyl-2,3-dihydro-1*H*-2-indolyliden)-2,4-hexadienyliden]malononitrile (THDM) in solutions and polymer matrices is studied at room temperature and 77 K under conditions of steady-state and pulsed laser excitation. A large bathochromic shift of the absorption spectra observed upon an increase in the solvent polarity is caused by a strong increase of the dipole moment in the ground state ( $\mu_g = 7.6$  D) on going to an excited Franck–Condon state ( $\mu_{FC} = 33.5$  D). Based on the solvatochromic data, the quadratic polarizability was calculated to be  $\beta = (3.2 \pm 0.6) \times 10^{-28}$  esu, which is close to the experimentally determined value  $\beta_{exp} = (3.9 \pm 0.2) \times 10^{-28}$  esu. A strong narrowing of the fluorescence spectra in comparison with the absorption spectra at room temperature is observed upon an increase in the solvent polarity caused by a decrease in the bond length alternation parameter and by weakening of vibronic interactions in the singlet excited state. The mirror symmetry of the absorption and fluorescence spectra of THDM in ethanol at 77 K is explained by the increase of the electrostatic interactions between the solvent and merocyanine molecules. The dynamic fluorosolvatochromism of THDM in the picosecond range is caused by molecules reorientations of the polar environment occurring during a time period consistent with the dielectric relaxation time of these molecules.

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## 1. Introduction

The high quadratic polarizability  $\beta$  values of conjugated organic dyes are of great interest in connection with their nonlinear optical (NLO) properties in view of their potential use for second-harmonic generation (SHG) [1–5] and electro-optic polymer-based devices. Conjugated merocyanines with electron donor (D) and acceptor (A) substituents have attracted considerable attention because of their remarkable intramolecular charge transfer (ICT) properties and their related second-order NLO response, with attractive applications for polymer-made modulators,

amplifiers, elements for optical information recording, telecommunication devices, and optical switches [1–3,6–9].

The D and A substituents are connected with polymethine chain (PC) of alternating single and double bonds playing the role of electron transmitters for the ICT. The ICT efficiency of a merocyanine dye is changed when going from the ground  $S_0$  state to the excited singlet Franck–Condon (FC) state  $S_1^{FC}$  and the lowest fluorescent  $S_1^f$  state. A maximal quadratic polarizability  $\beta$  value evaluated from SHG measurements is shown for merocyanines due to their high oscillator strength  $f_e$  of a  $S_1^{FC} \leftarrow S_0$  transition, to low energy of this transition, and to a large difference  $\Delta\mu$  between the dipole moments of the ground ( $\mu_g$ ) and excited FC ( $\mu_{FC}$ ) states [9]. In the case of such highly conjugated ICT molecules,  $\beta$  is calculated in the context of a two-state

\*Corresponding author. Fax: +375 17 2840 030.

E-mail address: [bondarev@imaph.bas-net.by](mailto:bondarev@imaph.bas-net.by) (S.L. Bondarev).

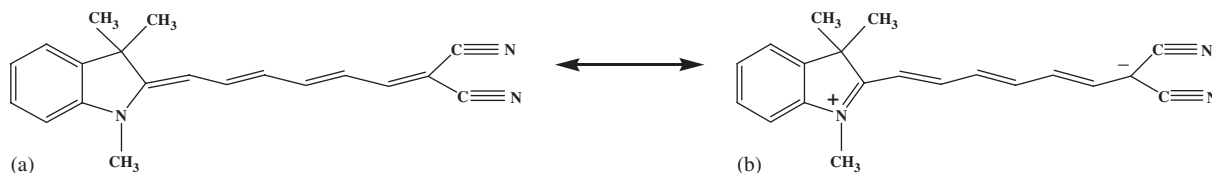


Fig. 1. Nonpolar (a) and bipolar (b) molecular structures of THDM.

model involving covalent (nonpolar) and zwitterionic (bipolar) states (see Fig. 1). The quadratic polarizability is found to correlate well with the bond length alternation (BLA) parameter of the PC whose value is minimal for the bipolar state of the merocyanine dye and maximal in the less polar state [10,11]. The  $\beta$  value can be determined, either directly from SHG measurements, or from indirect evaluation of  $\Delta\mu$  using the influence of environment polarity on absorption and emission spectra [12].

The electronic absorption spectra of merocyanines are characterized by intense long-wavelength bands, which are determined by  $(\pi, \pi^*)$  transitions  $S_1^{\text{FC}} \leftarrow S_0$ . As the length of the PC increases, the probability of the  $S_1^{\text{FC}} \leftarrow S_0$  transition increases, and binding each additional vinylene group to the PC is accompanied by a bathochromic shift of the long-wavelength absorption band. As in the case of asymmetric ionic cyanines, both the transition probability and the band shift strongly depend on the electronic asymmetry of the dye [13]. Upon electronic excitation, the dipole moment of a merocyanine molecule can either increase or decrease considerably. The sign of  $\Delta\mu$  affects the solvatochromic behavior of merocyanine dyes. An increase of the excited state dipole moment with respect to that of the ground state corresponds to a positive solvatochromism (bathochromic band shift upon the increase of solvent polarity), whereas a decrease leads to a negative solvatochromism (hypsochromic band shift when solvent polarity increases).

The fluorescence quantum yield  $\Phi_f$  and fluorescence lifetime  $\tau_f$  of some merocyanines, for example, the laser dye DCM [14,15], increases with solvent polarity, while  $\Phi_f$  of fluorine-substituted derivatives of DCM decreases [8,15]. It has been also revealed that  $\Phi_f$  and  $\tau_f$  of DCM and DA-substituted stilbenes increase at low temperatures and by inclusion into a polymeric matrix [15–17]. In the singlet excited fluorescent  $S_1^f$  state, the excited-state dipole moment of DCM exceeds that of the ground  $S_0$  state by 20 D, and a large Stokes shift ( $\sim 5000 \text{ cm}^{-1}$ ) between the maxima of the absorption and fluorescence spectra is observed in polar solvents [18]. The charge transfer from a locally excited state (i.e., from a FC planar state) to a dipolar twisted state (the so-called twisted intramolecular charge transfer (TICT) state [16,19]) in the DCM molecule in a polar solvent at 293 K occurs during a time interval smaller than 100 fs [20]. A further bathochromic shift of the fluorescence spectrum (fluorosolvatochromism) and the stabilization of the TICT conformation are determined by the properties of polar solvents, whose average solvation times are in the range 0.2–200 ps [21].

In this paper, we have studied the spectroscopic, photophysical, and nonlinear properties of 2-[(2*E*,4*E*)-6-(1,3,3-trimethyl-2,3-dihydro-1*H*-2-indolyliden)-2,4-hexadienyliden]malononitrile (THDM, Fig. 1) in solutions and polymer films using steady-state fluorescence and picosecond absorption spectroscopy at room and 77 K temperatures, as well as electric-field induced second-harmonic generation (EFISH) technique. Due to the large asymmetric charge distribution caused by a shift of the electron density from the electron donor fragment (3*H*-indolium) to the electron acceptor fragment (the dicyano group), this molecule may be considered as an asymmetric dye with a strong ICT. In this perspective, large dipole moments both in the ground and excited states of this dye are expected and may be connected with large changes in linear (steady-state and nonsteady-state solvatochromism, as well as quantum yield and lifetime of fluorescence) and nonlinear (quadratic polarizability  $\beta$ ) optical properties when going from nonpolar to polar liquid solutions.

## 2. Materials and methods

THDM was synthesized according to the method reported in Ref. [22]. Solvents of analytical grade were purified according to well-known procedures [23] with their purity being checked spectrally. The values of dielectric constants  $\epsilon$  and refractive indices  $n$  of pure solvents were taken from Ref. [23], and those of the mixed solvents ( $\epsilon_{12}$  and  $n_{12}$ , respectively) were estimated from the volume fractions ( $f$ ) of the co-solvents as

$$\epsilon_{12} = f_1 \epsilon_1 + f_2 \epsilon_2, \quad (1)$$

$$n_{12}^2 = f_1 n_1^2 + f_2 n_2^2, \quad (2)$$

where subscripts 1 and 2 represent the respective co-solvents. Solutions were not degassed since the photophysical and spectral characteristics of THDM measured in degassed and nondegassed solutions were identical. Polymer films were obtained from solutions of THDM with polyvinylethylal (PVE) in methylene chloride and THDM with polystyrene (PS) in toluene. The solutions were poured on glass substrates and evaporated.

Fluorescence studies were performed using a large-aperture setup described in Ref. [24]. The fluorescence quantum yield  $\Phi_f$  was measured with respect to  $\Phi_f$  of cresyl violet in methanol ( $\Phi_f = 0.65$  [25]). The optical density of the solutions at the excitation wavelength did not exceed 0.2. The values of  $\Phi_f$  were corrected taking into account refractive index changes of the solvent. The steady-state

absorption and fluorescence spectra of THDM are plotted as  $\varepsilon(\nu)/\nu$  (absorption) and  $I_f(\nu)/\nu^4$  (fluorescence) versus  $\nu$  ( $\text{cm}^{-1}$ ), in which the mirror symmetry rule for absorption and fluorescence spectra is most rigorously obeyed [26].

Transient absorption, bleaching, and gain spectra were recorded on a picosecond spectrometer [27]. Samples were excited by radiation from the second harmonic of a  $\text{Nd}^{3+}$ :phosphate glass laser ( $\lambda_{\text{exc}} = 528 \text{ nm}$ ) with a pulse duration of 4 ps. For probing, a picosecond continuum was used. The spectra were recorded at a dye concentration of  $\sim 2 \times 10^{-5} \text{ M}$  using a 1 mm thick cell. NLO molecular measurements were performed at 1.9  $\mu\text{m}$  in chloroform using the EFISHG technique [28]. Quantum chemical calculations were performed using semiempirical AM1 method with standard set of parameters [29].

3. Results and discussion

3.1. Spectroscopic and photophysical properties of THDM in liquid solvents and films at room temperature

The absorption and fluorescence spectra of THDM in *n*-hexane and dimethyl sulfoxide (DMSO) shown in Fig. 2 reveal a bathochromic shift (positive solvatochromism) when going from nonpolar *n*-hexane with dielectric constant  $\varepsilon = 1.9$  to polar aprotic DMSO ( $\varepsilon = 48.9$ ). The maximum values of bathochromic shifts are  $\sim 3000 \text{ cm}^{-1}$  for the absorption spectra and  $1160 \text{ cm}^{-1}$  for the fluorescence ones (Fig. 2 and Table 1). This means that the dipole moment of the THDM molecule is higher in the excited FC state than in the ground state, for which the nonpolar mesomeric form (Fig. 1a) dominates. It should be noted that the half-widths ( $\Delta\nu_{1/2h}^{\text{abs}}$ ) of the absorption spectra in solution (except the solution in DMSO) slightly differ from

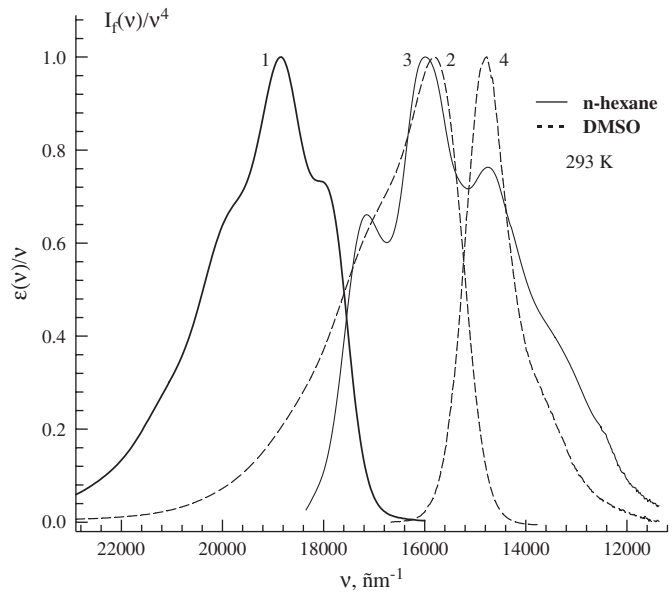


Fig. 2. Absorption (1, 2) and fluorescence (3, 4) spectra of THDM in *n*-hexane (1, 3) and DMSO (2, 4) at room temperature.

Table 1  
Spectral and photophysical characteristics of THDM in different solvents and polymer films at 293 K

Solvent	$\varepsilon$	$n$	$\lambda_{\text{max}}^{\text{abs}}$ (nm)	$\varepsilon_{\text{max}}^{\text{abs}}$ ( $\text{M}^{-1} \text{cm}^{-1}$ )	$f_e$	$\Delta\nu_{1/2h}^{\text{abs}}$ ( $\text{cm}^{-1}$ )	$\lambda_{\text{max}}^{\text{f}}$ (nm)	$\Delta\nu_{1/2h}^{\text{f}}$ ( $\text{cm}^{-1}$ )	$\Delta\nu_{\text{st}}$ ( $\text{cm}^{-1}$ )	$\Phi_f$	$\tau_f$ (ps)	$k_f \times 10^{-8}$ ( $\text{s}^{-1}$ )	$k_{\text{nr}} \times 10^{-8}$ ( $\text{s}^{-1}$ )
<i>n</i> -hexane	1.9	1.3749	532	68700	0.65	2800	625	3400	3050	0.001	$6 \pm 3$	1.7	1665
Toluene	2.4	1.4969	558	66800	0.7	3100	637	2700	2750	0.004	$22 \pm 4$	1.9	450
Chloroform	4.7	1.4433	582	76600	0.6	3110	657	1670	1960	0.013	$80 \pm 10$	1.6	62
Methylene chloride	8.9	1.4246	602	77700	0.8	3200	662	1300	1900	0.021	$100 \pm 20$	2.1	98
Ethanol	24.3	1.3613	611	86000	1.1	3200	665	1100	1800	0.061	$260 \pm 40$	2.3	36
acetonitrile	37.5	1.3442	609	78700	0.9	3100	663	1100	1750	0.041	$180 \pm 30$	2.3	53
DMSO	48.9	1.4783	632	98000	0.8	2400	674	1000	1500	0.150	$600 \pm 50$	2.5	14
PVE film			601			3300	660	1600	1800	0.180	$< 1000$ <sup>a</sup>	1.8	8
PS film			570			3200	645	2150	2300				

The error of determination of  $\varepsilon_{\text{max}}^{\text{abs}}$  amounted to  $\pm 2\%$ , while that of  $f_e$  and  $\Phi_f$  was within  $\pm (5-10)\%$ . The error of determination of the spectral characteristics was  $\pm 70 \text{ cm}^{-1}$ .

<sup>a</sup>The fluorescence decay in the PVE film at 293 K obeys a three-exponential law, and the table shows the average fluorescence lifetime.



those measured in PVE or PS films (Table 1). In contrast to the absorption spectrum of THDM in *n*-hexane, the spectrum of this dye in other solvents and polymeric films exhibits virtually no vibronic structure. The smoothing of the vibronic structure in the absorption spectra of THDM in moderately and strongly polar solvents (methylene chloride, ethanol, acetonitrile, and DMSO), as well as in an aromatic solvent, toluene, is explained by dipole–dipole interactions with the polar groups of the solvents and with strongly polarizing toluene molecules [1,13,30].

The oscillator strengths  $f_e$  of the long-wavelength transition  $S_0 \rightarrow S_1^{\text{FC}}$  of THDM in all solvents presented in the Table 1 were calculated according to the relation:

$$f_e = \frac{4.32 \times 10^{-9}}{n} \int \varepsilon_v dv, \quad (3)$$

where  $n$  is the refractive index of the solvent and  $\varepsilon_v$  is the molar decimal extinction coefficient ( $\text{M}^{-1} \text{cm}^{-1}$ ) of the chromophore. High values of  $f_e$  and  $\varepsilon_{\text{max}}^{\text{abs}}$  indicate that the  $S_0 \rightarrow S_1^{\text{FC}}$  transition is allowed, and is of ( $\pi$ ,  $\pi^*$ ) nature.

As shown in Fig. 2, the absorption and fluorescence spectra of THDM in *n*-hexane are qualitatively similar to each other. However, the fluorescence spectrum of this dye in DMSO is 2.4 times narrower than its absorption spectrum (Table 1). A strong narrowing of the fluorescence spectra was also observed for methylene chloride, ethanol, and acetonitrile. When considering Stokes shifts, i.e., the frequency intervals between the centers of gravity of absorption and fluorescence bands, they tend to decrease when going from nonpolar to polar solvents (Table 1). It should be noted that fluorescence spectra do not depend on excitation wavelength, while fluorescence excitation spectra do not depend on recording wavelength and coincide with absorption spectra.

Absorption and fluorescence spectra of THDM in *n*-hexane are very similar. Therefore, it can be supposed that the geometry of the molecule and the bond orders in the ground and excited states do not differ significantly. The vibronic structure of the THDM molecule in this solvent is determined mainly by the stretching vibrations of the carbon atoms of the conjugated system with a characteristic frequency of  $1300 \text{ cm}^{-1}$ . The BLA, i.e., the difference between the average length of the carbon–carbon single and double bonds, plays an important role in these molecules. Consequently, the electronic structure of THDM in *n*-hexane approaches that of polyenes and the contribution from the dipolar structure in the ground state of this compound is minimal. Indeed, absorption and fluorescence spectra of THDM in *n*-hexane are very similar to the corresponding spectra of well-known nonpolar compound  $\beta$ -carotene in isopentane [31]. In moderately polar solvents (methylene chloride) and strongly polar ones (acetonitrile, ethanol, and DMSO), the absorption and fluorescence spectra practically lose their vibronic structure and the half-widths of the fluorescence spectra become smaller than those of the absorption spectra by a factor of 2.5–3. In the strongly polarizing solvent toluene (whose

refractive index is high,  $n = 1.4969$ ) the vibronic structure is also absent. An increase in the solvent polarity also leads to a decrease in the BLA parameter [10], where both bond lengths and bond orders level off. This is especially true for excited fluorescence states. For this reason, the  $S_0 \leftarrow S_1^{\text{f}}$  transition is characterized by smaller changes in the equilibrium internuclear distances and, consequently, by a greater weakening of vibronic interactions than the  $S_0 \rightarrow S_1^{\text{FC}}$  transition. As a result, the fluorescence bands become narrower than the absorption bands. Notably, the fluorescence spectrum of the more polar PVE film is narrower than that of the nonpolar PS film ( $\Delta\nu_{1/2}^{\text{f}} = 1600$  and  $2150 \text{ cm}^{-1}$ , respectively), while the half-widths of the absorption spectra of both films are nearly the same (see Table 1).

As to the influence of solvent polarity on the energetic of THDM, it will be noticed that its fluorescence quantum yield  $\Phi_{\text{f}}$  increases from 0.001 in *n*-hexane to 0.15 in DMSO; i.e.,  $\Phi_{\text{f}}$  increases by 150 times. When going from *n*-hexane to DMSO, the lifetime  $\tau_{\text{f}}$  of the  $S_1^{\text{f}}$  state increases by two orders of magnitude (Table 1). The radiative  $k_{\text{r}}$  and nonradiative  $k_{\text{nr}}$  rate constants calculated from the fluorescence quantum yield and lifetime using

$$k_{\text{r}} = \frac{\Phi_{\text{f}}}{\tau_{\text{f}}}, \quad (4)$$

$$k_{\text{nr}} = \frac{1 - \Phi_{\text{f}}}{\tau_{\text{f}}} \quad (5)$$

are presented in the last columns of the Table 1. The solvent polarity has virtually no effect on the radiative rate constant, and, within the measurement error, the values of this parameter coincide. However, the nonradiative rate constants  $k_{\text{nr}}$  increase from  $14 \times 10^8 \text{ s}^{-1}$  in DMSO to  $1665 \times 10^8 \text{ s}^{-1}$  in *n*-hexane.

The effect of the solvent polarity on  $\Phi_{\text{f}}$  and  $\tau_{\text{f}}$  of the THDM molecule is similar to that of DCM [15,16]. In the case of the DCM molecule, a polar solvent stabilizes the emitting TICT conformation in the  $S_1^{\text{f}}$  state of the molecule, leading to a decrease in the probability of the nonradiative *trans*  $\rightarrow$  *cis* isomerization and, correspondingly, to an increase in  $\Phi_{\text{f}}$  and  $\tau_{\text{f}}$ . This fact is also supported by the increase in  $\Phi_{\text{f}}$  of the THDM-doped PVE film (see Table 1) when, as a result of an increase in the medium rigidity, the efficiency of the nonradiative processes due to photoisomerization decreases.

Attempts at characterizing transient absorption spectra of photoisomers in triplet or singlet excited states using picosecond spectroscopy in a variety solvents failed. Only time-resolved spectra of transient absorption, bleaching, and gain of THDM in different solvents with exponential lifetimes of the excited state  $S_1$  were detected. Besides, the steady-state absorption and fluorescence spectra before and after measurements were the same ones. Therefore, large nonradiative constants  $k_{\text{nr}}$  of THDM in nonpolar and polar solvents at 293 K have been interpreted in terms of high efficiently processes from excited *trans* isomer to

transient perpendicular quinoid form. The formation of *cis* isomers from this quinoid form is negligible, and the main channel of energy deactivation is connected with transitions to *trans* isomers in the ground state.

We also have tried to detect long-lived triplet states at 293 and 77 K using laser flash and steady-state phosphorescence experiments, respectively. However, our attempts to detect triplet states in THDM failed. With respect to that, the two simple merocyanines investigated in Ref. [32] show more efficient triplet-state formation, which is a manifestation of the presence of a low-lying singlet  $^1(n\pi^*)$  state. Apparently, this characteristic of simple merocyanines was not observed in THDM and more complex ones [6,13]. So, the main nonradiative process in THDM molecule is internal conversion  $S_1^f \rightarrow S_0$  determined by a reversible photoisomerization from excited *trans*<sup>\*</sup> to ground *trans* forms through transient perpendicular quinoid form.

### 3.2. Mirror symmetry between absorption and fluorescence spectra in ethanol at 77 K

The dramatic changes of the absorption and fluorescence spectra of THDM in ethanol solutions occur when going

from 293 to 77 K. As seen from Fig. 3, the absorption and fluorescence spectra at 77 K are characterized by a vibronic structure with a characteristic frequency  $\sim 1200\text{ cm}^{-1}$ . The absorption spectrum (centrum of gravity) shows a  $450\text{ cm}^{-1}$  bathochromic shift as compared to that at 293 K; its half-width decreases from  $3200\text{ cm}^{-1}$  at 293 K to  $1580\text{ cm}^{-1}$  at 77 K. It should be noted that at 77 K the fluorescence spectra do not depend on the excitation wavelength, while fluorescence excitation spectra do not depend on the recording wavelength and coincide with absorption spectra. Together with these strong spectroscopic changes, a large increase of  $\Phi_f$  and  $\tau_f$  was found on going from 293 to 77 K (see Table 2).

Absorption and fluorescence spectra of THDM in ethanol at 77 K (Fig. 3, curves 2 and 4) show practically ideal mirror symmetry. The distances between vibronic maxima of absorption and fluorescence spectra are in  $1170\text{--}1270\text{ cm}^{-1}$  range typical of polymethine dyes [13]. This mirror symmetry between absorption and fluorescence spectra was found only in ethanol frozen at 77 K as a transparent glass. In other solvents (toluene, acetonitrile, and DMSO) and PVE film spectra at 77 K display large half-widths and no vibronic structures. Besides, the fluorescence spectra of THDM in these media do depend on the excitation wavelength. So, the unusual spectroscopic behavior of THDM ethanol solutions at 77 K can be explained by the strong reorganization of solvent molecules around merocyanine molecule at low temperatures. That reorganization is confirmed by the smaller spectroscopic effects in the PVE solid film when going from 293 to 77 K, the reorganization of polymeric chains being impossible when cooled down to such low temperature values.

In general, the process of spectroscopic changes in THDM ethanol solutions due to temperature decrease can be interpreted as follows. As a result of the strong solvation of THDM molecules at 293 K, they display an electronic configuration that is intermediate between nonpolar (a) and bipolar (b) structures shown in Fig. 1. When temperature decreases, the intermolecular interactions between dye molecules become stronger as a result of a high order organization of solvent molecules in the field induced by the charge distribution of the chromophore. As a result, the dipolar structure (b) is formed in the ground  $S_0$  state. These dipolar structures (b) are characterized by narrow, nonsymmetrical vibronic bands, and a large decrease of vibronic interactions [13,33]. The solvent shell formed in the  $S_0$  state cannot be transformed into excited

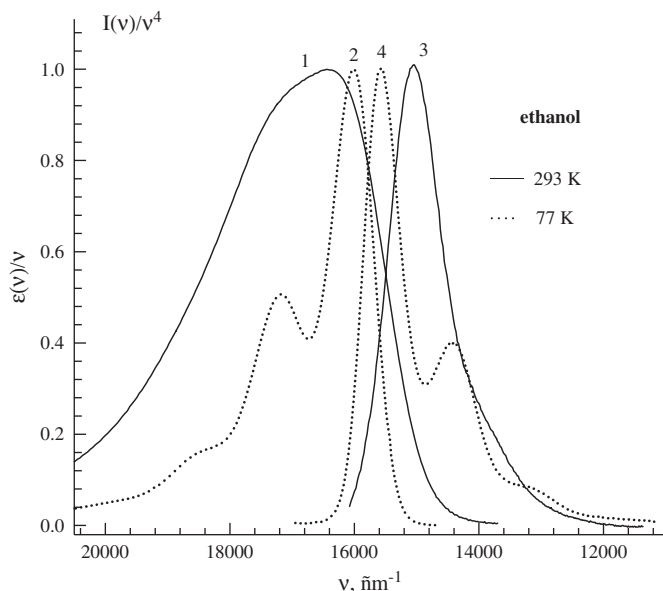


Fig. 3. Absorption (1, 2) and fluorescence (3, 4) spectra of THDM in ethanol at room temperature (1, 3) and 77 K (2, 4).

Table 2  
Spectroscopic and photophysical properties of THDM in ethanol at 293 and 77 K

$T$ (K)	$\lambda_{\text{max}}^{\text{abs}}$ (nm)	$\epsilon_{\text{max}}^{\text{abs}}$ ( $\text{M}^{-1}\text{ cm}^{-1}$ )	$f_e$	$\Delta\nu_{1/2h}^{\text{abs}}$ ( $\text{cm}^{-1}$ )	$\lambda_{\text{max}}^{\text{f}}$ (nm)	$\Delta\nu_{1/2h}^{\text{f}}$ ( $\text{cm}^{-1}$ )	$\Phi_f$	$\tau_f$ (ps)	$k_r$ ( $\text{s}^{-1}$ )	$k_{\text{nr}}$ ( $\text{s}^{-1}$ )
293	611	86000	1.10	3200	665	1100	0.061	$260 \pm 40$	$2.3 \times 10^8$	$36 \times 10^8$
77	624	—	—	1580	641	$\sim 1600$	0.69	$2800 \pm 100$	$2.4 \times 10^8$	$1.2 \times 10^8$

The error of determination of  $\epsilon_{\text{max}}^{\text{abs}}$  amounted to  $\pm 2\%$ , while that of  $f_e$  and  $\Phi_f$  was within  $\pm(5\text{--}10)\%$ . The error of determination of the spectral characteristics was  $\pm 70\text{ cm}^{-1}$ .

states due to the glass solid state of the medium. In that case, the  $S_1^{\text{FC}}$  and  $S_1^{\text{f}}$  energetic levels are close to each other. The same phenomena may occur for the  $S_0$  and  $S_1^{\text{FC}}$  levels. Therefore, the absorption and fluorescence spectra of THDM in ethanol at 77 K display small Stokes shift and practically ideal mirror symmetry (Fig. 3).

The directed reorganization and fixed environment of the solvent molecules in the merocyanine electric field takes place when going from the liquid to the glass solid state of ethanol. This leads to the formation of highly organized complexes of THDM molecules with ethanol at 77 K, a fact being confirmed by the fluorescence spectra independent of the excitation wavelength, and by the coincidence of fluorescence excitation and absorption spectra at various recording wavelengths. On the contrary, in the case of inhomogeneous oriented broadening, a bathochromic shift of the fluorescence bands occurs when the excitation wavelength increases [34]. Such an inhomogeneous broadening is absent for THDM spectra and, therefore, we are able to observe a good vibronic structure in the electronic bands. Obviously, the specific crystalline state of ethanol at low temperatures [35] promotes the formation of highly organized THDM/ethanol complexes.

### 3.3. Dipole moments $\mu_g$ , $\mu_{\text{FC}}$ and quadratic polarizability $\beta$

The large bathochromic shift of absorption spectra (Fig. 2) when increasing solvent polarity indicates that the dipole moment  $\mu_{\text{FC}}$  of the molecule in the FC excited state is greater than the THDM dipole moment  $\mu_g$  in the ground state, where a less polar mesomeric form (Fig. 1a) dominates. The ground state dipole moment  $\mu_g = 7.6$  D was calculated using the AM1 method [29]. The excited state  $\mu_{\text{FC}}$  dipole moment was determined by the well-known Lippert–Mataga method [36,37], which is based on the measurement of the absorption spectrum shift with respect to the solvent polarity function  $\Delta f$ :

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}, \quad (6)$$

where  $\varepsilon$  and  $n$  are the dielectric constant and the refractive index of the solvent. The Lippert–Mataga equation has the form [36,37]:

$$\nu_{\text{sol}} - \nu_0 = \frac{2\mu_g(\mu_g - \mu_{\text{FC}})}{hca^3} \Delta f, \quad (7)$$

where  $\nu_{\text{sol}}$  and  $\nu_0$  are the absorption maxima wavenumbers (centers of gravity) of the chromophore in the solvent and in vacuum (in  $\text{cm}^{-1}$ ), respectively;  $h$  is Planck's constant;  $c$  is the speed of light; and  $a$  is the Onsager radius, which is commonly taken to be equal to half of the length of the molecule. The Onsager radius  $a$  of the THDM molecule is 7 Å. In Fig. 4, the centers of gravity of the long-wavelength absorption bands of THDM in the eleven solvents are plotted versus  $\Delta f$ . The slope  $\text{tg } \alpha$  of the resulting straight line is equal to the term  $2\mu_g(\mu_g - \mu_{\text{FC}})/hca^3$  in Eq. (5). The section intercepted on the ordinate axis by the straight line

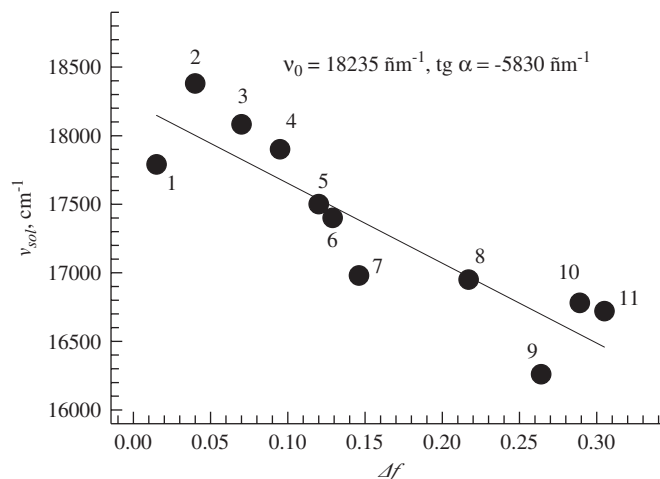


Fig. 4. Dependence of the centers of gravity of the absorption spectra on the polarity function of the solvents: 1, toluene; 2, methylene chloride + *n*-hexane (5:95); 3, methylene chloride + *n*-hexane (10:90); 4, methylene chloride + *n*-hexane (15:85); 5, methylene chloride + *n*-hexane (22:78); 6, methylene chloride + *n*-hexane (25:75); 7, chloroform; 8, methylene chloride; 9, DMSO; 10, ethanol; 11, acetonitrile.

determines the absorption frequency  $\nu_0$  of THDM in vacuum. The values of  $\text{tg } \alpha$  and  $\nu_0$  are given in the caption of Fig. 4. As a result of these calculations, we find that  $\mu_{\text{FC}} = 33.5$  D. Thus, upon transition from the ground state to the FC state, the dipole moment of the THDM molecule increases by 4.4 times and  $\Delta\mu = \mu_{\text{FC}} - \mu_g = 25.9$  D.

On the basis of the data obtained, one can estimate the quadratic polarizability  $\beta$ , using an equation derived from a two-level model [9]:

$$\beta = \frac{3e^2\hbar^2}{2m} \frac{W}{[W^2 - (2\hbar\omega)^2][(W^2 - (\hbar\omega)^2]} f_e \Delta\mu, \quad (8)$$

where  $e$  is the electron charge,  $\hbar$  is Planck's constant,  $m$  is the electron mass,  $W$  is the energy difference between the ground and the first excited states of the chromophore,  $\omega$  is the laser radiation frequency,  $f_e$  is the oscillator strength, and  $\Delta\mu$  is the difference between the dipole moments of the FC and the ground states.

The measurement of polarizability  $\beta_{\text{exp}}$  was performed in chloroform using EFISHG technique [28] at  $\omega = 9.9 \times 10^{14} \text{ s}^{-1}$  (1.9  $\mu\text{m}$ ). The values of  $W$  and  $f_e$  measured in chloroform are  $3.36 \times 10^{-12} \text{ erg}$  (589 nm) and 0.6, respectively. Taking into account that  $\Delta\mu = 25.9$  D, calculation derived from Eq. (6) gives  $\beta = (3.2 \pm 0.6) \times 10^{-28} \text{ esu}$ , a value compatible with the EFISHG value  $\beta_{\text{exp}} = (3.9 \pm 0.2) \times 10^{-28} \text{ esu}$ .

The polarizability  $\beta$  is calculated in the context of the two-level model of Ref. [9], in which the main process determining the value of this parameter is a one-dimensional ICT. Indeed, even in the ground state, the dipole moment of the THDM molecule is large (7.6 D), and, upon transition of the molecule to the excited state, this dipole increases considerably, reaching a value as high as 33.5 D.



Therefore, the transition  $S_0 \rightarrow S_1$  in the THDM molecule is mainly assigned to an ICT process. The large dipole moment of the molecule in the excited FC state (33.5 D) indicates that a charge as large as  $0.5 e^-$  (i.e., a half of the electron charge) is transferred from the electron donor group (3*H*-indolium) to the electron acceptor group (the dicyano group) over the whole length of the molecule (14 Å).

### 3.4. Dynamic fluorosolvatochromism

Time-resolved spectra of transient absorption, bleaching, and gain of THDM in ethanol at 293 K are presented in Fig. 5. This figure also shows steady-state absorption ( $\lambda_{\text{max}}^{\text{abs}} = 611$  nm) and fluorescence ( $\lambda_{\text{max}}^{\text{f}} = 665$  nm) spectra. Comparison between the gain spectra recorded at different delay times  $\Delta t$  after the exciting pulse shows that the spectra gradually narrow and are red-shifted. For  $\Delta t = 50$  ps, the maximum of the gain spectrum is observed at  $\lambda_{\text{max}} = 660$  nm. However, the transient absorption spectrum ( $\lambda_{\text{max}} = 480$  nm) does not exhibit any shift. The decay kinetic curves of the quantity  $\Delta D$  determined at different wavelengths of the time-resolved spectrum,  $\lambda = 480, 590$ , and  $660$  nm, are characterized by a lifetime of the excited state equal to  $260 \pm 40$  ps. The maximum of the gain spectrum at  $\Delta t = 500$  ps ( $\lambda_{\text{max}} = 663$  nm) is very close to the maximum of the steady-state fluorescence

spectrum ( $\lambda_{\text{max}}^{\text{f}} = 665$  nm). It is of interest to discuss the dynamics of the bathochromic shift of the THDM gain spectrum in ethanol. This can be done with the help of the function  $S_v(t)$ , which is commonly used in fluorosolvatochromism dynamic studies of dyes [20]:

$$s_v(t) = \frac{v(t) - v(\infty)}{v(0) - v(\infty)}. \quad (9)$$

Here  $v(t)$  is the wavenumber of the maximum gain frequency (in  $\text{cm}^{-1}$ ) at a time  $t$ ;  $v(\infty)$  is the maximum of the steady-state fluorescence band; and  $v(0)$  is the maximum of the fluorescence spectrum for  $t = 0$ , which is well approximated by the fluorescence spectrum of the dye in a normal hydrocarbon solvent, e.g., in 2-methylbutane [21]. In our case, for such a spectrum, we chose the fluorescence spectrum of THDM in *n*-hexane ( $\lambda_{\text{max}}^{\text{f}} = 625$  nm), which can be considered as a spectrum of emission from a locally excited (or FC) state.

The dependence of  $S_v(t)$  on  $\Delta t$  for THDM in ethanol is shown in the inset of Fig. 5. This dependence is well approximated by two exponentials with characteristic times  $\tau' = 9.1$  ps and  $\tau'' = 180$  ps. It is of interest to compare these data with the dielectric relaxation times of ethanol determined in Ref. [38] by a microwave method:  $\tau_1 = 1.63$  ps,  $\tau_2 = 8.97$  ps, and  $\tau_3 = 163$  ps. The authors of Ref. [38] connect, respectively, the time  $\tau_1$  with the time of breaking and formation of a hydrogen bond, the time  $\tau_2$

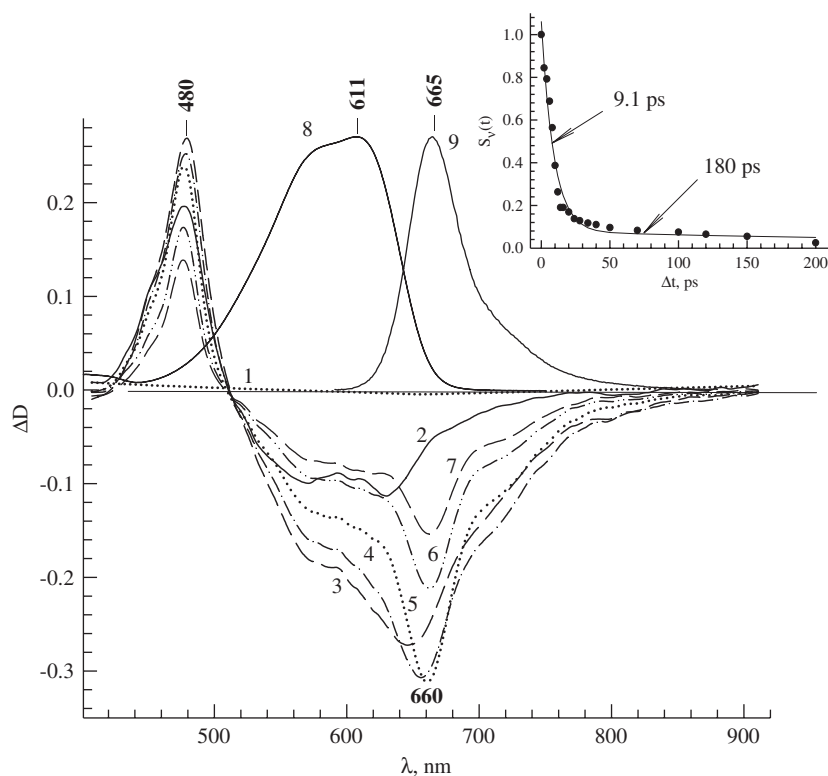


Fig. 5. Picosecond (1–7) and steady-state (8–9) spectra of THDM in ethanol at room temperature ( $\Delta D$  is the change in the optical density and  $\Delta t$  is the delay time after the exciting pulse at  $\lambda_{\text{exc}} = 528$  nm and  $E = 10 \mu\text{J}$ );  $\Delta t = 0$  (1), 6 (2), 10 (3), 15 (4), 50 (5), 120 (6), 200 ps (7). The steady-state absorption (8) and fluorescence (9) spectra are plotted in relative units. The inset shows the dependence of the function  $S_v(t)$  on the delay time  $\Delta t$ .

with the reorientation time of a monomer molecule, and the time  $\tau_3$  with the rotation time of an ethanol cluster. Our times  $\tau'$  and  $\tau''$  may correspond to  $\tau_2$  and  $\tau_3$  values. We were unable to estimate the time  $\tau_1$  because the time resolution of our picosecond spectrometer was insufficient for this purpose.

Gain spectra of THDM in *n*-hexane and toluene display no dynamic solvatochromism, contrary to the case of ethanol. The gain spectra of THDM in acetonitrile and DMSO vary with time in the same way as in ethanol in accordance with the dielectric relaxation times characteristic of these solvents [21]. In contrast to liquid solvents, the decay kinetics of  $\Delta D$  for THDM in a PVE film is approximated by at least three exponentials and the average decay time amounts to  $\sim 1$  ns. It seems that the film contains no less than three sets of emission centers with different conformations.

#### 4. Conclusions

From these investigations of the medium polarity influence on the spectral and photophysical properties of the THDM merocyanine dye, displaying a high quadratic polarizability, we show that:

1. A large bathochromic shift in the absorption spectra of THDM, as observed when increasing solvent polarity, which amounts to  $\sim 3000 \text{ cm}^{-1}$  when going from *n*-hexane to DMSO, is related to a large difference between the dipole moments of a molecule in the ground and the excited FC states ( $\Delta\mu = \mu_{\text{FC}} - \mu_{\text{g}} = 25.9 \text{ D}$ ) and, correspondingly, to a high value of the dipole moment  $\mu_{\text{FC}} = 33.5 \text{ D}$ .
2. Comparison between the experimentally determined quadratic polarizability  $\beta_{\text{exp}} = (3.9 \pm 0.2) \times 10^{-28} \text{ esu}$  and the polarizability calculated according to the two-level model  $\beta = (3.2 \pm 0.6) \times 10^{-28} \text{ esu}$  shows that the quadratic polarizability of the THDM molecule mainly originates from ICT processes. A very good agreement between these two independent methods for  $\beta$  evaluation is quite remarkable. The high value of  $\beta_{\text{exp}}$  allows to consider THDM as a promising material for creating various NLO devices.
3. An increase in the medium polarity leads to a narrowing of the fluorescence spectra and to an increase in the fluorescence quantum yield, which is explained by a decrease in the BLA parameter, as well as by weakening of vibronic interactions in the singlet excited state of the THDM molecule.
4. We show for the first time that the mirror symmetry of the absorption and fluorescence spectra of THDM in ethanol at 77 K is explained by the increase of the electrostatic interactions between the solvent and merocyanine molecules.
5. The dynamic fluorosolvatochromism of THDM in the picosecond range results from reorientations of surrounding polar solvent molecules occurring during time intervals consistent with the dielectric relaxation times of the solvent molecules.

A more detailed study of the mechanisms of initial spectral and kinetic changes, as well as charge transfer processes in the THDM molecule upon its transition from the FC state to lower lying excited states, requires the performance of experiments in the femtosecond time range.

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