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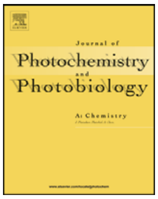

Structure and fluorescence properties of indole cyanine and merocyanine dyes with partially locked polymethine chain

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ABSTRACT

The fluorescent properties of a series of symmetric cationic cyanine dyes and merocyanines with trimethylene bridge connecting N-atom of the indole residue with α-position of the polymethine chain have been explored in detail. It is shown that the constraining group influences their fluorescent properties both by steric and electronic effects. It revealed an essential decrease of the fluorescence quantum yields of the constrained symmetric cyanine dyes in comparison with those of their analogues without bridge group in their chromophore. This effect diminishes essentially at polymethine chain lengthening. In the case of merocyanines the bridge group can cause a decrease as well a substantial increase of their fluorescence quantum yields depending on their type of solvatochromism and solvent polarity. The conclusions made on the basis of the experimental data are in good agreement with the results of semiempirical quantum-chemical calculations.

1. Introduction

Cyanine dyes with completely or partially locked polymethine chain get higher photo- and thermostability [1–3]. These features are crucial for their application in photorefractive or photoconductive media [4]. An increase of chromophore rigidity is also the common way of enhancement of dyes' fluorescence quantum yields Φ_f since the probability of the excited state nonradiative deactivation via intramolecular rotation about the polymethine chain bonds decreases [1–3,5]. However the latter is not a general rule. For example, merocyanine (**1**) (Scheme 1), the analogue of widely used as a fluorescent probe dye **MC-540**, was in detail studied in the work [1].

The authors of [1] have ascertained that incorporating the C-2=C-3 double bond into a small ring, while preventing isomerization at this site, has not had the desired effect of increasing the fluorescence quantum yield of dye **1** in comparison with **MC-540**. They have shown that two important factors combine to limit the effectiveness of this strategy. The constraining propyl chain causes sufficient structural distortion (the torsion angle N-1–C-2=C-3–C-4 in dye **1** is much greater than in the chromophore of **MC-540**) to seriously perturb the absorption spectrum and thereby to decrease the radiative rate constant. The second problem is that, having blocked isomerization at the first double bond, rotation occurs around the C-4=C-5 double bond. Although the yield of the resultant *cis*-isomer is substantially less than found for the parent dye, the rate constant for overall internal conversion remains competitive with both radiative decay and intersystem crossing to the triplet manifold. The inference was made that necessary to prevent isomerization by an alternative methodology for creation of clinically viable merocyanine dyes with high Φ_f values.

However, the constraining groups in the polymethine chain influence the spectral-luminescent properties of cyanine dyes also by their electronic effect. This issue is well studied for their absorption spectra [3]. The fluorescent researches are rare and unsystematic. Only the influence of the excited state chromophore planarity violations on the fluorescent properties of dyes is well-developed problem in this field (TICT and PICT states) [6,7].

The goal of the present work was an elucidation of the influence of trimethylene bridge group on the fluorescent properties of

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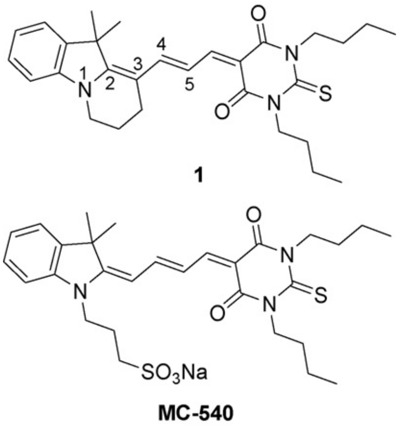


Scheme 1.

polymethine dyes **2**–**10** (Scheme 2) depending on their chemical structure and solvent polarity.

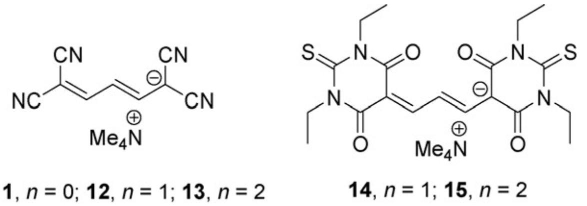
2. Materials and methods

The regularities in the absorption spectra of dyes **2**–**10** were described in Ref. [8].

The mathematical treatment of the fluorescence bands of dyes **2**–**10** by the method of moments [9] has allowed us to characterize quantitatively their position (M_f^{-1}) and form (σ^f, γ_1^f, γ_2^f, F^f). The parameter M^{-1} reflects the average position of the band (on the wavenumber scale it represents the band gravity centre: $\tilde{\nu} = 10^7/M^{-1}$). The parameter σ^f characterizes deviation of spectral band points from the gravity centre. Hence, it allows making a reliable quantitative comparison of the bandwidth regardless of the band shape that is an advantage over the traditionally used bandwidth at half-height. The asymmetry coefficient γ_1^f, the excess coefficient γ_2^f, and the fine structure coefficient F^f provide additional information on the band shape. The moments of the fluorescence and absorption bands were determined accordingly in coordinates $I_f(\tilde{\nu})/\tilde{\nu}^4$ and $I_a(\tilde{\nu})/\tilde{\nu}$ (I_f and I_a are intensity of fluorescence and absorption and $\tilde{\nu}$ is wavenumber) in which the law of mirror symmetry is most rigorously obeyed [9].

The deviations of the fluorescence band maxima D_λ^f and centres D_M^f were evaluated for merocyanines (**5**–**10**) using the spectral data of the parent cationic dyes **2**–**4** and anionic dyes **11**–**15** [10,11] (Scheme 3).

The spectral-luminescent properties and the electronic structure of cationic dyes **16**–**18** and merocyanines (**19**–**24**) (Scheme 4) necessary for analysis of the influence of the constraining propyl group on the properties of compounds **2**–**10** were studied in Refs. [5,9–11].

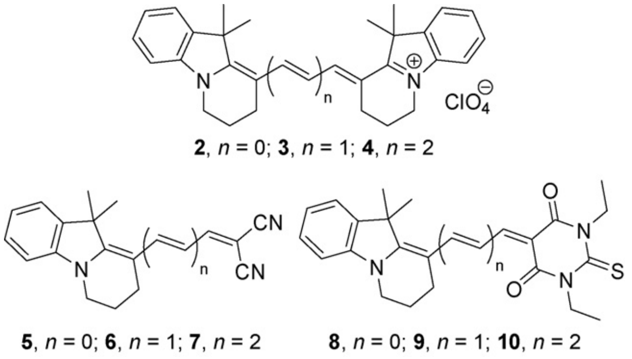


Scheme 3.

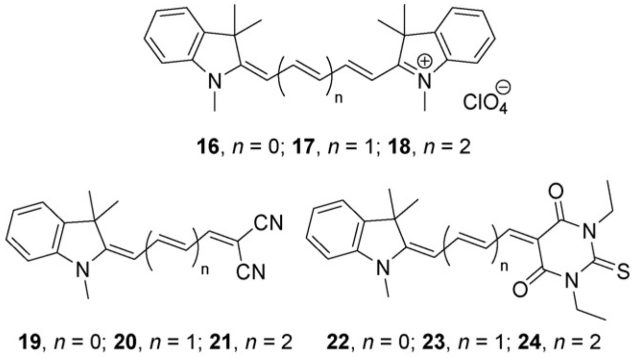
Dyes **2**–**10** were refined by chromatography on “Merck” silica gel 60 or neutral aluminium oxide 80. Their purity was checked by TLC-control (Silufol UV-254, CH_2Cl_2 as the eluent). Solvents were purified according to the known techniques [12]. Solutions of merocyanines were not degassed since the fluorescent characteristics for degassed and non-degassed solutions were shown to be identical. The fluorescence spectra were measured on the large-aperture setup high-transmission spectrometer described in Ref. [13]. The fluorescence quantum yields Φ_f of merocyanines (**5**–**10**) were measured in toluene and ethanol in relation to the Φ_f values of cresyl violet in methanol ($\Phi_f = 65\%$ [14]) and rhodamine 6G in ethanol ($\Phi_f = 95\%$ [15]). The Φ_f values of cationic dyes **2**–**4** were measured in relation to the Φ_f values of the corresponding dyes **16**–**18** in ethanol [9] ($\Phi_f = 3\%$, 25%, and 28%). The values of Φ_f were corrected taking into account refractive indexes of the solvent. The fluorescence spectra of dyes **2**–**4** and **16**–**18** were also measured in polymer films. The film samples with thickness of 70–80 μm (their thickness was measured with help of interference microscope MII-4 (Russia)) were located at the angle 45° to the excitation beam in order to avoid getting of excited light to the photomultiplier. The fluorescence light was measured in “a transmitted light scheme” without interfering influence of excited light. All fluorescence spectra were measured within concentration range 5×10^{-7}–3×10^{-6} mol/L. It was shown that all studied dyes did not form aggregate at these conditions.

The quantum-chemical calculations of the electronic structure of the dye molecules were performed for gas phase by AM1 method with a standard set of parameters [16]. Geometry optimizations with the use of limited Hartree–Fock method and Polak–Ribiere algorithm with an accuracy of 0.001 kcal Å^{-1} mol^{-1} had been preliminary carried out. Geometry optimization of the excited states was not carried out.

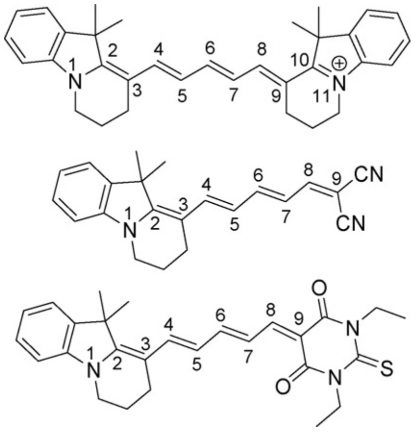
For analysis of bond length (bond order) alternation in the polymethine chain of the dyes the widely used parameters BLA (bond length alternation) and BOA (bond order alternation) [17] were



Scheme 2.



Scheme 4.



Scheme 5.

evaluated. Charge alternation in the chromophore of dyes both in the ground S_0 and excited S_1 states was calculated by the formula:

$$\Delta q_{\mathrm{av}} = \frac{\Delta q_{\Sigma}}{m} = \frac{\left(\sum_i |q_i - q_{i+1}|\right)}{m},$$

where q_i and q_{i+1} are charges on the neighbouring atoms of chromophore, m is a number of bonds for which alternation was evaluated. The parameter Δq_{av} was estimated for the chromophore N-1–C-2–C-3···–C-10–N-11 for cationic polymethines and N-1–C-2–···–C-9 for merocyanines (Scheme 5).

A value of quadratic changes of bond orders at excitation (δ) represents the vibronic interactions (VI) in absorption transition $S_1^{\mathrm{FC}} \leftarrow S_0$ [5]. It was evaluated for compounds **2**–**10**, **16**–**24** taking into account all bonds of a molecule except C–H ones.

$$\delta = \sqrt{\sum_{i=1}^{m} (P^{*} - P)_i^2},$$

where i is the bond number, m is the bond count, $P^{*} - P$ is a difference of i-bond orders in the excited and ground states.

3. Results and discussion

3.1. Fluorescent properties of cationic cyanine dyes 2–4

The spectral parameters $\lambda_{\max}^{\mathrm{f}}$, M_{f}^{-1}, σ^{f}, γ_1^{f}, γ_2^{f}, and F^{f} alongside with the fluorescence quantum yields Φ_{f}, the Stokes shifts SS_{λ} and SS_M, and the deviations D_{λ}^{f} and D_M^{f} are collected in Table 1.

Compounds **2**–**4** possess weak negative solvatofluorochromism typical for cationic cyanines (Table 1). Its range is less than the corresponding range of solvatochromism. It is well known that in the fluorescent state solvation of cationic cyanine dyes is considerably weakened and the influence of solvent polarity on their fluorescence spectra is determined mainly by the dispersion interactions (Bayliss function) [5,9]. Weakening of solute–solvent intermolecular interaction (IMI) in the fluorescent state of dyes **2**–**4** could be also presupposed from the corresponding values of Δq_{av} and $\Delta q_{\mathrm{av}}^{*}$ (Table 2).

The fluorescence bands of compounds **2**–**4** undergo long-wavelength shift with respect to those of dyes **16**–**18** (see Table 1 and [9]). The induced by constraining trimethylene group shifts are very close for their fluorescence and absorption spectra. In high-polar ethanol and DMF these shifts are somewhat less for the fluorescence bands (cf. the band centres M_{a}^{-1} [5,8] and M_{f}^{-1} (Table 1, [9])). As a result the values of Stokes shifts SS_M of dyes **2**–**4** are smaller than those of compounds **16**–**18**.

The fluorescence bands of dyes **3** and **4** (Table 1) are narrower, more asymmetric and more peaked, than the corresponding bands of compounds **16**–**18** [9] (cf. the parameters σ^{f}, γ_1^{f}, and γ_2^{f}). Since solute–solvent IMI weakly affect their fluorescent bandwidth, it is necessary to assume that the constraining group causes a decrease of VI in the fluorescence transition $S_1 \rightarrow S_0^{\mathrm{FC}}$ of dyes **3** and **4**, like it takes place in their absorption transition [8].

The fluorescence bands of dye **4** are narrower than its absorption bands in all used solvents (Fig. 1, Table 1, [8]). For vinylogue (**3**) it holds only in high-polar DMF and ethanol; in dichloromethane a slight growth of its fluorescence bandwidth occurs ($\sigma^{\mathrm{f}} > \sigma^{\mathrm{a}}$). But these effects are very slight and the absorption and fluorescence bands of dye **3** are close to mirror-like (Fig. 1).

Vinylogue (**2**) occupies special position. Owing to a strong molecule planarity distortion its fluorescence bands are substantially broader, symmetric, and sloping than those of its analogue **16**. Similarly to its absorption bands they are shifted in long-wavelength range in comparison with the spectral bands of dye **16** more than it takes place for the higher vinylogues. It results in a decrease of the first vinylene shifts (in a pair of dyes **2**–**3**) (Table 1). In contrast to the higher vinylogues the fluorescence bands of dye **2** are substantially broader than the absorption ones (Fig. 1). The analysis of the band form allows us to infer that the broadening of the fluorescence bands of dye **2** occurs due to strengthening of the VI in the fluorescent transition $S_1 \rightarrow S_0^{\mathrm{FC}}$ in comparison with the absorption transition $S_1^{\mathrm{FC}} \leftarrow S_0$ that becomes apparent in a growth of intensity of the higher vibronic transitions (Fig. 1).

The constrained chromophore, the greater values of the oscillator strength, a decrease of the VI should promote a growth of the fluorescence quantum yields of dyes **3** and **4** in comparison with their analogues **17** and **18**. However, contrary to these prerequisite their Φ_{f} values appeared much less (Table 1, [9]). The fluorescence quantum yield of compound **3** is almost 10 times less than that of its analogue **17**. Let us analyse the probable reasons of such phenomenon.

The long-wavelength shifts of the fluorescence bands of dyes **2**–**4** in comparison with those of dyes **16**–**18** are not so substantial to cause a considerable decrease of the Φ_{f} values due to amplification of internal conversion. Consequently, other factors cause the fluorescence quantum yields reduction.

Firstly, the bridge group causes some steric hindrances due to repulsion between $\mathrm{CH_2}$-group and H-atom at C-5. As a result, a rise of intramolecular rotations and torsions about the bonds C-3–C-4 and C-4–C-5 can take place that should result in a decrease of Φ_{f} value [18]. Our quantum-chemical calculation predicts some elongation of the bonds C-2–C-3 and C-3–C-4 in molecules **3** and **4** in comparison with those in molecules **17** and **18**. It also should facilitate intramolecular rotations and torsions about the bond C-3–C-4 of the polymethine chain (the bond C-2–C-3 is locked). Secondly, aliphatic six-atom ring being in a semichair form causes chromophore planarity distortion in dyes **2**–**4**, just as it takes place in the case of dyes **1** and **MC-540** [1]. But in the case of dyes **3** and **4** it does not perturb their absorption and fluorescence spectra and thereby cannot seriously decrease the radiative rate constant. Thirdly, quantum-chemical calculation predicts the stronger VI in a series **2**–**3** than in a series **16**–**18** (cf. the corresponding δ values in Table 2). This factor also can contribute to a decrease of Φ_{f} values of these dyes. Less decrease of the fluorescence quantum yield in a pair of the higher vinylogues (**18**–**4**) than in a pair **17**–**3** can be probably explained by weakening of the VI with polymethine chain lengthening, that one can see from band narrowing (Fig. 1) or from a decrease of the corresponding values of δ (Table 2).

Table 1
Characteristics of the fluorescence bands of dyes **2**–**10** measured in *n*-hexane, toluene, dichloromethane, DMF, and ethanol at 293 K

Dye	Solvent	λ^{f}_{max} (nm)	D^{f}_{λ} (nm)	Φ_f (%)	M^{-1}_{f} (nm)	D^{f}_{M} (nm)	σ^{f} (cm^{-1})	γ^{f}_{1}	γ^{f}_{2}	$F^{f} \times 10^{2}$	SS_{λ} (cm^{-1})	SS_{M} (cm^{-1})
2	CH_2Cl_2	588	–	–	619.8	–	1220	−0.85	1.2	3.8	476	2058
	DMF	588	–	–	621.3	–	1260	−0.79	1.1	3.2	568	2210
	EtOH	584	–	0.05	615.3	–	1230	−0.81	1.1	3.3	482	2106
3	CH_2Cl_2	682	–	–	706.5	–	815	−1.37	3.0	7.6	466	1437
	DMF	678	–	–	702.3	–	830	−1.34	3.0	7.2	495	1561
	EtOH	676	–	3.2	700.6	–	825	−1.32	2.8	6.8	498	1557
4	CH_2Cl_2	795	–	–	813.7	–	615	−1.17	1.9	6.3	459	1099
	DMF	794	–	–	815.5	–	670	−1.20	2.3	6.1	581	1609
	EtOH	789	–	15.0	810.5	–	655	−1.15	2.2	6.0	536	1434
5	Hexane	463	–	–	491.3	–	1570	−0.96	1.3	4.0	1496	3770
	Toluene	472	–	0.08	499.7	–	1520	−0.94	1.5	3.8	1336	3390
	CH_2Cl_2	472	32	–	502.8	32.1	1480	−0.92	1.4	3.8	1185	3310
	DMF	476	22	–	507.1	30.3	1485	−0.81	1.0	3.4	1263	3380
	EtOH	474	21	0.2	502.4	27.7	1480	−0.82	1.1	3.1	1324	3320
6	Hexane	(523) 553	–	–	575.2	–	1650	−0.78	0.8	4.4	682	3340
	Toluene	554	–	0.14	583.3	–	1165	−0.84	1.2	3.3	961	2640
	CH_2Cl_2	566	11.5	–	588.1	16.5	1040	−1.30	2.9	5.9	989	2340
	DMF	566	10	–	589.0	10.1	1045	−1.34	3.2	6.5	920	2240
	EtOH	562	9.5	0.9	583.3	13.6	1060	−1.34	3.2	6.5	866	2210
7	Hexane	(597) 638	–	–	672.5	–	1660	−0.76	0.8	3.6	763	3790
	Toluene	643	–	0.55	689.0	–	1190	−0.82	1.2	3.2	1226	3120
	CH_2Cl_2	671	14	–	695.1	8	875	−1.16	2.3	4.9	1071	2440
	DMF	677	5	–	697.4	4.2	830	−1.34	3.1	6.4	952	2200
	EtOH	670	8	8.2	691.2	5.4	855	−1.35	3.1	6.3	998	2330
8	Hexane	509	–	–	538.1	–	1515	−1.14	2.7	4.4	556	2090
	Toluene	524	–	0.1	550.3	–	1385	−1.19	2.8	4.7	679	2060
	CH_2Cl_2	534	–	–	560.8	–	1375	−1.20	2.9	4.8	958	2380
	DMF	531	–	–	558.1	–	1415	−1.16	2.7	4.7	970	2545
	EtOH	521	–	0.04	554.9	–	1455	−1.12	2.5	4.2	647	2590
9	Hexane	588	–	–	619.4	–	1110	−1.27	2.4	6.9	506	2021
	Toluene	614	–	18.0	632.9	–	880	−1.55	4.1	8.3	605	1528
	CH_2Cl_2	619	5.	–	639.7	3.9	870	−1.59	4.2	8.6	539	1438
	DMF	615	4.5	–	639.4	0	925	−1.57	4.1	8.5	462	1596
	EtOH	615	3	6.3	639.5	−2.1	930	−1.44	3.8	7.2	547	1760
10	Hexane	667 (719)	–	–	721.2	–	1105	−0.76	0.9	4.3	560	2701
	Toluene	712	–	40.0	738.0	–	840	−1.30	3.0	6.5	704	1932
	CH_2Cl_2	733	−1	–	749.5	−0.8	665	−1.43	3.5	7.8	602	1308
	DMF	727	3.5	–	746.3	1.1	720	−1.39	3.4	7.5	551	1453
	EtOH	723	3	12.2	745.4	−2.1	770	−1.37	3.4	6.3	537	1633

The less intensive peak positions are typed in parentheses. The corresponding data for dyes **16**–**24** besides Refs. [5,9–11] may be found in supplementary.

Table 2
The results of the quantum-chemical calculation of dyes **2**–**10**, **16**–**26** by methods AM1 and ZINDO/S (the last column only)

Dye	BLA (Å)	BOA	BOA*	δ	μ (D)	μ^{*} (D)	Δq_{av}	Δq^{*}_{av}	ΔE (eV)	
									AM1	ZINDO/S
2	−0.016	0.039	0.014	0.229	1.056	3.069	0.381	0.145	–	–
3	−0.001	−0.022	−0.019	0.156	0.723	3.049	0.38	0.142	–	–
4	0.003	−0.05	−0.017	0.117	0.314	2.862	0.373	0.159	–	–
5	0.068	−0.57	0.131	0.69	6.865	9.091	0.25	0.177	−0.601	−0.914
6	0.077	−0.62	0.068	0.827	7.463	11.52	0.21	0.112	−0.745	−1.119
7	0.083	−0.66	−0.006	0.929	7.7	13.76	0.174	0.094	−0.833	−1.416
8	0.055	−0.477	0.05	0.544	6.835	10.21	0.355	0.148	0.367	0.606
9	0.069	−0.553	0.036	0.717	7.631	13.06	0.297	0.123	0.395	0.402
10	0.076	−0.624	−0.015	0.864	7.622	15.52	0.238	0.118	0.422	0.407
16	−0.007	0.024	−0.021	0.258	2.254	3.711	0.442	0.089	–	–
17	−0.001	−0.029	−0.007	0.165	1.699	3.639	0.422	0.135	–	–
18	0.005	−0.066	−0.013	0.136	1.192	3.472	0.406	0.156	–	–
19	0.064	−0.546	0.2	0.714	7.196	8.877	0.292	0.143	−0.586	−0.816
20	0.077	−0.627	0.098	0.861	7.488	11.12	0.223	0.092	−0.712	−1.04
21	0.084	−0.665	0.011	0.953	7.64	12.99	0.18	0.091	−0.795	−1.187
22	0.047	−0.421	0.113	0.538	7.608	10.04	0.413	0.113	0.424	0.758
23	0.069	−0.564	0.062	0.753	7.689	12.62	0.313	0.097	0.457	0.483
24	0.079	−0.631	0	0.894	7.534	14.61	0.244	0.112	0.484	0.482
25	–	–	–	–	–	–	–	–	0.404	0.965
26	–	–	–	–	–	–	–	–	−0.273	0.691

The parameters concerning the first excited Franck–Condon state S_1^{FC} are marked with “asterisk”.

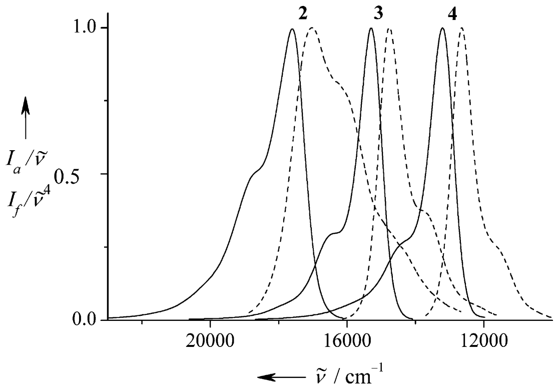


Fig. 1. Normalized UV–vis (solid) and fluorescent (dash) spectra of dyes **2–4** in ethanol.

The molecule of compound **2** is characterized by the considerable planarity distortion; the calculated torsion angle C-1–C-2–C-3–C-4 amounts to 12.8° while for the higher vinylogues it is less than 5°. Its fluorescence spectral bands are very broad and diffuse (Fig. 1) testifying to the strong VI in the fluorescent transition and low radiative rate constant. Therefore its Φ_f value is extremely small and amounts only to 0.05% (Table 1), while the fluorescence quantum yield of dye **16** amounts to 3% in ethanol.

The influence of intramolecular rotations and torsions on the Φ_f values of compounds **2–4** was examined by measuring of their spectral luminescence characteristics in the rigid PVE matrix (polyvinyl ethylal). The relative fluorescence quantum yields of dyes **2–4** were measured in relation to those of compounds **16–18**. The Φ_f values of carbocyanines (**2**) and (**16**) were also measured in relation to rhodamine 6G in the same polymer.

Inclusion of dyes **2–4** into polymer films has resulted in expected growth of their fluorescence quantum yields. Especially strong effect takes place in the case of carbocyanines (**2**) and (**16**) for which probability of intramolecular torsions is highest due to a close arrangement of their terminal groups and the greatest alternation of bond orders in chromophore (Table 2). Thus in ethanol the ratio of Φ_f values of rhodamine 6G and dyes **2** and **16** is 100:0.06:3.4, and in PVE film it amounts to 100:8.8:51 (λ_{exc} = 500 nm), *i.e.* the relative fluorescence quantum yields of compounds **2** and **16** have increased approximately 150 and 15 times. For vinylogues (**3**) and (**17**) the ratio of their Φ_f values is 12.8:100 in ethanol and 64:100 in PVE (λ_{exc} = 600 nm); for dyes **4** and **18** it is 54:100 in ethanol and 75:100 in PVE (λ_{exc} = 700 nm). These data specifies that intramolecular torsions and rotations are an important channel of deactivation of the excited state of dyes **2–4** but they subside with an increase of *n*. Transition from ethanol to PVE does not change the general tendency of a decrease of the fluorescence quantum yields of constrained symmetric cationic cyanines **2–4** in comparison with their analogues **16–18**. Therefore, the VI should be another important channel of deactivation of their fluorescent state.

3.2. Structure and solvatofluorochromism of merocyanines (5–10)

The analysis of the spectral-luminescent properties of the merocyanines was carried out in the context of the suggested by Dähne model of three ideal states (Scheme 6)—non-polar polyene (**A1**), ideal polymethine (**A2**) (the cyanine limit) and dipolar polyene (**A3**) [19].

The electronic structure of donor–acceptor substituted polyenes depending on their chemical structure and solvent polarity can vary continuously achieving any of the ideal states as well as all intermediate between them. Approach of a merocyanine to the structure **A2** is concerned with a bathochromic shift of its spectral bands, their narrowing (due to a decrease of the VI) and a growth of their intensity. Deviations decrease and vinylene shifts increase at that [19].

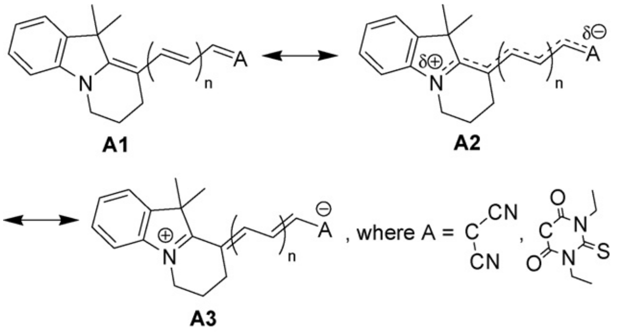
An increase of solvent polarity is accompanied with long-wavelength shifts of the fluorescence bands of merocyanines (**5–7**) (Table 1). The range of solvatofluorochromism of dyes **5–7** is very close to that of their analogues **19–21** [10], while the range of solvatochromism of dyes **5–7** is much less than that of dyes **19–21**. Probably, this fact is connected with a decrease of charge alternation in the chromophore of dyes **5–7** and **19–21** in the excited state (cf. the values of Δq_{av} and Δq^*_{av} in Table 2).

Long-wavelength shifts of the fluorescence bands of merocyanines **5–7** in comparison with those of dyes **19–21** are smaller than the corresponding shifts in their absorption spectra (Table 1, [8,10]). For example, the fluorescence maximum of merocyanine (**7**) in DMF is shifted at $\Delta\lambda^f_{max} = 6$ nm (130 cm^{-1}) with respect to its analogue **21**, while $\Delta\lambda^a_{max} = 12$ nm (300 cm^{-1}).

The fluorescence vinylene shifts at transition from merocyanine **5** to **6** both on the maxima (VS^f_λ) and on the band centres (VS^f_M) are close to the corresponding values of VS^a_λ, VS^a_M (cf. Table 1, [8]). They are less than the vinylene shifts between their analogues **19** and **20** that, apparently, is the consequence of additional long-wavelength shifts of spectral bands of dye **5** caused by strong planarity distortion of its molecule. The values of VS^f_λ and VS^f_M at transition from dye **6** to **7** are greater than those between **20** and **21** and exceed the value of 100 nm in solvents more polar than toluene (Table 1). Vice versa, in the absorption spectra of dyes **5–7** the second vinylene shifts are less than the first ones [8]. It allows us to suggest that in the fluorescent state S_1 they (perhaps except for vinylogue (**5**)) lie closer to the cyanine limit **A2** than in the ground state S_0. It is also confirmed by the deviation values D^f_M and D^f_λ (Table 1) which for dyes **6** and **7** are less than the values of D^a_λ and D^a_M [8].

The changes of width and shape of the fluorescence bands of dyes **5–7** (Table 1, Figs. 2 and 3) in comparison with their absorption bands are like to those in a series **19–21** [10]. The violation of the mirror symmetry of the absorption and fluorescence bands also takes place. The fluorescence bands of dye **5** are broader, more symmetrical and more sloping than its absorption bands. For the higher vinylogues the changes are opposite (with exception of the spectra in low-polar *n*-hexane). The fluorescence bandwidth of merocyanines (**5–7**) is less than that of their analogues **19–21** (Fig. 2); especially well-defined this tendency is in low-polar solvents (cf. Table 1, [10]). It is the case even for a pair of **5** and **19** for which one could expect the opposite, reasoning from the regularities observed in their absorption spectra [8]. From Fig. 2 one can see also that the trimethylene group induces a decrease of the relative intensity of the highest (0–2, 0–3) vibronic components of the spectral bands.

The Stokes shifts SS_λ and SS_M of dyes **5–7** decrease with a growth of medium polarity (Table 1). They change irregularly with chain lengthening reaching the minimal values for vinylogue (**6**).



Scheme 6.

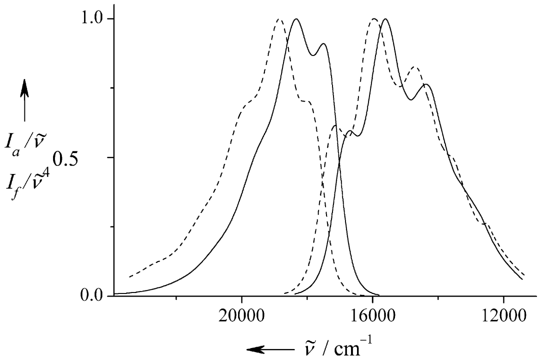


Fig. 2. Normalized UV–vis and fluorescent spectra of merocyanines (**7**) (solid) and (**21**) (dash) in *n*-hexane.

Thus, the regularities in the fluorescence spectra of dyes **5**–**7** are similar to those in the spectra of compounds **19**–**21**. But merocyanines (**5**–**7**) have somewhat greater vinylene shifts, smaller deviations; their fluorescence spectral bands are narrower than those of dyes **19**–**21**. Hence, both in the ground state S_0 and in the fluorescent state S_1 the electronic structure of merocyanines (**5**–**7**) is characterized by the weaker alternation of chromophore bond orders, *i.e.* by the greater contribution of the ideal polymethine structure **A2**, than merocyanines (**19**–**21**).

The fluorescence quantum yields of dyes **5**–**7** and **19**–**21** are very close (Table 1, [10]). The vinylogue (**7**) both in low-polar toluene and in high-polar ethanol has even the higher quantum yields than dye **21**. Apparently, the factors that promote a decrease of the Φ_f values of cationic polymethines **2**–**4** in comparison with dyes **16**–**18** should affect similarly in the case of merocyanines (**5**–**7**). But an increase of the electronic symmetry of dyes **5**–**7** in comparison with **19**–**21** both in the ground and in the excited state results in a growth of oscillator strength and in a decrease of the VI in the fluorescent transition $S_1 \rightarrow S_0^{FC}$. These two factors cause an increase of the radiative rate constants of dyes **5**–**7** preventing a reduction of their fluorescence quantum yields.

Merocyanines (**8**–**10**) derivatives of strongly electron acceptor *N*,*N*-diethylthiobarbituric acid, possess reversal solvatochromism while their analogues **22**–**24** possess distinct positive solvatochromism [8]. The same tendency holds in their fluorescence spectra. Maximal long-wavelength shifts of their fluorescence bands is observed in dichloromethane; transition both to low-polar *n*-hexane and toluene and to high-polar DMF and ethanol is accompanied by short-wavelength band shifts (Table 1). It is interestingly that the solvatofluorochromic range of dyes **8**–**10** is greater than their solvatochromic range (cf. Table 1, [8]). For positively solvatochromic dyes which possess the greater dipole moment in the excited state than in the ground one this is quite natural. Really, for coumarines [20], ketocyanines [5] and merocyanine DCM [21] the solvent polarity influences greatly their fluorescence spectra than the absorption ones. The opposite situation was observed for merocyanines with non-constrained polymethine chain which contain the same terminal groups that merocyanines (**5**–**10**) (as well as residues of 1,3-diphenylbenzimidazole, benzo[*cd*]indole, and 1,3-dimethylbarbituric acid) irrespectively of their sign of solvatochromism [10,11].

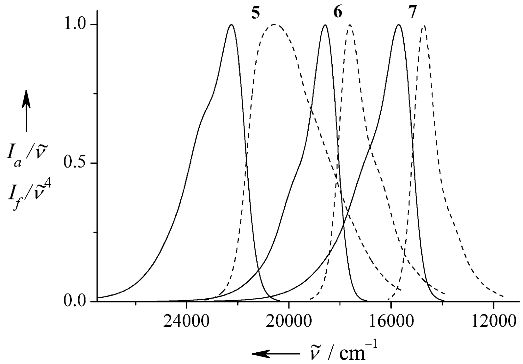


Fig. 3. Normalized UV–vis (solid) and fluorescent (dash) spectra of dyes **5**–**7** in DMF.

The fluorescence band vinylene shifts in a pair of merocyanines (**8**) and (**9**) are substantially less than those in a pair of dyes **22** and **23** (cf. Table 1, [11]). Evidently, similarly to pairs of vinylogues (**2**, **3**) and (**5**, **6**), this fact is concerned with the strong planarity distortion of the shortest vinilogue (**8**). The second vinylene shifts (between **9** and **10**) exceed those in a pair of dyes **23** and **24**. In all solvents except for *n*-hexane they exceed the value of 100 nm. The values of deviations D_λ^f and D_M^f in the fluorescence spectra of dyes **8**–**10** are close to zero (in a series of solvents in which they have been determined, Table 1). These data specify the vicinity of their excited S_1 state to the cyanine limit **A2**.

The maximal vinylene shift for a pair of **9** and **10** is observed in dichloromethane ($\mathrm{VS}_\lambda^\mathrm{f} = 114$ nm). Just in this solvent their absorption and fluorescence bands are narrowest, most asymmetric, most peaked, and lie in the most long-wavelength spectral range (see Table 1, the parameters σ^f, γ_1^f, γ_2^f). It specifies that dyes **8**–**10** achieve in dichloromethane the ideal polymethine state **A2** not only in the ground state S_0 but also in the fluorescent state S_1.

As against to their absorption bands, the fluorescence bands of dyes **8**–**10** get narrow regularly with the polymethine chain lengthening. For merocyanine (**8**) the values of σ^f considerably exceed σ^a. The absorption and fluorescence bands of vinylogue (**9**) have close width and the law of mirror symmetry is virtually carried out for them (Fig. 4). The σ^f values of dye **10** are less than the σ^a in all solvents.

The fluorescence bands of vinylogue (**8**) are broader than those of **22**. For pairs **9**–**23** and **10**–**24** the parameters σ^f are rather close; the effect of the constraining trimethylene group results in some narrowing of the bands in low-polar *n*-hexane and toluene and their broadening in high-polar media. This can be explained by a change of type of solvatofluorochromism from positive for merocyanines (**22**–**24**) to reversal for dyes **8**–**10**.

The Stokes shifts in a series **8**–**10** are less than those for malononitrile derivatives **5**–**7** (Table 1). They decrease also with the polymethine chain lengthening. The least SS_M values are in dichloromethane confirming the maximal electronic symmetry of the given dyes in this solvent.

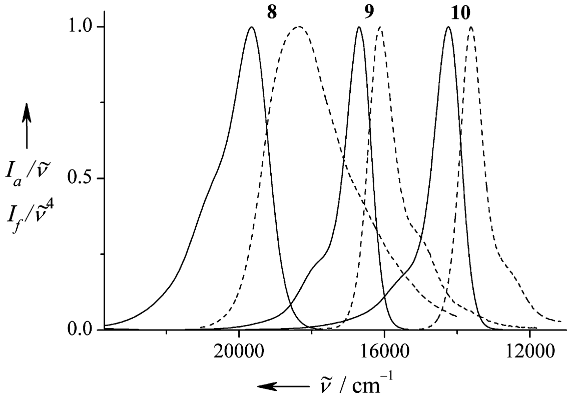


Fig. 4. Normalized UV–vis (solid) and fluorescent (dash) spectra of dyes **8**–**10** in dichloromethane.

Thus, the peculiarities of the fluorescence spectra of merocyanines (**8**–**10**) concerned with the presence of the constraining trimethylene group are similar to those in their absorption spectra. In dichloromethane their electronic structure achieves the cyanine limit **A2** both in the ground S_0 and in the excited state S_1. In low-polar *n*-hexane and toluene their ground state lies in the interval of structures **A1**–**A2** and their dipolarity should increase at excitation in a direction of the interval **A2**–**A3**. On the contrary, in high-polar DMF and ethanol the ground S_0 state of dyes **8**–**10** is shifted from **A2** toward **A3** and their dipole moment in the absorption transition should decrease, the fluorescent S_1 state should come nearer to structure **A2** from the side of non-polar polyene **A1**.

Merocyanine (**8**) has very low fluorescence quantum yields (Table 1), tens times less than those of dye **22**. Apparently, in this case the strong nonradiative deactivation of the excited state is concerned with strong planarity distortion of its molecule, just as it takes place for a pair of cationic dyes **2**–**16**. Quantum-chemical calculation demonstrates that the torsion angle N-1–C-2–C-3–C-4 grows from $\theta \approx 0^\circ$ up to $\theta \approx 0.7^\circ$, and the angle C-2–C-3–C-4–C-5 grows from $\theta \approx 0^\circ$ up to $\theta \approx 20.2^\circ$ at transition from **22** to **8**. Besides, the calculated C-3–C-4 bond order in the fluorescent state of compound **8** is less than those for **22** (1.3223 and 1.3792 accordingly) that should facilitate intramolecular torsions about this bond.

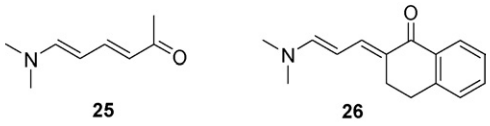
The Φ_f values of higher vinylogues (**9**) and (**10**) correlate well with changes of their electronic symmetry under the influence of the trimethylene bridge group. In high-polar ethanol their electronic structure diverts from the ideal polymethine (**A2**) and their fluorescence quantum yields are much less than those of dyes **23** and **24** (cf. Table 1, [11]). For example, in ethanol the Φ_f value of dye **10** amounts to 12.2% while the corresponding Φ_f value of dye **24** is 39%. However in low-polar toluene merocyanines (**9**) and (**10**) lie nearer to the cyanine limit than compounds **23** and **24**. It results in a growth of their Φ_f values. For the highest vinylogue (**10**) the Φ_f value in toluene is 40% while for dyes **24** it amounts only to 16% in the same solvent.

Discussing the influence of various structure factors on the fluorescent properties of merocyanines we did not consider one more, namely their $^1(\pi_H\pi_L^*)$ and $^1(n\pi_L^*)$ states relative positions. If their energies are close the interaction of the vibration sublevels of these states causes an increase of the internal conversion [18,22] deactivating nonradiatively the fluorescent $^1(\pi_H\pi_L^*)$ state, that causes a decrease of the fluorescence abilities of merocyanines.

In work [22] Ponterini et al. have shown that in the case of simple merocyanines (**25**) and (**26**) the low-lying $^1(n\pi_L^*)$ state essentially reduces their fluorescence quantum yields (Scheme 7).

A growth of medium polarity reduces energy of the $^1(\pi_H\pi_L^*)$ state of compound **26** more strongly than the $^1(n\pi_L^*)$ since the former is more dipolar. In ethanol the $^1(\pi_H\pi_L^*)$ state becomes the S_1 state and the fluorescence quantum yield of dye **26** increases more than ten times in comparison with that in toluene. Though the authors of [22] notes that this factor apparently is less important in the case of more complex dyes, we have analysed its possible influence on the Φ_f values of the explored merocyanines.

The relative energies $\Delta E = E^{\pi\pi} - E^{\pi\pi}$ of the $^1(\pi_H\pi_L^*)$ and $^1(n\pi_L^*)$ states of merocyanines (**5**–**10**), (**19**–**24**) and (**25**), (**26**) (Table 2) were calculated not only by AM1 method, but also by ZINDO/S method; the latter reflects electronic transitions in dye molecules more reasonably (geometry optimization was carried out by AM1 method in both cases).



Scheme 7.

As one can see from Table 2, the energy of the $^1(\pi_H\pi_L^*)$ state for dyes **5**–**7** and **19**–**21** is substantially less, than those of the $^1(n\pi_L^*)$ and the value of ΔE grows at lengthening of the polymethine chain. Hence, the $^1(n\pi_L^*)$ state cannot influence the Φ_f values of these compounds. This factor, ungearing one the important channels of deactivation of the fluorescent state for derivatives of malononitrile, was one of the main reasons why this residue had been chosen as a terminal group of merocyanines.

For the merocyanines based on *N*,*N*-diethylthiobarbituric acid the calculation predicts an arrangement of the $^1(\pi_H\pi_L^*)$ and $^1(n\pi_L^*)$ levels similar to that of compounds **25**, **26**. So, the fluorescence quenching via deactivation of the $^1(n\pi_L^*)$ state can be quite possible for dyes **8**–**10** and **22**–**24**. Contrary to this, their Φ_f values are higher than those of malononitrile derivatives (Table 1). With a growth of solvent polarity the energy of their $^1(\pi_H\pi_L^*)$ state like in the case of compound **26** should fall more strongly than that of the $^1(n\pi_L^*)$ one; it should result in an increase of the fluorescence quantum yields. However for merocyanines (**8**–**10**) the opposite situation is observed. Moreover, it follows from Table 2 that in gas phase the levels $^1(\pi_H\pi_L^*)$ and $^1(n\pi_L^*)$ of dyes **8**–**10** lie closer than those of their analogues **22**–**24**. From here one can expect, that in low-polar toluene the Φ_f values of the former will be lower. However the experiment shows the opposite. Hence, for them, as well as for derivatives of malononitrile, the deactivation of the excited state with participation of the $^1(n\pi_L^*)$ state is not dominating.

4. Conclusion

The fluorescent properties and electronic structure of cationic dyes and merocyanines with partially constrained polymethine chain has been studied in a wide range of solvent polarity. It was shown that the trimethylene bridge group connecting *N*-atom of indole nucleus with α-position of the polymethine chain causes similar effects on their absorption and fluorescence spectra. But for the latter this influence often is somewhat weaker.

The constraining group increases the dipolarity of the ground state of merocyanines. Thanks to this effect the positively solvatochromic merocyanines both in the ground S_0 and in the excited S_1 state lie closer to the ideal structure **A2** than the corresponding dyes without such trimethylene bridge. On the contrary, the electronic structure of negatively solvatochromic merocyanines deviates from the cyanine limit to dipolar polyene **A3** in the ground state and neutral polyene **A1** in the excited one.

Steric hindrances caused by constraining group result in some planarity distortion in chromophore of the dyes. For short-chain polymethines the planarity distortion of dye molecules is very substantial since strong repulsion of closely located terminal groups takes place. Also the constraining group provokes some lengthening of the adjacent to the ring C-3–C-4 bond. It facilitates intramolecular rotations and torsions around this bond and consequently causes an amplification of nonradiative deactivation of the excited state of dyes.

The results obtained for dyes **2**–**10** allow us to make a conclusion that studied bridge group can cause both a decrease and an increase of the fluorescence quantum yields of cyanines. The factors exerting negative influence on the Φ_f value (planarity distortion, intensification of intramolecular rotations and torsions, amplification of the VI in the fluorescent transition) are weakened essentially with lengthening of the polymethine chain both for cationic cyanine dyes and for merocyanines.

A growth of the fluorescence quantum yield of merocyanines is observed when the electron donating bridge group approaches their electronic structure to the ideal polymethine structure **A2**.

This is typical for positive solvatochromic dyes. On the contrary, for merocyanines with negative or reversal solvatochromism (in high-polar solvents) the trimethylene link causes the violation of uniformity of bond orders in the chromophore, the deviation of the electronic structure of dyes toward dipolar polyene **A3**, and a significant decrease of the Φ_f value takes place.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2008.06.020.

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