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Fluorescent Properties of 8-phenylBODIPY in Ethanol – Ethylene Glycol Mixed Solutions

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Abstract Fluorescent characteristics of two BODIPY dyes in solutions were investigated under the viscosity variations. Investigated dyes differ in the nature of 8-substituent of ligand molecule. Viscosity variation was achieved by changing of solvent composition in the binary system ethanol - ethylene glycol and solvent temperature. 8-Phenyl substituted BODIPY is found to exhibit properties of molecular rotor, i.e. its fluorescent characteristics are highly dependent on the viscosity or rigidity of the microenvironment. Increased temperature leads to a linear decrease of fluorescence parameters unlike the solvent composition variation where fluorescence change is nonlinear. The highest specific change in the fluorescence was observed in pure ethanol. Change in the nonradiative decay rate constant values with the increasing of viscosity indicates that the analyzed phenyl substituted complex is a true molecular rotor. Investigated 8-phenylBODIPY could be recommended as promising viscosity sensor in different organic media.

Keywords BODIPY · Molecular rotor · Dynamic viscosity · Fluorescence · Solvent effects

Introduction

Fluorescent molecular rotors are environment-sensitive molecules with strong dependency of their emission spectra on the polarity and viscosity of the solvent environment [1]. Molecular rotors' quantum yield depends on the ability to form twisted intramolecular charge-transfer states (TICT):

upon photoexcitation an electron is transferred from an electron donor group to an electron acceptor group within the same molecule. Rotation of the molecular groups in such systems provides the possibility of nonradiative energy dissipation of the excited state of the chromophore. Thus, there are two mechanisms of exited state energy dissipation: 1) the radiative energy dissipation – luminescence; 2) the nonradiative deactivation. TICT formation is dominantly governed by the solvent's microviscosity, but the polarity and the ability of the solvent for specific interactions with dissolved molecule play an additional role [2]. This mechanism opens the way to the measurement of local viscosity through molecular rotors. Nowadays molecular rotors are considered as promising replacement of widely used techniques for viscosity measurements. Traditional mechanical viscometers are not able to measure viscosity of microsystems and, more important, can't measure fluid viscosity in real-time conditions. At the present time fluorescent molecular probes are most suitable tools for real-time measurements of viscosity in both micro- and macrosystems [3]. Molecular rotors could be used for micro-viscosity measurements of biological samples in vivo, namely intracellular and intercellular fluids without compromising the integrity of the cell wall [4]. Ability for real-time viscosity control could be used for investigations of self-organizing and polymeric systems [5]. In particular, it is actual in studying of polycondensation processes during the synthesis of nano- and meso-porous materials by sol–gel technology, which is very popular nowadays [6].

Boron-dipyrromethene (BODIPY) based fluorophores are very perspective among the large variety of organic dyes, those spectral and photophysical characteristics are superior to the known values for dyes of other chemical groups [7]. Combination of intense fluorescent characteristics with the possibility for accurate tuning of the spectral properties of the compounds together with a high resistance of the chromophore to external chemical influences and the irradiation

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determines a wide variety of practical applications of BODIPY. At present, BODIPY based dyes are widely used in various fields of molecular sensing [8–11], in biochemistry and medicine [12–14], in optics [15]. BODIPY are used for polymeric matrices functionalization and their further usage for as replacement of liquid phase sensors and optical converters [16, 17]. Taking that into account, studying of BODIPY as a molecular rotors is perspective task of material science, analytical- and biochemistry [18]. The strongest fluorescent molecular rotor properties could be achieved when BODIPY with bulky substituent in 8-position of dipyrromethene ligand is used [19–21]. The detailed analysis of rotational behavior of several 8-sybstituted BODIPY dyes could be found in literature [22–24]. But the information about the solvent and viscosity influence on photophysical properties and appropriate radiative and nonradiative decay rate constants is limited.

In this work we studied photophysical characteristics of two BODIPY fluorophores, that differs in the nature of 8-substituent: H- in compound *1*, C_6H_5- in compound *2* (Fig. 1). Thus, *1* is the "nonrotating" reference sample for physical-chemical investigations of spectral characteristics of 8-phenyl substituted BODIPY *2*. This makes it possible to allow us to determine directly the mechanism of fluorescence gain or quenching in the systems of different viscosities. The change of viscosity of the medium was carried out by changing the molar ratio of components of the solvent in the ethanol-ethylene glycol mixtures and by varying the temperature of the solution.

Materials and Methods

Complexes of 4,4-difluoro-1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-s-indacene (*1*) and 4,4-difluoro-1,3,5,7-tetramethyl-2,6-diethyl-8-phenyl-4-bora-3a,4a-diaza-s-indacene (*2*) were synthesized, purified and characterized in accordance with the procedures described in the literature [25, 26]. Before characterization, the compounds were crushed and dried to constant weight under vacuum.
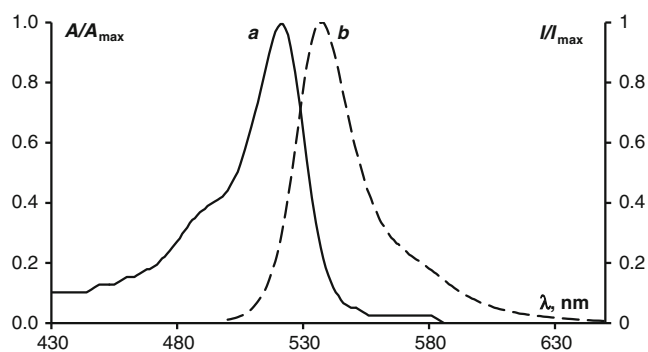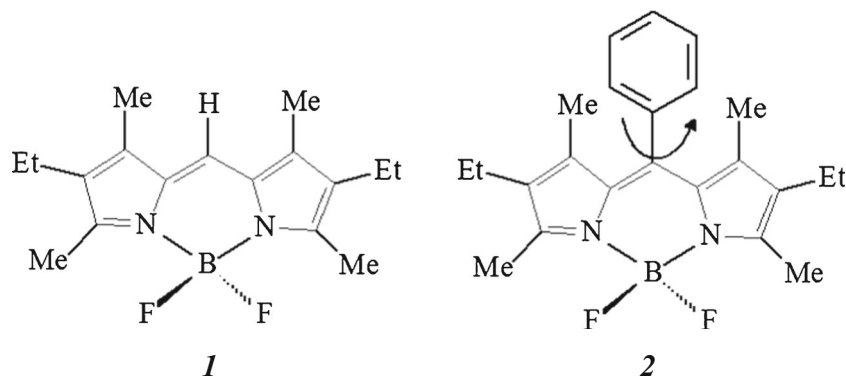

Fig. 2 EAS (**a**) and fluorescence spectrum (**b**) of *2* in ethanol

Ethanol and ethylene glycol (Chimmed, Russia) were all of analytical grade purified by standard techniques [27]. The residual water content (<0.02 %) was determined by the Karl Fischer method [28].

U.v.–vis. electronic absorption spectra (EAS) were recorded in the range of 350–800 nm on an SF-104 spectrophotometer (Aquilon, Russia) controlled with a PC using the software package UVWin 5.1.0. The accuracy of the measurements was±0.03 on the scale of optical density; wavelength accuracy was±0.05 nm. The fluorescence spectra were obtained with a Cary Eclipse fluorescence spectrometer (Varian-Agilent, US-Australia) controlled with a PC using the software package Cary Eclipse Scan Application 1.1. Spectra were measured in the wavelength range 500–900 nm and the excitation wavelength was 480 nm. The slit widths for excitation and emission ranged from 2.5 to 5 nm. Investigations were carried out in quartz cuvettes with a thickness of the absorbing layer of 2 and 10 mm. All experiments were performed in a temperature-controlled cell with Peltier PTC-2 module at fixed temperatures of 283 to 343 K.

Fluorescence quantum yield (φ) is defined as follows:

$$\varphi_x = \varphi_{st} \cdot \left(\frac{A_x}{A_{st}}\right) \cdot \left(\frac{B_{st}}{B_x}\right) \cdot \left(\frac{n_x^2}{n_{st}^2}\right)$$

where φ_{st} is the rhodamine 6G standard quantum yield in ethanol ($\varphi=0.95$, [29]), A_x and A_{st} are the integrated area under the corrected fluorescence spectra, B_x and B_{st} are the absorbance

Fig. 1 Structural formulas of the investigated compounds
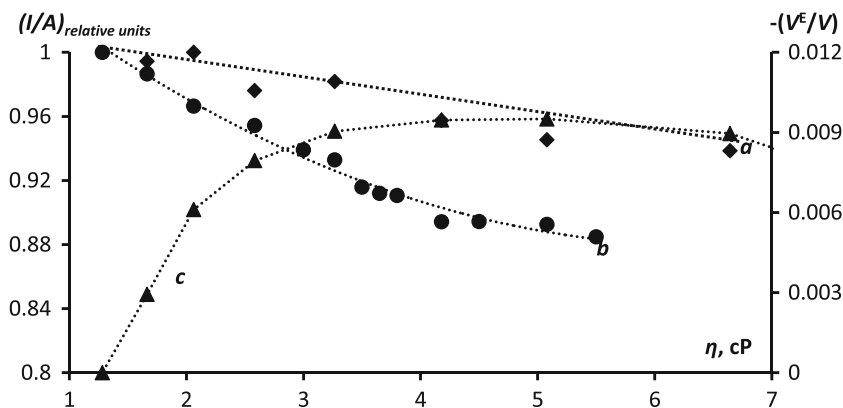
(optical density) at the excitation wavelength, n_x and n_{st} are the refractive indices of the solvents used for two solutions.

Quantum yield φ and solvent bulk viscosity η follow a power-law relationship that is widely referred to as the Forster-Hoffmann equation [30]:
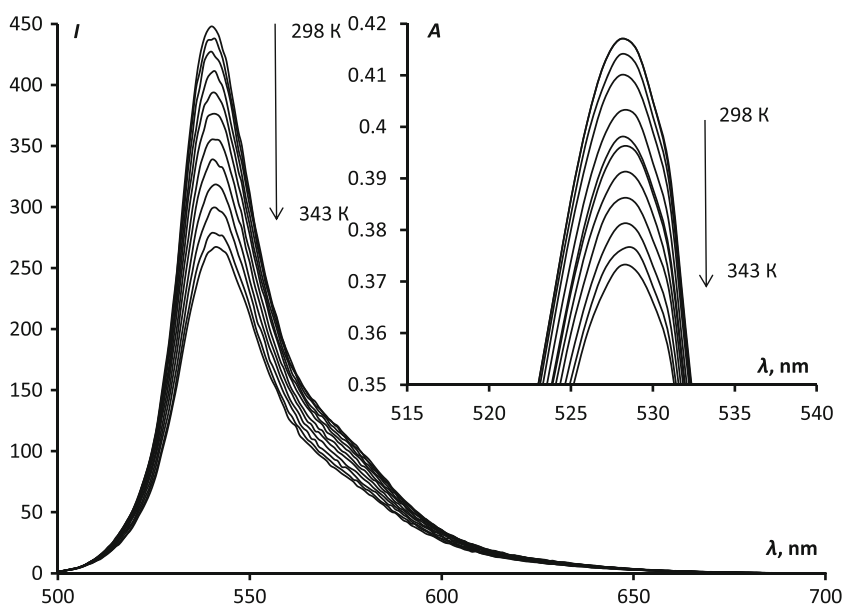
$$\log \varphi = x \cdot \log \eta + C$$

where C and x are solvent- and dye-dependent constants. This relationship has been experimentally shown to be valid in a wide range of viscosities and in both polar and nonpolar fluids.

The nonradiative (k_{nr}) and radiative decay constants (k_{fl}) were calculated from experimentally measured fluorescence quantum yield φ and calculated fluorescence lifetime τ according to the following equations:

$$\varphi = \frac{k_{fl}}{k_{fl} + k_{nr}}; \ \tau = \frac{1}{k_{fl} + k_{nr}}$$

In this study we used mixtures of ethanol (low viscosity solvent) and ethylene glycol (high viscosity solvent) to change the viscosity of the dye's solution in a broad range. The molar content of ethylene glycol was varied of 0 up to 91.12 % allowing us to achieve viscosity variation of 1.28 to 10.14 cP. Temperature influence was examined in the temperature range of 289 to 343 K, which allowed to investigate viscosity intervals from 1.347 up to 3.223 cP (in case of solvent with 40.46 % of ethylene glycol molar content) and from 3.093 up to 10.277 cP (in case of solvent with 91.12 % of ethylene glycol molar content).

Results and Discussion

Determining Solvent-Dependent Viscosity Behavior

EAS of the investigated complexes solutions are characterized by a high-intensity peak at 529 nm for 1 and 523 for 2,

Fig. 4 Fluorescence and absorption spectra (in incut) for 2 in ethanol - ethylene glycol mixture ($\chi_{ethylene\ glycol}$=0.2) at different temperatures

Fig. 5 Dependence of the relative fluorescence intensity at the emission maximum vs the temperature in ethanol – ethylene glycol mixture ($\chi_{ethylene\ glycol}$= 0.2) for the investigated compounds
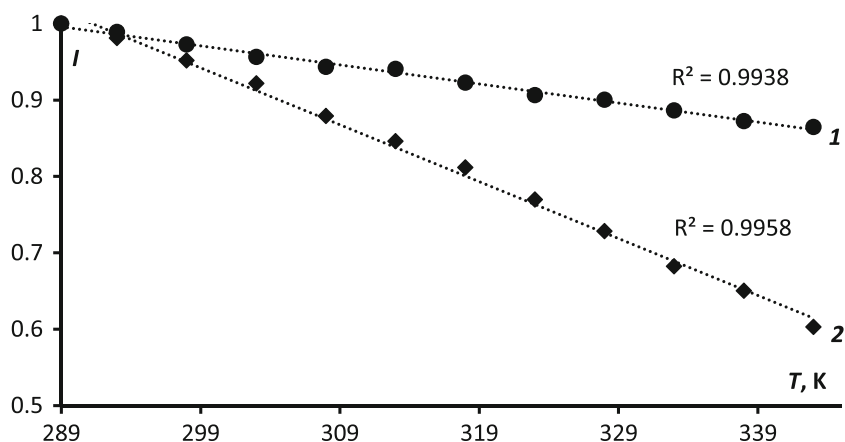
corresponding to an electronic transition $S_0 - S_1$ (Fig. 2). Conjugation of phenyl substituent to dipyrromethene π-electron system leads to the hypsochromic shift in EAS. The fluorescence spectra are "mirror" reflection of the absorption spectra. Fluorescence maxima are on 536 nm (*1*) and 535 nm (*2*). Stokes shift are increasing for *2* in comparison with *1* could be explained by nonradiative energy dissipation of the excited state of the molecule due to substituent rotation in *2*.

Effect of dynamic viscosity changes on the spectral characteristics of BODIPY is studied by varying the mole ratio of components in the system ethanol - ethylene glycol at the first stage. Increasing the content of ethylene glycol in solution leads to a linear decrease in fluorescence intensity for compound *1* (Fig. 3). The changes are more complex in the fluorescence spectra of *2*. There are two intervals for compound *2* on the curve of relative fluorescence vs viscosity: 1. in the range of 1.28 to~3.6 cP intense fluorescence drop is observed; 2. with an increase in viscosity above 3.8 cP fluorescence intensity drop decreases.

It is known that changing of the composition of the solvent and increasing the viscosity change leads to the structure changes of the molecular network in the studied binary system ethanol −ethylene glycol [31]. The geometric characteristics of the solvent change largely, resulting a nonlinear dependence of the excess molar volume of the solvent from the dynamic viscosity (Fig. 3). At low viscosities molecular network is formed preferably by ethanol molecules. Under the viscosity increasing the packing density of the solvent molecules peaks maximum and the presence of 8-substituent in *2*

play a significant role due to steric effects, which causes strong fluorescence quenching in the range of viscosities up to ~3.5 cP. It should be noted, that the fluorescence quenching by increasing the molar proportion of ethylene glycol in the viscosity range higher than 3.5 cP lead to a lesser fluorescence quenching for compound *2* confirming whose molecular rotor properties. The obtained results are in a good agreement with the literature data on spectral characteristics dependencies under the solvent nature variations [32, 33]. Specific interactions of phenyl substituent π-electron system with solvent molecules as well as van der Waals forces play significant role in fluorescence quenching. Increasing of the solvent dipole moment with increasing ethylene glycol molar content leads to the gain of orientation and dispersion interactions in the investigated system causing the fluorescence quenching.

Lack of linear dependence of the *2* photophysical characteristics on the dynamic viscosity due to the influence of packing effects makes the process of studying the molecular characteristics of the rotor by varying the composition of the solvent difficult for further practical application. Nevertheless, the understanding of the mechanisms of fluorescence quenching both by specific and nonspecific interactions allows deeper uncovering ways of directional control of the photophysical properties of these compounds.

Determining Temperature-Dependent Viscosity Behavior

The next step of our research was to determine the photophysical changes in case of viscosity changes under the

Fig. 6 Relative quantum yield vs temperature for *1* and *2* in ethanol
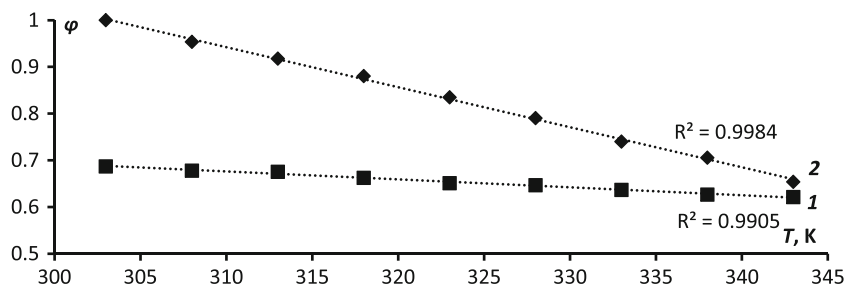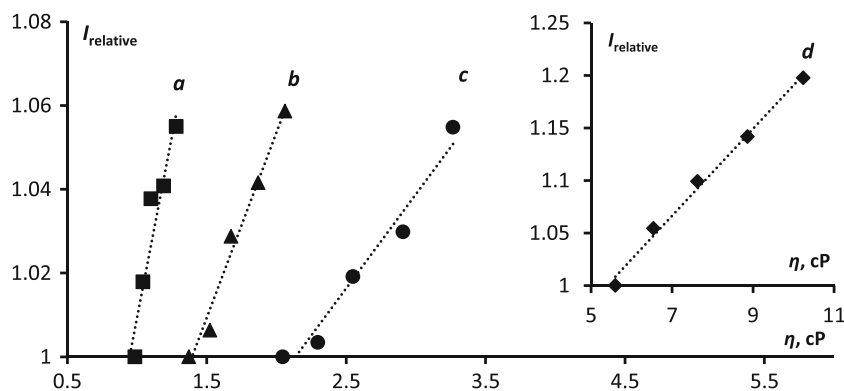
Fig. 7 Change in the relative fluorescence intensities with increasing the viscosity of the solutions of compound **2** in the ethanol - ethylene glycol mixtures: **a** − $\chi_{ethylene\ glycol}$=0; **b** − $\chi_{ethylene\ glycol}$=0.2; **c** − $\chi_{ethylene\ glycol}$=0.4; **d** − $\chi_{ethylene\ glycol}$=0.9

temperature variation. Temperature increasing leads to decreasing of the fluorescence intensity of investigated compounds solvents (Fig. 4). Temperature change does not influence significantly on absorption maximum position of compounds, but the temperature increasing from 298 to 343 K causes bathochromic shift of fluorescence maximum on 1.5 –2 nm. Increasing of the Stokes shift value is explained by increasing the probability of the fluorophore molecule transition to higher energy vibrational levels under the excitation.

The observed increase of the fluorescence intensity is consistent with the restricted rotation of the phenyl group in the medium of high viscosity preventing relaxation via the nonradiative exited state decay. Fluorescence intensity values depend on the temperature in a straight line for both studied compounds (Fig. 5), which is confirmed by

the high values of the correlation coefficients obtained for discussed dependencies. In the investigated temperature range fluorescence intensities change of 16 % for compound **1** and 40 % for compound **2**. This fact confirms the manifestation of the molecular rotor properties of the compound **2**.

It is known from literature [19], that it is more accurate to compare not fluorescence intensity but quantum yield changing under the dynamic viscosity variation (Fig. 6). But the obtained dependencies are the same as obtained for fluorescence intensity. Quantum yield linearly decrease with the temperature rising and viscosity decreasing respectively for both investigated compounds. This changing is more pronounced for compound **2**, which results in a higher value of the slope of approximating line. Higher quantum yield values in all investigated temperature range are obtained for 8-phenylBODIPY.

The magnitude of the fluorescent change in the investigated temperature range depends on the solvent composition (Fig. 7). Thus, in the less viscous solutions initially containing a small amount of ethylene glycol viscosity increase results in a greater change in the magnitude of spectral characteristics. The greatest relative change in fluorescence intensity is observed for the solution with the lowest initial dynamic viscosity. I.e. the studied compound **2** has optimal viscosity ranges in which the properties of the molecular rotor are most pronounced.
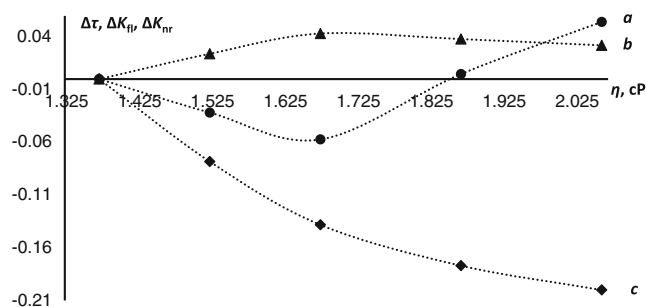
Table 1 Photophysical characteristics of **2** in ethanol – ethylene glycol mixed solvents in temperate range of 303 K to 323 K

Solvent molar ratio	$\chi_{ethanol}$=1; $\chi_{ethylene\ glycol}$=0				
η, cP	0.9859	1.043	1.1001	1.1911	1.2821
φ	0.551	0.557	0.557	0.578	0.585
K_{fl} ($\cdot 10^8$, s^{-1})	4.33	4.45	4.43	4.40	4.38
K_{nr} ($\cdot 10^8$, s^{-1})	2.90	2.88	2.78	2.73	2.66
τ, ns	1.38	1.36	1.39	1.40	1.42
Solvent molar ratio	$\chi_{ethanol}$=0.8; $\chi_{ethylene\ glycol}$=0.2				
η, cP	1.3722	1.5239	1.6756	1.8685	2.0614
φ	0.774	0.777	0.788	0.805	0.813
K_{fl} ($\cdot 10^8$, s^{-1})	4.68	4.65	4.62	4.69	4.74
K_{nr} ($\cdot 10^8$, s^{-1})	2.14	2.07	2.01	1.97	1.94
τ, ns	1.47	1.49	1.51	1.50	1.50
Solvent molar ratio	$\chi_{ethanol}$=0.6; $\chi_{ethylene\ glycol}$=0.4				
η, cP	2.0444	2.2969	2.5494	2.9083	3.2672
φ	0.949	0.954	0.937	0.962	0.993
K_{fl} ($\cdot 10^8$, s^{-1})	5.04	5.14	5.21	5.28	5.37
K_{nr} ($\cdot 10^8$, s^{-1})	1.42	1.38	1.39	1.41	1.30
τ, ns	1.55	1.53	1.51	1.49	1.50

Fig. 8 The changes of exited state lifetime, radiative and nonradiative decay constants for **2** in mixed solvent ($\chi_{ethanol}$=0.8; $\chi_{ethylene\ glycol}$=0.2) under the viscosity variations: **a** − k_{fl}, **b** − τ, **c** − k_{nr}

Table 2 Photophysical characteristics and constants of Forster-Hoffmann equation for 2 in ethanol – ethylene glycol mixtures

Solvent molar ratio	$\Delta\eta$, cP	ΔI	$\Delta\varphi$	$\Delta\varphi_{specific\ value}$	$X(\eta)$	$C(\eta)$	$X(\eta/T)$	$C(\eta/T)$
$\chi_{ethanol}$=1; $\chi_{ethylene\ glycol}$=0	0.2962	13.62	0.03	0.101	0.2420	−0.2589	0.1943	0.2283
$\chi_{ethanol}$=0.8; $\chi_{ethylene\ glycol}$=0.2	0.6892	15.33	0.04	0.058	0.1316	−0.1315	0.1137	0.1564
$\chi_{ethanol}$=0.6; $\chi_{ethylene\ glycol}$=0.4	1.2228	14.79	0.04	0.033	0.0875	−0.0542	0.0769	0.1420

Photophysical characteristics of *2* are measured for the viscosity range of 0.98–3.27 cP, in which the properties of the test compound as molecular rotor are more pronounced (Table 1).

There are two main factors in changing the photophysical characteristics of the compound – the change in the temperature and the change in the composition of the solvent. The relative quantum yield of fluorescence increases with the increase of the dynamic viscosity due to the temperature changes and increasing the content of ethylene glycol. However, the quantum yield is generally determined by the solvent composition. A similar situation is observed for the value of the excited state lifetime, which is almost independent of temperature and increases with the growth of ethylene glycol content in the mixture. The molecular rotor properties of the investigated compound *2* are confirmed by changes in radiative and nonradiative decay constants of the excited state of the molecule. Change in the viscosity of the solution of the fixed molar composition does not lead to significant change in value of the radiation decay constant of the excited state. At the same time with the growth of the viscosity, the nonradiative constant dramatically decreases (Fig. 8). Thus, *2* is truly a molecular rotor which displays both fluorescence intensity and lifetime sensitivity to viscosity changes of the environment. With the increase in ethylene glycol content in the system, the change of nonradiative decay constants per viscosity unit decreases.

The constants in the Forster-Hoffmann equation are calculated using the obtained data. The viscosity/temperature ratio is used to analyze the changes in the photophysical characteristics. Quantum yield φ and solvent bulk viscosity η follow the relationship: $\varphi \sim \left(\frac{\eta}{T}\right)^x$, where $x \leq 1$ and T is the temperature (Table 2).

The greatest change in the specific quantum yield values occurs in case of ethanol solution, with increasing the concentration of ethylene glycol the rotor properties decrease. The obtained values of Forster-Hoffmann constants also confirm our earlier conclusion about the various manifestation of the rotor properties in different viscosity ranges. The constants are change in the same manner for both η and η/T relations. However, if the change in X is almost the same for both described cases, the change in the numerical values of C is weaker when η/T relation is used, which makes the use of this form of the Forster-Hoffmann equation more convenient for practical analytical applications.

Conclusions

Spectral and photophysical characteristics of the two BODIPY complexes in ethanol - ethylene glycol mixtures are studied. *8*-Phenyl substituted BODIPY is found to exhibit properties of molecular rotor, i.e. its fluorescent characteristics highly dependent on the viscosity or rigidity of the microenvironment. In this paper the dependence of the photophysical characteristics of the complexes on the viscosity of the solvent is determined. Change in nonradiative decay rate constant values with increasing of viscosity indicates that the analyzed complex is the true molecular rotor, which forms TICT state. It is shown that the expression of the molecular rotor properties of the test compound is different in solvents of different viscosity. The highest specific change in fluorescence is observed in pure ethanol, which allows to recommend the compound as the analytical agent and the dependencies obtained by the authors as calibration plots for ethanol and other nonviscous media, and also for sol–gel systems, where the main solvent is ethanol. Studied compounds are not suitable for analysis of rheological characteristics of biological systems, because viscosities of bio systems are in the range of 2–50 cP, where molecular rotor properties of the compound under study are small. In addition, the features of solvation in various solvents should be taken into account, as this may have a dramatic effect on the spectral characteristics of studied compounds as it is shown by the authors. Obtained results provide additional insight into the mechanisms of BODIPY dyes solvation in general and can be used as another way for directional control of photophysical characteristics of this class of dyes.

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