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ORIGINAL ARTICLE

Synthesis and Spectral Characteristics of BODIPY Dyes with Two or Three Dipyrrin Domains

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Abstract

Several boron-dipyrrin (BODIPY) based fluorophores with two and three dipyrrin cores were synthesized and investigated in solvents under the concentration variation. Comparative analysis of spectral and photophysical changes under increasing the number of the cores in the dye molecule was made. Mutual influence of dipyrrin cores was detected leading to the increasing of the compounds rigidity and, thus, the absence of fluorescent molecular rotor effects under the viscosity variation. Aggregation induced quenching, which was observed for many mono-domain BODIPY dyes is reduced in case of investigated poly-domain compounds.

Keywords BODIPY · Spectral properties · Synthesis · Intramolecular rotation · Aggregation induced spectral changes

Abbreviations

ASE	Amplified spontaneous emission
EAS	Electronic absorption spectra
FRET	Fluorescence resonance energy transfer
PAI-1	Plasminogen activator type 1
ROS	Reactive oxygen species

Introduction

Highly luminescent materials have attracted considerable attention over the past decades due to their potential applications in medicinal diagnostics, molecular biology, molecular recognition, and material sciences. A particularly popular class of such dyes is the BODIPY family, in which a dipyrrin unit chelates BF_2 center, creating a boradiazaindacene unit. The BODIPY core offers good chemical and photochemical stability, both of which are two beneficial traits for a dye, especially for commercial applications. An especially appealing area for exploitation is the measurement of rheological properties of fluids and semi-mobile materials. Our laboratory has long been working with dyes – boron-dipyrrin based fluorophores (BODIPY), which have good photophysical properties, such as molar extinction coefficient, fluorescence intensity, quantum yield and others [1, 2]. Due to the presence of such properties, BODIPY can be applied in different fields of research to determine the properties of liquid-phase and solid-phase systems. 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 [3, 4]. Minor changes in the nature of the substituent in the 8- position does not deal high impact on the spectral properties, but the presence of nitrogen or oxygen donor atoms in phenyl moiety could be used for the sensing of the donor-acceptor interactions with solvent or dissolved compounds [5–7]. The changes of absorption and fluorescence spectra were found to be caused by specific and nonspecific interactions with biomolecules. It was shown that proteins could form molecular complexes with fluorophores [8]. Moreover, new trend in BODIPY chemistry is dye

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Highlights

- Several BODIPY-based fluorescent dyes were synthesized and characterized.
- The photophysical properties of poly-domain BODIPY dyes have been systematically investigated.
- Formation of J-type packing in the aggregated phase of BODIPY derivatives was observed.

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immobilization into polymer matrix using sol-gel technology where pH value can be used as influence factor during matrix synthesis and should be considered for further material usage [9]. It was shown that 8-substituted BODIPY dyes can exhibit a number of interesting properties that allow them to be used as fluorescent sensors for the properties of liquid-phase systems, bio systems [10, 11].

Although many examples of mono-BODIPY derivatives have been described, there are relatively few reports on multi-BODIPY dyes with conjugation in their frameworks. These conjugated multi-BODIPY dyes play very important role in light-harvesting and exhibit internal energy transfer [12–14]. Individual BODIPY domains can cooperate with each other, and not, that is, to act as separate units. When the parts of the BODIPY molecule interact, their polarization may occur, as a result of which a bathochromic shift will be observed in the absorption spectrum and the fluorescence spectrum. Tailor-made BODIPY dyes containing anchoring supports for surface attachment to, for example, metal surfaces, beads, paper, ceramics etc., would open up the possibility for real-time detection of fluid rheology at the liquid–solid boundary. There is the possibility of combining multiple BODIPY-based compounds together into a single entity for multiple sensing applications. For example, a dual rheology-ROS detector is not too difficult to imagine by careful design of the correct dipyrrin core and attached rotor [15]. A BODIPY–BODIPY rotor was shown to be a viable viscometer for various cellular, membrane-like environments, and its potential to be used for measuring the viscosity of molecular and ionic types of media was demonstrated [16]. But the question arises as to what BODIPY structures and how they should be related in order to observe an increase in their photophysical properties and manifestation of the properties of molecular rotors? At the moment, not so much studied these structures, so that you can draw any conclusions on this issue. For example, a triazine-based BODIPY trimer is a high molar extinction fluorophore, which is able to sense viscosity changes in various environments, including molecular solvents, lipid vesicles and several cancer cell lines [17]. Another single, dual and triple BODIPY complexes exhibit a high quantum yield due to excellent π-electron conjugation, and hence show good energy transfer mechanisms [12]. Under demanding transversal pumping conditions, the multi-branched BODIPYs exhibit enhanced laser actions with good efficiency in toluene solution. The high amplified spontaneous emission (ASE) conversion efficiency of the BODIPYs could be related to their higher fluorescence quantum yields and to its lower nonradiative deactivation processes. Photophysical and lasing properties are correlated: the higher the fluorescence quantum yields are, the higher the ASE efficiencies can be measured. Considering the easy synthetic protocol and the wide variety of possible substituents, we are confident that this strategy could be successfully extended for the development of efficient green emitting materials and devices [18].

A prototype in which two remote BODIPY units are linked by a long flexible chain, ROBOD, was synthesized and report on its ability to monitor changes in local viscosity. It is not intended that the two head groups interact in any way, and indeed there is no evidence to suggest that they do, but it is anticipated that the elongated structure might facilitate measuring changes in viscous flow, in addition to monitoring shear viscosity. Dyes such as Robod can be used to record how certain fluids respond to changes in applied pressure by techniques that are much simpler than conventional viscosity measurements. Similar studies can be applied to biological membranes and microheterogeneous media, such as micelles, vesicles, and organo-gels [19].

Monomeric, dimeric, trimeric and polymeric structures of C8 BODIPY and monomeric and dimeric aza-BODIPY were synthesized. Electrochemical studies show correlation of the number of active units with the amount of electrochemical peaks from monomer to oligomer. These characterizations of small oligomers of BODIPYs should help in development of new polymeric dyes for new applications [20]. Sensor connecting two BODIPYs at the *meso*-position shows a high sensitivity and selectivity for K^+ ions over other alkali and alkaline-earth metal ions (Na^+, Cs^+, Ca^{2+}, Ba^{2+}) in acetonitrile, ethanol, and ethanol–water mixtures [21]. Association of two BODIPY dyes possessing quite disparate optical properties and a crown ether provides an elegant way to obtain sensitive ratiometric fluorescent chemosensors for mercury(II) or for silver(I) [22].

Hence, BODIPY groups have proved to be useful in studies aimed at exploring protein structure. Little is still known about aggregation and the properties of aggregated BODIPY. BODIPY-BODIPY interaction is explored by investigating systems with a microscopically high, but macroscopically low concentration of BODIPY. Absorption and fluorescence spectra reveal different aggregation of BODIPY in the double-labeled cystein mutant of active PAI-1, and in lipid phases. Because the protein concentration is low there is a negligible intermolecular interaction between BODIPY groups in different protein molecules. The structure of PAI-1 allows the two BODIPY groups to be at distances short enough for an efficient orbital contact [23].

Compounds featuring one, two, or eight BODIPY donors and one porphyrin acceptor are light-harvesting arrays. Increasing the number of BODIPY donors from one to eight only increases the relative absorption [24]. To test distance-dependent FRET between the chosen donor and acceptor BODIPY dye pair, were prepared oligo(phenyleneethynylene)s of different lengths. Fluorescence spectroscopy in very dilute $CHCl_3$ solution showed that the FRET efficiency strongly decreases with increasing length of the rigid spacer [25].

Therefore, there is an increased interest in compounds that contain two or three BODIPY domains. If you take two or three BODIPY with a phenyl fragment and connect them through some spacer, then there may be an increase in photophysical characteristics with respect to the individual BODIPY compound. Thus, it may turn out that there will be no changes in the conversion to one domain of BODIPY, which means that these domains act as separate particles without any mutual interfacing. Our assumption is based on the fact that individual domains still have to influence each other, showing either a positive or negative synergistic effect.

In this paper, we will talk about the dual and the triple BODIPY, which include two and three BODIPY domains connected through a nitrogen and oxygen atoms. We aimed to study their photophysical characteristics, the effect of their structure on the properties of compounds for further use as pH sensors and molecular rotors due to the conjugation of two or three luminophores in one structure. Aggregation ability of the dual and triple BODIPY are also under discussion, in order to find the application of the effects studied in the future.

Material and Methods

Synthesis

Compounds ***1, 2, 4*** were synthesized in three successive stages with the one-pot method, to avoid the necessity of purifying the reaction mixture. The dipyrrin ligand was obtained on the first step. As starting compounds, an alkyl-substituted pyrrole, with a free alpha position, and tris(4-formylphenyl)amine, 4,4′ diformilphenylamine, or 4,4′ oxydilbenzaldehyde with the molar ratio of reagents 6:1, 4:1 or 4:1 respectively were used. The reaction was carried out for 12 h in a dichloromethane. The reaction mixture was acidified with a few drops of trifluoroacetic acid. In the second step the reaction mixture was injected by dichlorodicyanobenzoquinone as the oxidant. This resulted in the oxidation of methane bridge between pyrrole rings to methene and the emergence of a single conjugated electronic system of two pyrrole rings. After 15 min of stirring the excess of triethylamine was injected into the reaction mixture for removal of acidity and deprotonating the ligand obtained in the reaction mixture, then an excess of boron trifluoride etherate was added to provide the desired product. Triethylamine and etherate of boron trifluoride were injected in a molar ratio of 6:9 to the desired product.

Synthesis of unsubstituted analog (compound ***3***) was made in a similar method, but without addition of trifluoracetic acid in the first step. The reaction was carried out for 4 days in a dichloromethane in argon atmosphere. The following steps are the same as in the case of the synthesis of compounds ***1***, ***2***, ***4*** (Fig. 1).

Complex formation reaction was monitored spectrophotometrically by the change of the absorption spectra of the reaction mixture, and the appearance of the intensive fluorescence of the desired product.

The resulting compounds were washed from the excess reagents with water, dried, then purified by gel permeation chromatography. The eluent used was a 1:2 mixture of dichloromethane-hexane for compounds ***1***, ***2*** and ***4***, a 1:1 mixture of ethyl acetate-dichloromethane for compounds ***2*** and ***4***. After chromatography, the product was evaporated and recrystallized. The obtained BODIPY were identified by FTIR, ^{1}H NMR, MALDI TOF spectrometry.

Preparation of Compound (*1*) In a mixture of 0.100 g of 4,4′-diformyltriphenylamine and 0.163 g of 3-ethyl-2,4-dimethylpyrrole in dichloromethane (10 ml), acidified with two drops of trifluoroacetic acid, mixed for 12 h at room temperature. At the next stage into the reaction mass is added 0.075 g DDQ, in the molar ratio of DDQ:4,4′-bis(dipyrromethene)triphenylamine (alkylated) - 1:1. After 15 min of mixing 9 ml of triethylamine are injected into the reaction mixture, then etherate of Boron trifluoride to obtain compound 1. (0.05 g, 0.00006 mol). (yield 18%). ^{1}H-NMR (600 MHz, CCl_4): δ 1.15 (12H, t), 1.25 (12H, s), 1.80 (12H, d), 5.68 (4H, t), 5.85–5.90 (2H, dd), 6.47 (4H, s), 6.85 (1H, s), 7.27 (2H, s). MALDI-TOF: calculated ([C52H57B2F4N5]+) m/z = 849.67, found: m/z[M-3F+ C_2H_3N] = 837.23.

Preparation of Compound (*2*) In a mixture of 0.100 g of tris(4-formylphenyl)amine and 0.222 g of of 3-ethyl-2,4-dimethylpyrrole in dichloromethane (10 ml), acidified with two drops of trifluoroacetic acid, mixed for 12 h at room temperature. At the next stage into the reaction mass is added 0.681 g DDQ, in the molar ratio of DDQ:tris(4-dipyrromethanephenyl)amine (alkylated) - 1:1. After 15 min of mixing 9 ml of triethylamine are introduced into the reaction mixture, then etherate of Boron trifluoride to obtain compound 3. (0.07 g, 0.00006 mol). (yield 20%). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.05 (18H, t), 1.24 (9H, s), 1.54 (9H, s), 2.15 (12H, s), 2.33–2.40 (9H, dd), 2.58 (9H, s), 6.95 (6H, s), 7.75 (6H, s). MALDI-TOF: calculated ([C69H78B3F6N7]+) m/z = 1151.85, found: m/z[M-F-S] = 285.19.

Preparation of Compound (*3*) In a mixture of 0.1 g of tris(4-formilphenyl)amine and 0.12 g of pyrrole in dichloromethane (10 ml), mixed for 4 days at room temperature in argon. At the next stage into the reaction mass is added 0.0681 g DDQ, in the molar ratio of DDQ: tris(4-dipyrromethanephenyl)amine

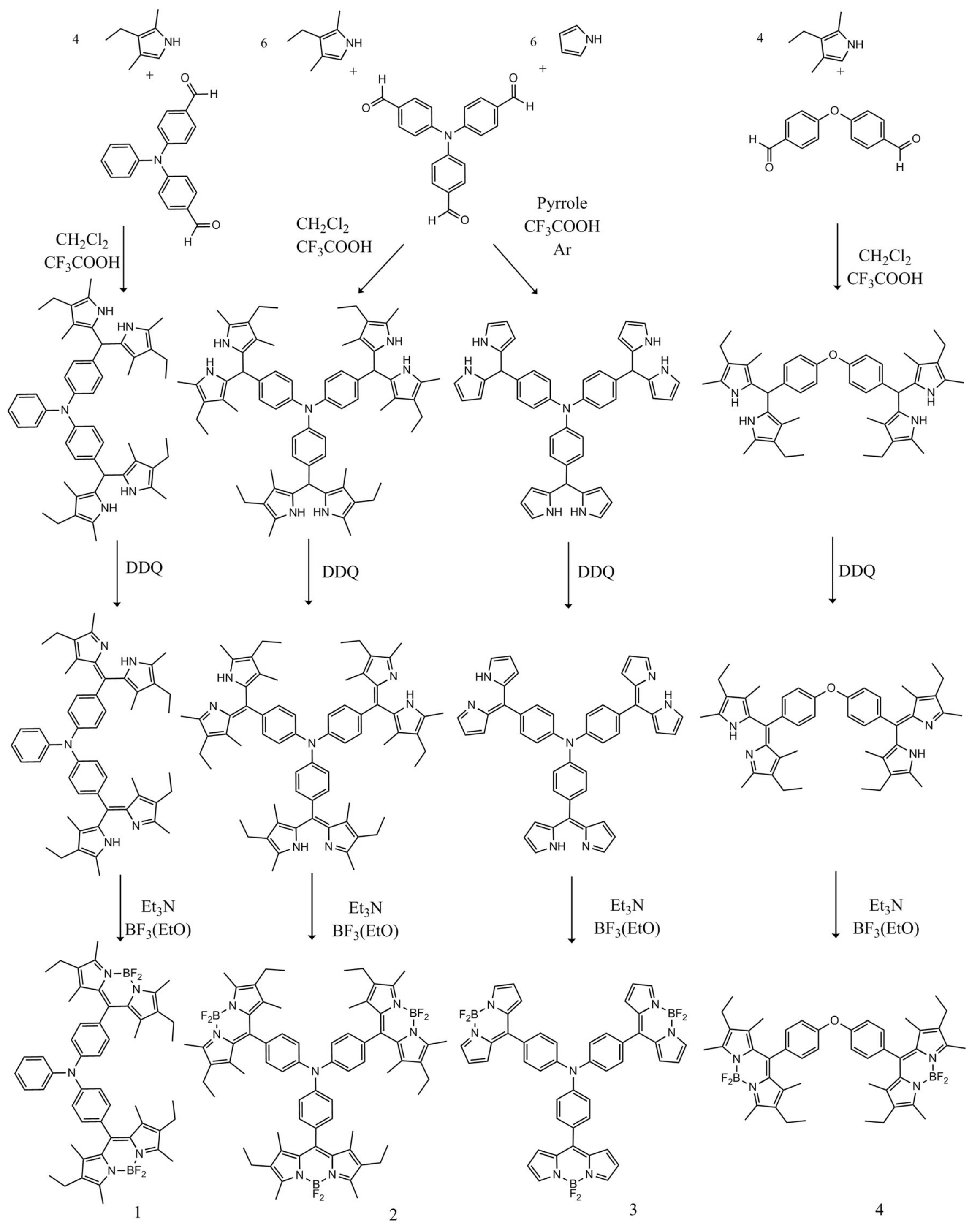


Fig. 1 Synthetic route to compounds

(unalkylated) - 1:1. After 15 min of mixing 9 ml of triethylamine are introduced into the reaction mixture, then etherate of Boron trifluoride to obtain compound 4. (0.02 g, 0.000025 mol). (yield 10%). ^{1}H-NMR (600 MHz, CCl_4): δ 5.70 (6H, t), 5.85–5.90 (6H, dd), 6.85 (6H, s), 5.47 (6H, s), 7,27 (6H, s). MALDI-TOF: calculated ([C45H30B3F6N7]+) m/z = 815.20, found: m/z[M + C_2H_3N] = 858.89.

Preparation of Compound (*4*) In a mixture of 0,05 g of 4-(4-formylphenoxy)benzaldehyde and 0,054 g of 3-ethyl-2,4-dimethylpyrrole in dichloromethane (10 ml), acidified with two drops of trifluoroacetic acid, mixed for 12 h at room temperature. At the next stage into the reaction mass is added 0,05 g DDQ, in the molar ratio of DDQ:4-(4-formylphenoxy)benzodipyrromethane - 1:1. After 15 min of mixing 9 ml of triethylamine are introduced into the reaction mixture, then etherate of Boron trifluoride to obtain compound 5. (0.035 g, 0.000045 mol). (yield 22%). ^{1}H-NMR (600 MHz, CCl_4): δ 1.15 (12H, t), 1.68 (12H, s), 2.36 (8H, dd), 2,72 (12H, s).

Equipment

UV–Vis electronic absorption spectra (EAS) were recorded in the range 360–700 nm on a SF-104 spectrophotometer (Aquilon, Russia) controlled with a PC through 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. The fluorescence spectra were measured in the wavelength range 500–700 nm and the excitation wavelength was 480 nm. The slit widths of excitation and emission ranged from 2.5 to 5 nm. Experiments were carried out in quartz cuvettes with a thickness of the absorbing layer of 2 and 10 mm. The ^{1}HNMR spectra for solutions of compounds in $CDCl_3$ were recorded on a Bruker AVANCE-500 spectrometer (Germany) with an operating frequency of 500 MHz.

The measurements were held in individual organic solvents of different nature and their mixtures. Solvents (Chimmed, Russia) were all of analytical grade purified by standard techniques [26]. The residual water content (<0.02%) was determined by the Karl Fischer method [27]. The changing of the viscosity was achieved by varying the solution temperature in range 293 to 343 K, and by varying the components molar ratios in mixtures of 2-propanol (low viscosity solvent) and glycerol (high viscosity solvent) to change the viscosity of the dyes' solution in a broad range 11.5–1444 cP.

Results and Discussion

Spectral Properties

On the first step we obtained spectral characteristics of investigated compounds in organic solvents (Table 1). The measurements were carried out in individual organic solvents of different nature and their mixtures. For the analyzed single, dual and triple BODIPY complexes with alkyl groups, the electronic absorption spectra in dichlormethane are characterized by intensive absorption maxima at 531 nm for compounds ***1*** and ***2***, 498 nm for ***3*** and 523 nm for ***4***. Depending on the extent of the π-electron conjugation between the BODIPY groups and the macromolecular system, the absorption intensity increased, but the bathochromic shifts were not observed in the absorption bands. In the transition from alkylated compounds to non-alkylated compounds, a hypsochromic shift was observed in the electronic absorption spectra that is in a good agreement with literature data on the influence of dipyrrin alkylation on spectral characteristics [1]. The influence of the heteroatom of the linker was unsuspected result, thus, changing Nitrogen to Oxygen cause 10 nm hypsochromic shift of the absorption band and Stokes shift increase (Table 1).

The average value of the molar absorption coefficient increases with the addition of supplemental BODIPY domains to the structure of the molecule to 150,000 l/(mol·cm), and in some solvents, even more than the individual BODIPY, in which it is about 60,000 l/(mol·cm) (Fig. 2).

The BODIPY complex exhibited the following maximum emissions: single-BODIPY at 547 nm, dual-BODIPY at 541 nm and triple-BODIPY at 540 nm. In the transition from single-BODIPY to the triple-BODIPY the average Stokes shifts of fluorescence (22–8 nm) decreases, which indicates that a system with several BODIPY cores has less possibilities for vibrational relaxation and, thus, increasing the number of dipyrrin moieties lead to increasing the molecule rigidity. In order to examine their fluorescence properties, the BODIPY complexes were dissolved in different solvents. At very low concentrations, they have sufficiently bright absorption, and their fluorescence does not differ much from fluorescence for simply single-phenyl-substituted BODIPY (Table 2).

The emission maxima of the compounds were affected by the solvent polarity with strong effects on the emission maxima being demonstrated with increasing solvent polarity. The quantum yields of the complexes calculated in C_6H_{12} were as follows for single-BODIPY (0.94), dual-BODIPY (0.83) and triple-BODIPY (0.85). Similarly, the quantum yields were calculated in other solvents and ranged from 0.03–0.91. The quantum yield depends on the values of the constants of radiation and non-radiative deactivation rate constants. The transition from the monomer to the trimmer decreases the quantum yield and the radiation deactivation rate constant, and non-radiation deactivation rate constant increases accordingly. The fluorescence lifetime of the complexes were calculated in C_6H_{12} for single-BODIPY, (1.8 ns), dual-BODIPY (0.61 ns) and triple-BODIPY (0.36 ns).

In comparison with single-BODIPY, the quantum yield of compound ***5*** is smaller, the radiative deactivation rate constant has not changed, but the non-radiative deactivation rate constant is much higher, and, therefore, the lifetime of the excited state has decreased. In comparison with the nitrogen-containing dual-BODIPY, the quantum

Table 1 Photophysical characteristics of compounds (λ_{abs} – wavelength of absorption maximum; λ_{fl} – wavelength of fluorescence maximum; $\Delta\lambda$ – Stokes shift) in individual organic solvents

	1			***2***			***3***			***4***		
	λ_{abs}, nm	λ_{fl}, nm	$\Delta\lambda$, nm	λ_{abs}, nm	λ_{fl}, nm	$\Delta\lambda$, nm	λ_{abs}, nm	λ_{fl}, nm	$\Delta\lambda$, nm	λ_{abs}, nm	λ_{fl}, nm	$\Delta\lambda$, nm
Benzene	535	542.1	7.5	529	542.5	14.0	499	508.1	9.1	525	540	15
Hexane	531	537.5	6.5	531	537.0	6.0	–	–	–	523	537	14
Cyclohexane	532	538.1	6.0	532	538.5	6.5	498	504.0	6.0	524	538	14
Dichlormethane	531	540.5	9.5	531	540.0	9.0	496	505.1	9.1	523	538	15
Ethylacetate	527	536.5	9.5	527	536.0	9.0	492	503.0	11.0	–	–	–
Ethanol	528	537.5	9.5	528	538.5	10.5	–	–	–	521	537	16
Pyridine	533	542.5	10.0	527	542.5	15.5	496	508.1	12.1	524	539	15
Dimethyl formamide	527	537.5	10.5	527	538.5	11.5	491	506.0	15.0	521	535	14
Dimethyl sulfoxide	528	539.5	11.5	528	538.5	10.5	493	507.0	14.0	522	537	15

yield and the radiation and non-radiative deactivation rate constants are also larger for the oxygen-containing dual-BODIPY the lifetime of the excited state is less.

Molecular Rotor Properties

The term “molecular rotors” refers to compounds whose molecules consist of two or more fragments that can rotate relative to each other. The major part is called the stator, and the smaller rotator or rotor. For systems, where the intramolecular conformational change depends on the viscosity of the local environment in the proximity of the molecule a linear dependence of the quantum yield (F) or fluorescence lifetime (τ) as a function of medium’s viscosity should be observed. This viscosity dependence of the quantum yield can be expressed using Foerster–Hoffman theory [17].

Earlier in our laboratory it was shown, that BODIPY with alkyl groups, in the structure of which there is a bulky phenyl or biphenyl fragment, as well as their derivatives, exhibit the properties of the fluorescent molecular rotor [5]. In this paper, it was interesting to study the manifestation of a similar effect for polydomain BODIPY (Fig. 3).

We examined how the emission of the compounds depended on the viscosity of the media. Solutions with different viscosities were prepared by changing temperature and mixing the appropriate amounts of 2-propanol and glycerol. The viscosity range under investigation was of 0.9–1457 cP. Emission intensity increased by 10% as viscosity increased, at the same time the absorbance is also increased. These values level each other, due to the quantum yield decreased by changing temperature in C_6H_{12} from 0.84 to 0.81. From a linear manner dependence of $\lg\Phi$ on $\lg\eta$ were obtained negative Foerster–Hoffman coefficients. This effect of “reverse” molecular rotors is manifested for both alkylated and non-alkylated compounds. Observed effects could be attributed with the temperature influence on spectral characteristics, not the viscosity. Same effects were earlier shown for many fluorophores [16]. Scanning of the potential energy surface of the investigated compounds show no differences in comparison with the individual dye molecules, thus, indicating the possibilities of intermolecular interactions in the investigated systems.

We assume, that the absence of fluorescent respond of investigated dyes on viscosity variation could be attributed with the increased rigidity of the molecules that is confirmed by the values of Stokes shifts. It is also possible that an increase in the viscosity leads to the formation of excimer forms. With the additional compaction of the molecular mesh due to the

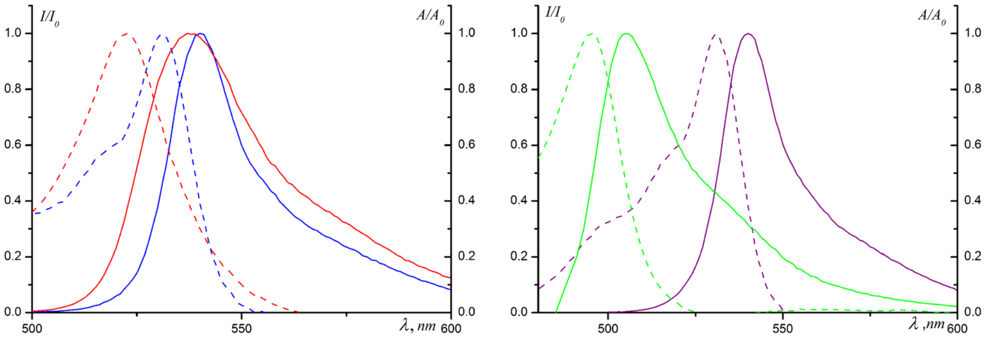


Fig. 2 Relative absorption (dashed line) and fluorescence (dotted line) spectra of investigated **compounds *1*** (blue line), ***2*** (purple), ***3*** (green), ***4*** (red line) in dichloromethane

Table 2 Photophysical characteristics of compounds (Φ – fluorescence quantum yield at 293 K; τ – excited state lifetime at 293 K; K_{rad} – radiative deactivation rate constant at 293 K; K_{nrad} – non-radiative deactivation rate constant at 293 K) in dichloromethane

	Φ	τ, ns	$K_{rad}\cdot10^8$, s^{-1}	$K_{nrad}\cdot10^9$, s^{-1}
mono BODIPY	0.94	1.8	5.03	0.52
1	0.83	0.61	1.5	1.6
2	0.85	0.36	2.37	2.69
3	0.14	0.12	1.33	9.2
4	0.8	0.1	8	9.3

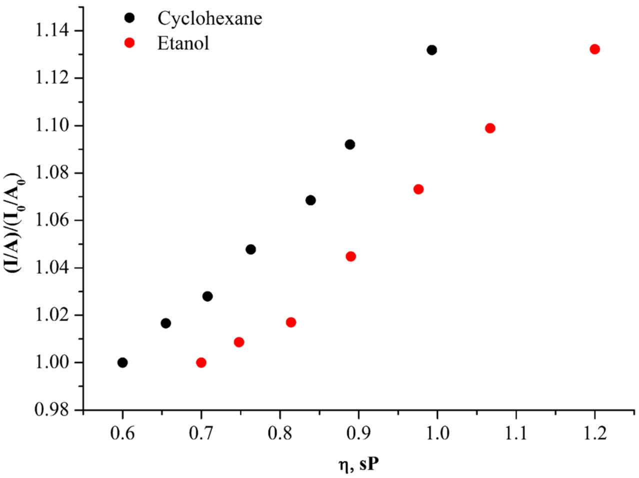


Fig. 4 Changes in the ratio of the fluorescence and absorption intensity (I /A) of compound ***4*** under the solvent viscosity

increase in solution viscosity, any interactions between BODIPY domains are possible, which results in quenching of the fluorescence (Fig. 4).

But for compound ***4***, containing oxygen atom at spacer group, with increasing viscosity, we observe an increase in the relative intensity of the fluorescence, indicating that this compound exhibits the properties of a fluorescent molecular rotor, but not as intense as a single-BODIPY [10]. This can be seen from the calculated values of the coefficient in the Foster-Hoffman equation for compound ***4*** (0.15) and single-BODIPY (0.46) in ethanol. The role of the nature of spacer atom requires additional investigation because it could be the factor of simple synthetic control under compounds spectral behavior.

Aggregation Initiated Spectral Changes

Although BODIPY complexes have high fluorescence in dilute solutions, their fluorescence drops or completely disappears in a solid state. This phenomenon is known as "concentration quenching". The main cause of fluorescence quenching processes is an association leading to the formation of aggregates of different structures. At the moment, there are several ways to modify the dyes in order to increase the fluorescence in the solid phase. One way to modify the BODIPY complexes is to expand the π-system of the substituent at the 8-position. It is established that the variation of the ratio of the monomeric and aggregated forms of such compounds can be used to fine tune the emission spectra of OLED devices based on BODIPY [28] (Fig. 5).

We conducted the experiments with oxygen-containing dual-BODIPY in two solvents (ethanol and cyclohexane), which differ from each other in polarity. With increasing concentration, the optical density increases, but the absorption peak does not shift. The dependence of the optical density on the concentration

Fig. 3 Changes in the ratio of the fluorescence and absorption intensity (I /A) of compound ***2*** (red) and ***3*** (green) under the solvent viscosity

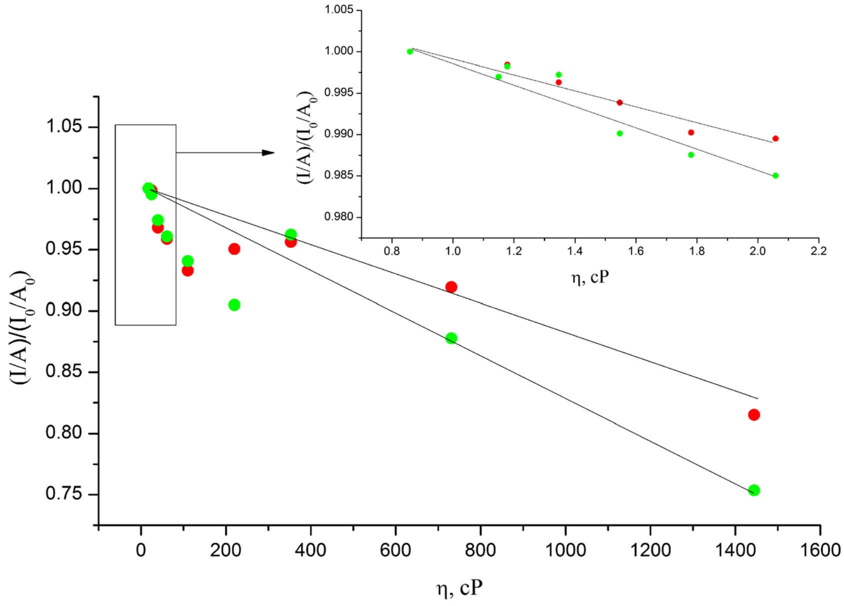
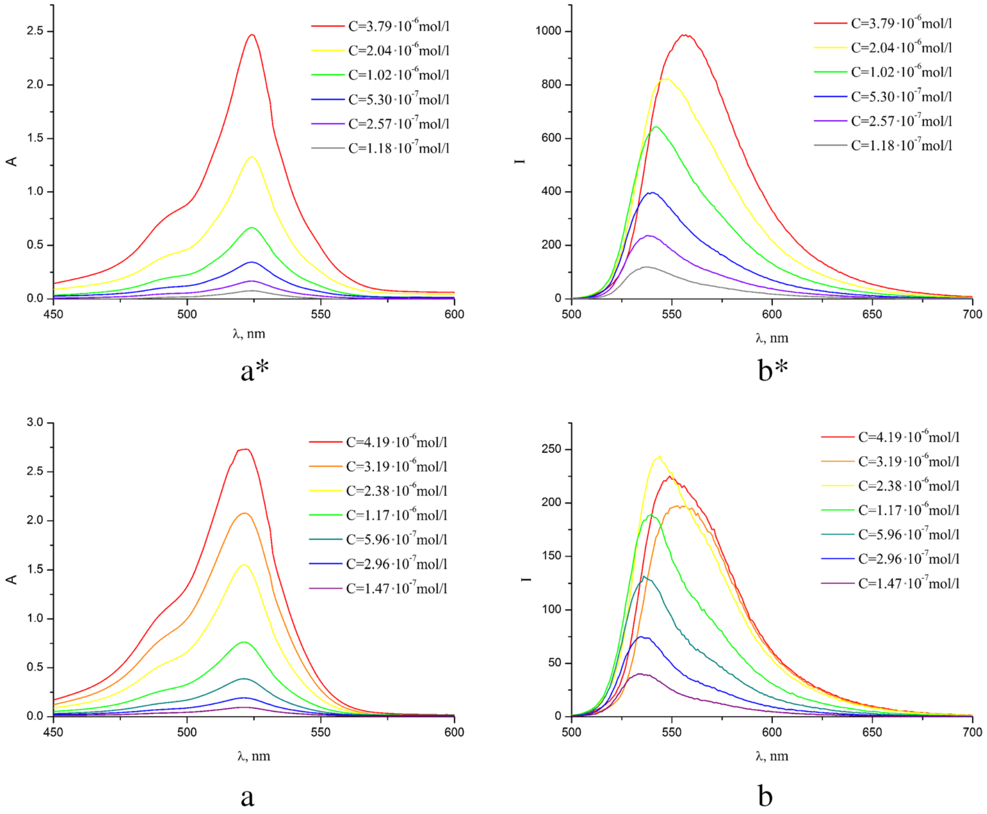


Fig. 5 EAS (A) and fluorescence (B) spectra of compound *4* in cyclohexane (A*) and in etanol (A) at varying concentrations



a* b*

a b

is linear and obeys the Lambert-Bouguer-Beer law. In turn, with increasing concentration, we observed a bathochromic shift of max fluorescence, which first of all illustrates the specific interaction of the compound molecules. Similar changes in the spectra were observed in ethanol (Table 3).

The results of the calculated photophysical characteristics show that in cyclohexane and ethanol the quantum yield and the lifetime of the excited state is increasing with decreasing concentration. In turn, the rate constant of radiative deactivation remains constant, and the rate constant of non-radiative deactivation decreases. We conclude that with an increase in the concentration of the oxygen-containing dual-BODIPY in the solution, the nonspecific interaction of the molecules takes place, namely, the light is reabsorbed.

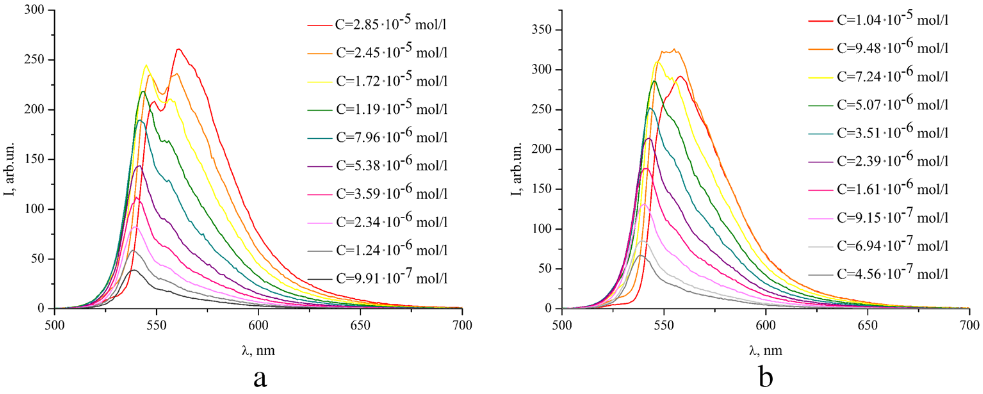
Table 3 Photophysical characteristics of compound *4* (Φ – fluorescence quantum yield at 293 K; τ – excited state lifetime at 293 K; K_{rad} – radiative deactivation rate constant at 293 K; K_{nrad} – non-radiative deactivation rate constant at 293 K) under the concentration variation

Cyclohexane						
$C \cdot 10^{-6}$, mol/l	4.54	3,79	2.04	1.02	0.53	0.25
Φ	0.07	0.15	0.23	0.35	0.35	0.48
$K_{rad} \cdot 10^{8}$, s^{-1}	7,98	7.97	7.96	7.68	7.66	7.66
τ, ns	0.005	0.019	0.028	0.045	0.046	0.063
$K_{nrad} \cdot 10^{10}$, s^{-1}	21.0	5.13	3.44	2.13	2.09	1.52
Ethanol						
$C \cdot 10^{-6}$, mol/l	4.19	3.19	2.38	1.17	0.59	0.29
Φ	0.09	0.14	0.21	0.29	0.35	0.35
$K_{rad} \cdot 10^{8}$, s^{-1}	9.88	9.88	8.72	8.72	9.03	9.34
τ, ns	0.009	0.014	0.024	0.033	0.039	0.037
$K_{nrad} \cdot 10^{10}$, s^{-1}	10.6	7.06	4.07	2.93	2.46	2.58

BODIPY dyes are widely used class of fluorescent probes, which attract continuous interest because their photophysical properties could be tuned via fairly straightforward synthetic transformations. J- and H-aggregates of BODIPY dyes were noted in a number of studies; however, these cases primarily involved aggregation in the solid or gel states or in organic solvent-water mixtures [29–31]. The aggregated forms of BODIPY dyes, especially in aqueous environments, tend to exhibit a red-shifed transition at ca. 600 nm. A few cases of BODIPY H-aggregates were reported, and in some instances the H- aggregates of BODIPY dyes were found to be non emissive [32]. On the other hand, in organic solvents, BODIPY dyes are known to be monomeric, especially at low concentration ranges, as conformed by the presence of a single peak in the emission spectra. Here, we present an unusual case of spectroscopically monomeric and aggregated forms of BODIPY in a cyclohexane.

We have observed the formation of red-shifed, relatively narrow emission band consistent with J-type packing in the aggregated phase of BODIPY derivatives (Fig. 6).

Fig. 6 Fluorescence spectra of compound ***1(A)*** and compound ***3(B)*** in cyclohexane at varying concentrations



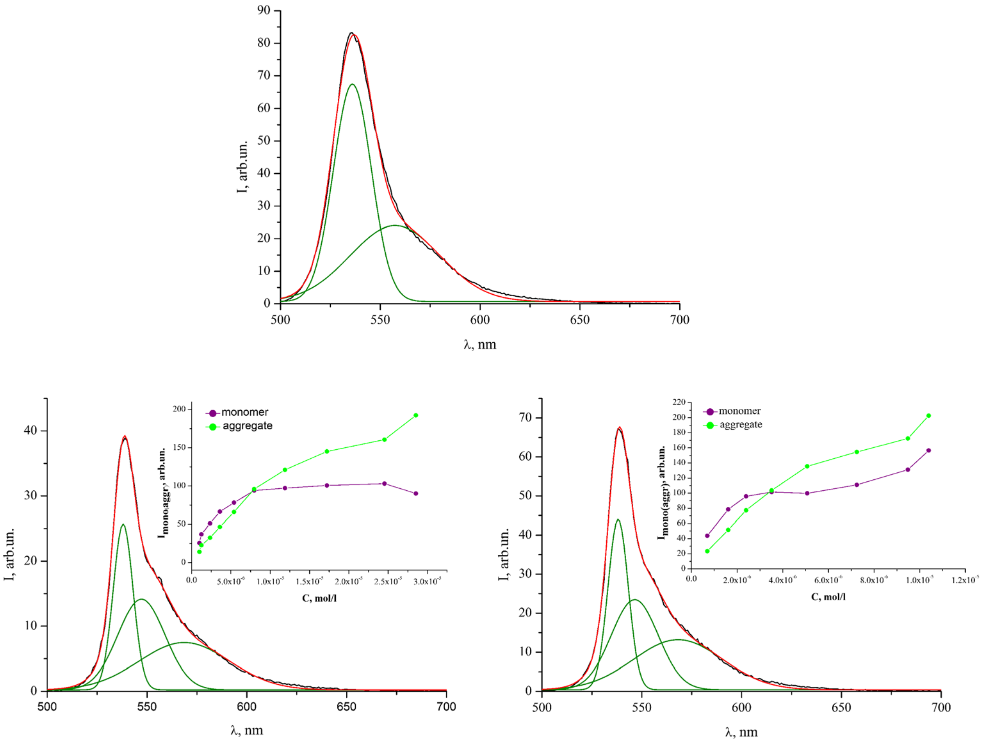
Obtained spectra were deconvoluted on separate Gauss curves. Mono-BODIPY was found to have two peaks in spectra: one for the S^1-S^0 transition and the small peak on the right shoulder of vibronic nature. For investigated ***1*** and ***2*** even at small concentrations three spectral peaks were observed. The third peak could be attributed to the formation of exited dimer in the solution or the reabsorption effects. But the absence of peak shifts under the concentration increase indicate the formation of eximer. Increasing of the concentration up to $2\cdot10^{-6}$ mol/l for 3 and $5\cdot10^{-6}$ mol/l lead to the growth of the monomeric and dimeric forms both. Above that concentration only dimeric form increase were observed. The difference in the concentration of the monomer stability demonstrate that alkyl moieties at dipyrrin units preserve aggregation in the exited state (Fig. 7).

It should be noted that dimeric form of compounds exhibit strong fluorescence to the contrast of mono-BODIPY.

Conclusions

Several BODIPY-based fluorescent dyes were synthesized and characterized. The photophysical properties of these dyes have been systematically investigated in different solvents and solvent mixtures. General spectral characteristics are the same as for monomeric BODIPY unit, with more pronounced absorption spectra and slightly weaker fluorescence. The absence of rotary effect under the viscosity variation indicated the high rigidity of the obtained structures. It was shown that separate BODIPY cores could interact with each other with

Fig. 7 The decomposition of the fluorescent spectra of compound ***mono-BODIPY*** (upper), ***1*** (bottom left) and ***2*** (bottom right) into individual bands using the Gaussian function



the formation of exited dimer, with less fluorescence quenching under the concentration increasing in comparison with the mono-BODIPY. Thus investigated complexes could be an interesting object for the obtainment of organized layers on some substrate for further usage as light converters in optics and sensoric.

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