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ORIGINAL ARTICLE

Effect of Aryl-, Halogen-, and Ms-Aza-Substitution on the Luminescent Properties and Photostability of Difluoroborates of 2,2′-Dipyrrometenes

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Abstract
Boron(III) complexes with alkyl-, phenyl-, and halogen-substituted 2,2′-dipyrromethenes (BODIPY) and meso-aza-dipyrrometenes (ms-aza-BODIPY) were synthesized. The structure relationship of the obtained coordination compounds with their luminescent characteristics is analyzed. Arylated BODIPY, in contrast to alkyl-substituted analogs, is more sensitive to interparticle interactions with a solvent, causing a decrease in the quantum yield by up to 40%. The introduction of phenyl substituents into the BODIPY molecule shifts the first absorption band bathochromic, significantly (32–37 nm) increases the Stokes shift in the emission spectrum, but reduces the probability of the $S_0 \rightarrow S_1$ electronic transition as compared to alkylated complexes. Replacing the methine carbon atom with nitrogen leads to quenching of ms-aza-BODIPY fluorescence compared to BODIPY up to 5–20%. The stability of 2,2′-dipyrromethenes difluoroborates to oxidative destruction under the influence of UV irradiation in cyclohexane solutions was evaluated. It has been shown that symmetric aryl substitution in pyrrole cycles of dipyrromethene significantly increases the photostability of the corresponding compounds as compared to alkyl-substituted analogs and is an effective method of obtaining boron (III) dipyrromethenates with practically useful properties. It has been established that the replacement of the methin ms-spacer of dipyrromethene by a nitrogen atom significantly reduces the photostability of ms-aza-dipyrromethenates of boron. Halogenation of β-positions of pyrrole cycles by a factor of 5–8 reduces the photostability of difluoroborates ms-aza-dipyrromethenes in comparison with a non-halogenated analogue.

Keywords Boron(III)dipyrromethenates · Synthesis · Electronic absorption spectra · Fluorescence · Photo-oxidative destruction

Introduction

One of the urgent tasks of modern science is to obtain new luminophores suitable for use in analytical chemistry, medicine, biology, and laser technology. Moreover, each specific practical task imposes its own requirements on the spectral properties of compounds, their photo- and thermal stability, chemical inertness and non-toxicity for living organisms, etc. At present, luminophores based on dipyrromethenes are of great scientific and practical interest. BF_2-dipyrromethenates (BODIPY) perfectly proved itself as fluorescent probes and dyes for visualizing individual components of biological systems [1–3], photosensitizers in photodynamic therapy [4–8], components of active media of dye lasers [9].

The ideas about the quantitative characteristics of photostability and the mechanisms of BODIPY photodegradation processes of dyes, depending on the characteristics of their molecular structure, the nature of the medium, characteristics of absorbed light quanta, etc., are very important for successful practical application.

To date, information on the photostability of dipyrromethenates is currently limited to data for only a small

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group of alkyl-substituted d-metals dipyrromethenates [10] and BODIPY [8, 11–16].

It should be expected that the indicators of BODIPY photostability can vary significantly, primarily due to the functional modification of the dye molecular structure, and also, depending on the redox properties of the medium, the nature of the solvent chosen, including its ability to solvation of the solute [17–19]. In this regard, the purpose of the work was to study the effect of various types of structural modification of BF_2-dipyrromethenes on their photostability in an organic medium under the action of UV-irradiation. As the objects of study, difluoroborates of alkyl-, phenyl-, and halogen-substituted dipyrromethenes and their meso-aza analogs **1**–**8** were selected (Fig. 1).

The BODIPY group of dyes is represented by compounds **1**–**5**. Complex 1 with unsubstituted β-positions of pyrrole fragments was chosen as the comparison compound with its structural analogues **2**, **3** and **4**, substituted in these positions with methyl-, heptyl- or benzyl-groups, respectively.

Compounds **6**–**8** form a meso-aza-BODIPY group, in whose molecules the aza-group plays the role of a spacer between the pyrrole core.

The phenyl substitution in 3,3′,5,5′-positions of the molecule is implemented in BODIPY **5** and meso-aza-BODIPY **6**–**8**. A small angle of rotation of the planes of the phenyl fragments relative to the dipyrromethene core provides a partial conjugation of their aromatic systems, which significantly affects the characteristics practically significant spectral-luminescent properties of these dyes [20], including, shifts their electronic spectra to the area of the phototherapeutic window.

Unlike meso-aza-BODIPY **6**, compounds **7** and **8** are halogenated at the β-positions of the pyrrole rings by chlorine and bromine atoms, respectively.

Experimental

Alkyl substituted dipyrrolylmethanes **1**–**4** were synthesized by condensation of the corresponding pyrroles with pyrrolealdehydes in methanol in the presence of hydrobromic acid [21]. The starting pyrroles and their formyl derivatives were obtained according to methods similar to those given in [22]. Compounds **5** and **6** were synthesized according to the procedures presented in [23]. Borfluoride complexes were prepared according to the general scheme by reacting the corresponding dipyrrolylmetene with boron trifluoride etherate in a medium of dried methylene chloride in the presence of triethylamine at room temperature (Fig. 2):

Compound **8** was obtained according to the method presented in [24], according to the scheme **1**:

Compound **7** was prepared similarly using chlorosuccinimide as chlorinating agent.

The PMR spectra of the synthesized compounds were recorded on a Bruker 500 spectrometer ($CDCl_3$, TMS internal standard) at the Upper Volga Regional Center for Physical and Chemical Research, collective center, G.A. Krestov Institute of Solution Chemistry of the Russian Academy of Sciences. Elemental analysis was performed on a FLASH EA1112 analyzer (Italy).

Difluoroborate 3,3′,5,5′-Tetramethyl-2,2′-Dipyrrolylmetene (1) Yield 66%. NMR spectrum ^1H, δ, ppm: 7.07 s (1H, *ms*-H), 6.07 s (2H, 4,4′-H), 2.55 s (6H, CH_3), 2.27 s (6H, CH_3). Found,%: H 6.0; C 62.83; N 11.18. $BC_{13}F_2H_{15}N_2$. Calculated,%: H 6.09; C 62.94: N 11.29.

Difluoroborate 3,3′,4,4′,5,5′-Hexamethyl-2,2′-Dipyrrolylmetene (2) Yield 96%. NMR spectrum ^1H, δ, ppm: 6.96 s (1H, *ms*-CH), 2.49 s (6H, 5,5′-CH_3), 2.16 s (6H, 3,3′-CH_3), 1.94 s (6H, 4,4′-CH_3). Found,%: H 6.85; C 65.18; N 10.04. $BC_{15}F_2H_{19}N_2$. Calculated,%: H 6.94; C 65.25; N 10.14.

Difluoroborate 3,3′,5,5′- Tetramethyl –4,4′- di-N-Heptyl –2,2′-Dipyrrolylmetene (3) Yield 97%. NMR spectrum ^1H, δ, ppm: 6.96 s (1H, *ms*-H), 2.50 s (6H, 5,5′-CH_3), 2.36 t (4H, J = 7.5 Hz, 4,4′-CH_2-Hp), 2.17 s (6H, 3,3′-CH_3), 1.44 q (4H,

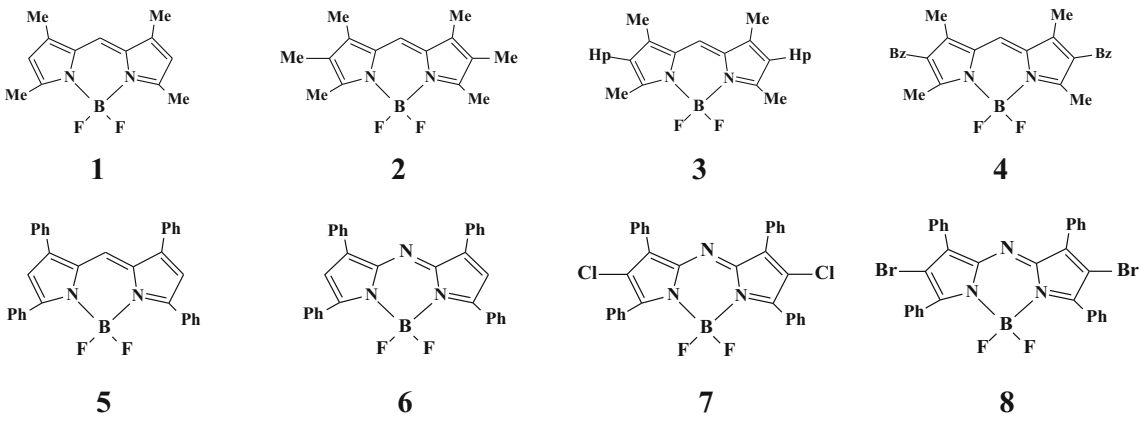
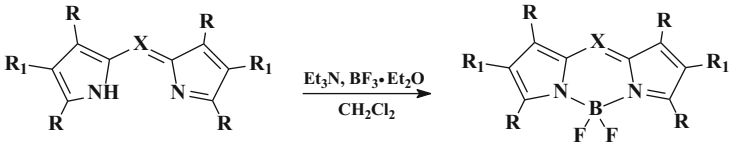


Fig. 1 Structures of the investigated compounds

Fig. 2 Synthesis scheme of compounds **1–8**



X=CH и R=CH_3, R_1=H (**1**); R_1=CH_3 (**2**); R_1=C_7H_{15} (**3**); R_1=CH_2-Ph (**4**); R=H, R_1=Ph (**5**).
X=N и R=Ph, R_1=H (**6**); R_1=Cl (**7**); R_1=Br (**8**).

CH_2-Hp), 1.32 m (16H, CH_2-Hp), 0.91 t (6H, J = 7.5 Hz, CH_3-Hp). Found, %: H 9.63; C 72.85; N 6.21. $BC_{27}F_2H_{43}N_2$. Calculated, %: H 9.75; C 72.96; N 6.30.

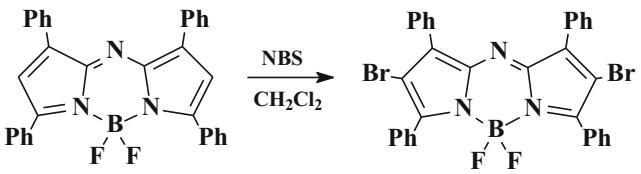
Difluoroborate 3,3′,5,5′-Tetramethyl-4,4′-Dibenzyl –2,2′-Dipyrrolylmetene (4) Yield 81%. NMR spectrum ^{1}H, δ, ppm: 7.29 t (4H, J = 7.3 Hz, 3″,5″-H-Ph), 7.21 t (2H, J = 7.3 Hz, 4″-H-Ph), 7.15 d (4H, J = 7.3 Hz, 2″,6″-H-Ph), 7.07 s (1H, *ms*-H), 3.80 s (4H, CH_2-Bz), 2.47 s (6H, 5,5′-CH_3), 2.18 s (6H, 3,3′-CH_3). Found, %: H 6.29; C 75.67; N 6.42. $BC_{27}F_2H_{27}N_2$. Calculated, %: H 6.35; C 75.71; N 6.54.

Difluoroborate 3,3′,5,5′- Tetraphenyl –2,2′- Dipyrrolylmetene (5) Yield 79%. NMR spectrum ^{1}H, δ, ppm: 7.43–7.58 m (8H, *o*-H-Ph), 7.17–7.40 m (12H, *m,p*-H-Ph), 6.76 s (2H, 4,4'-H), 5.40 s (1H, *ms*-H). Found, %: H 4.48; C 79.07; N 5.32. $BC_{33}F_2H_{23}N_2$. Calculated, %: H 4.67; C 79.85; N 5.64.

Difluoroborate 3,3′,5,5′- Tetraphenyl -*ms*-Aza-2,2′-Dipyrrolylmetene (6) Yield 85%. NMR spectrum ^{1}H, δ, ppm: 8.04–8.15 m (8H, *o*-H-Ph), 7.44–7.58 m (12H, *m,p*-H-Ph), 7.07 s (2H, 4,4'-H). Found, %: H 4.22; C 76.85; N 8.32. $BC_{32}F_2H_{22}N_3$. Calculated, %: H 4.46; C 77.28; N 8.45.

Difluoroborate 4,4′- Dichlor-3,3′,5,5′- Tetraphenyl -*ms*-Aza-2,2′- Dipyrrolylmetene (7) Yield 59%. NMR spectrum ^{1}H, δ, ppm: 7.47–7.54 m (12H, *m,p*-H-Ph), 7.83–7.99 m (8H, *o*-H-Ph). Found %: H 3.37; C 67.35; N 7.34. $BC_{32}F_2H_{20}Cl_2N_3$. Calculated %: H 3.56; C 67.88; N 7.42.

Difluoroborate 4,4′- Dibrom-3,3′,5,5′- Tetraphenyl -*ms*-Aza-2,2′- Dipyrrolylmetene (8) Yield 67%. NMR spectrum ^{1}H, δ, ppm: 7.46–7.51 m (12H, *m,p*-H-Ph), 7.74–7.91 m (8H, *o*-H-Ph). Found %: H 3.00; C 58.59; N 6.34. $BC_{32}F_2H_{20}Br_2N_3$. Calculated %: H 3.08; C 58.67; N 6.41.



Scheme 1 Synthesis of BODIPY **8**.

Electronic absorption spectra (EAS) and fluorescence of solutions of complexes **1–8** were recorded on a CM 2203 spectrofluorometer (SOLAR, Belarus) in the spectral range of 250–800 nm. The studies were carried out in quartz cuvettes with an absorbing layer thickness of l = 1 cm. The concentration of solutions of the complexes in organic solvents was ~10^{-7}–10^{-5} mol / l.

Fluorescence spectra were obtained under the same conditions with an optical density at the excitation wavelength not exceeding 0.1. Rhodamine 6G solution in ethanol (φ = 0.94) was used as a standard to determine the relative fluorescence quantum yield (φ) of BODIPY**1–5**, and Nile blue in ethanol (φ = 0.23) was used for BODIPY**6–8**.

The Stokes shift was calculated as the difference between the values of the maxima of the intense bands in the fluorescence and absorption spectra:

$$\Delta\lambda(\mathrm{nm}) = \lambda_{\max}^{fl} - \lambda_{\max}^{abs} \text{ and } \Delta\nu\left(\mathrm{cm}^{-1}\right) = \nu_{\max}^{fl} - \nu_{\max}^{abs}.$$

Universal interaction function (Δf), used as a solvent polarity parameter, is calculated using the Lippert-Matag equation [25]:

$$\Delta f = \left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right) - \frac{n_D^2 - 1}{2n_D^2 + 1},$$

ε the dielectric constant,
n_D refractive index (Table 1).

BODIPY **1–8** solutions in cyclohexane with a concentration of ~ $2 \cdot 10^{-5}$ mol/L were prepared to study the dyes photostability. A quartz cuvette with a solution was placed in a thermostatically controlled compartment (298.15 K) of the illuminator (mercury lamp DRL 250) equipped with a light filter (Carl Zeiss JENA) with a transmission of 365 nm. The luminous flux area was 2.02 cm^2 with the specific power of illumination W_{365} = 1.47 mW / cm^2 (UV power meter LH-106) at the point of installation of the cuvette. The electronic absorption spectrum of the dye solution was recorded at equal intervals of irradiation (from 5 to 30 min) on a SOLAR spectrometer CM2203 in the 300–700 nm wavelength range. The relative intensity of absorption (A_t/A_0) at the maximum of the

Table 1 The polarity parameters of organic solvents

Solvent	Δf	E_T^N
C_6H_{12}	0.002	0.01
C_7H_{16}	0.001	0.01
C_6H_6	0.003	0.11
C_6H_5-CH_3	0.014	0.10
$CHCl_3$	0.150	0.26
PrOH-1	0.270	0.62
EtOH	0.290	0.65
DMF	0.280	0.40

***Notes*:** Δf is empirical Lippert parameter [26], E_T^N is normalized Dimroth-Reichardt parameter [27]

long-wavelength absorption band was calculated as the ratio of the intensity of absorption after each irradiation (A_t) to the intensity of this band before irradiation (A_0). The half-life of the complexes was defined as the time during which the chromophore is destroyed by 50%.

Results and Discussion

Luminescent Properties

Compounds **1**–**8** were studied by the method of electron absorption spectroscopy and stationary fluorescence spectroscopy in solvents of different polarity, electron-and proton-donating ability. The results obtained are summarized in Table 2.

Figures 3 and 4 show the electronic absorption and fluorescence spectra of BODIPY 1–5 and meso-aza-BODIPY **6**–**8** under the same conditions. All synthesized dyes **1**–**8** have the EAS type in the visible region typical for this class of

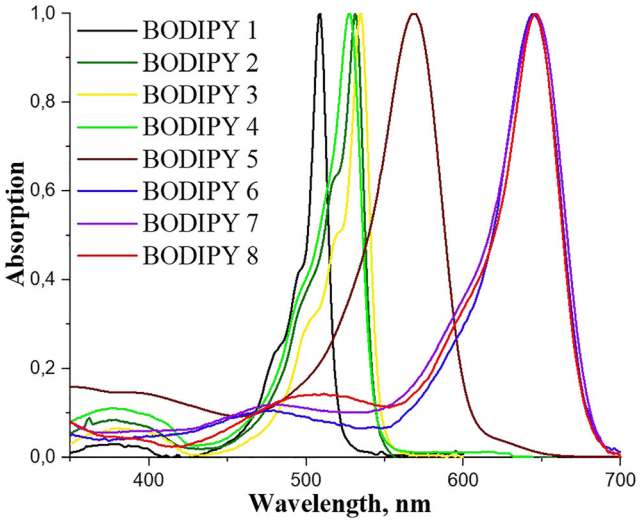


Fig. 3 Normalized electronic absorption spectra **1**–**8** in ethanol

compounds. The absorption spectra of complexes **1**–**4** in organic solvents contain one intense long-wave $S_0 \rightarrow S_1$ band with a maximum in the range of 503–536 nm and a low-intensity $S_0 - S_n$ broad band at 360–380 nm (Fig. 2).

The molar absorption coefficient of the $S_0 \rightarrow S_1$ band of complexes **1**–**8** is very high, log ε fits in the range of 3.96–4.99 (Table 2), and is comparable to that for other structurally related BODIPY [25].

Differences in functional substitution in β-positions of pyrrole dipyrromethene core are noticeably manifested in the quantitative characteristics of the EAS (Table 2).

Alkyl substitution makes it possible to achieve a bathochromic displacement of the maximum of the intense band by 22–25 nm compared to unsubstituted BODIPY **1**. Introduction of the phenyl groups to the 3,3 ‘, 5,5’-positions of the pyrrole cores of compound **5** significantly (up to 60–66 nm)

Table 2 Characteristics of electronic absorption spectra of BODIPYs **1**–**8** in organic solvents

Solvent	BODIPY (λ_{max}^{abs}, nm ($S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$); lgε, L/mol·sm)							
	1	2	3	4	5	6	7	8
C_6H_{12}	509 (4.96)	531 (4.75)	534 (4.92)	532(4.99)	569(4.30)	645(4.92)	644(4.85)	646 (4.53)
	366 (3.71)	379 (3.69)	379 (3.81)	378(3.88)	288(4.20)	308(4.45)	305(4.25)	291 (3.77)
C_7H_{16}	509 (4.89)	532 (4.73)	535 (4.89)	529(4.99)	569(4.30)	642(4.86)	643(4.77)	643 (4.15)
	367 (3.73)	379 (3.70)	383 (3.88)	376(4.02)	288(4.20)	308(4.43)	305 (4.26)	289 (3.38)
C_6H_6	509 (4.97)	533 (4.69)	535 (4.95)	533(4.98)	573(4.26)	653(5.02)	650 (4.95)	651 (4.91)
	366 (3.69)	379 (3.69)	381 (3.89)	378(3.93)	288(4.20)	308(4.49)	305 (4.38)	290 (4.09)
C_6H_5-CH_3	511 (4.85)	534 (4.71)	536 (4.87)	533(4.91)	572(4.79)	653(4.89)	652 (4.97)	651 (4.97)
	365 (3.73)	380 (3.73)	373 (3.87)	378(3.78)	288(4.24)	310(4.46)	304 (4.43)	289 (4.21)
$CHCl_3$	508 (4.95)	532 (4.83)	535 (4.96)	532(4.96)	569(4.36)	649(4.92)	648 (4.90)	648 (4.89)
	363 (3.74)	377 (3.89)	380 (3.89)	380(3.90)	288(4.26)	309(4.46)	309 (4.34)	285(4.09)
PrOH-1	503 (4.94)	528 (4.62)	529 (4.86)	527(4.93)	567(4.84)	642(4.86)	644 (4.67)	642(3.96)
	362 (3.75)	377 (3.69)	377 (3.89)	377(3.94)	287(4.44)	310(4.43)	305 (4.1)	289(3.64)
EtOH	505 (4.91)	529 (4.66)	532 (4.84)	526(4.91)	565(4.26)	646(4.85)	644 (4.71)	642(3.95)
	363 (3.74)	377 (3.76)	374 (3.91)	377(3.91)	287(4.18)	307 (4.45)	309 (4.15)	289(3.64)
DMF	503 (4.88)	526 (4.61)	529 (4.83)	527(4.84)	569(4.42)	654(4.97)	644 (4.90)	–
	364 (3.71)	377 (3.70)	379 (3.87)	379(3.84)	286(4.32)	307(4.46)	303 (4.39)	

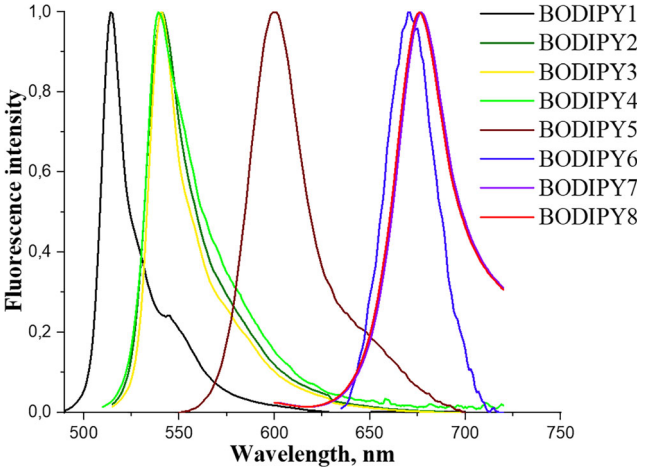


Fig. 4 The normalized fluorescence spectra of alkyl-substituted BODIPY **1**–**4**, tetraphenyl-substituted BODIPY **5** (*a*) and tetraphenyl-ms-aza-BODIPY 6–8 (*b*) in ethanol

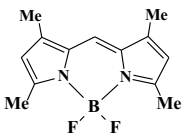
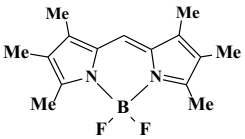
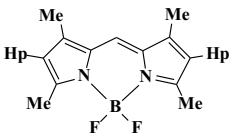
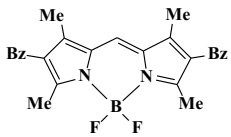
increases the bathochromic the shift of the intense band in the EAS, which is due to the change in the electron density in the chromophore due to the electronic effects of the substituents (Fig. 2, Table 2). The combination of phenyl and meso-aza-substitution makes it possible to achieve an even greater hyperchromic effect and a shift of the maximum of the long-wavelength band in the EAS of compounds **6**–**8** by 133–166 nm to the phototherapy window compared to BODIPY **1**. Such compounds with absorption in the long-wave region of the spectrum represent potential interest in application in PDT and in laser technology.

Halogenation gives a small (by 1–2 nm) shift of the maxima of the bands in the electronic absorption spectra of ms-aza-BODIPY **7**–**8** in comparison with the unsubstituted analogue **6**.

Compounds **1**–**4** are characterized by intense fluorescence with a maximum emission band in the region of 512–547 nm (Fig. 4 (a), Table 3). The phenyl substitution in molecule **5** bathochromic shifts the maximum of the band in the emission spectrum by 87–93 nm, depending on the nature of the solvent. Tetraphenyl-meso-aza-BODIPY **6**–**8** fluorescence is also significantly shifted to the red region with a maximum emission band in the 672–686 nm region (Fig. 4 (b)), which is interesting for their use in PDT.

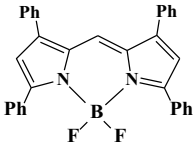
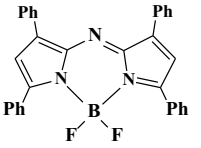
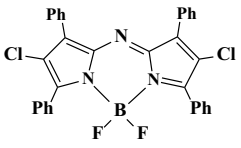
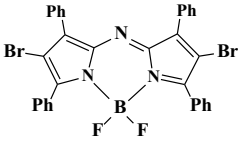
The emission band in the fluorescence spectrum of the complex mirrors the long-wavelength absorption band. For β-unsubstituted complex **1** the Stokes shift varies from 5 to 10 nm depending on the nature of the solvent (Table 3), which indicates a small energy expenditure on nonradiative relaxation processes. For methyl-, heptyl-, and benzyl-β-substituted compounds **2**–**4** the Stokes shift is slightly higher (6–15 nm). The introduction of aryl substituents in the 3,3′, 5,5′-position of the dipyrromethene molecule leads to a significant (32–37 nm) increase in the Stokes shift of BODIPY **5**. Replacing the methine spacer with an electronegative nitrogen atom stabilizes the lower free MO, reducing the energy gap of the electronic transition [28] and lowering the energy of nonradiative relaxation of complex **6** in aprotic and proton-donor solvents. The latter is manifested in a decrease in the Stokes shift of compound **6** relative to BODIPY **5** on average by 5 nm, and in proton-acceptor DMF - by 8 nm (Table 4).

Table 3 The luminescent characteristics of BODIPYs **1**–**4** in organic solvents

Solvent												
	λ^{fl}_{max}	Δλ	γ^{fl}	λ^{fl}_{max}	Δλ	γ^{fl}	λ^{fl}_{max}	Δλ	γ^{fl}	λ^{fl}_{max}	Δλ	γ^{fl}
C_6H_{12}	514	6	1.00	539	8	0.89	541	7	0.97	540	8	0.88
C_7H_{16}	514	5	0.97	540	8	0.97	542	8	0.85	538	9	0.89
C_6H_6	517	8	0.88	544	11	0.98	545	10	0.97	545	12	0.82
C_6H_5-CH_3	519	8	0.82	546	12	0.93	546	10	0.90	545	12	0.85
$CHCl_3$	516	8	0.90	538	6	0.91	545	10	0.96	547	15	0.91
PrOH-1	513	7	0.92	541	12	0.89	541	9	0.79	542	15	0.76
EtOH	512	9	0.88	538	11	0.89	540	11	0.92	540	14	0.78
DMF	513	10	0.99	539	13	0.93	541	13	0.86	540	13	0.84

λ_{ex} = 470–480 nm – for complex **1**; 495–500 nm – for complex **2**; 505–515 nm – for complex **3** и **4**

Table 4 The luminescent characteristics of BODIPYs **5–8** in organic solvents

Solvent												
	λ^{fl}_{max}	Δλ	γ^{fl}	λ^{fl}_{max}	Δλ	γ^{fl}	λ^{fl}_{max}	Δλ	γ^{fl}	λ^{fl}_{max}	Δλ	γ^{fl}
C_6H_{12}	601	32	0.91	672	27	0.20	673	29	0.07	675	29	0.02
C_7H_{16}	600	31	0.61	673	31	0.09	673	30	0.04	674	31	0.01
C_6H_6	605	32	0.45	681	28	0.10	682	32	0.11	686	35	0.01
C_6H_5-CH_3	605	33	0.44	682	29	0.15	682	30	0.16	685	34	0.01
$CHCl_3$	603	34	0.47	678	29	0.10	677	29	0.02	682	34	0.01
PrOH-1	600	33	0.57	674	32	0.07	676	32	0.07	676	34	0.01
EtOH	599	34	1.00	674	28	0.05	674	30	0.05	677	35	0.01
DMF	606	37	0.38	683	29	0.04	674	29	0.07	-	-	-

λ_{ex} = 520–525 nm – for complex **5**; 550–555 nm – for complex **6**; 570–590 nm – for complex **7** и **8**

The halogenation of the β-positions of the meso-aza-dipyrromethene causes a redistribution of the electron density in the BODIPY molecule (compounds **7**, **8**), again increasing the Stokes shift value by 2–5 nm. However, in aliphatic hexane, where Van der Waals interactions predominate, and the solvent itself does not undergo conformational rearrangements, the aza-substitution and halogenation of the β-positions of the pyrrole fragments does not manifest itself in the Stokes shift of compounds **6–8**.

The effect of functional substitution is noticeably manifested in the magnitudes of the quantum yield. The values of φ for alkyl BODIPY **1–4** and tetraphenyl-BODIPY **5** lie in the range of 38–100% without explicit correlation with the Lippert function (Δ*f*) (Fig. 5*a*) and Dimroth-Reichardt function (E_T^N) (Fig. 5*b*).

Replacing the methine spacer in structure **5** with an electronegative nitrogen atom causes a significant decrease in the BODIPY **6** fluorescence quantum yield (Table 4, Fig. 5 *a*, *b*). The maximum decrease in the quantum yield (up to 20 times) is observed in polar solvents and significantly less (up to 4 times) in saturated and aromatic hydrocarbons. The introduction of chlorine atoms into the β-positions of the pyrrole cycles of the chromophore has virtually no effect on the fluorescence quantum yield of the meso-aza-BODIPY **7** compared

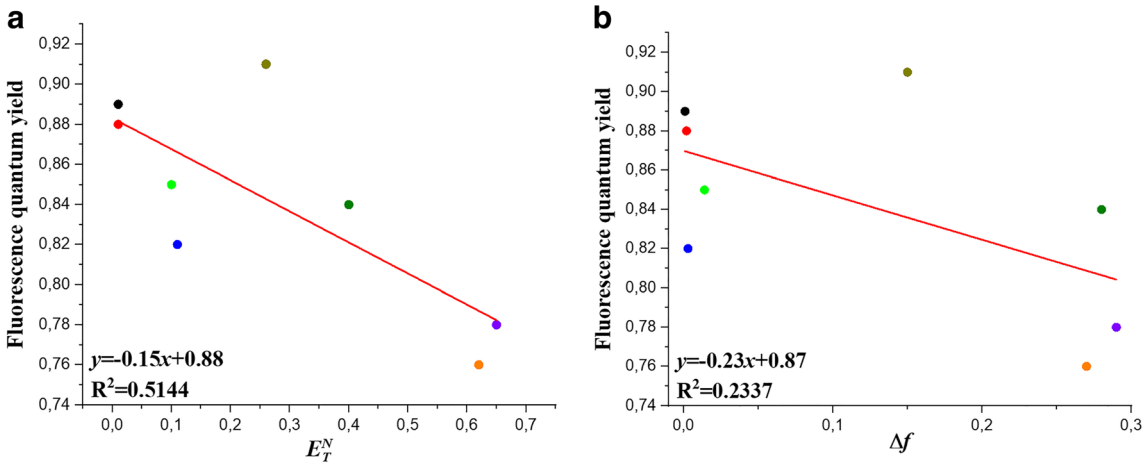


Fig. 5 Fluorescence quantum yield of BODIPY **4** from the Lippert function (Δ*f*) (**a**) and fluorescence quantum yield of BODIPY **4** from the Dimroth-Reichardt function (E_T^N) (**b**) (●-cyclohexane, ●–hexane, ●–toluene, ●–benzene, ●–chloroform, ●–propanol-1, ●–ethanol, ●-N,N-dimethylformamide)

with the unsubstituted analogue **6** [29]. However, bromination of β-positions in the meso-aza-BODIPY **8** molecule reduces the quantum yield by almost an order of magnitude (up to 1–1.5%) in both non-polar and polar solvents.

The solvatochromic effect for most compounds is manifested in the hypsochromic shift of the intense absorption band maximum in proton-donor (alcohols, chloroform) and electron-donor (DMF) solvents in comparison with aromatic (benzene, toluene) and aliphatic solvents (Table 2). As was shown earlier [30–32], specific solvation due to intermolecular hydrogen bond, π-stacking and other donor-acceptor interactions can be significantly enhanced by photoexcitation and, thus, can significantly affect the spectral shift, energy transfer, electron or proton transfer .

Photostability

Indicators of kinetic stability in solution under the influence of UV irradiation and in the presence of atmospheric oxygen are one of the key characteristics for dyes and phosphors used in practice, including diphroborates of dipyrrometenes. Spectral control confirmed that compounds **1**–**8** are stable in solutions of non-polar and aromatic solvents, and with diffused illumination their spectral-luminescent characteristics remain unchanged for a long time. However, with UV irradiation, complexes **1**–**8**, like all other dyes, are prone to fading at different rates, depending on the structural features of their molecules.

Changes in the electronic absorption spectrum in the process of photodestruction of dyes **1**–**8** in solutions and the corresponding dependences of the relative optical density at the maximum of the long-wavelength absorption band (A/A_o) on the UV irradiation time are presented in Figs. 6 and 7.

In all cases, the dyes destruction is accompanied by a decrease in the intensity of the $S_0 \rightarrow S_1$ band (Fig. 6) without shifting its position and ends with complete bleaching of the solution due to the destruction of the π-conjugation in the dipyrromethene chromophore.

Table 5 presents the observed photooxidation rate constants (k_{obs}) of complexes **1**–**8**, which were estimated by the equation $\ln(A_0/A_t) = k_{obs}\,t$, where A_0 and A_t are the initial and current optical densities at the maximum of the long-wave absorption band, t – time of irradiation of the sample with

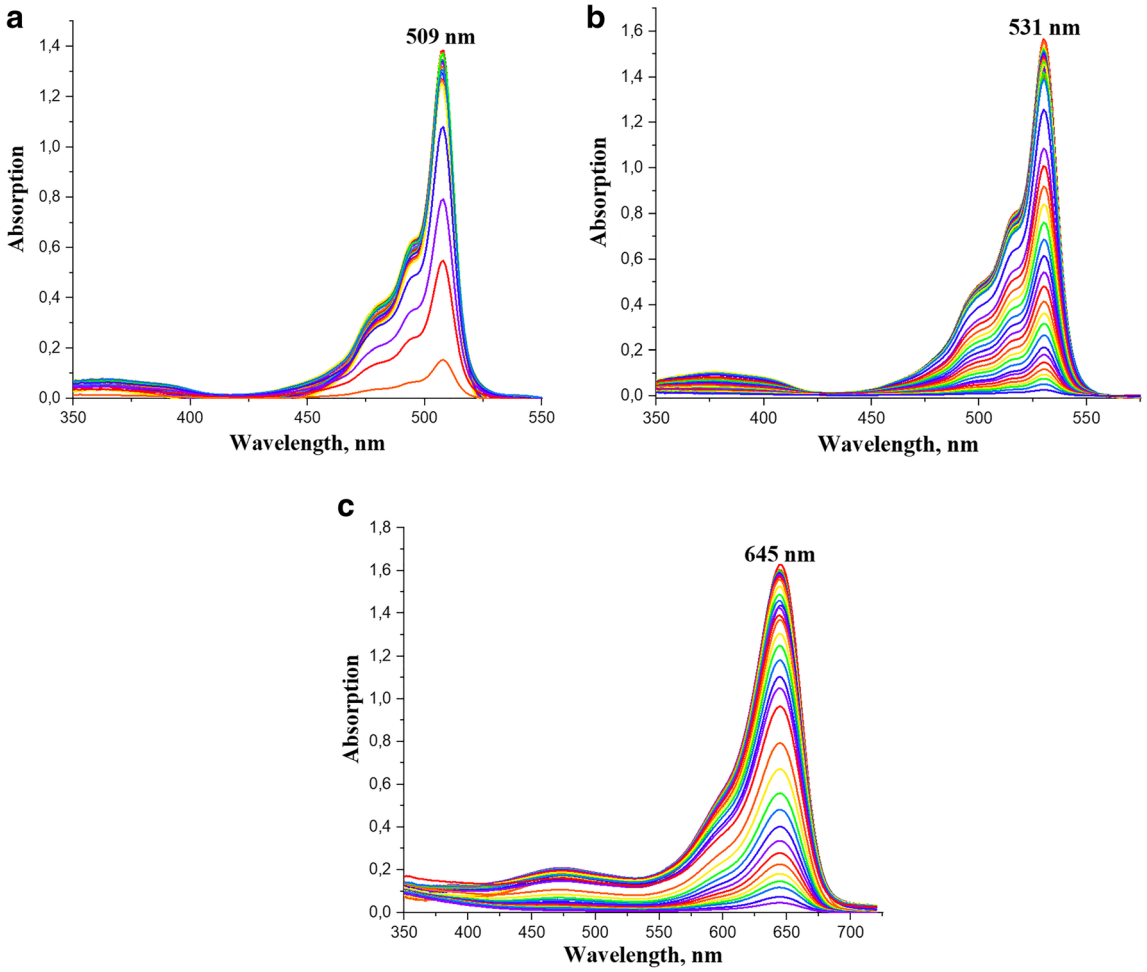


Fig. 6 Spectral changes when exposed to UV light solution in cyclohexane: **(a)** – $(CH_3)_4$-BODIPY, **(b)** - $(CH_3)_4$-Bz-BODIPY, **(c)** $(Ph)_4$-*mezo-aza*-BODIPY

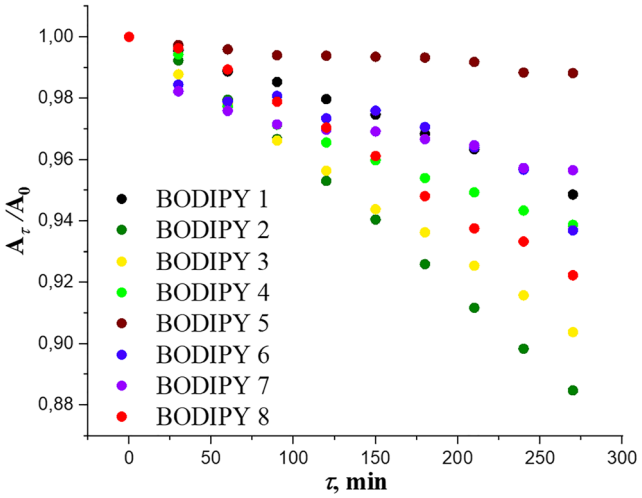


Fig. 7 Dependences of the relative optical density at the maximum of the long-wavelength absorption band (A/A_o) in EAS solutions of boron (III) dipyrromethenates **1**–**8** in cyclohexane on the time of UV irradiation

UV light. A similar approach to the calculation was applied by the authors of [33]. The half-life ($t_{1/2}$) of the complexes was determined from the dependence of A_t/A_0 on the irradiation time, during which the chromophore is destroyed by 50%, i.e. at $A_t/A_0 = 0.5$. Depending on the peculiarities of the molecular structure of compounds **1**–**8**, the value of $t_{1/2}$ in cyclohexane varies in a very wide range, from 19 to 240 h (Table 5).

Most of the dye destruction processes caused by the effects of absorbed light quanta are based on photo-oxidation reactions with oxygen [34], which occur due to photosensitized transformation of ordinary molecular oxygen, the main state of which is triplet, into singlet oxygen, which is easily attached via multiple bonds or embedded in single bonds of the chromophore molecule, initiating subsequent red-ox processes. By analogy with porphyrins [35], it can be assumed that the oxygen molecule passes into the singlet state when interacting with the dipyrromethenate molecule, which has passed as a result of absorption of light quanta into the excited state. Next, singlet oxygen interacts with the most active centers of the dye molecule, destroying its chromophore system.

Table 5 Quantitative characteristics of photodestruction processes of complexes **1**–**8** in cyclohexane

Compound	$k_{obs}\cdot10^6$, s^{-1}	$t_{1/2,\ hour}$
BODIPY		
1	3.17 ± 0.24	46
2	6.87 ± 0.63	19
3	6.33 ± 0.24	23
4	5.25 ± 0.74	31
5	0.52 ± 0.09	240
ms-aza-BODIPY		
6	4.65 ± 1.56	34
7	3.72 ± 0.69	41
8	4.01 ± 0.72	38

An earlier analysis of the energy levels of the boundary molecular orbitals (HOMO and LUMO) indicates that the most photoactive centers of the dipyrromethenic chromophores are the meso-spacer and the nitrogen atoms of the pyrrole cycles, in which the electron density is efficiently observed in the excited state, which favors the flow of red-ox - reactions on these groups and atoms [16].

The functionalization of the dipyrromethenic chromophore leads to various changes in the electron density in these active centers and, as a result, to the different resistance of dipyrromethene dyes to photo-oxidation.

The most rapid ($k_{obs} = 6.87\cdot10^{-6}$ s^{-1}) photo-oxidation process of BODIPY **2** with fully methylated pyrrole cycles takes place (Table 4). The half-life time of BODIPY **2** is only 19 h. An almost twofold decrease in the speed of the photodestruction process and an increase in the half-life are observed for BODIPY **1** compared to BODIPY **2**. It can be assumed that replacing the **1** methyl molecule with β hydrogen atoms in β-positions reduces the electron density in the chromophore due to a decrease I-induction effect in the substituents.

Substitution of β-positions with heptyl no longer has such a noticeable effect on the photostability of BODIPY **3** as compared with analogue **2**. Benzyl substituents somewhat stabilize the molecule, apparently due to the contribution of the phenyl fragment to the overall inductive effect of the substituent, which leads to a decrease in the photooxidation rate constant BODIPY **4** compared to almost identical (within the error) in stability by dyes **2** and **3**.

The presence of four phenyl substituents with pronounced *–I*-inductive together with *+C*-mesomeric effects in 3,3′,5,5′-positions of the pyrrole cores ensures the greatest photostability of complex **5**. The half-life of the phosphor **5** is maximal among the studied compounds - 240 h and the bleaching rate constant is almost an order of magnitude lower than that of **2**, **3**.

Replacing methinated carbon by a nitrogen atom, exhibiting a positive mesomeric effect, as already noted, leads to an increase in electron density in the molecule, including the active centers of the ms-aza-BODIPY **6** chromophore system, causing a sharp increase in its lability under UV irradiation Compared with BODIPY **5**. The halogenation of β-positions ms-aza-BODIPY increases the stability of difluoroborates **7** and **8** under the action of UV irradiation in accordance with the increase in electronegativity of the atoms of the introduced halogens.

Thus, it can be assumed that the process of photo-oxidative degradation of BODIPY and their aza-analogues under UV irradiation in solution proceeds according to the mechanism of photosensitized oxidation of the aromatic backbone of the dipyrromethene dye, including the stages of interaction of

excited chromophore molecules with molecular oxygen with its transfer to the singlet-excited state and the subsequent destruction of the chromophore system when interacting with singlet oxygen. In this case, the intensity of photo-oxidation is largely determined by the peculiarities of the redistribution of electron density at the active centers of the excited chromophore molecule, which directly depend on the electronic effects of groups and substituent atoms.

Conclusions

As a result of the research it was found that alkyl-substituted boron dipyrromethenates are powerful fluorophores with a quantum fluorescence yield of 80–99%, weakly dependent on the nature of the solvent. Their aryl-analogs are more sensitive to interparticle interactions with a solvent, leading to a decrease in the quantum yield in some cases to 40%. Replacing the methine carbon atom with nitrogen significantly quenches the fluorescence up to 5–20%. Introduction of phenyl fragments into BODIPY molecule shifts the first absorption band in a bathochromic manner, significantly (32–37 nm) increases the Stokes shift in the emission spectrum, but reduces the probability of the $S_0 \rightarrow S_1$ electronic transition as compared to alkylated complexes. Replacing the methine carbon atom with nitrogen additionally increases the bathochromic shift and ε values in the long-wavelength absorption band, however, it reduces the Stokes shift by 5–8 nm, depending on the nature of the solvent. The studied compounds are resistant to UV irradiation. The half- life of BODIPY**1**–**8** varies from 19 to 240 h. The half- life increases in the series of compounds ms-aza-BODIPY <alkyl-BODIPY <aryl-BODIPY.

References

1. Zhang J, Zhang L, Zhou Y, Acta M (2013) A highly selective fluorescent probe for the detection of palladium(II) ion in cells and aqueous media. Microchim Acta 180:211–217. https://doi.org/10.1007/s00604-012-0922-2
2. Kim SB, Cho DG (2012) Hg(II)-selective fluorescent indicator: one-step synthesis. Eur J Org Chem 2012:2495–2498. https://doi.org/10.1002/ejoc.201200126
3. Ran C, Xu X, Raymond SB (2009) Design, synthesis, and testing of Difluoroboron-Derivatized curcumins as near-infrared probes for in vivo detection of amyloid-β deposits. J Am Chem Soc 31: 15257–15261. https://doi.org/10.1021/ja9047043
4. Gorman A, Killoran J, O'Shea C (2004) In vitro demonstration of the heavy-atom effect for photodynamic therapy. J Am Chem Soc 126:10619–10631. https://doi.org/10.1021/ja047649e
5. Awuah SG, Polreis J, Biradar V (2011) Singlet Oxygen Generation by Novel NIR BODIPY Dyes. You Org Lett 13:3884–3887. https://doi.org/10.1021/ol2014076;
6. Pang W, Zhang XF (2012) Modulating the singlet oxygen generation property of meso–β directly linked BODIPY dimers. Chem Commun 48:5437–5439. https://doi.org/10.1039/C2CC30915G
7. Lim S, Thivierge C, Nowak-Sliwinska P (2010) In vitro and in vivo photocytotoxicity of boron dipyrromethene derivatives for photodynamic therapy. Med Chem 53:2865–2874. https://doi.org/10.1021/jm901823u
8. Lincoln R, Durantini Photochem AM (2017) Meso-Acetoxymethyl BODIPY dyes for photodynamic therapy: improved photostability of singlet oxygen photosensitizers. Photobiol Sci 16:178–184. https://doi.org/10.1039/c6pp00166a
9. Duran-Sampedro G, Agarrabeitia AR, Garcia-Moreno I (2012) Chlorinated BODIPYs: surprisingly efficient and highly Photostable laser Dyes. Eur J Org Chem 2012:6335–6350. https://doi.org/10.1002/ejoc.201200946
10. Trinh C, Kirlikovali K (2014) Symmetry-breaking charge transfer of visible light absorbing systems: zinc Dipyrrins. J Phys Chem 118:21834–21845. https://doi.org/10.1021/jp506855t
11. Cui A, Peng X (2007) Synthesis, spectral properties and photostability of novel boron–dipyrromethene dyes. J Photochem Photobiol A Chem 186:85–92. https://doi.org/10.1016/j.jphotochem.2006.07.015
12. Liras M, Pintado-Sierra M (2011) New BODIPY chromophores bound to polyhedral oligomeric silsesquioxanes (POSS) with improved thermo- and photostability. J Mater Chem 21:12803–12811. https://doi.org/10.1039/C1JM11261A
13. Wittmershaus B, Skibicki J (2001) Spectral properties of single BODIPY Dyes in polystyrene microspheres and in solutions. J Fluoresc 11:119–128. https://doi.org/10.1023/A:1016629518660
14. Nuraneeva EN, Guseva GB, Antina EV, Kuznetsova RT, Berezin MB, V'yugin AI (2016) Synthesis, spectral luminescent properties, and Photostability of Monoiodo- and Dibromo-substituted BF_2-Dipyrrinates. Russ J Gen Chem 86:840–847. https://doi.org/10.1134/S1070363216040149
15. Gupta M, Mula S, Tapan K (2017) Structure and solvent-induced tuning of laser property and photostability of a boradiazaindacene (BODIPY) dye. J Photochem Photobiol A Chem 349:162–170. https://doi.org/10.1016/j.jphotochem.2017.09.033
16. Nuraneeva EN, Antina EV, Guseva GB, Berezin MB, V'yugin AI (2018) Effects of halogen substitution on the photostability and thermal degradation of boron(III), zinc(II) and cadmium(II) dipyrrinato complexes. Inorg Chim Acta 482:800–806. https://doi.org/10.1016/j.ica.2018.07.026
17. Semejkin AS, Berezin MB, Chernova OM et al (2003) Interrelation of the structure and solvation characteristics of alkyl-substituted dipyrrolylmethenes, their oxa- and thia-analogs. Izv RAS Ser chemical 8:1712–1718
18. Berezin MB, Chernova OM, Pashanova NA et al (2001) The influence of functional substitution on the enthalpy characteristics of the solution of dipyrrolylmethenes. J Physical Chemistry 75:1242–1245
19. Antina EV, Guseva GB, Rumyantsev EV, Dudina NA (2009) Thermal properties of ligands, salts and metal complexes of linear oligopyrroles. Russ J Gen Chem 79:1900–1909. https://doi.org/10.1134/S1070363209090163
20. Antina EV, Berezin MB, Dudina NA et al (2014) Synthesis, spectral-luminescent properties of B(III) and Zn(II) complexes with alkyl- and aryl-substituted dipyrrins and azadipyrrins. Russ J Inorg Chem 59:1187–1194. https://doi.org/10.7868/S0044457X1410002X
21. Berezin MB, Semejkin AS (1999) E.V. Antina synthesis and physicochemical properties of alkyl-substituted dipyrrolylmetenes hydrobromides. General chemistry 69:2040–2047
22. Berezin MB, Semejkin AS (1993) Thermochemistry of substituted pyrroles. Russian Chem Bull 42:449–453

23. Antina EV, Berezin MB, Dudina NA, Burkova SL, Nikonova AY (2014) Synthesis, spectral-luminescent properties of B(III) and Zn(II) complexes with alkyl- and aryl-substituted dipyrrins and azadipyrrins. Russ J Inorg Chem 59:1187–1194. https://doi.org/10.1134/S0036023614100027
24. Dudina NA, Berezin MB, Semeikin AS, Antina EV (2015) Difluoroborates of phenyl-substituted Aza-Dipyrromethenes: preparation, spectral properties, and stability in solution. Russ J Gen Chem 85:2739–2742. https://doi.org/10.1134/S1070363215120130
25. Fischer M, Georges J (1996) Fluorescence quantum yield of rhodamine 6G in ethanol as a function of concentration using thermal lens spectrometry. Chem Phys Lett 260:115–118. https://doi.org/10.1016/0009-2614(96)00838-X
26. J.R. Lakowicz (ed.). Principles of fluorescence spectroscopy. Springer science & business media, 2013
27. Reichardt C (1994) Solvatochromic dyes as solvent polarity indicators. Chem Rev 94:2319–2358. https://doi.org/10.1002/chin.199509296
28. Castaneda A, Zaballa E et al (2018) Tailoring the molecular skeleton of Aza-BODIPYs to design Photostable red-light-emitting laser Dyes. ChemPhotoChem 2:1–12. https://doi.org/10.1002/cptc.201800225
29. Kuznetsova RT, Aksenova IV, Bashkirtsev DE, Prokopenko AA, Pomogaev VA, Antina EV, Berezin MB, Bumagina NA (2018) Photonics of coordination complexes of dipyrrins with p- and d-block elements for application in optical devices. J Photochem Photobiol A Chem 354:147–154. https://doi.org/10.1016/j.jphotochem.2017.08.068
30. Zhao G-J, Han K-L (2012) Hydrogen bonding in the electronic excited state. Acc Chem Res 45(3):404–413. https://doi.org/10.1021/ar200135h
31. Zhao G-J, Han K-L (2007) Early time hydrogen-bonding dynamics of Photoexcited Coumarin 102 in hydrogen-donating solvents: theoretical study. J Phys Chem A 111(13):2469–2474. https://doi.org/10.1021/jp068420j
32. Zhao G-J, Liu J-Y, Zhou L-C, Han K-L (2007) Site-selective Photoinduced Electron transfer from alcoholic solvents to the chromophore facilitated by hydrogen bonding: a new fluorescence quenching mechanism. J Phys Chem B 111:8940–8945. https://doi.org/10.1021/jp0734530
33. Ping C, Shuqing S, Yunfeng H, Zhiguo Q, Deshui Z (1999) Structure and solvent effect on the photostability of indolenine cyanine dyes. Dyes Pigments 41:227–231. https://doi.org/10.1016/S0143-7208(98)00088-6
34. Kautsky Request permissions H (1939) Quenching of luminescence by oxygen. Trans Faraday Soc 35:216–219
35. Berezin BD (1981) Coordination compounds of porphyrins and phthalocyanines. J Wiley Publ: Toronto 314