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Photonics of boron fluoride and zinc dipyrromethene complexes

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ABSTRACT

Spectral, photophysical, photochemical characteristics for mononuclear and binuclear dipyrromethenes in complexes with BF₂ (BODIPY), bis-BODIPY and bis-helicates ([Zn₂(L)₂]) are described. The role of substituents (type and location in the ligand) and the medium in which dipyrromethene complexes are placed (solvents, solid-state matrices), the effect of different complexing agents (p- and d-elements) on the photonics of the complexes are discussed. The results of studying the lasing and photochemical properties of complexes under the action of laser irradiation are presented. In addition, for the described complexes the stability in the ground and excited states in protic media are estimated. Based on the analysis of the results discussed possibilities of practical application of these compounds to creating various optical devices.

Key words: dipyrromethene, BODIPY, [Zn₂(L)₂], photonics of laser dyes, photostability, stability in protic media

1. INTRODUCTION

For the modern stage of the development of world science and industry, there is an increasing interest in the creation of various optical devices based on molecular compounds and their complexes. To create optical devices for different purposes (laser active media, limiters for high-power pulsed radiation and so on), dyes of different classes (Rhodamine [1], Coumarin [2]) are used. To date, the most promising compounds have emerged for use in the above-described devices - they are dipyrromethene complexes with p- and d-elements.

Dipyrromethene compounds have effective absorption and radiation in the visible region of the spectrum; they are sensitive to changes in structure and molecular environment [3, 4]. Thanks to the achievements of chemical synthesis, to date, numerous groups of dipyrromethenes have been created, but until now the study of their physicochemical properties for the subsequent creation of optical devices is essentially behind. Therefore, at this stage, these compounds are well known, mainly, only as active laser media based on boron fluoride complexes of alkyl-dipyrromethenes [5]. Practically, the complexes of dipyrromethenes with zinc ions and other d-elements remain unexplored.

From these positions, a systematic study of photoprocesses occurring in dipyrromethene complexes of different structures when interacting with solvents of different nature and phase state, optical radiation of different wavelengths and intensities is necessary to establish the possibility of using these compounds in various hi-tech optical devices. Therefore, the purpose of the work is to study the spectral-luminescent, lasing properties and photostability of different complexes of dipyrromethenes with boron fluoride and zinc, the optimal combination of which will indicate the direction of the most effective use of these dyes.

2. EXPERIMENTAL PART

2.1 Research objects

The objects of research in this work are mononuclear boron fluoride (BODIPY) and zinc ([Zn₂(L)₂]) complexes of dipyrromethenes, synthesized at the Institute of solution chemistry of Russian Academy of Sciences in detail, described in [3, 6, 7], with the control of the purity of the compounds by thin-layer chromatography, PMR, and IR spectroscopy. Figure 1 shows the structural formulas, names and designations of the compounds studied.

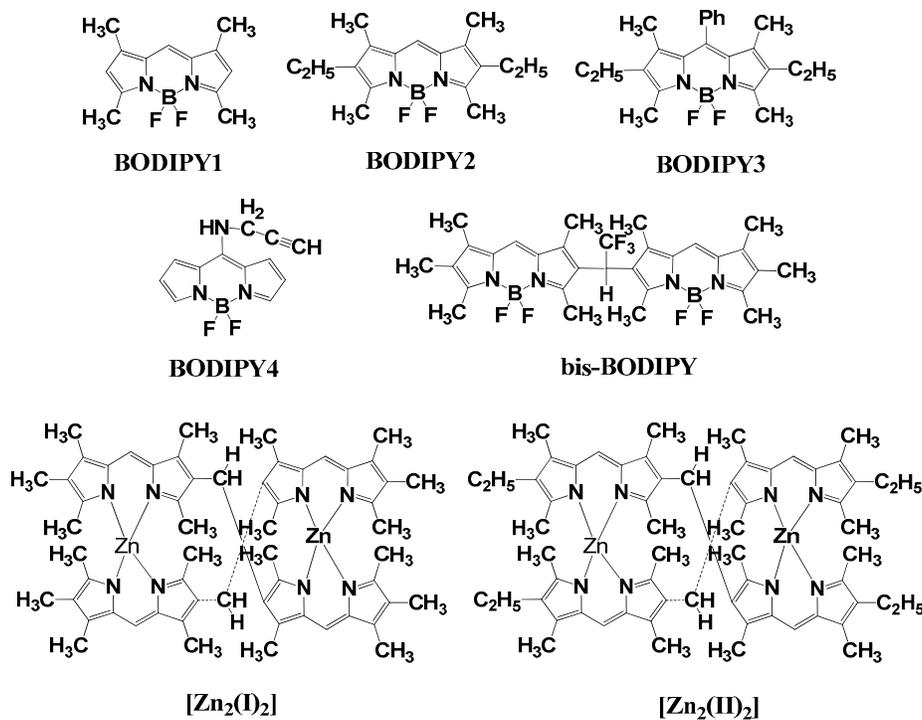


Figure 1. Structures and designations of the investigated compounds

As solvents, we used ethanol, ethyl acetate, and cyclohexane (all HPLC grade). The solubility of the compounds was reasonably good in these solvents, and no undesired effect of the solvent itself was observed for the employed excitation densities. The typical dye concentration was about 10^{-5} M. To study the stability in proton-donor media ethanol solutions were acidified using a high-purity 33% aqueous HCl (10.6 M).

Along with liquid solutions, solid-state bulk matrices and thin films were prepared. The technique for synthesising solid active media based on PMMA and modified PMMA – P(MMA + 8MMA-POSS) – formed by copolymer MMA with polyhedral silsesquioxane (8MMA-POSS) (Hybrid Plastics) in amount of 13 wt%, as well as the technology for fabricating laser elements on their basis (half-cylinders 1 – 1.3 cm high), were described in [8].

2.2 Research methods

Absorption and luminescent spectra were measured by spectrometers CM2203 (SOLAR, Belarus). The luminescence quantum yield was determined with an error of 10% by the reference method; as standards, a set of dyes with known luminescence yields (Coumarin 102 (C102), Rhodamin 6G (R6G)) were used. All described experiments were performed in a 1 cm quartz cell at a temperature of 298 K and atmospheric pressure.

Lasing and photochemical characteristics of the dipyrrromethene complexes were studied with excitation by the second and third harmonics of Nd-YAG laser (SOLAR, Belarus). Lasing and pumping energies were measured accurate within 3% with an OPHIR-NOVA (Israel) and GentecE-100 (Canada) instruments. Generation spectra were measured by an AVANTES laser spectrometer (Netherlands) with an accuracy of 0.5 nm. The efficiency of phototransformation was estimated from the change in the absorption spectra after laser irradiation, following the procedure described in [9].

To estimate the stability of dipyrrromethene complexes and the efficiency of protonated ligand formation, pK_a was chosen. This value characterizes the probability of detachment of the complexing agent and addition of a proton by a ligand base upon interaction with a proton-donor solvent. To determine the quantitative characteristics of stability a solutions of dipyrrromethene complexes with a gradually changing content of hydrochloric acid were studied via spectrophotometric titration. In this case, changes in the electronic absorption and fluorescence spectra were observed, along which titration curves were constructed to determine the pK_a values in S₀, S₁ⁿ, and S₁^{F-C} states [10].

3. RESULTS AND DISCUSSION

3.1 Spectral-luminescence, lasing and photochemical characteristics of solutions

Table 1 shows the results of spectral-luminescent, lasing and photochemical properties of BODIPY and binuclear complexes of bis-dipyrrromethenes with difluoroborate and zinc. From the table it follows that BF₂ complexes with alkyl- and phenyl-substituted dipyrrromethenes tend to effectively fluoresce and generate stimulated emission when excited in S₀-S₁-transition fluorescence in long-wave edge of the strip. In the case of the meso-phenyl substituent (BODIPY3), a small short-wave shift is observed due to a reduction in conjugation (phenyl leaves the plane of the core) and a decrease in the radiation efficiency when excited to high states. The propargylamine substituent in the meso position (BODIPY4) gives the largest short-wavelength shift of the spectra with sufficiently effective radiation, both fluorescence and stimulated emission generation.

Table 1. Spectral-luminescent, lasing and photochemical characteristics of dipyrrromethene complexes in solutions.

Compound, solvent	$\lambda_{\text{abs}}^{S_0-S_1}$, nm ($\epsilon, \text{M}^{-1}\text{cm}^{-1}$)	λ_{fl} , nm (λ_{ex} , nm)	γ_{fl} (λ_{ex} , nm)	λ_{laser} , nm (λ_{ex} , nm; W_{pump} MW/cm ²)	Eff _{las} , % (λ_{ex} , nm; W_{pump} MW/cm ²)	$\Phi_{\text{phot}} \times 10^5$ (λ_{ex} , nm)
BODIPY1, ethanol	504 (8×10 ⁴)	514 (440)	0.8 (440)	537 (355, 25)	20 (355, 25)	
BODIPY1, cyclohexene	509 (7×10 ⁴)	516 (460)	1.0 (460)	544 (355, 20)	15 (355, 20)	22 (355)
BODIPY2, ethanol	528 (6×10 ⁴)	545 (475)	0.8 (475)	560 (532, 25)	74 (532, 25)	7 (532)
BODIPY3, ethanol	522 (7×10 ⁴)	538 (470)	0.8 (470)	551 (532, 25)	56 (532, 25) 16 (355, 20)	4 (532) 260 (355)
BODIPY3, ethanol+DABCO	522	545 (355)		553 (355, 25)	20 (355, 20)	20 (355)
BODIPY4, ethyl acetate	409 (4×10 ⁴)	470 (370)	0.9 (370)	475 (355, 1)	38 (355, 10)	450 (355)
BODIPY4, ethyl acetate+DABCO	409	470 (370)		476 (355, 25)		90 (355)
bis-BODIPY, ethanol	537 (10×10 ⁴)	547 (480)	0.1 (480)	no las		47 (355) 0.04 (532)
bis-BODIPY, cyclohexene	542 (8×10 ⁴)	546 (480)	0.9 (480)	567 (532, 25)	1 (355) 14 (532)	0.3 (532)
[Zn ₂ (I) ₂], cyclohexene	530 (25×10 ⁴)	546 (470)	0.6 (470)	561 (532, 25)	7 (532, 25)	23 (532)
[Zn ₂ (II) ₂], cyclohexene	530 (24×10 ⁴)	548 (510)	0.9 (510)	560 (532, 20)	11 (532, 20)	4 (532)

The transition to binuclear nonplanar complexes BF₂ and zinc with bis-dipyrrromethenes leads to a significant increase the extinction coefficient of the S₀-S₁ transition and its splitting into two maxima (Figure 2). This is explained by the quadrupling of the absorbing chromophore and its non-planarity, i.e. the existence of both a planar (longwave band) and nonplanar (a band with a maximum at 476-480 nm) chromophore with a corresponding set of energy states.

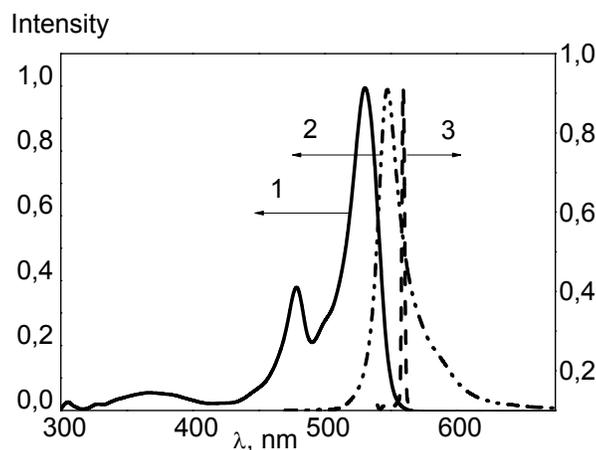


Figure 2. Normalized (1) absorption, (2) fluorescence, and (3) lasing spectra of $[Zn_2(II)_2]$ in cyclohexane.

Study of the lasing characteristics of dipyrromethenes complexes revealed the following features: a low threshold for the lasing ($W_{las} < 1.5-2 \text{ MW/cm}^2$). The BODIPY complexes were excited by second and third harmonic radiation Nd: YAG laser. The lasing spectra are located at the long-wave edge of the band nonreabsorbed fluorescence, i.e., generally at the maximum reabsorbed fluorescence at a selected concentration, and shifted slightly depending on the structure for the compounds studied. In the region of more intense excitation ($W > 40 \text{ MW/cm}^2$), the lasing spectrum shifts by 1.5-2 nm to the long-wavelength region, which is due to an increase in the concentration of higher-threshold solvates at such intensities that in this case generate in the longer-wave region. The half-width of the bands of nonselective generation under given excitation conditions is 2.5-3 nm.

Table 1 shows the effect of DABCO additives (known quencher of triplets and singlet oxygen) on the lasing and photostability characteristics of BODIPY3 and BODIPY4. In this case, its introduction into solutions increases the efficiency from 16 to 20% and reduces the quantum yield of the phototransformation of BODIPY3 (from 260 to 20×10^{-5}) under pumping in the UV region (355 nm). For BODIPY4 at the same pumping, DABCO reduces the yield of phototransformations from 450 to 90×10^{-5} . Given that DABCO has an alkaline reaction, these figures may reflect an increase in the stability of the complexes when interacting with proton-donating solvents, both in general and in the S_1^{F-C} excited state, in addition to photodecay through the T-state, which makes analysis of the results significantly more difficult and requires additional research.

3.2 Features of lasing of stimulated emission in solid-state media

Solutions of organic compounds for use in various optical devices have been studied for a long time, however, the largest convenience in practical work is associated with the use of solid-state polymer matrices doped with complex organic luminophores, in particular - BODIPY complexes [11]. For this reason, in this paper we study the lasing properties of different BODIPY structures embedded in the bulk PMMA and 8MMA-POSS matrices (Table 2).

Table 2. Spectral-luminescent and lasing characteristics of BODIPY complexes in solid-state matrices.

Compound, solvent	$\lambda_{abs}^{S_0-S_1}$, nm	λ_{fl} , nm (λ_{ex} , nm)	λ_{las} , nm (λ_{ex} , nm; W_{pump} , MW/cm^2)	Eff _{las} , %
				(λ_{ex} , nm; W_{pump} , MW/cm^2)
BODIPY2, PMMA	528	555 (450)	558.7 (532, 3)	38 (532, 3)
				70 (532, 20)
BODIPY2, PMMA+8MMA-POSS	536	557 (450)	566 (532, 3)	58 (532, 3)
				90 (532, 70)
BODIPY3, PMMA	522	551 (450)	558.6 (532, 20)	32 (532, 3)
				57 (532, 70)

Analyzing the data of Table 2, one can note the effect of the medium on the photophysical parameters. It follows from the above results that the transition from solutions to solid matrices of unmodified and modified PMMA slightly shifts the spectra of alkyl- and phenyl-derivatives of mono-dipyromethenate to the long-wave side, while the radiation efficiency remains practically unchanged.

Attention should be paid to the significant increase in the efficiency of BODIPY2 in a solid PMMA matrix with the addition of 8MMA-POSS, which is apparently due to the scattering of lasing and pumping photons on these particles. This can lead to lengthening the path of the photon in the resonator, reducing the lasing threshold, and increasing the efficiency. Confirmation of this explanation is the generation spectrum obtained by us, consisting of individual peaks with a half-width of 1 nm (Figure 3), which qualitatively agrees with the spectra and characterizes the existence of several resonators for amplifying scattered stimulated emission [12].

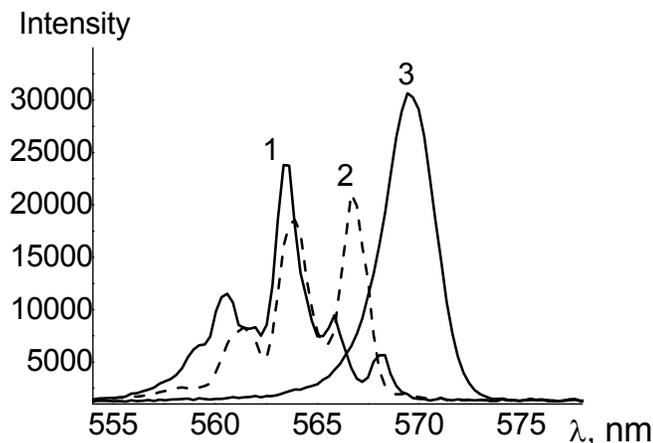


Figure 3. The lasing spectra of BODIPY2 in PMMA + 8MMA-POSS, $W_{\text{pump}} = 3 \text{ MW/cm}^2$: 1 and 2 - before irradiation (recorded in different parts of the lasing volume), 3 - after irradiation at $W_{\text{pump}} = 3 \text{ MW/cm}^2$, $\lambda_{\text{max}} = 569.7 \text{ nm}$.

A comparison of the BODIPY2 characteristics in the conventional PMMA matrix and in the modified matrix reveals the influence of 8MMA-POSS particles on the lasing characteristics of samples (increase in efficiency and reduction of threshold). Our results are in agreement with the data of [13] for a number of dyes in solutions and bulk polymer matrices, which are also indicative of enhanced efficiency and reduced threshold under generation of laser-like radiation in samples containing 8MMA-POSS nanoparticles (13 %) in comparison with unmodified samples.

3.3 Stabilities in proton-donor media

When synthesizing solid samples stained with BODIPY, the use of media with the addition of acids and alkalis. For the successful practical application of BODIPY-complexes, knowledge of the features of their behavior in various media, including in the presence of acidic and alkaline additives, is necessary. In this connection, such characteristics in proton-donor media of different acidity were studied to identify the most suitable for practical use in optical devices.

Table 3. Spectral shifts, $-\log[\text{HCl}]$ values in the corresponding state of BODIPY ethanol solutions with HCl.

Compound	λ_{abs} BODIPY, nm	λ_{abs} (H_2dpm^+), nm	$-\lg[\text{HCl}]$ (S_0)	$-\lg[\text{HCl}]$ ($S_1^{\text{F-C}}$)	$-\lg[\text{HCl}]$ (S_1^{fl})
BODIPY1	504	467	0.3	-2.9	0.2
BODIPY2	528	484	0.4	-3.0	0.4
BODIPY3	522	516	0.1	-0.1	1.1
BODIPY4	409	375	0.3	-3.8	0.3
bis-BODIPY	537	494	0.1	-3.2	0.4

According to the published data [14] and the studied spectral changes (Table 3), the mechanism of the process of protolytic dissociation of BODIPY includes the initial stages of binding of protons with electronegative fluorine atoms, which weakens the B-N, B-F coordination bonds and leads to their rupture with addition of a proton to pyrrole nitrogen and the formation of a protonated ligand form through an isosbestic point (Figure 4). Acid dissociation of bis-BODIPY proceeds in a similar manner, but the presence of an electron-withdrawing substituent in the central spacer leads to an increase in the stability of BODIPY in the ground and excited states compared to the mononuclear dipyrromethene.

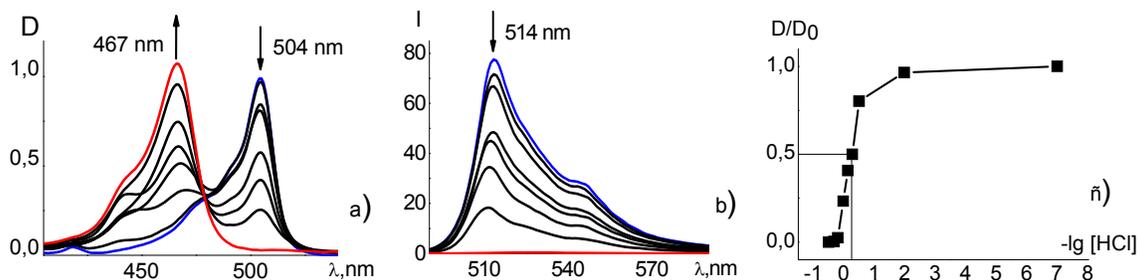


Figure 4. Changes in the absorption (a) and fluorescence (b) ($\lambda_{exc} = 480$ nm) spectra of BODIPY1 in ethanol upon the addition of 33% (10.6 M) HCl in amounts of 1 to 20%. The titration curve plotted from the drop in absorption at 505 nm (c).

A numerical evaluation of the stability of complexes in the ground and excited states was performed for a number of BODIPYs based on the 50% decay of complexes in proton-donor solvents, when the coordination bond N-B or N-Zn is weakened due to the interaction of the proton from the solution with the proton-acceptor center of the complex with the irreversible formation of the protonated ligand ($-\lg [HCl]_{50}$).

By analogy with the acid-base interaction of organic compounds by the method of Foster's cycles from the shifts of bands from the neutral complex to the protonated ligand, the probability of destruction of complexes in excited Frank-Condon states was determined (Table 3), which can be compared and correlated with the quantum yields of phototransformations (Table 1) in the case when phototransformation is carried out by the proton-donor mechanism. The efficiency of protonation upon excitation increases in comparison with the ground state, i.e. photostability decreases. The data presented indicate a decrease in the efficiency of protonation of complexes in the Frank-Condon excited state, i.e. the increase of photostability of complexes by the mechanism of decomplexation in proton-donor solvents. If the photostability does not correlate with this value, this means that the phototransformation is carried out by another mechanism: not through the photodetachment of the complexing agent in proton-donor media, but, for example, through the detachment of the protonated electron-withdrawing phenyl substituent, as suggested in the literature [15].

As for the zinc complexes of dipyrromethenes, it can be assumed that they have much less stability in proton-donor solvents compared to BODIPY. This is consistent with the reported in the literature increased "self-assembly" of complexes with zinc, which indicates their lightweight synthesis with two proton-acceptor centers and the possibility of application in optical devices [16, 17]. Further research is needed to confirm this point of view.

4. CONCLUSIONS

The results showed that alkyl-, phenyl-, meso-propargylamino-substituted dipyrromethene difluoroborates, as well as solutions of binuclear complexes of bis-dipyrromethene with BF_2 and zinc are recommended as photostable liquid and solid laser active media for the visible region with high efficiency, fluorescent probes, limiters of powerful pulsed radiation. The ways of miniaturization of laser media by introducing dyes into photostable solid-state matrices are outlined, which is important for practical use.

Quantum yield of phototransformations under UV-irradiation (355 nm) of dipyrromethenates are increased compared with visible irradiation. The best photostability for bis-BODIPY in ethanol under visible irradiation, and the smallest photostability for BODIPY4 compound under UV irradiation in ethylacetate are obtained. The ways to improve photostability by adding DABCO are presented.

Along with the determination of the quantum yields of phototransformations upon irradiation in the visible and UV regions, the stability of the complexes was determined upon interaction with a proton-donor solvent. The above results indicate an increase in stability in the singlet F-C state. The data obtained make it possible to state that the photostability of dipyrromethene complexes with BF_2 and Zn is sufficient for use in the optical devices under discussion.

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REFERENCES

- [1] Moreau, D., Lefort, C., Burke, R., Leveque, P. and O'Connor, R. P., "Rhodamine B as an optical thermometer in cells focally exposed to infrared laser light or nanosecond pulsed electric fields," *Biomed. Opt. Express* 6(10), 4105-4117 (2015).
- [2] Bazzicalupi, C., Caltagirone, C., Cao, Z., Chen, Q., Di Natale, C., Garau, A., Lippolis, V., Lvova, L., Liu, H., Lundstrom, I., Mostallino, M. C., Nieddu, M., Paolesse, R., Prodi, L., Sgarzi, M. and Zaccheroni, N., "Multimodal use of new coumarin-based fluorescent chemosensors: towards highly selective optical sensors for Hg²⁺ probing," *Chem. Eur. J.* 19, 14639-14653 (2013).
- [3] Antina, E. V., Guseva, G. B., Dudina, N. A. and V'yugin, A. I., "Synthesis, Stability in Solutions, and Spectral and Thermal Properties of Alkyl-Substituted 3,3'-Bis(dipyrromethene) Hydrobromides," *Rus. J. Inorg. Chem.* 55(8), 1172-1178 (2010).
- [4] Lakshmi, V., Sharma, R. and Ravikanth, M., "Functionalized boron-dipyrromethenes and their applications," *Reports in Organic Chemistry* 6, 1-24 (2016).
- [5] Pérez-Ojeda, M. E., Thivierge, C., Martín, V., Costela, A., Burgess, K. and García-Moreno I., "Highly efficient and photostable photonic materials from diiodinated BODIPY laser dyes," *Opt. Mater. Exp.* 1(2), 243-251 (2011).
- [6] Berezin, M. B., Semeikin, A. S., Antina, E. V., Pashanova, N. A., Lebedeva, N. Sh. and Bukushina, G. B., "Synthesis and physicochemical properties of hydrobromides of alkyl-substituted dipyrrolylmethenes," *Russ. J. Gen. Chem.* 69, 1949-1955 (1999).
- [7] Antina, E. V., Berezin, M. B., Dudina, N. A., Guseva, G. B., Antina, L. A. and V'yugin A. I., "Synthesis and spectral properties of zinc(II) helicates with 3,3'-bis(dipyrrolylmethenes) series," *Rus. J. Gen. Chem.* 80(6), 1216-1218 (2010).
- [8] Kuznetsova, R. T., Aksenova, Yu. V., Solodova, T. A., Kopylova, T. N., Tel'minov, E. N., Mayer, G. V., Berezin, M. B., Antina, E. V., Burkova, S. L. and Semeikin, A. S., "Lasing characteristics of difluoroborates of 2,2'-dipyrromethene derivatives in solid matrices," *Quantum Electron.* 44(3), 206-212 (2014).
- [9] Kuznetsova, R. T., Maier, G. V., Kopylova, T. N., Svetlichnyi, V. A., Tel'minov, E. N. and Filinov, D. N., "Phototransformations of organic compounds upon powerful laser excitation under nonlinear absorption conditions," *High Energy Chem.* 36(5) 338-343 (2002).
- [10] Aksenova, Iu. V., Kuznetsova, R. T., Tel'minov, E. N., Mayer, G. V., Antina, E. V. and Berezin, M. B. "Stabilities of a series of dipyrin difluoroborates in protic solvents in the ground and electron-excited states," *Rus. J. Phys. Chem. A* 90(2), 349-355 (2016).
- [11] Alvarez, M., Amat-Guerri, F., Costela, A., Garcia-Moreno, I., Liras, M. and Sastre, R., "Laser emission from mixtures of dipyrromethene dyes in liquid solution and in solid polymeric matrices," *Optics Commun.* 267, 469-479 (2006).
- [12] Cerdan, L., Costela, A., Garcia-Moreno, I., Garcia, O. and Sastre, R., "Laser emission from mirrorless waveguides based on photosensitized polymers incorporating POSS," *Opt. Express.* 18, 10247-10256 (2010).
- [13] Costela, A., Garcia-Moreno, I., Cerdan, L., Martin, V., Garcia, O. and Sastre, R., "Dye-doped POSS solutions: random nanomaterials for laser emission," *Adv. Mater.* 21, 1-4 (2009).
- [14] Romyantsev, E. V., Aleshin, S. N., Desoki, A., Marfin, Y. S. and Antina, E. V., "Kinetic resistance of borofluoride complexes of dipyrrolylmethenes to acids," *Rus. J. Inorg. Chem.* 58(5), 596-601 (2013).
- [15] Mula, S., Ray, A. K., Banerjee, M., Chaudhuri, T., Dasgupta, K. and Chattopadhyay, S. "Design and development of a new pyrromethene dye with improved photostability and laser efficiency: theoretical rationalization of photophysical and photochemical properties," *J. Org. Chem.* 73, 2146-2154 (2008).
- [16] Baudron, S. A., "Luminescent dipyrin based metal complexes," *Dalton Trans.* 42, 7498-7509 (2013).
- [17] Baudron, S. A., Ruffin, H. and Hosseini, M. W., "On Zn(II) 2,20-bisdipyrin circular helicates," *Chem. Commun.* 51, 5906-5909 (2015).