

Photonics and application of dipyrinates in the optical devices

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Abstract. In this paper spectral–luminescent, lasing, photochemical, and sensory characteristics of a number of Zn(II) and B(III) coordination complexes with dipyrinates with different structures are presented. We have discussed relations of the structure of investigated compounds and formed solvates with their optical characteristics. The results showed that alkyl substituted dipyrinates derivatives have excellent luminescent characteristics and demonstrated effective lasing upon excitation of Nd:YAG-laser. They can be used as active media for liquid tunable lasers. Zinc and boron fluoride complexes of dipyrinates with heavy atoms in structure don't have fluorescence but have long-lived emission due to increased nonradiative intersystem processes in the excited state by the mechanism of a heavy atom. For solid samples based on halogenated complexes was found dependency of the long-lived emission intensity of the oxygen concentration in gas flow. The presence of line segment indicates the possibility of the use of these complexes as a basis for creation of optical sensors for oxygen. Moreover, results of a study of halogen-substituted aza-complexes under irradiation are presented. Such complexes are promising for the creating media for generation of singlet oxygen (¹O₂), which is important for photodynamic therapy in medicine and photocatalytic reactions in the industry.

1. Introduction

To date, the study of complexes of dipyrinates with different structure is one of the most successful developing areas of modern chemistry. The increased interest to this class of compounds is associated with widespread complexes of dipyrinates in many branches of science, technology and medicine. The most perspective members of this family are boron fluorinated complexes of dipyrinates (BODIPY). Depending on the structure of the ligand and a solvent, they have optimal characteristics for the fluorophores (high fluorescence quantum yield, a good photostability). BODIPYs can be widely applied as active media for tunable dye lasers with high energy conversion outputs, as well as light harvesting arrays to develop antenna systems [1, 2]. Furthermore, dipyrinates can form stable complexes with ions of d-elements, such as Zn(II). In comparison with BODIPY, advantage complexes of d-metals with dipyrinates is easy to "self-assembly" in the "soft" conditions on complexing ions in solutions and in biological systems, as well as high sensitivity spectral-luminescence characteristics to changes in the structure of the chromophore and the nature of the solvent, which makes them very promising to fluorescent probes [3]. To successfully apply dipyrinates complexes and creation of various optical devices based on them must be systematic study of photochemical and photophysical properties and the establishment of their relationship from the structural features of the complexes. Therefore, the purpose of the work is to study the spectral–luminescent, lasing, photochemical, and sensory properties of a number of Zn(II) and B(III) coordination complexes with dipyrinates, the optimal combination of which will indicate the direction of the most effective use of these dyes.



2. Experimental details

In this work we studied the photophysical and photochemical characteristics of Zn(II) and B(III) complexes with dipyrinates with different alkyl and halogen substituted which were synthesized at the Institute of Solution Chemistry RAS. The structural formulas and denotations of the investigated compounds are given in Figure 1. The individuality and structure of synthesized compounds were verified using the thin layer chromatography, NMR, and IR spectroscopy methods in accordance with [4]. As solvents, we used ethanol, ethyl acetate, and cyclohexane (reagent grade).

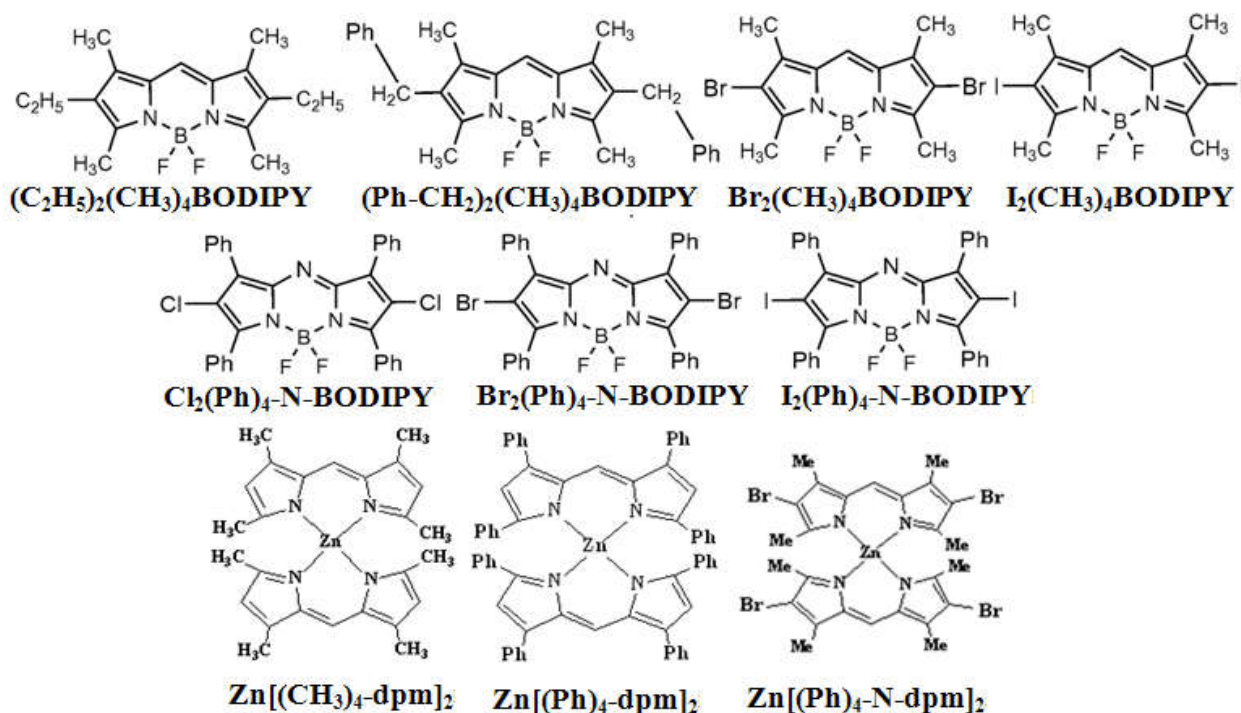


Figure 1. Structural formulas and denotation of investigated of dipyrinates.

The spectral and fluorescence characteristics of solutions were measured at room temperature on a SM2203 spectrometer (SOLAR, Belarus). Fluorescence, phosphorescence, and luminescence excitation spectra and lifetimes of the long-lived emission in frozen (77 K) non-degassed ethanol were measured accurate to 10% on a Cary Eclipse spectrometer (Varian) with an OptistatDN-100 cryostat (Oxford Instruments). The luminescence quantum yield was determined with an error of 10% by the reference method.

Lasing and photochemical characteristics of the dipyrinates complexes were studied with excitation by the second 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.

For the study the sensory properties the fibers of methylcellulose (MC-100, ReaChem) were pressed in tablets with thickness of about 1 mm and diameter of about 7 mm, which were impregnated by dyes solution in ethanol with different concentrations and dried under standard conditions. Polymer swelling in ethanol was not observed because of small quantities of solvent: volume of impregnating solution was 0.15 ml. After impregnating the volume of tablet increased by 20%. The sensor properties were investigated on the setup built around a CM2203 spectrometer consisted of a UFGS-4 device intended for generating gas mixture flow, a gas cell with the examined sample put in the cell block of the spectrometer, and a personal computer. Pure oxygen was used as a gas-analyte, and argon was used as a gas-diluent. A more detailed description of the experimental procedure has been described in [5].

3. Results and disacussion

Results of our investigations of spectral-luminescent, lasing, and photochemical characteristics are presented in the Table 1. Alkyl substituted BODIPY show excellent luminescent characteristics. Since the fluorescence quantum yield of such complexes in solutions is close to unity, stimulated emission was generated by pumping with the second harmonics of the Nd-YAG laser (532 nm). The solutions of $(C_2H_5)_2(CH_3)_4BODIPY$ and $(Ph-CH_2)_2(CH_3)_4BODIPY$ generates in the range of 557-560 nm and exceeds well known commercial laser dye in efficiency.

Table 1. Spectral luminescent, lasing, and photochemical properties of alkyl dipyrinates.

Compound, solvent	λ_{abs}^{max} , nm	λ_{fl}^{max} , nm (λ_{ex} , nm)	γ_{fl} (λ_{ex} , nm)	λ_{las} , nm (λ_{ex} , nm, W_{pump} , MW/cm ²)	Eff. las, % (λ_{ex} , nm, W_{pump} , MW/cm ²)	$\phi_{phot} \times 10^5$ (λ_{ex} , nm)
$(C_2H_5)_2(CH_3)_4$ BODIPY, ethanol	528	545 (457)	0.8 (475)	560 (532, 25)	74 (532, 25)	7 (532)
$(Ph-CH_2)_2(CH_3)_4$ BODIPY, cyclohexane	531	539 (500)	0.9 (500)	557 (532, 25)	76 (532, 25)	4 (532)

The solution of alkyl BODIPY generates with low threshold $W_{pump} < 1$ MW/cm², and, even at a laser-pump density of 1 MW/cm², the efficiency achieves 43%. With increasing excitation intensity, the maximum of lasing is shifted toward the long wavelength range by 1.5 nm (Figure 2). High generation efficiency and low yield of phototransformation point to the possibility of creating active media for tunable lasers based on alkyl derivatives of boron fluorinated complexes of dipyrinates.

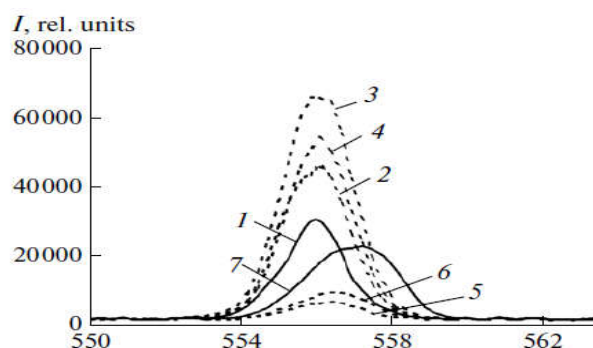


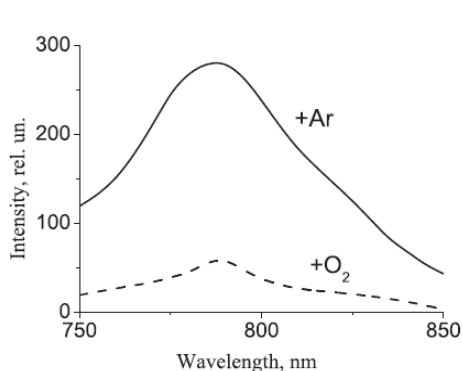
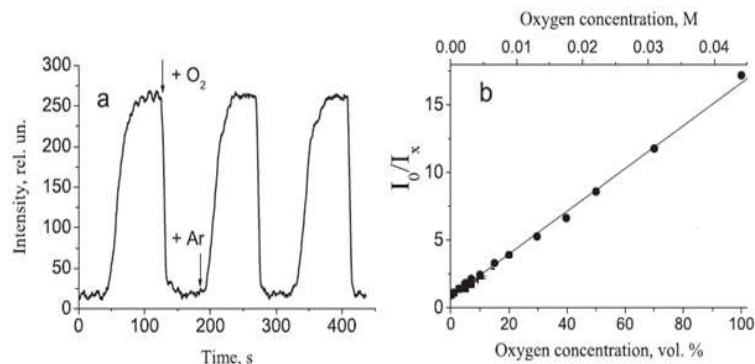
Figure 2. Lasing spectra of $(Ph-CH_2)_2(CH_3)_4BODIPY$ upon excitation by second harmonic of a Nd:YAG laser in cyclohexane (5×10^{-4} M, $\Delta\lambda_{1/2} = 2$ nm). Curves in: 1 – $\lambda_{max} = 556$ nm, $W = 0.5$ MW/cm²; 2 – $\lambda_{max} = 556$ nm, $W = 1.1$ MW/cm²; 3 – $\lambda_{max} = 556$ nm, $W = 1.3$ MW/cm²; 4 – $\lambda_{max} = 556$ nm, $W = 3.4$ MW/cm²; 5 – $\lambda_{max} = 556.3$ nm, $W = 6$ MW/cm²; 6 – $\lambda_{max} = 556.5$ nm, $W = 11$ MW/cm²; 7 – $\lambda_{max} = 557.5$ nm, $W = 46$ MW/cm².

Introduction bromine or iodine into the dipyrinates core enhances intersystem crossing, which leads to decrease of the fluorescence yield and to emergence a long-lived emission (Table 2). The replacement of the central atom boron(III) by zinc(II) adds to non-planarity of the chelates and contribution of non radiative processes in excitation energy deactivation, resulting in a decrease in the fluorescence yield. The higher efficiency of intersystem crossing and the higher triplet population in the zinc(II) dipyrinates complexes in comparison with BODIPY can be due to both the heavy atom effect and, possibly, an increased fraction of the unpaired “promoted” electrons in the non-planar transition metal chelates. This increase results in an appearance of the long lived emission of the zinc chelates in the form of phosphorescence and delayed fluorescence generated via the T-T annihilation mechanism.

Table 2. Spectral luminescent properties of halogenated dipyrinates of B(III) and Zn(II).

Compound in ethanol	$\lambda_{\text{abs}}^{\text{max}}$, nm	$\lambda_{\text{fl}}^{\text{max}}$, nm (λ_{ex} , nm)	γ_{fl} (λ_{ex} , nm)	λ_{ph} , nm *77 K	τ_{ph} , ms *77 K	$\Phi_{\text{phot}} \times 10^5$ (λ_{ex} , nm)
$\text{Br}_2(\text{CH}_3)_4\text{BODIPY}$	528	545 (470)	0.4 (480)	795	3.7	12 (532)
$\text{I}_2(\text{CH}_3)_4\text{BODIPY}$	535	550 (500)	0.04 (500)	792	0.6	35 (532)
$\text{Zn}[(\text{CH}_3)_4\text{-dpm}]_2$	485	492 (460)	0.008 (460)	740+820	11+4.2	7.5 (355)
$\text{Zn}[(\text{Ph})_4\text{-dpm}]_2$	525	602 (510)	0.01 (510)	600+830	0.7+17.7	1.2 (532)
$\text{Zn}[(\text{Ph})_4\text{-N-dpm}]_2$	588	350 (209)		760+810	0.2+2.2	5 (532)

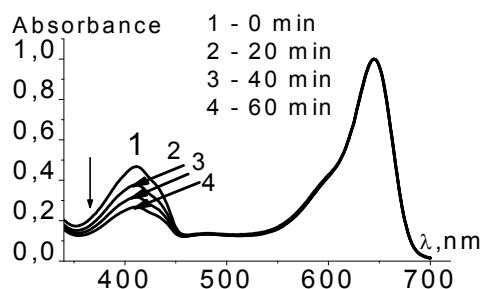
The obtained characteristics of long-lived emission from complexes allow us to recommend this compound for study of his interaction with oxygen with aim of creation oxygen sensor. Because sensory properties required evaluation at room temperature were prepared solid samples (matrices based on methyl cellulose, solid-state films based on polyvinyl butyral) to minimize nonradiative processes of the T-state characteristic of liquid solutions. For studied solid samples (matrices and films) noted the change in intensity of luminescence dipyrinates complexes under various conditions, i.e., quenching of phosphorescence in an oxygen atmosphere and its increase in argon (Figure 3). Measuring dependencies of the intensity of the phosphorescence of the oxygen concentration and plotting the calibration curve (Stern-Volmer dependences have linear portion (Figure 4)) can be used to determine the unknown concentration of oxygen. Thus, the obtained results point to the possibility of the use of dipyrinates complexes as a basis for creation of optical sensors for oxygen.

**Figure 3.** Luminescence spectra of $\text{I}_2(\text{CH}_3)_4\text{BODIPY}$ in methyl cellulose matrix in the argon and oxygen atmospheres at $\lambda_{\text{ex}}=520$ nm**Figure 4.** (a) Typical change in phosphorescence intensity ($\lambda_{\text{ex}}=520$ nm, $\lambda_{\text{em}}=790$ nm) of $\text{I}_2(\text{CH}_3)_4\text{BODIPY}$; (b) Stern-Volmer plots sequestered in methyl cellulose.

We also studied the spectral properties of halogenated tetraphenyl-aza-dipyrinates. They have a low fluorescence quantum yields due to increased intersystem processes by the mechanism of "heavy" atoms (Table 3). The absence of phosphorescence may be due to high efficient T-S₀ intersystem crossing and quenching triplet oxygen. According to the literature, there is evidence of generation singlet oxygen by similar structures [6]. Therefore, the efficiency of the formation of singlet oxygen when transferring the excitation energy from the BODIPY complexes to 1,3-diphenylisobenzofuran (DPBF well known as a "trap" of singlet oxygen) was measured. Under irradiation mixture a dye with DBPF was found decrease concentration of DPBF (Figure 5). This indicates the formation of singlet oxygen in solution by reacting triplet excited BODIPY ($\lambda_{\text{ex}}=640$ nm) with molecular O₂. So, halogenated aza-dipyrinates is promising for the creating media for generation of singlet oxygen (¹O₂), which is important for photodynamic therapy in medicine and photocatalytic reactions in the industry.

Table 3. Spectral luminescent properties of halogenated aza-dipyrrinates.

Compound, solvent	$\lambda_{\text{abs}}^{\text{max}}$, nm	$\lambda_{\text{fl}}^{\text{max}}$, nm (λ_{ex} , nm)	γ_{fl} (λ_{ex} , nm)	$\Phi_{\text{phot}} \times 10^5$ (λ_{ex} , nm)
$\text{Cl}_2(\text{Ph})_4\text{-N-BODIPY}$, ethyl acetate	644	674 (590)	0.26 (590)	1.3 (532)
$\text{Br}_2(\text{Ph})_4\text{-N-BODIPY}$, ethyl acetate	643	674 (560)	0.02 (560)	0.13 (532)
$\text{I}_2(\text{Ph})_4\text{-N-BODIPY}$, ethanol	647	674 (600)	0.32 (600)	0.18 (532)

**Figure 5.** The change in the absorption spectra of the mixture $\text{I}_2(\text{Ph})_4\text{-N-BODIPY}$ (3×10^{-5} M) and 1,3-DPBF (3×10^{-5} M) upon irradiation ($\lambda_{\text{ex}}=640$ nm) in ethanol in oxygen atmosphere

Substance used in optical devices must have a high photostability under regular excitation. And so the stability of the complexes in the ground and excited states is the most important characteristic for practical applications. To study this, photostability of dipyrinates in ethanol solutions was investigated under 2nd and 3rd harmonic of Nd:YAG-laser irradiation. Alkyl and halogen dipyrinates complexes exhibit high photostability (Table 1, 2, 3). Thereby this value of phototransformations quantum yield is quite enough for successful use in optoelectronic devices.

4. Conclusion

We have investigated the spectral–luminescent properties and lasing characteristics in relation to the excitation parameters (intensity and excitation wavelength) for new dipyrinates complexes. We have ascertained and analyzed relations of obtained characteristics with the molecular structure and properties of the solvent and its phase state (liquid, solid). Our results showed that dipyrinates derivatives can be used as active media for different optical devices: tunable lasers, sensors for determining the oxygen in the gas phase and so on.

References

- [1] Loudet A, Burgess K 2007 *Chem. Rev.* **107** 4891
- [2] Harriman A 2015 *Chem. Commun.* **51** 11745
- [3] Kuznetsova R T, Aksenova Yu V, Bashkirtsev D E, Prokopenko A A, Tel'minov E N, Mayer G V, Dudina N A, Antina E V, Nikonova A Yu, Berezin M B, Semeikin A S 2015 *High Energy Chem.* **49** 16
- [4] Dudina N A, Nikonova A Yu, Antina E V, Berezin M B, V'yugin A I 2013 *Khim. Geterotsikl. Soedin.* **12** 1878
- [5] Ermolina E G, Kuznetsova R T, Aksenova Yu V, Gadirov R M, Kopylova T N, Antina E V, Berezin M B, Semeikin A S 2014 *Sensors and Actuat. B* **197** 206
- [6] Zhang X, Yang X 2013 *J. Phys. Chem. B* **117** 5533