

PAPER • OPEN ACCESS

Experimental and theoretical research of photonics of zinc dipyrromethene complexes

To cite this article: A Prokopenko *et al* 2019 *J. Phys.: Conf. Ser.* **1145** 012045

View the [article online](#) for updates and enhancements.

You may also like

- [Influence of North Sumatra Maize \(*Zea mays L.*\) monoculture on soil properties using free Sentinel 2 imagery](#)
V. Novák, K. Kížová and R. A. M. Napitupulu
- [Observations of Love Wave Dispersion Properties Using Seismometers and Component Strainmeters](#)
Xiaolei Wang, Bing Xue, Xiaoyi Zhu et al.
- [Structural study of hydrogen absorption properties using Thermocalc software for application in energy storage](#)
D Bellon, A Martínez-Amariz and E Montes



ECS
The
Electrochemical
Society
Advancing solid state &
electrochemical science & technology

DISCOVER
how sustainability
intersects with
electrochemistry & solid
state science research

Experimental and theoretical research of photonics of zinc dipyrromethene complexes

A Prokopenko, R Kuznetsova and V Pomogaev

Laboratory of Photophysics and Photochemistry of Molecules, *Tomsk State University*, Tomsk 634050, Russia

E-mail: alexpr898@gmail.com

Abstract. Experimental study of photonics of selected complexes was presented. Electronic absorption and luminescence spectra in different solutions at room temperature (298 K) were shown. For dipyrromethene complexes with zinc phosphorescence was observed in ethanol solution at liquid nitrogen temperature (77 K). Also quantum yield of transformation under excitation of Nd:YAG laser was received. Their values are enough for successful use in modern optical devices. For one of the studied complex the theoretical calculations were made by Gaussian 09. Discussion of features relationships of the structure with the properties using quantum chemical calculations was carried out.

1. Introduction

The last decades were characterized by increased interest in the development of various optical devices based on complex molecular compounds. Depending on the structure, they are widely used including active laser media of tunable lasers, laser limiters, optical sensors in various fields of science and technology. Currently, dipyrromethenes with p- and d- elements are the most promising compounds to be applied as elements of these devices. The most perspective members of this family are boron fluorinated complexes of dipyrromethenes (BODIPY). BODIPYs can be widely used as active media for tunable dye lasers with high energy conversion outputs, optical sensors, fluorescence markers and others [1, 2]. In addition, dipyrromethenes can form stable complexes with ions of d- elements such as Zn(II). In comparison with BODIPY, an advantage of complexes of d-metals with dipyrromethenes is high sensitivity of the photonics characteristics to changes in the chromophore structure and nature of the solvent as well as easier “self-assembly” of these complexes. It makes them very promising for fluorescent probes dipyrromethenates have efficient absorption and emission in the visible spectral region and they are sensitive to structural changes in their molecular environment [3].

New derivatives are been synthesizing with increasing intensity but at the same time theoretical researches of their physical and chemical properties to develop optical devices is going essentially slower. However exactly theoretical calculations are the key to understanding of photonics for complex organic molecules in ground and excited states.

Therefore, the purpose of the present work is experimental and theoretical multiscale researches of photophysical and photochemical processes occurring in dipyrromethenes molecules and depending on their structure, nature of the solvent and the characteristics of the exciting radiation.



2. Methods and Materials

We investigated a series of zinc complexes of dipyrromethenes $[\text{Zn}(\text{dpm})_2]$ with different alkyl-, phenyl- and halogen- substituted compounds synthesized at the G.A. Krestov Institute of Solution Chemistry of the Russian Academy of Sciences by the methods described in [4]. The structural formulas and designations of the examined compounds are shown in figure 1. The individuality and structure of synthesized compounds were verified using methods of thin layer chromatography, NMR, and IR spectroscopy. As solvents, we used ethanol and cyclohexane (of reagent grade).

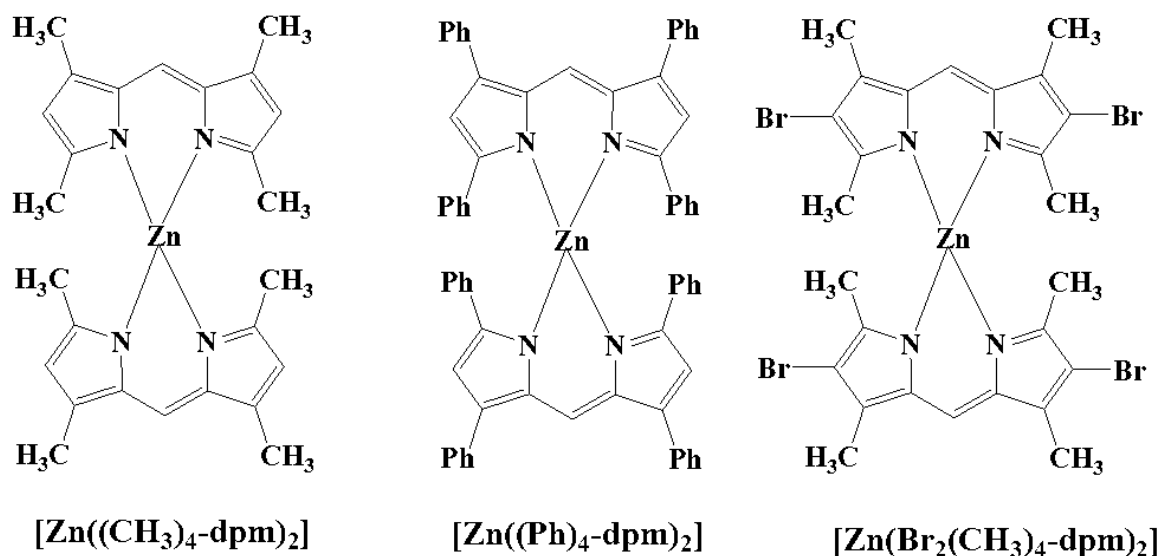


Figure 1. Structure formulas and denotation of investigated dipyrromethens.

The spectral and fluorescence characteristics of solutions were measured at room temperature on a CM2203 spectrometer (SOLAR, Belarus). The fluorescence, phosphorescence, and luminescence excitation spectra and lifetimes of long-lived emission in frozen (77 K) non-degassed ethanol were measured with accuracy up to 10 % on a Cary Eclipse spectrometer (Varian) equipped with an Optistat DN-100 cryostat (Oxford Instruments). The luminescence quantum yields were determined with an error of 10 % by the relative method.

The photochemical characteristics of the dipyrromethenes complexes were studied under excitation by the second and third harmonics of a Nd-YAG laser (SOLAR, Belarus). Lasing and pumping energies were measured to within 3 % error with OPHIR-NOVA (Israel) and Gentec EO (Canada) instruments. The efficiency of phototransformation was estimated from the change in the absorption spectra after laser irradiation, using the procedure described in detail in [5].

For better understanding of physical-chemical properties of complex organic molecules, not only experimental data but also theoretical investigations are needed. Quantum chemical calculations are successfully used to understand the spectral properties and physical mechanisms of such molecules. The advantages of this method are the possibilities of analysis of low excited states, related molecular orbitals, their types and localization, also ESP (electrostatic potential) mapping analysis to detect pathway of interaction with ions. Methods ab initio calculations were widely used, especially based on density functional theory (DFT). Quantum-chemical calculations using the TD-DFT (time-dependent density functional theory) the pbe0 and wb97xd potential accompanied with svp and cc-pvdz basis sets implemented in the Gaussian09 package were performed [6]. Types and localization of MO (molecular orbitals) responsible for electronic transitions were analysed. Schemes of excited energy decay were presented and analyzed, and the MO localization and electron density difference (EDD) were mapped and analyzed with the GaussView visualization suite.

3. Results and discussion

3.1. Experimental research of spectral luminescence properties

The spectral properties of zinc dipyrromethene complexes $[\text{Zn}(\text{dpm})_2]$ were previously studied in [5]. Alkyl-substituted zinc dipyrromethene complex have a maximum of absorption spectra in 485 nm. Incorporation of halogen atoms as substituents instead of alkyl groups into ligands leads to a slight change of the absorption and fluorescence spectra and also reduces the fluorescence efficiency because increases the intersystem crossing and phosphorescence yield (the heavy atom effect). The replacement of the methyl by the phenyl groups in the dipyrromethene ligand causes a bathochromic shift in the spectral and luminescence parameters. Replacement of the solvent has little effect on the spectroscopic, but significantly changes the photophysical characteristics of the compounds: the moving from cyclohexane to ethanol increases the share of nonradiative processes in deactivation of excitation energy due to "rearrangements" within the near specific solvate shell of complexes in ethanol, which are inhibited by freezing solutions, increasing the intensity of luminescence.

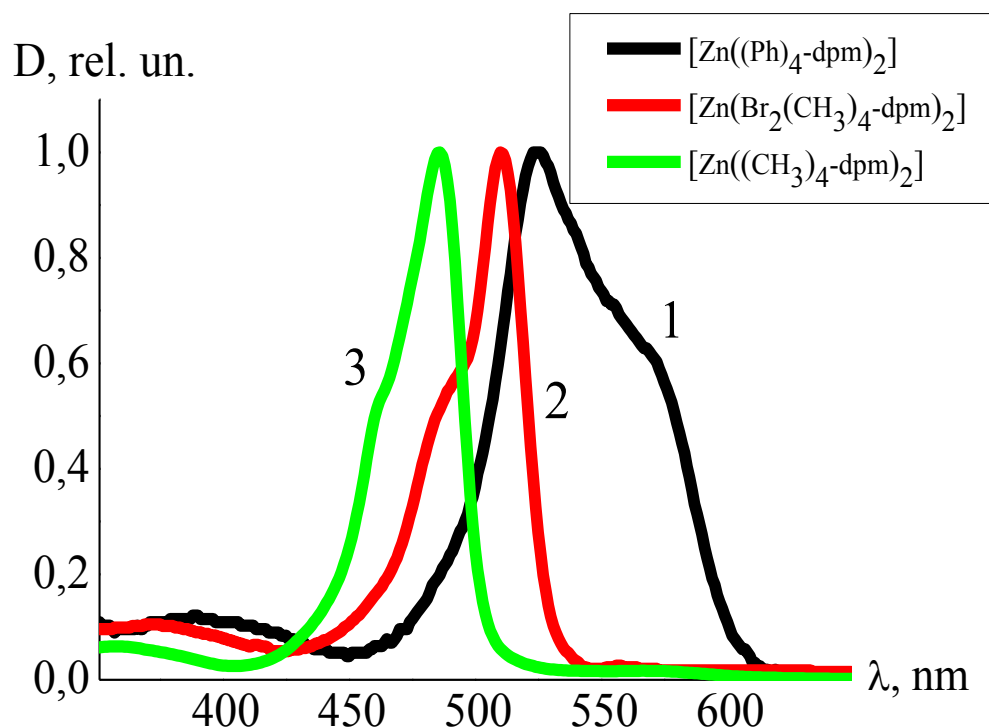


Figure 2. Normalized absorption spectra of zinc dipyrromethene complexes in ethanol (1 – $[\text{Zn}((\text{Ph})_4\text{-dpm})_2]$, 2 – $[\text{Zn}(\text{Br}_2(\text{CH}_3)_4\text{-dpm})_2]$, 3 – $[\text{Zn}((\text{CH}_3)_4\text{-dpm})_2]$).

All of investigated complexes have low fluorescence yield: 0.4 in cyclohexane and 1-2 orders lower in ethanol (table 1). The yield of fluorescence of the phenyl substituted chelate is higher than of alkyl substituted, a difference that can be due to π - π coupling of the aromatic systems of the closest phenyl rings of one ligand with the pyrrole rings of the other retarding their free rotation, which stimulates the nonradiative processes in $[\text{Zn}((\text{CH}_3)_4\text{-dpm})_2]$. It should be noted that $[\text{Zn}((\text{Ph})_4\text{-dpm})_2]$ have a double transitions (S_0 - $S_1 = 587$ and S_0 - $S_2 = 525$) while there are no such effects in $[\text{Zn}((\text{CH}_3)_4\text{-dpm})_2]$ and $[\text{Zn}(\text{Br}_2(\text{CH}_3)_4\text{-dpm})_2]$ (figure 2).

Due to zinc dipyrromethene complexes does not generate stimulated emission; therefore, possible excitation energy deactivation pathways in the chelate, including phosphorescence, were studied, for example, for creation of sensor media with quenching phosphorescence by oxygen.

Table 1. Spectral luminescent properties of zinc dipyrromethene complexes.

Compound, solvent	λ_{abs} , nm	λ_{fl} , nm (λ_{ex} , nm)	$\gamma_{\text{fl}} \pm 10\%$ (λ_{ex} , nm)	λ_{phos} , nm (λ_{ex} , nm), T=77 K	$\phi \times 10^5$ (λ_{ex} , nm)
[Zn((CH ₃) ₄ -dpm) ₂], cyclohexane	354 (12000) 488 (235000)	500 (350, 470)	0.05 (470) 0.03 (360)		
[Zn((CH ₃) ₄ -dpm) ₂], ethanol	346 (9750) 485 (146200)	491 (360, 460)	0.008 (460) 0.004 (360)	740+820 (360, 460)	7.5 (355)
[Zn((Ph) ₄ -dpm) ₂], cyclohexane	290 (120000) 400 (18000) 527 (197000) 572 (112000)	605 (290) 603 (520, 580)	0.3 (290) 0.4 (570)		
[Zn((Ph) ₄ -dpm) ₂], ethanol	290 (162000) 400 (12300) 525 (297000) 570 (116000)	602 (510, 570)	0.009 (310) 0.01 (510) 0.05 (570)	830 (290, 510, 560)	1.1 (532)
[Zn(Br ₂ (CH ₃) ₄ -dpm) ₂], ethanol	365 (6600) 503 (98000)	512 (350, 465)	0.005 (350) 0.007 (465)	744 (350, 465)	640 (355)

For these complexes the molecular photostability was determined. The value of quantum yield of phototransformation was about 10^{-5} . This value is quite enough for successful use in optical devices. For bromine substituted zinc dipyrromethene complexes photostability is the lowest and it is necessary to find ways to increase this value.

3.2. Theoretical calculation

In order to reproduce spectral features of zinc dipyrromethene complexes an adequate chromophore model and computational methods capable of correctly calculating the energies of the excited states and their photo-physical properties are needed.

Complexes with methyl group and bromine atom were used for calculation S_1 - S_4 excited states under absorption and excitation. For calculation of these states two functional (wb97xd and pbe0) and two basis (cc-pvdz and svp) were applied (table 2) [7]. The change of basis set has a small effect and only slightly shifts the position of absorption bands. While the replacement of the functional leads to the significant change of nature of transition, so S_1 - S_2 is becoming S_3 - S_4 with according to increase of oscillator strength. When calculating fluorescence triplets states were appeared. Their presence were confirmed experimentally by detection of phosphorescence. But the positions of calculated bands do not match with experiment.

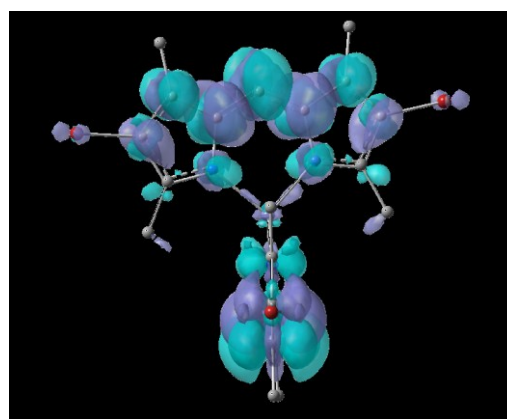
When analyzing the change in the electron density distribution for S_0 - S_1 transition, forming intensities of the corresponding absorption bands, the large electron density is localized on bromine atoms which is probably due to their high electronegativity. Under excitation in S_1 state, a modification of electron density occurs at the bromine atom and it change its effective charge to the opposite (figure 3).

Table 2. Calculated parameters of electron transitions for zinc dipyrromethene complexes.

Complex	Functional/basis	S ₁ , nm (f)	S ₂ , nm (f)	S ₃ , nm (f)	S ₄ , nm (f)
absorption					
[Zn((CH ₃) ₄ -dpm) ₂]	wb97xd/cc-pvdz	401 (0.6279)	401 (0.6284)	328 (0.0003)	328 (0.0003)
	pbe0/cc-pvdz	458 (0.0002)	458 (0.0002)	418 (0.6062)	394 (0.6066)
	pbe0/svp	459 (0.0002)	459 (0.0002)	392 (0.6206)	392 (0.6211)
[Zn(Br ₂ (CH ₃) ₄ -dpm) ₂]	wb97xd/cc-pvdz	414 (0.7186)	414 (0.7195)	335 (0.0010)	335 (0.0010)
	pbe0/cc-pvdz	474 (0.0008)	474 (0.0008)	418 (0.6024)	418 (0.6029)
	pbe0/svp	473 (0.0007)	473 (0.0007)	415 (0.6082)	415 (0.6088)
fluorescence					
[Zn((CH ₃) ₄ -dpm) ₂]	wb97xd/cc-pvdz	429 (0.3327)	T ₂ = 949	T ₃ = 429	
	pbe0/cc-pvdz	478 (0.0344)	467 (0.0001)	409 (0.3063)	T ₂ = 839 T ₃ = 468
	pbe0/svp	465 (0.0013)	464 (0.0004)	402 (0.4921)	
[Zn(Br ₂ (CH ₃) ₄ -dpm) ₂]	wb97xd/cc-pvdz	439 (0.4092)	T ₂ = 930	T ₃ = 426	
	pbe0/cc-pvdz	487 (0.0291)	482 (0.0004)	434 (0.3374)	T ₂ = 838 T ₃ = 483



a



b

Figure 3. Electron Density Difference EDD from S₀ to S₁ (a) and S₁ to S₀ (b) for [Zn(Br₂(CH₃)₄-dpm)₂] calculated by wb97xd-functional.

4. Conclusions

As a result of complex investigations of the photonics for three zinc dipyrromethene complexes with different substituents are presented. Experimental spectral luminescent characteristics in several solutions are shown. Also phosphorescence properties in frozen ethanol solutions were studied. For methyl and bromine substituted zinc dipyrromethene complexes theoretical study was conducted using quantum chemical calculations with different functional and basis sets. Electronic structures, the nature of involved molecular orbitals and electron density redistributions in excited states was

established. The electronic schemes qualitatively reflect the experimental data. Nevertheless, the level of calculations requires an improvement to obtain better quantitative results that is a task of the further research.

Acknowledgments

We kindly thank Dr. M.B. Berezin from the G.A. Krestov Institute of Solution Chemistry of the RAS for the synthesis of the presented dipyrromethene complexes.

This study was supported by the Russian Foundation for Basic Research (projects nos. 18-33-00284), the State Task of Russian Ministry of Education and Science (project no. 4.6027.2017/8.9) and The Tomsk State University competitiveness improvement programme.

References

- [1] Kuehne A and Gather M 2016 Organic Lasers: Recent Developments on Materials, Device Geometries, and Fabrication Techniques *Chem. Rev.* **116** 12823-12864
- [2] Xia H, Xu X and Song Q 2017 BODIPY-Based Fluorescent Sensor for the Recognition of Phosgene in Solutions and in Gas Phase *Anal. Chem.* **89** 4192-4197
- [3] Dudina N, Nikonova A, Antina E, Berezin M and Vyugin A 2014 Synthesis, spectral-luminescent properties, and photostability of zn(ii) complexes with dipyrins modified by the periphery and meso-spacer *Chemistry of heterocyclic compounds* **49** № 12 1740-1747
- [4] Antina L, Dudina N, Guseva G, Antina E, Berezin M and Vyugin A 2012 Characteristic features of formation, synthesis, and properties of binuclear zinc(II) helicates with alkyl-substituted 3,3'-bis(dipyrrolylmethenes) *Russian Journal of Inorganic Chemistry* **57** 261-269
- [5] Kuznetsova R, Aksenova Yu, Bashkirtsev D, Prokopenko A, Tel'minov E, Mayer G, Dudina N, Antina E, Nikonova A, Berezin M, and Semeikin A 2015 Photonics of Zinc(II) and Boron(III) Chelates with Methyl and PhenylSubstituted Dipyrromethenes and Azadipyrromethenes *High Energy Chemistry* **49** 16-23
- [6] Kuznetsova R, Aksenova Iu, Bashkirtsev D, Prokopenko A, Pomogaev V, Antina E, Berezin M and Bumagina N 2018 Photonics of coordination complexes of dipyrins with p- and d-block elements for application in optical devices *Journal of Photochemistry and Photobiology A: Chemistry* **354** 147-154
- [7] Pomogaev V, Ramazanov R, Ruudc K and Artyukhov V 2018 Insight into the fluorescence quenching of Trp214 at HSA by the Dimetridazole ligand from simulation *Journal of Photochemistry and Photobiology A: Chemistry* **354** 86-100