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Photonics of Halogenated Zinc(II) and Cadmium(II) Dipyrrromethene Complexes

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Abstract: This article compares spectroscopic properties of the series of dipyrrromethene dyes, namely their complexes of boron (III), zinc(II) and cadmium(II) with the halogenated ligands of the same structure. Absorption and emission spectra, lifetimes of long-lived emission and quantum yields of luminescence were studied as the functions of molecular structure of dipyrrromethene complexes. The role of the position and nature of a substituent in a ligand, polarity of a solvent and temperature of media were also investigated. The studies demonstrate that replacing the central atom boron(III) by zinc(II) decreases the fluorescence quantum yield, indicating the increased role of non-radiative processes in excitation energy deactivations such as intersystem crossings. In addition, according to the heavy atom effect, the efficiency of intersystem crossings in halogen-substituted zinc(II) and cadmium(II) dipyrrromethene complexes is higher than in the corresponding boron fluoride dipyrrromethenes (BODIPY), which leads to increase in phosphorescence at low temperatures (frozen solutions). The obtained results make it possible to carry out further investigations of potential sensory properties that are required for systematic use of halogenated dipyrrromethene complexes for the creation of modern optical oxygen sensors and singlet oxygen photosensitizers for photodynamic therapy or photocatalytic oxidative reactions.

Keywords: dipyrrromethene complexes; BODIPY; photonics; spectroscopy; luminescence; phosphorescence; luminescence lifetime; heavy atom effect



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1. Introduction

The current stage in the development of world fundamental and material science is characterized by an increased interest in the creation of various materials capable of transforming the energy of light into a work function [1,2]. Such optically active materials are often based on hybrid organic compounds and their complexes. Dipyrrromethene-based complexes of transition metals are of a particular interest among a variety of organic-based luminophores. The high interest in these compounds is due to their structural–optical property relationships and relative simplicity of synthesis. It is known that dipyrrromethene-based complexes are the simplest chromophores, with an open chain oligopyrrole structure and a porphyrin-like fragment coordinated to the central atom which increases the structural rigidity of the entire system [3,4]. These complexes possess advanced optical characteristics (effective absorption and emission) in the visible range of the electromagnetic spectrum. Additionally, they possess high photostability, which is relevant in the design of optical devices. These properties define the unique role of dipyrrromethene-based complexes of high demand in various areas of chemistry, physics and medicine [5,6].

Initially, the alkyl substituted complexes of BF₂-dipyrrromethenes with high fluorescence and stimulated emission yields in a wide spectral range were synthesized for use as active laser media [7–9]. It is also known that dipyrrromethene complexes are used as active media for fluorescent markers and probes [10–12]. Moreover, derivatives of dipyrrromethene complexes are potential sensors for detection of metal ions such as Pb(II),

Hg(II), Pt(II) and gases in an air mixture (COCl_2 , CO_2 , COS , SO_2 and SO_3) [13–18]. Such sensors are used in the areas of biological and medical research.

Despite significant success in the design and application of dipyrromethene-based materials, the search for new compounds with improved spectroscopic characteristics is still a rapidly growing area of research. A particular focus is on dipyrromethene complexes of d-metals. At the moment, the photonics of dipyrromethene complexes of zinc(II) and cadmium(II) are not well investigated, especially the mechanisms of photorelaxation via long-lived excited states. The available studies demonstrate non-negligible phosphorescence even in the absence of heavy substituents in the ligand (halogenation) [19–21]. In this regard, in addition to their practical potential, halogen-substituted dipyrromethene systems are of a great fundamental interest due to the influence of the heavy atom effect on the photochemical and photophysical properties occurring in these compounds. The solution of the classical fundamental problem of establishing the “structure–property” relationship will evince the pathway towards practical use of dipyrromethene compounds in the creation of new materials for biosensorics and photodynamic therapy.

2. Materials and Methods

The object of study was a set of halogenated dipyrromethene complexes of BF_2 , Zn(II) and Cd(II) with substituents of various structures (Figure 1). There are three groups based on the different complexing ions B(III), Zn(II) and Cd(II). Halogen substituents also form three groups: two complexes with substitution of two bromines in the α - and β -positions relative to the central complexing metal and one with one atom of iodine in β -position. Full structural formulas and notations are contained in Supplementary Materials (Tables S1 and S2). It should be noted that the naming scheme adopted in this article is not generally accepted nomenclature but improves the clarity of this article. Analytical chemistry of the studied compounds has been performed by means of mass, IR and NMR spectroscopy at the G.A. Krestov Institute of Solution Chemistry at the Russian Academy of Sciences [22,23].

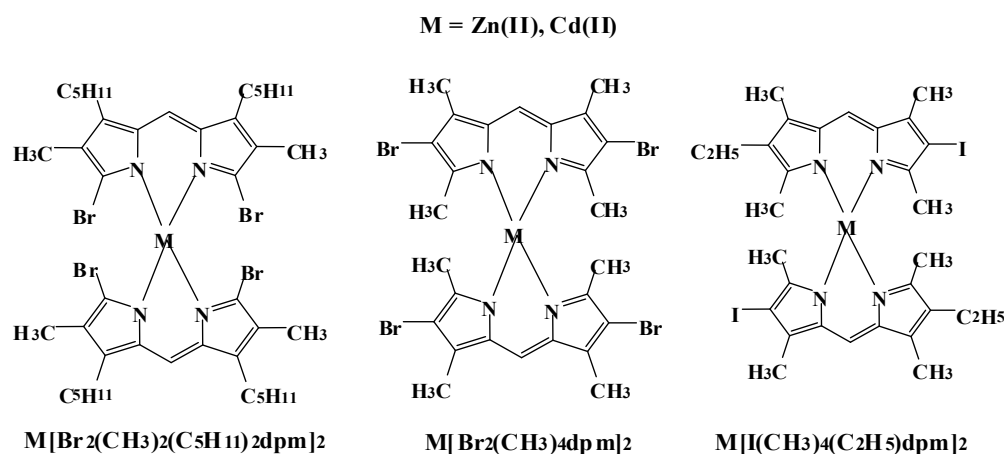


Figure 1. Structural formulas and designations of the studied dipyrromethene complexes.

Analytically pure ethanol, propanol-2, chloroform and cyclohexane were used as solvents (all HPLC grade). This set of solvents is basic and makes it possible to study the spectroscopic properties of compounds under diametrically opposite conditions. These solvents were used to test the impact of differences in polarity, protonic properties and ability to form hydrogen bonds on the spectral properties of target compounds.

The spectral–luminescent properties (the stationary absorption, fluorescence, phosphorescence, and luminescence excitation spectra) of liquid and frozen solutions of the studied dipyrromethene complexes were recorded with the accuracy of resolution of 0.5 nm and of 3% in intensity using Cary5000 (Agilent) and Cary Eclipse (Varian) spectrometers with Optistat DN cryostat (Oxford Instruments). The Cary Eclipse spectrometer also allows measuring the lifetime of long-lived emissions (for $\tau > 100 \mu\text{s}$) of compounds in frozen

solutions. Luminescence quantum yields were measured by the comparative method using the fluorescence data from the previously studied compound as reference: $(\text{CH}_3)_4\text{BODIPY}$ ($\lambda_{\text{fl}} = 514 \text{ nm}$, $\gamma_{\text{fl}} = 0.8$) [21]. An ethanolic solution of zinc tetraphenylporphyrin (ZnTPP) ($\lambda_{\text{phos}} = 780 \text{ nm}$, $\gamma_{\text{phos}} = 0.015$) was used as standard for phosphorescence measurements [24]. The error in determining the luminescence quantum yields does not exceed 10%.

3. Results

3.1. Spectral–Luminescent Characteristics at Room Temperature

The spectroscopic characteristics of zinc(II) and cadmium(II) dipyrromethene complexes are given in Table 1. They are compared to the previously studied properties of boron fluoride dipyrromethenes with similar substituents [21,25]. Comparative analysis of the spectral features of the studied complexes indicates a common shape of the spectra, which is characteristic of compounds of the dipyrromethene dyes family. There are two bands in the electronic absorption spectra. In the region of 330–400 nm, there is a band with a lower molar absorption coefficient corresponding to S_0 – S_2 absorption. The long wavelength band corresponding to S_0 – S_1 absorption is in the region of 450–550 nm and is the most sensitive to ligand substitution (Figure 2a,c). The typical fluorescence spectra appear as “mirror reflections” of the absorption spectra which is evidence that it is the same state that absorbs and emits (Figure 2b,d).

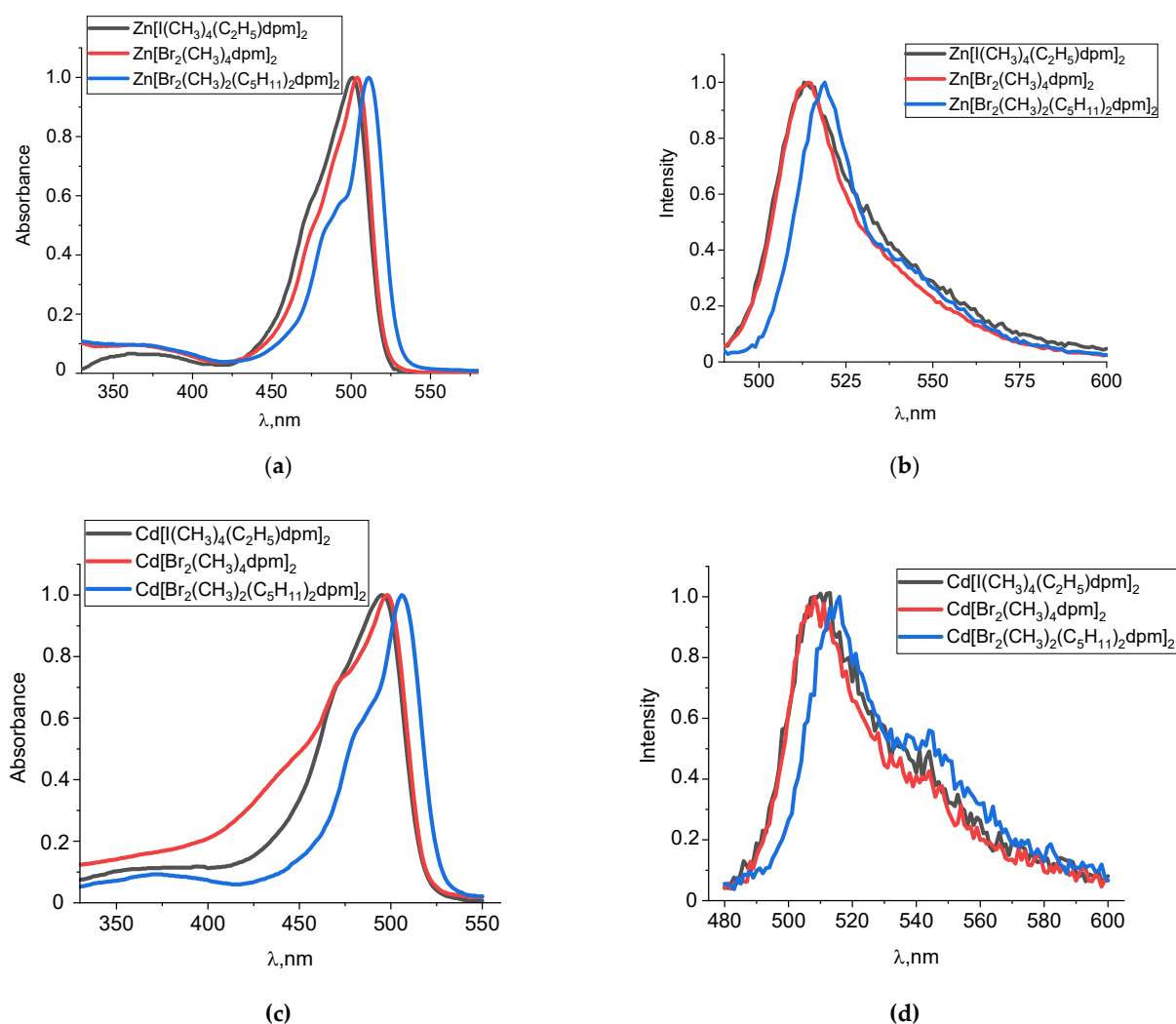


Figure 2. Normalized absorption (a,c) and fluorescence ($\lambda_{\text{ex}} = 470 \text{ nm}$) (b,d) spectra of zinc(II) (a,b) and cadmium(II) (c,d) dipyrromethene complexes in ethanol solutions at 298 K.

Table 1. Spectral and luminescent characteristics of BF₂, Zn(II) and Cd(II) dipyrromethene complexes at room temperature.

Compound	Solvent	$\lambda_{\text{abs}}, \text{nm}$	$\epsilon^* \times 10^{-4} (\text{S}_0\text{-S}_1), \text{M}^{-1}\text{cm}^{-1}$	$\lambda_{\text{fl}}, \text{nm} (\lambda_{\text{ex}}, \text{nm})$	$\gamma_{\text{fl}} \pm 10\%$
Br ₂ (CH ₃) ₂ (C ₅ H ₁₁) ₂ BODIPY	ethanol	381, 537	4.92	551 (475)	0.40
	propanol-2	378, 539	4.58	545 (475)	0.33
	chloroform	377, 546	4.54	553 (475)	0.43
	cyclohexane	376, 544	5.60	551 (475)	0.44
Br ₂ (CH ₃) ₄ BODIPY	ethanol	376, 528	5.10	545 (470)	0.40
	propanol-2	376, 531	4.84	547 (470)	0.27
	chloroform	378, 539	4.63	548 (470)	0.42
	cyclohexane	380, 538	5.76	547 (470)	0.44
I(CH ₃) ₄ (C ₂ H ₅)BODIPY	ethanol	380, 528	5.95	547 (470)	0.20
	propanol-2	373, 531	4.71	546 (470)	0.15
	chloroform	374, 534	4.62	547 (470)	0.22
	cyclohexane	375, 535	5.73	545 (470)	0.28
Zn[Br ₂ (CH ₃) ₂ (C ₅ H ₁₁) ₂ dpm] ₂	ethanol	373, 511	6.45	519 (480)	0.005
	propanol-2	372, 511	4.95	520 (480)	0.002
	chloroform	371, 510	5.05	522 (480)	0.003
	cyclohexane	373, 514	4.97	527 (480)	0.014
Zn[Br ₂ (CH ₃) ₄ dpm] ₂	ethanol	368, 504	6.81	514 (470)	0.007
	propanol-2	373, 505	5.04	515 (470)	0.004
	chloroform	372, 506	5.08	518 (470)	0.007
	cyclohexane	375, 509	5.10	520 (470)	0.13
Zn[I(CH ₃) ₄ (C ₂ H ₅)dpm] ₂	ethanol	370, 501	6.34	513 (480)	0.003
	propanol-2	374, 502	5.16	516 (470)	0.001
	chloroform	373, 505	5.09	518 (470)	0.001
	cyclohexane	373, 506	5.22	519 (480)	0.063
Cd[Br ₂ (CH ₃) ₂ (C ₅ H ₁₁) ₂ dpm] ₂	ethanol	373, 506	8.45	516 (470)	0.002
	propanol-2	372, 507	5.10	520 (470)	0.003
	chloroform	373, 509	5.03	525 (470)	0.003
	cyclohexane	373, 509	5.12	527 (470)	0.022
Cd[Br ₂ (CH ₃) ₄ dpm] ₂	ethanol	366, 498	8.82	508 (470)	0.002
	propanol-2	372, 501	4.96	511 (470)	0.002
	chloroform	372, 502	5.03	520 (470)	0.004
	cyclohexane	372, 504	5.10	518 (470)	0.027
Cd[I(CH ₃) ₄ (C ₂ H ₅)dpm] ₂	ethanol	370, 495	6.34	508 (470)	0.002
	propanol-2	373, 497	5.03	511 (470)	0.002
	chloroform	373, 498	5.09	518 (470)	0.001
	cyclohexane	373, 501	5.06	517 (470)	0.007

Substitution of boron with either zinc(II) or cadmium(II) leads to the hypsochromic shift of the absorption and fluorescence maxima by 24–33 nm in a series of complexes of the same type in terms of the ligand. For the dipyrromethene complexes of zinc(II) and cadmium(II), an increase in extinction coefficients is observed, which can be explained by a twofold increase in a number of chromophore ligands when compared to BODIPY complexes containing only one dipyrromethene ligand.

The monoiodine-substituted complex absorbs and emits at the shortest wavelength among the complexes of the same central atom (Table 1, Figure 2). In turn, the introduction of two heavy bromine atoms into α -positions to the pyrrole ring leads to a bathochromic shift of the main absorption and emission maxima by 5–9 nm relative to the β -dibromo-substituted analog. It should be noted that for boron fluoride and zinc(II) complexes, the α -bromination leads to a slight decrease in the extinction coefficients, which can be explained by the different inductive effect of alkyl substituents (CH₃/C₅H₁₁) and the additional influence on the polarization of intramolecular interactions of bromine atoms in α -positions to the central atom.

An increase in the polarity of the medium causes a general hypsochromic shift of the absorption and fluorescence maxima by 7–10 nm for BODIPY complexes and by 3–7 nm for zinc(II) and cadmium(II) complexes. At the same time, a slight decrease in intensity is observed, i.e., the molar extinction coefficient. The value of the Stokes shift is generally not large and is in the range of 6–19 nm for BODIPY complexes, 8–14 nm for zinc(II) complexes and 10–20 nm for cadmium(II) complexes. For BODIPY complexes, the Stokes shift increases in more polar solvents, which indicates an increase in the solvation interactions of excited molecules with a polar solvent compared to a non-polar one.

The nature of the solvent also has a significant effect on the luminescence efficiency of zinc(II) and cadmium(II) dipyrromethene complexes. Fluorescence quantum yield decreases in polar solvents such as ethanol and propanol-2 (Table 1). This is explained by the additional specific interaction of the solvent molecules with the central atom, which increases the yield of nonradiative relaxation in the deactivation of the excitation energy due to the internal reorganization of the first solvation sphere in the excited state in comparison with the main one.

3.2. Phosphorescence Properties in Frozen Solutions

According to the heavy atom effect, the halogen-substituted complexes of dipyrromethenes exhibit a decrease in the fluorescence efficiency and an increase in the intersystem crossing yield. Due to this, non-zero phosphorescence has been observed for these complexes in frozen ethanol and propanol-2 solutions. Unfortunately, attempts to register reliable phosphorescence spectra in chloroform and cyclohexane have not been successful. The solutions of these solvents formed frost on the cuvette walls, hindering the path for the optical beam. Polar solvents, such as ethanol and propanol-2, form optically transparent ice floes upon freezing and are suitable for recording phosphorescence at 77 K.

Previously, we studied the phosphorescence of halogen-substituted complexes of BODIPY [20,21,25]. The results of the phosphorescence of the zinc(II) and cadmium(II) complexes are shown in Table 2. The maxima of the long-lived emission spectra of the zinc(II) and cadmium(II) complexes are hypsochromically shifted relative to the analogous BODIPY complexes and are in the region of 735–745 nm. Phosphorescence spectra exhibit only single peak. For α -dibromo-substituted complexes of zinc(II) and cadmium(II), a clearer resolution of the vibrational structure is observed at the right edge of the phosphorescence spectrum (Figure 3). The coincidence of the phosphorescence excitation spectra with the absorption spectrum of halogen dipyrromethenates confirms that phosphorescence belongs to complexes $\text{Zn}[\text{Br}_2(\text{CH}_3)_2(\text{C}_5\text{H}_{11})_2\text{dpm}]_2$ and $\text{Cd}[\text{Br}_2(\text{CH}_3)_2(\text{C}_5\text{H}_{11})_2\text{dpm}]_2$ (Figure 4).

Table 2. Spectral and luminescent characteristics of BF_2 , Zn(II) and Cd(III) dipyrromethene complexes at temperature 77 K.

Compound	Solvent	$\lambda_{\text{phos}}, \text{ nm}$ ($\lambda_{\text{ex}}, \text{ nm}$)	$\tau_{\text{phos}}, \text{ ms}$ ($\lambda_{\text{ex}}/\lambda_{\text{em}}, \text{ nm}$)	$\gamma_{\text{phos}} \pm 10\%$
$\text{Br}_2(\text{CH}_3)_2(\text{C}_5\text{H}_{11})_2\text{BODIPY}$	ethanol	802 (480)	1.4 (475/802)	0.18
$\text{Br}_2(\text{CH}_3)_4\text{BODIPY}$	ethanol	795 (470)	3.7 (470/795)	0.01
$\text{I}(\text{CH}_3)_4(\text{C}_2\text{H}_5)\text{BODIPY}$	ethanol	787 (470)	1.5 (475/790)	0.52
$\text{Zn}[\text{Br}_2(\text{CH}_3)_2(\text{C}_5\text{H}_{11})_2\text{dpm}]_2$	ethanol	744 (470)	2.2 (470/740)	0.93
	propanol-2	745 (470)	2.7 (470/740)	0.73
$\text{Zn}[\text{Br}_2(\text{CH}_3)_4\text{dpm}]_2$	ethanol	740 (470)	5.8 (470/740)	0.68
	propanol-2	743 (470)	5.9 (470/740)	0.31
$\text{Zn}[\text{I}(\text{CH}_3)_4(\text{C}_2\text{H}_5)\text{dpm}]_2$	ethanol	739 (470)	2.4 (470/740)	0.48
	propanol-2	745 (470)	2.9 (470/740)	0.30
$\text{Cd}[\text{Br}_2(\text{CH}_3)_2(\text{C}_5\text{H}_{11})_2\text{dpm}]_2$	ethanol	735 (470)	2.3 (470/740)	1.01
	propanol-2	738 (470)	2.3 (470/740)	0.71
$\text{Cd}[\text{Br}_2(\text{CH}_3)_4\text{dpm}]_2$	ethanol	735 (470)	6.1 (470/740)	0.30
	propanol-2	735 (470)	6.0 (470/740)	0.35
$\text{Cd}[\text{I}(\text{CH}_3)_4(\text{C}_2\text{H}_5)\text{dpm}]_2$	ethanol	740 (470)	2.0 (470/740)	0.35
	propanol-2	739 (470)	2.4 (470/740)	0.36

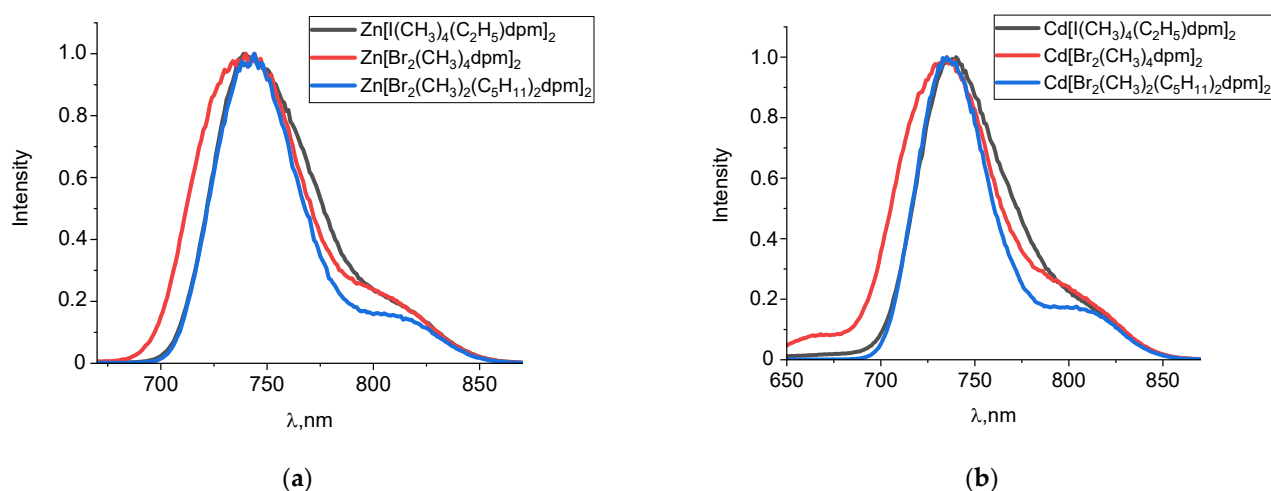


Figure 3. Normalized phosphorescence ($\lambda_{\text{ex}} = 470$ nm) spectra of zinc(II) (a) and cadmium(II) (b) dipyrromethene complexes in ethanol solutions at 77 K. Phosphorescence spectra of zinc(II) and cadmium(II) dipyrromethene complexes in propanol-2 solutions at 77 K are contained in Supplementary Materials (Tables S1 and S2).

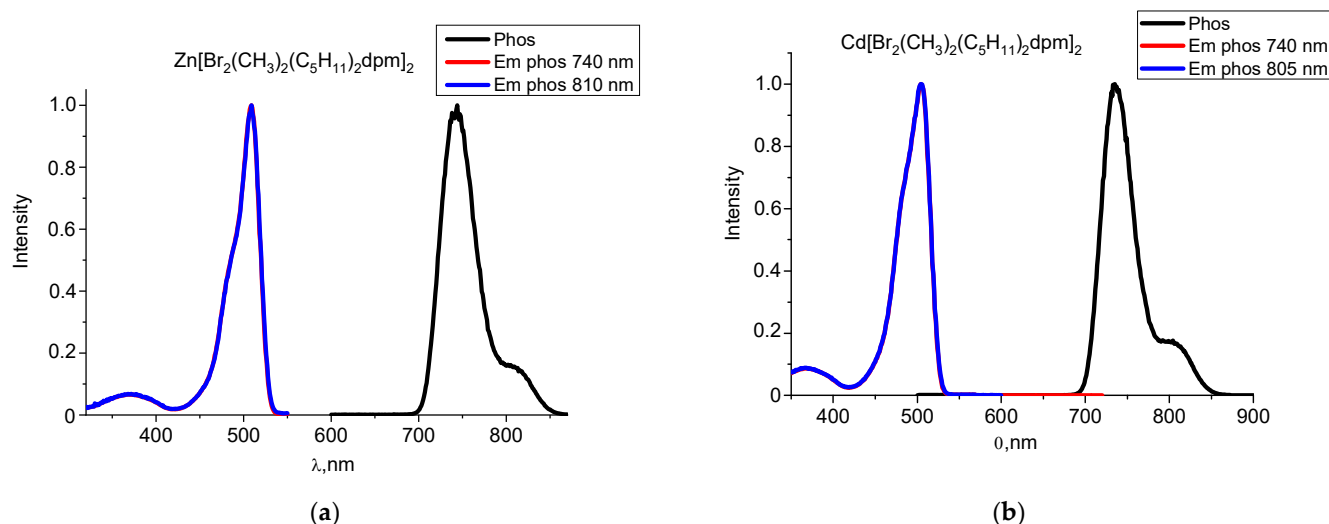


Figure 4. Normalized phosphorescence ($\lambda_{\text{ex}} = 470$ nm) and extinction of phosphorescence spectra of zinc(II) (a) and cadmium(II) (b) dipyrromethene complexes in ethanol solutions at 77 K.

The lifetimes of long-lived emissions were determined for the studied compounds (Figure 5). The complexes with β -dibromo substitution in the ligand possess an increased phosphorescence lifetime. This is the key value our study, as the long lifetime of triplet states indicates a higher probability of the formation of singlet oxygen via intersystem crossing [26–28]. This fact requires further studies on the probability of the formation of singlet oxygen.

The phosphorescence quantum yields for halogen-substituted BODIPY complexes decrease from bromine to iodine complexes according to the heavy atom effect. However, for zinc(II) and cadmium(II) complexes, this regularity is violated. The highest values of phosphorescence quantum yields were obtained for α -dibromo-substituted zinc(II) complexes. Similar values were obtained for cadmium(II) complexes with the same ligand. These results indicate the additional influence of both structural factors (namely the ability of metal complexes to coordinate several chromophore dipyrromethene groups) and a special electronic activity of bromination in the α -position in the ongoing photophysical processes.

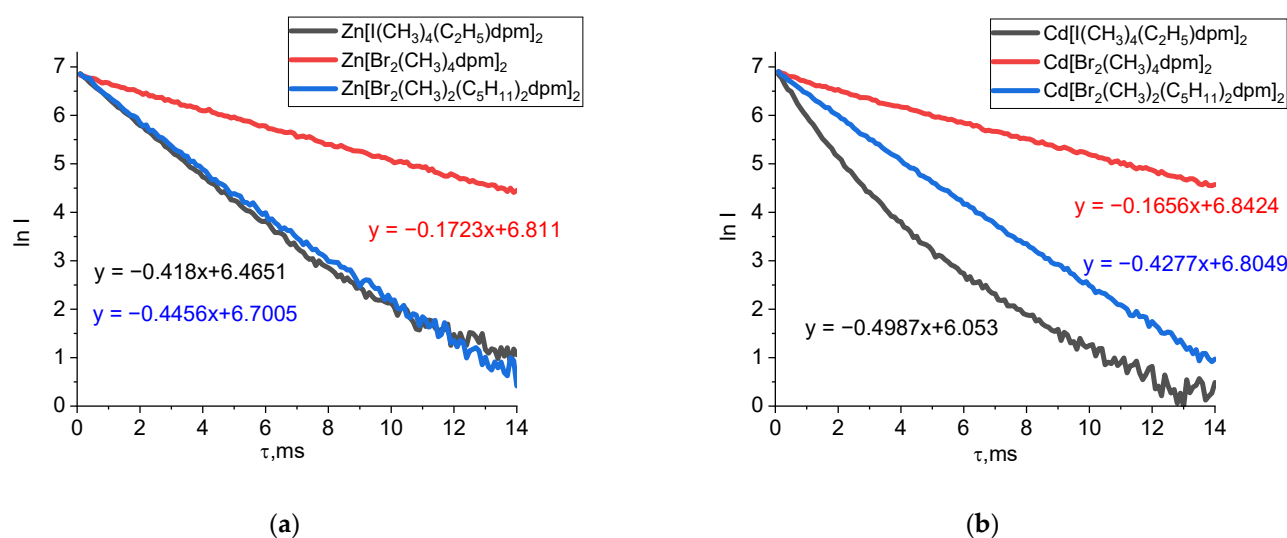


Figure 5. Dependence of the logarithm of phosphorescence attenuation on the lifetime ($\lambda_{\text{ex}} = 470$ nm, $\lambda_{\text{em}} = 740$ nm) of zinc(II) (a) and cadmium(II) (b) dipyrromethene complexes in ethanol solutions at 77 K. Dependence of the logarithm of phosphorescence attenuation on the lifetime of zinc(II) and cadmium(II) dipyrromethene complexes in propanol-2 solutions at 77 K are contained in Supplementary Materials (Tables S1 and S2).

4. Conclusions

The spectral properties of halogen-substituted zinc(II) and cadmium(II) complexes of dipyrromethenes were studied and compared with similar BODIPY complexes. The spectral characteristics of absorption and emission of the studied compounds were studied as the function of the ligand structure, polarity of solvents and temperature (298 K and 77 K). Results show that the photonics of dipyrromethenates is determined not only by the type of complexing metal but also by the substituents introduced into the ligand. Specifically, the nature and location of the substituents in the dipyrromethene core significantly affect the efficiency of the radiative T-S deactivation of the excitation energy. This work provides the basis for further studies on the phosphorescent properties of the dipyrromethene-based compounds, especially on the interactions with molecular oxygen in order to create diverse, active media for optical sensors and photodynamic therapy.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/colorants1030018/s1>, Table S1: Structural formulas, absorption and luminescence spectra of zinc(II) dipyrromethene complexes; Table S2: Structural formulas, absorption and luminescence spectra of cadmium(II) dipyrromethene complexes.

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Conflicts of Interest: The authors declare no conflict of interest.

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