

# The High Sensitive and Selective “Off-On” Fluorescent Zn<sup>2+</sup> Sensor Based on the Bis(2,4,7,8,9-pentamethyldipyrrolylmethene-3-yl)methane

Natalia A. Dudina · Elena V. Antina · Galina B. Guseva · Anatoly I. Vyugin

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**Abstract** A fluorescent chemosensor based on the 3,3'-bis(dipyrin) bearing two chromophoric dipyrin units was synthesized, which showed a strongly enhanced fluorescent intensity in the presence of Zn<sup>2+</sup> ions and a high selectivity toward Zn<sup>2+</sup> ions over a wide range of tested metal ions in organic solvents.

**Keywords** Fluorescence sensor · Zinc ions · Bis(dipyrin) · Selectivity · Sensitivity

## Introduction

Search of the fluorescent chemosensors with high selectivity, sensitivity and low detection limit has been receiving considerable attention because of their fundamental role in medical, environmental and biological applications. Chemosensors based on the rhodamine, bipyridine, porphyrins derivatives and other compounds were created [1–10]. Of particular interest are the chromophoric chemosensors, which as chelate ligands bind Zn<sup>2+</sup> cations to form stable complexes and with a sharp change in the chromophoric and fluorescent properties. This is very important for biological research, that such sensors are non-toxic and have a high absorption in the visible region, including in the phototherapeutic window. The porphyrins display such properties. However, the ligands and coordination compounds of most porphyrins are very weak fluorophores. This limits the use of porphyrin ligands as fluorescent sensors of metal cations.

Recently, the first data on new efficient fluorescent chemosensors Zn(II) on the basis of dipyrin—porphyrin related compounds were obtained. Dipyrins have weak fluorescence, although some of their complexes with metals, including Zn<sup>2+</sup> and others are strong fluorophores [11, 12].

In our previous studies established that, as dipyrins, open-chain tetrapyrrole porphyrin analogs—3,3'-bis(dipyrin)s and their salts with HBr (Scheme 1) exhibit weak fluorescence in solutions of organic solvents, but have a much more intense chromophoric properties ( $\epsilon \sim 10^5 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ) than dipyrins. As a result of easy self-assembly on the number of d-metal cations, ligands 3,3'-bis(dipyrin)s (H<sub>2</sub>L) form stable neutral dinuclear complexes of M<sub>2</sub>L<sub>2</sub> with double helix structure (Scheme 1) [13–16]. Due to the presence of four chromophoric dipyrin systems in a single molecule (Scheme 1), complexes M<sub>2</sub>L<sub>2</sub> are much stronger ( $\epsilon > 10^5 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ) chromophores than H<sub>2</sub>L and M(dpm)<sub>2</sub>.

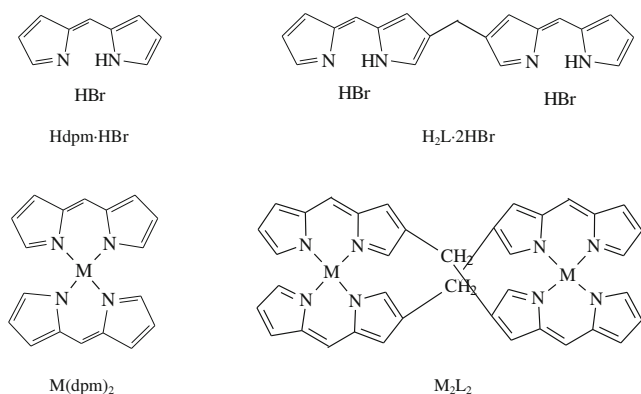
In subsequent studies [17, 18], we found that the synthesized helicates Zn<sub>2</sub>L<sub>2</sub> are strong fluorophores. The fluorescence quantum yield of helicate Zn<sub>2</sub>L<sub>2</sub> (where H<sub>2</sub>L—bis(2,4,7,8,9-pentamethyldipyrrolylmethene-3-yl)methane) in solutions of nonpolar solvents (for example, hexane, cyclohexane) reaches 0.91 [17, 18]. This implies that 3,3'-bis(dipyrin)s could be developed as “off-on” fluorescent Zn<sup>2+</sup> sensors.

In this paper we report a fluorescent “off-on” chemosensor based on the bis(2,4,7,8,9-pentamethyldipyrrolylmethene-3-yl)methane for fluorescence analysis of ions Zn<sup>2+</sup>, including, in the presence of other cations d-metals with which the ligands 3,3'-bis(dipyrin)s also form stable complexes.

## Experimental

Bis(2,4,7,8,9-pentamethyldipyrrolylmethene-3-yl)methane dihydrobromide (H<sub>2</sub>L·2HBr) was synthesized by according to the

N. A. Dudina (✉) · E. V. Antina · G. B. Guseva · A. I. Vyugin  
G.A. Krestov Institute of Solution Chemistry of the Russian  
Academy of Sciences, str. Academic, 1, 153045 Ivanovo,  
Russian Federation  
e-mail: nad@isc-ras.ru



**Scheme 1** Structures of dipyrin (Hdpm·HBr), 3,3'-bis(dipyrin) ( $\text{H}_2\text{L}\cdot 2\text{HBr}$ ) and their metal complexes

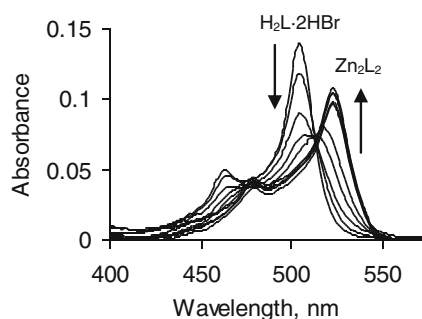
procedures reported in the following paper [19] and characterized by  $^1\text{H}$  NMR, IR, UV–vis spectroscopy and elemental analysis.

Rhodamine 6G in ethanol with fluorescence with quantum yield  $\Phi_f=0.94$  [20] was used as a standard for the determination of fluorescence quantum yields of  $\text{H}_2\text{L}\cdot 2\text{HBr}$ .

UV/Vis and fluorescence spectra in the visible (500–700 nm) range were recorded with a SM2203 SOLAR spectrofluorimeter.

The analysis of  $\text{H}_2\text{L}\cdot 2\text{HBr}$  activity as fluorescent chemosensor towards cations  $\text{Zn}^{2+}$  and the influence of other cations ( $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ) was carried out in solutions of organic solvents and their binary mixture (chloroform, propanol-1 and chloroform/propanol-1) in accordance with the data of the fluorescence spectra. The spectrophotometric titration was performed using the method of molar ratios. The molar series of solutions with constant concentration of ligand and varying the concentration of the zinc salt ( $[\text{Zn}(\text{AcO})_2]/[\text{H}_2\text{L}\cdot 2\text{HBr}]=0$  to 60) were prepared by adding of solution of Zn(II) acetate to the solution of  $\text{H}_2\text{L}\cdot 2\text{HBr}$  ( $5.0\times 10^{-7}$  M) in organic solvents.

Registration of the fluorescence spectra before and after addition of a metal salt or mixture of salts of several metals was performed.



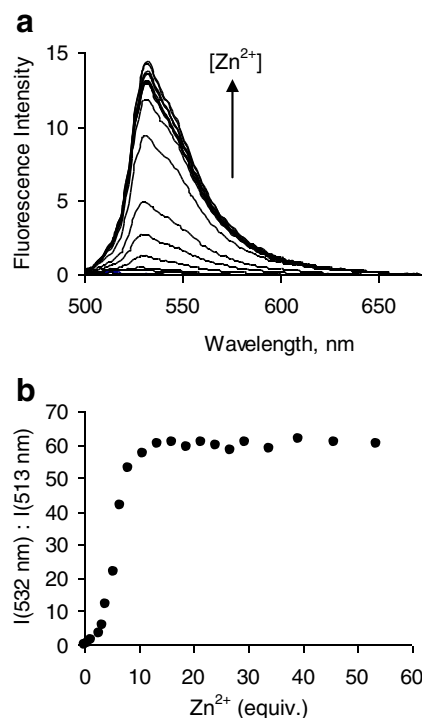
**Fig 1** Absorption spectra for  $\text{H}_2\text{L}\cdot 2\text{HBr}$  ( $5.0\times 10^{-7}$  M, const) in chloroform and in the presence of increasing concentration of  $\text{Zn}(\text{AcO})_2$ ,  $[\text{Zn}(\text{AcO})_2]/[\text{H}_2\text{L}\cdot 2\text{HBr}]=0$ –55

Solvents used were selected according to data on the solubility and fluorescence quantum yields of reagents and formed chelates. Chloroform (Chemically pure grade) was additionally purified by the standard methods [21]. Propanol-1 (UV-IR-HPLC-HPLC preparative, PAI) used without further purification.

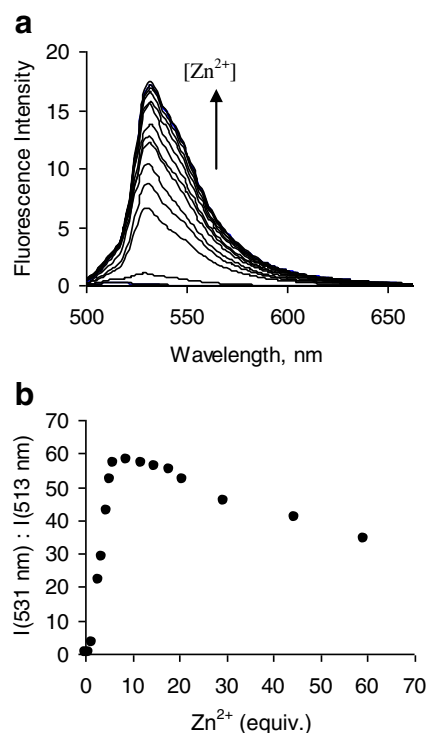
## Results and Discussion

During the spectrophotometric titration of the solution  $\text{H}_2\text{L}\cdot 2\text{HBr}$  ( $5.0\times 10^{-7}$  M) in chloroform by solution of  $\text{Zn}(\text{AcO})_2$  in the same solvent, the optical density of the ligand absorption band ( $\lambda_{\text{max}}=504$  nm) decreases and the characteristic absorption band of the complex  $\text{Zn}_2\text{L}_2$  with  $\lambda_{\text{max}}=523$  nm appears and grows. This process can be observed by the naked-eye: color of the solution changes from yellow-orange to crimson-red (Fig. 1).

Ligand  $\text{H}_2\text{L}$  and salt  $\text{H}_2\text{L}\cdot 2\text{HBr}$  in the different organic solvents (chloroform, DMF, benzene, etc.) exhibit very weak fluorescence with quantum yield  $\Phi_f=0.001$  and the maximum of the emission band in the range 513–517 nm. However, adding to a solution of  $\text{H}_2\text{L}\cdot 2\text{HBr}$  in chloroform of the solution of  $\text{Zn}(\text{AcO})_2$  in chloroform in the range of molar ratios  $[\text{Zn}^{2+}]/[\text{H}_2\text{L}\cdot 2\text{HBr}]=0$ –10 increases the intensity of fluorescence in  $\sim 60$  times with red-shift of the emission



**Fig 2** Fluorescence emission spectra of  $\text{H}_2\text{L}\cdot 2\text{HBr}$  ( $5.0\times 10^{-7}$  M, const) in chloroform in the presence of increasing concentration of  $\text{Zn}(\text{AcO})_2$  in chloroform;  $\lambda_{\text{ex}}=495$  nm;  $[\text{Zn}(\text{AcO})_2]/[\text{H}_2\text{L}\cdot 2\text{HBr}]=0$ –55 (a) and plot of fluorescence titration (b)



**Fig 3** Fluorescence emission spectra of  $\text{H}_2\text{L}\cdot 2\text{HBr}$  ( $5.0 \times 10^{-7}$  M, const) in chloroform in the presence of increasing concentration of  $\text{Zn}(\text{AcO})_2$  in propanol-1;  $\lambda_{\text{ex}}=495$  nm;  $[\text{Zn}(\text{AcO})_2]/[\text{H}_2\text{L}\cdot 2\text{HBr}]=0-60$  (a) and plot of fluorescence titration (b)

maximum to the 532 nm (excitation wavelength: 495 nm) (Fig. 2).

At 10-fold molar excess of  $\text{Zn}(\text{AcO})_2$  fluorescence reaches its maximum value, and a further increase of  $\text{Zn}^{2+}$  in the system does not affect the fluorescence behaviour. The fluorescence enhancement can be ascribed to the CHEF effect induced by chelation of  $\text{Zn}^{2+}$ .

During the titration solution  $\text{H}_2\text{L}\cdot 2\text{HBr}$  in chloroform by solution of  $\text{Zn}(\text{AcO})_2$  in propanol-1 (Fig. 3) in the range of

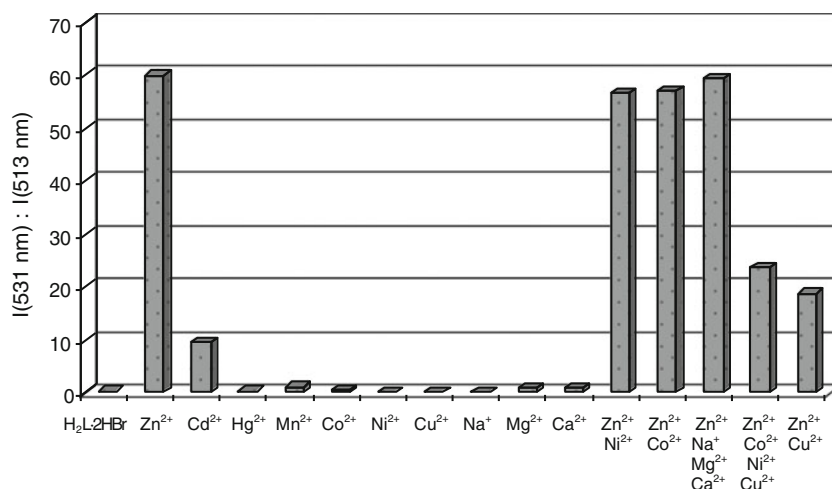
molar ratios  $[\text{Zn}^{2+}]/[\text{H}_2\text{L}\cdot 2\text{HBr}]=0-10$  fluorescence intensity also increases by 60 times with a red shift of the emission band of 531 nm. In the range  $[\text{Zn}^{2+}]/[\text{H}_2\text{L}\cdot 2\text{HBr}]$  of 10 to 20 fluorescence intensity varies only slightly, while the molar ratios of  $[\text{Zn}^{2+}]/[\text{H}_2\text{L}\cdot 2\text{HBr}]>20$  fluorescence intensity decreases by about 30 % (Fig. 3).

Decrease of fluorescence due to a significant increase of the alcohol content, in which the fluorescence quantum yield of the complex  $\text{Zn}_2\text{L}_2$  lower ( $\Phi_f=0.01$ ) than in chloroform ( $\Phi_f=0.025$ ) [17, 18]. As shown earlier [17, 18], this effect is due to specific interactions of oxygen and hydrogen atoms OH-groups of the alcohol with the metal atoms and nitrogen of helicate, which increases the probability of nonradiative processes.

It is known [22] that the ions of alkali and alkaline earth metals do not form stable complexes with 3,3'-bis(dipyrrin). As well as  $\text{Zn}^{2+}$ , only  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$  cations form with  $\text{H}_2\text{L}$  the stable binuclear homoligand double-stranded helicates  $\text{M}_2\text{L}_2$  [23–25]. The compounds  $\text{Co}_2\text{L}_2$ ,  $\text{Ni}_2\text{L}_2$ ,  $\text{Cu}_2\text{L}_2$  are not fluorophores, helicates  $\text{Cd}_2\text{L}_2$  and  $\text{Hg}_2\text{L}_2$  – weak fluorophores with fluorescence quantum yield in chloroform from 0 to 0.27.

Therefore, we investigated the selectivity and sensitivity of fluorescent  $\text{Zn}^{2+}$  sensor based on 3,3'-bis(dipyrrin) in the presence of these metal cations and mixtures thereof in a binary solvent chloroform/propanol-1 (24:1). We determined the fluorescence intensities of  $\text{H}_2\text{L}\cdot 2\text{HBr}$  ( $5.0 \times 10^{-7}$  M) in the presence of various metal ions and compared the results with that observed for free  $\text{H}_2\text{L}\cdot 2\text{HBr}$  (Fig. 4). Upon addition of the same amount (tenfold molar excess) of the various metal ions, respectively, only  $\text{Zn}^{2+}$  enhanced ( $I/I^0 \sim 60$ ) the emission of sensor. The addition of  $\text{Cd}^{2+}$  gave appreciable changes ( $I/I^0 \sim 10$ ) but in no case approached that observed with  $\text{Zn}^{2+}$ . As can be seen from Fig. 4, the addition to a solution of  $\text{H}_2\text{L}\cdot 2\text{HBr}$  in chloroform a tenfold molar excess individual ions  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Hg}^{2+}$ ,

**Fig 4** Fluorescence intensity of  $\text{H}_2\text{L}\cdot 2\text{HBr}$  ( $5.0 \times 10^{-7}$  M, const) at 531 nm ( $\lambda_{\text{ex}}=495$  nm) in chloroform/propanol-1 (24:1) upon the addition of 10.0 equiv. metal ions and their mixtures;  $\lambda_{\text{ex}}=495$  nm,  $\lambda_{\text{em}}=531$  nm



$\text{Na}^+$ ,  $\text{Mg}^{2+}$  or  $\text{Ca}^{2+}$  in propanol-1 ( $[\text{Mn}^{2+}] = [\text{Co}^{2+}] = [\text{Ni}^{2+}] = [\text{Hg}^{2+}] = [\text{Na}^+] = [\text{Mg}^{2+}] = [\text{Ca}^{2+}] = 5.0 \times 10^{-6}$  M) no effect on the weak fluorescence of the ligand. Among examined transition metal cations,  $\text{Cu}^{2+}$  quench the emission, owing to an electron or energy transfer between the metal cation and fluorophore known as the fluorescence quenching mechanism.

Moreover, a comparison of fluorescence intensities of  $\text{H}_2\text{L} \cdot 2\text{HBr}$  in the presence of  $\text{Zn}^{2+}$ -containing ion mixtures was also useful to reveal the influence of coexisting ions in the chloroform/propanol-1 environment on the  $\text{Zn}^{2+}$  sensing ability of  $\text{H}_2\text{L} \cdot 2\text{HBr}$ . Consequently, compound  $\text{H}_2\text{L} \cdot 2\text{HBr}$  ( $5.0 \times 10^{-7}$  M) was treated with 10 equiv.  $\text{Zn}^{2+}$  in the presence of different background metal ions (10 equiv.). The presence in solution a cations mixture of  $\text{Zn}^{2+}/\text{Co}^{2+}$  or  $\text{Zn}^{2+}/\text{Ni}^{2+}$  or  $\text{Zn}^{2+}/\text{Na}^+/\text{Mg}^{2+}/\text{Ca}^{2+}$  does not affect the fluorescence intensity and efficiency of the analysis of zinc ions: fluorescence response is reduced by less than 5 % in comparison with the solution containing only zinc ions. In the presence of  $\text{Cu}^{2+}$  ions the intensity of fluorescence of the solution  $\text{H}_2\text{L} \cdot 2\text{HBr} - \text{Zn}(\text{AcO})_2$  decreases by no more than 3 times. A similar effect is observed in solution in the presence of all four cations  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$ . The fluorescence of the complex resulting from the reaction of  $\text{Zn}^{2+}$  and compound  $\text{H}_2\text{L} \cdot 2\text{HBr}$  was not influenced by the alkali and alkaline earth metal ions.

The results show that the presence of  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Hg}^{2+}$  ions practically do not interfere with the fluorescence determination of  $\text{Zn}^{2+}$ , which indicating a high selectivity of the chemosensor towards  $\text{Zn}^{2+}$  ions. Sensitivity of spectrofluorimetric analysis of  $\text{Zn}^{2+}$ , estimated from a linear dependence of fluorescence intensity on the concentration of the complex  $\text{Zn}_2\text{L}_2$ , resulting in a wide range of concentrations in the studied media reaches  $10^{-9}$  M.

In summary, we have described a fluorescent sensor based on 3,3'-bis(dipyrrin) for the naked-eye and quantitative detection of  $\text{Zn}^{2+}$  cations in chloroform and mixtures of chloroform/propanol-1. Bis(2,4,7,8,9-pentamethyldipyrrolylmethene-3-yl)methane dihydrobromide is weakly fluorescent. As a result, the complexation of bis(2,4,7,8,9-pentamethyldipyrrolylmethene-3-yl)methane dihydrobromide with  $\text{Zn}^{2+}$  ions led to the formation complex  $[\text{Zn}_2\text{L}_2]$  that is accompanied by fluorescence change. Available fluorescent chemosensor showed a remarkable a high selectivity toward  $\text{Zn}^{2+}$  ion over a wide range of metal ions in mixtures of chloroform/propanol-1. The presence of background metal ions ( $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Hg}^{2+}$ ) showed small or no interference with the detection of  $\text{Zn}^{2+}$ , indicating that compound bis(2,4,7,8,9-pentamethyldipyrrolylmethene-3-yl)methane dihydrobromide could be used as an efficient highly sensitive, selective “off-on” fluorescent chemosensor for the determination trace amounts of  $\text{Zn}^{2+}$  cations.

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