

Influence of Solvation and Structural Contributions on Fluorescence of Dipyrriene Dyes

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Abstract The results of quantum-chemical and spectral researches of zinc^(II) complexes with alkylated dipyrriene and 3, 3'-, 2,3'- and 2,2'-bis(dipyrriene)s in non-polar and polar solvents and their binary mixtures are presented. It was investigated the efficiency of the fluorescence quenching of fluorophores depending on of the solvation and structural contributions. Found that 3,3'-bis(dipyrrieno)zinc^(II) demonstrates the highest sensitivity of the fluorescence to the presence of the electron-donor component compared with the studied complexes. The obtained results allow to offer dipyrriene and bis(dipyrriene) zinc^(II) complexes as new, highly sensitive and selective fluorescent sensors of the N- and O-containing toxicants.

Keywords Dipyrriene dyes · Zinc^(II) complexes · Frontier molecular orbitals · Spectral-luminescent properties · Fluorescence quenching · Detection limit

Highlights • Spectral properties of dipyrriene and bis(dipyrriene)s Zn^(II) complexes in organic solvents were investigated.

- HOMO→LUMO transition makes the main contribution to manifestation of the fluorescence of the dipyrriene dyes.
- The fluorescence quenching of the dipyrriene dyes depends on the structural factors and of the medium polarity.
- Specific solvation strongly affects the fluorescence properties of the dipyrriene dyes.
- Dipyrriene dyes are recommended as the fluorescent sensors of the medium polarity.

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Introduction

Currently an urgent task is to create of a highly sensitive and reliable express methods for the detection and of ecological monitoring in vitro and in vivo ultra quantities of the toxic N- and O-containing molecules. Therefore increasing attention is paid to the development and testing of new fluorescent sensors and hybrid materials based on them. Among the most promising of platform for creating of fluorescent probes are dipyrriene dyes namely the zinc^(II) dipyrrienes and bis(dipyrriene)s. These luminophors have the individual absorption and emissions spectra, high fluorescence sensitivity to the properties of the medium [1–3].

Analysis of published data shows, that in inert solvents (cyclohexane, hexane, benzene, etc.) the fluorescence quantum yield (φ) of the complexes on one or two orders higher, than in the polar medium [1, 4]. In electron-donor solvents (DMF, Py) the fluorescence intensity of the dyes is significantly reduced (about~500 times), and becomes almost zero. The solvent polarity as a rule usually due to the presence in its molecule groups with hetero atoms (O, N, S et al.) hence such solvents to a greater or lesser extent, exhibit properties of electron-donor ligands which capable to be coordinated by ions of unsaturated metals [5–7]. The first results of the study of supramolecular structures of the acyclic oligopyrroles are presented in the review articles H. Maeda [8, 9] and Yongshu Xie with colleagues [10]. The authors examine only supramolecular structures and ensembles formed by the interaction of acyclic oligopyrrole ligands with cations or anions have been considered. The supramolecular structures formed by metal complexes with neutral molecules are not considered in these reviews and the data on them is very limited. The data of X-ray analyses and TGA for the crystal solvates of metalloporphyrinates [11, 12] and dipyrrienes [Zn(dpm)₂] and [Cu(dpm)₂] have

been published previously [13, 14]. It was found that metalloporphyrinates form π - π -supramolecular complexes with non-polar aromatic molecules (benzene, toluene, caffeine, etc.) or the systems with electron-donating molecules (Py, DMF) [11]. These supramolecular complexes are stable in the solid phase and in solutions [11, 12] According to [13] dipyrinates and *bis*(dipyrinate)s of *d*-metals form with the electron-donor ligands the stable solvates of the composition $[M(\text{dpm})_2X_2]$ and $[Zn_2L_2X_n]$ respectively, when X – DMF or Py. In this supramolecular systems the interparticle interactions have a donor-acceptor nature. The process of the additional coordination of the molecule X with their inclusion in the inner coordination sphere of complexes $[Zn(\text{dpm})_2X_2]$, $[Zn_2L_2X_n]$ facilitated at excited of a molecule of a luminophor by the quantum of light, when the electron density changes on the nitrogen and metal atoms. It has been hypothesized, that the additional coordination is the main cause of the sharp fluorescence quenching of the zinc dipyrinates ($[Zn(\text{dpm})_2]$) and *bis*(dipyrinate)s $[Zn_2L_2]$ in the electron-donating solvents (Py, DMSO, DMF) [15]. Using the experimental and theoretical justification of the phenomenon causes [1–4], this property of ($[Zn(\text{dpm})_2]$) and $[Zn_2L_2]$ complexes can be used for developing of new fluorescent sensors of the electron-donor N- and O-containing molecules.

In order to substantiate the practical application of the dipyrine zinc^(II) complexes as a new fluorescent sensors of the electron-donor molecules, we carried out quantum-chemical and experimental studies of the spectral-luminescent properties of these dyes in the non-polar, polar solvents and their binary mixtures. We have proposed methods for identifying of the type of the N- and O-containing analytes and the limit of their detection. The results of the investigations are presented in this article.

For the purpose the detailed understanding of the main regularities of the influence of the structural factors and the macromolecular environment on fluorescence of the complexes as luminophores selected: Zn^(II) dipyrinate with hexamethylsubstituted 2,2'-dipyrine (1) and Zn^(II)*bis*(dipyrinate)s (2–4) with dekamethylsubstituted *bis*(dipyrin)s, differing 2,2'-, 2,3'- and 3,3'-positions attachment of the central methylene spacer to the proximal nuclei pyrrole ligands (Fig. 1).

Experimental

Investigated Compounds

The synthesis, X-ray and elemental analysis, NMR ¹H, UV- and IR-spectroscopy data for complexes 1–4 and respective ligands were described in previous works [2, 16–20]. Solid samples of investigated compounds were

trituated and dried to constant weight in vacuum before the experiments.

Solvents

Organic solvents (cyclohexane (C₆H₁₂), acetone, *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), triethylamine (TEA)) all of analytical grade were further purified according to standard procedures described in [21]. The residual water content (less than 0.02 wt.%) was monitored by amperometric Fischer titration [22].

Apparatus

UV/Vis and fluorescence spectra in the visible (300–700 nm) range were recorded with a SM2203 SOLAR spectrofluorimeter. The accuracy of the measurements in the registered wavelength interval (500–700 nm, $\lambda_{\text{ex}}=470$ ($[Zn(\text{dpm})_2]$) and $\lambda_{\text{ex}}=495$ nm ($[Zn_2L_2]$)) was ± 0.02 nm. Solutions with a concentration less than 1×10^{-6} mol/l were used to determine the characteristics of the fluorescence. Rhodamine 6G in ethanol with fluorescence with quantum yield $\varphi=0.94$ [23] was used as a standard for the determination of fluorescence quantum yields of $[Zn(\text{dpm})_2]$ and $[Zn_2L_2]$.

The equation for calculating the fluorescence quantum yield:

$$\varphi_x = \varphi_{st} \left(\frac{S_x}{S_{st}} \right) \cdot \left(\frac{I_{st}}{I_x} \right) \cdot \left(\frac{n_x}{n_{st}} \right)^2$$

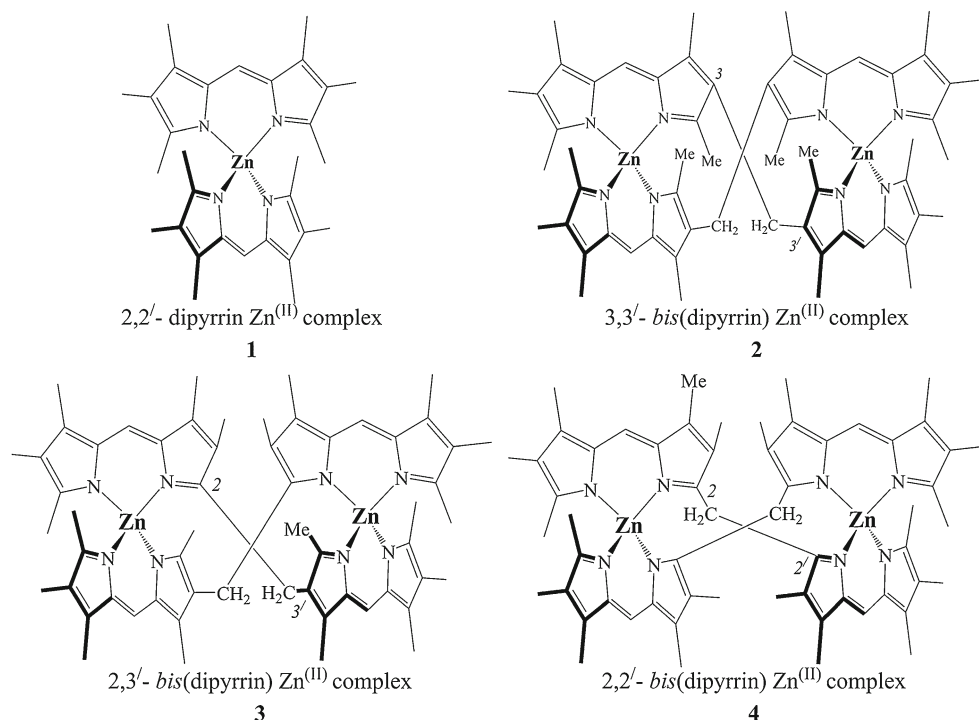
where φ_x - fluorescence quantum yield of substance, φ_{st} - fluorescence quantum yield of the standard (Rhodamine 6G), S - integrated fluorescence intensity (area under spectrum), I - fluorescence intensity, n - refractive index.

Calculations

All the computations were performed using the PC GAMESS v.12 program package [24]. The ground state (S_0) geometry of 1–4 was optimized using DFT method [25], which has been shown previously [26–29] well describes the geometric and electronic properties of molecules acyclic oligopirroles and their coordination compounds. As of the functional was chosen B3LYP (the B3LYP combines Becke's three parameter exchange functional (B3) [30] with the nonlocal correlation functional by Lee, Yang and Parr (LYP) [31]). The basis set used in both, DFT and TD-DFT methods for all the atoms was cc-pVTZ [32].

Calculations of the energy of electronic transitions from the ground to the immediate electronic states, the oscillator strengths and the corresponding wavelengths values held in the TD-DFT, B3LYP/ cc-pVTZ approach for the optimized structures of the Zn^(II)*bis*(dipyrinate)s.

Fig. 1 Zn^(II) complexes with hexamethylsubstituted 2,2'-dipyrrine and dekamethylsubstituted 3,3'-, 2,3'-, 2,2'-bis(dipyrrin)s



The polarizable continuum model (PCM) using dielectric constants cyclohexane, acetone, DMF, DMSO and triethylamine were used to evaluate solvation effects.

Molecular graphics and analyses were performed with the UCSF Chimera package [33] and ChemCraft 1.8 (<http://www.chemcraftprog.com>).

Results and Discussion

For the purpose of searching factors of management of spectral and luminescent properties of dipyrrole dyes the orbital energy analysis (E_{HOMO} , E_{LUMO}) and the width of the HOMO–LUMO energy gaps ($\Delta E_{\text{HOMO/LUMO}}$) analysis of 1–4 complexes was carried out. The electron density distribution of HOMO and LUMO orbitals for complexes obtained PCM/TD-DFT/B3LYP/cc-pVTZ and shown in Fig. 2 and Table 1. The quantum–chemical calculations showed that HOMO–LUMO transition makes major contribution to the fluorescence of the studied complexes. As might be expected for investigated systems, the next occupied levels are lower in energy (HOMO–1), the next free levels (LUMO+1) are higher in energy. Revealed, that these levels are insignificantly differed compared to the HOMO and LUMO energy values (Table 1). Such small differences between HOMO, HOMO–1 and LUMO, LUMO+1 lead to several possible optical transitions.

Analysis of the molecular orbitals shows that they represent combination of bonding and anti-bonding π -

orbitals. The first excited electronic state (S_1) arises at electron transition with HOMO on quasi-degenerate LUMO orbital. Figure 2 demonstrate the distribution of the electron density of molecular HOMO and LUMO orbitals in the dyes molecules.

As show quantum-chemical calculations, the nature of the ligands influences on the spectral-luminescent properties. Increasing of the oligomerization degree of the chelate ligand (at the transition from a bidentate 2,2'-dipyrrin-ligand, located in the structure of the complex 1 to tetradentate 2,2'-bis(dipyrrin) on the based of 3) reduces both the E_{HOMO} (on 0.10 eV) and the energy gap value (on 0.01 eV) (Fig. 2). The structural isomerism of the zinc bis(dipyrinate)s exerts a greater influence on the energy characteristics. Replacing of 3,3'-bis(dipyrrin) ligand to 2,3'- и 2,2'-analogues there is an increase E_{HOMO} (on 0.10 eV) and reducing ΔE (on 0.06 eV) (Fig. 2). The observed pattern in good agreement with experimentally observed trends of change of the fluorescence quantum yield of the dyes [2, 19, 34], Table 2. So, the value of φ for complex 2 twice as higher than that for 3 and almost in 30 times exceeds the fluorescence quantum yield of the biladiene complex 4. For example, in cyclohexane, for 2, 3 and 4 the values φ are 0.91, 0.39 and 0.036, respectively (Table 2).

To assess the influence of the nature of the solvent on the change of the spectral-luminescent properties of complexes we analyzed the of molecular orbitals HOMO and LUMO for molecules 1–4 by the method

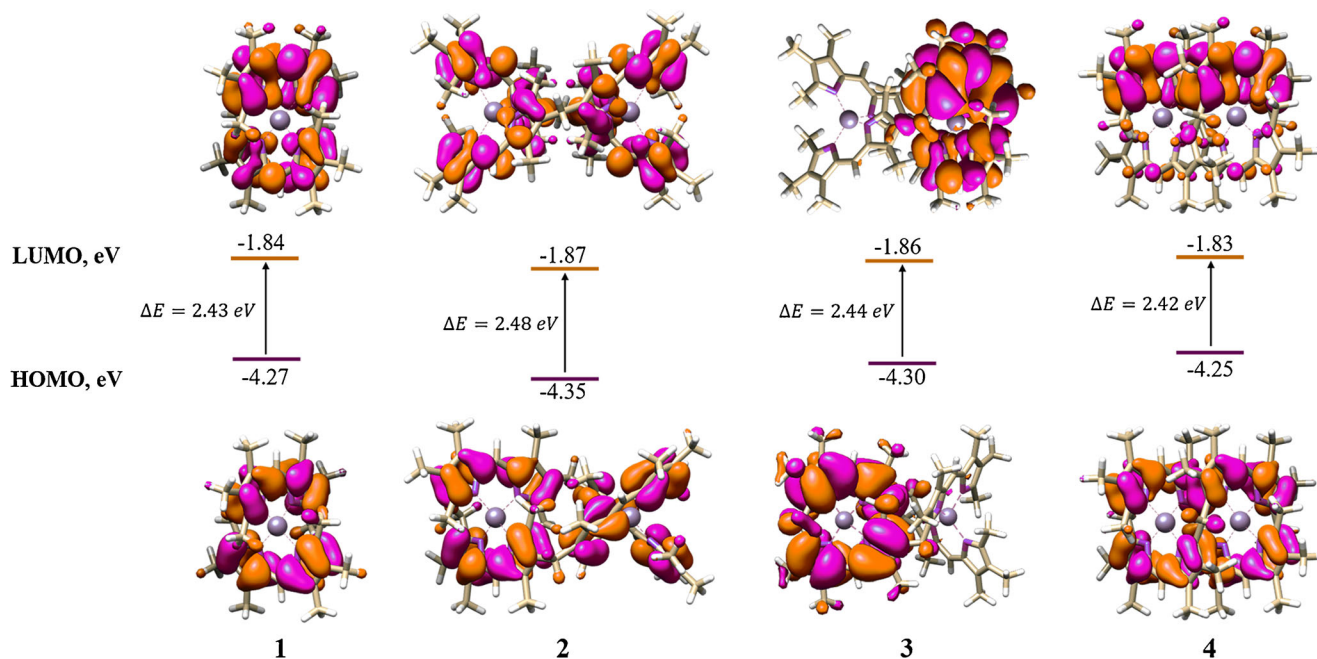


Fig. 2 The distribution of boundary molecular orbitals of 1–4 complexes and the energy gap values ($\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$), (PCM (cyclohexane) / TD-DFT/B3LYP/cc-pVTZ)

of TD-DFT/B3LYP/cc-pVTZ. Influence of the solvent (cyclohexane, acetone, DMF, DMSO and triethylamine) was considered in the model PCM. Calculations have shown that by increasing the electron-donor ability of the solvent, the HOMO→LUMO energy of the gap is reduced (Table 2).

The effect of reducing of the energy gap is associated with the redistribution of electron density on of dipyrin fragments and coordination centers of the complexes. Spectrofluorimetric studies confirmed the results of quantum-chemical prediction and demonstrated that the complexes indeed exhibit intense fluorescence in non-polar and weakly polar hydrocarbons (cyclohexane, hexane, benzene) [2, 19, 34] and in electron-donor solvents (DMF, DMSO, triethylamine) is observed the sharp (in some cases to zero) quenching of fluorescence (Table 2)

which is caused by specific interactions of the electron-donor solvents with atoms (Zn, N) of the coordination centers dyes [35].

In order to develop ideas about the practical uses of dipyrine Zn^(II) complexes as a new perspective fluorescent sensors to N- and O-containing analytes, we carried out spectrofluorimetric studies of the dependences of a fluorescence quantum yield of complexes from the composition of the binary mixtures on the basis of cyclohexane with additive of electron-donor solvent (X): acetone, DMF, DMSO and triethylamine.

The spectral studies showed, that in binary mixtures «cyclohexane – X» for 1 is observed the blue shift (2 to 3 nm) of the emission band maximum with increasing mole fraction (χ) of the electron-donor component (Fig. 3). The emission band maximum is shifted to the red or the blue area (of 1 to 12 nm)

Table 1 HOMO and LUMO energies (eV), HOMO – LUMO (H→L) transition energies (eV) of 1–4 complexes obtained by PCM (cyclohexane) / TD-DFT/B3LYP/ cc-pVTZ

	1	2	3	4
E_{HOMO}	-4.27	-4.35	-4.30	-4.25
$E_{\text{HOMO}-1}$	-4.34	-4.42	-4.46	-4.45
E_{LUMO}	-1.84	-1.87	-1.86	-1.83
$E_{\text{LUMO}+1}$	-1.81	-1.83	-1.80	-1.80
Transition energies (HOMO→LUMO)	2.43	2.48	2.44	2.42
Transition energies (HOMO→LUMO+1)	2.46	2.52	2.50	2.45
Transition energies (HOMO-1→LUMO)	2.50	2.55	2.60	2.62

Table 2 Fluorescence quantum yield (φ) of 1–4 complexes and the energy gap values of HOMO–LUMO transition (ΔE , eV), considering the solvent (PCM/TD-DFT/B3LYP/Def2-SVP)

Solvent	1	2	3	4
	$\varphi(\Delta E)$			
Cyclohexane	0.138 (2.43)	0.910 (2.48)	0.369 (2.44)	0.036 (2.42)
Acetone	0.006 (2.35)	0.143 (2.40)	0.005 (2.35)	0.001 (2.37)
DMF	0.005 (2.34)	0.002 (2.37)	0.001 (2.32)	0 (2.30)
DMSO	0.004 (2.28)	0.001 (2.34)	0.001 (2.29)	0.001 (2.27)
TEA	0.058 (2.19)	0.001 (2.30)	0.060 (2.24)	0.004 (2.19)

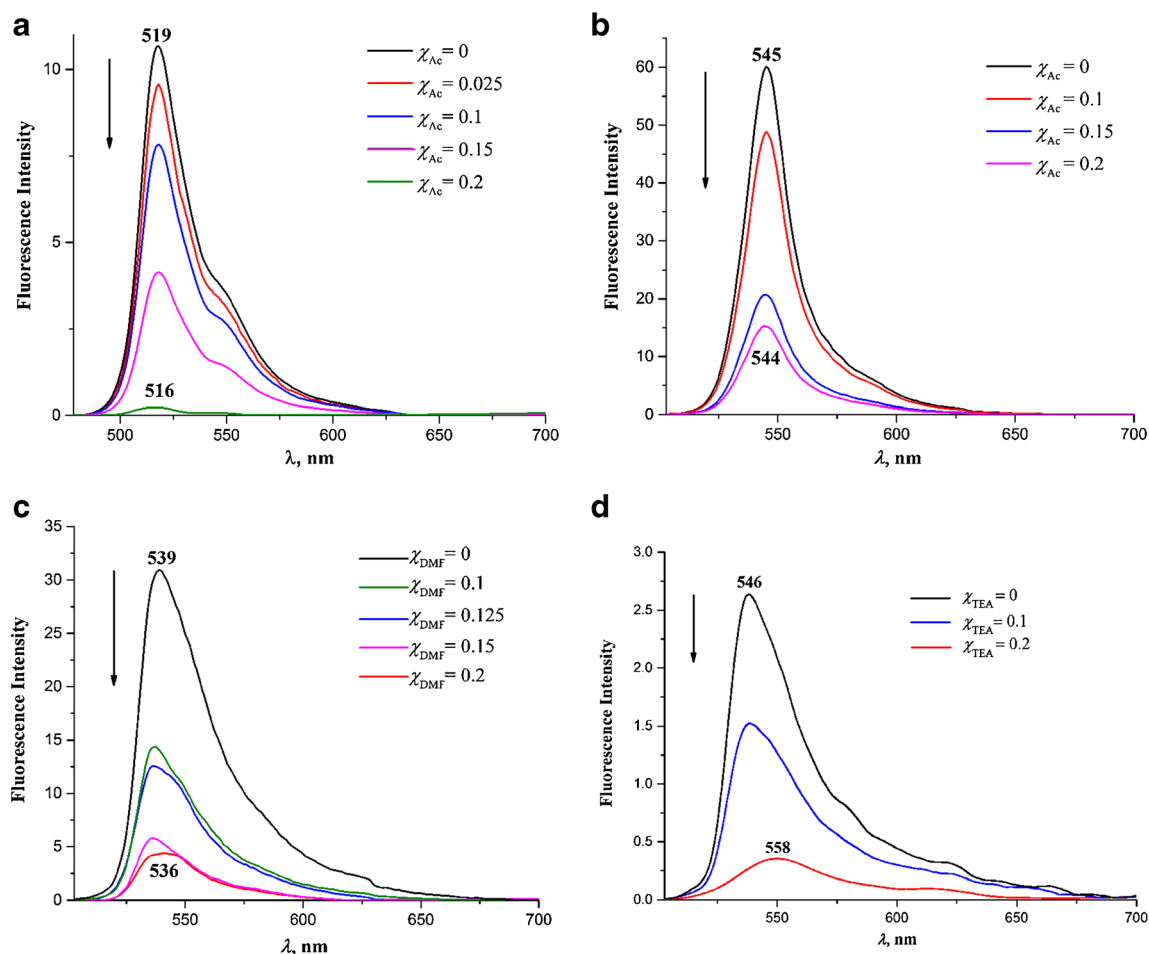


Fig. 3 Fluorescence spectra of the compounds 1–4 ($c \approx 1.0 \times 10^{-7}$ mol/l) in solutions of cyclohexane with different mole fraction of the electron-donor component: 1, DMSO (a), 2, acetone (b), 3, DMF (c), 4, TEA (d)

for $Zn^{(II)}$ bis(dipyrrinate)s with the addition of an electron donor component (Fig. 3).

The efficiency of fluorescence quenching of dipyrriene complexes depended on of the structural factors forming their dipyrriene and bis(dipyrriene) ligands and an electron-donating ability of the solvent (X). Helicat 2 demonstrates the greatest sensitivity of a fluorescence to presence X. For example, in mixtures on the basis of cyclohexane with the mole fraction of the triethylamine ($\chi_{TEA}=0.1$) fluorescence quantum yield 2 decreases by 10 times (Fig. 4b), while fluorescence quantum yield 1, 3 and 4 is reduced only in 2 and 3 times (Fig. 4. a, c, d).

In binary mixtures based on cyclohexane at the same mole fraction of the electron-donor component, for example when $\chi_{(X)}=0.1$ is observed a linear relationship of the fluorescence quantum yield of the dyes from a donor number (Gutman) of the co-solvent (Fig. 5.) In case of 1, 3 and 4 complexes, TEA doesn't correspond to general dependence, owing to less efficient fluorescence quenching. This fact may be explained by different composition of molecular complexes.

It should be noted that spectrofluorimetric research agree satisfactorily with the results of quantum-chemical prediction about changing fluorescence quantum yield of the dipyrriene fluorophores depending on the electron-donating ability of the solvent (Fig. 3, Table. 2).

Dependencies of the fluorescence quenching of the dyes on the concentration of the electron-donor component were described by the Stern-Volmer model using equation [36, 37]:

$$I_0/I = 1 + K_{SV}[X] \quad (1)$$

where I_0 и I are the fluorescence intensities of the fluorophores in the absence of the quencher and in the presence of various concentrations of the quencher, respectively, K_{SV} – quenching Stern-Volmer constant and $[X]$ – the concentration of the quencher.

Deviation up and the concavity in relation to the ordinate axis of the Stern-Volmer equation (Fig. 6) indicate [38] that quenching of fluorophore fluorescence due not only by collisions with quencher (dynamic quenching), but also due to the

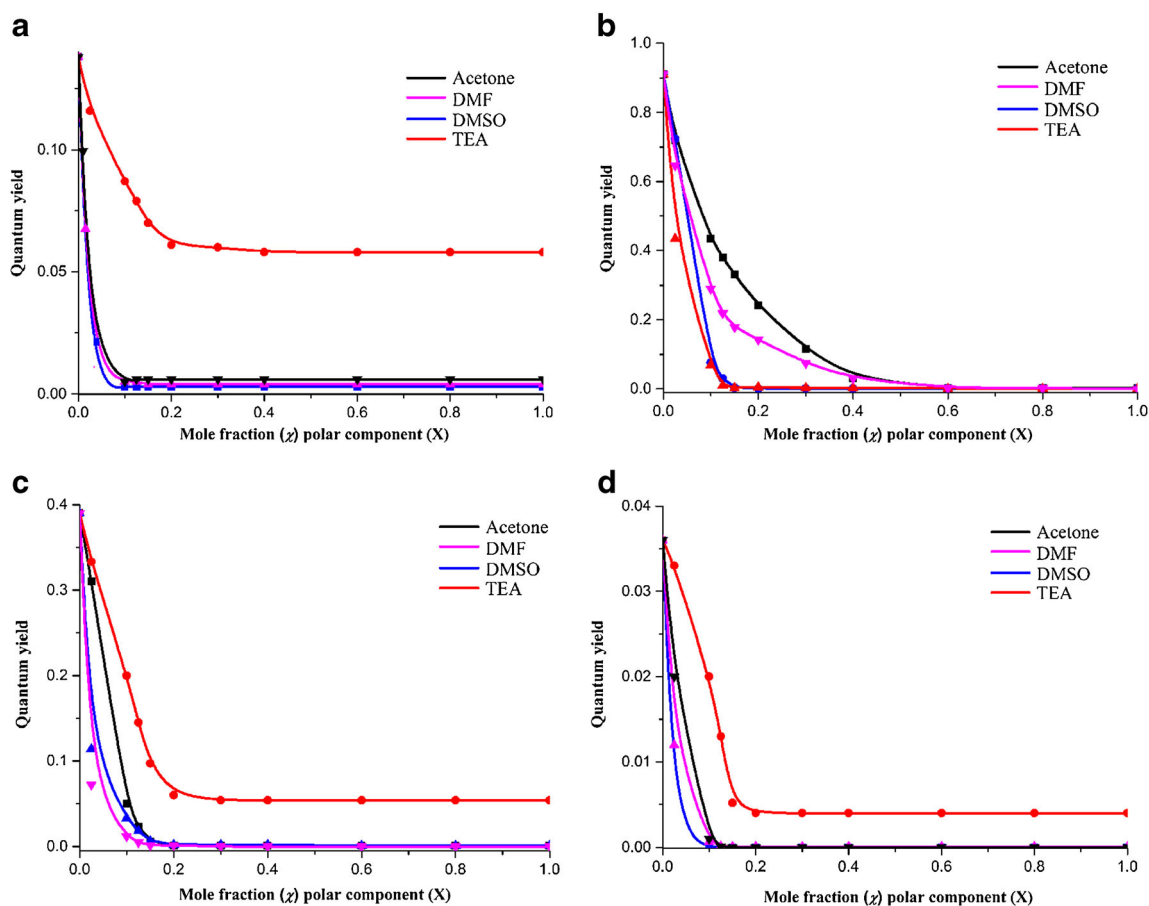


Fig. 4 The dependence of a fluorescence quantum yield (φ) 1 (a) and helicetes 2 (b), 3 (c), 4 (b) the mole fraction of the electron-donor component (X) in binary solvent X – cyclohexane, X – acetone, DMF, DMSO, TEA

formation of non-fluorescent stable complex of the fluorophore with the quencher (static quenching) in the ground state.

For a graphic definition of the dynamic (K_{dyn}) and static (K_{st}) quenching constants the equation (1) transformed to:

$$I_0/I = (1 + K_{\text{dyn}}[X]) (1 + K_{\text{st}}[X]) = 1 + K_{\text{app}}[X] \quad (2)$$

where $K_{\text{app}} = (K_{\text{dyn}} + K_{\text{st}}) + K_{\text{dyn}}n_{\text{st}} [X] = \frac{I_0/I - 1}{[X]}$ is the apparent rate constant of quenching.

The apparent constant was assessed by treating the linear portion according I_0/I from $[X]$ for a range of additives of the electron-donor components from 0 to 2.3 mol/l (Fig. 6).

Analysis of obtained data (Fig. 7) showed that for 2 apparent constants of quenching of a fluorescence increases linearly with increasing electron-donating ability of the solvent in the sequence: acetone \rightarrow DMF \rightarrow DMSO \rightarrow TEA (Fig. 7). For of 1, 3 and 4 complexes a similar pattern of change K_{app} is saved, except for trimethylamine. Moreover, for of 1, 3 and 4 complexes the apparent quenching constants in the presence of TEA is significantly lower, in compared with the values K_{app}

in the presence of the electron-donor DMF and DMSO. Observable effect is due to differences in the composition of the supramolecular complexes $[\text{Zn}(\text{dpm})_2\text{X}_n]$ and $[\text{Zn}_2\text{L}_2\text{X}_n]$, that requires carry out additional researches.

For justification of sensitivity characteristics of the fluorescence of the complexes to the type of quencher, i.e., the selectivity determining of the quencher with use of the considered luminophors, by analogy as described in [39] the approach, we carried out comparative analysis of the indicators of the relative changes fluorescence intensity at any selected wavelengths ($\frac{\Delta I_{\lambda_1}}{\Delta I_{\lambda_2}}$) in the emission spectra of solutions of individual complexes in different solvents. Processing of experimental data showed, that irrespective of a ratio of concentration of a luminophor and the detect analyte X, value $\frac{\Delta I_{\lambda_1}}{\Delta I_{\lambda_2}}$ remains constant for the selected wavelength, for example, at the band maximum in $\lambda_1 = 545$ nm and on its right slope in $\lambda_2 = 575$ nm, as shown in Fig. 8.

In accordance with [39], distinction values $\frac{\Delta I_{\lambda_1}}{\Delta I_{\lambda_2}}$, shown in Table 3, testify to high selectivity of luminophors 1–4 and prospects of their application for determining the type of the electron-donor impurity component in practice.

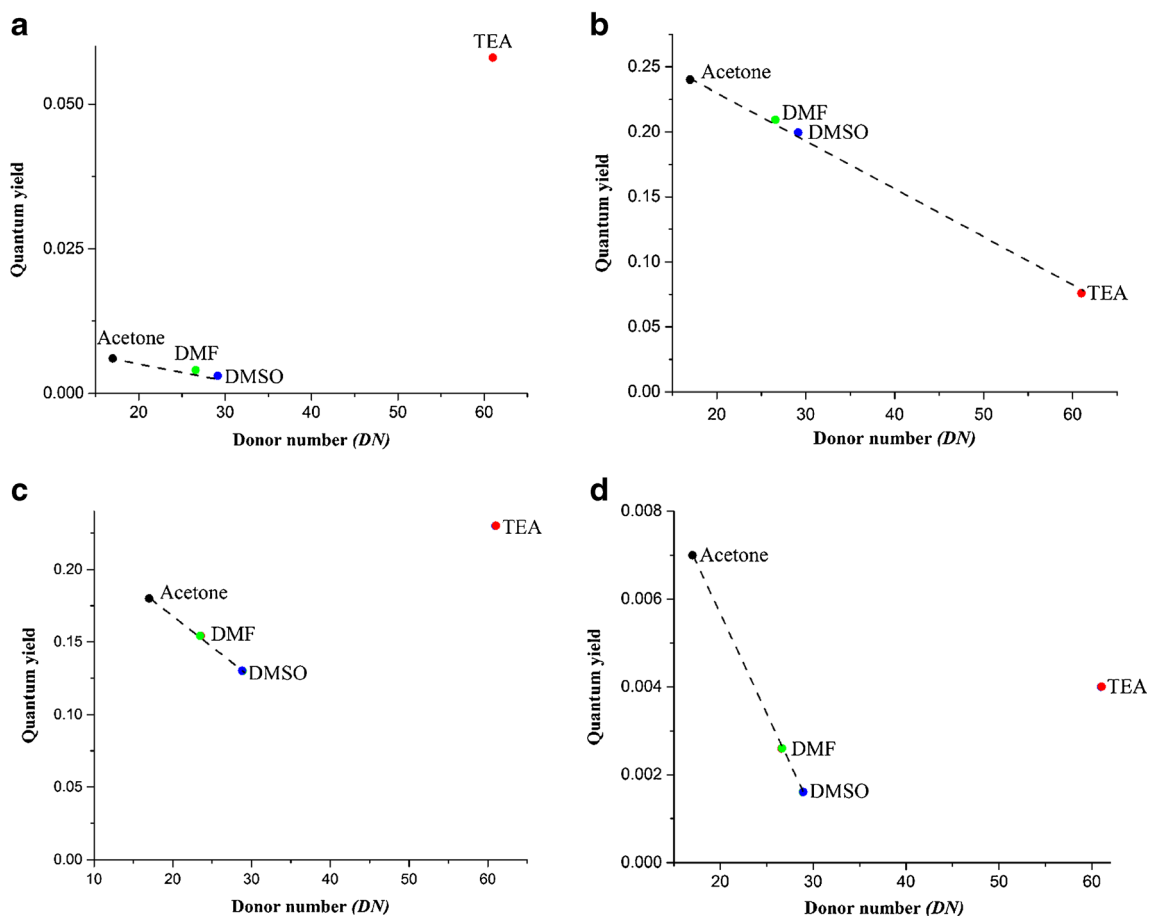
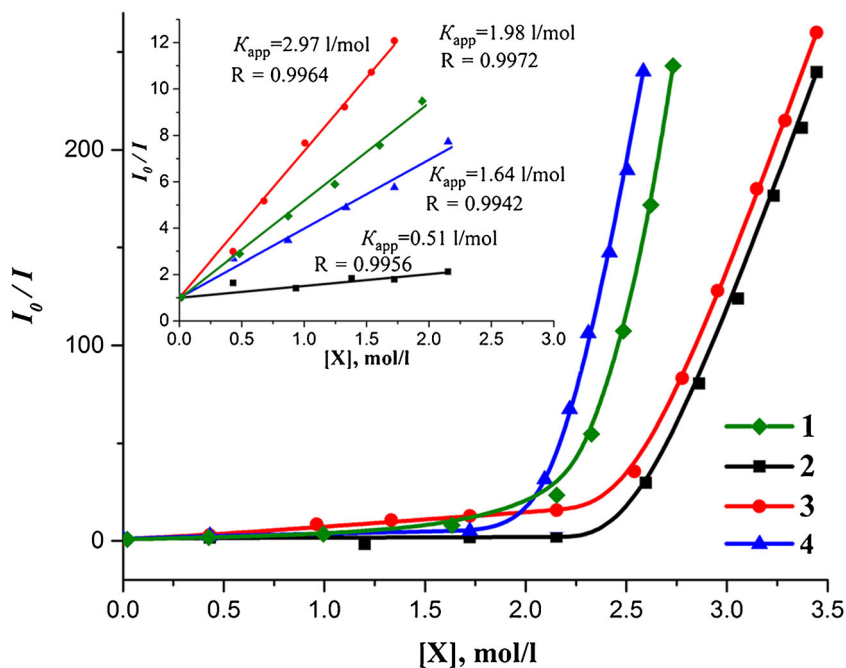


Fig. 5 Dependence of a fluorescence quantum yield of solutions $[Zn(dpm)_2]$ and $[Zn_2L_2]$ in mixes cyclohexane – X with $\chi_{(x)}=0.1$ from a donor number of the solvent by Gutman [7]: 1 (a), 2 (b), 3 (c); 4 (d)

Fig. 6 Dependence of the relative intensity I_0/I for 1–4 solutions ($\sim 1.0 \times 10^{-7}$ mol/l) in cyclohexane on the concentration of DMF; inset: Stern-Folmer's dependences, received by data processing for mixtures with additives DMF to 2.3 mol/l



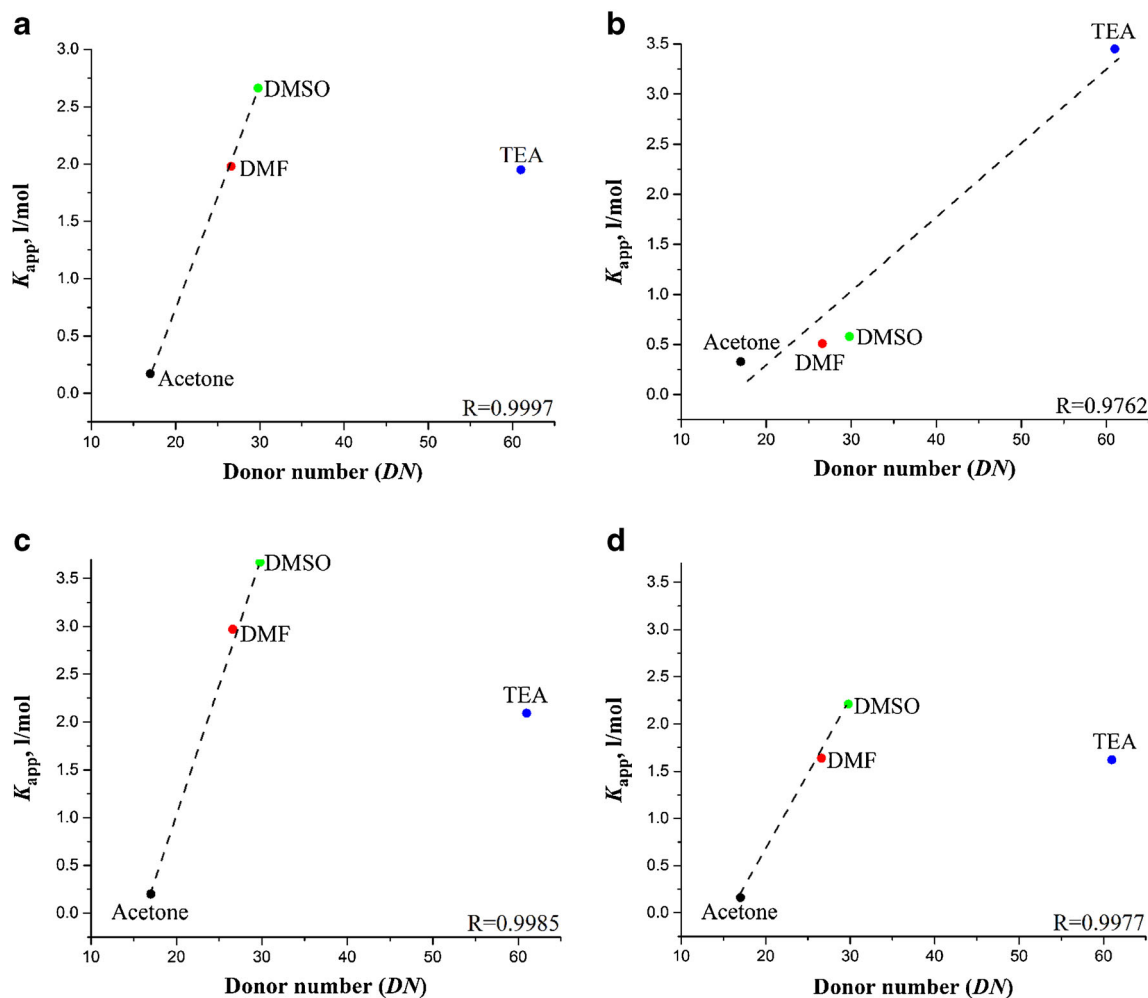


Fig. 7 Dependence of values apparent constants of quenching (K_{app} , l/mol) in mixtures X – cyclohexane from a donor number of the solvent by Gutman [7]: 1 (a), 2 (b), 3 (c), 4 (d)

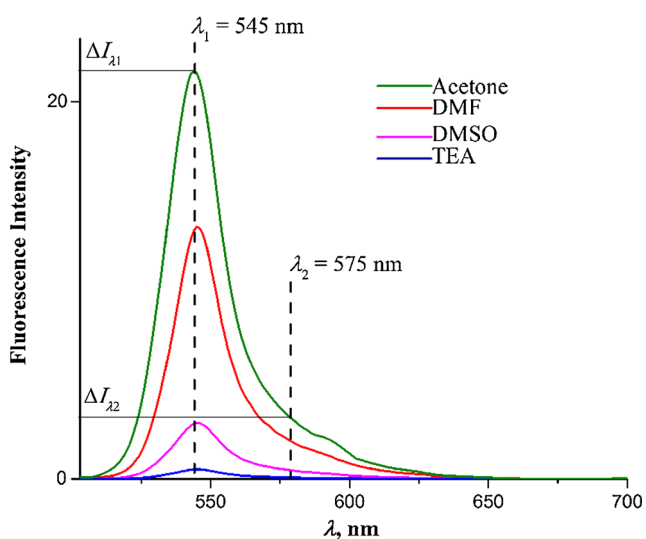


Fig. 8 The fluorescence spectra of 2 solutions (1.0×10^{-7} mol/l, $\lambda^l = 495$ nm) depending on the type of electron-donor component in cyclohexane

In Fig. 9 for 1–4 complexes are presented linear dependences $(I_{max} - I)/(I_{max} - I_{min})$ (where I_{max} , I , I_{min} are fluorescence intensities of $[Zn(dpm)_2]$ and $[Zn_2L_2]$ in cyclohexane, with addition $[X]$ and in the polar medium) from $\log[X]$, which cross points with an abscissa axis allow us to estimate the concentration of detection limit of the N-

Table 3 The change of the fluorescence intensity of $[Zn(dpm)_2]$ and $[Zn_2L_2]$ at two wavelengths ($\frac{\Delta I_{\lambda_{545}}}{\Delta I_{\lambda_{575}}}$) under the action of a electron-donor component (X) in cyclohexane

X	1	2	3	4
	$\frac{\Delta I_{\lambda_{545}}}{\Delta I_{\lambda_{575}}}$			
Acetone	3.537	5.468	2.253	1.982
DMF	3.740	5.826	3.405	2.134
DMSO	4.783	5.913	3.500	2.203
TEA	4.912	6.002	3.714	2.694

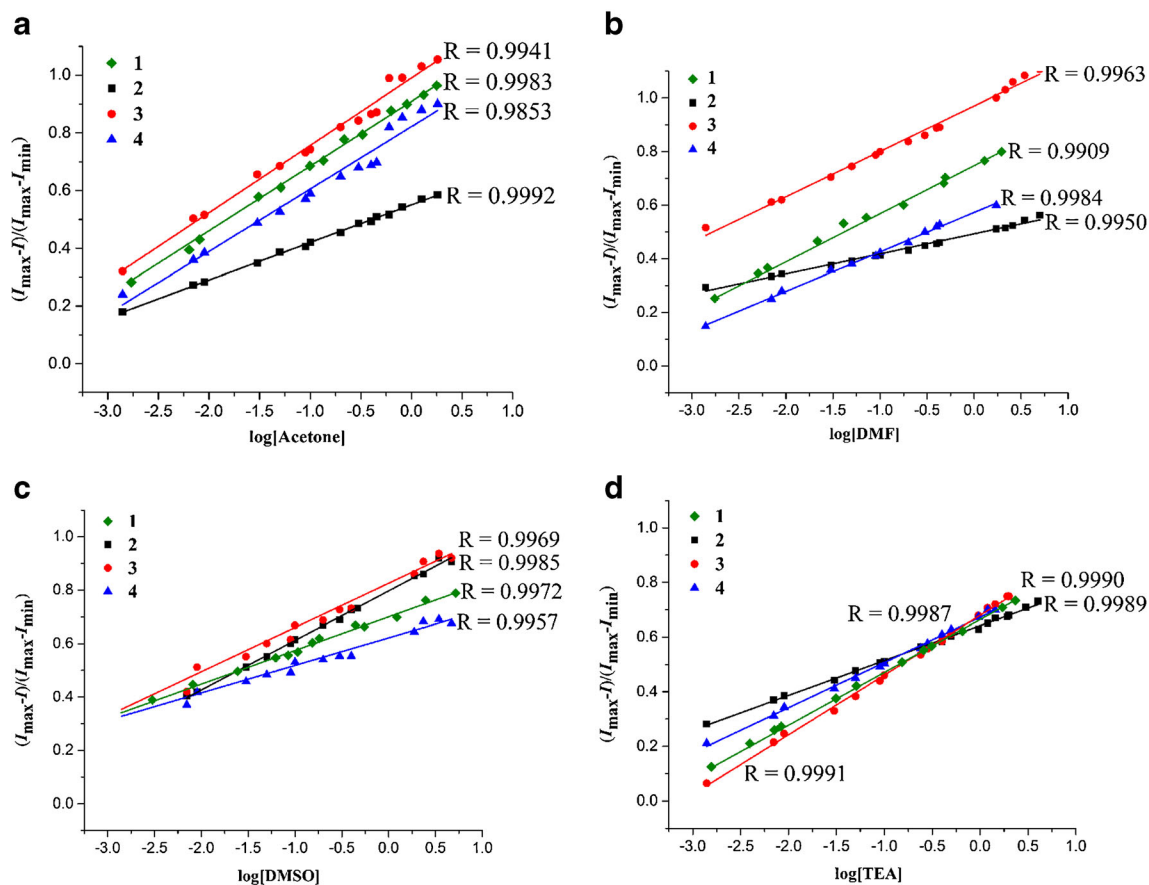


Fig. 9 Calibration according to the normalized fluorescence intensity $(I_{\max} - I) / (I_{\max} - I_{\min})$ $[\text{Zn}(\text{dpm})_2]$ and $[\text{Zn}_2\text{L}_2]$ on $\log[X]$ in cyclohexane: (a) – acetone, (b) – DMF, (c) – DMSO, (d) – TEA

and O- the containing analytes in the binary mixture X–cyclohexane. In cyclohexane the detection limits of the studied electron-donor compounds (acetone, DMF, DMSO, TEA) using a 1–4 are the range from 10^{-5} to 10^{-7} mol/l (Table 4).

Thus, strong performance of chemosensory sensitivity and selectivity, and sufficiently low detection limit ($\sim 10^{-5}$ – 10^{-7} mol/l) of the electron-donor component allow to recommend the $[\text{Zn}(\text{dpm})_2]$ and $[\text{Zn}_2\text{L}_2]$ as a new effective «On-Off» fluorescent sensors for express analysis of N- and O- containing analytes.

Table 4 The detection limits of the electron-donor component (X) in cyclohexane using fluorescent $[\text{Zn}(\text{dpm})_2]$ and $[\text{Zn}_2\text{L}_2]$ sensors

Complexes	The detection limits [X], mol/l			
	Acetone	DMF	DMSO	TEA
1	$3.3 \cdot 10^{-5}$	$2.1 \cdot 10^{-5}$	$8.2 \cdot 10^{-5}$	$7.2 \cdot 10^{-5}$
2	$6.0 \cdot 10^{-5}$	$2.5 \cdot 10^{-7}$	$8.4 \cdot 10^{-6}$	$9.4 \cdot 10^{-6}$
3	$2.7 \cdot 10^{-5}$	$1.9 \cdot 10^{-6}$	$4.5 \cdot 10^{-5}$	$7.8 \cdot 10^{-5}$
4	$9.3 \cdot 10^{-5}$	$4.2 \cdot 10^{-5}$	$5.0 \cdot 10^{-5}$	$8.7 \cdot 10^{-5}$

Conclusion

The results of quantum-chemical modeling (TD-DFT/B3LYP/cc-pVTZ) allow reliably predict major trends of the changes the spectral-luminescent properties of the dipyrriene and *bis*(-dipyrriene) zinc complexes depending on the characteristics of their molecular structure and properties of the medium.

Calculation of the energy of electronic transitions from the ground electronic state in the next showed that the main orbital contribution in the manifestation of the fluorescence of the dyes brings HOMO→LUMO transition.

Based on the experimentally established of linear correlations of the fluorescence quantum yield and calculated in the of the Stern-Volmer model of the apparent constants of fluorescence quenching of dipyrriene, *bis*(dipyrriene) Zn^{II} complexes with electron donor ligands we have substantiated the prospects of the practical application of the dyes as high sensitivity and selectivity «On-Off» fluorescent sensors of N- and O- containing analytes (10^{-5} – 10^{-7} mol/l).

As the analytical criterion of the identification of the analyte was proposed indicator of the relative change of intensity at different wavelengths of the fluorescence spectrum of the dipyrriene, *bis*(dipyrriene) zinc complexes, the numerical value

of which is determined by the nature of the electron donor N- or O-containing molecules (acetone, DMF, DMSO, TEA) and is independent from the selected wavelengths and concentration ratios of the solution components. The results showed that 3,3'-bis(dipyrinato)zinc^(II) complex demonstrates the highest sensitivity of the fluorescence to the presence of the electron-donor component compared with structurally-related 2,3'- and 2,2'-analogs.

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References

- Antina LA, Dudina NA, Guseva GB et al (2012) Characteristic features of formation, synthesis, and properties of binuclear zinc(II) helicates with alkyl-substituted 3,3'-bis(dipyrrolylmethenes). *Russ J Inorg Chem* 57:261–269. doi:10.1134/S0036023611120242
- Antina LA, Guseva GB, Vyugin AI et al (2012) Spectral and thermal properties of double-helicates binuclear Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) with 3,3'-bis(dipyrrolylmethenes). *Russ J Coord Chem* 38:529–536
- Marfin YS, Rummyantsev EV (2014) Analysis of solvation and structural contributions in spectral characteristics of dipyrin Zn(II) complexes. *Spectrochim Acta A Mol Biomol Spectrosc* 130:423–428. doi:10.1016/j.saa.2014.04.031
- Kuznetsova RT, Aksenov YV, Orlovskaya OO et al (2012) Study photoprocesses in coordination compounds of zinc(II) and boron(III) with open chain oligopyrroles for use in optical devices. *Russ J High Energ Chem* 46:464–475
- Filatov MA, Lebedev AY, Mukhin SN et al (2010) Pi-extended dipyrins capable of highly fluorogenic complexation with metal ions. *J Am Chem Soc* 132:9552–9554. doi:10.1021/ja102852v
- Gresser R, Hoyer A, Hummert M et al (2011) Homoleptic Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) complexes of bis-(phenyl)-diisoindol-aza-methene. *Dalton Trans* 40:3476–3483. doi:10.1039/c0dt01655a
- Gutmann V (1976) Solvent effects on the reactivities of organometallic compounds. *Coord Chem Rev* 18:225–255. doi:10.1016/S0010-8545(00)82045-7
- Maeda H (2009) Acyclic oligopyrroles as building blocks of supramolecular assemblies. *J Incl Phenom Macrocycl Chem* 64:193–214. doi:10.1007/s10847-009-9568-z
- Maeda H (2010) Anion recognition in supramolecular chemistry. doi: 10.1007/978-3-642-15444-7
- Ding Y, Tang Y, Zhu W, Xie Y (2015) Fluorescent and colorimetric ion probes based on conjugated oligopyrroles. *Chem Soc Rev* 44:1101–1112. doi:10.1039/c4cs00436a
- Antina EV, Vyugin AI (2012) Crystal solvates of porphyrins and metalloporphyrins. *Russ J Gen Chem* 82:1298–1306. doi:10.1134/S1070363212070201
- Bym MP, Curtis CJ, Hsiou Y et al (1993) Porphyrin sponge: conservation of host structure in over 200 porphyrin-based lattice clathrates. *J Am Chem Soc* 115:9480–9497
- Hill CL, Williamson MM (1985) Isolation and characterization of the principal kinetic product in the preparation of a sterically hindered tetra-arylporphyrin: X-ray structure of a bis(dipyrromethene) complex of zinc, Zn II (C₂₂H₁₃C₁₄N₂)₂: toluene. *J Chem Soc Chem Commun* 1228. doi: 10.1039/c39850001228
- Antina EV, Guseva GB, Vyugin AI (2006) Peculiarities of the interspecies interactions of metallocomplexes of structurally similar α , α -dipyrrolylmethene and porphyrin with organic solvents. *Russ J Phys Chem* 80:S1–S6. doi:10.1134/S0036024406130012
- Dudina NA, Antina EV, Guseva GB, Vyugin AI (2013) The high sensitive and selective “off-on” fluorescent zn²⁺ sensor based on the bis(2,4,7,8,9-pentamethyldipyrrolylmethene-3-yl)methane. *J Fluoresc* 24:13–17. doi:10.1007/s10895-013-1278-7
- Zakharova SP, Rummyantsev EV, Antina EV (2005) Coordination of alkyl-substituted biladiene-a, c by zinc(II), cadmium(II), and mercury(II) acetates in dimethylformamide. *Russ J Coord Chem* 31:849–855. doi:10.1007/s11173-005-0180-5
- Berezin MB, Antina EV, Dudina NA et al (2011) Synthesis, structure and fluorescence of a zinc(II) chelate complex with bis(2,4,7,8,9-pentamethyldipyrrolylmethen-3-yl)methane. *Mendeleev Commun* 21:168–170. doi:10.1016/j.mencom.2011.04.020
- Sheldrick WS, Engel J (1980) X-Ray crystal structure of the zinc complex of 1,2,3,7,8,12,13,17,18,19-decamethylbiladiene-a,c. *J Chem Soc Chem Commun* 5. doi: 10.1039/c39800000005
- Antina EV, Antina LA, Guseva GB et al (2014) Comparative analysis of physicochemical properties of dinuclear zinc(II) helicates with 2,2'-, 2,3'-, and 3,3'-bis(dipyrromethenes). *Russ J Inorg Chem* 59:578–586. doi:10.1134/S0036023614060023
- Antina EV, Gusev GB, Rummyantsev EV, Dudina NA (2009) Thermal properties of ligands, salts and metal complexes of linear oligopyrroles. *Russ J Gen Chem* 79:1900–1909. doi:10.1134/S1070363209090163
- Weissberger A, Proskauer E, Riddick J et al (1955) Organic solvents: physical properties and methods of purification. Interscience Publishers Inc., New York
- Bruttel P, Schlink R (2003), Water determination by Karl Fischer titration. Metrohm Monograph
- Fischer M, Georges J (1996) Fluorescence quantum yield of rhodamine 6G in ethanol as a function of concentration using thermal lens spectrometry. *Chem Phys Lett* 260:115–118
- Schmidt MW, Baldrige KK, Boatz JA et al (1993) General atomic and molecular electronic structure system. *J Comput Chem* 14:1347–1363. doi:10.1002/jcc.540141112
- Treutler O, Ahlrichs R (1995) Efficient molecular numerical integration schemes. *J Chem Phys* 102:346. doi:10.1063/1.469408
- Li W, Wang Y-B, Yang L-Y et al (2006) Spectroscopic and computational studies on the coordination-driven self-assembly complexes (ZnL)₂ and (NiL)₂ [L = bis(2,4-dimethyldipyrin-3-yl)methane]. *J Phys Chem B* 110:21958–21965. doi:10.1021/jp063105i
- Li W, Yang F, Wang Z, et al. (2009) Theoretical studies on structures and spectroscopic properties of self-assembled bis(2,4,8,10-tetramethyl-9-methoxycarbonylethyl)dipyrin-3-yl) methane with Co(II). 3375–3381
- Ksenofontov AA, Guseva GB, Antina EV, Vyugin AI (2014) Molecular structure of bis(dipyrrolylmethanates) of d-metals according to the quantum chemical calculations by the PM6 method. *J Struct Chem* 55:418–423. doi:10.1134/S0022476614030044
- Guseva GB, Ksenofontov AA, Antina EV (2015) Theoretical studies on the electronic structure and spectroscopic properties of zinc(II) bis(dipyrinate)s. *Comput Theor Chem* 1054:88–92. doi: 10.1016/j.comptc.2014.12.018
- Becke AD (1993) A new mixing of Hartree–Fock and local density-functional theories. *J Chem Phys* 98:1372. doi:10.1063/1.464304
- Lee C, Yang W, Parr RG (1988) Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys Rev B* 37:785–789. doi:10.1103/PhysRevB.37.785

32. Teets TS, Partyka DV, Updegraff JB, Gray TG (2008) Homoleptic, four-coordinate azadipyromethene complexes of d10 zinc and mercury. *Inorg Chem* 47:2338–2346. doi:[10.1021/ic701190g](https://doi.org/10.1021/ic701190g)
33. Pettersen EF, Goddard TD, Huang CC et al (2004) UCSF Chimera—a visualization system for exploratory research and analysis. *J Comput Chem* 25:1605–1612. doi:[10.1002/jcc.20084](https://doi.org/10.1002/jcc.20084)
34. Antina EV, Kuznetsova RT, Antina LA et al (2015) New luminophors based on the binuclear helicates of d-metals with bis(dipyrrin)s. *Dye Pigment* 113:664–674. doi:[10.1016/j.dyepig.2014.10.002](https://doi.org/10.1016/j.dyepig.2014.10.002)
35. Guseva GB, Antina EV, Ksenofontov AA et al (2014) Composition and thermal stability of bis(dipyrrolylmethenato)zinc(II) crystal solvates with N, N-dimethylformamide. *Thermochim Acta* 589: 31–36. doi:[10.1016/j.tca.2014.05.007S](https://doi.org/10.1016/j.tca.2014.05.007S)
36. Madhu S, Kalaiyarasi R, Basu SK et al (2014) A boron-dipyrrin–mercury(II) complex as a fluorescence turn-on sensor for chloride and applications towards logic gates. *J Mater Chem C* 2:2534. doi:[10.1039/c3tc32188f](https://doi.org/10.1039/c3tc32188f)
37. McLean TM, Moody JL, Waterland MR, Telfer SG (2012) Luminescent rhenium(I)-dipyrrinato complexes. *Inorg Chem* 51: 446–455. doi:[10.1021/ic201877t](https://doi.org/10.1021/ic201877t)
38. Lakowicz JR (2007) Principles of fluorescence spectroscopy. Springer Science & Business Media
39. Alfimov MV, Koshkin AV, Sazhnikov VA (2014) A method for detecting amines in the gas phase. The patent of the Russian Federation № 2532238. *Bulletin*. № 30