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Photo- and ionochromism of 5'-(4,5-diphenyl-1,3-oxazol-2-yl) substituted spiro[indoline-naphthopyrans]

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Abstract

Photo- and ionochromism of two spiro[indoline-naphthopyran] derivatives with a 4,5-diphenyl-1,3-oxazol-2-yl substituent at the 5'-position has been investigated. The cyclic forms exhibit fluorescence and phosphorescence. In the presence of metal ions such as Zn(II), Cu(II), Mn(II), Co(II), Ni(II), Cd(II) the merocyanine isomers of the 5'-(4,5-diphenyl-1,3-oxazol-2-yl) substituted spironaphthopyrans forms metal complexes whose composition and stability strongly depends on the nature of a metal ion. Zn(II), Cd(II) and Mn(II) ions form 1:1 complexes, whereas with Co(II), Ni(II) and Cu(II) ions the formations of 1:2 complexes was also observed. For the first time stepwise stability constants and spectral properties of the prepared mono- and bis-complexes have been determined. The complexes formed by Cd(II) and Zn(II) ions exhibit fluorescence in 580–700 nm spectral region. Complexes with Mn(II) at 77 K display unusual narrow band fluorescence with a maximum at 730–760 nm. At room temperature solutions of the complexes with Cd(II), Zn(II), Mn(II) demonstrate negative photochromic behavior which make them promising building blocks for the construction of photodynamic chemosensors for metal ions.

Keywords: Spiropyrans; Photochromism; Fluorescence; Complexation; Binding constants

1. Introduction

Photochromic organic molecules, including spiropyrans [1–3] and spirooxazines [4,5], are the subject of intense research due to their application in optical systems for registration and storage of information, sensor design, opto- and optobioelectronics as well as transportation systems and catalysis [6].

The mechanism for photochromic transformation of spironaphthopyrans (SNP) is based on the reversible heterolytic C_{spiro}–O bond cleavage in the cyclic isomer **A** followed by *cis–trans*-isomerization into the metastable merocyanine form **B**. The latter spontaneously or under the action of visible light undergoes the back rearrangement to the starting spiroform [1–3] (Scheme 1).

In the last years much attention was given to investigation into isomerization of spiropyrans and spirooxazines occurring under the action of certain substrates, for example metal ions [7]. Spiropyran and spirooxazine molecules used for this purpose contain an ionophore fragment in the *ortho*-position to pyran/oxazine oxygen atom converting to the phenolate oxygen of the colored isomers and complementarily coordinating to metal ions. A special part of this research is the study of spirocyclic photochromic compounds containing various crown-ether moieties as the ionophore fragment [8–10]. The influence of alkaline and alkaline-earth metal ions on the isomerization of these compounds was amply studied. Much less studied are the spirocyclic photochromic compounds the isomerization of which is influenced by transition and rare-earth metal ions. Among these compounds are derivatives of 6-nitroBIPS containing methoxy [11–13], piperidinomethyl [14] and other donor groups [15] in the position 8 as well as quinolinespiropyranindolines [16–20]. Recently a report on the synthesis and

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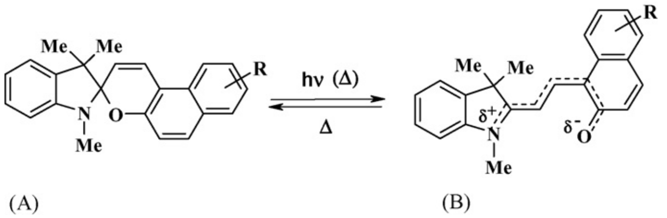


Scheme 1. Photo- and thermochromic transformation of SNP.

investigation into the use of new spirooxazines containing benzotiazole substituent in the position 5 as photochromic chelate reagents has been published [21,22].

This work deal with preparation and study of coordination ability of previously prepared [23] and new spironaphthopyrans containing diphenyloxazolyl group in the position 5′ of the naphthopyran moiety.

2. Experimental

^{1}H NMR spectra were recorded on a Varian Unity-300 spectrometer (300 MHz) in $CDCl_3$ at 20 °C; δ values and spin–spin coupling constants were measured within 0.01 ppm and 0.1 Hz, respectively. Electronic absorption spectra were recorded on a Varian Cary 100 spectrophotometer. Luminescence emission and excitation spectra were recorded on a Varian Cary Eclipse spectrofluorimeter. The quantum yield of fluorescence was determined using methylene blue in water ($\Phi_f = 0.02 \pm 0.005$) [24] as reference with optically matched samples having absorbances of 0.1 at $\lambda_{ex} = 540$ nm; the experimental error in Φ_f is ±20%. The CLINP software program [25,26] was used to calculate binding constants.

The solvents were MeOH, EtOH, MeCN, acetone, toluene (Aldrich), heptane, and Et_2O (reagent grade). Photolysis of solutions ($V = 2 \times 10^{-3}$ L) was carried out with a DRSh-250 mercury lamp with a set of interference filters for isolation of the spectral lines of mercury. The intensity of light used for irradiation of the solutions was 4×10^{16} and 6×10^{16} photons s^{-1}, for the spectral lines of 365 and 546 nm, respectively. Solutions of the complexes were prepared by mixing in dark equivalent volumes of the standard solutions of components ($C = 2 \times 10^{-4}$ M) followed by their dilution to with solvent to 10^{-2} L at 293 K. Metal ions were added to solutions as perchlorates. The constant ionic strength ($I = 0.01$) of the solutions under study was maintained by adding 0.2 M Bu_4NClO_4 (Acros).

Compounds (**4**) [23] and (**6**) [27] were prepared according to the previously reported procedures.

5’-(4,5-Diphenyl-1,3-oxazol-2-yl)-8’-methoxy-1,3,3-trimethylspiro[indoline-2,3’-[3*H*]naphtho[2,1-*b*]pyran] (**5**) was synthesized using the procedure already described [23]. The yield was 49%, m.p. 230–231 °C (from heptane–toluene, 1:1). Found (%): C, 81.35; H, 5.52; N, 4.69. $C_{39}H_{32}N_2O_3$. Calculated (%): C, 81.23; H, 5.59; N, 4.86. ^{1}H NMR, δ: 1.26 (s, 3H, 3-Me); 1.43 (s, 3H, 3-Me); 2.80 (s, 3H, 1-Me); 3.92 (s, 3H, 8’-OMe); 5.90 (d, 1H, H-2’, $J = 10.5$); 6.57 (d, 1H, H-7, $J = 7.7$); 6.90 (dt, 1H, H-5, $J = 7.4$ and $J = 0.9$); 7.09–7.18 (m, 4H, H-4, H-7’, PhH); 7.19–7.39 (m, 8H, H-6, H-9’, PhH); 7.59–7.63 (m, 3H, H-1’, PhH); 7.96 (d, 1H, H-10’, $J = 9.3$); 8.52 (s, 1H, 6’-H).

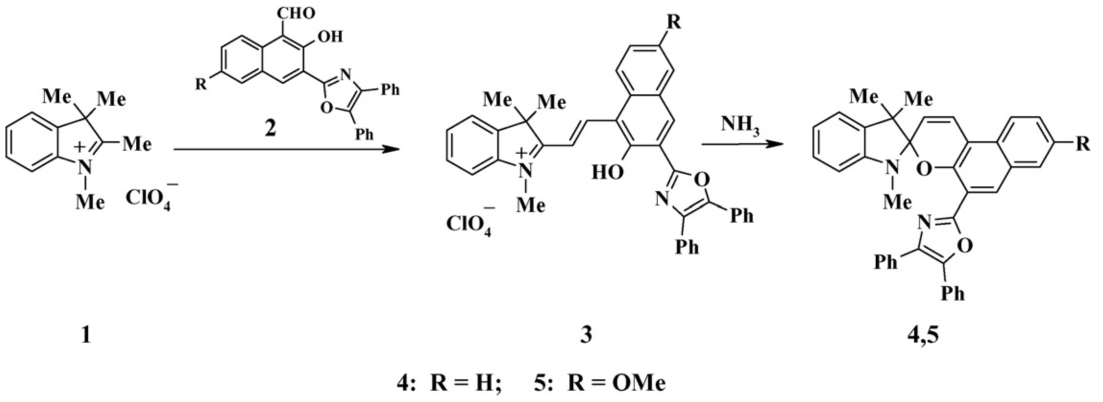
3. Results and discussion

3.1. Synthesis

Oxazole derivatives, especially those containing aromatic or heterocyclic substituents in the positions 2 and 5, are good fluorophore systems. They are widely used as fluorescent bleaching agents and can form complexes with transition metal ions [28,29]. We expected that these properties of the oxazolyl moieties might be properly exhibited in diphenyloxazolyl-functionalized fluorescent spiropyrans. Spiropyran (**4**) was obtained in two steps (Scheme 2) by the reaction of 3*H*-indolium perchlorate (**1**) with 3-diphenyloxazolyl substituted 2-hydroxynaphthaldehydes (**2**) in acetic acid followed by a treatment of 2-hydroxynaphthylvinylindolium perchlorate (**3**) with ammonia [23]. Spiropyran (**5**) was obtained by the same procedure.

3.2. Spectroscopic and photochemical properties

The cyclic form of the parent spironaphthopyran (**6**) is characterized by a structured absorption band with maxima at 346 and 362 nm (toluene). Electronic absorption spectra of 5’-



Scheme 2. Synthesis of 5’-(4,5-diphenyl-1,3-oxazol-2-yl) substituted SNP.

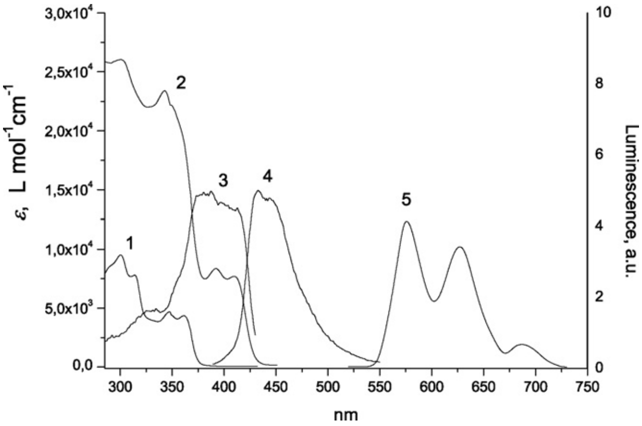


Fig. 1. Absorption spectra of compounds (**6**) (1) and (**5**) (2), fluorescence excitation (3) and emission (4) spectra of (**5**) in toluene at 293 K. Phosphorescence spectra of (**5**) (5) (toluene–ethanol–diethyl ether, 77 K).

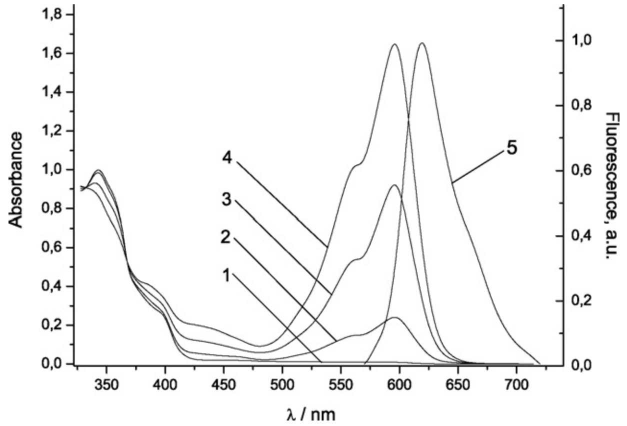


Fig. 2. Absorption spectra of spironaphthopyran (**4**) in toluene before (1) and after irradiation with 365 nm light for 30 (2), 60 (3) and 120 (4) s. Fluorescence spectrum of merocyanine **4B** in toluene (5). Concentration of (**4**)—5×10^{-5} M, $T = 200$ K.

diphenyloxazolyl substituted SNP (**4**), (**5**) contain also an additional low intense long-wavelength absorption band with two weak resolved maxima in the region 380–392 and 395–410 nm. The origin of the corresponding electronic transitions is due to charge transfer between the naphthopyran and diphenyloxazole fragments (Fig. 1, Table 1). Introduction of an electron donating methoxy-group in the position 8 of the naphthopyran moiety of SNP (**5**) leads to batochromic shift of this band relative to that in SNP (**4**) (Table 1).

In toluene at 293 K, the cyclic forms of SNP (**4**) and (**5**) exhibit weak fluorescence with maxima at 420 and 430 nm, correspondingly (Table 1). The fluorescence excitation spectra well coincide with the absorption ones (Fig. 1, Table 1). For SNP (**4**) and (**5**), phosphorescence characterized by structured bands with maxima in the region 574–576 and 625–626 is observed at 77 K (Fig. 1, Table 1). In contrast with (**4**) and (**5**), the cyclic form of the non-substituted SNP (**6**) has no luminescence under these conditions.

At the temperature higher than 273 K the photochromism of SNP (**4**)–(**6**) solutions is not observed due to the high rate of the back thermal recyclization reaction **B** → **A**. UV-irradiation of uncoloured solutions of SNP (**4**)–(**6**) at 200 K results in their coloration. This process is accompanied by an appearance of new long-wavelength absorption bands in the region 562–596 nm (Table 1, Fig. 2), which are typical of ring-opened merocyanines **B** [1–3] (Scheme 3).

Subsequent irradiation with the light corresponding to the absorption bands of **B** or heating solutions lead to decolouration and restoration of the bands related to the cyclic form **A**. The absorption bands of the merocyanine forms **B** of SNP containing electron-donating substituents (diphenyloxazolyl in (**4**), diphenyloxazolyl and methoxy groups in (**5**)) in the naphthopyran moiety of SNP are bathochromically shifted (Table 1) with respect to (**6**). The merocyanine forms **B** of (**4**)–(**6**) have intense fluorescence in the region 550–720 nm. The fluorescent maxima of **4B** and **5B** are shifted bathochromically relative to that of **6B** (Table 1).

3.3. Cation-induced isomerization in acetone solutions

An addition of equivalent amounts of Zn(II), Cu(II), Mn(II), Co(II) and Ni(II) salts to the almost colorless acetone solution of SNP (**4**) leads to significant changes in the absorption spectra. In the near UV region, a small growth of the absorption is observed, whereas in the visible region an appearance of new intense absorption bands takes place. The position of the absorption maxima of these bands depends on the nature of the metal ion (Table 2). The maxima of these absorption bands

Table 1
Wavelengths of the absorption maxima, corresponding absorption coefficients ε, luminescence emission and excitation λ_{max} of the isomeric forms of spiropyrans (**4**)–(**6**) in toluene (or toluene/ethanol/diethyl ether at 77 K) solutions

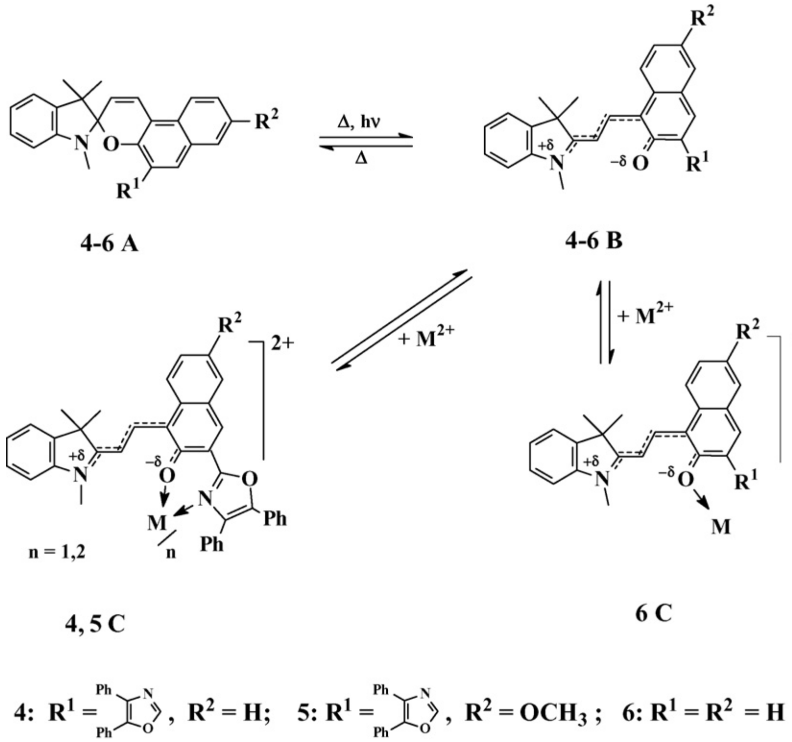
Compound	Isomeric form	λ_{max}^{abs} (nm) (ε, 10^{-4} L mol^{-1} cm^{-1})[a]	$\lambda_{max}^{ex,fl}$ (nm)	λ_{max}^{fl} (nm)	$\lambda_{max}^{ex,ph}$ (nm)[b]	λ_{max}^{ph} (nm)[b]
(**4**)	Sp	304 (28.11), 342 (22.15), 380[c], 395[c]	398, 404[a]	420, 432[a]	396	574, 625, 680[c]
	Mc	596	590[d]	618[d]	–	–
(**5**)	Sp	301 (26.04), 343 (23.40), 392 (8.35), 410 (7.696)	390, 410[a]	430, 446[a]	400	576, 626, 680[c]
	Mc	610	617[d]	646[d]	–	–
(**6**)	Sp	346 (13.59), 362 (11.93)	–	–	–	–
	Mc	562	558[d]	600[d]	–	–

[a] 293 K.
[b] 77 K.
[c] A shoulder.
[d] 200 K.

Table 2
Wavelengths of maximum absorption and corresponding absorption coefficients ε and luminescence λ_{max} of spironaphthopyran and of the complexes with merocyanines (**4**)–(**6**) in acetone solutions at 293 K

Ion	(**4**)				(**5**)				(**6**)			
	λ_{max}^{abs} (nm)	ε (10^{-4} L mol^{-1} cm^{-1})	$\Delta\lambda_{max}^{abs}$	λ_{max}^{fl} (nm) ($\Phi_f \times 10^3$)	λ_{max}^{abs} (nm)	ε (10^{-4} L mol^{-1} cm^{-1})	$\Delta\lambda_{max}^{abs}$	λ_{max}^{fl} (nm) ($\Phi_f \times 10^3$)	λ_{max}^{abs} (nm)	ε (10^{-4} L mol^{-1} cm^{-1})	$\Delta\lambda_{max}^{abs}$	λ_{max}^{fl} (nm)
Metal free												
SP	338	1.91	–	410	337	2.10		430	346	0.42	–	–
	375[a]	0.63			392[a]	0.58			359	0.40		
	392[a]	0.46			405[a]	0.54						
MC	588	–	–	620[b]	610	–	–	646[b]	562	–	–	600[b]
Complexes												
Mn	582	4.56	−6	733[c]	595	4.95	−15	766[c]	–	–	–	–
Co	571	4.46	−17	–	593	4.40	−17	–	–	–	–	–
	596[d]	11.84[d]	8[d]		623[d]	13.97[d]	13[d]	–				
Ni	580	4.77	−8	–	603	5.24	−7		–	–	–	–
	600[d]	13.84[d]	12[d]		628[d]	14.55[d]	18[d]	–				
Cu	560	4.52	−28	–	580	4.64	−30		–	–	–	–
	562[d]	11.31[d]	−26[d]		582[d]	11.14[d]	−28[d]	–				
Zn	566	4.70	−22	626 (5.50)	588	4.95	−22	649 (3.28)	558	–	−4	605
Cd	586	4.60	−2	628 (4.84)	609	5.10	−1	657 (3.34)	–	–	–	–

[a] A shoulder.
[b] 200 K.
[c] 77 K.
[d] Complex 1:2.



Scheme 3. Suggested mechanism of SNP transformations.

are hypsochromically shifted with respect to the merocyanine absorption. The largest shift is observed for solutions containing Cu(II) ions (Table 2). This spectral behavior is exemplified by the spectra of SNP (**4**) in the presence of metal perchlorates (Fig. 3). It is noteworthy that an addition of salts of alkali and alkaline-earth metal ions even in 100-fold excess does not have a significant effect on the spectra, which fact points to the absence of interaction with these ions. In the presence of Cd(II) ions significant coloration takes place only at 50-fold excess of the metal ions. Similar observations were made for SNP (**5**). In contrast with compounds (**4**) and (**5**), coloration of spiropyran (**6**) solutions is observed only at 100-fold excess of Zn(II). The absorption band of the product is also shifted to the blue region.

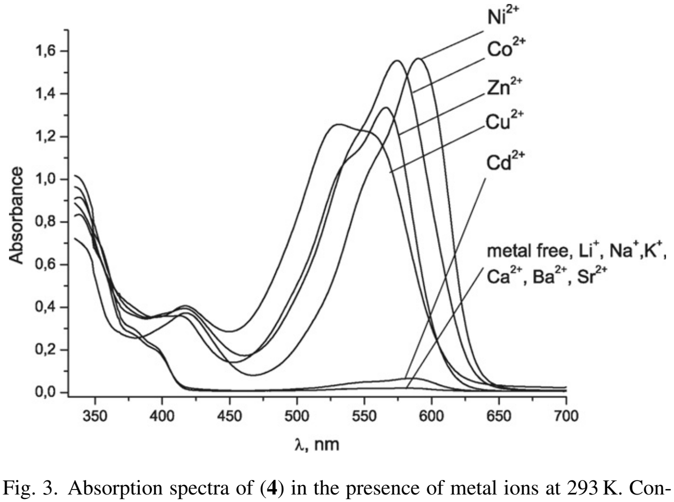


Fig. 3. Absorption spectra of (**4**) in the presence of metal ions at 293 K. Concentration of (**4**) and metal—4×10^{-5} M.

Two known types of the interaction between spiroheterocyclic photochromic compounds and metal ions are complexation with merocyanine isomer and redox reaction [30,31]. In both cases resulting products absorb in the visible region. In contrast with complexation, redox reaction is the irreversible process. To check the reversible character of the reaction between SNP and metal ions we added to the resulted colored solutions an excessive amount of competing complexing agent—disodium salt of ethylenediaminetetraacetic acid (EDTA) [32]. In all cases decoloration and recovery of the absorption spectrum characteristic of the initial cyclic isomer were observed. These data indicate that the reaction between metal ions and spiropyrans leads to the formation of complexes of type **C** (Scheme 3).

3.4. Stoichiometry and stability of resulting complexes

Composition of complexes **4C** was measured using spectrophotometric method of continuous variation (Job-method) that was previously successfully employed for determination of composition of complexes of metal ions with spiropyrans and chromenes [33–35]. Fig. 4 depicts the dependence of optical densities in the absorption maximum of a complex **4C** with Zn(II) ions versus composition of the isomolar solutions of the components. A clear maximum of this plot corresponds to the equimolar composition. It should be noted that the position of the maximum does not depend on the selection of the wavelength using for monitoring provided it is chosen within long-wavelength absorption band. Similar dependences were observed for the complexes with Mn(II) and Cd(II) ions. For Ni(II), Co(II) and Cu(II) ions the isomolar diagrams have other

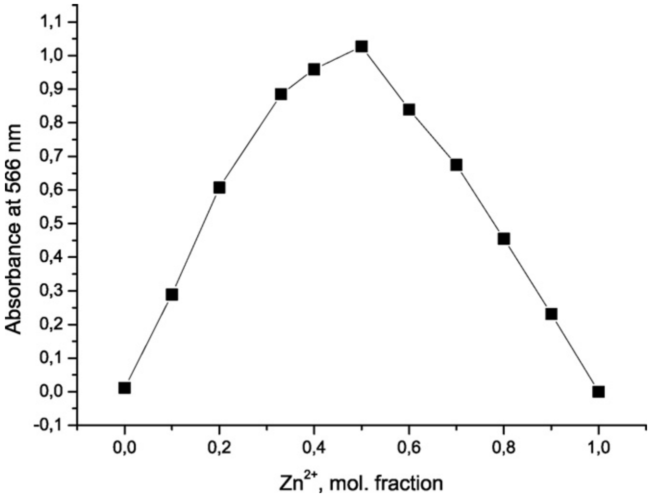


Fig. 4. Continuous variation plot of the (**4**)/Zn (C(**4**) + C(Zn) = 3 × 10^{-5} M) in acetone at 293 K.

shapes. Fig. 5 shows the Job's plot for Ni(II). The maximum on this plot corresponds to 1:2 (ion:SNP) ratio and the shape of the Job-plot diagram varies with the wavelength chosen for the examination. Such behavior can be explained by the contribution of the intermediate 1:1 complex to the absorbance (metal ion and merocyanine absorption in this region are inessential). The 1:2 complex absorbs predominantly at 600 nm, which corresponds to the maximum observed on the continuous variation diagram. At 580 nm, molar extinction coefficients for both complexes are of comparable value, which leads to that in this case the maximum on the diagram is less expressed and in the 1:1 region a "shoulder" on the curve is observed.

An important parameter of coordination compounds is binding constant which allows one to predict preferred metal ions to form stable complexes with spirocyclic compounds and, consequently, to estimate selectivity of the reaction between metal and spiropyrans. Approaches to estimation of binding constants depend on the type of formed complex. When metal ions are coordinated to the phenolate oxygen atom of the colored SNP form, merocyanine isomers are involved in the tautomeric and complexation equilibria [13]:

$$\mathrm{A} \rightleftharpoons \mathrm{B}, \qquad \mathrm{B} + \mathrm{M} \rightleftharpoons \mathrm{MB}, \qquad \mathrm{B} + \mathrm{MB} \rightleftharpoons \mathrm{MB_2}$$

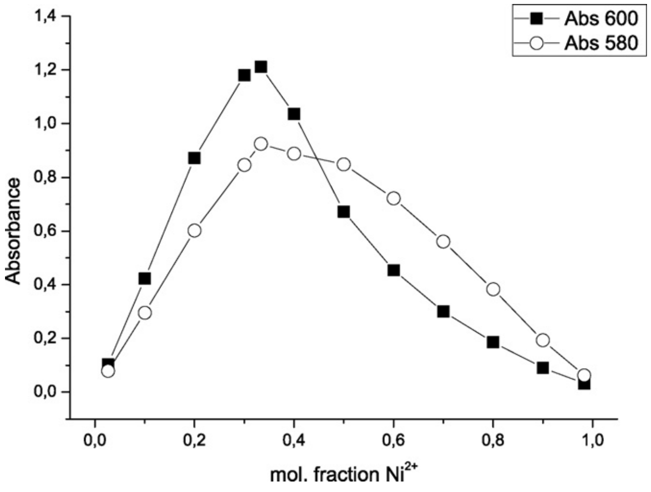


Fig. 5. Continuous variation plot of the (**4**)/Ni (C(**4**) + C(Ni) = 3 × 10^{-5} M) in acetone at 293 K.

In this case corresponding equilibrium constants can be described by the following equations:

$$K_\mathrm{T} = [\mathrm{B}]/[\mathrm{A}] \tag{1}$$

$$K_1 = [\mathrm{MB}]/([\mathrm{M}][\mathrm{B}]) \tag{2}$$

$$K_2 = [\mathrm{MB_2}]/([\mathrm{MB}][\mathrm{B}]) \tag{3}$$

It is difficult to accurately determine the constant K_T of the tautomeric equilibrium, because it is impossible to determine photometrically the equilibrium concentration of the colored isomer without knowing its molar extinction coefficient. At the same time it is difficult to determine this value using NMR spectroscopy because equilibrium amount of the merocyanine is low [36,37]. Therefore, we estimated the effective values of the complexation constants K^eff (which also include K_T) by analogy with acid–base equilibria [38].

$$K_i^\mathrm{eff} = [\mathrm{MB}_i]/([\mathrm{MB}_{i-1}][\mathrm{L}]^i) \tag{4}$$

Here $[L] = [A] + [B]$—equilibrium concentration of SNP not involved in the complexation. The correlation between K_i and K^eff is given by Eq. (5):

$$K_i^\mathrm{eff} = K_\mathrm{T} K_i/(1 + K_\mathrm{T}) \tag{5}$$

K^eff values have been determined spectrophotometrically. The absorption spectra of solutions containing a given amount of SNP and various amounts of metal ion have been recorded. Some important requirements of Eq. (5) validity should be noted. The injection of a metal salt during a measurement changes the ion strength of solution, which is a factor influencing K_T value. It is also known [39] that metal cation complexes with some styryl dyes form associates with counter-ions in solution, influence of this effect being increased with increasing metal salt concentration. To level these effects we added to the temperature-controlled solution stock electrolyte (t-Bu$_4$ClO$_4$) to maintain the constant ion strength on the level $I = 0.01$ M.

For Zn(II), Mn(II), Cd(II) ions at all concentrations used (starting from 10-fold deficiency to 20-fold excess), only the absorption band corresponding to 1:1 complex was observed. The dependence between the absorbance in the maximum versus overall metal ion concentration can be expressed [40] by Eq. (6):

$$\begin{aligned} A = A_0 + (A_\mathrm{max} - A_0)[C_\mathrm{L}^0 + C_\mathrm{M}^0 + 1/K_1^\mathrm{eff} \\ - [(C_\mathrm{L}^0 + C_\mathrm{M}^0 + 1/K_1^\mathrm{eff})^2 - 4C_\mathrm{L}^0 C_\mathrm{M}^0]^{1/2}]/2C_\mathrm{L} \end{aligned} \tag{6}$$

where A_0, A_max, A—correspondingly minimal, maximal and current value of optical density in spectral series; C_L, C_M—total SNP and metal concentrations. Changes in the absorption spectra of SNP (**4**) after addition of different amounts of zinc salt are shown in Fig. 6 as an example. The approximation of experimental data by function (6) is also shown in Fig. 6.

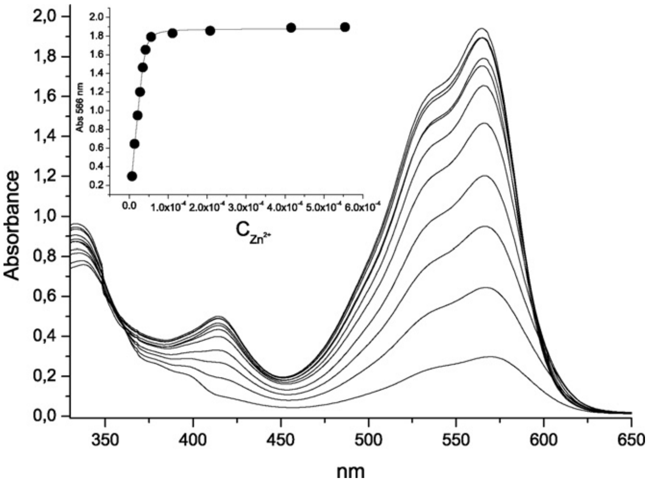


Fig. 6. Absorption spectra of (**4**) after addition of different amounts of $Zn(ClO_4)_2$ at 293 K. C(**4**) = 4×10^{-5} M (Inset: absorption changes at 566 nm vs. Zn(II) concentration. Points – experiment, continuous line – result of calculation).

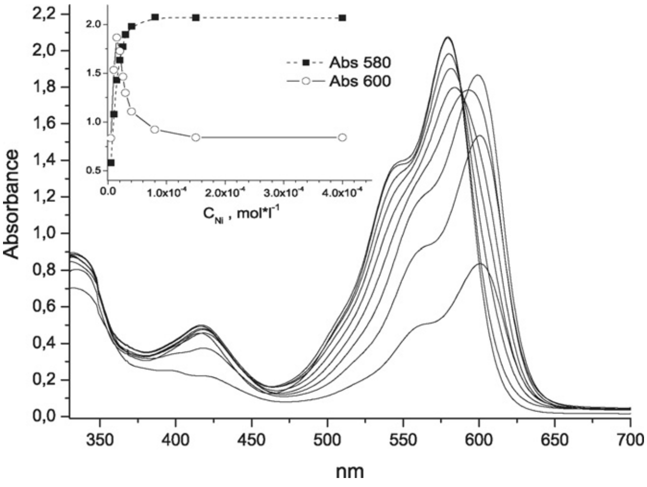


Fig. 7. Absorption spectra of (**4**) after addition of various amounts of $Ni(ClO_4)_2$ at 293 K. C(**4**) = 4.2×10^{-5} M. (Inset: absorption changes at 580 and 600 nm (full and open symbols) vs. Ni(II) concentration. Points – experiment, continuous line – result of calculation).

For 1:2 complexes of SNP with Co(II), Ni(II), Cu(II) ions it is impossible to obtain an explicit expression of the absorbance as a function of total metal ion concentration. In this case calculations were based on numerical interactive approach to the search of minimum of the functional (7) defined as

$$U = \sum_{i=1}^{n_s}\sum_{j=1}^{n_\lambda}(A_{\text{obs}} - A_{\text{calc}})^2 \to \min \qquad (7)$$

n_s indicates the number of solutions, n_λ is the number of wavelengths (readings for each spectrum), The values A_{obs} and A_{calc} correspond to the measured absorbance of the j-wavelength in the i-solution, and that estimated by the program for a given equilibrium model, respectively.

$$\begin{aligned}
&A_{\text{calc}} = \varepsilon_{\text{MB}}[\text{MB}] + \varepsilon_{\text{MB}_2}[\text{MB}_2] + \varepsilon_{\text{L}}^{\text{eff}}[\text{L}] + \varepsilon_{\text{M}}[\text{M}],\\
&[\text{MB}] = C_{\text{M}}K_1^{\text{eff}}[\text{L}]/(1 + K_1^{\text{eff}}[\text{L}] + K_1^{\text{eff}}K_2^{\text{eff}}[\text{L}]^2),\\
&[\text{MB}_2] = (C_{\text{M}}K_1^{\text{eff}}K_2^{\text{eff}}[\text{L}]^2)/(1 + K_1^{\text{eff}}[\text{L}] + K_1^{\text{eff}}K_2^{\text{eff}}[\text{L}]^2),\\
&C_{\text{L}} = [\text{MB}] + 2[\text{MB}_2] + [\text{L}] \qquad (8)
\end{aligned}$$

In an iterative nonlinear fitting procedure using least-square Newton–Gauss algorithm, K^{eff} and the molar absorption coefficients of complexes MB and MB_2 were optimized. In fitting procedure the absorbance measured at selected characteristic wavelengths in samples with various metal ion concentrations was used. A representative fit is presented in Fig. 7. The fits are generally good. Calculated effective stability constants are listed in Table 2.

The results obtained reveal a clear dependence of the stability of the 1:1 complexes and the Pearson's type of metal ions. Cd(II) cation (soft) forms less stable complexes than "harder" Co(II), Ni(II) ions. Stability of the 1:2 complexes is mainly determined by steric factors. The log K_2 value increases nearly by an order of magnitude in the row Co(II), Ni(II), Cu(II) in the order of increase in the effective cation radius. Molar extinction coefficient values for 1:1 complexes are comparable with those for complexes of 5'-benzotiazolyl substituted spirooxazines [22] and merocyanines [3]. Introduction of an oxazolyl fragment in *ortho*-position to pyran oxygen atom leads to significant increase in the stability of the complexes (Table 3).

3.5. Luminescent and photochemical properties of complexes

In the case of SNP (**4**) complexes with Zn(II) and Cd(II), weak fluorescence of the colored solutions was observed with maxima at 625 and 628 nm, correspondingly (Fig. 8, Table 2). Complexes with Mn(II) as well as mono- and bis-complexes with Co(II), Ni(II) and Cu(II) have no fluorescence at room temperature. Lowering temperature down to 77 K leads to the increase in the fluorescence intensity of Zn(II), Cd(II) complexes. At this condition the Mn(II) complex has a narrow band in the region 700–790 nm with a maximum at 733 nm (Fig. 8). The excitation spectrum coincides with the absorption of the complex. A similar band was observed for the complex of SNP (**4**) with Mn(II) ions in other polar media: acetonitrile, vitrescent mixture of ethanol with diethyl ether. Analogous spectral behavior demonstrate complexes with SNP (**5**), but in this case, fluorescence bands of Zn(II), Cd(II) and Mn(II) complexes are bathochromically shifted (Table 2).

Table 3
Logarithms of effective complexes stability constants

Ion	K_i^{eff}	(**4**)	(**5**)	(**6**)
Cd	K1	3.97 ± 0.12	3.65 ± 0.02	–
Mn	K1	4.47 ± 0.04	4.29 ± 0.03	–
Zn	K1	6.17 ± 0.08	5.90 ± 0.16	1.88 ± 0.05
Co	K1	6.85 ± 0.12	6.13 ± 0.12	–
	K2	4.66 ± 0.14	4.65 ± 0.15	
Ni	K1	6.81 ± 0.12	6.54 ± 0.13	–
	K2	5.18 ± 0.15	5.16 ± 0.11	
Cu	K1	8.75 ± 0.12	7.24 ± 0.07	–
	K2	5.21 ± 0.28	5.16 ± 0.23	

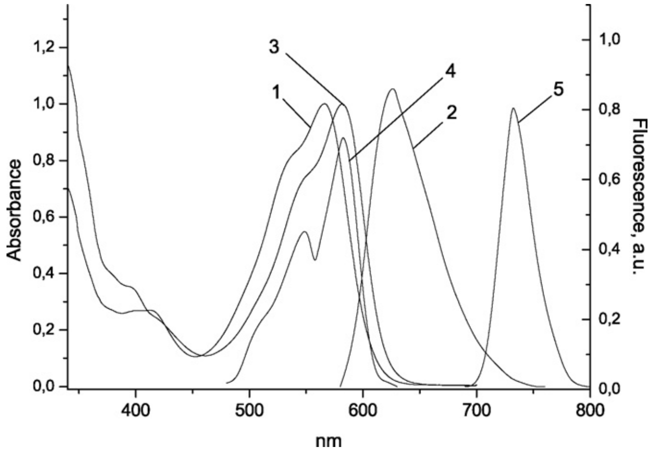


Fig. 8. Absorption (1) and emission (2) spectra of complex (**4**) with Zn^{2+}, absorption spectra of complex (**4**) with Mn(II) (3) in acetone solution at 293 K. Fluorescence excitation (4) and emission (5) spectra of complex (**4**) with Mn(II) in acetone at 77 K. $C(\mathbf{4}) = 2.1 \times 10^{-5}$ M, $C(Mn) = 2 \times 10^{-4}$ M.

Irradiation of solutions containing complexes SNP (**4**), (**5**) with Zn(II), Mn(II) and Cd(II) as well as SNP (**6**) with Zn(II) by the light with wavelength corresponding to their long-wavelength absorption at 293 K leads to effective decoloration. Color of the solutions fully restores after extinguishing the irradiation (Fig. 9). Kinetics of the dark process has monoexponential character and the observed rate constant for the repeated coloring recovery coincides with that observed after mixing of starting components. This fact evidences the photodissociation of complexes to the starting components, as it was previously proved for Zn(II) complexes with quinolinospiropyranindolines with the use of spectrophotometric and electrochemical methods [18]. Other complexes described in this paper are stable toward irradiation by visible light.

The results obtained can be explained on the base of the chelate structure of **4C**, **5C**. Hypsochromic shift of the absorption bands (Table 2) occurring upon formation of the complexes is caused by participation of merocyanine phenolic oxygen atom in coordination with metal ions [41]. On the other hand, the substantial difference in stability of **4C**, **5C** and **6C** indicates additional coordination of a metal ion to nitrogen atom of the diphenyloxazolyl substituent. The planar structure of the chelates formed by **4B**, **5B** and metal ions favor to interaction between the metal ion and the merocyanine π-system. As a result, complexes of Cu(II), Co(II) and Ni(II) display no photochromism and luminescence at room temperature and at 77 K because of effective quenching singlet excited state by the intramolecular energy transfer to the metal cation [12,13]. Fluorescence with a maximum at 733 (or 766 nm) observed for the Mn(II) complexes at 77 K contrasts to the properties typical of the complexes of merocyanines with non-transition metals with the narrower band width fluorescence at 570–720 nm [13] (4300 and $\sim$1630 cm^{-1}, correspondingly). These data can be explained by the sensitized luminescence of Mn(II) ion arising energy transfer from the excited merocyanine energy levels to the low lying metal excited states, which may correspond to the $^4T_1 \rightarrow {}^6A_1$ transition [42].

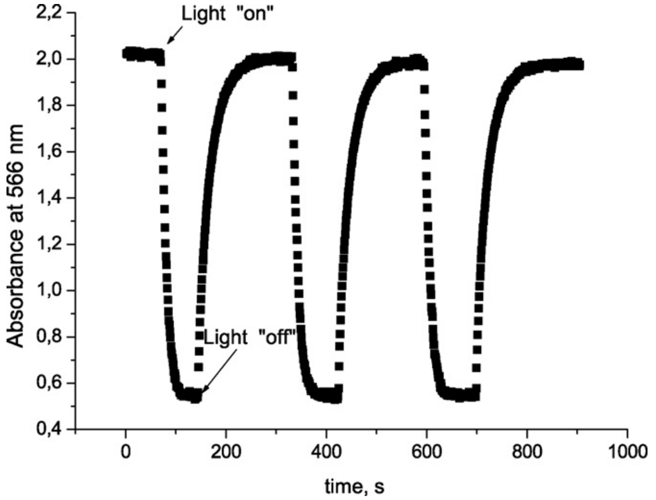


Fig. 9. Switching behaviour observed in the absorbance intensity at 566 nm with visible light irradiation. SNP (**4**)/Zn, $C(Zn) = C(\mathbf{4}) = 4.25 \times 10^{-5}$ M, $T = 293$ K.

4. Conclusions

Photochromic members of the family containing diphenyloxazolyl substituent in 5'-position in contrast with the unsubstituted SNPs, exhibits fluorescence of its ring-closed isomeric along with the phosphorescence. The presence of the methoxy group in the new compound leads to batochromic shift of absorption and fluorescent bands of SNP isomeric forms. Metal ions induce isomerization of the SNP and the formation of intensely colored complexes with the merocyanine isomeric forms. The complexation causes hypsochromic shift of the absorption of the merocyanine forms of SNP. Composition and stability of the formed complexes depend on the nature of the metal ions. In the case of Zn(II), Cd(II) and Mn(II) only 1:1 complexes are detected, whereas Co(II), Ni(II) and Cu(II) cations form also 1:2 complexes. For the first time stepped stability constants and spectral properties of mono- and bis-complexes have been determined. Stability of the 1:1 complexes increases in the order Cd(II) < Mn(II) < Zn(II) < Ni(II) < Co(II) < Cu(II) and slightly decreases for methoxy substituted diphenyloxazolyl SNP with respect to unsubstituted one. The complexes formed by diamagnetic (Cd(II) and Zn(II)) cations have fluorescence with maxima in the region 620–660 nm and exhibit negative photochromism—thermally reversible decoloration under the action of visible light.

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