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Benzothiazolyl substituted spiropyrans with ion-driven photochromic transformation

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### Abstract

The present work is devoted to the synthesis and detailed investigation of new 8-benzothiazole containing spiropyrans. The investigated spiropyrans exist under colorless spirocyclic isomers exhibiting positive photochromism with thermo- and photoinduced back reaction. UV light irradiation leads to their effective coloration with quantum yields up to 44 %. The efficiency of the back photocyclization induced by visible light does not exceed 0.1%. This feature distinguishes them from the previously studied benzoxazole analogs. The enhancement of electron-withdrawing properties of the indoline fragment substituents promotes an increase in photo-coloration efficiency. The lifetime of the colored form varies from 17 to 200.8 s (acetone, 293 K) depending on substituents. Due to the presence of the benzothiazole moiety, merocyanines can effectively bind Zn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Cd<sup>2+</sup>, Mn<sup>2+</sup> ions. The addition of salts of these ions to spiropyran solutions results in the stabilization of the merocyanine in the form of intensely colored complexes. Composition, stability and spectroscopic characteristics of complexes have been investigated depending on the metal ion nature and substituents in ligand

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molecules. The colored complexes possess negative photochromism. The visible light irradiation causes their bleaching with quantum yields up to 48%. The benzothiazole substituted spiropyrans demonstrate ion driving photochromic transformation.

#### **Keywords**

photochromism, spiropyrans, ionochromism, complexes, quantum yield

### 1. Introduction

Due to the variety of external stimuli capable of initiating the chromogenic isomerization reaction of spiropyran-indolines, this class of organic compounds was the subject of continuous studies for more than 60 years [1]. Under the influence of temperature, the colorless spirocyclic form of the spiropyran-indolines is capable of isomerizing into a colored merocyanine form, causing thermochromic properties [2]. Following thermochromism, the photochromic properties of the spiropyran-indolines were soon described [3-5]. Subsequently, changes in the redox potential [6–8], as well as mechanical stress [9–11], were added to the number of external stimuli affecting the isomerization of spiropyran-indolines. All this leads to a wide range of applications of spiropyrans, such as optical data recording and storage [12-14], photostimulated control of biological functions [15] and many other application [16]. Separately, it is possible to single out the ionochromism of spiropyrans associated with the stabilization of the colored form upon interaction with charged particles. The simplest example of ionochromism is acidochromism. It is the protonation of the merocyanine form of spiropyran at the phenolate oxygen atom with the formation of a colored styryl salt [17-20], which is typical for almost all spiropyrans. However, ionochromism associated with the interaction of spiropyrans with metal

ions seems to be more interesting, since the resulting complexes of the merocyanine form are more diverse in their photophysical and photochemical properties than protonated merocyanines. The latter is due to the fact that their properties depend not only on the structure of the spiropyran but also on the nature of the metal ion [21,22]. In addition, an outstanding feature of the ionochromic transformation of spiropyrans is a possibility to drive complex formation with the help of light irradiation. The light can produce a coordinationally active form of the spiropyran or lead to a decomplexation reaction [23]. This phenomenon finds its application in different fields such as photostimulated metal ion sensors for real-time environmental monitoring and clinical diagnostics [24-27], visualization [28-32] and tracking [33] of mobile forms of a metal ion in biological objects, photoswitchable magnetics [34] and adsorbents [35,36]. For effective ionochromic transformation of spiropyrans, it is desirable to have an additional ligand group in its structure, which, along with the phenolate oxygen atom of merocyanine, will participate in the binding of the metal ion. In addition to increasing the binding ability, such a modification of the structure of spiropyran significantly affects its photochromic characteristics. Among various ligand groups [37], azole substituents are effective modifiers of the structure of spiropyrans to enhance the ionochromic effect. Earlier, we have described in detail the photoand ionochromism of benzoxazole- [38] and oxadiazole-substituted [39] spirobenzopyranindolines. In order to gain deeper insight into the influence of the nature of the azole substituent on both the properties of spiropyran and its complexes this work is aimed at obtaining and studying the photo- and ionochromic properties of new 8-benzothiazole substituted spirobenzopyran-indolines (SPP).

### 2. Experimental part

### 2.1. Materials and methods

NMR spectra were recorded using a "Varian Unity-300" (300 MHz, <sup>1</sup>H) and Bruker "AVANCE-600" (600 MHz, <sup>1</sup>H; 150 MHz, <sup>13</sup>C; 60 MHz, <sup>15</sup>N) spectrometer at 20 °C, the signals were referred with respect to the signal of residual protons of deutero-solvent CDCl<sub>3</sub> (<sup>1</sup>H:7.24 ppm, <sup>13</sup>C: 77.0 ppm). All chemical shifts are reported in the standard  $\delta$  notation of parts per million. FTIR spectra were collected on a Varian Excalibur 3100 spectrometer. High-resolution mass spectra were obtained from a TOF mass spectrometer with an ESI source (Bruker maXis). The instrument was operated in positive mode using an m/z range of 50–3000. The capillary voltage of the ion source was set at 4500 V. The nebulizer gas pressure was 0.4 bar, the drying gas flow was set to 4.0 L/min. Elemental analysis was carried out using a KOVO CHN analyzer. Melting points were determined on a Boetius hot stage apparatus. The electronic absorption spectra and kinetic curves of thermal and photochemical reactions of the studied compounds have been recorded on an "Agilent 8453" spectrophotometer equipped with a temperaturecontrolled cell. Irradiation light was brought into the thermostated cell compartment at 90° from a 200W high-pressure mercury lamp "Newport" equipped with glass filters for the allocation of mercury lines. The irradiation intensity has been determined by the help of a "Newport 2935" optical power meter. The irradiation intensity at 365 and 546 nm has been found to be (0.7-2.6)  $\cdot 10^{-5}$  and  $(0.6-1.4) \cdot 10^{-4}$  Einstein  $\cdot L^{-1}s^{-1}$  correspondingly. In experiments of determination of photo-discoloration quantum yields of complexes 546 nm light flux has been attenuated by iris diaphragm up to  $3 \cdot 10^{-6}$  Einstein  $\cdot L^{-1}s^{-1}$ . Numerical simulations were carried out with the simulation-adjustment program SA 3.3 (non-commercial software, Laboratoire des IMRCP, Université Paul Sabatier, Toulouse, France) [40]. In order to prepare solutions toluene, acetone of the spectroscopic grade and metal perchlorates have been used. Fluorescence emission and excitation spectra were collected using an Eclipse Varian spectrofluorimeter. Fluorescence quantum yields have been determined by the relative Parker-Rees method using cresyl violet in ethanol ( $\varphi = 0.51$ ) [41] as a reference with optically matched samples having absorbance of 0.1-0.2 at  $\lambda_{ex} = 540$  nm; the experimental error 20%.

### 2.2. Synthesis

3H-Indolinium salts **2a-f** were obtained by previously described procedures [42-44].

5-(Benzo[*d*]thiazol-2-yl)-4-hydroxyisophthalaldehyde (3). A mixture of benzo[*d*]thiazolylphenol **4** (2.28 g, 10 mmol), hexamethylenetetramine (8.40 g, 60 mmol) and trifluoroacetic acid (30 mL) was refluxed for 8 h, cooled, and a mixture of conc. HCl (14 mL) and H<sub>2</sub>O (28 mL) was added. The reaction mixture was poured into H<sub>2</sub>O (130 mL), the solid was filtered off, washed with water, dried and recrystalized from chlorobenzene. Yield 72%, m.p. 196-197 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.50 (1H, dt, *J* = 7.7 Hz, *J* = 1.2 Hz, H-5'); 7.58 (1H, dt, *J* = 7.8 Hz, *J* = 1.2 Hz, H-6'); 7.98 (1H, dd, *J* = 7.9 Hz, *J* = 0.6 Hz, H-4'); 8.05 (1H, dd, *J* = 7.8 Hz, *J* = 0.9 Hz, H-7'); 8.41 (1H, d, *J* = 1.9 Hz, H-6); 8.55 (1H, d, *J* = 2.1 Hz, H-4); 9.99 (1H, s, 3-CHO); 10.60 (1H, s, 1-CHO); 14.21 (1H, s, 4-OH). Elemental analyses: Found: C, 63.66; H, 3.11; N, 4.81%; C<sub>15</sub>H<sub>9</sub>NO<sub>3</sub>S; requires: C, 63.59; H, 3.20; N, 4.94%.

8-(Benzo[*d*]thiazol-2-yl)-3',3'-dimethylspiro[chromene-2,2'-indoline]-6-carbaldehydes (1a-f) (general procedure). A mixture of 3*H*-indolium salt 2a-f (1 mmol), triethylamine (0.14 mL, 1 mmol), and aldehyde 3 (0.28 g, 1 mmol) in toluene (10 mL) and 2-propanol (4 mL) were refluxed for 12 h and evaporated. The residue was purified by column chromatography on  $Al_2O_3$  with benzene as eluent and recrystallized and recrystallized from a mixture of heptane-toluene (1:1).

### 8-(Benzo[d]thiazol-2-yl)-1'-benzyl-3',3'-dimethylspiro[chromene-2,2'-indoline]-6-

**carbaldehyde** (**1a**). Yield 42%, m.p. 207-208 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 1.37 (3H, s, 3'-Me); 1.42 (3H, s, 3'-Me); 4.16 (1H, d, *J* = 16.3 Hz, 1'-CH<sub>2</sub>Ph); 4.55 (1H, d, *J* = 16.3 Hz, 1'-CH<sub>2</sub>Ph); 6.08 (1H, d, *J* = 10.4 Hz, H-3); 6.43 (1H, d, *J* = 7.7 Hz, H-7'); 6.98 (1H, dt, *J* = 7.4 Hz, *J* = 1.0 Hz, H-5'); 7.14 (1H, dd, J = 7.7 Hz, *J* = 1.3 Hz, H-4'); 7.58 (1H, ddd, *J* = 7.9 Hz, *J* = 1.3 Hz, *J* = 0.7 Hz, H-7"); 7.03 (1H, d, *J* = 10.4 Hz, H-4); 7.16-7.35 (7H, m, H-6', H-5", PhH); 7.45

(1H, ddd, J = 8.3 Hz, J = 7.2 Hz, J = 1.3 Hz, H-6"); 8.04 (1H, ddd, J = 8.2, J = 1.0, J = 0.7, H-4"); 7.78 (1H, d, J = 2.0, H-5); 8.95 (1H, d, J = 2.0, H-7); 10.02 (1H, s, 6-CHO). IR (cm<sup>-1</sup>): 1694 (C=O), 1645 (C=N), 1597 (C=C), 928 (C<sub>spiro</sub>-O). Elemental analyses: Found: C, 77.11; H, 5.15; N, 5.15%; C<sub>33</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub>S; requires: C, 77.02; H, 5.09; N, 5.44%. MS (ESI-TOF) *m/z*: found: 515.1788 [M+H]<sup>+</sup>. C<sub>33</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub>S. Calcd: 515.1787.

**8-(Benzo**[*d*]thiazol-2-yl)-5'-bromo-1',3',3'-trimethylspiro[chromene-2,2'-indoline]-6carbaldehyde (1b). Yield 45%, m.p. 239-240 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.28 (3H, s, 3'-Me); 1.31 (3H, s, 3'-Me); 2.70 (3H, s, 1'-Me); 5.96 (1H, d, *J* = 10.4 Hz, H-3); 6.48 (1H, d, *J* = 8.2 Hz, H-7'); 7.06 (1H, d, *J* = 10.4 Hz, H-4); 7.25 (1H, d, *J* = 2.0 Hz, H-4'); 7.33 (1H, ddd, *J* = 8.1 Hz, *J* = 7.3 Hz, *J* = 1.1 Hz, H-5"); 7.38 (1H, dd, *J* = 8.2 Hz, *J* = 2.0 Hz, H-6'); 7.45 (1H, ddd, *J* = 8.3 Hz, *J* = 7.2 Hz, *J* = 1.3 Hz, H-6"); 7.65 (1H, ddd, *J* = 7.9 Hz, *J* = 1.3 Hz, *J* = 0.7 Hz, H-7"); 7.78 (1H, d, *J* = 2.1 Hz, H-5); 8.01 (1H, ddd, *J* = 8.2 Hz, *J* = 1.1 Hz, *J* = 0.7 Hz, H-4"); 8.92 (1H, d, *J* = 2.1 Hz, H-7), 9.99 (1H, d, 6-CHO). IR (cm<sup>-1</sup>): 1691 (C=O), 1600 (C=N), 1580 (C=C), 931 (C<sub>spiro</sub>-O). Elemental analyses: Found: C, 62.54; H, 4.01; N, 5.32%; C<sub>27</sub>H<sub>21</sub>BrN<sub>2</sub>O<sub>2</sub>S; requires: C, 62.67; H, 4.09; N, 5.41%. MS (ESI-TOF) *m/z*: found 517.0580 [M+H]<sup>+</sup>. C<sub>27</sub>H<sub>21</sub>BrN<sub>2</sub>O<sub>2</sub>S. Calcd: 517.0579 (<sup>79</sup>Br).

**8-(Benzo**[*d*]thiazol-2-yl)-5'-chloro-1',3',3'-trimethylspiro[chromene-2,2'-indoline]-6carbaldehyde (1c). Yield 46%, m.p. 243-244 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.28 (3H, s, 3'-Me); 1.31 (3H, s, 3'-Me); 2.71 (3H, s, 1'-Me); 5.96 (1H, d, *J* = 10.4 Hz, H-3); 6.52 (1H, d, *J* = 8.2 Hz, H-7'); 7.06 (1H, d, *J* = 10.4 Hz, H-4); 7.12 (1H, d, *J* = 2.1 Hz, H-4'); 7.23 (1H, dd, *J* = 8.2 Hz, *J* = 2.1 Hz, H-6'); 7.32 (1H, ddd, *J* = 8.2 Hz, *J* = 7.2 Hz, *J* = 1.2 Hz, H-5''); 7.43 (1H, ddd, *J* = 8.3 Hz, *J* = 7.2 Hz, *J* = 1.3 Hz, H-6''); 7.64 (1H, ddd, *J* = 7.9 Hz, *J* = 1.3 Hz, *J* = 0.7 Hz, H-7''); 7.78 (1H, d, *J* = 2.1 Hz, H-5); 8.01 (1H, ddd, *J* = 8.2 Hz, *J* = 1.0 Hz, *J* = 0.7 Hz, H-4''); 8.92 (1H, d, *J* = 2.1 Hz, H-7), 9.99 (1H, s, 6-CHO). IR (cm<sup>-1</sup>): 1691 (C=O), 1599 (C=N), 1581 (C=C), 933 (C<sub>spiro</sub>-O). Elemental analyses: Found: C, 68.43; H, 4.40; N, 6.01%; C<sub>27</sub>H<sub>21</sub>ClN<sub>2</sub>O<sub>2</sub>S; requires: C, 68.56; H, 4.48; N, 5.92%. MS (ESI-TOF) m/z: found 473.1085 [M+H]<sup>+</sup>. C<sub>27</sub>H<sub>21</sub>ClN<sub>2</sub>O<sub>2</sub>S. Calcd: 473.1085.

8-(Benzo[d]thiazol-2-yl)-1',3',3'-trimethyl-5'-(trifluoromethyl)spiro[chromene-2,2'indoline]-6-carbaldehyde (1d). Yield 48%, m.p. 212-213 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.30 (3H, s, 3'-Me); 1.37 (3H, s, 3'-Me); 2.77 (3H, s, 1'-Me); 5.99 (1H, d, J = 10.4 Hz, H-3); 6.65 (1H, d, *J* = 8.1 Hz, H-7'); 7.10 (1H, d, *J* = 10.4 Hz, H-4); 7.30 (1H, ddd, *J* = 8.1 Hz, *J* = 7.2 Hz, *J* = 1.0 Hz, H-5"); 7.39 (1H, d, J = 1.8 Hz, H-4'); 7.43 (1H, ddd, J = 8.3 Hz, J = 7.2 Hz, J = 1.2 Hz, H-6"); 7.50-7.59 (2H, m, H-6, H-7"); 7.79 (1H, d, *J* = 2.0 Hz, H-5); 8.00 (1H, ddd, *J* = 8.2 Hz, *J* = 1.7 Hz, J = 0.9 Hz, H-4"); 8.93 (1H, d, J = 2.0 Hz, H-7); 10.00 (1H, s, 6-CHO). <sup>13</sup>C NMR (150) MHz, CDCl<sub>3</sub>, δ): 19.37 (3'-Me), 25.22 (3'-Me), 29.18 (N'-Me), 51.97 (C-3'), 107.42 (C-7'), 108.76 (C-2/2'), 119.00 (C-4', q, J = 3.7), 119.56 (C-3), 119.98 (C-4a), 120.32 (C-7"), 121.16 (C-5"), 122.20 (5'-СF<sub>3</sub>, к, J = 32.1), 122.74 (С-4"), 124.16 (С-5'), 125.03 (С-4а"), 126.15 (С-6"), 125.80 (C-6', q, J = 4.0), 127.64 (C-5), 129.85 (C-6), 130.10 (C-4), 133.68 (C-7), 135.97 (C-8), 137.39 (C-3a'), 151.03 (C-7a'), 151.73 (C-7a"), 156.08 (C-1a), 160.52 (C-2"), 190.49 (6-CHO). <sup>15</sup>N NMR (60 MHz, CDCl<sub>3</sub>,  $\delta$ ): 97.30 (N-1'), 303.81 (N-3"). IR (cm<sup>-1</sup>): 1695 (C=O), 1600 (C=N), 1581 (C=C), 1096 (C-F), 920 (C<sub>spiro</sub>-O). Elemental analyses: Found: C, 66.45; H, 4.11; N, 5.42%; C<sub>28</sub>H<sub>21</sub>F<sub>3</sub>N<sub>2</sub>O<sub>2</sub>S; requires: C, 66.39; H, 4.18; N, 5.53%. MS (ESI-TOF) *m/z*: found  $507.1349 [M+H]^+$ . C<sub>28</sub>H<sub>21</sub>F<sub>3</sub>N<sub>2</sub>O<sub>2</sub>S. Calcd: 507.1348.

8-(Benzo[*d*]thiazol-2-yl)-1',3',3'-trimethyl-5'-nitrospiro[chromene-2,2'-indoline]-6carbaldehyde (1e). Yield 39%, m.p. 282-283 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 1.33 (3H, s, 3'-Me); 1.41 (3H, s, 3'-Me); 2.90 (3H, s, 1'-Me); 5.99 (1H, d, *J* = 10.4 Hz, H-3); 6.66 (1H, d, *J* = 8.7 Hz, H-7'); 7.14 (1H, d, *J* = 10.4 Hz, H-4); 7.32 (1H, ddd, *J* = 8.2 Hz, *J* = 7.3 Hz, *J* = 1.1 Hz, H-5"); 7.47 (1H, ddd, *J* = 8.4 Hz, *J* = 7.2 Hz, *J* = 1.3 Hz, H-6"); 7.57 (1H, ddd, *J* = 8.0 Hz, *J* = 1.3 Hz, *J* = 0.7 Hz, H-7"); 7.83 (1H, d, *J* = 2.0 Hz, H-5); 8.04 (1H, ddd, *J* = 8.2 Hz, *J* = 1.7 Hz, *J* = 0.9 Hz, H-4"); 8.07 (1H, d, *J* = 2.3 Hz, H-4'); 8.31 (1H, dd, *J* = 8.7 Hz, *J* = 2.3 Hz, H-6'); 8.97 (1H, d, *J* = 2.0 Hz, H-7); 10.03 (1H, s, 6'-CHO). IR (cm<sup>-1</sup>): 1692 (C=O), 1600 (C=N), 1581 (C=C), 931 (C<sub>spiro</sub>-O). ). Elemental analyses: Found: C, 66.95; H, 4.27; N, 8.77%; C<sub>27</sub>H<sub>21</sub>N<sub>3</sub>O<sub>4</sub>S; requires: C, 67.07; H, 4.38; N, 8.69%. MS (ESI-TOF) *m/z*: found 484.1326 [M+H]<sup>+</sup>. C<sub>27</sub>H<sub>21</sub>N<sub>3</sub>O<sub>4</sub>S. Calcd: 484.1325.

**8-(Benzo[d]thiazol-2-yl)-5'-bromo-3',3'-dimethyl-1'-propylspiro[chromene-2,2'indoline]-6-carbaldehyde (1f).** Yield 44%, m.p. 195-196 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 0.87 (3H, t, *J* = 7.4, 1'-CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); 1.27 (3H, s, 3'-Me); 1.29 (3H, s, 3'-Me); 1.53-1.70 (2H, m, 1'-CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); 2.98-3.15 (2H, m, 1'-CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); 5.96 (1H, d, *J* = 10.4 Hz, H-3); 6.51 (1H, d, *J* = 8.2 Hz, H-7'); 7.04 (1H, d, *J* = 10.4 Hz, H-4); 7.24 (1H, d, *J* = 2.0 Hz, H-4'); 7.32 (1H, ddd, *J* = 8.2 Hz, *J* = 7.2 Hz, *J* = 1.2 Hz, H-5"); 7.36 (1H, dd, *J* = 8.2 Hz, *J* = 2.0 Hz, H-6'); 7.44 (1H, ddd, *J* = 8.3 Hz, *J* = 7.2 Hz, *J* = 1.3 Hz, H-6"); 7.65 (1H, ddd, *J* = 7.9 Hz, *J* = 1.3 Hz, *J* = 0.7 Hz, H-7"); 7.77 (1H, d, *J* = 2.0 Hz, H-5); 8.01 (1H, ddd, *J* = 8.2 Hz, *J* = 1.1 Hz, *J* = 0.7 Hz, H-4"); 8.92 (1H, d, *J* = 2.0 Hz, H-7); 9.99 (1H, s, 6-CHO). IR (cm<sup>-1</sup>): 1690 (C=O), 1599 (C=N), 1580 (C=C), 943 (C<sub>spiro</sub>-O). Elemental analyses: Found: C, 63.92; H, 4.49; N, 5.04%; C<sub>29</sub>H<sub>25</sub>BrN<sub>2</sub>O<sub>2</sub>S; requires: C, 63.85; H, 4.62; N, 5.14%. MS (ESI-TOF) *m/z*: found 545.0893 [M+H]<sup>+</sup>. C<sub>29</sub>H<sub>25</sub>BrN<sub>2</sub>O<sub>2</sub>S. Calcd: 545.0892 (<sup>79</sup>Br).

### 2.3 Single crystal X-ray diffraction studies

The single crystals of complex **1f-Zn** have been grown from acetone solution. The data collection have been performed on an Agilent SuperNova diffractometer using microfocus X-ray source with copper anode ( $\lambda = 1.54184$ ) and Atlas S2 CCD detector. The diffraction data of **1f-Zn** were obtained at 103(4) K. Single crystals of C<sub>29</sub>H<sub>25</sub>BrN<sub>4</sub>O<sub>8</sub>SZn are triclinic, *a* = 10.8733(2) Å, *b* = 14.7522(3) Å, *c* = 20.6289(5) Å, *a* = 71.798(2)°, *β* = 76.023(2)°, *γ* = 73.251(2)°, *V* = 2968.00(12) Å<sup>3</sup>, *Z* = 4, *T* = 103(4) K,  $\mu$ (Cu K $\alpha$ ) = 3.882 mm<sup>-1</sup>, *Dcalc* = 1.645 g, space group P-1 (no. 2). 12404 reflections measured (6.888° ≤ 2Θ ≤ 152.554°), 12404 unique (R<sub>sigma</sub> = 0.0394) which were used in all calculations. Twinned data refinement Scales: 0.753(2); 0.247(2). The final *R*<sub>1</sub> was 0.0572 (I > 2 $\sigma$ (I)) and *wR*<sub>2</sub> was 0.1634 (all data). The collection of reflexes, determination and refinement of unit cell parameters were performed by using the

specialized CrysAlisPro 1.171.38.41 software suite [45]. The structures were solved by using ShelXT program [46], structure refinement was also performed with ShelXL program [47]. Molecular graphics were rendered and prepared for publication with the Olex2 software suite [48]. The complete X-ray diffraction datasets were deposited at the Cambridge Crystallographic Data Center (CCDC 1977817).

### 3. **Results and discussion**

### 3.1 Synthesis

8-Benzothiazolyl-6-formyl substituted spirobenzopyrans **1a-f** have been obtained by the interaction of 3*H*-indolium salts **2a-f** in the presence of triethylamine as a base with 5-benzothiazolyl substituted 4-hydroxy-isophthalaldehyde **3** obtained by Duff-formylation of the phenol **4** (Scheme 1).



Scheme 1. Synthesis of 8-Benzothiazolyl-6-formyl substituted spirobenzopyrans

The structure of the compounds **1a-f** has been established using <sup>1</sup>H NMR spectroscopy (<sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>15</sup>N NMR), heteronuclear correlation spectroscopy (COSY <sup>1</sup>H-<sup>1</sup>H, HSQC <sup>1</sup>H-<sup>13</sup>C, HMBC <sup>1</sup>H-<sup>13</sup>C, HMBC <sup>1</sup>H-<sup>15</sup>N), mass spectrometry and elemental analysis.

The <sup>1</sup>H NMR spectra of spiropyrans **1a-f** contain two signals of *geminal* methyl groups, which are prochiral due to the presence of a stereogenic tetrahedral carbon atom; signals of protons of the *N*-alkyl group (Me, Pr, CH<sub>2</sub>Ph) of the indoline moiety in the high field, as well as the signal of the formyl proton and several groups of interrelated proton signals in the low field region of the spectrum related to the indoline, benzopyran, and benzothiazole fragments.

Prochirality of the protons of the methylene group of *N*-benzyl substituent in the indoline fragment of spiropyran **1e** leads to diastereotopic splitting of proton signals of this group which appear as two one proton doublets at 4.16 and 4.55 ppm, respectively.

Full assignment of signals of hydrogen, carbon and nitrogen atoms of the spiropyran **1d** has been carried out based on the data of two-dimensional heteronuclear correlation spectroscopy COSY <sup>1</sup>H-<sup>1</sup>H, HSQC <sup>1</sup>H-<sup>13</sup>C, HMBC <sup>1</sup>H-<sup>13</sup>C, HMBC <sup>1</sup>H-<sup>15</sup>N.

The signal of the carbon atom of the 5'-trifluoromethyl group of the indoline fragment of the spiropyran **1d** appears at  $\delta$  122.20 ppm as a quartet with J = 32.1 Hz, and the signals of carbon atoms 4-C and 6-C appear as quartets at  $\delta$  119.00 (J = 3.7 Hz) and 125.80 ppm. (J = 4.0 Hz) respectively.

All of the mentioned above NMR spectroscopy data unambiguously confirm the structure of the obtained compounds **1a-f**. The absence of proton signals of the indoline and benzopyran moieties in the spectral regions typical for the open merocyanine form [49,50] indicates that the obtained spiropyrans are in the spirocyclic form in CDCl<sub>3</sub> solution.

### 3.2 Spectroscopic properties of spiropyrans

In toluene, the obtained spiropyrans **1a-f** are completely in cyclic form, which is evidenced by the absence of absorption in the visible spectral region at  $\lambda$ > 400 nm. The electronic absorption spectra of the cyclic forms **A** (Scheme 2) of spiropyrans **1a-f** are characterized by two absorption bands: a structured long-wavelength band with maxima in the range 344–346 and 361–364 nm ( $\varepsilon$  =7300–19600 and 6400–20100 M<sup>-1</sup>·cm<sup>-1</sup>) and a more intense short-wavelength band possessing maxima at 290 - 299 nm ( $\varepsilon$  = 21500 – 33000 M<sup>-1</sup>·cm<sup>-1</sup>) (Table 1, Fig. S1).

### Table 1

Data of absorption spectra ( $\lambda_{max}$ ,  $\varepsilon$ ) and kinetic properties ( $\tau(B)$ ,  $\Phi_{AB}$ ,  $\Phi_{BA}$ ) of SPP **1a-f**, *T*=293K (<sup>\*</sup> - shoulder).

		Toluene		Acetone			
SPP	isomer	$\lambda_{\max}$ , nm	$\tau(B),$	$\lambda_{\max}$ , nm	$\tau(B),$	Ф	Ф
		$(\boldsymbol{\varepsilon} \cdot 10^{-3}, \mathrm{M}^{-1} \cdot \mathrm{cm}^{-1})$	S	$(\boldsymbol{\varepsilon} \cdot 10^{-3}, \mathrm{M}^{-1} \cdot \mathrm{cm}^{-1})$	s	$\Psi_{AB}$	$\Psi_{BA}$
1a	Α	290 (21.5), 321 <sup>*</sup> (13.1), 346 (7.3), 364 (6.4)	23.1	346 (10.6), 363 (9.3)	101.8	0.16	0.0008
	В	444, 647	444, 647				
1b	Α	294 (25.5), 321 <sup>*</sup> (16.1), 345 (8.5), 363 (8.3)	25.4	345 (8.2), 362 (8.0)	177.7	0.20	0.0005
	В	448, 648		403 (16.2), 595 (49.1)			
1c	A	299 (24.8), 321 <sup>*</sup> (16.8), 345 (9.0), 363 (8.5)	23.6	345 (8.7), 362 (8.3)	200.8	0.17	0.0004

		Journ	<u>al Pre-r</u>	1001,04 (15 0)			
	B	447 647		404 (15.2),			
	D	117,017		595 (49.2)			
		$208(240) 320^*$					
		298 (24.9), 520		344 (8.5),			0.0007
	Α	(18.6), 344 (10.9),		2(1 (9 ()			
1d		362 (10.6)	22.7	361 (8.6)	33.0	0.15	
						0.15	
	B	119 611		407 (14.2),			
	D	++2, 0++		600 (39.8)			
		207 (22.0) 205					
	А	297 (33.0), 305		344 (21.6),			
		(22.6), 322 (22.7),					
		344 (19.6) 361		360 (23.6),			
1e		544 (17.0), 501	4.7	381* (14.0)	17.0	0.44	< 0.0001
		(20.1), 372 <sup>*</sup> (11.7)					
			0	415 (19.4),			
	В	466, 655					
				617 (54.6)			
		297 (33.0), 322*					
	•	(21.3) 346 (11.4)		346 363			
1f	A	(21.3), 340 (11.4),		540, 505			
		364 (11.0)	41.7		90.1	0.27	0.0010
				410.			
	В	444, 647		,			
				601 (44.7)			
1		1					1

Except for the nitro group, the substituents  $R^1$  and  $R^2$  in the indoline part of the spiropyran molecule have practically no effect on the position of the absorption bands of the spirocyclic form. The presence of a nitro group at position 5 of the indoline fragment significantly enhances the absorptivity of the cyclic form in the visible spectroscopic region due to the appearance of an additional charge transfer band [51].

Solutions of SPP **1a-f** in the more polar acetone are slightly colored (Fig. 1) due to the equilibrium between the cyclic and merocyanine forms (Scheme 2), which is significantly shifted

towards the cyclic form. The approximate values of the equilibrium constant estimated based on the data of the molar coefficients of the merocyanine forms (*vide infra*), did not exceed  $10^{-2}$ . In the case of nitro-substituted SPP **1e**, passing to a more polar solvent caused a bathochromic shift of the long-wavelength absorption band of the cyclic form by 9 nm, which is characteristic of the charge transfer band, while for the other SPPs, an increase in the polarity of the medium did not affect the position of the absorption bands of cyclic forms.



**Fig. 1**. Absorption spectra of SPP **1a-f** in acetone,  $C(SPP)=3 \cdot 10^{-5}$  M, T = 293 K.

The merocyanine isomers **B** of spiropyrans 1a-f in toluene are characterized by two absorption bands located in the region of 444 - 466 and 644 - 655 nm. The longest wavelength absorption has been demonstrated by the merocyanine of 5-nitro-substituted SPP 1e. When increased the polarity of the solvent, a hypsochromic shift of the absorption bands of merocyanines occurs. Based on the previously obtained data [38, 39], the influence of the nature of the azole substituent at position 8 of the benzopyran part of the molecule consists of a bathochromic shift of the absorption bands of the merocyanine in the range oxadiazole benzoxazole - benzothiazole.



Scheme 2. Transformation of studed SPP

## 3.3 Kinetics of thermal and photochemical transformations

Irradiation of SPP **1a-f** solutions with UV light in the absorption region of their spirocyclic isomers leads to their coloration as a result of the formation of the merocyanine isomer **B** (Fig. 2a, Scheme 2).



**Fig.2a**. Evolution of SPP **1b** spectra in acetone **Fig. 2b**. A relaxation kinetic curve of SPP **1b** upon UV light irradiation, T = 293 K,  $\lambda_{irr} = 365$  in acetone, T = 293 K. nm, time between spectra 10 s.

After switching off the irradiation source, discoloration of the solutions occurs due to the thermal recyclization reaction  $\mathbf{B} \to \mathbf{A}$ . The kinetics of the dark relaxation process  $\mathbf{B} \to \mathbf{A}$  in solutions of compounds **1a-e** are satisfactorily described by the monoexponential function (Fig. 2b). In the general case, the time constant of the relaxation process is  $\tau = (k_{BA} + k_{AB})^{-1}$ . However, taking into account that the equilibrium constant  $K = k_{AB}/k_{BA} << 1$ ,  $k_{AB} << k_{BA}$  and, therefore,  $\tau(B)$  $= k_{BA}^{-1}$ . The time constant of the relaxation process  $\tau(B)$  for spiropyrans **1a-e** is in the range 4.7– 200.8 s (Table 1) and is determined by both the structure of the molecule and the parameters of the medium. An increase in the kinetic stability of the merocyanine forms of SPP is observed with an increase in the polarity of the medium upon passing from toluene to acetone. At the same time, strong electron-withdrawing groups in the indoline fragment (CF<sub>3</sub>, NO<sub>2</sub>), on the contrary, reduce its stability.

Irradiating the preliminary colored solutions of SPP **1a-f** with visible light in the absorption region of the merocyanine forms accelerates the bleaching process (Fig.2b, for instance, irradiation of a colored solution of **1b** reduces relaxation time from 177.7 s to 123.4 s). This is a consequence of the presence of a reverse photochemical reaction of cyclization of the merocyanine form. Therefore, the investigated spiropyrans exhibit positive photochromism with thermal and photochemical back reactions. Thus, the general kinetic scheme characterizing the photochemical and thermal processes will have the following form (scheme 3):

$$A \xrightarrow[\stackrel{h\underline{v} (\Phi_{AB})}{\underbrace{\stackrel{h\underline{v} (\Phi_{BA})}{\underbrace{\underline{A} (k\_BA)}}} B$$

### Scheme 3.

The scheme 3 includes the forward photoinduced reaction of the formation of the

merocyanine from the spirocyclic form; spontaneous thermal process of the recyclization of the merocyanine into the initial spiroform; as well as the back photochemical pathway of the recyclization of the merocyanine form into the spirocyclic one. Taking into account that  $k_{AB} << k_{BA}$  the contribution of the forward thermal reaction of the merocyanine formation can be neglected. It means that  $k_{AB}$  can be supposed to equal to 0.

In order to evaluate the efficiency of the photo-coloration and photo-bleaching, the quantum yields  $\Phi_{AB}$  and  $\Phi_{BA}$  of the corresponding photoreactions have been calculated. For this purpose, the photokinetic method has been applied [52]. In accordance with Scheme 3, kinetic curves describing the photo-coloration of an SPP solution under UV light irradiation can be described by equation (1):

$$\frac{d[B]}{dt} = \Phi_{AB} \varepsilon_A^{irr} I_0^{irr} F^{irr} l^{irr} (C - [B]) - (\Phi_{BA} \varepsilon_B^{irr} I_0^{irr} F^{irr} l^{irr} + k_{BA})[B]$$
(1)

When the colored solution is irradiated with visible light,  $\Phi_{AB} = 0$  and equation (1) can be represented as:

$$-\frac{d[B]}{dt} = (\Phi_{BA} \varepsilon_B^{irr} I_0^{irr} F^{irr} l^{irr} + k_{BA})[B]$$
<sup>(2)</sup>

where  $F = (1-10^{-D'})/D'$  – photokinetic factor;

D' – total absorbance at the irradiation wavelength;

(') – indicates a certain irradiation wavelength;

 $I'_0$  – the intensity of monochromatic light;

 $\varepsilon'_{A}$  and  $\varepsilon'_{B}$  – molar absorption coefficients of isomeric forms A and B;

 $\Phi_{AB}$  and  $\Phi_{BA}$  – quantum yields of photoreactions  $A \rightarrow B$  and  $B \rightarrow A$ ;

C – the total concentration of SPP;

[*A*], [*B*] – the concentrations of the spirocyclic and the merocyanine form of SPP at a given time;

 $k_{\rm BA}$  – rate constant of thermal reaction **B** $\rightarrow$ **A**.

It is worth noting that equations (1)-(2) are acceptable under the premise that  $\Phi_{BA}$  values do not depend on the irradiation wavelength. In other words,  $\Phi_{BA}^{546} = \Phi_{BA}^{365}$ . The numerical solution of the system of equations (1) - (2) for two experiments: photocoloration

(Fig. 3a) and photobleaching (Fig. 3b) (taking into account C = [A] + [B] - mass balance equation and  $D(\lambda) = \varepsilon(\lambda)_A[A] + \varepsilon(\lambda)_B[B]$  – Beer's law for absorbance at selected wavelength) has allowed to obtain the  $\Phi_{AB}$  and  $\Phi_{BA}$  (Table 2).





Fig. 3a. Dependence of absorbance at the selected wavelength of SPP 1b in acetone  $(3.1 \cdot 10^{-5} \text{ M})$  at 293 K upon irradiation with UV ( $\lambda$ = 365 nm, I =  $1.4 \cdot 10^{-5}$  Einstein·L<sup>-1</sup>·cm<sup>-1</sup>) light.  $\lambda_{obs}$ = 365 ( $\Box$ ), 546 ( $\odot$ ) and 595 ( $\Delta$ ) nm. Points are experimental data, lines are results of kinetic modeling.

Fig. 3b. Dependence of absorbance at the selected wavelength of SPP 1b in acetone  $(3.1 \cdot 10^{-5} \text{ M})$  at 293 K upon irradiation with Vis ( $\lambda = 546 \text{ nm}$ , I =  $1.1 \cdot 10^{-4}$  Einstein·L<sup>-1</sup>·cm<sup>-1</sup>) light.  $\lambda_{obs} = 365 (\Box)$ , 546 ( $\circ$ ) and 595 ( $\Delta$ ) nm. Points are experimental data, lines are results of kinetic modeling.

As can be seen from the data presented, SPP **1a-f** are effective photochromic compounds characterized by the photo-coloration quantum yields as high as 0.44 for 5-nitro substituted SPP **1e**. At the same time, the efficiency of the reverse photobleaching reaction is more than two orders of magnitude lower, which markedly distinguishes benzothiazole substituted SPP **1a-f** from the previously described analogs bearing other azole moieties at position 8 of the

### 3.4 Ionochromic transformation of spiropyrans

Spiropyrans **1a-f** exhibited an ionochromic effect. The addition of Zn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, (in the form of well soluble perchlorates or nitrates) to solutions of SPP in acetone caused their slow staining. This is accompanied by the appearance of intense absorption bands in the visible region of the spectrum (Fig. 4), the position of the maxima of which depended both on the nature of the added ion and, in the case of Ni<sup>2+</sup>, Cu<sup>2+</sup>, on the concentration of the metal perchlorates. Upon addition of  $Cd^{2+}$ ,  $Mn^{2+}$  perchlorates the coloration has been observed only for SPP **1a-c**, **f**, while SPP 1d, e bearing strong acceptor groups in the indoline fragment have not exhibited an ionochromic effect in the presence of these ions. The appearance of the coloration of the SPP solutions is caused by the formation of complex compounds of the merocyanine form, whose stability, due to the bidentate site, including the phenolate oxygen atom and the azole heteroatom, becomes higher compared to unbound merocyanine (Scheme 3). The structure of the complex compound SPP 1f with zinc ions in the crystal has been studied by the XRD method. Single crystals of compound  $1f - Zn(NO_3)_2$  have been obtained in the form of orange plates by slow evaporation of acetone solution of SPP 1f with 1 equivalent of  $Zn(NO_3)_2$  at room temperature. We have used nitrate instead of zinc perchlorate in experiments on crystal growth since in the case of perchlorate, the complexes have greater solubility and therefore it was not possible to obtain acceptable crystals. The complex 1f-  $Zn(NO_3)_2$  crystallizes in the triclinic space group P-1 with two non-equivalent molecules in a centrosymmetric unit cell, the difference in the side chain conformation (Fig. S8 Suppl. Inform.). The coordination sphere of the Zn atom (refer to Figure 5) is described as a distorted octahedral. The zinc ion is coordinated by the nitrogen atom of benzothiazole and the phenol oxygen atom of merocyanine molecules and by the oxygen atoms of two chelating nitrate ions. The merocyanine ligand is in the TTC

conformation. The bond distances and angles are within expected values.



**Fig. 4**. Absorption spectra of pure SPP **1a** and absorption spectra obtained after addition of the excess of the metal perchlorates in acetone,  $C(1a)=3\cdot10^{-5}$  M,  $C(M^{2+})=1.5\cdot10^{-4}$  M, T=293 K.



**Fig.** 5. Molecular structure of compound **1f-** Zn(NO<sub>3</sub>)<sub>2</sub> in the solid-state. The second molecule difference in the side chain conformation is omitted for clarity. Selected bond lengths [Å]: Zn1–O1 1.943 (4), Zn1–O2 2.083 (4), Zn1–O3 2.344 (5), Zn1–O4 2.213 (6), Zn1–O5 2.115 (5), Zn1–N1 2.040 (5). Showing displacement ellipsoids drawn at the 50% probability level.

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The composition and stability of SPP complexes in acetone solutions have been determined by means of the spectrophotometric method, which we had described in detail earlier [38,53]. It has been revealed that, depending on the metal and substituents in the spiropyran molecule, both the formation of 1:1 complexes (metal-merocyanine) **MB** and stepwise formation of 1:1 (**MB**) and 1:2 (**MB**<sub>2</sub>) complexes are possible. In the latter case, the long-wavelength absorption band observed in the spectrum of the SPP solution showed a slight hypochromic shift with an increasing concentration of added metal perchlorates (Fig.6b, S7). In the case of the formation of only 1:1 complexes, an increase in the metal ion concentration has caused only an increase in the intensity of the long-wavelength absorption band, but not its shift (Fig.6a, S3, S4, S6). The experimental dependences of the absorbance of SPP solutions on the concentration of a metal ion have been satisfactorily described within the framework of the selected complexation models. The calculated values of the logarithms of the stability constants, as well as the spectroscopic properties of the complex compounds, are presented in Table 2.



Fig. 6a. Alteration of the absorption spectrum of SPP 1b upon the addition of different amounts of the cobalt perchlorate in acetone.  $C(1b) = 3.88 \cdot 10^{-5}$  M, T = 293 K. Insert – Dependence of the absorbance at the maximum



Fig. 6b. Alteration of the absorption spectrum of SPP 1b upon the addition of different amounts of the nickel perchlorate in acetone.  $C(1b) = 3.45 \cdot 10^{-5}$  M, T = 293 K. Insert – dependence of the absorbance at 520 absorption on the cobalt concentration. Pointsand 570 nm on the nickel concentration.are experimental data; the line is a result of the<br/>theoretical calculation.Points are experimental data; the line is a<br/>result of the theoretical calculation.

As can be seen from the data presented, SPP **1a-f** form moderately stable complexes with the studied ions. Their stability mainly increases in the range Cd<sup>2+</sup>, Mn<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup> that is typical for the ligands with N, O chelating cites. The enhancement of the electron-withdrawing properties of the substituent at position 5 of the indoline fragment suppresses the ability of spiropyrans to form complexes. It should also be noted that, in comparison with benzoxazolyl-substituted [38] spirobenzopyran-indolines, the benzothiazolyl-substituted SPPs under study form less stable complexes. Previously, a similar effect was observed for spironaphthopyran analogs and was associated with a decrease in the basicity of the phenolate oxygen atom of the merocyanine form upon passing from benzoxazole to benzothiazole [53]. Complexation causes a hypsochromic shift of the long-wavelength absorption band of the ligand by more than 100 nm. The complexes of the 1:2 composition exhibit longer wavelength absorption in comparison with the 1:1 complexes.

### 3.5 *Photoinitiated processes in the complexes*

Solutions of SPP complexes are sensitive to light. This is especially true for complexes with diamagnetic ions such as  $Cd^{2+}$ ,  $Zn^{2+}$ . Their solutions are not stable even at room lighting. As a result, the reaction of their formation must be carried out in the dark. Under the action of an intense source of visible radiation, solutions of the  $Cd^{2+}$ ,  $Zn^{2+}$  complexes completely decolorize in a short period of time. Solutions of paramagnetic ion complexes are more stable. An exception is the Mn complexes, whose solutions undergo rapid discoloration, like solutions of the  $Cd^{2+}$ ,

Zn<sup>2+</sup> complexes. The bleaching process is caused by photo-cyclization of merocyanine, which is accompanied by the release of a metal ion from the complex [54] and is thermally reversible. Thus, SPP **1a-f** complexes possess the property of negative photochromism.





**Fig. 7a.** Evolution of absorption spectra of a **1b**-Zn<sup>2+</sup> solution (5.04 · 10<sup>-5</sup> M) in acetone under continuous irradiation ( $\lambda_{irr} = 546$  nm,  $I = 2.7 \cdot 10^{-6}$  Einstein·L<sup>-1</sup>·s<sup>-1</sup>).

**Fig. 7b**. Kinetic traces from monitoring the absorbance at 491 nm (absorption maximum of the complex) and 546 nm (maximum of irradiation source) during the photoreaction under continuous 546 nm irradiation of a **1b**-Zn<sup>2+</sup> solution in acetone at 293 K (Fig.7a). The geometric shapes indicate experimental data, the solid lines are the calculated results.

In order to determine complex dissociation quantum yields a photokinetic method based on equation (2) and described in detail earlier [54] has been used. The kinetic equation describing the photodissociation of the complex under steady-state irradiation can be represented as:

$$-d[\boldsymbol{M}\boldsymbol{B}]/dt = I^{0} \boldsymbol{\Phi}_{r} (1 - 10^{-\varepsilon' |\boldsymbol{M}\boldsymbol{B}||}) - k_{\Delta} (C_{0} - [\boldsymbol{M}\boldsymbol{B}])$$
(3)

where  $I^0$  - incident photon flux (Einstein·L<sup>-1</sup>·s<sup>-1</sup>),  $\varepsilon'$  - molar extinction coefficient of **MB** at irradiation wavelength (M<sup>-1</sup>·cm<sup>-1</sup>), l - optical path length for the incident light (cm),  $k_{\Delta}$  – the observed rate constant for the complex formation of pseudofirst order,  $C_0$  is **MB** concentration at t = 0. The current value of the complex concentration [MB] can be obtained from the absorption spectra of a complex solution under its irradiation according to Beer's law [**MB**] =  $A_{\lambda}/\epsilon_{\lambda}l$ . The solution of the **MB** complex has been prepared in the dark by the addition of a metal perchlorate (taken at a 10-100 excess) to the SPP solution of the known concentration. These conditions can be calculated using complexation constant values thus providing the full transformation of the SPP into the complex of 1:1 composition. The experiment of the determination of the efficiency of photobleaching consisted of the irradiation of the exact volume of the MB complex solution with visible monochromatic light of the known intensity and simultaneously registration of the absorption spectra (Fig.7a). Kinetic curves at the absorption maximum of the complex and maximum of irradiation source were then fitted by the help of the equation (3) (Fig. 7b). The simulation results are shown in Table 2. The efficiency of photobleaching of the complexes sharply increases in the range of paramagnetic  $Co^{2+}$ ,  $Ni^{2+}$ , and  $Mn^{2+}$  ions and reaches 48% in the case of diamagnetic  $Zn^{2+}$  ions. The introduction of electron-withdrawing substituents into the indoline fragment significantly reduces the quantum yields of photoreaction. Compared with the complexes of benzoxazolyl- [38] and oxadiazolyl-substituted [39] spirobenzopyran-indolines, the complexes of the studied benzothiazolyl substituted analogs demonstrate the highest efficiency of the photobleaching reaction.

It should be also noted that complex compounds of SPP **1a-f** with  $Zn^{2+}$  and  $Cd^{2+}$  ions exhibit fluorescence in the red spectral region (table 2, fig.S5).

### Table 2

The calculated values of the effective complexation constants ( $K_i^{eff}$ ), the spectral absorption ( $\lambda_{max}$ ,  $\varepsilon$ ) and spectral luminescent properties ( $\lambda^{flu}$ ,  $\varphi^{flu}$ ) and the quantum yields ( $\Phi_{546}$ ) of photodissociation of SPP complexes with metals in acetone. T = 293 K.

SPP	М		MB	$MB_2$		
		$log K_1^{e\!f\!f}$	$\lambda_{max}$ , nm	$\lambda^{flu}$ , nm	$\varPhi_{546}$	$logK_2^{e\!f\!f}$

			$(\varepsilon \cdot 10^{-4} \mathrm{M}^{-1} \cdot \mathrm{cm}^{-1})$	$(\varphi^{flu})$			$(\varepsilon \cdot 10^{-4} \mathrm{M}^{-1} \cdot \mathrm{cm}^{-1})$
	Со	5.56±0.01	508 (2.81)	_	0.0007	_	_
	Cu	6.6±0.8	490 (3.41)	_	_	8.1±0.4	508 (5.56)
1.	Ni	5.9±0.1	527 (3.29)	_	0.0008	6.70±0.06	543 (5.42)
1a	Zn	6.00±0.02	502 (3.02)	626 (0.066)	0.47	_	-
	Cd	2.85±0.01	530 (3.73)	632 (0.067)	0.32	-	-
	Mn	3.63±0.01	522 (2.77)	_	0.084	_	-
	Co	5.85±0.02	511 (2.78)	-	0.0009	-	-
	Cu	6.16±0.07	486 (2.49)	-	-	6.03±0.05	503 (6.88)
1h	Ni	5.75±0.05	520 (3.21)	-	0.0009	6.30±0.04	537 (5.60)
10	Zn	5.68±0.03	493 (3.01)	622 (0.063)	0.46	- 1	-
	Cd	2.96±0.01	522 (3.72)	631 (0.075)	0.31	) -	-
	Mn	3.62±0.01	515 (2.80)	-	0.12	-	-
	Co	8.6±0.2	510 (2.85)	-	0.0009	6.7±0.1	514 (5.31)
	Cu	8.2±0.3	491 (2.93)	0	-	7.2±0.2	506 (5.13)
1c	Ni	6.50±0.08	519 (3.09)		0.0011	6.15±0.05	539 (6.70)
	Zn	5.55±0.02	492 (3.01)	621 (0.062)	0.48	-	-
	Cd	2.89±0.01	522 (3.89)	628 (0.064)	0.28	-	-
	Mn	3.70±0.01	514 (2.86)	-	0.14	-	-
	Co	4.18±0.02	517 (2.33)	-	0.0005	-	-
	Cu	6.82±0.08	494 (2.85)	-	-	6.59±0.06	511 (6.17)
1d	Ni	6.7±0.1	524 (3.31)	-	0.0004	7.1±0.1	546 (4.38)
	Zn	5.71±0.01	498 (2.66)	630 (0.115)	0.37	-	-
	Cd	1.83±0.01	526 (4.22)	634 (0.080)	0.13	-	-
	Mn	-	-	-	-	-	-
	Co	3.28±0.01	519 (3.02)	-	0.0003	-	-
	Cu	4.49±0.01	506 (3.14)	-	-	-	-
1e	Ni	4.27±0.01	545 (3.03)	-	0.0002	-	-
	Zn	3.06±0.08	512 (3.07)	626 (0.097)	0.25	-	-
	Cd	-	-	-	-	-	-
	Mn	-	-	-	-	-	-
	Co	5.89±0.03	519 (3.24)	-	0.0008	-	-
1f	Cu	6.7±0.1	498 (3.34)	-	-	5.91±0.06	510 (8.03)
	Ni	7.0±0.1	535 (3.84)	-	0.0008	6.3±0.1	545 (6.06)
	Zn	5.72±0.06	503 (3.73)	621 (0.081)	0.41	-	-
	Cd	3.13±0.01	528 (4.03)	626 (0.077)	0.27	-	-

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Mn	3.80±0.01	523 (2.72)	<u>- 10-p1001</u>	0.10	-	-		

#### 4. Conclusion

Synthetic procedures have been developed and new benzothiazolyl substituted spiropyrans have been obtained. The structure of new compounds has been established by means of NMR spectroscopy methods, as well as mass spectroscopy and elemental analysis. The obtained spiropyrans demonstrate positive photochromism with thermal and photochemical back reactions. The quantum efficiency of photo-coloration attains a value of 44%. In contrast to photo-coloration, the quantum yields of photobleaching reactions take extremely low values in the range 0.1–0.01%, which is the smallest indicator in the series of spiropyrans with known azole substituent fragments. The thermal bleaching reaction is characterized by a time constant that varies over a wide range from 4.7 to 200.8 s depending on the substituent mainly in the indoline part of the molecule and the polarity of the solvents. The thermal reaction is noticeably accelerated with the introduction of electron-withdrawing substituents at position 5 of the indoline fragment and upon passing from polar acetone to weakly polar toluene. All spiropyrans obtained exhibit ionochromic properties. When interacting with Cd<sup>2+</sup>, Mn<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup> metal ions, they form complexes of 1:1 and 1:2 compositions, the structure of which has been established in the case of SPP 1 by the help of different methods including X-ray diffraction. It has been established that electron-withdrawing substituents in the indoline part of SPP molecules inhibit the complexation reaction. Photoinitiated processes in complexes of merocyanine isomers with metal cations include both thermally reversible negative photochromism and fluorescence in the case of  $Zn^{2+}$  and  $Cd^{2+}$  ions. Thus, the obtained spiropyrans are a polychromogenic molecular system with ion-controlled photochromic properties, manifested as positive photochromism in the case of free SPP molecules and negative photochromism of complexes of SPP merocyanine isomers with metal ions.

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Appendix A. Supplementary data

Supplementary data related to this article can be found online at

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#### Journal Pre-proof

### **Highlights:**

- New 8-benzothiazole spiropyrans undergo positive photochromism.
- 8-benzothiazole spiropyrans form complexes with transition metal ions.
- Photo-reaction efficiency of the bound merocyanine is 3 orders of magnitude higher.
- Cation induced isomerization into merocyanine complex can be controlled by light.
- Photochromic transformations can be driven by transition metal ions.

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Anatoly V. Chernyshev: Conceptualization, Methodology, Investigation, Formal analysis, Validation, Writing - Review & Editing, Nikolai A. Voloshin: Methodology, Investigation, Validation, Writing - Original Draft, Irina A. Rostovtseva: Investigation, Validation, Visualization, Oleg P. Demidov: Investigation, Formal analysis, Validation, Visualization, Konstantin E. Shepelenko: Investigation, Ekaterina V. Solov'eva: Investigation, Validation, Elena B. Gaeva: Validation, Visualization, Writing - Original Draft, Anatoly V. Metelitsa: Writing - Review & Editing, Project administration, Funding acquisition.

#### **Declaration of interests**

\* The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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