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Chromogenic systems based on 8-(1,3-benzoxazol-2-yl) substituted spirobenzopyrans undergoing ion modulated photochromic rearrangements

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ABSTRACT

8-(1,3-Benzoxazol-2-yl) substituted spirobenzopyrans **1A** appear as a chromogenic system susceptible of switching between positive and negative photochromism under complexation with metal ions. The thermal and photochemical reactions accompanying metal ion-induced transformation of spiropyrans **1A** to the complexes formed by their photoinduced merocyanine isomers **1B** were investigated. In the dark, the colorless spiropyrans interact with Mn^{2+}, Cd^{2+} and Zn^{2+} transition metal ions to yield deeply colored 1:1 complexes possessing fluorescence, while Co^{2+}, Ni^{2+}, Cu^{2+} ions prefer to form non-fluorescent complexes with two merocyanines. Under irradiation with visible light solutions of the merocyanine-metal complexes undergo photobleaching. This effect was quantified using photokinetic method.

1. Introduction

Spiropyrans (SPP) belong to the widely known class of organic photochromic dyes. Undying interest in these compounds is caused by the wide possibilities of the directed alteration of their properties upon variation of the structure which stipulates their application in the different fields of photonics, chemo- and biosensorics and molecular electronics [1–3]. The colorless cyclic form of the spiropyran can be transformed into the colored quinoid zwitterionic isomer as a result of valence photo- or thermal isomerization. Presence of the oxygen atom acquiring partial negative charge in the merocyanine structure makes SPP a powerful ligand in the complexation reaction with metal ions that had been demonstrated for the first time by Philips [4] and Taylor [5] who employed SPP functionalized with donor centers ortho-positioned to the oxygen atom. This work initiated preparation of many other similarly designed SPP capable to bind metal ions [6–9]. A peculiar feature of metal complexes formed by merocyanine isomers of SPP is their ability to isomerize reversibly into the spirocyclic form under the action of light. This process is accompanied by a release of the metal ion from the complex [10]. Such a process allows ion transport through cell membranes [11–14]. It has been also the base of sensors design for repeated analyte recognition [15–17], visualization [18–20] and tracking [21] of mobile metal ions in biological objects. Also such type of complexes represents effective photochromic systems demonstrating negative photochromism [22,23]. In the last time this phenomenon finds more applications because primarily of less energy consuming activation compared to the classic UV stimulated photochromic systems [24]. Moreover, the transition metal complexes with photochromic ligands manifesting photoswitchable magnetic properties determined by the light-induced configurational isomerization rearrangements [25].

As we have previously shown, 8-benzoxazole substituted spirobenzopyrans (SBP) **1**–**4** appear as a photochromic system demonstrating positive photochromism of T- and P-type [26]. Before irradiation, SBP solutions in acetone are colorless because they are in the cyclic form **A** (Scheme 1) characterized by the absorption band with a maximum in the UV region (353–354 nm; $\varepsilon = 8.4–9.8{\cdot}10^3\,M^{-1}\,cm^{-1}$). Upon irradiation with the light of $\lambda_{irr} = 365$ nm coloration of the solutions is observed as the result of the C_{spiro}—O bond cleavage and the subsequent *cis*-trans isomerization of the formed merocyanines **B.** The process is characterized by the appearance of a long wavelength absorption band with a maximum in the 640–644 nm region ($\varepsilon = 6.1–6.4{\cdot}10^4\,M^{-1}\,cm^{-1}$). Quantum yield of the photocoloration reaction is equal to 0.023-0.051 and the reverse thermal relaxation process time is 49–68 s (T = 293 K) [26].

In the present work we intend to show that the situation is completely changed upon addition of the transition metal salts to the SBP **1**–**4** solutions. The new photochromic system appearing upon interaction of these spiropyrans with metal cations exhibits negative photochromism of T- and P- type.

In the previous work we have reported on the complexation

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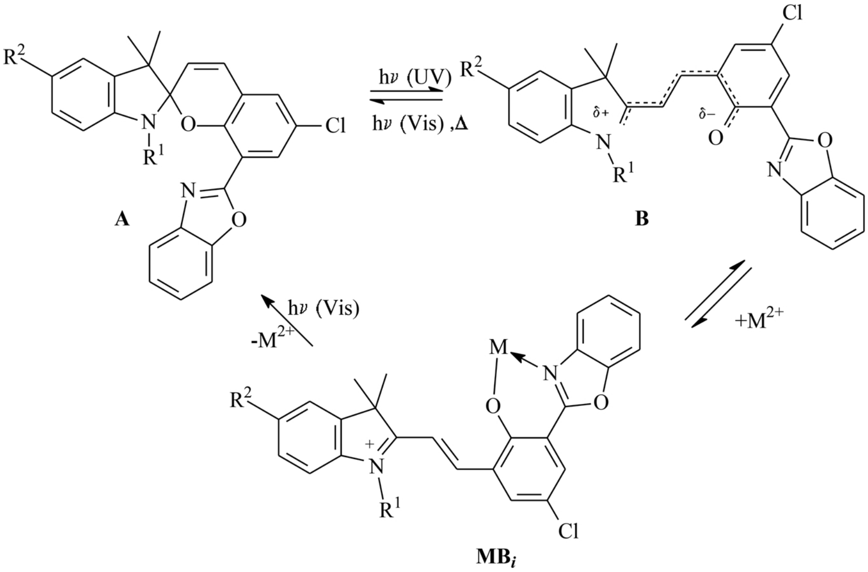

Scheme 1. **1**: R^1 = Me, R^2 = Cl; **2**: R^1 = Me, R^2 = Br; **3**: R^1 = Pr, R^2 = Br; **4**: R^1 = CH_2Ph, R^2 = H.

behavior of the series of 5′-benzoxazole-substituted spiro(indoline-naphthopyrans) (SNP) [27]. Taking into account differences in photo- and thermochromic behavior of the benzoxazole substituted SNPs [28] and SBPs [26], certain differences in ionochromic effect exhibited by the compounds can be expected. In this regard, the aim of the present work was also a quantitative comparative study of the complexation of a series of SBP **1–4**, the merocyanine form of which contains bidentate chelate site comprised of the phenolate oxygen and nitrogen atom of the azole cycle, and SNP.

2. Experimental part

The compounds **1–4** have been synthesized according to the procedure described in [26]. Spectral investigation has been carried out using equipment of the collective use center "Molecular spectroscopy" of the Southern Federal University. Electronic absorption spectra and kinetic curves of the investigated compounds were recorded on an "Agilent 8453" spectrophotometer equipped with the thermostatic cell. The irradiation of solutions with filtered light of a high pressure Hg lamp was performed on a "Newport 66902" equipment. To isolate monochromatic irradiation, interferential light filters (λ = 365, 546 nm) were used. The photon flux power was measured on a "Newport Power Meter 2903-C". The solutions for spectrophotometric investigations were prepared by mixing exact aliquots of standard $2{\cdot}10^{-4}$ M solutions of SBP and a metal salt with subsequent dilution in 10 ml flasks. The solutions were allowed to stand for 24 h under dark conditions for complete metal ion complexation.

Acetone of the spectroscopic grade ("Aldrich") were used to prepare solutions. Metal salts added in solutions were used as perchlorates ("Aldrich").

3. Result and discussion

An addition of the equivalent amounts of the Cu^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+} perchlorates to the colorless solutions of the spiropyrans **1–4** causes coloration that is a result of the merocyanine complex formation depicted in Scheme 1.

Alike previously studied benzoxazole derived SNP [27,29], the reaction of which with the mentioned ions proceeds for 2–5 min, in the case of SBP **1–4** this process being observed by the solution color evolution is significantly retarded and ends up in about 1 h. Moreover, in contrast with SNP the compounds **1–4** do not interact with alkaline earth metal and magnesium ions. In the case of Cd^{2+} and Mn^{2+} ions the coloration appears only under 10 fold excess of an ion. UV irradiation (λ_{irr} = 365 nm) influences the complexation reaction in a different way. In the case of Cu^{2+}, Ni^{2+}, Co^{2+} the irradiation activates merocyanine isomers generation and therefore accelerates reaction process. On the contrary, in the case of Zn^{2+} and Cd^{2+}, the UV irradiation leads to the solution decoloration. After switching off the irradiation source the color recovering is observed. The latter is typical for the thermal reaction of the complex formation. This difference can be related to the high efficiency of dissociation photoreaction of the Zn^{2+} and Cd^{2+} complexes comparing to Cu^{2+}, Ni^{2+}, Co^{2+}. Accounting for these observations all the further experiments related to the complexation of SBP **1–4** have been carried out using dark glass flasks at the low ambient illumination. The analysis of the formed complexes stoichiometry has been accomplished using spectrophotometry Job's method. It has been established that Mn^{2+}, Zn^{2+} and Cd^{2+} ions form 1:1 (metal-ligand) complexes. Fig. 1a shows a plot of maximum absorption of **2**-Zn^{2+} complex vs composition of isomolar solutions. The maximum of the curve corresponds to the equimolar composition. In such a case a maximum position does not depend on the wavelength selected for observation within a longwavelength absorption band. In the case of Cu^{2+}, Ni^{2+}, Co^{2+} the formation of 1:2 complexes has been recorded. There is a maximum of the Job diagram corresponding to metal ion molar fraction equal to 0.3 (Fig. 1b) and upon selecting of a shorter wavelength this maximum shifts towards the value 0.4, that is more probably related to simultaneous presence of 1:1 and 1:2 complexes in solution.

The detailed structure determination has been conducted for the **4**-Zn^{2+} complex. According to the X-ray analysis [30] the ligand in the **4**-Zn^{2+} complex has the merocyanine form and possesses *TTT* (trans-trans-trans) conformation unlike to the SNP analogues, in the case of which the ligand in the complex acquires *TTC* conformation [29]. The realization of the *TTT* merocyanine isomer in the **4**-Zn^{2+} complex can be caused by the presence of a bulk benzyl substituent at the nitrogen atom of the indoline fragment. This assumption is in a good agreement with the X-ray analysis data of the spirobenzopyran complexes containing substituents at the nitrogen atom of the indoline fragment other than a methyl group [31].

In order to estimate the influence of the metal ion feature and the ligand substituents on the efficiency of complex formation the determination of the corresponded stability constants has been carried out. The total ligand concentration (C_L) has been used for calculations [32]. In such a case the obtained values of stability constants are effective because they depend on the position of the tautomeric