

Spectral study of interaction between Silica nanoparticles and molecules of photochromic spirocompounds in solutions

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Abstract

A comparative spectral study of water–acetonitrile systems containing photochromic spiropyran and spirooxazine derivatives in the absence and in the presence of silica nanoparticles was carried out. The photoinduced formation of proton complexes between phenolic oxygen of the colored forms of spirocompounds and the surface hydroxyl groups of silica nanoparticles was established for all of the derivatives. The photoinduced proton complexes of the spiropyrans exhibit positive photochromism on the surface of silica nanoparticles. It is assumed that the previously discovered negative photochromism is due to the formation of proton complexes with not only phenolic oxygen, but also the OH group at the nitrogen atom of the indoline spiropyran moiety. These complexes can also exist in the absence of nanoparticles, because of interaction with water molecules.

Keywords: Photochromism; Proton Complexes; Silica Nanoparticles; Spectroscopy; Spirocompounds.

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INTRODUCTION

The development of photochromic nanostructured systems of the core–shell type based on silica nanoparticles (SiO₂) attracts attention due to the prospects of their use as fluorescent labels in biological and medical diagnostics, for the design of photochromic clothing and camouflage coatings in the textile industry, and for other applications.

Earlier studies using silica nanoparticles and mesoporous silica [1-6] demonstrated the possibility of obtaining systems with negative photochromism of spiropyrans [1-6]. Positive

photochromism on the surface of these nanoparticles is exhibited by nitro-substituted spiropyrans with a long methylene substituent in the indoline moiety [7] and by methyl methacrylate copolymer containing spiropyran moieties [8-10]. The molecules of nitro-substituted spiropyran and Rhodamine B fluorophore chemisorbed on the surface of silica nanoparticles provide photoinduced modulation of the fluorophore fluorescence due to inductive resonance energy transfer of excitation from the fluorophore to the merocyanine form of spiropyran [11].

Silica nanoparticles with adsorbed spirooxazine molecules [12-16] or silylated

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naphthopyrans (chromenes) [17-19], exhibiting positive photochromism, were used to obtain photochromic textiles.

Photochromic silica nanoparticles were also obtained using modified photochromic diarylethene molecules [20-22].

Analysis of relevant publications indicated that the interaction of spirocompounds with silica nanoparticles has not been adequately studied. Most of researches focus on photochromic nanoparticles and photochromic spirocompounds chemically grafted on silica nanoparticles.

Previously, we carried out a comparative spectral kinetic study of the photochromism of water-ethanol solutions of spirocompounds (spiropyrans and spirooxazines), chromenes, and diarylethenes in the absence or in the presence of silica nanoparticles and found that the interaction of photochromic molecules with nanoparticles occurs as either chemical or physical adsorption, depending on the structure of photochromic compounds [23]. This communication presents new results from the ongoing research of chemical adsorption processes of specially selected structurally different functionalized spiro compounds. This adsorption is accompanied by the formation of surface proton complexes of photoinduced merocyanine or merocyanine form of functionalized spirocompounds.

It is well known [24] that under UV irradiation, spirooxazines and nitro-substituted spiropyrans in

the initial colorless form A experience reversible photodissociation of the $-C-O$ bond and the subsequent dark *cis-trans* isomerization to give the colored open form B (Fig. 1). The latter spontaneously relaxes, after UV irradiation, into the initial closed form A. This process is accelerated under visible irradiation and with increasing temperature.

EXPERIMENTAL DETAILS

Silica nanoparticles Levasil 200 (Bayer, Germany) and functionalized spirooxazines **I**, **II** and spiropyrans **III**, **IV** (Fig. 2) were used in the study.

Photochromic 1, 3-dihydro-1, 3, 3-trimethylspiro[2H-indole-2, 3'-[3H]naphtho[2,1-b][1,4]oxazine]-9'-ol **I** was synthesized by a method reported in [25], and 1,3-dihydro-1, 3, 3-trimethylspiro[2H-indole-2, 3'-3H-naphtho[2, 1-b][1, 4]oxazine]-8-amine **II** was prepared as described in [26].

A well-known technique was also used to synthesize photochromic nitro-containing spiropyran **III** [27]. The synthesis and properties of compound **IV** were described previously [28].

Solutions of photochromic compounds with the concentration $C = 4 \times 10^{-4}$ M were prepared in acetonitrile (HPLC, ACS). They were kept in an ultrasonic bath (Sapphire, Russia) for 2 minutes for better dissolution. Water-acetonitrile solutions for the study were prepared using 50 μ l of an initial

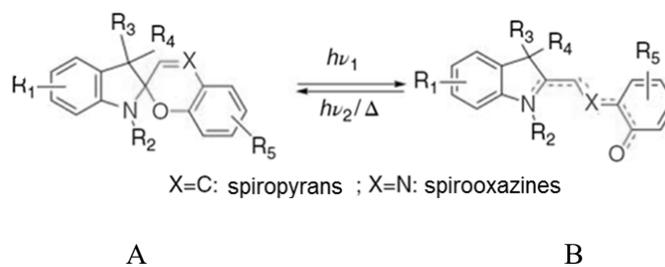


Fig.1. Photochromic transformations of spirocompounds.

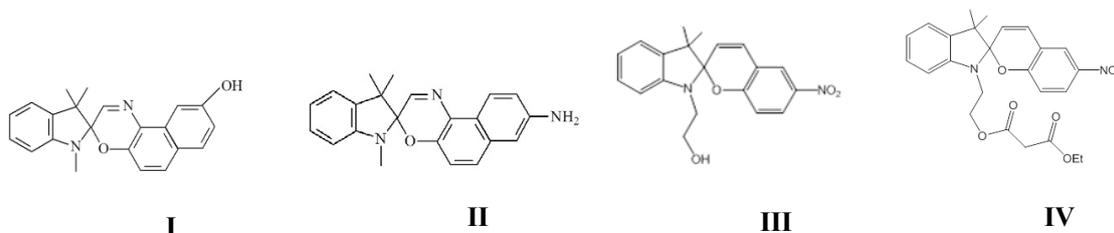


Fig. 2. Structures of studied photochromic spirocompounds.

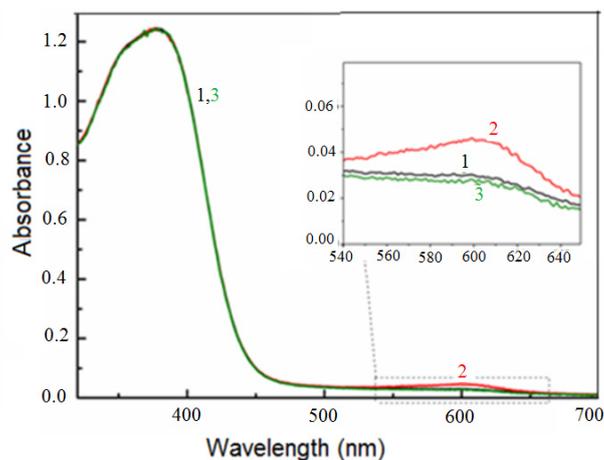


Fig. 3. Absorption spectra of a water–acetonitrile solution of spirooxazine I with silica nanoparticles before (1) and after UV irradiation (2) and after subsequent dark relaxation (3).

acetonitrile solution of a photochromic compound and 166 μl of a five-fold diluted solution of silicon nanoparticles. This ratio was optimal and was determined experimentally. Silica nanoparticles remained in solutions in a stable transparent state without precipitation for 24 h. The concentration of perchloric acid in the solutions was $C = 4 \times 10^{-2}$ M.

The spectral kinetic measurements were carried out using a Cary-60 UV-Vis spectrophotometer (Agilent Technologies). The baseline was recorded using an acetonitrile–water mixture (50 μl + 166 μl) in a quartz working cell with 2 mm optical path. The absorption spectra of the solutions were recorded in the same quartz working cell. After the initial absorption spectrum was measured, the mixture solution was irradiated with filtered UV light with simultaneous recording of the absorption spectra of the photoinduced merocyanine form. Then, UV radiation was terminated, and the spectra of this form were recorded during its relaxation in the dark. To analyze the absorption spectra of the photochromic molecules adsorbed on silica nanoparticles, difference spectra were used. To exclude light scattering by nanoparticles and absorption of photochromic molecules in the initial spiro form, difference spectra were obtained by subtracting the initial absorption spectrum of the solution containing silica nanoparticles and photochromic compounds in the spiro form from the photoinduced absorption spectrum of the solution containing photochromic compounds in the merocyanine or merocyanine form and silica

nanoparticles.

The irradiation was carried out with the light of a L8253 xenon lamp of the LC-4 illuminator (Hamamatsu) through optical filters that transmitted UV (250–400 nm) or visible (400–800 nm) radiation.

The solutions were irradiated with UV light for the time (several minutes) necessary to achieve the photoequilibrium state, at which the photoinduced absorbance at the maxima of the photoinduced absorption bands did not change. Bleaching under visible light was also achieved in a few minutes.

RESULTS AND DISCUSSION

Fig. 3 shows the absorption spectra of a solution containing spirooxazine I and silica nanoparticles. It can be seen that in the presence of silica nanoparticles, photochromic compound I exhibits photochromic transformations.

The efficiency of photochromic transformations of this and below-considered spiro compounds is significantly reduced in the presence of silica nanoparticles. This is apparently due to the decrease in the intensity of activating UV radiation as a result of light scattering by nanoparticles.

The photoinduced difference absorption spectra (Fig. 4) indicate the presence of interaction between the photoinduced photochromic molecules and the surface groups of silica nanoparticles. This is evidenced by appearance of a low-intensity absorption band with a maximum at 460 nm (Fig. 4, curve 1; Table 1). The same

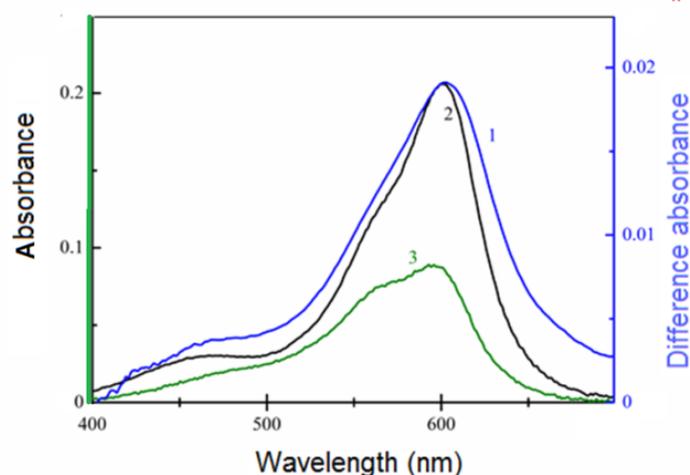


Fig. 4. Difference (1) and usual (2, 3) absorption spectra of the photoinduced absorption for compound I in a water-acetonitrile solution with (1) and without (2) silica nanoparticles and in acetonitrile (3).

Table 1. Spectral characteristics of photochromic compounds in various solvents with and without silica nanoparticles.

Compound	Solvent	Presence of nanoparticles	λ_{A}^{\max} , nm	λ_{B}^{\max} , nm
I	Acetonitrile	-	233, 337	563sh, 593
	Acetonitrile/water	+	234, 341	467нл, 564нл, 601
II	Acetonitrile	-	252sh, 277sh, 378	469, 603*
	Acetonitrile/water	+	257, 322sh, 388	621
III	Acetonitrile	-	252, 325sh, 379	443, 605нл, 640
	Acetonitrile/water	+	330sh, 393sh	475нл, 639*
IV	Acetonitrile	-	245, 267, 299, 343	561
	Acetonitrile/water	+	240sh, 271, 351	404, 510
V	Acetonitrile	-	242sh, 267sh, 344	427, 517sh*
	Acetonitrile/water	+	243, 268, 297sh, 337	569
VI	Acetonitrile	-	244, 273, 299sh, 346	397, 534
	Acetonitrile/water	+	269sh, 335	417, 525*

Note: λ_{A}^{\max} and λ_{B}^{\max} are wavelengths of the absorption maxima for the initial A and photoinduced B (*for difference absorption bands) forms of photochromic compounds. The maxima of the most intense absorption bands are shown in bold.

band appears in the photoinduced absorption spectrum of compound I in a water-acetonitrile solution (Fig. 4, curve 2; Table 1), but it is absent in the photoinduced difference spectrum of this compound in acetonitrile (Fig. 4, curve 3; Table 1). Absorption bands in this spectral region occur in the spectra of unsubstituted spirooxazines in the presence of acids, H_2SO_4 [29] and HCl [30], or upon proton beam irradiation [31].

A comparative analysis of the measured spectra and literature data prompts the assumption that the photoinduced formation of proton complexes in a water-acetonitrile solution in either the presence or the absence of silica nanoparticles is associated with hydrogen bond formation between the merooxazine form B of compound I and water molecules and/or surface hydroxyl groups of silica nanoparticles.

In the case of UV irradiation of amino-

substituted spirooxazine II, a short-wavelength absorption band also appears in a water-acetonitrile solution, both in the presence (Fig. 5, curve 1; Table 1) and in the absence (Fig. 5, curve 2; Table 1) of silica nanoparticles. However, in the presence of the nanoparticles, the short-wavelength absorption band was much more intense. Upon irradiation with visible light, this band reversibly disappeared, while after UV irradiation it appeared again.

This difference between the behaviors of hydroxy- and amino-substituted spirooxazines is attributable to the influence of substituent in the naphthyl ring on the basicity of spiro-oxygen (Fig. 6).

In the case of compound II, effective conjugation of the electron-donating amino group with spiro-oxygen is observed. Compound I, in which the substituent is in a different position,

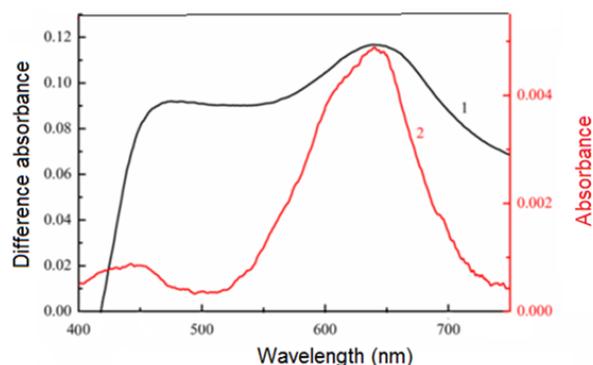


Fig. 5. Difference (1) and usual (2) spectra of photoinduced absorption of compound II in a water-acetonitrile solution with (1) and without (2) silica nanoparticles.

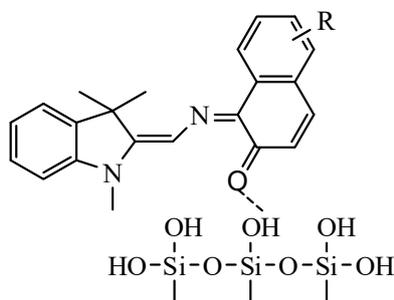


Fig. 6. Structure of the proton complex between a silica hydroxyl group and a photoinduced merooxazine molecule of spirooxazine.

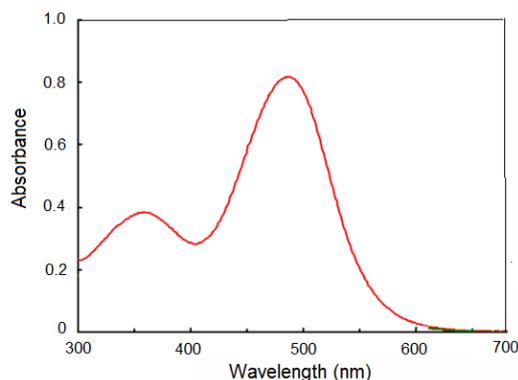


Fig. 7. Absorption spectra of acetonitrile solution of compound II in the presence of perchloric acid (1:100).

has no such conjugation. Therefore, in the case of compound II, spiro-oxygen is more basic and more efficiently forms a protonated complex with surface OH groups of silica nanoparticles.

A similar absorption band with a maximum at 485 nm is observed in the initial absorption spectrum of this compound in acetonitrile in the presence of perchloric acid (Fig. 7).

Coincidence of the absorption bands of spirooxazine II in acetonitrile in the presence of either silica nanoparticles or perchloric acid suggests that a protonated complex of this compound is formed on the surface of silica nanoparticles under UV irradiation.

Comparison with the results of spectral studies of unsubstituted spirooxazine, which does not form

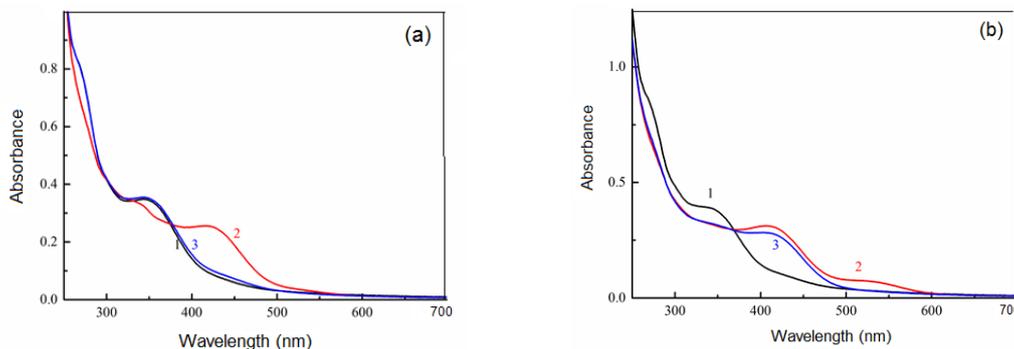


Fig. 8. Absorption spectra of a water-acetonitrile solution of spiropyran **III** (a) and **IV** (b) with silica nanoparticles before (1) and after UV irradiation (2) and after subsequent irradiation by visible light (3).

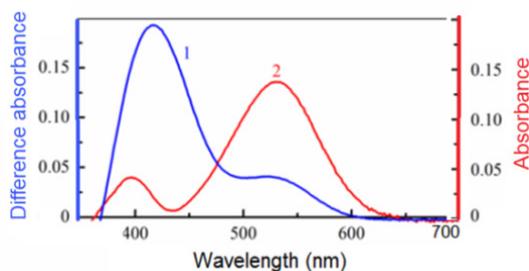


Fig. 9. Difference (1) and usual (2) spectra of photoinduced absorption of spiropyran **IV** in a water-acetonitrile solution in the presence (1) and in the absence (2) of silica nanoparticles.

protonated complexes with silica nanoparticles [23], shows that the introduction of substituents in the oxazine moiety of these compounds leads to photoinduced formation of protonated complexes on the surface of this type of nanoparticles. These complexes exhibit positive photochromism.

It should also be noted that the absorption bands of the photoinduced merooxazine form of spirooxazines in acetonitrile/water solutions are red-shifted; when the hydroxyl substituent is replaced by an amino group the magnitude of the shift increases (Table). Unlike spirooxazines, in the case of spiropyran, the photoinduced merocyanine form shows a more pronounced blue shift of the absorption bands (Table)

The photoinduced short-wavelength absorption bands at 427 and 417 nm are also observed in the absorption spectra of water-acetonitrile solutions containing silica nanoparticles and nitro-substituted spiropyran **III** (Fig. 8a; Table 1) and **IV** (Fig. 8b; Table 1). As in the case of spirooxazines, the appearance of these absorption bands is attributable to the formation of

protonated complexes, which arise as a result of interaction between the phenoxyl oxygen of the spiropyran merocyanine form and the surface hydroxyl groups of silica nanoparticles.

The spectral changes induced by the formation of the proton complex of spiropyran **III** in the presence of silica nanoparticles is consistent with the position of its absorption bands in the presence of an acid in polymer films (410 nm) [32, 33].

The long-wavelength absorption band with a maximum at 540 nm in the photoinduced absorption spectrum of spiropyran **IV** (Fig. 8b, curve 2; Table 1) is due to merocyanine form molecules that do not interact with silica nanoparticles.

Fig. 9 shows the photoinduced absorption spectra of solutions of **IV** in the absence and in the presence of silica nanoparticles, which clearly show the photoinduced formation of a new photoproduct.

A new short-wavelength absorption band is also observed in acetonitrile solutions of these

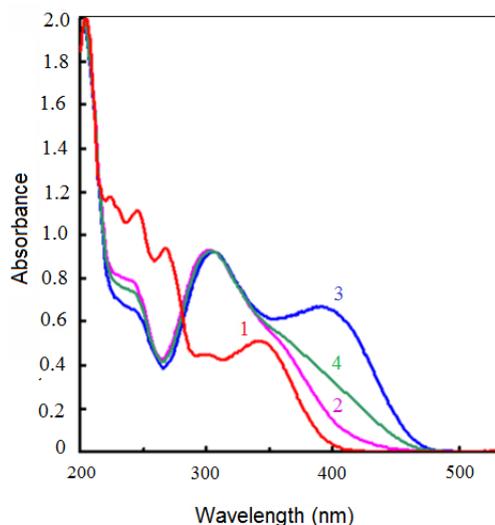


Fig. 10. Absorption spectra of compound III in acetonitrile in the absence (1) and in the presence of perchloric acid HClO_4 (1:100) before (2) and after UV irradiation (3) and after subsequent irradiation by visible light (4).

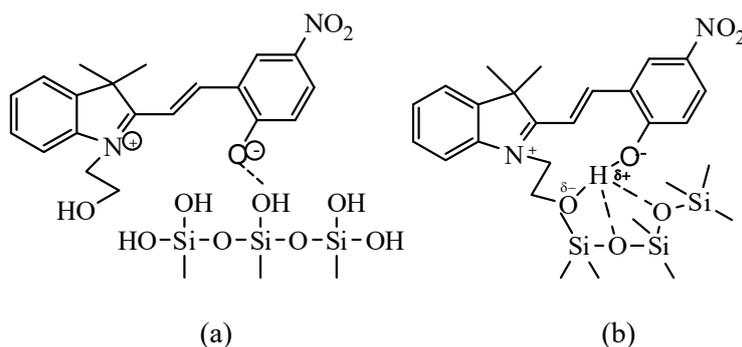


Fig. 11. Structure of the proton complexes (a) and (b) between silica surface groups and a photoinduced merocyanine molecule of spiropyran.

compounds in the presence of acids, in particular, for spiropyran III (Fig. 10).

As compared with the absorption spectrum of this compound in acetonitrile (Fig. 10, curve 1), a new band with a maximum at 310 nm and a shoulder at 375 nm appear in the spectrum (Fig. 10, curve 2). The 375 nm shoulder appearing in the absorption spectrum of the solution in the presence of acid before UV irradiation (Fig. 10, curve 2) suggests that some amount of the protonated complex is formed immediately after adding the acid to the solution. After UV irradiation, the concentration of the complex sharply increases (Fig. 10, curve 3), while on exposure to visible light, it decreases (Fig. 10, curve 4). Similar results were obtained for

indoline spiropyran and their hybrid molecules with fullerene C_{60} [34].

Analysis of the above results attests to the formation of proton complexes of these spiropyran on the surface of silica nanoparticles (Fig. 11a). These complexes exhibit positive photochromism. The observed negative photochromism [3, 4] is probably due to the formation of proton complexes with participation of the OH group at the nitrogen atom of the indoline spiropyran moiety (Fig 11b) [5].

The observed formation of protonated complexes for these spiropyran is consistent with the results of a spectral study of the interaction of nitro-substituted spiropyran containing a methoxy

group in the pyran moiety with silica nanoparticles [23]. The difference is that in the case of compounds III and IV, protonated complexes arise only under UV light. The interaction of methoxy-substituted spiropyran molecules with silica nanoparticles gives rise to protonated complexes before irradiation. Their concentration increases with subsequent exposure to UV or visible light. In the solid silicate matrix, the proton complexes of spiropyran III molecules exhibit negative photochromism [3, 4].

Analysis of the results of the spectral study of the interaction between photochromic spirooxazine and spiropyran molecules and hydroxyl groups of silica nanoparticles indicates the photoinduced formation of hydrogen-bonded proton complexes between the surface sites of silica nanoparticles and phenolate oxygen of the spiropyran and spirooxazine merocyanine forms. In the case of hydroxyl-containing spiro compounds, hydroxyl substituents, phenolate oxygen of the merocyanine form, and oxygen atoms of silica nanoparticles can participate in the formation of proton complexes³. The nitro-substituted spiropyran IV, devoid of a hydroxyl group, also forms proton complexes, but only between the phenolate oxygen of the merocyanine form and the surface groups of silica nanoparticles. Such complexes are less efficiently bleached by visible light. However, judging by the appearance of short-wavelength absorption bands in the spectra of water–acetonitrile solutions of spirocompounds, these complexes are also formed in water–acetonitrile solutions as a result of interaction of photochromic molecules with water molecules, apparently, via hydrogen bonding between water molecules, the indoline nitrogen atom, and the phenolate oxygen of the photoinduced open form of spiropyran and spirooxazines [35].

It should be noted that the process of dark bleaching of photoinduced proton complexes of the above spirocompounds is characterized by a rate constant more than an order of magnitude lower than that of their photoinduced merocyanine or merocyanine forms in solutions containing no nanoparticles. The bleaching process is significantly accelerated under visible radiation, which is absorbed by merocyanine forms.

CONCLUSION

The photochromic transformations of spiro compounds (spiropyran and spirooxazines) were

studied by spectroscopy in water–acetonitrile solutions in the absence and in the presence of silica nanoparticles and in acetonitrile in the presence of perchloric acid. Comparative spectroscopic analysis demonstrated the photoinduced formation of protonated complexes of the named compounds, exhibiting positive photochromism on the surface of silica nanoparticles. This opens up the possibility of obtaining new nanostructured photochromic materials.

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CONFLICT OF INTEREST

Authors have no conflict of interest

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