NJC





Cite this: New J. Chem., 2021, 45, 10287

Received 2nd March 2021, Accepted 2nd May 2021

DOI: 10.1039/d1nj01046h

rsc.li/njc

1. Introduction

Photochromic compounds are bistable structures whose physicochemical properties can be regulated by irradiation with UV or visible light. The possibilities for the practical use of photochromes are extremely diverse. The following recent reviews describe the practical application of photochromes in nanosystems,¹ as optically functionalized organic field-effect transistors (OFETs),² solar thermal fuels,³ multiaddressable photochromic architectures,⁴ fluorophores at the molecular and nanoparticle levels⁵ and modern all-visible-light-triggered compounds.⁶ The following reviews on the use of photochromic dyes for photocontrol in biomedicine,⁷ photoswitches in smart materials and biological systems⁸ and photoswitchable molecules in longwavelength light-responsive drug delivery⁹ should also be mentioned as they indicate the importance of photochromes for biological research.

Review studies^{7–9} show that the water-solubility of photochromes is a highly desirable characteristic for their use in the control of biological processes. In this regard, it should be noted that the recent research trend is the intensification of studies on the creation of photochromic materials reversibly transformed by irradiation in aqueous medium. Spiropyran derivatives are



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A novel water-soluble multicolor halo- and photochromic switching system based on a nitrile-rich acceptor[†]

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A directed synthesis of the first nitrile-rich dye showing visible-light-induced negative photochromism in aqueous medium was implemented. The possibility to change the color of an aqueous solution from yellow to magenta by varying the pH from 5 to 8 was shown. The synthesized dye was found to be a thermally unstable photochrome (T-type) whose photoinduced form returned to the initial state following the first order kinetic equation in the dark at room temperature. It was possible to change the dark reaction rate in a wide range and to block the photochromic process by pH regulation. The calculated pK_a^{1} of the initial form was more than 2.5 units higher than the pK_a^{1S} of the photoinduced form, which indicated the photoacidity of the dye in aqueous medium. This allowed the pH of the solution on 1.2 pH units to be reversibly changed under visible light irradiation, followed by dark relaxation. The obtained results revealed a new direction in the investigation of nitrile-rich negative photochromes, namely, the synthesis of water-soluble multicolor molecular switching systems sensitive to several factors.

among the well-studied groups of water-soluble photochromes. Representatives of this group are known as photoacids,^{10–13} photoswitchable ligands of biomolecules,¹⁴ molecular devices that mimic triode action,¹⁵ compounds with photoresponsive electrostatic¹⁶ or light-controlled self-assembly,¹⁷ water-soluble polymers,¹⁸ molecules showing light-induced cytotoxicity,¹⁹ light-driven hydrogels²⁰ and light-responsive metal–organic frameworks with high ON/OFF photoswitchable proton conductivity.²¹

Spiropyran photochromes are well studied due to their universality for imparting a wide variety of physicochemical properties to them.²² Other representatives of water-soluble photochromic molecules are also known. Thus, azobenzenes are promising as photoactive ultrathin films,²³ light-responsive surfactants²⁴ and photoswitchable drugs.²⁵ Thioindigo derivatives are reported for reversible spatial control in aqueous media by visible light,²⁶ diarylethene molecules are shown as photoswitchable and water-soluble fluorescent nano-aggregates,²⁷ as well as biomarkers for super-resolution optical imaging,28 and fulgide derivatives are described in the ultrafast reactions of the watersoluble photoswitches.²⁹ Fig. 1 shows examples of known watersoluble photochromes. It should be noted that a possibility to use visible light for switching is crucial, as it is a harmless and selective external trigger to regulate the properties of various media and materials.⁶ In addition, most of the studies describe the investigation of direct photochromes, compounds whose color appears or deepens upon irradiation. Reverse photochromes, which lose color under irradiation, are much

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[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/d1nj01046h



Fig. 1 Examples of known water-soluble photochromes, known nitrilerich photochromes and the object of the present study.

less common.^{30,31} This indicates a requirement of the intensification of research in this area.

The data described above demonstrate the importance of the search for novel groups of water-soluble visible-light-switchable photochromic dyes with wide possibilities for the regulation of their color and other physicochemical characteristics.

After the analysis of the literature data, we started to study the possibility of preparation of water-soluble photochromes based on the poorly studied group of reverse photochromes. Their essential structural part was the combination of a nitrilerich acceptor and a 2-vinylphenol fragment in the molecule (Fig. 1).³²⁻³⁸ The first representative of this group of photochromes was described in 2014; it included a tricyanofuran moiety with a salicylic aldehyde fragment in the structure.³² Later, the synthetic possibilities were expanded both for changing the structure of the nitrile-rich acceptor³⁴ and for introducing various substituents into the aromatic moiety.35 These several works showed the practical significance of photochromes of this group, because the possibility for photoregulation of acidic^{32,33} and fluorescence³⁶ properties had been reported. An example of a high-contrast photochromic transformation with 100% conversion of the initial intensely colored form to a colorless

one was also shown.³⁴ It should be noted that, among the described examples of **NRP**, there were no data on water-soluble species.

Thus, the purpose of this study was to synthesize the first water-soluble representative of nitrile-rich negative photochromes and to study the dependence of its color and photochromic properties on the acidity of aqueous medium.

2. Results and discussion

2.1 Synthesis and structure determination

The preparation of **NRP** was based on the reactions of salicylic aldehyde derivatives with a cyano-substituted acceptor.^{32–38} A sulfonate moiety was one of the common fragments used to impart water solubility to an organic molecule. For example, the introduction of this moiety allowed the synthesis of a number of water-soluble photochromes of the spiropyran series^{10,16} and thioindigo derivatives (Fig. 1).²⁶

At the initial stage, according to the known procedure³⁹ we synthesized azomethine 2 starting from salicylic aldehyde and aniline. Then, sulfonation of compound 2 by concentrated sulfuric acid to obtain an intermediate product 3 was carried out. Further, the azomethine protection was removed by heating compound 3 in the presence of sodium carbonate, which led to the formation of the desired sodium salt of 5-sulfosalicylic aldehyde 4. The tricyanofuran (TCF) acceptor was also prepared according to the literature, starting from 3-hydroxy-3-methylbutan-2-one and malononitrile.⁴⁰ The target product 1 was synthesized in 87% yield by the reaction of TCF with aldehyde 4 in the presence of a catalytic amount of sodium acetate in ethanol under an argon atmosphere under moderate heating (Scheme 1).

The structure of compound **1** was considered with the data of ¹H, ¹³C NMR and IR spectroscopy, mass spectrometry and elemental analysis. Thus, the ¹H NMR spectrum included a characteristic pair of doublets at 7.21 and 8.12 ppm with a coupling constant of 16.5 Hz. These signals corresponded to protons appeared after the double bond formation. The proton of the phenolic hydroxyl required for the photochromic reaction appeared at 11.08 ppm.

2.2 Study of absorption spectra in water at different pH values

As we expected, compound **1** was found to be water-soluble, thus allowing us to carry out the investigation of its optical absorption and photochromic behavior in aqueous medium,



 $\ensuremath{\mathsf{Scheme 1}}$ Directed synthesis of water-soluble nitrile-rich dye 1 and intermediates.



Fig. 2 UV-Vis spectra and photos of compound **1** at different pH values ($C = 2.5 \times 10^{-5}$ M, phosphate buffer, 20 °C).

which was the first time for the compounds of the **NRP** series (Fig. 1). We registered the absorption spectra for the solutions of compound **1** in phosphate buffers at constant pH from 2.08 to 9.94 (Fig. 2, Table 1).

 $\label{eq:table_$

рН	$\lambda_{ m abs} \ (m nm)$	A _{max}	$\lambda_{abs}(nm) \\ PSS^a$	A _{max}	Rate constant, $k(s^{-1})$	Half-life, $\tau_{1/2}$ (s) ^b	PC (%) ^c
2.08	422	0.819	413	0.451	$3.2 imes10^{-4}$	2166	0.45
3.08	420	0.828	414	0.451	$2.9 imes10^{-3}$	239	0.46
4.08	420	0.836	310	0.304	$2.06 imes10^{-2}$	33.6	0.55
			415	0.377			
4.54	420	0.818	310	0.439	$3.71 imes10^{-2}$	18.7	0.66
			415	0.277			
5.03	421	0.783	310	0.577	$5.01 imes10^{-2}$	13.8	0.79
			415	0.162			
6.03	419	0.679	310	0.717	5.88×10^{-2}	11.8	0.90
	535	0.143	415	0.070			
6.50	415	0.567	310	0.736	6.00×10^{-2}	11.5	0.87
	535	0.301	415	0.072			
			530	0.038			
7.02	410	0.370	310	0.657	$6.97 imes10^{-2}$	10.0	0.78
	536	0.509	410	0.079			
			535	0.134			
7.99	536	0.684	310	0.341	$6.91 imes10^{-2}$	10.0	0.26
			535	0.500			
8.95	537	0.705	_	_	_		—
9.94	537	0.702	_	_	_		—

^{*a*} Spectral data registered at photostationary state (PSS). ^{*b*} Half-life of the reverse thermal reaction was found to be 0.693/k. ^{*c*} Photoconversion (PC) was estimated as a percentage of the decrease of the main long-wavelength absorption band (at 420 nm or 535 nm) in the photostationary state.

Fig. 2 shows a significant difference in absorption spectra for different pH values. This indicates the sensitivity of compound **1** to the changes of acid–base characteristics of the medium. Thus, the absorption spectra were almost similar in acidic media at pH 2–4. They were characterized with an intensive band in the visible region of the spectrum centered at 420 nm. The second maximum in the visible region (535 nm) appeared starting from pH 6 and became dominant after pH 7, accompanied by a decrease of the band at 420 nm. At higher pH values, there was no significant change in the spectra. The intensity of the band centered at 535 nm was almost constant in the range of pH 8–10. Fig. 2 also included photos of solutions of compound **1**, showing significant color changes in the range of pH 5–8.

We associated the presence of two absorption bands in the visible region of the spectrum with phenol-phenolate equilibrium $1 \rightleftharpoons 1^-$ (Scheme 2) which was strongly affected by pH. Thus, in acidic media, phenolic form 1 prevailed with a maximum at 420 nm, while at neutral or basic pH values phenoxide form 1⁻ with a maximum at 535 nm became dominant. According to the constant absorbance at pH 8-10, we could conclude that compound 1 was completely in the anionic form 1⁻ at these pH values.

Relatively high molar absorptivity of both forms 1 and 1⁻ was found to be 33 500 and 35 400 $M^{-1} \times cm^{-1}$, respectively. The red-shifted absorption band of the phenolate form 1⁻ was probably associated with the stabilization of an anion by resonance structures, namely, quinoid form 1⁻Q and resonance hybrid 1⁻H (Scheme 2). The presence of an isosbestic point at 472 nm shown in Fig. 2 supported the existence of a reversible equilibrium between two forms. It should be noted that forms similar to 1⁻ and 1⁻Q were described in the literature for pH-sensitive analogues of compound 1 containing the hydroxyl group attached to the para-position of the phenyl ring.⁴¹

2.3 Determination of the acidity constant of the initial form

The absorption spectra of dye **1** (Fig. 2) registered at different pH values allowed us to estimate the logarithmic acidity constant pK_a^{1} . Fig. 3 shows absorbances at 420 nm and 535 nm, corresponding to forms **1** and **1**⁻, respectively, plotted against pH. An interception of the curves at pH 6.81 indicated the same concentration of both forms. This pH value corresponded to an approximate pK_a^{1} of compound **1**. To refine the obtained pK_a^{1} value, we used eqn (1):

$$\lg\left(\frac{\mathbf{A}^{1}-\mathbf{A}_{i}}{\mathbf{A}_{i}-\mathbf{A}^{1-}}\right) = \mathbf{p}\mathbf{H}_{i}-\mathbf{p}K_{a}^{1}$$
(1)

where A^1 is the absorbance of phenolic form **1**, A^{1-} is the absorbance of phenoxide $\mathbf{1}^-$ and A_i is the absorbance of the solution in respective buffers with pH_i. For the best results, $\lambda = 535$ nm was chosen, because of the greatest difference between the absorbance curves of the acidic and basic solutions. The obtained linear regression is shown in Fig. 3B. The interception of the fitted line with the *x*-axis at pH 6.6 corresponds to the pK_a¹ value of compound **1**.

The analysis of the phenol–phenolate equilibrium, as well as the determined pK_a^1 value, confirmed that the investigated dye



Scheme 2 Acid-base equilibrium and resonance structures of compound 1.



1 could be used as an aqueous pH indicator with maximum sensitivity in the range of pH 5–8.

2.4 Investigation of the photochromic properties in water at different pH values

An investigation of the photochromic properties of compound **1** in an aqueous medium as well as study of the medium acidity effect on the photochromic behavior is of considerable scientific interest. The results are promising for the creation of a multicolor dye **1** whose color can be adjusted not only by changing the pH, but also by irradiation.

The prepared solutions of compound **1** at different pH values from 2.08 to 9.94 were studied. The first absorption scan was carried out in the dark conditions to obtain the initial spectrum (marked as 'before irradiation' in Fig. 4). The second scan was carried out under light irradiation to register the spectrum of the photo-stationary state (PSS). Then, irradiation was stopped, and scans were continued in the dark at the maximum possible rate for fast reverse reactions (at pH 4–8) and at a medium rate for the slower ones (below pH 4). It was found that compound **1** underwent a photochromic transformation in a wide pH range. A different photoconversion degree

(PC) of compound **1** into the photoinduced spiro-form **1S** was observed depending on pH (Scheme 3, Table 1).

Thus, for the solutions at pH 2–4 a 45–55% decrease of the maximum at 420 nm was observed under irradiation. When increasing the pH value, the conversion degree also increased, reaching a maximum of about 90% at pH 6–6.5. It should be noted that at almost neutral media of pH 6–7, where comparable amounts of phenolic **1** and quinoid **1**⁻ forms were observed (420 nm and 535 nm maxima), a similar decrease of both visible bands was registered under irradiation. In the pH range of 7–8, a slight decrease in the degree of photoconversion was recorded. In basic media (pH 9–10) photochromism was not practically registered.

As an example, Fig. 4 (A and B) show the dynamics of spectral changes in the dark after the irradiation of solutions with pH 5.03 and 7.02. Fig. 4C also shows the photos of solutions of compound 1 at pH 5.03 and 7.02, as well as the corresponding color changes under irradiation by visible light. Similar transitions were observed for solutions at other pH values. Thus, we could conclude that compound 1 was a hybrid multicolor water-soluble molecular switch whose spectral properties were tunable both by the acid-base characteristics of the medium (halochromism) and by visible light irradiation (photochromism).



Fig. 4 Absorption spectra of compound **1** at pH 5.03 (A) and pH 7.02 (B) and photos of these solutions (C) before and after irradiation ($C = 2.5 \times 10^{-5}$ M, 20 °C).

An important and practically significant parameter of photochromic systems is the cyclicity of phototransformations. This process was investigated at different pH values from 2.08 to 7.99. Compound 1 showed good cyclicity of phototransformations and



Fig. 5 Cyclicity of photochromic transformation of compound 1 at pH 6.03 (C = 2.5×10^{-5} M, 20 °C).

fatigue resistance upon sequential irradiation by visible light and storage in the dark after ten cycles. Fig. 5 shows a plot of absorbance changes of solution **1** at 420 nm and pH 6.03 before and after irradiation.

As we could see from Fig. 5 the absorbance both before and after irradiation remained unchanged during cycles. Cyclicity at other pH values was also found to be excellent (ESI[†]).

2.5 Influence of pH on the rate of dark thermal reaction

Table 1, as well as Fig. 4A and B, shows that compound 1 was a thermally unstable photochrome (T-type). Its solutions irradiated by visible light restored the initial spectral pattern when being stored in the dark at 20 $^{\circ}$ C. Fig. 6 and 7 show the change of absorbance at 420 nm and the logarithm of the concentration of the photoinduced form **1S** for solutions at pH 3.08 (Fig. 6) and 6.50 (Fig. 7) plotted against time.

Fig. 6 and 7 show that the reaction order was similar at different pH values, which might indicate the same mechanism of the process in media with different acid/base parameters (Scheme 3).

A more thorough analysis on the kinetics of the dark thermal transformation of **1S** into **1** (Scheme 3) allowed the relationship between the acid/base characteristics of the medium and the half-life period $(\tau_{1/2})$ of the photoinduced form **1S** to be



Scheme 3 Possible photochromic transformations of compound 1.



Fig. 6 Kinetics of the reverse thermal transformation for compound **1** in H₂O at pH 3.08 (A), the plot of fitting the concentration of photo-induced form **[15]** in a first-order kinetic equation (B) ($C = 2.5 \times 10^{-5}$ M, phosphate buffer, 20 °C).



Fig. 7 Kinetics of the reverse thermal transformation for compound **1** in H₂O at pH 6.50 (A), the plot of fitting the concentration of photo-induced form [**1S**] in a first-order kinetic equation (B) ($C = 2.5 \times 10^{-5}$ M, phosphate buffer, 20 °C).

revealed (Table 1). Table 1 shows that the half-life period of **1S** was significantly longer at pH 2–3 than that at pH 5–8. Upon changing the pH from 2.08 to 4.08, the half-life of the dark reaction changed from 35 minutes to 0.5 minutes. At pH 4.5–5 the reaction rate changed insignificantly and in the range of pH 6–8 it remained almost similar ($\tau_{1/2}$: 10–11 s). This significant change in the dark thermal reaction rate upon pH changes is clearly demonstrated in Fig. 8, showing the negative logarithm of the reverse reaction rate constant *k* plotted against pH.

There were two almost linear sections which could be distinguished on the curve in Fig. 8. In the first section (in the range of pH 2–4), there was a sharp increase of the reverse reaction rate, while in the second one (in the range of pH 6–8) the reaction rate constant was almost similar. To explain these results, it was necessary to consider the structure of the metastable photoinduced form **1S** and the effect of the acid–base parameters of the medium in details.

The 1,3,3-tricyanopropene fragment of **1S** (Scheme 3) contained a mobile proton. Anion **1S**⁻ formed after deprotonation was efficiently stabilized by delocalization on three conjugated cyano groups. Therefore, the **1S** structure exhibited enhanced CH-acidic properties. In our opinion, the process of dark thermal transformation to the initial form **1** proceeded through this anionic form **1S**⁻. The greater amount of the anion **1S**⁻ led to the higher rate of dark reaction. It should be noted that the



Fig. 8 Dependence of the negative logarithm of the dark reaction rate constant on the pH value ($C = 2.5 \times 10^{-5}$ M, 20 °C).

existence of a similar equilibrium as $\mathbf{1S} \rightleftharpoons \mathbf{1S}^-$ was described in previous studies of **NRP** derivatives.³³ The evidence for the $\mathbf{1S}^-$ form of compound **1** was the absorption band centered at 310 nm (Fig. 4) according to previous work.^{33,43} However, the pH effect on the $\mathbf{1S} \rightleftharpoons \mathbf{1S}^-$ equilibrium had not been described prior to this study.

The fact that the lowest reverse reaction rate was observed at pH 2–3 supported our assumption, since in strongly acidic media the dissociation of CH-acid **1S** must be suppressed (Scheme 3). As it followed from the absorption spectra of the photoinduced form at pH 2–3, there was no clear maximum at 310 nm in PSS (ESI†), which was a proof for the suppression of the **1S** dissociation.

At the same time, a comparable dark reaction rate at pH 6–8 might indicate the complete ionization of the CH-acid. In other words, the maximum dark reaction rate was achieved with the complete dissociation of the **1S** form.

At the same time photochromism was almost not observed at pH 9–10. To explain this fact, it was necessary to consider the pH effect on the acid–base equilibrium of the initial form **1**. According to the estimated pK_a^{-1} of compound **1** at pH 9–10 the anionic form **1**⁻ predominated in the solution (Scheme 2). Therefore, we could conclude that the photochromic reaction occurred through the phenolic form **1**, while the phenoxide form **1**⁻ was apparently non-photochromic.

The observed dark reaction kinetics showed that by varying the pH we could significantly change the reverse reaction rate, accompanied by multicolor transformations (Fig. 2). Increasing the pH to 9–10 also allowed the photochromic process to be blocked.

From the obtained data, we could conclude that the investigation of **NRP** photochromes must be associated with the study of the effect of the acid-base characteristics of the medium on the ionization of both the initial **1** and photoinduced **1S** forms. In this regard, to obtain more accurate data on the tuning of photochromic behavior of compound **1**, it was necessary to estimate the acidity constant pK_a^{1S} of the photoinduced form.

2.6 Determination of the acidity constant of the photoinduced form

To determine the logarithmic acidity constant of the photoinduced form pK_a^{1S} , we considered that at pH 6–8 a comparable rate of the dark reaction of structure **1** formation was observed. As we assumed above, at these pH values acid **1S** was completely ionized and therefore the expected pK_a^{1S} value should be in the range of 3–4.

We used the data on the change in the intensity of the band centered at 310 nm, corresponding to the anionic spiro-form $1S^-$, from the spectra registered in the photo-stationary state (PSS) and fitted them in eqn (1). The resulting plot (Fig. 9) showed a linear regression of the logarithmic absorbance ratio between 1S and $1S^-$ forms plotted against pH. Its intersection with the *x*-axis at pH 3.9 corresponds to an apparent dissociation constant of the photoinduced form pK_a^{1S} .

The obtained pK_a^{1S} value of 3.9 was also supported by the dependence of the dark reaction rate constant k on the pH described above (Fig. 8). As it followed from Fig. 8, a dramatic change in the reverse reaction rate occurred near pH 4, namely, when the linear section was curved. According to the literature, this area can also be used to approximately estimate the pK_a value.⁴²

The established pK_a^{1} of 6.6 for the initial form **1** and pK_a^{1S} of 3.9 for the photoinduced form **1S** demonstrated that dye **1** was a compound with fully reversible photoacidity (Π) in aqueous medium, which could be estimated according to eqn (2)¹⁰ as 2.7.

$$\Pi = pK_a^1 - pK_a^{1S} \tag{2}$$

The observed difference between the pK_a values of the initial **1** and photoinduced **1S** forms had practical significance beside the theoretical one. This was due to the possibility of using such compounds for photo-regulated pH control of the aqueous media. In this regard, we estimated the possibility to regulate the acidity of the aqueous medium in the presence of compound **1**. We found that it was possible to change the pH from



Fig. 9 Linear regression of the logarithmic absorbance ratio between 1S and 1S⁻ forms vs. pH (C = 2.5×10^{-5} M, 20 °C).



Fig. 10 pH Changes of the aqueous solution of photoacid **1** upon sequential irradiation with visible light and storage in the dark (H₂O, $C = 1.0 \times 10^{-4}$ M, 20 °C).

5.6 to 4.4 (Fig. 10) by irradiation of 0.1 mmol solution of compound **1** in water.

As it is shown in Fig. 10, this process could be repeated several times. This valuable result made a significant contribution to the topical field of research on metastable photoacids allowing the pH of the aqueous media to be regulated.

3. Experimental

3.1 Materials and methods

The progress of reactions and the purity of products were monitored by TLC on Sorbfil plates (spots were visualized under UV light, by treatment with iodine vapor, or by heating). The IR spectra were recorded on an FSM-2201 spectrometer with Fourier transform from the samples dispersed in mineral oil. The NMR spectra were measured in DMSO- d_6 on Bruker DRX-500 and Varian 400 spectrometers using tetramethylsilane as an internal reference.

Elemental analyses were performed using a FlashEA 1112 CHN analyzer. The mass spectra were obtained on a Finnigan MAT INCOS-50 mass spectrometer. The UV spectra were recorded on an Agilent Cary 60 UV-Vis spectrophotometer. Melting points were determined on an OptiMelt MPA100 device. To study the photochromic behavior of compounds, the solutions were irradiated with non-filtered visible light using LED XM-LT6 CREE (spectral range of 400–700 nm, a luminous power density equal to 205 mW cm⁻²) for 0.5 min. Kinetic data of the dark thermal reaction were recorded at 20 °C. The syntheses of the starting compounds 2, 3 and 4,³⁹ as well as tricyanofuran TCF,⁴⁰ were carried out according to the described procedures.

3.2 Synthesis of sodium (*E*)-3-(2-(4-cyano-5-(dicyanomethylene)-2,2-dimethyl-2,5-dihydrofuran-3-yl)vinyl)-4-hydroxybenzenesulfonate 1

To a suspension of 0.199 g (1 mmol) of TCF in 3 ml 96% ethanol, 0.224 g (1 mmol) of aldehyde 4 and 0.82 mg (0.01 mmol)

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of sodium acetate were added under an argon atmosphere. The resulting mixture was stirred at 50 $^{\circ}$ C for 2 h and then for 2–3 h at room temperature until the complete consumption of **TCF** monitored by TLC. The obtained solid product was filtered off, washed 3 times with 2 ml of ethanol and then dried in a vacuum drying cabinet (1 torr) over CaCl₂ for 3 days.

3.3 Spectral characterization of compound 1

Orange solid; mp >330 °C (dec.); yield 87%; IR (mineral oil, v, cm⁻¹): 3400-3050 br. (OH), 2240, 2223 (C \equiv N), 1586 (C=C), 1041 (O=S=O). ¹H NMR (500.13 MHz, DMSO-*d*₆) δ : 1.79 (6H, s, 2CH₃), 6.90 (1H, d, *J* = 8.5 Hz, C₆H₃), 7.51 (1H, d, *J* = 16.5 Hz, CH =), 7.59 (1H, dd, *J* = 2.1, 8.5 Hz, C₆H₃), 8.04 (1H, d, *J* = 2.1, Hz, C₆H₃), 8.12 (1H, d, *J* = 16.5 Hz, CH =), 11.08 (1H, s, OH). ¹³C NMR (125.76 MHz, DMSO-*d*₆): δ 25.28, 53.85, 98.12, 99.27, 111.22, 112.04, 112.87, 115.81, 120.25, 128.38, 131.53, 140.19, 144.37, 158.72, 176.55, 177.25. MS, (EI, 70 eV): *m/z* (%) 303 (4), 184 (100). Anal. Calcd. for C₁₈H₁₂N₃NaO₅S: C, 55.35; H, 2.98; N, 10.37. Found: C, 55.17; H, 3.08; N, 10.19.

4. Conclusions

Thus, the first representative of nitrile-rich dyes exhibiting visible-light-induced negative photochromism in water over a wide pH range was synthesized. The pH sensitivity of this compound along with the possibility of adjusting the color of the aqueous solution from yellow to magenta by changing the pH was shown. The dark reaction rate of the synthesized photochrome increased with an increase of the pH of the aqueous medium, which was associated with an increase in the ionization of the photoinduced acid. The increase of pH to 9 and higher made it possible to block the photochromic reaction process due to the predominance of the non-photochromic phenoxide form of the dye. The difference in the found pK_a of the initial and photoinduced forms made it possible to carry out a fully reversible pH change of the aqueous solution on 1.2 units under irradiation using visible light. The observed kinetics of the dark reaction of the photoinduced form showed that varying the pH allowed the rate of the reverse reaction to be significantly changed along with multicolor transformations by changing the ratio of phenol and phenoxide forms. The obtained results allowed us to assert that the data described herein could become a powerful tool for modifying various physicochemical characteristics of nitrile-rich photochromes and, therefore, to be a starting point for a series of studies in this direction.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The research was performed with the financial support of the Russian Science Foundation (Grant no. 18-73-10065).

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